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Review

The Chemistry on Diterpenoids in 1977. Part-II[1]

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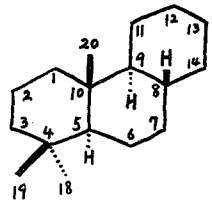
I. INTRODUCTION

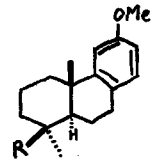
This is one of a series of our annual reviews on diterpenoids chemistry. The classification of the compounds is the same as that adopted in our reviews since 1969. This review covers the literatures published between July and December 1977 and also omissions in Part-I.

II. PODOCARPANE DERIVATIVES

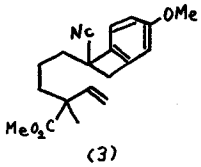


Podocarpane

The chirality of nucleophilic reactions of the 4β aldehyde and methyl ketone groups in the podocarpane derivatives (**1** and **2**) was investigated.[2] Thermolysis of cyanobenzocyclobutene **3** gave four stereoisomeric products (**4**–**7**). Their structures were clarified by the chemical conversion of each octahydrophenanthrene into the known compounds.[3]



(1) R = CHO
(2) R = COMe



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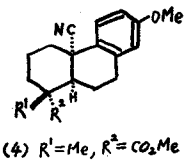
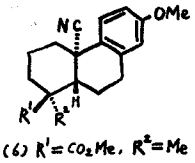
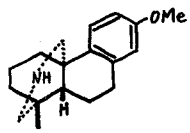


(4) R¹ = Me, R² = CO_2Me
(5) R¹ = CO_2Me, R² = Me



(6) R¹ = CO_2Me, R² = Me
(7) R¹ = Me, R² = CO_2Me

A synthesis of a diterpene alkaloid intermediate **8** from cyanobenzocyclobutene **9** was reported.[4] As an approach to the synthesis of podocarpic acid (**10**), an olefinic compound **11** was synthesized starting from 2-(2-phenylethyl)cyclohexane-1, 3-dione.[5]



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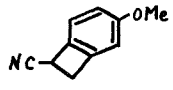

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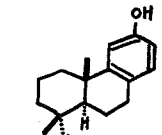

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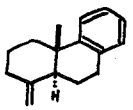


(11)

Syntheses of model systems for podocarpic acid and diterpene alkaloids were reported. The outline is illustrated in Chart 1.[6] The structure and stereochemistry of tricyclic intermediates (**16**) and other related compounds were also discussed.[7]

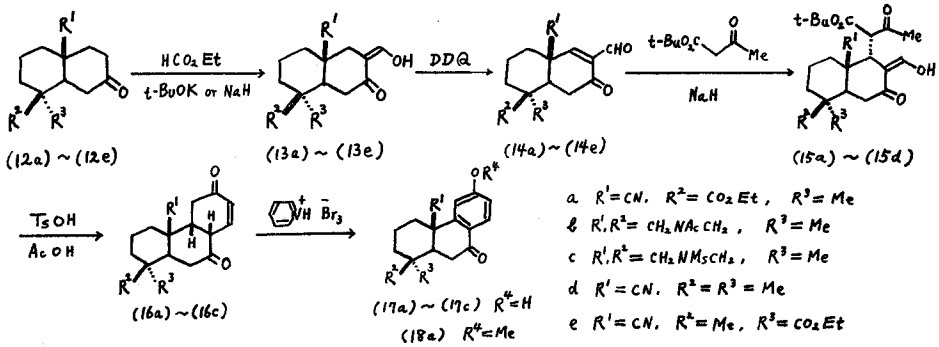
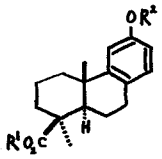


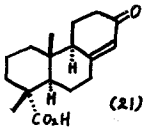
Chart 1

Treatment of ester **19** with lithium methanethiolate, CH_3SLi, at 25° for 2 hrs afforded the corresponding acid **20** in 98% yield. On treatment of compound **19** with CH_3SLi at 120° for 36 hrs, acid **10** was obtained in 95% yield.[8] The generation of a reactive phenyl selenide anion and its application to S_N2-type ester cleavage (*e.g.* **19**→**20**) were published.[9] The chemical basis for feeding adaptation of pine sawflies, *Neodiprion rugifrons* and *N. swainei*, was discussed determinating the content of a feeding deterrent chemical, 13-keto-8(14)-podocarpen-18-oic acid (**21**) in foliage.[10]



(19) $R^1=R^2=Me$

(20) $R^1=H$, $R^2=Me$



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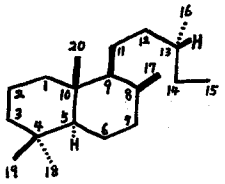
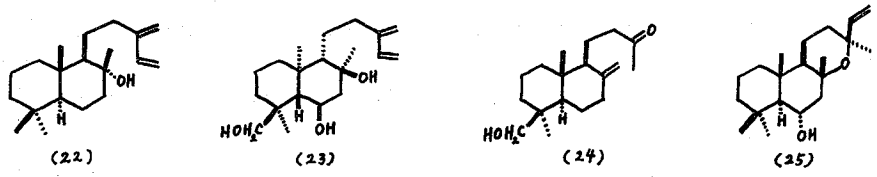
III. LABDANE DERIVATIVES

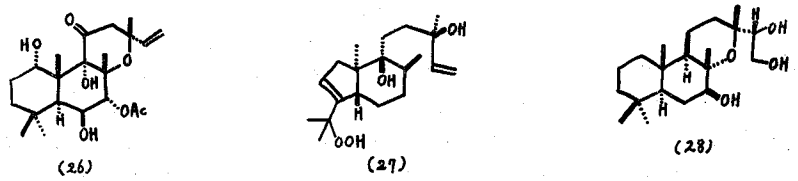


Labdane

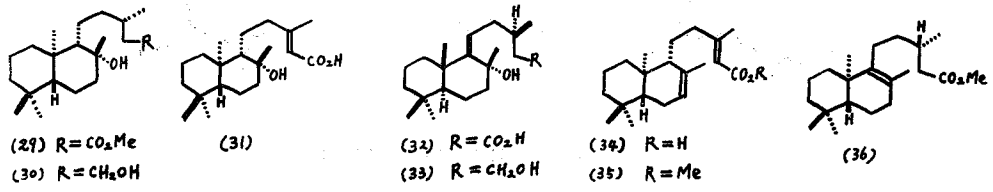
Isoabienol (**22**) was isolated from needles of *Pinus sylvestris*.[11] The absolute structure of andalusol (**23**), a new diterpene from a subspecies of *Sideritis arborescens*, was reported.[12] New labdane type diterpenes isolated from southern pine (*Pinus* spp.) tall oil were characterized as 19-hydroxy-15,16-dinorlabd-8(17)-en-13-one (**24**) and 8,13β-epoxy-14-labden-6α-ol (**25**).[13]



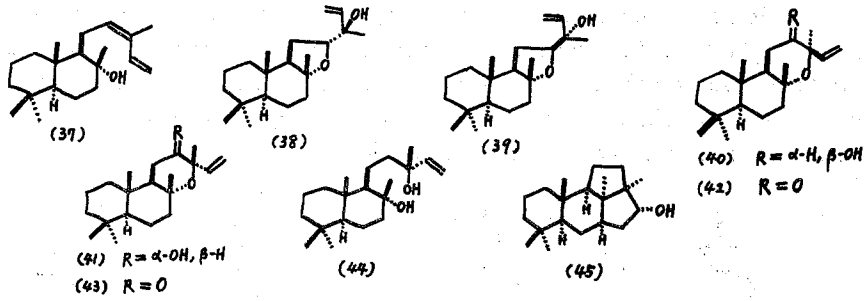
The structure **26** of coleonol, a diterpene possessing hypotensive and spasmolytic activities, isolated from the roots of *Coleus forskohlii*, was assigned on the basis of chemical and spectral evidence and X-ray crystallographic data.[14] A novel marine diterpenoid, neoconicinndiol hydroperoxide (**27**), was isolated from extracts of the red seaweed *Laurencia snyderiae* and its structure was finally determined by a single-crystal X-ray diffraction method.[15] A correction of the structure of borjatriol to formula **28** was reported on the basis of ^{13}C–NMR investigation.[16]



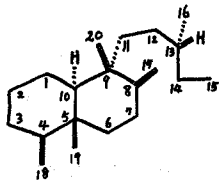
The ^{13}C–NMR spectra of some labdane diterpenes **29**–**36** were investigated and the signals assigned.[17] The substituent shielding effects in these compounds were also discussed.



On peracid oxidation, (12*Z*)-abienol (**37**) afforded two major products **38** and **39**, and also gave small amounts of **40** and **41**, which were converted to compounds **42** and **43** by Jones' oxidation.[18] Dehydration of sclareol (**44**) with perchloric acid yielded a complicated tetracyclic product **45**.[19] 15-Norlabdan-8-ol, labd-8(17)-en-15-ol, and 15-hydroxylabd-7-en-6-one were isolated from *Cistus ladaniferus* gum.[20]

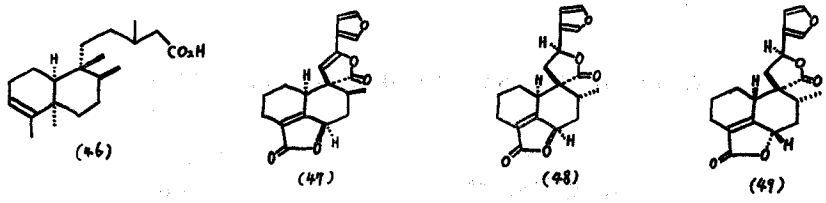


IV. CLERODANE DERIVATIVES

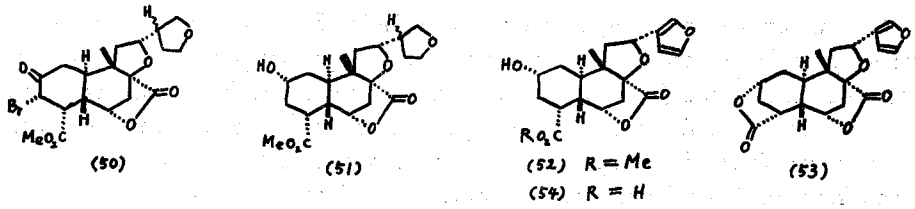


Clerodane

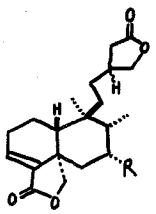
A new *cis*-clerodane diterpene was isolated from the aerial parts of *Macowania glandulosa* and its structure **46** was elucidated by spectroscopic methods and by chemical reactions.[21] The structure and stereochemistry of crotocaudin, a new norditerpene occurring as a minor constituent in *Croton caudatus* were established as **47** by the detailed investigation of the NMR spectroscopic study. The congener, teucvidin (**48**), was also isolated as a major component and its conversion to teucvin (**49**) was achieved.[22]



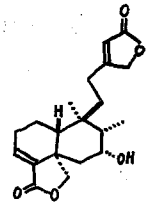
The X-ray analysis of 3-bromo-2-oxo-tetrahydrodiosbulbin-A (**50**) was performed using heavy-atom method. Thus the absolute structures of tetrahydrodiosbulbin-A (**51**), diosbulbin-A (**52**), -B (**53**), and -C (**54**), which could not be determined by chemicophysical methods, were clarified.[23]



The isolation of three new *trans*-clerodane type diterpenoids, **55**, **56**, and **57**, from the medicinal plant *Baccharis trimera* was reported. Proof for the proposed structure and definite evidence for the stereochemistry were provided by X-ray analysis of **57**.[24] The structures of bacchotricuneatin A (**58**) and B (**59**), two new diterpenes from *Baccharis tricuneata var. tricuneata*, were described.[25]



(55) R=H
(56) R=OH



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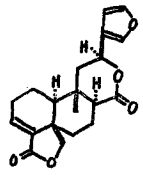

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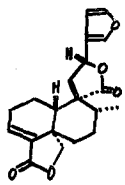
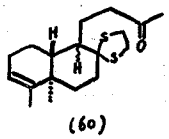


(59)

The isolation and structure elucidation of diterpenoids from *Teucrium polium*[26] and *T. hycanicum*[27] were reported.

Compound **60**, a valuable intermediate in the synthesis of various clerodane type diterpenes, was effectively prepared from **61**.[28] Kolavenic acid (**62**) was isolated from the roots of *Solidago altissima*. It showed the antibacterial activity. The antibacterial properties of the several compounds derived from **62** were also investigated.[29]



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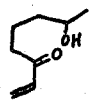

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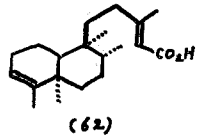

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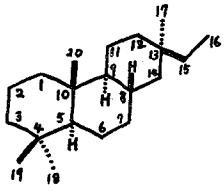
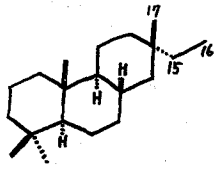
V. PIMARANE AND ISOPIMARANE DERIVATIVES





Pimarane and Isopimarane

A new diterpene, 8(14),15-pimaradiene-3β,18-diol (**63**) was isolated from southern pine (*Pinus* spp.) tall oil with some other type diterpenes.[13] A biosynthetic study on rosenolactone (**64**) using Deuterium Magnetic Resonance was published.[30] This investigation established that the 5-pro-*R* hydrogen of mevalonate becomes the 16*Z* hydrogen (H_a) of rosenolactone. Conversely the 16E hydrogen (Hb) of **64** is derived from the 5-pro-*S* hydrogen of mevalonate. The outline is shown in Chart 2.

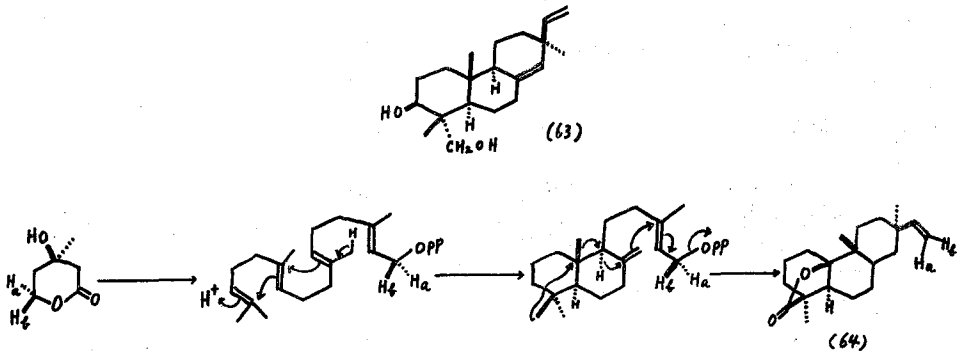
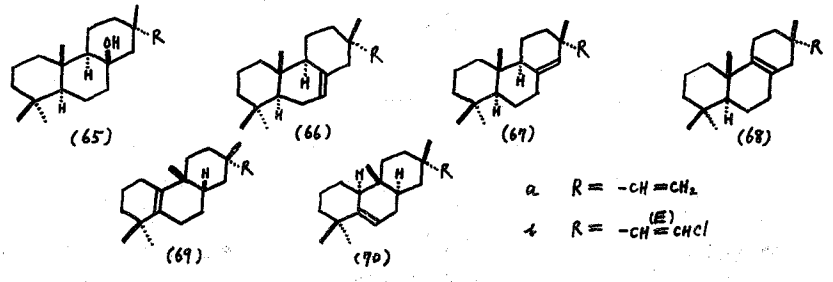
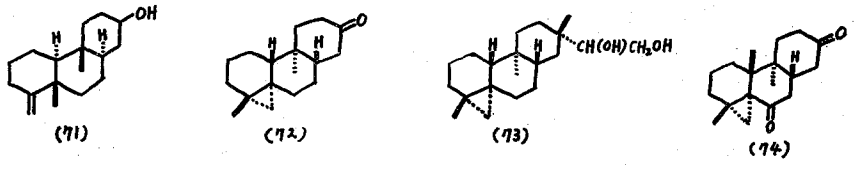


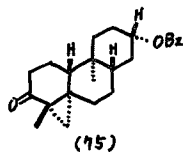
Chart 2

Acid-catalyzed dehydration of each of the 8β-hydroxy compounds **65a** and **65b** gave initially the olefinic isomers **66**, **67**, and **68**. After extended reaction times the rearranged olefinic compounds **69** and **70** were major products.[31]



The compound **71** was synthesized as an intermediate for pimarane derivatives.[32] The synthesis of the fundamental skeleton **72** of erythroxydiol X (**73**) isolated from *Erythroxylon monogynum* was investigated. The cycloprophyl ketones **74** and **75** were synthesized from the tricyclic oxo-acid **76** and the monomethylated $\alpha\beta$-unsaturated ketone **77**, respectively. Reduction of either compound **74** and **75** with lithium aluminum hydride in dioxane did not give the desired compound **72**, but the seven-membered ring compound **78**, presumably by hydrogenolytic cleavage of the cyclopropane ring.[33] The chemical conversion of virescenol A (**79**) into virescenol B (**80**) was published.[34] Oxidations of methyl sandaracomimarate, pimarate, isopimarate, $\Delta^{8,9}$-pimarate, and $\Delta^{8,9}$-isopimarate by *p*-nitroperbenzoic acid gave epoxides having both the α and β configurations, *e.g.* **81** and **82**. The compound **81** was isomerized in acidic chloroform to give **83**.[35]

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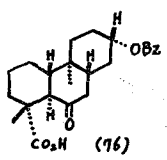
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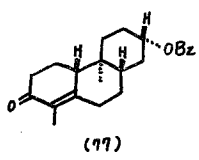
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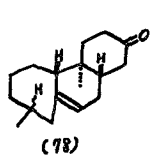
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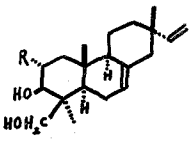
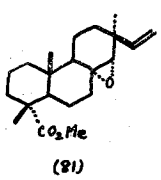

(79) R = OH
(80) R = H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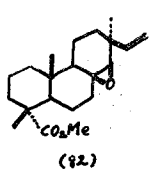
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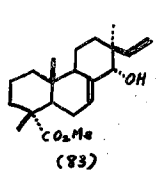
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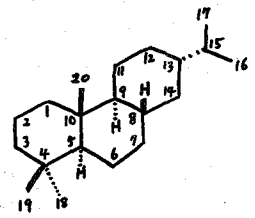
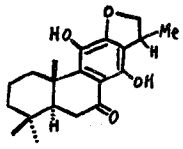
VI. ABIETANE DERIVATIVES


Abietane

A new diterpene-quinol, hyptol (**84**), was isolated from *Hyptis fructicosa* which also contained horminone (**85**) and 14-methoxytaxodione (**86**).[36]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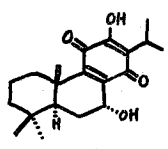
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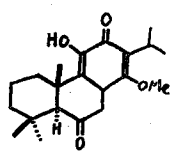
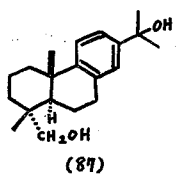
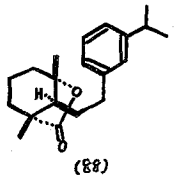

(86)

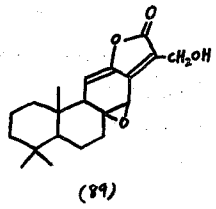
Arguments based on ^{13}C and ^{1}H NMR spectroscopy were presented to elucidate the structures of 12- and 14-monochlorodehydroabietic acid and 12, 14-dichlorodehydroabietic acid, which were major toxic components to fish in kraft mill caustic extraction effluents.[37]

Two new abietane type diterpenes, 8,11,13-abietatriene-15,18-diol (**87**) and 9,10-secoabieta-8,11,13-trien-18,10-olide (**88**) were obtained with some other new diterpene companions from southern pine (*Pinus* spp.) tall oil.[13]

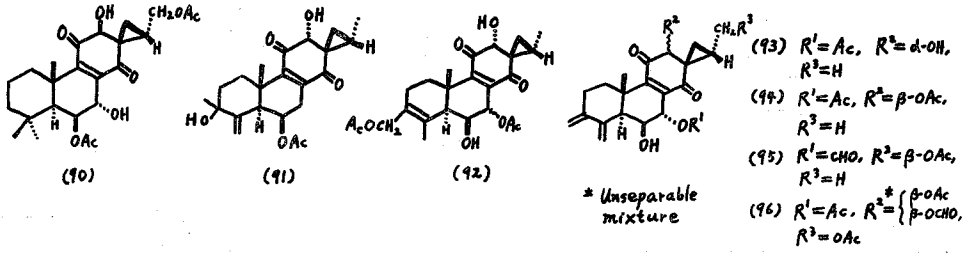
A new diterpene, caudicifolin (**89**) was isolated from *Euphorbia caudicifolia*.[38]


(87)

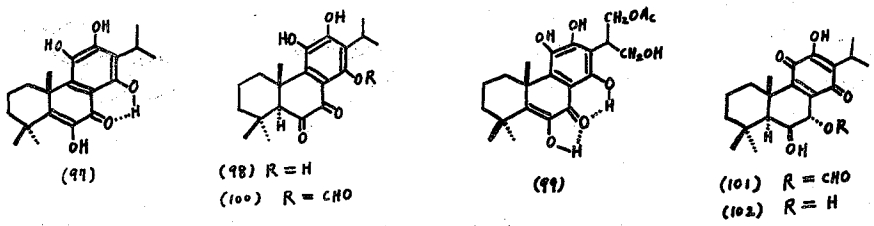

(88)


(89)

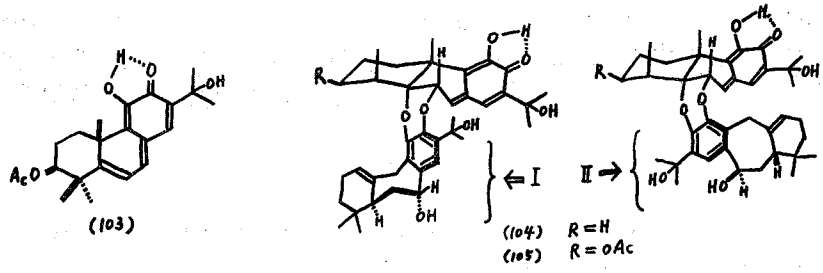
The structures of seven minor constituents "Syl-A (**90**), B (**91**), C (**92**), and D (**93**)" from *Solenostemon sylvaticus* and "Mon-A (**94**), B (**95**), and C (**96**)" from *S. monostachys* were reported.[39]



From leaf-glands of *Plectrauthus myrianthus*, the following diterpenoids were isolated: coleon U (**97**), V (**98**), W (**99**), 14-O-formyl-coleon-V (**100**), 7α-formyloxy-6β-hydroxyleanone (**101**) and the already known 6β,7α-dihydroxyleanone (**102**).[40]



Deeply colored quino-methane derivatives, 3β-acetoxy-fuerstione (**103**), nilgherron A (**104**, I or II), and nilgherron B (**105**, I or II) were isolated from *Plectranthus nilgherricus*.[41]



Ferruginol (**106**), a precursor for taxodione (**107**) synthesis, was prepared according to the sequence illustrated in Chart 3.[42]

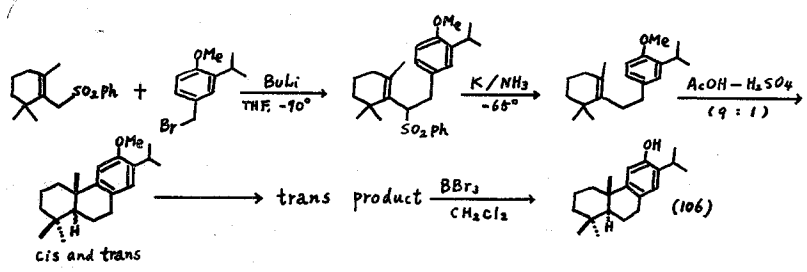
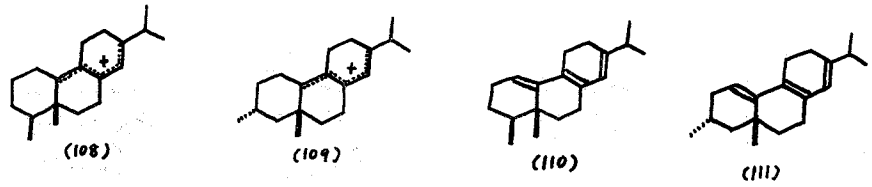


Chart 3

Abietic acid was recovered from fluorosulfonic acid below −40°. At higher temperatures an irreversible rearrangement took place to give stable carbocations **108** and **109**. Quenching the cations in aqueous sodium carbonate afforded a 1 : 2 mixture of trienes **110** and **111**.[43]



A new stereoselective synthesis of dehydroabietic acid (**113**) from the dinorketone (**112**) was efficiently achieved.[5] The outline is shown in Chart 4.

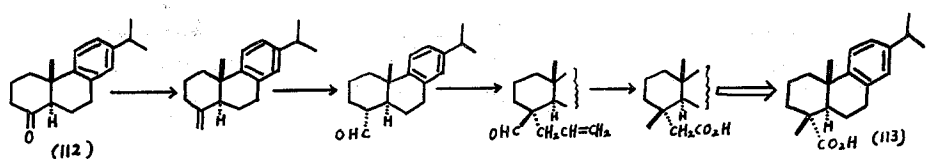
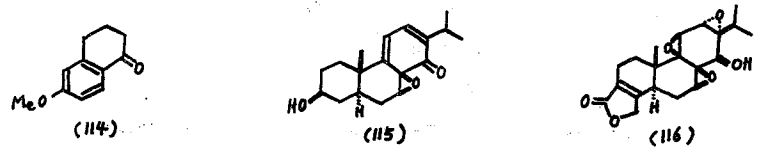


Chart 4

In a synthetic study of triptolide (**116**), a compound **115** was prepared from 6-methoxy-1-tetralone (**114**) *via* several steps.[44]



A total synthesis of methyl *rac*-dehydroabietate (**117**) was successfully performed.[45] The synthetic route is shown in Chart 5.

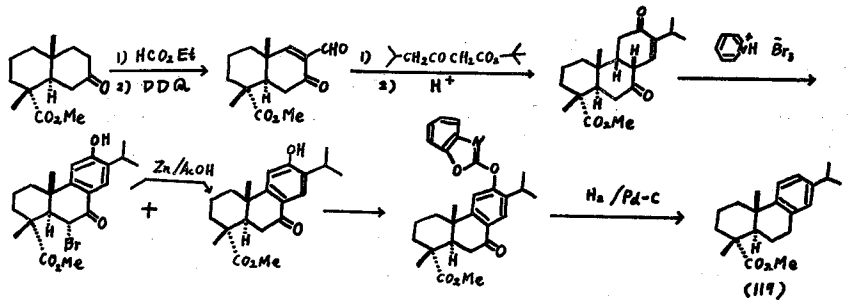
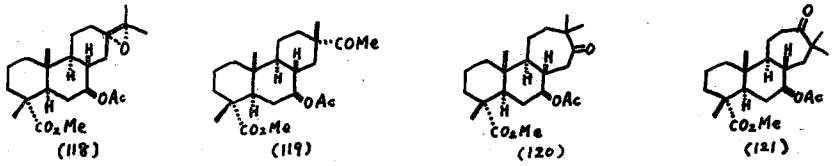
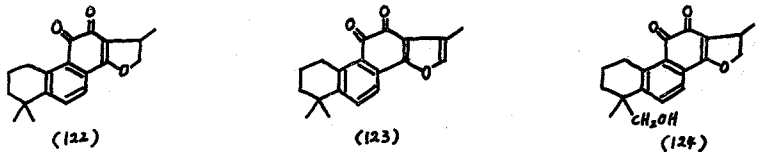


Chart 5

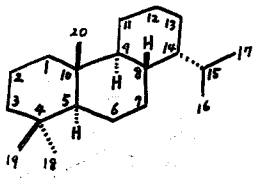
The α-epoxide **118** derived from *l*-abietic acid was treated with $BF_3 \cdot Et_2O$ in benzene to give the methyl ketone **119**, whereas the corresponding β-epoxide underwent a methylene migration (ring expansion) to give the cycloheptanone derivative **120** or **121**.[46] The compound **119** was converted to 13α-beyerane.



Isolation of cryptotansinone (**122**) from tansinone III [a mixture of tansinone II (consisting of II–A (**123**) and II–B (**124**)) and cryptotansinone (**122**)] as a Fe (III) complex was reported.[47]

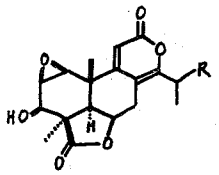


VII. TOTARANE DERIVATIVES

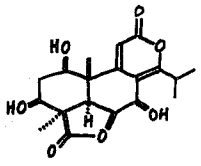


Totarane

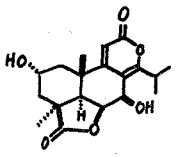
The structures of five new cytotoxic nor-diterpenoids, **125–129**, separated from *Podocarpus nagi* seed extract were elucidated.[48,49] Furthermore, three new nor-diterpenoids, **130–132**, were isolated from fresh root bark of the same plant.[50]



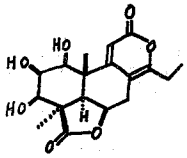
(125) R=OH
(126) R=CO_2Me



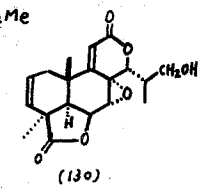
(127)



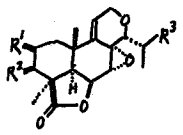
(128)



(129)



(130)

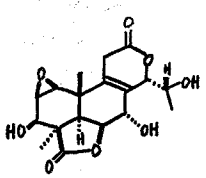


(131) $R^1=R^2=H$, $R^3=CH_2OH$

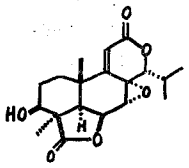
(132) $R^1,R^2=\!>O$, $R^3=Me$

From the seed of *Podocarpus macrophyllus*, inumakilactone D was isolated as a new minor norditerpene lactone, and the structure **133** was determined by X-ray analysis.[51]

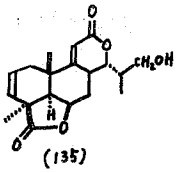
Chemical modifications of the ring A functional groups on the norditerpene dilactones, **134–136**, were investigated.[52]



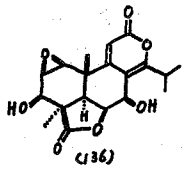
(133)



(134)

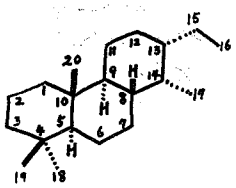


(135)



(136)

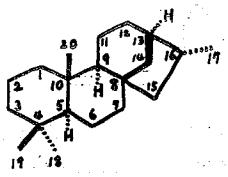
VIII. CASSANE DERIVATIVES



Cassane

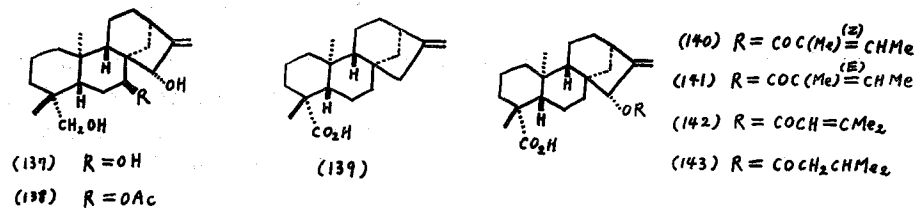
No papers have been published on the title topics in this period.

IX. KAURANE DERIVATIVES

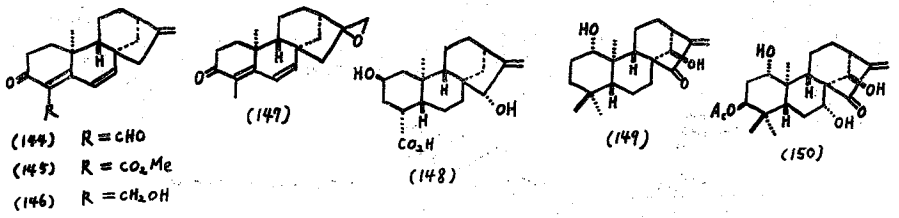


Kaurane

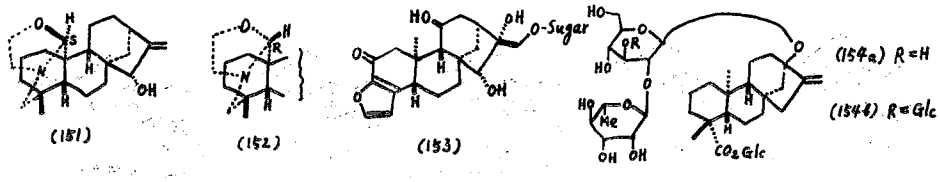
Two new diterpenes, eubotriol (**137**) and eubol (**138**), were isolated from *Sideritis euboea*.[53] From *Viguiera stenoloba var. chihuahuense* roots, five diterpenoids, **139–143**, were isolated. Kaurenoic acid (**139**) was also isolated together with beyerane type diterpenoids from *V. grammatoglossa* roots and *V. cordifolia* (roots and aerial part).[54]



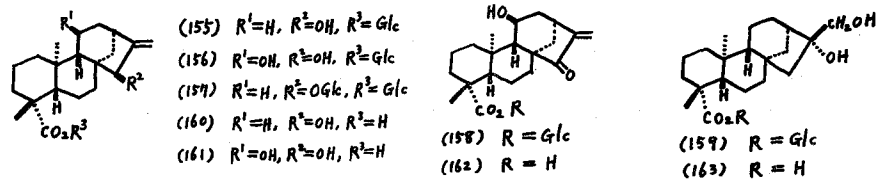
Investigation of seven *Arthrixia* species afforded besides known compounds four new norkaurene derivatives, **144–147**.[55] The occurrence of atractyloside and atractyligenin (**148**) in *Callilepis laureola* was reported.[56] A new antitumor and antibacterial diterpenoid, kamebanin, was isolated from *Isodon kameba* and the structure was determined as **149**.[57] The isolation and characterization of a new *ent*-kaurenoid diterpene, isodomedin (**150**), from *Isodon shikokianus var. intermedius* was published. This compound exhibits antibacterial and cytotoxic activities as well as antifeedant activity against the African army worm.[58]



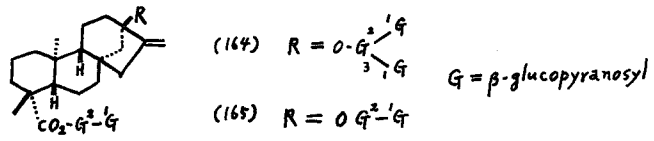
An X-ray crystal structure determination of veatchine revealed the coexistence of molecules which differ in configuration at C–20 atom, that is, **151** and **152**.[59] The crystal and molecular structure of mascaroside (**153**) isolated from coffee beans was determined by direct methods and X-ray analysis.[60] New diterpene glycosides, dulcosides A and B were isolated from *Stevia rebaudiana* and their structures were established as **154a** and **154b**, respectively. They showed moderate sweetness, *ca* 30 times more than that of sucrose.[61]



From the aerial part of *Stevia paniculata*, five new diterpene glucosides, paniculosides I–V were isolated and their structures, **155–159**, were formulated on comparison of ^{13}C NMR spectra of these glucosides with those of the aglycones, **160–163**.[62]



From the leaves of *Stevia rebaudiana*, additional two sweet glucosides, rebaudiosides-D (**164**) and -E (**165**), were isolated. Their structures were assigned on the basis of ^{13}C NMR evidences as well as the results of chemical and enzymatic hydrolysis and were substantiated by their preparation from the known compounds.[63]



By means of enzymatic and chemical procedures, stevioside (**166**) was converted efficiently into rebaudioside-A (**167**) which tastes sweeter and more pleasant than **166**[64] (see Chart 6).

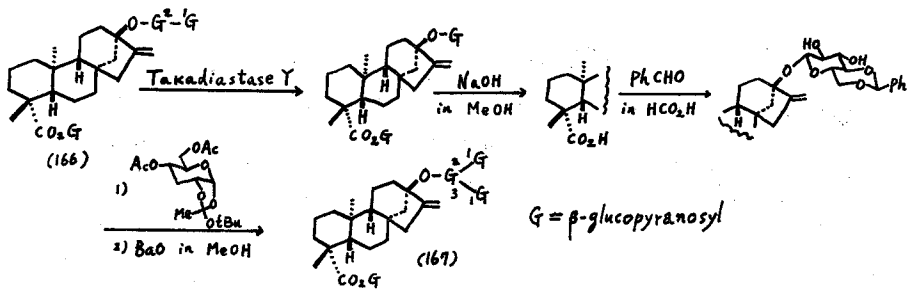
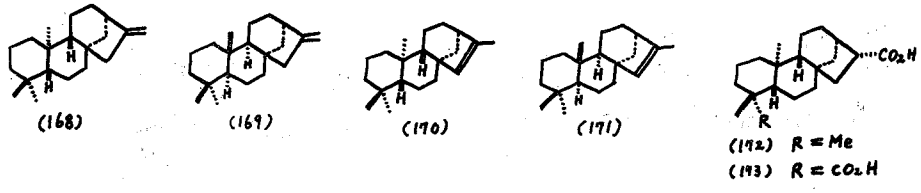


Chart 6

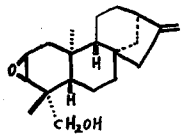
Reactions of *ent*-kaurenes and 13β-kaurenes with thallium(III) nitrate in glyme were investigated. Namely, the reaction of *ent*-kaur-16-ene (**168**) or 13β-kaur-16-ene (**169**) gave only allylic nitrate products in high yield. The reactions of *ent*-kaur-15-ene (**170**) and 13β-kaur-15-ene (**171**) with the same reagent were also investigated. Furthermore, a mutual allylic rearrangement of the allylic nitrate products was reported.[65]



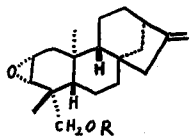
By the two successive oxidative rearrangements using thallium trinitrate, *ent*-kaur-16-ene (**168**) and kaurenoic acid (**139**) were stereoselectively converted into *ent*-16α-

kauran-17-oic acid (**172**) and *ent*-16α-kaurane-17,19-dioic acid (**173**), respectively.[66]

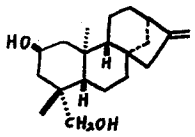
Reduction of 2,3-epoxides, **174**, **175**, and **176**, with hydride afforded equatorial alcohols, **177**, **178**, and **179**, respectively. Analogously, acidic hydrolysis of **180** and **181** afforded the diequatorial 2,3-diols **182** and **183**. The abnormal equatorial opening of these epoxides is attributed to the participation of the 19-hydroxy group (for the *ent*-2α,3α-epoxides) or to the steric effect of 18-methyl group (for the *ent*-2β, 3β-epoxides).[67]



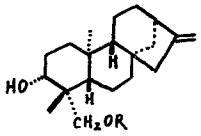
(174)



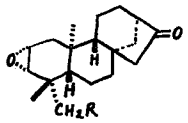
(175) R=H
(176) R=THP



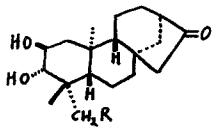
(177)



(178) R=H
(179) R=THP



(180) R=OH
(181) R=H



(182) R=OH
(183) R=H

A model reaction for a biosynthetic conversion of *ent*-kaurene into the grayanane skeleton was carried out using cholestane derivatives[68] (see Chart 7).

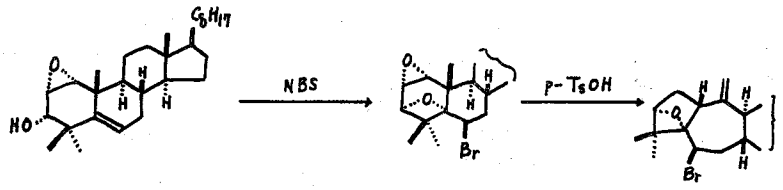


Chart 7

The reactivity of three secondary hydroxyl groups of grayanotoxin-(II) (**184**) toward acetylation and alkaline hydrolysis was investigated and on the basis of its evidence, chemical transformation of **184** into 3-dehydro grayanotoxin-II (**185**) was achieved[69] (see Chart 8). Furthermore, this transformation was also achieved by microbial oxidation with *Pseudomonas pseudomallei*.[70]

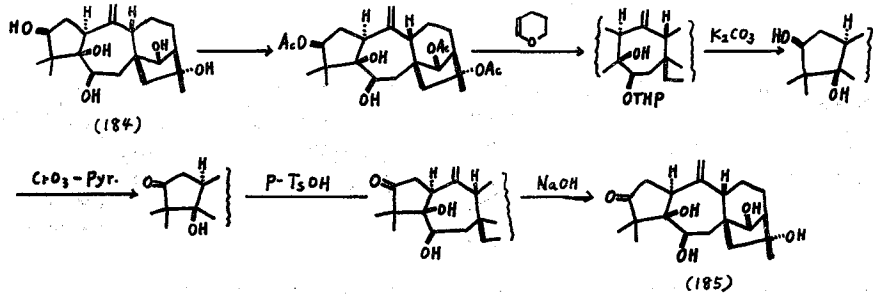
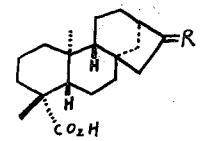


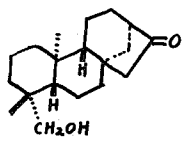
Chart 8

The microbiological transformations of three 19-oxygenated *ent*-kaurenes **139**, **186**, and **187** with *Rhizopus nigricans, Aspergillus ochraceous*, and *Calonectria decora* were investigated. The most common transformation observed is hydroxylation at the C–1 and C–7 positions. For *ent*-kaur-16-en-19-oic acid (**139**), allylic hydroxylation and hydration of the double bond also occurred.[71]

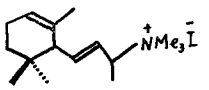
The plant growth retardant, compound **188**, was shown to block gibberellin biosynthesis in *Gibberella fujikuroi* between mevalonate and *ent*-kaur-16-ene. In the presence of the plant growth retardant, cultures of the fungus incorporate added *ent*-[^{14}C]-kaur-16-ene into gibberellin A_3, but kaur-16-ene, 13β-kaur-16-ene, and *ent*-kaur-15-ene are not metabolized to gibberellin analogs.[72]



(139) R = CH_2
(186) R = O



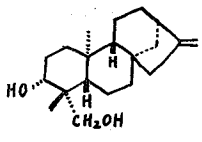
(187)



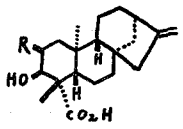
(188)

ent-Kaurene derivatives, **190** and **191**, were prepared from **189**, and their metabolites from cultures of the mutant B1–41a of *Gibberella fujikuroi* were analyzed by g.l.c.-mass spectrometry. The metabolism of **192**, **193**, and **194** was similarly investigated in cultures of the parent wild-type strain, GF–1a, in which gibberellin biosynthesis was blocked by a synthetic plant growth retardant[73] (see also Section XI).

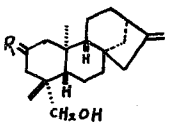
Inhibitory effect of the *Isodon* species diterpenoids on oxidative phosphorylation in rat liver mitochondria was investigated. Among them, isodonal (**195**) had the strongest effect.[74]



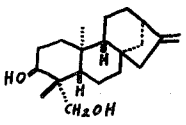
(189)



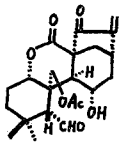
(190) R = H
(191) R = OH



(192) R = α-H, β-OH
(193) R = α-OH, β-H



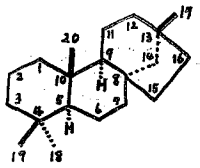
(194)



(195)

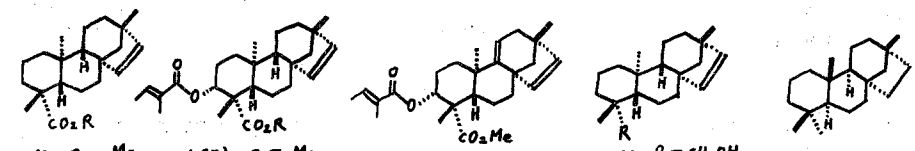
In a report on the circular dichroism of strained, bridged-ring, and other ketones, several ketones of kaurane were described.[75] The mass spectra of grayanotoxin III and some acetate and propionate esters were discussed.[76]

X. BEYERANE DERIVATIVES



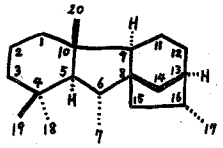
Beyerane

Isolation of beyerane type compounds, **196**, **197**, and **198**, from methylated extracts of *Dimorphotheca aurantiaca*, **199**, **200**, and **201** from *D. pseudoaurantiaca*, **199**, **201**, and **202** from *Viguiera grammatoglossa*, and **199** from *V. cordifolia* was reported.[54]



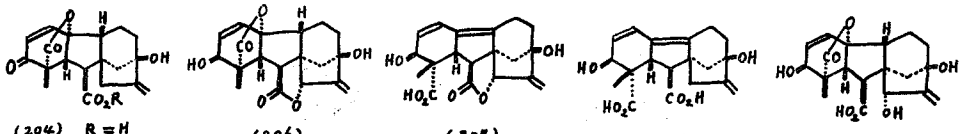
Isohibane (**203**) was synthesized from *l*-abietic acid *via* epoxide **118** and ketone **119**.[46] In a foregoing report on the circular dichroism of strained, bridged-ring, and other ketones, ketones of beyerane group were included.[75]

XI. GIBBERELLANE DERIVATIVES

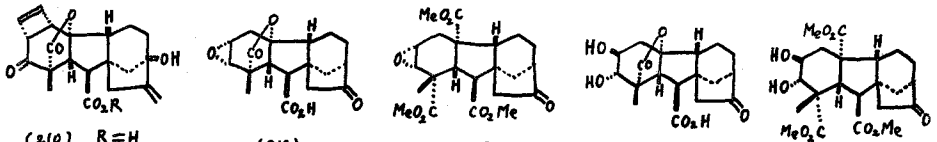


Gibberellane

Reduction of 3-dehydrogibberellin A_3 (**204**) with $NaBH_4$ and $LiAlH(O\text{-}^tBu)_3$, and of the ester **205** with $LiBH_4$, $NaBH_4$, or $Zn(BH_4)_2$ was investigated.[77] Acid-catalyzed hydrolysis of gibberellin A_3 derivative **206** gave the major product, monolactone acid **207**, as well as the minor products, **208** and **209**, without decarboxylation.[78]



Photochemical cycloaddition of acetylene to 3-dehydrogibberellin A_3 (**204**) and its methyl ester (**205**) gave adducts **210** and **211**, respectively. The reaction proceeded slowly, but more stereospecifically than the corresponding addition of ethylene. The adducts were converted to the corresponding 1β,2β-isomers *via* 1,3-acyl shift under continued photolysis.[79] Acidic hydrolysis of the *ent*-2β,3β-epoxides **212** and **213** afforded the diequatorial 2,3-diols **214** and **215**, respectively. The abnormal opening of these epoxides is attributed to the steric effect of the adjacent *ent*-4α-methyl group.[67]



(210) R=H
(211) R=Me
(212)
(213)
(214)
(215)

An efficient synthetic route to a lactone model for the gibberellin A ring was reported. The sequence is shown in Chart 9.[80]

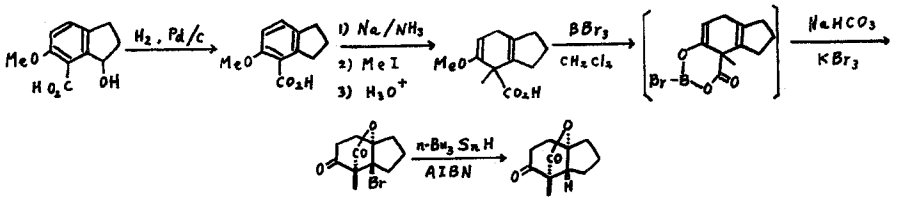
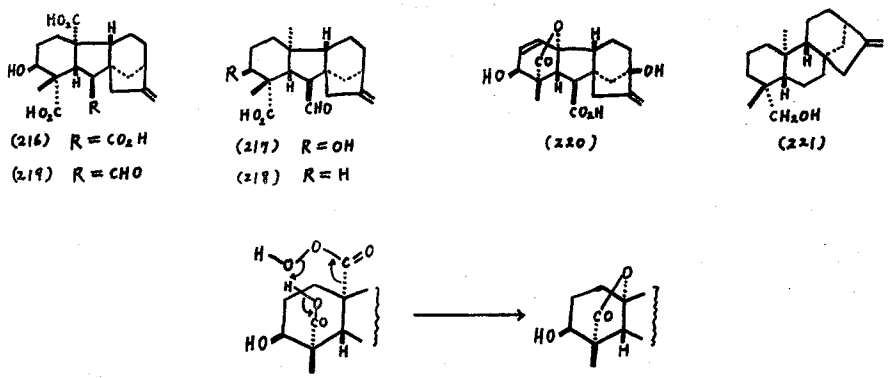


Chart 9

Gibberellin A_{13} (**216**) and A_{14} 7-aldehyde (**217**) were tentatively identified as metabolites of gibberellin A_{12} aldehyde (**218**) in a cell-free system derived from *Gibberella fujikuroi*; gibberellin A_{13} 7-aldehyde (**219**) is incorporated into gibberellin A_3 (**220**), and the C–20 carbon atom which is removed at this stage was isolated as carbon dioxide. A possible mechanism of C–20 removal in gibberellin biosynthesis is thought to involve a C–20 per-acid as shown in Chart 10.[81]



(216) R = CO_2H
(219) R = CHO
(217) R = OH
(218) R = H
(220)
(221)

Chart 10

The endogenous free gibberellins in two different stages of immature *Phaseolus vulgaris* seeds were investigated. In the early immature stage, feeding experiment of labeled GA_1, GA_4, GA_5, and GA_{20} indicated that GA_4 and GA_{20} were converted to GA_8 *via* GA_1 as shown in Chart 11. The interconversion of GA_5 to known gibberellins was not observed. Gibberellin glucosylating enzymes were not present in the early immature stage of the bean seeds but they appeared in the maturing process. The conversion of GA_4 to GA_4 glucosyl ester and GA_{20} to GA_{29} were shown in the maturing bean seeds.[82]

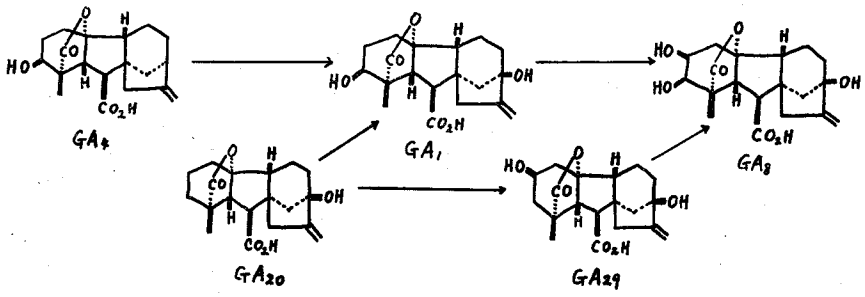
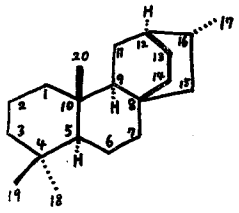


Chart 11

A report on metabolism of kaurenoids by *Gibberella fujikuroi* in the presence of the plant growth retardant was published[72] (see Section IX).

Transformations of 2- and 3-hydroxylated kaurenoids by *Gibberella fujikuroi* were investigated. The results show that the *ent*-3α-hydroxylated analogs of the normal gibberellin intermediates (**139** and **221**) are efficiently converted into 3–hydroxylated gibberellins. They indicated that the *ent*-2β-hydroxy-analog is converted into gibberellin A_3 (**220**) by dehydration and that the conversion of *ent*-kaurenoids into gibberellins is reduced by the presence of *ent*-2α- and *ent*-2β-hydroxyl groups.[73]

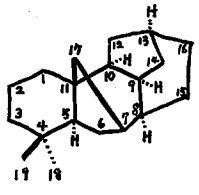
XII. ATISANE DERIVATIVES



Atisane

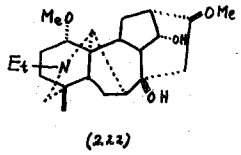
No papers have been published on the title topics in this period.

XIII. ACONANE DERIVATIVES

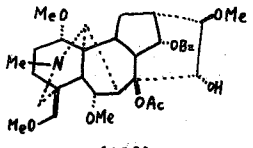


Aconane

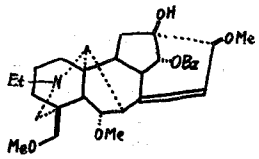
Sachaconitine (**222**) and isodelphinine (**223**) were isolated from *Aconitum miyabei*.[83] The ^{13}C–NMR spectra of the aconitine-type diterpenoid alkaloids were determined and applied in the structural determination of mithaconitine (**224**).[84]



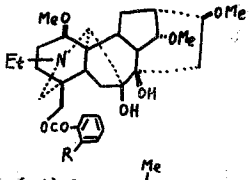
(222)



(223)

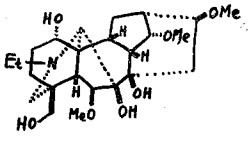


(224)

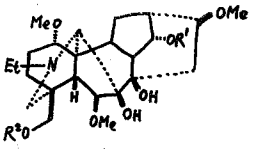


(225) R = HNCOCHCH$_2$CONH$_2$ (Me)

(226) R = HNCOCH$_2$CHCONH$_2$ (Me)



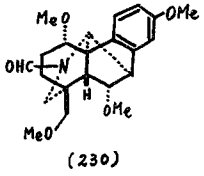
(227)



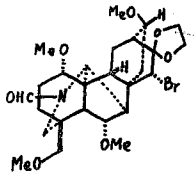
(228) R' = Me, R^2 = Ac

(229) R' = Ac, R^2 = -C(=O)-CH(NH$_2$)-Ph

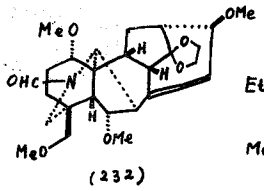
The alkaloid "delsemine" isolated from *Delphinium tricorne* was proved to be an inseparable mixture of **225** and **226**.[85] The structures of gigactonine (**227**) isolated from *Aconitum gigas*,[86] tricornine (**228**) isolated from *D. tricorne*,[87] and 0-acetyldelectine (**229**) isolated from *D. dictyocarpum*[88] were determined mainly by spectroscopic method. N-Oxyzongorine was isolated from *A. monticola*.[89] An excellent review describing the synthesis of aconite alkaloids was published.[90] A stereospecific total synthesis of chasmanine (**233**) was performed from the aromatic intermediate **230** by a photochemical route to the nordenudatine intermediate **231**, which was rearranged to **232** followed by functionalization.[91]



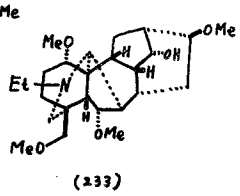
(230)



(231)



(232)



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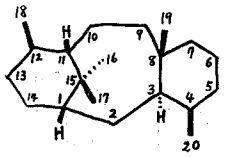
XIV. TAXANE DERIVATIVES



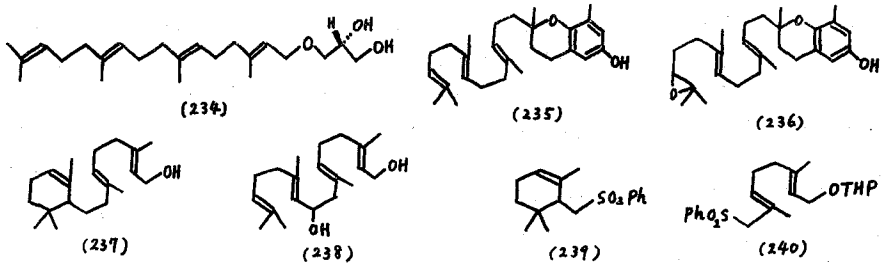
Taxane

No reports have been published on the title topics in this period.

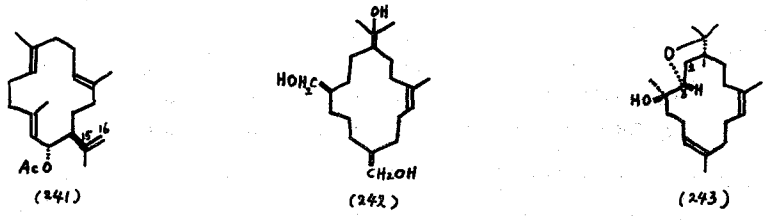
XV. THE OTHERS

A novel ether lipid, (—)-(*R*)-1-O-geranylgeranylglycerol (**234**) has been isolated

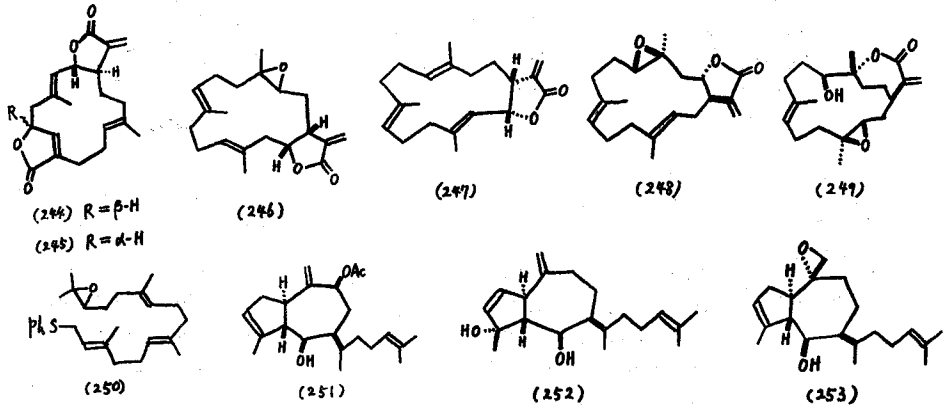
from the brown alga *Dilophus fasciola*.[92] From the lipid-soluble extract of the brown alga *Cystophora torulosa* two polyprenyl chromans **235** and **236** were isolated.[93] Caulerpol (**237**) and crinitol (**238**) isolated from marine algae were synthesized by the alkylation of lithium salt of benzenesulfonyl derivatives **239** and **240** followed by reductive cleavage of SO_2Ph and the protecting group.[94]



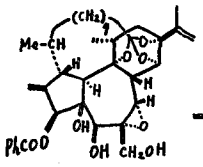
An X-ray crystallographic analysis of 15,16-dehydroepimukulol acetate (**241**) confirmed the modified diamond lattice conformation of the molecule.[95] The structure of a triol isolated from *Eremophila clarkei* was elucidated to be formulated as **242**.[96] A new epoxycembradienol was isolated from *E. georgei* and the structure **243** was advanced for the diterpene by spectroscopic and chemical means.[97] The structure **243** was further confirmed by an X-ray analysis.[98]



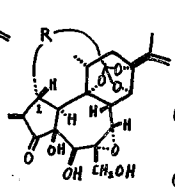
The structures of ovatodiolide (**244**) and isoovatodiolide (**245**), isolated from *Anisomeles indica*, have been established by X-ray crystallographic analyses.[99] Several cembranolide diterpenes, **246**[100], **247**[101], **248** (lobophytolide), and **249** (sinulariolide) were isolated from soft corals. The structures of the latter two were unambiguously determined by X-ray analyses.[102~104]



Synthetic approach to cembrene and thunbergol derivatives *via* the sulfoxide **250** has been published.[105] Two new and two known diterpenes were isolated from *Dictyota dichotoma*. The structures of the new diterpenes, dictyol B acetate (**251**) and dictyotadiol (**252**), were elucidated from spectral and X-ray crystallographic evidence.[106] Pachydictyol-A epoxide (**253**) was isolated from *D. flabellata*.[107] Highly irritant diterpenoids **254**–**257** were isolated from several species of Thymelaeaceae plants.[108] *Euphorbia tirucalli* was also found to contain highly irritant factors **258**–**262**.[109] Five diterpenoids **263**–**267** were isolated from *Pimelea* species.[110] Candletoxin A (**268**) and B (**269**) were isolated from *E. poisonii*.[111] Phorbol was epimerized to 4aα-phorbol (**270**) which was coverted into a number of 9- and 9a-esters.[112]



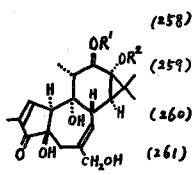
(254)



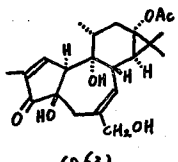
(255) (C-1)-R-
= (C-1)-CH(Me)-$(CH_2)_7$-

(256) (C-1)-R-
= (C-1)-$C_{13}H_{26}$-CH=CH-

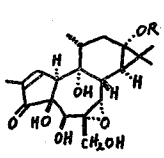
(257) (C-1)-R-
= (C-1)-CH(Me)-$(CH_2)_6$-CHOCOPh



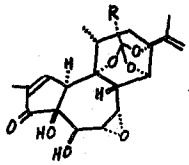
(258) R^1=COCH=CH-CH=CHCH_2Et, R^2=Ac
(259) R^1=COCH=CHCH=CHCH=CHCH_2Et, R^2=Ac
(260) R^1=CO(CH=CH)$_3$-CH_2Et, R^2=Ac
(261) R^1=CO(CH=CH)$_4$-$(CH_2)_3$Me, R^2=Ac
(262) R^1=Ac, R^2=CO(CH=CH)$_2$$CH_2$Et



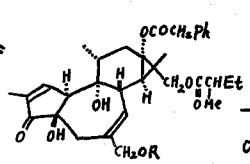
(263)



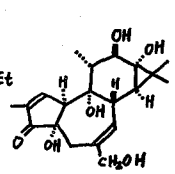
(264) R=CO$(CH_2)_{12}$Me
(265) R=CO(CH=CH)$_3$$(CH_2)_6$Me



(266) R=C_9H_{19}
(267) R=$C_{13}H_{27}$

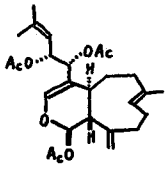


(268) R=Ac
(269) R=H

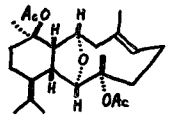


(270)

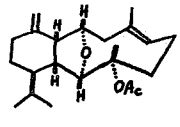
The structure of xenicin (**271**), isolated from a soft coral, *Xenia elongata*, was determined by an X-ray analysis.[113] Acetoxycladiellin (**272**) and cladiellin (**273**) were isolated from a soft coral (*Cladiella* species), and the structure of the former was established by a single crystal X-ray analysis.[114] Fourteen diterpenes **274**–**287** have been isolated from the digestive gland of the opisthobranch mollusc *Dolabella californica*.[115]



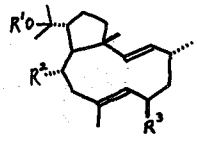
(271)



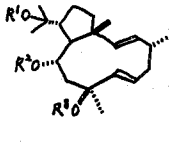
(272)



(273)

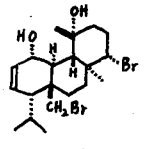


(274) R^1=Ac, R^2=OAc, R^3=H
(275) R^1=R^3=H, R^2=OAc
(276) R^1=R^3=H, R^2=OH
(277) R^1=H, R^2=R^3=OAc
(278) R^1=H, R^2=OAc, R^3=OH
(279) R^1=Ac, R^2=R^3=OH
(280) R^1=H, R^2=R^3=OH
(281) R^1=R^2=R^3=H

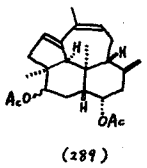


(282) R^1=R^2=R^3=Ac
(283) R^1=R^2=Ac, R^3=H
(284) R^1=R^3=Ac, R^2=H
(285) R^1=H, R^2=R^3=Ac
(286) R^1=Ac, R^2=R^3=H
(287) R^1=R^2=R^3=H

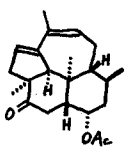
Neoconcinndiol hydroperoxide (**27**), a novel marine diterpenoid, was isolated from *Laurencia snyderiae* and its structure was determined by an X-ray diffraction experiment.[15] The structure of bromosphaerodiol (**288**), a minor bromoditerpene isolated from the red alga, *Sphaerococcus coronopifolius* has been established by chemical and spectroscopic methods.[116] Unusual tetracyclic diterpenes kempene-1 (**289**) and -2 (**290**) were isolated from *Nasutitermes* termite soldiers.[117] The structures of two new insecticidal substances, cinnzeylanin (**291**) and cinnzeylanol (**292**) isolated from barks of *Cinnamonum zeylanicum* were determined by the X-ray analysis and chemical reactions.[118]



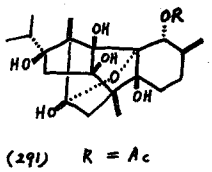
(288)



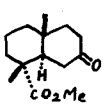
(289)



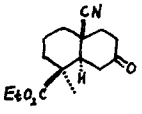
(290)



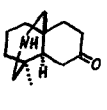
(291) R = Ac
(292) R = H



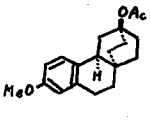
(293)



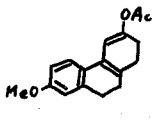
(294)



(295)



(296)



(297)

Bicyclic intermediates **293**, **294**, and several derivatives of **295** for the synthesis of resin acids and alkaloids were synthesized.[119] An intermediate **296** for the synthesis of complex diterpenoids was synthesized from **297**.[120]

A review on diterpenoid irritants and cocarcinogens in *Euphorbiaceae* and *Thymelaeaceae* was published.[121] A review under the title of "Synthesis of biologically active sesqui- and diterpenoids" was also published in Japanese.[122]

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