

REVIEW

The Chemistry on Diterpenoids in 1981

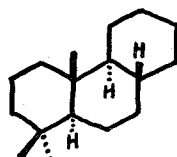
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Manabu NODE*, and Masahito OCHIAI*

Received June 1, 1984

I. INTRODUCTION

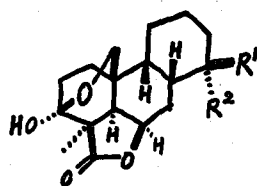
This is one of a series of our annual reviews on diterpenoid chemistry. The following abbreviations are used. [CN]: common name; [NS]: natural source; [REF]; reference number; [NC]: notes and comments.

II. PODOCARPANE DERIVATIVES



Podocarpane

1) Isolation and Structure Determination



1 $R^1 + R^2 = 0$

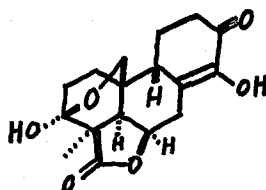
[CN] humirianthenolide A

2 $R^1 = H, R^2 = OH$

[CN] humirianthenolide B

[NS] *Humirianthera rupestris*

[REF] 1

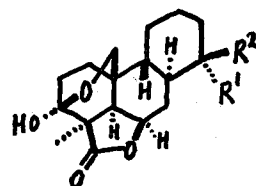


3

[CN] humirianthenolide D

[NS] *Humirianthera rupestris*

[REF] 1



4 $R^1 + R^2 = 0$

[CN] humirianthenolide E

5 $R^1 = H, R^2 = OH$

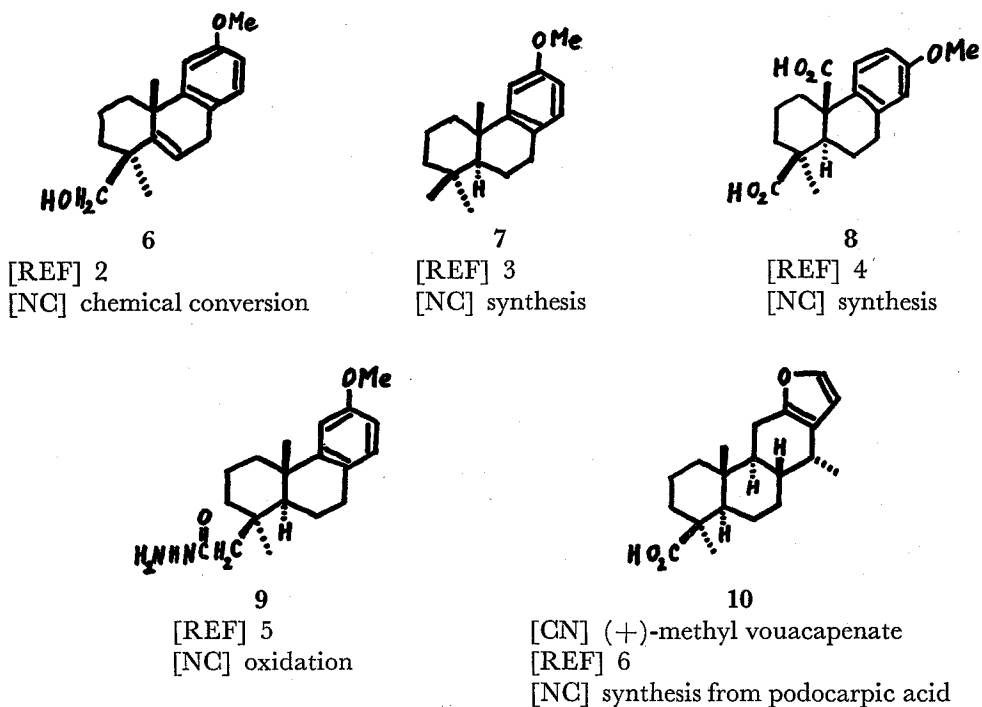
[CN] humirianthenolide F

[NS] *Humirianthera rupestris*

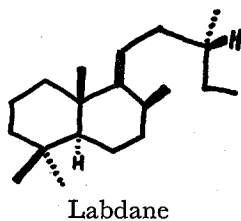
[REF] 1

* 藤田栄一, 富士 薫, 長尾善光, 野出 学, 落合正仁: Cancer Drug Research Laboratory, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

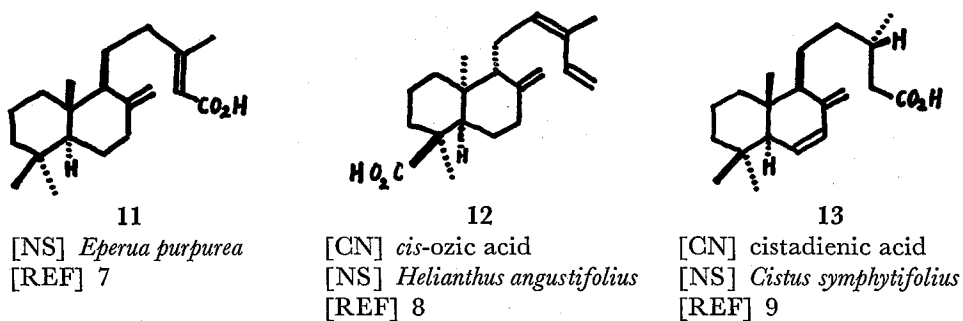
2) Synthesis and Reaction

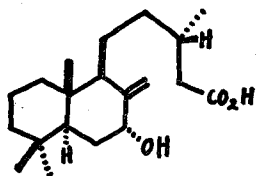


III. LABDANE DERIVATIVES



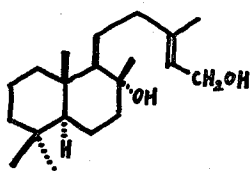
1) Isolation and Structure Determination





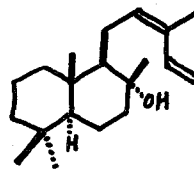
14

[CN] cistenolic acid
[NS] *Cistus symphytifolius*
[REF] 9



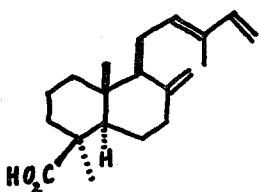
15

[NS] *Cistus symphytifolius*
[REF] 9



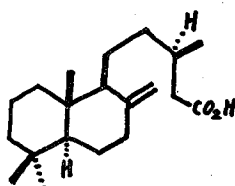
16

[CN] (+)-abienol
[NS] *Fleischmannia pycnocephaloides*
[REF] 10



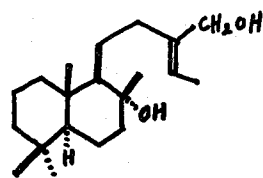
17

[NS] *Fleischmannia deborabellae*
[REF] 10



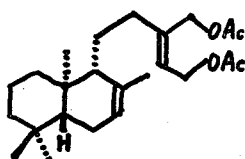
18

[NS] *Eperua purpurea*
[REF] 11



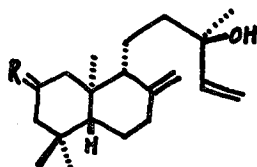
19

[NS] *Picea ajanensis*
[REF] 12

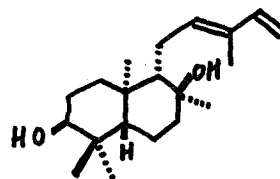


20

[NS] *Baccharis* species
[REF] 13

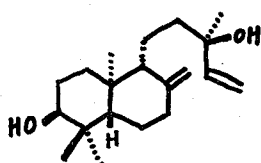


21 R = α -OH, H
22 R = β -OH, H
23 R = O
24 R = α -OCO(CH₂)₂CO₂H, H
[NS] *Baccharis oxydonta*
[REF] 14



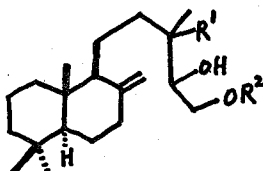
25

[NS] *Grazielia* species
[REF] 15

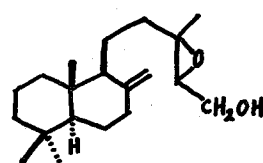


26

[NS] *Croton sublyratus*
[REF] 16

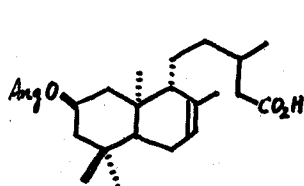


27 R¹=R²=H
28 R¹=OH, R²=H
29 R¹=OH, R²=Ac
[NS] *Hemizonia lutescens*
[REF] 17



30

[NS] *Hemizonia lutescens*
[REF] 17

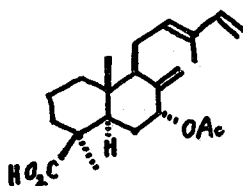


31

[CN] dihydrodendroidinic acid

[NS] *Pleurocoronis pluriseta*

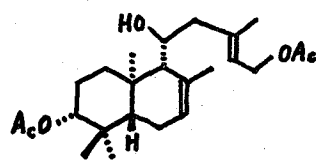
[REF] 18



32

[NS] *Chromolaena collina*

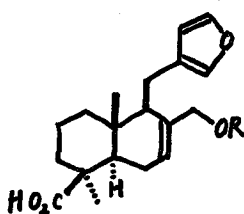
[REF] 19



33

[NS] *Lasiolaena santosii*

[REF] 20

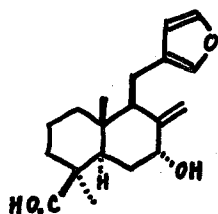


34 R=H

35 R=Ac

[NS] *Gutierrezia dracunculoides*

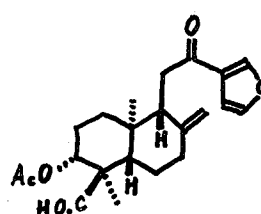
[REF] 21



36

[NS] *Gutierrezia dracunculoides*

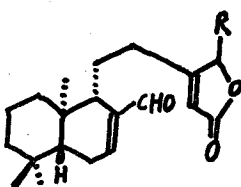
[REF] 21



37

[NS] *Dodonaea petiolaris*

[REF] 22



38 R=β-OH

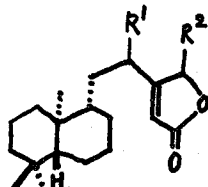
[CN] acritolongifolide A

39 R=α-OH

[CN] acritolongifolide B

[NS] *Acritopappus longifolius*

[REF] 23



40a R¹=H, R²=α-OH

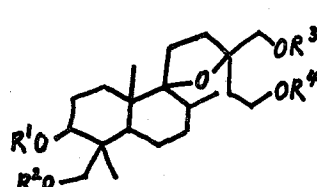
40b R¹=H, R²=β-OH

41a R¹=OH, R²=α-OH

41b R¹=OH, R²=β-OH

[NS] *Ageratum fastigiatum*

[REF] 24



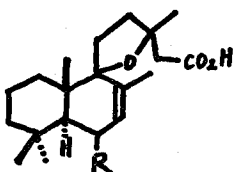
42 R¹=R³=Ac, R²=R⁴=H

43 R¹=R⁴=Ac, R²=R³=H

44 R¹=R³=H, R²=R⁴=Ac

[NS] *Lagochilus inebrians*

[REF] 25

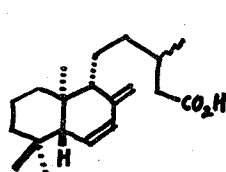


45 R=α-OH

46 R=β-OH

[NS] *Grindelia humilis*

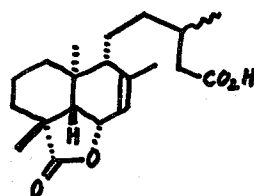
[REF] 26



47

[NS] *Hartwrightia floridana*

[REF] 27

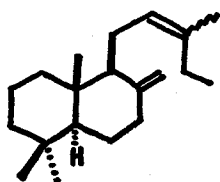


48

[NS] *Hartwrightia floridana*

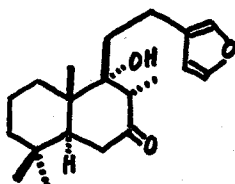
[REF] 27

2) Synthesis and Reactions



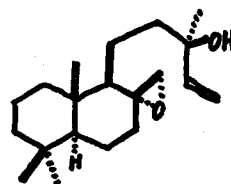
49

[REF] 28
[NC] photosensitized
oxygenation of 49
and related compds.



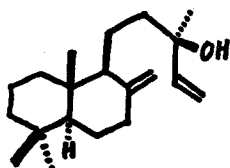
50

[CN] hispanolone
[REF] 29, 30, 31
[NC] chemical trans-
formation of 50



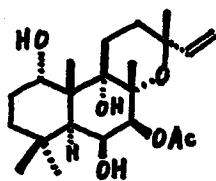
51

[REF] 32
[NC] acid-catalysed
rearrangement



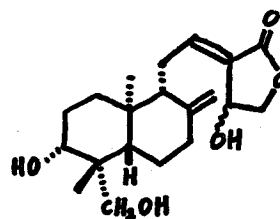
52

[CN] manool
[REF] 33
[NC] conversion to
isoagatholactone



53

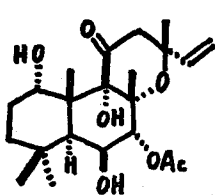
[CN] forskolin
[NS] *Coleus forskohlii*
[REF] 34
[NC] reactions



54

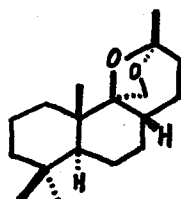
[CN] andrographolide
[REF] 35
[NC] reaction with
NaHSO₃

3) Miscellaneous Section



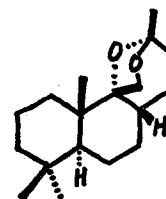
55

[CN] coleonol
[NS] *Coleus forskohlii*
[REF] 36
[NC] pharmacological
studies



56

[REF] 37
[NC] •synthesis from
manool
•odour studies



57

[REF] 37
[NC] •synthesis from
manool
•odour studies

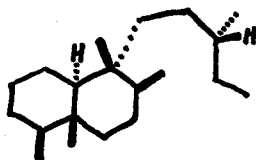
Additional references

[REF] 38 - 41
[NC] ¹³C NMR studies

[REF] 42
[NC] studies on optical
activity

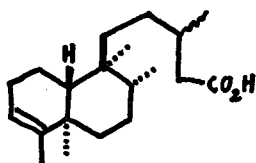
[REF] 43
[NC] separation by HPLC

IV. CLERODANE DERIVATIVES



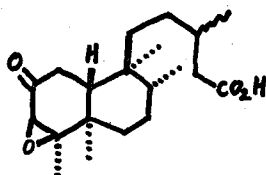
Clerodane

1) Isolation and Structure Determination



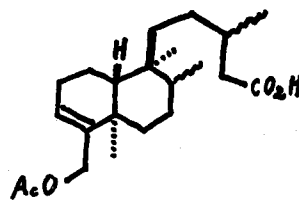
58

[NS] *Hartwrightia floridana*
[REF] 27



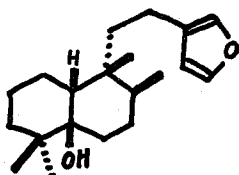
59

[NS] *Hartwrightia floridana*
[REF] 27



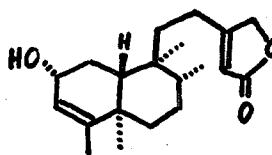
60

[NS] *Liatris scariosa*
[REF] 44



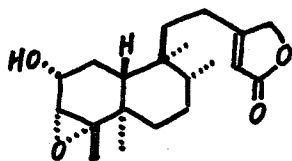
61

[NS] *Dysidea ambia*
[REF] 45



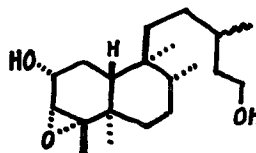
62

[NS] *Symphyopappus compressus*
[REF] 46



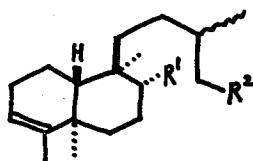
63

[NS] *Symphyopappus compressus*
[REF] 46

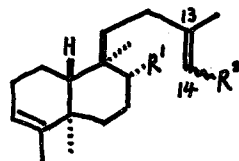


64

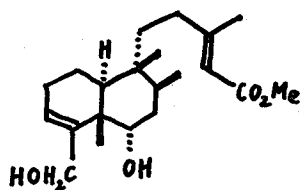
[NS] *Symphyopappus compressus*
[REF] 46



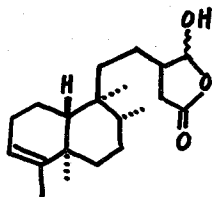
- 65 $R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{CHO}$
 66 $R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{CH}_2\text{OH}$
 67 $R^1 = \text{CH}_2\text{OH}$,
 $R^2 = \text{CH}_2\text{OCO}(\text{CH}_2)_{18}\text{Me}$
 68 $R^1 = \text{CH}_2\text{OH}$,
 $R^2 = \text{CH}_2\text{OCO}(\text{CH}_2)_{20}\text{Me}$
 69 $R^1 = \text{CHO}$, $R^2 = \text{CH}_2\text{OH}$
 [NS] *Symphyopappus reticulatus*
 [REF] 46



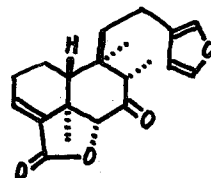
- 70 $R^1 = \text{CH}_2\text{OH}$, $R^2 = \text{CHO}$
 (13, 14 E and Z)
 71 $R^1 = \text{CO}_2\text{H}$, $R^2 = \text{CHO}$
 (13, 14 E and Z)
 72 $R^1 = R^2 = \text{CH}_2\text{OH}$ (13, 14 E)
 73 $R^1 = \text{CH}_2\text{OH}$,
 $R^2 = \text{CH}_2\text{OCO}(\text{CH}_2)_{18}\text{Me}$ (13, 14 E)
 74 $R^1 = \text{CH}_2\text{OH}$,
 $R^2 = \text{CH}_2\text{OCO}(\text{CH}_2)_{20}\text{Me}$ (13, 14 E)
 [NS] *Symphyopappus reticulatus*
 [REF] 46



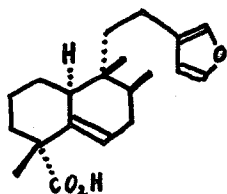
- 75
 [NS] *Pityrodia lepidota*
 [REF] 47



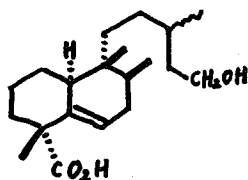
- 76
 [NS] *Balanthus viscidus*
 [REF] 48



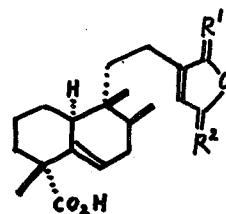
- 77
 [NS] *Pulicaria gnaphalodes*
 [REF] 49



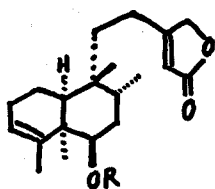
- 78
 [CN] koanophyllic acid A
 [NS] *Koanophyllon*
conglobatum
 [REF] 50



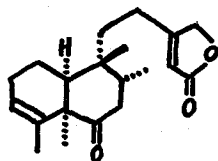
- 79
 [CN] koanophyllic acid B
 [NS] *Koanophyllon*
conglobatum
 [REF] 50



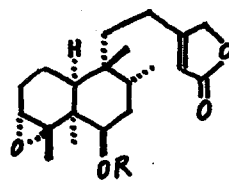
- 80 $R^1 = \text{O}$, $R^2 = \text{H}_2$
 [CN] koanophyllic acid C
 81 $R^1 = \text{H}_2$, $R^2 = \text{O}$
 [CN] koanophyllic acid D
 [NS] *Koanophyllon*
conglobatum
 [REF] 50



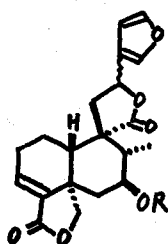
- 82 R=angeloyl
[CN] solidagolactone II
83 R=tigloyl
[CN] solidagolactone III
84 R=H
[CN] solidagolactone IV
85 R=Ac
[CN] solidagolactone VIII
[REF] 51
[NC] structure revision



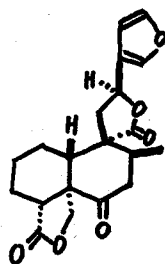
- 86
[CN] solidagolactone V
[REF] 51
[NC] structure revision



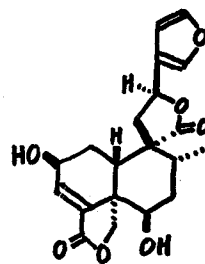
- 87 R=Ac
[NC] solidagolactone VI
88 R=angeloyl
[CN] solidagolactone VII
[REF] 51
[NC] structure revision



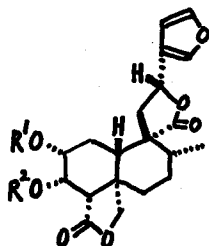
- 89 R=angeloyl
[NS] *Baccharis subdentata*
[REF] 14



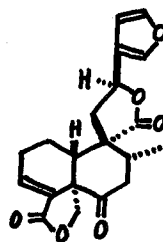
- 90
[NS] *Teucrium scordium*
[REF] 52



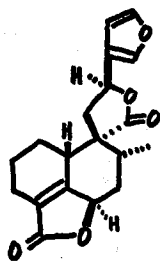
- 91
[CN] teugin
[NS] *Teucrium fragile*
[REF] 53



- 92 R¹=angeloyl, R²=senecioid
93 R¹=senecioid, R²=angeloyl
94 R¹=angeloyl, R²=2-methylbutyl
[NS] *Baccharis* species
[REF] 13



- 95
[CN] teuscordinon
[NS] *Teucrium scordium*
[REF] 54

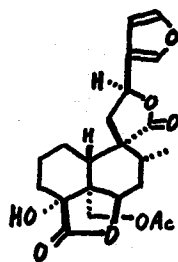


96

[CN] teuffin

[NS] *Teucrium viscidum*
var. *Miguelianum*

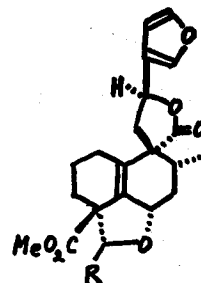
[REF] 55



97

[NS] *Teucrium* species

[REF] 56



98 R=β-OH

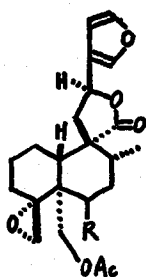
[CN] mallotucin C

99 R=α-OH

[CN] mallotucin D

[NS] *Mallotus repandus*

[REF] 57



100 R=β-OH

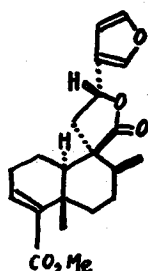
[CN] teucjaponin A

101 R=α-OH

[CN] teucjaponin B

[NS] *Truvtium japonicum*

[REF] 58

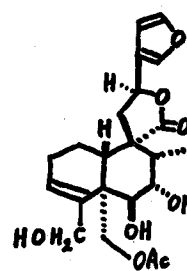


102

[CN] sonderianin

[NS] *Croton sonderianus*

[REF] 59

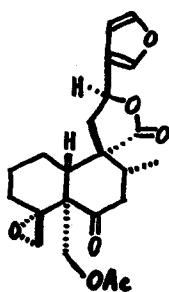


103

[CN] lolin

[NS] *Teucrium capitatum*

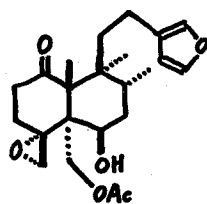
[REF] 60



104

[NS] *Teucrium gnaphalodes*

[REF] 61

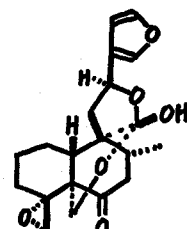


105

[CN] isofruticolone

[NS] *Teucrium gnaphalodes*

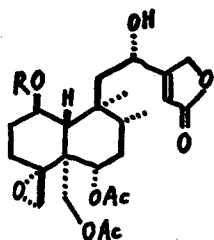
[REF] 61



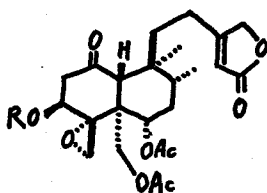
106

[NS] *Teucrium gnaphalodes*

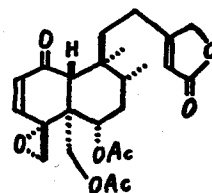
[REF] 61



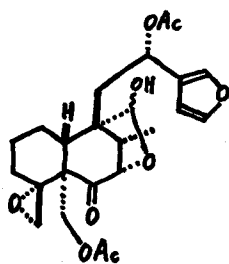
107 $R = \text{COC}(\text{Me}) = \text{CHMe}$
 [CN] ajugamarin
 [NS] *Ajuga nipponensis*
 [REF] 62



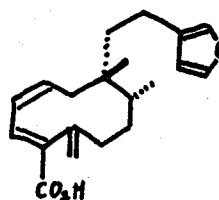
108 $R = \text{COCH}(\text{Me})\text{Et}$
 [CN] ajugareptansone A
 [NS] *Ajuga reptans*
 [REF] 63



109
 [CN] ajugareptansone B
 [NS] *Ajuga reptans*
 [REF] 63

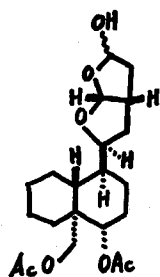


110
 [CN] auropolin
 [NS] *Teacrium polium*
 snbsp. *aureum*
 [REF] 64

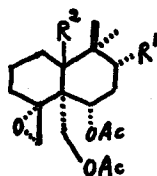


111
 [CN] conyzic acid
 [NS] *Conyza strict*
 [REF] 65

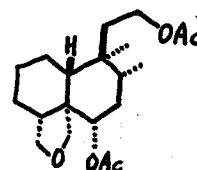
2) synthesis and Reactions



112
 [REF] 66
 [NC] •synthesis
 •insect
 antifeedant



113 $R^1 = \text{H}, R^2 = \beta\text{-H}$
 114 $R^1 = \text{H}, R^2 = \alpha\text{-H}$
 115 $R^1 = \text{Me}, R^2 = \beta\text{-H}$
 [REF] 67 - 69
 [NC] •synthesis
 •insect
 antifeedant



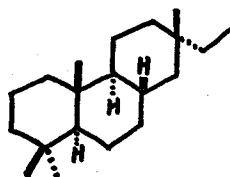
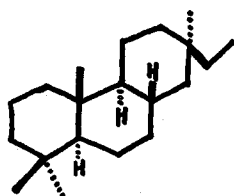
116
 [REF] 70
 [NC] synthesis

3) Miscellaneous Section

[REF] 71

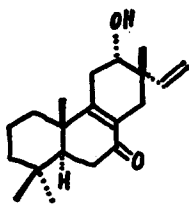
[NC] studies on insect antifeeding activity

V. PIMARANE AND ISOPIMARANE DERIVATIVES



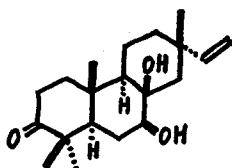
Pimarane and Isopimarane

1) Isolation and Structure Determination



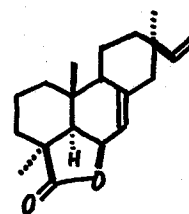
117

[NS] *Vellozia* species
[REF] 72



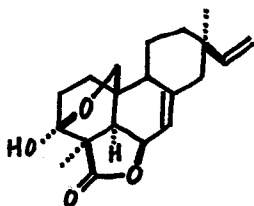
118

[NS] *Bromelia*
pinguin
[REF] 73



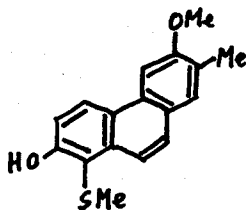
119

[CN] momilactone A
[NS] rice
[REF] 74
[NC] phytoalexin



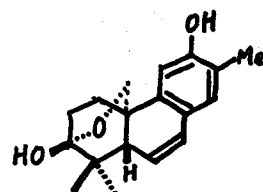
120

[CN] momilactone B
[NS] rice
[REF] 74
[NC] phytoalexin



121

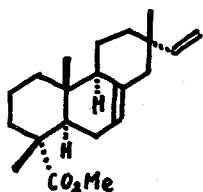
[CN] micrandrol C
[NS] *Micrandropsis*
scleroxylon
[REF] 75



122

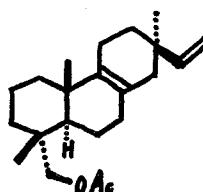
[CN] micrandrol D
[NS] *Micrandropsis*
scleroxylon
[REF] 75

2) Synthesis and Reaction



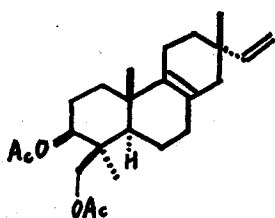
123

[REF] 76
[NC] superacid catalyzed
cyclization



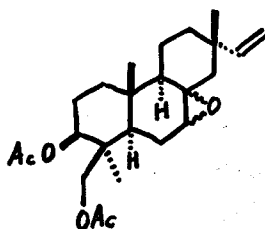
124

[REF] 77
[NC] photo-oxygenation



125

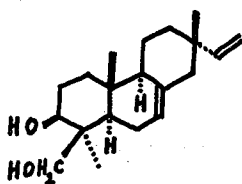
[REF] 77
[NC] photo-oxygenation



126

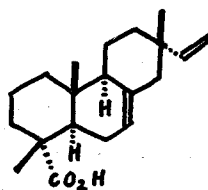
[REF] 78
[NC] chemical transformation

3) Miscellaneous Section



127

[CN] virescenol B
[REF] 79
[NC] bioxyntesis



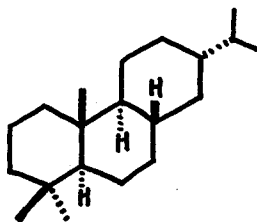
128

[CN] isopimaric acid
[REF] 80
[NC] biotransformation

Additional references

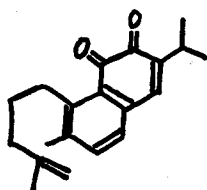
- [REF] 81 - 83
- [NC] ¹³C NMR studies
- [REF] 84
- [NC] studies on distribution of podolactone-type plant growth inhibitors
- [REF] 85
- [NC] studies on conformations for pimarane derivatives

VI. ABIETANE DERIVATIVES



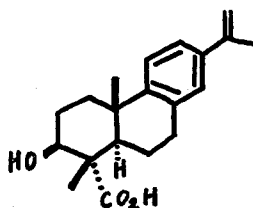
Abietane

1) Isolation and Structure Determination



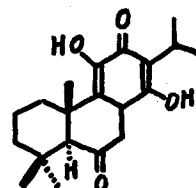
129

[CN] aethiopione
[NS] *Salvia aethiopis*
[REF] 86



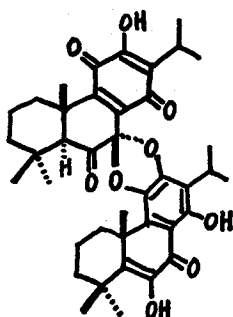
130

[NS] *Salvia tomentosa*
[REF] 87



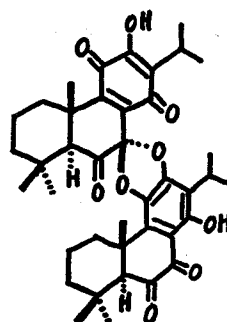
131

[NS] *Plectranthus grandidentatus*
[REF] 88



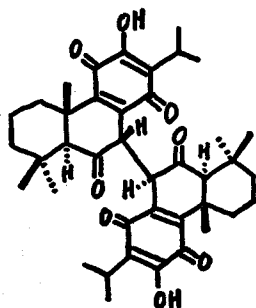
132 [CN] grandidone A

133 [CN] 7-epigrandidone A
[NS] *Plectranthus grandidentatus*
[REF] 88

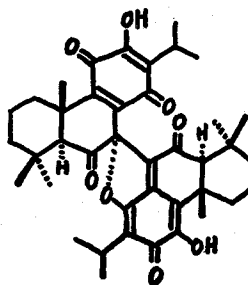


134 [CN] grandidone B

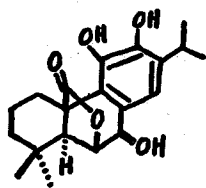
135 [CN] 7-epigrandidone B
[NS] *Plectranthus grandidentatus*
[REF] 88



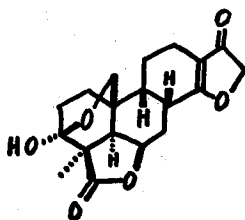
136
[CN] grandidone C
[NS] *Plectranthus*
grandidentatus
[REF] 88



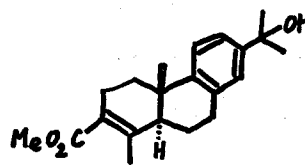
137 [CN] grandidone D
138 [CN] 7-epigrandidone D
[NS] *Plectranthus*
grandidentatus
[REF] 88



139
[CN] rosmanol
[NS] *Rosmarinus*
officinalis
[REF] 89
[NC] antioxidant

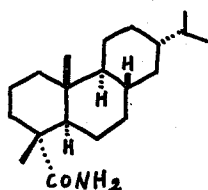


140
[CN] humiliathenolide C
[NS] *Humirianthera*
rupestris
[REF] 1

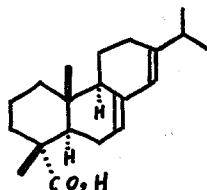


141
[NS] *Tripterygium wilfordii*
[REF] 90
[NC] isolation of cytotoxic
diterpenes. (tripdio-
loide, triptolide, etc.)

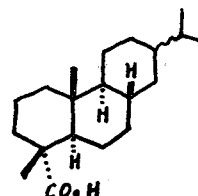
2) Synthesis and Reaction



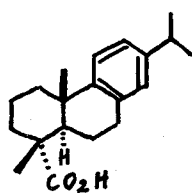
142
[REF] 91
[NC] lactonization
by photolysis
($\text{Pb}(\text{OAc})_4/\text{I}_2$)



143
[CN] abietic acid
[REF] 92
[NC] air oxidation

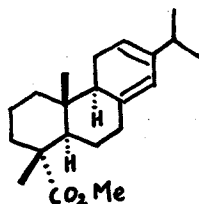


144
[REF] 93
[NC] carbonylation by
conc. H_2SO_4



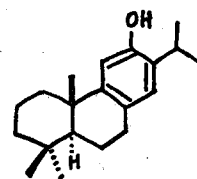
145

- [CN] dehydroabietic acid
[REF] 94
[NC] oxidation by
Co(acac)₂
[REF] 95
[NC] Synthesis of (+)-
fragrolide and (+)-
bemadienolide



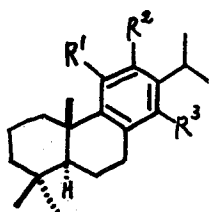
146

- [CN] methyl levopimarate
[REF] 96
[NC] addition of
ClSO₂NCO



147

- [CN] ferruginol
[REF] 97
[NC] synthesis from 145
[REF] 98
[NC] ozonolysis

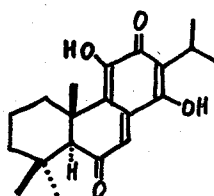


148 R¹=R²=OH, R³=H

149 R¹=R²=H, R³=OH

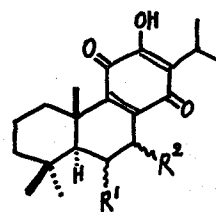
[REF] 98

- [NC] Chemical conversion
to isodrimenin, vali-
diviolide, winterin,
and confertifolin



150

- [CN] 14-hydroxytaxodione
[REF] 99
[NC] partial synthesis and
reactions of 150

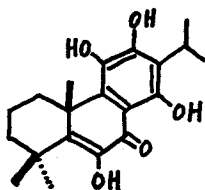


151 R¹=R²=α-OH

152 R¹=α-OH,
R²=β-OH

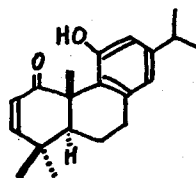
153 R¹=R²=β-OH
[REF] 100

- [NC] partial synthesis



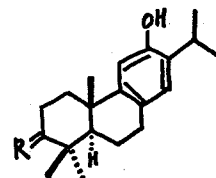
154

- [CN] coleoneU
[REF] 101 and 102
[NC] synthesis



155

- [REF] 103
[NC] synthesis



156 R=α-H, β-OH

[CN] hinokiol

157 R=O

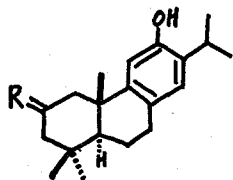
[CN] hinokione

[REF] 104

[NC] synthesis from
abietatrienol

[REF] 105

- [NC] total synthesis



158 R= α -OH, β -H

[CN] salviol

159 R=O

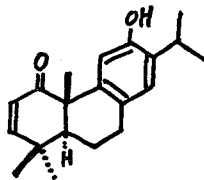
[CN] 2-oxoferruginol

[REF] 104

[NC] synthesis from
abietatrienol

[REF] 105

[NC] total synthesis



160

[CN] shonanol

[REF] 106

[NC] synthesis and
revised structure

131

[REF] 107

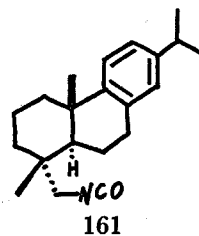
[NC] partial synthesis
(**131-138**)
from **131**

3) Miscellaneous Section

145

[REF] 108

[NC] biodegradation of dehydroabietic
acid (**145**) with *Mortierella isabellina*

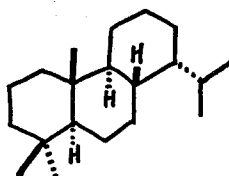


161

[REF] 109

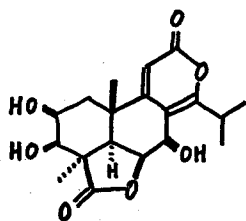
[NC] use in the synthesis of (*S*)-5-
hydroxy-6-*trans*-8, 11, 14-*cis*-
eicosatetraenoic acid

VII. TOTARANE DERIVATIVES



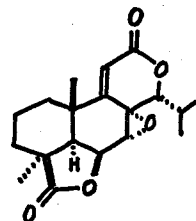
Totarane

1) Isolation and Structure Determination



162

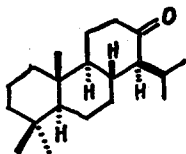
[CN] urbalactone
[NS] *Podocarpus urbanii*
[REF] 110



163

[CN] 2,3-dihydropodolide
[NS] *Podocarpus urbanii*
[REF] 110

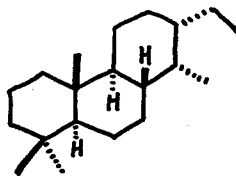
2) Synthesis and Reaction



164

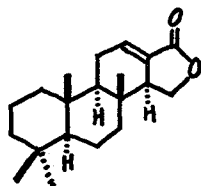
[REF] 111
[NC] Synthesis *via* cyclobutane ring-opening
of allene-enone photoadduct

VIII. CASSANE DERIVATIVES



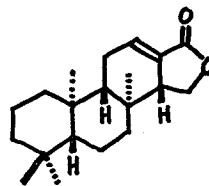
Cassane

1) Synthesis and Reaction



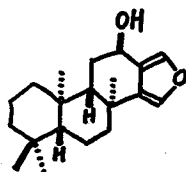
165

[CN] (+)-isoagatholactone
[REF] 33
[NC] synthesis from (+)-manool



166

[CN] *ent*-isoagatholactone
[REF] 112
[NC] synthesis from methyl isocopalate

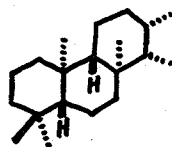


167

[CN] *ent*-13 (16),14-spongiadien-12 α -ol

[REF] 112

[NC] synthesis from methyl isocopalate



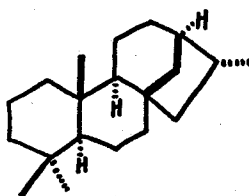
168

[CN] isocopalane

[REF] 112

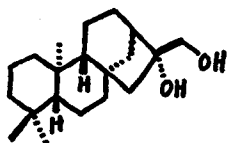
[NC] synthesis

IX. KAURANE DERIVATIVES



Kaurane

1) Isolation and Structure Determination



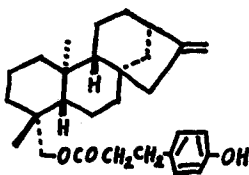
169

[NS] *Croton sublyratus*

[REF] 16

[NS] *Aristolachia elegans*

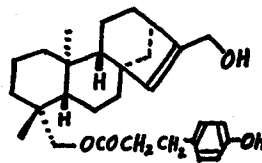
[REF] 113



170

[NS] *Baccharis quitensis*

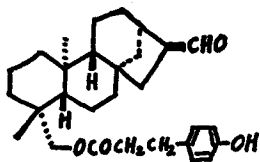
[REF] 14



171

[NS] *Baccharis quitensis*

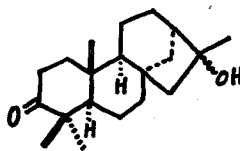
[REF] 14



172

[NS] *Baccharis quitensis*

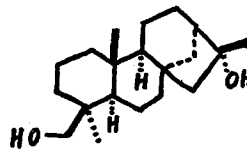
[REF] 14



173

[NS] *Bromelia pinguin*

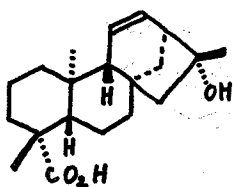
[REF] 73



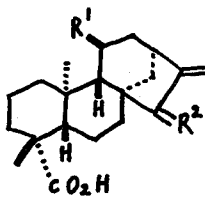
174

[NS] *Bromelia pinguin*

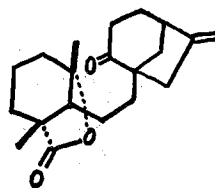
[REF] 73



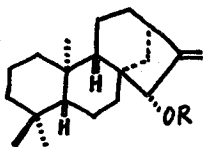
175
[NS] *Helianthus angustifolius*
[REF] 8



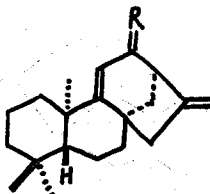
176 R¹=H,
R²= α -OTigl
177 R¹=OH, R²=O
178 R¹=OH,
R²= β -OH, H
[NS] *Grazielia* species
[REF] 15



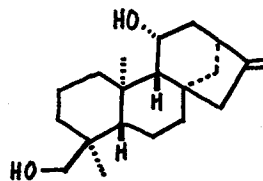
179
[NS] *Ageratum fastigiatum*
[REF] 24



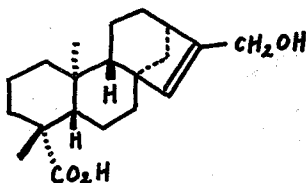
R=methylacryloyl
180
[NS] *Ichthyothere* species
[REF] 114



181 R= α -H, β -OH
182 R=O
[NS] *Vellozia caput-ardeae*
[REF] 115

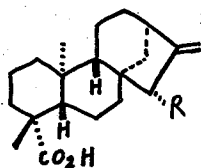


183
[NS] *Sideritis arborescens*
[REF] 116



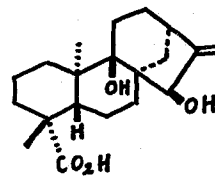
[NS] *Helianthus grosseserratus*
[REF] 117

184

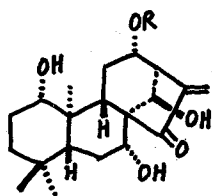


185 R=OH
[CN] grandifloric acid
[NS] *Helianthus grosseserratus*
[REF] 117
186 R=H
[NS] *Aristolochia triangularis*
[REF] 118
[NS] *Wedelia bupththalmiflora*
[REF] 119

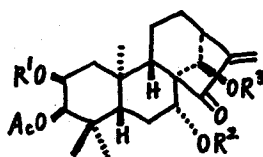
187 R=H; $\Delta^{9(11)}$
[CN] grandiflorenic acid
188 R=MeCH=CMcCOO-(Z)
189 R=MeCH=CMcCOO-(E)
190 R=Me₂CHCH₂COO-
191 R=Me₂CHCOO-
[NS] *Wedelia bupththalmiflora*
[REF] 119



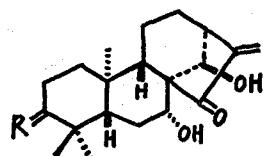
192
[CN] pterokaurene L₂
[NS] *Pteris longipes*
[REF] 120



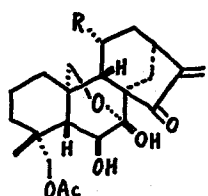
- 193 R=H
[CN] excisanin A
194 R=Ac
[CN] excisanin B
[NS] *Rabdosia excisa*
[REF] 121



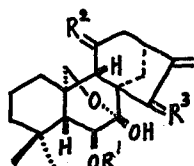
- 195 R¹=R²=R³=H
[CN] leukamenin A
196 R¹=Ac, R²=R³=H
[CN] leukamenin B
197 R¹=R³=Ac, R²=H
[CN] leukamenin C
198 R¹=R²=Ac, R³=H
[CN] leukamenin D
[NS] *Rabdosia umbrosa*
var. *leucantha* f. *kameba*
[REF] 122



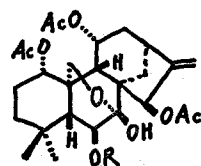
- 199 R=α-H, β-OAc
[CN] leukamenin E
200 R=O
[CN] leukamenin F
[NS] *Rabdosia umbrosa*
var. *leucantha* f. *kameba*
[REF] 122



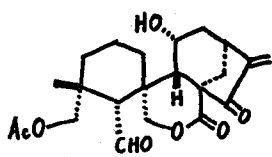
- 201 R=H
[CN] longikaurin C
202 R=OH
[CN] longikaurin D
203 R=OAc
[CN] longikaurin F
[NS] *Rabdosia longituba*
[REF] 123
[NC] antibacterial
diterpenoids



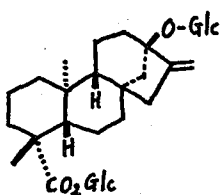
- 204 R¹=H, R²=α-H,
β-OAc, R³=O
[CN] longikaurin E
[NS] *Rabdosia longituba*
[REF] 123
205 R¹=OAc, R²=O,
R³=α-H, β-OH
[CN] rabdosianin C
[NS] *Rabdosia shikokiana*
[REF] 124



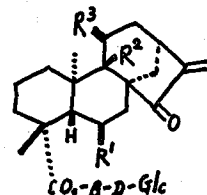
- 206 R=H
[CN] rabdosianin A
207 R=Ac
[CN] rabdosianin B
[NS] *Rabdosia shikokiana*
[REF] 124



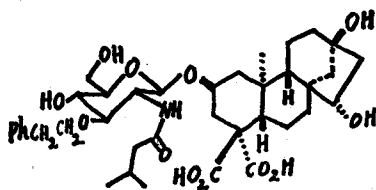
- 208
[CN] trichorabdal B
[NS] *Rabdosia trichocarpa*
[REF] 125
[NC] X-ray crystal structure
and transformation
into novel skeleton



- 209
[CN] rubusoside
[NS] *Rubus chingii*
[REF] 126
[NC] sweet principle

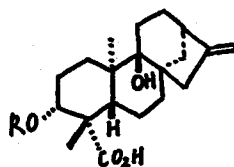


- 210 R¹=R³=H, R²=OH
211 R¹=R³=OH, R²=H
212 R¹=R²=OH, R³=H
[NS] *Pteris livida*
[REF] 127



213

[CN] wedeloside
[NS] *Wedelia asperima*
[REF] 128 and 129
[NC] toxicity and potential
antitumor activity

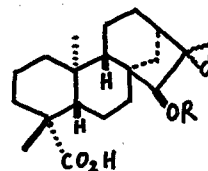


214 R=Ang

215 R=Cinn

[NS] *Wedelia trilobata*

[REF] 130

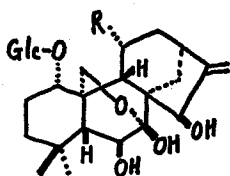


216 R=Ang

217 R=Tigl

[NS] *Aspilula parvifolia*

[REF] 130



218 R=OH

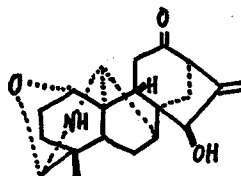
[CN] shikokiaside A

219 R=H

[CN] shikokiaside B

[NS] *Rabdosa shikokiana*
var. *shikokiana*

[REF] 131

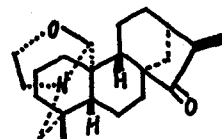


220

[CN] norsongoramine

[NS] *Delphinium tamarae*

[REF] 132

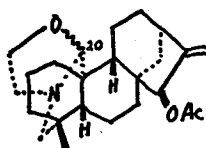


221

[CN] cuauchichicine

[REF] 133

[NC] revised structure and
¹³C-NMR and X-ray
crystallography



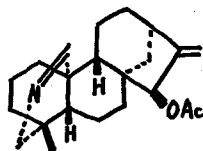
222

[CN] ovatine

[NS] *Garrya ovata* var.
lindheimeri

[REF] 133

[NC] mixture of C(20)
epimer

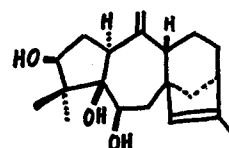


223

[CN] lindheimerine

[NS] *Garrya ovata* var.
lindheimeri

[REF] 133

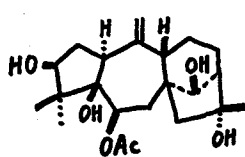


224

[CN] grayanotoxin XIX

[NS] *Leucothoe grayana*

[REF] 134

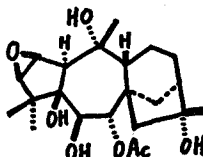


225

[CN] grayanotoxin XVI

[NS] *Leucothoe grayana*

[REF] 135



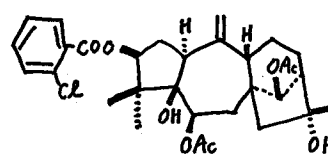
226

[CN] lyoniatoxin

[NS] *Lyonia ovalifolia*
var. *elliptica*

[REF] 136

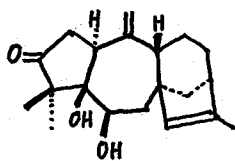
[NC] revised structure



227

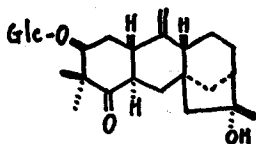
[REF] 137

[NC] X-ray analysis and
boat conformation
of C-ring



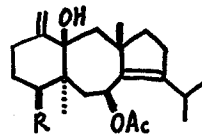
228

[CN] grayanotoxin XVIII
[NS] *Leucothoe grayana*
[REF] 138
[NC] X-ray analysis



229

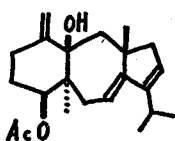
[CN] pierside B
[NS] *Pieris japonica*
[REF] 139
[NC] first example of a
leucothane glycoside



230 R=H

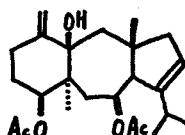
231 R=OH

[NS] *Dictyota divaricata*
[REF] 140
[NC] X-ray analysis



232

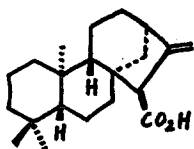
[NS] *Dictyota divaricata*
[REF] 140
[NC] X-ray analysis



233

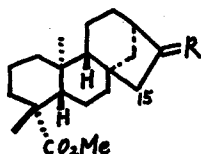
[NS] *Dictyota divaricata*
[REF] 140
[NC] X-ray analysis

2) Synthesis and Reaction



234

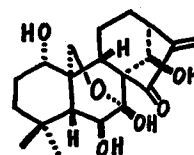
[REF] 141
[NC] carboxylation of
kaurene



235 R=F₂

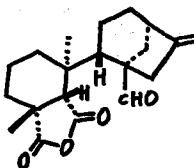
236 R=CF₃ (15-en)

[REF] 142
[NC] derived from
xylopic acid



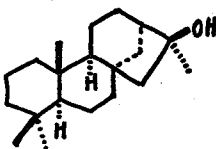
237

[CN] oridonin
[REF] 143
[NC] selective acetylation



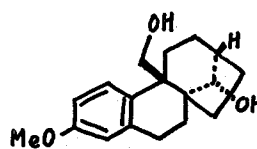
238

[CN] fujenal
[REF] 144 and 145
[NC] preparation of some
7-norgibberellanes
from 238



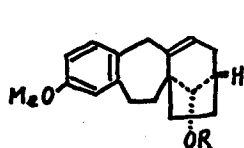
239

[CN] phyllocladan-16β-ol
[REF] 146
[NC] synthesis from
phyllocladene



240

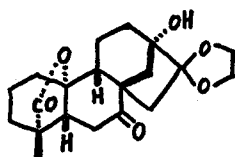
[REF] 147
[NC] synthetic approach
to grayanotoxins



241

[REF] 148

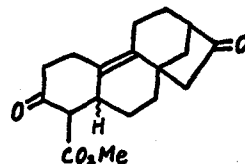
[NC] synthetic approach
to grayanotoxins



242

[REF] 149

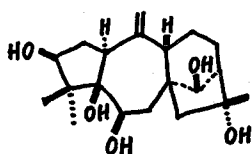
[NC] synthetic approach
to gibberellins



243

[REF] 150

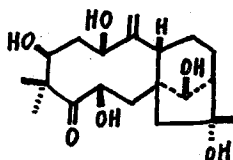
[NC] synthetic approach
to gibberellins



244

[REF] 151

[NC] ring opening with
 $\text{Pb}(\text{OAc})_4$

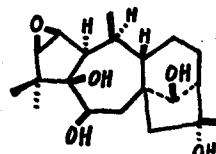


245

[CN] grayanol B

[REF] 152

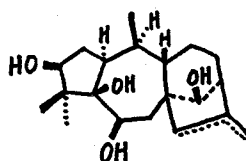
[NC] synthesis from 243



246

[REF] 153

[NC] conversion of 244
to 246 and 247

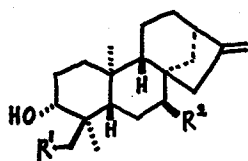


247

[REF] 153

[NC] conversion of 244
to 246 and 247

3) Miscellaneous Section



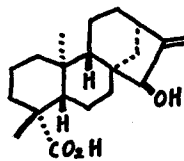
248 $\text{R}^1=\text{R}^2=\text{H}$

249 $\text{R}^1=\text{OH}$, $\text{R}^2=\text{H}$

250 $\text{R}^1=\text{R}^2=\text{OH}$

[REF] 154

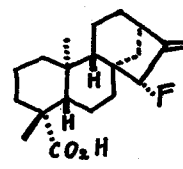
[NC] microbial
transformation of
248-250



251

[REF] 155

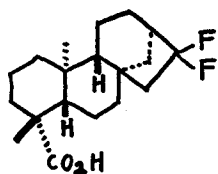
[NC] microbial production
of plant gibberellins
from 251 in *G. Fujikuroi*



252

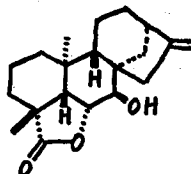
[REF] 156

[NC] microbial
production of fluoro
gibberellins from 252



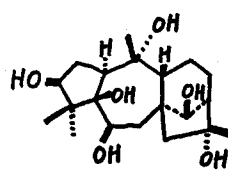
253

[REF] 157
[NC] microbial
transformation



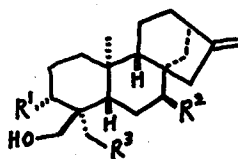
254

[REF] 158
[NC] kaurenolide
biosynthesis



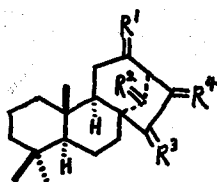
255

[CN] grayanotoxin III
[REF] 159
[NC] biosynthesis of
grayanotoxin



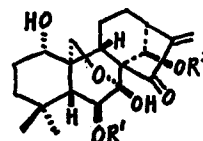
256

[REF] 160
[NC] ¹³C NMR studies



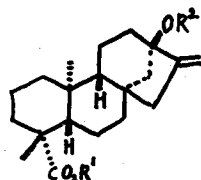
257

[REF] 161
[NC] ¹³C NMR studies



258

[REF] 162
[NC] antitumor activity
of acylated oridonin



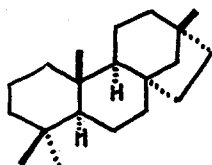
259

[CN] rebandioside-A, D, E
[REF] 163
[NC] structure-sweetness
relationship and
synthesis

Additional references

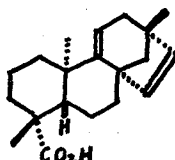
[REF] 164
[NC] sensory evaluation of
stevioside analogues

X. BEYERANE DERIVATIVES



Beyerane

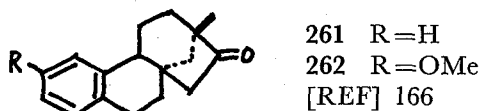
1) Isolation and Structure Determination



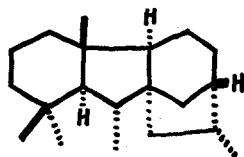
260

[CN] dehydrostachemic acid
[NS] *Viguiera* species
[REF] 165

2) Synthesis and Reaction

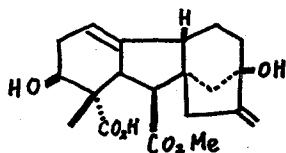


XI. GIBBERELLANE DERIVATIVES



Gibberellane

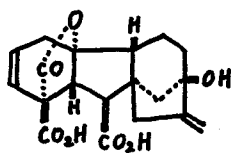
1) Isolation and Structure Determination



263

[REF] 167

[NC] X-ray analysis



264

[CN] gibberellin A₅₉

[NS] *Canavalia gladiata*

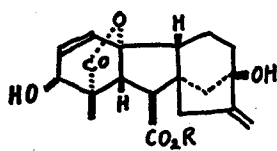
[REF] 168

Additional reference

[NS] *Chrysanthemum morifolium*

[REF] 169

2) Synthesis and Reaction



265

[CN] gibberellin A₃ (R=H)

[REF] 170

[NC] degradation

[REF] 171 (R=H)

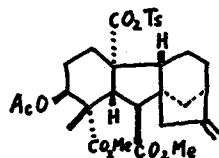
[NC] chemical conversion to GA₅

[REF] 172 (R=Me)

[NC] reaction with PPh₃

[REF] 173 (R=Me)

[NC] chemical conversion to GA₉ and GA₂₀

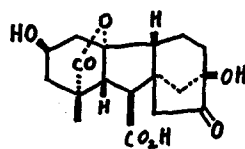


266

[CN] dimethyl ester of gibberellin A₁₃
20-toluene-*p*-sulfonyl anhydride

[REF] 174

[NC] methanolysis, reduction with NaBH₄



267

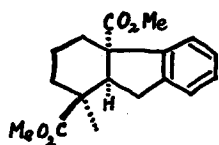
[CN] gibberellin A₂₉

[REF] 175

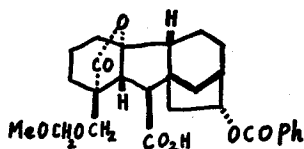
[NC] deuterated and tritiated GA₂₉

[REF] 176

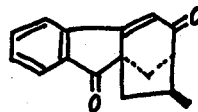
[NC] chemical conversion



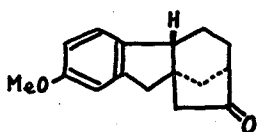
268
[REF] 177
[NC] synthesis



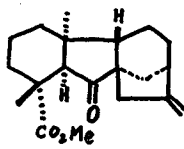
269
[REF] 178
[NC] synthesis



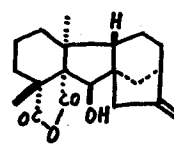
270
[REF] 179
[NC] synthesis



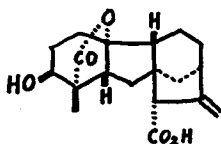
271
[REF] 180
[NC] synthesis



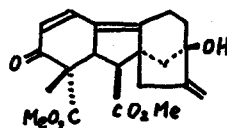
272
[REF] 144
[NC] preparation from fujenal



273
[REF] 144
[NC] preparation from fujenal



274
[CN] 7 (6→15βH)abeo-gibberellin A₄
[REF] 181
[NC] preparation from GA₄

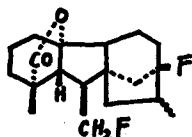


275
[REF] 182
[NC] photosensitized dimerization
[REF] 183
[NC] photoreduction
[REF] 184
[NC] photocycloaddition

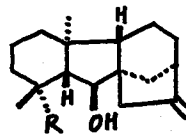
Additional references

- | | | | |
|-------------------|--------------------|--------------------|----------------------------------|
| [REF] 185 | [REF] 186 | [REF] 187 | [REF] 188 |
| [NC] chlorination | [NC] glucosylation | [NC] methylenation | [NC] reduction with K-selectride |

3) Miscellaneous Section



276
[REF] 189
[NC] feeding experiment

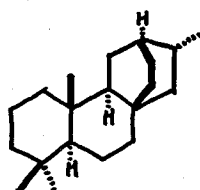


277 R = COOH
278 R = CH₂OH
[REF] 145
[NC] inhibitors of gibberellin biosynthesis

Additional references

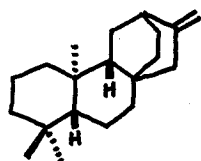
[REF] 109	[REF] 157	[REF] 156
[NC] bioassay	[NC] biotransformation of fluorogibberellins	[NC] biotransformation of fluorogibberellins
[REF] 155	[REF] 191	[REF] 192
[NC] microbial production of plant gibberellins	[NC] biosynthetic studies	[NC] biosynthesis in <i>Phaseolus coccineus</i>
[REF] 193	[REF] 194	[REF] 195
[NC] effect on the RNA- ase activity	[NC] gibberellins in callus of crown gall	[NC] chromatographic separation

XII. ATISANE DERIVATIVES



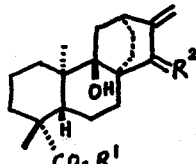
Atisane

1) Isolation and Structure Determination



279

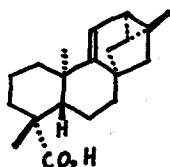
[CN] atisirene
[NS] *Thymus capitatus*
[REF] 196



280

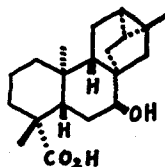
[CN] pteroatisene P₁ (R¹=H, R²=O)
pteroatisene P₂ (R¹=H, R²=α-H,
β-OH)
pteroatisenoside P₁ (R¹=β-D-
glucosyl, R²=O)

[NS] *Pteris purpureorachis*
[REF] 197, 120
[NC] X-ray analysis



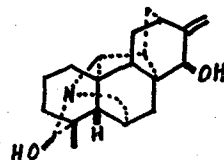
281

[CN] 9,11-dehydro
trachylobanic acid
[NS] *Viguiera* species
[REF] 165



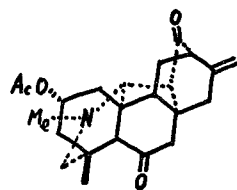
282

[CN] ciliaric acid
[NS] *Helianthus
grosseserratus*
[REF] 117



283

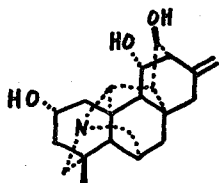
[CN] talatisine
[REF] 198
[NC] X-ray analysis



284

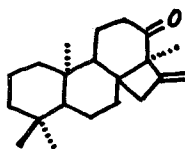
[CN] heterophylloidine
[NS] *Aconitum heterophylloides*
[REF] 199
[NC] X-ray analysis on a derivative

2) Synthesis and Reaction



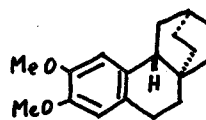
285

[CN] hetisine
[REF] 200
[NC] rearrangement with acids



286

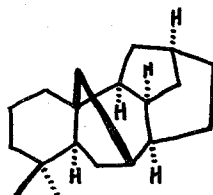
[REF] 201
[NC] rearrangement to the aconane skeleton



287

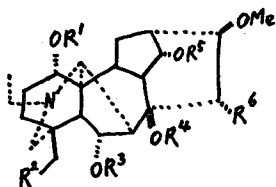
[REF] 202
[NC] synthesis from a benzylisoquinoline derivative

XIII. ACONANE DERIVATIVES



Aconane

1) Isolation and Structure Determination



288 $R^1=R^2=R^5=R^6=H$, $R^3=Ac$,
 $R^4=Me$

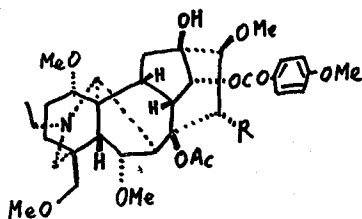
[CN] alkaloid A
[NS] *Delphinium bicolor*
[REF] 203
[NC] X-ray analysis

289 $R^1=R^3=Me$, $R^2=OMe$, $R^4=Ac$,
 $R^5=CO-C_6H_4-OMe$, $R^6=H$

[CN] foresaconitine
[NS] *Aconitum forestii*
[REF] 204

290 $R^1=R^4=R^5=H$, $R^2=OMe$,
 $R^3=Me$, $R^6=OH$

[CN] 15α -hydroxyneoline
[NS] *Aconitum* species
[REF] 205



291 R=H

[CN] crassicauline A

[NS] *Aconitum crassicaule*

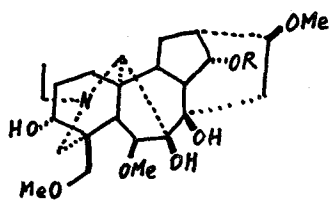
[REF] 206

292 R=OH

[CN] deoxyjesaconitine

[NS] *Aconitum subcuneatum*

[REF] 207



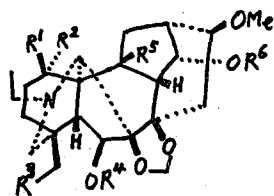
294 R=Me (acomonine)

295 R=H (iliensine)

296 R=-CO-C₆H₅
(14-benzoyliliensine)

[REF] 209

[NC] structure reinvestigation



302 R¹=R³=OMe, R²=R⁴=R⁵=R⁶=H (delcorine)

303 R¹=R³=OMe, R²=R⁴=R⁵=H, R⁶=Me (delcoridine)

[REF] 213

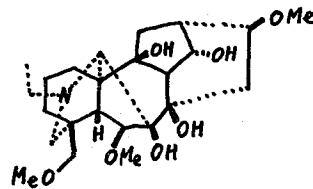
304 R¹=R³=H, R²=OMe, R⁴=Ac, R⁵=OH, R⁶=CO-CH(CH₃)CH₂CH₃ (glaucenine)

305 R¹=R³=H, R²=OMe, R⁴=Ac, R⁵=OH, R⁶=COCHMe₂ (glaucerine)

306 R¹=R³=H, R²=OMe, R⁴=Ac, R⁵=OH, R⁶=COPh (glaucephine)

[NS] *Delphinium glaucescens*

[REF] 212

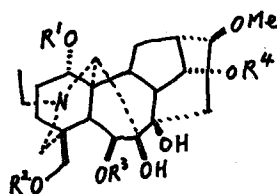


293

[CN] delcaroline

[NS] *Delphinium carolinianum*

[REF] 208



297 R¹=R³=R⁴=Me, R²=H

(lycoctonine)

298 R¹=R²=R³=Me, R⁴=H

(brownine)

[REF] 210

[NC] revision of the stereochemistry at C(1) for 37 alkaloids

299 R¹=R³=R⁴=H, R²=Me

[CN] delphinifoline

[NS] *Aconitum delphinifolium*

[REF] 211

[NC] X-ray analysis

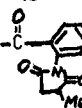
300 R¹=R²=R³=Me,

CH₃

R⁴=COCH(CH₃)CH₂CH₃ (glaucedine)

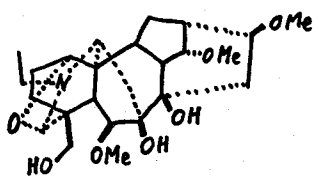
301 R¹=R⁴=Me, R²=

R³=H (glaudelsine)



[NS] *Delphinium glaucescens*

[REF] 212



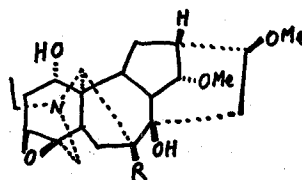
307

[CN] 18-hydroxy-14,15-dimethyloxagadine

[NS] *Consolida orientalis*

[REF] 214

[NC] X-ray analysis



308 R=H (monticamine)

309 R=OH (monticoline)

[NS] *Aconitum monticola*

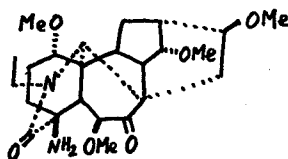
[REF] 215

Additisonal reference

[REF] 216

[NC] diterpene alkaloids from
Delphinium cardiopetalum

2) Synthesis and Reaction



310

[REF] 217

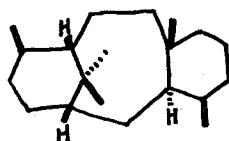
[NC] nitrous acid deamination

3) Miscellaneous Section

[REF] 218

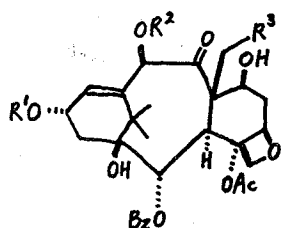
[NC] ^{13}C NMR spectra

XIV. TAXANE DERIVATIVES



Taxane

1) Isolation and Structure Determination



- 311 R¹=H, R²=Ac, R³=OH
(19-hydroxybaccatin IV)

- 312 R¹=CO-CH(Ph)CH(Me)NHCO-C(=CH₂),
R²=R³=H
(10-deacetylcephalomannine)

- 313 R¹=COCH(Ph)CH(OH)NHBz, R²=R³=H
(10-deacetyltaxol)

[NS] *Taxus wallichiana*

[REF] 219

[NC] antitumor diterpenoid

- 314 R¹=COCH(Ph)CH(Me)NHCO-C(=CH₂),
R²=Ac, R³=H

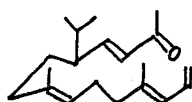
[CN] cephalomannine

[REF] 220

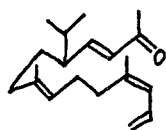
[NC] antileukemic diterpenoid, X-ray analysis

XV. THE OTHERS

1) Isolation and Structure Determination



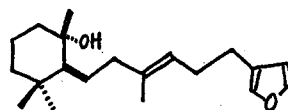
315



316

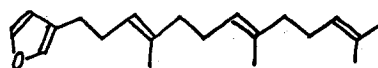
[REF] 221

[NC] from cigarette smoke



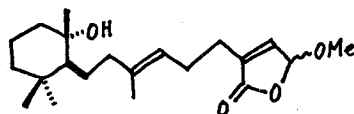
317

[CN] ambliol-A



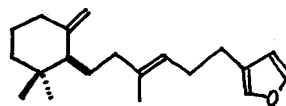
318

[CN] ambliofuran



319

[CN] ambliolide



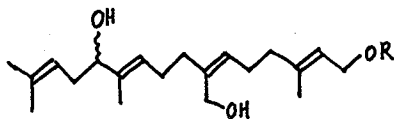
320

[CN] dehydroambliol-A

[NS] *Dysidea ambia*

[REF] 45

[NC] marine sponge metabolites

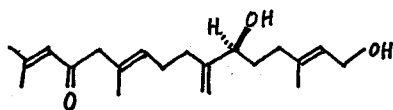


321 R=H

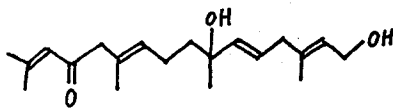
322 R=Ac

[NC] *Grazielia* species

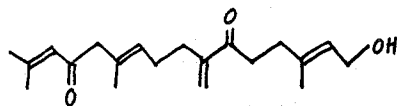
[REF] 15



323



324

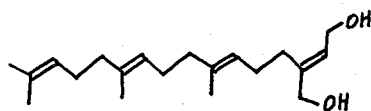


325

[NS] *Cystoseira crinita*

[REF] 222

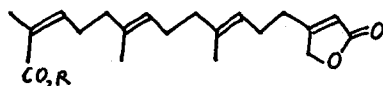
[NC] from brown alga



326

[NS] *Kingianthus paradoxus*

[REF] 223



327 R=H

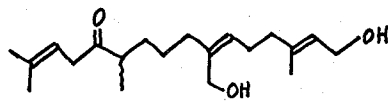
[CN] dimeroperatic acid

328 R=Me

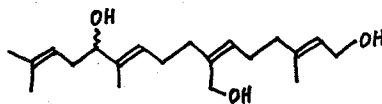
[CN] methyl dimeroperatate

[NS] *Dimerostemma asperatum*

[REF] 224



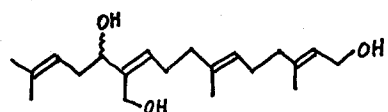
329



330

[NS] *Lasiolaena santosii*

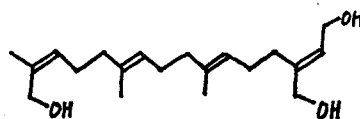
[REF] 20



331

[NS] *Zinnia tenuiflora*

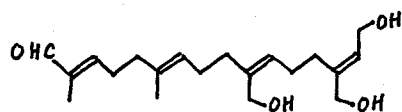
[REF] 225



332

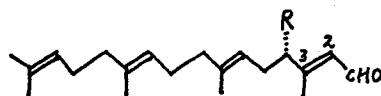
[NS] *Bejaranoa semistriata*

[REF] 226



333

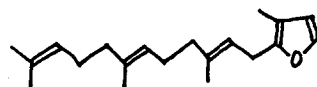
[NS] *Mikania officinalis*



334 R=H

335 R=H (2,3 Z)

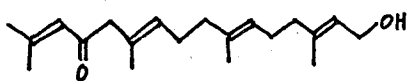
336 R=OH



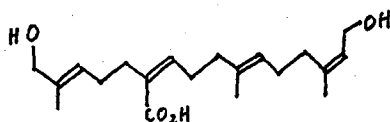
337

[NS] *Mikania sessilifolia*

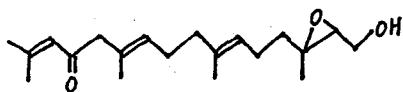
[REF] 227



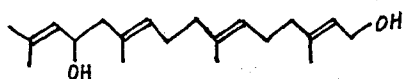
338
[CN] eleganolone



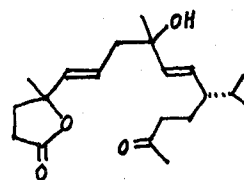
341
[NS] *Wyethia helenioides*
[REF] 229



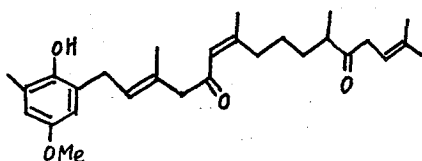
339
[CN] epoxyeleganolone



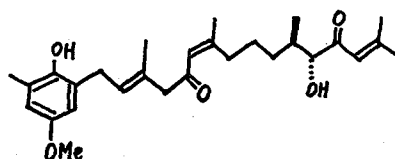
340
[CN] elegandiol
[NS] *Cystoseira elegans*
[REF] 228
[NC] seasonal variation of
a cyclic diterpenes



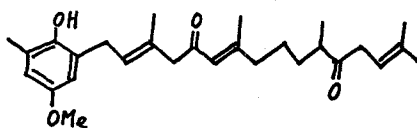
342
[REF] 230
[NC] from burley tobacco



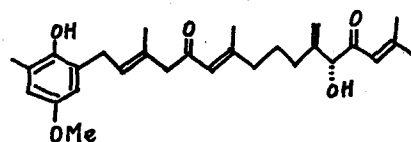
343
[CN] 5', 12'-dioxohalidrol



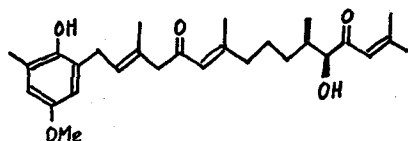
344
[CN] 12'- α -hydroxy-5', 13'-dioxohalidrol



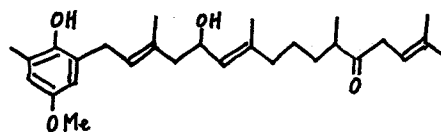
345
[CN] 5', 12'-dioxoisohalidrol



346
[CN] 12'- α -hydroxy-5', 13'-dioxoisohalidrol

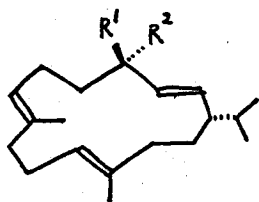


347
[CN] 12'- β -hydroxy-5', 13'-
dioxoisohalidrol

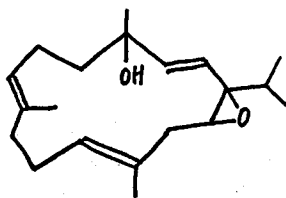


348
[CN] 5'-hydroxy-12'-oxohalidrol

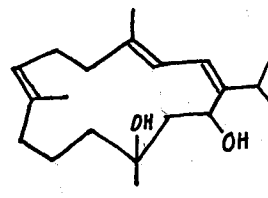
[NS] *Halidrys siliquosa*
[REF] 231



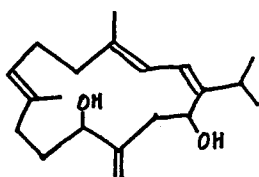
349 $R^1=OH$, $R^2=Me$
[CN] thunbegol (isocembrol)
350 $R^1=Me$, $R^2=OH$
[CN] 4-epiisocembrol
[NS] *Pseudotsuga menziesii*
[REF] 232



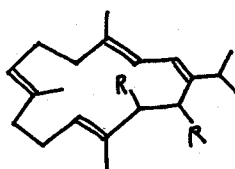
351
[CN] sarcophytol-C



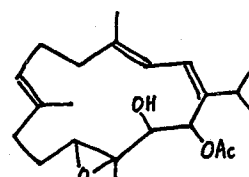
352
[CN] sarcophytol-D



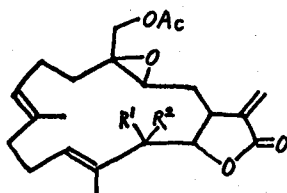
353
[CN] sarcoahytol-E
[NS] *Sarcophyton glaucum*
[REF] 233



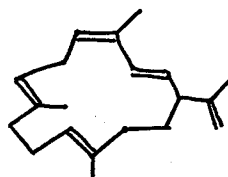
354 $R=H$
[CN] cembrene-C
355 $R=OH$
[CN] sarcophytol-B
[NS] *Alcyonium flaccidum*
[REF] 234



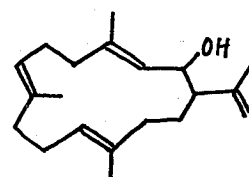
356
[CN] flaccidoxide
[NS] *A. flaccidum*
[REF] 234



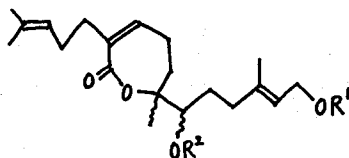
357 $R^1=R^2=H$
358 $R^1=H$, $R^2=OH$
359 $R^1=OH$, $R^2=H$
[NS] *Lobophytum crassum*
[REF] 234



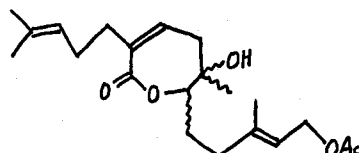
360
[CN] cembrenene



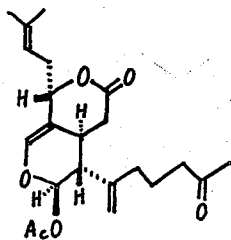
361
[CN] mayol
[NS] *Sinuralia mayi*
[REF] 235



362 $R^1=R^2=H$
[CN] acanthoaustralide
363 $R^1=Ac$, $R^2=H$
[CN] acanthoaustralide-1-O-acetate
[NS] *Acanthospermum australe*
[REF] 236

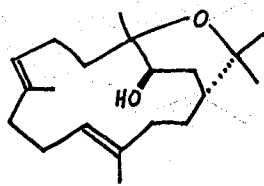


364
[CN] isoacanthoaustralide-1-O-acetate
[NS] *A. australe*
[REF] 236



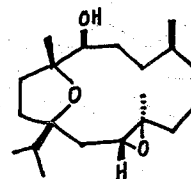
365

[CN] alcyonolide
[NS] *Akyonimu* species
[REF] 237



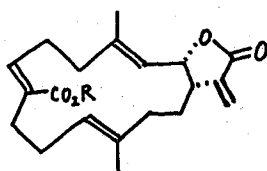
366

[CN] decaryiol
[NS] *Sarcophyton decaryi*
[REF] 238



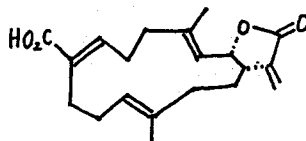
367

[CN] incensole oxide
[REF] 239
[NC] X-ray analysis



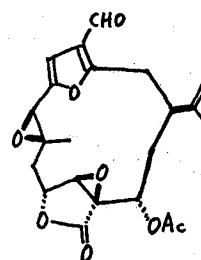
368

[CN] lobohedleolide
[NS] *Lobophytum hedleyi*
[REF] 240
[NC] X-ray analysis;
growth inhibition
of the Hella cells



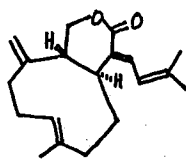
369

[CN] (7Z)-lobohedleolide
[NS] *L. hedleyi*
[REF] 240



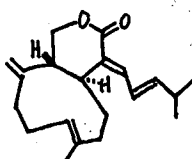
370

[CN] lophotoxin
[NS] *Lophogorgia alba*,
L. cuspidata, *L. rigida*,
L. chilensis
[REF] 241
[NC] new neuromuscular
toxin



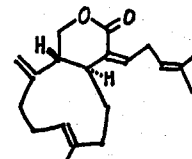
371

[CN] coraxeniolide-A



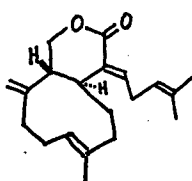
372

[CN] coraxeniolide-B



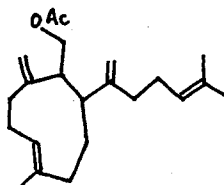
373

[CN] coraxeniolide-C



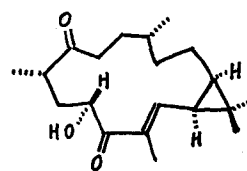
374

[CN] coraxeniolide-C'



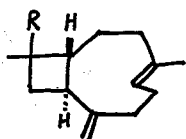
375

[CN] corabohcin
[NS] *Corallium* species
[REF] 242



376

[CN] crotonitenone
[NS] *Croton nitens*
[REF] 243

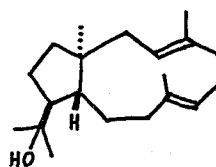


377 $R = \text{CH}_2\text{CH}_2\text{CH}(\text{O})\text{CMe}_2$

378 $R = \text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{Cl})\text{CMe}_2$

[NS] *Nephthea chabrolli*

[REF] 244

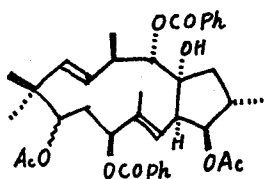


379

[CN] 18-hydroxy-3,7-dolablladiene

[NS] *Dictyota dichotoma*

[REF] 245

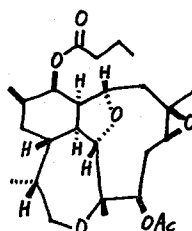


380

[NC] euphornin

[NS] *Euphorbia maddenii*

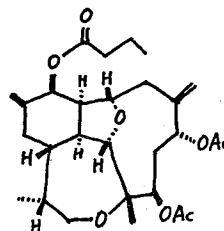
[REF] 246



381

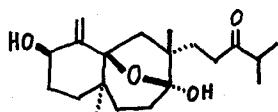
[NS] *Briareum asbestinum*

[REF] 247



382

[NC] from toxic extracts

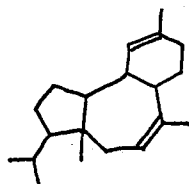


383

[CN] linearol

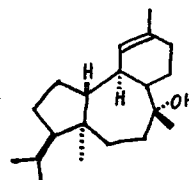
[NS] *Dictyota linearis*

[REF] 248



384

[CN] sphaerodiene



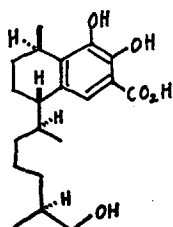
385

[CN] presphaerol

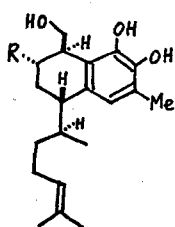
[NS] *Sphaerococcus coronopifolius*

[REF] 249

[NC] structure 385
(reassigned by
X-ray analysis)



386



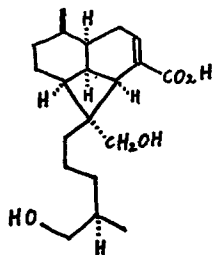
387 $R = \text{H}$

388 $R = \text{OH}$

[NS] *Eremophila* species

[REF] 250, 251

[NC] X-ray analysis

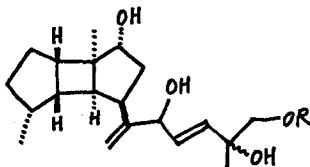


389

[NS] *Eremophila decipiens*

[REF] 252

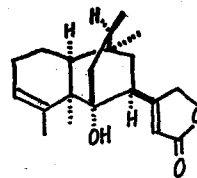
[NC] chemical degradation



390 R=H, 391 R=Ac

[NS] *Stoechospermum marginatum*

[REF] 253



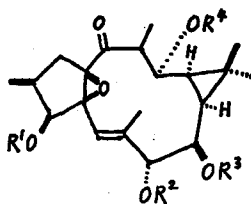
392

[CN] tricyclosolidagolactone

[NS] *Solidago altissima*

[REF] 254

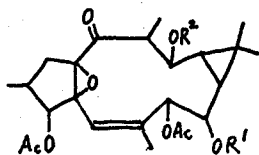
[NC] X-ray analysis



	R ¹	R ²	R ³	R ⁴
393	Ac	Ac	benzoate	Ac
394	Ac	Ac	angelate	Ac
395	Ac	Ac	tigliate	Ac
396	H	Ac	benzoate	Ac
397	H	Ac	angelate	Ac
398	H	H	tigliate	Ac
399	H	H	H	Ac
400	H	H	H	H
401	Ac	Ac	Ac	Ac

[NS] *Euphorbia kamerunica*

[REF] 255

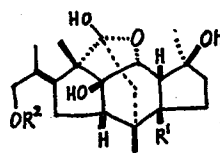


	R ¹	R ²
402	Ac	
403	H	
404	Ac	Ac

[NS] *Euphorbia kamerunica*

[REF] 256

[NC] from the cytotoxic fraction



405 R¹=R²=H

[CN] cinn cassiol D₁

406 R¹=H, R²=β-D-glc·pyr-

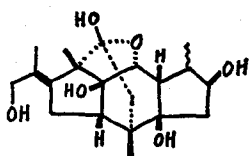
[CN] cinn cassiol D₁ glucoside

407 R¹=OH, R²=H

[CN] cinn cassiol D₂

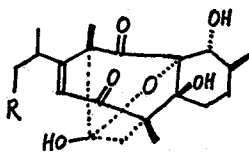
408 R¹=OH, R²=β-D-glc·pyr-

[CN] cinn cassiol D₂ glucoside



409

- [CN] cinn cassiol D₃
 [NS] *Cinnamomi cortex*
 [REF] 257
 [NC] from the fraction
 exhibiting anti-
 complement
 activity; X-ray
 analyses

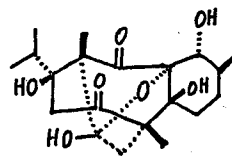


410 R = O-β-D-gluc·pyr

- [CN] cinn cassiol C₁
 glucoside

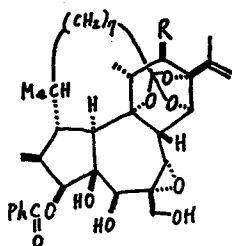
411 R = H

- [CN] cinn cassiol C₂



412

- [CN] cinn cassiol C₃
 [NS] *Cinnamomi cortex*
 [REF] 258
 [NC] from the fraction
 exhibiting anticom-
 plement activity

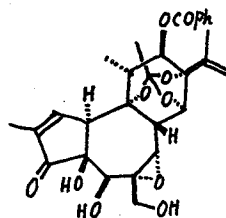


413 R = OAc

- [CN] linifolin A

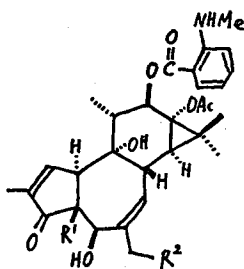
414 R = H

- [CN] linifolin B
 [NS] *Pimelea linifolia*
 [REF] 259
 [NC] fish toxin



415

- [CN] genkwadaphnin
 [NS] *Daphne genkwa*
 [REF] 260
 [NC] new antileukemic
 principle



416 R¹ = H, R² = OH

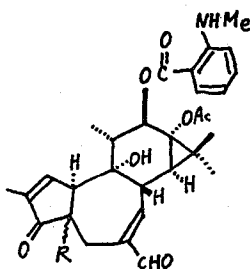
- [CN] sapintoxin B

417 R¹ = R² = H

- [CN] sapintoxin C

418 R¹ = R² = OH

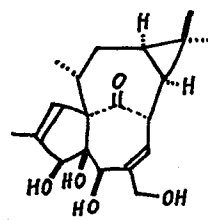
- [CN] sapintoxin D
 [NS] *Sapium indicum*
 [REF] 261, 262



419 R = β-H

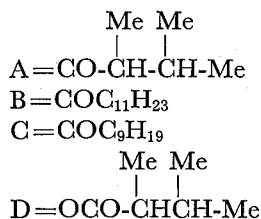
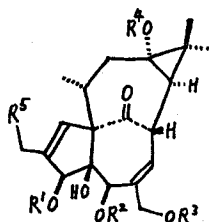
420 R = α-H

- [NS] *Sapium indicum*
 [REF] 263
 [NC] first natural tiglanes
 to exhibit a C-20
 aldehyde



421

- [CN] ingenol
 [NS] *Euphorbia ingens*
 [REF] 264

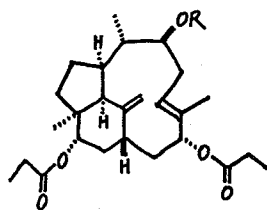


- 422 R²=R³=R⁵=H, R¹=A, R⁴=B
423 R¹=R³=R⁵=H, R²=A, R⁴=B
424 R¹=R²=R⁵=H, R³=A, R⁴=B
425 R¹=A, R²=R³=R⁵=H, R⁴=C
426 R¹=R⁴=A, R²=R³=H, R⁵=D
427 R¹=R³=H, R²=R⁴=A, R⁵=D
428 R¹=R²=H, R³=R⁴=A, R⁵=D

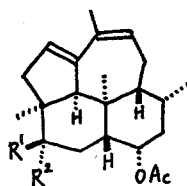
[NS] *Euphorbia cyparissias*

[REF] 265

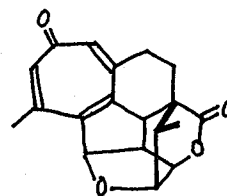
[NC] highly irritant activity



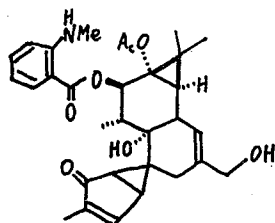
- 429 R=COEt
430 R=COMe
[NS] *Nasutitermes* species
[REF] 266
[NC] termite soldier
defense secretion



- 431 R¹=R²=O
432 R¹=OAc, R²=H
433 R¹=H, R²=OAc
[NS] *Bulbitermes singaporensis*
[REF] 267
[NC] defense secretion of the
nasute termite



- 434
[CN] harringtonolide
[NS] *Cephalotaxus*
harringtonia
[REF] 84
[NC] podolactone-type
plant growth
inhibition

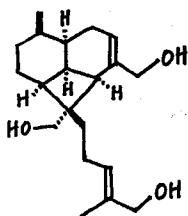


- 435
[CN] sapintoxin A
[NS] *Sapium indicum*
[REF] 268
[NC] irritant compound

Additional references

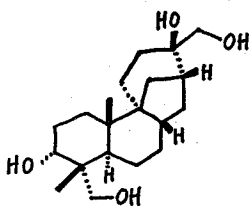
- [REF] 12
[NC] membrane diterpenoids from oleoresin of
Picea-ajanensis
[REF] 269, 270
[NC] phytochemical cultivation of Brazilian
velloziaceae
[REF] 271
[NC] diterpenoids of oleoresin of far east *Abies*
species
[REF] 272
[NC] new diterpenic acetate from a *Sideritis pusilla*

2) Synthesis and Reaction



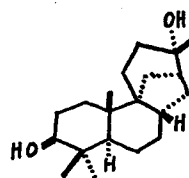
436

[CN] (+)trihydroxydecapadiene
[REF] 273
[NC] total synthesis



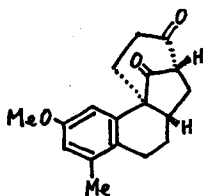
437

[CN] (+)aphidicolin
[REF] 274, 275
[NC] total synthesis



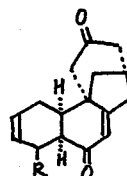
438

[CN] (+)maritimon
[REF] 276
[NC] total synthesis



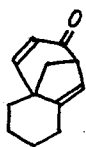
439

[REF] 277
[NC] synthesis of the basic skeleton of aphidicolan-type diterpenes

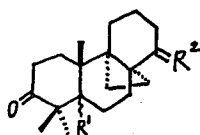


440 R=H, 441 R=OAc

[REF] 278
[NC] synthesis of the ring skeleton of aphidicolin and the related natural products

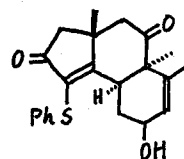


442



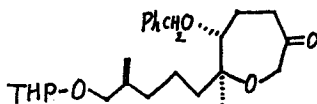
443 R¹=α-H, R²=O
444 R¹=β-H, R²=α-OH, β-H

[REF] 279
[NC] preliminary studies on the synthesis of aphidicolin



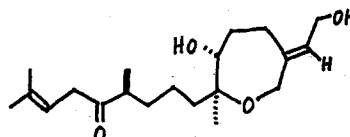
445

[REF] 280
[NC] synthesis of a potential intermediate directed towards cyathins



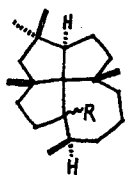
446

[REF] 281
[NC] stereoselective synthesis of a key intermediate for the total synthesis of (+)zoapatanol



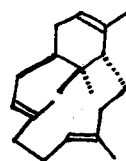
447

[CN] (+)zoapatanol
[REF] 282
[NC] total synthesis

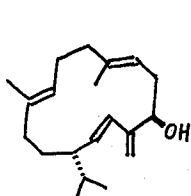


448 R= α -H
[CN] laurenane

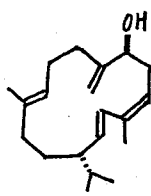
449 R= β -H
[CN] 1 β H-laurenane
[REF] 283



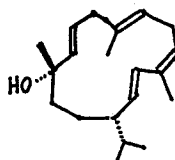
450
[REF] 284
[NC] synthesis of a geometrical isomer of anhydroverticillol



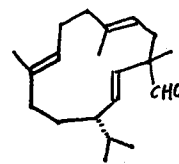
451



452

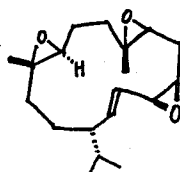


453



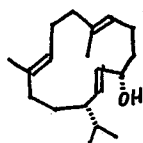
454

[REF] 285
[NC] photooxidation products of cembrene



455

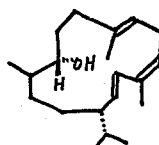
[REF] 286
[NC] complete epoxidation product of cembrene; X-ray analysis



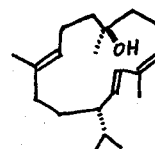
456

[CN] cembranol

453

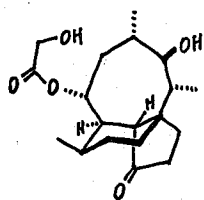


457



458

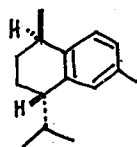
[REF] 287
[NC] reduction products of 11S,12S-epoxycembrene or 7S,8S-epoxycembrene by LiAlH₄; growth inhibition of red wheat



459

[REF] 288

[NC] chemical conversion from a pleuromutilin derivative

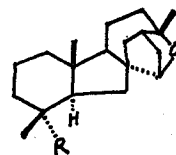


460

[CN] (1*R*,4*S*)-(-)-calamenene

[REF] 289

[NC] synthesis from dihydroxyserrulatic acid



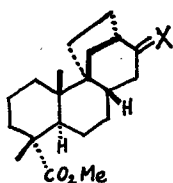
461 R=Me

462 R=CH₂OCOPh

463 R=CO₂Me

[REF] 290

[NC] chemical conversion (*in vitro* biosynthetic studies); X-ray analysis

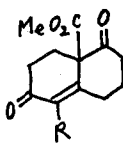


464 X=α-Me, β-OMe

465 X=α-OMe, β-Me

[REF] 291

[NC] cyclization products of methyl isopimarate and pimarate



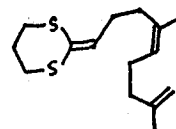
466 R=H

467 R=Me

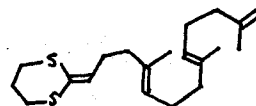
[CN] Wieland-Mischer ketone analogues

[REF] 292

[NC] intermediates in the synthesis of bruceantin



468



469

[REF] 293

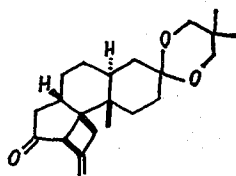
[NC] synthesis of *Z*- and *E*-polyunsaturated isoprenoids

Additional reference

[REF] 294

[NC] regiospecific and stereoselective 3α-hydroxylation of fusicoccin derivatives

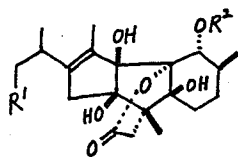
3) Miscellaneous Section



470

[REF] 295

[NC] X-ray analysis of a stemodin intermediate 470



471 R¹=H, R²=Ac

472 R¹=R²=H

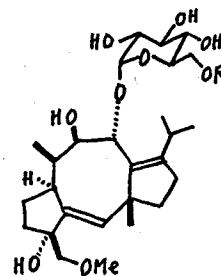
473 R¹=OH, R²=H

474 R¹=OAc, R²=H

475 R¹=O-glc(Ac), R²=H

[REF] 296

[NC] EI mass spectra of *Cassia* diterpenes



476 R=Me

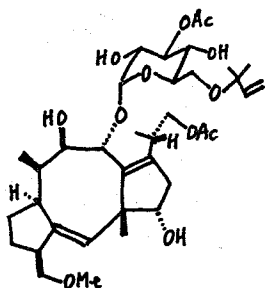
[CN] cotylenin-E

477 R=H

[CN] cotylenin-J

[REF] 297

[NC] germination-stimulating activity

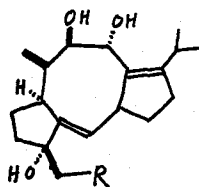


478

[CN] fusicoccin-A

[REF] 297

[NC] germination-stimulating activity



479 R=OMe

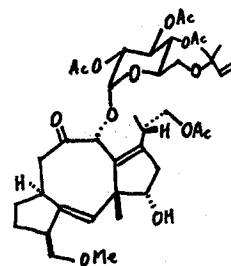
[CN] cotylenol

480 R=OH

[CN] 16-O-demethylcotylenol

[REF] 297

[NC] germination-stimulating activity

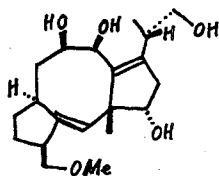


481

[CN] fusicoccin triacetate

[REF] 298

[NC] structure revision (481); preparation of 482

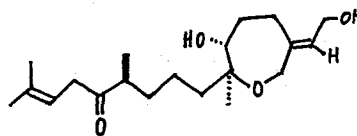


482

[CN] 9-epifusicoccin aglycone

[REF] 298

[NC] structure revision (481); preparation of 482

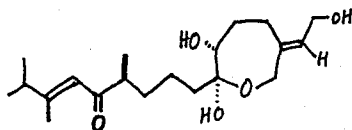


446

[CN] zoapatanol

[REF] 299

[NC] ¹³C NMR studies

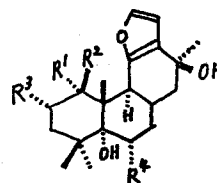


483

[CN] montanol

[REF] 299

[NC] ¹³C NMR studies



484 R¹=R³=OAc, R²=R⁴=H

485 R¹, R²=O, R³=H, R⁴=OAc

486 R¹, R²=O, R³=H, R⁴=OH

487 R¹, R⁴=OH, R²=R³=H

[RER] 300

[NC] ¹³C NMR studies of cassane diterpenoids; stereochemistry of the caesalpins

Additional reference

[REF] 301

[NC] computer-assisted structural interpretation of ^{13}C NMR spectral data

XVI. REVIEW ARTICLES

[REF] 302

[NC] irritant and defense substances

[REF] 303

[NC] terpenoid metabolites of mushrooms

[REF] 304

[NC] naturally occurring gibberellins (in Japanese)

[REF] 305

[NC] biologically active glucosides produced by fungi (in Japanese)

[REF] 306

[NC] fungal elicitors of the phytoalexin response

[REF] 307

[NC] chemistry of new natural sweet-principles (in Japanese)

[REF] 308

[NC] cocarcinogenesis and tumor promoters

[REF] 309

[NC] Chinese medicinal plants (in Japanese)

[REF] 310

[NC] decomposition of α -diazo ketones

[REF] 311

[NC] singlet oxygen in organic synthesis

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