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Effects of the Argentine ant venom on terrestrial amphibians

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Appendix S3 (page 13). The temporal and spatial overlap of *L. humile* ants with amphibians. Relative abundances over time of *Epidalea calamita* toadlets emerging from temporary ponds and (a) native ants or (b) *L. humile* ants. Invaded and uninvaded areas around ponds sampled in April May 2013 during amphibian emergence. Values represent the mean number (\pm SE) of toadlets per transect or ants per bait. Note the differences in axis scale between (a) and (b) regarding ants. (c) Mean (\pm SE) number of dead amphibians found along *L. humile* trails during the juvenile amphibian emergence period over three different seasons (May and June 2013, 2014, and 2018). (d, e, f) Examples of different phases of ant predation on amphibians: (d) ants attack *P. cultripes* toadlet; (e) freshly killed *H. meridionalis* covered by *L. humile*, around two hours after an attack; (f) skeleton of an *H. meridionalis* froglet, fewer than 12 h after an attack. Photo credits: Fernando Amor (d) and Elena Angulo (e,f).

Appendix S4 (page 14). The identification of *L. humile* venom. Longitudinal section of the abdomen of a, *Linepithema humile* and b, *Tapinoma cf. nigerrimum*. Partial chromatograms showing the iridodial/dolichodial iridomyrmecin complex of the pygidial glands of: c, *Linepithema humile* workers and d, *Tapinoma cf. nigerrimum* workers. e, List of compounds associated with the peaks in c and d. Iridomyrmecin and iridodials with different numbers are isomers. Note that the hydrocarbons may have originated from the cuticular intima lining the gland.

Supporting Information - Appendix S1

A. Study area and experimental individuals

A.1. Study area. The Doñana Biological Reserve (RBD, Spain, 36°59.491'N, 6°26.999'W) contains more than 1,100 temporary ponds, constituting the breeding grounds of eight amphibian species (Díaz-Paniagua et al., 2010). Juveniles of the various species emerge from these temporary ponds over a period of two to three weeks—in the spring for natterjack toads (*Epidalea calamita*) and in late spring or summer for Mediterranean treefrogs (*Hyla meridionalis*) and western spadefoot toads (*Pelobates cultripes*). In the 1970s, *Linepithema humile* was unintentionally introduced into the study area. Subsequently, it spread to occupy the natural habitats that surround temporary ponds, representing a patchy distribution. It has displaced native ants and established high-density colonies (Angulo et al., 2011).

A.2. Ethical issues. The experimental procedures were approved by the CSIC Ethical Committee and the regional government of Andalucía (CEBA-EBD 11-36, CEBA-EBD 11-36b, CSD2008-00040, 1043/MDCG/mect, 014-1073-00000613-FQH/MDCG/mect) and comply with Spanish legislation regarding the protection of wildlife used for scientific purposes. Some experiments were carried out at the Doñana Biological Station (EBD) in Seville, while others were performed at RBD. A B-M was the veterinarian in charge of animal health and welfare for the EBD and RBD experimental facilities. C D-P, P A-B, and E A were authorized to carry out animal experimentation by the Spanish MAGRAMA.

A.3. Housing of experimental animals. Juvenile amphibians were assigned to four different experiments: the ant-trail-exposure experiment was carried out in the field at RBD; the foraging-arena-exposure experiment was carried out in experimental facilities at RBD, under temperature and photoperiod conditions similar to those in the field; the iridomyrmecin-exposure and the dose-response experiments were carried out in the experimental facilities at EBD, under controlled conditions (23°C, 12:12 photoperiod, 60% humidity). In the first two experiments, juveniles were released back near their ponds of origin 48 h after the tests. In the last two experiments, juveniles were euthanized using an overdose of anaesthetic (5-min bath in tricaine methasulfonate [MS-222], 10 g/L dissolved in Ringer's lactate solution). In the iridomyrmecin-exposure experiment, euthanasia took place 48 h after the test. In the dose-response experiment, it took place approximately 10 min after dose application, immediately after the clinical evaluation.

We collected juvenile amphibians in the field near ponds shortly after emergence. We also collected tadpoles that were laboratory-raised until reaching metamorphosis. All specimens were kept in an experimental facility, either at RBD (raised in 55-L tanks, fed common aquatic plants, under ambient temperature and photoperiod) or EBD (raised in 5-L plastic containers, fed rabbit chow *ad libitum*, 23°C, 12:12 photoperiod). Juveniles were housed in groups (up to 10 individuals from the same pond of origin) in 20 x 30 x 20 cm terraria (with sandy substrate, pieces of cork as shelter, and a water container [in the case of *H. meridionalis*]), that were cleaned weekly. Every two days, we checked on the juveniles, misted the terraria with water, and provided individuals *ad libitum* with mealworms, *Drosophila* flies and small crickets dusted with a calcium supplement. During the experimental trials, juveniles were maintained individually in smaller containers.

A. 4. Sampling sizes. Each individual was used only once. Sampling/capture order determined the allocation of individuals to experimental groups: each new individual was assigned to a treatment on a rotating basis (i.e., treatments were alternated). Individuals were identified with a code; researchers were thus blind to treatment assignments when conducting analyses (i.e., histological, chemical analysis, clinical evaluation); behavioral tests were difficult to do blinded, especially in ant trails and foraging arenas where individuals could be at risk, or in the iridomyrmecin test in which the response occurred immediately after the administration, at the highest doses. However, it was blind in all the cases during the 48h of observations, that followed the behavioral tests. Because these were novel experiments, we had no estimates of variation for the dependent variables (i.e., the effect of the Argentine ant on juvenile amphibians), which prevented us from using power analysis to calculate a minimum sample size. Consequently, sample size was chosen so as to comply with ethical guidelines—we sought to limit the number of individuals used while ensuring that we

had adequate statistical power given the numbers and types of variables in each planned analysis. In some cases, sample sizes were unbalanced due to variation in availability of amphibian species in the field.

The total number of individuals used was as follows: 185 *P. cultripes* (30 for the ant-trail-exposure experiment, 94 for the foraging-arena-exposure experiment, 42 for the iridomyrmecin-exposure experiment, and 19 for the dose-response experiment); 137 *H. meridionalis* (27 for the ant-trail-exposure experiment, 75 for the foraging-arena-exposure experiment, and 35 for the dose-response experiment); and 152 *E. calamita* (125 for the foraging-arena-exposure experiment and 27 for the dose-response experiment).

A.5. Ant species. Two native ant species, commonly found in RBD, *Tapinoma* cf. *nigerrimum* and *Aphaenogaster senilis*, were used for comparisons with *L. humile*. *Tapinoma* cf. *nigerrimum* is a dolichoderine ant that is closely related to *L. humile*, with whom it shares many life-history traits (Arnan et al., 2012). *Aphaenogaster senilis* is a myrmecine ant, and served as a control for the two dolichoderine ants. Five colony fragments of *L. humile*, *T. cf. nigerrimum*, and *A. senilis* were maintained at RBD for the foraging-arena-exposure experiment. They were housed in dark, enclosed nesting boxes (10 cm in diameter; height of 10 cm for *A. senilis* and 5 cm for *T. cf. nigerrimum* and *L. humile*). Each nesting box was connected to an open foraging arena (30 x 10 x 10 cm), equipped with a small Petri dish where food was permanently supplied. Another five fragments of *L. humile* and *T. cf. nigerrimum* colonies were maintained at EBD. They were housed in open containers (30 x 10 x 10 cm) with a dark-colored tube functioning as a nest. These fragments were used for the dose-response experiment and to carry out chemical comparisons between the ant species. All ants were fed *ad libitum* fresh fruit, mealworms, and diluted honey.

B. Methodological details for the temporal and spatial overlap analysis of *L. humile* ants with amphibians

In April and May of 2013, during the period when newly metamorphosed *E. calamita* emergence from ponds, we established two plots that were separated by 400 m. One encompassed two invaded ponds (~15 and 25 m long, respectively), and the other comprised one uninvaded pond (53 m long). The transects for ant baiting and amphibian survey were carried out at the same locations to assess spatial overlap between ants (native or invasive) and amphibians. We recorded the number and species of ants and toadlets during each sampling session. Data on ant activity can be collected using a variety of standardized methods, such as the use of baits (Savolainen et al. 1988; Cerdá et al. 1997; Sanders & Gordon 2003). In this case diluted honey in water together with biscuits were used. Ants were identified by eye, and when necessary, a sample in alcohol was taken without disturbing the ants at the bait, to confirm the identity in the laboratory.

We wanted to demonstrate the directionality of interactions between ants and amphibians, i.e., do amphibians eat ants or are ants aggressive towards amphibian. Given that ants are relatively sessile organisms (relative to their nest), interactions would occur during foraging. This is why we searched for ant trails near the ponds where amphibian emerge. The amphibian would likely interact with ants when dispersing from the pond. But during preliminary observations we observed that amphibian were dying in the Argentine ant trail. Thus, we focused our sampling in counting dead juveniles.

C. Methodological details for the ant-trail-exposure experiment

We searched for at least six trails of each ant species in the field; in the case of *A. senilis*, trails were induced and maintained using bait as described in Cerdá et al. (2009). The experiment was carried out during 20 days in June, mornings or evenings, when the ants were active. We only used two amphibian species because juveniles of *B. calamita* were not available at this time of the year. We carefully positioned juveniles of *P. cultripes* and *H. meridionalis* 3 cm away from trails of the three ant species. Each amphibian was kept in place using an inverted plastic Petri dish (5.5 cm in diameter, 1.4 cm in height), enabling it to move and turn around but not to escape. The sides of the dish were perforated with eight to ten holes large enough to allow ants (either *L. humile* or *T. nigerrimum*) to enter. For the larger *A. senilis* tests we used cages (8 x 8.5 x 3 cm, with a mesh width of 5 x 5 mm). The dish or cage was held in place by hand, preventing any disturbance to

the ant trail. The ants took time to discover the amphibians. Following initial contact with the ants, the amphibians were kept in place for 2 additional minutes and then released (the dish/cage was carefully removed). They were observed for up to 10 min thereafter, or until they moved at least 1 m away from the trail, whichever came first. Then they were observed for an additional 48 h in the laboratory to evaluate the effects. No amphibian died during the 10-min trials.

D. Methodological details for the foraging-arena-exposure experiment

Five artificial colony fragments (as described below) were used per ant species. Each colony received an average of six different juveniles of each of the three amphibian species, but only one juvenile per day. This frequency of exposure to the ants realistically mimic in field situation during juvenile emergence from ponds. Behavioral tests were done in the afternoon, when both ants and juvenile amphibian were active.

E. Chemical analysis by gas chromatography

For qualitative analyses of pygidial glands secretion, the glands were carefully dissected out and immersed in hexane for content extraction for at least 24h. For compound quantifications, whole ants were used rather than dissected gland to avoid possible spillage during dissection. Decyl-alcohol (99%) was used as an internal standard. The samples were run by GC/MS (Agilent) using an HP-5MS capillary column, temperature programmed from 60°C (1 min hold) to 320°C at a rate of 10°C min⁻¹. Compound identification was done from the fragmentation pattern as compared to synthetic compounds.

Iridomyrmecin quantification was performed by gas chromatography (GC-FID - Shimadzu 2010 equipped with a 30 m x 0.25 mm i.d.-BPX5, 0.25 mm capillary column). Helium was used as the carrier gas (flow rate of 35.1 ml.min⁻¹). The injection port and detector temperatures were set to 280°C and 310°C, respectively. The GC oven was temperature programmed from 60°C with a 1-min initial hold to 300°C at a rate of 10°C.min⁻¹, and a final hold of 20-min. Decyl-alcohol (99%) was used as an internal standard, and the calibration curve for quantifying iridomyrmecin concentrations in the samples was constructed using synthetic iridomyrmecin (Chauhan & Schmidt 2014). The quantity of iridomyrmecin was determined by calculating the area under the peak relative to the internal standard for the different samples and corrected by the calibration curve.

To assess the percentage of iridomyrmecin of a worker 's fresh body weight, we sampled 10 ants from five laboratory colonies (used in the foraging-arena experiment) of each ant species and weighed them (in groups of 10) to obtain species-specific mean fresh weight.

F. Methodology of the dose-response experiments

Each amphibian received a single dose of mashed-ant solution (obtained from a known number of either *L. humile* or *T. cf. nigerrimum* workers) and was clinically evaluated 10 min later. The dose assigned for each test depended on the effects observed in previously tested individuals, to be higher or lower respectively. Doses were also adjusted according to the weight of the amphibian tested (number of ants/g of juvenile) and calculated in order to fill in the gaps in the dose-response curve. For ethical reasons, a minimal number of amphibians was used, and ant dosage levels were limited to what was necessary to obtain adequate dose-response curves (11 and 16 *E. calamita*, 14 and 5 *P. cultripes*, and 21 and 14 *H. meridionales* for the *L. humile* and the *T. cf. nigerrimum* curve respectively).

After the 10 min exposure to the ant doses, we performed a clinical evaluation of each individual and classified them as affected or unaffected, based on the presence (or absence) of neurological damage (Kahn 2005), including: 1) Motor response (we extended and released a leg and noted whether retraction occurred) and nociception response (presence/absence of reaction to pain inflicted by pressing a toe with tweezers), which reflected effects on the spinal cord; 2) Photopupillary reflexes (presence/absence of response to light changes) and ocular motility (ability to follow a light with the eyes), which reflected the midbrain response

(i.e., in the ocular [II] and oculomotor [III] cranial nerves); and 3) The palpebral reflexes (whether the eyelid closed when we touched the medial and lateral canthus of the eye), which reflected the response of the medulla oblongata and the pontine nucleus (i.e., in the trigeminal [V] and facial [VII] cranial nerves) .

Sample preparation of amphibian tissues for lesion examination through histological analysis was carried out in the Unit of Histology of the Andalusian Molecular Biology and Regenerative Medicine Centre (<https://www.cabimer.es/web3/unidades-apoyo/histologia/>), following the methods described in Rojas et al. (2005).

Literature cited

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- Savolainen R, Vepsäläinen K 1988 A competition hierarchy among boreal ants: impact on resource partitioning and community structure. *Oikos* **51**:135-155.

Supporting Information - Appendix S2

Literature review on the functional ecology of iridomyrmecin

We searched the ISI Web of Science for the word “iridomyrmec*” to obtain published articles about iridomyrmecin (accessed 15 November 2018). The search returned 61 articles. We increased this total by finding additional articles cited therein. In each publication, at the first mention of iridomyrmecin, we noted the function of iridomyrmecin as assessed by the authors. We established the following categories for these functions: defense, insecticide, antibiotic, alarm, antibacterial, trail pheromone, cat-attracting chemical, necrophoresis, or no function specified. Publications could fall into more than one category. We also categorized each article with respect to its main subject: synthesis of iridomyrmecin, iridomyrmecin in other species, chemical composition of exocrine secretions, chemical structure, insecticide, trail pheromone, defensive compound, pharmacological research, antibiotic, necrophoresis, or alarm pheromones (Supporting Information Table S1). Finally, we analyzed (i) the relative importance of each described function of iridomyrmecin in the literature and (ii) which other species have and use iridomyrmecin and for what purpose.

The review unearthed 116 articles published between 1948 and 2018. When iridomyrmecin was assigned a function at its first mention in the text (N = 93), the two most frequently cited functions were “defense” and “insecticide” (See Table 1a, below). Most of the ant species with iridomyrmecin belong to the Dolichoderine family and notably the genera *Iridomyrmex*, *Tapinoma*, and *Dolichoderus* (See Table 1c, below). However, not all species in these genera have iridomyrmecin (e.g. *T. melanocephalum*, Tomalski et al 1987). Iridomyrmecin has also been found in non-Dolichoderinae ants (i.e. *Pheidole biconstricta*, Davidson et al. 2005), in non-ant insects, (i.e. parasitic wasps and anthicide beetles, See Table S1c, below) and in plants (Riddick et al. 2008). In all cases, iridomyrmecin has been reported to be an effective repellent. However, while Pavan and Ronchetti (1955) found that iridomyrmecin has insecticidal and antibiotic properties, they did not show that this compound was toxic for vertebrates (i.e., tests performed with dogs, rodents, and humans).

Supporting Information Table 1. Context in which iridomyrmecin appears in previous Literature. **(a)** The functions for iridomyrmecin at the first mention in the text. Some studies refer to more than one function, so proportions here are referred to the total number of functions (138). **(b)** Main goal of the article. Data come from 116 articles expanding from 1948 to 2018. **(c)** Other animal taxa having and using iridomyrmecin.

a. Function of iridomyrmecin		abbreviation (a)	%
No function specified		NS	33
Defense		DEF	22
Insecticide		INS	22
Antibiotic		ANT	7
Antibacterial		AntB	6
Alarm		AL	4
Trail		TR	3
Cat attracting chemical		CA	3
Necrophoresis		NE	1

b. Main goal of the article		abbreviation (b)	%
Synthesis of iridomyrmecin		SYN	28
Iridomyrmecin in other species		OtSp	15
Chemical composition of exocrine secretions		ExS	14
Chemical structure		CH	13
Defensive compound		DEF	9
Trail pheromone		TR	6
Pharmacologic research		PH	5
Insecticide		INS	5
Antibiotic		ANT	4
Necrophoresis		NE	1
Alarm pheromones		AL	1

c. Iridomyrmecin in other animal taxa			abbr. (c)
Ant	Subfamily Dolichoderinae	<i>Conomyrma</i> sp.	Cono
		<i>Dolichoderus scabridus</i>	Dsca
		<i>Iridomyrmex nitidiceps</i>	Inip
		<i>Iridomyrmex pruinosus</i>	Ipru
		<i>Iridomyrmex purpureus</i>	Ipur
		<i>Tapinoma erraticum</i>	Terr
		<i>Tapinoma</i> cf. <i>nigerrimum</i>	Tnig
		<i>Tapinoma sessile</i>	Tsess
		<i>Tapinoma simrothi</i>	Tsim
			Subfamily Myrmicinae
Non-ant	Athicid beetle	<i>Formicomus pedestris</i>	Fped
		<i>Formicomus rubricollis</i>	Frub
		<i>Microhoria terminate</i>	Mter
	Parasitic wasp	<i>Alloxysta brevis</i>	Abre
		<i>Alloxysta victrix</i>	Avic
		<i>Aphidius uzbekistanicus</i>	Auzb
		<i>Leptopilina heterotoma</i>	(Lhet)

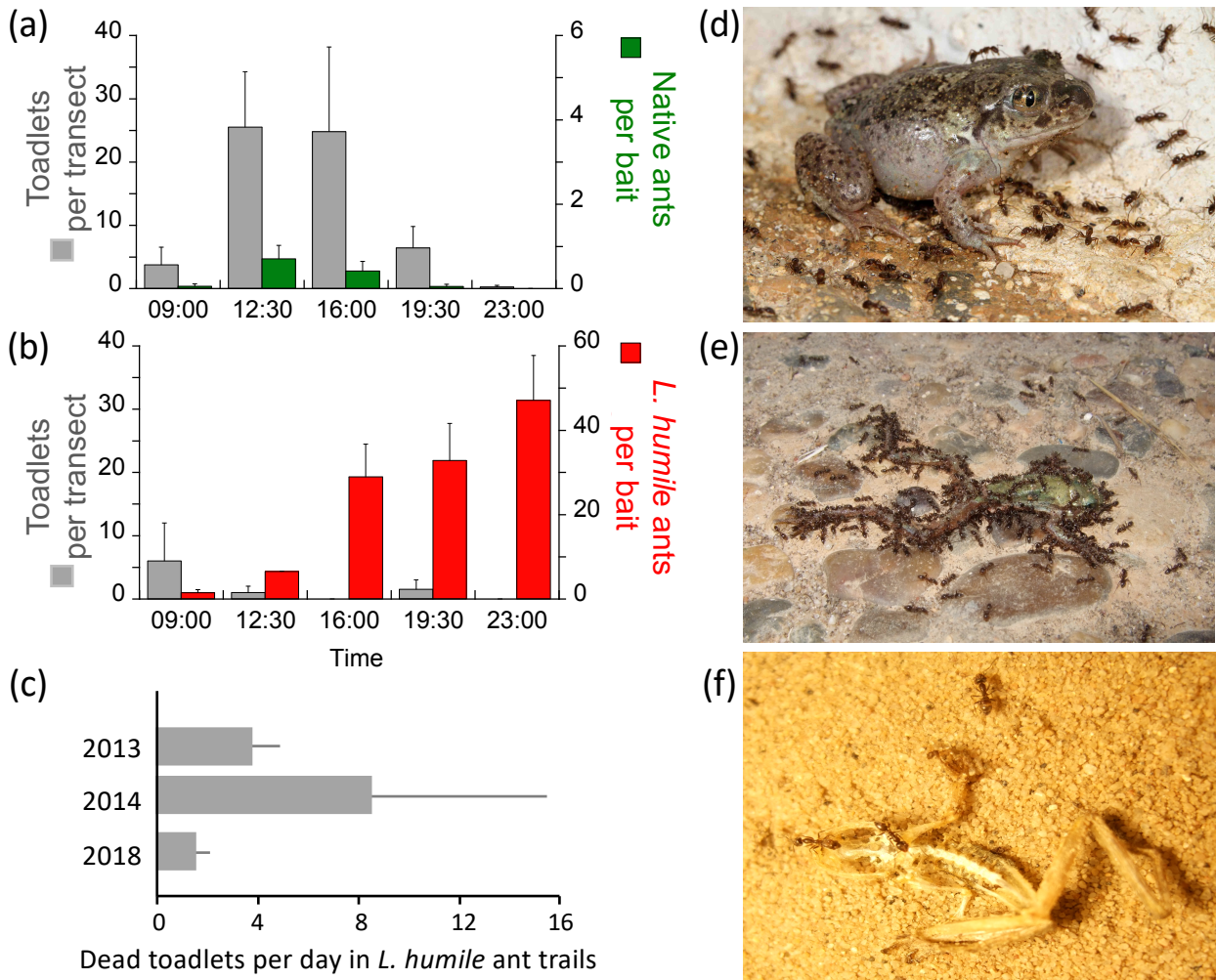
Year	Reference	a	b	c
2018	Pfeiffer, L; Ruther, J; Hofferberth, J; Stökl, J. Interference of chemical defence and sexual communication can shape the evolution of chemical signals. <i>Scientific Reports</i> 8 (321)	DEF	OtSp	Lhet
2018	Weizel, KF; Lee, SH; Dossey, AT; Chauhan, KR; Choe, D-H. Verification of Argentine ant defensive compounds and their behavioral effects on heterospecific competitors and conspecific nestmates. <i>Scientific Reports</i> 8 (1477)	DEF	DEF	
2017	Bol, S; Caspers, J; Buckingham, L; Anderson-Shelton, GD; Ridgway, C; Buffington, CAT; Schulz, S; Bunnik, EM. Responsiveness of cats (Felidae) to silver vine (<i>Actinidia polygama</i>), Tatarian honeysuckle (<i>Lonicera tatarica</i>), valerian (<i>Valeriana officinalis</i>) and catnip (<i>Nepeta cataria</i>). <i>BMC Vet Res</i> 13:1–15	CA	OtSp	
2016	Adachi, M; Miyazawa, Y; Nishikawa, T. Improved Syntheses of (+)-Iridomyrmecin and (-)-Isoiridomyrmecin, Major Components of Matatabilactone. <i>Nat Product Commun</i> 11:883–886	CA	SYN	
2016	Lin, L; Cheng, XL; Li, MZ; Wang, T; Dong, MH; Wang, ZY; Liao, M. Antitumor effects of iridomyrmecin in HeLa cervical cancer cells are mediated via apoptosis induction, loss of mitochondrial membrane potential, cell cycle arrest and down-regulation of PI3K/Akt and up-regulation of lncRNA CCAT2 expression. <i>Bangladesh J Pharmacol</i> 11:856–862	NS	PH	
2016	Rehova, L; Dracinsky, M; Jahn, U. A general approach to iridoids by applying a new Julia olefination and a tandem anion-radical-carbocation crossover reaction. <i>Org Biomol Chem</i> 14:9612–9621	CA	OtSp	
2016	Scaffidi, A; Algar, D; Bohman, B; Ghisalberti, EL; Flematti, G. Identification of the Cat Attractants Isodihydronepetalactone and Isoiridomyrmecin from <i>Acalypha indica</i> . <i>Aust J Chem</i> 69:169–173	CA	OtSp	
2016	Stökl, J; Herzner, G. Morphology and ultrastructure of the allomone and sex-pheromone producing mandibular gland of the parasitoid wasp <i>Leptopilina heterotoma</i> (Hymenoptera: Figitidae). <i>Arthropod Struct Dev</i> 45:333–340	DEF	OtSp	Lhet
2015	Ebrahim, SAM; Dweck, HKM; Stokl, J; Hofferberth, JE; Trona, F; Weniger, K; Rybak, J; Seki, Y; Stensmyr, MC; Sachse, S; Hansson, BS; Knaden, M. <i>Drosophila</i> Avoids Parasitoids by Sensing Their Semiochemicals via a Dedicated Olfactory Circuit. <i>PLoS Biol</i> 13: e1002318	DEF	OtSp	Lhet
2015	Neff, RR. Identification and characterization of trail pheromones and queen pheromones in the Argentine ant, <i>Linepithema humile</i> . PhD thesis - University of California - Riverside, 164 pp	NS	TR	
2015	Stökl, J; Machacek, Z; Ruther, J. Behavioural flexibility of the chemical defence in the parasitoid wasp <i>Leptopilina heterotoma</i> . <i>Sci Nat-Heidelberg</i> 102:1–4	DEF	OtSp	Lhet
2014	Cerdá, X; van Oudenhove, L; Bernstein, C; Boulay, RR. A list and some comments about the trail pheromones of ants. <i>Nat Product Commun</i> 9:1115–1125	TR	TR	Tnig
2014	Chauhan, KR; Schmidt, W. Biorational synthesis of iridomyrmecin diastereomers from catnip oil. <i>Tetrahedron Lett</i> 55:2534–2536	DEF	SYN	
2013	Fischman, CJ; Adler, S; Hofferberth, JE. Divergent Diastereoselective Synthesis of Iridomyrmecin, Isoiridomyrmecin, Teucriumulactone, and Dolicholactone from Citronellol. <i>J Org Chem</i> 78:7318–7323	NS	SYN	
2013	Weiss, I; Rossler, T; Hofferberth, J; Brummer, M; Ruther, J; Stokl, J. A nonspecific defensive compound evolves into a competition avoidance cue and a female sex pheromone. <i>Nat Commun</i> 4: 2767	DEF	OtSp	Lhet
2012	Choe, DH; Villafuerte, DB; Tsutsui, ND. Trail Pheromone of the Argentine Ant, <i>Linepithema humile</i> (Mayr) (Hymenoptera: Formicidae). <i>PLoS One</i> 7: e45016	TR	TR	
2012	Hilgraf, R; Zimmermann, N; Lehmann, L; Troger, A; Francke, W. Stereoselective synthesis of trans-fused iridoid lactones and their identification in the parasitoid wasp <i>Alloxysta victrix</i> , Part II: Iridomyrmecins in the parasitoid wasp <i>Alloxysta victrix</i> . <i>Beilstein J Org Chem</i> 8:1256–1264	ANT	OtSp	Avic
2012	Stökl, J; Hofferberth, J; Pritschet, M; Brummer, M; Ruther, J. Stereoselective chemical defense in the <i>Drosophila</i> parasitoid <i>Leptopilina heterotoma</i> is mediated by (-)-Iridomyrmecin and (+)-Isoiridomyrmecin. <i>J Chem Ecol</i> 38:331–339	DEF	OtSp	Lhet
2012	Van Oudenhove, L; Boulay R; Lenoir A; Bernstein C; Cerdá X. Substrate temperature constrains recruitment and trail following behavior in ants. <i>J Chem Ecol</i> 38:802–809	NS	TR	Tnig
2012	Zimmermann, N; Hilgraf, R; Lehmann, L; Ibarra, D; Francke, W. Stereoselective synthesis of trans-fused iridoid lactones and their identification in the parasitoid wasp <i>Alloxysta victrix</i> , Part I: Dihydronepetalactones. <i>Beilstein J Org Chem</i> 8:1246–1255	NS	SYN	Avic
2011	Martinez, MJ; Weis, EM. Field observations of two species of invasive ants, <i>Linepithema humile</i> Mayr, 1868 and <i>Tetramorium bicarinatum</i> Nylander, 1846 (Hymenoptera: Formicidae), at a suburban park in Southern California. <i>Pan-Pac Entomol</i> 87(1):57-61	INS	DEF	
2009	Choe, DH; Millar, JG; Rust, MK. Chemical signals associated with life inhibit necrophoresis in Argentine ants. <i>P Natl Acad Sci USA</i> 106:8251–8255	NE	NE	

2008	Morgan, ED. Chemical sorcery for sociality: Exocrine secretions of ants (Hymenoptera: Formicidae). <i>Myrmecol News</i> 11:79–90	ANT	ExS	
2008	Riddick, EW; Brown, AE; Chauhan, KR. <i>Harmonia axyridis</i> adults avoid catnip and grapefruit-derived terpenoids in laboratory bioassays. <i>B Insectol</i> 61:81–90	DEF	OtSp	
2007	Lu, Y; Zhao, YP; Wang, ZC; Chen, SY; Fu, CX. Composition and antimicrobial activity of the essential oil of <i>Actinidia macrosperma</i> from China. <i>Nat Prod Res</i> 21:227–233	NS	OtSp	
2006	Chang, MY; Hsu, RT; Lin, CY; Chen, BF; Lin, ST; Chang, NC. Formal synthesis of (+/-)-hop ether, (+/-)-isoboonein, and (+/-)-iridomyrmecin. <i>Heterocycles</i> 68:271–282	AL, DEF	SYN	
2006	Schollhorn, B; Mulzer, J. Stereocontrolled formation of three contiguous stereogenic centers by free radical cyclization – Synthesis of (+)-iridomyrmecin and (-)-isoiridomyrmecin – Formal synthesis of delta-skythantine. <i>Eur J Org Chem</i> 2006 (4):901–908	ANT	SYN	
2006	Zhao, YP; Wang, XY; Wang, ZC; Lu, Y; Fu, CX; Chen, SY. Essential oil of <i>Actinidia macrosperma</i> , a catnip response kiwi endemic to China. <i>J Zhejiang Univ – Sc B</i> 7:708–712	NS	OtSp	
2005	Davidson, DW; Clark, DA; Jones, TH. Gastral exocrine products of a myrmicine ant strongly overlap pygidial gland products of Dolichoderinae. <i>Insect Soc</i> 52:305–308	AL, DEF	ExS	Pbic
2000	Petersen, G; Matthiesen, C; Francke, W; Wyss, U. Hyperparasitoid volatiles as possible foraging behaviour determinants in the aphid parasitoid <i>Aphidius uzbekistanicus</i> (Hymenoptera: Aphidiidae). <i>Eur J Entomol</i> 97:545–550	DEF	OtSp	Auzb
1999	Hodgson, DM; Gibbs, AR; Drew, MGB. Mechanism and applications of lithium amide-induced asymmetric rearrangements of 4-substituted and 4,4-disubstituted cyclopentene oxides to cyclopentenols. <i>J Chem Soc Perk T 1</i> 1999: 3579–3590:	NS	SYN	
1998	Billen, J; Morgan, ED. Pheromone Communication in social insects: sources and secretions. In “Pheromone Communication in Social Insects: Ants, Wasps, Bees and Termites (Vander Meer RK, Breed MD, Espelie KE, Winston ML, eds) Westview Press, Boulder, pp 3-33	AL	ExS	
1998	Horikawa, T; Norimine, Y; Tanaka, M; Sakai, K; Suemune, H. Synthesis of optically active 9 α [3.3.0]octane skeleton using transannular reaction. <i>Chem Pharm Bull</i> 46:17–21	NS	SYN	
1997	Chiu, JY; Chiu, CT; Chang, NC. Total synthesis of (+/-)-patriscabrol and (+/-)-boschnialactone. <i>J Chin Chem Soc– Taip</i> 44:59–63	NS	SYN	
1997	Hemp, C; Dettner, K. Morphology and chemistry of mesothoracic glands in anthicid beetles (Coleoptera : Anthicidae). <i>Entomol Gen</i> 22:97–108	DEF	OtSp	Fges, Fped, Mter
1997	Hodgson, DM; Gibbs, AR. An enantioselective epoxide rearrangement – Claisen rearrangement approach to prostaglandins and (+)-iridomyrmecin. <i>Synlett</i> 1997 (6):657–658	NS	SYN	
1997	Nangia, A; Prasuna, G; Rao, PB. Synthesis of cyclopenta[c]pyran skeleton of iridoid lactones. <i>Tetrahedron</i> 53:14507–14545	DEF, INS, ANT	SYN	
1997	Stepanov, AV; Veselovsky, VV. Stereocontrolled synthesis of (+)- and (-)-iridomyrmecin from citronellene enantiomers. <i>Russ Chem Bull</i> 46:1606–1610	NS	SYN	
1996	Nangia, A; Prasuna, G. Studies on Horner-Wadsworth-Emmons reaction in base sensitive ketones: Synthesis of (-)-mitsugashiwalactone and formal synthesis of (+)-iridomyrmecin, (-)-isoiridomyrmecin and (+)-teucriumlactone. <i>Tetrahedron</i> 52:3435–3450	NS	SYN	
1996	Priano, M; Pavan, M. Chemical secretions of Formicidae (Hymenoptera, Formicidae). <i>Insect Social Life</i> 1:173–177	NS	ExS	
1995	Ohba, M; Haneishi T; Fujii, T. Syntheses of several cyclopentano-monoterpene lactones using 1,3-dioxin vinyllogous ester. <i>Chem Pharm Bull</i> 43:26–31	NS	SYN	
1994	Lee, E; Yoon, CH. Stereoselective favorskii rearrangement of carvone chlorohydrin – expedient synthesis of (+)-dihydronepetalactone and (+)-iridomyrmecin. <i>J Chem Soc Chem Comm</i> 4:479–481	NS	SYN	
1994	Völkl, W; Hübner, G; Dettner, K. Interactions between <i>Alloxysta brevis</i> (Hymenoptera, Cynipoidea, Alloxystidae) and honeydew-collecting ants: How an aphid hyperparasitoid overcomes ant aggression by chemical defense. <i>J Chem Ecol</i> 20:2901–2915	NS	OtSp	Abre
1993	Sakail, K. Chiral rhodium complex-catalyzed asymmetric cyclization and its application to the synthesis of natural-products. <i>J Syn Org Chem Jpn</i> 51:733–743	NS	SYN	
1992	Agnel, G; Owczarczyk, Z; Negishi, E. Diastereoselective zirconocene-promoted bicyclization-carbonylation of allylically methyl-substituted enynes – synthesis of (+)-iridomyrmecin. <i>Tetrahedron Lett</i> 33:1543–1546	NS	SYN	
1992	Kigawa, M; Tanaka, M; Mitsuhashi, H; Wakamatsu, T. Synthesis of iridolactones isolated from silver vine. <i>Heterocycles</i> 33:117–120	NS	SYN	
1992	Yokoyama, Y; Tsuchikura, K. Doubly allylic strain – controlled diastereoselective intramolecular Michael addition and a synthesis of (+/-)-iridomyrmecin. <i>Tetrahedron Lett</i> 33(20):2823–2824	NS	SYN	
1991	Simon, T; Hefetz, A. Trail-following responses of <i>Tapinoma simrothi</i> (Formicidae, Dolichoderinae) to pygidial gland extracts. <i>Insect Soc</i> 38:17–	TR, AL	TR	Tsim

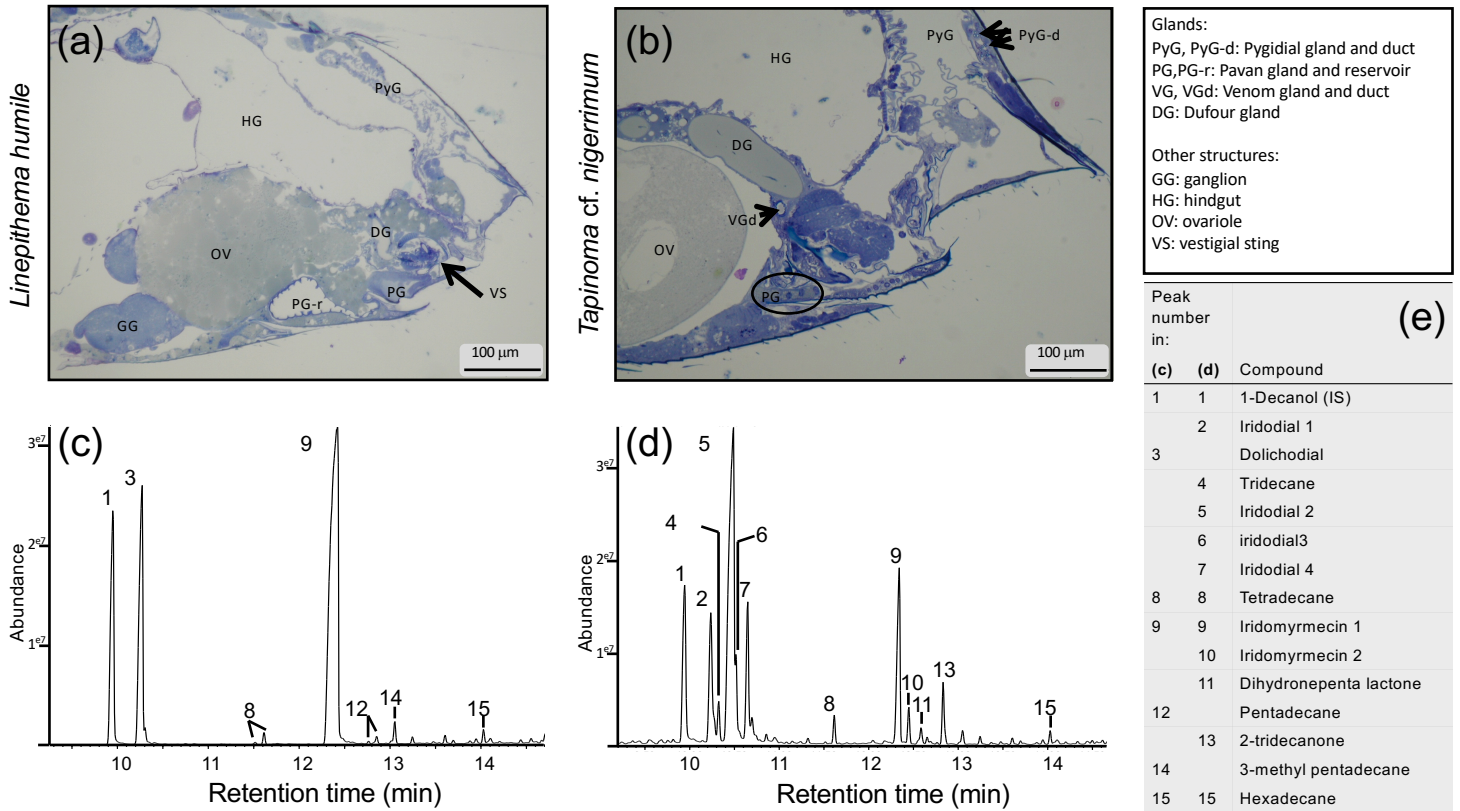
25				
1989	Wang, TF; Yang, CF. Baeyer-Villiger oxidation of bicycloheptanone to cyclopentapyranone – a novel synthesis of iridomyrmecin, isoiridomyrmecin, and boschnialactone. J Chem Soc Chem Comm 24:1876–1878	DEF	SYN	
1987	Tomalski, MD; Blum, MS; Jones, TH; Fales, HM; Howard, DF; Passera, L. Chemistry and functions of exocrine secretions of the ants <i>Tapinoma melanocephalum</i> and <i>Tapinoma erraticum</i> . J Chem Ecol 13:253–263	AL, DEF	ExS	Terr
1986	Oppolzer, W; Jacobsen, EJ. Enantioselective syntheses of (+)-alpha-skytanthine, (+)-delta-skytanthine and (+)-iridomyrmecin by an intramolecular magnesium-ene reaction. Tetrahedron Lett 27:1141–1144	NS	SYN	
1984	Attygalle, AB; Morgan, ED. Chemicals from the glands of ants. Chem Soc Rev 13:245–278	INS	ExS	Inip, Ipru, Dsca
1984	Cavill, GWK; Robertson, PL; Brophy, JJ; Duke, RK; McDonald, J; Plant, WD. Chemical ecology of the meat ant, <i>Iridomyrmex purpureus</i> sens. Strict. Insect Biochem 14:505–513	NS	ExS	Ipur
1983	Hefetz, A; Lloyd, HA. Identification of new components from anal glands of <i>Tapinoma simrothi pheonicium</i> . J Chem Ecol 9:607–613	NS	ExS	Tsim
1982	Cavill, GWK; Robertson, PL; Brophy, JJ; Clark, RD; Orton, CJ; Plant, WD. Defensive and other secretions of the Australian cocktail ant, <i>Iridomyrmex nitidiceps</i> . Tetrahedron 38:1931–1938	DEF	DEF	Inip
1981	Blum, MS. Chemical defenses of arthropods. 9. Lactones, pp. 239-246. Academic Press, Inc (London). ISBN 0-12-108380-2	INS	DEF	
1981	Grieco, PA; Srinivasan, CV. Stereochemical consequence of the coupling of lithium dimethylcuprate with a cyclopentenyl allylic lactone - total synthesis of dl-iridomyrmecin. J Org Chem 46:2591-2593	NS	SYN	
1981	Van Vorhis Key, SE; Gaston, LK; Baker, TC. Effects of gaster extract trail concentration on the trail following behaviour of the Argentine ant, <i>Iridomyrmex humilis</i> (Mayr). J Insect Physiol 27:363–370	INS	TR	
1980	Cavill, GWK; Davies, NW; McDonald, FJ. Characterization of aggregation factors and associated compounds from the Argentine ant, <i>Iridomyrmex humilis</i> . J Chem Ecol 6:371–384	DEF	ExS	
1980	El-Naggar, LJ; Beal JL. Iridoids. A review. Journal of Natural Products 43(6):649-707	DEF	ExS	
1979	Smith, RM; Brophy, JJ; Cavill, GWK; Davies, NW. Irididials and nepetalactone in the defensive secretion of the coconut stick insects, <i>Graeffea crouani</i> . J Chem Ecol 5:727–735	NS	OtSp	
1978	Blum, MS; Hermann, HR. Venoms and venom apparatuses of the Formicidae: Dolichoderinae and Aneuretinae. In Arthropod venoms, pp 871-894. Ed Bettini Handbook of Experimental Pharmacology	INS	DEF	
1978	Yamada, Y; Sanjoh, H; Iguchi, K. Synthesis of (+/-)-iridomyrmecin from the biogenetic precursor. Chem Lett 7:1405–1406	NS	SYN	
1977	Wheeler JW, Olagbemiro T, Nash A, Blum MS. Actinidine from the defensive secretions of dolichoderine ants. J Chem Ecol 3:241–244	DEF	DEF	Cono
1976	Cavill, GWK, Houghton, E, McDonald, FJ, Williams, PJ. Isolation and characterisation of dolichodial and related compounds from the Argentine ant, <i>Iridomyrmex humilis</i> . Insect Biochem 6:483–490	DEF	ExS	
1975	Lieberburg, I; Kranz, PM; Seip, A. Bermudian ants revisited: the status and interaction of <i>Pheidole megacephala</i> and <i>Iridomyrmex humilis</i> . Ecology 56(2):473-478	INS	DEF	
1975	Matthews, RS; Whitesell, JK. Transannular cyclizations. Stereoselective synthesis of cyclopentanoid monoterpenes. J Org Chem 40(22):3312-3313	INS	SYN	
1974	Cavill GWK, Houghton E. Volatile constituents of the Argentine ant, <i>Iridomyrmex humilis</i> . J Insect Physiol 20:2049–2059	DEF	ExS	
1971	Cavill, GWK; Clark, DV. Ant secretions and cantharidin. In Naturally occurring insecticides. pp. 271-305. Ed Marcel Dekker	INS	INS	
1970	Cavill, GWK. Chemistry of some insect secretions. Liversidge Research Lecturer No. 18 – School of Chemistry, The University of New South Wales, Kensington, N.S.W. 2033. Pp 5-18	INS, DEF	ExS	
1969	Blum, MS. Alarm pheromones. Annu Rev Entomol 14:57–80	AL	AL	
1968	McGurk, DJ; Frost, J; Waller, GR; Eisenbraun, EJ; Vick, K; Drew, WA; Young, J. Iridodial isomer variation in Dolichoderine ants. J Insect Physiol 14:841–845	DEF	CH	Ipru
1967	Cavill, GWK, Clark, DV. Insect venoms, attractants, and repellents – VIII. Isidihydronepetalactone. J Insect Physiol 13:131–135	DEF	ExS	
1967	Overberber, GC; Kaye, H. Optical rotatory dispersion and conformation of some optically active epsilon-caprolactones. J Am Chem Soc 89(22):5646-5649	NS	CH	
1966	Eisner, T; Meinwald, J. Defensive secretions of Arthropods. Science 153:1341–1350	DEF	DEF	
1965	Sakan, T; Isoe, S; Hyeon, SB; Katsumura, R; Maeda, T; Wolinsky, J; Dickerson, D; Slabaugh, M; Nelson, D. The exact nature of matatabilactone and the terpenes of <i>Nepeta cataria</i> . Tetrahedron Lett 6(46):4097-4102	NS	CH	

1965	Wolinsky, J; Gibson, T; Chan, D; Wolf, H. Stereospecific syntheses of iridomyrmecin and related iridolactones. <i>Tetrahedron</i> 21:1247–1261	DEF, INS, ANT	SYN	
1964	McConnell, JF; Mathieson, AM; Schoenborn, BP. The crystal structure of monoterpene iridomyrmecin at -150°C. <i>Acta Cryst</i> 17:472–477	NS	CH	
1964	Sisido, K; Isida, T; Utimoto, K. A synthesis of iridomyrmecin. <i>J Org Chem</i> 29:3361–3365	NS	SYN	
1963	Falbe, J; Weitkamp, H; Korte, F. Zur synthese bicyclischer lactone vom typ des D,L-iridomyrmecins. <i>Tetrahedron</i> 19:1479–1482	NS	SYN	
1962	Roth, LM, Eisner, T. Chemical defences of arthropods. <i>Annu Rev Entomol</i> 7:107–136	DEF, INS	DEF	
1962	Korte, F; Kochen, W; Ludwig, G; Rechmeier G; Schreiber HJ; Stiasni M; Vogel J. 14C-markierte Insektizide aus der Reihe der halogenierten Kohlenwasserstoffe und des Iridomyrmecins. <i>Angew Chem – Ger Edit</i> 74:503	INS	INS	
1962	Korte, F; Schreiber HJ. Insektizide im Stoffwechsel, IV. Iridomyrmecin-[3-14C]. <i>Liebigs Ann Chem</i> 656:145–148	INS	SYN	
1962	McConnell, JF; Mathieson, AM; Schoenborn, BP. Conformation of iridomyrmecin and isoiridomyrmecin. <i>Tetrahedron Lett</i> 10:445–448	NS	CH	
1961	Cavill, GWK; Hinterberger, H. The Chemistry of Ants. V. Structure and Reactions of Dolichodial. <i>Aust J Chem</i> 14:143–149	NS	CH	
1961	Dolejs, L; Mironov, A; Sorm, F. On terpenes. 121. Structure of bulnesol and stereochemistry of guaiol, nepetalinic acids and iridomyrmecins. <i>Collect Czech Chem Comm</i> 26:1015–1020	NS	CH	
1960	Cavill, GWK. The cyclopentanoid monoterpenes. <i>Reviews of Pure and Applied Chemistry</i> . 10(3):169-183	INS	ExS	
1960	Cavill, GWK; Hinterberger, H. The chemistry of ants. IV. Terpenoid constituents of some <i>Dolichoderus</i> and <i>Iridomyrmex</i> species. <i>Aust J Chem</i> 13:514–519	NS	CH	Dsca
1960	Dolejs, L; Mironov, A; Sorm, F. Structure of bulnesol stereochemistry of guaiol, nepetalinic acids and iridomyrmecins. <i>Tetrahedron Lett</i> 11:18–21	NS	CH	
1959	Clark, KJ; Fray, GI; Jaeger, RH; Robinson, R. Synthesis of D- and L- isoiridomyrmecin and related compounds. <i>Tetrahedron</i> 6:217–224	NS	SYN	
1959	Jaeger, RH; Robinson, R. The conversion of Deuterium-isoiridomyrmecin into Deuterium-iridomyrmecin <i>Tetrahedron Lett</i> 1(15):14-18	NS	CH	
1959	Korte, F; Falbe, J; Zschocke, A. Alpha-hydroxyalkyliden-lacton-umlagerung .9. Synthese des D,L-Iridomyrmecins und verwandter bicyclischer Lactone. <i>Tetrahedron</i> 6:201–216	INS, ANT	SYN	
1959	Sakan, T; Fujino, A; Murai, F; Busuga, n Y; Suzuui, A. The structure of Matatabilactone. <i>Bull Chem Soc</i> 32(10):1154-1155	NS	CH	
1959	Wilson, EO; Pavan, M. Glandular sources and specificity of some chemical releasers of social behavior in dolichoderine ants. <i>Psyche</i> 66:70–76	TR	TR	
1958	Clark, KJ; Fray, GI; Jaeger, RH; Robinson, R. Eine synthese des D- und L-Iso-Iridomyrmecins. <i>Angew Chem – Ger Edit</i> 70:704	NS	SYN	
1958	Clark, KJ; Fray, GI; Jaeger, RH; Robinson, R. Configuration of iridodial, isoiridomyrmecin and iridomyrmecin. <i>Chem & Industry</i> 45:1473	NS	CH	
1958	Korte, F; Falbe, J; Zschocke, A. Synthese des D,L-Iridomyrmecins und verwandter Lactone. <i>Angew Chem – Ger Edit</i> 70:704	NS	SYN	
1958	Pavan, M; Trave, R. Études sur les Formicidae. IV Sur le venin du Dolichodéride <i>T. nigerrimum</i> . <i>Insect Soc</i> 5:299–308	INS, AntB	DEF	
1958	Wendler, NL; Slates, HL. Studies in the Iridomyrmecin series - abnormal ring closure of a 1,6-keto aldehyde. <i>J Am Chem Soc</i> 80:3937–3939	NS	CH	
1957	Cavill, GWK; Locksley, HD. The chemistry of ants. II. Structure and configuration of iridolactone (isoiridomyrmecin). <i>Aust J Chem</i> 10:352–358	NS	CH	
1956	Cavill, GWK; Ford, DL; Locksley, HD. The chemistry of ants. I. Terpenoid constituents of some Australian <i>Iridomyrmex</i> species. <i>Aust J Chem</i> 9: 288–293	ANT, INS	ExS	
1955	Fusco, R.; Trave, R.; Vercellone, I. Ricerche sull'iridomirmecina, l'insetticida naturale secreto dalla <i>Iridomyrmex humilis</i> Mayr. <i>La Chimica e l'Industria</i> 37(4):251–259	INS	INS	
1955	Fusco R, Trave R, Vercellone A. La struttura dell'iridomirmecina. <i>La Chimica e l'Industria</i> 37:958-959	INS	CH	
1955	Pavan, M. Sull'attività fitoinibente della iridomirmecina su <i>Lupinus albus</i> . <i>Boll Soc Ital Biol Sper</i> 31:967–969	ANT, AntB	PH	
1955	Pavan, M; Baggini, A. Ricerche sull'attività fitoinibitrice dell'iridomirmecina su <i>Lupinus albus</i> . <i>Boll Zool</i> 22:393–404	INS	PH	
1955	Pavan, M; Ronchetti, G. Studi sulla morfologia esterna e anatomia interna dell' operaia di <i>Iridomyrmex humilis</i> Mayr e ricerche chimiche e biologiche sulla iridomirmecina. <i>Atti Soc It Sc Nat</i> 94:379–477	INS, AntB	PH	
1955	Pavan, M; Valcurone, ML. Antagonismo della iridomirmecina verso l'effetto oncogeno della colchicina e del gammaesano su <i>Lupinus albus</i> .	DEF	PH	

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1952	Pavan, M. Iridomyrmecin as insecticide. IX Int Congr Entomol Amsterdam 17-24 August 1951, 1: 321–327	INS, AntB	INS
1952	Pavan, M. Primo contributo sperimentale allo studio farmacologico della iridomirmecina. Arch Int Pharm Thér 89: 223–228.	AntB, INS	PH
1952	Pavan, M. Sugli antibiotici di origine animale. II. Ricerche personali. Boll Ist Mil 31(5-6):232-245	AntB, INS	ANT
1951	Pavan, M. Sull'attività insetticida della iridomirmecina. Mem Soc Ent It 30:107–132	INS	INS
1950	Pavan, M. Potere insetticida della iridomirmecina e significato della sostanza nella biologia di <i>Iridomyrmex humilis</i> Mayr (<i>Formica argentina</i>). La Ricerca Scientifica 20:1835–1855	INS	INS
1950	Zyka, J. New antibiotics, chloromycetin, aureomycin, and iridomyrmecin. Cas Cesk Lek 63(15):172-173	INS, AntB	ANT
1949	Pavan, M. Ricerche sugli antibiotici di origine animale. Nota riassuntiva	AntB	ANT
1948	Pavan, M; Nascimbene, A. Studi sugli antibiotici di origine animale. I. Su un principio antibiotico di <i>Iridomyrmex pruinosus humilis</i> Mayr. (nota prev.). Boll Soc Med Chir Pavia 62:193–197	ANT	ANT
1948	Pavan, M; Nascimbene, A. Studi sugli antibiotici di origine animale. X. Nuovi risultati sulla iridomirmecina . Boll Soc Med Chir Pavia 62:295–298	ANT	ANT



Supporting Information S3. *Linepithema humile* ants overlap temporally and spatially with amphibians Relative abundances over time of *Epidalea calamita* toadlets emerging from temporary ponds and (a) native ants or (b) *L. humile* ants. Invaded and uninvaded areas around ponds sampled in April May 2013 during amphibian emergence. Values represent the mean number (\pm SE) of toadlets per transect or ants per bait. Note the differences in axis scale between (a) and (b) regarding ants. (c) Mean (\pm SE) number of dead amphibians found along *L. humile* trails during the juvenile amphibian emergence period over three different seasons (May and June 2013, 2014, and 2018). (d, e, f) Examples of different phases of ant predation on amphibians: (d) ants attack *P. cultripres* toadlet; (e) freshly killed *H. meridionalis* covered by *L. humile*, around two hours after an attack; (f) skeleton of an *H. meridionalis* froglet, fewer than 12 h after an attack. Photo credits: Fernando Amor (d) and Elena Angulo (e,f).



Supporting Information S4. Identification of *Linepithema humile* ant venom. Longitudinal section of the abdomen of **a**, *Linepithema humile* and **b**, *Tapinoma cf. nigerrimum*. Partial chromatograms showing the iridodial/dolichodial iridomyrmecin complex of the pygidial glands of: **c**, *Linepithema humile* workers and **d**, *Tapinoma cf. nigerrimum* workers. **e**, List of compounds associated with the peaks in **c** and **d**. Iridomyrmecin and iridodials with different numbers are isomers. Note that the hydrocarbons may have originated from the cuticular intima lining the gland.