AD NUMBER

AD832802

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies only; Administrative/Operational Use; MAR 1968. Other requests shall be referred to Department of the Army, Atrtn: Department of the Army, Attn: Public Aairs Office, Washington, DC 20310.

AUTHORITY

OCRD D/A ltr, 12 Sep 1988

DEFENSIVE SECRETIONS OF ARTHROPODA

Final Technical Report

By

Prof. Mario PAVAN
Istituto di Entomologia Agraria
dell'Università di Pavia

march 1968

EUROPEAN RESEARCH OFFICE

United States Army

Contract Number DA-91-591-EUC-3898

Prof. Mario PAVAN

234

Mario PAVAN

Istituto di Entomologia Agraria
dell'Università di Pavia

DEFENSIVE SECRETIONS OF ARTHROPODA

PART I - INTRODUCTION.

Chap. 1 - Aims.

In this study we intend to set out data and considerations regarding *Arthropoda* defensive secretions and the chemically well defined substances of which they are composed.

Biological and chemical researches are part of the study of *Arthropoda* defensive secretions. The sector where researches were most advanced in the past was biology, whereas chemistry had made little progress until about twenty years ago.

We now believe the situation to be the following; biological studies have made clear that the offensive and defensive function of particular substances is very widespread in the large group of *Arthropoda*; the chief zoological groups comprising interesting species are known, and, for the most part, the organs which produce the defensive substances; physiological activity tests have also been made in many cases with isolated substances or with variously purified extracts. This opened an extremely vast field of work for chemists, but chemical researches were undertaken late compared with the development from biological investigations. In fact only in the last twenty years have chemists turned once more with renewed and deepening interest to this kind of study. There are many reasons for this. The biological observation regarding the production and the employement of defensive secretions and anatomical research of productive organs precede the chemical study of the secretions themselves; the initial phase of research is much easier than collecting a sufficient mass of animals, and above all than the subsequent extraction of substances for chemical studies. This second part also implies a close and intense collaboration between biologists and chemists which is not easy, and the availability of huge sums for financing the mass of work necessary to complete chemical researches; in fact these generally require enormous quantities of material and long, complicated extractions followed by difficult structural studies.

Over the last twenty years the technique of chemical research has made such great strides as to allow for definite results with smaller quantities of material, sometimes with just a few specimens of an insect species; this progress is of fundamental importance for the development of the present phase of research. New chemical research conditions make collaboration between biologist and chemist easier, as indispensable as always. These fact and the interest shown in results already obtained explain the recent increase in researches also in the chemical field.

For the above reasons, a comparison between the mass of important work revealing new and significant facts in various biological fields (morphology, anatomy, physiology, ecology) - and that of equal value carried out in chemistry - would certainly show that the biological publications are much more numerous than those of a strictly chemical nature. This means that chemists have a wealth of preliminary indications regarding materials and subjects not yet exmploited.

If one makes a comparison between the chemical studies of Arthropoda and vegetable venoms quite different results are revealed: we have a sufficient knowledge of a relatively small number of the vegetable species known (numbering about 330.000) whereas our knowledge is very limited regarding a large number of known Arthropoda species (about 884.944 species). The reasons for this can easily be divined.

In my part of the research, begun in 1947 and carried on with various and invaluable collaborators, the following 15 new natural substances were found and isolated for the first time:

1. iridomyrmecin (1947) from the worker and queen of Iridomyrmex humilis Mayr (Hymenoptera Formicidae);

The isoiridomyrmecin, chemically obtained (1948) from the iridomyrmecin in the research with Fusco, Trave and Vercellone (bibl. 232, 230, 128, 129) has been found as a natural products in ants by Cavill and Co. 1956 (60).

2. pederin (1963) from the adult beetle Paederus fuscipes Curt. (Coleoptera Staphylinidae);
3. iridodial (1956) from the workers of Tapinoma nigerrimum Nyl. (in the researches by Trave and Pavan (339)) and from workers of the genera Dolichoderus and Iridomyrmex in the contemporaneous researches by Cavill and Co., (60) (Hym. Formic.);
4. dendrolasin (1966) from the worker of Lasius (Dendrolasius) fuliginosus Latr. (Hym. Formic.);
5. pseudopederin (1961) from the adult beetle Paederus fuscipes Curt. (Coleopt. Staph.);
6. pederone (1967) from the adult beetle Paederus fuscipes Curt. (Coleopt. Staph.);
7. cossin A (1966) from the larva of Cossus cossus L. (Lepidoptera, Cossidae)
8. cossin B " " " " " "
9. cossin C " " " " " "
10. cossin 1 " " " " " "
11. cossin 2 " " " " " "
12. cossin 3 " " " " " "
13. cossin B_1 " " " " " "
14. cossin C_1 " " " " " "
15. zeuzerina (1967) from the larva of Zeuzera pyrina L. (Lepidopt.Cossidae);

In analogous researches carried out by other authors the following new substances were isolated as natural defensive products:

16. dolichodial (1960) from the worker of Dolichoderus (Hymenoptera Formicidae);

17.-18. cybisterone and 6-dihydrocybisterone (1967) from genera Cybister (Coleopt. Carabidae).

Chemical and biological investigations were carried out on these products new to chemical literature. There derived therefrom studies and practical results in the field of synthesis of analogous products (for example, isoiridomyrmecin, periidrodendrolasin, etc.).

These considerations induced me to make an inventory of the zoological area hitherto exploited and the results obtained in the chemical sector. Therefore, in this paper, after introducing the subject and placing the Arthropoda group in the animal kingdom (Chap. 5-9), I I shall give a list of the composition of the defensive secretion for each animal species (Chap. 10-17), and then, for each substance defined, a list of the animal species in whose secretions, it has been found (Chap. 18-20).

I also thought it opportune to devote a special chapter to each of the new substances, or groups of similar new substances, in which I have collected and arranged the available data (Chap. 21-28).

Lastly, in the concluding chapter, I have tried to see the subject of Arthropoda defensive secretions in the light of comparative, chemical, biological , biochemical and ecological finding, as might be seen by a naturalist considering the chemical aspects of these problems as primary factor of our knowledge of living beings generally and particularly of defensive secretions.

Chap. 2 -Precedents.

There are already remarkable works, both partial and comprehnsive, on the subject of this paper. Among the most recent papers on chemical and biological synthesis I will mention that by Kaiser and Michl (1958), two of my notes (1958) and that by Eisner and Roth (1962), and the recent note of Weatherston 1967. It is not possible to quote here all the contemporary researchers who have made remarkable contributions in this sector: I shall refer to them in the literature. I shall only mention, among the most active groups of researchers generally, those of Blum and Coll., Cardani and Coll., Casnati and Coll.; Cavill and Coll.; Eisner and Coll., Fusco, Trave and Coll.; Korte and Coll.; Quilico and

Coll.; Schildknecht and Coll.

Many important synthetic studies on the subject can be found in biological literature, amongst which for example Phisalix (1922), Fredericq 1924, Pawlowsky 1927, Deegener 1928, Maas 1937. A volume of literatura on animal venoms was published by Harmon and Pollard, 1948.

Recently meetings and international congresses have taken place on animal venoms where the sector regarding Arthropoda was granted an important or exclusive part (Venoms, 1956; XI International Congress of Entomology, Vienna 1960, Symposiums no. 3 and 4; International Symposium on Animal Venoms, Sao Paulo 1966: First Int. Symposium on Animal Toxins, Atlantic City 1966).

Chap. 3 - Remarks.

Frequent mention is made in the literature on defensive secretions of Arthropoda of substances contained in secretions which are chemically defined but where solid documentation is lacking. Also Roth and and Eisner 1962 show this. It is quite clear we cannot take such data into consideration in our synthesis; they might, however, serve to show a field of work to be considered anew. A typical example is that of the toxic substance of Coleoptera Staphylinidae of the Paederus genus, which several authors have first supposed to be identical with cantharidin; others then claimed it was identical (a fact which was repeated for several decades in world literature), whereas it was a product which we proved to be new and which we called pederin, with physical and biological properties quite different from those of cantharidin and an entirely different structure. Another example is that of the odorous products of the anal glands of the Dolichoderinae ants (for example Tapinoma) which in the literature are referred to as amylic and butyric esters, a smell of rancid butter, etc. whereas research by other authors and ourselves have shown it to be methyleptenon, propylisobutylchetone, etc.

Throughout this paper we shall frequently refer to the zoological systematics summarized in Tables 1-4. When I refer to the Myriapoda group I intend the entire Pauropoda, Diplopoda, Chilopoda and Symphila.

Chap. 4 - Acknowledgments.

My interest in the studies on insect defensive secretions goes back to 1947 when I discovered and isolated iridomyrmecin. Since than - as we have seen - various other new natural substances are derived from the development of my researches. These have been carried out contemporarily as activity of the Istituto di Anatomia Comparata dell'Università di Pavia, directed by Prof. M. Vialli, and of the Istituto di Entomologia Agraria dell'Università di Pavia, of which I am the Director. In the course of these researches, which are still being developed, I have had invaluable collaborators from the University of Pavia and other italian and foreign universities. I found the help of my assistants in the Institute under my direction to be precious: Dr. A. Baggini, Dr. A. Gabba, Dr. M. Valcurone. I should particularly like to mention my colleagues prof. G. Bo, A. Nascimbene and E. Testori, for their kind collaboration during the first years of research. The Italian Company (Soc. Montecatini, Soc. Montedison, Soc. Farmitalia) and the Consiglio Nazionale delle Ricerche have furnished me with basic equipment.

The Muséum National d'Histoire Naturelle of Paris helped me in faciliting my stay at the Station Experimentale de La Maboké (Boukoko, Republique Centrafricaine); the Institut National pour l'étude Agronomique du Congo (Kinshasa) allowed me to carry out profitable study in the laboratories of Yangambi (Kisangani); the Universidad Central de Venezuela, granted me a sojourn at the laboratories of the Facultad de Agronomia de Maracay at Rancho Grande.

Particular importance must be given to the aid received from European Research Office of the United States Government, which allowed me to make invaluable progress.

Important studies have been devoted to the materials deriving from my researches at the Laboratorio medico-micrografico della Provincia di Pavia, directed by prof. L. Bianchi, and at the following Institutes and University Faculties:

- Istituto di Chimica del Politecnico di Milano, directed by prof. A. Quilico.
- Istituto di Chimica Industriale dell'Università di Milano, directed by prof. R. Fusco.
- Cattedra di Chimica del Politecnico di Milano, directed by prof. C. Cardani.
- Istituto di Chimica dell'Università di Sassari, directed by prof. R. Trave.
- Istituto di Chimica Organica dell'Università di Pavia, directed by prof. P. Grünanger.
- Cattedra di Chimica Biologica dell'Università di Pavia, directed by prof. A. Castellani.
- Istituto di Farmacologia dell'Università di Bari, and then Parma, directed by prof. V. Erspamer.
- Istituto di Microbiologia dell'Università di Milano, directed by prof. R. Deotto.
- Istituto di Patologia e Clinica Medica Veterinaria dell'Università di Parma, directed by prof. I. Vaccari.

PART II - ARTHROPODA: PRODUCERS OF DEFENSIVE SECRETIONS AS CONSIDERED IN THE WHOLE OF THE ANIMAL KINGDOM.

Chap. 5 - Arthropoda: producers of secretions in the animal kingdom.

In the Animal Kingdom 1.200.000 species have hitherto been counted and systematically described, distributed into 22 Types.

The Type Arthropoda is the most numerous with about 884.944 species described, distributed into 12 Classes:

1. Onychophora		73 species	7. Crustacea	25.000 species
2. Pauropoda	Myriapoda	50 "	8. Merostomata	5 "
3. Diplopoda	Myriapoda	7.000 "	9. Arachnida	33.873 "
4. Chilopoda	Myriapoda	2.350 "	10. Pycnogonida	440 "
5. Symphila	Myriapoda	50 "	11. Pentastomida	60 "
6. Insecta		815.763 "	12. Tardigrada	280 "

According to present evaluation, it is presumed that the number of existing Arthropoda species, not yet scientifically described, may be 5-10 times greater than those known at present.

Of this number of species of the Arthropoda Type, less than 10% of those described may be considered producers of defensive secretions, which means at least 82.538 species.

Literature data available show that hitherto chemical definition of certain defensive secretion components has been made for only 426 species of Arthropoda. Naturally, on the other hand, there is a very large number of species which have been ascertained as producers of defensive substances, but about which we have no definite chemical data.

In Table 1 the quantitative data of the species presumed to produce defensive secretions have been comparatively summarized, and also of those for which there are precise chemical data of the secretion components themselves.

Table 1 - Species of Arthropoda described (2), species presumably producers of defensive secretions (3) and species with chemically known secretion components (4).

1. Type ARTHROPODA	2. presumed no. of species described	3. presumed no. of species producing defensive secretions	4. no. of species with known chemically defined defensive secretions
Classes			
1. Onychophora	73		
2. Pauropoda (Myriapoda)	50	8.000 (Myriapoda)	
3. Diplopoda (Myriapoda)	7.000		43
4. Chilopoda (Myriapoda)	2.350		2
5. Symphila (Myriapoda)	50		
6. Insecta	815.763	50.000	342
7. Crustacea	25.000	1.000	2
8. Merostomata	5		
9. Arachnida	33.873	23.538	37
10. Pycnogonida	440		
11. Pentastomida	60		
12. Tardigrada	280		
Totali	884.944	82.538	426

From the ecological point of view, the 884.944 species of *Arthropoda* hitherto known are arrangeable in *land species* and *water species*. To be precise these are:

- *land*: *Onychophora*, *Tardigrada*, *Myriapoda*, *Arachnida* (with the exception of a few limnobius species of *Araneae* and *Acara*), part of *Crustacea Isopoda*, most the *Insecta* (with the exception of a few thousands of *Coleoptera* and *Heteroptera*): in all at least 860.000 species;
- *water* (marine or limnobius): almost all the *Crustacea* (with the exception of some *Isopoda*) *Pycnogonida*, *Pentatomida*, *Merostomata* and a few thousands species of *Insecta* (especially *Coleoptera* and *Heteroptera*): in all about 25.000 species.

The species of *Arthropoda* whose poisonous substances are chemically known, belong mostly to the land species (*Insecta*, *Myriapoda*, *Arachnida*). Of the water species only five species belonging to *Coleoptera Dytiscidae* have chemically defined defensive substances.

PART III - THE DEVELOPMENT OF CHEMICAL RESEARCHES ON THE DEFENSIVE SECRETIONS OF VARIOUS ARTHROPODA GROUPS.

Chemical research of Arthropoda defensive secretions has taken differing developments according to the various groups. This is in relation to varying frequency of interesting species in various groups, to the degree of importance of defensive phenomena, to the varying possibilities of procuring species for researches. The lines these surveys took are summarized in the following chapters.

Chap. 6 - Chemical research on Diplopoda and Chilopoda poisons.

The Onychophora and Pauropoda are small land animals which are not generally considered to produce poisonous substances.

The Diplopoda (Chap. 10) include, the order of Glomerida of which only four species have been chemically studied. Presumably all Glomerida possess active poisonous organs, as certainly do the various European species of the Glomeris genus which we have examined. Polydesmida produce interesting defensive substances which have hitherto been studied in American, African and European species. During our orientative researches of European and African fauna, we have determined at least fifty species producing defensive secretions. Research was carried out as far as defining the venom components of three of these species (Polydesmus collaris collaris Koch, Gomphodesmus pavani Dem., Orthomorpha coarctata Sauss.). Presumably 6.500 species of Diplopoda produce defensive substances.

The group of Juliformia (Chap. 10) which include the Orders Julida, Spirobolida, Spirostreptida and Cambalida, has at least 2.000 species which may practically be numbered among the producers of defensive venoms. From studies carried out hitherto on 26 species it appears that the defensive secretions are mostly composed of quinones. Full research defining the various components was carried out on one of these species (Archiulus (Schizophyllum)sabulosus L.). We have also ascertained the production of quinonic poisons in 40 species of European, American and African fauna.

Chilopoda (Chap. 10) of which about 2.350 species are known, partially produce poisonous substances which they inject into their prey by biting. The sting of numerous species is also feared by man due to the local effects it produces. The chemistry of such poisons in two species has been studied but research appears to be not yet complete.

Chap. 7 - Chemical research on Insecta poisons.

Of the 31 Orders into which the Insecta are divided (comprising 815.763 species described), the chemical composition of defensive secretions has been studied in 10 Orders, in all 342 species. The Orders in which research has been more profound are: Coleoptera (146 species), Hymenoptera (96 species), Heteroptera (44 species).

Of about the 300.000 species of Coleoptera known, 146 (Chap. 14) have been studied up to date. It is estimated that at least 10.000 species produce defensive substances. Of these we may mention certain of the Staphylinidae (in which, from various species of the genus Paederus, pederin, pseudopederin, pederone have been extracted), as well as Carabidae, Tenebrionidae, and Meloidae which, in this order, have hitherto furnished most of the known data on defensive secretions.

Heteroptera (Chap. 12) comprising 31.000 known species, offer many interesting aspects: in fact, besides the adults with various types of glands producing defensive substances, also the younger forms produce defensive venoms in many species. Reduviidae, too, produce poisonous substances to be injected into their prey by means of the oral apparatus, substances which have been studied as far as the definition of some components only in one case (Platymeris). Also Corixoidea produce poisonous substances injected into the prey by means of the oral apparatus, but these have not yet been studied.

Heteroptera species probably producing toxin secretions, are 26.000.

Hitherto data have been collected from 44 species of Heteroptera permitting us to chemically identify certain components of the defensive secretions.

In the order of Hymenoptera 96 species have been studied out of 200.000 known (Chap. 15); most of these are Formicidae. The venom of Apidae has been studied (especially of Apis mellifera), but presents certain important aspects not yet clarified. Few precise chemical data are known about Vespidae venoms, which are also extremely interesting. The number of species which probably produce poisonous secretions is estimated to be 10.000.

Chap. 8 - Chemical research on Crustacea Isopoda poisons.

The Class of Crustacea (Chap. 16) with 25.000 species described, almost totally water species, includes only two land species of the Isopoda order, whose defensive secretions have been studied. The Isopoda comprise 4.000 species of which numerous land species (perhaps 1.000) producing defensive substances with a complex structure. The defensive secretions of the water species, both lymnobious and marine, are not known.

Chap. 9 - Chemical research on Arachnida poisons.

The Arachnida class (Chap. 17) comprising about 34.000 described species, mostly land dwelles (with the exception of a few Araneae species and part of the Acari), includes at least 23.000 species which are presumably producers of poisonous substances. The two orders with the most interesting venoms are Scorpiones (600 species) and Araneae (20.000 species). The number of species hitherto studied is small compared with such vast quantity of material available (37 in all, mainly Scorpiones and Araneae) and precise chemical data on the composition of their venoms are scarce. This is due to the difficulties inherent in the proteic nature of the toxic principles present in the venoms. The study of Arachnida venoms is also interesting from a practical point of view because of the numerous and occasionally serious cases of poisoning in man caused by the sting of Scorpiones and Araneae.

Table 2 - Number of Arthropoda Onychophora and Myriapoda (Pauropoda, Diplopoda, Chilopoda, Symphila) species described (2.), of the species presumed to produce defensive secretions (3.), and of the species producing chemically defined defensive substances (4.).

1. Type A R T H R O P O D A	2. presumed no. of species described	3. presumed no. of species producing defensive secretions	4. no. of species with known chemically defined defensive secretions
Cl. ONYCHOPHORA...........	73		
(M Y R I A P O D A)....	(9.450)	(7.550)	(45)
Cl. PAUROPODA.............	50	0	
Cl. DIPLOPODA.............	7.000	6.500	43
Ord. Polyxenida			
Glomerida	500	500	4
Glomeridesmida			
Chordeumida			1
Polydesmida	2.500	2.500	12
Juliformia: Julida			4
Juliformia: Spirobolida			9
Juliformia: Spirostreptida	2.000 (Julida–Cambalida)	2.000 (Julida–Cambalida)	12
Juliformia: Cambalida			1
Sup.Ord. Colobognatha			
Cl. CHILOPODA	2.350	1.000	2
Ord. Geophilomorpha			
Scolopendromorpha	420		2
Lithobiomorpha			
Scutigeromorpha			
Cl. SYMPHILA	50	50	

Table 3 - Number of Insecta species described (2.), of the species presumed to produce defensive secretions (3.), and of the species producing chemically defined defensive substances (4.).

1. Type ARTHROPODA Class INSECTA	2. presumed no. of species described	3. presumed no. of species producing defensive secretions	4. no. of species with known chemically defined defensive secretions
Ord. 1. Collembola	2.000		
2. Protura	90		
3. Diplura	380		
4. Thysanura	350		
5. Ephemeroptera	1.500		
6. Odonata	4.870		
7. Blattodea	2.500	100	15
8. Mantodea	1.800		
9. Isoptera	2.000	150	4
10. Zoraptera	19		
11. Plecoptera	1.490		
12. Embioptera	149		
13. Grylloblattodea	5		
14. Dermaptera	1.100	150	1
15. Phasmida	2.000	100	1
16. Orthoptera	15.000	500	1
17. Psocoptera	1.000		
18. Mallophaga	2.675		
19. Siphunculata	400		
20. Thysanoptera	3.170		
21. Heteroptera	31.000	26.000	44
22. Homoptera	26.500		
23. Neuroptera	4.670		
24. Mecoptera	350		
25. Trichoptera	4.470		
26. Lepidoptera	120.000	2.000	28
27. Diptera	85.000	1.000	6
28. Siphonaptera	1.100		
29. Coleoptera	300.000	10.000	146
30. Strepsiptera	175		
31. Hymenoptera	200.000	10.000	96
Class INSECTA	815.763	50.000	342

Table 4 - Number of Crustacea, Merostomata, Arachnida, Pycnogonida, Pentastomida species described (2.), of the species presumed to produce defensive secretions (3.), and of the species producing chemically defined defensive substances (4.).

1. Type A R T H R O P O D A	2. presumed no. of species described	3. presumed no. of species producing defensive secretions	4. no. of species with known chemically defined defensive secretions
Cl. CRUSTACEA (*)........ (35 Orders)	25.000	1.000	2
Ord. Isopoda...........	4.000	1.000	2
Cl. MEROSTOMATA..........	5		
Cl. ARACHNIDA............	33.873	23.538	37
Ord. Scorpiones........	600	600	16
Pseudoscorpiones	1.000	500	
Pedipalpi: Uropygi...........	98	98	1
Pedipalpi: Amblypigi.........	60		
Pedipalpi: Palpigradi........	20		
Ricinulei.........	15		
Solifugae.........	600		
Opiliones.........	2.340	2.340	1
Araneae...........	20.000	20.000	19
Acari.............	9.140		
Cl. PYCNOGONIDA..........	440		
Cl. PENTASTOMIDA.........	60		
Cl. TARDIGRADA...........	280		

(*) A list of the Crustacea Order, mostly formed by water animals (marine or lymnobius) for which there are no known defensive venoms, is omitted with the exception of the Order Isopoda.

PART IV - THE ARTHROPODA SPECIES PRODUCERS OF DEFENSIVE SECRETIONS AND CHEMICALLY DEFINED SUBSTANCES.

In Chapters 10-17 I have given a list of the Orders and the Families systematically arranged and, in alphabetical order, the species of Arthropoda producing defensive secretions with one or more chemically known components. The indication of known products is followed by the number or numbers corresponding to the publications listed in Part VIII, Bibliography.

Cap. 10 - Myriapoda Diplopoda and Chilopoda and chemically defined substances of defensive secretions.

(M Y R I A P O D A)

Cl. D I P L O P O D A

Ord. GLOMERIDA

Fam. Glomeridae

Glomeris marginata Vill.

glomerin: 315, 317; glomerin and omoglomerin: 191, 302, 316.

Glomeris conspersa Koch

glomerin, omoglomerin: 302.

Glomeris hexasticha Brandt

glomerin, omoglomerin: 302.

Loboglomeris rugifera Verh.

glomerin: 302.

Ord. CHORDEUMIDA

Fam. Chordeumidae

Abacion magnum Loomis

p-cresol (= p-methyl-phenol): 107, 348B, 363; phenol: 103, 106.

- IV 2 -

Ord. POLYDESMIDA

Fam. Strongilosomidae

Orthomorpha coarctata Sauss (= O. coarctata Sch.)

benzaldehyde, phenol, guaiacol, hydrocyanic acid, benzoic acid: 199.

Orthomorpha gracilis Koch (= Fontaria gracilis Koch, Paradesmus (Fontaria) gracilis Koch, Oxydus gracilis Koch)

hydrocyanic acid: 50, 93, 104, 140, 157, 179, 199, 348 B, 349, 363; benzaldehyde, hydrocyanic acid: 50, 125, 180, 265, 354.

Fam. Eurydesmidae

Apheloria corrugata Wood

hydrocyanic acid, benzaldehyde: 50, 348 B; benzaldehyde, hydrocyanic acid, mandelonitrile: 104, 105, 108, 118, 157, 363; hydrocyanic acid: 278.

Cherokia georgiana Bollman

hydrocyanic acid: 50, 104, 157, 348 B.

Leptodesmus haydenianus Wood

hydrocyanic acid: 77.

Nannaria sp.

hydrocyanic acid: 50, 104, 157, 278, 348 B.

Pachydesmus crassicutis (Wood)

β-glucosidase + cyanogenic glucoside ⟶ hydrocyanic acid, benzaldehyde, glucose, a disaccharide: 32, 363, 363; hydrocyanic acid, benzaldehyde, sugars: 50.

Rhysodesmus vicinus Sauss. (= Polydesmus vicinus Sauss., Polydesmus (Fontaria) vicinus Sauss.)

glucoside of p-isopropil mandelic nitrile ⟶ hydrocyanic acid, glucose, cuminaldehyde: 32, 104, 218, 363; hydrocyanic acid, glucoside of p-isopropil mandelic nitrile: 50; hydrocyanic acid, cuminaldehyde: 348 B.

Fam. Polydesmidae

Gomphodesmus pavani Dem.

D-(+)-mandelic nitrile, benzoic acid, benzaldehyde, hydrocyanic acid, mandelonitrile benzoate: 7.

Polydesmus virginiensis Drury (= Polydesmus (Fontaria) virginiensis Drury, Fontaria virginiensis Drury)

hydrocyanic acid: 61, 179, 180, 195, 199, 265, 354, 363.

Polydesmus collaris collaris Koch

mandelonitrile benzoate, benzaldehyde, hydrocyanic acid: 50, 157, 363, benzoic acid, hydrocyanic acid, benzaldehyde, mandelonitrile benzoate: 4 A; benzaldehyde, hydrocyanic acid: 348 B.

Pseudopolydesmus serratus (Say)

hydrocyanic acid, undeterminated components in a mixture: 278, hydrocyanic acid: 50, 104, 157, 348 B, 363.

(JULIFORMIA)

Ord. JULIDA

Archiulus (Schizophyllum) sabulosus L. (= Archiulus sabulosus L., Schizophyllum sabulosum L.)

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 9, 198, 199, 245, 246, 248, 278, 310, 348 B, 355, 363; 1,4-benzoquinone, quinones and their methyl derivatives: 199, 2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone, 2-methyl-hydroquinone, 2-methyl-3-methoxy-hydroquinone: 157, 301.

Brachyulus unilineatus Koch

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 157, 293, 299, 310, 348 B;

Cylindroiulus teutonicus Pocock

2-methyl-1,4-benzoquinone, 2-metil-3-methoxy-1,4-benzoquonone: 157, 293, 299, 310, 348 B.

Schizophyllum mediterraneum (= *Julus terrestris* L.)

1,4-benzoquinone: 10, 13, 41, 50, 125, 177, 179, 201, 245, 246, 263, 265, 276, 278, 310, 333 B, 335, 348 B, 363, 1,4-benzoquinone, other quinones and their methyl derivatives: 199.

Ord. SPIROBOLIDA

Chicobolus spinigerus Wood

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 50, 157, 198, 278, 348 B, 363.

Floridobolus penneri Causey

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4+benzoquinone: 50, 157, 198, 278, 348 B, 363.

Narceus annularis Raf.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4+benzoquinone: 50, 175, 198, 278, 348 B, 363.

Narceus gordanus Chamb.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4+benzoquinone: 50, 175, 198, 278, 348 B, 363.

Orthocricus arboreus (Sauss.)

quinones: 363.

Pachybolus laminatus Cook

1,4-benzoquinone, other quinones and their methyl derivatives: 199; 2-methyl-1,4-benzoquinone: 8, 10, 15, 50, 245, 246, 278, 310, 335, 348 B, 363.

Rhinocricus sp.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 157, 293, 299, 310; 2-methyl-hydroquinone, 2-methyl-3-methoxy-hydroquinone: 294.

Rhinocricus insulatus (Chamberlin)

trans-2-dodecenal, 2-methyl-1,4-benzoquinone: 157, 348 B, 355, 363.

Trigonoiulus lumbricinus Gerst.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 50, 157, 198, 278, 348 B, 363.

Ord. SPIROSTREPTIDA

Aulonopygus aculeatus Attems

2-methyl-1,4-benzoquinone: 8.

Aulonopygus aculeatus barbieri

2-methyl-1,4-benzoquinone: 8.

Doratogonus annulipes Carl

2-methyl-1,4-benzoquinone, 3-methoxy-2-methyl-1,4-benzoquinone: 106, 348 B.

Orthoporus conifer (Attems)

3-methoxy-2-methyl-1,4-benzoquinone: 106, 348 B.

Orthoporus flavior Chamberlin e Mulaik

2-methyl-1,4-benzoquinone, 3-methoxy-2-methyl-1,4-benzoquinone: 106, 348 B.

Orthoporus punctilliger Chamberlin

2-methyl-1,4-benzoquinone, 3-methoxy-2-methyl-1,4-benzoquinone: 106, 348 B.

Spirostreptus sp.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 293.

Spirostreptus castaneus Attems

1,4-benzoquinone, other quinones and their methyl derivatives: 199; 1,4-benzoquinone: 8, 10, 50, 106, 245, 246, 278, 310, 333B, 335, 348 B, 363.

Spirostreptus multisulcatus Dem.

2-methyl-1,4-benzoquinone: 8.

Spirostreptus virgator Silv.

2-methyl-1,4-benzoquinone: 8, 106, 348 B; 1,4-benzoquinone, o ther qui,ones and their methyl derivatives: 10, 50, 199, 245, 278, 310, 355, 363.

Fam. Odontopygidae

Peridontopyge aberrans Attems

2-methyl-1,4-benzoquinone: 8

Peridontopyge vachoni

2-methyl-1,4+benzoquinone: 8

Ord. CAMBALIDA

Cambala hubrichti Hoffman

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 106, 348 B.

Cl. C H I L O P O D A

Ord. SCOLOPENDROMORPHA

Ethmostigmus spinosus (*)

lysins, anti-coagulin, diastase, invertase, proteolytic enzymes: 78.

Scolopendra viridicornis Newport

5-hydroxytryptamine: 352, 353.

(*) Salivary glands and the third pair of glands mixed with a minimum of fat body and pigmented body: 78.

Chap. 11 - Insecta Blattodea, Isoptera, Dermaptera, Phasmida, Orthoptera and chemically defined substances of defensive secretions.

Ord. BLATTODEA (= DYCTIOPTERA)

Fam. Diplopteridae

Diploptera punctata (Eschscholtz)

glucoside which contains benzoquinone + β-glucosidase ⟶ p.benzoquiiones: 19, 32, 133, 325; 1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, undeterminated components in a mixture: 278; 1,4-benzoquinone and two derivatives: 99, 109; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 33, 80, 133, 245, 246, 333 B, 335, 348 A, 348 B; quinones: 134, 355 B.

Fam. Blattidae

Cutulia sororor (Brunner)

trans-hex-2-enal: 70, 83 A, 278, 348 A, 348 B.

Eurycotis biolleyi Rehn

water, D-gluconic acid, γ-gluconolactone, δ-gluconolactone, 2-hexenal: 83 A.

Eurycotis decipiens (Kirby)

D-gluconic acid, 2-hexenal, water, γ-gluconolactone, δ-gluconolactone: 83, 83 A, 348 A.

Eurycotis floridana Walk.

trans-hex-2-enal: 15, 18, 19, 24, 28, 44, 80, 109, 111, 131, 133, 156, 163, 220, 247, 277, 278, 280, 347, 348 A, 348 B; D-gluconic acid, 2-hexenal: 83 A.

Pelmatosilpha coriacea Rehn

trans-hex-2-enal: 19, 83 A, 157, 348 A, 348 B.

Platyzosteria armata Tepper

unbranched unsaturated aldehyds: 348 A.

Platyzosteria castanea Brunner

2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (traces), 2-methylene pentanal (traces), 2-methyl butanol, 2-methylene butyric acid: 348 A.

Platyzosteria coolgardiensis Tepper

unbranched insaturated aldehyds: 348 A.

Platyzosteria jungii (Tepper)

2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (traces), 2-methylene pentanal (traces), 2-methyl butanol, 2-methylene butyric acid: 348 A.

Platyzosteria morosa Shelford

2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (traces), 2-methylene pentanal (traces), 2-methyl butanol, 2-methylene butyric acid: 348 A.

Platyzosteria novae seelandiae Brunner

trans-hex-2-enal, undeterminated compounds in a mixture: 278; trans-hex-2-enal: 348 A, 348 B.

Platyzosteria ruficeps Shelford

2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (traces), 2-methylene pentanal (traces), 2-methyl butanol, 2-methylene butyric acid: 348 A.

Platyzosteria scabra Brunner

unbranched unsaturated aldehydes: 348 A.

Platyzosteria scabrella Tepper

unbranched unsaturated aldehydes: 348 A.

Ord. ISOPTERA

Fam. Termitidae

Nasutitermes sp. (soldiers)

24-methylene cholesterol: 292; α-pinene, β-pinene: 134, 358.

Nasutitermes hexitiosus (Hill)

α-pinene, β-pinene and/or other monoterpenoid hydrocarbons: 200, 348 B.

Nasutitermes graveolus (Hill)

α-pinene, β-pinene and/or other monoterpenoid hydrocarbons: 200, 348 B.

Nasutitermes walkeri (Hill)

α-pinene, β-pinene and/or other monoterpenoid hydrocarbons: 200, 348 B.

Ord. DERMAPTERA

Fam. Forficulidae

Forficula auricularia L.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 100, 138, 278, 307, 348 B; 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, hydroquinones: 299; 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 2-methyl-hydroquinone, 2-ethyl-hydroquinone: 157, 301.

Ord. PHASMIDA

Fam. Pseudophasmidae

Anisomorpha buprestoides (Stoll)

anisomorphal: 66, 101, 111, 157, 187, 189, 348 B, 67 C, 274 A.
(anisomorphal = dolichodial)

Ord. ORTHOPTERA

Fam. Acrididae

Poekilocerus bufonius Klug

histamine: 282; histamine, digitalis-like compound: 111, 221; histamine, calotropin, calactin: 118, 283.

Chap. 12 - Insecta Heteroptera and chemically defined substances of defensive secretions.

Ord. HETEROPTERA

Fam. Corixidae

Corixa dentipes Thoms

4-keto-trans-hex-2-enal: 4 A, 266.

Sigara falleni (Fieb)

4-keto-trans-hex-2-enal: 4 A, 157, 266, 348 B.

Fam. Belostomatidae

Lethocerus indicus Lep.

trans-hex-2-enyl-butyrrate: 4 A, 92; trans-hex-2-enyl-acetate: 4 A, 24, 44, 80, 156, 220, 266, 278.

Fam. Reduviidae

Platymeris rhadamanthus Gaerst.

six, eight proteins, three proteolytic fractions: alkaline endopeptidase, hyaluronidase, protease, phospholipase: 97; six protein fractions: three with trypsin-like proteolytic activity, one with strong hyaluronidase activity and one with weak phospholipase activity, histamine ?, neurotoxic activity: 11, 96, 111, 278.

Cimex lectularius L.

trans-hex-2-enal, trans-oct-2-enal: 4 A, 299; hyaluronidase, histamine: 193; hyaluronidase, histamine and substance wich contracts muscle: 11, 163.

Fam. Coreidae

Acanthocephala femorata Fabr.

trans-hex-2-enal: 4 A, 24, 80, 157, 348 B.

Acanthocoris sordidus (Thunberg)

trans-hex-2-enal, n-hexanal, unidentified carbonyl compound: 4 A, 364.

Agriopocoris froggatti Miller

acetic acid (trace), n-hexanal (°), n-hexanol, n-hexyl-acetate:

4 A: 348; n-hexanal: 348 B.

(c) In one sample of aged bugs the scent consisted entirely of hexanal.

Amorbus alternatus Dallas

acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348, n-hexanal: 348 B.

Amorbus rhombifer (§) Westwood

acetic acid,(*) n-hexanal, n-hexanol, n-butyl butyrate, n-hexyl acetate: 4 A; 348; n-hexanale: 348 B.

(§) One sample contained a compound believed to be butyric acid: 348.

(*) This fraction from the gas chromatograph contained a high concentration of n-butanal: 348.

Amorbus rubiginosus Guérin

n-hexanal, undeterminated compounds in a mixture: 278; n-hexanal : 347, 348 B; acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348.

Aulacosternum nigrorubrum Dallas

acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348; n-hexanal: 348 B.

Hygia opaca (Uhler)

n-hexanal: 4 A, 364.

Leptocoris apicalis Westw.

trans-oct-2-enal, trans-dec-2-enal,n-octyl acetate: 4 A.

Mictis caja Stål.

acetic acid, n-hexanal, n-hexanol, n-butyl butirate, n-hexyl acetate: 4 A, 348; n-hexanal: 348 B.

Mictis profana Fabr.

n-hexanal, undeterminated compounds in a mixture: 278; acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348; n-hexanal: 347, 348 B.

Pachycolpura manca Breddin

acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348; n-hexanal: 348 B.

Plinachtus bicoloripes Scott

n-hexanal: 4 A, 364.

Riptortus clavatus (Thunberg)

n-butanal: 4 A, 364.

Fam. Hyocephalidae

Hyocephalus sp.

acetic acid (trace), n-hexanal, n-hexanol, n-hexyl acetate (traces?): 4 A, 348; n-hexanal: 348 B.

Fam. Pentatomidae

Aelia fieberi Scott

trans-dec-2-enal, trans-oct-2-enal: 4 A, 364.

Biprorulus bibax

n-tridecane, n-dodecane, trans-dec-2-enal, trans-dec-2-henyl acetate: 4 A, 132, 220.

Brachymena quadripustulata Fabr.

trans-hex-2-enal: 4 A, 18, 132, 278, 348 B.

Carpocoris purpureipennis (De Geer)

n-tridecane: 4 A, 274.

Dolychoris baccarum L.

trans-hex-2-enal, trans-oct-2-enal, trans-dec-2-enal, two carbonyl products (20% + 2%): 4 A, 132, 157, 294, 299, 314; trans-hex-2-enal, trans-oct-2-enal, trans-dec-2-enal: 348 B.

Eurygaster sp.

trans-hex-2-enal, trans-oct-2-enal, 20% of undeterminated carbonyl compounds: 4 A, 132, 299.

Euschistus servus Say

According to Blum e Traynham, 1960, the gross chemistry of the secretion from scent glands is very similar to that of Oebalus pugnax (F.).

Graphosoma rubrolineatum (Westwood)

trans-dec-2-enal, n-hexanal: 4 A, 364.

Menida Scotti (Puton)

trans-dec-2-enal, unidentified carbonyl compound: 4 A, 364.

Musgraveia sulciventris Stål

n-tridecane, n-dodecane, trans-oct-2-enal, trans-dec-2-enal, trans-hex-2-enal (traces), trans-oct-2-enyl acetate, three very minor constituents: 132.

Nezara antennata Scott

trans-dec-2-enal: 4 A, 364.

Nezara viridula L.

4-keto-hex-2-enal: 134; trans-dec-2-enal, unidentified carbonyl compound: 4 A, 364; according to Blum and Traynham, 1960, the gross chemistry of the secretion from scent glands is very similar to that of Oebalus pugnax (F.); trans-hex-2-enal, trans-hept-2-enal, trans-dec-2-enal; 4-keto-trans-hex-2-enal, n-tridecane: 348 B.

Nezara viridula L. var. smaragdula F.

trans-hex-2-enal, trans-dec-2-enal, one dicarbonyl compound, tridecane: 4 A, 132, 347; propanal, trans-but-2-enal, methyl-ethyl-ketone, ethyl-propyl-ketone, 4-keto-hex-2-ene, trans-hex-2-enal, 4-keto-trans-hex-2-enal, trans-hex-2-enyl acetate, trans-oct-2-enal, methyl-heptyl-ketone (traces), n-undecane, 4- keto-trans-oct-2-enal, trans-oct-2-enyl acetate, n-dodecane, trans-dec-2-enal, cis-dec-2-enal (traces), n-tridecane, trans-dec-2-enyl acetate: 4 A, 132; trans-hex-2-enal, dec-2-enal, tridecane, undeterminated compounds in a mixture: 278; thirteen volatile components including: n-dodecane (n-tridecane), n-dec-2-enal, trans-hex-2-enal, an α-β dicarbonyl compound: 4 A, 132, 135.

Oebalus pugnax F.

trans-hept-2-enal, n-tridecane, six components including: an unsaturated dicarbonyl, a monocarbonyl, an alcohol,an acid: 4 A, 27, 132; n-tridecane, trans-hept-2-enal, dicarbonyl compound: 4 A, 13, 28, 132; 2-heptenal, n-tridecane: 80; trans-hept-2-enal, n-tridecane, undeterminated components in a mixture: 278.

<u>Palomena viridissima</u> P.

<u>trans</u>-hex-2-enal, <u>trans</u>-oct-2-enal, <u>trans</u>-dec-2-enal, unknown carbonyl compounds: 4 A, 132, 299.

<u>Poecilometis strigatus</u> Westw.

<u>trans</u>-hex-2-enal, <u>trans</u>-oct-2-enal, a dicarbonyl compound: 4 A, 132, 347; <u>trans</u>-hex-2-enal, 2-octenal, undeterminated components in a mixture: 278; <u>trans</u>-hex-2-enal, <u>trans</u>-oct-2-enal: 348 B.

<u>Rhoecocoris sulciventris</u> Stål

<u>trans</u>-hex-2-enal, <u>trans</u>-oct-2-enal, a dicarbonyl compound, <u>n</u>-tridecane: 4 A, 347; <u>n</u>-tridecane, <u>trans</u>-oct-2-enal, <u>trans</u>-oct-2-enyl acetate, <u>n</u>-dodecane, <u>trans</u>-dec-2-enal, <u>trans</u>-hex-2-enal (traces), three very minor constituents: 4 A, 220; <u>trans</u>-hex-2-enal, 2-octenal, <u>n</u>-tridecane, undeterminated components in a mixture: 278; <u>trans</u>-hex-2-enal, <u>trans</u>-oct-2-enal: 348 B.

<u>Tessaratoma aethiops</u> Dist.

adults: <u>trans</u>-hex-2-enal, <u>trans</u>-oct-2-enal, 4-keto-<u>trans</u>-hex-2-enal, <u>trans</u>-oct-2-enyl-acetate, <u>n</u>-tridecane: 4 A.

larvae: <u>trans</u>-oct-2-enal, 4-keto-<u>trans</u>-hex-2-enal, <u>n</u>-tridecane: 4 A.

<u>Scotinophara lurida</u> Burmeister

<u>trans</u>-dec-2-enal, <u>trans</u>-oct-2-enal, <u>trans</u>-hex-2-enal, unidentified carbonyl compound: 4 A, 364.

Fam. <u>Plataspidae</u>

<u>Ceratocoris cephalicus</u> Mont.

<u>n</u>-tridecane: 4 A.

Fam. <u>Cydnidae</u>

<u>Macroscytus</u> sp.

4-keto-<u>trans</u>-hex-2-enal, <u>trans</u>-oct-2-enyl acetate, <u>trans</u>-dec-2-enyl acetate, <u>n</u>-dodecane, <u>n</u>-tridecane: 4 A.

<u>Scaptocoris divergens</u> Froeschner

propenal, propanal, <u>trans</u>-but-2-enal, <u>trans</u>-hex-2-enal, pentenal, <u>trans</u>-hept-2-enal, <u>trans</u>-oct-2-enal, furan, methyl-furan, 2-me thyl-1,4-benzoquinone, unidentified quinone: 4 A, 132, 157, 277; trans-hex-2-enal, trans-hept-2-enal, trans-oct-2-enal: 348 B.

Cap. 13 - Insecta Lepidoptera and Diptera and chemically defined substances of defensive secretions.

Ord. LEPIDOPTERA

Fam. Cossidae

Cossus cossus L.

cossin A, cossin B, cossin C: 248, 250, 396, 338; cossin 1, cossin 2, cossin 3, cossin A, cossin B, cossin C, cossin B_1, cossin C_1: 334.

Zeuzera pyrina L.

zeuzerina:

Fam. Anthroceridae

Procris geryon (Hueb)

hydrocyanic acid: 161.

Zygaena filipendulae (L.)

hydrocyanic acid: 161; acetylcholine: 321 B.

Zygaena lonicerae (von Sch.)

histamine: 124, 161; hydrocyanic acid: 161; acetylcholine: 321 B.

Fam. Pyralidae

Eurrhypara hostulata L.

histamine: 124.

Fam. Geometridae

Abraxas grossulariata (L.)

histamine: 124.

Fam. Notodontidae

Cerura vinula L. (= Dicranura vinula L.)

larvae: formic acid, undeterminated components in a mixture: 278; larvae: formic acid: 36, 91, 125, 137, 172, 180, 193, 217, 245, 263, 341, 348 B, 355 B; larvae: acetic acid, formic acid, methacrylic acid, tiglic acid: 134; larvae: formic acid, aminoacids: 303.

Datana ministra

larvae: formic acid: 149.

Dicranura furcula

larvae: formic acid: 180.

Schizura concinna (Abb. e Smith) (= Notodonta concinna Abb. e Smith)

larvae: hydrochloric acid: 36, 90, 91, 193, 245, 341; formic acid: 149.

Schizura leptinoides Grote

formic acid: 278, 348 B.

Fam. Lymantriidae

Euproctis flava Brem.

hairs: histamine or histamine-like substances, pharmacologically active proteins: 163.

Porthesia sp.

hairs: formic acid, organic base, enzyme (probably): 125.

Fam. Arctiidae

Arctia caja L.

imago: choline ester, non dyalizable heat-labile toxic substance: 16; choline ester (β,β-dimethylacrylyl-choline): 17, 278, 281, 283, 355 B; choline ester (β,β-dimethylacrylyc-choline), histamine (traces): 124; methanol (probably): 281.

Hypocrita jacobaeae L.

histamine: 124.

Spilosoma lubricipeda L.

imago: histamine: 124, 281.

Fam. Thaumetopoeidae

Cnethocampa sp.

hairs: larvae: formic acid: 173.

Thaumetopoea pityocampa Schiff. (Cnetocampa pityocampa)

larvae, hairs: histamine or histamine-like substances, pharmacologically active proteins: 163; larvae, hairs: histamine (probably): 355 B; larvae: formic acid: 263.

Fam. Saturniidae

Automeris sp.

hairs, larvae: 5-hydroxytryptamine: 352.

Automeris (illustris ?)

hairs: 5-hydroxytryptamine: 353.

Dirphia sp.

hairs: histamine: 11, 340; hairs: histamine, pharmacologically active proteins: 163.

Fam. Lasiocampidae

Dendrolimus spectabilis Btlr.

hairs: histamine or histamine-like substances, pharmacologically active proteins: 163.

Dendrolimus undans Walk.

hairs: histamine or histamine-like substances, pharmacologically active proteins: 163.

Fam. Papilionidae

Papilio machaon L.

larvae: isobutyric acid, 2-methylbutyric acid: 110, 111, 348 B.

Fam. Danaidae

Danaus plexippus L.

pupae and adults: digitalis-like toxin: 222; imago tissue: two heart poisons: 283.

Fam. Megalopygidae

Megalopyge sp.

hairs: histamine, pharmacologically active proteins: 163; hairs: histamine: 11, 340.

Megalopyge urens Berg.

hairs: globuline: 117.

Ord. DIPTERA

Fam. Fungivoridae

Ceroplatus sp.

oxalic acid: 80.

Ceroplatus lineatus F.

oxalic acid: 181, 245.

Platyura sp.

oxalic acid: 80.

Platyura discoloria Mg.

oxalic acid: 181, 245.

Platyura fasciata

oxalic acid: 181, 245.

Platyura nigricornis F.

oxalic acid: 181, 245.

Cap. 14 - Insecta Coleoptera and chemically defined substances of defensive secretions.

Ord. COLEOPTERA

Fam. Carabidae

Abax ater Villers

methacrylic acid, tiglic acid: 157, 299, 311.

Abax ovalis Dftsch.

methacrylic acid, tiglic acid: 157, 299, 311.

Abax parallelus Dftsch.

methacrylic acid, tiglic acid: 157, 299, 311.

Acinopus sp.

formic acid: 111, 299, 348 B.

Apotomopterus albr. Esakii Mor.

methacrylic acid, tiglic acid: 299, 311.

Apotomopterus insulicula Chaud.

methacrylic acid, tiglic acid: 157, 299, 311.

Brachynus sp.

nitrogen oxides: 91, 341.

Brachynus crepitans L.

quinones (phenolic precursors + H_2O_2): 108; hydroquinone, 2-me thyl hydroquinone + H_2O_2 ⟶ 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, H_2O + O_2: 8, 9, 39, 80, 98, 133, 156, 245, 246, 278, 290, 298, 335, 348 B, 355 B; nitrogen oxides, nitrous acid: 125.

Brachynus explodens Duft.

hydroquinone, 2-methyl-hydroquinone + H_2O_2 ⟶ 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, H_2O + O_2: 133, 278, 298, 348 B.

Brachynus sclopeta Fabr.

hydroquinone, 2-methyl-hydroquinone + H_2O_2 ⟶ 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, H_2O + O_2: 133, 278, 298, 348 B.

Calathus sp.

formic acid: 111, 299, 348 B.

Calosoma prominens Lec.

salicylaldehyde: 107, 111, 114, 134, 157, 348 B.

Calosoma sycophanta L.

salicylaldehyde, metacrilic acid, tiglic acid: 51, 138.

Carabus sp.

butyric acid: 91, 125, 217, 341.

Carabus auratus L.

metacrilic acid, tiglic acid: 157, 299, 311.

Carabus auronitens Fbr.

metacrilic acid, tiglic acid: 157, 299, 311.

Carabus cancellatus Illig.

metacrilic acid, tiglic acid: 299, 311.

Carabus convexus Fbr.

metacrilic acid, tiglic acid: 157, 299, 311.

Carabus coriaceus L.

metacrilic acid, tiglic acid: 157, 299, 311.

Carabus cyaneus F.

metacrilic acid, tiglic acid: 299, 311.

Carabus granulatus L.

metacrilic acid, tiglic acid: 157, 299, 311.

Carabus irregularis Fbr.

methacrylic acid, tiglic acid: 157, 299, 311.

Carabus procerulus Chaud.

methacrylic acid: 157, 299, 311.

Carabus Ullrichi Germ.

methacrylic acid, tiglic acid: 157, 299, 311.

Carabus violaceus L.

methacrylic acid, tiglic acid: 157, 299, 311.

Carterus sp.

formic acid: 111, 299.

Chlaenius cordicollis Kirby

m-cresol: 107, 111, 348 B.

Cychrus sp.

butyric acid: 217.

Cychrus rostratus Lin.

methacrylic acid: 111, 299, 311.

Damaster oxuroides Schaum

methacrylic acid: 111, 157, 299, 311.

Harpalus dimidiatus Rossi

formic acid: 293, 299.

Pheropsophus africanus Dej.

nitrous acid: 131, 245; nitrous acid or nitrites: 137, 278, 341, 342.

Pheropsophus agnatus

formic acid: 125.

Pheropsophus catoirei Dej.

1,4-benzoquinone, 2-methyl-1,4-benzoquinone: 278, 298, 348 B.

Pseudophonus griseus Panz.

formic acid: 107, 157, 293, 299, 309, 348 B.

Pseudophonus pubescens Müll.

formic acid: 107, 293, 299, 309, 348 B.

Pterostichus metallicus Fbr.

methacrylic acid, tiglic acid: 157, 299, 311.

Pterostichus niger Schall.

methacrylic acid, tiglic acid: 157, 299, 311.

Pterostichus vulgaris L.

methacrylic acid, tiglic acid: 157, 299, 311.

Fam. Dytiscidae

Acilius sulcatus L.

cortexone, cybisterone,6-dihydrocybisterone: 300 A; cortexone, 6-dehydrocortexone, cybisterone,6-dihydrocybisterone, 6-dehydro progesterone: 300 B.

Cybister lateralimarginalis De Geer

p-hydroxybelzaldehyde, methyl-p-hydroxy-benzoate, stile unknown carboxylic acid: 299; cybisterone: 300 A, 305; p-hydroxybenzaldehyde, methyl-p-hydroxy-benzoate: 348 B.

Dytiscus latissimus L.

p-hydroxybenzaldehyde, methyl-p-hydroxy-benzoate, benzoic acid: 299, 348 B.

Dytiscus marginalis L.

benzoic acid, p-hydroxybenzaldehyde: 293; benzoic acid, p-hydroxybenzaldehyde, methyl-p-hydroxy-benzoate: 157, 294, 299, 312, 348 B; benzoic acid: 300; unidentified aliphatic α-β-unsaturated ketone: 297, 347; 11-desoxycorticosterone: 295 A, 304, 305; 11-desoxycorticosterone, benzoic acid, methyl-p-hydroxy-benzoate, p-hydroxybenzaldehyde: 295; cortexone, 6-dihydrocybisterone, cybisterone: 300 A.

Hydroporus palustris L.

p-hydroxybenzaldehyde: 299, 348 B.

Ilybius fenestratus Fabr.

testosterone: 296.

Ilybius fuliginosus Fabr.

testosterone: 296.

Fam. Silphidae

Phosphuga atrata L.

ammonia (4,5% solut.): 157, 313.

Silpha obscura L.

ammonia (4,5% solut.): 157, 313.

Oeceoptoma thoracicum L. (O. thorcica L.)

ammonia (4,5% solut.): 157, 313.

Fam. Staphylinidae

Paederus columbinus Lap.

pederin, pederone: 49.

Paederus fuscipes Curt.

pederin, pseudopederin: 46, 47, 48: pederin: 5, 45, 80, 131, 133, 150, 156, 163, 169, 184, 235, 236, 238, 240, 242, 244, 245, 246, 251, 253, 278, 319, 323, 348 B, 355 B; pederin, pseudopederin, pederone: 49

Paederus melanurus Arag.

pederin: 45; pederin, pederone: 49.

Paederus litoralis Gravh.

pederin: 45.

Paederus rubrothoracicus Goeze

pederin: 45.

Paederus rufocyaneus Bernh.

pederin: 45.

(*)

(*) According to Stepanova e Coll., 1961 (Farm.Zhur., Kiev), 16: 156, in Paederus caligatus Erichs there is cantharidin. In all the similar species of Paederus we never found cantharidin.

Fam. Meloidae

Cissites cephalotes Oliv. (C. axillosa)

cantharidin: 94, 163.

Cyaneolytta gigas F. (Lytta gigas)

cantharidin: 94.

Cyaneolytta violacea Brandt (Lytta violacea)

cantharidin: 94.

Decapotama lunata Pall. (Mylabris lunata)

cantharidin: 94.

Eletica wahlbergia Fahr.

cantharidin: 94.

Epicauta adspersa Klug (Lytta adspersa Klug)

cantharidin: 94, 125, 137, 163.

Epicauta femoralis Er. (Cantharis femoralis)

cantharidin: 94.

Epicauta gorhami Mars.

cantharidin: 94, 163.

Epicauta hirticornis Haag (Cantharis hirticornis)

cantharidin: 94.

Epicauta pennsylvanica Deg. (Lytta atrata)

cantharidin: 94.

Epicauta ruficeps Ill. (Lytta ruficeps)

cantharidin: 94, 163.

Epicauta velata Gerst. (Cantharis velata)

cantharidin: 94.

Epicauta vittata F. (Lytta vittata, Cantharis vittata)

cantharidin: 82, 94, 125, 137, 163, 263.

Horia debyi Fairm.

cantharidin: 94, 163.

Lydus trimaculatus Fischer

cantharidin: 94.

<u>Lytta conspicua</u> Waterh. (<u>Mylabris conspicua</u>)

cantharidin: 94.

<u>Lytta sanguinea</u> Haag (<u>Huechys sanguinea</u>)

cantharidin: 94.

<u>Lytta vesicatoria</u> L. (<u>Cantharis vesicatoria</u>)

cantharidin: 5, 88, 94, 125, 136, 137, 163, 169, 240, 263, 319, 342, 344, 351, 355 B.

<u>Macrobasis albida</u> Say.

cantharidin: 94, 163, 344.

<u>Macrobasis cinerea</u> F. (<u>Lytta cinerea</u>)

cantharidin: 94.

<u>Meloe</u> sp.

cantharidin: 125, 131, 186, 236, 278.

<u>Meloe angusticollis</u> Say

cantharidin: 94.

<u>Meloe majalis</u> L.

cantnaridin: 94, 125.

<u>Meloe proscarabeus</u> L.

cantharidin: 94, 157.

<u>Meloe variegatus</u> Donov. (<u>Mylabris variegata</u>)

cantharidin: 94.

<u>Meloe violaceus</u> Marsch.

cantharidin: 94.

<u>Mylabris balteata</u> Pall. (<u>Mylabris punctum</u> Duges)

cantharidin: 79, 94, 163.

<u>Mylabris bifasciata</u> De Geer (<u>Zonabris bifasciata</u> De Geer)

cantharidin: 94, 163. (confirmed by personal researches)

<u>Mylabris calida</u> Pall. (<u>Mylabris maculata</u>)

cantharidin: 94.

<u>Mylabris cichorii</u> L. (<u>Zonabris cichorii</u> L.)

cantharidin: 94, 125, 136, 163, 263, 344.

Mylabris colligata Redt.

cantharidin: 94.

Mylabris crocata Pall. (Mylabris duodecimpunctata)

cantharidin: 94.

Mylabris dicincta Bertol.

cantharidin: 94 (confirmed by personal researches)

Mylabris dilloni Guer.

cantharidin: (unpublished)

Mylabris ertli Voigts

cantharidin: (unpublished)

Mylabris escherichi Voigts semireducta Pic.

cantharidin: (unpublished)

Mylabris holosericea Klug

cantharidin: 79, 94.

Mylabris macilenta Mars.

cantharidin: 94.

Mylabris oculata Thunb.

cantharidin: 94.

Mylabris phalerata Pall. (Mylabris sidae, Zonabris phalerata Pall.)

cantharidin: 94, 136, 163.

Mylabris praestans Gerst.

cantharidin: (unpublished)

Mylabris pustulata Thunb.

cantharidin: 79, 94, 163, 263.

Mylabris quadripunctata L. (Mylabris melanura)

cantharidin: 79, 94, 163.

Mylabris quatuordecimpunctata Pall.

cantharidin: 94, 125, 263.

Mylabris schoenherri Billb.

cantharidin: 163.

Mylabris tripartita Gerst.

cantharidin: 94.

Mylabris tristigma Gerst.

cantharidin: (unpublished)

Mylabris variabilis Pall.

cantharidin: 79, 94, 163, 319.

Psalydolytta castaneipennis Makel

cantharidin: (unpublished)

Fam. Tenebrionidae

Blaps gibba L.

various benzoquinones: 245, 246, 248, 335.

Blaps gigas Lap. Cast.

1,4-benzoquinone: 10, 201, 245, 246, 335; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299; quinone or quinones: 333 B.

Blaps judaeorum Miller

quinones: 278.

Blaps lethifera Marsh.

1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 299, 308, 348 B.

Blaps mortisaga L.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 299, 308, 348 B; two benzoqinones: 306.

Blaps mucronata Latr.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 299, 308, 348 B; various benzoquinones: 245, 246, 248, 335.

Blaps nitens Cast.

quinones: 278.

Blaps requieni Sol.

various benzoquinones: 248; 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 299, 308, 348 B.

Diaperis boleti L.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 293, 299, 348 B.

<u>Diaperis hispilabris</u> Say

2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, undetermi nated components in a mixture: 80, 278.

<u>Diaperis maculata</u> Ol.

2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone: 80, 245, 246, 278, 333 B, 335, 348 B.

<u>Eleodes hispilabris</u>

1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzo quinone: 348 B.

<u>Eleodes longicollis</u> Le Conte

1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzo quinone, caprylic acid, n-tridecane, glucose: 348 B; 1,4-benzo quinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, carbonyl components: 71, 111, 190, 192, 278; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 1-tride cene, 1-undecene, 1-nonene (probably), caprylic acid, gluco-se: 108, 157, 188; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 102; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 1-tridecene, 1-undecene, glucose, 1-nonene (probably): 153.

<u>Eleodes obsoleta</u> (Say)

a quinone compound possessing alkyl groups: 33.

<u>Gnaptor spinimanus</u> Pall.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 308, 348 B.

<u>Helops aeneus</u> Montrouz

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299, 348 B.

<u>Helops quisquilius</u> Strm.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 293, 299, 348 B.

Latheticus oryzae Wat.

unknown quinones: 245, 246, 335; 2-ethyl-1,4-benzoquinone and/ or 2-methyl-1,4-benzoquinone: 177.

Morica planata tingitana Baudi

2-methyl-1,4-benzoquinone: 278, 308, 348 B.

Opatroides punctulatus Brull.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299, 348 B.

Opatrum sabulosum L.

2-methyl-1,4+benzoquinone, 2-ethyl-1,4-benzoquinone: 293, 299, 348 B.

Pimelia confusa Sen.

2-methyl-1,4-benzoquinone: 278, 308, 348 B.

Scaurus dubius Sol.

1,4-benzoquinone: 293.

Scaurus uncinus Forst.

1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzo quinone: 299.

Scotobates calcaratus (Fabr.)

unknown quinones: 245, 246, 335.

Tenebrio molitor L.

2-methyl-1,4-benzoquinone: 278, 291, 299, 348 B; 2-methyl-1,4-hydroquinone: 301.

Tenebrio obscurus Fabr.

1,4-benzoquinone: 278, 308, 348 B.

Tribolium sp.

quinones: 240, 341, 355 B.

Tribolium castaneum Herbst.

quinone: 85, 86; p-benzoquinone derivatives: 168; 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone: 133, 333 B; 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-methoxy-1,4-benzo quinone: 9, 10, 80, 131, 177, 245, 246, 278, 335, 348 B.

Tribolium confusum J. du Val.

quinone: 85, 86, 279; p-benzoquinone derivatives: 168; 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone: 80, 133, 278, 348 B; 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, unknown quinones: 245, 246, 335.

Tribolium destructor Uytt.

unknown quinones: 245, 246, 335; cresol, unknown aromatic component: 219; 2-ethyl and/or 2-methyl-1,4-benzoquinone: 177.

Uloma impressa Melsh.

unknown quinones: 245, 246, 335.

Fam. Alleculidae

Prionychus ater Fabr.

1,4-benzoquinone: 293; 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299.

Fam. Cerambycidae

Aromia moscata L.

salicylaldehyde: 348 B.

Fam. Chrysomelidae

Blefarida evanida Baly

larvae: protein substance (probably): 163

Diamphidia simplex Peringuey(= Diamphidia locusta)

larvae: protein substance (probably): 163; larvae: toxalbumin: 163; toxic saponin: 355 B.

Melasoma populi L. (= Chrysomela populi L.)

salycilaldehyde (*): 87, 91, 114, 125, 131, 137, 156, 199, 217, 235, 236, 238, 240, 245, 246, 247, 248, 278, 341, 348 B, 355 B, 359.

(*) According to Claus (1862) there is a matter of salicylic acid. Other authors as well reported this initial observation.

Melasoma saliceti Weise

salicylaldehyde (larvae): 152.

Phyllodecta vitellinae L.

salicylaldehyde: 91, 114, 133, 156, 199, 245, 278, 341, 345, 348 B.

Plagiodera sp.

salicylaldehyde: 114, 278, 348 B.

Plagiodera versicolor Laich.

larvae: salicylaldehyde: 152.

Chap. 15 - Insecta Hymenoptera and chemically defined substances of defensive secretions.

Ord. HYMENOPTERA

Fam. Brachonidae

Habrobracon hebetor Say (= Microbracon hebetor Say)

protein, protein-like substance: 176, 352.

Fam. Apidae

Apis mellifera L.

histidine, histamine, lecithin, hyaluronidase, phospholipase A: 156, 246; histamine: 81, 176, 288, 352; apitoxin (polypeptide): 38; lecithinase A, direct hemolitic factor: 211; lecithinase, hyaluronidase: 158; protein toxin, lecithinase A, spreading factors, riboflavin, histamine, magnesium, copper: 35; formic acid, histamine, apitoxin (polypeptide - protease), riboflavin (vit.B_2), lecithinase A, 5-hydroxytryptamine (*), kinin (*), spreading hyaluronidase-like factors: 37; alanine, arginine, aspartic acid, cystine, cysteine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalaline, proline, serine, threonine, tryptophane, tyrosine, valine, histamine, lecithin, hyaluronidase, phospholipase A: 163, 245, 261; tryptophane, choline, glycerol, phosphoric acid, palmitic acid, unsaturated fatty acid, volatile fatty acid (butyric acid?): 318; histamine, apitoxin (=polypeptide - protease): 137, 175; 5-hydroxytryptamine: 352; hyaluronidase activity: 159, 286 A; histamine, five protein fractions: 321 A; fraction I: glycine, alanine, valine, leucine, isoleucine, serine, threonine, lysine, arginine, aspartic acid, glutamic acid, tryptophane, proline; fraction II: the same aminoacids of fraction I + phenylalanine, tyrosine, histidine, methionine, cystine: 122; histamine, mellitin (containing thirteen aminoacids), phospholipase A, hyaluronidase: 169; protein substances, phospholipase A, hyaluronidase: 143, 144, 208, 214; hyaluronidase, phospholipase A, toxin, two unknown ninhydrin-positive components: 141; fraction I: direct hemolytic activity, fraction II: phospholipase A with indirect hemolytic activity: 123; histamine, protein like substance containing 8% of tryptophane, sterol-like substance, protein: 164; fraction 0, fraction I (toxic), glycine, alanine, valine, leucine, isoleucine, serine, threonine, lysine, arginine, aspartic acid, glutamic acid, tryptophane, proline, Fraction II: the same aminoacids of fraction I + tyrosine, cystine, methionine, phenylalanine, histidine, phospholipase A, hyaluronidase, histamine: 11, 207; isoamyl acetate: 34, 183, 320, 358; histamine, apamin, mellitin, phospholipase A, hyaluronidase: 324; 10-hydroxy-2-decenoic acid: 320 B; water, alanine, arginine, cystine, glutamic acid, histidine, proline, asparagine (*), glycine (*), isoleucine (*), leucine (*), lysine (*), ornithine (*), phenylalanine (*), serine (*), threonine (*), tyrosine (*), valine (*), α-aminobutyric acid (*), β-isoaminobutyric acid (*), histamine, fructose, glucose, five-six lecithin-like compounds, two steroids (possibly), histapeptide (alanine, glycine, proline, alanine, $gluNH_2$, histamine), small peptides (probably fourteen), apamin (ten aminoacids), mellitin, enzymes including phospholipase and hyaluronidase, four antigenic proteins, eleven unidentified compounds: 212 A.

(*) traces.

- According to Fredericq 1924 (125) Apis mellifera venom contains: hydrochloric acid, phosphoric acid, organic base.
- According to Pawlowsky 1927 (263) Apis mellifera venom contains: formic acid, hydrochloric acid, phosphoric acid, protein substances, organic base, tryptophane, choline, glycerol, palmitic acid, high molecular unsatured fatty acid (probably): 263.
- Owing to the complexity of the bibliographic data, we list the chemically determined substances from bee venom: glycerol, choline, histamine, 5-hydroxytryptamine, formic acid, butyric acid (probably), palmitic acid, 10-hydroxy-2-decenoic acid, isoamylacetate, glycine, alanine, serine, β-iso-aminobutyric acid α-aminobutyric acid, threonine, valine, aspartic acid, asparagine, leucine, isoleucine, glutamic acid, glutamine, ornithine, cysteine, cystine, methionine, lysine, arginine, proline, histidine, fenilalanine, tyrosine, tryptophane, apamin, mellitin, kinin, apitoxin (polypeptide-protease), histapeptide (alanine, glycine, proline, alanine, $gluNH_2$, histamine), riboflavin, lecithin, phospholipase A, hyaluronidase,lecithinase, lecithinase A, glucose, fructose.

Bombus pratorum L.

hyaluronidase: 245, 246; lecithinase, hyaluronidase: 158; hyaluronidase activity: 159.

Lestrimelitta limao (Fr. Smith)

citral: 21.

Xylocopa sp.

an organic base connected with an acid: 263.

Fam. Vespidae

Dolichovespula media De G.

5-hydroxytryptamine: 245, 246.

Polistes gallicus L.

5-hydroxytryptamine: 75, 115, 245, 246, 353.

Polistes omissa Weyrauch

hyaluronidase, acetylcholine: 11; hyaluronidase, esterase: 286 A.

Polistes versicolor (Ol.)

5-hydroxytryptamine: 353.

Polybia occidentalis scutellaris

5-hydroxytryptamine: 353.

Synoeca surinama

5-hydroxytryptamine: 352, 353.

Vespa crabro L.

5-hydroxytrr/itamine: 353; 5-hydroxytryptamine, histamine, kinin: 352; acetylcholine, phospholipase B, 5-hydroxytryptamine: 245, 246; histamine, 5-hydroxytryptamine, acetylcholine, free amino acids: 66, 163, 169; hyaluronidase, histamine, acetylcholine: 11; histamine, 5-hydroxytryptamine, acetylcholine, kinin, phospholipase A, phospholipase B: 324; 5-hydroxytryptamine, acetyl choline, kinin, hystamine: 287 B, acetylcholine: 321 B.

Vespula germanica Fab. (= Vespa germanica Fabr.)

hystamine: 176; pipecolinic acid: 194; 245; 246; acetylcholine, cholinesterase, hyaluronidase, phospholipase B, kinin, 5-hydro xytryptamine: 182.

Vespula media

5-hydroxytryptamine: 115.

Vespula vulgaris L. (= Vespa vulgaris L.)

hystamine, cholinesterase, hyaluronidase, phosphilipase B, 5-hydroxytryptamine, kinin: 245, 246; hystamine, kinin: 352; 5-hydroxytryptamine: 75, 209, 240, 353; 5-hydroxytryptamine, hysta mine, kinin: 66, 115, 151, 288, 183 A; hystamine, 5-hydroxytrytta mine, free amino acids: 163; hystamine, 5-hydroxytryptamine, potent unidentified smooth muscle stimulant substance: 160; hystamine, 2-5-hydroxytryptamine, kinin, hemolytic factor, hyaluronidase, phospholipase A, phospholipase B, cholinesterase: 169;

cholinesterase, hyaluronidase, lecithinase: 158; hyaluronidase, 5-hydroxytryptamine, kinin, histamine: 11; hystamine, 5-hydroxytryptamine, kinin, phospholipase A, phospholipase B, hyaluronidase: 324; hyaluronidase: 286 A.

Fam. Formicidae

Subfam. Ponerinae

Ectatomma tuberculatum (Olivier)

proteinaceous substance: 147.

Myrmecia forficata Fabr.

hystamine, one or more histamine-like compounds: 89.

Myrmecia gulosa (Fabr.)

eight fractions: hystamine, hyaluronidase, phospholipase C, kinin-like substances, direct hemolytic factor: 66, 67, 68.

Odontomacus hematoda insularis Guerin

proteinaceous substance: 147.

Pachycondila sp.

formic acid: 213.

Pachycondila harpax

formic acid: 193; proteinaceous substance: 147.

Paltothyreus tarsatus (Fabr.)

dimethyldisulfide, dimethyltrisulfide: 53.

Paraponera clavata F.

polypeptide containing at least eleven amino acids including: aspartic acid, lysine, leucine, isoleucine, alanine, glutamic acid: 147.

Subfam. Pseudomyrminae

Pseudomyrmex pallidus (Fr. Smith)

basic protein: 23, 333 A.

Subfam. Dolichoderinae

Conomyrma pyramica (Roger)

2-heptanone: 29

Dolichoderus sp.

dolichodial: 270

Dolichoderus (Acanthoclinea) clarki (Wheeler)

dolichodial, 4-methyl-2-hexanone: 30, 31, 52, 61, 66, 249, 348 B; dolichodial: 55, 62, 63, 64, 80, 187, 249, 250.

Dolichoderus (Acanthoclinea) dentata Forel

dolichodial: 52, 55, 61, 63, 187, 249, 250, 348 B.

Dolichoderus (Diceratoclinea) scabridus (Roger)

dolichodial: 250; iridodial; 2-methyl-2-hepten-6-one, isoiridomyrmecin, dolichodial: 52, 55, 61, 63, 187, 249, 348 B.

Iridomyrmex sp.

dolichodial: 270.

Iridomyrmex conifer For.

iridodial: 59, 73, 131, 139, 185, 270, 351; iridodial, 2-methyl-2-hepten-6-one: 52, 55, 60, 61, 66, 245, 246, 261, 278, 332, 339, 348 B; iridodial, 2-methyl-2-hepten-6-one: 62, 80, 156.

Iridomyrmex detectus Sm.

2-methyl-2-hepten-6-one: 58, 163, 169; iridodial: 1 A, 59, 73, 131, 139, 185, 270, 351; 2-methyl-2-hepten-6-one, iridodial: 52, 55, 60, 61, 63, 66, 133, 241, 245, 246, 261, 278, 332, 339, 348 B; iridodial, 2-methyl-2-hepten-6-one, propyl isobutyl ketone: 62, 80, 130, 156.

Iridomyrmex gracilis Lowne

terpenoid constituents: 60.

Iridomyrmex gracilis var. rubriceps Forel

terpenoid constituents: 60.

Iridomyrmex humilis Mayr (I. pruinosus Roger humilis Mayr)

iridomyrmecin: 5, 30, 40, 52, 55, 60, 61, 62, 66, 80, 128, 129, 130, 131, 133, 134, 139, 144 A, 154, 155, 156, 163, 165, 166 A, 169, 185, 202, 204, 223, 224, 225, 226, 227, 228, 229, 230, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 245, 246, 248, 249, 250, 252, 254, 257, 258, 260, 261, 262, 264, 267, 269, 270, 271, 274 A, 275 A, 278, 319, 321, 331, 332, 332 A, 337, 339, 348 B, 351, 356, 355 B, 361.

Iridomyrmex myrmecodiae Em.

dolichodial: 52, 55, 61, 63, 130, 187, 348 B.

Iridomyrmex nitidiceps

iridodial: 270; iridodial, 2-methyl-2-hepten-6-one: 52, 55, 61, 63, 66, 348 B.

Iridomyrmex nitidus Mayr

isoiridomyrmecin: 40, 52, 55, 60, 61, 62, 63, 64, 65, 66, 72 A, 73, 130, 131, 133, 139, 156, 185, 202, 241, 245, 246, 261, 270, 332, 339, 348 A, 351, 361; isodihydronepetalactone, isoiridomyrmecin: 56.

Iridomyrmex pruinosus Roger

methyl-n-amyl-ketone: 21, 29, 30, 31, 52, 66, 320, 356, 357.

Iridomyrmex rufoniger Lowne

iridodial, 2-methyl-2-hepten-6-one, dolichodial: 55, 63, 348 B; dolichodial: 52, 61, 187; iridodial: 59; terpenoid constituents: 60.

Liometopum microcephalum Panz.

2-methyl-2-hepten-6-one, acetic acid, butyric acid, isovaleric acid, formic acid: 52, 130.

Tapinoma erraticum Latr.

2-methyl-2-hepten-6-one: 261, 332.

Tapinoma nigerrimum Nyl.

iridodial: 59, 139, 270; 2-methyl-2-hepten-6-one, propyl isobutyl ketone: 183, 359; 2-methyl-2-hepten-6-one, propyl isobutyl ketone, a dialdehyde: 350, 2-methyl-2-hepten-6-one, propyl iso butyl ketone, iridodial: 30, 42, 52, 55, 61, 62, 66, 80, 130, 131, 133, 156, 182, 204, 245, 246, 248, 249, 250, 278, 332, 332 A, 339, 348 B, 351, 356; propyl isobutyl ketone: 31.

Subfam. Myrmicinae

Atta sexdens rubropilosa For.

citral: 21, 42, 43, 53, 66, 80, 133, 134, 139, 182, 202, 204, 249, 250, 270, 278, 332 A, 348 B, 355 B, 356, 357, 358.

Crematogaster (Atopogyne) africana Mayr

trans-hex-2-enal: 15, 19, 30, 53, 66, 80, 132, 134, 157, 348 B.

Crematogaster lineolata (Say) clara Mayr

formic acid (traces): 193.

Crematogaster scutellaris scutellaris Oliv.

formic acid: 137, 203, 204, 205, 224, 226, 228, 231, 233, 256, 259, 264, 319.

Daceton armigerum (Latreille)

proteins: 25.

Monomorium antarcticum Wheeler

proteins and free amino acids: 20.

Monomorium pharaonis (L.)

proteins and free amino acids: 20.

Myrmica rubida Latr.

formic acid: 66, 245, 246, 328.

Myrmica ruginodis Nyl.

formic acid: 66, 245, 246, 328.

Myrmicaria natalensis Fred.

D-limonene, L-limonene: 134, 248, 278, 348 B; D-limonene, L-limonene, acetic acid, propionic acid, isovaleric acid, isobutyric acid (traces): 66, 139, 249, 250, 270.

Pheidole fallax Mayer

an indole base (probably scatole): 174.

Pogonomyrmex badius (Latr.)

proteins and free amino acids: 148.

Solenopsis saevissima Fr.Smith

nitrogenous base: 23; amine: 26; hemolytic, non protein, alkaline principle (probably a amine): 4.

Solenopsis saevissima var. richteri For.

high molecular weight nitrogen-containing unsaturated compound (alkaloid?): 22; solenopsin: 249, 250; strongly hemolytic component (probably a amine): 11.

Solenopsis xyloni McCook

amine: 26.

Subfam. Formicinae

Acanthomyops sp.

citronellal, citronellol: 53, 139, 249, 250, 270.

Acanthomyops claviger Roger

citronellal: 357; citronellal, citral: 21, 53, 66, 72, 111, 145, 157, 183, 189, 348 B, 356, 358: citronellal, citral, mixture of undeterminated components: 278; citronellal, citral, formic acid: 134; monoterpene aldehydes: 174.

Cataglyphis bicolor (Fab.)

formic acid: 66, 163, 180, 245, 246, 327, 330, 333 A.

Camponotus aethiops Latr.

formic acid: 66, 163, 245, 246, 330.

Camponotus americanus Mayr

formic acid: 193.

Camponotus compressus F. thoracica F.

formic acid: 163.

Camponotus fumidus Roger

formic acid: 193.

Camponotus ligniperda Latr.

formic acid: 11, 66, 163, 179, 245, 246, 326, 327, 330, 332 A.

Camponotus maculatus Fabr.

formic acid: 66, 245, 246, 301, 330, 333 A.

Camponotus maculatus Fabr. sansabeanus Bkly

formic acid: 193.

Camponotus thoracicus F.

formic acid: 66, 245, 246, 330.

Colobopsis truncata Spin.

formic acid: 66, 163, 245, 246, 330.

Lasius alienus Först.

formic acid: 66, 163, 203, 204, 224, 226, 228, 231, 234, 245, 246, 256, 259, 260, 264, 330.

Lasius bicornis affinis Sch.

formic acid: 163, 203, 204, 205, 223, 224, 226, 228, 231, 234, 235, 255, 256, 259, 260, 264.

Lasius (Chthonolasius) bicornis (Foerst.)

metyl-undecyl- ketone: 30; palmitic acid, *n*-undecane, methyl-*n*-undecyl-ketone: 53, 249, 267.

Lasius (Chthonolasius) umbratus Nyl.

n-undecane, methyl-*n*-undecyl-ketone: 66, 80, 133, 272; 332 A; palmitic acid, *n*-undecane, methyl-*n*-undecyl-ketone: 53, 249, 267; methyl-*n*-undecyl-ketone: 30.

Lasius (Dendrolasius) fuliginosus Latr.

dendrolasin: 5, 53, 54, 69, 131, 139, 156, 163, 169, 204, 240, 242, 245, 247, 248, 249, 261, 269, 270, 270 A, 271, 272, 273, 278, 286 B, 319, 332, 332 A, 339, 348 B, 351, 355 A, 356, 357, 358, 360; formic acid, dendrolasin: 66, 80, 134, 245, 246, 250; dendrolasin, *n*-undecane, palmitic acid: 249, 267; formic acid: 163, 180, 203, 204, 205, 223, 224, 226, 228, 231, 233, 235, 255, 256, 259, 260, 264, 326, 327, 330; 6-methyl-hept-5-en-2-one (traces), perillen *cis*-citral, *trans*-citral, dendrolasin, farnesal, two unidentified compounds: 13 A.

Lasius flavus F.

formic acid: 66, 163, 179, 245, 246, 326, 327, 330.

Lasius niger L.

formic acid: 66, 163, 203, 204, 205, 213, 224, 226, 228, 231, 234, 245, 246, 256, 259, 260, 264, 330.

Lasius niger x alienus

formic acid: 203, 204, 205, 224, 226, 228, 231, 234, 256, 259, 260, 264.

Formica cinerea Mayr

formic acid: 66, 163, 245, 246, 330.

Formica exsecta Nyl.

formic acid: 66, 163, 245, 246, 330.

Formica exsecta Nyl. pressilabris Nyl.

formic acid: 163.

Formica exsectoides Forel.

formic acid: 1 B, 58, 163, 278.

Formica fusca L.

formic acid: 66, 163, 213, 245, 246, 327, 330.

Formica fusca L. glebaria Nyl.

formic acid: 66, 163, 245, 246, 326, 330.

Formica fusca L. gnava Bkly

formic acid: 193, 213.

Formica nigricans Em.

formic acid: 165, 332 A; formic acid, ammonia: 215.

Formica picea Nyl.

formic acid: 66, 163, 245, 246, 330.

Formica polyctena Först.

formic acid: 157, 165, 183, 216, 287, 332, 332 A, 333; formic acid, ammonia: 215.

Formica pratensis Retz.

formic acid: 66, 119, 137, 157, 163, 165, 169, 203, 204, 205, 224, 226, 228, 231, 234, 235, 245, 246, 256, 259, 260, 264, 326, 327, 328, 330, 331; formic acid, ammonia: 215.

Formica pressilabris Nyl.

formic acid: 66, 245, 246, 330.

Formica rufa L.

formic acid, amino acids, odorous substances: 333, formic acid: 11, 66, 119, 137, 157, 163, 165, 167, 179, 180, 242, 245, 246, 261, 263, 278, 319, 326, 327, 329, 330, 332, 332 A, 333 A, 346, 351, 355 B; n-undecane: 267, 272, 289; formic acid, ammonia: 215.

Formica rufibarbis F.

formic acid: 66, 163, 245, 246, 326, 327, 330.

Formica sanguinea Latr.

formic acid: 66, 163, 245, 246, 326, 327, 330.

Formica truncicola Nyl.

formic acid: 66, 245, 246, 326, 327, 330.

Plagiolepis pygmaea Latr.

formic acid: 66, 163, 245, 246, 330, 332 A.

Polyergus rufescens Latr.

formic acid: 66, 163, 245, 246, 330.

Chap. 16 - Crustacea Isopoda and chemically defined substances of defensive secretions.

Cl. CRUSTACEA

Ord. ISOPODA

Fam. Porcellionidae

Porcellio scaber (Latr.)

cis-dec-3-en-1-ol, trans-dec-3-en-1-ol, cis/trans-non-en-1-ol, nonan-1-ol, unsaturated component: 57 (1).

Fam. Armadillididae

Armadillidium sp.

octan-1-ol: 57 (1).

(1) See pag. 42.

Chap. 17 - Arachnida Scorpiones, Uropygi, Araneae and chemically defined substances of defensive secretions.

Cl. A R A C H N I D A

Ord. SCORPIONES

Fam. Buthidae

Androctonus australis (L.)

neurotoxic basic proteins: 196, 197, 352; scorpamins: 212; two toxic fractions each containing: aspartic acid, threonine, serine, glutamic acid, proline, glycine, alanine, cystine, valine, isoleucine, leucine, tyrosine, phenylalanine, lysine, histidine, arginine, tryptophane: 195.

Buthacus arenicola (E. Simon)

lecithinase, coagulase: 6.

Buthotus minax

5-hydroxytryptamine: 352, 353.

Buthus australis Hector

hyaluronidase activity: 163.

Buthus martensii Karsch

buthotoxin: 163, 169, 212.

Buthus occitanus (Am.) (= Buthus europaeus ?)

neurotoxic proteins: 196, 197, 352; scorpamin: 212; hyaluroni-

---

(1) The defensive action of alcohols found is only supposed and the organ producing the substances is not yet known (Cavill and Coll., 1966, 57).

The mucilaginous substances from glands of uropoda in many species of terrestrial Isopods, have probably a defensive action.

According to T. Paulucci Maccagno 1951-52 (Sul secreto delle ghiandole tegumentali lobate degli Isopodi terrestri. Bull.Ist.Mus. Zool.Univ.Torino, 3 (14): 177-184, 1951-52) Porcellio scaber and P. laevis secretions contain: proteins with indole and benzene groups, tyrosine, cystine, mucoproteins, mucins, neutral fats, chlorides, urea, uric acid.

dase activity: 159, 163; aspartic acid, threonine, serine, glutamic acid, proline, glycine, alanine, cystine, valine, isoleucine, leucine, tyrosine, phenylalanine, lysine, histidine, arginine, tryptophane: 195.

Centruroides gracilis Gervais

5-hydroxytryptamine: 353.

Centruroides sculpturatus Ewing

peptide or with peptides closely associated substance, polysaccharide (probably): 324; sixteen protein fractions: 324 A.

Isometrus maculatus (De Geer)

hyaluronidase activity: 163.

Leiurus quinquestriatus H. e E.

5-hydroxytryptamine: 3, 353; 5-hydroxytryptamine and enzymes: 286, 5-hydroxytryptamine, peptide compound or compounds: 212; two low molecular basic proteins, 5-hydroxytryptamine: 2, 352.

Tityus bahiensis Perty

a low-molecular substance attached to protein: 163, 212; protein-like substances, lysine: 169; 5-hydroxytryptamine: 353.

Tityus serrulatus Lutz e Mello

a low-molecular substance attached to protein: 163, 212; protein-like substances, lysine: 169; 5-hydroxytryptamine: 353.

Fam. Scorpionidae

Heterometrus maurus L. (= Scorpio maurus L.)

hyaluronidase activity: 159, 163; lecithinase, anticoagulase:6.

Fam. Vejovidae

Vejovis sp.

5-hydroxytryptamine: 353.

Vejovis spinigerus

5-hydroxytryptamine: 353.

Fam. Chactidae

Euscorpius italicus (Herbst)

adenosine triphosphatase, hyaluronidase activity: 163; hyaluronidase activity: 120.

Ord. UROPYGI

Fam. Thelyphonidae

Mastigoproctus giganteus (Lucas)

acetic acid, caprylic acid, H_2O: 112, 113, 204, 249, 250, 278, 348 B.

Ord. OPILIONES

Fam. Gonyleptidae

Heteropachyloidellus robustus Roewer (*)

2,3-dimethyl-1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, 2,3,5-trimethyl-1,4-benzoquinone: 9, 10, 80, 116, 121, 245, 246, 248 B, 278, 335.

Ord. ARANEAE

Fam. Theraphosidae

Acanthoscurria atrox Vellard

glutamic acid, γ-aminobutyric acid, aspartic acid, four protein fractions: 169; 5-hydroxytryptamine: 353; four protein fractions, free amino acids: 163.

Acanthoscurria sternalis Pocock

5-hydroxytryptamine: 353.

Aphonopelma sp.

ten protein fractions: 324 A.

(*) This species is cited also as undeterminated genus and species of Fam. Gonyleptidae.

Grammostola actaeon Pocock

glutamic acid, γ-aminobutyric acid, four protein fractions: 169; four protein fractions, free amino acids: 163.

Grammostola mollicoma Ausserer

glutamic acid, γ-aminobutyric acid, four protein fractions: 169; four protein fractions, free amino acids: 163.

Grammostola pulchripes Simon

four protein fractions, free amino acids: 163.

Lasiodora klugii Koch

glutamic acid, γ-aminobutyric acid: 169; four protein fractions, free amino acids: 163.

Pamphobetus roseus M.-Leitao

four protein fractions, free amino acids: 163.

Pamphobeteus soracabae M.-Leitao

glutamic acid, γ-aminobutyric acid: 169; four protein fractions, free amino acids: 163.

Pamphobeteus tetracanthus M.-Leitao

glutamic acid, γ-aminobutyric acid: 169; four protein fractions, free amino acids: 163.

Pterinopelma vellutinum M.-Leitao

5-hydroxytryptamine: 353.

Fam. Lycosidae

Lycosa erythrognata Luc. (=L. raptoria Wlk.)

glutamic acid, aspartic acid, lysine, proteins, hyaluronic acid, histamine, nitrogen, inorganic phosphates: 169; 5-hydroxy tryptamine 353; hyaluronidase-like substance, trypsin: 162.

Scaptocosa raptoria Wlk.

proteins, free amino acids including glutamic acid, proteolytic ferment, L-amino acid dehydrogenase, hyaluronidase: 163.

Fam. Theridiidae

Latrodectus mactans F.

five-six protein compounds: free amino acids and high content of glutamic acid: 284; twelve amino acids including glutamic acid: 285; seven protein and three non-protein fractions: 184D.

Latrodectus tredecimguttatus Rossi

six protein fractions: 14, 163; three toxic protein components: 126, 127, 184 D, 206, 343; two active protein fractions: 352, lipoprotein: 163.

Fam. Argiopidae

Araneus diadematus Clerck

hyaluronidase: 163.

Fam. Ctenidae

Ctenus nigriventer Keys (= Phoneutria nigriventer Keys)

proteins, hyaluronic acid: 169; hyaluronidase like substance, trypsin: 162; proteolytic enzyme, L-amino acid dehydrogenase, hyaluronidase: 163.

Phoneutria fera Perty (= Ctenus ferus Perty) (1)

5-hydroxytryptamine: 352, 353; proteins, free amino acids including glutamic acid: 163.

---

(1) According to Lang K., Lehnartz E. (1960) 169, the secretion of Phoneutria fera Perty (= Ctenus nigriventer Keys) contains: glutamic acid, aspartic acid, lysine, histamine, inorganic phosphates.

PART V - CHEMICALLY DEFINED SUBSTANCES OF DEFENSIVE SECRETIONS OF ARTHROPODA AND THE SPECIES IN WHICH THEY ARE PRESENT.

Chap. 18 - Remarks.

In this chapter I have listed the substances that we presume to be present in Arthropoda defensive secretions, including the list of the species in which it has been found for each one. The species are arranged systematically and are followed by the code of the zoological group to which they belong. The codes used are the following:

ARA - Arachnida Araneae
BLA - Insecta Blattodea
CHOR - Diplopoda Chordeumida
COL - Insecta Coleoptera
CRU - Crustacea Isopoda
DER - Insecta Dermaptera
DIP - Insecta Diptera
GLO - Diplopoda Glomerida
HET - Insecta Heteroptera
HYM - Insecta Hymenoptera
ISO - Insecta Isoptera
JUL - Diplopoda Juliformia
LEP - Insecta Lepidoptera
OPI - Arachnida Opiliones
ORT - Insecta Orthoptera
PHA - Insecta Phasmida
POL - Diplopoda Polydesmida
SCOL - Chilopoda Scolopendromorpha
SCORP - Arachnida Scorpiones
URO - Arachnida Uropygi

Chap. 1^ - Organic substances.

HYDROCARBONS

n-undecane

Formica rufa L., Lasius (Chthonolasius) bicornis Foerst., L. (Ch.) umbratus Nyl., L. (Dendrolasius) fuliginosus Latr. (HYM); Nezara viridula L. var. smaragdula Fabr. (HET).

n-dodecane

Biprorulus bibax , Musgraveia sulciventris Stål., Nezara viridula L. var. smaragdula F., Rhoecocoris sulciventris Stål, Macroscytus sp. (HET).

n-tridecane

Biprorulus bibax , Carpocoris purpureipennis (De Geer), Ceratocoris cephalicus Mont., Euschistus servus Say., Macroscytus sp., Mysgraveia sulciventris Stål, Nezara viridula L., N. viridula L. var. smaragdula Fabr., Oebalus pugnax Fabr., Rhoecocoris sulciventris Stål, Tessaratoma aethiops Dist. (adults and larvae) (HET); Eleodes longicollis Le Conte (COL).

1-nonene

Eleodes longicollis Le Conte (probably) (COL).

1-undecene

Eleodes longicollis Le Conte (COL).

1-tridecene

Eleodes longicollis Le Conte (COL).

SULFIDES

dimethyldisulfide

Paltothyreus tarsatus (Fabr.) (HYM).

dimethyltrisulfide

Paltothyreus tarsatus Fabr. (HYM).

ALCOHOLS

methanol

Arctia caja L. (LEP).

glycerol

Apis mellifera L. (HYM).

n-hexanol

Agriopocoris froggatti Mill., Amorbus alternatus Dallas, A. rhombifer West., A. rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Mictis caja Stål, M. profana Fabr., Pachycolpura manca Breddin, Hyocephalus sp. (HET).

2-methyl butanol

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

2-methylene butanol

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

ottan-1-ol

Armadillidium sp. (CRU).

nonan-1-ol

Porcellio scaber (Latr.) (CRU).

cis-non-3-en-1-ol

Porcellio scaber (Latr.) (CRU).

trans-non-3-en-1-ol

Porcellio scaber (Latr.)(CRU).

cis-dec-3-en-1-ol

Porcellio scaber (Latr.) (CRU).

trans-dec-3-en-1-ol

Porcellio scaber (Latr.) (CRU).

cossin 1 (*)

Cossus cossus L., larvae (LEP).

cossin 2 (*)

Cossus cossus L., larvae (LEP).

cossin 3 (*)

Cossus cossus L., larvae (LEP).

(*) For cossin A, cossin B, cossin C, cossin B_1, cossin C_1, see Esters.

AMINES AND AMINO ALCOHOLS

choline

Apis mellifera L. (HYM).

histamine

Poekilocerus bufonius Klug (ORT);

Abraxas grossulariata L., Arctia caja L. (§), Dendrolimus spectabilis Btlr. (§), D. undans Walk. (§), Dirphia sp., Euproctis flava Brem. (§), Eurrhypara hostulata L., Hypocrita jacobaeae L., Megalopyge sp., Spilosoma lubricipeda L., Thaumetopoea pityocampa Sch.(§), Zygaena lonicerae von Sch. (LEP);

Cimex lectularius L., Platymeris rhadamanthus Gaerst. (§) (HET);

Apis mellifera L., Myrmecia forficata Fabr., M. gulosa Fabr., Vespa crabro L., Vespula germanica Fabr., V. vulgaris L. (HYM);

Lycosa erythrognata Luc. (ARA).

(§) probably.

5-hydroxytryptamine

Scolopendra viridicornis Newport (SCOL);

Automeris sp. (hairs, larvae), Automeris (illustris?) (hairs) (LEP);

Apis mellifera L., Dolichovespula media De G., Polybia occidentalis scutellaris , Polistes gallicus L., P. versicolor (Ol.),

HYDROCARBONS

$CH_3-(CH_2)_9-CH_3$ n-UNDECANE

$CH_3-(CH_2)_{11}-CH_3$ n-TRIDECANE

$CH_2=CH-(CH_2)_8-CH_3$ 1-UNDECENE

$CH_3-(CH_2)_{10}-CH_3$ n-DODECANE

$CH_2=CH-(CH_2)_6-CH_3$ 1-NONENE

$CH_2=CH-(CH_2)_{10}-CH_3$ 1-TRIDECENE

SULFIDES

$CH_3(S_2)CH_3$ DIMETHYLDISULFIDE

$CH_3(S)_3CH_3$ DIMETHYLTRISULFIDE

ALCOHOLS

CH_3OH METHANOL

$CH_3-(CH_2)_4CH_2OH$ n-HEXANOL

CH_2OH
$CH-OH$
CH_2OH
GLYCEROL

C_2H_5
$CH_3-CH-CH_2OH$
2-METHYL BUTANOL

C_2H_5
$CH_2=C-CH_2OH$
2-METHYLENE BUTANOL

$CH_2OH-(CH_2)_6-CH_3$ OTTAN-1-OL

$CH_2OH-CH_2-CH=CH-(CH_2)_4-CH_3$ CIS,TRANS-NON-3-EN-1-OL

$CH_2OH-(CH_2)_7CH_3$ NONAN-1-OL

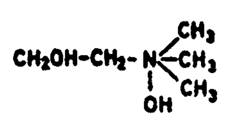
$CH_2OH-CH_2-CH=CH-(CH_2)_5-CH_3$ CIS,TRANS-DEC-3-EN-1-OL

$CH_2=CH-(CH_2)_6-CH=CH-(CH_2)_3-CH_2OH$ COSSIN 1

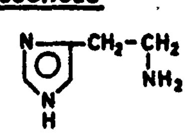
$CH_2=CH-(CH_2)_6-CH=CH-CH=CH-CH_2-CH_2OH$ COSSIN 2

$CH_2=CH-(CH_2)_5-CH=CH-CH=CH-(CH_2)_2-CH_2OH$ COSSIN 3

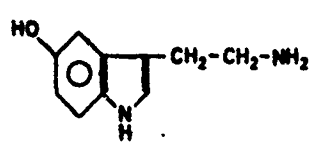
AMINES AND AMINO ALCOHOLS



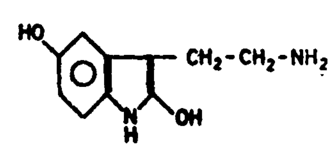
CHOLINE



HISTAMINE



5-HYDROXYTRYPTAMINE



2,5-HYDROXYTRYPTAMINE

Synoeca surinama , Vespa crabro L., Vespula germanica Fbr., V. media , V. vulgaris L. (HYM);

Buthotus minax , Centruroides gracilis Gervais, Leiurus quinquestriatus H. et E., Tityus bahiensis Perty, T. serrulatus L.M., Vejovis sp., V. spinigerus (SCORP);

Acanthoscurria atrox Vellard, A. sternalis Poc., Lycosa erythrognatha Luc., Phoneutria fera Perty, Pterinopelma vellutinum M-Leitao (ARA).

2,5-hydroxytryptamine

Vespula vulgaris L. (HYM).

SATURATED ALDEHYDES

propanal

Scaptocoris divergens Froesch (HET).

n-butanal

Riptortus clavatus (Thunberg), Amorbus rhombifer West. (HET).

2-methyl-butanal

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

n-hexanal

Acanthocoris sordidus (Thunberg), Agriopocoris froggatti Miller, Amorbus alternatus Dallas, Amorbus rhombifer West., Amorbus rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Graphosoma rubrolineatum (Westwood), Hygia opaca (Uhler), Hyocephalus n.sp., Mictis caja Stål, Mictis profana Fabr., Pachycolpura manca Breddin, Plinachtus bicoloripes Scott (HET).

UNSATURATED ALDEHYDES

trans-prop-2-enal

Nezara viridula L. var. smaragdula F., Scaptocoris divergens Froesch. (HET).

2-methylene propanal

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

trans-but-2-enal

Nezara viridula L. var. smaragdula F., Scaptocoris divergens Froesch. (HET).

2-methylene butanal

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

2-methylene butanal dimer

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

pentenal

Scaptocoris divergens Froesch. (HET).

2-methylene pentenal

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

trans-hex-2-enal

Cutilia sororor (Brunner), Eurycotis decipiens (Kirby), E. floridana Walk., Pelmatosilpha coriacea Rehn, Platyzosteria novae seelandiae Brunner (BLA);

Acanthocoris sordidus (Thunberg), Acantocephala femorata Fab., Brachymena quadripustulata Fabr., Cimex lectularius L., Dolychoris baccarum L., Eurygaster sp., Musgraveia sulciventris Stål, Nezara viridula L., N. v. var. smaragdula Fabr., Palomena viridissima P., Poecilometis strigatus Westwood, Rhoecocoris sulciventris Stål, Scaptocoris divergens Froeschner, Scotinophara lurida Burmeister, Tessaratoma aethiops Dist. (adults) (HET);

Crematogaster (Atopogyne) africana Mayr (HYM).

trans-hept-2-enal

Euschistus servus Say, Oebalus pugnax Fabr., Nezara viridula L., Scaptocoris divergens Froesch. (HET).

trans-oct-2-enal

Aelia fieberi Scott., Cimex lectularius L., Dolychoris baccarum L., Eurygaster sp., Leptocoris apicalis West., Musgraveia sulciventris Stål, Nezara viridula L. var. smaragdula Fabr., Palomena viridissima P., Poecilometis strigatus Westwood, Rhoecocoris sulciventris Stål, Scaptocoris divergens Froeschner, Scotinophara lurida Burmeister, Tessaratoma aethiops Dist. (adults and larvae) (HET).

trans-dec-2-enal

Aelia fieberi Scott., Biprorulus bibax , Dolichoris baccarum L., Graphosoma rubrolineatum West., Leptocoris apicalis West., Menida scotti Puton, Musgraveia sulciventris Stål, Nezara antennata Scott., N. viridula L., N. v. L. var. smaragdula Fabr., Palomena viridissima P., Rhoecocoris sulciventris Stål, Scotiniphara lurida Burmeister (HET).

cis-dec-2-enal

Nezara viridula L. var. smaragdula F. (HET).

trans-dodec-2-enal

Rhinocricus insulatus Chamberlin (JUL).

AROMATIC ALDEHYDES

benzaldehyde

Apheloria corrugata Wood, Orthomorpha coarctata Sauss., O. gracilis Koch, Pachydesmus crassicutis Wood, Polydesmus collaris collaris Koch, Gomphodesmus pavani Dem. (POL).

p-hydroxybenzaldehyde

Cybister lateralimarginalis D.G.Dytiscus latissimus L., D. marginalis L., Hydroporus palustris L. (COL).

salicylaldehyde

Aromia moschata L., Calosoma prominens Lec., C. sycophanta L. (adults), Melasoma populi L., M. saliceti Weise (larvae), Phyllodecta vitellinae L., Plagiodera sp., Plagiodera versicolor Laich. (larvae) (COL).

cuminaldehyde

Rhysodesmus vicinus Sauss. (POL).

SATURATED KETONES

methyl-ethyl-ketone

Nezara viridula L. var. smaragdula F. (HET).

methyl-heptyl-ketone

Nezara viridula L. var. smaragdula F. (HET).

ethyl-propyl-ketone

Nezara viridula L. var. smaragdula F. (HET).

methyl-n-amyl-ketone

Conomyrma pyramica (Roger), Iridomyrmex pruinosus Roger (HYM).

methyl-n-undecyl-ketone

Lasius (Chthonolasius) bicornis Foerst, L. (Ch.) umbratus Nyl.(HYM).

4-methyl-2-hexanone

Dolichoderus (Acanthoclinea) Clarki (Wheeler) (HYM).

n-propyl-isobutyl-ketone

Iridomyrmex conifer For., Iridomyrmex detectus Sm., Tapinoma nigerrimum Nyl. (HYM).

UNSATURATED KETONES

2-methyl-2-hepten-6-one

Dolichoderus (Diceratoclinea) scabridus Roger, Iridomyrmex conifer For., I. detectus Sm., I. nitidiceps Andre, I. rufoniger Lowne, Lasius (Dendrolasius) fuliginosus Latr., Liometopum microcephalum Panz., Tapinoma nigerrimum Nyl., T. erraticum Latr. (HYM).

ALDEHYDES

SATURATED

$CH_3-(CH_2)_4-CHO$
n-HEXANAL

CH_3-CH_2-CHO
PROPANAL

$CH_3-CH_2-CH_2-CHO$
n-BUTANAL

$CH_3-CH(C_2H_5)-CHO$
2-METHYL-BUTANAL

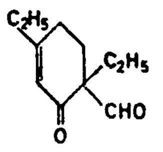
UNSATURATED

$CH_2=CH-CHO$
TRANS-PROP-2-ENAL

$CH_2=C(CH_3)-CHO$
2-METHYLENE PROPANAL

$CH_3-CH=CH-CHO$
TRANS-BUT-2-ENAL

$CH_2=C(C_2H_5)-CHO$
2-METHYLENE BUTANAL


2-METHYLENE BUTANAL DIMER

$CH_3-CH_2-CH=CH-CHO$
PENTENAL

$CH_2=C(C_3H_7)-CHO$
2-METHYLENE PENTENAL

$CH_3-CH_2-CH_2-CH=CH-CHO$
TRANS-HEX-2-ENAL

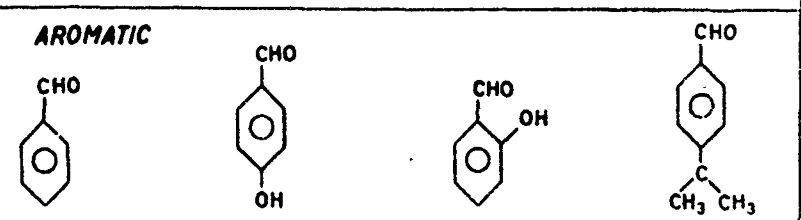
$CH_3-(CH_2)_3-CH=CH-CHO$
TRANS-HEPT-2-ENAL

$CH_3-(CH_2)_4-CH=CH-CHO$
TRANS-OCT-2-ENAL

$CH_3-(CH_2)_6-CH=CH-CHO$
CIS,TRANS-DEC-2-ENAL

$CH_3-(CH_2)_8-CH=CH-CHO$
TRANS-DODEC-2-ENAL

AROMATIC



BENZALDEHYDE p-HYDROXYBENZALDEHYDE SALICYLALDEHYDE CUMINALDEHYDE

KETONES

SATURATED

$CH_3-CO(CH_2)_6-CH_3$
METHYL-HEPTYL-KETONE

$CH_3-CH_2-CO-(CH_2)_2-CH_3$
ETHYL-PROPYL-KETONE

$CH_3-CH_2-CO-CH_3$
METHYL-ETHYL-KETONE

$CH_3-(CH_2)_4-COCH_3$
METHYL-n-AMYL-KETONE

$CH_3-(CH_2)_{10}-COCH_3$
METHYL-n-UNDECYL-KETONE

$CH_3-CO-CH_2-CH(CH_3)-CH_2-CH_3$
4-METHYL-2-HEXANONE

$(H_3C)_2CH-CH_2-CO-CH_2-CH_2-CH_3$
n-PROPYL-ISOBUTYL-KETONE

UNSATURATED

$CH_3-CH_2-CO-CH=CH-CH_3$
4-KETO-HEX-2-ENE

$(H_3C)_2C=CH-CH_2-CH_2-CO-CH_3$
2-METHYL-2-HEPTEN-6-ONE

KETO ALDEHYDES

$CH_3-CH_2-CO-CH=CH-CHO$
4-KETO-TRANS-HEX-2-ENAL

$CH_3-(CH_2)_3-CO-CH=CH-CHO$
4-KETO-TRANS-OCT-2-ENAL

4-keto-hex-2-ene

Nezara viridula L. var. smaragdula F. (HET).

UNSATURATED KETO ALDEHYDES

4-keto-trans-hex-2-enal

Corixa dentipes Thoms, Macroscytus sp., Nezara viridula L., N. v. L. var. smaragdula Fabr., Sigara falleni (Fieb.), Tessaratoma aethiops Dist. (adults and larvae) (HET).

4-keto-trans-oct-2-enal

Nezara viridula L. var. smaragdula F. (HET).

CARBOXYLIC ACIDS

formic acid

Cerura vinula L. (larvae), Cnethocampa sp., Datana ministra (larvae), Dicranura furcula Boisduval (larvae), Portesia sp. (hairs), Schizura concinna Abbot and Smith (larvae), S. leptinoides Grote, Thaumetopoea pityocampa Sch. (larvae) (LEP);

Acinopus sp., Calathus sp., Carterus sp., Harpalus dimidiatus Rossi, Pheropsophus agnatus , Pseudophonus griseus Panz., P. pubescens Müll (COL);

Acanthomyops claviger (Roger), Apis mellifera L., Camponotus aethiops Latr., C. americanus Mayr, C. compressus F. thoracica F., C. fumidus Roger, C. ligniperda Latr., C. maculatus Fabr., C.m. sansabeanus Bkly, C. thoracicus F., Cataglíphys bicolor Fabr., Colobopsis truncata Sprin., Crematogaster lineolata clara Mayr, Cr. scutellaris scutellaris Oliv., Formica cinerea Mayr, F. exsecta Nyl., F. e. Nyl. pressilabris Nyl., F. exectoides Forel, F. fusca L., F.f. L. glebaria Nyl., F. f. L. gnava Bkly, F. nigricans Em., F. picea Nyl., F. polyctena Först., F. pratensis Retz., F. pressilabris Nyl., F. rufa L., F. rufibarbis F., F. sanguinea Latr., F. truncicola Nyl., Lasius alienus Först., L. bicornis affinis Sch., L. (Dendrolasius) fuliginosus Latr., L. flavus F., L. niger L., L. n. x alienus Först., Liometopum microcephalum Panz. (*), Myrmica rubida Latr., M. ruginodis Nyl., Pachycondila sp., P. harpax (Fabr), Plagyolepis pygmaea Latr., Polyergus rufescens Latr. (HYM).

acetic acid

Agriopocoris froggatti Miller, Amorbus alternatus Dallas, A. rhombifer West., A. rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Hyocephalus sp., Mictis caja Stål, M. profana Fabr., Pachycolpura manca Breddin (HET);
Cerura vinula L. (larvae) (LEP);
Liometopum microcephalum Panz., Myrmicaria natalensis Fred. (HYM);
Mastigoproctus giganteus (Lucas) (URO).

propionic acid

Myrmicaria natalensis Fred. (HYM).

butyric acid

Carabus sp., Cychrus sp. (COL);
Apis mellifera L. (*), Liometopum microcephalum Panz. (HYM).

isobutyric acid

Papilio machaon L.,(larvae)(LEP);
Myrmicaria natalensis Fred. (HYM).

2-methyl butyric acid

Papilio machaon L.,(larvae)(LEP).

isovaleric acid

Liometopum microcephalum Panz., Myrmicaria natalensis Fred. (HYM).

caprylic acid

Eleodes longicollis Lec. (COL);
Mastigoproctus giganteus (Lucas) (URO).

palmitic acid

Apis mellifera L., Lasius (Chthonolasius) bicornis Foerst., L. (Ch.) umbratus Nyl., L. (Dendrolasius) fuliginosus Latr. (HYM).

(*) probably.

methacrylic acid

Cerura vinula L.,(larvae)(LEP);

Abax ater Villers, A. ovalis Dftsch., A. parallelus Dftsch., Apotomopterus albrechti Esakii A. Mor., A. insulicula Chaud., Calosoma sycophanta L., Carabus auratus L., C. auronitens Fbr., C. cancellatus Illig., C. convexus Fbr., C. coriaceus L., C. cyaneus F., C. granulatus L., C. irregularis Fbr., C. procerulus Chaud., C. Ullrichi Germ., C. violaceus L., Cychrus rostratus Lin., Damaster oxuroides Schaum, Pterostichus metallicus Fbr., Pt. niger Schall., Pt. vulgaris L.(COL).

2-methylene butyric acid

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

tiglic acid

Cerura vinula L.,(larvae)(LEP);

Abax ater Villers, A. ovalis Dftsch., A. parallelus Dftsch., Apotomopterus albrechti Esakii A. Mor., A. insulicula Chaud., Calosoma sycophanta L., Carabus auratus L., C. auronitens Fabr., C. cancellatus Illig., C. convexus Fbr., C. coriaceus L., C. cyaneus F., C. granulatus L., C. irregularis Fbr., C. ullrichi Germ., C. violaceus L., Pterostrichus metallicus Fbr., P. niger Schall., P. vulgaris L. (COL).

10-hydroxy-2-decenoic acid

Apis mellifera L. (HYM).

D-gluconic acid

Eurycotis biolleyi Rehn, E. decipiens (Kirby), E. floridana Walk.(BLA).

ascorbic acid

Chrysocoris stolli Wolf (HET).

hyaluronic acid

Ctenus nigriventer Keys, Lycosa erythrognatha Luc. (ARA).

benzoic acid

Gomphodesmus pavani Dem., Orthomorpha coarctata Sauss., Polydesmus collaris collaris Koch (POL);

Dytiscus latissimus L., D. marginalis L. (COL).

pipecolinic acid

Vespula germanica Fabr. (HYM).

oxalic acid

Ceroplatus lineatus F., Platyura discoloria Mg., Pl. fasciata Meigen, Pl. nigricornis F., Pl. sp., Ceroplatus sp. (DIP).

PHENOLS

phenol

Abacion magnum Loomis (CHOR);

Orthomorpha coarctata Sauss. (POL).

guaiacol

Orthomorpha coarctata Sauss. (POL).

cresol

Tribolium destructor Uytt. (COL).

m-cresol

Chlaenius cordicollis Kirby (COL).

p-cresol

Abacion magnum Loomis (CHOR).

FURANS

furan

Scaptocoris divergens Froesch. (HET).

methyl furan

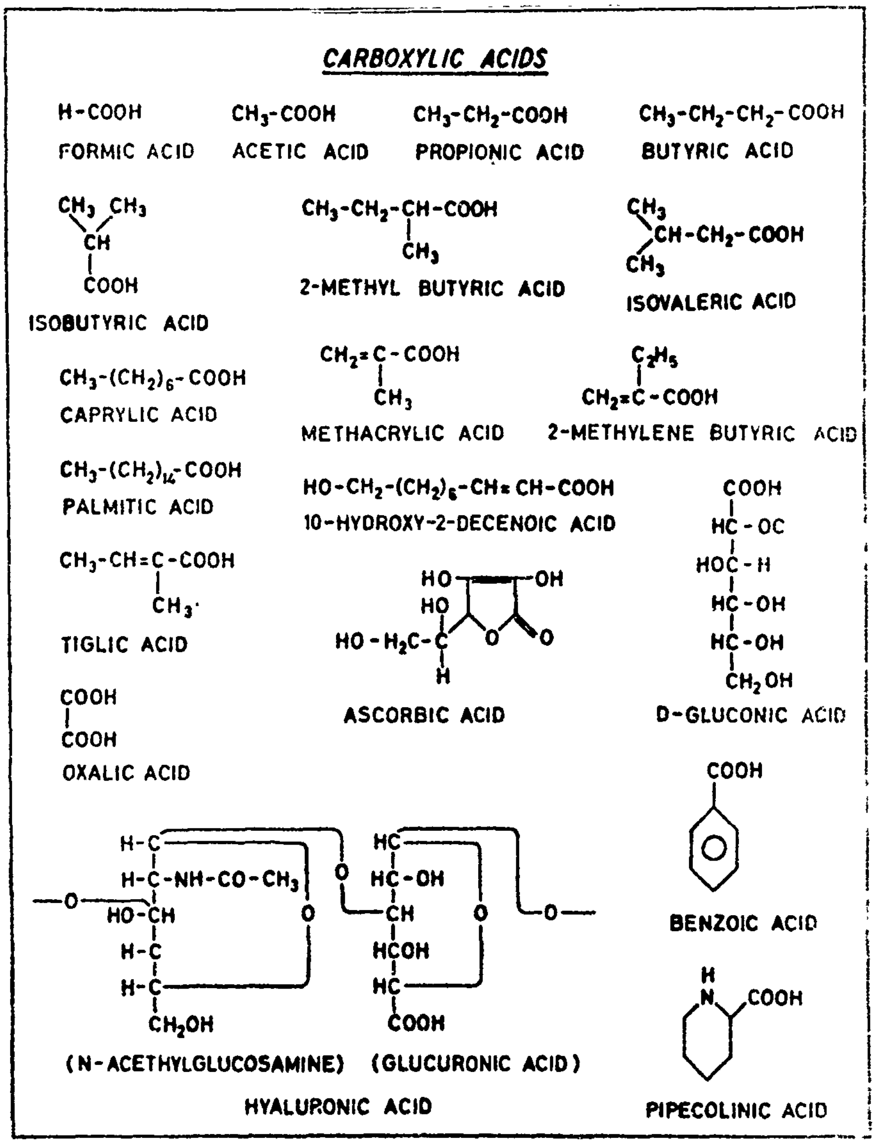
Scaptocoris divergens Froesch. (HET).

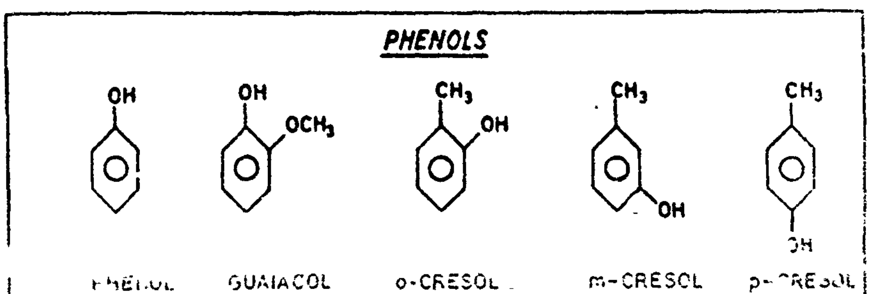
perillen

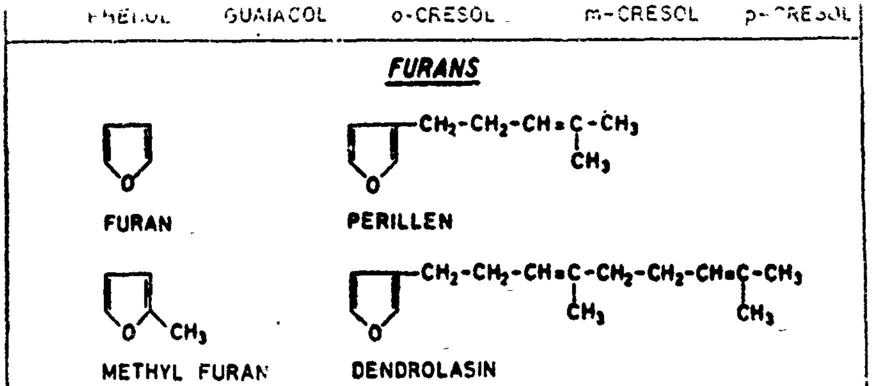
Lasius (Dendrolasius) fuliginosus Latr. (HYM).

dendrolasin

Lasius (Dendrolasius) fuliginosus Latr. (HYM).


CARBOXYLIC ACIDS
H-COOH
FORMIC ACID
CH3-COOH
ACETIC ACID
CH3-CH2-COOH
PROPIONIC ACID
CH3-CH2-CH2-COOH
BUTYRIC ACID
ISOBUTYRIC ACID
CH3-CH2-CH-COOH
2-METHYL BUTYRIC ACID
CH-CH2-COOH
ISOVALERIC ACID
CH3-(CH2)6-COOH
CAPRYLIC ACID
CH2=C-COOH
METHACRYLIC ACID
CH2=C-COOH
2-METHYLENE BUTYRIC ACID
CH3-(CH2)14-COOH
PALMITIC ACID
HO-CH2-(CH2)6-CH=CH-COOH
10-HYDROXY-2-DECENOIC ACID
CH3-CH=C-COOH
TIGLIC ACID
ASCORBIC ACID
D-GLUCONIC ACID
OXALIC ACID
BENZOIC ACID
(N-ACETHYLGLUCOSAMINE)
(GLUCURONIC ACID)
HYALURONIC ACID
PIPECOLINIC ACID


PHENOLS
GUAIACOL
o-CRESOL
m-CRESOL


FURANS
FURAN
-CH2-CH2-CH=C-CH3
PERILLEN
-CH2-CH2-CH=C-CH2-CH2-CH=C-CH3
METHYL FURAN
DENDROLASIN

ESTERS

isoamyl acetate

Apis mellifera L. (HYM).

n-hexyl acetate

Agriopocoris froggatti Miller, Amorbus alternatus Dallas, A. rhombifer West., A. rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Hyocephalus sp., Mictis caja Stål, M. profana Fabr., Pachycolpura manca Breddin (HET).

n-octyl acetate

Leptocoris apicalis Westw. (HET).

trans-hex-2-enyl acetate

Lethocerus indicus (Lep. and Serv.), Nezara viridula L. var. smaragdula F. (HET).

trans-oct-2-enyl acetate

Macroscytus sp., Musgraveia sulciventris Stål., Nezara viridula L. var. smaragdula F., Rhoecocoris sulciventris Stål., Tessaratoma aethiops Dist. (adults) (HET).

trans-dec-2-enyl acetate

Biprorulus bibax , Macroscytus sp., Nezara viridula L. var. smaragdula F. (HET).

cossin A (*)

Cossus cossus L. (larvae) (LEP).

cossin B (*)

Cossus cossus L. (larvae) (LEP).

cossin C (*)

Cossus cossus L. (larvae) (LEP).

cossin B_1 (*)

Cossus cossus L. (larvae) (LEP).

(*) For cossin 1, cossin 2, cossin 3, see alcohols.

cossin C_1 (*)

Cossus cossus L. (larvae) (LEP).

n-butyl butyrrate

Amorbus rhombifer West., Mictis caja Stål. (HET).

trans-hex-2-enyl butyrrate

Lethocerus indicus (Lep. and Serv.) (HET).

methyl p-hydroxy benzoate

Cybister lateralimarginalis D.G. Dytiscus latissimus L., D. marginalis L. (COL).

acetylcholine

Polistes omissa Weyrauch, Vespa crabro L., Vespula germanica Fbr. (HYM);

Zygaena filipendulae L., Z. lonicerae (Von Sch.) (LEP).

ββ-dimethylacrylyl-choline

Arctia caja L. (imago) (LEP).

LACTONES

γ-gluconolactone

Eurycotis biolleyi Rehn, E. decipiens (Kirby) (BLA).

δ-gluconolactone

Eurycotis biolleyi Rehn, E. decipiens (Kirby) (BLA).

AMIDES

pederin

Paederus columbinus Lap., P. fuscipes Curt., P. melanurus Arag., P. litoralis Gravh., P. rubrothoracicus Goeze, P. rufocyaneus Bernh.(COL).

pseudopederin

Paederus fuscipes Curt. (COL).

(*) For cossin 1, cossin 2, cossin 3, see alcohols.

ESTERS

$CH_3-CH(CH_3)-(CH_2)_2-OCOCH_3$
ISOAMYL ACETATE

$CH_3-(CH_2)_5-OCOCH_3$
n-HEXYL ACETATE

$CH_3-(CH_2)_7-OCOCH_3$
n-OCTYL ACETATE

$CH_3-(CH_2)_2-CH=CH-CH_2-OCOCH_3$
TRANS-HEX-2-ENYL ACETATE

$CH_3-(CH_2)_4-CH=CH-CH_2-OCOCH_3$
TRANS-OCT-2-ENYL ACETATE

$CH_3-(CH_2)_6-CH=CH-CH_2-OCOCH_3$
TRANS-DEC-2-ENYL ACETATE

$CH_2=CH-(CH_2)_8-CH=CH-(CH_2)_3-CH_2OCOCH_3$ COSSIN A

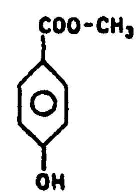
$CH_2=CH-(CH_2)_6-CH=CH-CH=CH-CH_2-CH_2OCOCH_3$ COSSIN B

$CH_2=CH-(CH_2)_5-CH=CH-CH=CH-(CH_2)_2-CH_2OCOCH_3$ COSSIN C

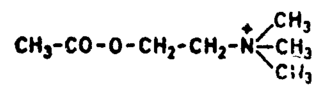
COSSIN B_1 (*) COSSIN C_1 (**)

$CH_3-(CH_2)_3-OCO-(CH_2)_2-CH_3$
n-BUTYL BUTYRATE

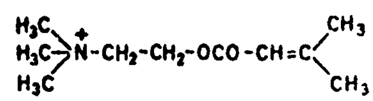
$CH_3-(CH_2)_2-CH=CH-CH_2-OCO-(CH_2)_2-CH_3$
TRANS-HEX-2-ENYL BUTYRATE



METHYL p-HYDROXY BENZOATE

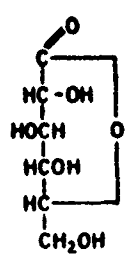


ACETYLCHOLINE

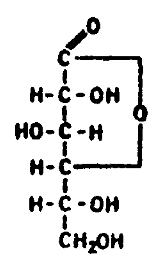


ββ-DIMETHYLACRYLYL-COLINE

LACTONES

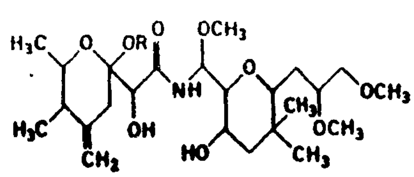


δ-GLUCONOLACTONE

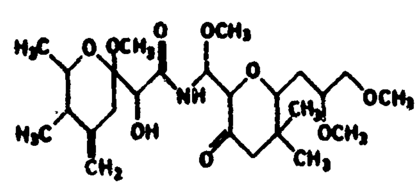


γ-GLUCONOLACTONE

AMIDES



PEDERIN R = CH_3
PSEUDOPEDERIN R = H



PEDERONE

pederone

Paederus columbinus Lap., P. fuscipes Curt., P. melanurus Arag.(COL).

NITRILES

hydrocyanic acid

Apheloria corrugata Wood, Cherockia georgiana Bollman, Gomphodesmus pavani Dem., Leptodesmus (Polydesmus) haydenianus Wood, Nannaria sp., Orthomorpha coarctata Sauss., O. gracilis Koch, Pachydesmus crassicutis Wood, Polydesmus collaris collaris Koch, P. (Fontaria) virginiensis Drury, Pseudopolydesmus serratus Say, Rhysodesmus vicinus Sauss. (POL);

Zygaena filipendulae L., Z.lonicerae (von Schev.), Procris geryon (Hueb.) (LEP).

D-(+)-mandelic nitrile

Apheloria corrugata Wood, Gomphodesmus pavani Dem. (POL).

mandelonitrile benzoate

Gomphodesmus pavani Dem., Polydesmus collaris collaris Koch (POL).

glucoside of p-isopropil mandelonitrile

Rhysodesmus vicinus Sauss. (POL).

AMINO ACIDS

glycine

Apis mellifera L. (HYM).

Androctonus australis L., Buthus occitanus Am. (SCORP).

alanine

Apis mellifera L., Paraponera clavata F. (HYM);

Androctonus australis L., Buthus occitanus Am. (SCORP).

serine

Apis mellifera L. (HYM);

Androctonus australis L., Buthus occitanus Am. (SCORP).

α-aminobutyric acid

Apis mellifera L. (HYM).

β-iso-aminobutyric acid

Apis mellifera L. (HYM).

γ-aminobutyric acid

Acanthoscurria atrox Vellard, Grammostoma actaeon Pocock, Gr. mollicoma Ausserer, Lasiodora klugii Koch, Pamphobeteus soracabae M.-Leitao, P. tetracanthus M.-Leitao (ARA).

threonine

Apis mellifera L. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

valine

Apis mellifera L. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

aspartic acid

Apis mellifera L., Paraponera clavata F. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP);
Acanthoscurria atrox Vellard, Lycosa erythrognata Luc. (ARA).

asparagine

Apis mellifera L. (HYM).

leucine

Apis mellifera L., Paraponera clavata F. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

isoleucine

Apis mellifera L., Paraponera clavata F. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

glutamic acid

Apis mellifera L., Paraponera clavata F. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

Acanthoscurria atrox Vellard, Grammostoma actaeon Pocock, Grammostoma mollicoma Ausserer, Lasiodora klugii Koch, Latrodectus mactans F., Lycosa erythrognata Luc., Pamphobeteus soracabae M.-Leitao, P. tetracanthus M.-Leitao, Phoneutria fera Perty, Scaptocosa raptoria Perty (ARA).

glutamine

Apis mellifera L. (HYM).

ornithine

Apis mellifera L. (HYM).

cysteine

Apis mellifera L. (HYM).

cystine

Apis mellifera L. (HYM); Androctonus australis L., Buthus occitanus Am. (SCORP).

methionine

Apis mellifera L. (HYM).

lysine

Apis mellifera L., Paraponera clavata F. (HYM);
Androctonus australis L., Buthus occitanus Am., Tityus bahiensis Perty, T. serrulatus L. e Mello (SCORP);
Lycosa erythrognata Luc. (ARA).

arginine

Apis mellifera L. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

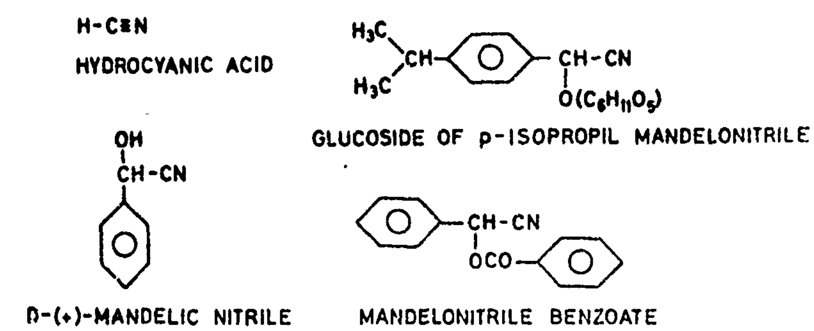
proline

Apis mellifera L. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

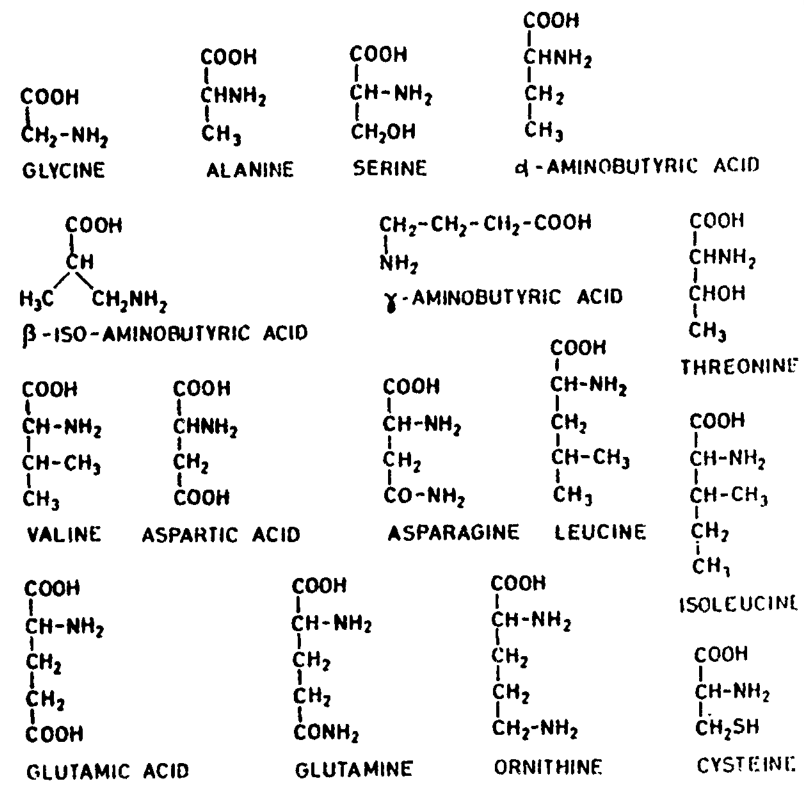
histidine

Apis mellifera L. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

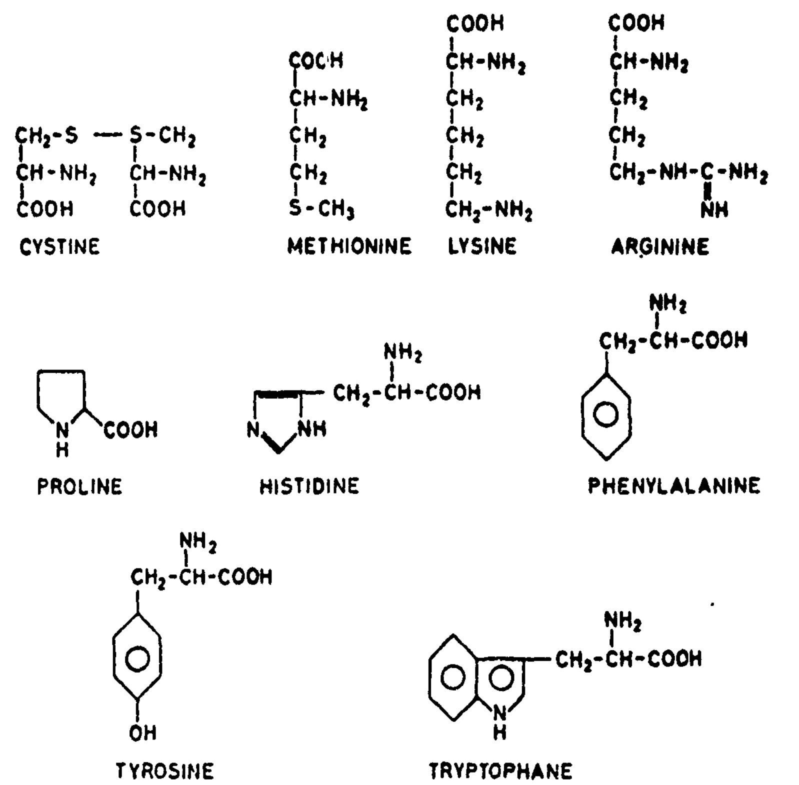
NITRILES



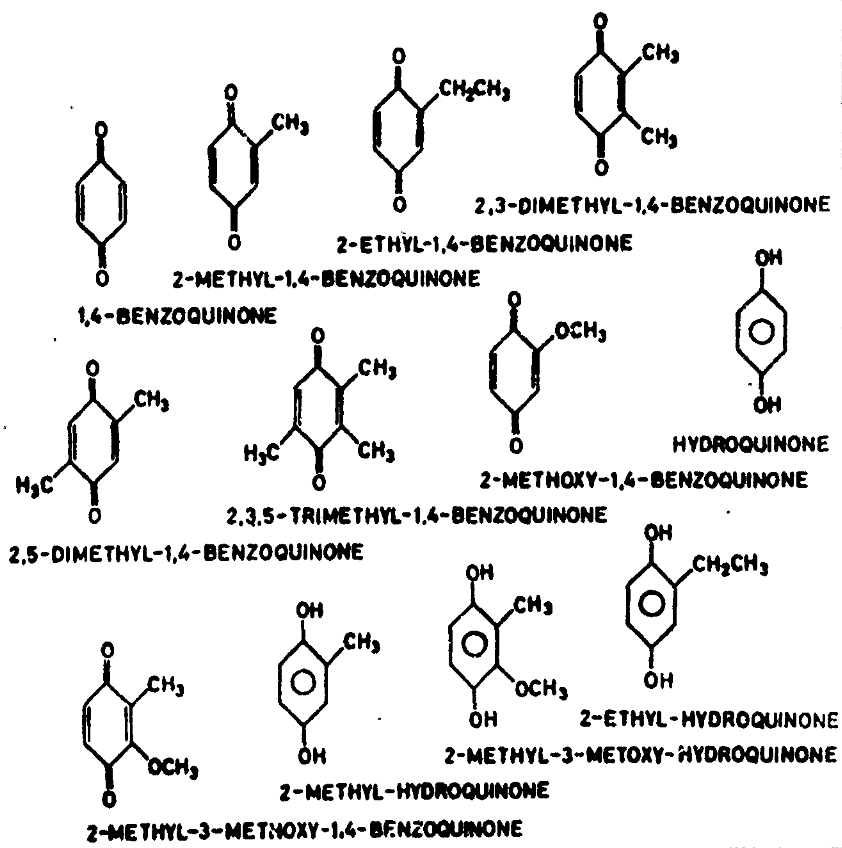
AMINO ACIDS



AMINO ACIDS



QUINONES



phenylalanine

Apis mellifera L. (HYM);

Androctonus australis L., Buthus occitanus Am. (SCORP).

tyrosine

Apis mellifera L. (HYM);

Androctonus australis L., Buthus occitanus Am. (SCORP).

tryptophane

Apis mellifera L. (HYM);

Androctonus australis L., Buthus occitanus Am. (SCORP).

QUINONES

1,4-benzoquinone

Archiulus (Schizophyllum) sabulosus L., Pachybolus laminatus Cook, Schizophyllum mediterraneum , Spirostreptus castaneus Attems, Sp. virgator Silv. (JUL);

Diploptera punctata (Esch.) (BLA);

Blaps gigas L., Bl. lethifera Marsh., Brachynus crepitans L., B. explodens Duft., B. sclopeta Fabr., Eleodes hispilabris , E. longicollis Le Conte, Pheropsophus catoirei Dej, Prionychus ater Fabr., Scaurus dubius Sol., S. uncinus Först., Tenebrio obscurus Fabr.(COL).

2-methyl-1,4-benzoquinone

Archiulus (Schizophyllum) sabulosus L., Aulonopygus aculeatus Attems, A. aculeatus barbieri , Brachyulus unilineatus Koch, Cambala hubrichti Hoffman, Chicobolus spinigerus Wood, Cylindrojulus teutonicus Pocock, Doratogonus annulipes Carl, Floridobolus pennery Causey, Narceus annularis Raf., N. gordanus Chamb., Orthoporus flavior Chamberlin e Mulaik, Or. punctilliger Chamberlin, Pachybolus laminatus Cook, Peridontopyge aberrans Attems, P. vachoni , Rhinocricus sp., Rh. insulatus Chamberlin, Spirostreptus sp., Sp. multisulcatus Dem., Sp. virgator Silv., Trigonoiulus lumbricinus Gerst (JUL);

Diploptera punctata (Esch.) (BLA);

Forficula auricularia L. (DER);

Scaptocoris divergens Froesch. (HET);

Blaps gigas L., Bl. lethifera Marsh., Bl. mortisaga L., Bl. mucronata Latr., Bl. requiénii Solier, Brachynus crepitans L., Br. explodens Duft., Br. sclopeta Fabr., Diaperis boleti L., D. maculata Ol., D. hispilabris Say, Eleodes hispilabris , E. longicollis Le Conte, Gnaptor spinimanus Pall., Helops aeneus Montrouz, H. quisquilius Strm., Latheticus oryzae Wat., Morica planata/tingitana Baudi, Opatroides punctulatus Brull., Opatrum sabulosum L., Pimelia confusa Sen., Pheropsophus catoirei Dej, Prionychus ater Fabr., Scaurus uncinus Först., Tenebrio molitor L., Tribolium castaneum Herbst., Tr. confusum J. du V. (COL).

2-ethyl-1,4-benzoquinone

Diploptera punctata (Esch.) (BLA);

Forficula auricularia L. (DER).

Blaps gigas L., Bl. lethifera Marsh., Bl. mortisaga L., Bl. mucronata Latr., Bl. requienii Solier, Diaperis boleti L., D. maculata Ol., D. hispilabris Say, Eleodes hispilabris , E. longicollis Le Conte, Gnaptor spinimanus Pall., Helops aeneus Montrouz, H. quisquilius Strm., Latheticus oryzae Wat., Opatroides punctulatus Brull., Opatrum sabulosus L., Prionychus ater Fabr., Scaurus uncinus Förtst., Tribolium castaneum Herbst, Tr. confusum J. du V., Tr. destructor Uytt. (COL).

2,3-dimethyl-1,4-benzoquinone

Heteropachyloidellus robustus Roewer (OPI).

2,5-dimethyl-1,4-benzoquinone

Heteropachyloidellus robustus Roewer (OPI).

2,3,5-trimethyl-1,4-benzoquinone

Heteropachyloidellus robustus Roewer (OPI).

2-methoxy-1,4-benzoquinone

Tribolium castaneum Herbst (COL).

2-methyl-3-methoxy-1,4-benzoquinone

Archiulus (Schizophyllum) sabulosus L., Brachyulus unilineatus Koch, Cambala hubrichti Hoffman, Chicobolus spinigerus Wood, Cylindroiulus teutonicus Pocock, Doratogonus annulipes Carl, Floridobolus penneri Causey, Narceus annularis Raf., N. gordanus Chamb., Orthoporus conifer Attems, Or. flavior Chamberlin and Mulaik, Or. punctilliger Chamberlin, Rhinocricus sp., Spirostreptus sp., Trigonoiulus lumbricinus Gerst. (JUL).

hydroquinone

Brachynus crepitans L., Br. explodens Duft., Br. sclopeta Fabr.(COL).

2-methyl-hydroquinone

Archiulus (Schizophyllum) sabulosus L., Rhinocricus sp. (JUL).
Forficula auricularia L. (DER);
Brachynus crepitans L., Br. explodens Duft., Br. sclopeta Fabr.,
Tenebrio molitor L. (COL).

2-ethyl-hydroquinone

Forficula auricularia L. (DER).

2-methyl-3-methoxy-hydroquinone

Archiulus (Schizophyllum) sabulosus L., Rhinocricus sp. (JUL).

SUGARS

glucose

Pachydesmus crassicutis Wood, Rhysodesmus vicinus Sauss. (POL);
Eleodes longicollis Lec. (COL);
Apis mellifera L. (HYM).

fructose

Apis mellifera L. (HYM).

TERPENIC DERIVATIVES

HYDROCARBONS

D,L-limonene

Myrmicaria natalensis Fred. (HYM).

α,β-pinene

Nasutitermes sp. (soldiers), N. exitiosus (Hill.), N. graveolus Hill., N. walkeri Hill.(ISO).

ALCOHOLS

citronellol

Acanthomyops sp. (HYM).

ALDEHYDES

citral

Acanthomyops claviger Roger, Atta sexdens rubropilosa For., Lasius (Dendrolasius) fuliginosus Latr., Lestrimelitta limao (Fr. Smith) (HYM).

citronellal

Acanthomyops sp., A. claviger Roger (HYM).

farnesal

Lasius (Dendrolasius) fuliginosus Latr. (HYM).

iridodial

Dolichoderus (Diceratoclinea) scabridus Roger, Iridomyrmex conifer For., Ir. detectus Sm,, Ir. nitidiceps (Andre), Ir. rufoniger Lowne, Tapinoma nigerrimum Nyl. (HYM).

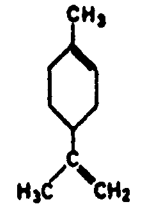
dolichodial

Anisomorpha buprestoides Stoll (PHA);

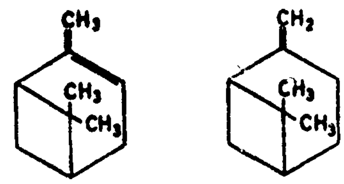
Dolichoderus sp., D. (Acanthoclinea) Clarki Wheeler, D. (Ac.) dentata Forel, D. (Diceratoclinea) scabridus Roger, Iridomyrmex sp., Ir. myrmecodiae Em., Ir. rufoniger Lowne (HYM).

TERPENIC DERIVATIVES

HYDROCARBONS

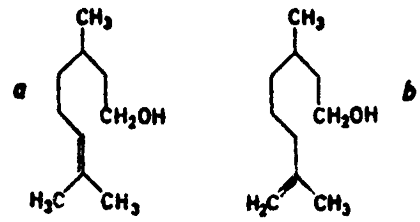


D,L-LIMONENE



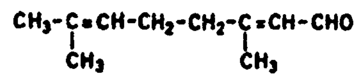
α,β-PINENE

ALCOHOLS

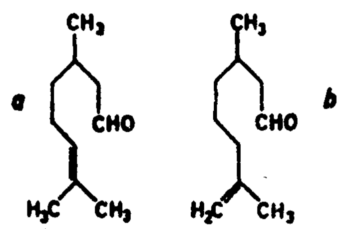


CITRONELLOL (MIXTURE OF a,b)

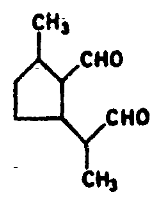
ALDEHYDES



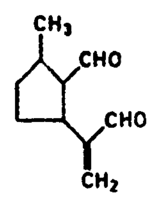
CITRAL



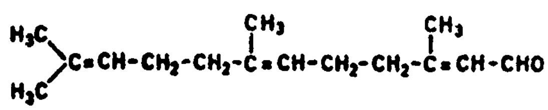
CITRONELLAL (MIXTURE OF a,b)



IRIDODIAL

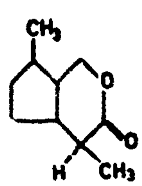


DOLICHODIAL

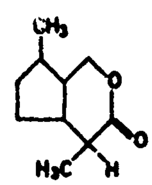


FARNESAL

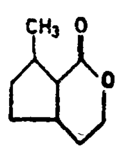
LACTONES, ANHYDRIDES



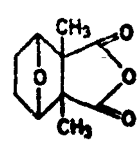
IRIDOMYRMECIN



ISOIRIDOMYRMECIN



ISODIHYDRONEPETALACTONE



CANTHARIDIN

LACTONES, ANHYDRIDES

iridomyrmecin

Iridomyrmex humilis Mayr (HYM).

isoiridomyrmecin

Dolichoderus (Diceratoclinea) scabridus Roger, Iridomyrmex nitidus Mayr (HYM).

isodihydronepetalactone

Iridomyrmex nitidus Mayr (HYM).

cantharidin

Cissites cephalotes Oliv., Cyaneolytta gigas F., C. signifrons Fahr., C. violacea Brandt, Decapotama lunata Pall., Eletica wahlbergia Fahr., Epicauta adspersa Klug, Ep. femoralis Er., Ep. gorhami Mars., Ep.hirticornis Haag, Ep. pennsylvanica Deg., Ep. ruficeps Ill., Ep. velata Gerst., Ep. vittata F., Horia debyi Fairm., Lydus trimaculatus Fischer, Lytta conspicua Waterh., L. sanguinea Haag, L. vesicatoria L., Macrobasis albida Say, M. cinerea F., Meloe sp., Me. angusticollis Say, Me. majalis L., Me. proscarabeus L., Me. variegatus Donov., Me. violaceus Marsh., Mylabris balteata Pall., My. bifasciata De Geer, My. calida Pall., My. cichorii L., My. colligata Redt., My. crocata Pall., My. dicincta Bertol., My. dilloni Guer., My. escherichi Voigts ~~My. ertli Voigts~~, My. semireducta Pic., ~~My. holoser~~icea Klug, My. macilenta Mars., My. oculata Thunb., My. phalerata Pall., My. praestans Gerst., My. pustulata Thunb., My. quadripunctata L., My. quatuordecimpunctata Pall., My. schoenherri Billb., My. tripartita Gerdt., My. tristigma Gerst., My. variabilis Pall., Psalydolytta castaneipennis Makel (COL).

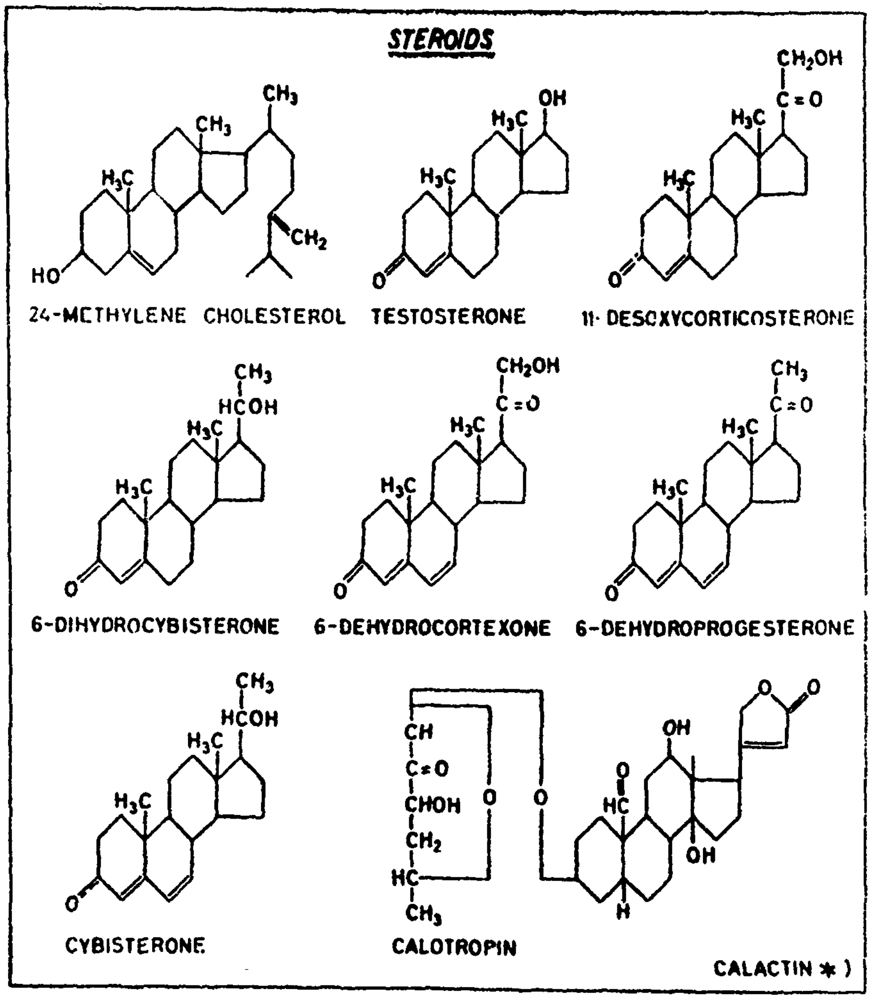
STEROIDS

24-methylene cholesterol

Nasutitermes sp. (soldiers) (ISO).

testosterone

Ilybius fenestratus Fabr., Ilybius fuliginosus Fabr. (COL).


STEROIDS
24-METHYLENE CHOLESTEROL
TESTOSTERONE
11- DESOXYCORTICOSTERONE
6-DIHYDROCYBISTERONE
6-DEHYDROCORTEXONE
6-DEHYDROPROGESTERONE
CYBISTERONE
CALOTROPIN
CALACTIN *)

__11-desoxycorticosterone__

__Acilius sulcatus__ , __Dytiscus marginalis__ L. (COL).

__6-dihydrocybisterone__

__Acilius sulcatus__ , __Dytiscus marginalis__ L. (COL).

__6-dehydrocortexone__

__Acilius sulcatus__ (COL).

__6-dehydroprogesterone__

__Acilius sulcatus__ (COL).

__cybisterone__

__Acilius sulcatus__ , __Cybister lateralimarginalis__ De Geer, __Dytiscus marginalis__ L. (COL).

__calotropin__

__Poekilocerus bufonius__ Klug (ORT).

__calactin__

__Poekilocerus bufonius__ Klug (ORT).

__ALKALOIDS__

__glomerin__

__Glomeris marginata__ Vill., __Gl. conspersa__ Koch, __Gl. hexasticha__ Brandt, __Loboglomeris rugifera__ Verh. (GLO).

__omoglomerin__

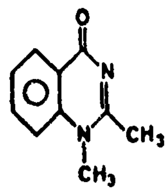
__Glomeris marginata__ Vill., __Gl. conspersa__ Koch, __Gl. hexasticha__ Brandt (GLO).

__FLAVOPROTEINS__

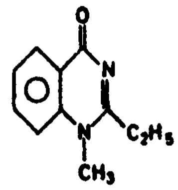
__riboflavin__

__Apis mellifera__ L. (HYM).

ALKALOIDS

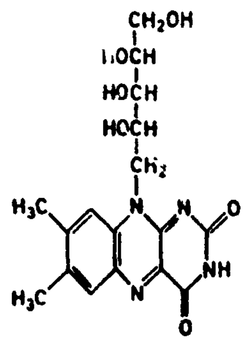


GLOMERIN



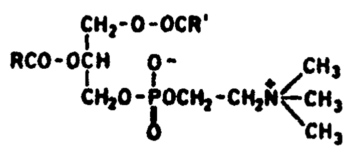
OMOGLOMERIN

FLAVOPROTEINS



RIBOFLAVIN

PHOSPHATIDES



LECITHIN

PHOSPHATIDES

lecithin

Apis mellifera L. (HYM).

ENZYMES

adenosine triphosphatase

Euscorpius italicus (Herbst) (SCORP).

L-amino acid dehydrogenase

Ctenus nigriventer Keys., Scaptocosa raptoria Walk (ARA).

cholinesterase

Vespula germanica Fbr., V. vulgaris L. (HYM).

alkaline phosphatase

Chrysocoris stolli Wolf (HET).

phospholipase A

Apis mellifera L., Vespa crabro L., Vespula vulgaris L. (HYM).

phospholipase B

Vespa crabro L., Vespula germanica Fbr., V. vulgaris L. (HYM).

phospholipase C

Myrmecia gulosa (F.) (HYM).

β-glucosidase

Pachydesmus crassicutis Wood (POL);

Diploptera punctata (Escholtz) (BLA).

hyaluronidase

Cimex lectularius L., Platymeris rhadamanthus Gaerst. (HET);

Apis mellifera L., Bombus pratorum L., Myrmecia gulosa Fabr., Polistes omissa Veyrauch, Vespa crabro L., Vespula germanica Fbr., V. vulgaris L. (HYM);

Araneus diadematus Clerck, Ctenus nigriventer Keys, Scaptocosa raptoria Walk (ARA).

invertase

Ethmostygmus spinosus (SCOL).

trypsin

Ctenus nigriventer Keys., Lycosa erithrognata Luc. (ARA).

Chap. 20 - Inorganic substances.

In the literature consulted the presence of inorganic substances has been found in the defensive secretions of various Arthropoda. For some of them a further and more carefully investigation by new methods is necessary:

hydrogen peroxide

Brachynus crepitans L., B. explodens Duft., B. sclopeta Fabr. (COL).

ammonia

Phosphuga atrata L., Silpha obscura L., Oeceoptoma thoracicum L. (COL);

Formica nigricans Em., F. polyctena Först., F. pratensis Retz., F. rufa L. (HYM).

nitrogen oxides

Brachynus crepitans L., Br. sp. (COL).

hydrochloric acid

Notodonta concinna (Abb. and Smith) (LEP).

nitrous acid

Brachynus crepitans L., Pheropsophus africanus Dej. (COL).

nitrites

Pheropsophus africanus Dej.(COL).

inorganic phosphates

Lycosa erythrognata Luc., Phoneutria fera Perty (ARA).

Water is also present as a carrier in many defensive secretions. Some Authors mention it:

Mastigoproctus giganteus (Lucas) (URO);

Schizura leptinoides Grote (LEP);

Brachynus crepitans L., B. explodens Duft., B. sclopeta Fabr. (COL);

Eurycotis biolleyi Rehn, E. decipiens (Kirby) (BLA);

Apis mellifera L. (HYM).

Organic substances not chemically defined.

Some organic and not defined substances are indicated in the literature as parts of the defensive secretions. Other products even if not chemically defined are described in the literature with a particular name, e.g.: scorpamin, buthotoxin.

We are reporting these brief data as well, for their indicative significance.

QUINONES

quinones

Orthocricus arboreus (Sauss.), Schyzophyllum mediterraneum , Spirostreptus castaneus Attems (JUL);

Blaps gibba L., Bl. judaeorum Miller, Bl. nitens Cast., Scotobates calcaratus , Tribolium sp., Uloma impressa Melsh., (COL).

quinones with alkyl groups

Schizophyllum mediterraneum , Spirostreptus castaneus Attems (JUL);

Eleodes obsoleta (Say) (COL).

SUGARS

disaccharide

Pachydesmus crassicutis Wood (POL).

polysaccharide

Centruroides sculpturatus Ewing (SCORP).

AMINO ACIDS

free amino acids

Chrysocoris stolli Wolf (HET);

Cerura vinula L. (larvae) (LEP);

Formica rufa L., Monomorium antarcticum Wheeler, M. pharaonis (L.), Pogonomyrmex badius (Latr.), Vespa crabro L., Vespula vulgaris L. (HYM);

Acanthoscurria atrox Vellard, Grammostoma actaeon Pocock, Gr.mollicoma Ausserer, Gr. pulcripes Simon, Lasiodora Klugii Koch, Latrodectus mactans L., Pamphobeteus roseus M.-Leitao, P. soracabae M.-Leitao, P. tetracantus M.-Leitao, Scaptocosa raptoria Wlk, Phoneutria fera Perty (ARA).

PEPTIDES

kinin

Apis mellifera L., Vespa crabro L., Vespula germanica Fbr., V.vulgaris L. (HYM).

apamin

Apis mellifera L. (HYM).

mellitin

Apis mellifera L. (HYM).

ENZYMES

anticoagulase

Scorpio arenicola L. (SCORP).

coagulase

Buthacus arenicola (E. Simon) (SCORP).

diastase

Ethmostygmus spinosus (SCOL).

alkaline endopeptidase

Platymeris rhadamanthus Gaerst. (HET).

enzymes

Leiurus quinquestriatus H. and E. (SCORP).

protease

Platymeris rhadamanthus Gaerst. (HET).

proteolytic enzymes

Ethmostygmus spinosus (SCOL).

esterase

Polistes omissa Weyrauch (HYM).

phospholipase (= lecithinase)

Platymeris rhadamanthus Gaerst. (HET);

Apis mellifera L., Bombus pratorum L., Vespula vulgaris L. (HYM);

Buthacus arenicola (E. Simon), Scorpio maurus L. (SCORP).

VARIOUS SUBSTANCES

indole base (probably scatole)

Pheidole fallax Mayr (HYM).

buthotoxin

Buthus martensi Karsch (SCORP).

toxic saponin

Diamphidia simplex Peringuey (= D. locusta Fairmaire) larvae (COL).

scorpamin

Androctonus australis L., Buthus occitanus Am. (SCORP).

toxalbumin

Diamphidia simplex Peringuey (= D. locusta Fairmaire) larvae (COL).

PART VI - NEW SUBSTANCES FOUND FOR THE FIRST TIME IN ARTHROPODA DEFENSIVE SECRETIONS.

Chap. 21 - Iridomyrmecin and iridoids present in Arthropoda.

Iridomyrmecin.

In 1948, with the collaboration of A. Nascimbene (223, 254) in the microbiological field, we pointed out the existence of an unknown antibacteric factor, which we called iridomyrmecin, in the Dolichoderin Ant Iridomyrmex humilis Mayr. This substance was obtained in a pure crystalline state in 1948 (258). Recognizing its insecticide property (229), we demonstrated its presence in the anal gland secretions and its employment by the ant as an offensive and defensive means against Insects. The centesimal composition $C_{10}H_{16}O_2$ was made known at the IX International Congress of Entomology at Stockholm, 1948 (published in 1952 (232)).

Iridomyrmecin is contained in a rough liquid state in a reservoir of the "anal glands" opening between the 4th and 5th urotergum. A full extraction carried out on three lots in different seasons revealed that the worker (weighing an average of 0,35 mg) contains from 3,453 gamma (about 1/100 of its body weight) (average of a lot of 20 million workers), to 2,930 gamma in the other lots examined.

Workers just formed have depigmented and delicate bodies, and their anal gland reservoir is empty; during their early life they stay confined to the underground nest; they come out and face external life when their bodies are strong and pigmented, and the iridomyrmecin venom reserve is developed.

Structure.

The structure, first partially (april 1955) and then completely (november 1955) was published by Fusco, Trave and Vercellone (128, 129).

Iridomyrmecin is a lactone of a cycloparaffin, more exactly of · (2-oxy-methyl-cyclopentyl) propionic acid [(1)].

Structural research was made easier by the discovery that bicarbossilic acid obtained by iridomyrmecin oxydization is identical to one of the isomer nepetalinic acids obtained by trasformation of another natural product of vegetal origin, nepetalactone.

[figure 1]

Nepetalactone is contained in the essential oil (catnip oil) of Nepeta cataria, a labiate widespread throughout Europe, Asia, America and Africa. McElvain and Eisenbraun are classic references on the products of this plant (e.g. 184 D, E; 185 A). Feline attracting substances are present in the leaves of Actinidia polygama Miq. (Actinidiacea is known in Japan as "matatabi")[(2)]; various works by Sakan and coll. starting from 1959 (286 C-N)show them to be present in iridomyrmecin, isoiridomyrmecin, dihydronepetalactone, isodihydronepetalactone and neonepetalactone. Actinidine is also found in the same plant, with a carbon atomic structure identical to that of iridomyrmecin and

---

(1) Isoiridomyrmecin, obtained by transformation of iridomyrmecin with alcaline alcoholates, was made known in 1948 in Stockholm at the IX International Congress of Entomology (232) and in a paper in 1951 (230); later thoroughly described by Fusco, Trave and Vercellone 1955 (128, 129). Cavill, Ford and Locksley 1956 (60) found it as a natural product in the defensive secretions of Iridomyrmex nitidus Mayr and Dolichoderus scabridus Roger Dolichoderine Ants, and they gave it the name of iridolactone; this name is used synonimously with isoiridomyrmecin as it was the earlier term for this substance. In the literature the term iridolactone was later used to refer brievly to the two isomers.

(2) Bates and Sigel 1963 (10 D), affirm that the trans-cis-isomer of nepetalactone proves extremely attractive to cats, while the cis-trans -isomer is much less attractive or inactive altogether. Sakan, Isoe, Hyeon, Katsumura, Maeda, Wolinsky, Dickerson, Slabaugh, Nelson 1965 affirm that the three iridoids dihydronepetalactone, isodihydronepetalactone, neonepetalactone are equally attractive to cats.

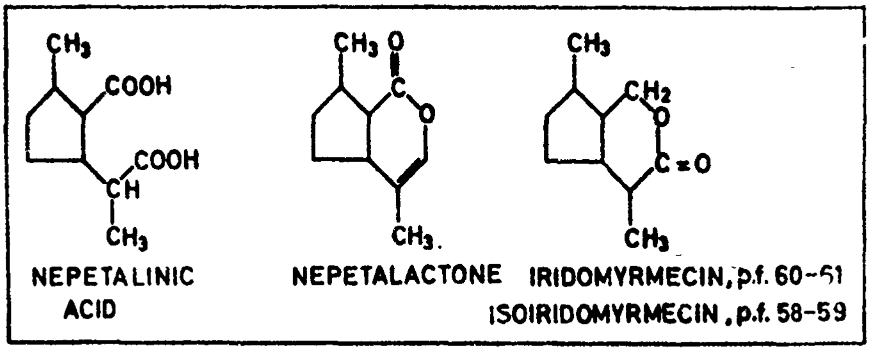

NEPETALINIC ACID
NEPETALACTONE
IRIDOMYRMECIN, p.f. 60-61
ISOIRIDOMYRMECIN, p.f. 58-59

Fig. 1

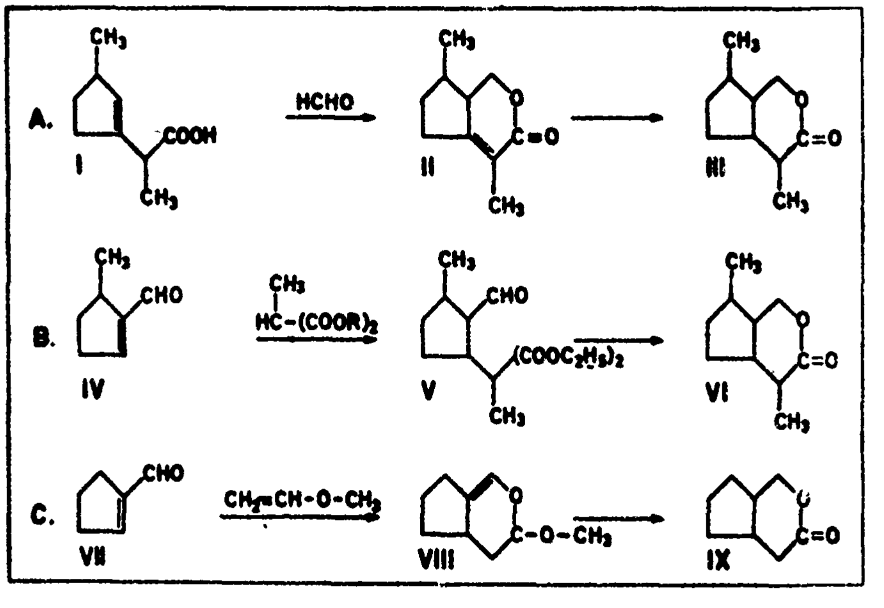

A.
B.
C.
HCHO
CH=CH-O-CH

Fig. 2

and correlated. Many other products of vegetal origin have the same structural relationship as the basic substance iridomyrmecin; collectively they are referred to as iridoids. Among these we may mention skytanthine, dehydroskytanthine, hydroxyskytanthine found in the Apocinacea of South America Skytanthus acutus Meyen (Casinovi and coll. 49 A-E; Marini-Bettolo and coll. 181 A, B; Djerassi and coll.[1]), harpagoside, harpagide, harpagide acetate, asperuloside, aucubin, catalposide, genepin, guaiol, loganin, monotropein, unedoside, verbenalin, etc.

Synthesis of iridomyrmecin and other iridoids.

Various syntheses of iridomyrmecin have been obtained in different ways. This has made it possible to obtain the synthesis of several other iridoids and to acquire information about the probable biogenetical pathways of these substances in plants and Insects. The first syntheses date back to 1958 (Korte and coll.; Clark and coll.); others followed and activity in this field is still going on.

In 1958 Korte, Falbe and Zschocke (166 B) obtain the synthesis of D,L-iridomyrmecin and of the correlate bicyclic lactones, and in 1959 (155 C) they publish further developments. In the first of these two papers the Authors give the three following schemes of synthesis.

[figure] 2

In the same year, 1958, Clark, Fray, Jaeger and Robinson (72 B) obtain the synthesis of D and L-isoiridomyrmecin starting from citronellal; in 1959 (73) starting from D-citronellal of natural origin, they synthetize D-iridodial[2] and D-isoiridomyrmecin. The L-

(1) DJERASSI C., KUTNEY J.P., SHAMMA M., SHOOLERY J.N. and JOHNSON L., 1961. Chem.Ind.: 210.

(2) Iridodial was found simultaneously by Trave and Pavan (339) and Cavill and coll. 1956 (60). Research went on with a mutual exchange of information between the two groups, but the Italians declared they would wait for the publication of the data of Cavill and coll. before publishing their own.

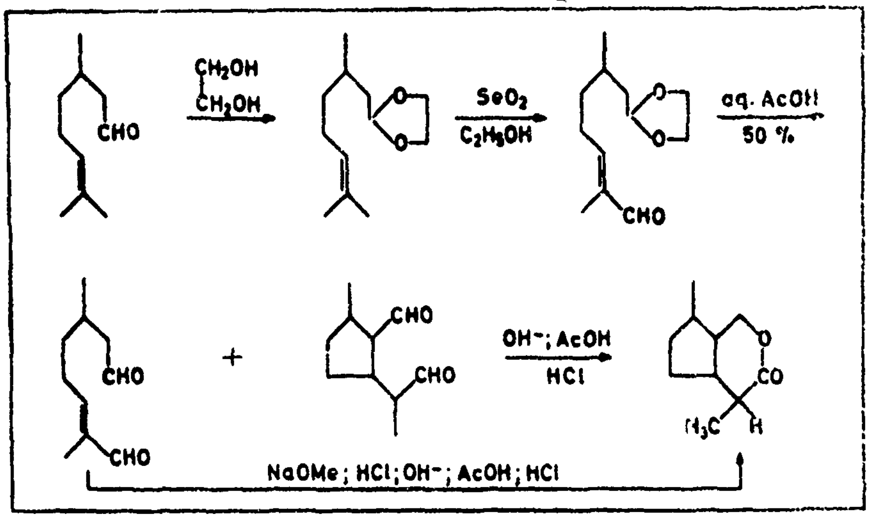

CH₂OH
CH₂OH
CHO
SeO₂
C₂H₅OH
aq. AcOH
50 %
CHO
CHO
CHO
+
CHO
CHO
OH⁻; AcOH
HCl
O
CO
H₃C
H
NaOMe; HCl; OH⁻; AcOH; HCl

Fig. 3

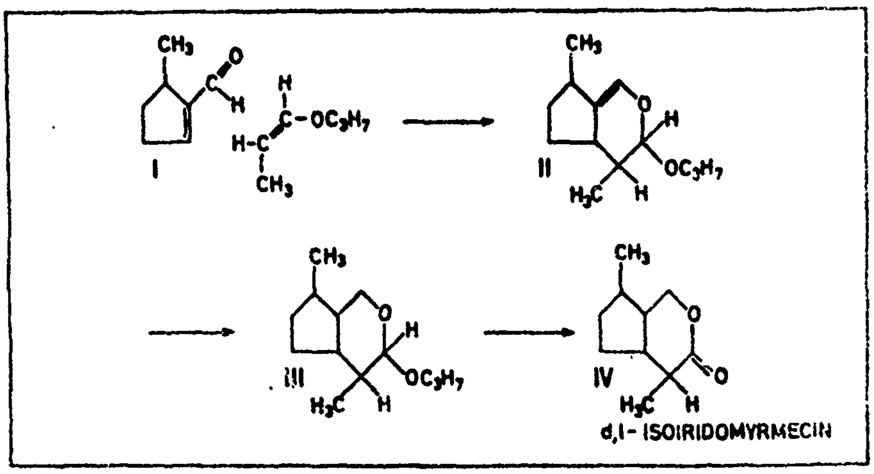
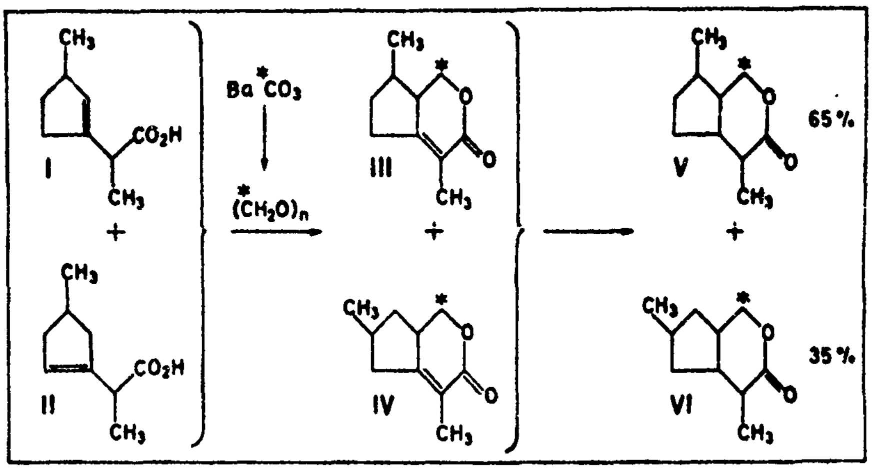
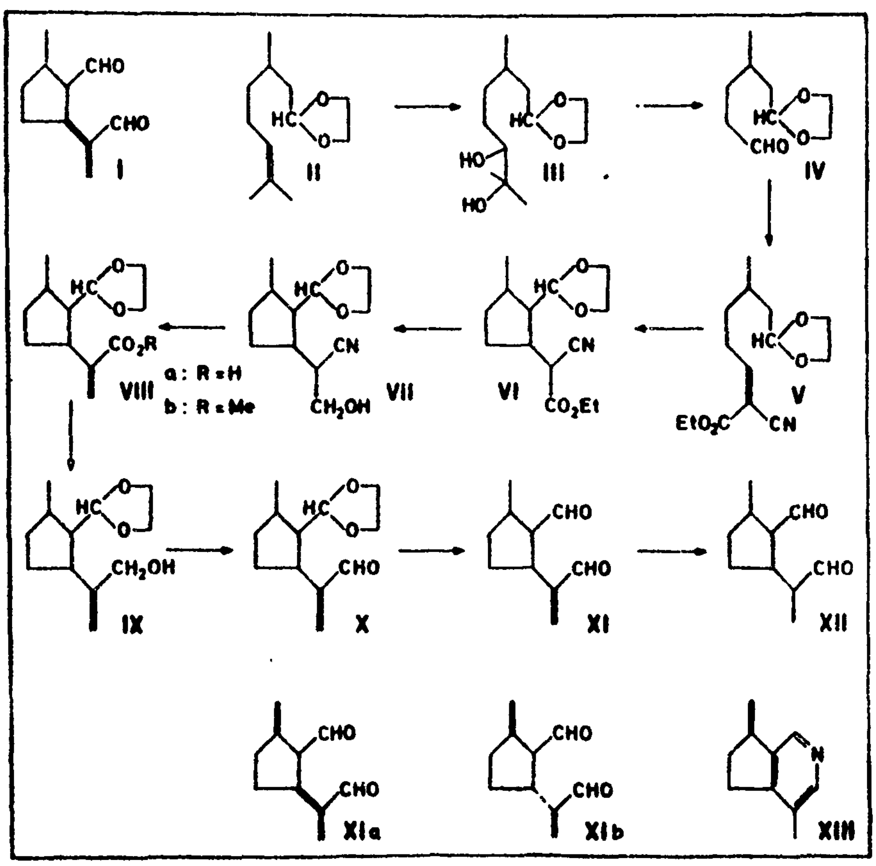

CH₃
O
H
H
C-OC₃H₇
H-C
CH₃
I
CH₃
O
H
II
OC₃H₇
H₃C
H
CH₃
O
H
III
OC₃H₇
H₃C
H
CH₃
O
IV
O
H₃C
H
d,l- ISOIRIDOMYRMECIN

Fig. 4



CH3
CO2H
I
CH3
+
CH3
CO2H
II
CH3
Ba*CO3
*(CH2O)n
CH3
*
O
O
III
CH3
+
CH3
*
O
O
IV
CH3
CH3
*
O
65 %
O
V
CH3
+
CH3
*
O
35 %
O
VI
CH3

Fig. 5



CHO
CHO
I
HC
O
O
II
HO
HO
III
CHO
IV
CO2R
VIII
a : R = H
b : R = Me
CN
CH2OH
VII
VI
CN
CO2Et
V
EtO2C
CN
CH2OH
IX
CHO
X
CHO
CHO
XI
CHO
CHO
XII
CHO
CHO
XIa
CHO
CHO
XIb
N
XIII

Fig. 6

citronellal, obtained from pinene through a series of chemical transformations, was also transformed into L-iridodial and L-isoiridomyrmecin.

[figure]3

Büchel and Korte 1960 (40) deal extensively with their systems of synthesis of iridomyrmecin type lactones.

Korte, Büchel and Zschocke 1961 (166 A) obtain the synthesis of D,L-isoiridomyrmecin in the pathways shown in the following diagram. Isoiridomyrmecin is epimerized into iridomyrmecin during gas chromatography at 240°C.

[figure]4

Korte and Schreiber 1962 (166 D) obtained the synthesis of marked iridomyrmecin -(3-^{14}C), using Barium carbonate -^{14}C as in the diagram illustrated below. The marked substance was transformed with ox liver homogenate into the corresponding hydroxycarbonilic acid. Aedes aegypti larvae have a poor absorption of marked iridomyrmecin.

[figure]5

In two papers of 1962 (67 A) and 1964 (67 C) Cavill and Whitfield make known the synthesis of natural dolichodial enantiomorph (fig. 6 , I), analagous to Clark and Coll.'s synthesis of iridodial, starting from ethyl acetylene α-(2-formyl-3-methylcyclopentyl)-cyanacetate, obtained from the transformation of D(+)citronellal. With hydrogenation of the mixture of XIa and XIb synthetic products (cis and trans dolichodial isomers) iridodial identical to that produced by Clark and coll. starting from D-citronellal was obtained. D-actinidine (XIII) is obtained from bis-2,4-dinitrophenylhydrazone of iridodial (XII) derived from hydrogenation of synthetic dolichodial.

[figure]6

The synthesis of (-)iridomyrmecin (Table 7 III) and correlated lactones (VIII and IX) is obtained by Gibson 1964 (131 A) starting from trans-pulegenic acid (I) derived from (+)pulegone. Treatment with

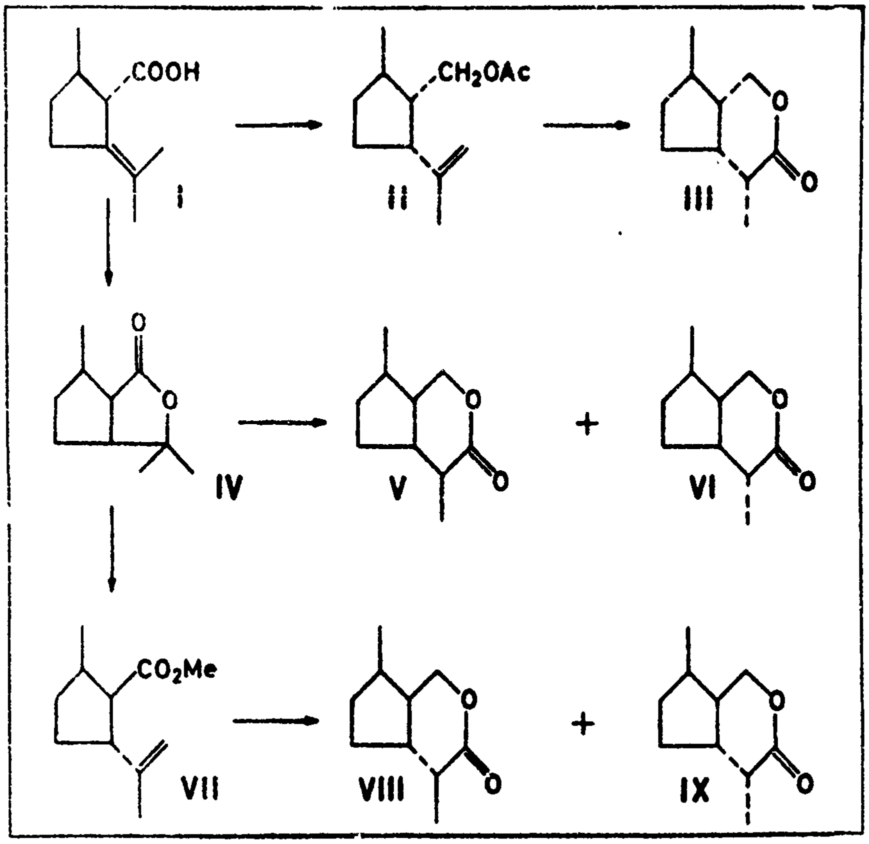

COOH
I
CH2OAc
II
O
O
III
O
O
IV
O
O
V
+
O
O
VI
CO2Me
VII
O
O
VIII
+
O
O
IX

Fig. 7

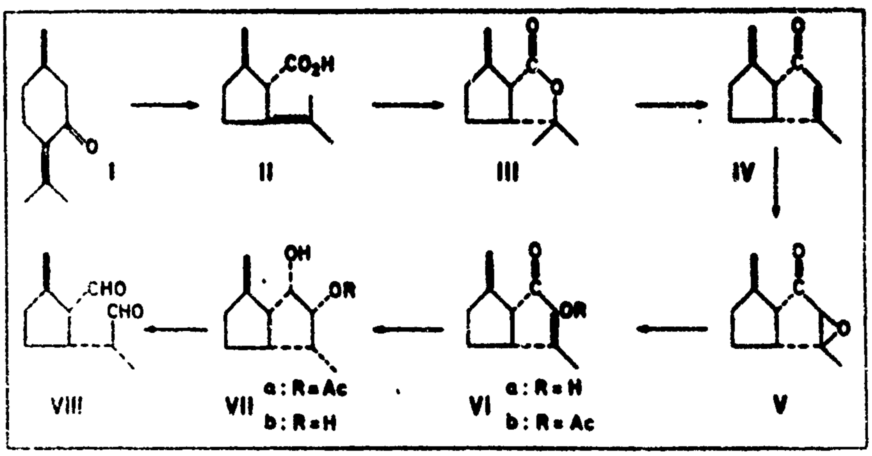

O
I
CO2H
II
O
O
III
O
IV
V
OR
O
VI
a: R=H
b: R=Ac
OH
OR
VII
a: R=Ac
b: R=H
CHO
CHO
VIII

Fig. 8

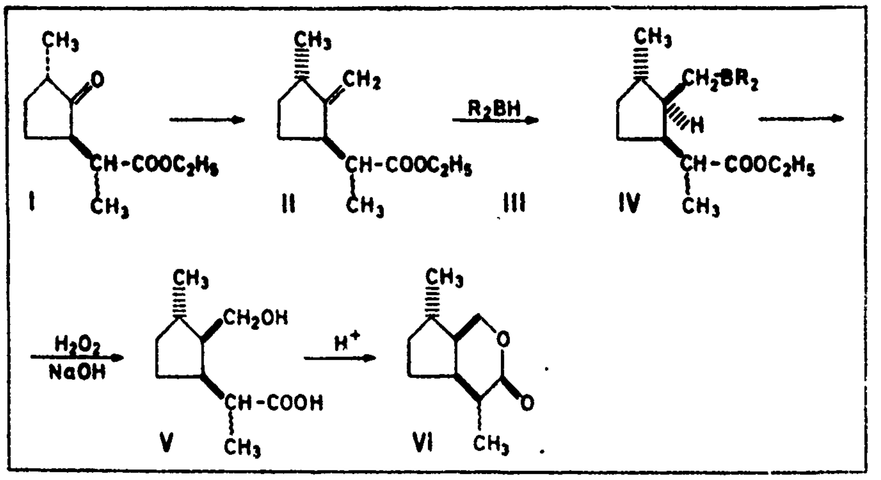

CH3
O
CH-COOC2H5
I
CH3
CH2
II
R2BH
III
CH2BR2
H
IV
H2O2
NaOH
CH2OH
CH-COOH
V
H+
O
VI

Fig. 9

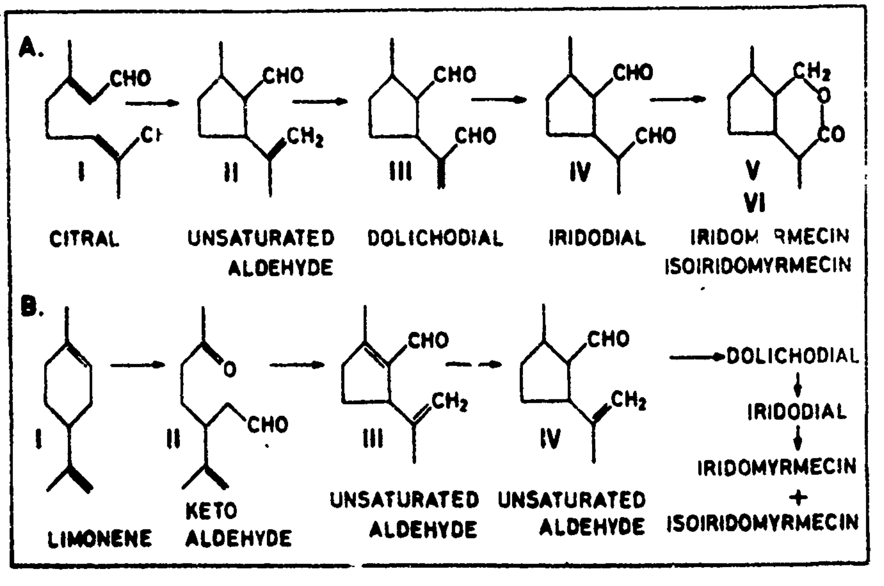

A.
CHO
CITRAL
UNSATURATED ALDEHYDE
DOLICHODIAL
IRIDODIAL
IRIDOMYRMECIN
ISOIRIDOMYRMECIN
B.
LIMONENE
KETO ALDEHYDE
UNSATURATED ALDEHYDE
UNSATURATED ALDEHYDE
DOLICHODIAL
IRIDODIAL
IRIDOMYRMECIN
+
ISOIRIDOMYRMECIN

Fig. 10

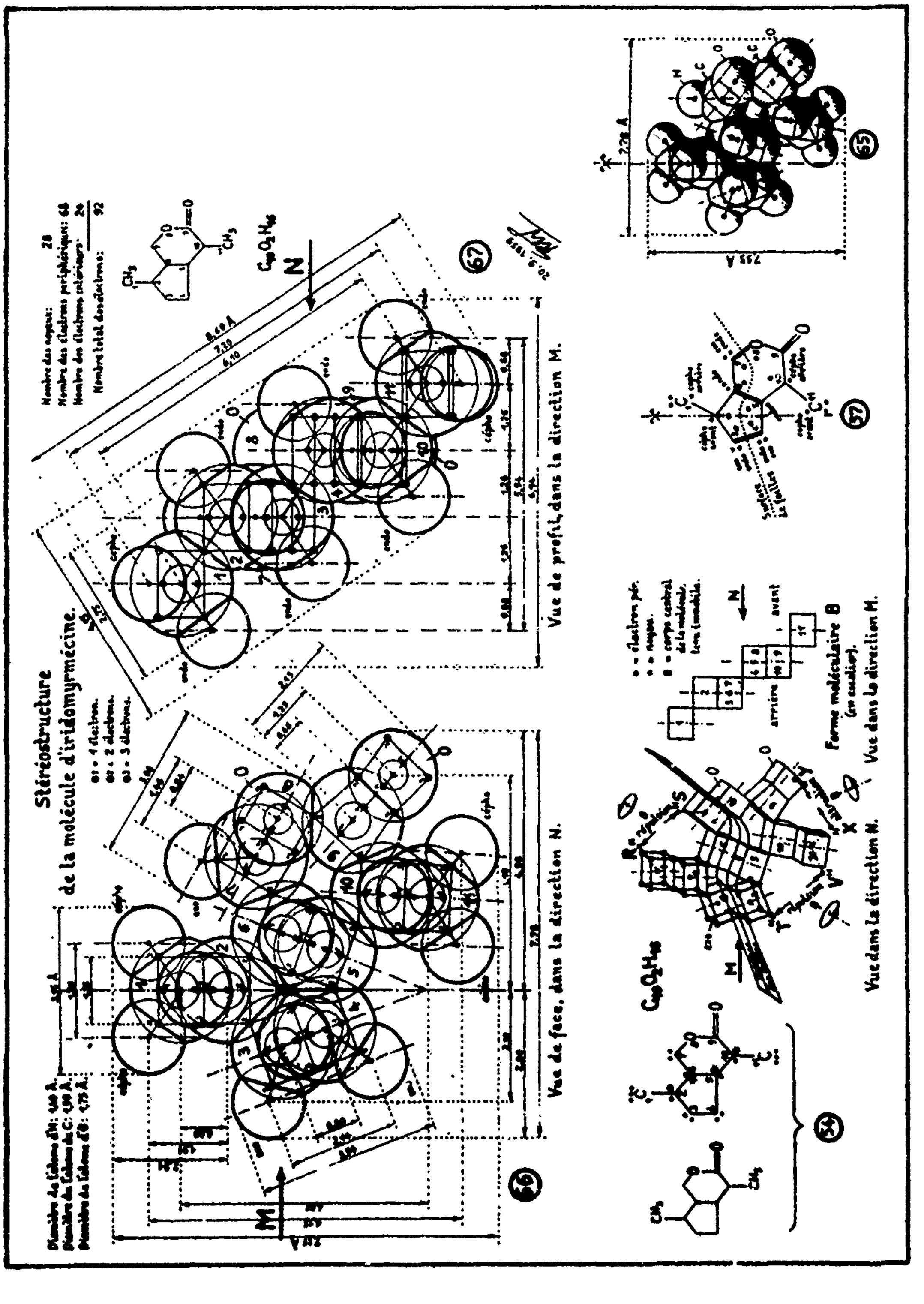

Stéréostructure
de la molécule d'iridomyrmécine.
Vue de face, dans la direction N.
Vue de profil, dans la direction M.
Forme moléculaire B
(en escalier).
Vue dans la direction M.
Vue dans la direction N.
arrière
avant
56
57
54
55
67

Fig. 11

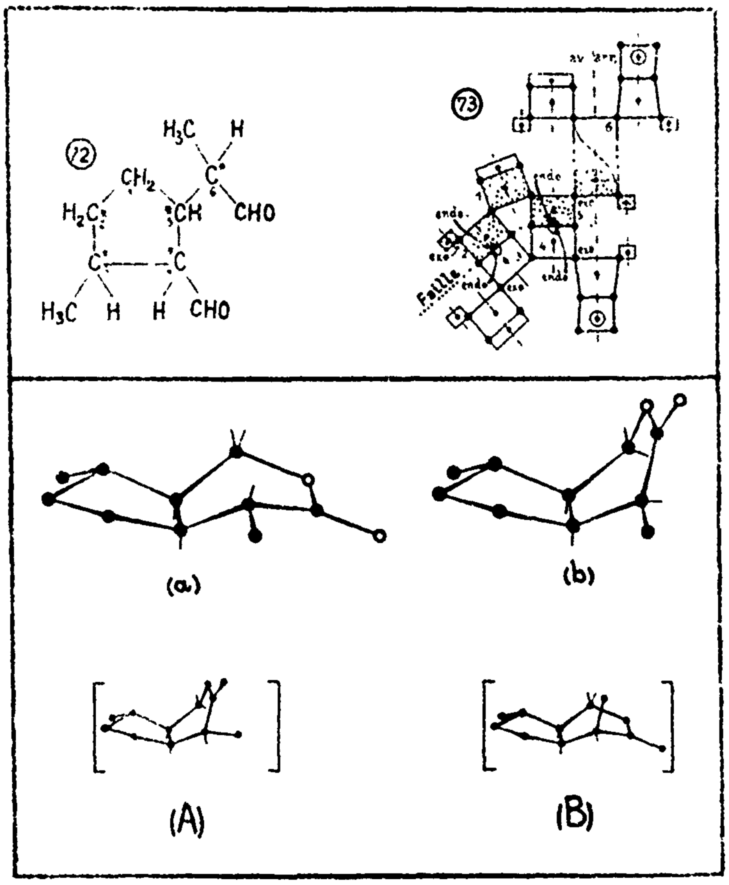


Fig. 12

a base gives (+)isoiridomyrmecin.

[figure] 7

Achmad and Cavill 1963, 1961 (1, 1A), starting from trans-pulegenic acid obtained from (+)pulegone (Table 8 I) obtain the synthesis of enantiomorph VIII of natural iridodial and correlate products. By successive treatment synthetic iridodial VIII gave a product identical to natural iridodial.

[figure] 8

Sisido, Utimoto and Isida 1964 (321), obtain a synthesis of iridomyrmecin starting from a derivate of cyclopentanone, ethyl 2-(3--methyl-2-oxocyclopentyl) propionate (IV) as in Table 9 .

[figure] 9

Wolinsky, Gibson, Chan and Wolf 1965 (361), starting from trans-pulegenic acid, describe the stereospecific synthesis of 6 of the 8 possible iridolactones, meaning by the term iridolactone, in agreement with other authors, iridomyrmecin and isoiridomyrmecin together. They presents probable biosynthesis pathways starting from citronellal, citral and limonene (fig. 10).

Among the various syntheses of iridoids not yet found as natural substances in insects we may mention those of Cavill, Ford, Hinterberger, Solomon 1958 (59) and 1961 (59 A) regarding bisnoriridodial, bisnoriridolactone, and correlate substances, and those of Garanti 1962 (129 B), who synthetize nor-isoiridomyrmecin from trans-nor-nepetalic acid going through nor-nepetalactone, and the researches on nor--nepetalactone synthesis by Trave, Merlini, Garanti 1958 (337).

Weckering 1960 (351) presents the bicyclic skeleton stereostructure of iridomyrmecin (Table 11); from these he derives the detailed structural formula (Table 12). Iridodial is represented by Weckering with the stereoelectronic structure in Table 12 . I should also like to mention the works of McConnel and Schoenborn 1962 (184 D), McConnel, Mathieson and Schoenborn 1962 (184 B) and 1964 (184 C) on iridomyrmecin and isoiridomyrmecin crystalline structure.

Biogenesis of iridomyrmecin and correlate products (iridoids).

It is interesting to note how both iridomyrmecin just as related products from the group of iridoids formed by plants and Insects on an identical carbon atom skeleton, follow the same isoprenic rule.

There is no definite information on the ways of biogenic derivation of iridomyrmecin. Hypotheses have been made about its biosynthesis, but experimental demonstration is still lacking. The newly formed worker, deprived of the normal regurgitated food fed to it by older workers, and nourished mainly with sucrous solutions, is able to build up its own dose of iridomyrmecin. This, however, may happen at the cost of organic substances already present in the organism since the beginning of experimentation. As already pointed out ( ), the structure of iridomyrmecin and correlates might go back to head-to-tail concatenation of two isoprenic residues (table). Mevalonic acid might be its precursors as is the case for other terpenic structures. Iridodial, in the opinion of various authors, may be considered as a precursor of iridomyrmecin and isoiridomyrmecin. See Chap. VII, for experiments of incorporation of products with radioactive carbon (mevalonic acid, sodium acetate, etc.) for the formation in vivo of various iridoids in plants and animals.

We have seen that citronellal is considered to be a possible natural precursor (see diagram on page fig. 10); by irradiation of citral (table 10 , diagram A) aldehyde (II) was obtained which can produce dolichodial by enzyme. oxydization; this, after reduction to iridodial and disproportion, can produce iridomyrmecin and isoiridomyrmecin. Oxydization of (-) limonene to linear ketoaldehyde and successive aldolic cyclization leads to an unsaturated aldehyde as in diagram B of table ; then enzyme reduction can prouce an unsaturated aldehyde from which it is possible to go on to dolichodial, iridodial, irido and isoiridomyrmecin as in diagram A.

[figure] 10

The synthesis of iridoids from citral, a typical acyclic monoterpene, and from limonene, a typical cyclohexanoid derivative, are considered as probable also in nature. It is remarkable that hitherto iridoids appear to be present only in Insects and plants.

Biological activities of iridomyrmecin.

Antibacteric and antimitotic activity.

Iridomyrmecin show weak antibacteric properties as pointed out at the beginning of our research with A. Nascimbene (254, 257, 223, 224, 260, etc.).

According to Hamasaki 1961 (144 A), the development of fungi (Mucor mandhricus, Rhizopus javanicus, Aspergillus oryzae, A. niger, Penicillium chrysogenum Q 176) is completely inhibited with a concentration of 1×10^{-3} g/cc of D(+)-isoiridomyrmecin, but only partially in a concentration of 2×10^{-4} g/cc. It is inactive on bacteria Pseudomonas fluorescens, Escherichia coli, Staphylococcus aureus in vitro, while it completely inhibits Bacillus aureus in a concentration of 1×10^{-3} g/cc.

Insecticide activity (229, 232, 260, 245, 246, 275 A).

The insecticide activity that I found in 1959 (see 229) justifies the existence of iridomyrmecin in nature as def sive products of the ant species producing it.

Experiments on the insecticide activity carried out on 39 species of Arthropoda also by actographic recording have pointed out the toxic activity of iridomyrmecin against insects found in agricultural, forestal, economic, industrial, sanitary and veterinary fields, and also against animal Acari parasites. Generally speaking, Arthropoda which are most sensitive on coming into contact with iridomyrmecin, show a precocious agitated reaction in respect to the action of DDT-pp' and HCH. According to Ronchetti 1958 (275 A) its toxicity for Arthropoda, particularly high between 50 and 100 gamma per cm^2, is greater than that of DDT-pp' for most of the experimentated species, and in a few cases also that of gammahexane, while its toxicity for warm-blooded animals is remarkably lower than that of the latter insecticides.

Iridomyrmecin exerts a contact toxic activity of various degrees on almost all the Arthropoda species examined: therefore, no real specificity of action or non-action on particular systematic groups is apparent. However, Formicidae in general are particularly sensitive to iridomyrmecin, as if Iridomyrmex humilis Mayr had at its disposal an offensive-defensive venom created precisely for its struggle against ants, which are the deadliest enemies of the species. This is proved by the fact that in taking possession of new ground and later expansion it provides for thorough elimination of any species of indigenous ant. Such action is so thorough as to cause changes in the balance of the fauna.

Iridomyrmex humilis Mayr is itself very sensitive to contact with its own venom.

According to Clark, Fray, Jaeger and Robinson 1959 (73) there is no difference between the insecticide activity of natural iridomyrmecin and the two epimeric lactones. Cavill and Clark 1967 (56) confirm that irido and isoiridomyrmecin are highly lethal, this being the factor that proves their efficiency in defending the species (see also Cavill and coll. 1961 (59 A)).

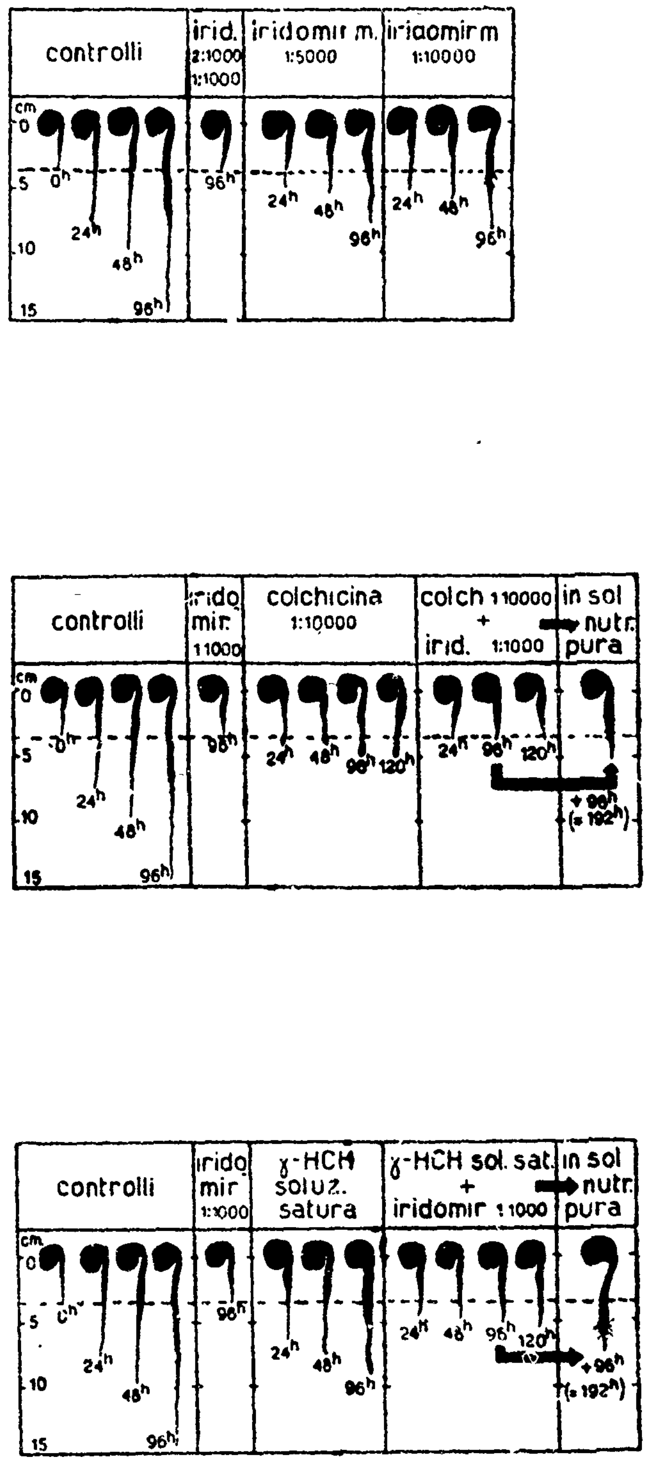

controlli
irid. 2:1000 1:1000
iridomir m. 1:5000
iridomir m 1:10000
cm
0
5
10
15
0h
24h
48h
96h
controlli
irido mir 1:1000
colchicina 1:10000
colch 1:10000 + irid. 1:1000
in sol nutr. pura
120h
+96h (=192h)
controlli
irido mir 1:1000
γ-HCH soluz. satura
γ-HCH sol. sat. + iridomir 1:1000
in sol nutr. pura

Fig. 13

Fitoinhibiting and antimitotic activity (237, 245, 246, 252, 260, 262).

Iridomyrmecin powder sprinkled on the leaves of various plants causes noticable toxic reactions. When applied in the Macht test(development of the germ of Lupinus albus Leguminosae seeds), it slows down the radical development completely or partially, depenging on the concentration in the alimentary liquid, the plant may start developing again when moved to a pure alimentary environment.

When applied together with colchicine (which produces the well known c-tumour) or with HCH gamma isomer (which produces a typical swelling of the root) it eliminates the tumoral action of the two products. Later transfer into a pure nutritive solution allows a fresh start of normal growth without the typical tumoral alteration. In appropriate conditions therefore it opposes the oncogenous stimulus of colchicine and gammahexane and it eliminates the effects on Lupinus albus.

[schematic diagrams of the Lupinus] fig. 13

Iridomyrmecin applied in a dose of 1:1000 to Allium cepa procures, after 4 hours, inhibition of the roots which later wither. The number of mitotic phases diminishes abruptly until the 4th hour of treatment and ceases at 24 hours. The reduction of the total number of stages appears due to the incapacity of the cell to enter the prophase. [~~figure~~]

The apical meristem cells of the roots and the rare cases of mitotic phases present did not show any noticable alterations. Only after 48 hours do the cells become smaller and the nuclei no longer coloured by Feulgen reaction.

The addition of 1:1.000.000 iridomyrmecin inhibits the development causing cytoplasmatic lysis, nuclear pycnosis and remarkable cellular rarefaction on cultures of chicken embryo heart fibroblasts; a 1:2.000.000 dose produces weaker effects.

<u>Toxicity and systemic action on warm-blooded animals</u> (233, 245, etc.).

Iridomyrmecin has very low toxicity for warm-blooded animals. When applied in powder or oily solution to human skin over long periods, it does not provoke any cutaneous reaction.

In the white rat the average tethal dose through the stomach is 1,5 g to 1 Kg of animal (0,225 g for DDT, 0,190-0,225 g for gammahexane, 0,0125 g for parathion); a 4% oily solution with a dose of 0,5 g of iridomyrmecin per Kg, administered <u>per endoperitonaeum</u>, has no lethal effects, while1 g per Kg is getting close to DL 50. Toxicity is therefore very low.

When injected into the white rat in oily solution with a dose of 0,25/Kg <u>per endoperitonaeum</u>, it enters the organs (liver, lungs kidneys, spleen, brain, blood) where it is active for a short time. It overcomes the hemato-encephalic barrier because it is also active for a short time in the brain. If in hydroalcoholic solution it persists in its active form in the organs for a longer period.

Pharmacological experiments <u>in vivo</u> (cardiac rhythm, pressure and breathing in an anesthesized dog) and in isolated organs (uterus of female rat <u>in estrum</u>) showed that iridomyrmecin, even in large doses, does not have any systemic toxic action; larger doses have shown a slightly depressive action on pressure and a limited respiratory stimulation.

The substance has therefore extremely low acute and systemic toxicity for worm-blooded animals.

Chap. 22 - Dendrolasin.

In literature the Ant Lasius (Dendrolasius) fuliginosus was remarkable for the odour it produced which has been defined in various ways. This species lives in colonies, sometimes composed of hundreds of thousands of ants, living cavities in tree-trunks. On being disturbed the workers emit a characteristic smell, similar to lemon peel or vegetal juices (for example that of the Labiata Melissa officinalis L., called citronel or lemoncine, of the Verbenacea Lippia citriodora H.B.K. or also of Andropogon citratus D.C.). This typical and very persistent smell is due to the complex mandibular gland secretion emitted from the base of the jaws.

Dendrolasin was the first component of the mandibular gland secretion of Formica Lasius (Dendrolasius) fuliginosus Latr. to be isolated (Pavan 1956, 240), and chemically defined (Quilico, Piozzi, Pavan 1956, 271; 1957, 273). It is a liquid product which is preserved ready for use in the reservoir of the glands mentioned (~~see Table~~). The crude secretion is composed of various substances, including the following: methylheptenone, perillen, cis-citral, trans-citral, farnesal (Bernardi, Cardani, Ghiringhelli, Selva, Baggini, Pavan, 1967, 13A).

The emission of this mandibular gland secretion causes alarm and the secretion has a repellent and therefore defensive function, particularly regarding other ants. Insecticide activity due to contact is usually low, but it proved notably stronger than equal doses of DDT-pp' on the various species of Ants tested; L. (D.) fuliginosus itself is very resistent to its own secretion (~~Table~~).

Structure.

Dendrolasin ($C_{15}H_{22}O$), new to chemical literature, proved to be a (4:8-dimethylnon-3:7-dienyl) furan. Quilico, Grünanger, Piozzi 1957, 270A, broadened their research to include the synthesis of tetra-

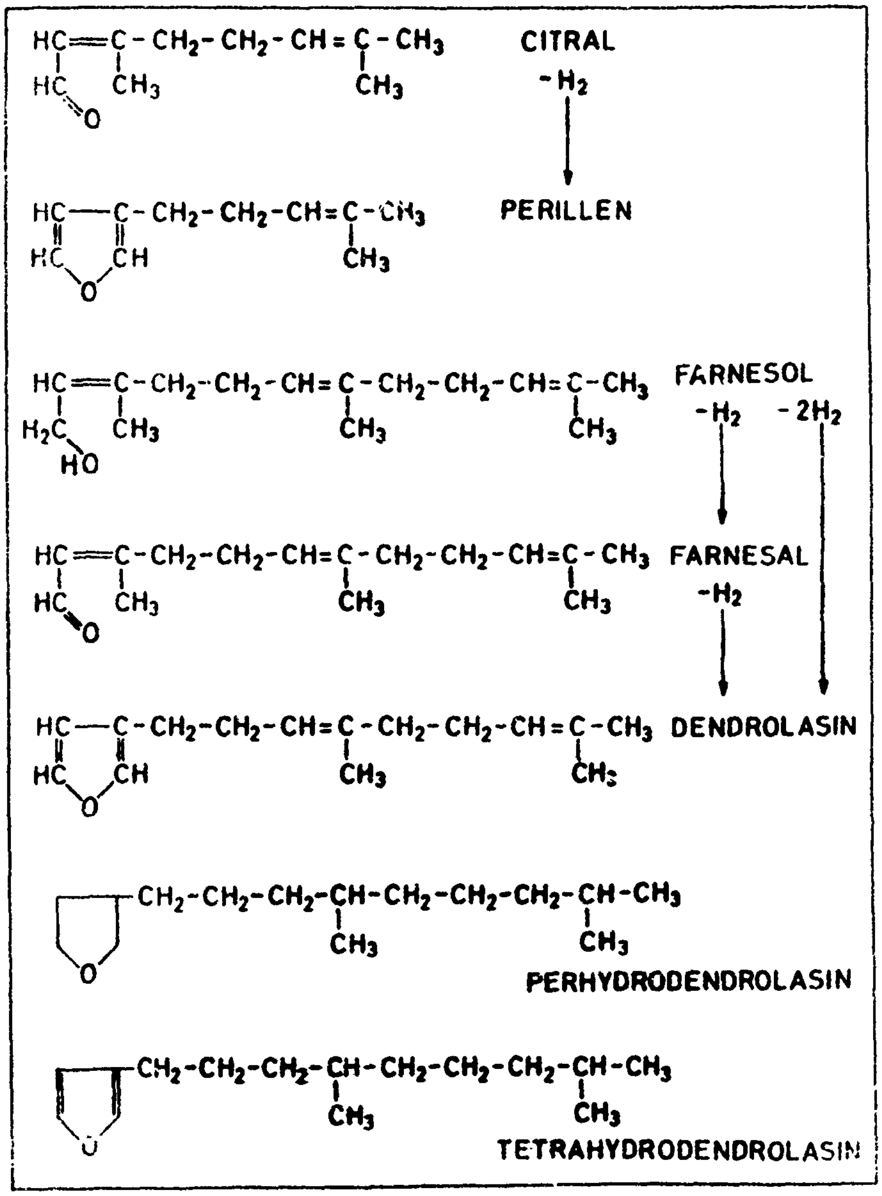

CITRAL
$-H_2$
PERILLEN
FARNESOL
$-H_2$
$-2H_2$
FARNESAL
$-H_2$
DENDROLASIN
PERHYDRODENDROLASIN
TETRAHYDRODENDROLASIN

Fig. 14

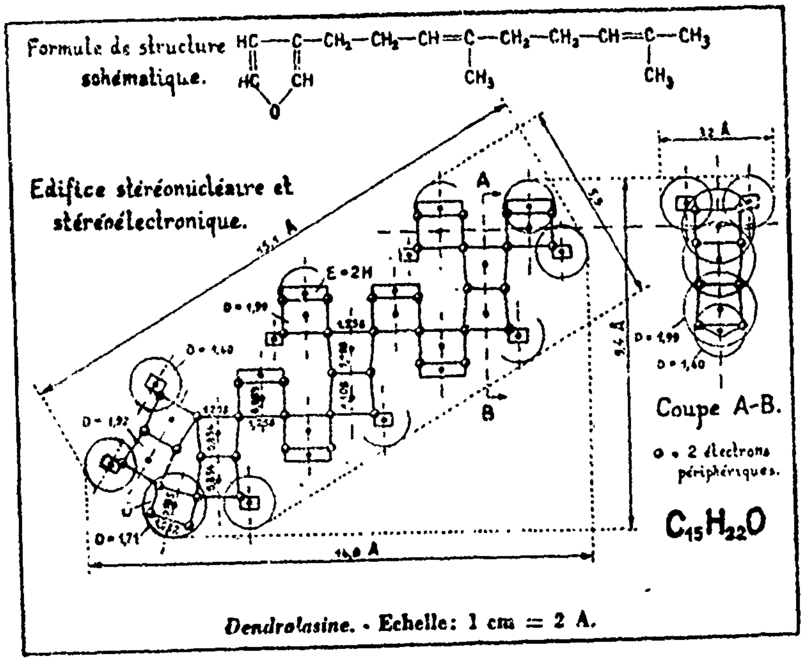


Fig. 15

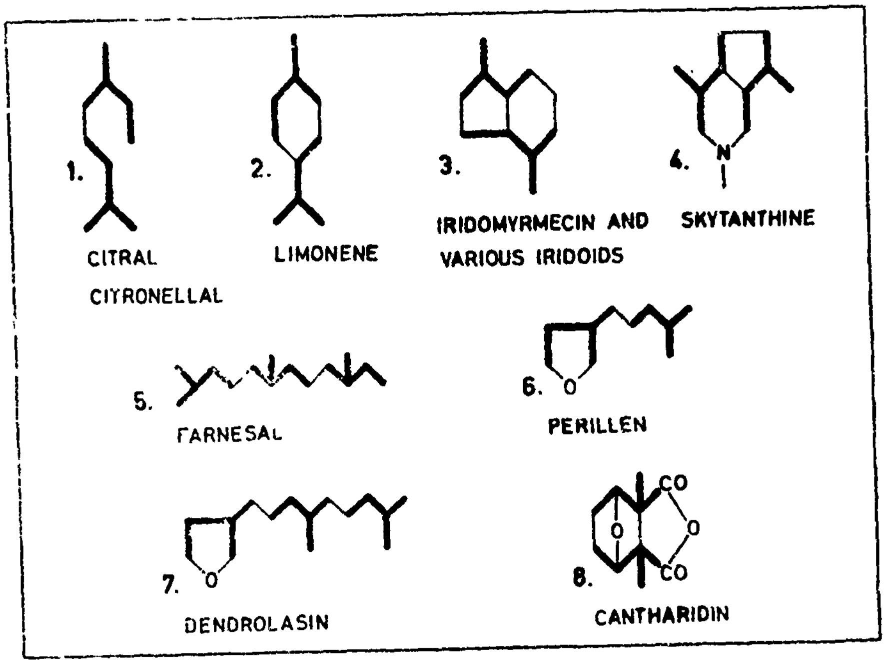


Fig. 16

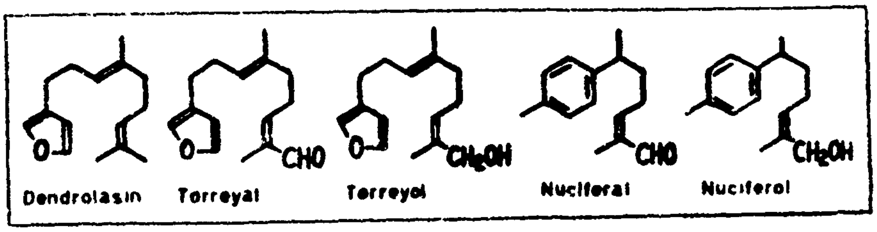


Fig. 17

hydro and perihydrodendrolasin (fig. 14 ;) confirming the structure indicated for dendrolasin. Weckering, 1960, 351, has published the stereonuclear and stereoelectronic structure of dendrolasin (fig. 15).

Dendrolasin biogenesis is still unknown. It has been pointed out (271, etc.) that the structure of the substance may correspond to the union of isoprenic residues; this is also likely for several other Arthropoda defensive secretions and for products of vegetal origin (see for example Chap. 21): in particular for citral and perillen (2 isoprenic units) and for farnesal and dendrolasin (3 isoprenic units), present in the secretion (see fig. 16). The simultaneous presence of these four products and their structural affinities pose the problem of the possible relative relationships of biogenetic derivation, which are under research at present. For the time being we may mention that radioactive dendrolasin was obtained by feeding the subjects with marked mevalonic acid: this suggested a transformation of mevalonic acid into farnesylpirophosphate and later oxidation and furanic ring cyclization (Castellani and Pavan 1966, 54). Several products which are structurally correlated with dendrolasin (e.g. perillen) are found in plants and recently dendrolasin was found (286B) in two plants (Ipomoea batatas and Torreya nucifora Sieb. and Zucc.) together with four new sesquiterpenes nuciferal, nuciferol, torreyal, torreyol (Sakai and coll. 1963, 286B, see table 17). Comparative biogenetic study of these products present in plants and of those correlate with dendrolasin present in Insects offers an interesting line of work. The structural relationship existing between dendrolasin and farnesol and farnesal (see table 14), factors of the young hormone produced by the corpus allatum of insects, induced Wigglesworth (1963, 355A) to examine the properties of dendrolasin, which were found to be weak.

When exposed to air dendrolasin polymerizes, changing into an insoluble solid product; polymerization is activated in an acid ambient. The presence of a solid cohesive in the "cardboard" with which L. (D.) fuliginosus builds its nest, can be interpreted as polymerized dendrolasin.

Chap. 23 - Pederin, pseudopederin, pederone.

The toxic activity of several species of the Paederus genus (Coleoptera Staphylinidae) on the skin and eyes of warmblooded animals and man, met with in every continent, was pointed out in numerous publications the first of which was by Da Silva 1912 (1). In literature the toxic substance responsible for dermatitis was generally identified as cantharidin, even though some authors stated that this substance was out of the question (2). For a more detailed knowledge of the subject, see Pavan-Bo 1952 (3) and Pavan 1963, 251.

Skin and eye affections due to Paederus were called "pederosi" by Maugeri and Candura 1964 (4).

The problem of the identification of the toxic substance was solved when it was obtained in its pure crystalline state from Paederus fuscipes Curt. Being a new product in chemical literature, I called this substance pederin (Pavan-Bo 1953, 253). The differential chemical, physical and biological features of cantharidin and pederin are shown in Table 18 .

Pederin is present usually with a percentage of 1% per weight of P. fuscipes that is 1 gamma per specimen, with considerable individual variations and percentages up to 10 times greater in the female.

---

(1) DA SILVA P., 1912. Le Paederus columbinus est vésicant. Arch. de Parasit., Paris, 15: 3.

(2) We do not believe that P. caligatus Er., closely related to P. fuscipes Curt., contains cantharidin, as was recently stated in Stepanova O.S., Alt'er E.N., Viranova L.I., 1961. (Study of P. caligatus extract). Farm.Zhur., 16: 56-57 (in russian).

(3) PAVAN M., BO G., 1952. Ricerche sulla differenziabilità, natura e attività del principio tossico di Paederus fuscipes Curt. (Col. Staph.). Mem.Soc.Ent.It., 31: 67-82.

(4) MAUGERI S., CANDURA F., 1964. Diffusione e prevenzione delle zoonosi. Atti II Congr.Naz.Medicina Rurale: 57-191.

from Pavan and Bo, 1953 (253)

Table 18

Possibility of differentiation between cantharidin and pederin.

Data of differentiation	Cantharidin	Pederin
I: ORIGIN:	Coleoptera Meloidae (various species of the genera *Lytta, Meloë, Zonabris, Epicauta, Milabris,* etc.)	Coleoptera Staphylinidae (*Paederus fuscipes* Curt. and probably other species belonging to the genus *Paederus*).
II: CHEMICAL TESTS		
1) Solubility		
a) Chloroform, carbon tetrachloride, acetone, ethyl ether, ethyl acetate, ethyl acetoacetate, benzene, toluene, xylene, tetralin, ethylene chlorohydrin, acetic anhydride, acetic acid, hydrochloric acid, sulfuric acid, nitric acid.	+	+
b) petroleum ether, glycerin, ammonia (33%)	0	0
c) water, physiological solution, carbon disulfide, methanol, ethanol (cold and warm), butyl alcohol, isobutyl alcohol, benzyl alcohol, amyl alcohol, ethylene glycol, triethylene glycol, propylene glycol, decalin.	0	+
d) sodium hydroxide N.	+	0
III: PHYSICAL TESTS		
Melting point (¹)	218°C	112°C
3) May be extracted by the following methods:		
MARFORI and PIUTTI 1935.	+	0
STASS-OTTO-DRAGENDORFF-OGIER (DOURIS 1935).	+	0
Deutsches Arzneibuch 1938.	+	0
STASS-OTTO-OGIER (DOURIS 1951).	+	0

¹) Microdetermination with Kofler's apparatus.

IV: BIOLOGICAL TESTS

4) Reaction on human beings: skin	*Acute*: Typical vesication (bulla with serum). (1) (2). *Chronic*: Unknown	*Acute*: (1) (2): epidermic necrotization (without bulla or serum). *Chronic*: (1)(2): desquamation for many months.
5) Reaction on albino mouse:		
a) skin of the head	Slight local swelling, desquamation, depilation without scalp and return of hair (2)	Huge edema of the anterior half of the body. Scalp, reconstitution of tissue with permanent loss of hair (2).
b) skin of the back	Desquamative dermatitis (2)	Dermatitis with necrosis (2)
c) pulmonary histological test	Exudates (3)	No exudates (2)
d) renal histological test	Glomerulonephritis (3)	Kidney undamaged (3)
6) Attraction for insects (4)		
a) *Anthomyia pluvialis* L. (5)	+	0
b) *Anthicus quadriguttatus* Rossi (6)	+	0
c) *Formicomus pedestris* Rossi 6)	+	0
d) *Notoxus monoceros* L. (6)	+	0

1) Experimental and accidental tests, and literature data.
2) Cf. PAVAN-BO 1952 and BO-VALCURONE 1953.
3) PETRI 1930.
4) PAVAN, unpublished.
5) Diptera Anthomyidae.
6) Coleoptera Anthicidae.

from Pavan and Bo, 1953 (253)

During the course of chemical researches on P. fuscipes inconsistent traces of another new substances have been found; this substances was called pseudopederin (Quilico, Cardani, Ghiringhelli, Pavan 1961,269A) and a third called pederone (Cardani, Ghiringhelli, Quilico, Selva, 1967, 49), present in quantities of 25-50 mg per Kilo of insects.

Pederin was also found in the following species: P. fuscipes Curt., P. melanurus Ar., P. lithoralis Gravh., P. rubrothoracicus Goeze (all european but fuscipes is also widespread in Asia), P. rufocyaneus Bernh. (Mozambico), P. columbinus Cast. (South America).

Pseudopederin was found in P. fuscipes. Pederone was found in P. fuscipes and columbinus.

Structure.

Research on the structure of pederin and derivates required about 100 kilos of P. fuscipes (25 million individuals) which we obtained by carefully organized collection with teams of dozens of men in the countryside around the Pianura Padana and personnel for laboratory preparation [1].

The centesimal composition and structure of pederin ($C_{25}H_{45}O_9N$) and pseudopederin ($C_{24}H_{43}O_9N$) were the subject of a first publication (Quilico, Cardani, Ghiringhelli, Pavan 1961,269A) and were later completely defined in Cardani, Ghiringhelli, Mondelli, Quilico 1965, 46; 1966,47).

From the excellent studies on structure by Quilico, Cardani and coll., we learn that pederin - by hydrolysis with water - loses methanol and changes into pseudopederin; this through the action of barium

(1) This working, though careful, caused every year (since 1958 till 1965) many hospitalizations for "pederosi" and consequent complications.

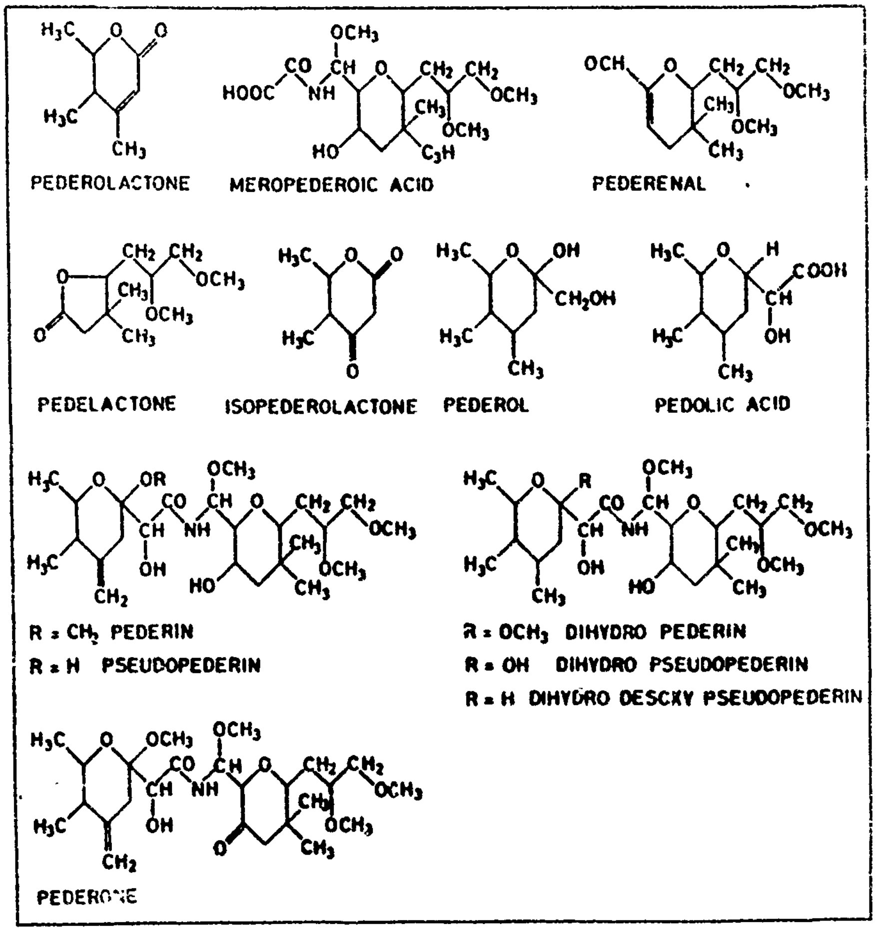

PEDEROLACTONE
MEROPEDEROIC ACID
PEDERENAL
PEDELACTONE
ISOPEDEROLACTONE
PEDEROL
PEDOLIC ACID
R = CH3 PEDERIN
R = H PSEUDOPEDERIN
R = OCH3 DIHYDRO PEDERIN
R = OH DIHYDRO PSEUDOPEDERIN
R = H DIHYDRO DESOXY PSEUDOPEDERIN
PEDERONE

Fig. 19

metoxyde or of piperidine, gives pederolactone and meropederoic acid. The structure of the former, determined by the results of ozonization and spectrographic data, was confirmed by sinthesis. The structure of meropederoic acid was determined following its acid hydrolysis which leads to pederenal, a substance that, by ozonolysis and later hydrolysis, gives pedelactone. By permanganic oxydation of pedelactone HIO_4 oxydation subject to previous bromidric hydrolysis and NMR spectrum we were able to define the structure of this compound its derivatives.

The fact that isopederolactone was obtained by pseudopederin oxydation with lead tetracetate, together with the interpretation of the results of hydrogenation with Adams catalyzer and Pd on carbon helped to establish the position of CH_2=; the existence of two rings was confirmed by obtaining non-hydroxylated diacetylpederin and ritransformation in pederin by LiAlH reduction; the derivation of pederol from acid hydrolysis of dihydropederin and dihydropseudopederin and of pedolic acid from acid hydrolysis of dihydrodesoxy-pseudopederin confirmed the structure given to pederin and pseudopederin and their hydroderivatives (1).

Biological properties.

Numerous publications describe the symptoms and development of skin and eye lesions caused by pederin; the biographical data are to be found in our previous publications, particularly Pavan 1963, 251, for bibliographical data.

Pederin is found throughout the insect's body, but the producing organ is not known. It is not employed for defensive purposes and

(1) In 1964 Matsumoto and coll. (184), dealing with partial pederin structure, published that the substance previously isolated by Ueta from P. fuscipes, to which the centesimal formula $C_{21}H_{39}O_9$ had been attributed (decidedly different from that of pederin), was to be identified with pederin, which we had isolated.

there is no organ for expelling it from the body. It acts on homeotherm skin only on direct contact with the skin, as in the case where the insect is squashed, not through mere contact with the insect, even when prolonged. Pederin does not gave insecticide or repellent properties.

Applied to human skin in small doses (lower than 1 gamma) pederin provokes a slight redenning and temporary pigmentation, but higher doses (for example 1 gamma, corresponding generally to the average content of one specimen of *Paederus fuscipes*) quickly cause a local reaction of necrotic type, with the appearance of blisters and sores: this in general develops aseptically and promptly heals without any traces of scarred tissues. This was found to be true for extensive accidental and voluntary sores, even when repeated many times on the same part of the body. This kind of cutaneous reaction, first from necrotization following from inhibition of the tissue development and later from stimulation of development, directed us towards a research on the inhibiting and stimulating properties of tissues *in vitro* and *in vivo*, in plants and animals and human tissues degenerated for other reasons. Therefore, this part was studied more thoroughly either directly or with various collaborators (Bo, Brega, De Carli, Deotto, Erspamer, Falaschi, Sirtori, Testori, Vaccari, Valcurone) or by other authors (Fioretti, Ghione, Soldati, 1966, 323) in Italy. This subject was also partially studied in Japan (Hisada, Emura 1965, 150) with *P. fuscipes* extracts. These researches, extensively dealt with in Pavan 1963, 251, but part of which is still under investigation and unpublished, gave the following results.

Pederin causes a fall in the number of lymphocytes in the circulating blood of rats, and of neutrophiles in the circulating blood of guinea pigs. In the partially hepatectomized rat it causes a stimulation of rigeneration, increasing the number of mitoses.

The treatment of tumoral fragments (sarcoma 180) before grafting between rats reduces taking faculties or inhibits them completely, depending on the concentrations and treatment times adopted. Soldati and coll. 1966 confirmed the inhibiting activity of very small doses on both normal cells and tumoral cells cultivated in vitro (HeLa and KB strains). The substance is lethal for Protozoa of the Trichomonas genus. It also exercises a strong phytoinhibition on plants cultivated in vitro such as Lupinus albus (Leguminosae) (fig.); treatment with pederin of the same white lupin inhibits also the development of the typical tumours from colchicin and gammahexane (fig.). It acts as an antimitotic on Allium cepa, blocking the metaphase before the formation of the spindle and causing typical chromosomic alterations and general cytotoxic effects.

The application of very small doses of the substance (gamma 0,05) on large bedsores in extremely elderly chronic patients resulted in a reduction of the sore in a short time and in complete recovery in numerous cases.

On the other hand, following up our research, Hisada and Emura 1965, 150, employed metanolic extracts of P. fuscipes in the treatment of a graftable ascite rat tumour (MTK strain - sarcoma III) obtaining almost complete regression after a long period of treatment. They believe that the antimitotic action is proved, and that the DNA synthesis system is repressed but not damaged by pederin.

In several in vitro cultures of animal tissues pederin proved to have remarkable inhibiting properties on development in very small doses.

Brega, Falaschi, De Carli and Pavan [(1)], proved that in vitro the substance inhibits the development of various strains of human and mammal tissues, with a concentration of 1,5 nanogram per ml [(2)]. The analysis of macromolecular synthesis by radioacti-

(1) Studies on the mechanism of action of pederin. J. Cell Biology, 36: 485, 1968.

(2) This is the most powerful antimitotic known, much more active than puromycin.

Table

Minimum inhibitory concentrations (M.I.C.) in nanogram/milliliter (ng/ml) of pederin on different strains and cell lines.
(from Brega, Falaschi, De Carli and Pavan: Studies on the mechanism of action of pederin. J.Cell Biology, 36: 485, 1968).

Strain or line	M.I.C. ng/ml	Strain or line	M.I.C. ng/ml
EUE	1.5	MEF	1.5
E6D	1.5	CE	1.5
HeLa	1.5	BHK	1.0
KB	1.5	Z 1	3.1
Hep	1.5	M 1	3.9
Senger	1.5		

Cell strains or lines and culture procedures

The minimum inhibitory concentration was determined both on heteroploid cell lines and diploid strains. All other experiments were performed with the EUE line only.

1) Cell lines.
   EUE: a human cell line isolated by Terni and Lo Monaco.
   E6D: an EUE clonal subline deficient for alkaline phosphatase, isolated by De Carli *et al*.
   HeLa: Gey *et al*.
   Hep 2: Fjelde.
   MEF: a cell line isolated in 1964 from a mouse embryo by Dr. Murthy at the Research Laboratories of the Lepetit Corporation, Milan, Italy.
   KB: Eagle.
   BHK 21: Stoker and MacPherson.

2) Cell strains.
   Z 1: A diploid cell strain derived for human thyroid, grown in our laboratory for 5 months.
   M 1: a diploid cell strain derived from human amnion, grown in our laboratory for 6 months.

ve precursors shows that pederin causes an almost immediate blocking of DNA and proteic synthesis, without however affecting RNA synthesis nor DNA polymerizing activity. It appears to act directly on the amino acid polymerization system, and that the effect on DNA is secondary.

Pseudopederin and pederone phytoinhibiting, dermatitic and toxic activity on white mice is of a roughly similar order (though the endoperitoneal toxicity in particular is lower for pederone), and is still far lower than that of pederin; pederone is different from pederin and pseudopederin inasmuch in doses applied it does not have antimitotic effects on Allium cepa. Pederin is, as already mentioned, very active on various animal and human cellular strains cultivated in vitro (for example etheroploid embryonal human epithelium, HeLa carcinoma of the uterus, etc.), followed by pederone and lastly by the least active pseudopederin. The very slight toxicity which accompanies pederone makes this product interesting and opens up further prospectives of study.

The pharmacological tests of pederin on warm-blooded animals have shown an acute systematic inactivity up to very heavy doses (251). Data on lethal doses for various animals are also shown in 251.

Chap. 24 - Cossins and Zeuzerin.

Cossins.

The larva of Cossus cossus L. Lepidoptera (C. ligniperda Fabr.) living in the trunk of various trees emanates a characteristic smell showe origin is in the secretion of the mandibular glands, which are supplied with a large reservoir whose excreting duct opens at the base of the jaw.

The smell and the secretion responsible for it attracted the attention of Henseval who, in 1897, published data which we found to be mistaken [1].

Composition of the secretion.

The larva secretion, taken directly from the animal dissected under narcosis, is citrin coloured and of oily consistency. The smell is penetrating and very persistent [2].

The first chemical researches were made in 1959 and various components were isolated. The partial data which we published in 1960 (336, 338), were modified and later replaced by the latest final publication (Trave, Garanti, Marchesini, Pavan 1966, 334).

Gaschromatographic analysis proved the secretion to be composed of seven main components which, being new to chemical literature, we called cossin 1, cossin 2, cossin 3, cossin A, cossin B, cossin C, cossin B_1, cossin C_1; the respective structures are shown in table .

Therefore the seven cossins are:
cossin 1: tetradeca-5,13-dienol; cossin 2: tetradeca-3,5-13-trienol; cossin 3: tetradeca-4,6,13-trienol; cossin A: acetate of cossin 1; cossin B: acetate of cossin 2; cossin C: acetate of cossin 3; cossin B_1: acetate of cossin 2 with a different steric configuration: cossin C_1: acetate of cossin 3 with a different steric configuration.

In an attempt to find a naturalistic justification of the secretion, a preliminary research of insecticide activity through contact and breathing was made. The trials through contact were made by comparative experimentation with equal doses of DDT-pp': at 100 gamma/cm^2

---

(1) Henseval 1897 states that the secretion is composed of a cyclic substance containing sulphur, corresponding to the centesimal composition $C_{22}H_{35}S$.

(2) In those places where the larva are found during springtime when they leave the trunks to bury themselves in the ground as a preparation for nymphosis, their typical smell is present in the air, and it is possible to trace where they passed and dug into the ground.

on the 13 species of Blattodea, Isoptera, Orthoptera, Emiptera, Lepidoptera and Coleoptera experimented, the secretion generally does not show any activity or, in a few cases, a very reduced activity compared with that of DDT-pp', while on 8 Imenoptera Formicidae species it has a remarkably toxic effect, generally greater than DDT-pp'. Ants are to be considered as possible enemies of the Cossus cossus larvae, because they may be competitors for the same habitat. However, the substance has a very low toxicity for Formica lugubris Zett. and Lasius (Dendrolasius) fuliginosus Latr.

Phisalix 1922 (265) also mentions the fact that the secretion has a certain toxicity for the fly, and is active on the Oospora cinnamea Fungus, an insect parasite; this seems to suggest a protective action. On the contrary, it does not seem to have any influence on wood, so that its employment as an auxiliary means in the attack upon wood fibres during the excavation of the tunnel seems useless.

PART VII - ASPECTS OF STUDIES ON ARTHROPODA DEFENSIVE SECRETIONS.

Distribution in the zoological orders of those chemically defined substances found in Arthropoda defensive secretions.

1. The chemically defined substances hitherto known to be present in Arthropoda defensive secretions amount to at least 194 In Table 5 they have been arranged in categories according to chemical affinity, and indicating the zoological order in which they have been found.

Table 5 - Distribution in the zoological orders of those chemically defined substances found in Arthropoda defensive secretions.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) / Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA								Cl. I				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthopt
HYDROCARBONS													
1. *n*-undecane													
2. *n*-dodecane													
3. *n*-tridecane													
4. 1-nonene													
5. 1-undecene													
6. 1-tridecene													
SULFIDES													
7. dimethyldisulfide													
8. dimethyltrisulfide													
ALCOHOLS													
9. methanol													
10. glycerol													
11. *n*-hexanol													
12. 2-methyl-butanol									+				
13. 2-methylene butanol									+				
14. ottan-1-ol													
15. nonan-1-ol													
16. *cis*-non-3-en-1-ol													
17. *trans*-non-3-en-1-ol													
18. *cis*-dec-3-en-1-ol													
19. *trans*-dec-3-en-1-ol													
20. cossin 1													
21. cossin 2													
22. cossin 3													

A.

ch are pre- tances OPODA) CRUSTACEA)	Cl. DIPLOPODA								Cl. INSECTA											Cl. ARACHNIDA			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
														+				+					
														+									
														+			+						
																	+						
																	+						
																	+						
																		+					
																		+					
															+								
																		+					
														+									
									+														
									+														
																			+				
																			+				
																			+				
																			+				
																			+				
																			+				
															+								
															+								
															+								

B.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) / Substances which are present in the defensive secretions of Arthropoda	Cl. DIPLOPODA								C			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmid…
AMINES AND AMINO ALCOHOLS												
23. choline												
24. histamine												
25. 5-hydroxytryptamine								+				
26. 2,5-hydroxytryptamine												
SATURATED ALDEHYDES												
27. propanal												
28. *n*-butanal												
29. 2-methyl butanal									+			
30. *n*-hexanal												
UNSATURATED ALDEHYDES												
31. *trans*-prop-2-enal												
32. 2-methylene propanal									+			
33. *trans*-but-2-enal												
34. 2-methylene butanal									+			
35. 2-methylene butanal dimer									+			
36. pentenal												
37. 2-methylene pentanal									+			
38. *trans*-hex-2-enal									+			
39. *trans*-hept-2-enal												
40. *trans*-oct-2-enal												
41. *trans*-dec-2-enal												
42. *cis*-dec-2-enal												
43. *trans*-dodec-2-enal					+							

A.

ch are pre- tances OPODA) CRUSTACEA)	Cl. DIPLOPODA								Cl. INSECTA											Cl. ARACHNIDA			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
																		+					
													+	+	+			+					+
								+							+			+		+			+
																		+					
															+								
															+								
									+														
															+								
															+								
									+														
															+								
									+														
									+														
															+								
									+														
									+						+			+					
															+								
															+								
															+								
															+								
					+																		

B.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) / Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA								Cl. I				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
<u>AROMATIC ALDEHYDES</u>													
44. benzaldehyde			+										
45. *p*-hydroxybenzaldehyde													
46. salicyl aldehyde													
47. cumin aldehyde			+										
<u>SATURATED KETONES</u>													
48. methyl-ethyl-ketone													
49. methyl-heptyl-ketone													
50. ethyl-propyl-ketone													
51. methyl-*n*-amyl-ketone													
52. methyl-n-undecyl-ketone													
53. 4-methyl-2-hexanone													
54. *n*-propyl-isobutyl-ketone													
<u>UNSATURATED KETONES</u>													
55. 2-methyl-2-hepten-6-one													
56. 4-keto-hex-2-ene													
<u>UNSATURATED KETO ALDEHYDES</u>													
57. 4-keto-*trans*-hex-2-enal													
58. 4-keto-*trans*-oct-2-enal													
<u>CARBOXYLIC ACIDS</u>													
59. formic acid													
60. acetic acid													
61. propionic acid													
62. butyric acid													
63. isobutyric acid													

A

ich are pre- stances ILOPODA) s CRUSTACEA)	Cl. DIPLOPODA								Cl. INSECTA											Cl. ARACHNIDA			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
			+																				
																	+						
																	+						
			+																				
														+									
														+									
														+									
																		+					
																		+					
																		+					
																		+					
																		+					
														+									
														+									
														+									
															+		+	+					
														+	+			+			+		
																		+					
																	+	+					
															+			+					

B.

Zoological order in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) / Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA								Cl. IN				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
64. 2-methyl butyric acid													
65. isovaleric acid													
66. caprylic acid													
67. palmitic acid													
68. methacrylic acid													
69. 2-methylene butyric acid									+				
70. tiglic acid													
71. 10-hydroxy-2-decenoic acid													
72. D-gluconic acid									+				
73. ascorbic acid													
74. hyaluronic acid													
75. benzoic acid			+										
76. pipecolinic acid													
77. oxalic acid													
<u>PHENOLS</u>													
78. phenol		+	+										
79. guaiacol			+										
80. cresol													
81. <u>m</u>-cresol													
82. <u>p</u>-cresol		+											
<u>FURANS</u>													
83. furan													
84. methylfuran													
85. perillen													
86. dendrolasin													

A.

are pre- tances OPODA) CRUSTACEA)	Cl. DIPLOPODA								Cl. INSECTA											Cl.ARACHNI			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
															+								
																		+					
																	+				+		
																		+					
															+		+						
									+														
															+		+						
																		+					
									+														
														+									
																							+
			+														+						
																		+					
																+							
		+	+																				
			+																				
																	+						
																	+						
		+																					
														+									
														+									
																		+					
																		+					

B

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) / Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA								Cl. I				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orth
ESTERS													
87. isoamyl acetate													
88. *n*-hexyl acetate													
89. *n*-octyl-acetate													
90. *trans*-hex-2-enyl-acetate													
91. *trans*- oct-2-enyl acetate													
92. *trans*-dec-2-enyl-acetate													
93. cossin A													
94. cossin B													
95. cossin C													
96. cossin B_1													
97. cossin C_1													
98. *n*-butyl butyrrate													
99. *trans*-hex-2-enyl butyrrate													
100. methyl-*p*-hydroxybenzoate													
101. acetylcholine													
102. β,β-dimethyl-acrylyc-choline													
LACTONES													
103. γ-gluconolactone									+				
104. δ-gluconolactone									+				
AMIDES													
105. pederin													
106. pseudopederin													
107. pederone													

A.

are pre- nces ODA) RUSTACEA)	Cl. DIPLOPODA								Cl. INSECTA											Cl. ARACHNIDA			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
																		+					
														+									
														+									
														+									
														+									
														+									
															+								
															+								
															+								
															+								
															+								
														+									
														+									
																	+						
															+			+					
															+								
									+														
									+														
																	+						
																	+						
																	+						

B.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) / Substances which are present in the defensive secretions of Arthropoda	Cl. DIPLOPODA								Cl. I				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthopte
NITRILES													
108. hydrocyanic acid			+										
109. D-(+)-mandelic nitrile			+										
110. glucoside of p-isopropil mandelonitrile			+										
111. mandelonitrile benzoate			+										
AMINO ACIDS													
112. glycine													
113. alanine													
114. serine													
115. α-aminobutyric acid													
116. β-iso-aminobutyric acid													
117. γ-aminobutyric acid													
118. threonine													
119. valine													
120. aspartic acid													
121. asparagine													
122. leucine													
123. isoleucine													
124. glutamic acid													
125. glutamine													
126. ornithine													
127. cysteine													
128. cystine													
129. methionine													
130. lysine													

A.

re pre- ces DA) USTACEA)	Cl. DIPLOPODA								Cl. INSECTA											Cl. ARACHNIDA			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
			+												+								
			+																				
elonitrile			+																				
			+																				
																		+		+			
																		+		+			
																		+		+			
																		+					
																		+					
																							+
																		+		+			
																		+		+			
																		+		+			+
																		+					
																		+		+			
																		+		+			
																		+		+			+
																		+					
																		+					
																		+					
																		+		+			
																		+					
																		+		+			+

B.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) / Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA								Cl. INSE[CTA]					
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	[illegible]
131. arginine														
132. proline														
133. histidine														
134. phenylalanine														
135. thyrosine														
136. tryptophane														
QUINONES														
137. 1,4-benzoquinone				+	+	+			+					
138. 2-methyl-1,4-benzoquinone				+	+	+	+		+		+			[illegible]
139. 2-ethyl-1,4-benzoquinone									+		+			
140. 2,3-dimethyl-1,4-benzoquinone														
141. 2,5-dimethyl-1,4-benzoquinone														
142. 2,3,5-trimethyl-1,4-benzoquinone														
143. 2-methoxy-1,4-benzoquinone														
144. 2-methyl-3-methoxy-1,4-benzoquinone				+	+	+	+							
145. hydroquinone														
146. 2-methyl-hydroquinone				+	+						+			
147. 2-ethyl-hydroquinone											+			
148. 2-methyl-3-methoxy-hydroquinone				+	+									
SUGARS														
149. glucose			+											
150. fructose														
TERPENIC DERIVATIVES														
HYDROCARBONS														
151. D,L-limonene														

A.

are pre- ances PODA) CRUSTACEA)	Cl. DIPLOPODA								Cl. INSECTA											Cl. ARACHNIDA			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
																		+		+			
																		+		+			
																		+		+			
																		+		+			
																		+		+			
																		+		+			
				+	+	+			+								+						
				+	+	+	+		+		+			+			+						
									+		+						+						
one																						+	
one																						+	
uinone																						+	
																	+						
zoquinone				+	+	+	+																
																	+						
				+	+						+						+						
											+												
none				+	+																		
			+														+	+					
																		+					
																		+					

B.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class INSECTA) / Substances which are present in the defensive secretions of Arthropoda	Cl. DIPLOPODA								Cl. I				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
152. α,β-pinene										+			
ALCOHOLS													
153. citronellol													
ALDEHYDES													
154. citral													
155. citronellal													
156. farnesal													
157. iridodial													
158. dolichodial												+	
LACTONES, ANHYDRIDES													
159. iridomyrmecin													
160. isoiridomyrmecin													
161. isodihydronepetalactone													
162. cantharidin													
STEROIDS													
163. 24-methylene cholesterol										+			
164. testosterone													
165. 11-desoxycorticosterone													
166. 6-dihydrocybisterone													
167. cybisterone													
168. 6-dehydrocortexone													
169. 6-dehydroprogesterone													
170. calotropin													+
171. calactin													+

A.

h are pre- tances OPODA) INSECTA)	Cl. DIPLOPODA								Cl. INSECTA											Cl. ARACHNIDA			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
										+													
																		+					
																		+					
																		+					
																		+					
																		+					
												+						+					
																		+					
																		+					
																		+					
																	+						
										+													
																	+						
																	+						
																	+						
																	+						
																	+						
																	+						
													+										
													+										

B

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) / Substances which are present in the defensive secretions of Arthropoda	Cl. DIPLOPODA								Cl. INS				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
ALKALOIDS													
172. glomerin	+												
173. omoglomerin	+												
FLAVOPROTEINS													
174. riboflavin													
PHOSPHATIDES													
175. lecithin													
ENZYMES													
176. adenosine triphosphatase													
177. L-amino acid dehydrogenase													
178. cholinesterase													
179. alkaline phosphatase													
180. phospholipase A													
181. phospholipase B													
182. phospholipase C													
183. β-glucosidase			+						+				
184. hyaluronidase													
185. invertase								+					
186. trypsin													

A.

ch are pre- stances LOPODA) s CRUSTACEA)	Cl. DIPLOPODA								Cl. INSECTA											Cl. ARACHNILA			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida *	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	($) Isopoda	Scorpiones	Uropygi	Opiliones	Aranea
	+																						
	+																						
																		+					
																		+					
																				+			
e																							+
																		+					
														+									
																		+					
																		+					
																		+					
			+						+														
														+				+					+
								+															
																							+

B.

Defensive secretions of Hymenoptera (2-6).

2. In the group of social Hymenoptera (Apidae, Vespidae, Formicidae there are species with more simple venoms and others with the most complicated venoms hitherto known within the entire group of Arthropoda. In fact they go from the venom of many Formicidae, composed of a watery solution of formic acid, to those of the Apis mellifera (and presumably many other Apidae and Vespidae) which are estremely complex and where dozens of different substances belonging to entirely different chemical categories may be found.

3. Various types of glands producing defensive substances exist in Hymenoptera Formicidae

a) in the head the mandibular glands, present in all the Families, from which so far citrale, dendrolasin, farnesal, a substance similar to this but not yet defined (Chthonolasius), various sulphides (Paltothyreus), 2-hexenal and various other odorous substances have been extracted.

b) The venomous apparatus in the abdomen, in many species with an atrophied sting. This apparatus comprises two glands (acid and alkaline) (*): it usually produces venom in small quantities, complex however, meant to be injected into the prey in those cases where the sting is active (for example in many Ponerinae, Myrmicinae, etc.). In many Formicinae with atrophied sting the glands producing formic acid in considerable quantities is extremely developed, as for example in the species of the Formica rufa group: these eject venom in visible quantities even as far as 20-30 centimeters.

In Dolichoderinae besides the poison apparatus with a sting (usually atrophied and inefficient), typically formed of an acid gland and an alkaline gland, we also find the so-called "anal

(*) The alkaline or Dufour gland in various species appears to produce a trail substance (see Gabba 1967).

glands" which are characteristic of this group; they produce the known venoms without formic acid and containing iridomyrmecin, iridodial, dolicodial, methylheptenone, etc. The first species studied was Iridomyrmex humilis Mayr from which iridomyrmecin was obtained. This gave rise to an interesting series of studies in several continents, results of which are summarized in Table 6.

Table 6

Species of Formicidae Dolichoderinae	Products of the anal glands
Iridomyrmex humilis Mayr	iridomyrmecin
I. nitidus Mayr	isoiridomyrmecin
I. myrmecodiae (Em.)	dolichodial
I. rufoniger Lowne	dolichodial; iridodial; methylheptenone
I. detectus (Smith)	iridodial, methylheptenone
I. conifer For.	" "
I. nitidiceps (André)	" "
I. pruinosus (Roger)	methyl-n-amyl-ketone
Conomyrma pyramica (Roger)	"
Tapinoma nigerrimum Nyl.	iridodial; methylheptenone, propyl-isobutyl-ketone
Dolichoderus (Acanthoclinea) clarcki (Wheeler)	dolichodial; 4-methyl-2-hexanone
D. (A.) dentata (Forel)	dolichodial
D. (Diceratoclinea) scabridus (Roger)	iridodial; dolichodial, isoi[illegible]omyrmecin, methylheptenone
Liometopum microcephalum Panz.	methylheptenone

4. Hitherto studies have been particularly carried out on products of the "mandibular glands", the "anal glands" and "acid gland", with reference to the defensive secretions of the Formicidae.

Studies are only just beginning however on the species provided with an efficient sting (for example Solenopsis, Paraponera, Myrmica, etc.). These venoms are usually complex and in many cases have similar effects to those produced by the poison from Apidae and Vespidae. These poisons are of particular biological interest due to the effects they produce on animals generally (1).

5. The data collected concerning Hymenoptera Formicidae show a clear distinction between Formicinae and Dolichoderinae: Dolichoderinae always lack formic acid in the anal glands; this on the contrary, is the active factor always present in the venom produced by the acid gland of Formicinae.

The substances produced by the anal glands of Dolichoderinae are partially connected with the terpenes (iridomyrmecin, iridodial, etc.); also straight-chain substances are lacking in certain species (for example methylheptenone, propyl-isobutyl-ketone); in certain cases (for example Liometopum microcephalum Panz.) only straight-chain substances are to be found. (For example methylheptenone in Liometopum microcephalum Panz., methyl-n-amyl-ketone in Conomyrma pyramica (Roger)).

6. We now know a furanic substance in Formicinae Ants, dendrolasin, the first representative of furans found in animals, produced by the mandibular glands. A substance not yet chemically defined and presumably related to dendrolasin is present in Lasius (Chthonolasius) umbratus Nyl., a species systematically close to those which produce dendrolasin. Here again we can see the initial outline of a group of substances produced by Formicidae, with certain chemical and systematic-zoological uniformity.

---

(1) With regard to this we are waiting for the final results of the chemical study on solenopsine, extracted from the poison of Solenopsis geminata F. by Blum and coll. It seems to be an alcaloid but final data are still lacking.

The two dendrolasin and formic acid defensive secretions, contemporarily present in the same species, are produced by different organs.

Furans are closely related to dendrolasin and are present in plants (for exemple perillen, alfa-clausenane). Dendrolasin was later discovered also in the sweet potato and Torreya nucifera.

Heteroptera defensive secretions (7-8).

7. Defensive substances in Heteroptera adults are produced by a metathoracic odoriferous apparatus, by the Brindley glands and the thoraco-abdominal ventral glands.

In the young forme (larvae) there are dorso-abdominal glands which later generally disappear with imaginal metamorphosis, but which remain, sometimes reduced in number, in the imagines of numerous species; in certain cases they develop considerably even after the final imago, particularly in the male.

The metathoracic odoriferous apparatus, which is present in almost all Heteroptera, has its outlet on the surface of the body, often in the metasternum and by the sides of the metacoxal articulations.

The Brindley glands, paired, dorsal, present in Reduvidae s.l. and Pachynomidae, are placed at the base of the abdomen near the edge and open outwards in a region which seems to belong to the metathorax.

The thoraco-abdominal ventral glands in Reduvidae of the sub-families Phymarinae, Elasmodeminae e Holoptilinae are formed by a pair of sacculated invaginations of the thoraco-abdominal membrane.

8. The defensive secretions of all the above mentioned glands are formed of very volatile substances which the insect cán squirt in unilateral or bilateral jets.

The 35 substances described hitherto in about forty species are mostly straight-chain substances; only in one case (Scaptocoris divergens Fr.) are cyclic substances present together with the previous ones. In Table 7 the known data have been summarily collected.

Often we find no indication in literature of the glands from which the secretions have been collected and examined, however, they are usually taken from the metathoracic glands. Only one species studied by us (Tessaratoma aethiops Dist.) has comparatively well known metathoracic gland secretions, both from adults and larvae: the secretion of the latter did not contain two of the five components present in adult secretions.

A.

HETEROPTERA	Acido acetico CH_3COOH	Acido butirrico $CH_3-(CH_2)_2-COOH$	n-esanolo $CH_3-(CH_2)_4-CH_2OH$	propenale $CH_2=CH-CHO$	trans-but-2-enale $CH_3-CH=CH-CHO$	pentenale $CH_3-CH_2-CH=CH-CHO$	trans-es-2-enale $CH_3-(CH_2)_2-CH=CH-CHO$	trans-ept-2-enale $CH_3-(CH_2)_3-CH=CH-CHO$	trans-ott-2-enale $CH_3-(CH_2)_4-CH=CH-CHO$	trans-dec-2-enale $CH_3-(CH_2)_6-CH=CH-CHO$	cis-dec-2-enale $CH_3-(CH_2)_6-CH=CH-CHO$	propanale CH_3-CH_2-CHO	n-butanale $CH_3-(CH_2)_2-CHO$	n-esanale $CH_3-(CH_2)_4-CHO$	metiletilchetone $CH_3-CO-CH_2-CH_3$	metil-eptilchetone $CH_3-CO-(CH_2)_6-CH_3$	etil-propilchetone $CH_3-CH_2-CO-(CH_2)_2-CH_3$	4-cheto-trans-es-2-enale $CH_3-CH_2-CO-CH=CH-CHO$	4-cheto-trans-ott-2-enale $CH_3-(CH_2)_3-CO-CH=CH-CHO$	4-cheto-es-2-ene $CH_3-CH_2-CO-CH=CH-CH_3$	n-esil-acetato $CH_3-(CH_2)_5-O\,COCH_3$
Fam. Corixidae																					
Corixa dentipes (Thoms.)																		+			
Sigara falleni (Fieb.)																		+			
Fam. Belostomatidae																					
Lethocerus indicus Lep.																					
Fam. REDUVIDAE																					
Platymeris rhadamanthus Ger.																					
Fam. Cimicidae																					
Cimex lectularius L.							+		+												
Fam. Coreidae																					
Acanthocephala femorata Fab.							+														
Acanthocoris sordidus (Thunberg.)							+							+							
Agriopocoris froggatti Miller	tr.		+											+							+
Amorbus alternatus Dallas	+		+											+							+
Amorbus rhombifer Westwood	+	+?	+										+	+							+
Amorbus rubiginosus (Guer.)	+		+											+							+
Aulacosternum nigrorubrum Dallas	+		+											+							+
Hygia opaca (Uler)														+							
Leptocoris apicalis Westwood									+	+											
Mictis caja Stål	+		+											+							+
Mictis profana (Fabricius)	+		+											+							+
Pachycolpura manca Breddin	+		+											+							+
Plinachtus bicoloripes Scott														+							
Riptortus clavatus (Thunberg)													+								
Fam. Hypocephalidae																					

TABELLA

B.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
trans-dec-2-enale $CH_3-(CH_2)_6-CH=CH-CHO$								+																		
cis-dec-2-enale $CH_3-(CH_2)_6-CH=CH-CHO$																										
propanale $CH_3-CH_2\cdot CHO$																										
n-butanale $CH_3-(CH_2)_2-CHO$			+									+														
esanale $CH_3-(CH_2)_4\cdot CHO$	+			+	+	+	+		+	+	+	+	+	+	+											
metiletilchetone $CH_3-CO-CH_2-CH_3$																										
metil-eptilchetone $CH_3-CO-(CH_2)_6-CH_3$																										
etil-propilchetone $CH_3-CH_2\cdot CO\cdot(CH_2)_2-CH_3$																										
4-cheto-trans-es-2-enale $CH_3-CH_2-CO-CH=CH-CHO$																								+	+	
4-cheto-trans-ott-2 enale $CH_3-(CH_2)_3-CO-CH=CH-CHO$																										
4-cheto-es-2-ene $CH_3-CH_2-CO-CH=CH-CH_3$																										
n-esil-acetato $CH_3-(CH_2)_5-O\ COCH_3$	tr				+	+	+			+	+	+	+	+												
n-butil-butirrato $CH_3-(CH_2)_3-OCO-(CH_2)_2-CH_3$							+					+														
n-ottil-acetato $CH_3-(CH_2)_7-O\ CO\ CH_3$								+																		
trans-es-2-enil-acetato $CH_3-(CH_2)_2-CH=CH-CH_2-O\ CO\ CH_3$																						+				
trans-ott-2-enil-acetato $CH_3-(CH_2)_4-CH=CH-CH_2-O\ CO\ CH_3$																										
trans-dec-2 enil-acetato $CH_3-(CH_2)_6\ CH=CH-CH_2-O\ CO\ CH_3$																										
trans-es-2-enil-butirrato $CH_3-(CH_2)_2-CH=CH-CH_2-O\ CO(CH_2)_2\ CH_3$																						+				
n-undecano $C_{11}H_{24}$																										
n-dodecano $C_{12}H_{26}$																										
n tridecano $C_{13}H_{28}$																										
furano																										
metilfurano																										
metil-chinone																										
acido ascorbico																										
istamina																				+?						
endopeptidasi alcalina																				+						
fosfolipasi																				+						
fosfolipasi alcalina																										
ialuronidasi																				+						
proteasi																				+						

Leptocoris apicalis Westwood									+	+												
Mictis caja Stal	+		+											+							+	+
Mictis profana (Fabricius)	+		+											+							+	
Pachycolpura manca Breddin	+		+											+							+	
Plinachtus bicoloripes Scott														+								
Riptortus clavatus (Thunberg)													+									
Fam. Hyocephalidae																						
Hyocephalus n. sp.	tr		+											+							tr.	
Fam. Pentatomidae																						
Aelia fieberi Scott									+	+												
Biprorulus bibax										+												
Brachymena quadripustulata (F.)							+															
Carpocoris purpureipennis (De Geer)																						
Chrysocoris stolli Wolf																						
Dolycoris baccarum L.							+		+	+												
Eurygaster sp.							+		+													
Euschistus servus Say (1)																						
Graphosoma rubrolineatum (Westwood)										+				+								
Menida Scotti Puton										+												
Musgraveia sulciventris Stål							+		+	+												
Nezara antennata Scott										+												
Nezara viridula L.										+												
Nezara viridula var. *smaragdula* F.				+	+		+		+	+	tr.				+	tr.	+	+	+	+		
Oebalus pugnax F.								+														
Palomena viridissima P.							+		+	+												
Poecilometis strigatus Westw							-		+													
Rhoecocoris sulciventris Stal (3)							+		+	+												
Scotinophara lurida Burmeister							+		+	+												
Tessaratoma aethiops Dist							+		+⁰									+⁰				
Fam. Plataspidae																						
Ceratocoris cephalicus Montandon																						
Fam. Cydnidae																						
Macroscytus sp																		+				
Scaptocoris divergens Froeschner				+	+	+	+	+	+			+										

C.

(1) Secondo Blum e Traynham, 1960, il secreto ha una composizione del tutto uguale a quella di *Oebalus pugnax* (F.).

+⁰ Trovato anche nelle forme giovanili (n. e a.)

tr. = tracce.

N. B. Mukerji e Sharma, 1966, trovano *trans*-2-eptenale $CH_3CH_2CH_2CH=CH\,CH_2CH_2\cdot CHO$ in un Pentatomide dell'India che denominano Black Hemiptera Bug

+													+																	
				+							+	+																		
				+							+																			
				+							+																			
				+																										
			+																											
				+							tr.																			
+																														
+																+			+	+										
																				+										
																								+				+		
+																														
+				+																										
+																														
+															+				+	+										
+																														
+																														
+	tr.				+	tr.	+	+	+	+				+	+	+		+	+	+										
																				+										
+																														
+															+				+	+										
+																														
								+°							+					+°										
																				+										
								+							+	+			+	+										
		+																			+		+							

...ulus pugnax (F.).

...atomide dell'India che denominano Black Hemiptera Bug

D.

Examples on zoological specialization (9-10).

9. Examples of specialization in the production of defensive substances are given by Coleoptera and Myriapoda.

For example, in Colecptera cantharidin is only present in the species belonging to Meloidae; pederin, pseudopederin and pederone only in the Staphylinidae species; tiglic acid in the Carabidae; and quinones prevalently in the Tenebrionidae.

Myriapoda Diplopoda Juliformia contain numerous quinones; in Myriapoda Diplopoda Polydesmidae however we find the production of cyanogenic substances.

10. Several quinones closely related to each other have been found in three groups of Arthropoda considered distant from a systematic point of view (Myriapoda, Insecta, Arachnida).

Considering Insecta as producers of quinones we might almost say Coleoptera Tenebrionidae specialize in the production of these substances although there are examples in Carabidae (Brachynus), Blattodea (Diploptera), and Dermaptera (Forficula), systematically very distant from the first mentioned.

Complexity of venom (11-14).

11. Regarding the complexity of composition in these poisons, they go from those with only one known substance different from water (e.g. formic acid, oxalic acid, salicylic aldehyde, iridomyrmecin, trans-hex-2-enal, cantharidin, etc.), to those which are composed of several constituents.

The most complicated cases ~~seem to~~ in Insecta be those of Apis mellifera and Vespidae who produce venoms containing many complex substances, also enzymatic. Very complex venoms are to be found in Arachnidae, particularly Araneae and Scorpiones, but although studies of these animals are numerous, a well defined composition cannot yet be attributed to

Table 8 - Components of defensive secretions of <u>Diplopoda Juliformia</u>.

<u>Diplopoda Juliformia</u>	1,4-benzoquinone	2-methyl-1,4-benzoquinone	2-methyl-3-methoxi-1,4-benzoquinone	2-methyl-hydroquinone	2-methyl-3-methoxi-hydroquinone	quinones	trans-dodec-2-enal
<u>Archiulus (Schizophyllum) sabulosus</u> L.	+	+	+	+	+		
<u>Aulonopygus aculeatus</u> Attems		+					
<u>Aulonopygus aculeatus barbieri</u>		+					
<u>Brachyulus unilineatus</u> Koch		+	+				
<u>Cambala hubrichti</u> Hoffman		+	+				
<u>Chicobolus spinigerus</u> Wood		+	+				
<u>Cylindroiulus teutonicus</u> Pocock		+	+				
<u>Doratogonus annulipes</u> Carl		+	+				
<u>Floridobolus penneri</u> Causey		+	+				
<u>Narceus annularis</u> Raf.		+	+				
<u>Narceus gordanus</u> Chamb.		+	+				
<u>Orthocricus arboreus</u> (Sauss.)						+	
<u>Orthoporus conifer</u> (Attems)			+				
<u>Orthoporus flavior</u> Chamb. e Mulaik		+	+				
<u>Orthoporus punctilliger</u> Chamb.		+	+				
<u>Pachybolus laminatus</u> Cook	+	+					
<u>Peridontopyge aberrans</u> Attems		+					
<u>Peridontopyge vachoni</u>		+					
<u>Rhinocricus</u> sp.		+	+	+	+		
<u>Rhinocricus insulatus</u> Chamb.		+					+
<u>Schizophyllum mediterraneum</u>	+						
<u>Spirostreptus</u> sp.		+	+				
<u>Spirostreptus castaneum</u> Attems	+						
<u>Spirostreptus multisulcatus</u> Dem.		+					
<u>Spirostreptus virgator</u> Silv.	+	+					
<u>Trigonoiulus lumbricinus</u> Gerst.		+	+				

Table 9 - Components of defensive secretions of Diplopoda Polydesmida (1) (from Barbetta-Casnati-Pavan 1966).

Diplopoda Polydesmida	Benzoic acid	Benzaldehyde	[Cuminaldehyde]	Hydrocyanic acid	[Phenol]	[Guaiacol]	[Glucoside of p-isopropil mandelonitrile]	Mandelonitrile benzoate	D-(+)-mandelic nitrile	[Glucose]	[Disaccarid]
Apheloria corrugata (Wood)		+		+					+(b)		
Cherokia georgiana (Bollmann)				+							
Gomphodesmus pavani Dem.	+	+		+				+(a)	+		
Kanngria sp.				+							
Orthomorpha coarctata Sauss.	+	+		+	[+]	[+]					
Orthomorpha gracilis Koch (= Fontaria gracilis Koch, Paradesmus (Fontaria) gracilis Koch, Oxydus gracilis Koch)		+		+							
Pachydesmus crassicutis (Wood)		+		+						[+]	[+]
Polydesmus collaris collaris (Koch)	+	+		+				+(a)			
Polydesmus (Fontaria) virginiensis Drury (= Polydesmus virginiensis Drury, Fontaria virginiensis Drury)				+							
Pseudopolydesmus serratus (Say)				+							
Rhysodesmus vicinus Sauss. (= Polydesmus vicinus Sauss., Polydesmus (Fontaria) vicinus Sauss.)			[+]	+			[+]				

(1) Substances between parentheses have not been isolated: they are recognized by purely indicative methods.

(a) Isolated and certainly identified product, probably evolved from mandelonitrile in the course of separative processes due to benzoic acid reaction.

(b) Product which has been roughly identified as mandelonitrile by indicative methods unsuitable for defining its steric structure.

these poisons: this is due to the fact that they mostly contain active proteinic substances which are difficult to identify.

12. There are cases of venoms consisting of a single straight-chain substance (e.g. formic acid, oxalic acid; trans-hex-2-enal) and others in which the venom is composed of several straight-chain substances, as for instance, in several species of Heteroptera.

There are cases where the venom is formed of a single cyclic substance (e.g. iridomyrmecin; cantharidin; salicylic aldehyde) and others where it is composed of several cyclic substances (e.g. in Coleoptera of Paederus genus with the presence of pederin, pseudopederin, pederone; in the cases of various quinones which are to be found together in the poison of individual species of Juliformia; in the Glomerida species, where both glomerin and omoglomerin are present simultaneously).

There are also numerous examples of poisons composed of straight-chain and cyclic substances together, with either the former or the latter prevailing.

13. Considering straight-chain substances we note that many of these are simple in nature (formic acid, oxalic acid, trans-hex-2-enal, methylheptenone, propyl-isobutyl-ketone, etc.), compared to the relative complexity of some cyclic substances (salicylic aldehyde, dendrolasin, iridomyrmecin, cantharidin, quinones, 5-hydroxytryptamine, glomerin, pederin, etc.).

Among the more complex straight-chain substances we find for example tridecane, tridecene, the various cossins, etc. Among the more complex cyclic substances we may mention pederin, glomerin and omoglomerin, cortexone,24-methylene cholesterol,riboflavin, etc.

14. It is perhaps worthwhile recalling that in those poisons known among saturated fatty acids the first, formic acid, the most dissociated of the series, is the most usual, although 7 other successive elements are present (acetic, propionic, butyric, isobutyric, isovaleric, caprylic, palmitic acid); therefore of saturated dicarboxylic acids

only the first and strongest is known to be present hitherto - oxa lic acid.

It is a remarkable fact that the most simple substance of all the poisons chemically known, formic acid, is mostly produced and used by a clearly defined group of Ants of the Family Formicinae, and is only to be found in a few other cases besides Ants.

The natural significance of defensive secretions (16-19).

16. With regards to the meaning of Arthropoda poisonous secretions, it seems clear that most of them have an active defensive and offensive aim concerning other animals. When the venom can be used directly there is an organ to produce it, a reservoir where it is pre served and a mechanism for volontary expulsion; in the other cases (e.g. pederin, pseudopederin, pederone) the toxic substance is diffu sed throughout the organism and an expulsion mechanism is missing. Ho wever, Coleoptera Meloidae which produce cantharidin, also found throu ghout the organism, can exude drops of haemolymph, carriers of the poi son, by autohaemorrhoea.

17. Once the productive organ has been identified usually the o rigin of the chemically known substances of the poisons under study may be more or less exectly defined. The organs producing the poisons differ extremely as to place and significance. The productive organs of the typical Arthropoda poison pederin, are not known; the toxic substance is present in the haemolymph of the insect.

18. The reaction to these poisons regarding the same species whi ch produce them is variable, going from extreme sensibility (e.g. in the case of Iridomyrmex humilis Mayr for iridomyrmecin), to a relative resistence (e.g. Lasius (Dendrolasius) fuliginosus Latr. for dendrolasin; Melasoma populi L. for salicylic aldehyde), to cases of complete resistence (e.g. Paederus fuscipes Curt. for pederin; Lytta vesicatoria L. for cantharidin; Julida for quinones; Polydesmida for cyanogenic poisons, etc.).

19. Where the poison is spread throughout the body we have the interesting problem of how the tissues of the organism, which are saturated with this poison, resist: a particularly interesting problem, especially for those Arthropoda which produce substances highly active on animal tissues like cantharidin and pederin. In fact pederin acts as a powerful antimitotic in a dose of 1/000 of a gamma per cc on various types of animal tissues, and human tissues, normal and pathological, cultivated in vitro. Paederus fuscipes Curt. contains, on an average, 1 gamma of pederin to 4 mg, which corresponds to a concentration of 1 to 4000! Cantharidin, too, exercises a remarkable inhibiting action on tissues of homothermic animals. The resistance mechanism of the tissues of Insects regarding this action is of great general interest and still to be investigated.

Possible meanings of the biological properties of defensive secretions (20-22).

20. Regarding the avantages of animals producing these substances, we may divide the biological properties of poison secretions in properties for which there is a natural justification (e.g. insecticide, repellents), and properties which are difficult to justify as being to the advantage of the producing species (e.g. properties of pederin which stimulate or inhibit the growth of tissues, the phyto-inhibiting action of iridomyrmecin, etc.). On the other hand, these biological properties may be numerous and that which finds a natural justification is not necessarily the one to which a greater value can be attributed.

Some of the biological properties we have seen can be justified not only in the fight against competitors, but also as serving other needs of the species. For example, the phyto-inhibiting action of Bee poison, might also serve to block the pollen collected in the hive. Here we might make a comparison with the paralizing property for victims, contained in the poisons of certain predatory Hymenoptera (Sphecidae, etc.), but whose chemical components are not known. The antibacterial property may be justified because it can contribute to the inhibition of the bacteria present in the honey stored in the beehive, as seems to be the case with Bees when squirting honey into the cells.

21. Considering the toxic action on animal organisms, there are poisons which over a wide zoological range (e.g. those of certain Formicidae, of Bees, Wasps, and Myriapods etc.) including both lower animals and warmblooded animals, and this is in the defensive interest of the producing species; there are poisons which act in a more limited but still fairly wide range (e.g. those of Dolichoderinae active over a wide range of Insects); poisons which have a limited specific action like dendrolasin, selective against Ants which are the chief enemies of the producing species; poisons which apparently act on warmblooded animals only, as for exemple pederin and cantharidin.

There is also a poison, cantharidin, which exercises a strong attraction over certain species of Insects (Diptera of the Anthomyia genus; Coleoptera of the Anthicidae family) which are attracted by tiny quantities of this substance. This fact also occurs in nature as individuals of the species producing cantharidin can be found with the Insects attracted clinging to them. Here we are not aware of the significance that this may have for the species producing cantharidin.

22. We can legitimately consider as toxic secretions the repellent substances of several Insecta (for example Brachynus, Paltothyreus, Dendrolasius, etc.) and of Polydesmidae protected by a cyanogenic secretion exuded freely over the surface of the body: the cyanogenic secretion produced by Gomphodesmus and Orthomorpha has been found to have a protective role in nature, for example against the Doryline Ants, the most savage African Insects which attack any living being.

Toxic substances in Arthropoda and plants (23-27).

23. Both Arthropoda and plants produce insecticides. It may be of interest to point out, in cases of known chemical substances, the essential difference between the groups of substances employed by certain Insecta in the fight against other Insecta and the groups of entirely different insecticides known in plants (e.g. pyretrine, rotenone, nicotine, etc.).

24. Regarding the natural toxic substances we may make a comparison of a purely speculative nature between the animal and vegetable kingdom. Unfortunately we are limited in this comparison due to our lack of knowledge; on the other hand, in order to pursue this comparison, we must also include examples of poisons whose chemical structure is not known.

Regarding animals we usually find poisons which appear to be confined within those special organs in which they are produced and from which they are later secreted, and, rarer, poisons spread throughout the whole organism. In plants it is usually the case to find poisonous substances spread throughout or covering most of the organism, and rarer to find them concentrated exclusively in particular organs. For plants this would mean a greater resistance to their own poisonous substances, probably seated in a particular cellular organisation capable of accumulating, so to speak, these substance in the expectation, in certain cases, of getting rid of it as may happen in the case of shedding leaves or other parts of the plant. The loss of part of the body to get rid of harmful substances is not known among Arthropoda. The spontaneous ejection of haemolymph in Insecta capable of self-haemorroea is not purification from poisoning but an act of defence.

It is not clear why most of the plants which produce poisonous substances should do so (e.g. the countless number of cases of alkaloids). However, and perhaps generally amongst animals, it seems the production of poison takes place according to very precise methods in order to achieve the aims of the species. There is even the extreme case of the thrifty Melasoma populi larvae, which, after ejecting the poison, absorb the drops not used into their reservoir again so the poison can be used later.

25. Plants contain a great abundance of alkaloids and glucosides although representatives of other large chemical groups are not lacking. This category of substances form part of Arthropoda poison only in a few cases. We may mention, for example, the cyanogenic glucoside of the Myriapoda Polydesmida, the glomerin and omoglomerin alkaloids.

Analogies may be found between the urticating poisons of numerous plants (e.g. Urtica, Mucuna, etc.) and the urticating hairs of Lepidoptera larvae (for example Thaumetopoea pityocampa Sch.) or of Lepidoptera adults (for example the various species of Anaphe). The urticating secretion of these plants contains histamine and 5-hydroxytryptamine. It seems the secretion of the urticating hairs of Lepidoptera, however, contains substances capable of freeing histamine from the tissues. In any case the entire subject still has to be studied, first analitically and then comparatively.

Other comparisons are possible, for example, between the cutaneous effects (necrosis) produced by numerous plants, e.g. Rhus toxicodendron L., and those produced by certain Arthropoda, e.g. Araneae of the genus Lycosa and Insecta Coleoptera of the Paederus genus: however, the chemical structures of poisons produced by plants, Araneae and Paederus are completely different. Whereas the above mentioned Araneae use the poison in defence, in the case of plants and Paederus the defensive effect does not derive from an obvious direct action but from the experience and awareness of the being facing the toxic organisms.

26. Some curare type paralizing substances are known in plants. Substances which paralize other Insecta are known in the poison of certain Hymenoptera (Habrobracon, numerous species of Sphecidae, etc.), but at present it is not possible to even vaguely indicate a chemical relationship with curare. This subject too must be studied ex novo because the comparison between paralizing venoms produced by Insecta is unknown.

Examples of a direct and analogous defence action of plants and Arthropoda against certain animals, and also partly against man, are the plant Symplocarpus foetidus (L.) Nutt., which gives off fetid gases, and the ants Megaponera foetens F. and Paltothyreus tarsatus Fabr. which emit a strong fecal smell perceivable at a distance. We have seen that in the African Ant Paltothyreus tarsatus the fetid secretion from the mandibular glands contains sulphides (dimethyldisulphide and dimethyltrisulphide) which have a defensive action. Sulphides of this type are present also in plants.

Another example is the plant Rafflesia arnoldi R. Br. which emits an offensive smell, and Brachynus (Insecta Coleoptera) which explosively produce a cloud of protective vapour, both irritating and with an unpleasant smell. In the two plants quoted, according to certain authors, the smells might serve to attract pollinating Insects; no attraction value can be attributed to the smells of the Insects just quoted, whose primary function is to repel preying animals.

27. The fetid secretion from the mandibular glands of the Paltothyreys tarsatus Ant contains sulphides; as seen, substances of this type are also contained in plants. Dendrolasin, found for the first time in the mandibular secretion of the Ant Lasius (Dendrolasius) fuliginosus, was later found in Japan in sweet potato fusel oil (Ipomoea batatas) by Hirose et al. 1961, in the wood of Torreya nucifera together with other products of a similar structure, like torreyal

and torreyol [1], by Sakan et al. 1963.

Iridomyrmecin, discovered in the "anal glands" of the Iridomyrmex humilis Ant, was also later discovered in a japanese plant, Actinidia polygama Miq., together with isoiridomyrmecin, dihydronepetalactone, isodihydronepetalactone and neonepetalactone (Sakan et al.). An alkaloid (actinidine) is present in the same plant with the same carbon atomic structure as iridomyrmecin. A similar substance, skytanthine,is present in the plant Skytanthus acutus Meyen, from South America.

Biogenesis of Arthropoda venoms (28).

28. We still have only limited information about the biogenesis of the most characteristic products of Arthropoda venoms. Several products may be considered as resulting from a variously patterned union of isoprenic residues according to the known Ruzicka rules (see also Chap.), as shown also in the diagram below.

/Figure/

Several authors obtained the synthesis for the iridoids present in Insecta and plants from citral , citronellal and limonene (see chap. 21). It is believed that these may also be the biogenetic origins, down to iridomyrmecin and correlate molecules. It has also been suggested that mevalonic acid, precursor of terpenic structures, may be the origin of iridoid structure, and therefore also of skytanthines (Casinovi and C. 1964, 49 E), alkaloids which are provided, as we have seen, with the same carbon atomic skeleton as iridoids. Meinwald, Happ, Labows and Eisner 1966 (189), have shown by radioactive substances that in the Anisomorpha buprestoides phasmid dolichodial (= anisomorphal) is synthesized from the normal precur-

(1) Not to be confused with torreyol $C_{15}H_{26}O$ which according to Sakan et al. 1963 is identical to δ-cadinol.

sors of terpenes, that is from acetate, mevalonate (mevalonic lactone) and malonate. Parallel experiments on the Nepeta cataria plant have brought to light the use of radioactive acetate and mevalonate for the formation of nepetalactone.

In the Acanthomyops claviger Ant the mandibular gland secretion includes citronellal and citral. Happ and Meinwald 1965 (145) obtained radioactive citral and citronellal by feeding workers with 1-^{14}C-acetate sodium, 2-^{14}C-acetate sodium, mevalonic 2-^{14}C-lactone. This suggests that the mevalonic acid pathway may have been utilized for terpenes biosynthesis.

To study dendrolasin biogenesis in Lasius (Dendrolasius) fuliginosus Latr. ants were fed with 2-^{14}C mevalonic acid: radioactive isolated dendrolasin was obtained. The biogenetic pathway that appears likely in this case is a transformation of mevalonic acid into farnesylpyrophosphate with successive oxydization and cyclization of the third isoprenic unity into furanic ring (Castellani and Pavan 1966) (54). The presence of other substances (methylheptenone, perillen, cis-citral, trans-citral, farnesal) in part (perillen, farnesal) correlate with dendrolasin (Bernardi, Cardani, Ghiringhelli, Selva, Baggini, Pavan 1967, 13 A) in the mandibular gland secretion of this species is a fact that makes the study of the biogenesis of these products and their interrelationships particularly interesting.

The presence of dendrolasin in Torreya nucifera Sieb and Zucc. and Ipomoea batatas plants (Sakai and coll. 1963, 286 B; Hirose and coll. 1961) poses also the comparative problem of its biogenesis in animals and plants.

Formic acid, which is widespread in Insects and plants, may derive from several biogenetic pathways, as assumed by O'Rourke 1950 (213) among others. In our preliminary experiments of feeding Formica lugubris Zett. with radioactive serine, we obtained marked formic acid (Castellani, Laterza, Pavan still underway).

Salicyl aldehyde, present in the Melasoma populi L. larvae, for example, is thought to derive from salicyn as in the following diagram (Pavan 1953, 235; 1958, 245, 246).

[figure]

For the Arthropoda quinones we may mention the possible derivations reported in the diagrams of table (Pavan 1958, 245, 246), and 5-hydroxytryptamine, according to several Authors, probably derived from tryptophane (see Pavan 1958, 245, 246).

[figure]

In the Nezara viridula (Fabr.) Heteropter the incorporation of acetate with radioactive C takes place in the products of the complex aliphatic compound mixture of the defensive secretion (Gordon, Waterhouse, Gilby 1963, 135). On the whole, then, an interesting field of research lies ahead.

Effects of Arthropoda poison on man (29).

29. The known data may also be considered from the point of view of their relevance to man. In fact, Arthropoda have both negative and positive aspects for man, which is also true for their poisons.

Some of the poisons mentioned appear neither directly nor indirectly harmful to man. In fact, for many poisons there is no reaction on the part of a human organism, for example those produced by the anal glands of Dolichoderinae, dendrolasin. Formic acid produced by Formicinae Ants is slightly caustic and asphyxiating for man. The poisons injected by Apidae, Vespidae, and numerous Formicidae, cause varying reactions, also serious. The defensive secretions of many Coleoptera Carabidae cause skin irritation and burns if in contact with the cornea; the quinonic poisons of various species of Coleoptera and Myriapoda Diplopoda can produce slight burns if squirted into the eye, but only provoke a temporary pigmentation when in contact with the skin. The salicyl aldehyde poison of Coleoptera larvae is only offensive due to its bitter smell. The vesicatory poisons with a basis of cantharidin, and lastly the most serious necrotizing poison, pederin, produce, when brought into contact with skin vesication (cantharidin), or sores due to necrotization of the tissues (pederin). Venoms injected by various Araneae (for example those in South America) provoke extensive and serious skin necrotization. The venoms of numerous species of Scorpiones and many Araneae (for example of the genus Latrodectus) can provoke serious general reactions and even death.

Useful aspects of Arthropoda defensive secretions (30).

30. Among the possible useful functions for man, to quote only a few of the most practical, worth noting is Bee poison which has recognized therapeutic applications (rheumatism) and is officially adopted in the pharmacopea of several countries. The secretion of Polydesmida (Myriapoda, Diplopoda) are used for arrow poison in Mexico due to the liberating power of hydrocyanic acid under the influence of particular enzymes present in the blood of the prey. Cantharidin has been widely used in therapy as a rubefacient and I have personally observed its use as an ingredient of the arrow poison made from plants by the Babinga pygmies of Equatorial Africa. The larvae of Coleoptera Chrysomelidae of the genera Diamphidia in Botswana are used by Bushmans, the people of Kalahari, when preparing arrow poisons. Its active principle are not chemically known. Formic acid, originally obtained from Ants three centuries ago, is applied in numerous ways in various important sectors of the chemical and pharmaceutical industries. Pederin presents aspects which might be of interesting development due to its effect on the growth of tissues: for example we were able to heal decubitus sores with quantities of the

substance equal to hundredths of a gamma; but it is also the most active antimitotic known. As an insecticide iridomyrmecin shows us the line to take the study of poison with a certain selective action, non-toxic for warm-blooded animals. Cantharidin was useful in distinguishing and procuring interesting phytoinhibitors, a property which, as we have seen, is common to other Insecta products. Dendrolasin showed us a natural chemical structure with selective repellent action employed by animals in nature, particularly effective against other species of Ants, direct competithors of the species which produces it.

The mere fact that it indicated the way to be followed in probable researches in nature and in laboratory sinthesis of insecticidal or repellent substances, endowed with a reduced range of action and very low toxicity for warmblooded animals, is enough to justify our interest in this kind of research. These aims have been recognized in high quarters by the most qualified organization also at an international level (for example O.I.L.B., International Organization for Biological Control ; U.I.C.N., International Union for Conservation of Nature and Natural Resources; Council of Europe; FAO; UNESCO, etc.)n which are concerned about the effects of wide indiscriminate use of ever more toxic, long lasting insecticides with a more extensive range of action.

Also what is known about antimitotic substances, especially when they are as powerful as pederin, for example, provides a sufficient motive for a through naturalistic, applied biological and chemical enquiry into the sector of biologically active substances produced by Arthropoda.

General remarks (31-33).

31. In order to try and see the entire problem of the relationship between the field of studied opened and the results reached in a general and vaster framework, we might consider some statistics; examining the number of animal species known in comparison to those whose poisons have been studied, and in particular regarding the species of whose poisons we know one or more chemical constituents, we note a striking disproportion which gives us an idea of how much still remains to be studied. As we have seen, today the number of animal species scientifically described amounts about 1.200.000, most of which are Arthropoda (884.944 species) with Insecta clearly predominating (815.763 species).

Among the largest Orders we find Coleoptera, Hymenoptera and Heteroptera which also have the largest number of poison producing species, and therefore presumably a large part of the species described in these Orders are of interest to our studies. According to very cautious calculations the poisonous species included in the Insecta group might be at least 50.000. Only 342 of these have been more or less studied, among which 146 Coleoptera, 96 Hymenoptera (of which as many as 81 Formicidae), and 44 Heteroptera.

If we add to these presumably interesting species of Insecta those belonging to other Arthropoda, it is clear we may calculate as over 82.000 the number of species of Arthropoda scientifically described, and presumably producers of offensive and defensive substances. The species of Arthropoda from which chemically defined substances forming part of the poison have been extracted and recognized, are only 426. Therefore a vast field of work is left for biologically and chemically integrated researches.

Considering only the list of chemically new natural substances found in the poisons of Insecta, it must be pointed out that from the 342 species of Insecta studied 18 of these substances have been extracted, 15 of which deriving from our researches (1-15) and 3 from the researches of Cavill and Coll. (16), and Schildknecht (17-18). These new substances are the following:

1. iridomyrmecin	10. cossin 1
2. pederin	11. cossin 2
3, iridodial	12. cossin 3
4. dendrolasin	13. cossin B_1
5. pseudopederin	14. cossin C_1
6. pederone	15. zeuzerina
7. cossin A	16. dolichodial
8. cossin B	17. cybisterone
9. cossin C	18. diidrocybisterone

No chemically new substance has been hitherto found in the venoms of Arthropoda species other than Insecta.

The above findings may be seen in an even more interesting prospect if we think that the animal species actually existing, but not yet scientifically known and described, can be estimated to be 5-10 times as numerous as those that are known at present.

The limited knowledge we already have is indicative of the multiformity of existing conditions and the importance they may have for our biological knowledge, particularly in the field of biochemistry. They indicate the existence of fields completely unknown for vertebrates and clearly demonstrate how the Arthropoda world is, in a certain way, a world into itself.

32. I feel it might be useful to now consider methodologically the individual and complex contributions at the various stages of our research. It is clear that at the beginning of research any problem which might arise is fundamentally an entomological problem in its widest sense: in fact the entomologist will identify the species most suitable for research by following previous indications or by deliberately taking new roads. Continuing in the development of the problem

the entomologist will apply himself above all to anatomy and physiology. The phase of essential chemical research to isolate biologically active factors will require collaboration with the chemist and continuous biological control of the results deriving from chemical experiments.

When the biologically active factors are isolated, the part which the chemist must play in the study of their structural characterization is of fundamental importance and involves considerable difficulty, above all due to the small quantity of substance with which he must sometimes work. In this phase the entomologist's collaboration lies in supplying the largest possible quantities of raw material.

After this study is concluded, the structural data and the pure substances must be returned to the entomologist to verify their origin and their complex meaning in nature. In this phase the entomologist will fit these data in with the general biological and zoological knowledge, and will consequently be able to single out new lines of collaborative research to be taken with the chemist. The chemist on the other hand will have opened the truly important scientific and practical field of the synthesis of analogous products; the biologist that of comparisons between the biological activities of the new products over an ever vaster range of animal and plant tests.

33. The group of studies regarding the defensive secretions of Arthropoda, carried out especially in the last 20 years, as we have seen, has supplied chemical literature with many new substances; we must add to these synthetic products modelled on them, but which generally have not been considered here; it has also brought to light their biological properties, it has partially explained their function in nature, it has opened new fields of research with possibilities of interesting applications to various sectors of agriculture, medicine, etc.

I should particularly like to emphasize once more how only by a close collaboration of entomological research, in the narrowest sense, with biological and biochemical researches it has been possible to arrive at the wealth of new facts summarily presented in this paper.

The data I have attempted to expound, first analytically and then summarily, in this conclusion, show how wide and full of prospects our future work is, both to fill in the missing links in the sector already known, and to extend and deepen our knowledge of entire huge and extremely interesting fields of work whose existence we are aware of, but which still remain almost completely unexplored.

PART VIII - BIBLIOGRAPHY.

1. ACHMAD S.A., CAVILL G.W.K., 1963. A stereospecific synthesis of the enantiomer of natural iridodial, and of natural nepetalactone. Proc.Chem.Soc.: 166.

1A. ACHMAD S.A., CAVILL G.W.K., 1965. Insect venoms, attractants, and repellents. VII. A stereospecific synthesis of iridodial. Aust.J.Chem., 18: 1989-1996.

1B. ACREE F. Jr., HAVILLAND E.E., HALLER H.L., 1946. Nature of the venom of (the ant) Formica exsectoides. J. Econ.Ent., 39: 661-662. (C.A., 41: 1338e, 1947).

2. ADAM K.R., SCHMIDT H., STÄMPFLI R., WEISS W., 1966. The effect of scorpion venom on single myelinated nerve fibres of the frog. Brit.J.Pharmacol., 26 (3): 666-677.

3. ADAM K.R., WEISS C., 1956. 5-Hydroxytryptamine in Scorpion venom. Nature, 178 (4530): 421-422.

4. ADROUNY G.A., DERBES V.J., JUNG R.C., 1959. Isolation of a hemolytic component of fire ant venom. Science, 130 (3373): 449.

AMEND G., see 210, Habermann W. and coll.

APLIN R., see 283, Rothschild M. and coll.

APPEL H.H., see 49A, Casinovi G.C. and coll.

ARAI T., see 153A, Inouye H. and coll.

ARDAO M.I., see 116, Estable C. and coll.
see 117, Estable C. and coll.
see 121, Fieser L.F. and coll.

4A. BAGGINI A., BERNARDI R., CASNATI G., PAVAN M., RICCA A., 1966. Ricerche sulle secrezioni difensive di insetti emitteri eterotteri (Hem. Heteroptera). EOS, 42 (1-2): 7-26.

5. BAGGINI A., PAVAN M., VALCURONE M.L., 1957. Sull'attività della cantaridina sul Lupinus albus. Atti Soc.It.Sc.Nat., 96 (1): 5-19.

BAGGINI A., see 13B, Bernardi R. and coll.
see 252, Pavan M. and coll.

6. BALOZET L., 1956. Scorpion venoms and antiscorpion serum. pag.141-144 in: BUCKLEY E.E., PORGES N. (Ed.): Venoms. American Association for the Advancement of Science, Washington: 1-467.

7. BARBETTA M., CASNATI G., PAVAN M., 1966. Sulla presenza di D-(+)-mandelonitrile nella secrezione difensiva del miriapode Gomphodesmus pavani Dem. (Diplopoda Polydesmoidea). Mem.Soc.Ent.It., 45: 169-176.

8. BARBIER M., 1959. Séparations de p-benzoquinones naturelles par chromato-plaques. J.Chromat., 2: 649-651.

9. BARBIER M., 1960. La sécrétion de venins p-benzoquinoniques chez certain arthropodes. La Nature, 3305: 388.

10. BARBIER M., LEDERER E., 1957. Sur les benzoquinones du venin de trois espèces de Myriapodes. Biochimia, 22 (1-2): 236-240.

10A. BATES R.B., 1957. The racemic 3-methylcyclopentane-1,2-dicarboxylic acids and the stereochemistry of nepetalactone and related compounds. Dissert.Abstr., 17: 2414-2415.

10B. BATES R.B., EISENBRAUN E.J., McELVAIN S.M., 1958. The configuration of the nepetalactone and related compounds. J.Amer.Chem.Soc., 80 (13): 3420-3424.

10C. BATES R.B , EISENBRAUN E.J., McELVAIN S.M., 1958. The dl-3-methylcyclopentane-1,2-dicarboxylic acids and the configuration of the nepetic acids. J.Am.Chem.Soc., 80 (13): 3413-3420.

10D. BATES R.B., SIGER C.W., 1963. Terpenoids. Cis-trans- and trans-cis-nepetalactones. Experientia, 19 (11): 564-565.

BATTY C.S., see 353, Welsh J.H. and coll.

11. BEARD R.L., 1963. Insect toxins and venoms. Ann.Rev.Entomol., 8: estratto 1-18.

12. BEAUREGARD H., 1890. Les insectes vésicants. Félix Alcan Ed., Paris: 1-544.

13. BEHAL A., PHISALIX C., 1900. La quinone, principe actif du venin du Julus terrestris. Bull.Muséum Hist.Nat.Paris, 6 (7): 388-390.

13A. BENTLEY T.W., JOHNSTONE R.A.W., GRIMSHAW J., 1967. Aspects of mass spectra of organic compounds. Part IV. Cyclopentane monoterpenes of the iridoid group. J.Chem.Soc. (C), : 2234-2240.

13B. BERNARDI R., CARDANI C., GHIRINGHELLI D., SELVA A., BAGGINI A., PAVAN M., 1967. On the component of secretion of mandibular glands of the ant Lasius (Dendrolasius) fuliginosus. Tetrahedron Letters, 40: 3893-3896.

BERNARDI R., see 4A, Baggini A. and coll.

14. BETTINI S., TOSCHI FRONTALI N., 1960. Biochemical and toxicological aspects of Latrodectus tredecimguttatus venom. XI Int.Kongr. Ent., Wien, Verh.B.III: 115-121.

15. BEVAN C.W., BIRCH A.J., CASWELL H., 1961. An insect repellent from black cocktail ants. J.Chem.Soc. (1): 488.

BETTINI S., see 206, Neri L. and Coll.
see 343, Vicari G. and coll.

BIANCHI E., see 49B, Casinovi G.C. and coll.
see 49C, Casinovi G.C. and coll.

15A. BIRCH A.J., GRIMSHAW J., JUNEJA H.R., 1961. Aucubin. J.Chem.Soc.: 5194-5197.

BIRCH A.J., see 15, Bevan C.W. and coll.

BIRRINGER H., see 296, Schildknecht H. and coll.

16. BISSET G.W., FRAZER J.F.D., ROTHSCHILD M., SCHACHTER M., 1959. A choline ester and other substances in the garden tiger moth, Arctia caja (L.). J.Physiol., 146: 38-39.

17. BISSET G.W., FRAZER J.F.D., ROTHSCHILD M., SCHACHTER M., 1960. A pharmacologically active choline ester and other substances in the garden tiger moth, Arctia caja L. Proc.R.Soc.London, B, 152: 255-262.

18. BLUM M.S., 1961. The presence of 2-hexenal in the scent gland of the pentatomid Brachymena quadripustulata. Ann.Entom.Soc.Am., 54 (3): 410-412.

19. BLUM M.S., 1964. Insect defensive secretions: hex-2-enal-1 in Pelmatosilpha coriacea (Blattaria) and its repellent value under natural conditions. Ann.Entom.Soc.Am., 57 (5): 600-602.

20. BLUM M.S., 1966. The source and specificity od trail pheromones in Termitopone, Monomorium and Huberia, and their relation to those of some other ants. Proc.R.Ent.Soc.Lond.(A), 41 (10-12): 155-160.

21. BLUM M.S., 1966. Chemical releaser of social behavior. VIII. Citral in the mandibular gland secretion of Lestrimelitta limao (Hymenoptera:Apoidea: Melittidae). Ann.Ent.Soc.Am., 59 (5): 962-964.

22. BLUM M.S., CALLAHAN P.S., 1960. Chemical and biological properties of the venom of the imported fire ant (Solenopsis saevissima var. richteri Forel) and the isolation of the insecticidal component. XI Int.Kongr.f.Entom., Wien, Verh.B.III: 290-293.

23. BLUM M.S., CALLAHAN P.S., 1963. The venom and poison glands of Pseudomyrmex pallidus (F. Smith). Psyche, 70 (2): 69-74.

24. BLUM M.S., CRAIN R.D., CHIDESTER J.B., 1961. Trans-2-hexenal in the scent gland of the hemipteran Acanthocephala femorata. Nature, 189 (4760): 245-246.

25. BLUM M.S., PORTOCARRERO C.A., 1966. Chemical releaser of social behavior. X. An attine trail substance in the venom of a non trail laying myrmicine, Daceton armigerum (Latreille). Psyche, 73 (2): 150-155.

26. BLUM M.S., ROBERTS J.E.Jr., NOVAK A.F., 1961. Chemical and biological characterization of venom of the ant Solenopsis xyloni McCook. Psyche, 68 (2-3): 73-74.

27. BLUM M.S., TRAYNHAM J.G., 1960. The chemistry of the pentatomid scent gland. XI Int.Kongr.f.Entom., Wien, Verh.B.III: 48-52.

28. BLUM M.S., TRAYNHAM J.G., CHIDESTER J.B., BOGGUS J.D., 1960. n-tridecane and trans-2-heptenal in scent gland of the rice stink bug Oebalus pugnax (F.). Science, 132 (3438): 1480-1481.

28A. BLUM M.S., WALKER J.R., CALLAHAN P.S., NOVAK A.F., 1958. Chemical, insecticidal, and antibiotic properties of fire ant venom. Science, 128: 306-307.

29. BLUM M.S., WARTER S.L., 1966. Chemical releaser of social behaviour. VII. The isolation of 2-heptanone from Conomyrma pyramica (Hymenoptera: Formicidae: Dolichoderinae) and its modus operandi as a releaser of alarm and digging behaviour. Ann.Ent.Soc.Am ., 59 (4): 774-779.

30. BLUM M.S., WARTER S.L., MONROE R.S., CHIDESTER J.C., 1963. Chemical releasers of social behaviour. I. Methyl-n-amyl ketone in Iridomyrmex pruinosus (Roger) (Formicidae: Dolichoderinae). J. Ins. Physiol., 9: 881-885.

31. BLUM M.S., WARTER S.L., TRAYNHAM J.G., 1966. Chemical releasers of social behaviour. VI. The relation of structure to activity of ketones as releasers of alarm for Iridomyrmex pruinosus (Roger). J.Ins.Physiol., 12: 419-427.

32. BLUM M.S., WOODRING J.P., 1962. Secretion of benzaldehyde and hydrogen cyanide by the millipede Pachydesmus crassicutis (Wood). Science, 138 (3539): 512-513.

BLUM M.S., see 147, Hermann H.R. and coll.
see 148, Hermann H.R. and coll.
see 362, Woodring J.P. and coll.
see 363, Woodring J.P. and coll.

33. BLUMBERG D.R., 1961. The repugnatorial glands of the tenebrionid beetle (Coleoptera) Eleodes obosoleta (Say). Trans.Amer.Ent.Soc., 87: 45-55.

BO G., see 253, Pavan M. and coll.

33A. BOBBITT J.M., SPIGGLE D.W., MAHBOOB S., Von PHILIPSBORN W., SCHMID H., 1962. Catalpa glycosides. II. The structure of catalposide. Tetrahedron Letters, (8): 321-329.

34. BOCH R., SHEARER D.A., STONE B.C., 1962. Identification of iso-amyl acetate as an active component in the sting pheromone of the honey bee. Nature, 195 (4845): 1018-1020.

BOCH R., see 320, Shearer D.A. and coll.

BOGGUS J.D., see 28, Blum M.S. and coll.

35. BONIMOND J.P., 1951. Le venin d'abeilles. Ed.Bière, Paris: 1-72.

BORCHERT P., see 321A, Slotta K. and coll.

36. BORDAS M.L., 1909. Les glandes céphaliques (glandes séricigènes et glandes mandibulaires) des chenilles de Lépidoptères. Ann.Sci. Nat.Zool., 10 (3-6): 125-198.

BRANDER J., see 215, Osman M.F.H. and coll.

37. BRANGI G.P., PAVAN M., 1954. Sulle proprietà antibatteriche del miele, propoli, pappa reale e veleno di Apis mellifera L. (Hym. Apidae). Mem.Soc.Entom.It., 33: 19-32.

38. BRANGI G.P., PAVAN M., 1954. Sulle proprietà antibatteriche del veleno di Apis mellifica L. (Hym.Apidae). Ins.Soc., 1 (3): 209-217.

BRASIL N.P., see 116, Estable C. and coll.

38A. BRIGGS L.H., CAIN B.F., LE QUESNE P.W., SHOOLERY J.N., 1963. The structure of asperuloside. Tetrahedron Letters,(2): 69-74.

BRIGHT R.D., see 184E, McElvain S.M. and coll.
see 185A, McElvain S.M. and coll.

BRUENS C.T., see 193, Melander A.L. and coll.

39. BRUNET P.C.J., 1965. The metabolism of aromatic compounds. pag.49-77 in: GOODWIN T.W. (Ed.): Aspects of insect biochemistry. Academic Press, London: 1-107.

40. BÜCHEL K.H., KORTE F., 1960. Zur Chemie der Iridolactone. XI Int. Kongr.Ent., Wien, Verh.Bd.III: 60-65.

BÜCHEL K.H., see 166A, Korte F. and coll.

40A. BÜCHI G., MANNING R.E., 1960. Structure of verbenalin. Tetrahedron Letters, 26: 5-12.

41. BURTT E., 1947. Exudate from millipedes with particular reference to its injurious effects. Trop.Dis.Bull., 44 (1): 7-12.

42. BUTENANDT A., 1959. Wirkstoffe des Insektenreiches. Naturwiss., 46 (15): 461-471.

43. BUTENANDT A., LINZEN B., LINDAUER M., 1959. Über einen Duftstoffe aus der Mandibeldrüse der Blattschneiderameise Atta sexdens rubropilosa Forel. Arch.Anat.Micr.Morph.Exper., 48 bis: 13-19.

44. BUTENANDT A., NGUYEN-DANG TAM, 1957. Über einen geschlechtsspezifischen Duftstoff der Wasserwanze Belostoma indica Vitalis (Lethocerus indicus Lep.). Ztschr.f.Physiol.Chem., 308: 277-283.

BUTSUGAN Y., see 286E, Sakan T. and coll.
see 286F, Sakan T. and coll.
see 286G, Sakan T. and coll.
see 286H, Sakan T. and coll.
see 286I, Sakan T. and coll.
see 286L, Sakan T. and coll.
see 286M, Sakan T. and coll.

CAIN B.F., see 38A, Biggs L.H. and coll.

CALLAHAN P.S., see 22, Blum M.S. and coll.
see 23, Blum M.S. and coll.
see 28A, Blum M.S. and coll.

CANDURA F., see 184A, Maugeri S. and coll.

CAPEN R.G., see 344, Viehoeber A. and coll.

45. CARDANI C., GHIRINGHELLI D., MONDELLI R., PAVAN M., QUILICO A., 1965. Propriétés biologiques et composition chimique de la pédérine. Ann.Soc.Ent.Fr. (N.S.), 1 (4): 813-816.

46. CARDANI C., GHIRINGHELLI D., MONDELLI R., QUILICO A., 1965. The structure of pederin. Tetrahedron Letters, 29: 2537-2545.

47. CARDANI C., GHIRINGHELLI D., MONDELLI R., QUILICO A., 1966. Struttura della pederina. Gazz.Chim.It., 96: estratto 3-38.

48. CARDANI C., GHIRINGHELLI D., QUILICO A., 1964. Chemical investigations on pederin. Int.Symp.Chem.Nat.Prod., Kyoto.

49. CARDANI C., GHIRINGHELLI D., QUILICO A., SELVA A., 1967. The structure of pederone a novel substance from Paederus (Coleoptera Staphylinidae). Tetrahedron Letters (41): 4023-4025.

CARDANI C., see 13B, Bernardi R. and coll.

49A. CASINOVI C.G., DELLE MONACHE F., GRANDOLINI G., MARINI BETTOLO G.B., APPEL H.H., 1963. Two new alkaloids from Skytanthus acutus Meyen. Chemistry and Industry: 984.

49B. CASINOVI G.C., DELLE MONACHE F., MARINI BETTOLO G.B., BIANCHI E., GARBARINO J.A., 1961. Synthesis in the skytanthine series. Sci.Repts.Ist.Super.Sanità, 1:588-590.

49C. CASINOVI C.G., DELLE MONACHE F., MARINI BETTOLO G.B., BIANCHI E., GARBARINO J.A., 1962. Ricerche nella serie della Skytanthina. Nota II. Sintesi di tre stereoisomeri a configurazione nota della Skytanthina. Gazzetta Chimica Italiana, 92: 479-487.

49D. CASINOVI C.G., GARBARINO J.A., MARINI BETTOLO G.B., 1961. La struttura dell'alcaloide dello Skytanthus acutus Meyen. Gazzetta Chimica Italiana, 91: 1037-1044.

49E. CASINOVI C.G., GIOVANNOZZI-SERMANNI G., MARINI BETTOLO G.B., 1964. Studi preliminari sulla biosintesi delle skitantine. Gazzetta Chimica Italiana, 94: 1356-1368.

CASINOVI C.G., see 181A, Marini Bettolo G.B. and coll.
see 181B, Marini Bettolo G.B. and coll.

50. CASNATI G., NENCINI G., QUILICO A., PAVAN M., RICCA A., SALVATORI T., 1963. The secretion of the myriapod Polydesmus collaris collaris(Koch). Experientia, 19: 409-411.

51. CASNATI G., PAVAN M., RICCA A., 1965. Sulla costituzione del veleno dell'insetto Calosoma sycophanta L. (Coleoptera Carabidae). Ann.Soc.Ent.Fr. (N.S.), 1 (3): 705-710.

52. CASNATI G., PAVAN M., RICCA A., 1964. Ricerche sul secreto delle glandole anali di Liometopum microcephalum Panz. Boll.Soc.Ent. It., 94 (9-10): 147-152.

53. CASNATI G., RICCA A., PAVAN M., 1967. Sulla secrezione difensiva delle glandole mandibolari di Paltothyreus tarsatus (Fabr.). Chim. Ind., Milano, 49: 57- .

CASNATI G., see 4A, Baggini A. and coll.
see 7, Barbetta M. and coll.

54. CASTELLANI A.A., PAVAN M., 1966. Prime ricerche sulla biogenesi della dendrolasina. Boll.Soc.Ital.Biol.Sper., 42 (20 bis), com. 221.

CASWELL H., see 15, Bevan C.W. and coll.

55. CAVILL G.W.K., 1960. The cyclopentanoid monoterpenes. Rev.Pure Appl. Chem., 10 (3): 169-183.

56. CAVILL G.W.K., CLARK D.V., 1967. Insect venoms, attractants, and repellent. VIII. Isodihydronepetalactone. J.Insect Physiol., 13: 131-135.

57. CAVILL G.W.K., CLARK D.V., HINTERBERGER H., 1966. Some volatile constituents of terrestrial slaters. Aust.J.Chem., 19: 1495-1501.

58. CAVILL G.W.K., FORD D.L., 1953. The chemistry of Ants. Chem.and Ind., : 351.

59. CAVILL G.W.K., FORD D.L., HINTERBERGER H., SOLOMON D.H., 1958. Synthesis of 1:5-dials including bisnoriridodial. Chem.and Ind.: 292.

59A. CAVILL G.W.K., FORD D.L., HINTERBERGER H., SOLOMON D.H., 1961. Bisnoriridodial, bisnoriridolactone, and related compounds. Austr. J.Chem., 14 (2): 276-283.

60. CAVILL G.W.K., FORD D.L., LOCKSLEY H.D., 1956. The chemistry of ants. I. Terpenoid constituents of some australian Iridomyrmex species. Austr.J.Chem., 9 (2): 288-293.

61. CAVILL G.W.K., HINTERBERGER H., 1960. Dolichoderinae ant extractives. XI Int.Kongr.Entom., Wien, Verh.Bd.III: 53-59.

62. CAVILL G.W.K., HINTERBERGER H., 1960. Dolichodial and related compounds. XI Int.Kongr.Entom., Wien, Verh.Bd.III: 284-289.

63. CAVILL G.W.K., HINTERBERGER H., 1960. The chemistry of ants. IV Terpenoid constituents of some Dolichoderus and Iridomyrmex species. Austr.J.Chem., 13 (4): 514-519.

64. CAVILL G.W.K., HINTERBERGER H., 1961. The chemistry of ants. V. Structure and reactions of dolichodial. Austr.J.Chem., 14 (1): 143-149.

65. CAVILL G.W.K., LOCKSLEY H.D., 1957. The chemistry of ants. II. Structure and configuration of iridolactone (isoiridomyrmecin). Austr.J.Chem., 10 (3): 352-358.

66. CAVILL G.W.K., ROBERTSON P.L., 1965. Ant venoms, attractants and repellents. Science, 149 (3690): 1337-1345.

67. CAVILL G.W.K., ROBERTSON P.L., WHITFIELD F.B., 1964. Venom and venom apparatus of the bull ant, Myrmecia gulosa (Fabr.). Science, 146 (3640): 79-80.

67A. CAVILL G.W.K., WHITFIELD F.B., 1962. Synthesis of the Enantioner of Natural Dolichodial. Proc.Chem.Soc.: 380-381.

67B. CAVILL G.W.K., WHITFIELD F.B., 1964. Ethyl 2-cyano-6-methyl-8,8-ethylenedioxyoct-2-enoate and its transformation products. Austr.J.Chem., 17 (11): 1245-1259.

67C. CAVILL G.W.K., WHITFIELD F.B., 1964. Insect venoms, attractants, and repellents. VI. Synthesis of the dolichodials. Aust.J.Chem., 17: 1260-1269.

68. CAVILL G.W.K., WILLIAMS P.J., 1967. Constituents of Dufour's glands in Myrmecia gulosa. J.Ins.Physiol., 13: 1097-1103.

69. CAVILL G.W.K., WILLIAMS P.J., WHITFIELD F.B., 1967. α-farnesene, Dufour's gland secretion in the ant Aphaenogaster longiceps (F. Sm.). Tetrahedron Letters (23): 2201-2205.

CAVILL G.W.K., see 1, Achmad S.A. and coll.
see 1A, Achmad S.A. and coll.

70. CHADHA M.S., EISNER T., MEINWALD J., 1961. Defense mechanism of arthropods. III. Secretion of 2-hexenal by adults of the cockroach Cutilia soror (Brunner). Ann.Ent.Soc.Am., 54 (5): 642-643.

71. CHADHA M.S., EISNER T., MEINWALD J., 1961. Defence mechanism of arthropods. IV. Para-benzoquinones in the secretion of Eleodes longicollis Lec. (Coleoptera: Tenebrionidae). J.Ins.Physiol., 7 (1): 46-50.

72. CHADHA M.S., EISNER T., MONRO A., MEINWALD J., 1962. Defence mechanisms of arthropods. VII. Citronellal and citral in the mandibular gland secretion of the ant Acanthomyops claviger (Roger). J.Ins.Physiol., 8: 175-179.

CHADA M.S., see 187, Meinwald J. and coll.
see 198, Monro A. and coll.

CHAN D., see 361 Wolinsky J. and coll.

CHIDESTER J.B., see 24, Blum M.S. and coll.
see 28, Blum M.S. and coll.
see 30, Blum M.S. and coll.

72A. CHOPARD L., 1962. Les Zygènes papillons à acide cyanhydrique. Nature, Paris (3325): 206-207.

72B. CLARK K.J., FRAY G.I., JAEGER R.H., ROBINSON Sir R., 1958. Eine Synthese des D-und L-Iso-Iridomyrmecins. Ang.Chemie, 70 (22-23): 704.

72C. CLARK K.J., FRAY G.I., JAEGER R., ROBINSON R., 1958. Configuration of iridodial, isoiridomyrmecin and iridomyrmecin. Chemistry and Industry (45): 1473.

73. CLARK K.J., FRAY G.I., JAEGER R.H., ROBINSON Sir R., 1959. Synthesis of D-and L-isoiridomyrmecin and related compounds. Tetrahedron, 6: 217-224.

CLARK D.V., see 56, Cavill G.W.K. and coll.
see 57, Cavill G.W.K. and coll.

74. CLAUS C., 1862. Ueber die seitendrüsen der Larve von Chrysomela populi. Z.Wiss.Zool., 11: 309-314.

75. COLLIER H.O.J., 1958. The occurrence of 5-hydroxytryptamine (HT) in nature. pag. 5-19 in LEWIS G.P. (Ed.): 5-Hydroxytryptamine", Pergamon Press, London: 1-253.

76. COOK O.F., 1900. Camphor secreted by an animal (Polyzonium). Science, 12 (301): 516-521.

COLLOTTI C., see 343, Vicari G. and coll.

76A. COOKSON R.C., HUDEC J., KNIGHT S.A., WHITEAR B., 1962. Cyclization of citral by light. Tetrahedron Letters,(2): 79-81.

76B. COOKSON R.C., HUDEC J., KNIGHT S.A., WHITEAR B.R.D., 1963. The photochemistry of citral. Tetrahedron, 19: 1995-2007.

77. COOLIDGE K.R., 1909. Secretion of hydrocyanic acid by Leptodesmus haydenianus Wood. Canadian Entomol., 41: 104.

78. CORNWALL J.W., 1916. Some centipedes and their venom. Ind.J.Med.Res., 3 (3): 541-557.

79. COTTE J., 1920. Teneur en cantharidine de certains Mylabris. C.R.Soc. Biol., 83: 106-108.

CRAIN R.D., see 24, Blum M.S. and coll.

80. CRESCITELLI F., GEISSMAN T.A., 1962. Invertebrate pharmacology: selected topics. Ann.Rev.Pharmacol., 2: 143-192.

81. CREWE W., GORDON R.M., 1949. The histology of the lesions caused by the sting of the hive-bee (Apis mellifica). Ann.Trop.Med.Parasit., 43 (3-4): 341-344.

82. CUENOT L., 1890. Le sang des Meloe et le role de la cantharidine dans la biologie des Coléoptères vésicants. Bull.Soc.Zool.France, 15: 126-128.

83. DATEO G.P., ROTH L.M., 1967. D-gluconic acid: isolation from the defensive secretion of the cockroach Eurycotis decipiens. Science, 155 (3758): 88-89.

83A. DATEO G.P., ROTH L.M., 1967. Occurrence of Gluconic acid and 2-hexenal in the defensive secretions of three species of Euryccotis (Blattaria: Blattidae: Polyzosteriinae). Ann.Ent.Soc.Am., 60 (5): 1025-1030.

84. DE COURSEY J.D., 1954. Addendum to Tribolium castaneum (Herbst) as a source of an antibacterial agent. Nav.Med.Field.Res.Lab. Camp Lejeune North Carolina, 5: 81-88 (cyclost.).

85. DE COURSEY J.D., WEBSTER A.P., TAYLOR W.W. Jr., LEOPOLD R.S., KATHAN R.H., 1953. An antibacterial agent from Tribolium castaneum (Herbst). Ann.Ent.Soc.Am., 46 (3): 386-392.

86. DE COURSEY J.D., WEBSTER A.P., TAYLOR W.W. Jr., LEOPOLD R.S., KATHAN R.H., 1953. Tribolium castaneum (Herbst) as a source of an antibacterial agent. Nav.Med.Field Res.Lab.Camp Lejeune North Carolina, 4: 125-136 (cyclost.).

87. DEEGENER P., 1928. Haut und Hautorgane. pag. 1-60 in SCHRÖDER C.: Handbuch der Entomologie. G. Fischer, Verlag, Jena: 1-

88. DEFIEL F., 1922. An experimental investigation of the supposed poisonous qualities of the granary weevil, Calandra granaria. Amer. J.Trop.Med., 2: 199-211.

89. DE LA LANDE I.S., THOMAS D.W., TYLER M.J., 1963. Pharmacological analysis of the venom of the "bulldog" ant Myrmecia forficata. pag. 71-75 in RAUDONAT H.W., VANECEK J. (Ed.): Recent advances in the pharmacology of toxins. Pergamon Press, London: 1-240, 1965.

DELLE MONACHE F., see 49A, Casinovi C.G. and coll.
see 49B, Casinovi C.G. and coll.
see 49C, Casinovi C.G. and coll.
see 181A, Marini Bettolo G.B. and coll.
see 181B, Marini Bettolo G.B. and coll.

90. DENHAM C.S., 1888. The acid secretion of Notodonta concinna. Insect Life, Washington, 1: 143.

DERBES V.J., see 4, Adrouny G.A. and coll.

91. DETHIER V.G., 1947. Chemical insect attractants and repellents. The Blakiston Co.Philadelphia: 1-289.

DETWILER J.D., see 149, Herricj G.W. and coll.

92. DEVAKUL V., MAARSE H., 1964. A second compound in the odorous gland liquid of the giant water bug Lethocerus indicus (Lep. and Serv.). Anal.Biochem., 7: 269-274.

DICHERSON D., see 286N, Sakan T. and coll.

DILGEN Sir St.F., see 97A, Eisenbraun E.J. and coll.

93. DIMMOCK G., 1882. On some glands which open externally on insects. Psyche, 3: 387-401.

94. DIXON A.F.G., MARTIN-SMITH M., SMITH S.J., 1963. Isolation of cantharidin from Meloë proscarabeus. Can.Pharm.J., 96: 501-503.

94A. DJERASSI C., NAKANO T., JAMES A.N., ZALKOW L.H., EISENBRAUN E.J., SHOOLERY J.N., 1961. Terpenoids. XLVII. The structure of enipin. J.Org.Chem., 26: 1192-1202.

94B. DOLEJS L., MIRONOV A., SORM F., 1960. Structure of bulnesol, stereochemistry of guaiol, nepetalinic acids and iridomyrmecins. Tetrahedron Letters, 11: 18-21, 1960.

94C. DOLEJS L., MIRONOV A., SORM F., 1961. On terpenes. CXXI. Structure of bulnesol and stereochemistry of guaiol, nepetalinic acids and iridomyrmecins. Collection Czechoslov.Chem.Commun., 26: 1015-1020.

DÖRFEL H., see 122, Fischer F.G. and coll.

DUBINI M., see 267, Piozzi F. and coll.

95. ECKERT D., PAASONEN M., VARTIAINEN A., 1951. On histamine in the gnat (Culex pipiens). Acta pharmacol.toxicol., 7: 16-22.

96. EDWARDS J.S., 1960. Spitting as a defensive mechanism in a predatory Reduviid. XI Int.Kongr.f.Entom., Wien, Verh.Bd.III: 259-263.

97. EDWARDS J.S., 1961. The action and composition of the saliva of an assassin bug Platymeris rhadamanthus Gaerst. (Hemiptera, Reduviidae). J.Exp.Biol., 38: 61-77.

97A. EISENBRAUN E.J., HANEL P.G., SCHORNO K.S., DILGEN F., OSIECKI J., 1967. The synthesis of racemic and (3R)-methylcyclopentane-1,2-dicarboxylic acids (nepetic acids). J.Org.Chem., 32: 3010-3017.

EISENBRAUN E.J., see 10B, Bates R.B. and coll.
see 10C, Bates R.B. and coll.
see 94A, Djerassi C. and coll.
see 184F, McElvain S.M. and coll.
see 185, McElvain S.M. and coll.
see 273A, Regnier E.J. and coll.

98. EISNER T., 1958. The protective role of the spray mechanism of the bombardier beetle Brachynus ballistarius Lec. J.Ins.Physiol., 2 (3): 215-220.

99. EISNER T., 1958. Spray mechanism of the cockroach Diploptera punctata. Science, 128 (3316): 148-149.

100. EISNER T., 1960. Defense mechanisms of arthropods. II. The chemical and mechanical weapons of an earwig. Psyche, 67 (3): 62-70.

100A. EISNER T., 1964. Catnip: its raison d'être. Science, 146 (3649): 1318-1320.

101. EISNER T., 1965. Defensive spray of a phasmid insect. Science, 148 (3672): 966-968.

102. EISNER T.,1966. Beetle's spray discourages predators. Nat.Hist., 75 (2): 42-47.

103. EISNER T., EISNER H.E., 1965. Mystery of a millipede. Hydrogen cyanide gas is made by insect, new studies show. Nat.Hist., 74 (3): 30-37.

104. EISNER H.E., EISNER T., HURST J.J., 1963. Hydrogen cyanide and benzaldehyde produced by millipedes. Chem.and Industry: 124-125.

105. EISNER T., EISNER H.E., HURST J.J., KAFATOS F.C., MEINWALD J., 1963. Cyanogenic glandular apparatus of a millipede. Science, 139 (3560): 1218-1220.

106. EISNER T., HURST J.J., KEETON W.T., MEINWALD J., 1965. Defense mechanism of arthropods. XVI. Para-benzoquinones in the secretion of spirostreptoid millipedes. Ann.Ent.Soc.Am., 58 (2): 247-248.

107. EISNER T., HURST J.J., MEINWALD J., 1963. Defense mechanism of arthropods. XI. The structure, function, and phenolic secretions of the glands of a chordeumoid millipede and a carabid beetle. Psyche, 70 (2): 94-116.

108. EISNER T., McHENRY F., SALPETER M.M., 1964. Defense mechanisms of arthropods. XV. Morphology of the quinone-producing glands of a tenebrionid beetle (Eleodes longicollis Lec.). J.Morph., 115 (3): 355-399.

109. EISNER T., McKITTRICK F., PAYNE R., 1959. Defense sprays of roaches. Pest Control, 27: 11-12, 44-45.

110. EISNER T., MEINWALD Y.C., 1965. Defensive secretion of a caterpillar (Papilio). Science, 150 (3704): 1733-1735.

111. EISNER T., MEINWALD J., 1966. Defensive secretions of Arthropods. Science, 153 (3742): 1341-1350.

112. EISNER T., MEINWALD J., MONRO A., GHENT R., 1960. The defensive spray of a Whipscorpion. XI Int.Kongr.f.Entom., Wien, Verh.B.III: 110-114.

113. EISNER T., MEINWALD J., MONRO A., GHENT R., 1961. Defence mechanisms of Arthropods. I. The composition and function of the spray of the whipscorpion, Mastigoproctus giganteus Lucas (Arachnida; Pedipalpida). J.Insect Physiol., 6: 272-298.

114. EISNER T., SWITHENBANK C., MEINWALD J., 1963. Defense mechanisms of arthropods. VIII. Secretion of salicylaldehyde by a carabid beetle. Ann.Ent.Soc.Am., 56 (1): 37-41.

EISNER H.E., see 103, Eisner T. and coll.
see 105, Eisner T. and coll.

EISNER T., see 70, Chadha M.S. and coll.
see 71, Chadha M.S. and coll.
see 72, Chadha M.S. and coll.
see 104, Eisner H.E. and coll.
see 153, Hurst J.J. and coll.
see 187, Meinwald J. and coll.
see 188, Meinwald J. and coll.
see 189, Meinwald J. and coll.
see 190, Meinwald J. and coll.
see 191, Meinwald Y.C. and coll.
see 192, Meinwald J. and coll.
see 198, Monro A. and coll.
see 278, Roth L.M. and coll.
see 355, Wheeler J.W. and coll.

EL KAREMI M.M.A., see 143, Habermann E. and coll.

EMURA M., see 150, Hisada Y. and coll.

115. ERSPAMER V., 1955. Osservazioni critiche sulle ipotesi concernenti il significato biologico della 5-idrossitriptamina (enteramina, serotonina). Medicina, Parma, 5: 1-34.

116. ESTABLE C., ARDAO M.L., BRASIL N.P., FIESER L.F., 1955. Gonyleptidine.J.Am.Chem.Soc., 77: 4942.

117. ESTABLE C., FERREIRA-BERRUTI P., ARDAO M.I., 1945. Contribucion al conocimiento de la toxina de Megalopyge urens y de su accion farmacodinamica. Arch.Soc.Biol.Montevideo, 12 (3): 186-198.

118. v.EUW J., FISHELSON L., PARSONS J.A., REICHSTEIN T., ROTHSCHILD M., 1967. Cardenolides (heart poison) in a grasshopper feeding on milkweeds. Nature, 214 (5083): 35-39.

119. FABRE M.P., 1905. II. Le venin des hyménoptères. Bull.Acad.Méd., 53 (3): 487-509.

119A. FALBE J., WEITKAMP H., KORTE F., 1963. Zur Synthese bicyclischer Lactone vom Typ des D,L-Iridomyrmecins. Tetrahedron, 19: 1479-1482, 1963.

FALBE J., see 166B, Korte F. and coll.
see 166C, Korte F. and coll.

120. FAVILLI G., 1954. Occurrence of spreading factors and some properties of hyaluronidases in animal parasites and venoms. pag.281-289 in BUCKLEY E.E., PORGES N. (Ed.): Venoms. American Association for the Advancement of Science, Washington: 1-467, 1956.

FERREIRA-BERRUTTI P., see 117, Estable C. and coll.

121. FIESER L.F., ARDAO M.I., 1956. Investigation of the chemical nature of gonyleptidine. J.Am.Chem.Soc., 78: 774-781.

FIESER L.F., see 116, Estable C. and coll.

FIORETTI A., see 323, Soldati M. and coll.

122. FISCHER F.G., DÖRFEL H., 1953. Das Gift der Honigbiene. II. Mitteilung. Die Aminosäuren-Zusammensetzung der Bienengift-Fraktionen. Biochem.Ztschr., 324: 465-475.

123. FISCHER F.G., NEUMAN W.P., 1953. Das Gift der Honigbiene. I. Mitteilung. Trennung und chemische Charakterisierung der beiden Hauptfraktionen. Biochem.Ztsch., 324: 447-464.

FISCHER P., see 176, Leclercq M. and coll.

FISHELSON L., see 118, v.EUW J. and coll.

FORD D.L., see 58, Cavill G.W.K. and coll.
see 59, Cavill G.W.K. and coll.
see 59A, Cavill G.W.K. and coll.
see 60, Cavill G.W.K. and coll.

FORSS D.S., see 347, Waterhouse D.F. and coll.

FRANK M., see 206, Neri L. and coll.

123A. FRAY G.I., ROBINSON Sir R., 1960. Synthesis of analogues of the iridolactones. Tetrahedron, 9: 295-297, 1960.

FRAY G.I., see 72B, Clark K.J. and coll.
see 72C, Clark K.J. and coll.
see 73, Clark K.J. and coll.

124. FRAZER J.F.D., ROTHSCHILD M., 1960. Defence mechanisms in warninggly-coloured moths and other insects. XI Int.Kongr.f.Entom., Wien, Verh.Bd.III: 249-256.

FRAZER J.F.D., see 16, Bisset G.W. and coll.
see 17, Bisset G.W. and coll.

125. FREDERICQ L., 1924. Die Sekretion von Schutz-und Nutzstoffen. Hand. Vergl.Physiol., 2: 1-256.

126. FRONTALI N., GRASSO A., 1964. Separation of three toxicologically different protein components from the venom of the spider _Latrodectus tredecimguttatus_. Arch.Biochem.Biophys., 106: 213-218.

127. FRONTALI N., GRASSO A., 1964. Biochemical and toxicological characteristics of three protein components of the venom of the spider _Latrodectus tredecimguttatus_. Proc.12th Int.Congr.Ent., London: 229, 1965.

FRONTALI N., see 343, Vicari G. and coll.

127A. FUJINO A., 1960. Chemical studies of effective components contained in Matatabi (_Actinidia polygama_ Miq.). III. Chemical structure of Actinidine. Nippon Kagaku Zasshi, 81 (8): 1327-1332.

FUJINO A., see 286C, Sakan T. and coll.
see 286D, Sakan T. and coll.
see 286E, Sakan T. and coll.
see 286F, Sakan T. and coll.
see 286G, Sakan T. and coll.
see 286H, Sakan T. and coll.
see 286I, Sakan T. and coll.
see 286L, Sakan T. and coll.
see 286M, Sakan T. and coll.

128. FUSCO R., TRAVE R., VERCELLONE A., 1955. La struttura dell'iridomirmecina. Chim.Ind.Milano, 37 (12): 958-959.

129. FUSCO R., TRAVE R., VERCELLONE A., 1955. Ricerche sull'iridomirmecina, l'insetticida naturale secreto dalla Iridomyrmex humilis Mayr. Chim.Ind., Milano, 37 (4): 251-258.

129A. GABBA A., 1967. Aspetti dell'organizzazione negli insetti sociali. 2. la sostanza della traccia nei Formicidae. Natura, 58 (2): 150-172.

129B. GARANTI L., 1962. Sintesi della nor-isoiridomirmecina. Chim.Ind., Milano, 44 (10): 1105-1114.

GARANTI L., see 334, Trave R. and coll.
see 335, Trave R. and coll.
see 336, Trave R. and coll.
see 337, Trave R. and coll.

GARBARINO J.A., see 49B, Casinovi G.C. and coll.
see 49C, Casinovi G.C. and coll.
see 49D, Casinovi G.C. and coll.

130. GASPAR C., 1966. Les fourmis et l'agriculture (Hymenoptera Formicidae). Ann.Gembloux, 72: 235-243.

130A. GEISSMAN T.A., KNAACK W.F.Jr., KNIGHT J.O., 1966. Unedoside, a novel iridoid compound. Tetrahedron Letters, (12): 1245-1249.

GEISSMAN T.A., see 80, Crescitelli F. and coll.

GHENT R., see 112, Eisner T. and coll.
see 113, Eisner T. and coll.

131. GHILIAROV M.S., 1958. Sostanze biologicamente attive prodotte da Insetti. I progressi della biologia contemporanea, 46, 2 (5): 208-216 (in russo).

GHIONE M., see 323, Soldati M. and coll.

GHIRINGHELLI D., see 13B, Bernardi R. and coll.
see 45, Cardani C. and coll.
see 46, Cardani C. and coll.
see 47, Cardani C. and coll.
see 48, Cardani C. and coll.
see 49, Cardani C. and coll.

131A. GIBSON T.W., 1964. I. The synthesis of (-)-iridomyrmecin and related iridolactones. II. The chemistry of camphene sultone. Dissert.Abstr., 24 (12): 4994-4995.

GIBSON T., see 361, Wolinsky J. and coll.

132. GILBY A.R., WATERHOUSE D.F., 1965. The composition of the scent of the green vegetable bug, Nezara viridula. Proc.R.Soc., B, 162: 105-120.

GILBY A.R., see 135, Gordon H.T. and coll.
see 348, Waterhouse D.F. and coll.

133. GILMOUR D., 1961. The biochemistry of insects. Academic Press, London: 1-343.

134. GILMOUR D., 1965. The metabolism of insects. Oliver & Boyd, Edinburgh: 1-195.

GIOVANNOZZI-SERMANNI G., see 49E, Casinovi G.C. and coll.

GONZALES J.D., see 321B, Slotta K.H. and coll.

135. GORDON H.T., WATERHOUSE D.F., GILBY A.R., 1963. Incorporation of ^{14}C-acetate into scent constituents by the green vegetable bug. Nature, 197 (4869): 818.

GORDON R.M., see 81, Crewe W. and coll.

136. GORNITZ K., 1937. Cantaridin als Gift und Anlockungsmittel für Insekten. Arb.Phys.Angew.Ent. Berlin-Dahlem, 4 (2): 116.

137. GRANDI G., 1951. Introduzione allo studio dell'entomologia. Ed.Agricole, Bologna, 2 vol.: 1-950, 1-1332.

138. GRANDI G., 1966. Istituzioni di entomologia generale. Ed. Calderini, Bologna: 1-655.

GRANDOLINI G., see 49A, Casinovi G.C. and coll.

GRASSO A., see 126, Frontali N. and coll.
see 127, Frontali N. and coll.

GRIMSHAW J., see 13A, Bently T.W. and coll.
see 15A, Birch A.J. and coll.

139. GRÜNANGER P., QUILICO A., PAVAN M., 1960. Sul secreto odoroso del Formicide Myrmicaria natalensis Fred. Acc.Naz.Lincei, 28 (3): 293-300.

GRÜNANGER P., see 270, Quilico A. and coll.
see 270A, Quilico A. and coll.

139A. GRUVEL J., 1957. Les Coléoptères vésicants. R. Foulon, Paris: 1-63.

GUISO M., see 287A, Scarpati M.L. and coll.

140. GULDENSTEEDEN-EGELING C., 1882. Ueber Bildung von Cyanwasserstoffsäure bei einem Myriapoden. Arch.Ges.Physiol.Pflügers, 28 (11-12): 576-579.

141. HABERMANN E., 1957. Eigenschaften und Anreicherung der Hyaluronidase von Bienengift. Biochem.Ztschr., 329: 1-10.

142. HABERMANN E., 1963. Recent studies on Hymenoptera venoms. pag.53-62 in RAUDONAT H.W., VANECEK J. (Ed.): Recent Advances in the Pharmacology of Toxins. Pergamon Press, London: 1-240, 1965.

143. HABERMANN E., EL KAREMI M.M.A., 1956. Antibody formation by protein components of bee venom. Nature, 178 (4546): 1349.

144. HABERMANN E., NEUMANN W.P., 1957. Reinigung der Phospholipase A des Bienengiftes. Biochem.Ztschr., 328: 465-473.

HABERMANN E., see 208, Neumann W. and coll.
see 209, Neumann W. and coll.
see 210, Neumann W. and coll.
see 211, Neumann W. and coll.

HACKMAN R.H., see 347, Waterhouse D.F. and coll.

HALLER H.L., see 1B, Acree F.Jr. and coll.

144A. HAMASAKI T., 1961. On the antibiotic activity of D(+)-isoiridomyrmecin. Trans.Tottori Soc.Agric.Sc., 13: 84-85.

HANEL P.G., see 97A, Eisenbraun E.J. and coll.

HANSEN H., see 211, Neumann W. and coll.

145. HAPP G.M., MEINWALD J., 1965. Biosynthesis of arthropod secretions. I. Monoterpene synthesis in an ant (<u>Acanthomyops claviger</u>). J. Chem.Soc., 87 (11): 2507-2508.

HAPP G.M., see 189, Meinwald J. and coll.

146. HARMON R.W., POLLARD C.B., 1948. Bibliography of animal venoms. University Florida Press, Gainesville: 1-340.

HATALA R.J., see 184D, McCrone J.D. and coll.

HAVILLAND E.E., see 1B, Acree F.Jr. and coll.

HENDERSON G., see 212A, O'Connor R. and coll.

HENDRICKSON J.B., see 274A, Richards J.H. and coll.

147. HERMANN H.R., BLUM M.S., 1966. The morphology and histology of the Hymenopterous poison apparatus. I. <u>Paraponera clavata</u> (Formicidae). Ann.Ent.Soc.Am., 59 (2): 397-409.

148. HERMANN H.R., BLUM M.S., 1967. The morphology and histology of the hymenopterous poison apparatus. II. <u>Pogonomyrmex badius</u> (Formicidae). Ann.Ent.Soc.Am., 60 (3): 661-668.

149. HERRICK G.W., DETWILER J.D., 1919. Notes on the repugnatorial glands of certain notodontid caterpillars. Ann.Ent.Soc.Am., 12:44-48.

HINTERBERGER H., see 57, Cavill G.W.K. and coll.
see 59, Cavill G.W.K. and coll.
see 59A, Cavill G.W.K. and coll.
see 61, Cavill G.W.K. and coll.
see 62, Cavill G.W.K. and coll.
see 63, Cavill G.W.K. and coll.
see 64, Cavill G.W.K. and coll.

HIROSE Y., see 286B, Sakai T. and coll.

150. HISADA Y., EMURA M., 1965. Cytological effects of chemicals on tumors. XXVIII. Notes on the effect of extract from Paederus fuscipes on a transplantable rat ascites tumor. J.Fac.Sci. Hokkaido Univ., Ser.VI, Zool., 15: 684-692.

150A. HOKARI S., 1963. Poison. Sekkasha, Tokyo: 1-269. (in giapp.).

151. HOLDSTOCK D.J., MATHIAS A.P., SCHACHTER M., 1957. A comparative study of kinin, kallidin, and bradykinin. Brit.J.Pharmacol., 12: 149-158.

152. HOLLANDE A.-CH., 1909. Sur la fonction d'excrétion chez les insectes salicicoles et en particulier sur l'existence des dérivés salicylés. Thèse Faculté Méd.Pharm., Lyon, (1): 1-72.

HOLOUBEK K., see 297, Schildknecht H. and coll.
see 298, Schildknecht H. and coll.
see 299, Schildknecht H. and coll.
see 300, Schildknecht H. and coll.

HORI H., see 166, Koidsumi K. and coll.

HOTZ D., see 300A, Schildknecht H. and coll.
see 300B, Schildknecht H. and coll.

HOWLAND R.B., see 279, Roth L.M. and coll.

HUDEC J., see 76A, Cookson R.C. and coll.
see 76B, Cookson R.C. and coll.

153. HURST J.J., MEINWALD J., EISNER T., 1964. Defense mechanisms of arthropods. XII. Glucose and hydrocarbons in the quinone-containing secretion of Eleodes longicollis. Ann.Ent.Soc.Am., 57 (1): 44-46.

HURST J.J., see 104, Eisner H.E. and coll.
see 105, Eisner T. and coll.
see 106, Eisner T. and coll.
see 107, Eisner T. and coll.
see 187, Meinwald J. and coll.
see 355, Wheeler J.W. and coll.

HYEON S.B., see 286N, Sakan T. and coll.
see 2860, Sakan T. and coll.

153A. INOUYE Y., ARAI T., MIYOSHI Y., YAOI Y., 1963. Über die Struktur des Monotropeins. Tetrahedron Letters, (16): 1031-1038.

154. INOUYE Y., 1955. A new insecticidal compounds of animal origin. Plant Protection, 9: 41 (in giapponese).

155. INOUYE Y., 1956. Chemistry of iridomyrmecin. Plant Protection, 10: 17-18 (in giapponese).

156. INOUYE Y., OHNO M., 1959. Insect poisons. Kagaku no Ryoeki, 13 (9): 648-658 (in giapponese).

ISIDA T., see 321, Sisido K. and coll.
see 320C, Sisido K. and coll.

ISOE S., see 286N, Sakan T. and coll.
see 2860, Sakan T. and coll.

157. JACOBSON M., 1966. Chemical insect attractants and repellents. Ann.Rev.Ent., 11: 403-422.

157A. JAEGER R.H., ROBINSON Sir R., 1959. The conversion of D-isoirido myrmecin into D-iridomyrmecin. Tetrahedron Letters (15): 14-18.

JAEGER R.H., see 72B, Clark K.J. and coll.
see 72C, Clark K.J. and coll.
see 73, Clark K.J. and coll.

JAMES A.N., see 94A, Djerassi C. and coll.

158. JAQUES R., 1955. Vergleichende Fermentuntersuchungen an tierischen Giften (Cholinesterase, "Lecithinase", Hyaluronidase). Helvet. Physiol.Acta, 18: 113-120.

159. JAQUES R., 1954. The hyaluronidase content of animal venoms. pag. 291-293 in BUCKLEY E.E., PORGES S. (Ed.): Venoms. American Association for the Advancement of Science, Washington: 1-467, 1956.

160. JAQUES R., SCHACHTER M., 1954. The presence of histamine, 5-hydroxytriptamine and a potent, slow contracting substance in wasps venom. Brit.J.Pharmacol.Chemoth., 9 (1): 53-58.

JOHNSON B.D., see 324A, Stahnke H.L. and coll.

JOHNSON P.R., see 184E, McElvain S.M. and coll.

JOHNSTONE R.A.W., see 13A, Bentley T.W. and coll.

161. JONES D.A., PARSONS J., ROTHSCHILD M., 1962. Release of hydrocyanic acid from crushed tissues of all stages in the life-cycle of species of the Zygaeninae (Lepidoptera). Nature, 193 (4810): 52-53.

JUNEJA H.R., see 15A, Birch A.J. and coll.

JUNG E.C., see 4, Adrouny G.A. and coll.

KAFATOS F.C., see 105, Eisner T. and coll.

162. KAISER E., 1954. Enzymatic activity of spider venoms. pag.91-93 in BUCKLEY E.E., PORGES S. (Ed.): Venoms. American Association for the Advancement of Science, Washington: 1-467, 1956.

163. KAISER E., MICHL H., 1958. Die Biochemie der tierischen Gifte. Franz Deuticke, Wien: 1-258.

KATSUMURA R., see 286N, Sakan T. and coll.

KAWASHIMA J., see 184, Matsumoto T. and coll.

163A. KEEGAN H.L., MACFARLANE W.V. (Ed.), 1963. Venomous and poisonous animals and noxious plants of the Pacific Region. Pergamon Press, London: 1-456.

KEETON W.T., see 106, Eisner T. and coll.

164. KELLAWAY C.H., 1939. Animal poisons. Ann.Rev.Biochem., 8: 541-556.

165. KIETCZEWSKI B., WISNIEWSKI J., 1963. Arbeitsschutz bei der künstlichen Kolonievermehrung der Ameisen durch einfache Nestaufteilung. Ztschr.Ang.Ent., 52 (3): 298-301.

KLOFT W., see 216, Osman M.F.H. and coll.

KNAACK W.F., see 130A, Geissman T.A. and coll.

KNIGHT J.O., see 130A, Geissman T.A. and coll.

KNIGHT S.A., see 76A, Cookson R.C. and coll.
see 76B, Cookson R.C. and coll.

KOCH K.F., see 190, Meinwald J. and coll.

166. KOIDSUMI K., MAKINO K., HORI H., 1954. Studies on the antimicrobial function of insect lipids. I. Antifungal action of epicuticular lipid. Jap.J.Appl.Zool., 19 (3): 112-116. (in giapp.).

166A. KORTE F., BÜCHEL K.H., ZSCHOCKE A., 1961. Synthese des d, l-Iso iridomyrmecins. Chem.Ber., 94 (8): 1952-1955.

166B. KORTE F., FALBE J., ZSCHOCKE A., 1958. Synthese des D,L-Iridomyrmecins und verwandter Lactone. Ang.Chem., 70 (22-23): 704.

166C. KORTE F., FALBE J., ZSCHOCKE A., 1959. α-Hydroxyalkyliden-Lacton-Umlagerung-IX. Synthese des D,L-Iridomyrmecins und verwandter bicyclischer Lactone. Tetrahedron, 6: 201-216.

166D. KORTE F., SCHREIBER H.J., 1962. Insektizide im Stoffwechsel, IV. Iridomyrmecin- 3-14C. Liebigs Ann.Chem., 656: 145-148.

KORTE F., see 40, Büchel K.H. and coll.
see 119A, Falbe J. and coll.

167. KOSTOWSKI W., 1966. A note on the effects of some psychotropic drugs on the aggressive behaviour in the ant, Formica rufa. J.Pharm.Pharmac., 18: 747-749.

KRÄMER H., see 299, Schildknecht H. and coll.
see 301, Schildknecht H. and coll.

KUROZUMI S., see 320C, Sisido K. and coll.

LABOWS J., see 189, Meinwald J. and coll.

168. LADISCH R.K., McQUE B., 1953. Methods of obtaining quinones from flour beetles. Science, 118 (3064): 324-325.

169. LANG K., LEHNARTZ E., 1960. Handbuch der Physiologisch-und Patho-logisch-chemischen analysis. Springer Verlag, Berlin, 4 (2): 837-844.

170. LATTER O.H., 1892. XVIII. The secretion of potassium hydroxide by Dicranura vinula (imago) and the emergence of the imago from the cocoon. Trans.Ent.Soc.London (4): 287-292.

171. LATTER O.H., 1895. XIV. Further notes on the secretion of potassium hydroxide by Dicranura vinula and similar phenomena in other Lepidoptera. Trans.Ent.Soc.London (B): 399-412.

172. LATTER O.H., 1897. VI. The prothoracic gland of Dicranura vinula, and other notes. Trans.Ent.Soc.London (2): 113-125.

173. LAUDON IN ELBING., 1891. XIII. Einige Bemerkungen über die Processionraupen und die Aetiologie der Urticaria endemica. Virch. Arch.Anat., 125: 220-238.

174. LAW J.H., WILSON E.O., McCLOSKEY J.A., 1965. Biochemical polymorphism in ants. Science, 149 (3683): 544-546.

175. LECLERCQ M., 1949. Les pigûres d'insectes venimeux en Belgique. Rev.Méd.Liège, 4 (6): 162-169.

176. LECLERCQ M., FISCHER P., LECONTE J., 1949. Nouvelle propriété des venins d'une guêpe et d'une abeille. Arch.Internat.Physiol., 57 (2): 241-244.

LECONTE J., see 176, Leclercq M. and coll.

LEDERER E., see 10, Barbier M. and coll.

LEHNARTZ E., see 169, Lang K. and coll.

LE QUESNE P.W., see 38A, Briggs L.H. and coll.

176A. LICHTI H., von WARTBURG A., 1964. Zur Konstitution von Harpagosid. Tetrahedron Letters (15): 835-843.

LINDAUER M., see 43, Butenandt A. and coll.

LINZEN B., see 43, Butenandt A. and coll.

LISSITZKY S., see 196, Miranda F. and coll.
see 197, Miranda F. and coll.

LOCKSLEY H.D., see 60, Cavill G.W.K. and coll.
see 65, Cavill G.W.K. and coll.

177. LOCONTI J.D., ROTH L.M., 1953. Composition of the odorous secretion of Tribolium castaneum. Ann.Ent.Soc.Am., 46 (2): 281-289.

178. LOMAN J.C.C., 1887. Freies Jod als Drüsensecret. Tijdschr.Ned. Dierk.Ver., 1: 106-108.

LONG T.E., see 286, Russel F.E. and coll.

MAARSE H., see 92, Devakul V. and coll.

179. MAASS T.A., 1937. Gift-tiere. Tabulae Biologicae. Junk.W.ed., 's Gravenhage, 13: 1-272.

MACFARLANE W.V., see 163A, Keegan H.L. and coll.

MAEDA T., see 286N, Sakan T. and coll.

MAENO S., see 184, Matsumoto T. and coll.

MAHBOOB S., see 33A, Bobbit J.M. and coll.

MAKINO K., see 166, Koidsumi K. and coll.

180. MALOEUF N.S.R., 1938. Secretions from ectodermal glands of Arthropods. Quart.Rev.Biol., 13: 169-195.

MANNING R.E., see 40A, Büchi G. and coll.

181. MANSBRIDGE G.H., 1933. On the biology of some Ceroplatinae and Macrocerinae (Diptera, Mycetophilidae). With an appendix on the chemical nature of the web fluid in larvae of Ceroplatinae (by BUSTON H.W.). Trans.Ent.Soc.London, 81 (1): 75-90; 90-92.

MARCHESINI A., see 334, Trave R. and coll.

181A. MARINI BETTOLO G.B., CASINOVI C.G., DELLE MONACHE F., 1962. Stereochemistry of Skytanthus alkaloids. Sci.Repts.Ist.Super.Sanità, 2: 195-200.

181B. MARINI BETTOLO G.B., CASINOVI C.G., DELLE MONACHE F., 1965. Ricerche nella serie della skitantina. III. Stereochimica degli alcaloidi dello Skytanthus acutus. Ann.Ist.Super.Sanità, 1: 257-262.

MARINI BETTOLO G.B., see 49A, Casinovi C.G.
see 49B, Casinovi C.G.
see 49C, Casinovi C.G.
see 49D, Casinovi C.G.
see 49E, Casinovi C.G.

MARKWARDT F., see 214, Ortel S. and coll.

MARTIN-SMITH M., see 94, Dixon A.F.G. and coll.

182. MASCHWITZ U., 1964. Gefahrenalarmstoffe und gefahrenalarmierung bei sozialen hymenopteren. Ztschr.Vergl.Physiol., 47: 596-655.

183. MASCHWITZ U., 1966. Alarm substances and alarm behavior in social insects. Vitamins and Hormones, 24: 267-290.

MASCHWITZ U., see 296, Schildknecht H. and coll.
see 300B, Schildknecht H. and coll.
see 302, Schildknecht H. and coll.
see 304, Schildknecht H. and coll.
see 305, Schildknecht H. and coll.
see 317, Schildknecht H. and coll.

183A. MATHIAS A.P., SCHACHTER M., 1958. The chromatographic behaviour of wasp venom kinin, kallidin and bradykinin. Brit.J.Pharmacol., 13 (3): 326-329.

MATHIAS A.P., see 151, Holdstock D.J. and coll.

MATHIESON A.McL., see 184B, McConnel J.F. and coll.
see 184C, McConnel J.F. and coll.

184. MATSUMOTO T., TSUTSUI S., YANAGIYA M., YASUDA S., MAENO S., KAWASHIMA J., UETA A., MURAKAMI M., 1964. The partial structure of pederin. Bull.Chem.Soc.Japan, 37 (12): 1892-1893.

184A. MAUGERI S., CANDURA F., 1964. Diffusione e prevenzione delle zoonosi. Atti II Congr.Naz.Med.Rurale, 25-26 aprile: 57-191.

McCLOSKEY J.A., see 174, Law J.H. and coll.

184B. McCONNEL J.F., MATHIESON A.McL., SCHOENBORN B.P., 1962. Conformation of iridomyrmecin and isoiridomyrmecin. Tetrahedron Letters, (10): 445-448.

184C. McCONNEL J.F., MATHIESON A.McL., SCHOENBORN B.P., 1964. The crystal structure of the monoterpene iridomyrmecin at -150°C. Acta Cryst., 17: 472-477.

McCONNEL J.F., see 318B, Schoenborn B.P.and coll.

184D. McCRONE J.D., HATALA R.J., 1966. Isolation and characterization of a lethal component from the venom of Latrodectus mactans mactans. pag.29-34 in RUSSEL F.E., SAUNDERS P.R. (Ed.): Animal toxins. Pergamon Press, London: 1-428, 1967.

184E. McELVAIN S.M., BRIGHT R.D., JOHNSON P.R., 1941. The constituents of the volatile oil of catnip. I. Nepetalic acid, nepetalactone and related compounds. J.Am.Chem.Soc., 63: 1558-1563.

184F. McELVAIN S.M., EISENBRAUN E.J., 1955. The constituents of the volatile oil of catnip. III. The structure of nepetalic acid and related compounds. J.Am.Chem.Soc., 77: 1599-1605.

185. McELVAIN S.M., EISENBRAUN E.J., 1957. The interconversion of nepetalic acid and isoiridomyrmecin (iridolactone). J.Org.Chem., 22: 976-977.

185A. McELVAIN S.M., WALTERS P.M., BRIGHT R.D., 1942. The constituents of the volatile oil of catnip. II. The neutral components. Nepetalic anhydride. J.Am.Chem.Soc., 64: 1828-1831.

McELVAIN S.M., see 10B, Bates R.B. and coll.
see 10C, Bates R.B. and coll.

McHENRY F., see 108, Eisner T. and coll.

186. McINDOO N.E., 1916. The reflex "bleeding" of the coccinellid beetle Epilachna borealis. Ann.Ent.Soc.Am., 9: 201-223.

McKITTRICK F., see 109, Eisner T. and coll.

McQUE B., see 168, Ladisch R.K. and coll.

187. MEINWALD J., CHADHA M.S., HURST J.J., EISNER T., 1962. Defense mechanisms of Arthropods. IX. Anisomorphal, the secretion of a phasmid insect. Tetrahedron Letters, 1: 29-33.

188. MEINWALD Y.C., EISNER T., 1964. Defense mechanisms of arthropods. XIV. Caprylic acid: an accessory component of the secretion of Eleodes longicollis. Ann.Ent.Soc.Am., 57 (4): 513-514.

189. MEINWALD J., HAPP G.M., LABOWS J., EISNER T., 1966. Cyclopentanoid terpene biosynthesis in a phasmid insect and in catmint. Science, 151 (3706): 79-80.

190. MEINWALD J., KOCH K.F., ROGERS J.E.Jr., EISNER T., 1966. Biosynthesis of Arthropod secretions. III. Synthesis of simple p-benzoquinones in a beetle (Eleodes longicollis). J.Am.Chem.Soc., 88: 1590-1592.

191. MEINWALD Y.C., MEINWALD J., EISNER T., 1966. 1,2-Dialkyl-4(3H)-Quinazolinones in the defensive secretion of a millipede (Glomeris marginata). Science, 154 (3748): 390-391.

192. MEINWALD J., ROGERS J.E.Jr., EISNER T., 1964. Quinone biosynthesis in Arthropods. Int.Symp.Chem.Nat.Products, Kyoto: 138-139.

MEINWALD J., see 70, Chadha M.S. and coll.
see 71, Chadha M.S. and coll.
see 72, Chadha M.S. and coll.
see 105, Eisner T. and coll.
see 106, Eisner T. and coll.
see 107, Eisner T. and coll.

see 110, Eisner T. and coll.
see 111, Eisner T. and coll.
see 112, Eisner T. and coll.
see 113, Eisner T. and coll.
see 114, Eisner T. and coll.
see 145, Happ G.M. and coll.
see 153, Hurst J.J. and coll.
see 191, Meinwald Y.C. and coll.
see 198, Monro A. and coll.
see 355, Wheeler J.W. and coll.

193. MELANDER A.L., BRUENS C.T., 1906. The chemical nature of some insect secretions. Bull.Wisconsin Nat.Hist.Soc., 4 (1-2):22-36.

MERLINI L., see 337, Trave R. and coll.
see 338, Trave R. and coll.

194. MICHL H., 1957. Über das Vorkommen von Pipecolinsäure in tierischen Giften. Monatsh.Chem., 88 (4): 701-702.

MICHL H., see 163, Kaiser E. and coll.

MILLER-BENSHAUL D., see 212, Nitzan (Tischler) M. and coll.

194A. MINATO H., 1961. Studies on Sesquiterpenoids. II. Absolute configuration of Guaiol. (2). Absolute configuration of the methyl group at C-10 in Guaiol, and of Nepetalinic acids and iridolactones. Chemical & Pharmaceutical Bull., 9 (8): 625-631.

195. MIRANDA F., 1964. Purification et caracterisation des neurotoxines des venins de scorpions (Scorpamines). Application des méthods utilisées à l'isolement d'autres neurotoxines de pH basique (neurotoxines des venins de serpents). Thèses Fac. Sci.Univ.d'Aix-Marseille, N° d'ordre 124: 1-187.

196. MIRANDA F., ROCHAT H., LISSITZKY S., 1960. Sur la neurotoxine du venin des scorpions. I. Purification a partir du venin de deux espèces de scorpions nord-africains. Bull.Soc.Chim.Biol. 42 (4): 379-391.

197. MIRANDA F., ROCHAT H., LISSITZKY S., 1961. Sur la neurotoxine du venin des scorpions. II. Utilisation de l'électrophorèse sur papier pour l'orientation et le contrôle de la purification. Bull.Soc.Chim.Biol., 43 (7-8): 945-952.

MIRONOV A., see 94B, Dolejs L. and coll.
see 94C, Dolejs L. and coll.

MIYOSHI Y., see 153A, Inouye H. and coll.

MONDELLI R., see 45, Cardani C. and coll.
see 46, Cardani C. and coll.
see 47, Cardani C. and coll.

198. MONRO A., CHADHA M., MEINWALD J., EISNER T., 1962. Defense mechanisms of arthropods. VI. Para-benzoquinones in the secretion of five species of millipedes. Ann.Ent.Soc.Am., 55 (2): 261-262.

MONRO A., see 72, Chadha M.S. and coll.
see 112, Eisner T. and coll.
see 113, Eisner T. and coll.

MONROE R.S., see 30, Blum M.S. and coll.

199. MONTEIRO H.J., 1961. Constituents of the secretion of Orthomorpha coarctata Schibart. Anais Ass.Brasil.Quim., 20: 29-31.

200. MOORE B.P., 1964. Volatile terpenes from Nasutitermes soldiers (Isoptera, Termitidae). J.Insect Physiol., 10: 371-375.

201. MOREAU L., 1932. La secrétion du Blaps gigas. Bull.Soc.Linn.Provence, 5: 34-37.

202. MURAI F., 1960. Chemical studies of effective components contained in matatabi (Actinidia polygama Miq.). II. Chemical structure of matatabi lactone. Nippon Kagaku Zasshi, 81 (8): 1324-1326.

MURAI F., see 286C, Sakan T. and coll.
see 286D, Sakan T. and coll.
see 286E, Sakan T. and coll.
see 286F, Sakan T. and coll.
see 286G, Sakan T. and coll.
see 286I, Sakan T. and coll.
see 286L, Sakan T. and coll.

MURAKAMI M., see 184, Matsumoto T. and coll.

NAKANO T., see 94A, Djerassi C. and coll.

203. NASCIMBENE A., PAVAN M., 1948. Studi sugli antibiotici di origine animale. II. Ricerche su alcune Formicidae ad acido formico. Boll.Soc.Med.Chir.Pavia, 62 (1-2): 199-202.

204. NASCIMBENE A., PAVAN M., 1948. Studi sugli antibiotici di origine animale. III. Sul significato dell'acido formico in estratti acquosi ad azione antibatterica di alcuni Formicidae. Boll.Soc.Med.Chir.Pavia, 62 (1-2): 203-206.

205. NASCIMBENE A., PAVAN M., 1950. Studi sugli antibiotici di origine animale. VIII. Ricerche su varie specie di Formicidae produttrici di acido formico. Bull.Soc.Med.Chir.Pavia, 64 (3-4): 369-384.

NASCIMBENE A., see 254, Pavan M. and coll.
see 255, Pavan M. and coll.
see 256, Pavan M. and coll.
see 257, Pavan M. and coll.

see 258, Pavan M. and coll.
see 259, Pavan M. and coll.

NELSON D., see 212A, O'Connor R. and coll.
see 286N, Sakan T. and coll.

NENCINI G., see 50, Casnati G. and coll.

206. NERI L., BETTINI S., FRANK M., 1965. The effect of Latrodectus mactans tredecimguttatus venom on the endogenous activity of Periplaneta americana nerve cord. Toxicon, 3: 95-99.

207. NEUMANN W., 1954. Neuere Untersuchungen über die Giftstoffe von Bienen und Schlangen. Naturwiss., 41 (13): 322-326.

208. NEUMANN W., HABERMANN E., 1954. Beiträge zur Charakterisierung der Wirkstoffe des Bienengiftes. Arch.Exper.Path.Pharmakol., 222: 367-387.

209. NEUMANN W., HABERMANN E., 1954. Paper electrophoresis separation of pharmacologically and biochemically active components of bee and snake venoms. pag. 171-174 in: BUCKLEY E.E., PORGES N. (Ed.): Venoms. American Association for the Advancement of Science, Washington: 1-467, 1956.

210. NEUMANN W., HABERMANN E., AMEND G., 1952. Zur papierelektrophoretischen Fraktionierung tierischer Gifte. Naturwiss., 39 (12): 286-287.

211. NEUMANN W., HABERMANN E., HANSEN H., 1953. Differenzierung von zwei hämolyzierenden Faktoren im Bienengift. Arch.Exper.Path. Pharmakol., 217: 130-143.

NEUMANN W.P., see 123, Fischer F.G. and coll.
see 144, Habermann E. and coll.

NGUYEN-DANG TAM, see 44, Butenandt A. and coll.

NIEGISCH W.D., see 280, Roth L.M. and coll.

NISHIMURA K., see 286B, Sakai T. and coll.

212. NITZAN (TISCHLER) M., MILLER-BENSHAUL D., SHULOV A., 1963. Studies on the dialyzable fraction of the venom of the yellow scorpion, Leiuris quinquestriatus H. et E. Israel J.Exp.Med.,11 (2): 54-63.

NOVAK A.F., see 26, Blum M.S. and coll.
see 28A, Blum M.S. and coll.

212A. O'CONNOR R., HENDERSON G., NELSON D., PARKER R., PECK M.L., 1966. The venom of the honeybee (Apis mellifera). I. General character. pag. 17-22 in: RUSSEL F.E., SAUNDERS P.R. (Ed.): Animal toxins. Pergamon Press, London: 1-428, 1967.

OHNO M., see 156, Inouye Y. and coll.

ONO T., see 2860, Sakan T. and coll.

213. O'ROURKE F.J., 1950. Formicid acid production among the Formicidae. Ann.Ent.Soc., 43 (3): 437-443.

214. ORTEL S., MARKWARDT F., 1955. Untersuchungen über die antibakteriellen Eigenschaften des Bienengiftes. Die Pharmazie, 10 (12): 743-746.

OSIECKI J., see 97A, Eisenbraun E.J. and coll.

215. OSMAN M.F.H., BRANDER J., 1961. Weitere Beiträge zur Kenntnis der chemischen Zusammensetzung des Giftes von Ameisen aus der Gattung Formica. Z.Naturf., 16b: 749-753.

216. OSMAN M.F.H., KLOFT W., 1961. Untersuchungen zur insektiziden Wirkung der verschiedenen Bestandteile des Giftes der Kleinen Roten Waldameise Formica polyctena Foerst. Insectes Sociaux, 8 (4): 383-395.

PAASONEN M., see 95, Eckert D. and coll.

217. PACKARD A.S., 1895. The eversible repugnatorial scent glands of insects. J.New York Ent.Soc., 3: 110-127.

218. PALLARES E.S., 1946. Note on the poison produced by the Polydesmus (Fontaria) vicinus Lin. Arch.Biochem., 9: 105-108.

219. PALM N.B., 1946. Structure and physiology of the stink glands in Tribolium destructor Uytt. (Col.).Opuscola Entomol., 119-132.

PANIZZI L., see 287A, Scarpati M.L. and coll.

220. PARK R.J., SUTHERLAND M.D., 1962. Volatile constituents of the bronze orange bug, Rhoecocoris sulciventris. Austr.J.Chem., 15 (1): 172-174.

PARKER R., see 212A, O'Connor R. and coll.

221. PARSONS J.A., 1963. Heart poison from a toxic grasshoper. Biochem. Pharmacol., 12: 126-127.

222. PARSONS J.A., 1965. A digitalis-like toxin in the monarch butterfly, Danaus plexippus L. J.Physiol., 178: 290-304.

PARSONS J.A., see 118, v.Euw and coll.
see 161, Jones D.A. and coll.
see 282, Rothschild M. and coll.
see 283, Rothschild M. and coll.

223. PAVAN M., 1948. Iridomirmecina, nuovo antibiotico estratto dalla Formica argentina (Iridomyrmex pruinosus humilis Mayr). Atti I° Congr.Naz.Antibiotici, Milano: 247-251.

224. PAVAN M., 1949. Ricerche sugli antibiotici di origine animale. Nota riassuntiva. Ricerca Scient., 19 (9): 1011-1017.

225. PAVAN M., 1948. Iridomirmecine, antibiotique nouveau extrait de la Fourmi argentine. XIII Congr.Int.Zool., Paris: 500-501.

226. PAVAN M., 1948. Recherches sur les antibiotiques d'origine animale. XIII Congr.Int.Zool., Paris: 501-504.

227. PAVAN M. (1948), 1950. Iridomyrmecin, an antibiotic substance extracted from the argentine ant (*Iridomyrmex pruinosus humilis* Mayr). VIII Int.Congr.Ent., Stockolm: 863-865.

228. PAVAN M. (1948), 1950. Summary of original research on antibiotic substances of insects. VIII Int.Congr.Ent.Stockolm: 866-869.

229. PAVAN M., 1950. Potere insetticida della "iridomirmecina" e significato della sostanza nella biologia di *Iridomyrmex humilis* Mayr (Formica argentina). Ricerca Scient., 20 (12): 1853-1855.

230. PAVAN M., 1951. Sull'attività insetticida della iridomirmecina. Mem.Soc.Ent.It., 30: 107-132.

231. PAVAN M., 1952. Die antibiotica tierischer Herkunft. Ztschr.Hygiene, 134: 136-161.

232. PAVAN M., 1952. "Iridomyrmecin" as insecticide. IX Int.Congr.Ent., 1: 321-327.

233. PAVAN M., 1952. Primo contributo sperimentale allo studio farmacologico della iridomirmecina. Arch.Int.Pharmacodyn.Thér., 89 (2): 223-228.

234. PAVAN M., 1952. Sugli antibiotici di origine animale. Boll.Ist. Sieroter.Milanese, 31 (3-4): 195-208; (5-6): 232-245.

235. PAVAN M., 1953. Studi sugli antibiotici di origine animale. I. Sul principio attivo della larva di *Melasoma populi* L. (*Col. Chrysomelidae*). Arch.Zool.It., 38: 157-184.

236. PAVAN M., 1955. Gli insetti come fonte di prodotti biologicamente attivi. Chim.Ind., Milano, 37 (9): 714-724.

237. PAVAN M., 1955. Sull'attività fitoinibente della iridomirmecina su *Lupinus albus*. Boll.Soc.It.Biol.Sper., 31 (7-8): 967-969.

238. PAVAN M., 1955. Sulla estrazione e cristallizzazione della iridomirmecina. Chim.Ind., Milano, 37 (8): 625-627.

239. PAVAN M., 1955. Studi sui *Formicidae*. I. Contributo alla conoscenza degli organi gastrali dei *Dolichoderinae*. Natura, 46: 135-145.

240. PAVAN M., 1956. Studi sui Formicidae. II. Sull'origine, significato biologico e isolamento della dendrolasina. Ricerca Scientifica, 26 (1): 144-150.

241. PAVAN M., 1956. Formiche e processionarie in foresta. Informatore fitopatologico, 6 (4): 50-52.

242. PAVAN M., 1956. La lotta biologica con Formica rufa L. contro gli insetti dannosi alle foreste. Min.Agric.For., Roma, Collana Verde 3: 1-20.

243. PAVAN M., 1957. La formica argentina e l'iridomirmecina. Illustrazione Scientifica, 9 (86): 3-9.

244. PAVAN M., 1957. Su un recente lavoro sui Coleotteri vescicanti. Boll.Soc.Ent.It., 87 (7-8): 131-133.

245. PAVAN M., 1958. Significato chimico e biologico di alcuni veleni di insetti. Ed.Tipografia Artigianelli, Pavia: 1-75.

246. PAVAN M. (1958), 1959. Biochemical aspects of insect poisons. IV Int.Congr.Bioch., XII: Bioch.of Insects, Pergamon Press, London: 15-36.

247. PAVAN M., 1959. La dendrolasina. Not.For.Mont. (64-65): 1737-1740, 1782.

248. PAVAN M., 1960. Estrazione e purificazione di alcuni componenti delle secrezioni difensive degli Artropodi. XI Int.Congr. Entom., Wien, Verh.Bd.III: 276-283.

249. PAVAN M., 1961. Données chimiques et biologiques sur les secretions des Formicidae et Apidae. Atti IV Congr. U.I.E.I.S., 12: 19-37.

250. PAVAN M., 1961. Sviluppi delle ricerche sulle secrezioni di insetti. Atti Accad.Naz.It.Ent., Rend., 8: 228-242.

251. PAVAN M., 1963. Ricerche biologiche e mediche su pederina e su estratti purificati di Paederus fuscipes Curt. (Coleoptera Staphylinidae). Tip.Ponzio, Pavia: 1-93.

252. PAVAN M., BAGGINI A., 1955. Ricerche sull'attività fitoinibente dell'iridomirmecina su Lupinus albus. Boll.Zool., 22 (2): 393-404.

253. PAVAN M., BO G., 1953. Pederin, toxic principle obtained in the crystalline state from the beetle Paederus fuscipes Curt. Physiol.Comp. Oecol., 3 (2-3): 307-312.

254. PAVAN M., NASCIMBENE A., 1948. Studi sugli antibiotici di origine animale. I. Su un principio antibiotico di Iridomyrmex pruinosus humilis Mayr. Boll.Soc.Med.Chir.Pavia, 62 (1-2): 193-197.

255. PAVAN M., NASCIMBENE A., 1948. Studi sugli antibiotici di origine animale. IV. Sulla presenza di sostanze antibiotiche nella testa di Dendrolasius fuliginosus Latr. e Lasius bicornis affinis Sch. Boll.Soc.Med.Chir.Pavia, 62 (1-2): 207-210.

256. PAVAN M., NASCIMBENE A., 1948. Studi sugli antibiotici di origine animale. VI. Riassunto dello studio di 40 specie animali, 17 delle quali con risultati positivi. Boll.Soc.Med.Chir.Pavia, 62 (1-2): 229-234.

257. PAVAN M., NASCIMBENE A., 1948. Studi sugli antibiotici di origine animale. VII Ricerche su Iridomyrmex pruinosus humilis Mayr. (Hymen. Formicidae). Igiene Sanità Pubblica, 4 (3-4): 129-141.

258. PAVAN M., NASCIMBENE A., 1948. Ricerche sugli antibiotici di origine animale. X. Nuovi risultati sulla iridomirmecina. Boll.Soc. Med.Chir.Pavia, 62 (1-2):295-298.

259. PAVAN M., NASCIMBENE A., 1949. Studi sugli antibiotici di origine animale. IX. Sui rapporti fra estratti di Formicidae, acido formico e alcuni formiati. Atti Soc.It.Sc.Nat., 88 (3-4): 136-141.

260. PAVAN M., RONCHETTI G., 1955. Studi sulla morfologia esterna e anatomia interna dell'operaia di Iridomyrmex humilis Mayr e ricerche chimiche e biologiche sulla iridomirmecina. Atti Soc. It.Sc.Nat., 94 (3-4): 379-477.

261. PAVAN M., TRAVE R., 1958. Etudes sur les Formicidae. IV. Sur le venin du Dolichodéride Tapinoma nigerrimum Nyl. Insectes Soc., 5 (3): 299-308.

262. PAVAN M., VALCURONE M.L., 1955. Ricerche sull'antagonismo dell'iridomirmecina verso l'attività oncogena della colchicina e del gammaesano su Lupinus albus. Boll.Zool., 22 (2): 405-419.

PAVAN M., see 4A, Baggini A. and coll.
see 5, Baggini A. and coll.
see 7, Barbetta M. and coll.
see 13B, Bernardi R. and coll.
see 37, Brangi G.P. and coll.
see 38, Brangi G.P. and coll.
see 45, Cardani C. and coll.
see 50, Casnati G. and coll.
see 51, Casnati G. and coll.
see 52, Casnati G. and coll.
see 53, Casnati G. and coll.
see 54, Castellani A.A. and coll.
see 139, Grünanger P. and coll.
see 203, Nascimbene A. and coll.
see 204, Nascimbene A. and coll.

see 205, Nascimbene A. and coll.
see 267, Piozzi F. and coll.
see 270, Quilico A. and coll.
see 271, Quilico A. and coll.
see 272, Quilico A. and coll.
see 273, Quilico A. and coll.
see 334, Trave R. and coll.
see 335, Trave R. and coll.
see 336, Trave R. and coll.
see 338, Trave R. and coll.
see 339, Trave R. and coll.
see 359, Wilson E.O. and coll.

263. PAWLOWSKY E.N., 1927. Gifftiere und ihre giftigkeit. Gustav Fischer, Jena: 1-516.

PAYNE R., see 109, Eisner T. and coll.

PECK M.L., see 212A, O'Connor R. and coll.

von PHILIPSBORN W., see 33A, Bobbit J.M. and coll.

PHISALIX C., see 13, Behal A. and coll.

264. PERRY W.J., 1951. Bactericidal and insecticidal activity of iridomirmecina. American Embassy, Off.Nav.Res., London, Technical Report: 1-7.

265. PHISALIX M., 1922. Animaux venimeux et venins. Masson & C., Paris: 1-656.

PICARELLI Z.P., see 340, Valle J.R. and coll.

266. PINDER A.R., STADDON B.W., 1965. Trans-4-oxohex-2-enal in the odoriferous secretion of Sigara falleni (Fieb.) (Hemiptera-Heteroptera). Nature, 205 (4966): 106-107.

267. PIOZZI F., DUBINI M., PAVAN M., 1959. Ricerche chimiche sui Formicidi. Boll.Soc.Ent.It., 89 (3-4): 48-50.

PIOZZI F., see 270A, Quilico A. and coll.
see 271, Quilico A. and coll.
see 272, Quilico A. and coll.
see 273, Quilico A. and coll.

POLLARD C.B., see 146, Harmon R.W. and coll.

268. PORTA A., 1902. Ricerche sull'apparato di secrezione e sul secreto della Coccinella 7-punctata L. Anat.Anz., 22 (9-10): 177-193.

PORTOCARRERO C.A., see 25, Blum M.S. and coll.

PRADO J.L., see 340, Valle J.R. and coll.

269. QUILICO A., 1962. Alcune nuove prospettive nella lotta contro gli insetti nocivi. Atti del Convegno sul tema: Equilibri biologici e insetticidi. Acc.Naz.Lincei, Roma, 359 (58): 57-71.

270. QUILICO A., GRÜNANGER P., PAVAN M., 1960. Sul componente odoroso del veleno del formicide Myrmicaria natalensis Fred. XI Int. Kongr.Entom., Wien, Verh.B.III: 66-68.

270A. QUILICO A., GRÜNANGER P., PIOZZI F., 1957. Synthesis of tetrahydro and perhydro-dendrolasin. Tetrahedron, 1: 186-194.

271. QUILICO A., PIOZZI F., PAVAN M., 1956. Sulla dendrolasina. Ricerca Scient., 26 (1): 177-180.

272. QUILICO A., PIOZZI F., PAVAN M., 1957. Ricerche chimiche sui Formicidae; sostanze prodotte dal Lasius (Chthonolasius) umbratus Nyl. Rend.Ist.Lomb.Sc.Lett., Cl.Sc., 91: 271-279.

273. QUILICO A., PIOZZI F., PAVAN M., 1957. The structure of dendrolasin. Tetrahedron, 1: 177-185.

QUILICO A., see 45, Cardani C. and coll.
see 46, Cardani C. and coll.
see 47, Cardani C. and coll.
see 48, Cardani C. and coll.
see 49, Cardani C. and coll.
see 50, Casnati G. and coll.
see 139, Grünanger P. and coll.

RAMSTAD E., see 320A, Sheth K. and coll.

273A. REGNIER F.E., EISENBRAUN E.J., WALLER G.R., 1967. Nepetalactone and epinepetalactone from Nepeta cataria L. Phytochem., 6: 1271-1280.

REICHSTEIN T., see 118, v.Euw and coll.
see 283, Rothschild M. and coll.

274. REMOLD H., 1963. Scent-glands of land-bugs, their physiology and biological function. Nature, 198 (4882): 764-768.

RICCA A., see 4A, Baggini A. and coll.
see 50, Casnati G. and coll.
see 51, Casnati G. and coll.
see 52, Casnati G. and coll.
see 53, Casnati G. and coll.

274A. RICHARDS J.H., HENDRICKSON J.B., 1964. The biosynthesis of steroids, terpenes, and acetogenins. Ed.Benjamin, Inc., New York.

ROBERTS J.E.Jr., see 26, Blum M.S. and coll.

ROBERTSON P.L., see 66, Cavill G.W.K. and coll.
see 67, Cavill G.W.K. and coll.

269A. QUILICO A., CARDANI C., GHIRINGHELLI D., PAVAN M., 1961. Pederina e pseudopederina. La Chimica e L'ind., 43: 1434-1436.

ROBINSON Sir R., see 72B, Clark K.J. and coll.
see 72C, Clark K.J. and coll.
see 73, Clark K.J. and coll.
see 123A, Fray G.I. and coll.
see 157A, Jaeger R.H. and coll.

274B. ROBIQUET M., 1812. Expériences sur les Cantharides. Ann.Chim. (Paris), 76: 302.

275. ROCCI U., 1915. Di una sostanza velenosa contenuta nelle Zigene. Atti Soc.Ligustica Sc.Nat.Geog., 26 (3): 71-107.

ROCHAT H., see 196, Miranda F. and coll.
see 197, Miranda F. and coll.

ROGERS J.E.Jr., see 190, Meinwald J. and coll.
see 192, Meinwald J. and coll.

275A. RONCHETTI G., 1958. Ricerche sull'attività insetticida dell'iridomirmecina. Mem.Soc.Ent.It., 37: 55-86.

RONCHETTI G., see 260, Pavan M. and coll.

276. ROSSI G.L., 1903. Le glandole odorifere dell'Iulus communis. Ztschr. Wiss.Zool., 74 (1): 63-80.

277. ROTH L.M., 1961. A study of the odoriferous glands of Scaptocoris divergens (Hemiptera: Cydnidae). Ann.Ent.Soc.Am., 54 (6): 900-911.

278. ROTH L.M., EISNER T., 1962. Chemical defenses of arthropods. Ann. Rev.Ent., 7: 107-136.

279. ROTH L.M., HOWLAND R.B., 1941. Studies on the gaseous secretion of Tribolium confusum Duval. I. Abnormalities produced by Tribolium confusum Duval by exponsure to a secretion given off by the adults. Ann.Ent.Soc.Am., 34: 151-175.

280. ROTH L.M., NIEGISCH W.D., STAHL W.H., 1956. Occurrence of 2-hexenal in the cockroach Eurycotis floridana. Science, 123 (3199): 670-671.

ROTH L.M., see 83, Dateo G.P. and coll.
see 83A, Dateo G.P. and coll.
see 177, Loconti J.D. and coll.
see 325, Stay B. and coll.

ROTH S.C., see 321, Slotta K.H. and coll.

280A. Lord ROTHSCHILD, 1965. A classification of Living animals. Longmans, London, sec.Ed.: 1-134.

281. ROTHSCHILD M., 1961. Defensive odours and Müllerian mimicry among insects. Trans.Roy.Ent.Soc.Lond., 113 (5): 101-121.

282. ROTHSCHILD M., PARSONS J., 1962. Pharmacology of the poison gland of the locust Poekilocerus bufonius Klug. Proc.R.Ent.Soc.London, C, 27 (6): 21-22.

283. ROTHSCHILD M., REICHSTEIN T., PARSONS J., APLIN R., 1966. Poisons in aposematic insects. The Royal Society. Conversation 12 May (cyclost.).

ROTHSCHILD M., see 16, Bisset G.W. and coll.
see 17, Bisset G.W. and coll.
see 118, v. Euw J. and coll.
see 124, Frazer J.F.D. and coll.
see 161, Jones D.A. and coll.

284. RUSSEL F.E., 1961. Injuries by venomous animals in the United States. J.Am.Med.Ass., 177: 903-907.

285. RUSSEL F.E., 1965. Venomous animals and their toxins. Smithsonian Inst. (4631): 477-487.

285A. RUSSEL F.E., SAUNDERS P.R. (Ed.), 1967. Animal toxins. Pergamon Press, London: 1-428.

286. RUSSEL F.E., LONG T.E., 1965. Effects of venoms on neuromuscular transmissions. pag. 101-116 in VIETS H.R. (Ed.): Myasthenia Gravis. C.C.Thomas, Springfield.

286A. SAID E.E., 1960. Enzymological study of the venom of Polistes omissa Weyr. Bull.Soc.Ent.Egypte, 44: 167-170.

286B. SAKAI T., NISHIMURA K., HIROSE Y., 1963. The constituent of the volatile oil from the wood of Torreya nucifera. Tetrahedron Letters, 18: 1171-1173.

286C. SAKAN T., FUJINO A., MURAI F., 1960. Chemical studies of effective components contained in Matatabi (Actinidia polygama Miq.). I. Separation of active componènts - Matatabi-lactone and Actinidine. Nippon Kagaku Zasshi, 81 (8): 1320-1324.

286D. SAKAN T., FUJINO A., MURAI F., 1960. Chemical studies of effective components contained in Matatabi (Actinidia polygama Miq.). IV. Induction (induced reaction) of Actinidine from Matatabi lactone. Nippon Kagaku Zasshi, 81 (9): 1444-1445.

286E. SAKAN T., FUJINO A., MURAI F., BUTSUGAN Y., 1960. Chemical studies of effective components contained in Matatabi (Actinidia polygama Miq.). VI. Stereochemical structure of Actinidine. Nippon Kagaku Zasshi, 81 (9): 1447-1450.

286F. SAKAN T., FUJINO A., MURAI F., BUTSUGAN Y., SUZUI A., 1959. On the structure of actinidine and matatabilactone, the effective components of Actinidia polygama. Bull.Chem.Soc.Japan, 32 (4): 315-316.

286G. SAKAN T., FUJINO A., MURAI F., SUZUI A., BUTSUGAN Y., 1959. The synthesis of actinidine. Bull.Chem.Soc.Japan, 32 (10): 1157.

286H. SAKAN T., FUJINO A., MURAI F., SUZUI A., BUTSUGAN Y., 1959. The structure of matatabilactone. Bull.Chem.Soc.Japan, 32 (10): 1154-1155.

286I. SAKAN T., FUJINO A., MURAI F., SUZUI A., BUTSUGAN Y., 1960. The synthesis of dl-Nepetalactone. Bull.Chem.Soc.Japan, 33 (12): 1737-1738,

286L. SAKAN T., FUJINO A., MURAI F., SUZUI A., BUTSUGAN Y., TERASHIMA Y., 1960. The absolute structure of Actinidine. Bull.Chem.Soc. Japan, 33 (5): 712.

286M. SAKAN T., FUJINO A., SUZUI A., BUTSUGAN Y., 1960. Chemical studies of effective components contained in Matatabi (Actinidia polygama Miq.). V. Synthesis and optical property of DL-Actinidine. Nippon Kagaku Zasshi, 81 (9): 1445-1447.

286N. SAKAN T., ISOE S., HYEON S.B., KATSUMURA R., MAEDA T., WOLINSKY J., DICKERSON D., SLABAUGH M., NELSON D., 1965. The exact nature of matatabilactone and the terpenes of Nepeta cataria. Tetrahedron Letters, 46: 4097-4102.

286O. SAKAN T., ISOE S., HYEON S.B., ONO T., TAKAGI I., 1964. Iridodiols, the effective components of Actinidia polygama for Chrysopidae. Bull.Chem.Soc.Japan, 37 (12): 1888-1889.

SALPETER M.M., see 108, Eisner T.and coll.

SALVATORI T., see 50, Casnati G. and coll.

287. SAUERLÄNDER S., 1961. Das Gift von Formica polyctena Först. als ein möglicher Schutzmechanismus dieses Insektes gegen Microorganismen. Naturwiss., 48 (19): 629-630.

SAUNDERS P.R., see 285A, Russel F.E. and coll.

287A. SCARPATI M.L., GUISO M., PANIZZI L., 1965. Iridoids. I. Harpagide acetate from Melittis melissophyllum. Tetrahedron Letters, (39): 3439-3443.

287B. SCHACHTER M., 1964. Kinins-a group of active peptides. Ann.Rev. Pharmacol., 4: 281-292.

288. SCHACHTER M., THAIN E.M., 1954. Chemical and pharmacological properties of the potent, slow contracting substance (kinin) in Wasp venom. Brit.J.Pharmacol., 9 (5): 352-359.

SCHACHTER M., see 16, Bisset G.W. and coll.
see 17, Bisset G.W. and coll.
see 151, Holdstock D.J. and coll.
see 160, Jaques R. and coll.
see 183A, Mathias A.P. and coll.

289. SCHALL C., 1892. Undecan als Hauptbestandtheil des flüchtigen Amei senöls. Ber.Deutschen Chem.Ges., 25: 1489-1490.

290. SCHILDKNECHT H., 1957. Zur Chemie des Bombardierkäfers. Angew.Chem. 69 (1-2): 62.

291. SCHILDKNECHT H., 1959. Über das flüchtige Sekret von gemeinen Meh lkäfer. II. Mitteilung über Insekten-Abwehrstoffe. Angew. Chem., 71 (15-16): 524.

292. SCHILDKNECHT H., 1960. Untersuchungsmethoden zur Aufklärung chemi scher Abwehrstoffe von Insekten. IX. Mitteilung über Insekten abwerstoffe. XI Int.Kongr.Ent., Wien, Verh.B.III: 269-275.

293. SCHILDKNECHT H., 1961. Über Insekten- und Pflanzenabwehrstoffe, ih re Isolierung und Aufklärung. Angew.Chem., 73 (17-18): 629.

294. SCHILDKNECHT H., 1962. Abwerhrstoffe von Insekten, ihre Isolierung und Aufklärung. Angew.Chem., 74: 473.

295. SCHILDKNECHT H., 1965. Beetle gives human hormone. Chem.Eng.News, april 18: 27-28.

295A. SCHILDKNECHT H., 1966. Vertebrate hormones as defense substances in Dytiscides. Mem.Inst.Butantan Simpo.Internac., 33 (1): 121-133.

296. SCHILDKNECHT H., BIRRINGER H., MASCHWITZ U., 1967. Testosteron als Abwehrstoff des Schlammschwimmers Ilybius. Angew.Chem., 79 (12): 579-580.

297. SCHILDKNECHT H., HOLOUBEK K., 1959. Über einen Inhaltsstoff der Wehrdrüsen des Gelbrandkäfers. III. Mitteilung über Insekten-abwehrstoffe. Angew.Chem., 71 (15-16): 524-525.

298. SCHILDKNECHT H., HOLOUBEK K., 1961. Die Bombardierkäfer und ihre Explosionschemie. V. Mitteilung über Insekten-Abwehrstoffe. Angew.Chem., 73 (1): 1-7.

299. SCHILDKNECHT H., HOLOUBEK K., WEIS K.H., KRÄMER H., 1964. Defensi- ve substances of the arthropods, their isolation and identifi cation. Angew.Chem.Int.Edit., 3 (2): 73-82.

300. SCHILDKNECHT H., HOLOUBEK K., WOLKENSTÖRFER M., 1962. Über einen Inhaltsstoff der Pygidialblasen von Gelbrandkäfer. X. Mittei lung über Insektenabwehrstoffe. Z.Naturf., 17b (2): 81-83.

300A. SCHILDKNECHT H., HOTZ D., 1967. Identifizierung der Nebensteroide das Prothorakalwehrdrüsensystems des Gelbrandkäfers Dytiscus marginalis. Angew.Chem., 79 (20): 902-903.

300B. SCHILDKNECHT H., HOTZ D., MASCHWITZ U., 1967. Über Arthropoden-Abwehrstoffe XXVII. Die C_{21}-Steroide der Prothorakalwehrdrü- sen von Acilius sulcatus. Zeitsch.Naturf., 22b (9): 938-944.

301. SCHILDKNECHT H., KRÄMER H., 1962. Zum Nachweis von Hydrochinonen neben Chinonen in den Abwehrblasen von Arthropoden. XV.Mitteilung über Insektenabwehrstoffe. Z.Naturf., 17b (10): 701-702.

302. SCHILDKNECHT H., MASCHWITZ U., WENNEIS W.F., 1967. Neues„Stoffe aus dem Wehrsekret der Diplopodengattung Glomeris. Über Arthropoden-Abwehrstoffe. XXIV. Naturwiss., 54 (8): 196-197.

303. SCHILDKNECHT H., SCHMIDT H., 1963. Die chemische Zusammenzetzung des Wehrsekretes von Dicranura vinula. XVII. Mitteilung über Insektenabwehrstoffe. Z.Naturf., 18b (7): 585-587.

304. SCHILDKNECHT H., SIEWERDT R., MASCHWITZ U., 1966. Ein Wirbeltierhormon als Wehrstoff des Gelbrandkäfers (Dytiscus marginalis). Angew.Chem., 78 (7): 392.

305. SCHILDKNECHT H., SIEWERDT R., MASCHWITZ U., 1967. Über Arthropodenabwerstoffe, XXIII. Cybisteron, ein neuss Arthropoden-Steroid. Liebigs Ann.Chem., 703: 182-189.

306. SCHILDKNECHT H., WEIS H., 1960. Über das flüchtige Sekret vom Totenkäfer (Blaps mortisaga L.). IV. Mitteilung über Insektenabwehrstoffe. Z.Naturf., 15b (3): 200.

307. SCHILDKNECHT H., WEIS H., 1960. Zur Kenntnis des Pygialdrüsen-Sekretes vom gemeinen Ohrwurm, Forficula auricularia. VI Mitteilung über Insektenabwehrstoffe. Z.Naturf., 15b (11): 755-757.

308. SCHILDKNECHT H., WEIS K.H., 1960. Über die Tenebrioniden-Chinone bei lebendem und totem Untersuchungsmaterial. VII. Mitteilung über Insektenabwehrstoffe. Z.Naturf., 15b (11): 757-758.

309. SCHILDKNECHT H., WEIS K.H., 1961. Die chemische Natur des Wehrsekretes von Pseudophonus pubescens und Ps. griseus. VIII. Mitteilung über Insectenabwehrstoffe. Z.Naturf., 16b (6): 361-363.

310. SCHILDKNECHT H., WEIS K.H., 1961. Chinone als aktives Prinzip der Abwehrstoffe von Diplopoden. Z.Naturf., 16b (12): 810-816.

311. SCHILDKNECHT H., WEIS K.H., 1962. Die Abwehrstoffe einiger Carabiden, insbesondere von Abax ater. XII. Mitteilung über Insekten abwehrstoffe. Z.Naturf., 17b (7): 439-447.

312. SCHILDKNECHT H., WEIS K.H., 1962. Zur Kenntnis der Pygidialblasensubstanzen vom Gelbrandkäfer (Dytiscus marginalis L.). XIII. Mitteilung über Insektenabwehrstoffe. Z.Naturf., 17b (7):448-452.

313. SCHILDKNECHT H., WEIS K.H., 1962. Über die chemische Abwehr der Aaskäfer. XIV. Mitteilung über Insectenabwehrstoffe.Z.Naturf., 17b (7): 452-455.

314. SCHILDKNECHT H., WEIS K.H., VETTER H., 1962. α,β-ungesättigte Aldehyde als Inhaltsstoffe der Stinkblasen der Blattwanze <u>Dolycoris baccarum</u> L. XI. Mitteilung über Insektenabwehrstoffe. Z.Naturf., 17b (5): 350-351.

315. SCHILDKNECHT H., WENNEIS W.F., 1966. Über Arthropoden (Insekten) Abwehrstoffe. XX. Strukturaufklärung des Glomerins. Z.Naturf., 21b (6): 552-556.

316. SCHILDKNECHT H., WENNEIS W.F., 1967. Über Arthropoden-abwehrstoffe. XXV. Anthranilsaure als Precursor der Arthropoden-Alkaloide. Glomerin und Homoglomerin. Tetrahedron Letters, 19: 1815-1818.

317. SCHILDKNECHT H., WENNEIS W.F., WEIS K.H., MASCHWITZ U., 1966. Glomerin, ein neues Arthropoden-Alkaloid. Z.f.Naturf., 21b (2): 121-127.

SCHMIDT H., see 2, Adam K.R. and coll.
see 33A, Bobbit J.M. and coll.
see 303, Schildknecht H. and coll.

318. SCHMIDT-LANGE W., 1941. Die Keimtötende Wirkung des Bienengiftes. München.Med.Wschr., 88 (34): 935-936.

318A. SCHNEIDER O.C., 1934. Las emanaciones del chinchemoyo (<u>Paradoxomorpha crassa</u> (Blanch), Kirby). Rev.Chil.Hist.Nat., 38: 44-46.

318B. SCHOENBORN B.P., McCONNEL J.F., 1962. The crystal structure of the monoterpene isoiridomyrmecin $C_{10}H_{16}O_2$. Acta Cryst., 15: 779-785.

SCHOENBORN B.P., see 184B, McConnel J.F. and coll.
see 184C, McConnel J.F. and coll.

SCHORNO K.S., see 97A, Eisenbraun E.J. and coll.

SCHREIBER H.J., see 166D, Korte F. and coll.

319. SCORTECCI G., 1966. Insetti. Labor, Milano, 1: 1-879; 2: 1-1045.

SELVA A., see 13B, Bernardi R. and coll.
see 49, Cardani C. and coll.

320. SHEARER D.A., BOCH R., 1965. 2-Heptanone in the mandibular gland secretion of the honey bee. Nature, 206 (4983): 530.

SHEARER D.A., see 34, Boch R. and coll.

320A. SHETH K., RAMSTAD E., WOLINSKY J., 1961. The structure of loganin. Tetrahedron Letters, (12): 394-397.

SHOOLERY J.N., see 94A, Djerassi C. and coll.
see 38A, Briggs L.H. and coll.

SHOLOV A., see 212, Nitzan (Tischler) M. and coll.

SIEWERDT R., see 304, Schildknecht H. and coll.
see 305, Schildknecht H. and coll.

SIGEL C.A., see 10D, Bates R.B. and coll.

320B. SIMPSON J., 1966. Repellency of the mandibular gland scent of worker honey bees. Nature, 209 (5022): 531-532.

320C. SISIDO K., KUROZUMI S., UTIMOTO K., ISIDA T., 1966. Stereochemistry of 1,2-dimethyl-3-isopropylcyclopentane. J.Org.Chem., 31: 2795-2802.

321. SISIDO K., UTIMOTO K., ISIDA T., 1964. A synthesis of iridomyrmecin. J.Org.Chem., 29: 3361-3365.

SLABAUGH M., see 286N, Sakan T. and coll.

SLATES H.L., see 353A, Wendler N.L. and coll.

321A. SLOTTA K., BORCHERT P., 1954. Histamina e toxinas proteicas no veneno de abelha. Mem.Inst.Butantan, 26: 279-295.

321B. SLOTTA K.H., GONZALEZ J.D., ROTH S.C., 1967. The direct and indirect hemolytic factors from animal venoms. pag. 369-377 in RUSSEL F.E., SAUNDERS P.R. (Ed.): Animal toxins. Pergamon Press, London: 1-428.

322. SMIRNOV D.A., 1911. Sulla costituzione ed importanza delle ghiandole odorifere della Aromia moscata L. (in russo). Trav.Soc. Impér.Natural.St.Pétersbourg. Section Zool.Physiol., 40 (3-4): 1-15.

SMITH S.J., see 94, Dixon A.F.G. and coll.

323. SOLDATI M., FIORETTI A., GHIONE M., 1966. Cytotoxicity of pederin and some of its derivatives on cultured mammalian cells. Experientia, 22 (3): 176-178.

SOLOMON D.G., see 59, Cavill G.W.K. and coll.
see 59A, Cavill G.W.K. and coll.

SORM F., see 94B, Dolejs L. and coll.
see 94C, Dolejs L. and coll.

SPIGGLE D.W., see 33A, Bobbit J.M. and coll.

STADDON B.W., see 266, Pinder A.R. and coll.

STAHL W.H., see 280, Roth L.M. and coll.

324. STAHNKE H.L. (1963), 1965. Some pharmacological and biochemical characteristics of Centruroides sculpturatus Ewing scorpion venom. II Int.Pharmacol.Meeting, Praga 1963, 9: 63-70.

324A. STAHNKE H.L., JOHNSON B.D., 1967. Aphonopelma tarantula venom. pag. 35-40 in: RUSSEL F.E., SAUNDERS P.R. (Ed.): Animal toxins. Pergamon Press, London: 1-428.

STÄMPFLI R., see 2, Adam K.R. and coll.

325. STAY B., ROTH L.M., 1962. The colleterial glands of cockroaches. Ann.Ent.Soc.Am., 55 (1): 124-130.

STONE B.C., see 34,Boch R. and coll.

325A. STRUBEL A., 1925. Thelyphonus caudatus L. Eine biologische Skizze. Verh.Naturh.Ver.Preuss.Rheinl., 82: 301-314.

326. STUMPER R., 1921. Etudes sur les fourmis. Recherches critiques sur l'odorat. Bull.Soc.Ent.Belg., 3 (1): 24-30.

327. STUMPER R., 1922. Le venin des fourmis en particulier l'acide formique. Ann.Sc.Nat.,Paris: 105-112.

328. STUMPER R., 1951. Sur la sécrétion d'acide formique par les fourmis. C.R.Acad.Sc., 233: 1144-1146.

329. STUMPER R., 1951. Il veleno delle formiche. Selezione Scientifica, 3 (23): 57-61.

330. STUMPER R., 1952. Données quantitatives sur la sécrétion d'acide formique par les fourmis. C.R.Acad.Sc., 234: 149-152.

331. STUMPER R., 1953. Über schutz und Trutzsekrete der Ameisen. Naturwiss., 40 (2): 33-34.

332. STUMPER R., 1959. Un nouveau constituant odorant du venin acide de Fourmis. C.R.Acad.Sc., 249: 1154-1156.

332A. STUMPER R., 1960. Die Giftsekretion der Ameisen. Naturwiss., 17 (20): 457-463.

333. STUMPER R., 1964. Über die Ameisensäure-Sekretion der Formicinen. Naturwiss., 51 (12): 277-279.

333A. SUDD J.H., 1967. An introduction to the behaviour of Ants. Publ. Arnold E., London: 1-200.

SUTHERLAND M.D., see 220, Park R.J. and coll.

SUZUI A., see 286F, Sakan T. and coll.
see 286G, Sakan T. and coll.
see 286H, Sakan T. and coll.
see 286I, Sakan T. and coll.
see 286L, Sakan T. and coll.
see 286M, Sakan T. and coll.

SWITENBANK C., see 114, Eisner T. and coll.

TAKAGI I., see 286O, Sakan T. and coll.

TAYLOR W.W.Jr., see 85, De Coursey J.D. and coll.
see 86, De Coursey J.D. and coll.

TERASHIMA Y., see 286L, Sakan T. and coll.

THAIN E.M., see 288, Schachter M. and coll.

THOMAS D.W., see 89, De La Lande I.S. and coll.

333B. THOMSON R.H., 1957. Naturally occurring quinones. Butterworths Scientific Public., London: 1-302.

TOSCHI-FRONTALI M., see 14, Bettini S. and coll.

334. TRAVE R., GARANTI L., MARCHESINI A., PAVAN M., 1966. Sulla natura chimica del secreto odoroso della larva del lepidottero Cossus cossus L. Chim.Ind., Milano, 48 (11): 1167-1177.

335. TRAVE R., GARANTI L., PAVAN M., 1959. Ricerche sulla natura chimica del veleno del miriapode Archiulus (Schizophyllum) sabulosus L. Chim.Ind., Milano, 41: 19-29.

336. TRAVE R., GARANTI L., PAVAN M., 1960. Sul secreto delle glandole mandibolari della larva di Cossus cossus L. (C. ligniperda Fabr.) (Lepidoptera). XI Int.Kongr.Ent., Wien, Verh.B.III: 73-76.

337. TRAVE R., MERLINI L., GARANTI L., 1958. Ricerche sulla sintesi del nor-nepetalattone. Chim.Ind., Milano, 40: 887-895.

338. TRAVE R., MERLINI L., PAVAN M., 1960. Sulla natura chimica del secreto della larva del Lepidottero Cossus ligniperda Fabr. Rend.Ist.Lomb.Sc.Lett., Cl.Sc.(B), 94: 151-155.

339. TRAVE R., PAVAN M., 1956. Veleni degli insetti. Principi estratti dalla formica Tapinoma nigerrimum Nyl. Chim.Ind., Milano, 38: 1015-1019.

TRAVE R., see 128, Fusco R. and coll.
see 129, Fusco R. and coll.
see 261, Pavan M. and coll.

TRAYNHAM J.G., see 27, Blum M.S. and coll.
see 28, Blum M.S. and coll.
see 31, Blum M.S. and coll.

TSUTSUI S., see 184, Matsumoto T. and coll.

TSUYUKI T., see 364, Yamamoto I. and coll.

TYLER M.J., see 89, De La Lande I.S. and coll.

UETA A., see 184, Matsumoto T. and coll.

UTIMOTO K., see 320C, Sisido K. and coll.
see 321, Sisido K. and coll.

VALCURONE M.L., see 5, Baggini A. and coll.
see 262, Pavan M. and coll.

340. VALLE J.R., PICARELLI Z.P., PRADO J.L., 1954. Histamine content and pharmacological properties of crude extracts from setae of ur ticating caterpillar. Arch.Int.Pharmacodyn.Thér., 98 (3): 324-334.

VARTIAINEN A., see 95, Eckert D. and coll.

341. VECCHI M.A., 1960. La glandola odoripara dell'Apis mellifica L. Boll.Ist.Ent.Univ.Bologna, 24: 53-66.

VERCELLONE A., see 128, Fusco R. and coll.
see 129, Fusco R. and coll.

VETTER H., see 314, Schildknecht H. and coll.

342. VIALLI M., 1939. Ricerche preliminari sul secreto di Pheropsophus africanus Dej. (Col.Car.). Riv.Biol.Col., 2 (4): 273-277.

343. VICARI G., BETTINI S., COLLOTTI C., FRONTALI N., 1965. Action of Latrodectus mactans tredecimguttatus venom and fractions on cells cultivated in vitro. Toxicon, 3: 101-106.

344. VIEHOVER A., CAPEN R.G., 1923. Domestic sources of cantharidin. I. Macrobasis albida Say. J.Assoc.Offic.Agr.Chem., 6 (4): 489-492.

345. WAIN R.L., 1943. The secretion of salicylaldehyde by the larvae of the brassy willow beetle (Phyllodecta vitellinae L.). Ann.Rep. Agric.Hort.Res.Sta., Long Ashton: 108-110.

WALKER J.R., see 28A, Blum M.S. and coll.

WALLBANK B.E., see 348A, Waterhouse D.F. and coll.

WALLER G.R., see 273A, Regnier F.E. and coll.

346. WALLIS D., 1966. L'aggressività negli insetti sociali. Sapere, 57 (676): 211-215.

WALTERS P.M., see 185A, McElvain S.M. and coll.

WARTER S.L., see 29, Blum M.S. and coll.
see 30, Blum M.S. and coll.
see 31, Blum M.S. and coll.

Von WARTBURG A., see 176A, Lichti H. and coll.

347. WATERHOUSE D.F., FORSS D.A., HACKMAN R.H., 1961. Characteristic o-dour components of the scent of stink bugs. J.Insect Physiol., 6 (2): 113-121.

348. WATERHOUSE D.F., GILBY A.R., 1964. The adult scent glands and scent of nine bugs of the superfamily Coreoidea. J.Insect Physiol., 10: 977-987.

348A. WATERHOUSE D.F., WALLBANK B.E., 1967. 2-methylene butanal and related compounds in the defensive scent gland of Platyzosteria cockroaches (Blattidae: Polyzosteriinae). J.Ins.Physiol., 13 (11): 1657-1669.

WATERHOUSE D.F., see 132, Gilby A.R. and coll.
see 135, Gordon H.T. and coll.

348B. WEATHERSTON J., . The chemistry of Arthropod Defensive substances. Quarterly Reviews :287-313.

349. WEBER M., 1882. Ueber eine Cyanwasserstoffsäure bereitende Drüse. Arch.Mikro.Anat., 21: 468-475.

350. WEBER N.A., 1961. Use of poison by the ant, Tapinoma nigerrimum (Hymenoptera: Formicidae). Proc.Ent.Soc.Washington, 63: 217-218.

WEBSTER A.P., see 85, De Coursey J.D. and coll.
see 86, De Coursey J.D. and coll.

351. WECKERING R., 1960. III. Stereoelectronie de poisons de fourmis et de coleoptères. XI Int.Kongr.Ent., Wien, Verh.Bd.III: 102-109.

WEIS K.H., see 299, Schildknecht H. and coll.
see 306, Schildknecht H. and coll.
see 307, Schildknecht H. and coll.
see 308, Schildknecht H. and coll.
see 309, Schildknecht H. and coll.
see 310, Schildknecht H. and coll.
see 311, Schildknecht H. and coll.
see 312, Schildknecht H. and coll.
see 313, Schildknecht H. and coll.
see 314, Schildknecht H. and coll.
see 317, Schildknecht H. and coll.

WEISS C., see 2, Adam K.R. and coll.
see 3, Adam K.R. and coll.

WEITKAMP H., see 119A, Falbe J. and coll.

352. WELSH J.H., 1964. Composition and mode of action of some invertebrate venoms. Ann.Rev.Pharmacol., 4: 293-304.

353. WELSH J.H., BATTY C.S., 1963. 5-hydroxytryptamine content of some arthropod venoms and venom-containing parts. Toxicon, 1: 165-173.

353A. WENDLER N.L., SLATES H.L., 1958. Studies in the iridomyrmecin series. Abnormal ring closure of a 1,6-Keto aldehyde. J.Am.Chem. Soc., 80 (15): 3937-3939.

WENNEIS W.F., see 302, Schildknecht H. and coll.
see 315, Schildknecht H. and coll.
see 316, Schildknecht H. and coll.
see 317, Schildknecht H. and coll.

354. WHEELER W.M., 1890. Hydrocyanic acid secreted by Polydesmus virginiensis Drury. Psyche, 5: 442.

355. WHEELER J.W., MEINWALD J., HURST J.J., EISNER T., 1964. Trans-2-dodecenal and 2-methyl-1,4-quinone produced by a millipede. Science, 144 (3618): 540-541.

WHITEAR B.R.D., see 76A, Cookson R.C. and coll.
see 76B, Cookson R.C. and coll.

WHITFIELD F.B., see 67, Cavill G.W.K. and coll.
see 67A, Cavill G.W.K. and coll.
see 67B, Cavill G.W.K. and coll.
see 67C, Cavill G.W.K. and coll.
see 69, Cavill G.W.K. and coll.

355A. WIGGLESWORTH V.B., 1963. The juvenile hormone effect of farnesol and some related compounds: quantitative experiments. J.Ins. Physiol., 9: 105-119.

355B. WIGGLESWORTH V.B., 1964. The life of Insects. Weidenfeld and Nicolson, London:

WILLIAMS P.J., see 68, Cavill G.W.K. and coll.
see 69, Cavill G.W.K. and coll.

356. WILSON E.O., 1963. The social biology of ants. Ann.Rev.Ent., 8: 345-368.

357. WILSON E.O., 1963. Pheromones. Sci.Am., 208 (5): 100-114.

358. WILSON E.O., 1965. Chemical communication in the social insects. Science, 149 (3688): 1064-1071.

359. WILSON E.O., PAVAN M., 1959. Glandular sources and specificity of some chemical releasers of social behaviour in Dolichoderine ants. Psyche, 66 (4): 70-76.

WILSON E.O., see 174, Law J.H. and coll.

360. WINTERINGHAM F.P.W., 1965. Some distinctive features of insect metabolism, pag.29-37 in GOODWIN (Ed.): Aspects of insect biochemistry. Academic Press, London:

WISNIEWSKI J., see 165, Kietczewski B. and coll.

WOLF H., see 361, Wolinsky J. and coll.

361. WOLINSKY J., GIBSON T., CHAN D., WOLF H., 1965. Stereospecific synthesis of iridomyrmecin and related iridolactones. Tetrahedron, 21: 1247-1261.

WOLINSKY J., see 286N, Sakan T. and coll.
see 320A, Sheth K. and coll.

WOLKENSTÖRFER M., see 300, Schildknecht H. and coll.

362. WOODRING J.P., BLUM M.S., 1963. The anatomy and physiology of the repugnatorial glands of Pachydesmus crassicutis (Diplopoda). Ann.of Ent.Soc.Am., 56 (4): 448-453.

363. WOODRING J.P., BLUM M.S., 1965. The anatomy, physiology and comparative aspects of the repugnatorial glands of Orthocricus arboreus (Diplopoda: Spirobolida). J.Morph., 116: 99-108.

WOODRING J.P., see 32, Blum M.S. and coll.

364. YAMAMOTO I., TSUYUKI T., 1964. Odoroûs principles from stink bugs. I.U.P.A.C. Int.Symp.Chem.Nat.Prod., Kyoto: 133-134.

YANAGIYA M., see 184, Matsumoto T. and coll.

YAOI Y., see 153A, Inouye H. and coll.

YASUDA S., see 184, Matsumoto T. and coll.

ZALKOW L.H., see 94A, Djerassi C. and coll.

ZSCHOCKE A., see 166A, Korte F. and coll.
see 166B, Korte F. and coll.
see 166C, Korte F. and coll.

Pavia, 15.III.1968

EUROPEAN RESEARCH OFFICE
Zimmer 030 (Q-3)
IG Farben Hochhaus
6000 FRANKFURT/MAIN (GERMANY)

Final Technical Report
(third year) under Contract
DA-91-591-EUC-3898.

1) Subject of the research:
   1a) Search in tropical regions will me made for Arthropods (Insects, Arachnids, Crustacea and Myriapoda) which produce toxic substances. Methods will be developed for Arthropods. The crude extracts will be tested for biological effects. Those substances showing promise will be further concentrated and purified followed by biological, chemical, and physical study of the purified products.
   1b) The contractor will provide the service of a botanist who will travel to the Congo where he will study the process for producing poisoned arrows has practised by the native doctors (sorcerers). He will study the source of raw materials, the production of the poison from these materials, and will obtain samples of the raw materials and the poisonous product for subsequent study by the contractor and the U.S. Army.

2) Name of Contractor: Prof. M. PAVAN, Istituto di Entomologia Agraria dell'Università di Pavia, Via Taramelli 24, Pavia (Italy).

3) Contract number: DA-91-591-EUC-3898.

4) Type and number of report: Final Technical Report.

5) Period covered by report: 1.V.1967 - 30.VI.1967.

6) "The research reported in this document has been made possible through the support and sponsorship of the US Department of Army, through its European Research Office. This report, not necessarily in final form, is intended only for the internal management use of the Contractor and the US Department of Army".

The Contractor:
prof. Mario Pavan, director of
Istituto di Entomologia Agraria
dell'Università di Pavia (Italy)
Via Taramelli 24

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

Istituto di Entomologia Agraria
dell'Universita di Pavia
Pavia, Italy

2a. REPORT SECURITY CLASSIFICATION

2b. GROUP

3. REPORT TITLE

DEFENSIVE SECRETIONS OF ARTHROPODA

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Technical Report, January 1966 - March 1968

5. AUTHOR(S) (Last name, first name, initial)

PA[illegible], Mario

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 1968	218	364

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA-91-591-EUC-3898	
b. PROJECT NO. IC522301A060	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) Prop. E-711
d.	

10. AVAILABILITY/LIMITATION NOTICES

Qualified requesters may obtain copies of this report from DDC.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

AMC

13. ABSTRACT The report starts with the calculation that out of 885,000 known species of arthropods (of which 815,000 are insects) at least 82,500 species can synthesize poisons. The constituents of these poisons have been identified in part for only 426 species, of which 342 are insects. Arthropods of particular interest in this respect have been listed and the chemical compounds identified in the poison of each species indicated. The following are new compounds, identified for the first time in arthropod poisons: 1. iridomyrmecin; 2. pederin; 3. iridodial; 4. dendrolasin; 5. pseudopederin; 6. pederone; 7. cossin A; 8. cossin B; 9. cossin C; 10. cossin 1; 11. cossin 2; 12. cossin 3; 13. cossin B_1; 14. cossin C_1; 15. zeuzerina; 16. dolichodial; 17. cybisterone; 18. diidro-cybisterone. A chapter is devoted to each compound and a comprehensive concluding chapter and bibliography terminate this report.

DD FORM 1 JAN 64 1473

UNCLASSIFIED

BEST AVAILABLE COPY →

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Defensive Secretions						
Arthropod Poisons						
Plant Poisons						
Insect Poisons						
Iridomyrmecin						
Pederin						
Iridodial						
Dendrolasin						
Pseudopederin						
Pederone						
Cossins						
Zeuzerina						
Dolichodial						
Cybisterone; Diidrocybisterone						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2*a*. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7*a*. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8*a*. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through ______________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through ______________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through ______________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

UNCLASSIFIED

Security Classification