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Review

The Chemistry on Diterpenoids in 1975. Part-II

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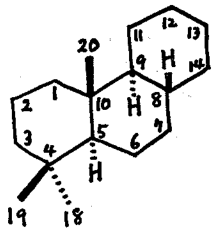
I. INTRODUCTION

This is one of a series of our annual reviews[1~12] on diterpenoids chemistry. The classification of the compounds is the same as that adopted in our reviews since 1969.

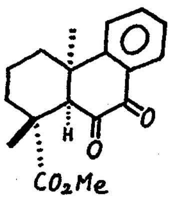
This review covers the literatures published between July and December 1975 and also omissions in part-I.

II. PODOCARPANE DERIVATIVES

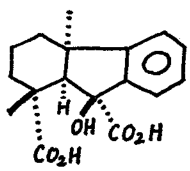


Podocarpane

The benzylic acid rearrangement of the dioxo ester **1** derived from abietic acid gave a gibberellane derivative **2**, whose stereochemistry was determined unequivocally.[13)]



(1)



(2)

A method for angular functionalized methylaton *via* bromocyclopropane **4**, which was obtained by the abnormal Reimer-Tiemann reaction of **3** with bromoform followed

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by cyclization, was reported.[14] The bromocyclopropane **4** has a high reactivity towards various nucleophiles to give the ring-opened products. Thus, variously functionalized methyl group can be introduced into the angular position by a choice of nucleophiles. (Chart 1)

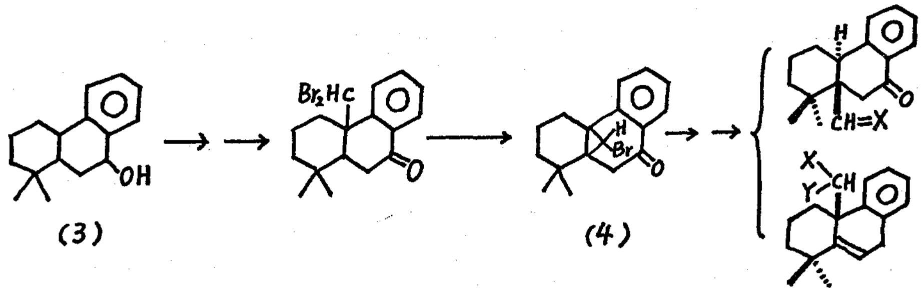


Chart 1

Reactions of methyl dehydroabietate derivatives **5** and **6** with aluminum chloride were examined.[15] Epimerization at C–10 and/or deisopropylation might depend on the hydroxy group on the aromatic ring. The results are summarized in Chart 2.

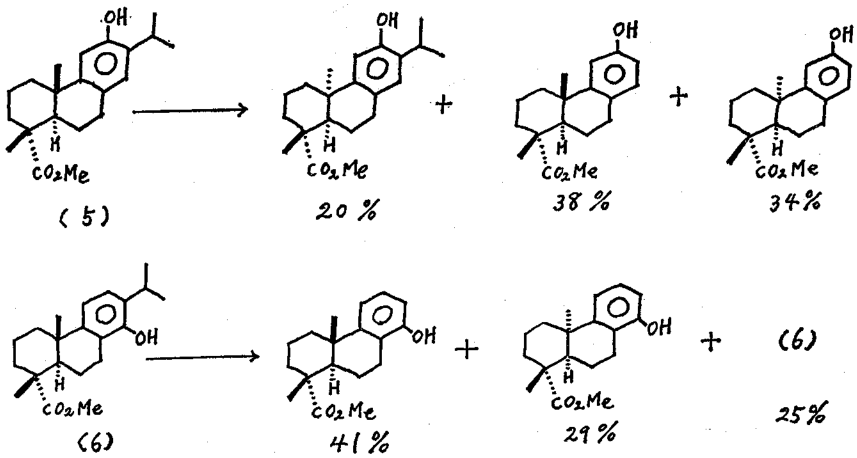
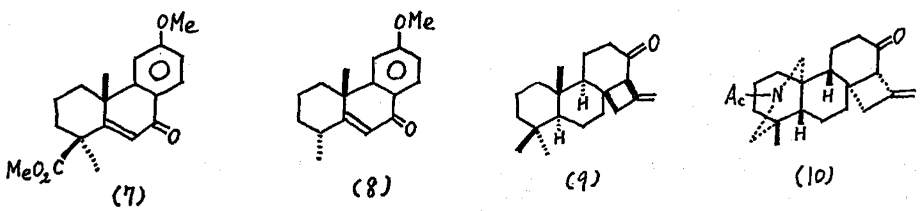


Chart 2

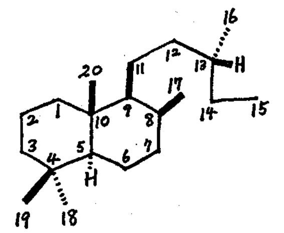
Selective cleavage of β-keto and vinylogous β-keto esters by 3-quinuclidinol was published.[16] An application of the reaction to the podocarpane derivative **7** giving rise to **8** was noted.



The stereochemistry of the products (*e.g.* **9** and **10**) from the photoaddition between podocarpane derivatives having α, β-unsaturated ketone moiety and olefins was discussed by the relative stability of the excited state.[17]

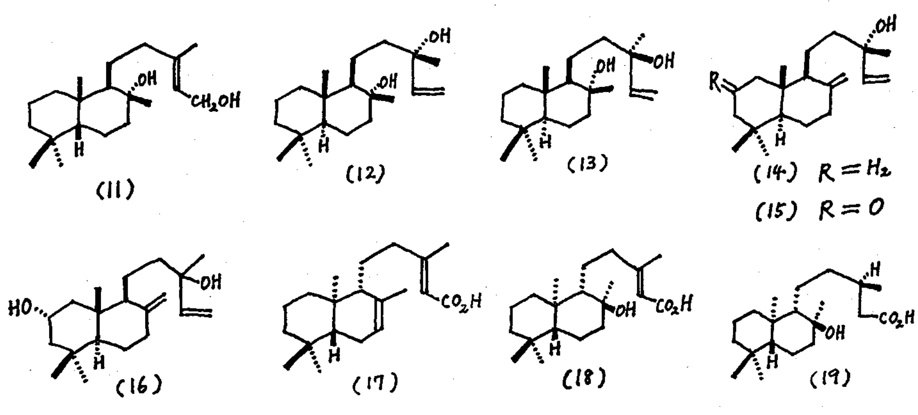
Carbon-13 nuclear magnetic resonance spectra of a series of ring C substituted podocarpane derivatives were reported.[18]

III. LABDANE DERIVATIVES

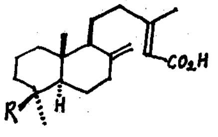


Labdane

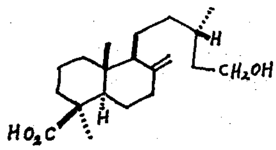
A new diterpenoid, vulgarol (**11**), was isolated from *Marrubium vulgare*.[19] The major metabolite of *Nicotiana glutinosa* was identified as a mixture of **12** and **13**, and the minor metabolite of this species was tentatively assigned the structures **14**, **15**, and **16**. Their potential technological significance is also discussed.[20] Three *ent*–labdane type diterpenes **17**, **18**, and **19** were isolated from *Hymenea coubaril*.[21]



Agathic acid (**20**), agatholic acid (**21**) and imbricatolic acid (**22**) as well as abietane type diterpene, sugiol, were isolated from *Araucaris angustifolia*.[22] A number of labdane oxides, 18-deoxylazarcardenasol (**23**) and 18-benzoxylazarcardenasol (**24**) from *Palafoxia rosea*,[23] gomeraldehyde (**25**), 13-epigomeraldehyde (**26**), gomeric acid (**27**) and 13-epigomeric acid (**28**) from *Sideritis gomerae*,[24] and barbatol (**29**) from *S. arborescens*,[25] were isolated and characterized. *ent*-Labd-13-ene-8α, 15-diol was also isolated from *S. gomerae*.[24]



(20) R = CO_2H
(21) R = CH_2OH



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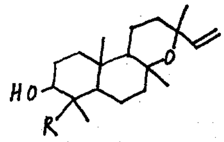
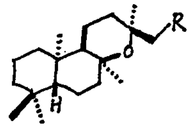
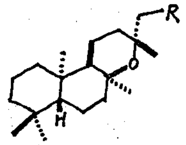


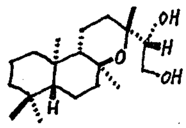
(23) R = Me
(24) R = CH_2OCOPh



(25) R = CHO
(27) R = CO_2H

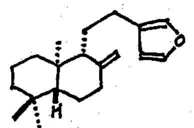


(26) R=CHO
(28) R= CO_2H



(29)

Two diterpenes, **30** and **31**, were isolated from *Pamburus missionis*.[26] The crystal and molecular structures of two highly oxygenated labdane type diterpenes, lasiocoryin (**32**)[27] and nepetaefolin (**33**),[28] were determined by X-ray analyses.



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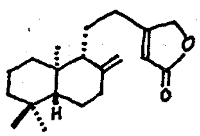

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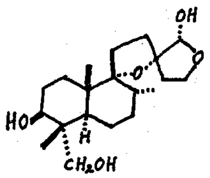

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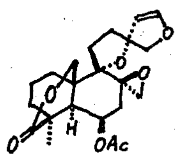


(33)

Chemical conversion of manool (**14**) into anticopalic acid (**34**) has been reported.[29] The outline is shown in Chart 3. Manool (**14**) was also converted into beyerane derivatives,[30] which is described in section X.

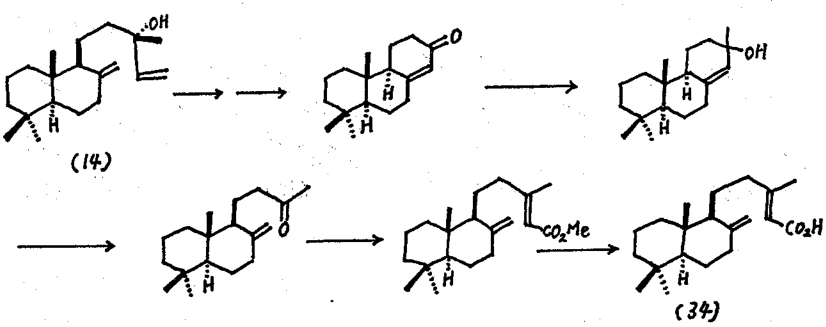
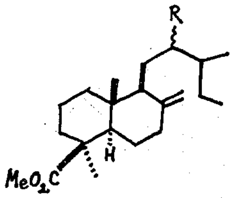
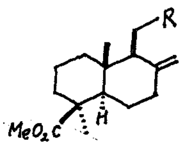


Chart 3

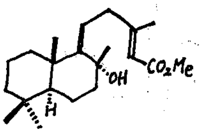
A formal total synthesis of methyl 12S- and 12R-hydroxylabd-8(17)-en-19-oates, (**35**) and (**36**) respectively, isolated from *Juniperus phoenicea*,[31] has been achieved.[32] The labdane side chain was formed by the nucleophilic addition of s-butyllithium to the bicyclic acid **37** or the aldehyde **38**, prepared from podocarpic acid.



(35) R = α-OH
(36) R = β-OH



(37) R = CO2H
(38) R = CHO



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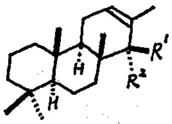
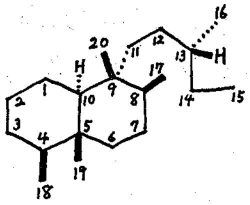


(40) R' = CO2Me
R2 = H
(41) R' = H
R2 = CO2Me

Oxidation of sclareol (**13**) led to a complex mixture. The structure of each component was characterized.[33] Acid catalyzed cyclization of methyl anticopalate (**39**) and methyl Z-anticopalate gave rise to **40** and its 14-epimer **41**.[34] Methyl isoanticopalate (**40**) was selectively attacked from the α-side on hydroboration, PtO_2–H_2 reduction, and OsO_4 oxidation, whereas no selectivity was recognized on its 14-epimer (**41**).[35]

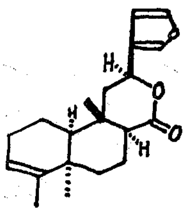
Studies on carbon-13 NMR spectra of several labdane derivatives were published.[36]

IV. CLERODANE DERIVATIVES



Clerodane

Diterpenoid **42** was isolated from *Evodia floribunda*.[37] Columbin (**43**) and its C–8 epimer, isocolumbin were isolated from *Dioscoreophyllum cumminsii*.[38]



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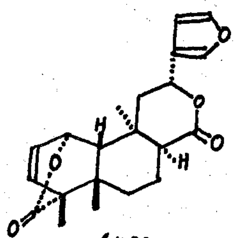

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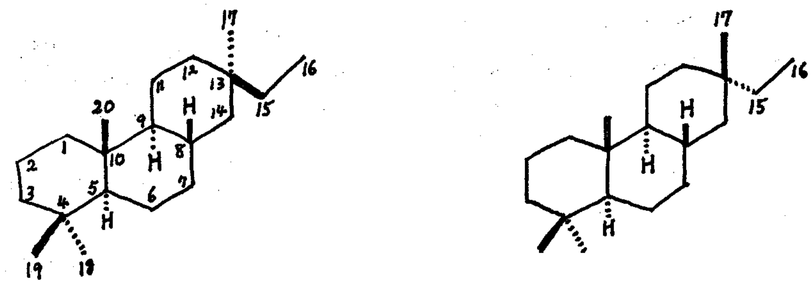
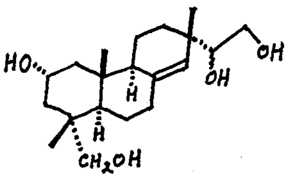
V. PIMARANE AND ISOPIMARANE DERIVATIVES



Pimarane and Isopimarane

The structure of hallol isolated from *Podocarpus hallii* was determined as **44**.[39] Isopimarane type diterpenes, **45** and **46**, as well as kaurane derivatives were isolated from *Siegesbeckia pubescens*.[40] *Sideritis reverchonii* was found to contain eight known diterpenoids including lagascol (**47**) and lagascatriol (**48**) together with a new diterpenoid belonging to beyerane type.[41]



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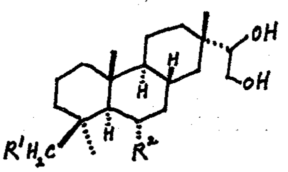
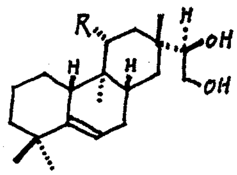


(45) R¹=OH ; R²=H

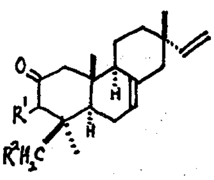
(46) R¹=H ; R²=glucose



(47) R=H

(48) R=OH

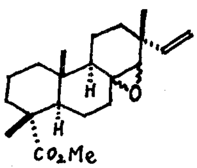
Reduction of **49** with Zn–AcOH, Li–NH_3, or Me_2CuLi gave **50**, whereas **51** was obtained together with **50** by Ca–NH_3 reduction of **49**.[42] Epoxidation of methyl sandaracopimarate gave the α- and β-epoxides **52** in 1 : 1 ratio.[43] The tetracyclopentadecene **53** was prepared by tosylation of 3-oxo-19-hydroxyisopimaradiene (**54**) followed by cyclization with t-BuOK-t-BuOH.[44]



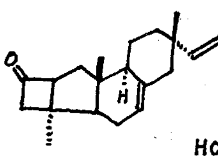
(49) R¹=R²=OAc

(50) R¹=H; R²=OAc

(51) R¹=R²=H



(52)



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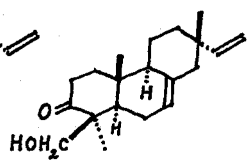
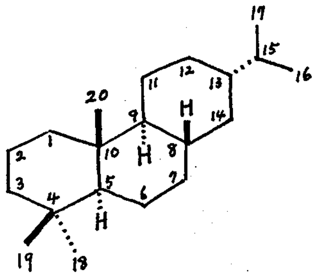


(54)

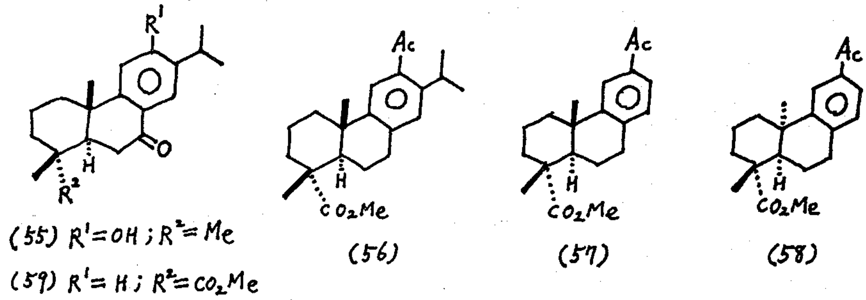
In a review titled "Growth regurating substances of plant origin", a number of diterpenoids including pimarane type are described.[45]

VI. ABIETANE DERIVATIVES



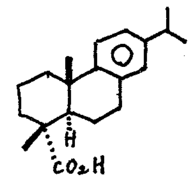
Abietane

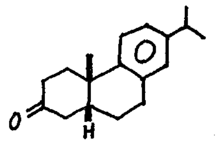
Sugiol (**55**) was isolated from *Araucaria angnstifolia*[22] and *Libocedrus bidwillii*.[46]

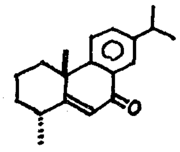


Reactions of methyl dehydroabietate derivatives having electron-donating group at aromatic C-ring with aluminum chloride were examined.[15] (See section II, Chart 2.) Reaction of 12-acetyl ester **56** with aluminum chloride gave predominant *trans*-isomer **57** accompanied by the *cis*-isomer **58**. In the other case of reactions of methyl dehydroabietate derivatives having electron-withdrawing group, 7-oxo ester **59** did not react even under the drastic conditions. But 7-oxo ester having a hydroxyl or a methoxyl group at 12 or 14-position was deisopropylated to give only the respective *trans*-deisopropyl isomer.[47]

Conversion of dehydroabietic acid (**60**) to a steroid skeleton was attempted. Synthesis of the 3-oxo compound **61** having a steroid type A ring was successfully completed from **62** or **63** derived from **60** *via* intermediates **64** and **65**.[48,49]


(60)


(61)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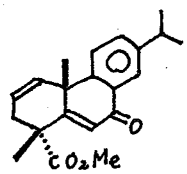
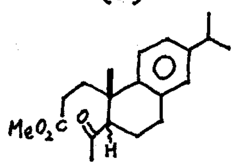
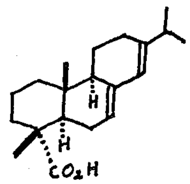

(63)


(64) 5β-H
(65) 5α-H


(66)

Compound **1** derived from abietic acid (**66**) was converted into compound **2**.[13] (See Section II.) A ring substitution of hydrofluorene compound derived from abietic acid (**66**) was accomplished.[50] (See also Section XI.)

Kaurene and 13β-kaur-16-ene (phyllocladene) were synthesized from abietic acid (**66**).[51] (See Section IX.) The phenacylidene ester **67** underwent novel rearrangements on refluxing with an excess of aluminum chloride to afford **68** and **69** in 57 and 5% yields.[52] (See Chart 4.)

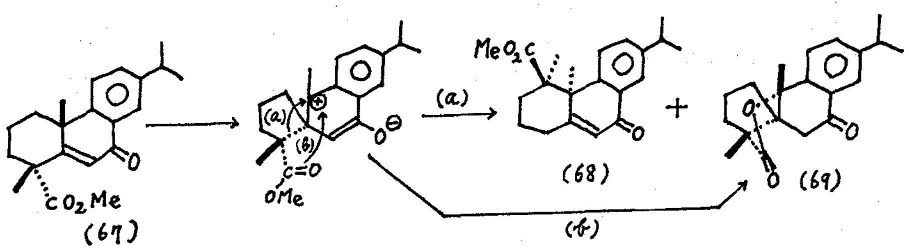
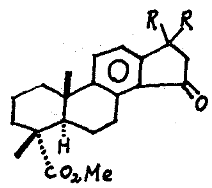
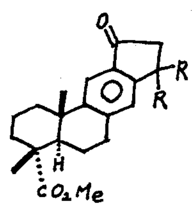


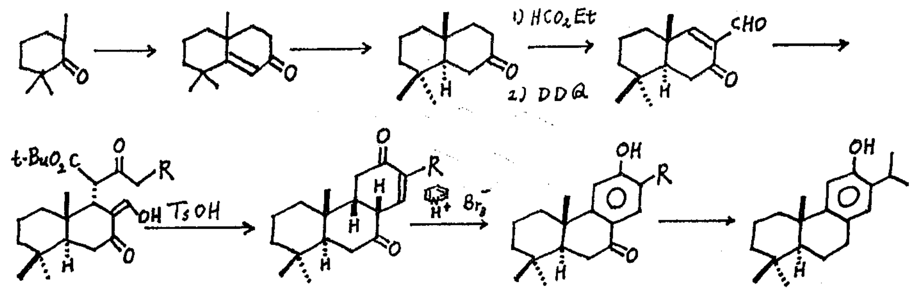
Chart 4

The steroidal D-rings (**70** and **71**), along with **72** and **73**, were synthesized by the use of a part or whole of the carbon units of the isopropyl group of abietic acid (**66**).[53]


(70) R=H
(71) R=Me


(72) R=H
(73) R=Me

Total synthesis of *rac*-sugiol (**55**), *rac*-nimbiol (**74**), and *rac*-ferruginol (**75**) was achieved.[54] The sequence is shown in Chart 5.



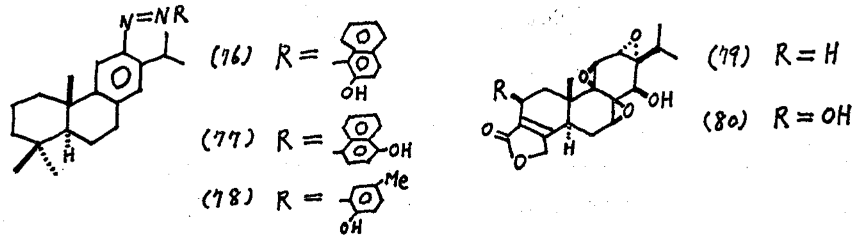
R= CH(Me)2 or Me

(55) R= CH(Me)2
(74) R = Me

(75)

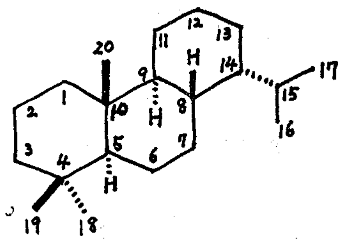
Chart 5

The azodehydroabietic acids, **76**, **77**, and **78**, were prepared.[55] Treatment of abietyl ohloride with excess amines gave abietamides, which were reduced to abietylamines by $LiAlH_4$.[56] Abietic acid (**66**) was oxidized by passing oxygen at 30–150°.[57]



Antileukemic diterpenoid, triptolide (**79**) and tripdiolide (**80**) were cited in a short review article.[58] (See also Section VII.)

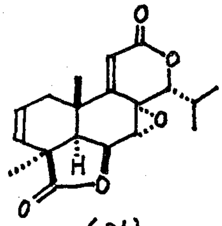
VII. TOTARANE DERIVATIVES



Totarane

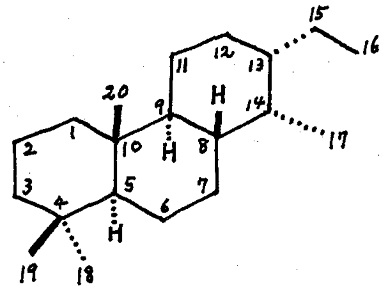
The structure of podolide (**81**), an antileukemic norditerpene dilactone isolated from *Podocarpus gracilior*, was determined by an X-ray analysis.[59]

A review on the growth regulating substances of plant origin, in which several totarane derivatives were cited, was published.[45] (See also Sections V and XV.) Also in the foregoing review,[58] several totaranes were cited.



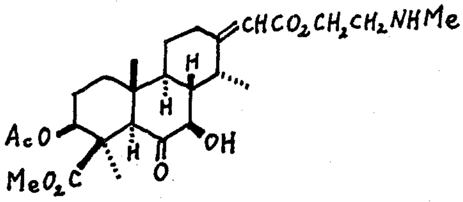
(81)

VIII. CASSANE DERIVATIVES



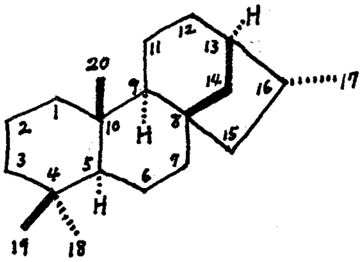
Cassane

The structure of 3β-acetoxynorerythrosuamine (**82**), a highly cytotoxic alkaloid from *Erythrophleum chlorostachys*, was determined.[60]



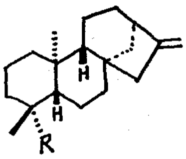
(82)

IX. KAURANE DERIVATIVES

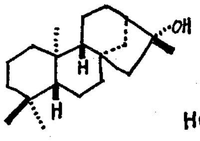


Kaurane

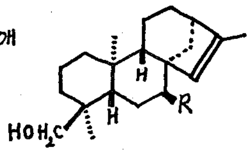
From *Cacalia bulbifera*, *ent*-16-kauren-19-ol (**83**), *ent*-16-kauren-19-al (**84**), *ent*-16–kauren-19-oic acid (**85**), and *ent*-kauran-16-ol (**86**) were isolated.[61] Sideridiol (**87**), and foliol (**88**) were isolated from *Sideritis chamaedryfolia*, and siderol (**89**) from *S. hyssopifolia*, and foliol (**88**), sidol (**90**), and linearol (**91**) from *S. luteola*.[62]



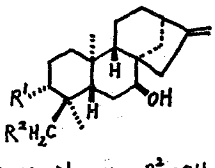
(83) R = CH_2OH
(84) R = CHO
(85) R = CO_2H



(86)

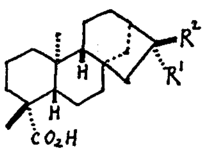


(87) R = OH
(89) R = OAc

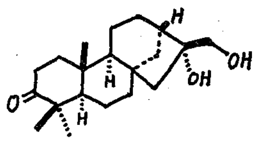


(88) R^1=OH ; R^2=OH
(90) R^1=OAc ; R^2=OH
(91) R^1=OH ; R^2=OAc

From *Coffea arabica* beans, *ent*-16-kauren-19-ol (**83**) was isolated.[63] The compounds **92**, **93**, and **94** were isolated from *Siegesbeckia pubescens*, and **93** and **94** showed antiinflammatory activity.[40] (See also Section V.) The structure and absolute configuration of calliterpenone was established as 3-oxo-13β-kaurane-16α,17-diol (**95**). This conclusion confirmed the structure proposed by Ahmad and Zaman, and the formula suggested previously by Chatterjee *et al.* was revised.[64]

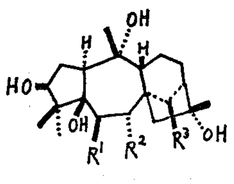


(92) R^1 = OH ; R^2 = CH_2OH
(93) R^1 = H ; R^2 = CH_2OH
(94) R^1 = H ; R^2 = CO_2H

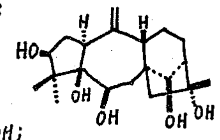


(95)

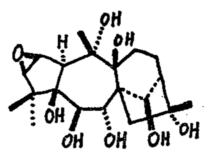
From the leaves of *Pieris japonica* were isolated deacylpieristoxin-B, pieristoxin-C, asebotoxin-I (**96**), graayanotoxin-II (**97**), graynotoxin-III (**98**), and two new diterpenes, pieristoxin F and pieristoxin G, to which the structures **99** and **100** were presumed, respectively.[65]



(96) R^1=OH; R^2=H; R^3=OCOEt
(98) R^1=OH; R^2=H; R^3=OH
(99) R^1=OAc; R^2=OH; R^3=OCOEt



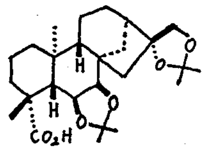
(97)



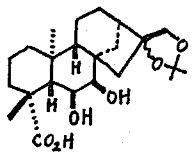
(100)

The mass spectra of carbon-13-labeled kaurene and some related compounds were investigated.[66]

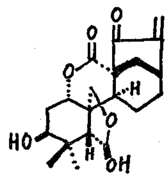
C–α and C–β, previously isolated from seed of *Phaseolus coccineus*, were shown respectively to be **101** and **102**.[67] (See also Section XI.) The synthesis of gibberellin A_{15} methyl ester and gibberellin A_{37} methyl ester from enmein (**103**), and their more direct total synthesis *via* the key intermediate **104** were published.[68] (See also Section XI.)



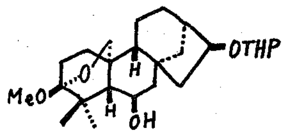
(101)



(102)

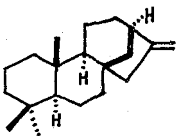


(103)

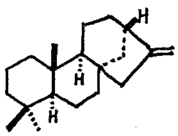


(104)

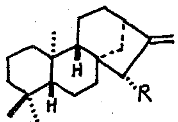
The full details of the previous communication of the synthesis of 16-kaurene (**105**) and 13β-kaur-16-ene (**106**) from abietic acid (**66**) were published.[51] (See also Section VI.) The formation of the allylic nitrates, **107** and **108**, in the reactions of both *ent*-16-kaurene (**109**) and *ent*-15-kaurene (**110**) with thallium trinitrate (TTN), and a [3, 3]-sigmatropic rearrangement between **107** and **108**, were published.[69]



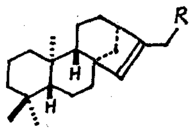
(105)



(106)

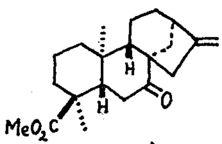


(107) R=ONO₂
(109) R=H

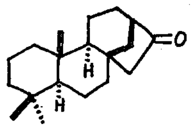


(108) R=ONO₂
(110) R=H

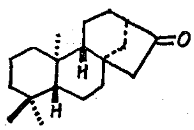
Benzilic acid-type rearrangement of lactone derived from compound **111** by treatment with oxygen in t-BuOK-t-BuOH gave a gibberellane derivative.[70] (See also Section XI.) Incubation of 17-norkauran-16-one (**112**) and *ent*-17-norkauran-16-one (**113**) with *Rhizopus nigricans* gave mixtures of mono- and dihydroxy-derivatives (**114–117** and **118–121**, respectively).[71]



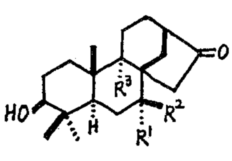
(111)



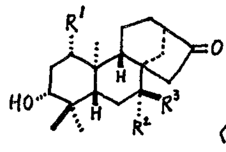
(112)



(113)

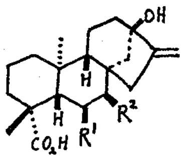


(114) R¹=R²=R³=H
(115) R¹=R³=H; R²=OH
(116) R¹=OH; R²=R³=H
(117) R¹=R²=H; R³=OH

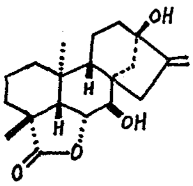


(118) R¹=R²=R³=H
(119) R¹=R³=H; R²=OH
(120) R¹=R²=H; R³=OH
(121) R¹=OH; R²=R³=H

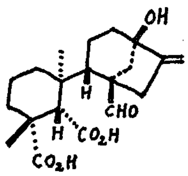
Steviol (**122**) was rapidly metabolized by the mutant B1–41a of *Gibberella Fujikuroi.* The initial product, *ent*-7α-hydroxy derivative **123**, was further metabolized to **124**, **125**, **126**, and several gibberellins.[72] (See also Section XI.)



(122) $R^1=R^2=H$
(123) $R^1=H$; $R^2=OH$
(124) $R^1=R^2=OH$



(125)



(126)

In *Gibberella fujikuroi* cultures, *ent*-[3β–^{3}H, 17–^{14}C]kaurene was converted to gibberellic acid with retention of the tritium label at the 3α-position. The evidence for the stereochemistry of 3-hydroxylation also permitted the stereochemistry of the 'proton-initiated' cyclization step in gibberellic acid biosynthesis to be deduced.[73] (See Chart 6).

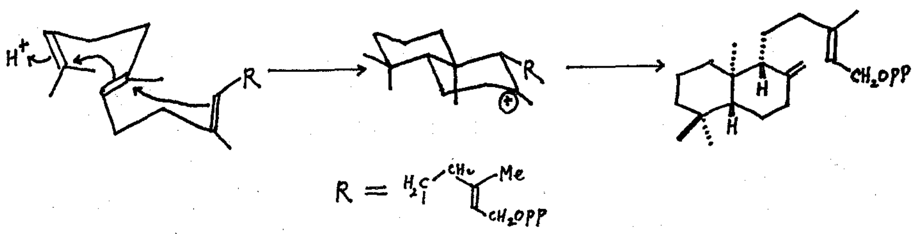
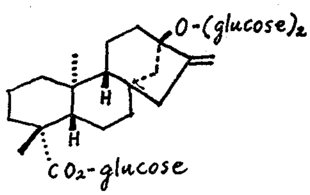


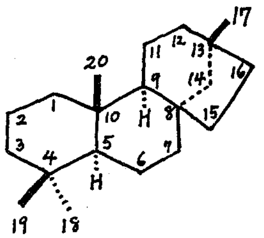
Chart 6

Thinchrograph analysis was established for simple quantitative analysis of stevioside (**127**) in *Stevia rebaudiana*,[74] and for the same purpose, the optimal condition for the enzymic hydrolysis of **127** and quantitative analysis of the resulting steviol (**122**) by gas chromatography were studied.[75]



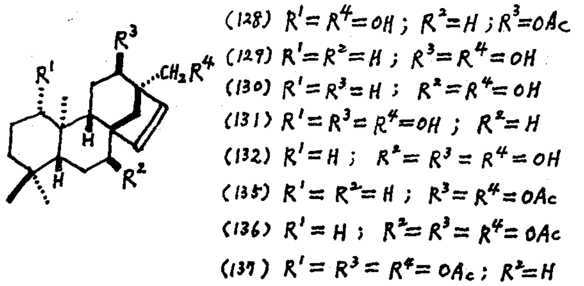
(127)

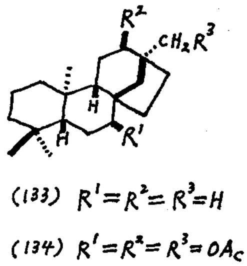
X. BEYERANE DERIVATIVES*



Beyrane

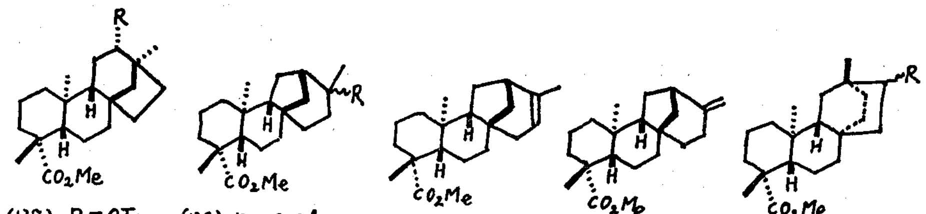
A new diterpenoid acetate was isolated from *Sideritis reverchonii* and its structure was estimated to be 12-acetyl jativatriol (*ent*-12α-acetoxy-15-beyerene-1β, 17-diol) (**128**). Furthermore, eight known diterpenoids including beyerene type compounds, tobarrol (**129**), benuol (**130**), jativatriol (**131**), and conchitriol (**132**), were also isolated.[41] A communication about analysis of ^{13}C NMR spectra of *ent*-beyerane (**133**), *ent*-7α, 12α, 17-triacetoxybeyerane (**134**), and *ent*-beyerene derivatives, **135**, **136**, and **137** were published. A good agreement between experimental and calculated ^{13}C chemical shifts for *ent*-beyerane (**133**) was shown.[76]





The solvolysis of the *ent*-methyl 12β-tolylsulfonyloxybeyeran-19-oate (**138**) was published. Acetolysis gave only products resulting from a single Wagner-Meerwein shift [the *ent*-14(13→12)*abeo*-beyeranes, **139**, **140**, **141**, and **142**], whereas formolysis and trifluoroacetolysis gave products from further rearrangement in addition to the starting beyerane system [formates of *ent*-12-methyl-17-noratisanol (**143**) and *ent*–beyeranol (**144**); trifluoroacetates of **143**, **144**, and **145**]. The rearrangements were discussed in terms of intermediate carbocation stabilities and lifetimes in the various solvents.[77] The X-ray analysis of the *p*-bromobenzoate (**146**) derived from the product **139** of the solvolysis of **138** was undertaken.[78]

* See also section IX, ref. 75.



(138) R=OTs (144) R=OH

(139) R=β-OAc (140) R=α-OAc (146) R=β-$OCOC_6H_4Br$

(141)

(142)

(143) R=α-OH (145) R=β-OH

Synthesis of beyerane type compounds through a photochemical cycloaddition of $\Delta^{8(14)}$ podocarpen-13-one to ethylene or 1, 2-dichloroethylene was reported.[30] The sequence is shown in Chart 7.

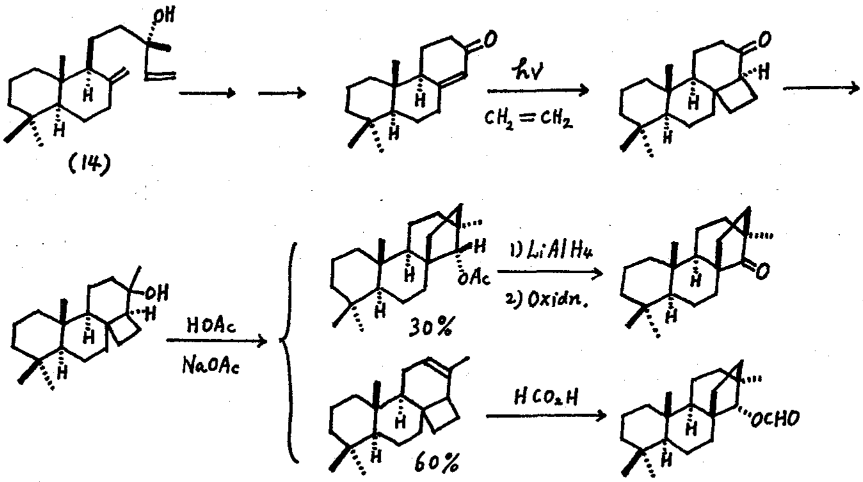
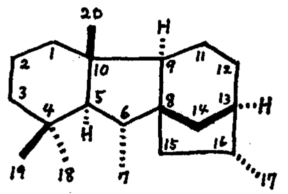


Chart 7

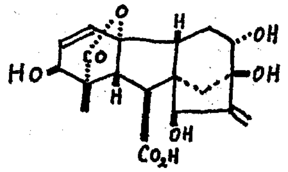
XI. GIBBERELLANE DERIVATIVES



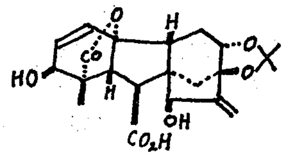
Gibberellane

Besides polyoxygenated *ent*-kauranes, occurrence of Gibberellins A_8, A_{17}, A_{20}, and A_{28} in *Phaseolus coccineus* seed was shown by GC–MS characterization of the hydrolysis products.[67] Isolation of gibberellins A_5 and A_{32}, and gibberellin

A_{32} acetonide from *Prunus persica* was reported[79] and the structures of gibberellin A_{32} and its acetonide were elucidated to be **147** and **148** respectively.[80] The latter compound was concluded to be an artifact product from gibberellin A_{32} in the isolation process.[80]



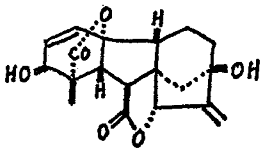
(147)



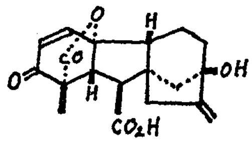
(148)

The ^{13}C NMR spectra of some C_{19} gibberellins were assigned and the labeling pattern of gibberellin A_3 from [2–^{13}C]mevalonic acid was confirmed.[81] The mass spectra of trimethylsilyl ethers of six gibberellin-β-glucopyranosyl ethers and five gibberellin-β-D-glucopyranosyl esters were discussed. The fragmentation patterns were shown to be affected by the structural variations of the aglycones.[82]

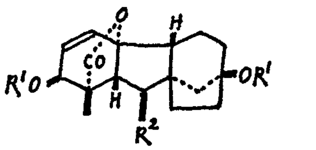
It was shown that the lactone ring of gibberellin A_3 was destroyed by gamma-ray irradiation in dilute solution, whereas the basic gibberellane skeleton remained intact.[83] Oxidation of gibberellin A_3 by MnO_2 gave lactone **149**. 3-Dehydrogibberellin A_3 (**150**) and its methyl ester were shown to be subject to Michael addition at C–1.[84] Partial synthesis of gibberellin-A_3-(7)-aldehyde (**152**) from 7-alcohol **151** was carried out by its oxidation with N-chlorosuccinimid-dimethylsulfoxide complex at $-25°$ to aldehyde followed by alkaline hydrolysis.[85] The alcohol (**151**) was obtained together with carboxylic acid **153** by $NaBH_4$ reduction of a dimeric anhydride **154** which was derived from **153** by dehydration with DCC.[86]



(149)



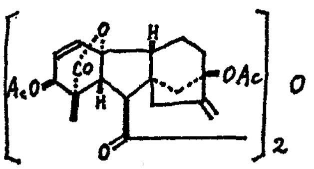
(150)



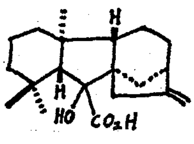
(151) $R^1 = Ac$; $R^2 = CH_2OH$

(152) $R^1 = H$; $R^2 = CHO$

(153) $R^1 = Ac$; $R^2 = CO_2H$



(154)



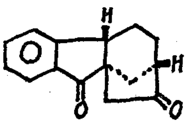
(155)

3-Dehydrogibberellin A_3 (**150**) upon $n \rightarrow \pi^*$-excitation of the enone chromophore was transformed in good yield to the corresponding ring A phenolic acid. The corresponding methyl ester under the same UV-irradiation conditions underwent intermolecular cycloaddition leading to two dimerization products. For explanation of this divergent crystal-controlled photoreactivity an X-ray analysis of **150** was performed, and the molecular packing determined.[87]

As described in Section II, the stereochemistry of the hydroxy diacid **2**, which was obtained by the benzylic acid rearrangement of the dioxo ester **1**, was determined.[13] Moreover, the rearranged compound **2** and its dimethyl ester were concluded to have a nonsteroidal form.[13]

Several hydrofluorenes with A-ring substituent were synthesized from l-abietic acid.[50]

The gibberellane derivative **155** was prepared starting from epicandicandiol using benzilic acid-type rearrangement as a key step.[70] A synthesis of *rac*-compound **156** starting from methyl *p*-hydroxybenzoate was reported.[88] The 2-carboethoxymethyl-6-methoxy-indenone (**157**) was synthesized in good yield. Diels-Alder addition of **157** to 1, 3-butadiene afforded compound **158**. The corresponding acid **159** was cyclized to **160**, which on catalytic hydrogenation gave **161**.[89]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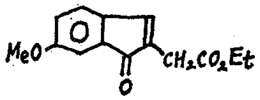
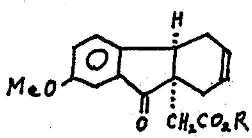
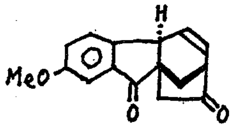

(157)


(158) R = Et
(159) R = H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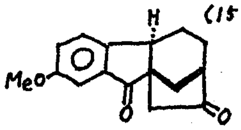
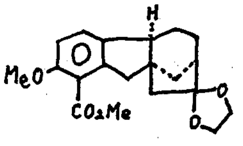
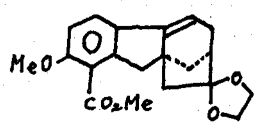

(161)

The synthesis from suitable indane derivatives of tetracyclic compounds **162** and **163**, possible intermediates for the total synthesis of gibberellin A_4, was published.[90]


(162)


(163)

The syntheses of gibberellin A_{15} methyl ester (**164**) and gibberellin A_{37} methyl ester (**165**) from enmein (**103**) and their total syntheses from the relay compound **104**[91] which has been derived from 5-methoxy-2-tetralone (**166**) were published.[68] The sequence is shown in Chart 8.

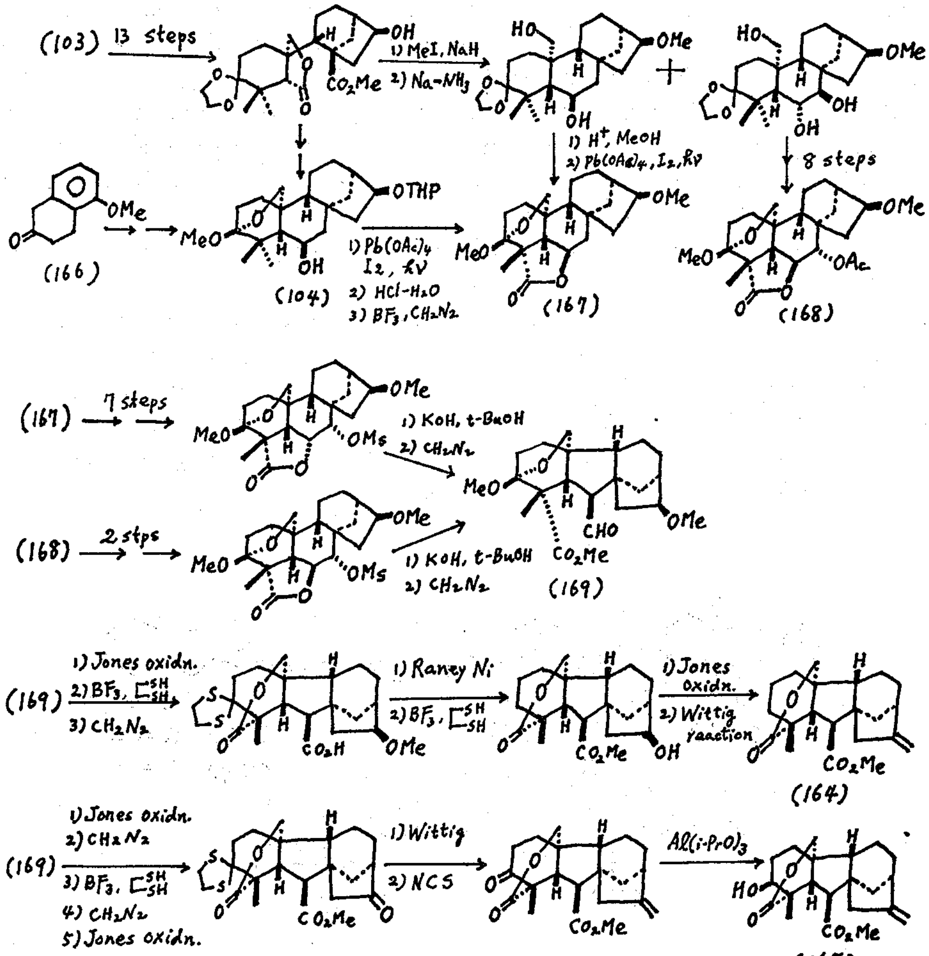
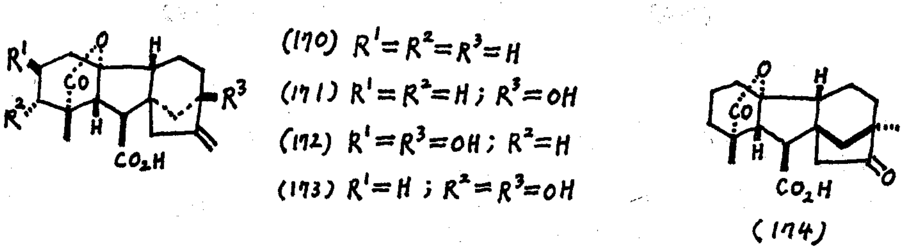


Chart 8

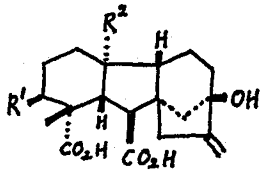
The metabolism of gibberellins A_9 (**170**), A_{20} (**171**), and A_{29}(**172**) in immature seed of *Pisum sativum* CV. Progress No. 9 was investigated. The results of this experiment using tritiated gibberellins suggested that *in vivo* GA_9 (**170**) may not be the principal precursor of GA_{20} (**171**) and that conversion of GA_{20} to GA_{29} is normal metabolic sequence.[92] Furthermore, [^{3}H]GA_{20} (**171**) was injected into mature leaves of *Bryophyllum daigremontianum* under long- and short-day conditions. It was converted to GA_{29} (**172**), 3-epi-GA_1 (**173**), C/D-ring-rearranged GA_{20} (**174**), and two minor metabolites.[93]



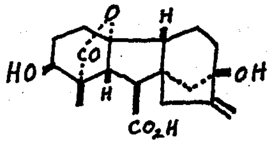
Translocation and metabolism of [^{3}H]gibberellins (A_1, A_4, A_5, and A_{20}) by light-grown *Phaseolus coccineus* seedlings were investigated.[94)]

Radioactive gibberellin A_3 applied to seedlings of *Pharbitis nil* strain Violet was converted to one single metabolite which was tentatively identified as GA_3-glucoside.[95)]

The initial metabolism of steviol (**122**) to 13-hydroxylated *ent*-kauranes by mutant B1–41a of *Gibberella fujikuroi* was described in Section IX.[72)] Further metabolism produced GA_{12} (**175**), GA_1 (**176**) as the major products and GA_{18} (**177**) as the minor product. From GA_{12} (**175**) were metabolized GA_{17} (**178**), GA_{19} (**179**), and GA_{20} (**171**).[72)]



(175) R¹ = H ; R² = Me
(177) R¹ = OH ; R² = Me
(178) R¹ = H ; R² = CO₂H
(179) R¹ = H ; R² = CHO

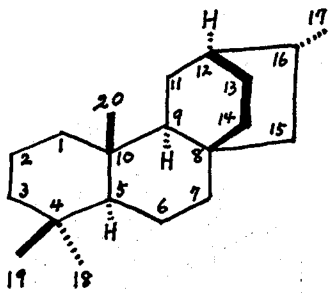


(176)

Stereochemistry in the biosynthesis of gibberellin A_3, (especially of cyclization and hydroxylation) was studied.[73)] (See Section IX.) Several biochemical reports on gibberellins and related compounds were published.[96~104)]

A review about utilization of gibberellin for modification of barley grain into malt without germination was published.[105)]

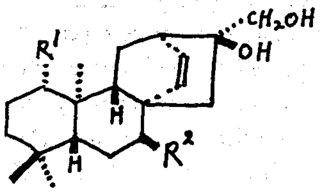
XII. ATISANE DERIVATIVES



Atisane

From *Sideritis reverchonii*, two known atisane type diterpenes [serradiol (**180**) and sideritol (**181**)] were isolated.[41)]

Chemical and crystallographic data were presented for a new diterpenoid, *ent*–atis-13-en-7α, 16α, 17-triol (**182**), isolated from *Sideritis angustifolia* as a minor component together with the major diterpene sideritol (**181**).[106)]



(180) $R^1 = R^2 = H$
(181) $R^1 = OH$; $R^2 = H$
(182) $R^1 = H$; $R^2 = OH$

A communication about chemical conversion of kobusine (**183**) involving cleavage of the bridged C–14, C–20 bond by a novel fragmentation reaction was published. The outline of the conversion sequence is shown in Chart 9.[107]

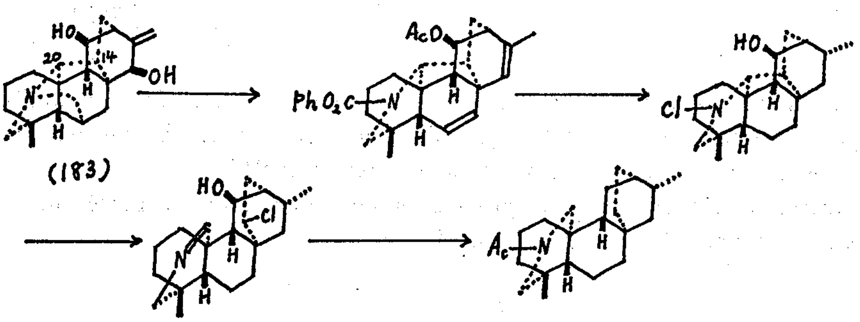
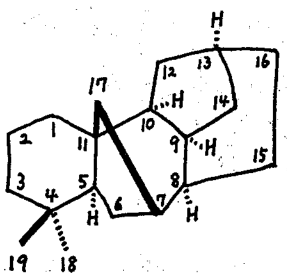


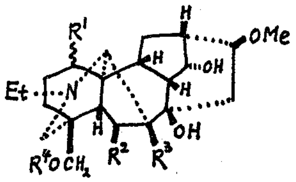
Chart 9

XIII. ACONANE DERIVATIVES



Aconane

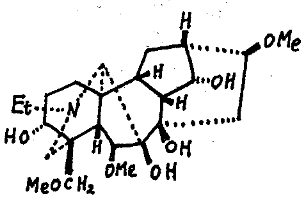
The structure of delectine (**184**), new diterpene alkaloid from *Delphinium dictyocarpum*, was determined by spectroscopy and chemical transformations into O, O-dimethyllycoctonine.[108] The structure of iliensine (**185**) was determined by IR, NMR, and mass spectroscopy and chemical transformations into O-methylacomonine and nor-anhydroxyiliensine (**186**).[109] The structure of aconorine (**187**), isolated from *Aconitum orientale*, was determined by spectroscopy and chemical transformation into columbianine (**188**), isolated from *A. columbianum*.[110]



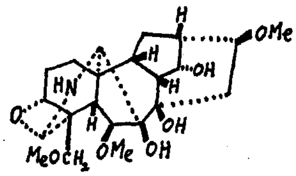
(184) R^1=β-OMe; R^2=OMe; R^3=OH; R^4=$-\overset{O}{\overset{\|}{C}}-C_6H_4(H_2N)$

(187) R^1=α-OMe; R^2=R^3=H; R^4=$-\overset{O}{\overset{\|}{C}}-C_6H_4(AcNH)$

(188) R^1=α-OMe; R^2=R^3=R^4=H

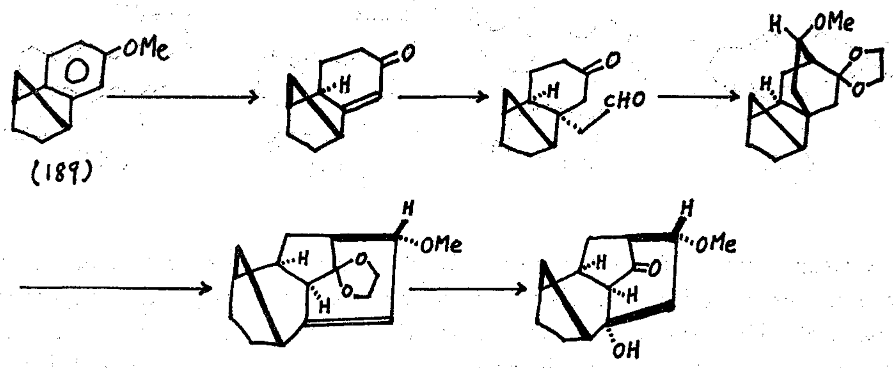


(185)



(186)

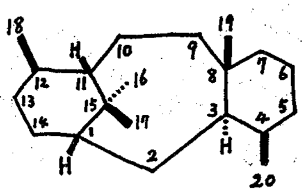
A simple and stereospecific conversion of compound **189** to the aconite alkaloid model (delphinine-type) **190** was published. The outline of this synthetic route is shown in Chart 10.[111]



(189) (190)

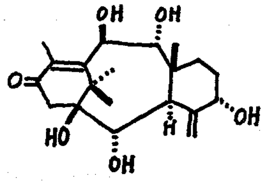
Chart 10

XIV. TAXANE DERIVATIVES



Taxane

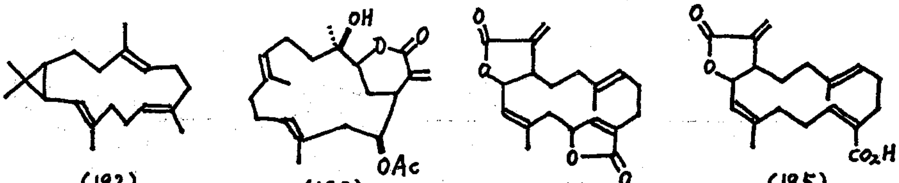
Taxicin-I (**191**) was cited in a review related to the method for preparation of bridgehead-olefins.[112]



(191)

XV. THE OTHERS

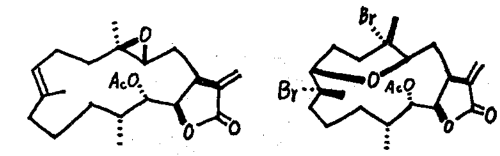
The capacity of cell-free extracts of castor bean seedlings for synthesis of casbene (**192**) was compared for seedlings which had been germinated under sterile conditions and seedlings which were intentionally exposed to fungal cultures. It is suggested from the several investigations that casbene may serve the castor bean plant as a phytoalexin.[113]



(192) (193) (194) (195)

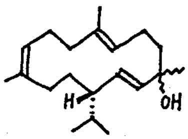
Crassin acetate (**193**) was shown to be the principal antineoplastic agent present in the marine invertebrates such as *Pseudoplexaura parosa*, *P. flagelosa*, *P. wagenaari* and *P. crucis*.[114] The structures of ovatodiolide (**194**) and anisomelic acid (**195**) isolated from *Anisomeles malabalica* were determined by the spectral and chemical evidence.[115]

The X-ray analysis of eupalmerin acetate (**196**), a diterpene lactone in the gorgonian *Eunicea palmeri*, and of eupalmerin acetate dibromide (**197**) was published.[116]

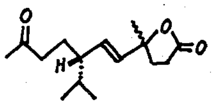


(196) (197)

A new thunbergan-type nor-isoprenoid lactone **199** was obtained from Greek tobacco. The carbon skeleton of this compound indicates that it is derived from a thunbergane precursor **198**.[117]

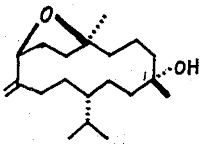


(198)

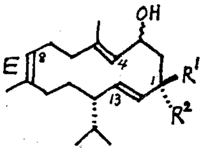


(199)

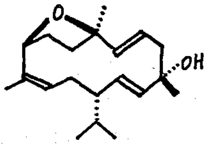
In order to clarify the absolute configuration of the tobacco thunberganoids, X-ray analysis of 5, 8-oxido-3, 9(17), 13-duvatrien-1α-ol (**200**) and chemical degradation of 4, 8, 13-duvatriene-1β, 3-diol (**201**) were performed. Correlation of the degradative product of **201** with a known tobacco constituent, solanone, established the absolute stereochemistry the carbon-1 of **201**. Since the hydroxyether **200** had already been correlated with the diol **201**, the absolute configuration of **200** was established. Several other components encountered in tobacco were assigned structures **202**–**211** by the same manner as mentioned above.[118)]



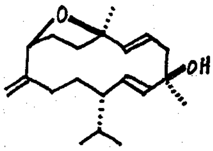
(200)



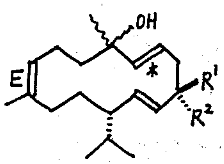
(201) R^1=OH; R^2=Me
(204) R^1=Me; R^2=OH



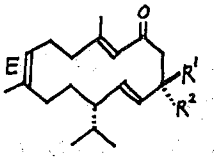
(202)



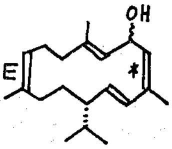
(203)



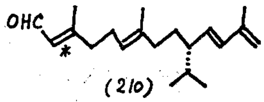
(205) R^1=OH; R^2=Me
(206) R^1=Me; R^2=OH



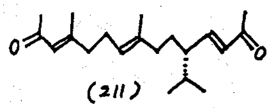
(207) R^1=Me; R^2=OH
(208) R^1=OH; R^2=Me



(209)



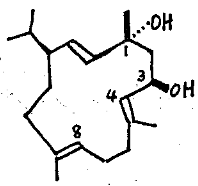
(210)



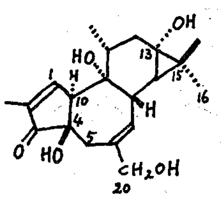
(211)

(Double bonds marked with "E" are *trans*, although here more conveniently portrayed as *cis*, and those labeled "*" are of undetermined configuration.)

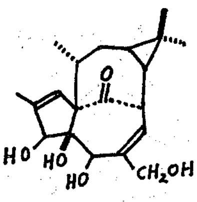
The structure of a new type of plant growth inhibitor extracted from immature Tobacco leaves was shown to be 4, 8, 13-duvatriene-1, 3-diol (**212**).[119)]



(212)



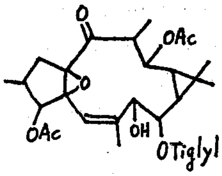
(213)



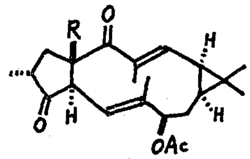
(214)

The presence of 12-deoxy-phorbol (**213**) or ingenol (**214**) in several succulent *Euphorbia* species of Nigeria was reported.[120] New diester of **213**, that is, 12-deoxy-4β-hydroxyphorbol–13-dodecanoate-20-acetate was isolated from latex of *Euphorbia coerulescens* and *E. fortissima*. 12-Deoxy-4β-hydroxyphorbol-13-octenoate-20-acetate was isolated from *E. polyacantha*.[121] A method was reported for the micro-identification of 12-deoxy–phorbol (**213**) and its esters having inflammatory toxicity based on thin layer chromatography-mass spectrometry.[122]

3, 12-Di-O-acetylingol 8-tiglate (**215**) and some known diterpene esters of the irritant and cocarcinogenic latex of *Euphorbia lactea* were reported.[123]



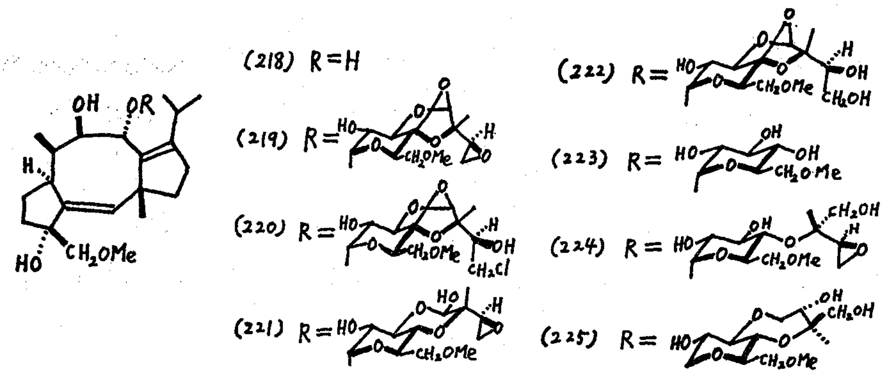
(215)



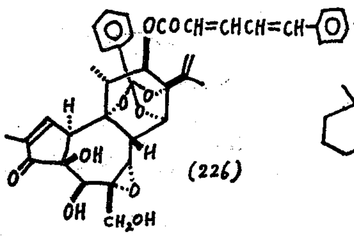
(216) R = OH

(217) R = H

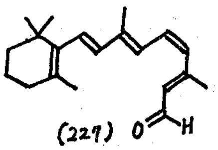
The crystal structures of compounds, **216** and **217**, were determined by X-ray diffraction method.[124] The structure of cotylenol, the aglycone of cotylenins, leaf grows substances produced by a fungus, was assigned **218** on the basis of degradative and spectroscopic evidence.[125] The structures of cotylenins A (**219**), B(**220**), C(**221**), D(**222**), and E(**223**) were also determined.[126] Cotylenins F(**224**) and G(**225**) were isolated from the culture filtrate of a fungus (*Cladosporium* species).[127] Cotylenin G was chemically derived from cotylenin F by treatment with a strong base.



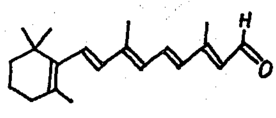
The structure **226** of mezerein, one of the toxic components of the plant *Daphne mezerum*, was established by the X-ray diffraction study.[128]



(226)

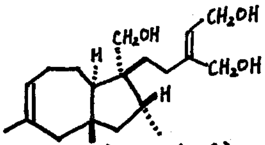


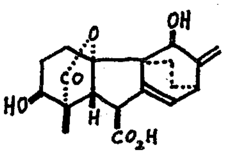
(227)

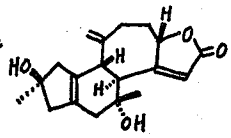


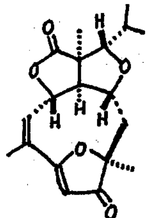
(228)

A ¹³C–NMR study of *cis-trans* isomeric vitamin A, carotenoids and related compounds was reported.[129] The molecular mechanism of visual excitation was investigated experimentally; 11-*cis*- (**227**) and all-*trans*-retinal (**228**) were studied.[130] Portulal (**229**) and antheridiogen (**230**) were described in the foregoing review[45] on the growth regulating substances of plant origin.


(229)


(230)

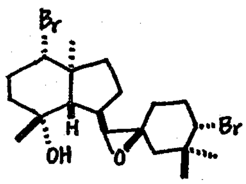

(231)

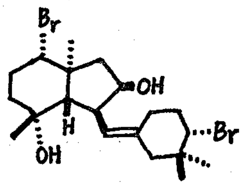

(232)

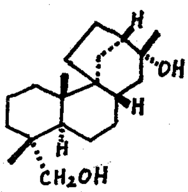
Determination of the structure and relative configuration of crotofolin A(**231**) was performed using the X-ray analysis. It was shown to have a new carbon skeleton and its biogenesis was presumed.[131]

Eremantholide A, a novel tumor-inhibiting compound from *Eremanthus elaeagnus*, was successfully isolated by utilizing countercurrent distribution, extensive chromatography and high pressure liquid chromatography. Its structure and relative configuration were substantiated as **232** by the X-ray determination. But it is not certain whether it should be regarded as a nor-diterpenoid or as a tetrahomosesquiterpenoid, although the latter possibility is strongly favored on phytochemical grounds.[132]

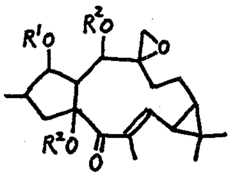
Irieol A (**233**) and iriediol (**234**), dibromoditerpenes of a new skeletal class from *Laurencia*, were isolated and the structures were determined by X-ray diffraction methods.[133]


(233)


(234)


(235)

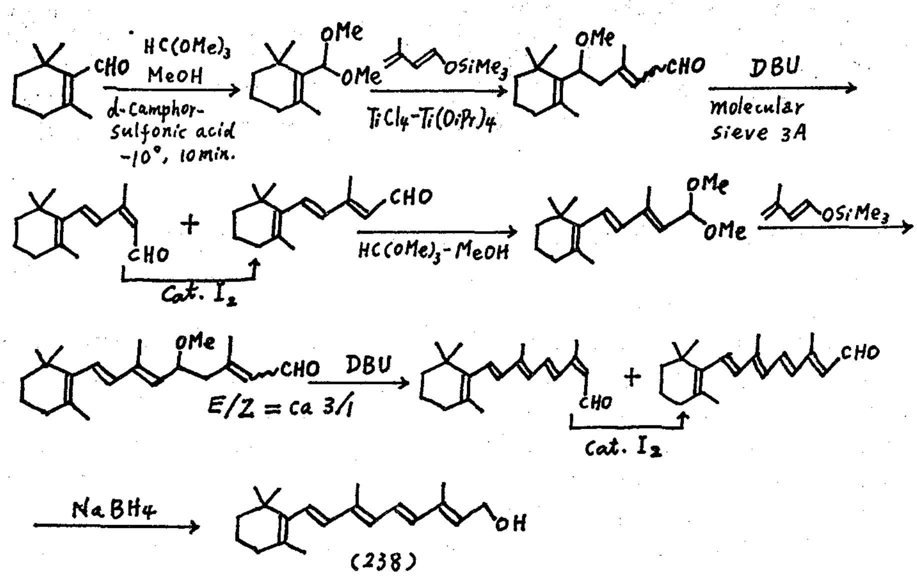
The structure and absolute stereochemistry of stemarin, a novel skeletal tetracyclic diterpene isolated from *Stemodia maritima*, were determined as **235** by means of spectral and X-ray crystallographic analyses.[134] The solvolysis of *ent*-methyl 12β-p-tolylsulfonyloxybeyeran-19-oate (**138**) was investigated at room temperature in buffered acetic, formic, and trifluoroacetic acids.[77] (See Section X.) Photochemical cleavage of the cyclopropane ring in 6, 20-epoxylathyrol (**236**) and the corresponding parent alcohol **237** was described.[135]



(236) R^1= $PhCH_2CO$; R^2= Ac

(237) R^1 = R^2 = H

A new synthesis of vitamin A (**238**) was successfully performed. The outline is shown in Chart 11.[136]



(238)

Chart 11

An interesting biogenetic type synthesis of cembrene type compounds was reported, in which geranyl geranic acid chloride (**239**) was selectively converted to the macrocyclic cembrene skeleton. The outline is illustrated in Chart 12.[137]

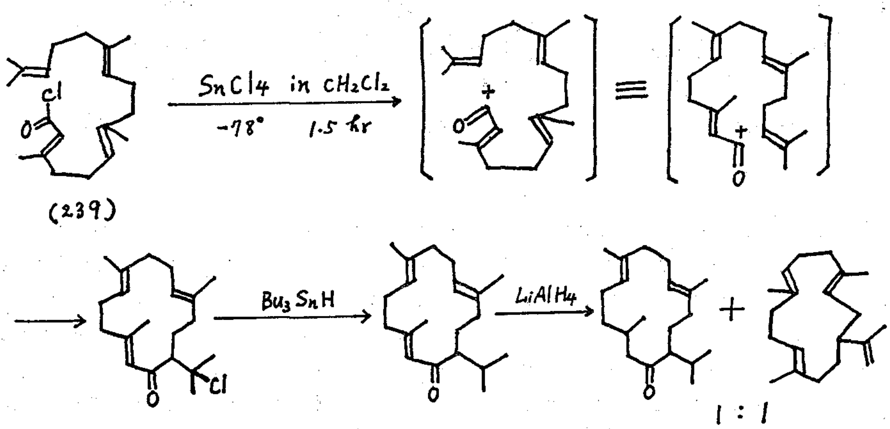
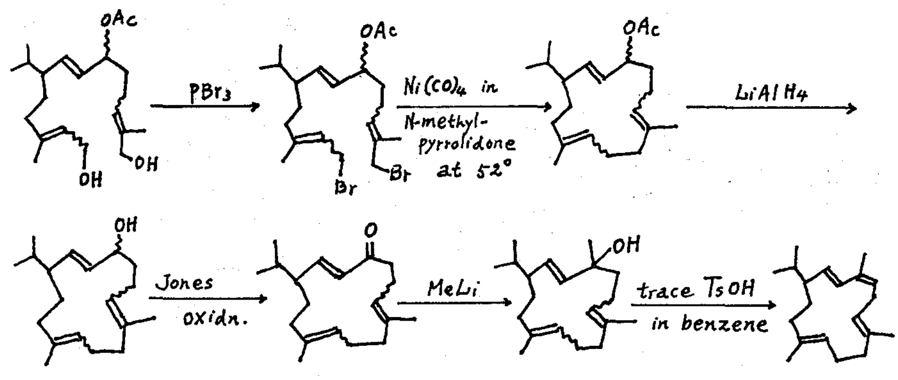


Chart 12

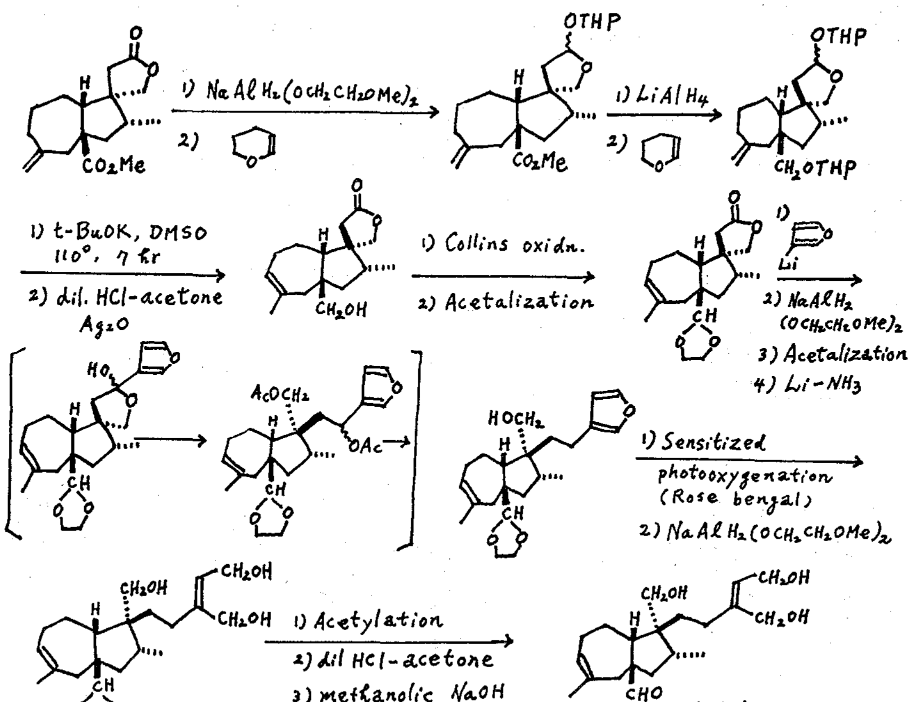
The full paper of synthesis of *rac*-cembrene (**240**) was published. The convergent synthetic method, which employed a nickel carbonyl catalyzed coupling of a terminal allylic bromide as the important key step, is shown in Chart 13.[138)]



(240)

Chart 13

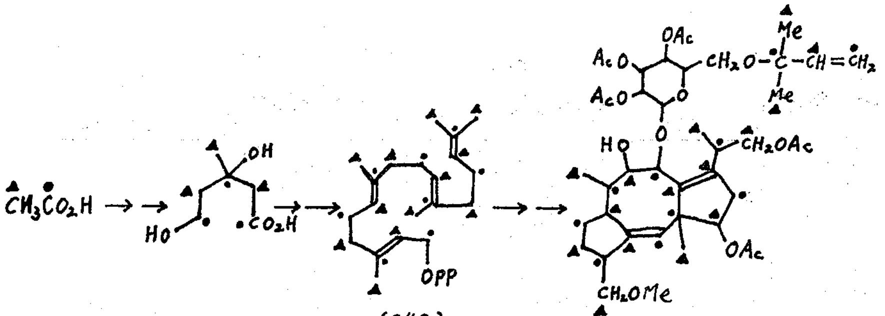
Total synthesis of portulal (**241**) was accomplished according to the sequence shown in Chart 14.[139)]



(241)

Chart 14

The biosynthesis of fusicoccin (**243**) from [1–^{13}C]- and [2–^{13}C]-acetate was investigated. The positions of labeled atoms in biosynthesized fusicoccin were determined by ^{13}C NMR spectroscopy. The results (Chart 15) were consistent with fussicoccin being formed by direct cyclization of a precursor such as geranyl geraniol pyrophosphate (**242**).[140]



(242) (243)

Chart 15

Measurements were described of fusicoccin-stimulated H^+ efflux in barley (*Hordeum vulgare*) roots when K^+ and Na^+ concentrations were varied.[141]

In a review[142] on the activation of Grignard reagents by transition metal compounds, the synthesis of Δ^7-pimaradiene and of beyerene from manool was cited.[143]

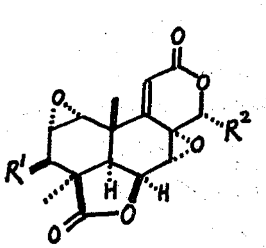
A Japanese brief review related to the absolute feeding reterrent was published, in which several clerodane type diterpenes were described.[144]

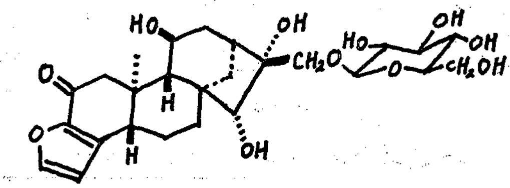
Addendum to VI. ABIETANE DERIVATIVES

Eleven hinokiol derivatives were prepared and their NMR investigations especially on their chemical shift variations with functional groups were carried out.[145]

Addendum to VII. TOTARANE DERIVATIVES

Hallactone B (**244**), inumakilactone B (**245**), and nagilactone A were isolated from *Podocarpus polystachyus* and their structures determined on the basis of IR, NMR, and mass spectra.[146]





(244) $R^1=H$; $R^2=CMe(OH)CH_2SO_2Me$

(245) $R^1=OH$; $R^2=CH=CH_2$

(246)

Addendum to IX. KAURANE DERIVATIVES

The absolute configuration of mascaroside was determined by the X-ray crystallography as shown in formula **246**.[147]

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