Bull. Inst. Chem. Res., Kyoto Univ., Vol. 52, No. 3, 1974

Review

The Chemistry on Diterpenoids in 1971

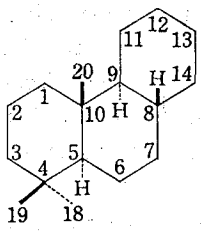
Eiichi FUJITA*

Received May 7, 1974

I. INTRODUCTION

This is one of a series of annual reviews[1~7] on diterpenoids chemistry by the author. In principle, in each section the full papers were first described and the short communications followed. The order of the journals followed the alphabet of their names.

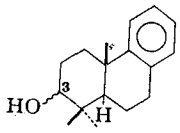
II. PODOCARPANE DERIVATIVES**



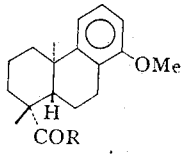
Podocarpane

Oxidiative cyclization of 4,8-dimethyl-1-phenyl-3,7-nonadiene with benzoyl peroxide was tried. From the *trans*-3-ene, podocarpane derivatives **1** (18%) and **2** (2~3%) were formed, while the *cis*-isomer gave only very low yield (3%) of **1**.[8]

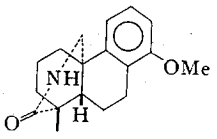
Racemic acid **3** was converted into azide **4**, which, without purification, was irradiated with a high-pressure



1: 3β-OH
2: 3α-OH



3: R=OH
4: R=N_3



5

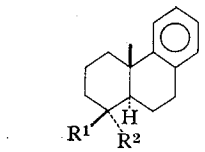
mercury lamp to give a δ-lactam **5**.[9] Since this lactam had been converted into the *Garrya* alkaloids, this completed another formal total synthesis of garryine, veatchine, and atisine.

Deisopropyldehydroabietane derivatives and related substances, **6**–**11**, were synthesized and their UV spectra and ORD curves were analyzed.[10]

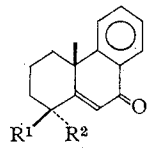
Lithium in liquid ammonia reduction of ester **12** and hydroxy acid **13** with concomitant decarboxylation provided a good route to moderate yields of the α,β-unsaturated ketones, **14** and **15**. The ketone **15** was also prepared in improved yield by another method.[11]

* 藤田栄一: Laboratory of Physiological Activity, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

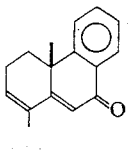
** See also ref. 108 (Section IX).



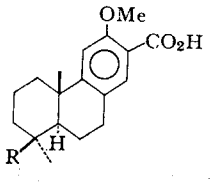
6: R^1=H, R^2=Me
7: R^1=Me, R^2=H



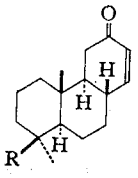
8: R^1=H, R^2=Me
9: R^1=Me, R^2=H
10: R^1=R^2=Me



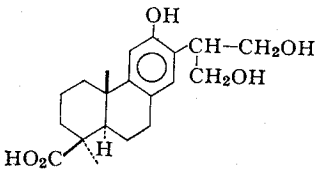
11



12: R=CO_2Me
13: R=CH_2OH



14: R=CO_2H
15: R=CH_2OAc

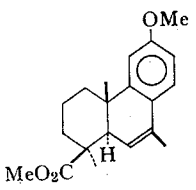


16

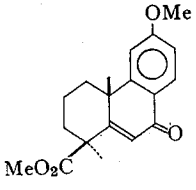
The reactions of boron trifluoride and dimethyl sulfoxide on ring-A epoxy derivatives of 18-norabieta-8,11,13-triene and 12-methoxy-18-norpodocarpa-8,11,13-triene were carried out, and the mode of formation of the products were discussed.[12] The stereochemistry of 6-bromo-7-oxo derivatives of diterpenoids possessing an aromatic ring C was discussed. The assignment of configuration of 6-bromo substituents from NMR and NOE data was examined and limitations to the use of the ORD curves were discussed.[13]

The structure of pododacric acid, a trihydroxy diterpenoid acid obtained from New Zealand *Podocarpus* species, was determined as **16** and confirmed by partial synthesis from podocarpic acid.[14]

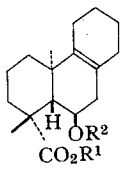
The dichromate oxidation of **17** to **18** was reported, and the mechanism pathway of the oxidation was provided.[15]



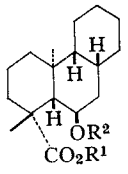
17



18



19: R^1=R^2=H
20: R^1=Me, R^2=Ac

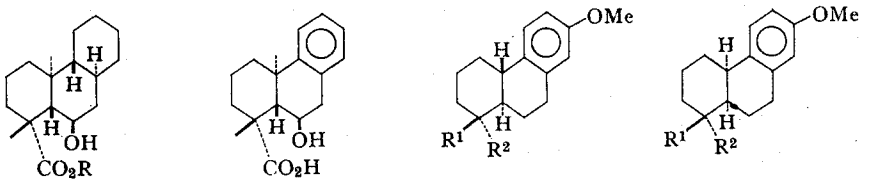


21: R^1=R^2=H
22: R^1=Me, R^2=H
23: R^1=Me, R^2=Ac

Reduction of *ent*-6α-hydroxypodocarpa-8,11,13-trien-19-oic acid derivatives provided a route of synthesizing compounds **19** to **25**.[16] Epimerization of 6β-hydroxy group at lactonization was recognized on compounds **19** and **21** as experienced about **26**, but not on **24**.[17]

All four possible racemates of 1-carboxy-1-methyl-7-methoxy-1,2,3,4,9,10,11,12-octahydrophenanthrenes, **27**–**30**, were synthesized.[18]

Compounds **31** and **32** were synthesized and their solvolytic rearrangement was investigated. Products arising from acetolysis of **31** and **32** and their yields are shown in Scheme 1.[19]

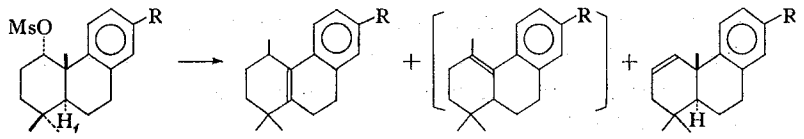


24: R=H
25: R=Me

26

27: R^1=CO_2H, R^2=H
28: R^1=H, R^2=CO_2H

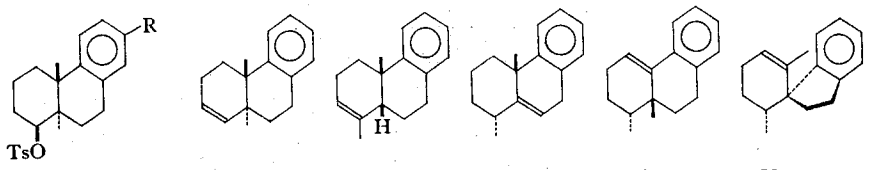
29: R^1=CO_2H, R^2=H
30: R^1=H, R_2=CO_2H



31: R=H ⟶ 80% 17% 3%
32: R=OMe ⟶ 88% 9% 3%

Scheme 1

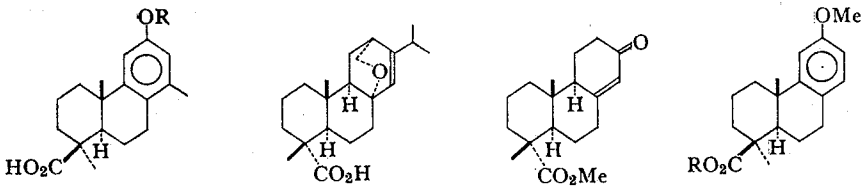
Buffered solvolysis of **33a** afforded the unrearranged olefin **34**, the singly backbone rearranged olefins, **35** and **36**, the doubly backbone rearranged olefin **37**, and aryl migrated olefin **38**. Similar products were obtained from solvolysis of **33b**.[20]



33a: R=H
33b: R=OMe

34 **35** **36** **37** **38**

Racemic 14-methylpodocarpic acid (**39**) and O-methyl-14-methylpodocarpic acid (**40**) were synthesized.[21]



39: R=H
40: R=Me

41

42

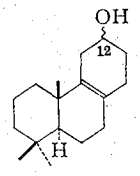
43: R=Me
44: R=H

Phenols of the podocarpic acid series were oxidized in ring B at room temperature with 2,3-dichloro-5,6-dicyanobenzoquinone in alcoholic solvents. Two equivalents of the quinone yielded mainly the corresponding 7-ketones, while the use of three equivalents provided a convenient one-step synthesis of the 5,6-dehydro-7-ketones.[22]

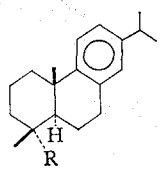
Levopimaric acid-formaldehyde adduct **41** was converted into methyl podocarp-8 (14)-en-13-on-18-oate (**42**) *via* five steps.[23]

Cleavage of sterically hindered esters, *e.g.* methyl O-methylpodocarpate (**43**), was achieved by the use of boron trichloride to yield 90% of O-methyl podocarpic acid (**44**).[24]

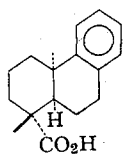
The conformation of ring C in alcohols **45** and **46** was investigated by NMR, and they



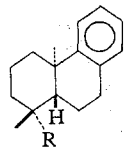
45: 12β-OH
46: 12α-OH



47: R=CO_2N
48: R=CN



49

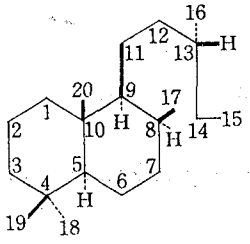


50: R=CO_2Me
51: R=CN

were shown to have the preferred half-chair conformation in ring C. This conformation was exactly analogous to that preferred in ring A of the 5(10)-estrene series. The close correspondence of molecular rotation differences between these two series provided further support for these conclusions.[25]

Transformations of the diterpene A/B ring juncture to the antipodal system were carried out starting from **47** and **48**. Acid **47** was converted into A/B *cis* product **49** by reverse Friedel-Crafts reaction, and methyl ester of **49** was subjected to isomerization into **50** by treatment with 10% palladium-carbon in refluxing triglyme for 3 hours. Ester **50** was converted into methyl *ent*-podocarpate. Similarly, nitril **48** was transformed into **51**.[26]

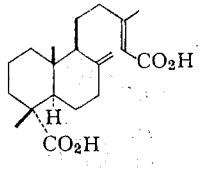
III. LABDANE DERIVATIVES*



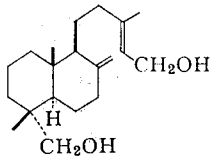
Labdane

A diterpene acid, dehydropinifolic acid, was isolated from the needles of *Pinus silvestris* and shown to have structure **52**.[27] The labdane diterpenes, 4-epiagathadiol (rayadiol) (**53**), 18-hydroxymanool (torreferol) (**54**), and 18-hydroxy-13-epimanool (13-epitorreferol) (**55**) were isolated from the non-steam volatile fraction of the leaves of *Torreya nucifera*.[28]

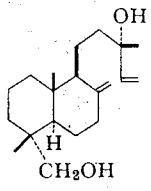
Copalic acid (**56**), *ent*-3-hydroxylabda-8(20),13-dien-



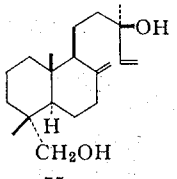
52



53



54

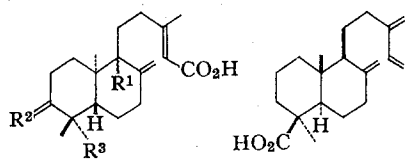


55

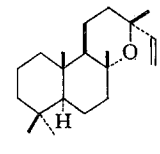
15-oic acid (**57**), and *ent*-agathic acid (**58**) were isolated from *Copaiba* oil. Their structures were determined by their spectroscopic data and those of their derivatives and by comparison with their known derivatives.[29]

A new diterpenoid acid, labda-8(17), 13(16), 14-trien-19-oic acid (**59**) was isolated from the oleoresin of *Callitris columellaris*. The known diterpenoids were also isolated.[30] The structures of fourteen products derived from the selenium dehydrogenation of manool (**72**) were determined.[31]

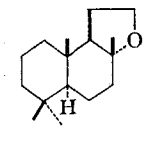
* See also section V (ref. 63).



56: $R^1=\beta$-H, $R^2=H_2$, $R^3=Me$ **59**
57: $R^1=\beta$-H, $R^2=H$, OH, $R^3=Me$
58: $R^1=\beta$-H, $R^2=H_2$, $R^3=CO_2H$

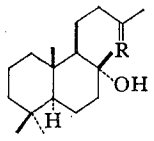


60

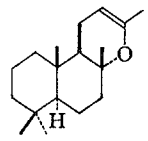


61

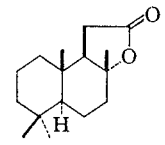
Manoyl oxide (**60**) was converted into the known five-membered oxide **61** with an ambergris-type odor, *via* intermediates **62–66**. The oxide **61** was also prepared from manoyl oxide in two steps by oxidation with chromic anhydride followed by reduction of the lactone **65** with diborane.[32]



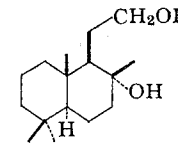
62: R=CHMe
63: R=O



64

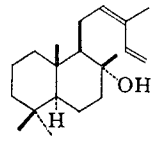


65

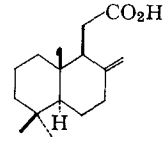


66

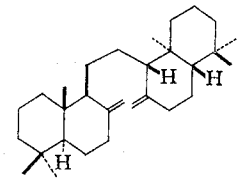
A synthesis of α-onoceradiene (**69**) from abienol (**67**) was reported *via* the Kolbe electrolysis of the key intermediate **68**. The observed molecular rotation did not fit the predicted value.[33]



67

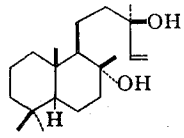


68

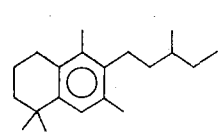


69

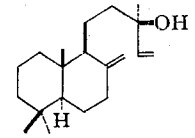
Structure **71** was assigned[34] to the hydrocarbon first prepared by Ruzicka[35] through the high temperature acid-catalyzed dehydration of sclareol (**70**).



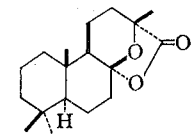
70



71



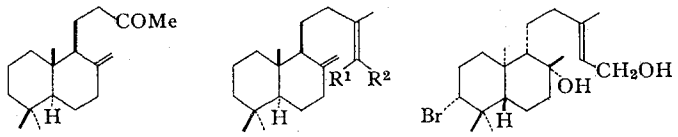
72



73

Some products from the oxidation of manool (**72**) were examined. Potassium permanganate gave, *inter alia*, the hitherto unreported compound **73**, while sodium dichromate gave the methyl ketone **74**, and, as the major product, a mixture of (Z)- and (E)-α,β-unsaturated aldehyde **75**. Some oxidations of **74** were examined.[36]

The selenium dehydrogenation of agathic acid (antipode of **58**) was carried out, and a consistent scheme from dehydrogenation of intermediates was proposed. The dehydro-

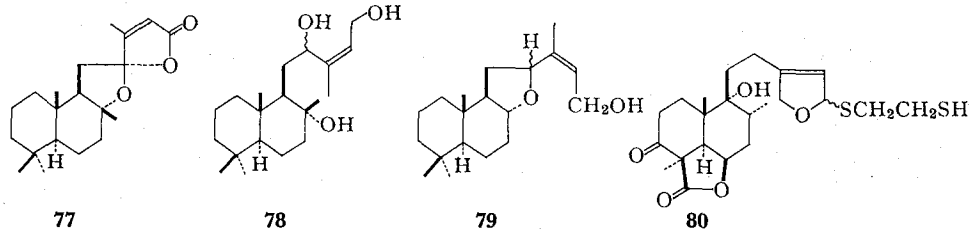


74 **75**: (R^1=CHO, R^2=H) +(R^1=H, R^2=CHO) **76**

genation of methyl sandaracopimarate was also examined.[37]

Two bromo-compounds, aplysin and aplysinol, had been isolated and characterized. The third minor bromo-compound, aplysin 20, had also been isolated from *Aplysia kurodai*.[38] The structure of aplysin 20 was determined by X-ray analysis as **76**.[39]

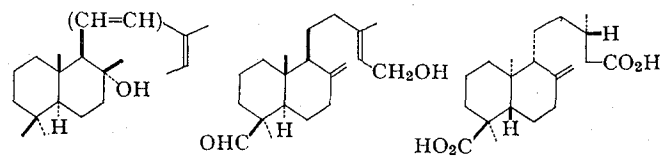
Triol **78** derived from α-levantenolide (**77**) by treatment with lithium aluminum hydride was cyclized to compound **79** by treatment with stannic chloride.[40]



77 **78** **79** **80**

3-Ketomarrubiin was treated with ethane-1,2-dithiol in the presence of boron trifluoride etherate to yield a 2,5-dihydro-2-(2-mercaptoethylthio)-furan derivative (**80**).[41]

Diterpenoids from the oleoresin of *Pinus koraiensis* were separated by column chromatography. As the labdane derivatives, neoabienol (**81**) and isoagatholal (**82**) were isolated. The trisubstituted double bond in neoabienol was shown to have the Z-configuration.[42]

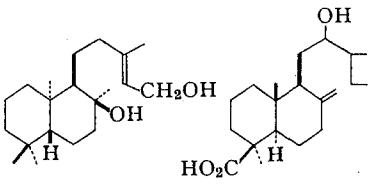


81 **82** **83**

From the oleoresin of *Copaifera langsdorfii, ent*-8(17)-labdene-15,18-dioic acid (**83**) was isolated.[43] Anticopalic acid (antipode of **56**) was found to be a major resin acid in the bark and in the wood of *Pinus monticola*.[44] From a light petroleum extract of *Juniperus phoenicea,* manoyl oxide, diol **84**, and a new hydroxy acid **85** were isolated.[45]*

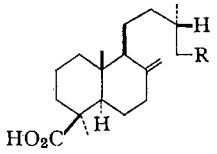
From *Cistus labdaniferus,* labdane-8α,15,19-triol was isolated.[46]** A new diterpene, imbricataloic acid (**86**) was found to be present as a major constituent in *Pinus elliottii* needles and *Cortex* oleoresin. The closely related imbricatoloic acid (**87**), previously reported only in *Araucaria imbricata,* was found in small amounts in slash pine needle extract.[47]

* See also section V.
** See also section IV.



84

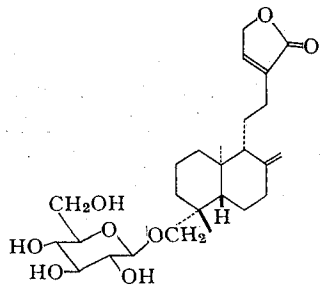
85



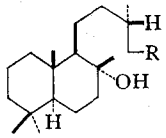
86: R=CHO
87: R=CH_2OH

The investigation on the second, minor crystalline component, neoandrographolide isolated from the shrub of *Andrographis paniculata* led to the structure and stereochemistry shown in **88**.[48]

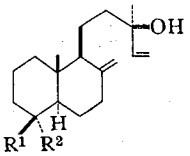
The reduction of methyl labdanolate (**89**) with lithium aluminum hydride gave labdane-8,15-diol (**90**) which with tosyl chloride in pyridine gave the monotosylate. Treatment of the monotosylate with lithium aluminum hydride gave tetrahydroabienol. Thus, the 13-R configuration of tetrahydroabienol was determined.[49]



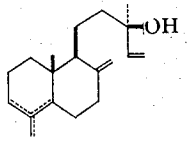
88



89: R=CO_2Me
90: R=CH_2OH



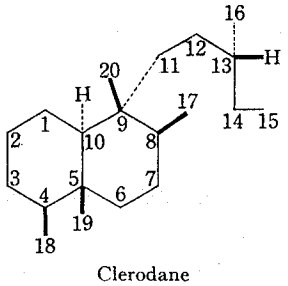
91: R^1=OH, R^2=Me
92: R^1=Me, R^2=OH
93: R^1=CHO, R^2=Me
95: R^1=OOH, R^2=Me
96: R^1=Me, R^2=OOH



94

The isolation in small amount from *Araucaria excelsa* of two new nor-diterpene diols **91** and **92** had been reported, but a pure sample of torulosal (**93**), which was among the components of the oleoresin from *A. excelsa,* kept five hours at room temperature without any solvent, when adsorbed on alumina or silica gel and then eluted with benzene yielded only 40% of starting aldehyde beside a less polar fraction containing a mixture of noralkenes **94** (9%) and a more polar fraction containing four substances. Two of them were **91** (0.6%) and **92** (5.5%). The other two were proved to be **95** (10%) and **96** (14%). Thus, these nor diterpenes may be artefacts.[50]

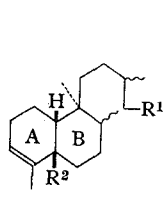
IV. CLERODANE DERIVATIVES



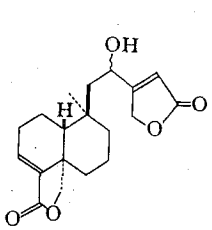
Clerodane

Cistus monspeliensis was found to contain almost exclusively compounds having the skeleton **97** with a cis-junction of A and B.[46]

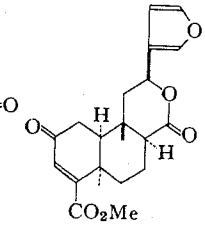
Chloroform extraction of *Olearia heterocarpa* yielded a new diterpene dilactone, olearin. On chemical and spectroscopic evidence, the structure of olerarin was elucidated. Correlation of olearin with a diterpene of the known stereochemistry defined the absolute con-



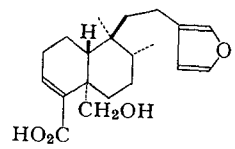
97



98



99

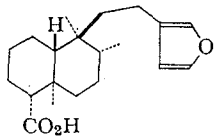


100

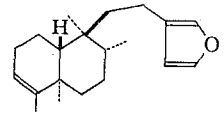
figuration at all but one center as **98**.[51]

The diterpene tinophyllone was isolated from the root and bark of *Tinomiscium philippinense*. Mainly on the basis of physical data and taking into account its occurrence in a plant of the same family (Menispermaceae) as that of *Jatrorrhiza palmata* from which columbin has been isolated, its planar structure was proposed by G. Aguilar-Santos.[52] An X-ray crystallographic examination confirmed the structure and determined its relative stereochemistry as **99**.[53]

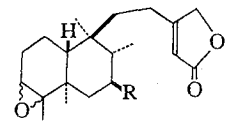
The structure of a diterpene carboxylic acid, hautriwaic acid, isolated from *Dodonea viscosa,* was confirmed as **100** by chemical and spectroscopic studies.[54] The structures of two new diterpenoids isolated from bulbs of *Annona coriacea* were established as **101** and **102**.[55] From extracts of the roots of *Solidago Shortii*, two new diterpenoids were isolated, and their structures were determined as **103** and **104**.[56]



101

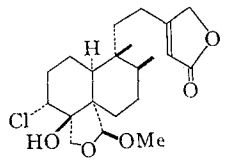


102

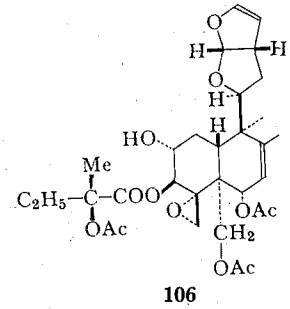


103: R=H
104: R=O-angeloyl

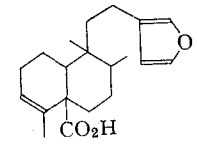
The molecular structure of the first naturally occurring chloro-diterpene, gutierolide, isolated from the alcoholic percolate of the above ground part of the annual herb, *Gutierrezia dracunculoides,* was determined as **105** by X-ray crystallographic analysis. The formula shows its absolute configuration.[57]



105



106

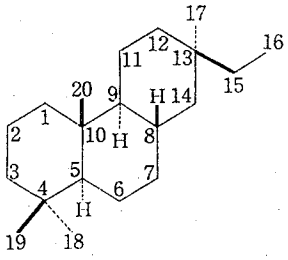


107

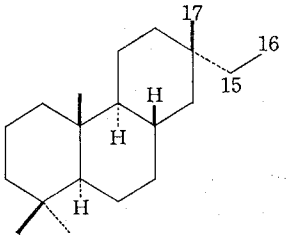
The structure of Clerodendrin A, a bitter principle of *Clerodendron tricotomum* and antifeeding repellent for the larvae of *Spodoptera littoralis,* was shown to be **106**. An X-ray analysis of the *p*-bromobenzoate chlorohydrin confirmed its structure and absolute

configuration as **106**.[58] Maingayic acid, a piscicidal constituent of *Callicarpa maingyi*, was investigated, and structure **107** was proposed.[59]

V. PIMARANE AND ISOPIMARANE DERIVATIVES

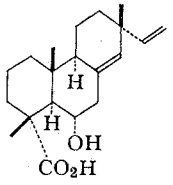


Pimarane

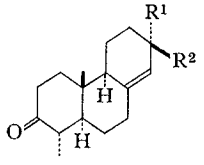


Isopimarane

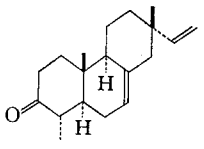
A major constituent of a light petroleum extract of *Juniperus phoenicea* was sandaracopimaric acid. 6α-Hydroxysandaracopimaric acid (**108**) was also isolated.[45]



108

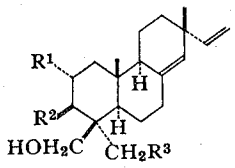


109: R^1=Me, R^2=vinyl
110: R^1=vinyl, R^2=Me

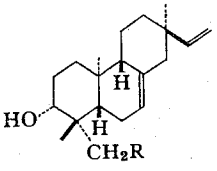


111

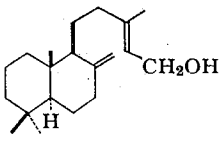
Three 19-nor-pimarane and isopimarane derivatives, **109–111**, were isolated from the light petroleum extract of the bark of *Pinus silvestris*.[60] Examination of the bark of *Dacrydium colensoi* showed the presence of the diterpenoids, sandaracopimaradien-19-ol (**112**), —3β, 19-diol (**113**), —2α, 18,19-triol (**114**), —3β, 18,19-triol (**115**), and —2α, 3β, 18,19-tetraol (**116**).[61]



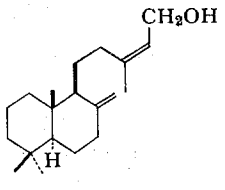
112: R^1=R^2=R^3=H
113: R^1=R^3=H, R^2=OH
114: R^1=R^3=OH, R^2=H
115: R^1=H, R^2=R^3=OH
116: R^1=R^2=R^3=OH



117: R=OH
118: R=H



119

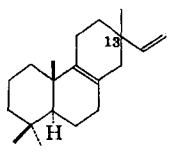


120

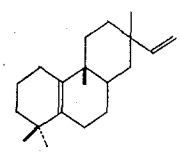
Oblongifoliol and deoxyoblongifoliol, components of *Croton oblongifolius*, were assigned the structures **117** and **118**, respectively.[62]

Manool, 13-epimanool, and the related alcohols **119** and **120** were converted by acid

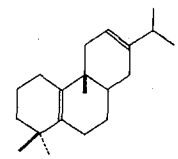
via pimaradienes **121** and **122** into rearranged pimaradienes **123** and **124**. Prolonged treatment with acid led to a rearranged abietadiene derivative **125**.[63]



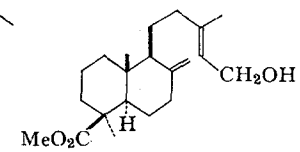
121: 13α-Me
122: 13β-Me



123: 13α-Me
124: 13β-Me

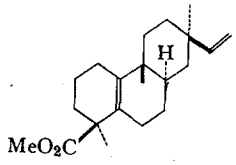


125

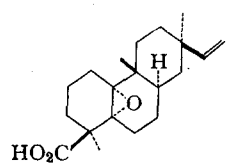


126

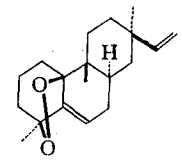
13α-Methyl compound **127** which was transformed with acid from methyl isocupressate **126** was converted *via* the epoxide **128** into the unsaturated lactone **129**, and thence into deoxyrosenonolactone (**130**) and rosenonolactone (**131**).[64]



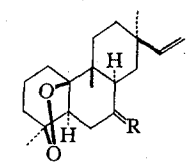
127



128

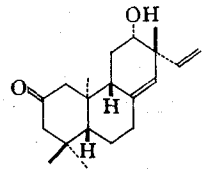


129

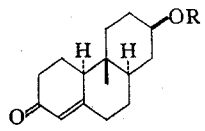


130: R=H_2
131: R=O

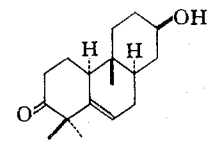
The light petroleum extract of the stems of *Macaranga tanarius* yielded in addition to several other terpenoids a new diterpene ketol, macarangonol, to which structure **132** was assigned.[65]



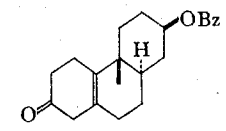
132



133: R=H
137: R=Bz



134



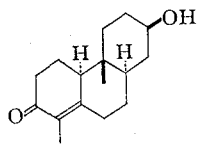
135

Ether extracts from the cones of *Cedrus atlantica* yielded sandaracopimaric and isopimaric acid. Those from *C. libani* yielded sandaracopimaric acid.[66]*

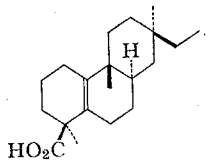
The enamine methylation of the αβ-unsaturated ketone **133** did not result in the C-methylation but in the N-methylation. The direct monomethylation of the same ketone under a controlled condition did not give a monomethylated derivative but a dimethylated αβ-unsaturated ketone **134**. However, when the βγ-unsaturated ketone **135** was methylated under a controlled condition, the expected monomethylated αβ-unsaturated ketone **136** was obtained. In this connection, the deconjugation of the αβ-unsaturated ketone **137** with trichloroacetic anhydride was also studied.[67]

Rosein III, a metabolite of *Trichothecium roseum*, was converted into **138**, and also more directly to a mixture of rosenonolactone dihydro derivative (**140**) and isorosenono-

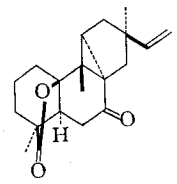
* See also section VI.



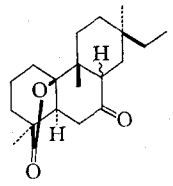
136



138

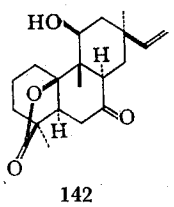


139

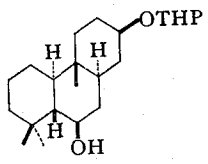


140: 8α-H
141: 8β-H

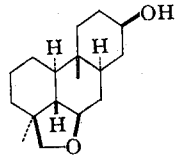
lactone dihydro derivative (**141**) *via* a novel cyclopropane intermediate (**139**). These correlations of rosein III with rosenonolactone in association with the spectroscopic evidences of derivatives substantiated its structure and absolute configuration as 11-β-hydroxyrosenonolactone (**142**).[68,69] The conformation of isorosein III, a C-8 isomer of rosein III, was also clarified.



142

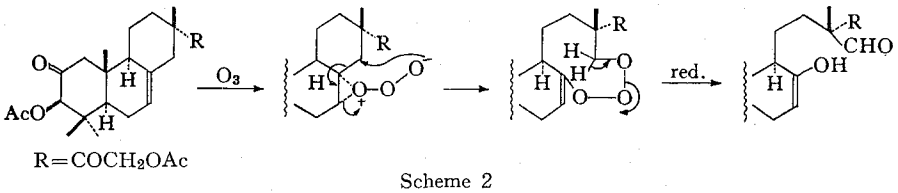


143



144

Certain "abnormal" ozonolyses, including those of several isopimarane derivatives, were explained in terms of the rearrangement of the peroxyepoxide as shown in Scheme 2.[70]

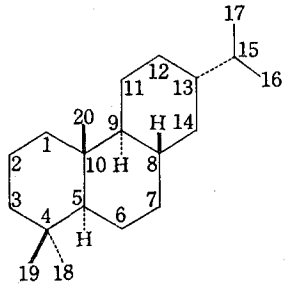


R=$COCH_2OAc$

Scheme 2

Potential intermediates for the syntheses of rosenonolactone type diterpenoids were prepared. Compound **143** was subjected to the reaction with lead tetraacetate and iodine followed by acid hydrolysis to give ether **144**.[71]

VI. ABIETANE DERIVATIVES



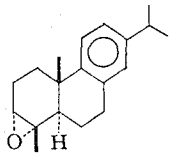
Abietane

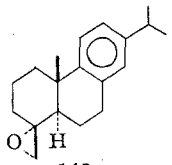
The reactions of boron trifluoride and dimethyl sulfoxide on the 3α,4α-epoxy- (**145**), 4α,19-epoxy- (**146**) and 4α,5α-epoxy- (**147**) derivatives of 18-norabieta-8,11, 13-triene were studied.[12]*

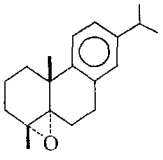
Methyl dehydro-15-hydroxy-abietan-18-oate was isolated by column chromatography from the oleoresin of *Pinus koraiensis*.[42]**

Ether extracts from the cones of *Cedrus atlantica* yielded abietic, levopimaric, palustric, dehydroabietic

* See also section II. ** See also section III.


145

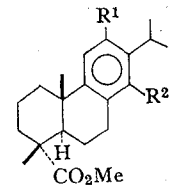

146

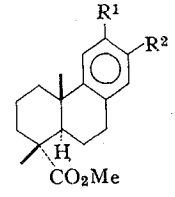

147

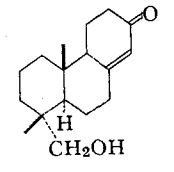
and neoabietic acids, and abieta-8,11,13-trien-7-one. The extracts of *C. libani* also yielded the same acids, abieta-8,11,13-triene, and abieta-7,13-diene.[66]†

Use of N-lithio ethylenediamine as a dehydrogenation agent of diterpene acids was investigated and (+)-dehydroabietic acid was prepared from (—)-abietic acid.[72]

Functionalization of the isopropyl group of methyl abieta-8,11,13-trien-18-oate (**148**) was achieved by intramolecular cyclizations of the 12-carboxy derivative (**149**) with lead tetraacetate and by thermolysis of the diazomethyl ketone (**150**). Nitration of methyl 12-acetylabieta-8,11,13-trien-18-oate (**151**) gave the products **152** and **153**, arising from nitrodeacylation and nitrodealkylation reactions, respectively. The nitro ketone **153** was converted into methyl 13-hydroxypodocarpa-8,11,13-trien-18-oate (**154**) in 26% overall yield from the ester **148**. Birch reduction of the methyl ether of **154** afforded the enone **155**, a potentially useful intermediate for synthesis.[73]

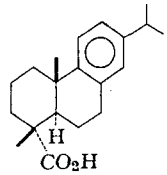


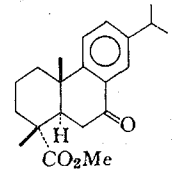


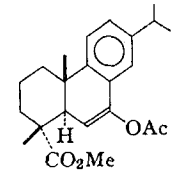

155

148: $R^1=R^2=H$
149: $R^1=CO_2H$, $R^2=H$
150: $R^1=COCHN_2$, $R^2=H$
151: $R^1=Ac$, $R^2=H$
152: $R^1=R^2=NO_2$
153: $R^1=Ac$, $R^2=NO_2$
154: $R^1=H$, $R^2=OH$

The preparation of 6-oxygenated derivatives of abieta-8,11,13-trien-18-oic acid, that is, dehydroabietic acid (**156**) was developed by peracid oxidation of the enol acetate **158** derived from the C-7 ketone **157**.[74]


156

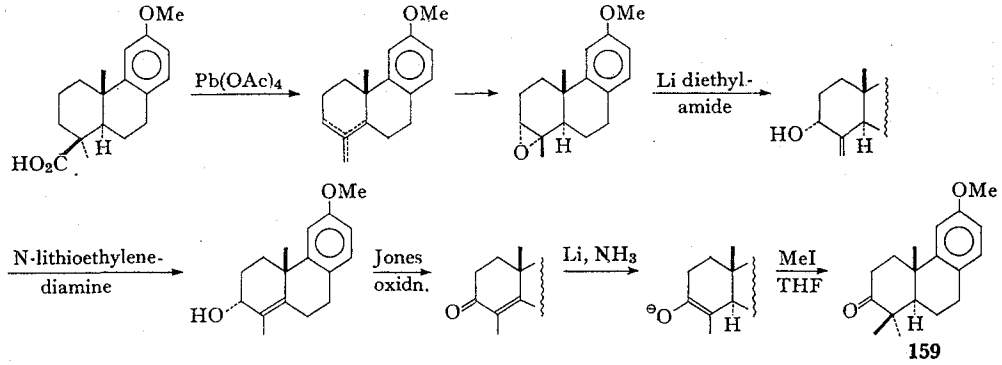

157


158

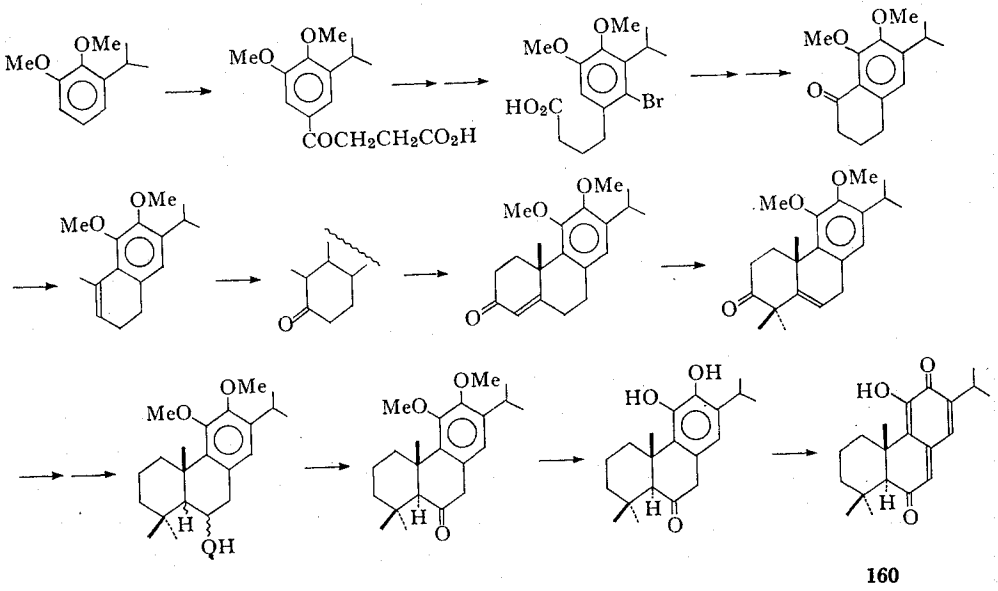
A synthesis of (+)-hinokione methyl ether (**159**) was carried out as shown in Scheme 3.[75]

The total synthesis of *rac.*-taxodione, (**160**) a tumor inhibitor, was done through the steps shown in Scheme 4.[76]

† See also section V.



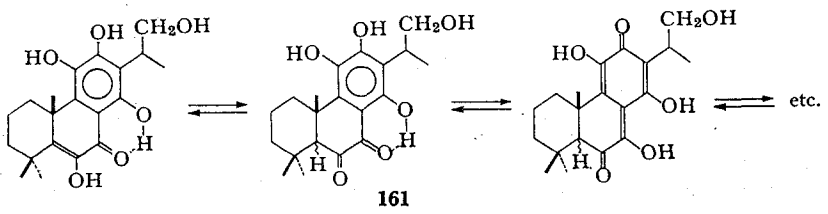
Scheme 3



Scheme 4

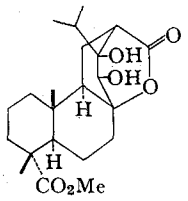
Methyl 12-chlorosulfonyl-dehydroabietate was prepared by treating methyl dehydroabietate in carbon tetrachloride with chlorosulfonic acid at −5°.[77] The thermal behavior of methyl dehydroabietate at 600–800° was investigated.[78] Methyl 12-acetyldehydroabietate was converted into some derivatives.[79] Dehydroabietic acid was converted to dehydroabietylnitrile, dehydroabietylamine, and their derivatives.[80]

Structure of coleon C, a new yellow diterpenoid hydroquinone, isolated from the leaves and inflorescences of *Coleus aquaticus* was elucidated as **161**.[81]

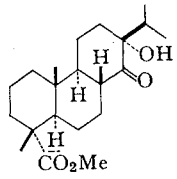


161

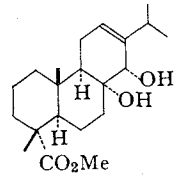
Nitration of methyl dehydroabietate by fuming nitric acid in acetic anhydride gave 27% of 14-nitro- and 47% of 12-nitroderivatives.[82] Pyrolysis of a dihydroxylactone **162** gave **163** or **164**. Decarboxylation of **165** also gave **163**. These unusually facile decarboxylations were discussed.[83]



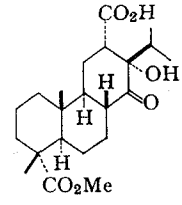
162



163

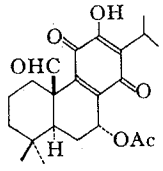


164

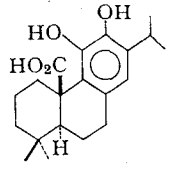


165

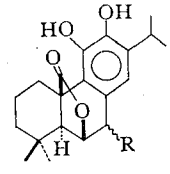
Dehydroabietane was isolated from the oleoresin of *Pinus pallasiana*.[84] The structure of nemorone isolated from *Salvia nemorosa* roots was determined as **166**.[85]



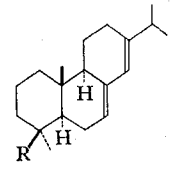
166



167

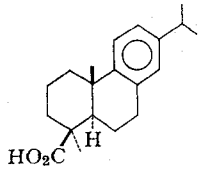


168: R=β-NH_2
169: R=α-NH_2

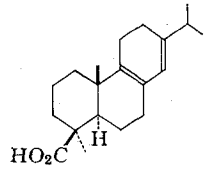


170: R=CO_2H
173: R=CHO
174: R=CH_2OH

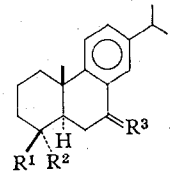
Derivatives of dehydroabietic acid with alkaloids salsolidine and cytisine were investigated.[86] The main terpene component (**167**) of *Rosmarinus officinalis* gave in the presence of ammonia a mixture of rosmaricine (**168**) and isorosmaricine (**169**). Chemical transformations and NMR studies confirmed their structure and stereochemistry as shown.[87] As the minor constituents of *Juniperus phoenicea,* 4-epi-abietic (**170**), 4-epi-dehydroabietic acid (**171**), 4-epi-palustic acid (**172**), 4-epi-abietal (**173**), and acid 4-epiabietol (**174**) were isolated.[88] 18-(**175**) and 19-Norabieta-8,11,13-trien-4-ol (**176**) and 18-hydroxy-8,11,13-abietatrien-7-one (**177**) were isolated from *Pinus banksiana.* In *Pinus monticola,* the presence of three 19-norabietateraenes was recognized.[89]



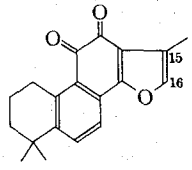
171



172



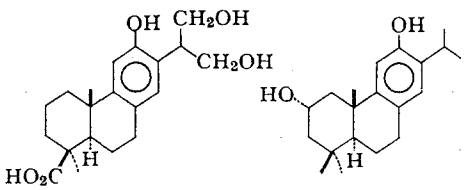
175: R^1=Me, R^2=OH, R^3=H_2
176: R^1=OH, R^2=Me, R^3=H_2
177: R^1=Me, R^2=CH_2OH, R^3=O
180: R^1=CHO, R^2=Me, R^3=H_2



178
179: 15,16-dihydro-derivative

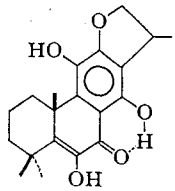
Syntheses of tanshinone-II (**178**) and cryptotanshinone (**179**) were carried out through fourteen steps of reactions from 1,2,4-trimethoxybenzene.[90] Preparation of dehydroabietic acid from rosin was reported.[91]

Chemical conversion of dehydroabietic acid into 4-epi-dehydroabietic acid (**171**) *via* 4-epi-dehydroabietal (**180**) was accomplished.[92] The structure of pododacric acid isolated from heartwoods of *Podocarpus dacrydioides* and *P. totara* was determined as **181**.[93] A new diterpenoid phenol, salviol, was isolated from *Salvia miltiorrhiza* and its structure was determined as **182**.[94]



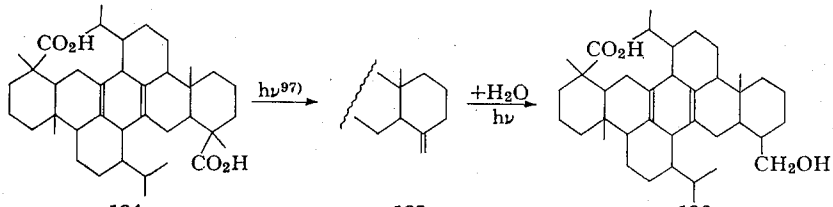
181

182



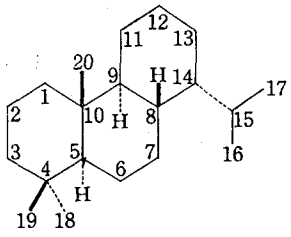
183

Structure **183** was assigned to lycoxanthol, a yellow hydroquinone diterpenoid isolated from *Lycopodium lucidulum*.[95] The UV-irradiation to "Kolophonium" which was mainly consisted of abietic acid provided evidence for its dimerization into diabietic acid (**184**) and conversion of the latter into diabietolic acid (**186**), the monomer of polyester succinite. Thus, a sequence of three chemical conversions which abietic acid must encounter during formation of succinite was clarified as follows: 1) dimerization of abietic acid into diabietic acid (**184**); 2) transformation of **184** into diabietenic acid (**185**); 3) transformation of **185** into **186**.[96]



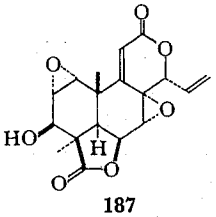
184 **185** **186**

VII. TOTARANE DERIVATIVES

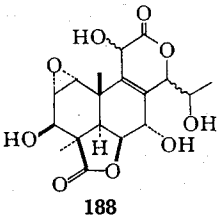


Totarane

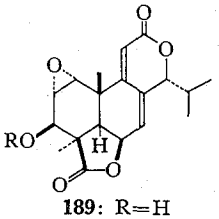
The structures **187** and **188** were suggested for inumakilactones B and C, which were isolated from the seeds of *Podocarpus macrophyllus,* respectively.[98] Structures, **189** and **190,** were established, respectively, for ponalactone A and its glucoside isolated from the leaves of *Podocarpus nakaii*. Both compounds exhibited plant growth inhibitory activities.[99]



187

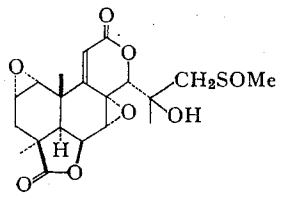


188

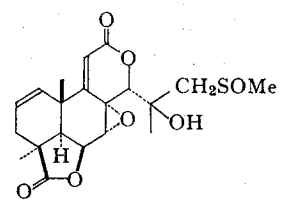


189: R=H
190: R=glu

The structures of podolactones C and D isolated from *Podocarpus neriifolius* were shown to be **191** and **192** respectively.[100]

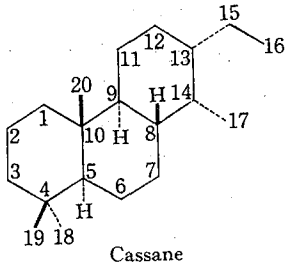


191



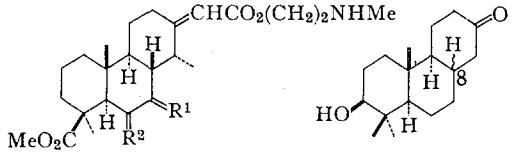
192

VIII. CASSANE DERIVATIVES



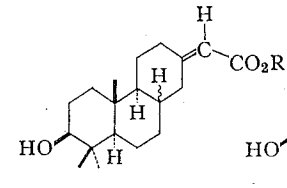
Cassane

From the bark of *Erythrophleum guineense,* an alkaloid norcassamine (**193**) was isolated as the main product.[101] The bark also contained norcassamidine (**194**), which was proved to be identical with erythrophleine. The originally ascribed structure was now revised. The structures of two minor alkaloids, norerythrosuamine (**195**) and dehydro-norerythrosuamine (**196**) were clarified with the aid of mass spectrometry. "Muawin", originally regarded to be a single compound was shown to be a mixture of these alkaloids, hence the name must be canceled.[101]

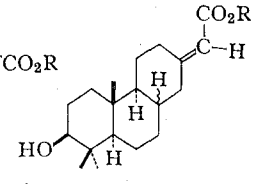


193: R^1=O, R^2=H_2
194: R^1=α-H, β-OH, R^2=H_2
195: R^1=α-H, β-OH, R^2=O
196: R^1=R^2=O

197: β-H at C-8
198: α-H at C-8



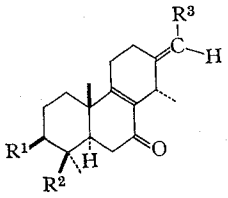
199: R=Et, β-H at C-8
201: R=Et, α-H at C-8
203: R=$(CH_2)_2NMe_2$, β-H at C-8
205: R=$(CH_2)_2NMe_2$, α-H at C-8



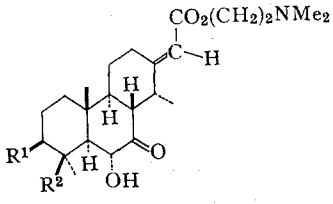
200: R=Et, β-H at C-8
202: R=Et, α-H at C-8
204: R=$(CH_2)_2NMe_2$, β-H at C-8
206: R=$(CH_2)_2NMe_2$, α-H at C-8

Reaction of tricyclic ketones **197** and**198** with triethyl phosphonoacetate, respectively, was investigated. The products were separated into the uniform racemic isomers **199** and **200**, **201**, and **202**, respectively. Transesterification of these compounds gave the corresponding 2-dimethylaminoethyl esters *i.e.* **203**, **204**, **205**, and **206**.[102] The structures of the four isomers *i.e.* 3-oxo-derivatives of **199**, **200**, **201**, and **202** were confirmed by detailed NMR investigations.[103] Catalytic hydrogenation of 3-dehydro-derivatives (3-ketones) of **199** and **200** gave 13α and 13β-ethoxycarbonylmethyl derivatives, which were separated.[104] 8-Dehydrocassaic acid (**207**) was isolated by hydrolysis of impure cassaine preparations, which indicated the original existence of 6-hydroxycassaine (**208**).

That 8-dehydrocassamine (**209**) was prepared from erythrophleguine (**210**) supported this.[105]



207: R^1=OH, R^2=Me, R^3=CO_2H

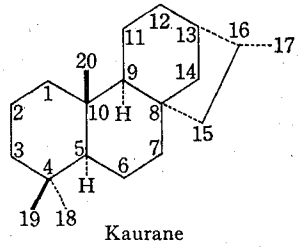


208: R^1=OH, R^2=Me

209: R^1=H, R^2=CO_2Me, R^3=$CO_2(CH_2)_2NMe_2$

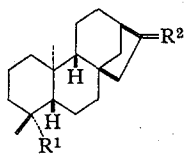
210: R^1=H, R^2=CO_2Me

IX. KAURANE DERIVATIVES

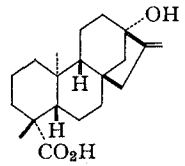


Kaurane

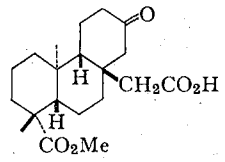
From the oleoresin of *Capaifera longsdorfii*, *ent*-16-kauren-19-oic caid (**211**) and ent-kauran-19-oic acid were isolated.[43] From extracts of the roots of *Solidago Shortii*, *ent*-16-kauren-19-oic acid was isolated.[56] *ent*-16β-Hydroxykaurane (**212**) was shown to be the main component of the white covering on the moss *Saelania glaucescens*.[106] The occurrence of *ent*-16-kauren-19-oic acid (**211**) and *ent*-16-kauren-19-ol (**213**) in the



211: R^1=CO_2H, R^2=CH_2
212: R^1=Me, R^2=α-OH, β-Me
213: R^1=CH_2OH, R^2=CH_2



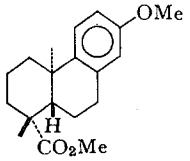
214



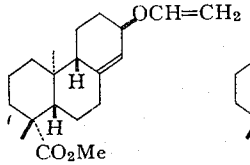
215

Australian member of the Compositae family *Abrotanella nivigena* was reported.[107]

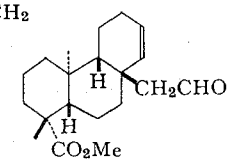
Total syntheses of *rac.*-steviol (**214**) and *rac.*-16-kauren-19-oic acid (**211**) were accomplished.[108] A synthesis of methyl *rac.*-8α-carboxymethylpodocarpan-13-on-19-oate (**215**), a degradation product of steviol, was also done. From the known starting material (**216**),[109] aldehyde **218** was synthesized *via* vinyl ether **217**. The compound **215** was synthesized from **218** *via* **219** and **220**. The aldehyde **218** was converted into ketones **221** and **222**. The minor product **221** was transformed into a tetracyclic compound



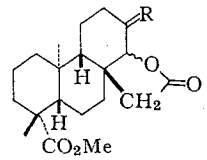
216



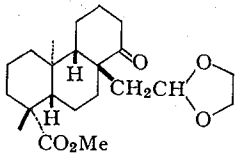
217



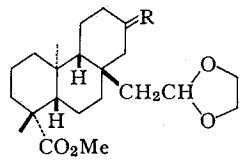
218



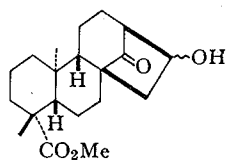
219: R=H, OH
220: R=O



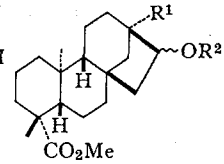
221



222: R=O
224: R=CHMe
225: R=α-Ac, β-H



223



226: R^1=COMe, R^2=H
227: R^1=NHAc, R^2=Ac

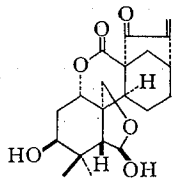
223, which was converted into *rac.*-16-kauren-19-oic acid (**211**). On the other hand, the major ketone **222** was subjected to the Wittig reaction to give olefin **224**, which was cyclized into **226** *via* **225**. The acetyl group at C-13 in **226** was transformed to a hydroxy group *via* **227** prepared using the Beckmann rearrangement. The subsequent Jones oxidation, Wittig reaction, and hydrolysis gave *rac.*-steviol (**214**).[108]

The mass spectra of *ent*-16-kaurene, *ent*-16-kaurene-12, 18-diol, and *ent*-kaurane-12, 18-diol were investigated and their fragmentation patterns were discussed.[110] *ent*-16-Kauren-18-oic acid, *ent*-kauran-18-oic acid and their 7- or 12-oxo derivatives were also investigated mass spectrometrically.[111] An additional report on the mass spectra of *ent*-16-kaurene-15,18-diol and its derivatives was published.[112]

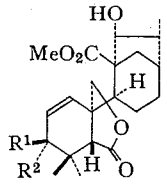
In leaf-extracts of *Rhododendron* species, the contents of grayanotoxin-I were determined by a German group.[113] According to the report, a suggestion that the other grayanotoxins *i.e.* grayanotoxin-II to -VIII were not likely to be naturally occurring compounds but artifacts was provided on the basis of the thin layer chromatographic investigations.

ent-17-Hydroxy-15-kauren-19-oic acid was isolated from *Enhydra fluctuans* and characterized.[114]

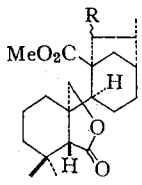
A full paper on a common stereoelectronic requirement which was recognized in epimerizations and *retro*-Dieckmann-type cleavages of some diterpene alcohols and ketones in enmein and gibberellin series was published by us.[115] A stereoelectronic factor controlling epimerisations of the C-15 alcohols **229**–**232** derived from enmein (**228**), which have a *cis*-relationship between the 15-hydroxy and 16-methyl groups, into the corresponding *trans*-alcohols (**233**)–(**236**) also operated in the *retro*-Dieckmann-type cleavage of the related C-15 ketones **237** and **238** to give the carboxylic acids **239** and **240**. The mechanism of these reactions were discussed.[115]



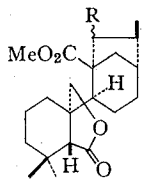
228



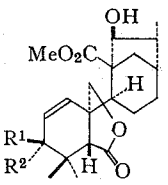
229: R^1=OH, R^2=H
230: R^1=H, R^2=OH



231: R=α-OH
235: R=β-OH

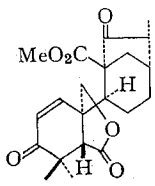


232: R=β-OH
236: R=α-OH

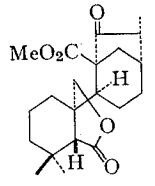


233: R^1=OH, R^2=H
234: R^1=H, R^2=OH

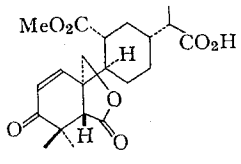
A stereoselective synthesis of *rac.*-12-oxo-7,9-ethano-*cis*-$\Delta^{1,2}$-octalin (**241**) was accomplished.[116]



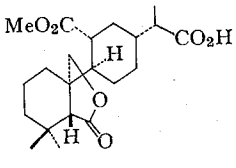
237



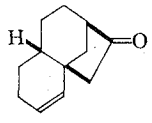
238



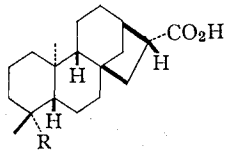
239



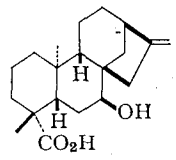
240



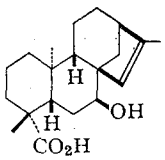
241



242: R=CHO
243: R=OH



244

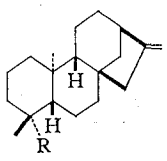


245

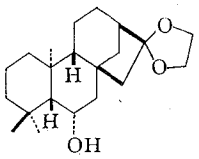
The mass spectra of natural and modified kaurenolides were reported.[117] From the bark of *Annona senegalensis, ent*-kauran-16-ol, *ent*-16-kauren-19-oic acid (**211**), *ent*-16-epi-kauran-19-al-17-oic acid (**242**), and *ent*-16-epi-19-norkauran-4β-ol-17-oic acid (**243**) were isolated.[118]

[17-^{14}C] *ent*-16-Kauren-19-oic acid was converted to several products in cell-free preparations of endosperm from immature *Echinocystis macrocarpa* seeds. One of these products was identified as *ent*-16-kauren-7α-ol-19-oic acid (**244**). A second product was tentatively identified as *ent*-15-kauren-7α-ol-19-oic acid (**245**). The former (**244**) stimulated leaf sheath growth in seedlings of the drawf-5 mutant of *Zea mays*. Also it was convertible to gibberellin A_3 in *Gibberella fujikuroi* mycelial suspensions. Thus, it was suggested that **244** was a normal intermediate in gibberellin biosynthesis.[119]

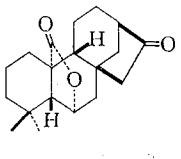
The resin of *Espeletia grandiflora* was shown to contain *ent*-16-kauren-19-ol (**246**), *ent*-16-kauren-19-al (**247**), *ent*-16-kaurene, and *ent*-16-kauren-19-oic acid (**211**).[120]



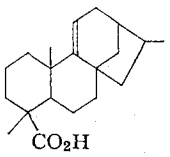
246: R=CH_2OH
247: R=CHO



248



249

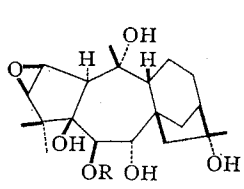


250

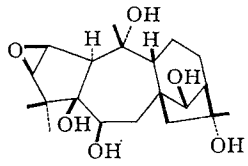
Photo-oxidation of compound **248** in the presence of iodine and lead tetraacetate followed by hydrolysis yielded the five-membered ring lactone **249**.[121] The mass spectra of xylopic acid (**250**), isolated from the light petroleum extracts of the pericarp of *Xylopia aethiopica*, and of its derivatives were investigated.[122]

The A,B-ring juncture of lyoniol-A (**251**) was shown to be *trans* on the basis of the ORD investigation of the 10-keto compound derived from lyoniol-A.[123] The structure of lyoniol-B was established as **252**.[124]

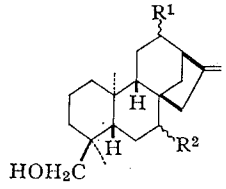
From the leaves of *Tripetaleia paniculata*, a toxic substance, rhodojaponin III (**253**) was isolated.[125] Structures, **254** and **255**,[126] which had been assigned, respectively, for candicandiol and epicandicandiol isolated from *Sideritis candicans var. eriocephala*,



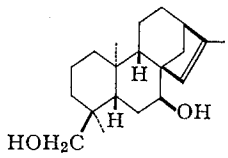
251: R=Ac
252: R=H



253



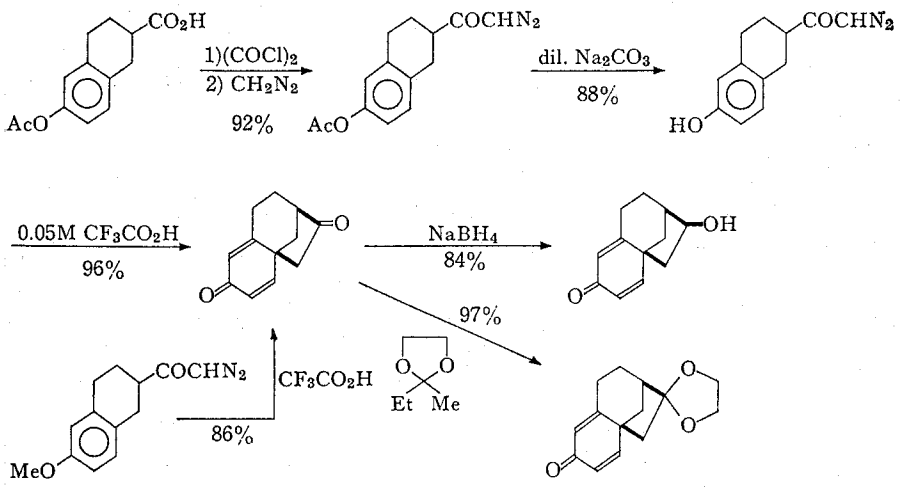
254: R^1=α-OH, R^2=H
255: R^1=β-OH, R^2=H
256: R^1=H, R^2=α-OH
257: R^1=H, R^2=β-OH



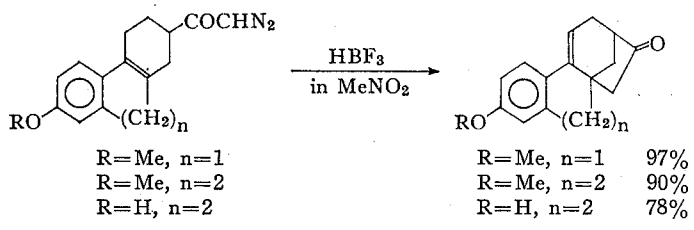
258

were revised to **256** and **257** by correlation with sideridiol (**258**).[127]

A new annelation reaction, initiated by the protonated diazomethylcarbonyl function, was developed and a variety of intermediates for the total synthesis of tetracyclic diterpenoids were prepared as shown in Scheme 5.[128]



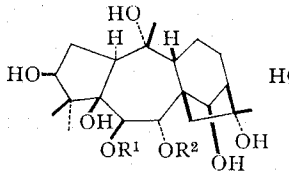
60% overall yield



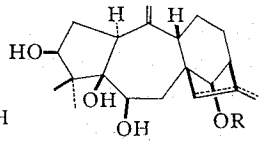
R=Me, n=1	97%
R=Me, n=2	90%
R=H, n=2	78%

Scheme 5

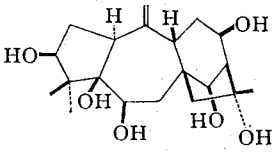
The stereochemistry of asebotoxin-IV and -V, toxins of *Pieris japonica,* was determined to be **259** and **260**, respectively.[129]



259: R^1=OCOEt, R^2=H
260: R^1=Ac, R^2=OCOEt



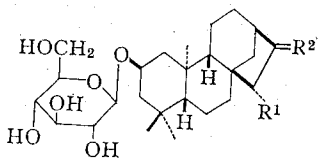
261: R=H, $\Delta^{16,17}$
262: R=Ac, $\Delta^{15,16}$
263: R=Ac, $\Delta^{16,17}$



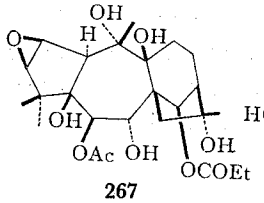
264

From the leaves of *Leucothoe grayana,* four novel toxins, grayanotoxin-VIII, -IX, -X, and -XI were isolated and their structures, **261**, **262**, **263**, and **264**, were determined, respectively.[130]

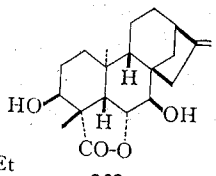
Two new diterpenoid glucosides, creticosides A and B, were isolated from *Pteris cretica,* and structures, **265** and **266**, were assigned to A and B, respectively.[131]



265: R^1=OH, R^2=CH_2
266: R^1=H, R^2=α-OH, β-Me

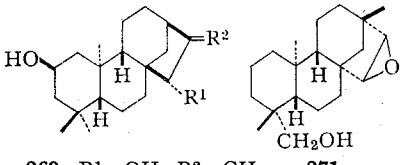


267



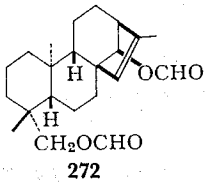
268

A new toxic diterpenoid, asebotoxin VII, was isolated from the flowers of *Pieris japonica* and structure **267** was assigned to it.[132] 3β,7β-Dihydroxykaurenolide (**268**) was isolated as a new metabolite from *Gibberella fujikaroi.*[133] The structures of two new diterpenoids, compounds A and B, were elucidated to be **269** and **270**.[134]

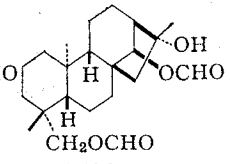


269: R^1=OH, R^2=CH_2
270: R^1=H, R^2=α-OH, β-Me

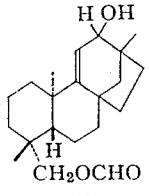
271



272



273



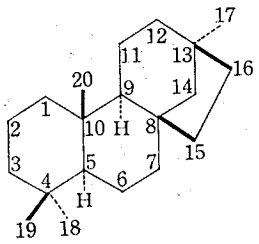
274

The acid-catalyzed rearrangement of a diterpenoid epoxide (**271**) was investigated. Under several different conditions, the products, **272**, **273**, and **274**, were obtained.[135]

X. BEYERANE DERIVATIVES*

A partial synthesis of isohibaene (**275**) starting with nezukol (**276**) was accomplished. As the key step, the intramolecular insertion reaction of a ketocarbene generated by

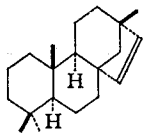
* See also section XII (ref. 186).



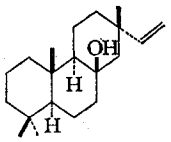
Beyerane

cuprous oxide-catalyzed decomposition of diazoketone (**277**) under irradiation gave ketone **278**.[136] It was also found that isohibaene underwent rearrangement into a mixture of phyllocladene and isophyllocladene by iodine catalytically.[136]

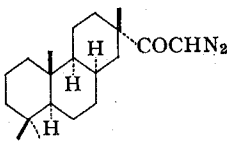
Nitrous acid deamination of methyl *ent*-16-amino-beyeran-19-oate (**279**) in acetic acid gave predominant rearrangement to methyl *ent*-16-acetoxykauran-19-oate



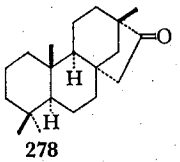
275



276

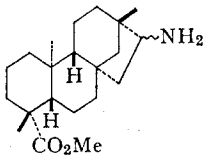


277

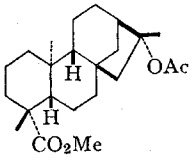


278

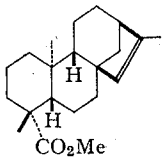
(**280**) accompanied by small amounts of the isomeric kaurene esters, **211** and **281**. Acetolysis of tosylate **282** and decomposition of the tosylhydrazone **283** under protic conditions afforded the same rearranged, unsaturated esters, **211** and **281**. In the latter reaction, methyl *ent*-13α,16-cycloatisan-19-oate (**284**), the C-4 epimer of methyl trachylobanoate, was also produced.[137]



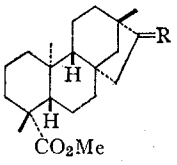
279



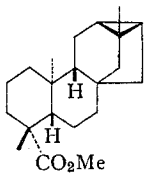
280



281

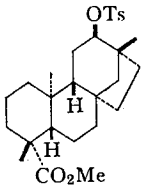


282: R=α-H, β-OTs
283: R=NNHTs

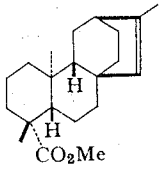


284

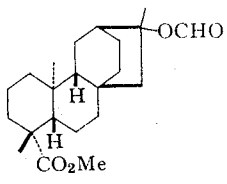
Acetolysis of tosylate **285** gave the isoatisirene ester **286** while formolysis of tosylate **285** yielded methyl *ent*-16-formyloxyatisan-19-oate (**287**). The various rearrangements observed formally corresponded to the ring D rearrangements suggested for the biogenesis of these tetracyclic diterpenes.[137]



285

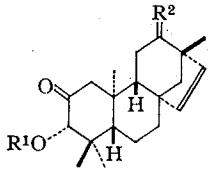


286

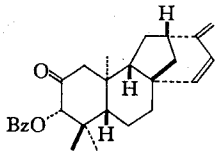


287

A tetracyclic ketol **288** was isolated as the major heartwood diterpene from *Androstachys johnsonii* and characterized. Mesylate **289** was easily converted into a new rearranged compound **290**. Thus, the latter type skeleton was suggested to occur in nature.[138]

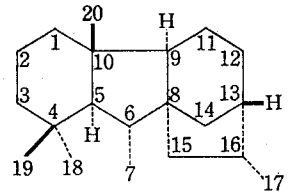


288: R^1=H, R^2=O
289: R^1=Bz, R^2=α-OMs, β-H



290

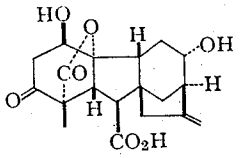
XI. GIBBERELLANE DERIVATIVES



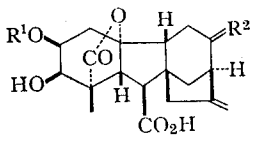
Gibberellane

The structures of the two new gibberellins, GA_{33} and GA_{34}, isolated from immature seeds of evening-glory (*Calonyction aculeatrum*) were determined to be **291** and **292**, respectively.[139] Gibberellin A_{26} (**293**) and GA_{27} (**294**) were isolated from Japanese morning-glory (*Pharbitis nil*) and their structures were confirmed.[140]

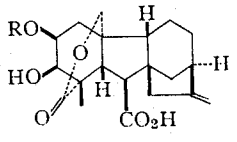
Seven gibberellin glucosides (F-I～F-VII) were



291

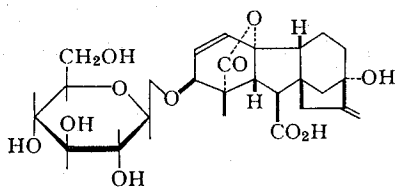


292: R^1=H, R^2=H_2
293: R^1=H, R^2=O
298: R^1=β-glucosyl, R^2=0

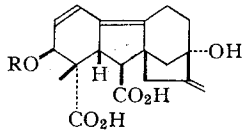


294: R=H
300: R=β-glucosyl

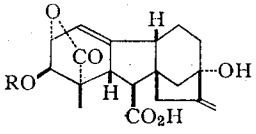
isolated from immature seeds of Japanese morning-glory. The structures were elucidated to be 3-O-β-glucosyl-GA_3 (**295**), 3-O-β-glucosyl-gibberellenic acid (**296**), 3-O-β-glucosyl-isogibberellin A_3 (**297**), 2-O-β-gulcosyl-GA_{26} (**298**), 2-O-β-glucosyl-GA_8 (**299**), 2-O-β-glucosyl-GA_{27} (**300**), and 2-O-β-glucosyl-GA_{29} (**301**), respectively.[141]



295

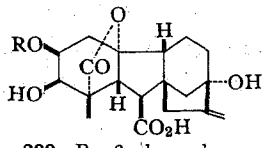


296: R=β-glucosyl

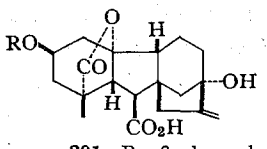


297: R=β-glucosyl

Two gibberellin-like substances were isolated from the immature pods of yellow broom (*Cytisus scoparius*). Although structures **302** and **303** were assigned to these substances, **303** was quite possible to be an artifact, so the name of gibberellin A_{35} was al-

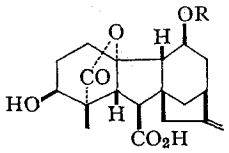


299: R=β-glucosyl

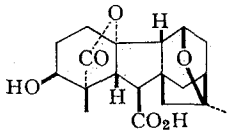


301: R=β-glucosyl

located to **302** only. Another new gibberellin glucoside was also isolated, and it was proved to be 11-O-β-D-glucosylgibberellin A_{35} (**304**).[142]



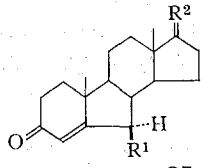
302: R=H
304: R=β-glucosyl



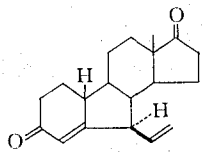
303

A review on structure, biosynthesis and effects of gibberellins was published.[143]

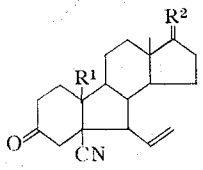
B-Nor-Δ^4-3-ketosteroids such compounds as **305**～**310** were synthesized starting from Δ^5-3β-hydroxysteroids.



305: R^1=CH(O,O), R^2=O
306: R^1=CH_2OAc, R^2=O
307: R^1=CH_2OH, R^2=O
308: R^1=CH=CH_2, R^2=O
309: R^1=CH=CH_2, R^2=H_2



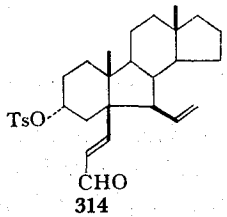
310



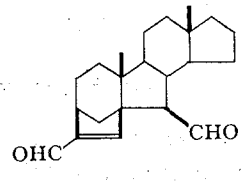
311: R^1=Me, R^2=O
312: R^1=Me, R^2=H_2
313: R^1=H, R^2=O

Hydrocyanation by treatment with diethylammonium cyanide was successful for only the 6β-vinyl derivatives (**308**, **309**, and **310**) and gave the corresponding 3-keto-5β-cyano-compounds (**311**, **312**, and **313**).[144]

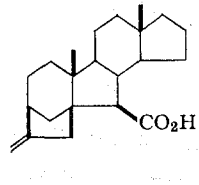
5β-Cyano-6β-vinyl-B-nor-5β-androstan-3-one (**312**) was transformed stereoselectively to 3α-tosyloxy-5β(trans-β-formyl)vinyl-6β-vinyl-5β-androstane (**314**) by the eight-step synthesis. The latter, after selective ozonization, was subjected to a new cyclization method involving participation of 6β-hemiacetal function to afford 3β,5β-etheno derivative **315**, which on subsequent oxidation and the Wolff-Kishner reduction led to modified gibberellin type compound **316**.[145]



314

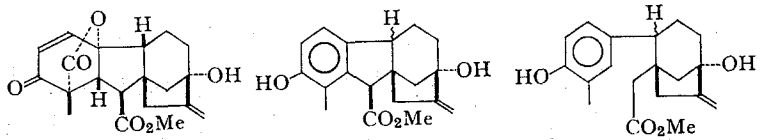


315



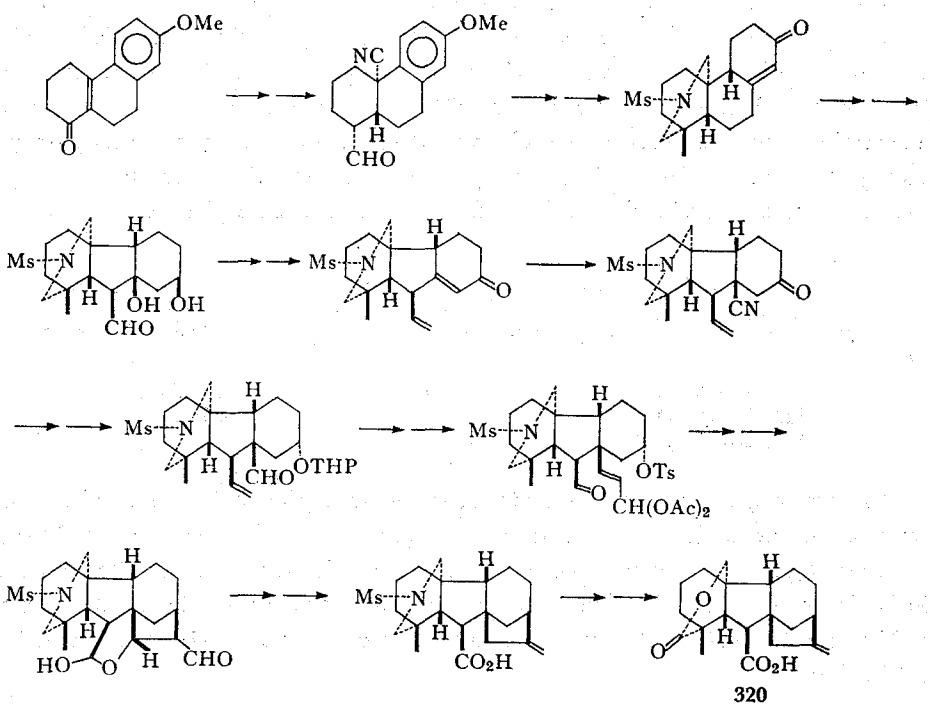
316

Photoconversion of **317** in *t*-butanol gave **318** in 25% yield. The photolysis of **317** in benzene gave **318** in 20% yield. Photolysis of **317** in benzyl alcohol gave **319**.[146)]



317 **318** **319**

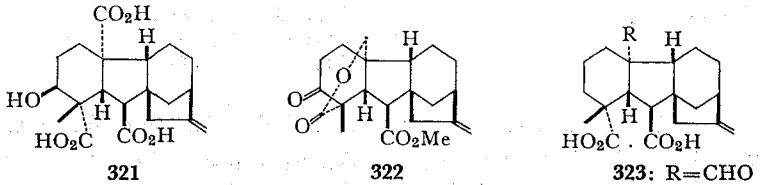
The stereocontrolled total synthesis of *rac.*-gibberellin A_{15} (**320**) was accomplished,[147b)] and its full paper was published. The main route was already shown in the review in 1970 of this series, according to the communication published in 1970[147a)], but the more simplified outline of the synthetic route is again shown in Scheme 6.



320

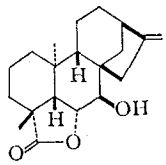
Scheme 6

Gibberellin A_{12} (**321**) was converted to the methyl ester (**322**) of 3-oxogibberellin A_{15} and some related δ-lactones.[148)]

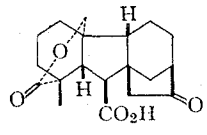


321 **322** **323**: R=CHO **324**: R=CO_2H

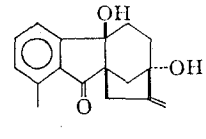
Isolation, structure elucidation, and correlation with gibberellin A_{13} and A_{15} of two new gibberellins, A_{24} (**323**) and A_{25} (**324**), were reported.[149] A partial synthesis of gibberellin A_{15} norketone (**326**) from 7-hydroxykaurenolide (**325**) was accomplished.[150]



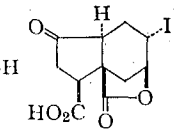
325



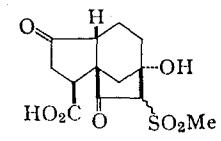
326



327

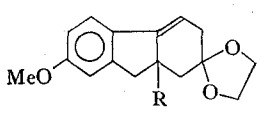


328

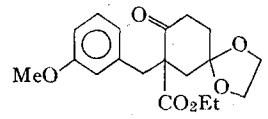


329

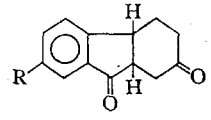
The structure **327** was assigned to a new metabolite of *Gibberella fujikuroi*.[151] Studies of the synthesis of the B, C, and D rings of gibberellic acid were carried out. Compound **329** was synthesized *via* lactone **328**, but attempts to remove the extraneous D ring keto group from sulfone were unsuccessful.[152] The crystal structure of **328** was shown to have the *trans* jucture between rings B and C by an X-ray analysis.[153] Catalytic hydrogenation of methoxycarbonyl derivative **330** gave a *cis*/*trans* product ratio of 15:85, while the hydroxymethyl derivative **331** gave a ratio of 95:5. A route involving condensation of *m*-methoxybenzyl chloride with the anion of 2-ethoxycarbonyl-4,4-ethylene dioxy-cyclohexanone yielded **332** readily. This condensation and the subsequent polyphosphoric acid cyclization of **332** led to **333** in an overall yield of about 33%.[154]



330: R=CO_2Me
331: R=CH_2OH
333: R=CO_2Et



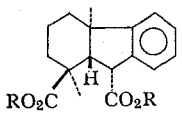
332



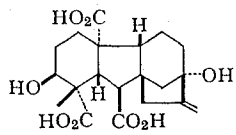
333: R=H
334: R=OMe

An efficient synthesis of hexahydrofluorene-2,9-dione (**333**) and 7-methoxyhexahydrofluorene-2,9-dione (**334**) from the appropriate phenyl pyruvic acid was published.[155]

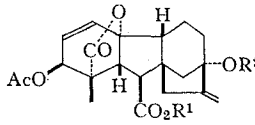
A new type of sweet compound having structure **335** was reported. Its sodium salt **336** is also very sweet. Relative sweetness of **335** to sucrose was 1300–1800, and that of **336** was 1600–2000. Their relative bitterness to caffein was 12–18 for **335** and 12–13 for **336**.[156]



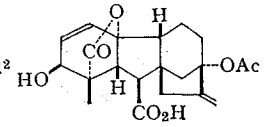
335: R=H
336: R=Na



337



338: R^1=R^2=H
339: R^1=H, R^2=Ac
340: R^1=Me, R^2=H
341: R^1=Me, R^2=Ac



342

A new C_{20} gibberellin, A_{28}, was isolated from fruits of *Lupinus luteus* and shown to have structure **337**.[157] Gibberellins A_1, A_3, A_5, A_6, A_8, A_{17}, A_{19}, and A_{20} were identified in the seed of *Phaseolus mulfiflorus* by GC-MS. In the seed of *P. vulgaris* gib-

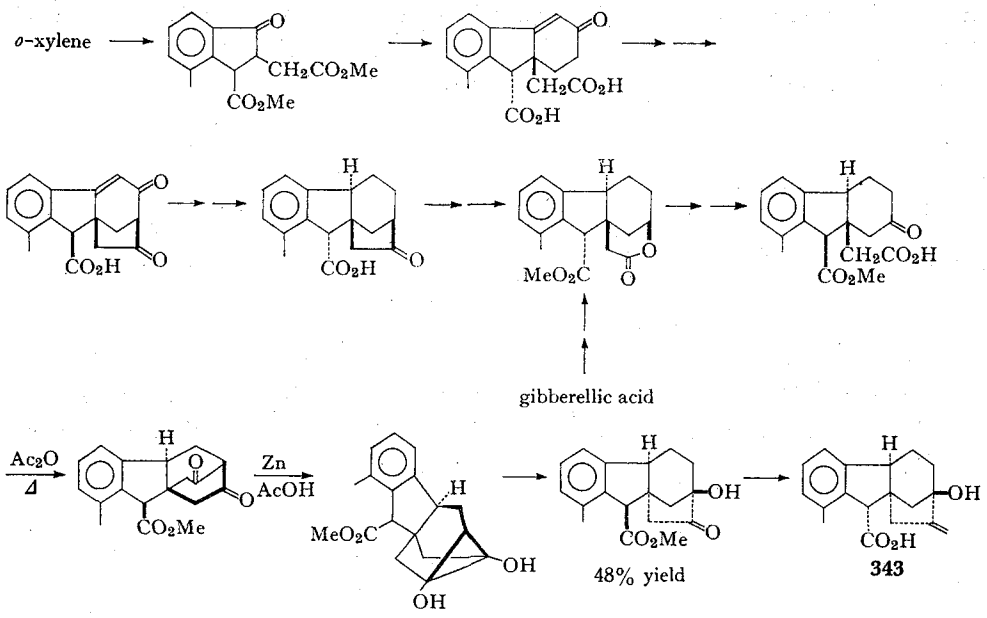
berellins A_6 and A_8 were identified by GC-MS. Gas-liquid chromatography analyses of the amounts of gibberellins in the developing seed of *P. mulfiflorus* and *P. vulgaris* were also reported.[158]

Growth-promoting effects of gibberellins and their glucosides isolated from immature seeds of *Pharbitis nil* were compared using six bioassay systems, and the results were published.[159]

The fungus *Phoma medicaginis var. pinodella* was shown to split off the O(3)-acetyl group of gibberellic acid acetates, **338** and **339**, and their methyl esters, **340** and **341**, without affecting O(13)-acetyl, 19,10-lactone, and methyl ester groups. Fungal deacetylation of OO(3,13)-diacetylgibberellic acid (**339**) yielded O(13)-acetylgibberellic acid (**342**), a new compound.[160]

Several biological and also biochemical works on gibberellins were published.[161~166] The number 3 of the lists of references for the physiologically active substances in plants was published and some gibberellins were added in this list.[167]

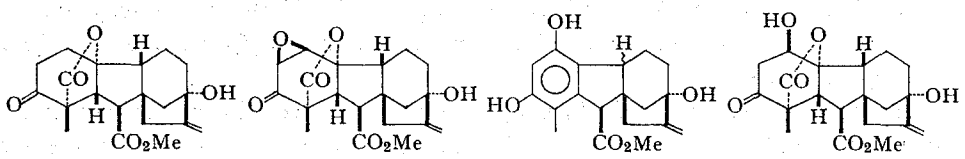
A total synthesis of *rac.* epiallogibberic acid (**343**) was accomplished employing a novel skeletal rearrangement. The outline is shown in Scheme 7.[168]



Scheme 7

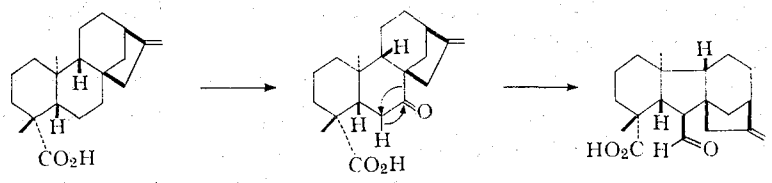
The photolysis of the 3-oxo derivative (**317**) of gibberellin A_3 methyl ester was reported as a preliminary report and described above.[146] Now, the full paper of this work was published by the same authors.[169] The photolysis of **317** in *t*-butanol or benzene gave rise to the tetracyclic phenol **318** (C-9: βH), while in benzyl alcohol **317** was transformed into the tricyclic phenol **319** (C-9: βH) and the reduced ketone **344**. The epoxy ketone **345** on photolysis in dioxan afforded the resorcinol **346**; at higher temperature the latter was accompanied by the hydroxy ketone **347**.

An evidence presented by the tracer experiments suggested that the ring contraction



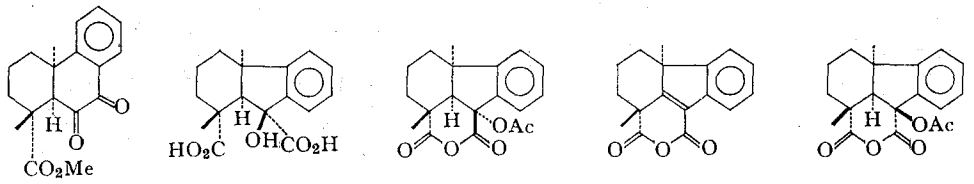
344 345 346 347

of a kauranoid diterpene to a gibberellane derivatives was accompanied by a hydrogen migration from C-6 to C-7 as shown in Scheme 8.[170]



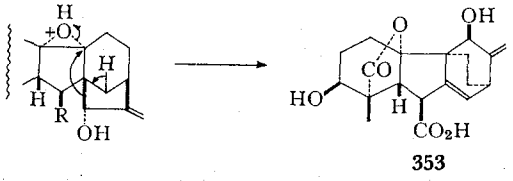
Scheme 8

Compound **348** derived from abietic acid was subjected to benzilic acid rearrangement to yield benzilic acid derivative **349**, acid anhydrides **350** and **351**. Benzilic acid **349** on acetylation gave rise to an epimerization at C-6 to yield **350**.[171] These facts resulted in the revise of the previously assigned structure **352**.[173]



348 349 350 351 352

Structure **353** including absolute configuration was assigned to the antheridium-inducing factor, antheridiogen-An, isolated from culture media of the fern *Anemia phyllitidis*. The biogeneisis was suggested as shown in Scheme 9.[173]



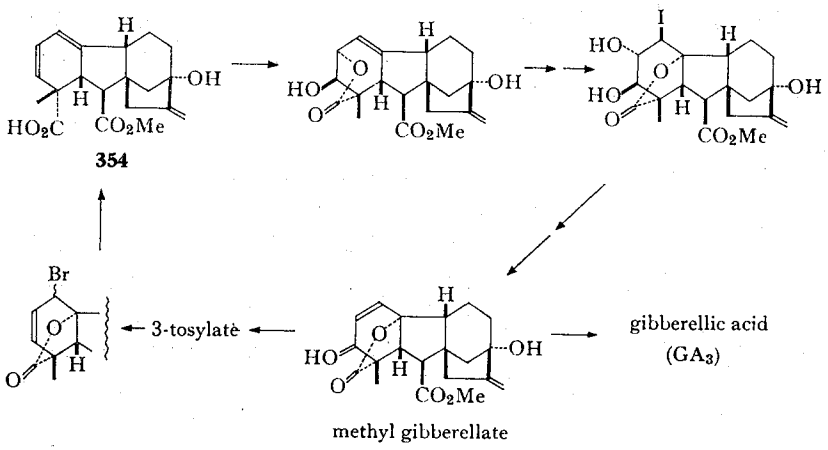
353

Scheme 9

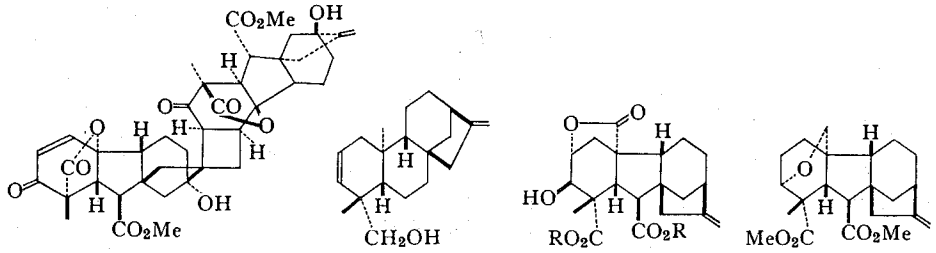
Compound **354** derived from methyl gibberellate was converted back to gibberellic acid by the following route shown in Scheme 10.[174]

The enone **317** was shown to be photoreactive in solid state yielding a cyclobutane photodimer as a main product, for which structure **355** was proposed.[175]

The structure of a new metabolite formed by feeding *ent*-2,16-kauradien-19-ol (**356**) to *Gibberella fujikuroi* was determined as **357** by chemical conversions of its methyl ester

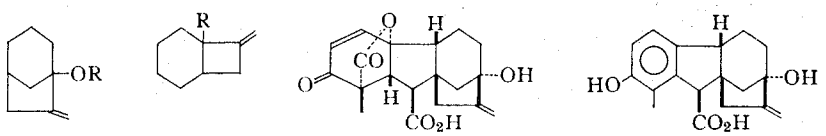


Scheme 10

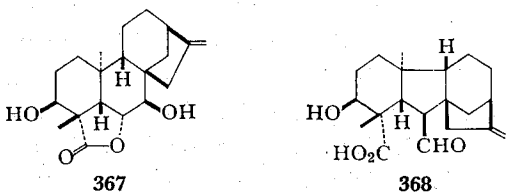


(**358**) to compound **359** *via* two routes. A bioassay against d_1-maize showed a significant response which was comparable with that observed with gibberellins A_5, A_6, A_{18}, and A_{22}.[176]

1-Hydroxy-7-methylene bicyclo [3.2.1.] octane (**360**), a gibberellin-steviol C/D ring model, was synthesized *via* **361**, **362**, **363**, and **364**.[177]

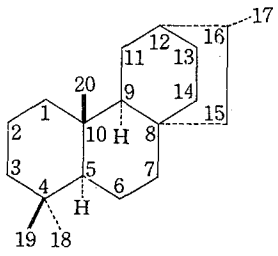


The enone **365** was also photoreactive in solid state and converted into the A-ring aromatized product **366**.[178]



A partial synthesis of aldehyde **368**, a probable biosynthetic intermediate of gibberellins, from the lactone **367** isolated from the culture filtrate of *G. fujikuroi* was carried out.[179]

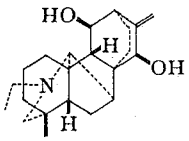
XII. ATISANE DERIVATIVES



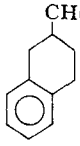
Atisane

The crystal and molecular structure of denudatine was established as **369** by an X-ray analysis.[180] The tricyclic dienones **371**, **372**, and **374** were prepared by the Ar_1-6 cyclization of a diastereomeric mixture of **370** and of **373**.[181]

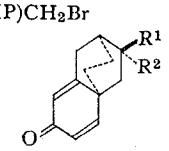
The structure of an *Aconitum* alkaloid, miyaconitine, was determined by the X-ray analysis of crystals of the hydrobromide dihydrate. It was established that



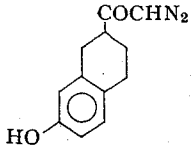
369



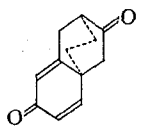
370



371: R^1=OH, R^2=H
372: R^1=H, R^2=OH



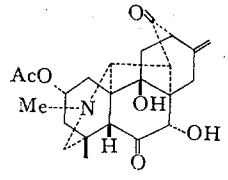
373



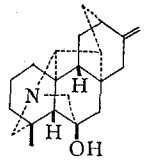
374

miyaconitine has structure **375** and is a novel type of *Aconitum* alkaloid.[182]

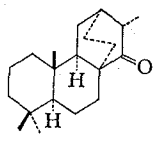
The structure of spiradine A, initially isolated from the shrub *Spiraea japonica*,[183] was determined as **376** by the X-ray analysis of its methiodide.[184]



375



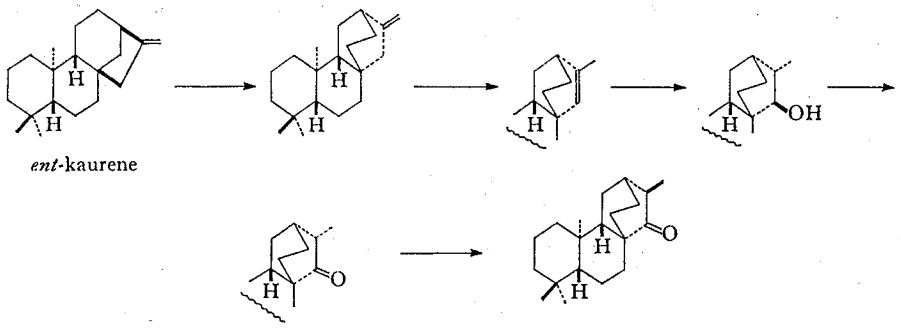
376



377

Synthesis of a neoatisiranone, the enantiomer of a ketone obtained by the acid-catalyzed rearrangement of isophyllocladene epoxide, confirmed the constitution and stereochemistry of the ketone to be **377**. The route of the synthesis of the enatiomer of **377** is shown in Scheme 11.[185]

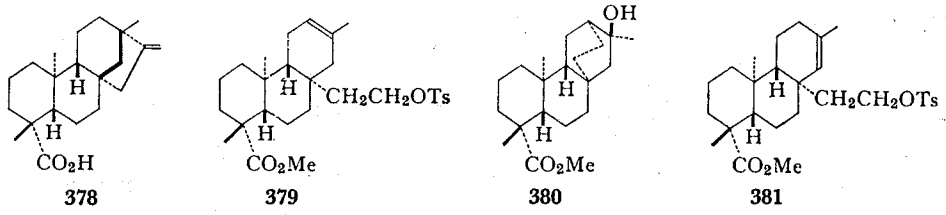
Structure modifications of isosteviol (**378**) were investigated. Various 15- and 16-substituted methyl *ent*-beyeran-19-oates were prepared by means of functional interconversion in ring D. Ring C functionalization at positions 12 and 14 was accomplished by degradation to the unsaturated tricyclic tosylate esters **379** and **381** followed by recyclization Thus, buffered formolysis of **379** at room temperature afforded after partial hydrolysis *ent*-atisane derivative **380**. Formolysis of **381** at 80° gave *ent*-beyerane derivative **382**. Dehydration of **380** produces the exocyclic and endocyclic unsaturated



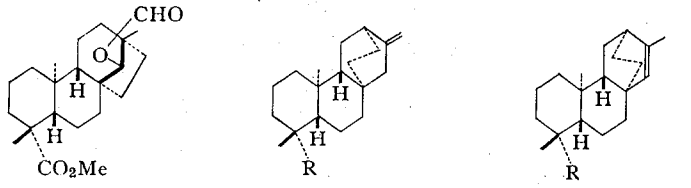
ent-kaurene

Scheme 11

esters **383** and **384** which were separately converted into atisirene (**385**) and isoatisirene (**386**).[186]



378 **379** **380** **381**

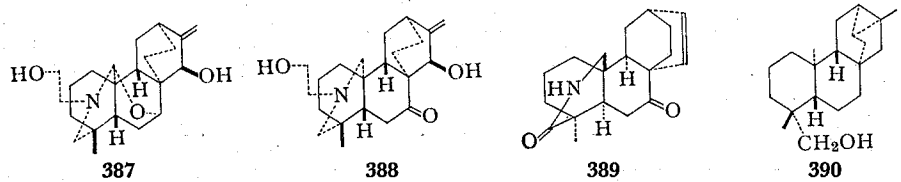


382

383: R=CO_2Me
385: R=Me

384: R=CO_2Me
386: R=Me

A number of optically active tetracyclic intermediates possessing a carbonyl group at C-7 and a bicyclo [2.2.2] octane C,D-ring system for a synthetic approach to the diterpenoid alkaloids, ajaconine (**387**) and atidine (**388**), was synthesized from methyl O-methyl–7-ketopodocarpate. The ORD curves of these compounds provided interesting insight into the effect of C,D ring substituents on the conformation of the B-ring. A pentacyclic unsaturated ketolactam **389**, useful for further conversion to ajaconine and atidine, was synthesized.[189]

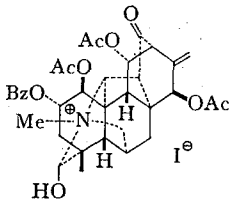


387 **388** **389** **390**

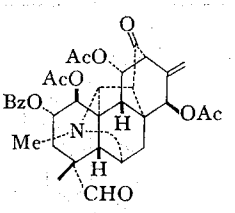
The Eu(dpm)$_3$-shifted NMR spectrum of a new diterpene provided independent evidence for its structure **390**.[188]

An X-ray crystallographic study of vakognavine hydroiodide clarified its structure

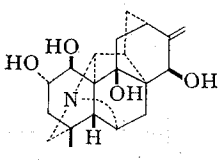
to be **391**. That vakognavine base, an alkaloid of *Aconitum palmatum,* exists as **392** was shown by the presence of an aldehyde signal in the NMR spectrum.[189]



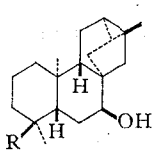
391



392



393

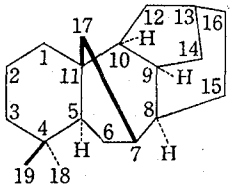


394: R=CH_2OH
395: R=Me

The structure of hypognavinol was established as **393** by a single crystal X-ray analysis of its methiodide.[190]

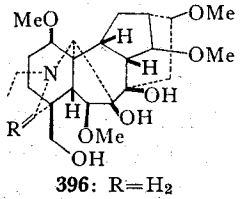
Two new diterpenes, trachinodiol (**394**) and trachinol (**395**), were isolated from *Sideritis canariensis* and characterized.[191]

XIII. ACONANE DERIVATIVES

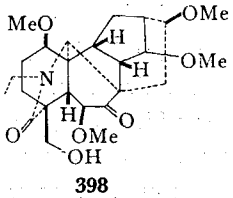


Aconane

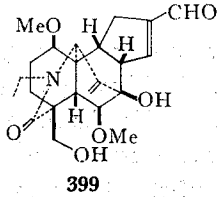
The lactam **397** derived from lycoctonine (**396**) underwent acid-catalyzed dehydration of the *vic*-glycol system to give anhydro-oxolycoctonine (**398**). More vigorous acid treatment converted these (**397** and **398**) to lycoctamone (**399**). Proof of structure and a mechanism for the formation of this compound were presented. The analogous derivatives were also produced from other alkaloids of the lycoctonine family.[192]



396: R=H_2
397: R=O



398

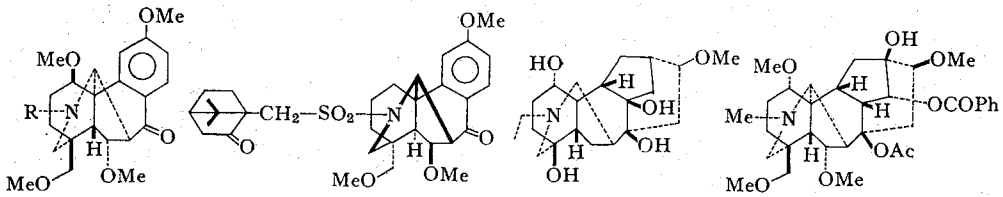


399

Resolution of the racemic relay compound synthesized as a key intermediate for the total synthesis of delphinine was accomplished. Thus, racemic compound **400** was treated with L-camphorsulfonyl chloride to yield sulfonamide **401** and optically active base **400** which was proved to be identical with the corresponding degradation product from delphinine.[193]*

The *N*-acyl group of oxonitine, an oxidation product of aconitine, was found to be a mixture of *N*-acetyl and *N*-formyl groups. It was rigorously proved that the aromatization product of oxonitine was a mixture of **402** and **403** and consequently also "oxonitine" must be a mixture of the *M*-acetyl and *N*-formyl derivatives.[194]

* See also ref. 197.



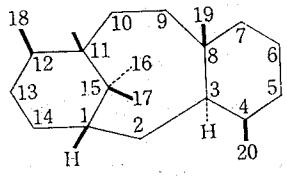
400: R=H
402: R=CHO
403: R=Ac

401 **404** **405**

The structure **404** for an alkaloid lapaconidine separated from *Aconitum leucostomum* was proposed on the basis of chemical and spectroscopic data.[195] An investigation on pyrolysis of *Aconitum* alkaloids was carried out.[196]

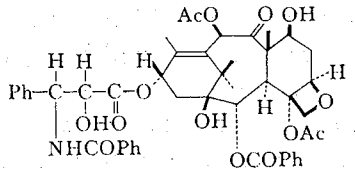
Configuration of the ring A methoxyl group in delphinine and aconitine was reversed and thus delphinine was shown to be prepresented by **405**, on the basis of the X-ray crystallography of a degradation product oxalate derivative.[197]

XIV. TAXANE DERIVATIVES



Taxane

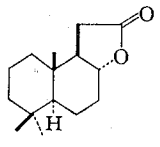
The structure of a novel compound named taxol, isolated from the stem bark of *Taxus brevifolia,* was determined as **406**. Taxol has potent antileukemic and tumor inhibitory properties and is the first compound possessing taxane ring which has been demonstrated to have such activity.[198]



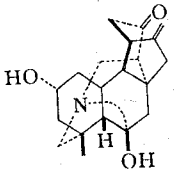
406

XV. THE OTHERS

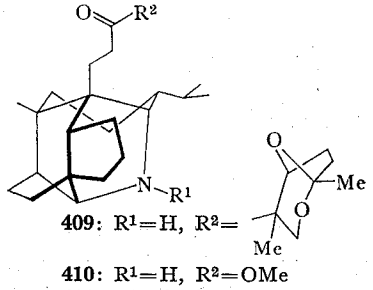
Norambreinolide (**407**) which can be considered a degradation product of diterpenoid was isolated from cigar tobacco.[198]



407



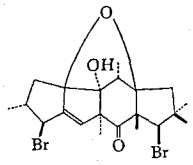
408



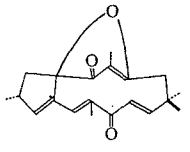
409: R^1=H, R^2=
410: R^1=H, R^2=OMe
411: R^1=$COCH_2Br$, R^2=OMe

The X-ray crystallographic analysis of delnudine hydrochloride established the structure of the alkaloid as **408**.[199] Fifty-one resin acid methyl esters (22 with abietane, 6 with pimarane, 8 with isopimarane, 8 with labdane, and 7 with miscellaneous skeletons) were purified to 99% by an appropriate combination of $AgNO_3$-alumina column, gel permeation, and preparative gas-liquid chromatography and their NMR, IR, UV, and mass spectra recorded.[200]

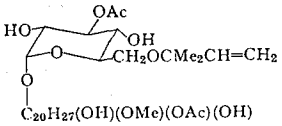
Structures including absolute configurations of new alkaloids, secodaphniphylline and methyl homosecodaphniphyllate, isolated from *Daphniphyllum macropodum,* were determined as **409** and **410**, respectively, by the X-ray analysis of methyl *N*-bromoacetylhomosecodaphniphyllate (**411**).[201] Crystal structure of jatrophone dihydrobromide was established as **412** and the original jatrophone as **413**.[202]



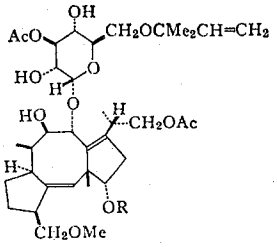
412



413



414



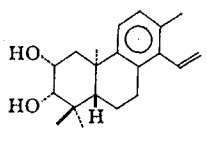
415: R=H

416: R=I-C$_6$H$_4$-SO$_2$-

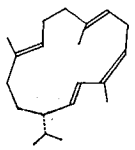
Fusicoccin, a phytotoxic glycoside metabolite by *Fusiciccum amygdali,* was shown to be **414**.[203] Combining X-ray crystallography of the aglycone derivative with chemical evidence afforded the complete structure **415** of fusicoccin.[204] Independently, the X-ray crystallography of *p*-iodobenzenesulfonate was carried out and the structure **416** was established for fusicoccin A *p*-iodobenzenesulfonate.[205]

The CD of some tertiary carboxylic acids was examined over the range −10 to −160°. The percentage changes in $\Delta\epsilon$ were ca. 25% for diterpene-4β(axial)-carboxylic acids and very small for diterpene-4α(equatorial) carboxylic acids. The examined compounds are 18- and 19-oic acids or their methyl esters of podocarpane, labdane, abietane, cassane, and kaurane.[206]

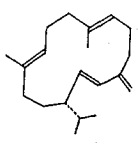
Detailed evidence supported the structure **417** for cleistanthol obtained from heartwood of *Cleistanthus schlechteri var. schlechteri.*[207]



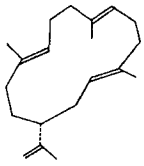
417



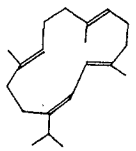
418



419



420



421

A method for preparing ^{3}H-labeled ryanodine was published. Thus, the alkaloid was brominated, and the bromoryanodines were separated by thin layer chromatography. The bromo-derivatives were hydrogenated to give ryanodine. They were treated with

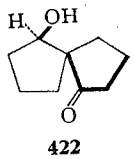
^3H to yield labeled ryanodine. Isotope exchange did not occur when the labeled alkaloid was incubated in aq. media at pH 7.0 and 30°.[208]

A short review on the structure and synthesis of diterpenes was published in Japanese.[209]

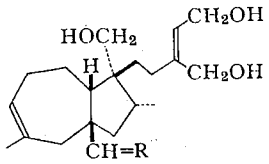
Stereochemistry of cembrene and related diterpenoids was investigated. The unconjugated double bonds in cembrene (**418**), isocembrene (**419**), and neocembrene (**420**) had the *trans* configuration; the conjugated trisubstituted double bond of cembrene the *cis* configuration. The asymmetric center of neocembrene was R. Hydrogenations of cembrene and isocembrene were also studied.[210]

α-, β-, and γ-Pinacenes, isolated from oleoresin of *Pinus koraiensis* and *P. sibirica* by column chromatography were stereoisomers of α-pinacene (**421**), which differed in the configuration of their conjugated double bonds. Isomerization of cembrene (**418**) with iodine in CCL_4 gave 7% α-pinacene, 45% β-pinacene, and 8% γ-pinacene.[211]

Starting from compound **422**, compound **423** was synthesized, which represented the main skeleton of the ginkgolides.[212]

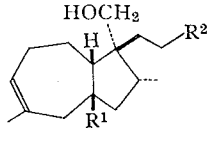


422

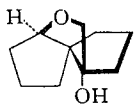


424: R=O

425: R=NNHSO$_2$–C$_6$H$_4$–Br

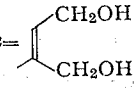


426: R^1=CHO, R^2=

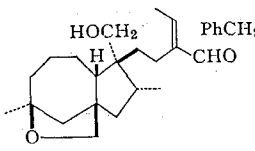


423

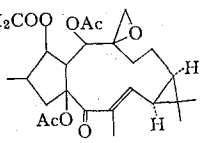
427: R^1=CH$_2$OH, R^2=



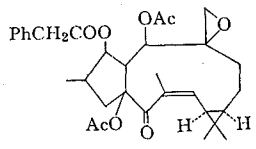
The crystal structure of portulal *p*-bromophenylsulfonyl-hydrazone was determined by a three-dimensional X-ray analysis as **425**. Thus, the absolute structure of portulal, a plant growth regulator from *Portulaca grandiflora,* was established as **424**.[213] Portulal was oxidized with active manganese dioxide to give a γ-lactone **426**. The aldehyde group of portulal was reduced with $LiALH_4$ to yield portulol (**427**), which was converted to an αβ-unsaturated aldehyde **428**. The physiological activity of these compounds was tested.[214]



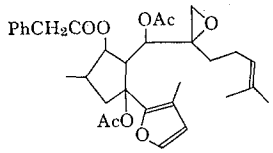
428



429



430



431

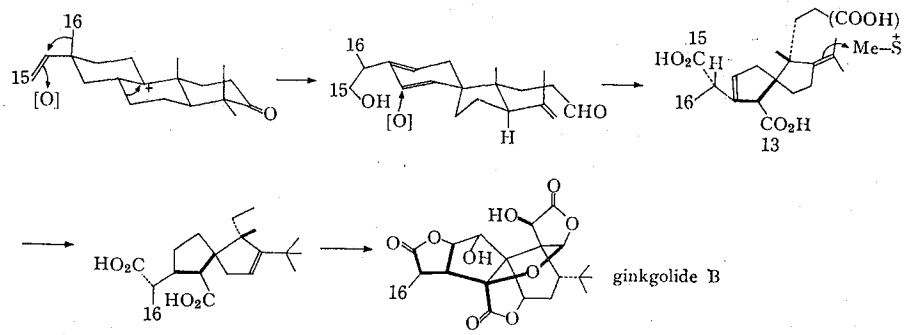
Correlation of Mills' and Brewster's rules with the Cotton effects of cyclic olefins was investigated using 74 substituted olefins including several diterpenoids having exocyclic methylene group in their molecule.[215] A review of the synthesis of polyprenyl alcohols was published.[216] In a review "Chemicals from plants", stevioside and steviol

are described.[217]

Photochemistry of the extended conjugated system, 3-oxoprop-1-enylcyclopropane, of the diterpene, epoxylathyrol (**429**) was investigated. The system was shown to be isomerized by light to the *cis*, non-planar, enone **430**, and thence to the fragmentation product **431**, a furan.[218]

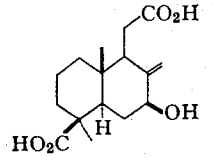
Detailed analysis of a number of exocyclic olefins showed that the sign of $\pi \rightarrow \pi^*$ absorption can be related to absolute configuration by use of the Octant rule. As the diterpenes, *ent*-kaurene, phyllocladene, and 13(15)-abieten-18-oic acid were used for this investigation.[219]

Biosynthesis of ginkgolide B in *Gingko biloba* was investigated, and its diterpenoid nature and the origin of the *tert*-butyl group were confirmed. The biosynthetic pathway is shown in Scheme 12.[220]

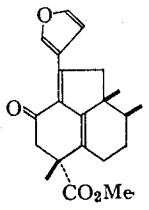


Scheme 12

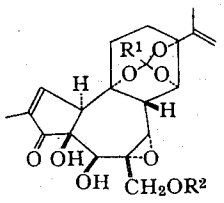
The third C_{16} terpenoid metabolite, LL-Z1271β, was isolated from the fermentations of an *Acrostalagmus* species, and characterized as **432**.[221]



432

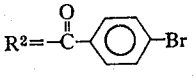


433



434: $R^1=\underset{H}{\overset{H}{C}}=C-CH=CH-(CH_2)_8-Me$, $R^2=H$

435: $R^1=\underset{H}{\overset{H}{C}}=C-CH=CH-(CH_2)_8-Me$,

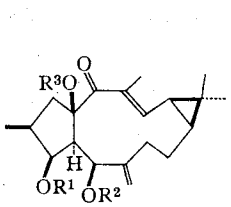


The structure of chettaphanin-II isolated from *Adenochlaena siamensis* was determined to be **433**. The stereochemistry was established by the X-ray analysis.[222]

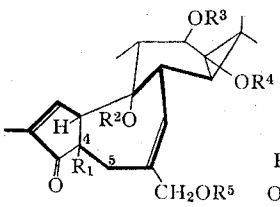
Huratoxin, a piscicidal constituent, was isolated from the sap of *Hura crepitans*.

The results of some degradations of huratoxin, coupled with other chemical and spectral data, led to the structure **434** for huratoxin, and its absolute configuration was established by X-ray analysis of *p*-bromobenzoate **435**.[223,224]

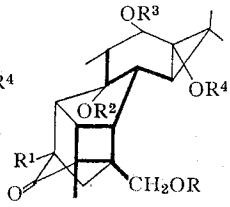
A diacetate-benzoate **437** and a diacetate-nicotinoate **438** of new diterpene lathyrol **436** and a monoester of diterpene ingenol were isolated from the seed oil or latex of *Euphorbia lathyris*. The biogenesis of the diterpene from Euphorbiaceae was discussed.[225]



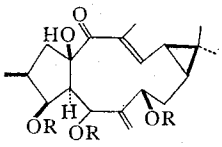
436: $R^1=R^2=R^3=H$
437: $R^1-R^3=2Ac$, 1Bz
438: $R^1-R^3=2Ac$, $1COC_6H_4N$



439



440



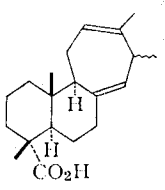
441: R=H
442: R=Ac

A short review for phorbol esters and their physiological activity was published in Japanese.[226] Stimulation for choline incorporation was recognized in phorbol esters.[227]

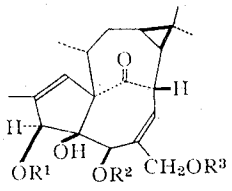
Irradiation of several 4α-phorbol derivatives (**439**) with UV light of 254 nm yielded the isomeric lumi-products (**440**).[228]

Structure **441** of 7-hydroxylathyrol, a further diterpene from *Euphorbia lathyris*, was confirmed and extended by X-ray diffraction analysis of **442**.[229]

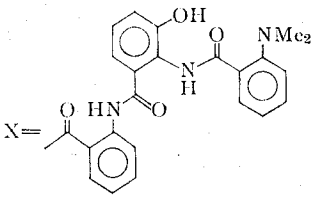
The structure of strobic acid, a new resin acid from *Pinus strobus*, was shown to be **443**.[230]



443



444: $R^1=X$, $R^2=H$, $R^3=Ac$
445: $R^1=R^2=H$, $R^3=X$



Isolation of two new alkaloids, milliamines A and B, from the roots of *Euphorbia Millii* and their structure elucidation were reported. Milliamines A and B were assiged structures **444** and **445**, respectively.[231]

REFERENCES

(1) E. Fujita, *Bull. Inst. Chem. Res. Kyoto Univ.*, **43**, 278 (1965).
(2) E. Fujita, *ibid.*, **44**, 239 (1966).
(3) E. Fujita, *ibid.*, **45**, 229 (1967).
(4) E. Fujita and T. Fujita, *ibid.*, **47**, 522 (1969).
(5) E. Fujita, *ibid.*, **48**, 111 (1970).
(6) E. Fujita, *ibid.*, **48**, 294 (1970).
(7) E. Fujita, *ibid.*, **49**, 423 (1971).

(8) M. Julia, *Accounts of Chem. Res.*, **4**, 386 (1971).
(9) K. Mori, K. Saeki, and M. Matsui, *Agr. Biol. Chem.*, **35**, 956 (1971).
(10) E. Wenkert and J. de Pavia, *An Acad. Brasil. Cienc.* **43**, 579 (1971). (*Chem. Abstr.*, **77**, 140323x [1972].)
(11) R. C. Cambie, W. A. Denny, T. R. Klose, and L. N. Mander, *Australian J. Chem.*, **24**, 99 (1971).
(12) R. C. Cambie, R. A. Franich, and T. J. Fullerton, *ibid.*, **24**, 593 (1971).
(13) R. C. Cambie, D. R. Crump, W. A. Denny, and T. J. Fullerton, *ibid.*, **24**, 1237 (1971).
(14) R. C. Cambie and K. P. Mathai, *ibid.*, **24**, 1251 (1971).
(15) T.-L. Ho, *Can. J. Chem.*, **49**, 2501 (1971).
(16) A. Tahara, Y. Ohtsuka, N. Umino, K. Nagasawa, and K. Hirao, *Chem. Pharm. Bull.* (*Tokyo*), **19**, 1756 (1971).
(17) A. Tahara and Y. Ohtsuka, *ibid.*, **19**, 1768 (1971).
(18) U. R. Ghatak and N. R. Chatterjee, *Indian J. Chem.*, **9**, 804 (1971).
(19) H. W. Whitlock, Jr., P. B. Reichardt, and F. M. Silver, *J. Amer. Chem. Soc.*, **93**, 485 (1971).
(20) H. W. Whitlock, Jr. and L. E. Overman, *ibid.*, **93**, 2247 (1971).
(21) U. R. Ghatak and N. R. Chatterjee, *J. Chem. Soc.* (*C*), 190 (1971).
(22) J. W. A. Findlay and A. B. Turner, *ibid.* **547** (1971).
(23) W. Herz and V. Baruaro, *J. Org. Chem.* **36**, 3271 (1971).
(24) C. S. Manchand, *Chem. Comm.*, 667 (1971).
(25) S. G. Levine, I. Y. Chen, A. T. McPhail, and P. Coggon, *Tetrahedron Lett.*, 3459 (1971).
(26) S. W. Pelletier, Y. Ichinohe, and D. L. Herald, Jr., *ibid.*, 4179 (1971).
(27) T. Norin, S. Sundin, and O. Theander, *Acta Chem. Scand.*, **25**, 607 (1971).
(28) Y. Sayama, K. Kyogoku, and H. Murayama, *Agr. Biol. Chem.*, **35**, 1068 (1971).
(29) J. R. Mahajan and G. A. L. Ferreira, *An. Acad. Brasil. Cienc.*, **43**, 611 (1971). (*Chem. Abstr.*, **77**, 140339g [1972].)
(30) R. M. Carman and H. C. Deeth, *Australian J. Chem.*, **24**, 353 (1971).
(31) R. M. Carman and W. Craig, *ibid.*, **24**, 361 (1971).
(32) R. C. Cambie, K. N. Joblin, and A. F. Preston, *ibid.*, **24**, 583 (1971).
(33) R. M. Carman and H. C. Deeth, *ibid.*, **24**, 1099 (1971).
(34) R. M. Carman and W. Craig, *ibid.*, **24**, 1919 (1971).
(35) L. Ruzicka and M. M. Janot, *Helv. Chim. Acta*, **14**, 645 (1931).
(36) P. C. Cambie, K. N. Joblin, and A. F. Preston, *Australian J. Chem.*, **24**, 2365 (1971).
(37) R. M. Carman and W. J. Craig, *ibid.*, **24**, 2379 (1971).
(38) S. Yamamura and Y. Hirata, *Tetrahedron*, **19**, 1485 (1963).
(39) S. Yamamura and Y. Hirata, *Bull. Chem. Soc. Japan*, **44**, 2560 (1971); H. Matsuda, Y. Tomiie, S. Yamamura, and Y. Hirata, *Chem. Comm.*, 898 (1967).
(40) T. Kato, S. Kanno, M. Tanemura, A. Kurozumi, and Y. Kitahara, *Bull. Chem. Soc. Japan*, **44**, 3182 (1971).
(41) B. Rindone and C. Scolastico, *J. Chem. Soc.* (*C*), 3339 (1971).
(42) V. A. Raldugin and V. A. Pentegova, *Khim. Prir. Soedin.*, 595 (1971). (*Chem. Abstr.*, **76**, 153961h [1972].)
(43) M. Ferrari, U. M. Pagnoni, F. Pelizzoni, V. Lukeš, and G. Ferrari, *Phytochemistry*, **10**, 905 (1971).
(44) D. F. Zinkel, J. K. Toda, and J. W. Rowe, *ibid.*, **10**, 1161 (1971).
(45) C. Tabacik and Y. Laporthe, *ibid.*, **10**, 2147 (1971); *Tetrahedron Lett.*, 3141 (1968).
(46) C. Tabacik and M. Bard, *Phytochemistry*, **10**, 3093 (1971).
(47) B. P. Spalding, D. F. Zinkel, and D. R. Roberts, *ibid.*, **10**, 3289 (1971).
(48) W. R. Chan, D. R. Taylor, C. R. Willis, R. L. Bodden, and H.-W. Fehlhaber, *Tetrahedron*, **27**, 5081 (1971); *Tetrahedron Lett.*, 4803 (1968).
(49) P. F. Vlad and A. G. Russo, *Zhur. Obshchei Khimi*, **41**, 232 (1971). (*Chem. Abstr.*, **75**, 2067b [1971].)
(50) R. Caputo, L. Mangoni, L. Previtera, and R. Iaccarino, *Tetrahedron Lett.*, 3731 (1971).
(51) J. T. Pinhey, R. F. Simpson, and I. L. Batey, *Australian J. Chem.*, **25**, 2621 (1971).
(52) G. Aguilar-Santos, *Chem. and Ind.* (*London*), 1074 (1965).
(53) L. Brehm, O. J. R. Hodder, and T. G. Halsall, *J. Chem. Soc.* (*C*), 2529 (1971).
(54) H.-Y. Hsü, Y. P. Chen, and H. Kakisawa, *Phytochemistry*, **10**, 2813 (1971).
(55) M. Ferrari, F. Pellizzoni, and G. Ferrari, *ibid.*, **10**, 3267 (1971).

(56) T. Anthonsen and G. Bergland, *Acta Chem. Scand.*, **25**, 1924 (1971).
(57) W. B. T. Cruse, M. N. G. James, A. A. Al-Shamma, J. K. Beal, and R. W. Doskotch, *Chem. Comm.*, 1278 (1971).
(58) N. Kato, S. Shibayama, K. Munakata, and C. Katayama, *ibid.*, 1632 (1971).
(59) C. Nishino, K. Kawazu, and T. Mitsui, *Tetrahedron Lett.*, 1541 (1971).
(60) T. Norin and B. Winell, *Acta Chem. Scand.*, **25**, 611 (1971).
(61) R. C. Cambie, R. J. Madden, and J. C. Parnell, *Australian J. Chem.*, **24**, 217 (1971).
(62) V. N. Aiyar and T. R. Seshadri, *Indian J. Chem.*, **9**, 1055 (1971). (*Chem. Abstr.*, **76**, 14741y [1972].)
(63) T. McCreadie and K. H. Overton, *J. Chem. Soc.* (*C*), 312 (1971).
(64) T. McCreadie, K. H. Overton, and A. J. Allison, *ibid.*, 317 (1971).
(65) W. H. Hui, K. K. Ng, N. Fukamiya, M. Koreeda, and K. Nakanishi, *Phytochemistry*, **10**, 1617 (1971).
(66) T. Norin and B. Winell, *ibid.*, **10**, 2818 (1971).
(67) A. K. Banerjee, T. Nakano, and M. C. de Hazos, *Rev. Latinoamer. Quim.*, **2**, 135 (1971).
(68) N. Kiriyama, Y. Yamamoto, and Y. Tsuda, *Chem. Comm.*, 37 (1971).
(69) N. Kiriyama, Y. Yamamoto, and Y. Tsuda, *Yakugaku Zasshi*, **91**, 1078 (1971).
(70) P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burgess, *J. Amer. Chem. Soc.*, **93**, 3044 (1971).
(71) T. Nakano and A. K. Banerjee, *Tetrahedron Lett.*, 165 (1971).
(72) A. Blade-Font, T. De Mas Rocabayera, and S. Aguik Salomo, *Afinidad*, **28**, 1301 (1971). (*Chem. Abstr.*, **76**, 127180h [1972[].)
(73) R. C. Cambie and R. A. Franich, *Australian J. Chem.*, **24**, 117 (1971).
(74) R. C. Cambie and R. A. Franich, *ibid.*, **24**, 571 (1971).
(75) R. C. Cambie and T. J. Fullerton, *ibid.*, **24**, 2611 (1971).
(76) T. Matsumoto, Y. Tachibana, J. Uchida, and K. Fukui, *Bull. Chem. Soc. Japan*, **44**, 2766 (1971).
(77) C. Kokkinos and Chr. Marcopoulos, *Bull. Soc. Chim. France*, 863 (1971).
(78) R. F. Severson, W. H. Schuller, and R. V. Lawrence, *Can. J. Chem.*, **49**, 4027 (1971).
(79) P. Catsoulacos, *Chem. Therap.*, **6**, 449 (1971).
(80) I. I. Bardyshev and V. Ya. Paderin, *Dokl. Akad. Nauk Beloruss. SSR*, **15**, 823 (1971). (*Chem. Abstr.*, **76**, 4027f [1972].)
(81) P. Rüedi and C. H. Eugster, *Helv. Chim. Acta*, **54**, 1606 (1971).
(82) A. S. Levinson, *J. Org. Chem.*, **36**, 3062 (1971).
(83) W. Herz and V. Baburao, *ibid.*, **36**, 3899 (1971).
(84) P. F. Vlad, A. G. Russo, M. N. Koltsa, and V. N. Paukov, *Khim. Prir. Soedin.*, **7**, 20 (1971).
(85) A. S. Romanova, G. F. Pribylova, P. I. Zakharov, V. I. Sheichenko, and A. I. Ban'lovskii, *ibid.*, **7**, 199 (1971). (*Chem. Abstr.*, **75**, 36375p [1971].)
(86) M. P. Irismetov, M. I. Goryaev, and R. N. Bagmanova, *ibid.*, **7**, 671 (1971). (*Chem. Abstr.*, **76**, 85968p [1972].)
(87) L. D. Yakkontova, V. I. Sheichenko, and O. N. Tolkachev, *ibid.*, **7**, 416 (1971). (*Chem. Abstr.*, **75**, 141010p [1971].)
(88) C. Tabacik and C. Poisson, *Phytochemistry*, **10**, 1639 (1971).
(89) J. W. Rowe, A. Nagasampagi, A. W. Burgstahler, and J. W. Fitzsimmons, *ibid.*, **10**, 1647 (1971).
(90) M. Tateishi, T. Kusumi, and H. Kakisawa, *Tetrahedron*, **27**, 237 (1971).
(91) I. I. Bardyshev and V. Ya. Paderin, *Vestsi Akad. Nauk Belarus. SSR, Ser. Khim. Navuk*, 108 (1971). (*Chem. Abstr.*, **74**, 125868y [1971].)
(92) S. W. Pelletier and D. L. Herald, Jr., *Chem. Comm.*, 10 (1971).
(93) R. C. Cambie and K. P. Mathai, *ibid.*, 154 (1971).
(94) T. Hayashi, T. Handa, M. Ohashi, and H. Kakisawa, *ibid.*, 542 (1971).
(95) R. H. Burnell and M. Moisnas, *ibid.*, 897 (1971).
(96) G. Mischer and R. C. A. Rottländer, *Tetrahedron Lett.*, 1295 (1971).
(97) R. Rottländer, *ibid.*, 4127, 4129 (1969).
(98) S. Ito, M. Sunagawa, M. Kodama, H. Honma, and T. Takahashi, *Chem. Comm.*, 91 (1971).
(99) S. Ito, M. Kodama, M. Sunagawa, M. Koreeda, and K. Nakanishi, *ibid.*, 855 (1971).
(100) M. N. Galbraith, D. H. S. Horn, and J. M. Sasse, *ibid.*, 1362 (1971).
(101) J. Friedrich-Fiechtl and G. Spiteller, *Chem. Ber.*, **104**, 3535 (1971).
(102) H. Hauth and D. Stauffacher, *Helv. Chim. Acta*, **54**, 1278 (1971).

(103) H. Hauth, P. Niklaus, and D. Stauffacher, *Helv. Chim. Acta.*, **54**, 1289 (1971).
(104) H. Hauth and D. Stauffacher, *ibid.*, **54**, 2197 (1971).
(105) R. L. Clarke, *Phytochemistry*, **10**, 851 (1971).
(106) E. Nilsson and O. Martensson, *Acta Chem. Scand.*, **25**, 1486 (1971).
(107) T. Anthonsen and S. Chantharasakul, *ibid.*, **25**, 1925 (1971).
(108) K. Mori and M. Matsui, *Agr. Biol. Chem.*, **35**, 918 (1971).
(109) K. Mori and M. Matsui, *Tetrahedron*, **22**, 879 (1966).
(110) B. R. Gonzalez, *An. Quim.*, **67**, 59 (1971). (*Chem. Abstr.*, **75**, 20674z [1971].)
(111) B. R. Gonzalez, *ibid.*, **67**, 73 (1971). (*Chem Abstr.*, **75**, 20673y [1971].)
(112) B. R. Gonzalez, *ibid.*, **67**, 85 (1971). (*Chem. Abstr.*, **75**, 20686e [1971].)
(113) S. von Kürten, S. auf dem Keller, P. Pachaly, F. Zymalkowski, G. Tauberger, and M. Moussawi, *Arch. Pharm.*, **304**, 753 (1971).
(114) E. Ali, P. P. G. Dastidar, and S. C. Pakrashi, *Indian J. Chem.*, **9**, 1166 (1971). (*Chem. Abstr.*, **76**, 14743a [1972].)
(115) E. Fujita and Y. Nagao, *J. Chem. Soc.* (*C*), 2902 (1971).
(116) R. A. Finnegan and P. L. Bachman, *J. Org. Chem.*, **36**, 3196 (1971).
(117) A. I. Kalinovskii, E. P. Serebryakov, A. V. Simolin, V. F. Kucherov, and O. S. Chizhov, *Org. Mass Spectrom.*, **5**, 33 (1971).
(118) I. T. U. Eshiet, A. Akisanya, and D. A. H. Taylor, *Phytochemistry*, **10**, 3294 (1971).
(119) F. T. Lew and C. A. West, *ibid.*, **10**, 2065 (1971).
(120) F. Piozzi, S. Passannati, M. P. Paternostro, and V. Sprio, *ibid.*, **10**, 1164 (1971).
(121) Z. O. Collera, M. C. Perezamador, and F. G. Jimenez, *Rev. Latinoamer. Quim.*, **2**, 129 (1971). [*Chem. Abstr.*, **76**, 99858q (1972).]
(122) A. M. Osman, M. B. E. Fayez, M. El-Garby Younes, M. H. A. El-Gammal, and A. Abdel Salam, *U. A. R. J. Chem.*, **14**, 15 (1971). [*Chem. Abstr.*, **77**, 88709m (1972).]
(123) M. Yasue, J. Sakakibara, and T. Kato, *Yakugaku Zasshi*, **91**, 358 (1971).
(124) T. Kato, J. Sakakibara, and M. Yasue, *ibid.*, **91**, 1194 (1971).
(125) M. Yasue, J. Sakakibara, and H. Ina, *ibid.*, **91**, 1252 (1971).
(126) a) J. L. Bretòn, A. G. Gonzàlez, J. M. Rocha, F. M. Panizo, B. R. Gonzàlez, and S. Valverde, *Tetrahedron Lett.*, 599 (1969).
b) B. R. Gonzàlez, S. Valverde, and J. M. Rocha, *Ana. Re. Soc. esp. Fis. Quim. B*, **66**, 503 (1970).
(127) F. Piozzi, P. Venturella, A. Bellino, M. P. Paternostro, B. R. Gonzàlez, and S. Valverdo, *Chem. and Ind.*, 962 (1971).
(128) D. J. Beames, T. R. Klose, and L. N. Mander, *Chem. Comm.*, 773 (1971).
(129) H. Hikino, M. Ogura, M. Fuzita, K. Ito, and T. Takemoto, *Chem. Pharm. Bull.* (*Tokyo*), **19**, 856 (1971).
(130) H. Hikino, T. Ohta, S. Koriyama, Y. Hikino, and T. Takemoto, *ibid.*, **19**, 1289 (1971).
(131) C.-H. Chen and T. Murakami, *ibid.*, **19**, 1498 (1971).
(132) H. Hikino, M. Ogura, and T. Takemoto, *ibid.*, **19**, 1980 (1971).
(133) J. H. Bateson and B. E. Cross, *Tetrahedron Lett.*, 3407 (1971).
(134) C.-M. Chen and T. Murakami, *ibid.*, 1121 (1971).
(135) R. D. H. Murray, R. W. Mills, and J. M. Young, *ibid.*, 2393 (1971).
(136) K. Kitadani, K. Ito, and A. Yoshikoshi, *Bull. Chem. Soc. Japan*, **44**, 3431 (1971).
(137) R. M. Coates and E. F. Bertram, *J. Org. Chem.*, **36**, 3722 (1971).
(138) K. H. Pegel, L. P. L. Piacenza, L. Phillips, and E. S. Waight, *Chem. Comm.*, 1346 (1971).
(139) N. Murofushi, T. Yokota, and N. Takahashi, *Agr. Biol. Chem.*, **35**, 441 (1971).
(140) T. Yokota, N. Murofushi, N. Takahashi, and S. Tamura, *ibid.*, **35**, 573 (1971).
(141) T. Yokota, N. Murofushi, N. Takahashi, and S. Tamura, *ibid.*, **35**, 583 (1971).
(142) H. Yamane, I. Yamaguchi, N. Murofushi, and N. Takahashi, *ibid.*, **35**, 1144 (1971).
(143) I. Macháčková and Z. Zmrhal, *Chemické Listry*, **65**, 1256 (1971).
(144) W. Nagata, M. Narisada, T. Wakabayashi, Y. Hayase, and M. Murakami, *Chem. Pharm. Bull.* (*Tokyo*), **19**, 1567 (1971).
(145) W. Nagata, T. Wakabayashi, M. Narisada, M. Yamaguchi, and Y. Hayase, *ibid.*, **19**, 1582 (1971).
(146) I. A. Gurvich, N. S. Kobrina, E. P. Serebryakov, and V. F. Kucherov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 2037 (1971). [*Chem. Abstr.*, **76**, 24944f (1972).]
(147) (a) W. Nagata, T. Wakabayashi, Y. Hayase, M. Narisada, and S. Kamata, *J. Amer. Chem. Soc.*,

92, 3202 (1970); (b) W. Nagata, T. Wakabayashi, M. Narisada, Y. Hayase, and S. Kamata, *J. Amer. Chem. Soc.* **93**, 5740 (1971).
(148) B. E. Cross and J. C. Stewart, *J. Chem. Soc.* (*C*), 245 (1971).
(149) D. M. Harrison and J. MacMillan, *ibid.*, 631 (1971).
(150) B. E. Cross and I. L. Gatfield, *ibid.*, 1539 (1971).
(151) B. E. Cross and R. E. Markwell, *ibid.*, 2980 (1971).
(152) L. J. Dolby, S. Esfandiari, C. A. Elliger, and K. S. Marshall, *J. Org. Chem.*, **36**, 1277 (1971).
(153) C. A. Maier, J. A. Kapecki, and I. C. Paul, *ibid.*, 1299 (1971).
(154) H. W. Thompson, *ibid.*, **36**, 2577 (1971).
(155) F. E. Ziegler and M. E. Condon, *ibid.*, **36**, 3707 (1971).
(156) A. Tahara, T. Nakata, and Y. Ohtsuka, *Nature*, **233**, 619 (1971).
(157) H. Fukui, K. Koshimizu, and T. Mitsui, *Phytochemistry*, **10**, 671 (1971).
(158) R. C. Durley, J. MacMillan, and R. J. Pryce, *ibid.*, **10**, 1891 (1971).
(159) T. Yokota, N. Murofushi, N. Takahashi, and M. Katsumi, *ibid.*, **10**, 2943 (1971).
(160) G. Schneider, G. Sembdner, I. Focke, and K. Schreiber, *ibid.*, **10**, 3009 (1971).
(161) W. Nagl, *Planta*, **96**, 145 (1971).
(162) G. W. M. Barendse, *ibid.*, **99**, 290 (1971).
(163) J. D. Ross and J. W. Bradbeer, *ibid.*, **100**, 288 (1971).
(164) J. D. Ross and J. W. Bradbeer, *ibid.*, **100**, 303 (1971).
(165) R. J. Jones, J. L. Stoddart, J. MacMillan, and C. Cloke, *ibid.*, **101**, 231 (1971).
(166) I. D. J. Phillips, *ibid.*, **101**, 277 (1971).
(167) N. Takahashi, *Shokubutsu no Kagaku Chosetsu* (*Chemical Regulation of Plants*), **6**, 190 (1971).
(168) K. Mori, *Tetrahedron*, **27**, 4907 (1971).
(169) I. A. Gurvich, N. S. Kobrina, E. P. Serebryakov, and V. F. Kucherov, *ibid.*, **27**, 5901 (1971).
(170) J. R. Hanson and J. Hawker, *Chem. Comm.*, 208 (1971).
(171) A. Tahara, T. Nakata, Y. Ohtsuka, and S. Takada, *Chem. Pharm. Bull.* (*Tokyo*), **19**, 2653 (1971).
(172) J. F. Grove and B. J. Riley, *J. Chem. Soc.*, 1105 (1961).
(173) K. Nakanishi, M. Endo, U. Näf, and LeRoy F. Johnson, *J. Amer. Chem. Soc.*, **93**, 5579 (1971).
(174) E. J. Corey, T. M. Brennan, and R. L. Carney, *ibid.*, **93**, 7316 (1971).
(175) G. Adam, *Tetrahedron Lett.*, 1357 (1971).
(176) I. F. Cook, P. R. Jefferies, and J. R. Knox, *ibid.*, 2157 (1971).
(177) F. E. Ziegler and J. A. Kloek, *ibid.*, 2201 (1971).
(178) G. Adams and B. Voigt, *ibid.*, 4601 (1971).
(179) P. Hedden and J. MacMillan, *ibid.*, 4939 (1971).
(180) F. Brisse, *Acta Cryst.*, **B27**, 1047 (1971).
(181) B. J. Beames and L. N. Mander, *Australian J. Chem.*, **24**, 343 (1971).
(182) H. Shimanouchi, Y. Sasada, and T. Takeda, *Bull. Chem. Soc. Japan*, **44**, 3020 (1971).
(183) V. I. Frolova, A. I. Bankovskii, A. D. Kuzovkov, and M. M. Molodozhnikov, *Med. Prom. S. S. S. R.*, **18**, 19 (1964).
(184) K. Sasaki, N. Sakabe, and Y. Hirata, *J. Chem. Soc.* (*B*), 354 (1971).
(185) P. A. Gunn, R. McCrindle, and R. G. Roy, *J. Chem. Soc.* (*C*), 1018 (1971).
(186) R. M. Coates and E. F. Bertram, *J. Org. Chem.* **36**, 2625 (1971).
(187) J. B. Nabors, D. H. Miles, B. Kumar, and L. H. Zalkov, *Tetrahedron*, **27**, 2385 (1971).
(188) O. Achmatowicz, Jun., A. Ejchart, J. Jurczak, L. Kozerski. and J. St. Pyrek, *Chem. Comm.*, 98 (1971).
(189) S. W. Pelletier, K. N. Iyer, L. H. Wright, and M. G. Newton, *J. Amer. Chem. Soc.*, **93**, 5492 (1971).
(190) S. W. Pelletier, S. W. Page, and M. G. Newton, *Tetrahedron Lett.*, 795 (1971).
(191) A. G. González, J. L. Bretón, B. M. Fraga, and J. G. Luis, *ibid.*, 3097 (1971).
(192) M. H. Benn, J. D. Connolly, O. E. Edwards, L. Marion, and Z. Stojanac, *Can. J. Chem.*, **49**, 425 (1971).
(193) K. Wiesner, E. W. K. Jay, and L. Poon-Jay, *Experientia*, **27**, 363 (1971).
(194) K. Wiesner and L. (P.) Jay, *ibid.*, **27**, 758 (1971).
(195) V. A. Telnov, M. S. Yunusov, Ya. V. Rashkes, and S. Yu. Yunusov, *Khim. Prirodn. Soedin.*, 622 (1971).
(196) M. S. Yunusov, Ya. V. Rashkes, and S. Yu. Yunusov, *ibid.*, 626 (1971).
(197) K. B. Birnbaum, K. Wiesner, E. W. K. Jay, and L. Jay, *Tetrahedron Lett.*, 867 (1971).

(198) H. Kaneko, *Agr. Biol. Chem.*, **35**, 1461 (1971).
(199) K. B. Birnbaum, *Acta Cryst.*, **B27**, 1169 (1971).
(200) D. F. Zinkel, L. C. Zank, and M. F. Wasolowski, *Diterpene Resin Acids*, 191 (1971).
(201) K. Sasaki and Y. Hirata, *J. Chem. Soc.* (*B*), 1565 (1971).
(202) R. C. Haltiwanger and R. F. Bryan, *ibid.*, 1598 (1971).
(203) K. D. Barrow, D. H. R. Barton, E. Chain, C. Conlay, T. C. Smale, R. Thomas, and E. S. Waight, *J. Chem. Soc.* (*C*), 1259 (1971).
(204) (a) E. Hough and D. Rogers, unpublished.
(b) K. D. Barrow, D. H. R. Barton, E. Chain, U. F. W. Ohnsorge, and R. Thomas, *J. Chem. Soc.* (*C*), 1265 (1971).
(205) M. Brufani, S. Cerrini, W. Fedeli, and A. Vaciago, *J. Chem. Soc.* (*B*), 2021 (1971).
(206) W. P. Mose and P. M. Scopes, *ibid.*, 1572 (1971).
(207) E. J. McGarry, K. H. Pegel, L. Phillips, and E. S. Waight, *ibid.*, 904 (1971). Preliminary commun.: *idem.*, *Chem. Comm.*, 1074 (1969).
(208) A. S. Fairhurst, *J. Label Compounds*, **7**, 133 (1971). (*Chem. Abstr.*, **75**, 49375p [1971].)
(209) K. Kato and Y. Kitahara, *Kagaku to Yakugaku no Kyoshitsu* **32**, 19 (1971); *ibid.*, **33**, 31 (1971).
(210) V. A. Raldugin, A. I. Rezvukhin, and V. A. Pentegova, *Khim. Prir. Soedin.*, 598 (1971). (*Chem. Abstr.*, **77**, 5630e [1972].)
(211) V. A. Raldugin, N. K. Kashtanova, and V. A. Pentegova, *ibid.*, 604 (1971). (*Chem. Abstr.*, **77**, 5628k [1972].)
(212) K. Wenigs, W. Bähr, and M. P. Rao, *Liebigs Ann. Chem.*, **753**, 100 (1971).
(213) S. Yamazaki, S. Tamura, F. Marumo, and Y. Saito, *Acta Cryst.*, **B27**, 2090 (1971).
(214) Y. Abe, E. Taniguchi, M. Eto, and Y. Oshima, *Nippon Nogeikagaku Kaishi*, **45**, 169 (1971).
(215) A. I. Scott and A. D. Wrixon, *Tetrahedron*, **27**, 4787 (1971).
(216) K. Sato and S. Inoue, *Yuki Goseikagaku Kyokaishi* (*J. Synth. Org. Chem. Japan*), **29**, 237 (1971).
(217) T. Reynolds, *Chem. and Ind.*, 443 (1971).
(218) A. Balmain and G. Ourisson, *Chem. Comm.*, 268 (1971).
(219) M. Fetizon, I. Hanna, A. I. Scott, A. D. Wrixon, and T. K. Devon, *ibid.*, 545 (1971).
(220) K. Nakanishi and K. Habaguchi, *J. Amer. Chem. Soc.*, **93**, 3546 (1971).
(221) G. A. Ellestad, R. H. Evans, Jr., and M. P. Kunstmann, *Tetrahedron Lett.*, 497 (1971).
(222) A. Sato, M. Kurabayashi, A. Ogiso, and H. Mishima, *ibid.*, 839 (1971).
(223) K. Sakata, K. Kawazu, T. Mitsui, and N. Masaki, *ibid.*, 141 (1971).
(224) K. Sakata, K. Kawazu, and T. Mitsui, *Agr. Biol. Chem.*, **35**, 1084, 2113 (1971).
(225) W. Adolf and E. Hecker, *Experientia*, **27**, 1393 (1971).
(226) K. Kawazu and T. Mitsui, *Kagaku to Seibutsu*, **9**, 823 (1971).
(227) G. Kreibich, E. Hecker, R. Süss, and V. Kinzel, *Naturwissenschaften*, **58**, 323 (1971).
(228) E. Härle and E. Hecker, *Liebigs Ann. Chem.*, **748**, 134 (1971).
(229) P. Narayanan, M. Röhrl, K. Zechmeister, D. W. Engel, W. Hoppe, E. Hecker, and W. Adolf, *Tetrahedron Lett.*, 1325 (1971).
(230) D. F. Zinkel and B. P. Spalding, *ibid.*, 2459 (1971).
(231) D. Umemura and Y. Hirata, *ibid.*, 3673 (1971).