

Review

The Chemistry on Diterpenoids in 1975 Part-I

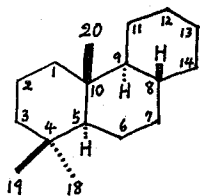
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Received May 6, 1976

I. INTRODUCTION

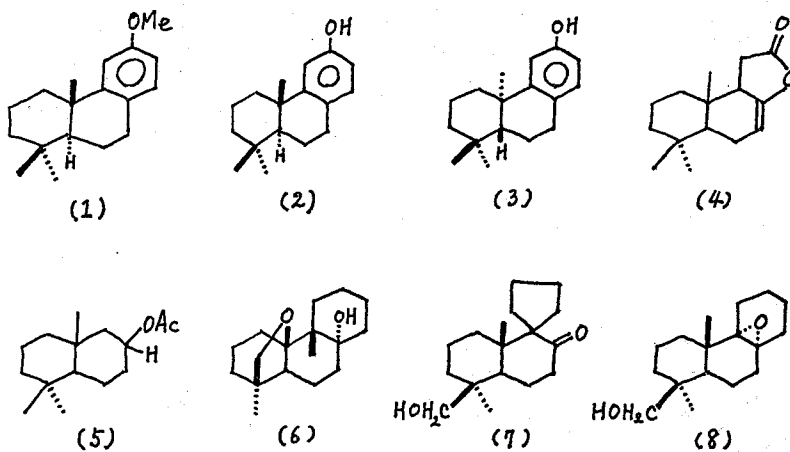
This is one of a series of our annual reviews¹⁻¹¹⁾ on diterpenoids chemistry. The classification of the compounds is the same as that adopted in our reviews since 1969. This review covers the literature published between January and June 1975.

II. PODOCARPANE DERIVATIVES



Podocarpane

Unusual partial inversion of configuration at two remote centers on demethylation

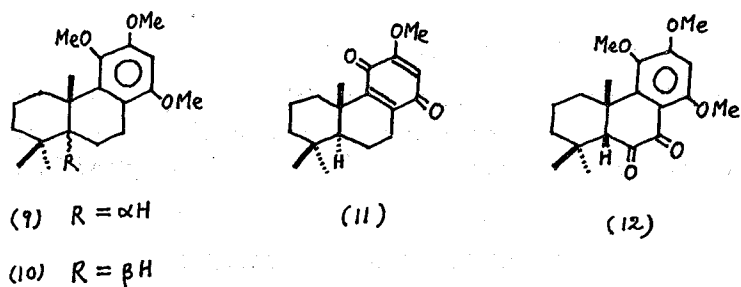


Formulae (1)-(8)

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of (+)-12-methoxypodocarpa-8, 11, 13-triene (**1**) was reported.¹²⁾ Thus, treatment of optically pure **1** with HI/HBr/AcOH and a trace of H_3PO_2 gives, as a major product, a non-racemic mixture of (+)-podocarpa-8, 11, 13-trien-12-ol (**2**) and its enantiomer **3**. Ozonolysis of **2** and subsequent transformations afforded the lactone **4**, a tobacco flavoring agent, and the bicyclic acetate **5**, a compound with a woody odor.¹³⁾ The compounds **6** and **7** were obtained by the boron trifluoride induced rearrangement of **8**.¹⁴⁾

Chromium trioxide oxidation of trimethoxypodocarpatriene (**9**) gave a quinone **11**, whereas under similar conditions **10** gave a diketone **12**.¹⁵⁾



Formulae (9)-(12)

Methyl and ethyl esters of sterically hindered diterpenoic acids were easily hydrolyzed into the parent carboxylic acids by the action of acetic or chloroacetic acid in quinoline or DMF.¹⁶⁾ A new method of geminal alkylation *via* α-trimethylenedithiocyclobutanones was reported. The synthesis of **13** in Chart 1 demonstrates the synthetic utility of the new method.¹⁷⁾

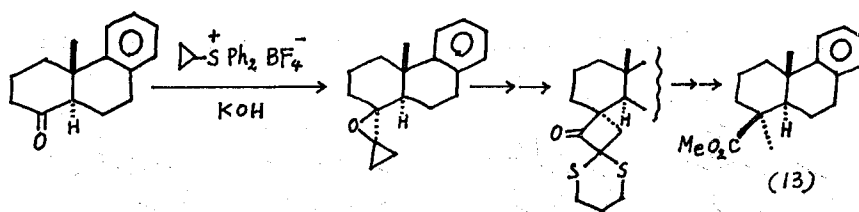
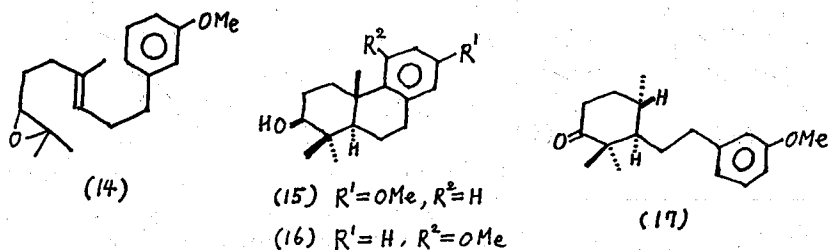


Chart 1

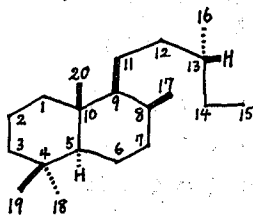
Cyclization of the epoxide **14** gave the podocarpa derivatives **15** and **16** along with **17**.¹⁸⁾



Formulae (14)-(17)

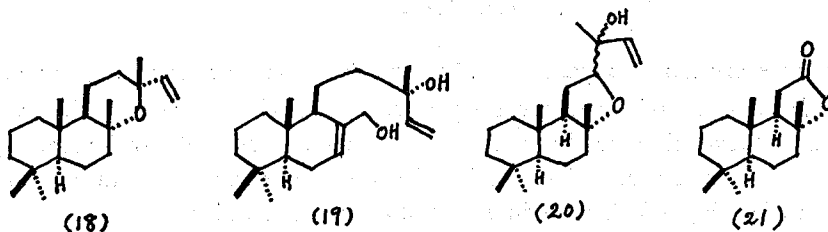
Detailed discussion on the dehydration reactions in the mass spectra of podocarpan-12- and -14-ols has been presented.¹⁹⁾

III. LABDANE DERIVATIVES



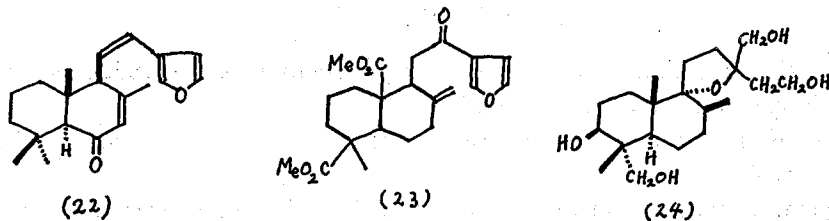
Labdane

Manoyloxide (**18**) along with other diterpenes was isolated from the cypress essential oil.²⁰⁾ *Sagittaria sagittifolia* was proven to contain a new diterpene, sagittariol (**19**).²¹⁾ The structures of four isomeric diterpenes (**20**) isolated from Green tobacco were determined by spectroscopic means and conversion into 12-norambreinolide (**21**).²²⁾



Formulae (18)–(21)

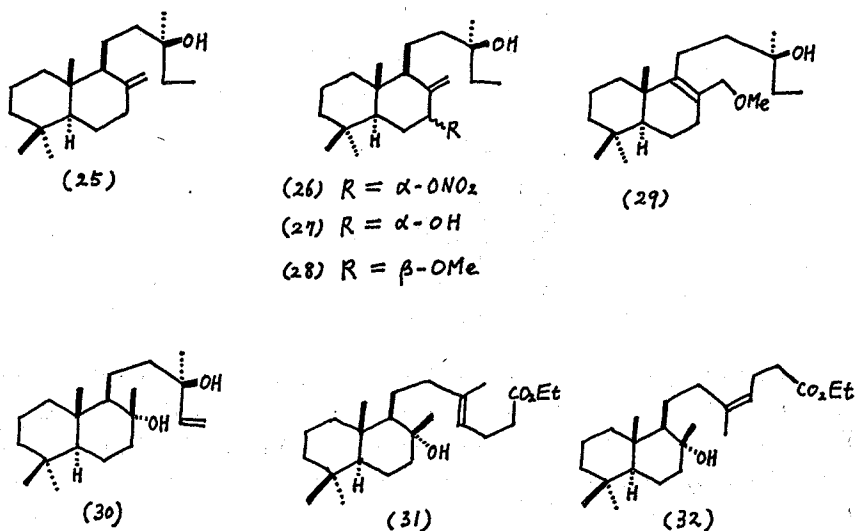
A new diterpene, hedychenone (**22**) was isolated from *Hedychium spicatum*.²³⁾ The growth inhibitor for silkworm larvae from *Avocado* leaves was identified as dimethyl sciadinonate (**23**).²⁴⁾ The structure of lagochilin (**24**) was determined by an X-ray analysis.²⁵⁾



Formulae (22)–(24)

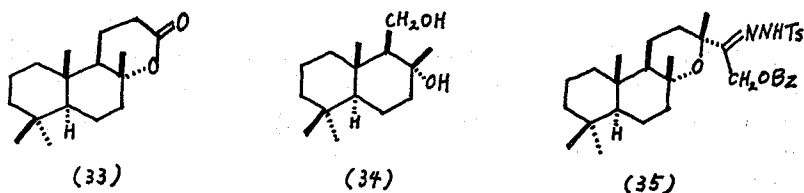
The reaction of labd-8(17)-en-13-ol (**25**) with thallium (III) nitrate in methanol gave rise to the isolation of **26**, **27**, **28**, and **29**. The reaction mechanism is briefly discussed.²⁶⁾ Transesterification of sclareol (**30**) with triethylorthoacetate and subsequent rearrangement gave (E)- and (Z)-ethyl 8-hydroxylabd-13-en-15-ylacetate **31**

and **32**. Cyclization of these esters with tin(IV) chloride in benzene was also described.²⁷⁾



Formulae (25)–(32)

A simple method of degradation of the readily available labdane group of diterpenes to drimanic sesquiterpenes was reported.²⁸⁾ The illustrative example is the conversion of (+)-ambreinolide (**33**) into (+)-drimane-8, 11-diol (**34**) by the reaction with D. D. Q. followed by ozonolysis and reduction. The structures of the products obtained by NaBH_4 or LiAlH_4 reduction of **35** were discussed.²⁹⁾



Formulae (33)–(35)

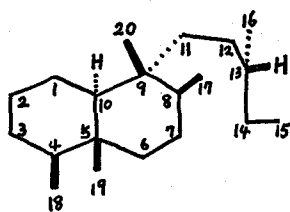
A total carbon shift analysis of several representatives of the labdane family using ^{13}C -NMR spectroscopy was presented.^{30, 31)}

The effect of sclareol (**30**) on the germination and growth of rust fungi *in vitro* was described.³²⁾

Several labdane derivatives are cited in the following three review articles. Their titles are "Chemicals from Trees"³³⁾ "Neutrals in Southern Pine Tall Oil",³⁴⁾ and "Halogenated Organic Compounds from Marine Plants."³⁵⁾

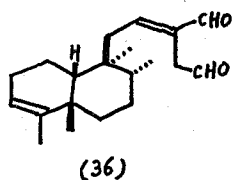
IV. CLERODANE DERIVATIVES

The first diterpene possessing a *cis*-clerodane skeleton, linaridial (**36**) was isolated

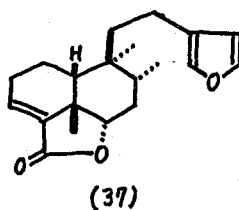


Clerodane

from *Linaria japonica*.³⁶⁾ An X-ray analysis of a key diterpene **37** from *Solidago arguta*, published at nearly the same time, served another example of *cis*-clerodane-type diterpene.³⁷⁾



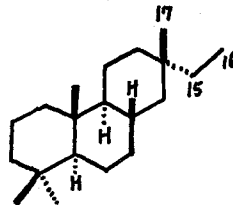
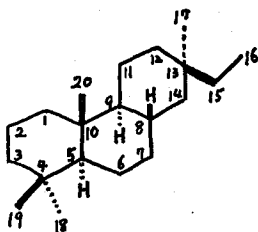
(36)



(37)

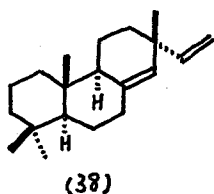
Formulae (36)-(37)

V. PIMARANE AND ISOPIMARANE DERIVATIVES

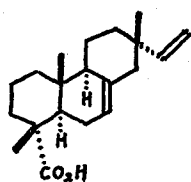


Pimarane and Isopimarane

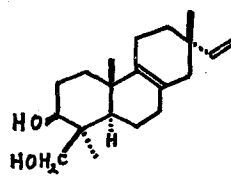
Sandaracopimara-8(14), 15-diene (**38**) and isopimaric acid (**39**) were isolated from the cypress essential oil²⁰⁾ and *Podocarpus lambertius*,³⁸⁾ respectively. The structure of iso-virescenol B (**40**), an aglycon of glycoside in the culture media of the fungus *Acremonium luzulae*, was determined by an X-ray analysis.³⁹⁾



(38)



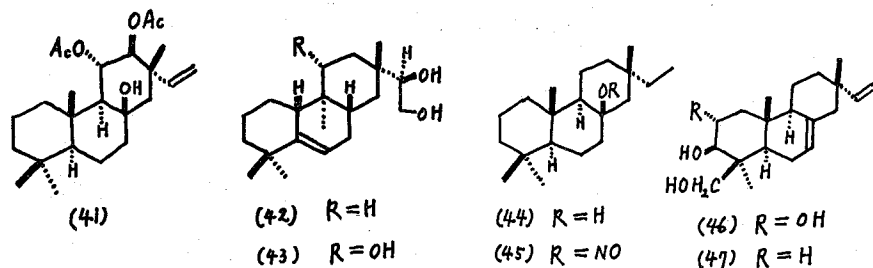
(39)



(40)

Formulae (38)-(40)

A new diterpene **41** was isolated from *Osteospermum subulatum*.⁴⁰⁾ Lagascol (**42**) and the known lagascatrion (**43**) along with other type of diterpenes were isolated from *Sideritis serrata*.⁴¹⁾

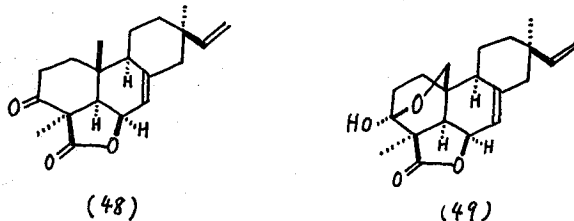


Formulae (41)-(47)

Functionalization of 10-methyl group in isopimaran-8 β -ol (**44**) was accomplished by the hypiodite oxidation and by the photorearrangement of its nitrite **45**.⁴²⁾

Biosynthetic origin of the substituents at C-4 of virescenols A (**46**) and B (**47**) was determined by ¹³C-NMR spectroscopy.⁴³⁾

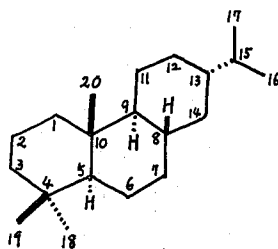
Structure and physiological properties of momilactones A (**48**) and B (**49**), growth regulating substances in rice husk, were reviewed in Japanese.⁴⁴⁾



Formulae (48)-(49)

Autoxidation of isopimaric acid gave acidic products, which were characterized.⁴⁵⁾ Pimaranes and isopimanes are also cited in the foregoing reviews.^{33,34)}

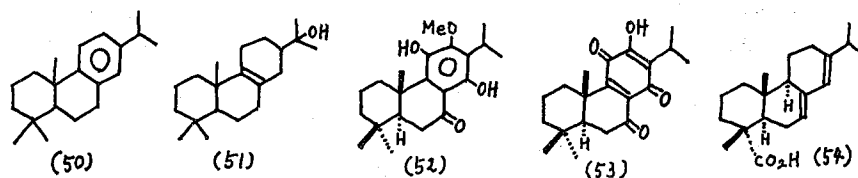
VI. ABIETANE DERIVATIVES



Abietane

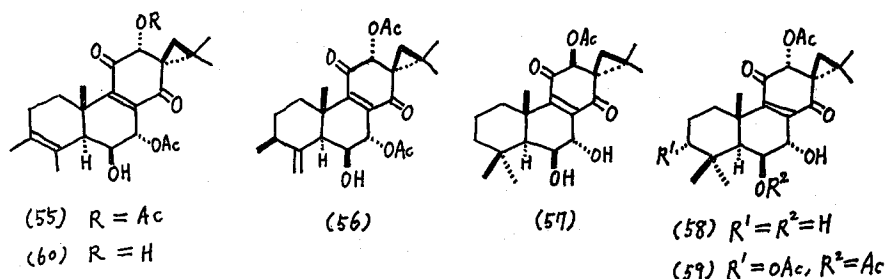
Dehydroabietane (**50**) has been isolated from the cypress essential oil (*Cupressus sempervirens*).²⁰⁾ From leaves of *Podocarpus lambertius*, 8-abieten-15-ol (**51**) was iso-

lated.³⁸⁾ Inuroyleanol (**52**) and 7-keto-royleanone (**53**) have been isolated from the roots of *Inula royleana* and their structures established.⁴⁶⁾ Some diterpenoids related to abietic acid (**54**) as common resin acids of pine were described in a review on chemicals from trees.³³⁾ In a review on neutrals in southern pine tall oil, abietane type diterpenoids were also described.³⁴⁾



Formulae (50)–(54)

Five new spiro-abietane diterpenes, coleone M (**55**), N (**56**), P (**57**), Q (**58**), and R (**59**), were isolated from *Plectranthus caninus*. Coleon O (**60**) was found in similar glands of *Coleus somaliensis*.⁴⁷⁾



Formulae (55)–(60)

A review containing abietane type diterpenoid pigments was published.⁴⁸⁾

Synthetic transformations of dehydroabietic acid derivative **61** shown in Chart 2 were reported. Furthermore, compound **62** was also obtained in 25% yield by reduction of the corresponding nitro compound and in 40% yield by amination of the corresponding bromo compound.⁴⁹⁾

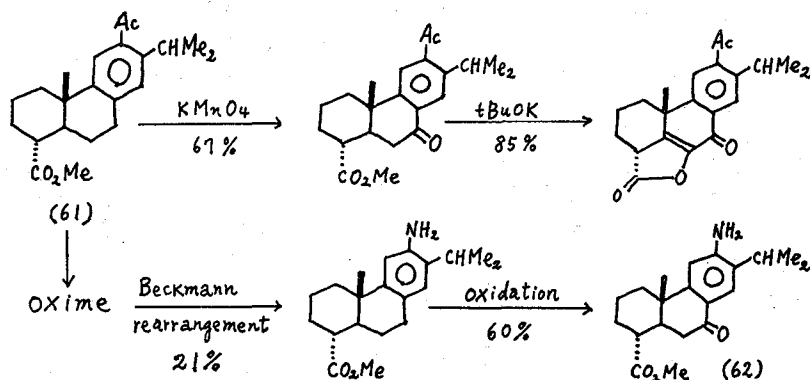
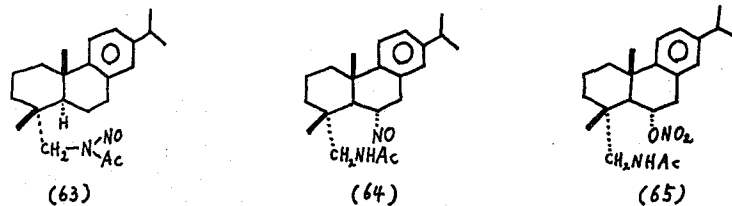


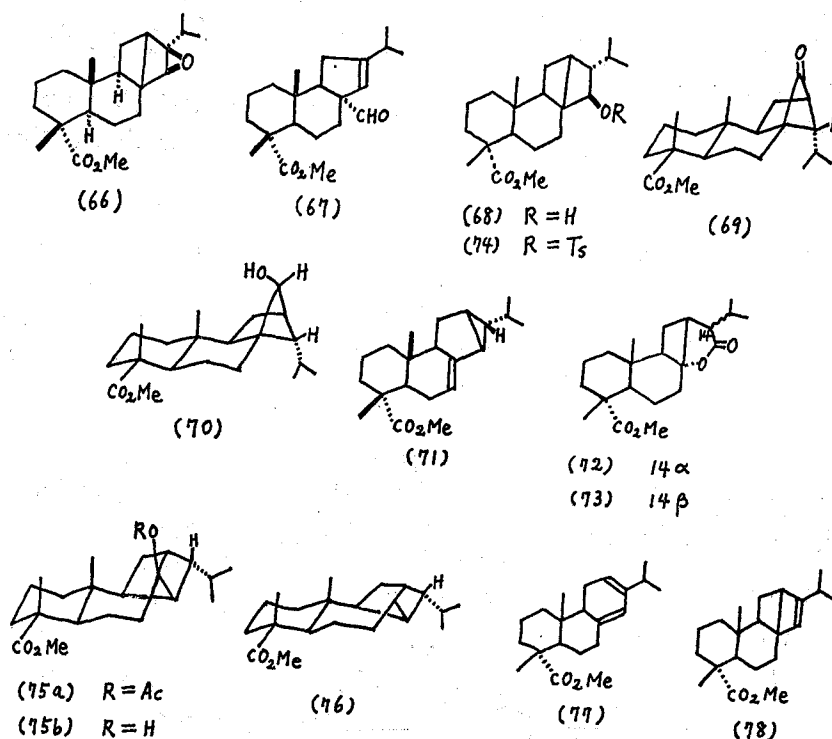
Chart 2

Applications of oxidative and non-oxidative photorearrangements of nitrosoamides were illustrated.⁵⁰ Namely, *N*-nitroso-*N*-acetyldehydroabietylamine (**63**) rearranged to give stable 6 α -nitroso (**64**) and 6 α -nitrate (**65**) derivatives respectively.



Formulae (63)–(65)

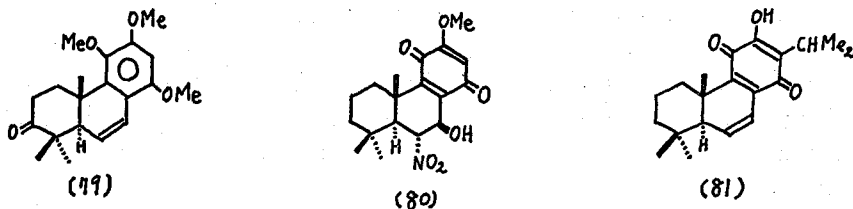
Unexpected rearrangements of photolevopimaric acid derivatives were published. Thus, treatment of **66** with Lewis acids resulted in rearrangement to **67**. Jones oxidation of **68** proceeded with rearrangement to bicyclo [2.1.1.] hexanone **69**. Treatment of **70** with tosyl chloride resulted in rearrangement to **71**. An unusual oxidation of **68** to the lactones **72** and **73** with Fétizon's reagent was observed. Solvolytic reactions of tosylate **74** resulted in rearrangement to **75** and **76**.⁵¹ The compounds **66** and **68** were prepared from **78**, derived from methyl levopimarate (**77**) by irradiation, by epoxidation and hydroboration-oxidation, respectively.



Formulae (66)–(78)

rac-Dehydroroyleanone (**81**) was synthesized from 3-oxo-trimethoxy-podocar-

patetraene (79) via 80.⁵²⁾



Formulae (79)–(81)

The total synthesis of *rac*-royleanone (82) was achieved.⁵³⁾ The sequence is shown in Chart 3.

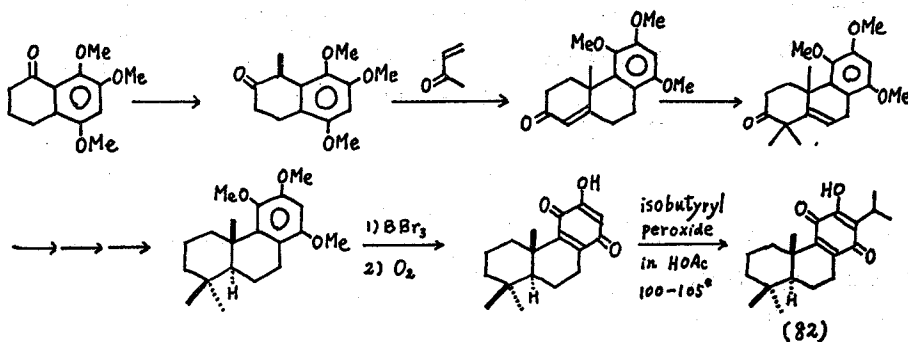
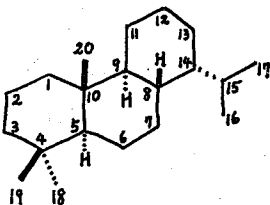


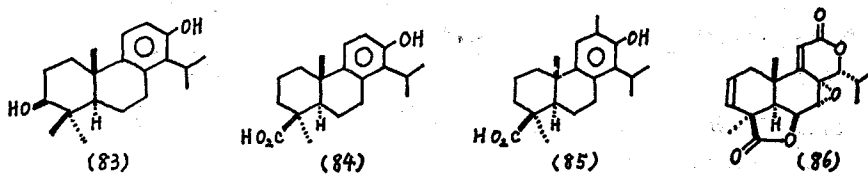
Chart 3

VII. TOTARANE DERIVATIVES



Totarane

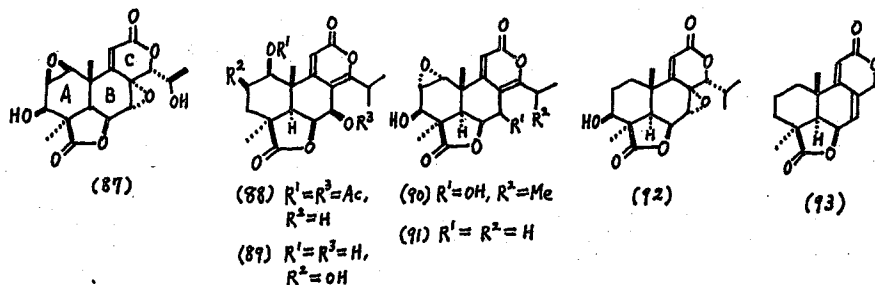
In a review on diterpenoid pigments, modified totarane type compounds were described.⁴⁸⁾ From bark of *Podocarpus lambertius*, 3 β -hydroxytotarol (83), 4 β -carboxynortotarol (84), macrophylic acid (85) were isolated.³⁸⁾



Formulae (83)–(86)

The structure of podolide (**86**), a new antileukenic norditerpene dilactone from *Podocarpus gracilior*, was established by the X-ray analysis. The absolute configuration was assigned on the basis of the observation of a negative Cotton effect in the CD spectrum.⁵⁴

The structure of inumakilactone (**87**) was solved by a single crystal X-ray analysis.⁵⁵ It was confirmed that the structure of the bisnorditerpenoid molecule was different from that previously proposed⁵⁶ in respect of the orientation of the epoxy group on ring A.

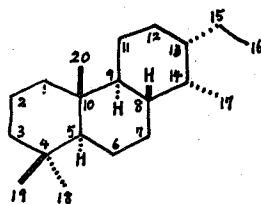


Formulae (87)–(93)

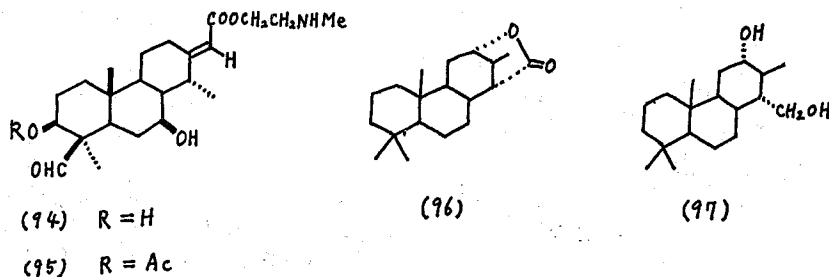
The molecular structure of nagilactone A diacetate derived from X-ray analysis,⁵⁷ as shown in (**88**), was shown to be consistent with that previously proposed⁵⁸ on the basis of the chemical and spectroscopic data.

Antitumor activity of nagilactones, B (**89**), C (**90**), D (**91**), and E (**92**), and a related lactone (**93**) was evaluated.⁵⁹

VIII. CASSANE DERIVATIVES



Cassane

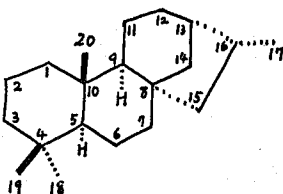


Formulae (94)–(97)

Isolation of unstable alkaloids from *Erythrophleum chlorostachys* was reported.⁶⁰⁾ Among them, structures of cytotoxic alkaloids, norerythrostachaldine (**94**) and its naturally occurring 3 β -acetate (**95**), were established.⁶¹⁾

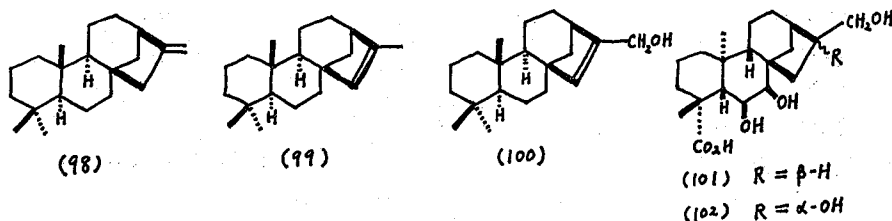
Preparation of lactone (**96**) from diol (**97**) with silver carbonate on Celite was published.⁶²⁾

IX. KAURANE DERIVATIVES



Kaurane

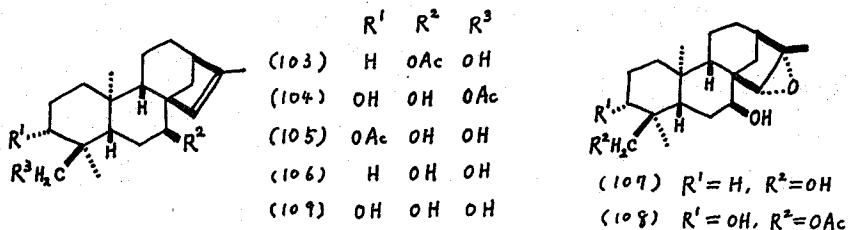
From leaves of *Podocarpus lambertius*, phyllocladene (**98**), isophyllocladene (**99**), and 17-isophyllocladenol (**100**) were isolated.³⁸⁾



Formulae (98)–(102)

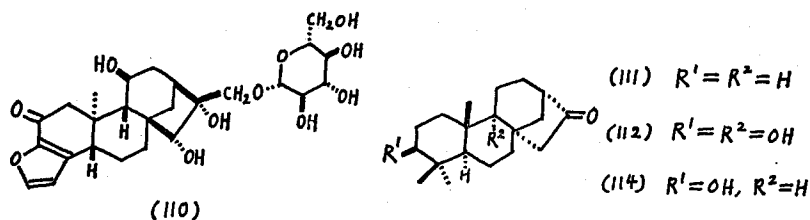
ent-6 α , 7 α , 17-Trihydroxy-16 α H-kauran-19-oic acid (**101**) and *ent*-6 α , 7 α , 16 β , 17-tetrahydroxykauran-19-oic acid (**102**) were identified by GC-MS from the endosperm of *Echinocystis macrocarpa*.⁶³⁾ (See also Section XI.) In the essential oil of *Araucaris araucana*, *ent*-kaurene was shown to be contained together with other diterpenoids.⁶⁴⁾

From *Sideritis theezans*, siderol (**103**), isolinearol (**104**), isosidol (**105**), sideridiol (**106**), sideroxol (**107**), a new diterpene shown to be epoxy-isolinearol (**108**), and isofoliol (**109**) were identified.⁶⁵⁾



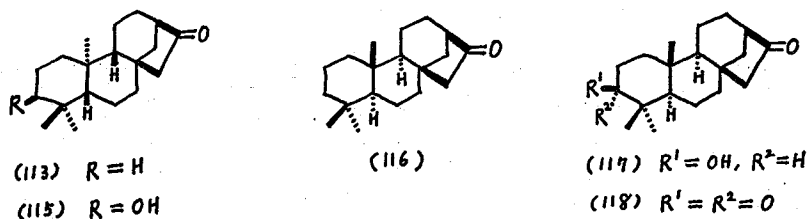
Formulae (103)–(109)

The structure of **110** for mascaroside, a bitter glycoside from *Coffea vianneyi*, was elucidated by spectral data⁶⁶⁾ and X-ray analysis.⁶⁷⁾



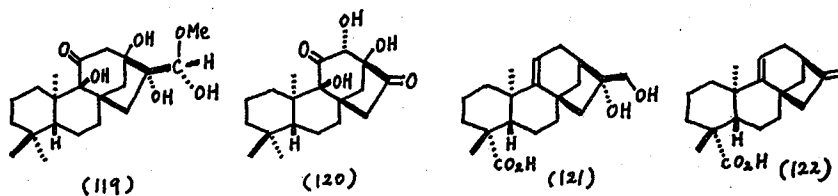
Formulae (110)–(112) and (114)

Microbial oxidation of 17-norkauran-16-one (**111**) by the fungus *Rhizopus nigricans* produced a dihydroxy compound (**112**) and the structure was established by X-ray analysis of the acetate derivative.⁶⁸⁾ It was reported⁶⁹⁾ that incubation of **111** and **113** with *Aspergillus niger* gave C-3 equatorial alcohols **114** and **115**, respectively, whereas compound **116** gave 3 β -alcohol **117** and 3-ketone **118** which was identical with corresponding compound derived from calliterpenone.



Formulae (113) and (115)–(118)

Two new antibacterial metabolites, phlebiakauranol (**119**) and phlebianorkauranol (**120**) were isolated from *Phlebia strigosozonala* and shown to have highly oxygenated kaurane structures by X-ray analysis.⁷⁰⁾



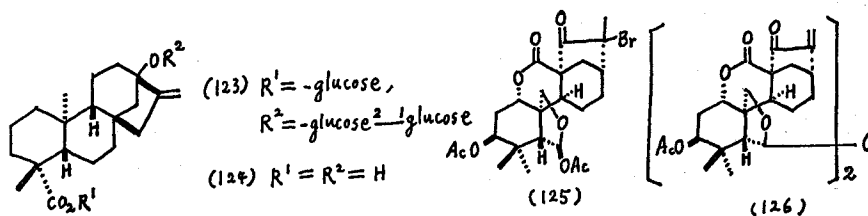
Formulae (119)–(122)

16, 17-Dihydroxy-9(11)-kauren-18-oic acid (**121**) was isolated from roasted coffee beans (*Coffea arabica*) and synthesized from compound **122**.⁷¹⁾ Several experiments for stevioside productivity of *Stevia rebaudiana* were reported.⁷²⁾

Enzymic hydrolysis of stevioside (**123**) to steviol (**124**) was undertaken using crude hesperidinase.⁷³⁾

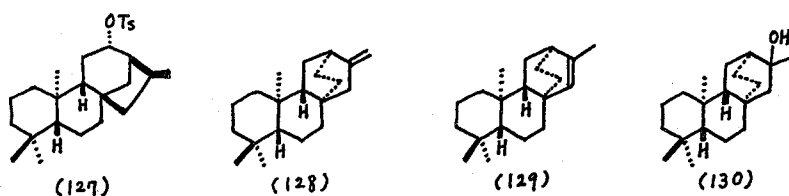
16-Bromodihydroenmein diacetate (**125**) was dehydrobrominated with lithium

chloride in DMF to give a product, the structure of which was elucidated as the intermolecular ether (126).⁷⁴⁾



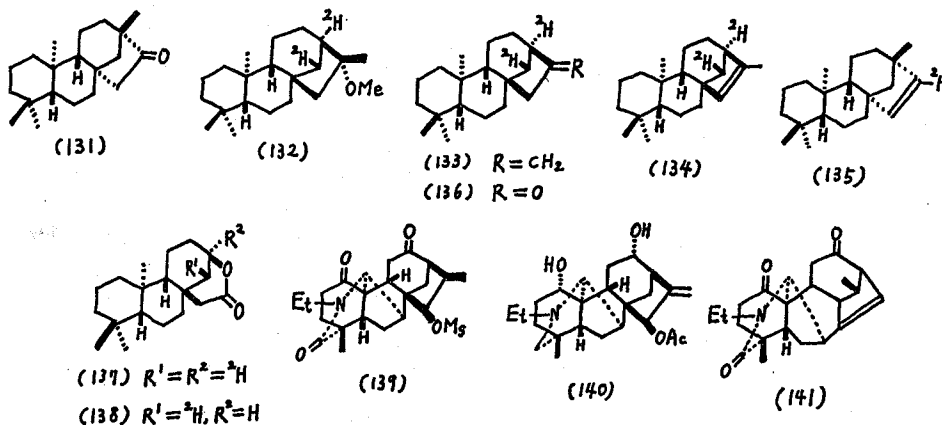
Formulae (123)–(126)

The formolysis of tosylate 127 followed by basic hydrolysis gave mixtures which contained atisane type products [128, 129, and 130] of 1, 3-hydride shift.⁷⁵⁾



Formulae (127)–(130)

Rearrangement of the phenylsulfonylhydrazone of *ent*-beyeran-16-one (131) with sodium methoxide in [²H] methanol yielded *ent*-[13, 14 α -²H₂]16-methoxykaurane (132), *ent*-[13, 14 α -²H₂]kaur-16-ene (133), and *ent*-[13, 14 α -²H₂]kaur-15-ene (134) together with *ent*-[16-²H]beyer-15-ene (135). Bridgehead enolization of *ent*-17-nor[13, 14 α -²H₂]kauran-16-one (136) was demonstrated by oxidation of the ketone, before and after heating with potassium *t*-butoxide, to the lactones 137 and 138, respectively.⁷⁶⁾ (See also section X.)



Formulae (131)–(141)

A novel rearrangement of the mesylate 139, derived from lucidusculine (140)

into olefine **141** was described.⁷⁷⁾

A short synthesis of optically active *d*-isophyllocladene (**99**) and *d*-phyllocladene (**98**) was published.⁷⁸⁾ Namely, rearrangement of the ketone **142** leads to *d*-isophyllocladen-14-one (**143**), which can be converted into **99** or **98**, as shown in Chart 4.

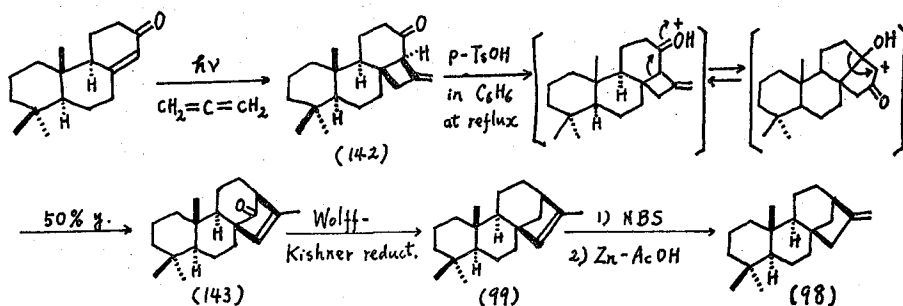


Chart 4

The stereoselective synthesis of *d*-phyllocladene (**98**) from *l*-abiestic acid (**54**) was reported.⁷⁹⁾ The sequence is shown in Chart 5.

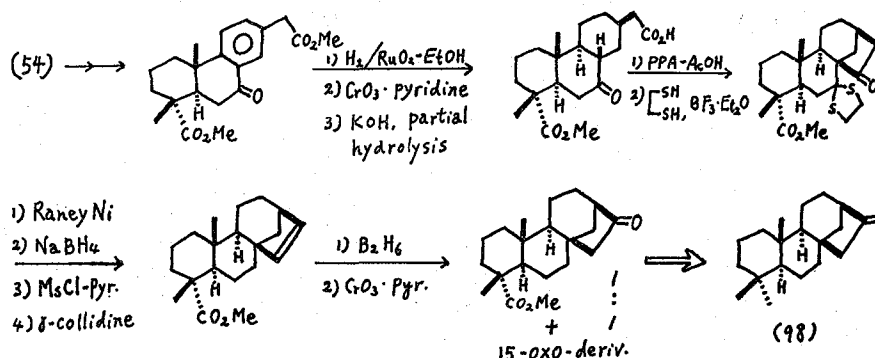
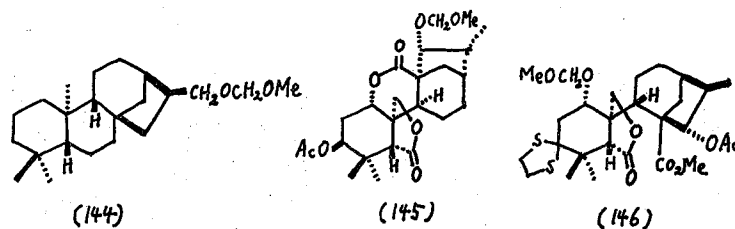


Chart 5

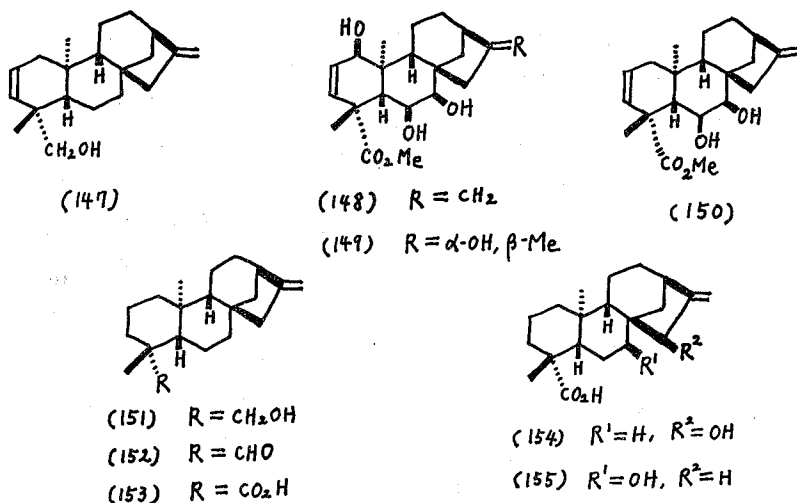
In a communication on an improved method for methoxymethylation, preparation of compounds **144**, **145**, and **146** was described.⁸⁰⁾



Formulae (144)-(146)

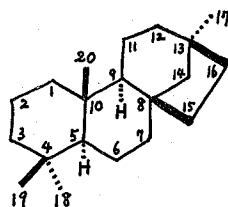
From incubation of [17-¹⁴C]-labeled dienol **147** in *Gibberella fujikuroi*, three acidic *ent*-kauranoid metabolites were isolated as their methyl esters [**148**, **149**, and **150**].⁸¹⁾

Metabolism of *ent*-[17-¹⁴C]kaurenol (**151**) and *ent*-[17-¹⁴C]kaurenal (**152**) by germinating *Hordeum distichon* was investigated and the initial steps of the biosynthetic pathway to gibberellins, that is, *ent*-kaurenol, *ent*-kaurenal, *ent*-kaurenoic acid (**153**), to *ent*-7 α -hydroxy kaurenoic acid were proved.⁸²⁾ Metabolic pathways from *ent*-kaurenoic acid (**153**)⁹⁷⁾ and *ent*-15 α -hydroxy-kaurenoic acid (**154**)⁸⁷⁾ to the fungal gibberellins were investigated. (See Section XI.) In the ring B contraction step in gibberellin biosynthesis, *ent*-7 α -hydroxy-kaurenoic acid (**155**) was discussed.¹⁰¹⁾ (See Section XI.)



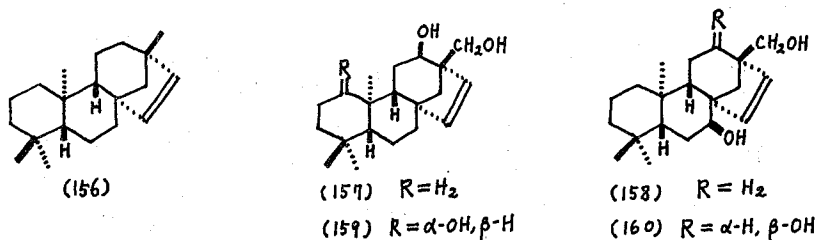
Formulae (147)–(155)

X. BEYERANE DERIVATIVES



Beyerane

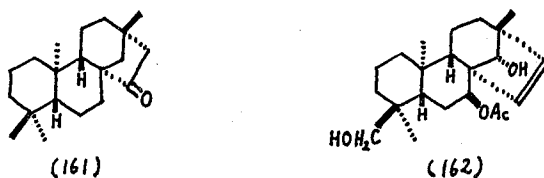
d-Hibaene (**156**) was found in the essential oil of *Araucaria araucana*.⁶⁴⁾ Two



Formulae (156)–(160)

new beyerane type diterpenes, tabarral (**157**) and benuol (**158**), were isolated from *Sideritis serrata*. The previously reported diterpenes, jativatriol (**159**) and conchitriol (**160**), were also obtained from the same source.⁴¹⁾

Rearrangement of the phenylsulfonylhydrazone of *ent*-beyeran-16-one (**131**) was reported. In the paper, the NMR spectra of ketones **131** and **161** were discussed in detail.⁷⁶⁾

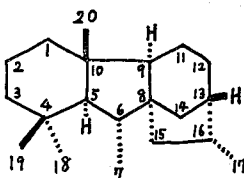


Formulae (161)–(162)

Correlation of the diterpenoids jativatriol (**159**) and sideritol (**209**) was published.⁸³⁾

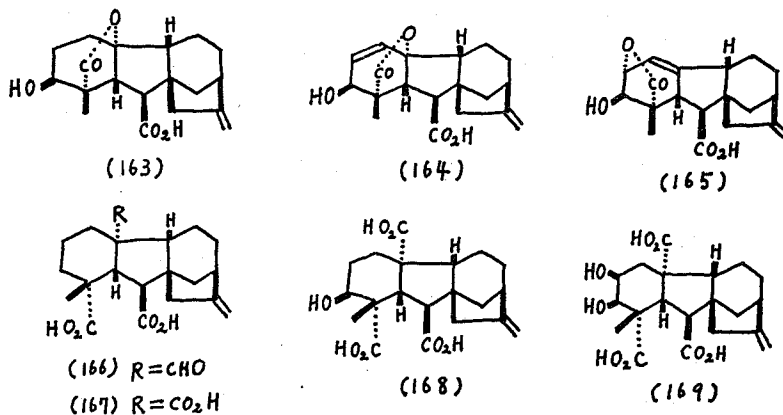
The *Sideritis* diterpene SP-2 was identified as **162** by the chemical conversion of **162** into *ent*-beyerane.⁸⁴⁾

XI. GIBBERELLANE DERIVATIVES



Gibberellane

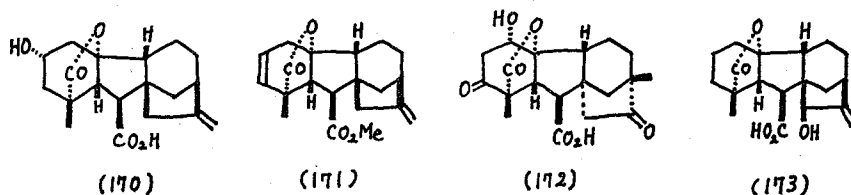
The following gibberellin constituents of the endosperm of *Echinocystis macrocarpa* were identified by GC-MS. They are GA₄ (**163**), GA₇ (**164**), iso-GA₇ (**165**), GA₂₄



Formulae (163)–(169)

(166), GA₂₅(167), two isomers of GA₁₃(168), and GA₄₃(169), respectively. The structure of a new gibberellin, GA₄₃, was established by partial synthesis.⁶³⁾

The structure of a new gibberellin (A₄₀) isolated from the culture filtrate of *Gibberella fujikuroi* was determined as 170 on the basis of ¹³C NMR measurements and conversion into deoxygibberellin A₅ methyl ester (171).⁸⁵⁾



Formulae (170)–(173)

The structure and stereochemistry of a 1-hydroxy-3-oxo-gibberellin derivative was established to be 172 by X-ray analysis.⁸⁶⁾

A new gibberellin (A₄₅) (173) was obtained from seeds of *Pyrus communis*. Its biosynthesis from a kaurene precursor was also investigated.⁸⁷⁾ (See Section IX.) The ¹³C NMR spectra of a series of gibberellins were measured and analyzed almost completely. The spectrum of ¹³C-enriched gibberellins (mixture of A¹ and A³) produced by *Gibberella fujikuroi* fed with sodium [1-¹³C] acetate was also reported.⁸⁸⁾

The gaschromatography of gibberellins and gibberellin-O-glucosides treated with silylating reagents was reported.⁸⁹⁾ Mass spectra of several gibberellins were detected.⁹⁰⁾

The partial synthesis of gibberellin A₃₇(174) from gibberellin A₁₃(168) was published. Selective reduction of the least reactive carboxy-group (C₁₀-COOH) in gibberellin A₁₃ was successively achieved through formation of the 20, 3-lactone 175, which gave the 3 α -hydroxy-epimer 176 of gibberellin A₃₇. This epimer was converted into gibberellin A₃₇(174) via Meerwein-Ponndorf reduction of 177. The sequence is illustrated in Chart 6.⁹¹⁾ Meerwein-Ponndorf reduction of the 3-oxogibberellins 177, 178, and 179 gave 50% or greater yields of the 3 β -epimers, whereas the 3-oxo-20, 19-lactone 180 afforded the 3 α -hydroxy-epimer predominantly.⁹¹⁾

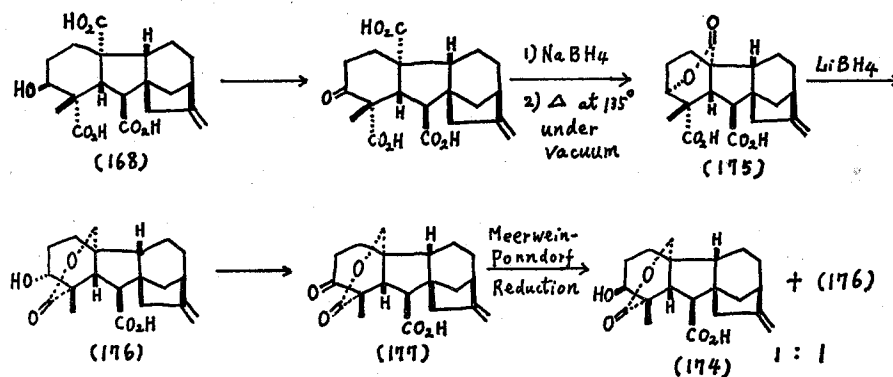
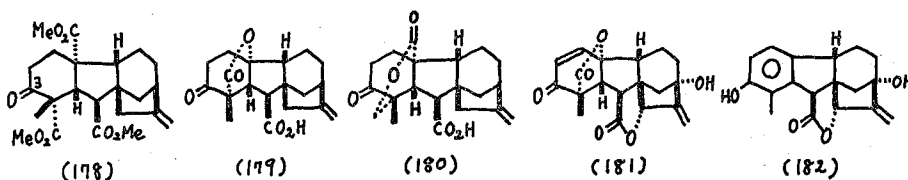


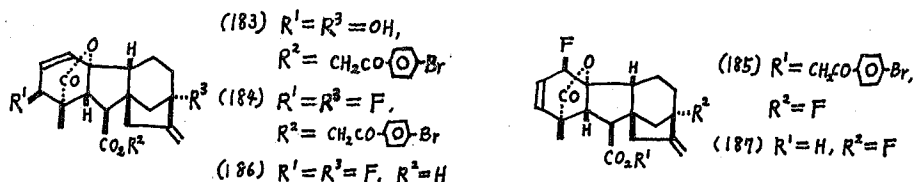
Chart 6

Dilactone **181** was irradiated with a Hg high pressure lamp for 82 hr under argon at 25–30° to give 50% yield of lactone **182** by the intramolecular photoaromatization.⁹²⁾



Formulae (178)–(182)

p-Bromophenacyl ester **183** of gibberellic acid was treated with a large excess of the fluoroamine in methylene chloride at room temperature to yield two isomeric difluoro-esters which were identified as **184** and **185** by their spectroscopic properties. De-esterification of the esters **184** and **185** with Zn dust in glacial acetic acid at room temperature gave the corresponding difluorogibberellins **186** and **187**.⁹³⁾



Formulae (183)–(187)

The partial synthesis of 6 β -methyl-7-nor-gibberellin-A₃ (**189**) from compound **188** was performed. The outline is shown in Chart 7.⁹⁴⁾

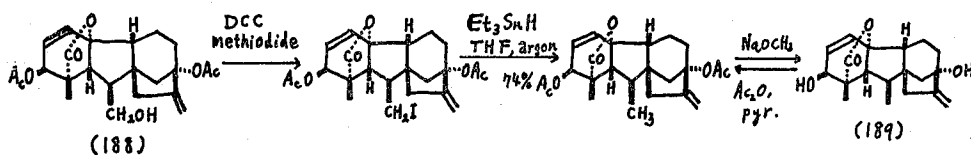
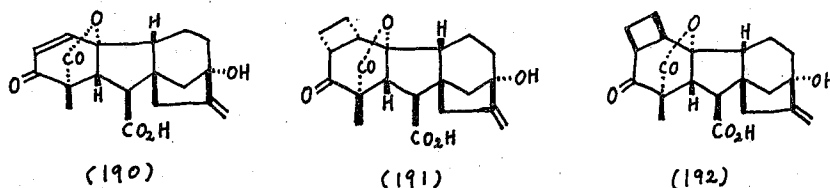


Chart 7

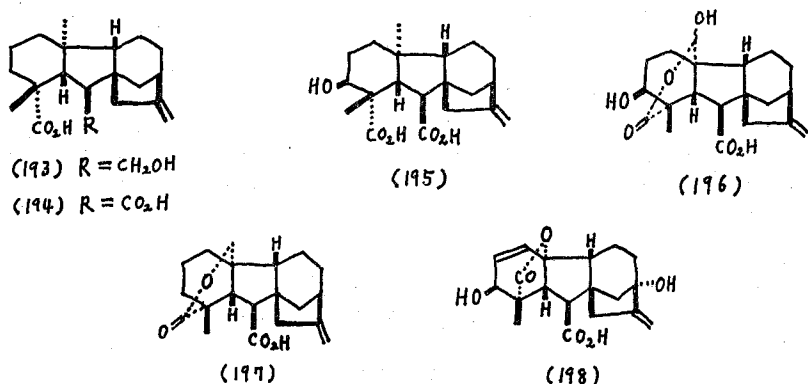
Photochemical cycloaddition of ethylene to 3-dehydro-gibberellin A₃ (**190**) yielded a mixture of adducts **191** and **192** in a ratio of 3:1.⁹⁵⁾



Formulae (190)–(192)

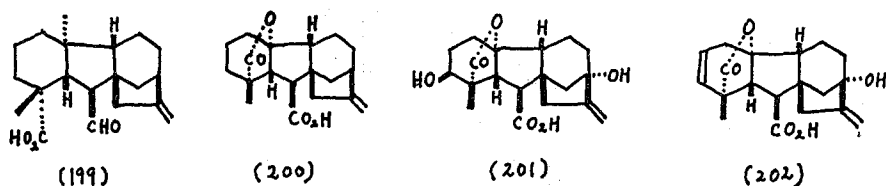
The biosynthetic relationship of the gibberellins in *Gibberella fujikuroi* was reported. A comparison of the results of feeding gibberellin A₁₂ alcohol **193** and gibberellin A₁₂

(194), in terms of the distribution of mevalonate, to *G. fujikuroi*, revealed that there was a divergence between the pathways leading to the 3-hydroxylated and the non-3-hydroxylated gibberellins at the C-7 aldehyde stage. The distribution of label between the C₁₉ and C₂₀ gibberellins after 6 and 24 hours incubations suggested that the free C₂₀ gibberellins [A₁₄ (195), A₃₇ (174), A₃₆ (196), and A₁₃ (168) or A₁₅ (197), A₂₄ (166), and A₂₅ (167)] might not lie on the direct pathway to the C₁₉ gibberellins. Gibberellins A₄ (163) and A₇ (164) were transformed into gibberellic acid (198). Incubation of gibberellin A₁₂ (194) with *G. fujiduroi* might be used to prepare gibberellins A₂₄ (166) and A₂₅ (167).⁹⁶⁾



Formulae (193)–(198)

Metabolic pathways from *ent*-kaurenoic acid to the fungal gibberellins were investigated using mutant B1-41a of *Gibberella fujikuroi*. The metabolism of substrates normally produced by wild-type strains of *G. fujikuroi* was determined in resuspended cultures of the mutant B1-41a at pH 3.5 and 7.0. The metabolites were identified by GC-MS and GC-Radiocounting. From the results at pH 3.5 the metabolic steps from *ent*-kaurenoic acid to the fungal gibberellins were deduced. The oxidation level at which C-20 is lost in the formation of C₁₉-gibberellins could not be determined. *ent*-7-Oxokaurenoic acid did not serve as a precursor of gibberellin A₁₂ aldehyde (199). At pH 7.0 the pathway from gibberellin A₁₂ (194) was diverted completely to 3-deoxygibberellins such as gibberellin A₉ (200).⁹⁷⁾

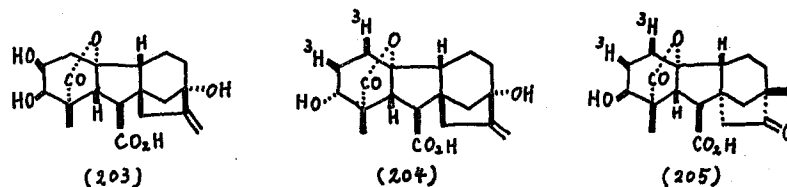


Formulae (199)–(202)

The effect of gibberellins on growth of pea seedling internode was reported. Elongation of internode segments of dwarf pea seedling exercised 4 mm below the plumular hook was stimulated by GA₃ (198) but not by GA₁ (201) or GA₅ (202).

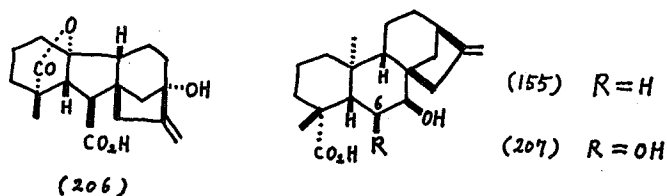
However, all three gibberellins induced cell elongation in the region from which this segment was isolated on application to intact seedlings.⁹⁸⁾

An enzyme from *Phaseolus vulgaris* seeds which hydroxylates GA₁ (201) to GA₈ (203) was characterized. This hydroxylase was specific for GA₁ and did not hydroxylate either pseudo-GA₁-[³H] (204) or rearranged 16-keto-GA₁-[³H] (205).⁹⁹⁾



Formulae (203)–(205)

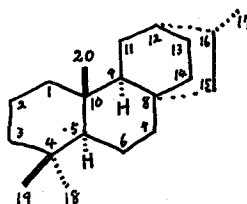
Tritium-labeled gibberellins [GA₁ (201), GA₄ (163), GA₅ (202), GA₈ (203) and GA₂₀ (206)] were fed to immature bean seeds 18 days after anthesis and their metabolic pathways were investigated.¹⁰⁰⁾



Formulae (206)–(207)

The mechanism of ring contraction (155 → 199) and 6β-hydroxylation (155 → 207) using the endosperm preparation of *Cucurbita maxima* seed and the ³H: ¹⁴C double labeled substrate of 155 was studied. It was demonstrated that the formation of GA₁₂-aldehyde (199) and *ent*-6α, 7α-dihydroxykaurenoic acid (207) involves the loss of one hydrogen atom from the 6-position in *ent*-7α-hydroxykaurenoic acid (155).¹⁰¹⁾

XII. ATISANE DERIVATIVES

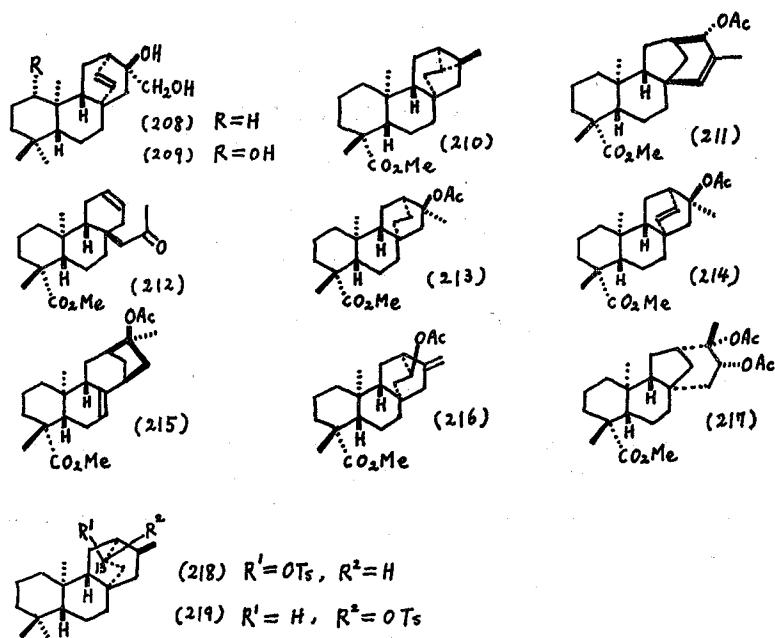


Atisane

The essential oil of *Araucaria araucana* included *ent*-atisirene (128) and *ent*-isoatisirene (129).⁶⁴⁾

From *Sideritis serrata*, two atisane type diterpenes were isolated with some other type

diterpenes. They were serradiol (**208**) and sideritol (**209**). The former was new.⁴¹⁾ Treatment of methyl *ent*-trachyloban-19-oate (**210**) with thallic oxide in acetic acid afforded many products. The paper on formation of the major products had been published.¹⁰²⁾ Now, the structures of seven minor products, **211**–**217**, and the mechanism of the oxidative cleavage were reported.¹⁰³⁾



Formulae (208)–(219)

The room temperature formolysis of the tosylates, **218** and **219**, followed by basic hydrolysis, gave mixtures which contained products [**128**, **129**, and **130**] of 1, 3-hydride shift.⁷⁵⁾ On formolysis of kaurane tosylate **127**, the same result was obtained. (See Section IX.)

A convenient synthesis of trachylobane (**221**) *via* a reductive homoallylic cyclization of compound **220** with LiAlH₄ was reported. (See Chart 8).¹⁰⁴⁾

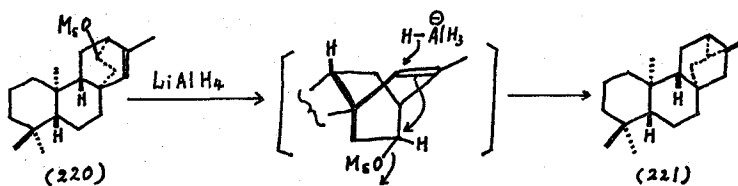


Chart 8

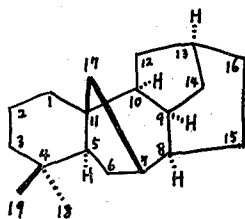
The diterpenoids sideritol (**209**) and jativatril (**159**) were correlated by transformation of each into diketone **222**.⁸³⁾

A chemical conversion of atisine (**223**) into lycocotnine type compounds was published. The detail is described in Section XIII.



Formulae (222)-(223)

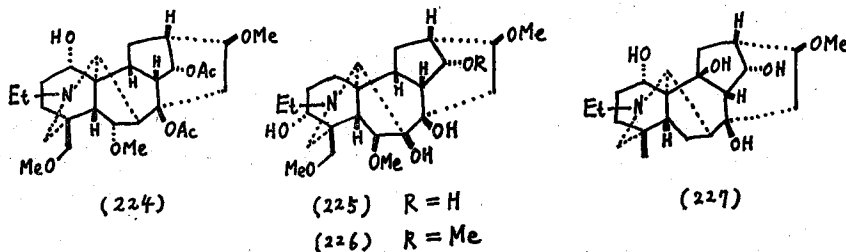
XIII. ACONANE DERIVATIVES



Aconane

The structural relationships among various aconitine-type alkaloids were re-examined on the basis of the structure of delphisine (224).¹⁰⁵⁾

The structure of iliensine (225), isolated from *Delphinium biternatum*, was determined by means of the spectroscopic methods.¹⁰⁶⁾



Formulae (224)-(227)

The structure of acomonine (226) isolated from *Aconitum monticola* was determined on the basis of spectroscopic and chemical evidence.¹⁰⁷⁾ Karacolidine was isolated from tubers of *Aconitum karacolicum* and its structure 227 was elucidated by NMR and mass spectroscopy and chemical transformations.¹⁰⁸⁾

The chemical conversion of atisine (223) into the ketone 228 possessing a lycocotone skeleton and the X-ray structure determination of the product were published. The outline of the conversion sequence is shown in Chart 9.¹⁰⁹⁾

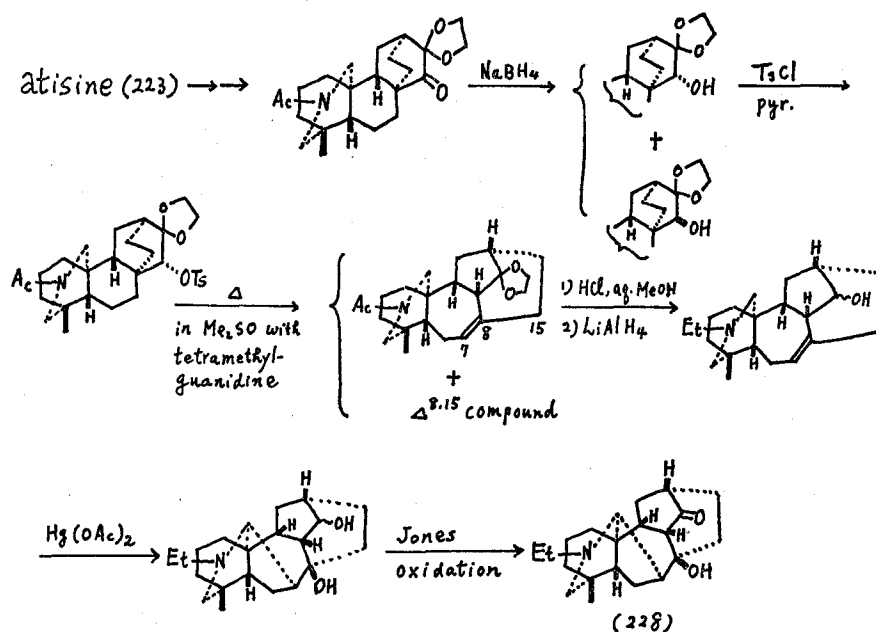
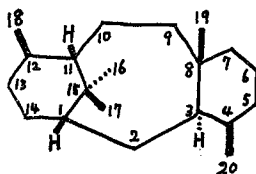


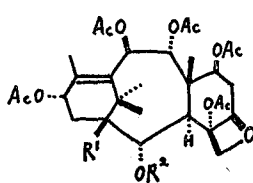
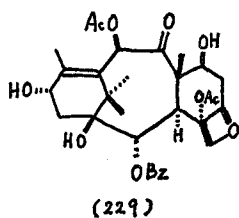
Chart 9

XIV. TAXANE DERIVATIVES



Taxane

The structures of baccatin-III (229), -IV (230a), -VI (230b), -VII (231) and 1-dehydroxybaccatin-IV (232) were determined.¹¹⁰⁾



(230a) $R^1 = \text{OH}$, $R^2 = \text{Ac}$

(230b) $R^1 = \text{OH}$, $R^2 = \text{Bz}$

(231) $R^1 = \text{OH}$, $R^2 = \text{COC}_2\text{H}_5$

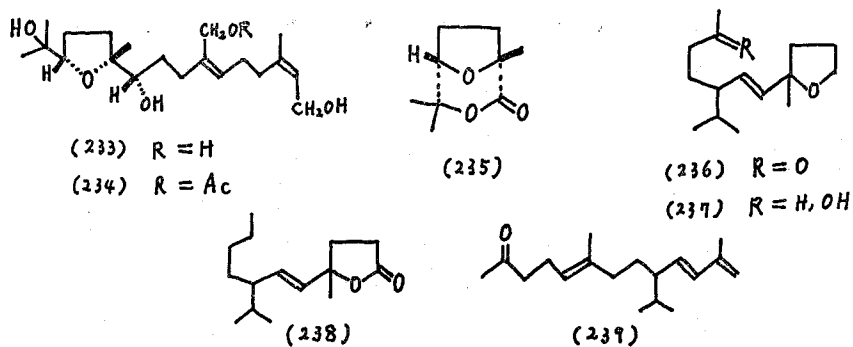
(232) $R^1 = \text{H}$, $R^2 = \text{Ac}$

Formulae (229)-(232)

XV. THE OTHERS

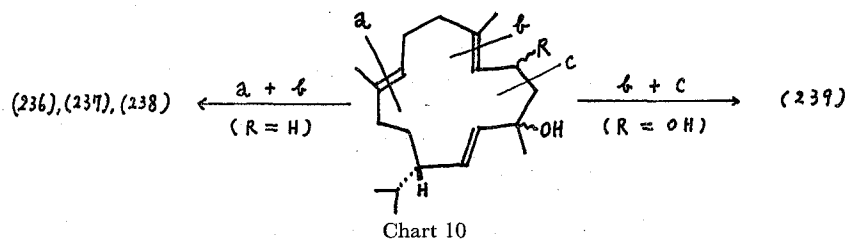
The geranylnerol derivative ligantrol (233) and its monoacetate (234) were iso-

lated from *Liatris elegans* and their structures established. The absolute stereochemistry assigned to C-11 and C-14 (11R, 14S) was deduced by degradation to a known lactone **235** of established absolute configuration.¹¹¹⁾

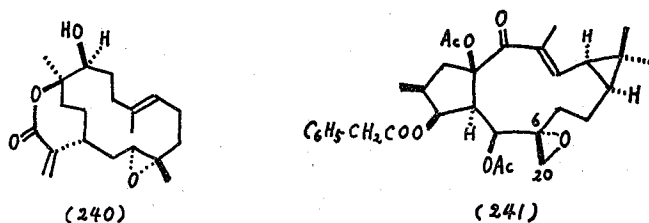


Formulae (233)–(239)

Four novel constituents of *Nicotiana tabacum* were identified as **236**, **237**, **238**, and **239**. Their possible formation from cembrene-type precursors was briefly discussed.¹¹²⁾ (See Chart 10.)



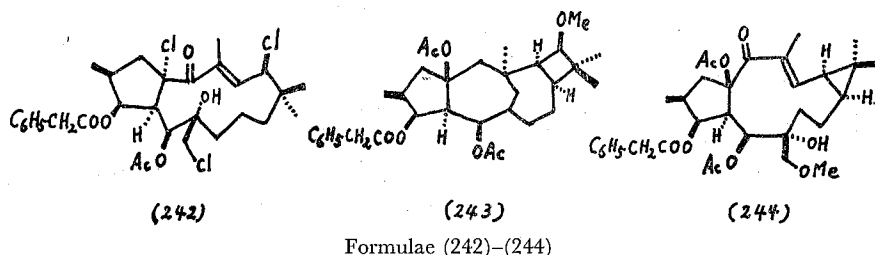
Sinulariolide, a novel diterpene lactone was isolated from *Simularia flexibilis*. Its absolute structure was established by X-ray diffraction as depicted in **240**.¹¹³⁾ 6, 20-Epoxyathyrol (**241**) was isolated from *Macaranga tanarius*.¹¹⁴⁾ From the seed oil of *Euphorbia lathyris* the known diterpenoids **241**, ester L₃, and ester L₂ were isolated.¹¹⁵⁾



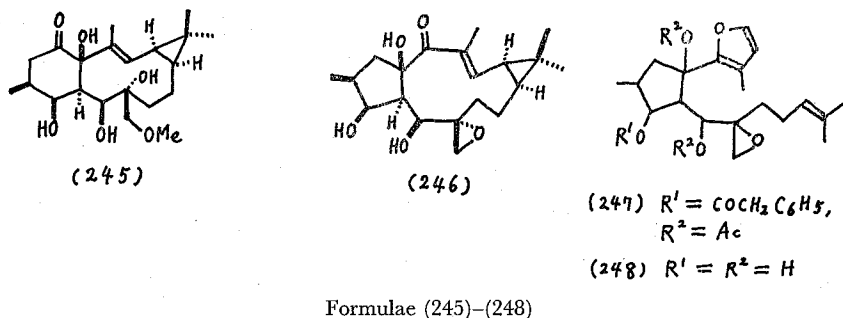
Formulae (240)–(241)

Reaction of **241** with acids in THF led to simple fission of the epoxy ring and yielded the corresponding hydrin derivatives. When anhydrous methanol was used as the solvent, reaction of **241** with hydrochloric acid gave the novel macrocyclic trichloride **242** which has the jatropane skeleton. Reaction with sulfuric acid afforded

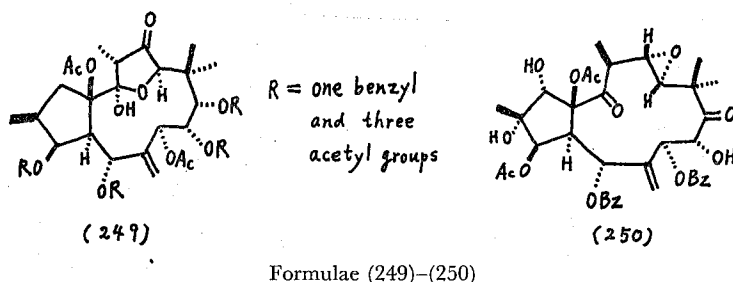
the transannular cyclization product **243** and methoxyhydrin **244**.¹¹⁶⁾



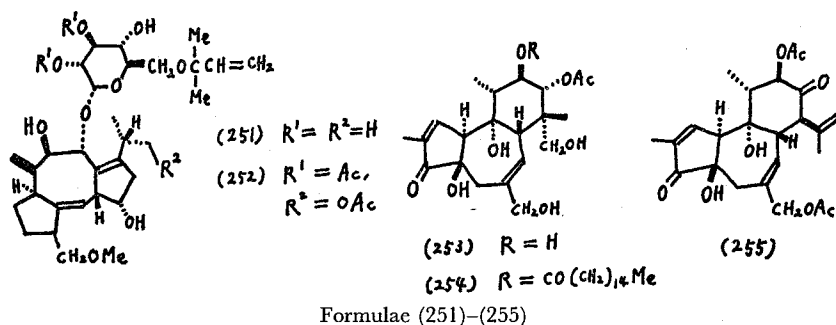
Reaction of **241** with barium methoxide afforded **245**, whereas the reaction with sodium methoxide gave **246**.¹¹⁷⁾ The photochemical reactions of **241** and **246** were shown to afford **247** and **248**, respectively.¹¹⁸⁾



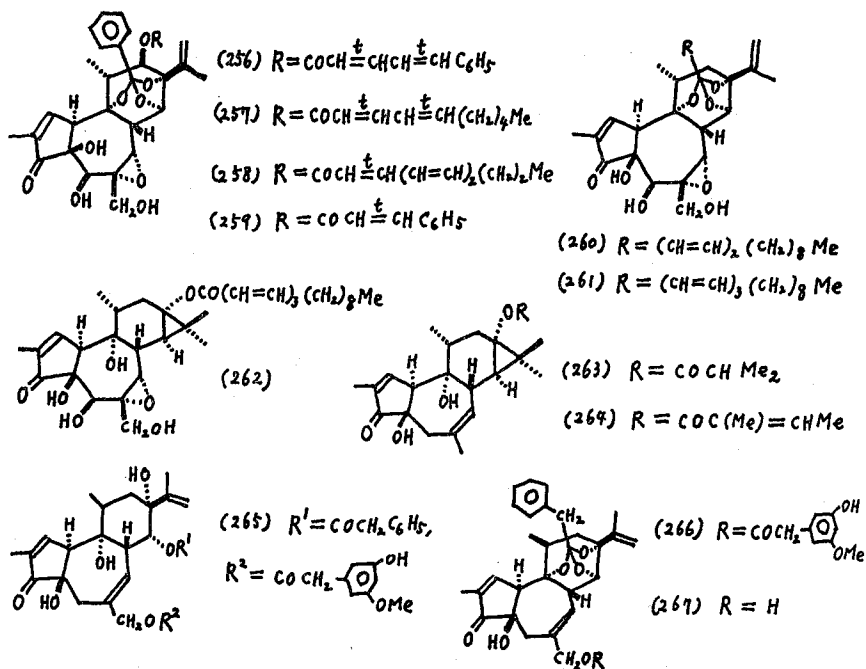
Two new toxic compounds, named kansuine A and B were isolated from *Euphorbia kansui*, and the structures were determined as **249** and **250**, respectively.^{119, 120, 121)}



The structure **251** of fusicoccin J, a minor glucoside produced by *Fusicoccum amygdali*, was determined by its synthesis from fusicoccin (**252**).¹²²⁾ The carbon-13 NMR spectra of **252** and its derivatives were investigated.¹²³⁾ From *Aleurites fordii* fruits, two new diterpenes were isolated. The structure **253** was assigned by its chemical transformation into **255**. The structure of another toxic constituent was established as **254** by partial synthesis from **253**.¹²⁴⁾



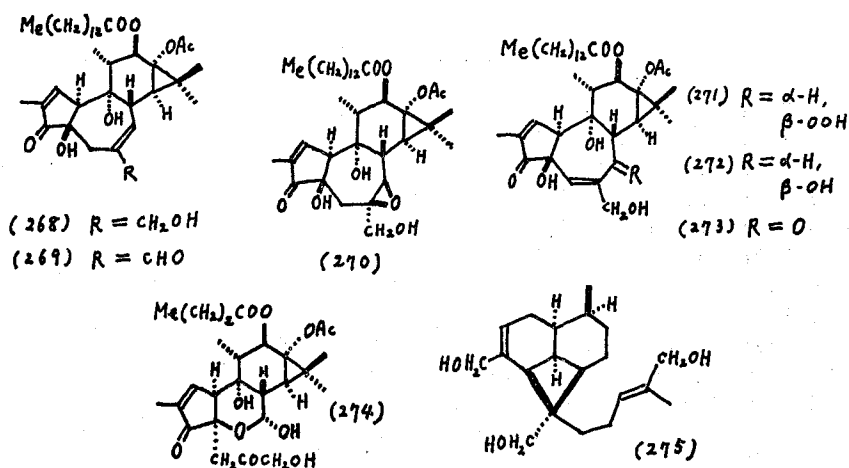
From *Daphne mezereum* an antileukemic principle, mezerein (256) was isolated and characterized.¹²⁵⁾ The novel antileukemic diterpenes, gnididin, gniditrin and gnidicin were isolated from *Gnidia lamprantha*, and their structures were determined as 257, 258, and 259, respectively.¹²⁶⁾ New irritant compounds 260, 261, and 262 were isolated from *Hippomane mancinella*.¹²⁷⁾ From *Euphorbia resinifera*, two yellow-orange staining, non-irritant compounds 263 and 264 as well as three blackish-brown staining irritant *Euphorbia* factors RL20 (265), RL9 (266) and RL14 (267) were isolated. Similarly, compound 266 was isolated from *Euphorbia unispina*.¹²⁸⁾



Autoxidation of phorbol ester 268 gave 269~274 characterized by T. L. C. and partial synthesis.¹²⁹⁾

A new diterpene triol 275 was isolated from *Eremophila decipiens*.¹³⁰⁾

Spectroscopic and degradative methods with 1, 2-¹³C₂-acetate and 2-¹⁴C-4R-



Formula (268)-(275)

³H-mevalonate precursors showed that aphidicolin (276) arises from initial chair-boat cyclization of the diterpene chain followed by successive H-shift, cyclization and rearrangement steps, as shown in Chart 11.¹³¹⁾

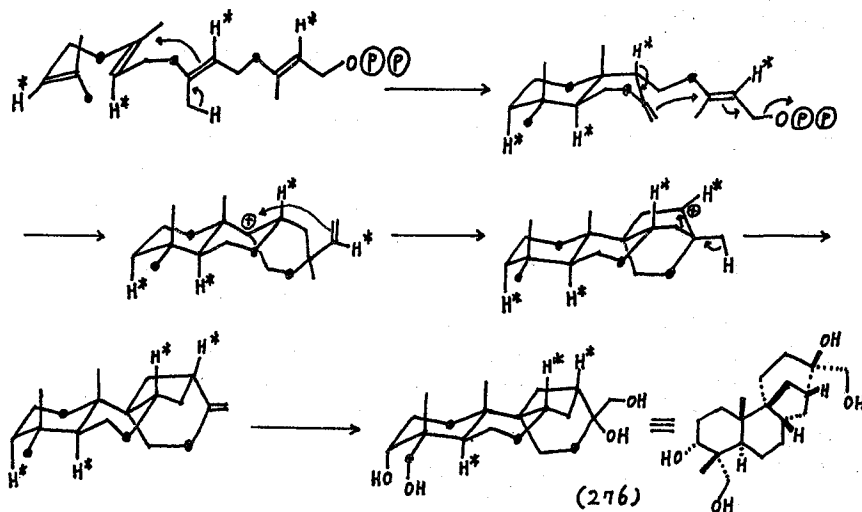


Chart 11

The review on the biogenetic type synthesis and reaction of terpenoids was published.¹³²⁾

The papers "Stereochemistry of diterpene alkaloids in acylation and alkaline hydrolysis"¹³³⁾ "Structure of vulgarol, a new diterpenoid from *Marrubium vulgare*"¹³⁴⁾ and "Structure of aconorine"¹³⁵⁾ were published. Cembrene, dehydroabietinal, palustral, epimanool, epitorulosol, larixol, larixol acetate, and isoprimaryinol were isolated from oleoresins of *Larix sibirica*, *L. sukaczawii*, and *L. czekanovskii*.¹³⁶⁾

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