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The Chemistry on Diterpenoids in 1979. Part-II[1]

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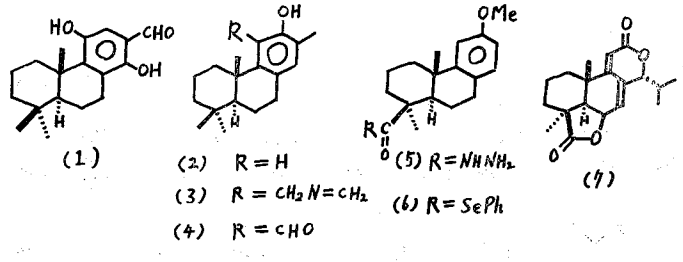
I. INTRODUCTION

This is one of a series of our annual reviews on diterpenoid chemistry. The classification of the compounds is the same as that used in our reviews since 1969. This review covers literature published between July and December 1979 and also omissions in the previous reviews.

II. PODOCARPANE DERIVATIVES

A new bisnorditerpene, premnolal (**1**), was isolated from *Premna latifolia*.[2] The crystal structure of 13β-hydroxymethylpodocarpane-8β-carboxylic acid lactone and the circular dichroism of this and related lactones were reported.[3] Treatment of phenol **2** with hexamethylenetetramine and F_3CCO_2H followed by hydrolysis gave **3**, whose rearrangement in the presence $KOCMe_3$-$HOCMe_3$ followed by hydrolysis gave **4**.[4] The reaction of N-acylhydrazine **5** with benzeneseleninic acid in the presence of triphenylphophine afforded a high yield of selenolester **6**.[5] Nagilactone F (**7**) was synthesized from (+)-podocarpic acid.[6]



III. LABDANE DERIVATIVES

Isolation of new labdane type diterpenoids, 19-noranticopalic acid (**8**) from *Agathis lanceolata* resin,[7] **9** from *Bishovia boliviensis*,[8] **10–12** from *Gutierrezia lucida*,[9] **13–15** from *G. mandonii*,[9] daniellol (**16**) from *Xanthocephalum linearifolium*,[10] **17** from *Porella perrottetiana*,[11] lagochirzidin (**18**) from *Lagochilus hirsutissimus*,[12] and leonitin(**19**) from *Leonotis* species,[13] was reported.

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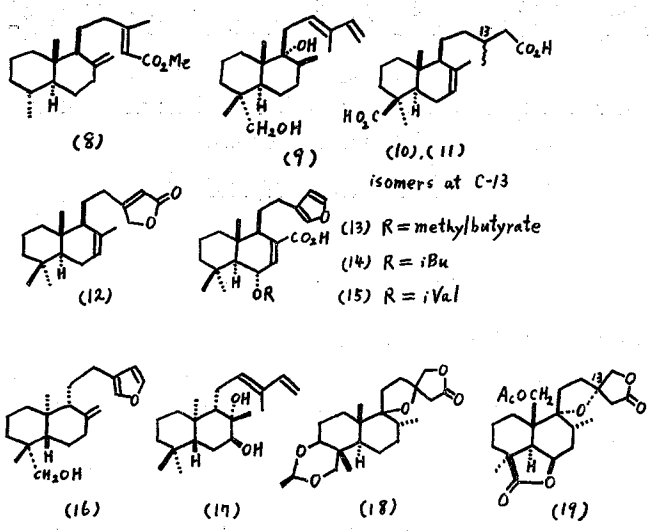
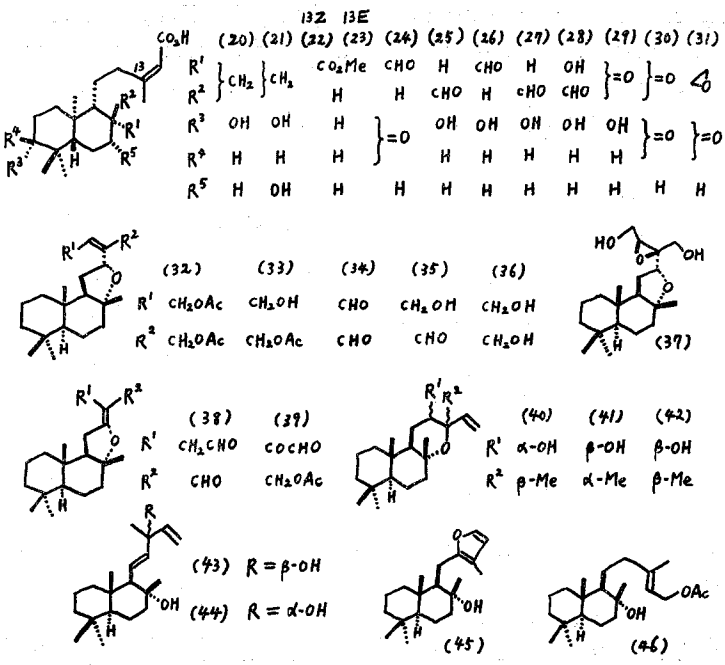


From *Ayapana amygdalina* were isolated twelve new labdane diterpenoids **20**–**31**.[14] The investigation of four *Silphium* species (*S. perfoliatum, S. asteriscus, S. integrifolium,* and *S. terebinthinaceum*) afforded eight new labdane diterpenoids **32**–**39**.[15] Seven new labdanic diterpenoids **40**–**46** were isolated from *Nicotiana tabacum.*[16]

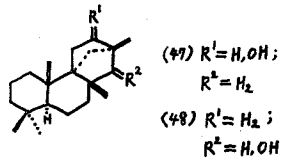


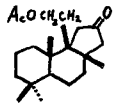
Chemical shifts in the ^{1}H and ^{13}C NMR spectra for lagochilin confirmed their utility in the structure determination of labdane type diterpenoids.[17] In the report of a semiquantitative prediction of the intensity of the Cotton effect of allyl alcohols

and ethers, labdane type allyl ethers were described.[18] The effect of the azide group in ^{13}C NMR was investigated. It was shown to be useful in the determination of the configuration of tetrasubstituted carbon atoms bearing an azide group.[19] C–C bond formation on reduction of organomercurial and its application to biomimetic synthesis of strobane carbon skeleton were published.[20]

Cyclization of an isomeric mixture of *ent*-copalol by concd. H_2SO_4-HCO_2H gave alcohols **47** and **48**. The former compound was converted to **49**.[21] The sensitized photo-oxygenation of (12E)-abienol (**50**) was studied.[22]

In a Japanese review titled on "Studies on Tobacco Aroma", labdanoid diterpenes were described.[23]





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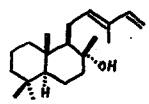

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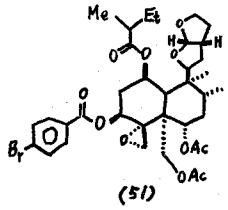
IV. CLERODANE DERIVATIVES

The structure and absolute configuration of ajugareptansin (isolated from *Ajuga reptans*) *p*-bromobenzoate (**51**) were determined by an X-ray study.[24] The absolute configurations of ajugarins (**52–54**) were determined. It was shown that the caryoptins and ajugarins are enantiomeric and both should be reversed from those previously proposed.[25] A clerodan derivative B (**55**), which was shown to be an epimeric mixture, was isolated from *Leonurus cardiaca*.[26]



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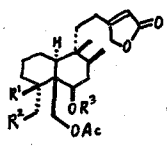
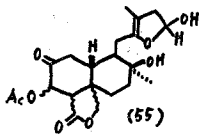


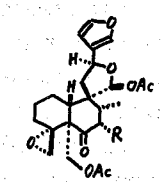
(52) R¹,R²= O<; R³=Ac
Ajugarin-I
(53) R¹,R²= O<; R³=H
Ajugarin-II
(54) R¹=R²=OH; R³=Ac
Ajugarin-III



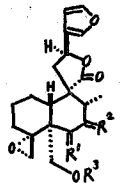
(55)

The investigation of two *Teucrium* species afforded seven new diterpenoids **56**,[27] **57**, **58**[28] (*T. polium* L.), and **59–62** (*T. eriocephalum*).[29]

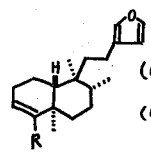
Isolation of new clerodane type diterpenoids, hardwickiic acid (**63**) from *Hardwickia pinnata*,[30] **64** from *Baccharis tricuneata var. lineata*,[31] and gensnerofolins A (**65**) and B (**66**) from *Salvia gensneraefolia*[32] was reported.



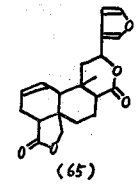
(61) R=OH
(62) R=H



	(56)	(57)	(58)	(59)	(60)
R^1	O	α-H, β-OH	α-OAc, β-H	O	O
R^2	O	H_2	H_2	H_2	H_2
R^3	Ac	Ac	H	H	Ac



(63) R=CO_2H
(64) R=$CH_2OCCH_2CO_2H$



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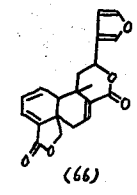

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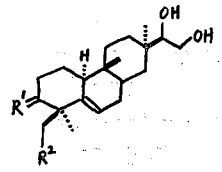
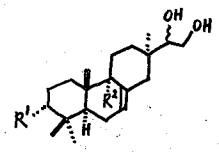
V. PIMARANE AND ISOPIMARANE DERIVATIVES

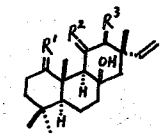
The structures of three pimarane type diterpenoids from *Palafoxia rosea* reported previously were corrected to **67**–**69**. The structures of the other two diterpenoids were also corrected to **70** and **71**.[33] From *Premna latifolia*, three new hydroxysandaracopimar-15-enes (**72**–**74**) were isolated.[2] A new diterpenoid, compactone (**75**), was isolated from *Vellozia compacta*.[34] The Cotton effect of olefins in the pimaric acid series was reported.[35]



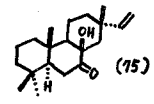
(67) R^1=α-H, β-OH; R^2=OH
Jesromotetrol
(68) R^1=O; R^2=H
(69) R^1=α-H, β-OH; R^2=H



(70) R^1=H; R^2=OH
(71) R^1=OH; R^2=H



(72) R^1=H_2; R^2=O; R^3=H
(73) R^1=α-H, β-OH; R^2=H_2; R^3=H
(74) R^1=α-H, β-OH; R^2=H_2; R^3=OH



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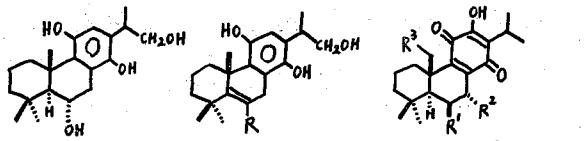
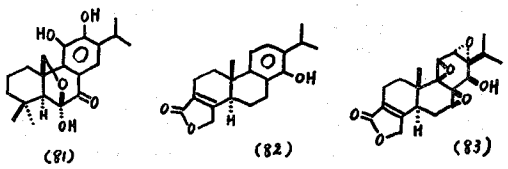
VI. ABIETANE DERIVATIVES

From *Premna latifolia*, three new abietane type diterpenoids, nellionol (**76**), dehydronellionol (**77**) and anhydronellionol (**78**) were isolated.[2] 6β-Hydroxyroyleanone (**79**), 7α-acetyloxy-6β, 20-dihydroxyroyleanone (**80**) and carnosolone (**81**) were isolated

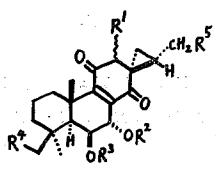
together with a novel dimeric diterpene of hitherto unknown structure from *Coleus carnosus*.[36] Two new diterpne lactones, hypolide (**82**) and tripterolide (**83**) were isolated from *Tripterygium hypoglucum* and *T. regelii*, respectively.[37] Structures of eleven new diterpenoids **84–94** (coleons) from *Solenostemon sylvaticus* and *Coleus garckeanus* were established.[38]



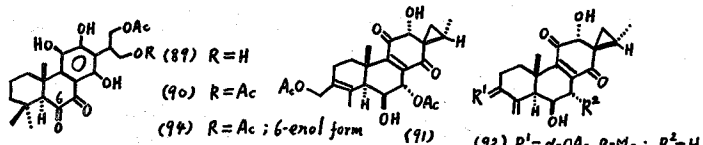
(76) (77) R = OH (78) R = H (79) $R^1=R^2=R^3=H$ (80) $R^1=R^3=OH$; $R^2=OAc$



(81) (82) (83)

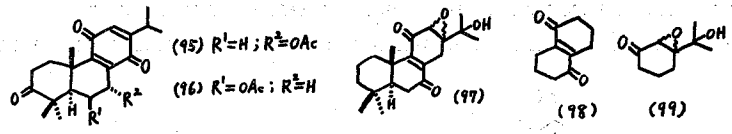


(84) $R^1=\alpha$-OAc; $R^2=H$; $R^3=Ac$; $R^4=OAc$; $R^5=H$
(85) $R^1=\alpha$-OH; $R^2=Ac$; $R^3=R^4=R^5=H$
(86) $R^1=\beta$-OH; $R^2=Ac$; $R^3=R^4=R^5=H$
(87) $R^1=\alpha$-OH; $R^2=Ac$; $R^3=R^5=H$; $R^4=OAc$
(88) $R^1=\beta$-OH; $R^2=R^4=H$; $R^3=Ac$; $R^5=OAc$



(89) R=H (90) R=Ac (94) R=Ac; 6-enol form (91) (92) $R^1=\alpha$-OAc, β-Me; $R^2=H$ (93) $R^1=CH_2$; $R^2=OAc$

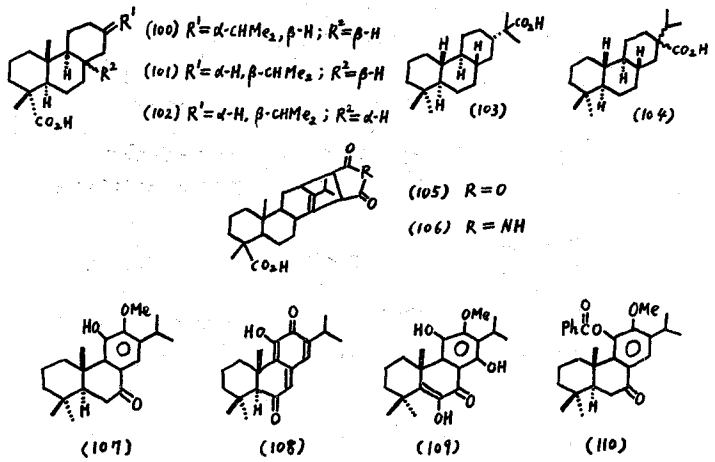
The structure **95** proposed for a hydrogenation product of barbatusin was revised to **96**.[39] The structure-activity relationship of callicarpone (**97**), was examined by synthesizing a series of compounds having certain of its structural features. Enedione compound **98** showed inhibitory activity against the mycobacterium and two yeasts, while epoxy hydroxy ketone **99** showed against mycobacterium.[40]



(95) $R^1=H$; $R^2=OAc$ (96) $R^1=OAc$; $R^2=H$ (97) (98) (99)

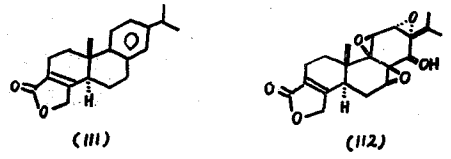
Carbon-13 NMR spectroscopy for diterpenoids of the dehydroabietane series was published.[41] Reactions of tetrahydroabietic acids **100–102**, respectively, in concentrated sulfuric acid led to decarbonylation, followed by a novel skeletal

rearrangement, and recarbonylation to give *inter alia* **103** and **104**.[42] Chemical transformation of maleopimaric acid (**105**) into maleopimarimide (**106**) under the effects of ammonia was published.[43] A synthesis of (±)-cryptojaponol (**107**) and (±)-taxodione (**108**) was reported; for the synthesis of highly substituted catechols, a new method involving the decarboxylation of an α, β-epoxyenone was employed.[44]



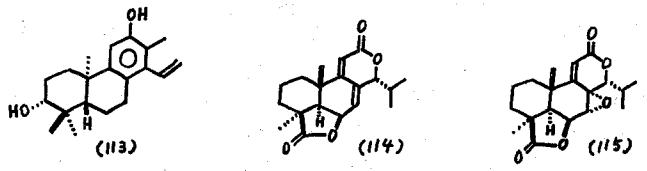
Coleon U 12-methyl ether (**109**) was synthesized from optically active **110** which was previously prepared from (+)-ferruginol.[45] It constituted a formal total synthesis of **109**.

Isodehydroabietanolide (**111**), which is anticipated to be a pivotal intermediate in synthetic approach to triptolide (**112**), was synthesized by two dissimilar routes.[46]



VII. TOTARANE DERIVATIVES

Spruceanol (**113**) was isolated from *Cununia spruceana* and was found to have the cytotoxic and antitumor activity.[47] Nagilactone F (**114**) and G (**115**), totarol, 19-oxototarol and macrophyllic acid were isolated from *Podocarpus milanjianus* and *P. sellowii*.[48] The compound **2** was synthesized from (+)-podocarpic acid.[6]

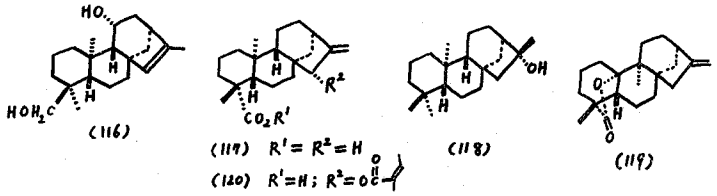


VIII. CASSANE DERIVATIVES

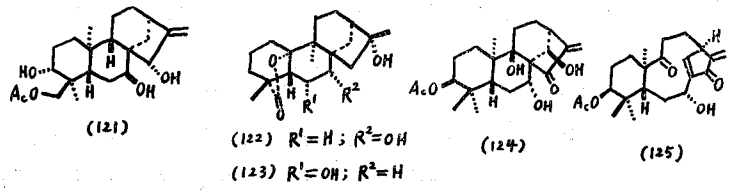
No papers have been published on the title topics in this period.

IX. KAURANE DERIVATIVES

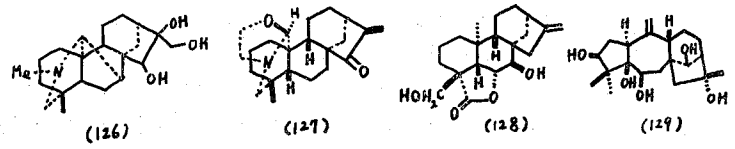
A new diterpene **116** was isolated from *Sideritis chamaedryfolia*.[49] *Ent*-kaur-16-en-19-oic acid (**117**) and *ent*-kauran-16α-ol (**118**) were isolated from *Didymocarpus oblonga*.[50] A new diterpene, tetrachyrin (**119**), and **117** were isolated from *Tetrachyron orizabaensis var. websteri* and *Helianthus debilis*. The latter species also afforded angeloylgrandifloric acid (**120**).[51]



Triol **121** was isolated from *Sideritis scardica*.[52] Two new diterpenes, eupatalfin (**122**) and eupatoralbin (**123**) were isolated from *Eupatorium album*.[53] Isolation of new diterpepenes, shikoccidin (**124**) and shikoccin (**125**) from *Rabdosia shikokiana var. occidentalis* was reported.[54]

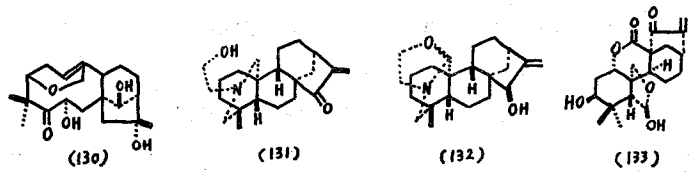


A diterpene alkaloid, dictysine (**126**) was isolated from *Delphinium dictyocarpum*.[55] The structure of cuauchichicine was revised to **127**.[56] The mass spectra of some *ent*-15-ketokaurane derivatives were discussed.[57]

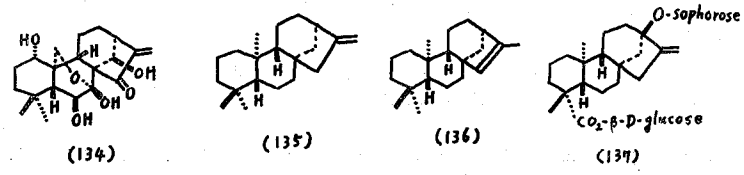


The preparation of some kaurenolides from **128** was reported.[58] Grayanotoxin-II (**129**) was converted to ketone **130** on treatment with thallium (III) nitrate.[59] A selective reduction of the oxazolidine ring of diterpene alkaloid derivatives was achieved using sodium cyanoborohydride and thus, dihydrocuauchichicine (**131**) was obtained from cuauchichicine (**127**).[60] Acid-catalyzed rearrangement of garryfoline (**132**) to

cuauchichicine (**127**) was studied by deuterium labeling experiments.[61]



Biosynthesis of enmein (**133**) and oridonin (**134**) from mono- or di-oxygenated kaurenoids was investigated.[62] Synthesis of *ent*-kaur-16-ene (**135**) and *ent*-kaur-15-ene (**136**) in cell-free systems from etiolated shoots of normal and DW ARF–5 maize seedlings was reported.[63] Some analogs of stevioside (**137**) were synthesized, and their relative sweetness was discussed.[64]

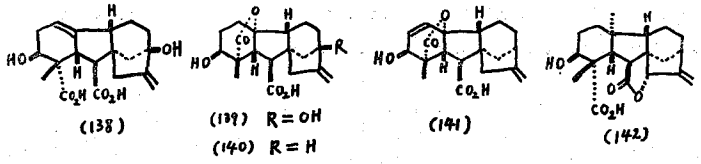


X. BEYERANE DERIVATIVES

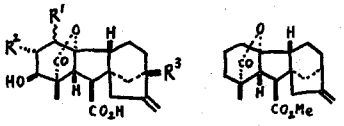
No papers have been published on the title topics in this period.

XI. GIBBERELLANE DERIVATIVES

The occurrence of $\Delta^{1(10)}$ gibberellin A_1 counterpart **138** together with gibberellin A_1 (**139**), A_4 (**140**) and A_7 (**141**) in embryo cultures of carrot and anise was reported.[65]

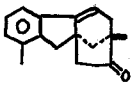


A new gibberellin **142** was isolated from cultures of *Gibberella fujikuroi* and its biological activity was discussed.[66] Three new gibberellins A_{54} (**143**), A_{55} (**144**), and A_{56} (**145**) were shown to occur in the culture broth of *G. fujikuroi*.[67] Gibberellin A_4 (**140**) was identified by combined gas chromatography-mass spectrometry in the culture medium of *Sphaceloma manihoticola*.[68] Gibberellin A_9 methyl ester (**146**) was identified in the culture of *Lygodium japonicum*.[69] Gibberellin A_1 (**139**) was identified in embryo culture of *Phaseolus coccineus*.[70]

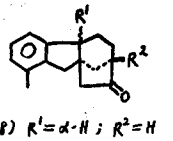


(143) $R^1=\beta$-OH; $R^2=R^3=H$
(144) $R^1=\beta$-OH; $R^2=H$; $R^3=$OH
(145) $R^1=H$; $R^2=R^3=$OH

(146)

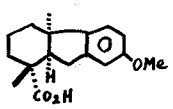


(147)

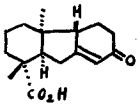


(148) $R^1=\alpha$-H; $R^2=H$
(149) $R^1=\alpha$-H; $R^2=$Me
(150) $R^1=\beta$-H; $R^2=H$
(151) $R^1=\beta$-H; $R^2=$Me

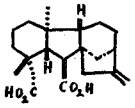
Stereocontrolled total syntheses of **147–151** were reported.[71] Acids **152** and **153**, important synthons towards gibberellin A_{12} (**154**) synthesis, were prepared.[72] Reductive cyclization of ethynyl ketone **155** followed by acid hydrolysis afforded a tricyclic intermediate **156** for the synthesis of gibberellic acid.[73] Regioselective synthesis of enol ether **157** was published.[74] A simple construction of ring A of gibberellic acid was reported; methyl gibberellate (**158**) was prepared from aldehyde **159**.[75]



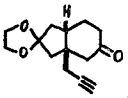
(152)



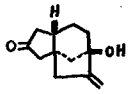
(153)



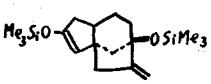
(154)



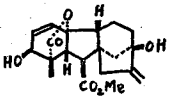
(155)



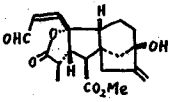
(156)



(157)



(158)



(159)

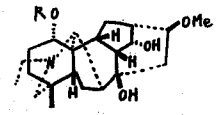
Hydroxylation of C–11 and C–18, oxidation of C–18, and cleavage of ring B of some kaurenolides by *G. fujikuroi* were reported.[76] Break in bud dormancy in virus-infected stem cuttings of *Euphorbia pulcherrima* was found to occur because of the higher quantity of gibberellins present in them than in healthy cuttings in the dormant period of the plant.[77]

XII. ATISANE DERIVATIVES

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

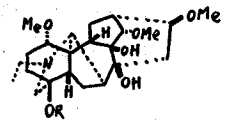
XIII. ACONANE DERIVATIVES

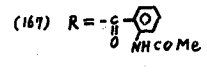
The structures of vilmorrianine B and D were determined to be **160** (=karakoline I) and **161**, respectively.[78] The principal toxin of *Delphinium brownii* was found to be methyllycaconitine (**162**) which acts as a potent neuromuscular blocking agent.[79] A new base cashmiradelphine (**163**) and known alkaloids **164–168** were isolated from *D. cashmirianum*.[80]



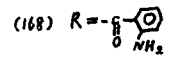
(160) R = H

(161) R = Me

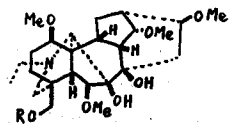


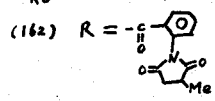


(167) R = -C(=O)-C6H4-NHCOMe

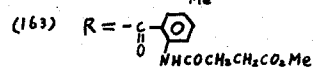


(168) R = -C(=O)-C6H4-NH2

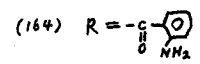




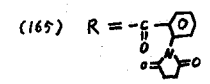
(162) R = -C(=O)-C6H4-N(C(=O)Me)C(=O)



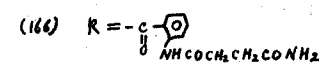
(163) R = -C(=O)-C6H4-NHCOCH2CH2CO2Me



(164) R = -C(=O)-C6H4-NH2

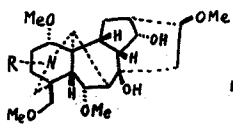


(165) R = -C(=O)-C6H4-N(C(=O))C(=O)



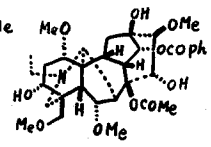
(166) R = -C(=O)-C6H4-NHCOCH2CH2CONH2

A stereo and regioselective synthesis of (±)-13-deoxydelphonine (**169**) and chasmanine (**170**) from *o*-cresol was reported.[81,82] The structure of nitronitrosoaconitic acid which is an oxidation product of aconitine (**171**) with nitric acid was confirmed to be **172** by spectroscopic methods.[83] The ^{13}C NMR spectra of some C_{19}-diterpenoid alkaloids and their derivatives were reported.[84]

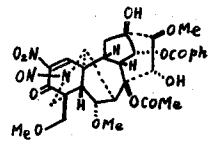


(169) R = Me

(170) R = Et



(171)



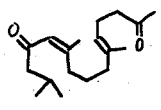
(172)

XIV. TAXANE DERIVATIVES

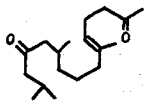
No papers were published in this period.

XV. THE OTHERS

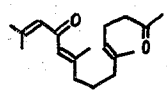
From the brown alga, *Sargassum micracanthum*, eight new farnesylacetone derivatives **173–180** were isolated.[85]



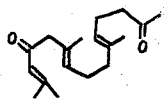
(173)



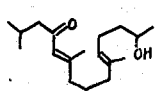
(174)



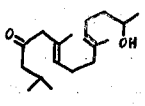
(175)



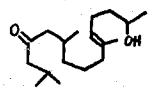
(176)



(177)



(178)



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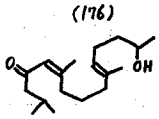
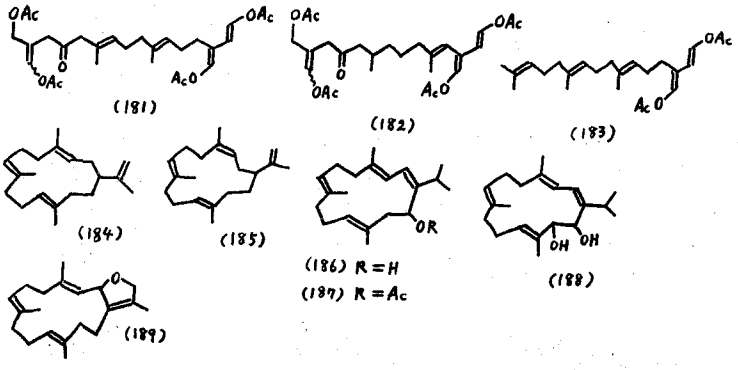
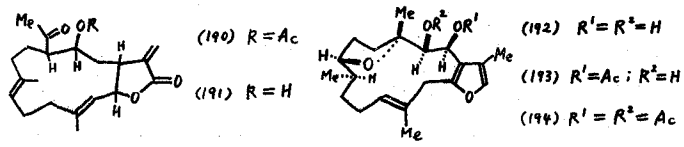


(180)

Two new diterpenes, chlorodesmin (**181**) and dihydrochlorodesmin (**182**), each containing 3 enol acetate groups, were isolated from Great Barrier Reef collections of the green alga *Chlorodesmis fastigiata.* Dihydrotrifarin (**183**) was also characterized.[86] A new acyclic diterpenoid, peucelinendiol, was isolated from the roots of *Peucedanum oreoselinum* and was assigned the structure (+)-(E)-7-hydroxymethyl-2, 6, 10, 14-tetramethyl-2, 9, 13-pentadecatrien-6-ol.[87] In a Japanese review "Studies on Tobacco Aroma", thunberganoid diterpenes were described.[23] Cembrene A (**184**) and (3Z)-cembrene A (**185**) were isolated from the frontal gland secretion of a Termite soldier, *Cubitermes umbratus.*[88] Structures of sarcophytol-A (**186**), sarcophytal-A acetate (**187**), sarcophytol-B (**188**), and sarcophytonin-A (**189**) isolated from the soft coral, *Sarcophyton glaucum,* were reported.[89]

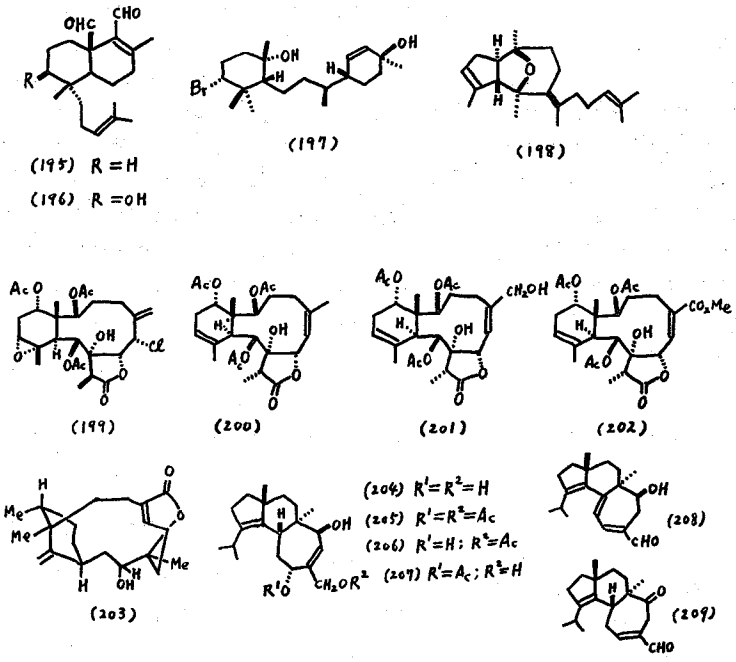


Two diterpenes, **190** and **191**, were isolated from the Japanese soft coral *Lobophytum pauciflorum.*[90] Pachyclavulariadiol (**192**) and its naturally occurring mono- and diacetylated derivatives, **193** and **194**, were isolated from the Australian soft coral *Pachyclavularia violacea.*[91]



Two new diterpenes, perrottetianal A (**195**) and B (**196**), were isolated from the liverwort *Porella perrottetiana.*[11] A new bicyclic monobromoditerpenoid **197** exhibiting marginal cytotoxicity was isolated from the sea hare *Aplysia dactylomela,* and its absolute structure was established by X-ray diffraction.[92] Dictyoxide (**198**), a new diterpene isolated from the brown alga *Dilophus ligulatus,* was reported.[93] The structure elucidations of four minor metabolites, **199–202**, of the sea pen *Stylatula* species, were published.[94]

The structure and stereochemistry of cleomeolide (**203**), a novel diterpene lactone isolated from *Cleome icosandra,* were determined by X-ray analysis and NMR and CD spectra.[95] Six new cyathin-type diterpenoid metabolites **204–209** were produced from the bird's nest fungus *Cyathus earlei.*[96] Biosynthetic studies utilizing [1-^{13}C],

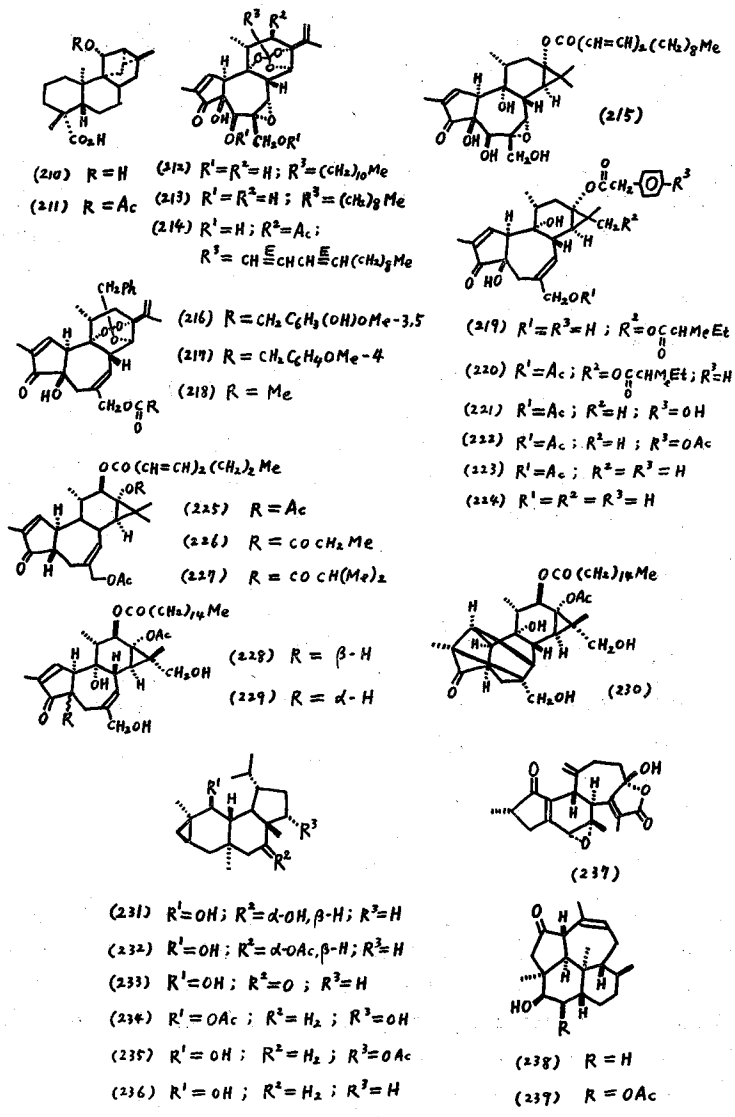


[2–^{13}C], and [1, 2–$^{13}C_2$] acetate indicated that 11-O-acetyl-cyathatriol (**207**) is formed from acetate *via* the isoprenoid pathway.[97]

The aerial parts of *Helichrysum fulvum* afforded two new diterpenic acids, **210** and **211**.[98] Montanin (**212**) was isolated as the cytotoxic and antitumor active constituent of *Cunuria spruceana*.[47] Systematic extraction of *Pimelea simplex*, which causes St. George disease of cattle, led to the isolation of the diterpenoid orthoester, simplexin (**213**), as an active principle. Other toxic substances, **214** and **215** were characterized. Simplexin was obtained also from *P. trichostachya*.[99] Resiniferonol esters, **216–218**, 12-deoxy-16-hydroxyphorbol esters, **219** and **220**, and the deoxyphorbol esters, **221–224**, were isolated from *Euphorbia poissonii*. Their irritant potency was also evaluated.[100] The new 4-deoxyphorbol triesters, **225**, **226**, and **227**, isolated from the latex sap of *Euphorbia biglandulosa*, showed an irritating action on the skin of mice, toxicity on fishes, and inhibition against the oxidative phosphorylation of isolated heart mitchondria.[101] Three new diterpenes **228**, **229**, and **230** and a known compound were isolated from the leaves of *Aleurites fordii* as the piscicidal constituents.[102]

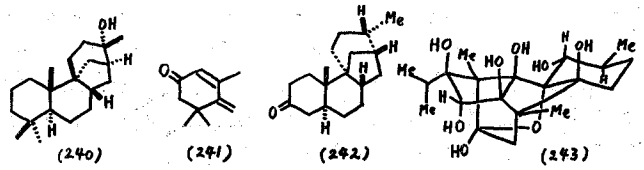
Six new diterpenes, **231–236**, containing a novel fused 3, 6, 6, 5-tetracyclic ring system were isolated from the liverwort, *Mylia verrucosa*.[103] A novel and highly functionalized diterpene, crotofolin E (**237**) was isolated from *Croton corylifolius*.[104] Two new tetracyclic diterpenes, **238** and **239**, were obtained from the defense secretion of the neotropical termite *Nasutitermes octopilis*.[105]

The structure of a new diterpenoid lactone from *Lagochilus hirsutissimus* was published.[106] New diterpenes, coleonol-D, coleol, and coleonone, were isolated from *Coleus forskohlii*.[107] The structure and stereochemistry of the hypothetical hydrocarbon dodecahedrane was discussed.[108]



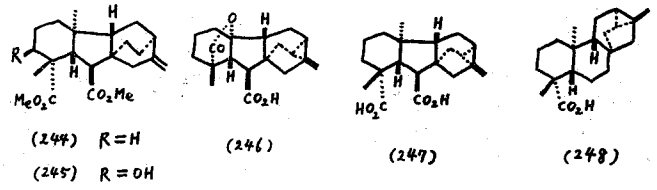
The conformation and proton magnetic resonance characteristics of the substituted 4a-methyloctahydrophenanthrenes were described.[109] The completely analyzed Fourier transform ^{13}C NMR spectra were reported on the trachylobane diterpenes.[110] The ^{13}C NMR spectrum of the diterpene phorbol was reported and the signals of all carbons assigned.[111]

Regio- and stereo-controlled synthesis of the unusual tetracyclic diterpene, deoxystemodin (**240**) was reported.[112] The 1, 6-conjugate addition reaction of *m*- and *p*-methoxybenzylmagnesium halides to the monocyclic linear dienone **241** was investigated for the diterpene synthesis.[113]



The regio- and stereoselective syntheses of C–2 and C–3 functionalized 4a-methyloctahydrophenanthrenes were described.[114] As an synthetic approach to the aphidicolane-type diterpenes, compound **242** was successfully prepared.[115] The stereocontrolled total synthesis of the complex diterpene, (+)-ryanodol (**243**) was accomplished *via* the elegant sequence of reactions.[116]

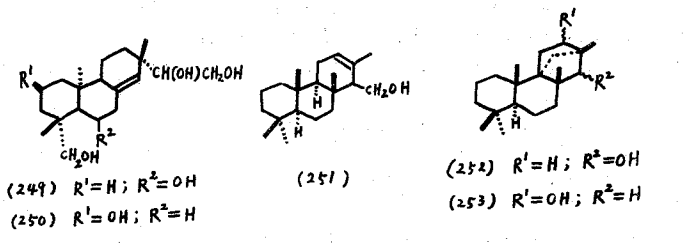
When *Gibberella fujikuroi* was cultured in the presence of AMO 1618, the biosynthesis of *ent*-kaur-16-ene was found to be inhibited. However, the post-kaurene metabolism was not disturbed. Thus, *ent*-7α-hydroxyatis-16-en-19-oic acid was incubated with *G. fujikuroi* in the presence of AMO 1618 for 6 days, and two new metabolites, atisagibberellins were detected and isolated as their methyl esters **244** and **245**.[117] 12, 16-Cyclogibberellins A_9 (**246**) and A_{12} (**247**) were isolated from the microbiological transformation of trachylobanic acid (**248**) by *Gibberella fujikuroi*, mutant B1–41a.[118]

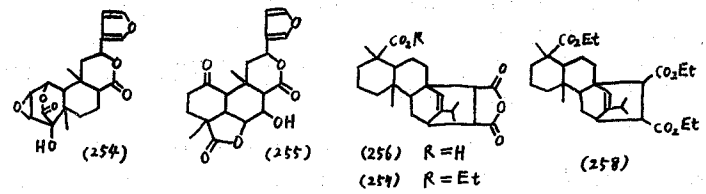


ADDENDA

The structure of the diterpenoid previously isolated from *Siegesbeckia pubescens* and considered to be **249** was revised to **250** on the basis of its ^{13}C NMR spectrum.[119]

Cyclization of acetate of $\Delta^{8(20),13}$ and $\Delta^{8(9),13}$-labdadien-15-ols by HCO_2H–H_2SO_4 yielded a mixture containing compounds **251**, **252**, and **253**.[120] The structures





of teucrins H_1–H_4 were reported.[121] The structure of tinosporide isolated from the fresh stem of *Tinospora cordifolia* was revised to **254** from the previously suggested structure **255**, on the basis of its spectral data and by the chemical correlations.[122] In an industrial-type process, base-catalyzed esterification of maleopimaric acid **256** gave ethyl ester **257** and triethyl ester **258**.[123]

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