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Review

The Chemistry on Diterpenoids in 1973

Eiichi FUJITA, Kaoru FUJI, Yoshimitsu NAGAO, and Manabu NODE*

Received June 30, 1975

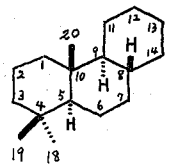
I. INTRODUCTION

This is one of a series of annual reviews[1~9] on diterpenoids chemistry. The classification is the same as that adopted in this series since 1969.

In each section, the related compounds of the similar structures are collected to form groups. In each group, isolation and structure determination are first described, synthesis and reaction are secondly, and biosynthesis and the others are finally followed. In each compound or sometimes in each group, the full paper(s) is first described and the short communication(s) is followed.

In 1970 of this series,[7] a biogenesis of the alkaloids of *Daphniphyllum macropodum* was described,[10] and they have been regarded as diterpenoids.[6] Recently, however, biosynthesis of daphnilactone-B was studied by tracer experiments,[11] and the results supported squalene to be the precursor of the alkaloid. Therefore, we exclude these *Daphniphyllum* alkaloids from our reviews.

II. PODOCARPANE DERIVATIVES



Podocarpane

A very short and highly stereoselective total synthesis of *dl*-podocarpic acid (**1**) was reported.[12] The outline is shown in Chart 1.

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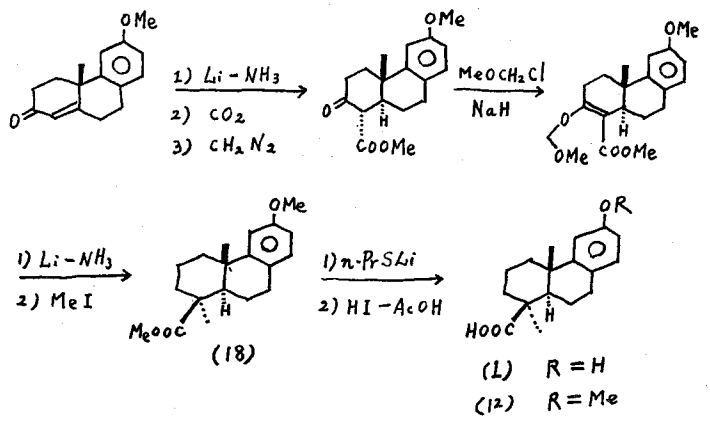
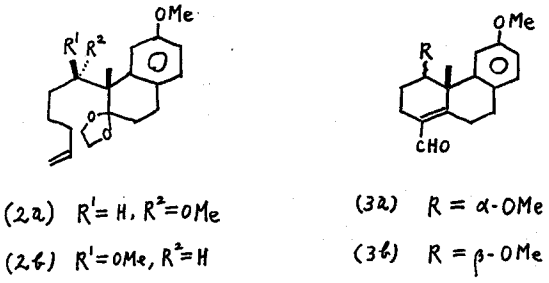


Chart 1

An annelation procedure for the synthesis of polysubstituted terpenoid intermediates was developed by Wiesner *et al.*[13] Thus the key compounds (**2a**) and (**2b**) afford (**3a**) and (**3b**) in 50% overall yield respectively by osmium tetroxide oxidation followed by periodate oxidation and the cyclization of the resulting aldehydes.



A skeletal transformation of compound **4**, derived from *l*-abietic acid, was carried out as shown in Chart 2.[14] The cyclization of **5** gives **6** regarded as a mother skeleton of aconitine.

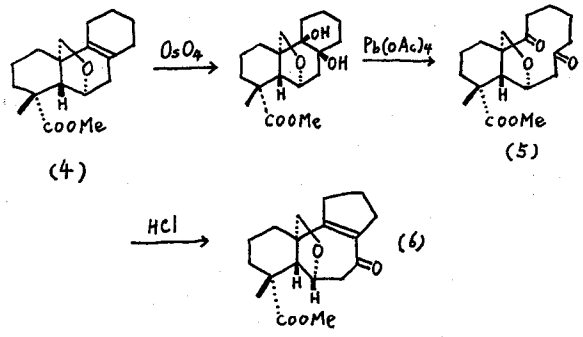
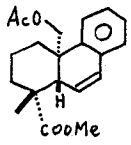


Chart 2

Compounds **7**, **8**, and **9**, derived from *l*-abietic acid were autoxidized to the

corresponding benzonilidene derivatives **10** and **11**.[15]



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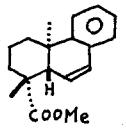

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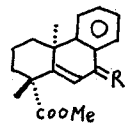
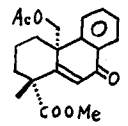
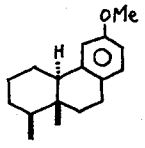


(9) R=H₂
(11) R=O



(10)

Reaction of methyl ether (**12**) of podocarpic acid with phosphoryl chloride resulted in reductive backbone rearrangement to give **13**.[16]



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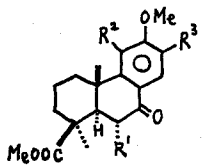
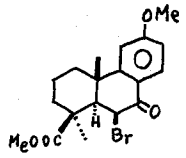


(14) $R^1=R^2=H$, $R^3=NO_2$
(15) $R^1=R^3=H$, $R^2=NO_2$
(16) $R^1=Cl$, $R^2=H$, $R^3=NO_2$
(17) $R^1=Cl$, $R^2=NO_2$, $R^3=H$

Chlorination of 7-oxopodocarpic acid esters (**14**) and (**15**) was conveniently achieved by HCl-H_2O_2 in AcOH giving **16** and **17**, respectively.[17] O-Alkyl cleavage of methyl esters by 1,5-diazabicyclo-[5.4.0]-undecene-5 (DBU) was demonstrated in podocarpic acid derivatives. Thus, **18** (Chart 1) gives rise to methyl ether (**12**) of podocarpic acid by the action of DBU in 96.7% yield. Treatment of **19** with 2 eq. of DBU in *o*-xylene at 165° for 15 min. affords **20** in 90.5% yield, while on treatment under the same condition for 5 hours **19** gives **21**, which is produced by dehydrobromination, O-alkyl cleavage of the ester, and decarboxylation.[18]



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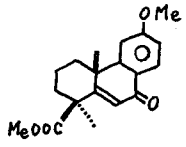

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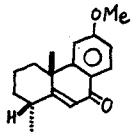


(21)

On the other hand, N-phenylbenzamidine was shown to be a relatively mild and selective dehydrobrominating agent.[19] It gave much higher yields of **20** from **19** than the stronger base sodium methoxide and without concomitant O-alkyl cleavage reported for dehydrohalogenating agents DBU and 1,5-diazabicyclo-[4.3.0]-nonene-5 (DBN).

A new approach to geminal alkylation was applied to synthesize methyl desoxypodocarpate (**23**) starting from **22** (Chart 3).[20] High yield and stereoselectivity in all steps are remarkable.

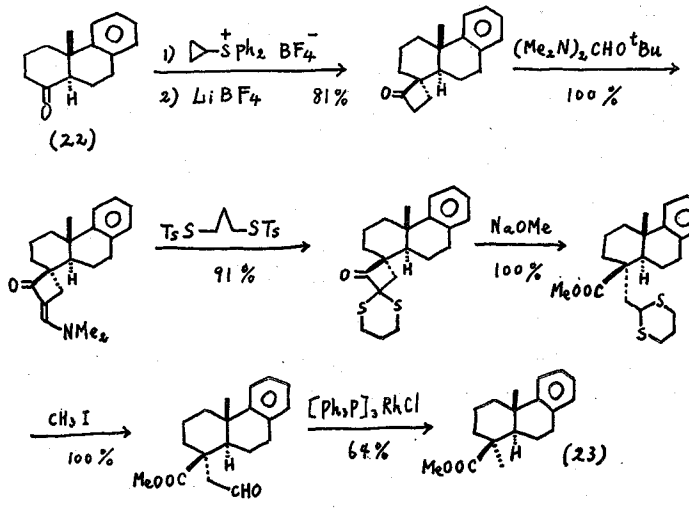
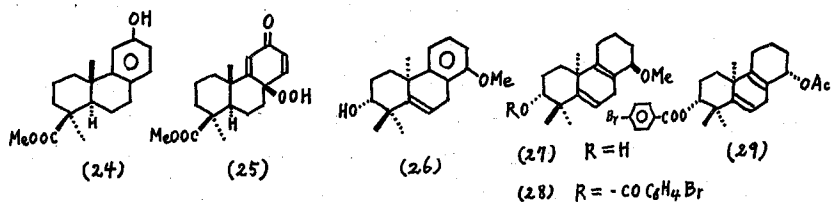


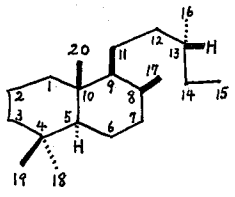
Chart 3

Tetraperoxymolybdate, $(Mo[O_2)_4]^{-2}$, oxidizes *p*-alkylphenols to afford a dienone hydroperoxide of *p*-quinol type. Thus, methyl podocarpate (**24**) gave rise to **25** in 55% yield by the reagent.[21] (for another example: see abietane section VI)



The structure of an unusual product from the Birch reduction of **26** was determined as **27** by an X-ray analysis of the *p*-bromobenzoate (**28**).[22] The methoxy group is reactive enough to be replaced with an acetoxy group, and the *p*-bromobenzoate of the product was analyzed by an X-ray method to confirm the structure (**29**).[23]

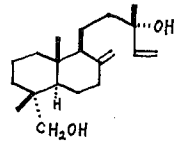
III. LABDANE DERIVATIVES



Labdane

Oleoresins from most species of the genus *Larix* were analyzed by GLC for their diterpene composition. The results were discussed in the chemotaxonomical point of

view.[24] The two new diterpenes, (13S)-labda-8(17),14-diene-13,18-diol (**30**) and 18-norlabda-8(17), 13-diene-4α, 15-diol (**31**) were isolated together with some known diterpenes from *Pinus contorta* bark.[25]



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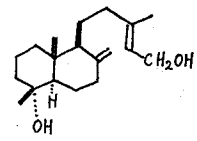

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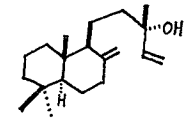
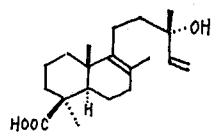


(32)

13-Epimanool (**32**) has been identified in the benzene extractives from the bark of *Pinus radiata*.[26] Three isomeric diterpenes **33**, **34**, and **35** were isolated from *Agathis robusta*.[27]

Diterpene acid constituents of two Amazonian species, *Hymenaea oblongifolia* and *H. parvifolia,* were screened and a new resin acid named guamaic acid (**36**) was isolated from the latter. *ent*-Pinifolic acid and *ent*-13-epilabdanolic acid were also isolated from *H. oblongifolia* and *H. parvifolia,* respectively.[28] Junicedric acid (**37**) was isolated from *Juniperus oxycedrus*.[29] The absolute structure of lithofellic acid (**38**) was determined by physical and chemical means.[30]



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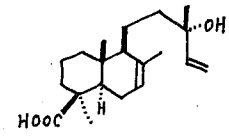

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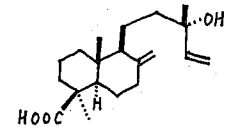

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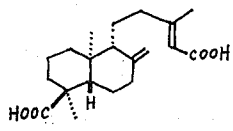

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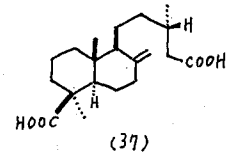

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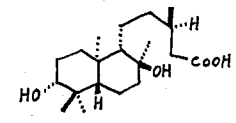
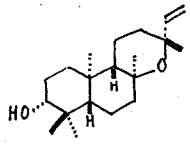


(38)

Sideritis canariensis was found to contain two new diterpenes, tibenol (**39**) and a derivative of trachylobane.[31] The structure of the latter will be described in the section of atisane. The structure of a new diterpene, borjatriol (**40**), isolated from *Sideritis mugronensis,* was established.[32]



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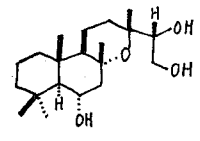

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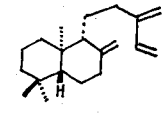
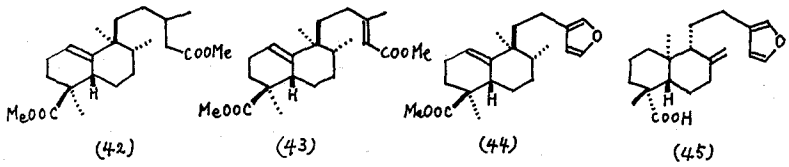


(41)

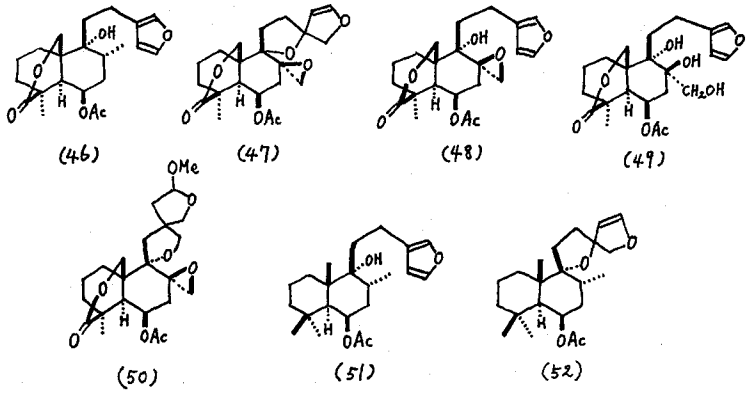
The resin obtained from *Hymenaea courbaril* was esterified with diazomethane and

subjected to GLPC analysis. Four new components (**41**～**44**) were evident.[33] Identity of daniellic acid (**45**) with illurinic acid was shown by Mills.[34]



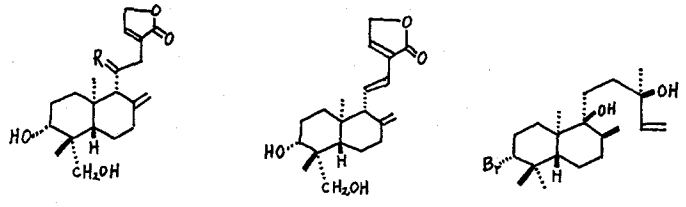
(42) (43) (44) (45)

The structure of dubiin (**46**) isolated from *Leonotis dubia* was elucidated.[35] Three new diterpenes, nepetaefolin (**47**), nepetaefuran (**48**), and nepetaefuranol (**49**) were isolated from *Leonotis nepetaefolia*.[36] The facile conversion of **47** to **48** was noted and the interconversion of **48** and **49** was carried out. Methoxynepetaefolin (**50**) was also isolated from the same plant.[37] Rotundifuran (**51**) and prerotundifuran (**52**) were isolated from *Vitex rotundifolia*.[38]



(46) (47) (48) (49) (50) (51) (52)

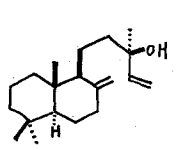
An X-ray crystallographic analysis established the structure **52** of prerotundifuran.[39] Three new diterpenoids **53**, **54**, and **55** were isolated from *Andrographis paniculata*.[40] A brominated diterpene (**56**) was isolated from the marine source, *Laurencia concinna*, and the structure was determined by X-ray crystallography.[41]



(53) R = H₂
(54) R = O
(55) (56)

A series of papers concerning the transformation of manool (**57**)[44] and dihydromanool.[42,43] Attempted allylic oxidation of dihydromanool (**58**) with $Pb(OAc)_4$/NBS

gave an unexpected tribromoorthoacetate (**59**) as a major product besides a small amount of the expected acetate (**60**). The mechanism to account for the formation of the bromo-orthoacetate is proposed.[42] Aqueous permanganate oxidation of **58** gave rise to unusual products **61** and its epimer at C-12 which are functionalized at an unactivated carbon atom as well as normal oxidiation products **62** and **63**.[43]



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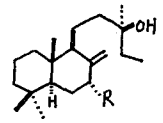
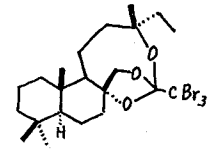
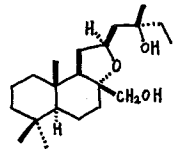


(58) R=H
(60) R=OAc



(59)

Some perfumes **64**, **65**, and **66** having an acetal group in the molecule were synthesized from manool (**57**).[44]



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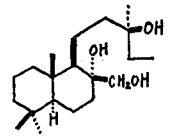

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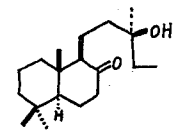

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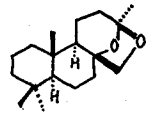

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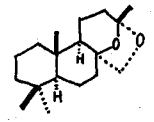
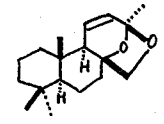
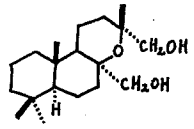


(65)

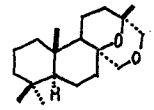


(66)

Attempted preparation of **68** on refluxing **67** in benzene with *p*-TsOH resulted in the formation of **69** and **65** in 58% and 9% yield, respectively, and a possible mechanism was postulated.[45] Syntheses of *cis*-abienol and Δ^{13}-*cis*- and Δ^{13}-*trans*- neoabienols were reported.[46]



(67)



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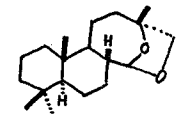
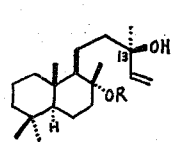


(69)

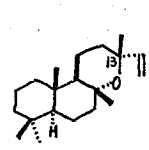
Sclareol 8-acetate (**70**) on heating at 125° for 2 hrs. gave manool (**57**) in 75% yield.[47] Correlation of manoyl oxide (**71**) and sclareol (**72**) configurations with respect to C-13 was achieved.[48]

The autoxidation of torulosal (**73**) was studied to prove that the naturally occurring 4-hydroxy-nor-diterpenes, **74** and **75**, are the artifacts.[49] 13-Epiisomanool (**76**) having S

configuration at C-13 was synthesized[50] and the optical rotation was compared with that of 13-R isomer (isomanool) to correct errors in the previous literature.[51]



(70) R = Ac
(72) R = H



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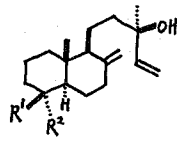
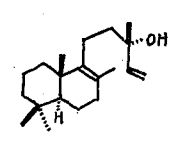
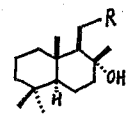


(73) R' = CHO, R² = Me
(74) R' = OH, R² = Me
(75) R' = Me, R² = OH



(76)

The Brewster's rule was modified to deal with the optical rotation of tertiary alcohols using several labdane type alcohols having partial structures (**77**) and (**78**).[52]



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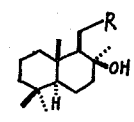
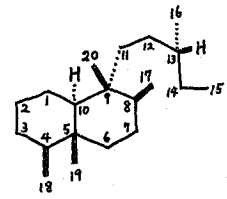


(78)

Some halogenated diterpenes of labdane and clerodane types are described in a review on the topics of naturally occurring halogenated organic compounds.[53]

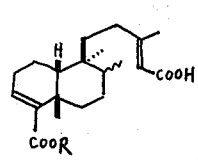
ent-13-Epimanoyl oxide and its 3-ketone were isolated from *Solidago missouriensis*.[93]

IV. CLERODANE DERIVATIVES

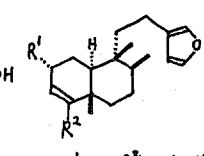


Clerodane

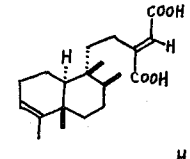
A new diterpene, haplopappic acid (**79**) and its mono-methyl ester (**80**) were isolated from *Haplopappus foliosus* and *H. angustifolius*.[54] The diterpene alcohols, **81** and **82**, and a hydroxy acid isolated as the ester **83** were obtained from *Dodonaea boroniaefolia*. Their structures were elucidated by some chemical correlations. The structure of a diacid (**84**) isolated from *Cyanostegia angustifolia* was also elucidated.[55]



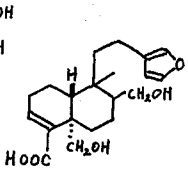
(79) R = H
(80) R = Me



(81) R' = H, R² = CH₂OH
(82) R' = OH, R² = CH₂OH
(83) R' = OH, R² = COOMe

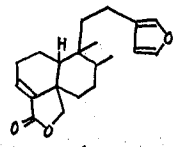


(84)



(85)

Further details are given for the assignment of absolute stereochemistry to the acetoxy-hydroxy-acid (**85**) from *D. attenuata* and the lactone (**86**) from the *var. linearis*.[56] Junceic acid (**87**) and the related epoxide (**88**) along with other type of diterpenoids were isolated from *Solidago juncea*.[57]



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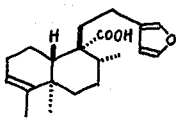

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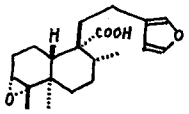
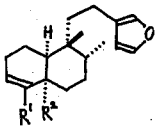
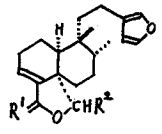


(88)

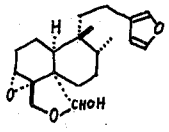
The structures of solidagoic acids A and B isolated from *Solidago gigantea var. serotina* were formulated as **89** and **90**,[58] however, the absolute configuration was tentatively assigned.



(89) R^1=Me, R^2=COOH
(90) R^1=CH_2OAng, R^2=COOH
(91) R^1=CHO, R^2=Me
(92) R^1=R^2=CHO
(93) R^1=CH_2OH, R^2=Me
(94) R^1=Me, R^2=CH_2OH
(95) R^1=R^2=CH_2OH

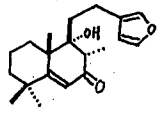


(96) R^1=O, R^2=H
(97) R^1=H_2, R^2=OH

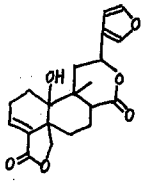


(98)

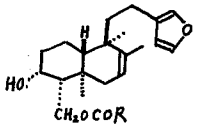
Further investigation of diterpenoid constituent of the same plant resulted in the isolation of eight new diterpenoids (**91**～**98**)[59] whose structures were determined by correlation with solidagoic acid A (**89**). Allylic oxidation of the natural and the related compounds with the chromium trioxide-pyridine complex is reported. Formal total synthesis of compound Y (**99**), isolated from *Leonotis leonurus* previously,[60] was accomplished in the course of this investigation.



(99)

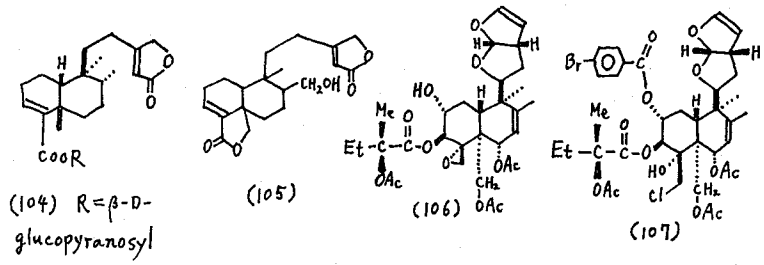


(100)



(101) R = CH_2CHMe_2
(102) R = $CHMeCH_2Me$
(103) R = $CMe=CHMe$

A new diterpene (**100**) with an intensive bitter taste was isolated from *Salvia rubescens*.[61] *Hinterhubera imbricata* was found to contain 3-hydroxyimbicatol isovalerate (**101**), α-methylbutylate (**102**), and angelate (**103**).[62] Marrubiaside (**104**) and marrubialactone (**105**) were isolated from *Leonurus marrubiastrum*.[63]



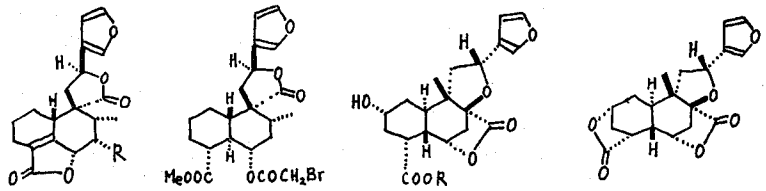
(104) R=β-D-glucopyranosyl

(105)

(106)

(107)

The structure of clerodendrin A (**106**), a bitter principle having an antifeeding repellent activity, isolated from *Clerodendron tricotomum* was determined by chemical methods[64] and by an X-ray analysis of the *p*-bromobenzoate chlorohydrin (**107**).[65] The structures of two novel norditerpenes, teucrin A (**108**)[66,67] and teucvin (**109**)[68] were determined. Though the configuration at C-12 has not been elucidated in the former, the whole structure of the latter including absolute stereochemistry was determined by the chemical method and an X-ray analysis of the key compound (**110**).



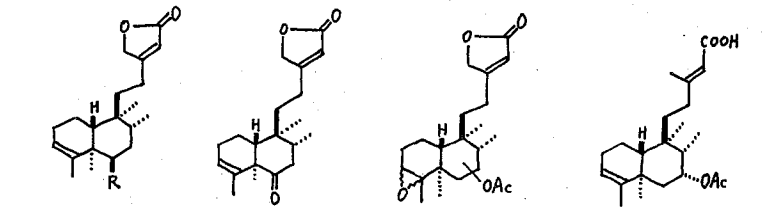
(108) R=OH
(109) R=H

(110)

(111) R = H
(113) R = Me

(112)

The structures of diosbulbins-A, -B, and -C were revised to **111**, **112**, and **113** respectively on the basis of the chemical and spectroscopic reinvestigations.[69] Six bitter principles (**114**~**119**) were isolated from *Solidago altissima*.[70]



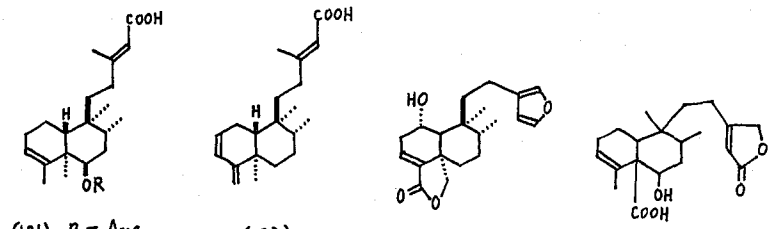
(114) R = H
(115) R = OAng
(116) R = OTig
(117) R = OH

(118)

(119)

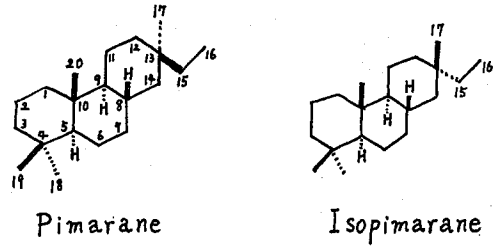
(120)

The stereostructures of the ring B of the acidic bitter principles from *Solidago altissima*, solidagonic acid, 6-angeloyloxy-, and 6-tigloyloxykolavenic acid were determined as **120**, **121**, and **122** respectively.[71] A new diterpene carboxylic acid, dehydrokolavenate (**123**) was isolated from *Solidago altissima* in the form of its methyl ester.[72]

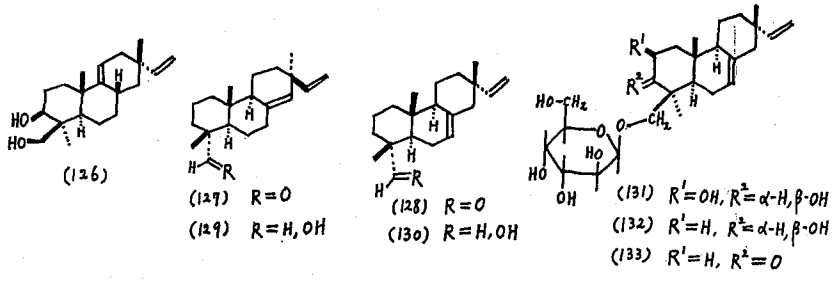


Bacchofertin[73] from *Baccharis conferta* and melissodoric acid[74] from *Salvia melissodora* were assigned structures, **124** and **125**, respectively, based on chemical and spectral data.

V. PIMARANE AND ISOPIMARANE DERIVATIVES



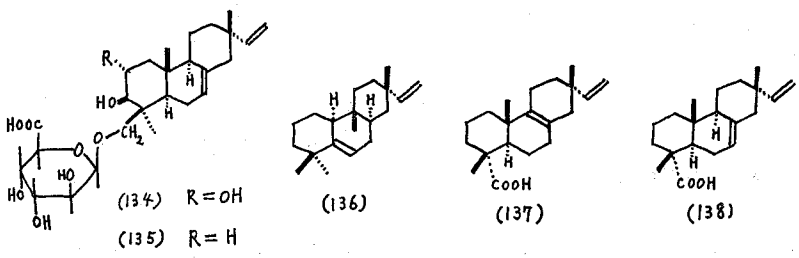
The structure of a new diterpene isolated from *Newcastlia viscida*, was assigned as isopimara-9(11),15-diene-3β,19-diol (**126**) by the conversion into isopimara-8,15-diene and by the spectroscopic data.[75]



Some known diterpenes, pimaral (**127**), isopimaral (**128**), pimarol (**129**), and isopimarol (**130**) were isolated with the new labdane type diterpenes (See. Labdane derivs.) from the bark of *Pinus contorta*.[25]

Several diterpene glycosides had been isolated from *Oospora virescens*. They were virescenosides A (**131**), B (**132**), and C (**133**). In addition, two novel metabolites, virescenosides F and G, were obtained and their structures were established as **134** and **135**. They are the first natural glycosides of altruronic acid.[76]

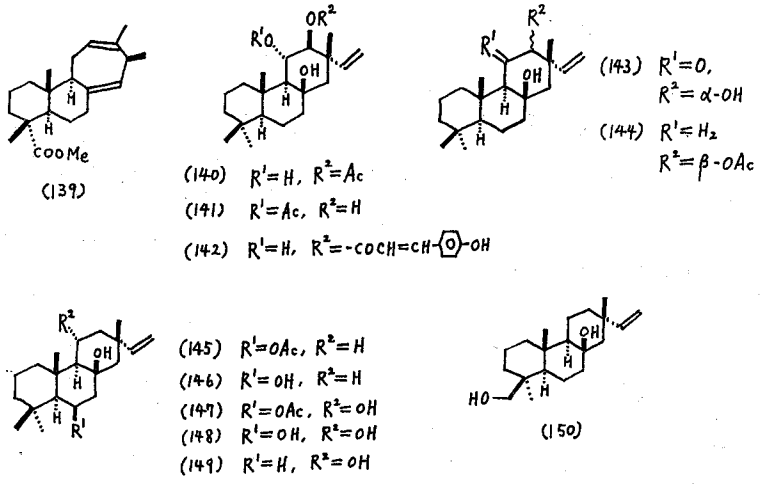
From the leaves and stems of *Podocarpus nubigena* was isolated rimuene (**136**)[77] with some totarane type diterpenes (See Totarane derivatives).



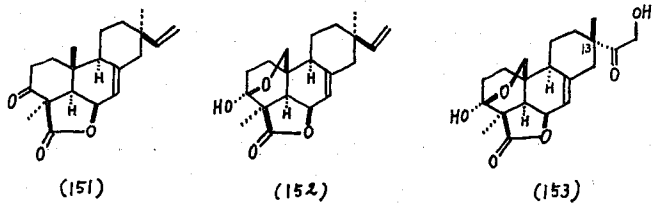
As diterpenes of *Pinus quadifolia,* Δ^8-isopimaric (8,15-isopimaradien-18-oic) acid (**137**), isopimaric acid (**138**), and methyl strobate (**139**) were reported.[78]

Oleoresins from most species of the genus *Larix* were analyzed by means of GLC for their diterpene composition. Common to all are the abietadiene and isopimaradiene acids usual in Pinaceae with the corresponding aldehydes and alcohols in small amounts.[24]

From different representatives of the genera *Garuleum* and *Osteospermum*, eleven new isopimarane type diterpenes (**140**~**150**) were isolated.[79]

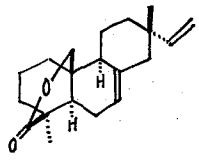


The structures of momilactone-A (**151**) and -B (**152**), growth inhibitors from rice, *Oryza sativa,* were proposed.[80]



The full paper on the structure of a new diterpene isolated from *Annona coriacea*

was published. The absolute chemistry (**153**) except the configuration at C-13 was confirmed on the bases of chemical and spectral evidence.[81] Subsequently, the C-13 configuration of annonalide (**153**) was clarified using ^{1}H and ^{13}C NMR analyses of the degradation product **154**.[82]



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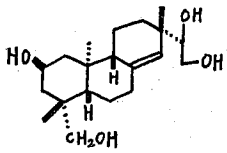

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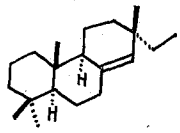
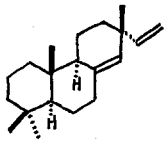


(156)

An isopimaran type diterpene, kirenol (**155**), and some other kaurane type diterpenes (See kaurane derivs.) were obtained from *Siegesbeckia pubescens*.[83]

Optical activity associated with isolated olefinic bonds was investigated using three olefinic compounds **156**, **157**, and **158**.[84]



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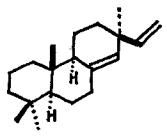

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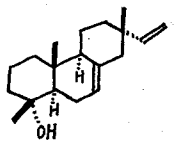


(159)

An autoxidation of isopimaric acid (**138**) in benzene at 70~75° in the presence of $CoCl_3$ yielded 10~15% of neutral product, 18-norisopimara-7,15-dien-4-ol (**159**) and additionally some oxo derivatives.[85]

The acid-catalyzed migration (shown in Chart 4) of the C-13 vinylidene grouping to C-14 in an isopimarane type diterpene (**160**) was reported.[86]

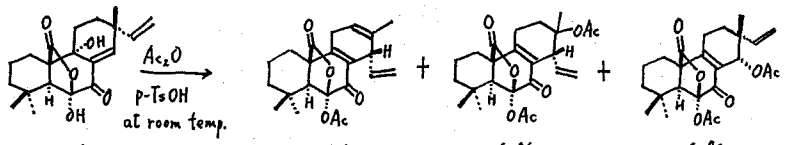


Chart 4

The chemical conversion of isopimaric acid (**138**) to a C-4 cyanomethylated compound (**161**) was developed.[87] The outline is shown in Chart 5.

A synthesis of $\Delta^{8(9)}$-sandaracopimaradiene (**163**) from a keto-hydroxy compound **162** was performed according to the sequence shown in Chart 6.[88]

The photolysis of compound **164** yielded a diketone **165**.[89] (See also beyerane section.) The 10→9 methyl group shift, with concomitant lactonization, effected by Lewis acid treatment of 12,12-ethylenedioxy-8α,9α-epoxy podocarban-19-oic acid (**166**) resulted

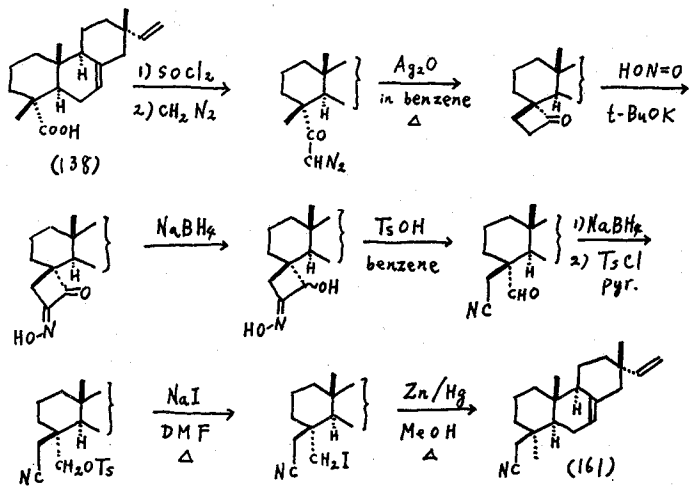


Chart 5

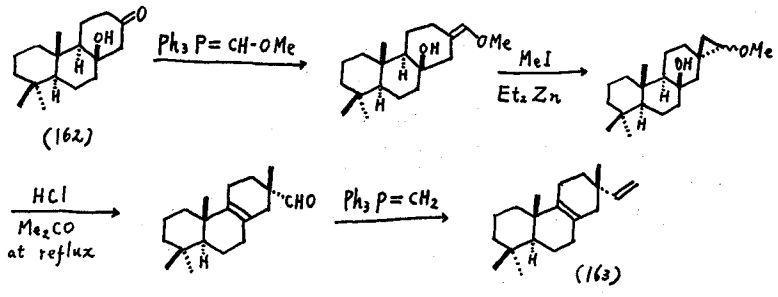
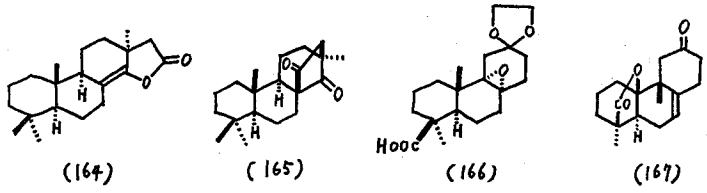
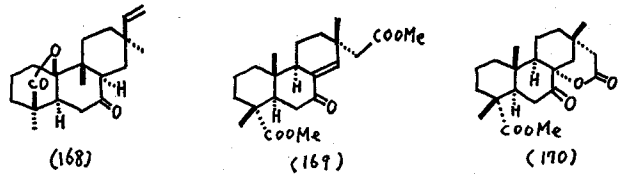


Chart 6

in the formation of the major product **167**,[90] and this compound was converted into rosenonolactone (**168**).

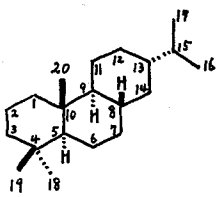


The unstable cisoid enone diester, dimethyl 7-oxoisopimar-8(14)-ene-16,18-dioate (**169**), a potential intermediate for the pimarane to cassane rearrangement, was synthesized regiospecifically from isopimaric acid (**138**) *via* keto-lactone **170**.[91]



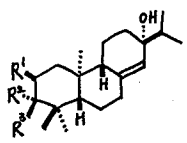
The preparation of pure maleopimaric acid from tall oil rosin was reported.[92]

VI. ABIETANE DERIVATIVES



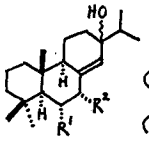
Abietane

Missourienols A (**171**), C (**172**), and some labdane type diterpenes were isolated from *Solidago missouriensis*. Their structure were deduced from the spectroscopic and chemical evidence.[93]



(171) R^1=H, R^2, R^3=O

(172) R^1=OAc, R^2=R^3=H



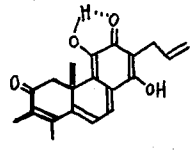
(173) R^1=OH, R^2= OCOC$_4$H$_7$

(174) R^1=OCOC$_4$H$_7$, R^2= OH

(175) R^1=H, R^2=OH

The constitution and stereochemistry of new abietane type diterpense, junceanol W (**173**), X (**174**), and Y (**175**), were clarified on the basis of their chemical and spectroscopic properties.[57]

The structure of coleon F (**176**), isolated from the glands on the leaves of *Coleus barbatus* and a *Coleus* species P. R. O. Bally No. 10431, was elucidated.[94]



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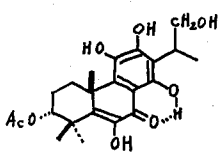
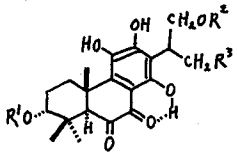
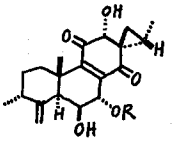


(177)



(178) R^1=Ac, R^2=R^3=H

(179) R^1=H, R^2=Ac, R^3=OAc

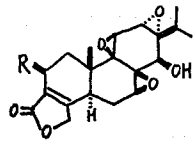


(180) R = H

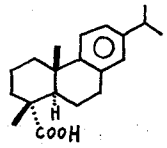
(181) R = Ac

Three diterpenoid hydroquinones, coleons H (**177**), I (**178**), and K (**179**),[95] and two diterpenoids with a cyclopropane ring, coleons G (**180**) and J (**181**)[96] were isolated from *Coleus somaliensis*.

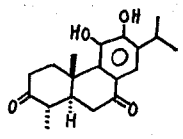
The crystal and molecular structures and absolute configuration of two anti-leukaemic diterpenoid triepoxides, triptolide (**182**) and tripdiolide (**183**), were determined by X-ray analysis.[97]



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



(184)



(185)

Under special conditions, *Flavobacterium Resinovorum* grown on dehydroabietic acid (**184**) as sole carbon and energy source, metabolized **184** into a diphenol diketone **185**. The unique behavior of bacterial attack at C-3 before the degradation of the cyclic system was confirmed.[98]

A metabolic pathway of dehydroabietic acid (**184**) was investigated using two new strains, *Pseudomonas* sp. and *Alcaligenes Eutrophus*.[99] An outline (Chart 7) of the degradative pathway of **184** by these two species in comparison with *Flavobacterium Resinovorum* were discussed.

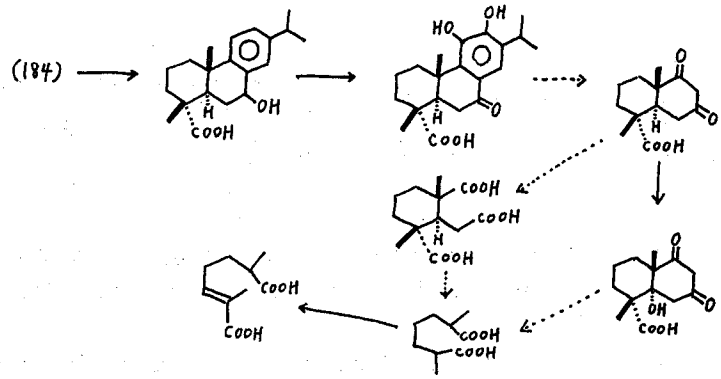
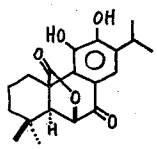


Chart 7

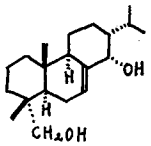
The structure of galdosol (**186**), a new diterpene from *Salvia canariensis* was reported.[100]

A dihydroxyabietene isomer **187**[101] and some other diterpene components[102] were isolated from *Nepta teydea*.

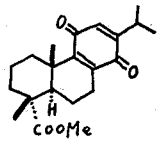
Oxidation of methyl dehydroabietate with H_2O_2-CF_3CO_2H afforded a compound **188**. The stereochemistry of **188** was established by a degradation study. The CD of this compound showed that quinonic chromophore is optically active; two Cotton effects of opposite sign were observed.[103]



(186)

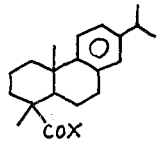


(187)

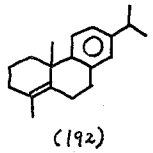


(188)

Dehydroabietic acid (**184**) was allowed to react with diketene, acetic acid, acetic anhydride, isopropenyl acetate, acetyl chloride, and acetone on Vycor rod at 450°C in a hot tube. Dehydroabietic anhydride (**189**) and acetyl dehydroabietate (**190**) were pyrolyzed at 450°C and dehydroabiethyl chloride (**191**) was pyrolyzed over a temperature range of 290~500°C. The major olefin products were compounds **192**, **193**, **194**, and **195**. In the presence of the ketene-producing reagents the olefins were oxidized to afford substantial amounts of retene (**196**).[104]



(189) X = dehydroabietate
(190) X = OCOMe
(191) X = Cl



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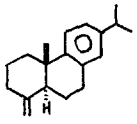

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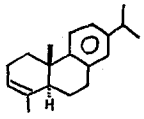

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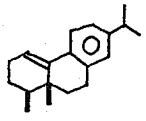

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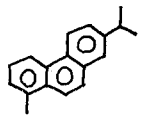
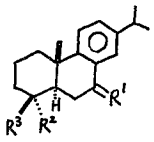


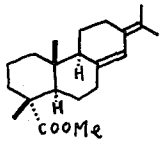
(196)

The autoxidations of dehydroabietinal (**197**) and dehydroabietic acid (**184**) were investigated. In the former reaction,[105] 6% of the hydrocarbon **198**, 16% of the hydroperoxide **199**, 23% of the hydroperoxide isomer **200**, 4% of the hydroxide **201**, and some of the hydroxide isomer **202** were obtained. The latter case[85] yielded 10~15% of the hydroxides **201** and **202**, and a few % of **203** after the methylation.



(197) $R^1=H_2$, $R^2=CHO$, $R^3=Me$
(198) $R^1=H_2$, R^2, $R^3=Me$ and H
(199) $R^1=H_2$, $R^2=Me$, $R^3=OOH$
(200) $R^1=H_2$, $R^2=OOH$, $R^3=Me$
(201) $R^1=H_2$, $R^2=Me$, $R^3=OH$
(202) $R^1=H_2$, $R^2=OH$, $R^3=Me$
(203) $R^1=O$, $R^2=COOMe$, $R^3=Me$

In relation to the photochemistry of alkenes, the previous irradiation experiment[106] of methyl neoabiatate (**204**) in methanol into the dienyl methyl ether (**205**) was briefly discussed.[107]



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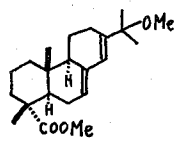

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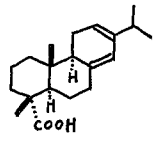

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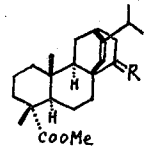
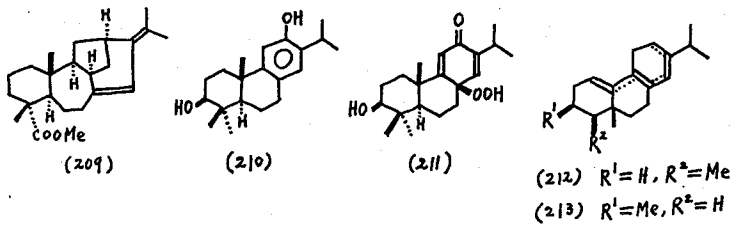


(207) R=O
(208) R=α-H, β-OH

Levopimaric acid (**206**) was transformed into the ketone **207** by the Diels-Alder reac-

tion with α-acetoxy acrylonitrile. The compound **207** was reduced to the alcohol **208**, the solvolysis of whose tosylate proceeded predominantly with rearrangement and elimination to give methyl 16-isopropylidene-7,17-secoacon-8(15)-en-18-oate (**209**).[108]

Oxidation of hinokiol (**210**) with tetraperoxymolybdate gave the dienone hydroperoxide **211** in good yield (55%).[21]



Nitration of various dehydroabietic acid derivatives was examined and it was found that nitration was affected by the structure.[109]

Levopimaric acid (**206**) in chlorosulfonic acid and CH_2Cl_2 underwent a novel rearrangement to give a mixture of C_{19}-triens, **212** and **213** in 88% yield after treatment with iced Na_2CO_3. The possible mechanism (Chart 8) and the further reactions of the mixture of **212** and **213** were discussed.[110]

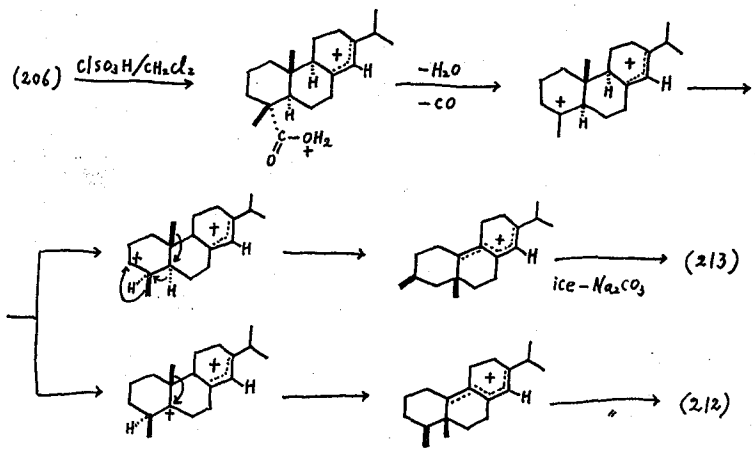
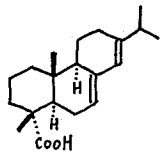


Chart 8

A skeletal transformation of compound **4** derived from *l*-abietic acid (**214**) into an aconane type skeleton **6** in shown in Chart 2.[14]

7-Oxo esters, **215** and **216**, derived from *l*-abietic acid (**214**) were converted to half esters **217** and **218** respectively. Intramolecular cyclization of **218** afforded the expected 11-methoxy oxo ester **219**, however, that of **217** yielded the undesirable bicycle[3.3.1] nonane ester **220** *via* a methoxy migration of the methoxy carbonyl group.[111] On the other hand, the cyclization of methoxycyano acid (**222**) derived from 7-oxo-dehydroabietamide (**221**) gave the expected 11-methoxy-7-oxo-dehydroabietonitrile (**223**).[112]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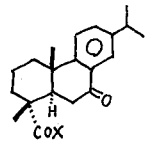
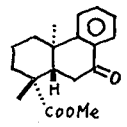

(215) X = OMe
(221) X = NH2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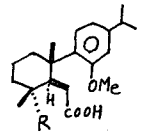
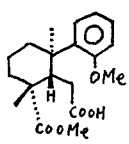

(217) R = COOMe
(222) R = CN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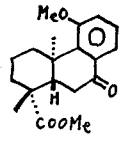
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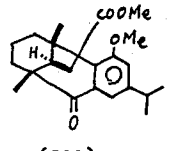
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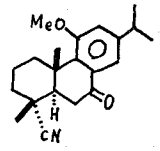

(223)

Miltirone (**224**), a diterpenoid quinone isolated from the roots of *Salvia miltiorrhiza*, was synthesized from *p*-bromoanisole.[113] The sequence is shown in Chart 9.

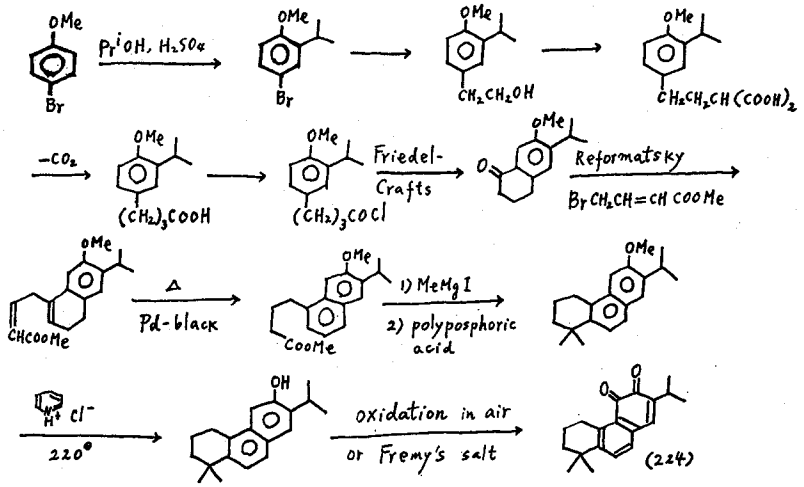
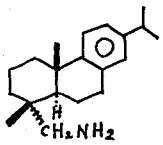


Chart 9

l-Abietic acid was converted into kaurene and phyloocladene. The details will be described in section IX.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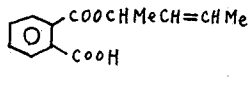
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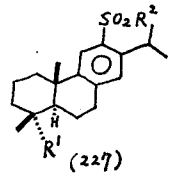

(227)

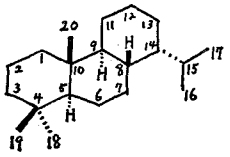
Dehydroabietylamine (**225**) was prepared in 84% yield by amination of dehydroabietic acid with NH_3, followed by reduction with $LiAlH_4$. Treatment of **226** with **225** at 0°

gave 18% (+)-(**226**) dehydroabietylamine salt, which was hydrolyzed by NaOH to 80% (+)-(**226**).[114]

Several dehydroabietylsulfonamides (**227**) were synthesized by treating **227** (R^2=Cl) with the corresponding amines. The acid derivatives of **227** (R^1=CO_2Me, R^2=OH, OAg, OMe) were similarly prepared. The yields were 32~97%.[115]

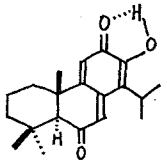
The syntheses of *cis*-abienol, Δ^{13} *cis*-neoabienols and Δ^{13} *trans*-neoabienols were reported.[116]

VII. TOTARANE DERIVATIVES



Totarane

The light petroleum extract of *Maytenus dispermus* was shown to contain three new diterpenes: maytenoquinone (**228**), 12-methoxytotarol (dispermol) (**229**), and 12-hydroxy-7-oxototarol (dispermone) (**230**), together with the known sugiol.[117]



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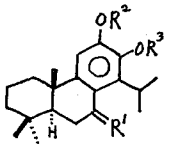
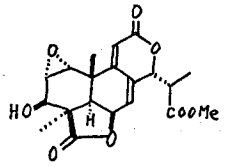


(229) R^1=H_2, R^2=Me, R^3=H

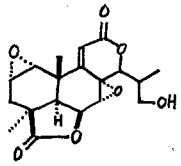
(230) R^1=O, R^2=R^3=H



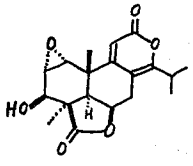
(231)

From the leaves and stems of *Podocarpus nubigena* was isolated a new diterpene, nubilactone-A (**231**) with some known components.[77]

One of the unidentified compounds from a methanalic extract of the heartwood of *Podocarpus hallii* was identified as the known norditerpene lactone, sellowin-A (**232**), which strongly inhibited growth of a pea stem hook segments giving a typical podolactone type response.[118]



(232)



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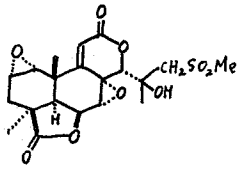
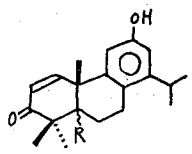


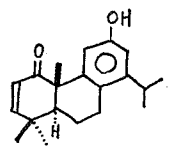
(234)

The structures of hallactones A and B, insect toxins from *Podocarpus hallii*, were

shown to be the norditerpene lactones **233**, and **234**, respectively.[119] The synthesis of *dl*-12-hydroxy-3-oxototara-1,8,11,13-tetraene (**235**), a proposed structure for shonanol, was reported.[120] The spectral data of the synthetic **235** and its *cis*-isomer **236**, however, were different from those of natural shonanol.[121]



(235) R = α-H
(236) R = β-H



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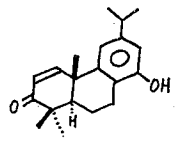

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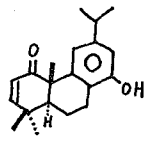
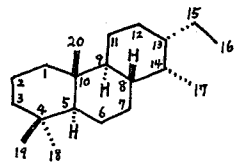


(239)

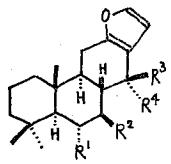
For structure elucidation of shonanol, a totarane type compound **237** and two podocarpane derivatives **238** and **239** were synthesized. However, it was recognized that these synthesized compounds were not identical with shonanol.[122]

VIII. CASSANE DERIVATIVES



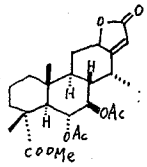
Cassane

Eight new diterpenoids isolated from *Pterodon emarginatus* were assigned the structures and stereochemistry of **240** to **247**.[123]



(240) $R^1 = R^2 = OAc$, $R^3 = H$, $R^4 = Me$
(241) $R^1 = H$, $R^2 = OAc$, $R^3 = H$, $R^4 = Me$
(242) $R^1 = R^2 = OH$, $R^3 = COOH$, $R^4 = H$
(243) $R^1 = R^2 = OH$, $R^3 = COOMe$, $R^4 = H$
(244) $R^1 = OH$, $R^2 = OAc$, $R^3 = COOMe$, $R^4 = H$
(245) $R^1 = OAc$, $R^2, R^3 = O{\cdot}CO$, $R^4 = H$
(246) $R^1 = R^2 = R^3 = OH$, $R^4 = Me$
(247) $R^1 = R^2 = OAc$, $R^3, R^4 = :CH_2$

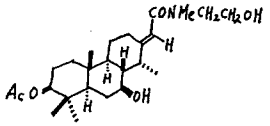
From the fruits of *Pterodon pubescens* were isolated two new diterpenes, a vinhaticoic acid derivative **248** and a non-cyclic component **249**.[124]



(248)

$Me_2C(OH)CH(OH)(CH_2)_2CMe=CH(CH_2)_2CMe=CH-(CH_2)_2CMe=CHCH_2OH$

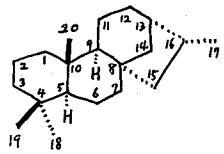
(249)



(250)

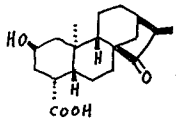
A new diterpene alkaloid **250** was isolated from the bark of *Erythrophleum suaveolens*. The NMR of **250** showed conformational isomerism because of a barrier to internal rotation.[125]

IX. KAURANE DERIVATIVES

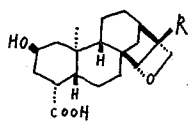


Kaurane

A C_{19} terpene acid occurring as glucuronide was isolated from human urine. Spectroscopic data and chemical degradations allowed to attribute to the acid the structure **251**.[126] This acid is excreted in human urine in daily amounts between 2 and 40 mg.

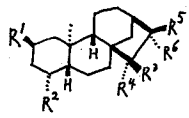


(251)



(252) R = H

(253) R = Br



(254) $R^1=R^3=OH$, $R^2=CH_2OH$, $R^4=R^6=H$, $R^5=Me$

(255) $R^1=R^4=OH$, $R^2=CH_2OH$, $R^3=R^5=H$, $R^6=Me$

(256) $R^1=R^4=OH$, $R^2=CH_2OH$, $R^3=R^6=H$, $R^5=Me$

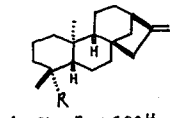
(257) $R^1=OAc$, $R^2=COOH$, $R^3=H$, $R^4=OH$, $R^5=Br$, $R^6=CH_2Br$

(258) $R^1=R^4=OH$, $R^2=COOMe$, $R^3=H$, $R^5=Br$, $R^6=CH_2Br$

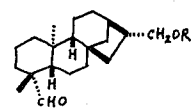
The oxetane ring of isoatractyligenin (**252**) and 16-bromo-isoatractyligenin (**253**) was proved to have α, α orientation, by comparison of triol **255** arising from the reduction of **252** with triols **254** and **256** having sure configuration at C–15 and C–16.[127] Addition of bromine on the exocyclic double bond of atractyligenin and its methyl ester gave derivatives **257** and **258** with 16 β-Br, 16 α-CH_2Br configuration. Product **258** was obtained also by reaction of hydrobromic acid on the methyl ester of **253**.

ent-16-Kauren-19-oic acid (**259**) was isolated from *Solidago juncea*,[57] and *Mikania mongenansis*.[128]

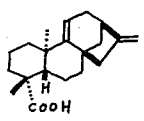
The root extract of *Anona squamosa* was found to contain five diterpenes (**260**~**264**), their structure being elucidated.[129]



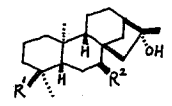
(259) R = COOH
(260) R = CH_2OH
(261) R = CHO
(262) R = CH_2OAc



(263) R = H
(264) R = Ac

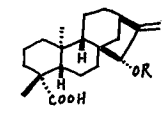


(265)

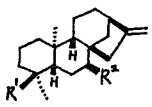


(266) R' = Me, R^2 = H
(273) R' = CH_2OH, R^2 = H
(274) R' = Me, R^2 = OH

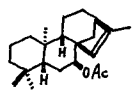
From the light petroleum extract of the dried leaves and bark of *Espletia littlei*, *ent*-kaur-9(11),16-dien-19-oic acid (**265**) was isolated. From *E. humbertii*, **265**, *ent*-kauran-16-ol (**266**), and *ent*-15 β-acetoxy-16-kauren-19-oic acid (**267**) were isolated. Isolations of **265** and *ent*-15 β-hydroxy-16-kauren-19-oic acid (**268**) from *E. timotensis* were also reported.[130]



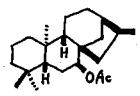
(267) R = Ac
(268) R = H



(269) R' = Me, R^2 = OH
(270) R' = CH_2OH, R^2 = H
(271) R' = CH_2OH, R^2 = OAc
(272) R' = CH_2OH, R^2 = OH
(275) R' = Me, R^2 = Ac



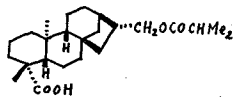
(276)



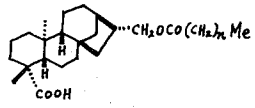
(277)

Three new diterpenes candol-A (*ent*-16-kauren-7α-ol) (**269**), candol-B (*ent*-16-kauren-18-ol) (**270**) and epicandicandiol 7 β-monoacetate (*ent*-7 α-acetoxy-16-kauren-18-ol) (**271**) as well as epicandicandiol (**272**) were isolated from *Sideritis candicans*.[131] Two new diterpenes, vierol (*ent*-kaurane-16,18-diol) (**273**) and powerol (*ent*-kaurane-7 α,16-diol) (**274**) were isolated from *Sideritis canariensis*. Partial synthesis of **273** from epicandicandiol (**272**) and some chemical conversions of **274** were described. The chemical transformations of epicandicandiol (**272**) into *ent*-7α-acetoxy-16-kaurene (**275**), *ent*-7α-acetoxy-15-kaurene (**276**), and *ent*-7α-acetoxy-kaurane (**277**) were also reported.[132]

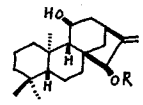
Substances A, B, C, and D were isolated from *Siegesbeckia pubescens*, and structures **278** and **279** were assigned to A and B, respectively.[83]



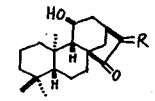
(278)



(279) a mixture of n = 10, 12, 14, and 16

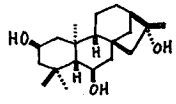


(280) R = Ac
(281) R = H



(282) R = α-H, β-Me
(283) R = CH_2

Four new 11 β-hydroxylated *ent*-kaurene derivatives were isolated from *Solenostoma triste*, and structures **280** to **283** were assigned to them.[133] From the rhizomes of *Pteris cretica* was isolated triol **284**.[134]



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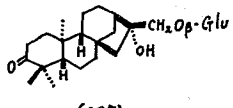

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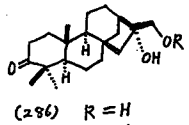
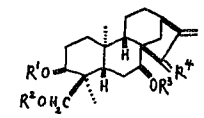


(286) R = H
(287) R = Ac

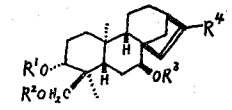
A bitter diterpene glucoside, sugereoside, was isolated from the leaves of *Ilex sugerokii var. bevipedunculata* and *I. sugerokii var. longipedunculata,* and structure **285** was given to it.[135]

The structures of calliterpenone and its monoacetate had been proposed as *ent*-kaurane derivatives,[136] but now, the revised structures **286** and **287** of 13β-kaurane derivatives were proposed.[137]

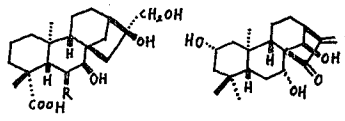
Seven kinds of diterpenes, **288** to **294**, were isolated from aerial parts of *Sideritis leucantha*. The compounds **289**, **290**, and **295** were found in *S. linearifolia*.[138]



(288) $R^1 \sim R^3 = H$, $R^4 = H, OH$
(289) $R^1 = Ac$, $R^2, R^3 = H$, $R^4 = H_2$
(290) $R^1 = R^3 = H$, $R^2 = Ac$, $R^4 = H_2$
(295) $R^1 \sim R^3 = H$, $R^4 = H_2$



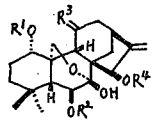
(291) $R^1 \sim R^3 = H$, $R^4 = Me$
(292) $R^1 \sim R^3 = H$, $R^4 = CH_2OH$
(293) $R^1 = Ac$, $R^2, R^3 = H$, $R^4 = Me$
(294) $R^1, R^3 = H$, $R^2 = Ac$, $R^4 = Me$



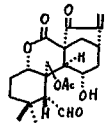
(296) R = H
(297) R = OH
(298)

During the isolation of gibberellins from immature seeds of *Calonyction aculeatum,* two polyhydroxykauranoic acids, **296** and **297**, were isolated and characterized.[139]

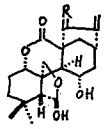
Mebadonin (**298**) was isolated from *Isodon Kameba* and the crystal and molecular structure was determined by means of X-ray analysis.[140] Shikokianidin isolated from *Isodon shikokianus* was formulated as **299** on the basis of chemical and spectroscopic evidence.[141]



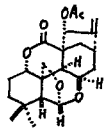
(299) $R^1 = R^2 = R^4 = Ac$, $R^3 = O$
(302) $R^1 = R^2 = R^4 = H$, $R^3 = \alpha$-H, β-OAc



(300)

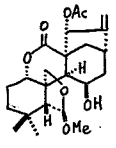


(301) R = O
(303) R = α-OH, β-H

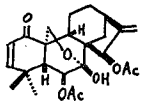


(304)

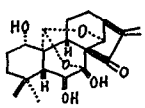
Isolation of the known isodonal (**300**) and epinodosin (**301**) from *Isodon japonicus* and structure elucidation of sodoponin (**302**) and epinodosinol (**303**), novel diterpenoids in the same plant, were reported.[142] Structures and absolute configurations of isodoacetal (**304**),[143] nodosinin (**305**),[143] odonicin (**306**),[143] and ponicidin (**307**),[144] were determined by means of chemical and physical methods. They are novel diterpenoids isolated from *I. japonicus*.



(305)



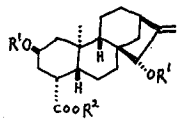
(306)



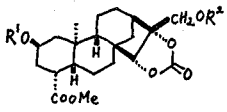
(307)

Isolation of grayanotoxins I, II, and III from *Agauria polyphylla* was reported.[145]

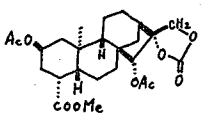
The performic oxidation of the kaurenic double bond of atractyligenin (**308**) and the derivatives afforded cyclic carbonates between the 15α-hydroxy and 16α-hydroxy grousp or the 16α-hydroxy and 17-hydroxy groups. For instance, the methyl ester **309** gave **310**, **311**, and **312** and diacetate (**313**) of **309** yielded **314** and **315**.[146]



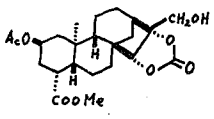
(308) $R^1 = R^2 = H$
(309) $R^1 = H$, $R^2 = Me$
(313) $R^1 = Ac$, $R^2 = Me$



(310) $R^1 = R^2 = H$
(311) $R^1 = CHO$, $R^2 = H$
(312) $R^1 = R^2 = CHO$

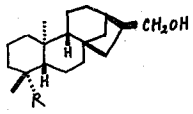


(314)

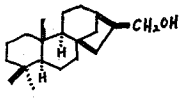


(315)

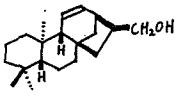
ent-Kauran-17-ol (**316**), the corresponding C–19 ester (**317**), and 13β-kauran-17-ol (**318**), on reaction with lead tetraacetate-iodine in refluxing cyclohexane, suffered intramolecular attack mainly at C–11. Thus, **316** gave as major products the 11-en-17-ol **319** and the 11β-iodo-12β, 17-ether **320**, along with minor amounts of the 9,11-en-12β, 17-ether **321**, the 11β, 17-ether **322**, and resulting from attack at C–12, the 12 β-17-ether **323**. The 13β-kauranol **318** gave the 11β, 17-ether **324** and the 9,11-en-12β, 17-ether **325**.[147]



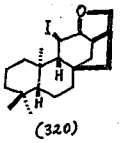
(316) R = Me
(317) R = COOMe



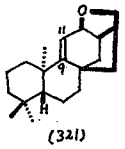
(318)



(319)

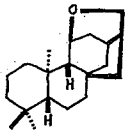


(320)



(321)

(323) 9,11-2H



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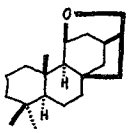
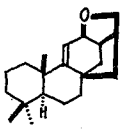
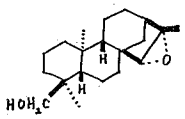


(324)

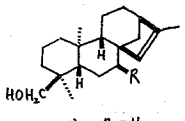


(325)

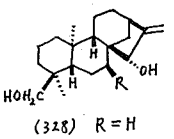
Treatment of *ent*-15β,16β-epoxykauran-18-ol (**326**) with boron trifluoride-ether complex in dimethyl sulfoxide or direct photo-oxygenation of *ent*-15-kauren-18-ol (**327**) gave the expected *ent*-16-kaurene-15β,18-diol (**328**), which was suggested to be identical with natural candidiol. Treatment of *ent*-15β,16β-epoxykaurane-7α,18-diol (**329**) (natural sideroxol) with the same reagent or photo-oxygenation of *ent*-15-kaurene-7α, 18-diol (**330**) (natural sideridiol) gave *ent*-16-kaurene-7α, 15β, 18-triol (**331**).[148]



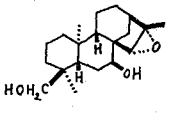
(326)



(327) R = H
(330) R = OH

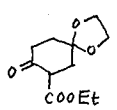


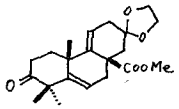
(328) R = H
(331) R = OH



(329)

A stereoselective synthesis of 3β,17-diacetoxy-13β-kaur-16-en-15-one (**335**) from ethyl 5,5-ethylenedioxy-2-oxocyclohexane carboxylate (**332**) proceeding in ten stages *via* podocarpane derivatives, **333** and **334**, was published.[149]


(332)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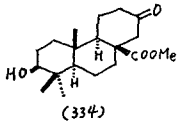
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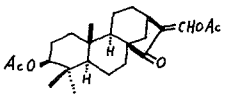
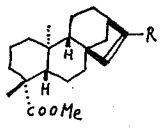
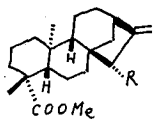
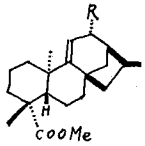

(335)

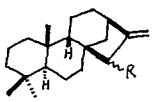
Methyl *ent*-15-(**336**) and 16-kauren-19-oate (**337**) in pyridine were irradiated with fluorescent tubes using haematoporphirin as a sensitizer to yield 15α-ol **338** and 17-ol **339**, respectively. Methyl *ent*-kaur-9(11)-en-19-oate (**340**) was irradiated to give 12α-ol **341**, from which the 12 epimer was derived.[150]

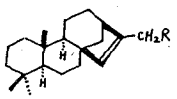

(336) R = Me
(339) R = CH_2OH

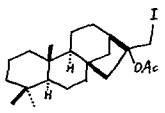

(337) R = H
(338) R = OH


(340) R = H
(341) R = OH

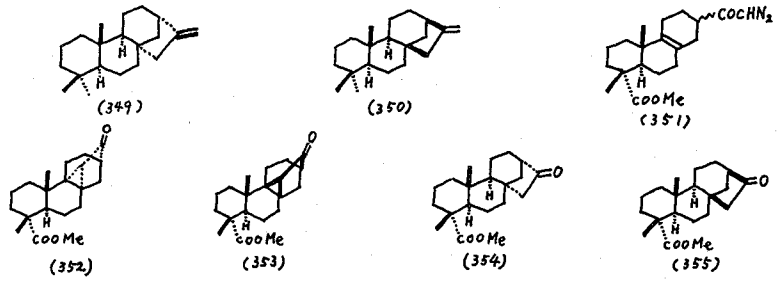
Treatment of an alkene with a thallium (I) carboxylate and iodine was found to give the corresponding α-iodocarboxylate in high yield, thereby affording a regiospecific and inexpensive modification for the Prevost reaction. Thus, 13β-kaur-16-ene (phyllocladene) (**342**) on treatment with thallium (I) acetate and iodine gave **343**, **344**, and **345** in the yields of 30, 40, and 30% respectively, while 13β-kaur-15-ene (**346**) on the same procedure gave **344** and **343** in 56 and 38% yields, respectively. Treatment of **342** with thallium (I) benzoate and iodine afforded **347** and **348** in 54 and 46% yields, respectively, and the same treatment of **346** also gave 55% of **347** and 45% of **348**.[151]


(342) R = H
(343) R = OAc
(348) R = OBz


(344) R = OAc
(346) R = H
(347) R = OBz

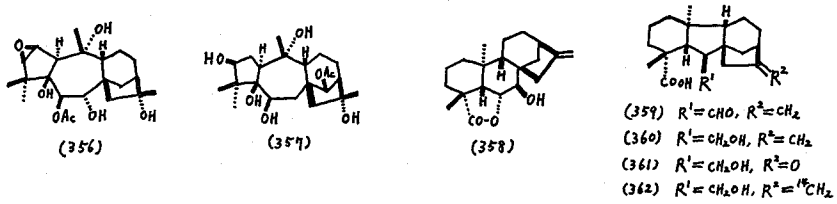

(345)

16-Kaurene (**349**) and 13β-kaurene (phyllocladene) (**350**) were derived from *l*-abietic acid (**214**) *via* several steps of reactions. The key reactions involved conversion of an epimeric mixture of diazoketone **351** into a mixture of two cyclopropyl ketones **352** and **353** and transformations of separated **352** and **353** into norketoesters **354** and **355**, respectively.[152]

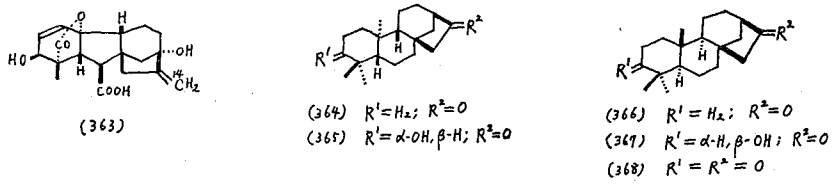


A short review on the total synthesis of steviol carried out in 1972 was published in Japanese.[153]

Correlation of lyoniol-A (lyoniatoxin) (**356**) with grayanotoxin-I (**357**), whose absolute structure had been determined by X-ray crystallography,[154] was achieved chemically, thus establishing the structure of lyoniol-A.[155]



A combination of chemical and microbiological methods was used for the preparation of [^{14}C]-gibberellic acid; 7β-hydroxykaurenolide (**358**) was converted into a norketone **361** of gibberellane type *via* 7α-hydroxykaurenolide, 7-bromobenzenesulfonate, gibberellane derivatives, **359** and **360**, then the ketone **361** was subjected to hot Wittig reaction to yield a labeled alcoholic acid **362**, which was incubated with *Gibberella fujikuroi* to yield [17-^{14}C]-gibberellic acid (**363**).[156]



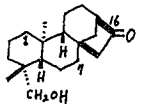
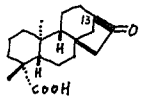
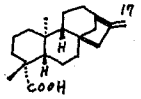
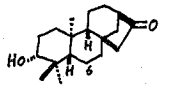
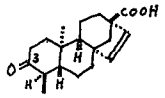
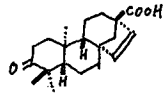
Soluble enzyme preparation from pea *Pisum sativum* shoot tips incorporated mevalonic-2-^{14}C into *ent*-kaurene-^{14}C, squalene-^{14}C, and other products. The assay for either *ent*-kaurene or squalene was quite direct; both products were obtained apparently free of radioactive contaminants by TLC on silica gel G in hexane. Biosynthesis of *ent*-kaurene in the cell-free extracts of pea under several conditions was investigated.[157]

Barley grains were found to contain hydrocarbons, including a material indistinguishable from *ent*-kaurene by GLC, and which after appropriate chemical conversions contained material behaving like *ent*-kauran-16,17-diol, *ent*-kaurene norketone and *ent*-17-norkaurane on TLC and GLC. The presence of *ent*-kaurene was confirmed by conversion to *ent*-kauran-16-ol and, following formation of acetate-[^{3}H], recrystallization to constant

specific activity with unlabeled carrier. In the initial ca. 15 hours of germination preceding the rise in endogenous gibberellins, the level of *ent*-kaurene fell. Exogenous *ent*-kaurene-[^{14}C] was not metabolized by intact barley gains. *ent*-Kaurane-16,17-epoxide was found non-enzymically by boiled extracts. Unboiled homogenates also formed *ent*-kauran-17-ol and *ent*-kaurane-16,17-diol. The diol appeared to be formed from the epoxide, but the *ent*-kauran-17-ol did not. No recognized gibberellin precursors were detected. Nevertheless, endogenous *ent*-kaurene may be the stored biosynthetic precursor of gibberellins in germinating barley grains.[158]

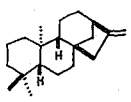
Microbiological transformations of tetracyclic diterpenes were reported. The results are summarized in Table I.[159]

Table I.

Substrate	Substrate modification in major products obtained (%)		
	Aspergillus ochraceous	*Calonectria decora*	*Rhizopus migricans*
	% 16β–OH (10)	1α–OH(10) 7α–OH(10)	1α–OH(20) 7α–OH(20)
	13–OH(5) 13, 16β–OH(5)	1α–OH(5) 7α–OH(15) 7β–OH(40)	1α–OH(30) 7α–OH(30) 7β–OH(5)
	16α, 17–OH(20)	15α, 7α–OH(30) 15α–OH(5) 7α–OH(5)	7β–OH(25)
	6β–OH(30) 7α–OH(25)	7α–OH(40)	1α–OH(25) 7α–OH(35)
	3β–OH	6β–OH(50)	—
	—	6β–OH(50)	—

Incubation of *ent*-17-norkauran-16-one (**364**) with *Aspergillus niger* gave *ent*-3β-hydroxy-17-norkauran-16-one (**365**), while 17-nor-13β-kauran-16-one (**366**) gave 3β-hydroxy-17-nor-13β-kauran-16-one (**367**) and the corresponding 3-ketone (**368**).[160]

Biosynthesis of enmein (**370**) and oridonin (**371**) from *ent*-16-kaurene (**369**) was investigated; *ent*-16-kaurene (**369**) was shown by tracer experiments to be incorporated into enmein (**370**) and oridonin (**371**) in *Isodon japonicus*.[161]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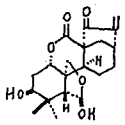
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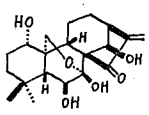
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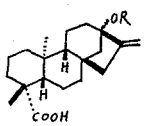
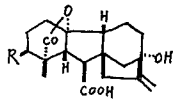
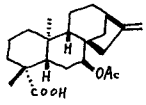

(372) R = H
(374) R = Ac

The low substrate specificity of enzymes operating beyond the genetic defect in mutant Bl–41a of the fungus, *Gibberella fujikuroi*, was shown by the metabolism of the non-fungal diterpene steviol (**372**) and some of its derivatives to higher plant gibberellins and their derivatives. The results are summarized as follows: (1) Steviol was rapidly converted to 7β-ol derivative and then several gibberellane derivatives, of which gibberellin A_1 (GA_1) (**373**) was the major metabolite. (2) Steviol acetate (**374**) was metabolized to GA_{20} acetate, whose hydrolysis yielded ca. 30% of overall yield of GA_{20} (**375**). (3) Steviol methyl ester was metabolized to mono- and dihydroxysteviol methyl esters and not to GAs. (4) *ent*-7α Acetoxykaurenoic acid (**376**) was metabolized to monohydroxy derivative. (5) Isosteviol (**377**)* was metabolized to several gibberellane derivatives and hydroxylated isosteviols.[162]


(373) R = OH
(375) R = H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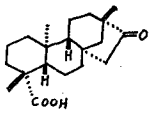
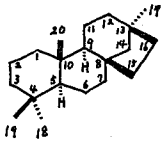
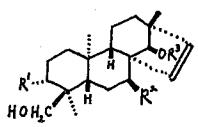

(377)

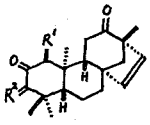
X. BEYERANE DERIVATIVES



Beyerane

The *ent*-beyerane derivatives **378**, **379**, and **380** were isolated as minor components of the extracts of *Sideritis pusilla*.[163] They were deacetylated to isopusillatriol, pusillatriol, and pusillatetraol, respectively.


(378) R^1 = OH, R^2 = H, R^3 = Ac
(379) R^1 = R^3 = H, R^2 = OAc
(380) R^1 = OH, R^2 = OAc, R^3 = H


(381) R^1 = H, R^2 = α-OH, β-H
(382) R^1 = H, R^2 = α-OTs, β-H
(383) R^1 = OAc, R^2 = H_2
(384) R^1 = OH, R^2 = H_2

Acetolysis of tetracyclic diterpenoid 3-equatorial, 3-axial or 1-axial sulfonate-2-ketones resulted in attack at the 1-axial position. Jones oxidation of the derived 1-hydroxy-2-

* Beyerane series.

ketone resulted in an unexpected ring contraction-decarboxylation giving a 2-nor-1-ketone. Thus, the equatorial tosylate **382** derived from *ent*-3β-hydroxybeyer-15-en-2,12-dione (**381**) with tosyl chloride in pyridine was subjected to acetolysis at reflux in sodium acetate buffered acetic acid to give the axial *ent*-1α-acetoxybeyer-15-en-2,12-dione (**383**) as the major product. Compound **383** underwent practically instantaneous hydrolysis with dilute base at room temperature to give the corresponding alcohol **384**, which on Jones oxidation with excess reagent at 0° resulted in the 2-nor-1-ketone **385** *via* a tentatively postulated route as shown in Chart 10.[164]

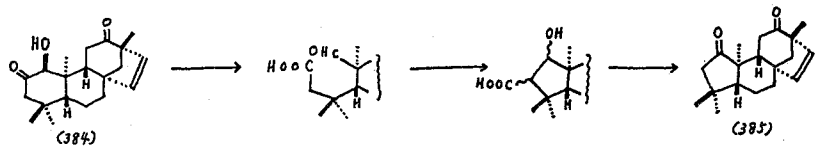
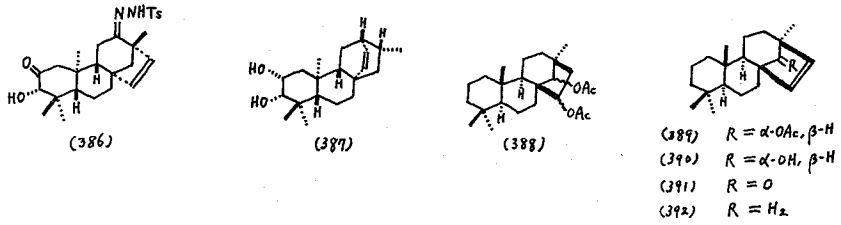


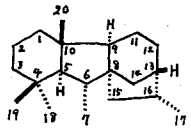
Chart 10

The hydride induced shift of an *ent*-beyer-15-ene-12-*p*-tosylhydrazone **386**, a bicyclo [3.2.1]octene system, to the hitherto undescribed *ent*-15S-atis-13-ene **387**, a bicyclo [2.2.2]octene system, was observed on treatment of the former with $NaBH_4$ in ethanol-dioxan at 0° or at reflux; the extreme unreactivity of the double bond in the product was reported.[165]



Photolysis of **164**, a product of dehydration of one of the earlier overoxidation products of pimaradine **158**, yielded diketone **165**, as described in Section V. Reduction of the latter with $LiAlH_4$ and acetylation of the resultant diol gave a diacetate **388**, whose pyrolysis led to 14 α-acetoxyhibaene (**389**). Reductive removal of the acetyl group of **389** and subsequent Jones oxidation of the resultant alcohol **390** produced 14-ketohibaene (**391**), whose Wolff-Kishner reduction afforded hibaene (**392**) and its dehydroderivative.[89]

XI. GIBBERELLANE DERIVATIVES

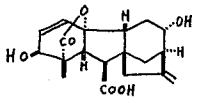


Gibberellane

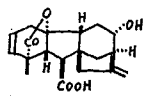
The main gibberellin in immature seed of *Pisum sativum* was identified as gibberellin A_{20} by GC-MS.[166]

Four novel gibberellins, GA_{30}, GA_{31}, GA_{33}, and GA_{34} together with five known gibberellins were isolated from *Calonyction aculeatum* and their structures were determined to be **393**, **394**, **395**, and **396**, respectively.[167]

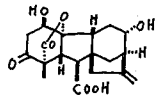
The structure of GA_{40} was determined as **397** mainly by ^{13}C NMR spectra.[168]



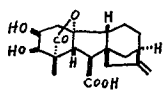
(393)



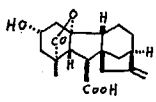
(394)



(395)



(396)

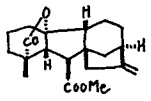


(397)

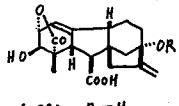
CD and ORD of twelve gibberellin derivatives with an aromatic A ring together with two related compounds were measured. Those curves provided information to determine the configurations at C–9 and C–6.[169]

An application of axial-haloketone rule to several lactones including gibberellin A_9 methyl ester (**398**) was discussed.[170]

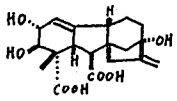
A qualitative and quantitative analysis of the decomposition of unbuffered and buffered (pH 3∼8) aqueous solutions of gibberellic acid (GA_3) on autoclaving was recorded. The identified products, which varry in composition with pH, were iso-GA_3 (**399**), iso-GA_3 hydroxy acid (**400**), gibberellenic acid (**401**), allogibberic acid (**402**), epiallogibberic acid (**403**), and dehydroallogibberic acid (**404**).[171]



(398)



(399) R = H
(400) R = Ac



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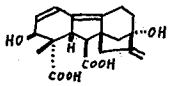

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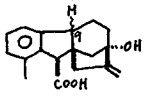
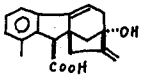


(402) 9α-H
(403) 9β-H



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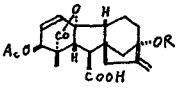
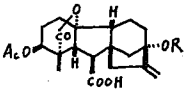


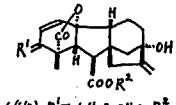
(405) R = Ac
(406) R = H



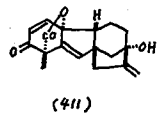
(406) R = Ac
(407) R = H

Selective deacetylation of 3,13-di-O-acetylgibberellic acid (**405**), 3,13-di-O-acetylgibberellin A_1 (**406**), and 13-O-acetyl isogibberellic acid (**407**) with $HgCl_2$ in Soerensen phosphate buffer (pH 8.0) gave 3-O-acetylgibberellic acid (**408**), 3-O-acetylgibberellin A_1 (**409**), and isogibberellic acid (**399**), respectively.[172]

The oxidation of gibberellic acid (**410**) with neutral manganese dioxide involves the



(410) R^1=α-H,β-OH; R^2=H
(411) R^1=O ; R^2=H
(412) R^1=α-H,β-OH ; R^2=Me



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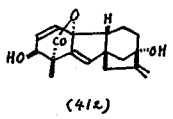
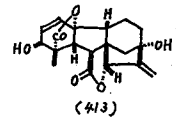
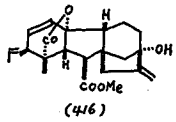


(412)



(413)



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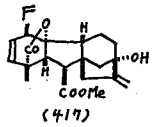
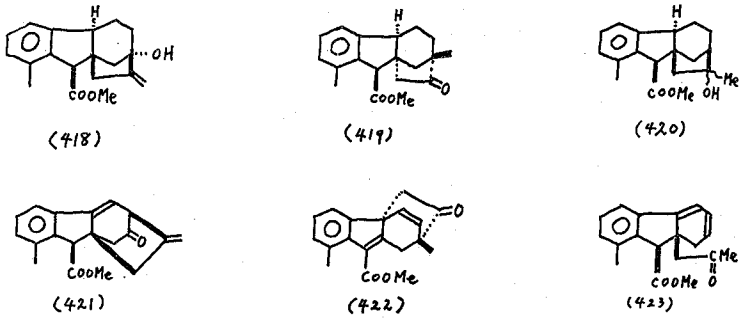


(417)

free carboxylic group and gives rise to three anomalous products which correspond to oxidative decarbonylation (**411**, **412**) or lactonization (**413**). Optimal condition for a normal allylic oxidation of **410** have been found using alkaline MnO_2 in acetone which gives yields of keto acid (**414**) up to 56%.[173]

The preparation of two fluorogibberellins (**416** and **417**) from methyl gibberellate (**415**) by treatment with diethyl(2-chloro-1,1,2-trifluoroethyl)amine was reported.[174]

A full paper on rearrangements between the rings C and D during reactions with DDQ was published. The materials used were gibberellin-type compounds in which ring A was aromatic. Thus **418**, **419**, and **420** produced **421**, **422**, and **423**, respectively.[175]



A total synthesis of racemic epiallogibberic acid (**403**) was accomplished.[176,177] A key intermediate (**426**) was synthesized from **424** *via* forming a covalent magnesium alkoxide (**425**) by an intramolecular aldol condensation.[178] The outline is shown in Chart 11.

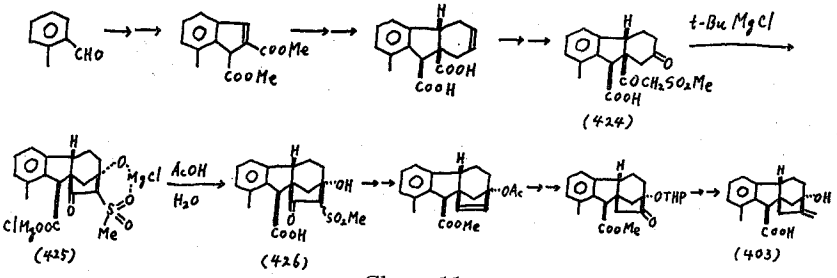
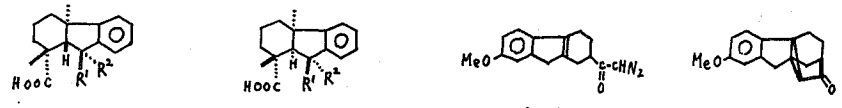


Chart 11

Among four stereoisomers (**427**, **428**, **429**, and **430**) of hydrofluorene derivatives recently derived from pine rosin, only **427** has a strong sweetness, and others have no taste.[179] Correlation between its sweetness and structure was studied. The improved method for its synthesis was also examined.[180]



Decomposition of some $\gamma\delta$-unsaturated α-diazomethyl ketones (*e.g.* **431**) which had been published[181,182] resulted in a significant increase in the yields of the corresponding intramolecular keto-carbenoid addition products (*e.g.* **432**), when an "activated CuO catalyst" under irradiation with a tungusten lamp was used. The substituents effect in controlling the stereoselectivity in the catalytic hydrogenation of the double bond between C–9 and C–11 in the gibberellane derivatives was also evaluated.[183]

Synthetic methodology for effecting the conversion of **433** to **434** was demonstrated by a stereospecific synthesis of the model system **436**. The key step in this sequence is the internal Diels-Alder cyclization of **435**. The outline is shown in Chart 12.[184]

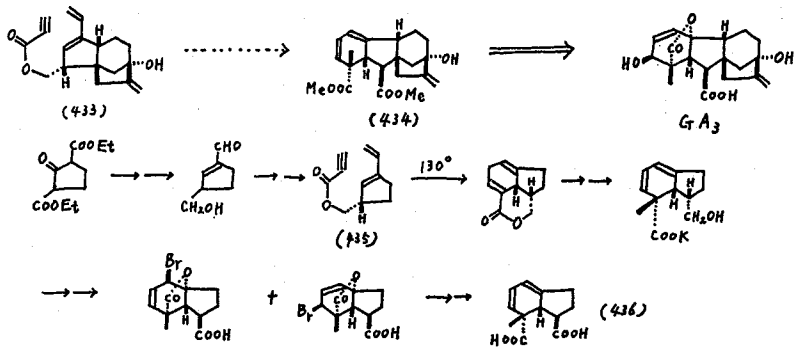
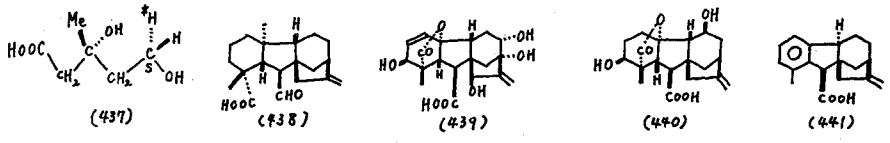


Chart 12

A mutant R–9 of *Gibberella fujikuroi* has been isolated and shown to be blocked for GA_1 and GA_3 biosynthesis, but not for GA_4, GA_7 and other gibberellins. Cultures of this mutant convert low concentrations of [1,2-$^3H_2$]-GA_1 into GA_3 in a radiochemical yield of 2.7%.[185]

Incorporation of four 5-pro-S mevalonoid hydrogen atoms into gibberellic acid (**410**) and location of two of these at C–6 and C–14 respectively has been shown by tritium labelling. The exo-15-H of methyl gibberate (**419**) has been shown to exchange more rapidly than the endo-H and this has been used to demonstrate that the β-exo hydrogen at C_{14} of **410** is derived from a 5-pro-S (*H in **437**) of mevalonic acid.[186]



Gibberellic acid and GA_7 were identified in extracts of germinating barley as their ^{14}C-Methyl esters. Germinating barley incorporated 2-^{14}C-mevalonic acid into several terpenes, but incorporation into GA_3 and the gibberellin intermediate *ent*-kaurene could not be detected.[187]

Interconversions of GA_5 to GA_3 in seedling of dwarf *Pisum sativum*[188] and of GA_1 to GA_8 in seedling of dwarf *Oryza sativa*[189] were shown by tritium labelling. Identifications of GA_3 and GA_8 were made by gas-liquid radiochromatography using three stationary phases.

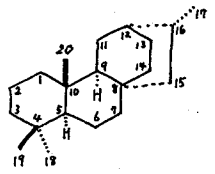
3-Hydroxylation of GA_{12}-aldehyde (**438**) in *Gibberella fujikuroi* strain REC-193A was studied, and the results showed that 3-hydroxylation was the first step in the conversion of gibberellin A_{12}-aldehyde into gibberellins A_{14}, A_4, and A_7.[190]

The plant growth-promoting activities of new gibberellins, GA_{30} (**393**), GA_{31} (**394**), GA_{32} (**439**), GA_{33} (**395**), GA_{34} (**396**), GA_{35} (**440**), and GA_{35} glucoside were evaluated in seven bioassays. In general GA_{30} (**393**), GA_{31} (**394**), and GA_{35} (**440**) showed fairly high biological activities, whilst GA_{33} (**395**), GA_{34} (**396**), and GA_{35} (**440**) glucoside were almost inactive. GA_{32} (**439**) was highly active, behaving similarly to GA_3 (**410**).[191]

Allogibberic acid (**402**) was identified as the compound responsible for the inhibition of flowering in *Lemna perpusilla*. 13-Deoxyallogibberic acid (**441**), a product of autoclaving aqueous GA_7 solutions, also inhibited flowering and was about 10 times more active than allogibberic acid.[192]

The mutant Bl-41a (a UV-induced mutant) of *Gibberella fujikuroi* was shown to be blocked for gibberellin biosynthesis at the step between *ent*-kaurenal and *ent*-kaurenoic acid. Steps beyond the block were examined by feeding, to the mutant, substrates which occurred beyond this point in the parent strain GF-1a.[193]

XII. ATISANE DERIVLTIVES

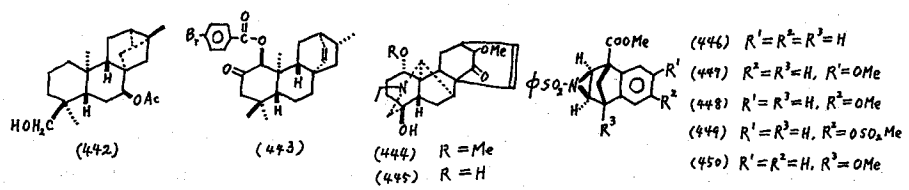


Atisane

A new diterpene *ent*-7α-acetoxy-13α,16-cycloatisan-18-ol (**442**) was isolated from *Sideritis canariensis*.[31]

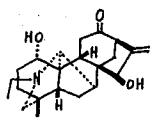
The molecular structure of *ent*-1α-*p*-bromobenzoyloxy-16S-atis-13-en-2-one (**443**) was determined by X-ray crystallographic analysis.[194]

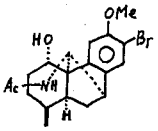
Some chemical reactions and the mass spectral fragmentations of anhydrodemethanollappaconine (**444**) and anhydrodemethanollappaconidine (**445**) and their derivatives were investigated.[195]



A general synthesis and a rearrangement control of various substituted benzobicycloheptane aziridines (**446**～**450**) was published. In this report, it was shown that the rearrangements may be used as a convenient approach to the synthesis of ring B bridged diterpene alkaloid.[196]

In the light of a possible synthesis of the alkaloid songorine (**451**), prior attempts to look for potential intermediates resulted in the synthesis of compound **452**. As the stereochemistry of **452** could not be fully established from spectroscopic data, an X-ray structure analysis was undertaken and established as shown to be **452**.[197]


(451)


(452)

A simple conversion of the tricyclic ester **453**[196] into the pentacyclic songorine intermediate **454** was reported. The process was stereospecific and it operated in an overall yield of 7.8%. The outline of the synthetic route is shown in Chart 13.[198]

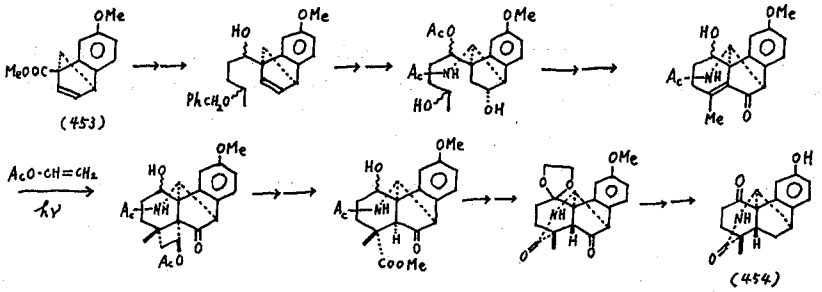
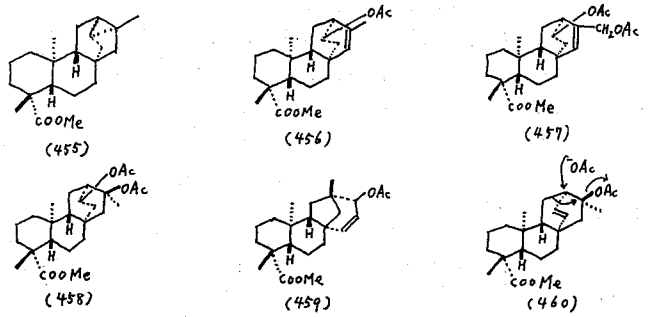

(453) (454)

Chart 13

Reaction of methyl *ent*-13α,16-cycloatisan-19-oate (**455**) with thallic acetate gave four major products including the *ent*-atisane derivatives, **456**～**458**. The fourth compound, **459**, may be derived from an *ent*-atisane intermediate like **460** by contraction of ring D.[199]


(455) (456) (457) (458) (459) (460)

A total synthesis of *dl*-trachylobane (**461**) was carried out as shown in Chart 14.[200]

A convenient and efficient method for the construction of the tricyclo[3.2.1.0]octane system, involving a homoallylic cyclization as shown in Chart 15, was reported.[201]

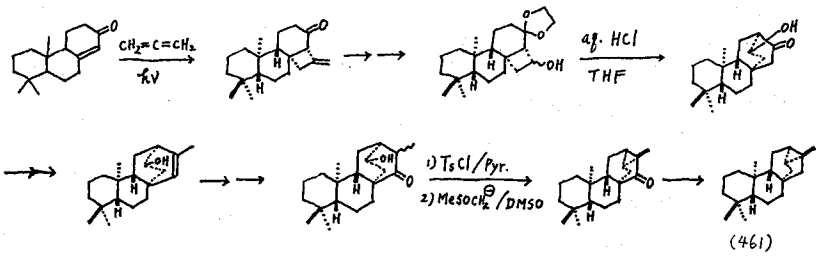


Chart 14

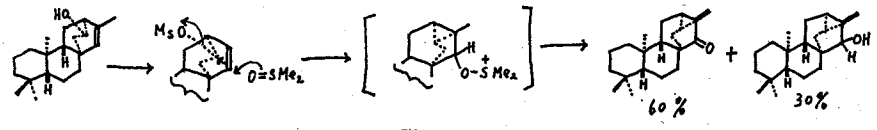
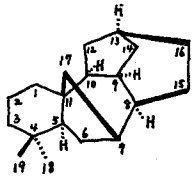


Chart 15

The hydride induced conversion of an *ent*-beyer-15-ene-12-*p*-tosylhydrazone into the novel *ent*-16S-atis-13-ene system was described.[165] (See section X, beyerane derivatives.)

XIII. ACONANE DERIVATIVES

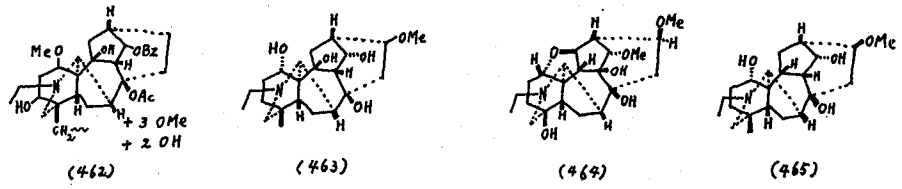


Aconane

From *Aconitum kalakolicum,* two alkaloids, aconifine (**462**) and karakolidine (**463**) were isolated.[202]

The structure **464** was proposed for an alkaloid excelsine isolated from the root of *Aconitum excelsum* on the basis of chemical and spectroscopic data.[203]

Karacoline, isolated from tubers of *Aconitum karacolicum,* was shown to have structure **465**, as determined by spectral and chemical data.[204]

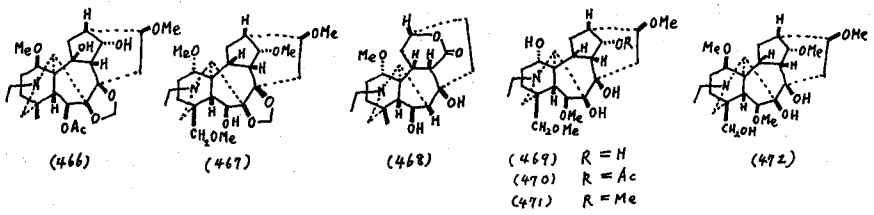


The structure of dictyocarpine, isolated from *Delphinium dictyocarpum,* was determined as **466** by NMR spectral data.[205]

The structure of delcorine (**467**), isolated from the above ground parts of *Delphinium*

corumbosum, was determined by IR, NMR, and mass spectroscopy, and chemical transformations.[206]

Chemical and spectroscopic studies have shown that heteratisine, a diterpene lactone alkaloid occurring as a monobenzoyl ester in the roots of *Aconitum heterophyllum, has* stereostructure **468**.[207] has



(466) (467) (468) (469) R = H (470) R = Ac (471) R = Me (472)

Delcosine (**469**), acetyldelcosine (**470**), and delsoline (**471**) were isolated from *Delphinium ajacis* seeds and were analyzed by mass spectrometry.[208]

The carbon-13 magnetic resonance spectra of the diterpenoid alkaloids *e.g.* lycoctonine (**472**), have been determined at 22.63 MHz in the Fourie mode.[209]

Chemical conversion of levopimaric acid (**206**) into a secoaconane derivative **209** is described in Section VI.[108]

The construction of the substituted C/D ring system of delphinine-type alkaloids was published. The route is shown in Chart 16.[210]

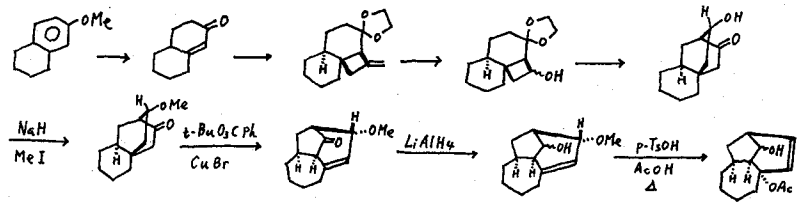
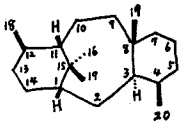


Chart 16

XIV. TAXANE DERIVATIVES



Taxane

No reports were published in this year.

XV. THE OTHERS

Pachydictyol A, an exceptional diterpene alcohol was isolated from the brown algal, *Pachydictyon coriaceum*, and the structure of this marine natural product was determined as **473** on the basis of the X-ray analysis of its *p*-bromophenylurethane derivative. It

showed a mild antibiotic activity against *Staphylococcus aureus*. A possible biosynthetic route of this substance was suggested as shown in Chart 17.[211]

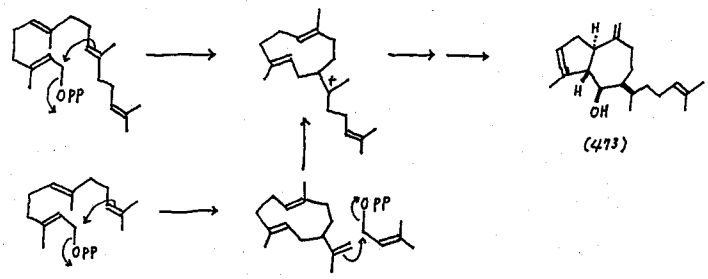
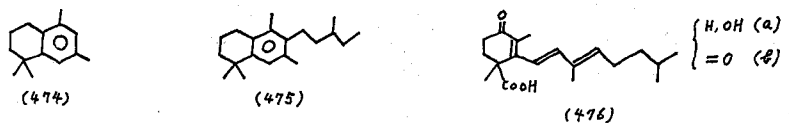


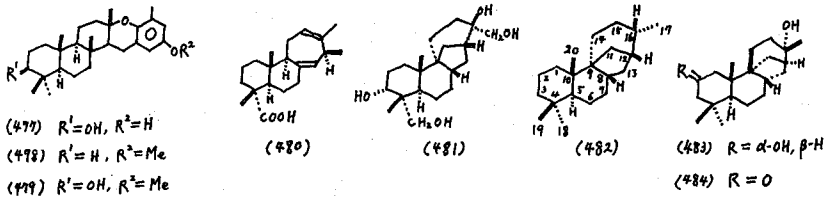
Chart 17

1,2,3,4-Tetrahydro-1,1,5,7-tetramethyl-6-(3-methylpenyl)naphthalene (**475**) was synthesized from tetrahydro-tetramethylnaphthalene **474**, and its identity with Ruzicka's hydrocarbon (acid-catalyzed dehydration product of sclareol) was confirmed.[212]



A "metabolic grid" related to the formation of trisporic acids (**476***a*, *b*) in (+)- and (−)-mating-types of *Blakeslea trispora* was reported.[213]

The structure of taondiol (**477**), a new aromatic terpenoid compound isolated from the marine alga *Taonia atomaria* was elucidated and its biogenesis discussed. 3-Desoxy-taondiol methyl ether **478** was synthesized.[214]



Subsequently, total synthesis of *dl*-taondiol methyl ether (**479**) was reported.[215] The route is shown in Chart 18.

The full paper on the structure of strobic acid (**480**), a diterpene resin acid from *Pinus strobus*, was published.[216b] The preliminary communication had been reported in 1971.[216a]

The structure and absolute configuration of the novel tetracyclic diterpenoid aphidicolin (**481**), an antimitotic and antiviral metabolite of *Cephalosporium aphidicola* were determined. Possible biosynthetic routes to aphidicolin were also discussed.

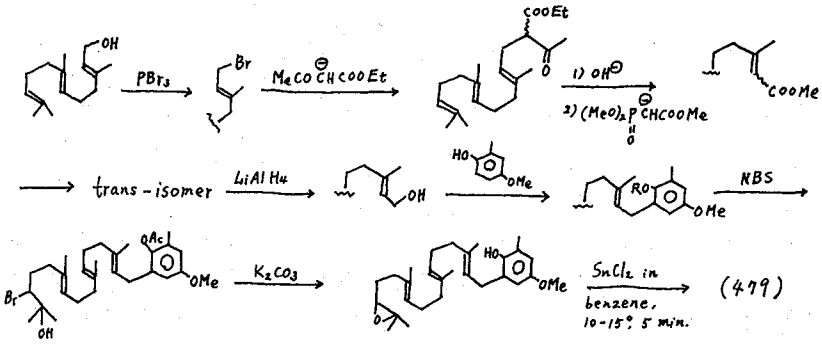
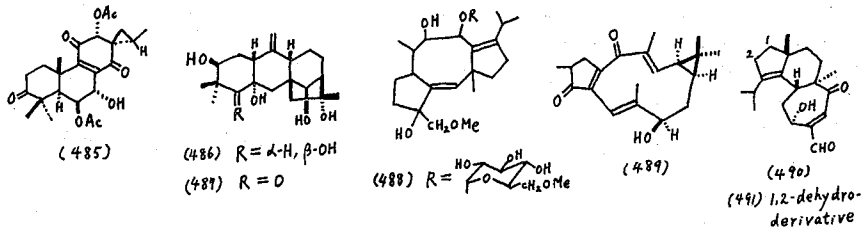


Chart 18

Aphidioclin is the first reported member of a new class of tetracyclic diterpenoids. The hypothetical parent hydrocarbon (**482**) was named aphidicolane and numbered as shown.[217]



The structures of stemodin and stemodinone, leaf constituents of *Stemoda maritima* obtained from the Palisadoes peninsula of Jamaica, were determined as **483** and **484**, respectively, on the basis of a single-crystal X-ray analysis of stemodinone.[218]

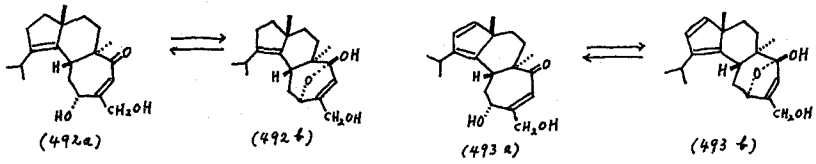
Barbatusin was isolated from the leaves of *Coleus barbathus* and its molecular structure **485** was established by X-ray and spectrochemical investigations.[219]

Two novel diterpenoids, leucothol B and D, were isolated from the leaves of *Leucothoe grayana*. Chemical and spectroscopic investigations showed that leucothol B and D had structures **486** and **487**, respectively.[220]

A new diterpene glycoside cotylenin E (**488**) was isolated from the culture filtrate of a fungal strain 501–7W.[221]

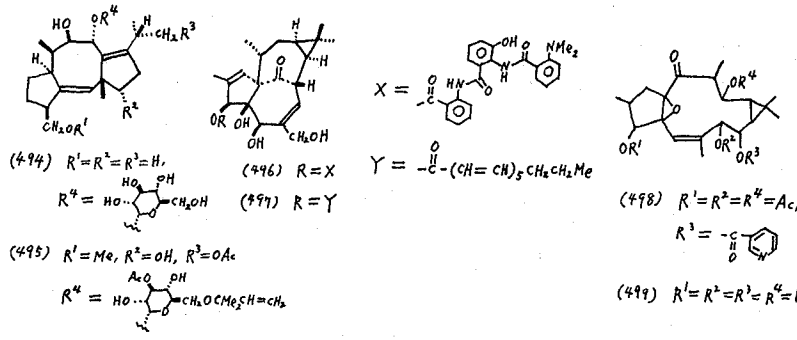
The structure and relative stereochemistry of bertyadionol (**489**), a member of a new class of diterpenes, were elucidated by chemical and physical methods. It was isolated from an ethereal solution of the neutral residues of *Bertya cuppressoidea*.[222]

Cyathin B_3, a metabolite of the bird's nest fungus *Cyathus helenae,* was shown to possess structure **490**. Cyathin C_3 was shown to be 1,2-dehydrocyathin B_3 (**491**).[223] Cyathin B_3 was correlated with cyathin A_3 and cyathin C_3 with allocyathin B_3, and cyathin A_3 and allocyathin B_3 were assigned structures **492** and **493**, respectively.[224] In the solid state cyathin A_3 exists in the hemiketal form **492b**, while allocyathin B_3 is in the hydroxy-ketone form **493a**.



(492a) (492b) (493a) (493b)

The structure (**494**) of fuscicoccin H, a minor phytotoxic glycoside produced by *Fusicoccum amygdali* was determined by degradative studies and by chemical correlation with the known fusicoccin series. Feeding experiments showed that fusicoccin H can act as a precursor of fusicoccin (**495**). This strongly suggested that fuscioccin is a diterpenoid and not a degraded sesterterpenoid.[225]



(494) $R^1=R^2=R^3=H$, $R^4=$ HO, OH, CH_2OH

(495) $R^1=Me$, $R^2=OH$, $R^3=OAc$, $R^4=$ AcO, OH, $CH_2OCMe_2CH=CH_2$

(496) R=X (497) R=Y

X = OH, O, NMe_2, HN, O

Y = O, $-C-(CH=CH)_5CH_2CH_2Me$

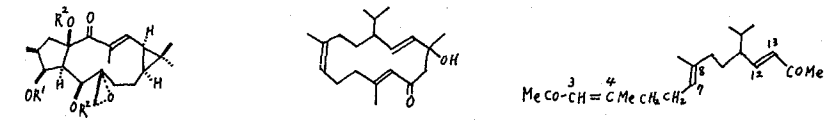
(498) $R^1=R^2=R^4=Ac$, $R^3=-C(=O)-$ pyridyl

(499) $R^1=R^2=R^3=R^4=H$

The isolation and structure elucidation of irritant substances milliamine C (**496**), obtained from *Euphorbia millii*, and ingenol 2,4,6,8,10-tetradecapentaenoate (**497**) from *E. jolkini* were reported.[226]

A derivative (**498**) of a new macrocyclic diterpene alcohol which was named ingol (**499**) was isolated from acetone soluble compounds of the latex of *Euphorbia ingens*.[227]

Isolation of phenylacetate diacetate (**500**) of epoxylathyrol (**501**) whose structure had been determined,[228] from Caper-squrge seed (*Lathyridis* seed) was reported.[229]



(500) $R^1=COCH_2C_6H_5$, $R^2=Ac$

(501) $R^1=R^2=H$

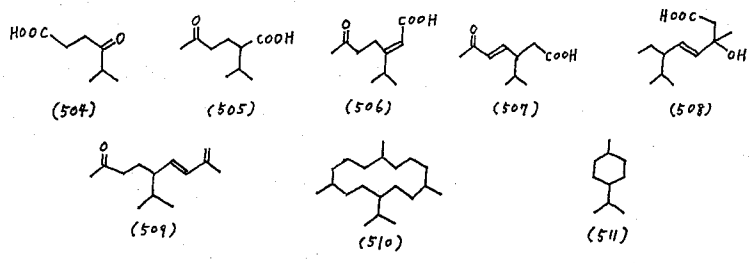
(502)

(503) $Me\,CO\text{-}CH=C(Me)\,CH_2CH_2$, 12, 13, COMe

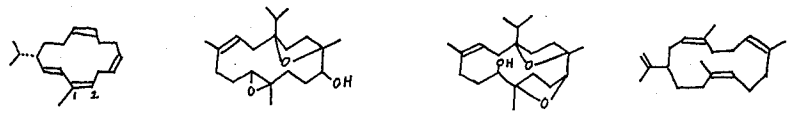
Isolation, for the first time from a natural source, of three compounds which were produced in the tobacco leaf during a natural fermentation process was reported. These compounds are 4,8,13-duvatrien-1-ol-3-one (**502**) and 11-isopropyl-4,8-dimethyl-3,7,12-pentadecatriene-2,14-dione (**503**). The latter was obtained in two stereo forms, as isomers-A (3,4-*cis*-double bond) and -B (3,4-*trans*-double bond).[230]

Structures of two new diterpenoids, cembrene-A and mukulol were discussed.[231] Cembrene-A is one of the two most elementary tetraenes derivable from geranyl-geranyl pyrophosphate by C-1 to C-14 cyclization. Mukulol is also a cembrane derivative and is biogenetically closely to cembrene-A.

The volatile acids of sun-cured Greek tobacco were studied.[232] Examination of this material by GC-MS supplemented by other spectroscopic methods and in some instances by synthesis, permitted the identification of nearly a hundred compounds. About half of them have not yet been encountered previously in tobacco or tobacco smoke, and the majority of the new compounds were straight and branched-chain unsaturated acids and aromatic acids. Five of the oxygenated acids were evidently seco- or nor- terpenoids. These acids, namely 5-methyl-4-oxohexanoic (**504**), 2S-isopropyl-5-oxo-hexanoic (**505**), 3-isopropyl-6-oxo-2E-heptenoic (**506**), 3 ζ-isoprophyl-6-oxo-4E-heptenoic (**507**) and 3ζ-hydroxy-3ζ-methyl-6ζ-isopropyl-4E-octenoic acid (**508**), like many other tobacco constituents such as solanone (**509**), solanol, and norsolanadione, may be regarded as nor-derivatives of diterpenoids possessing the thunbergane skeleton (**510**). Although this view is strengthened by the presence of a number of such macrocyclic diterpenoids in tobacco, it should be noted that four of them, **504**, **505**, **506**, and **507** may equally well be viewed as nor or seco-monoterpenoids of the *p*-mentahane series (**511**).



Oleoresins from most species of the genus *Larix* were analyzed[24] by GLC for their diterpene composition, and in some species thunbergene (**512**) and thunbergol (**513**) were recognized. Common to all are the abietadiene and isopimaradiene acids usual in Pinaceae with the corresponding aldehydes and alcohols in small amounts. Epimanool also occurred in all, but larixol and its acetate was confined to *L. decidua* and *L. gmelini*, and epitorulosol to the remainder. In the hybrid *L. Xeurolepis* both of these last two compounds were present.

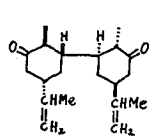


Reinvestigation led to revision of the structure **514** assigned[233a] previously to isoincensole-oxide from Frankincense resin to **515**.[233b]

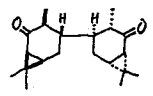
In a review of "Recent Results in Insect Pheromone Chemistry",[234a] nasutene is described as follows: "Stuart showed that *Nasutitermes* termites mark a trail with substance deposited from the sternal glad. More subsequently isolated from extracts of whole *N. exitiosus* termites a trail-active fraction. The molecule was characterized as a diterpene hydrocarbon, $C_{20}H_{32}$, with four double bonds and one ring. On the basis of UV and

NMR spectra and of microozonolysis experiments, this substance (nasutene) has been tentatively assigned structure **516**.[234b] The cembrane skeleton was confirmed by comparison of perhydrocembrene with perhydronasutene, which proved identical. The precise location and stereochemistry of the double bond are not certain. This substance also elicited trail-following in *N. walkeri* and *N. graveolus*. It remains to be seen if this substance originates in the sternal gland."

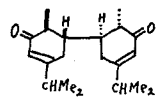
The structures of α-, β-, and γ-dicarvelone prepared by Wallach in 1899 and 1914 (Wallach's dicarvelones) were determined as **517**, **518**, and **519**, respectively, according to their IR and NMR spectra and ORD curves.[235]



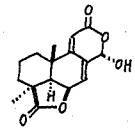
(517)



(518)



(519)



(520)

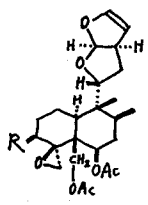
Biosyntheses of a C_{16}-terpenoid lactone **520** from [2-^{13}C]acetic acid and [2-^{14}C, 5-$^{3}H_2$] mevalonic acid showed that this lactone, a plant growth regulater, was derived from a diterpenoid precursor.[236]

A short review on prenyltransferase was published in Japanese.[237] A series of reviews about diterpenoids was published also in Japanese.[238]

Isolation of a new diterpene base from *Aconitum pubiceps* was reported,[239] but the details are not known.

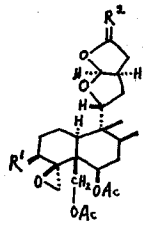
Addendum to IV. CLERODANE DERIVATIVES

The isolation and structural elucidation of caryoptin (**521**), dihydrocaryoptin (**522**) and caryoptin hemiacetal (**523**), three new insect antifeeding diterpenoids from *Caryopteris divaricata,* were reported. In addition, clerodin (**524**), clerodin hemiacetal (**525**), previously isolated from *Clerodendron infortunatum,* and dihydroclerodin-I (**526**) were also isolated.[240]



(521) R = OAc

(524) R = H



(522) R' = OAc, R² = H₂

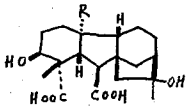
(523) R' = OAc, R² = H, OH

(525) R' = H, R² = H, OH

(526) R' = H, R² = H₂

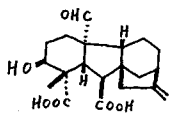
Addendum to XI. GIBBERELLANE DERIVATIVES

New gibberellins, that is, A_{41} (**527**) and A_{42} (**528**) were isolated from the culture filtrates of *Gibberella fujikuroi*, strain TP 70. Gibberellins A_{16}, A_{36}, and A_{37} were also isolated. The structure **529** ⇄ **530** was deduced for gibberellin A_{36} from spectroscopic data and confirmed by chemical conversion with gibberellin A_{13}.[241]

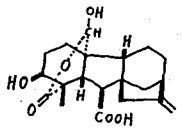


(527) R = COOH

(528) R = Me



(529)



(530)

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