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Triterpenoids

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This review covers the isolation and structure determination of triterpenoids reported during 2012 including squalene derivatives, lanostanes, holostanes, cycloartanes, cucurbitanes, dammaranes, euphanes, tirucallanes, tetranortriterpenoids, quassinoids, lupanes, oleananes, friedelanes, ursanes, hopanes, serratanes, isomalabaricanes and saponins; 348 references are cited.

1. Introduction

There is continued interest in the anticancer activities of triterpenoids[1–3] and their potential for treatment or prevention of diabetes and Alzheimer's disease.[4] The oral absorption and metabolism of triterpenoid saponins has been reviewed.[5] Surveys of triterpenoids from *Ceriops*,[6] and *Ilex*[7] species and *Sapindus mukorossi*,[8] have appeared.

2. The squalene group

Sapelenins G **1**–J **4** are further anti-inflammatory squalene derivatives from the bark of Cameroonian *Entandrophragma cylindricum*.[9] The highly oxidised squalene derivative **5** has been isolated from Peruvian *Protium subserratum*.[10] The structures of saiyacenols A **6** and B **7**, from the red alga *Laurencia viridis*, support the accepted pathway for the formation of the aplysiols.[11] The mechanism of triterpene biosynthesis in *Botryococcus braunii* has been reviewed.[12]

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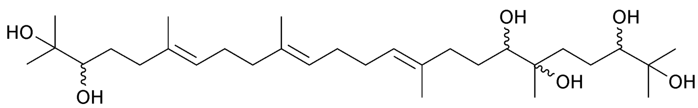
3. The lanostane group

New protostanes include alisol Q acetate **8** (ref. 13) and alisol X **9** (ref. 14) from *Alisma orientale* and the epoxy-ketone **10** from the leaves of *Aglaia odorata*.[15] The tetraterpenes abiestetranes A **11** and B **12**, from *Abies fabri*,[16] and abibalsamins A **13** and B **14**, from the oleoresin of *Abies balsamea*,[17] appear to have arisen by Diels–alder cycloadditions of rearranged lanostanes with the monoterpene β-myrcene. The structure of **13** was confirmed by X-ray analysis. A series of rearranged lanostanes, neoabiestrines A **15**–F **20**, has been reported from *Abies recurvata*.[18] The structures of neoabiestrine A **15** were confirmed by X-ray analysis. The compounds showed some cytotoxic activity. The mariesane lactone **21** has been obtained from *Abies sibirica*.[19] The tetranor derivative **22** and the 3,4-secolanostane **23** have been found in *Abies holophylla*.[20]

Pseudoferic acids A **24**, B **25** and C **26** are interesting new 16,24-cyclised lanostanes from *Pseudolarix kaempferi*.[21] The stems of *Schisandra glaucescens* contain the ring A-cleaved lanostanes schiglausins A **27**-H **34**, together with the intact derivatives schiglausins I **35** and J **36**.[22] The structure of schiglausin A **27** was confirmed by X-ray analysis. Schiglausin H **34** is the methyl ester of micranoic acid A. An impressive array of rearranged, ring A-cleaved and intact lanostanes, kadpolysperins A **37**–N **50**, has been isolated from *Kadsura polysperma*.[23] Kadcoccitones A **51** and B **52** are unusual rearranged lanostane derivatives from *Kadsura coccinea* where they occur with kadcoccitone C **53**, whose structure was confirmed by X-ray analysis.[24] Secococcinic acids G **54**–K **58** are further constituents of *Kadsura coccinea*.[25] Three esters **59–61** of 3-epidehydrotumulosic acid have been obtained from *Wolfiporia extensa*.[26] Other new lanostanes include lanosta-5,15-dien-3α-ol **62** from *Arctium lappa*[27] and inonotsuoxodiols B **63** and C **64**, epoxyinonotsudiol **65** and methoxyinonotsutriol **66** from *Inonotus obliquus*.[28]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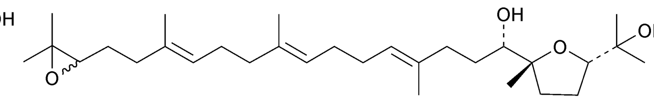
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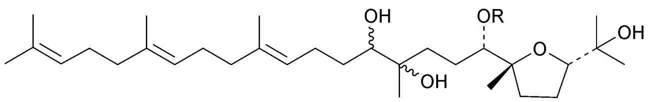
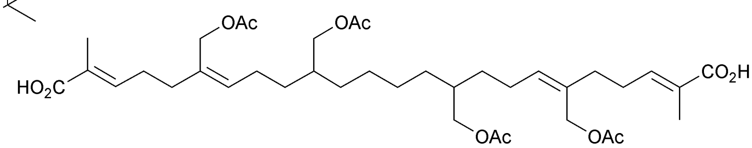

3 R = H
4 R = Ac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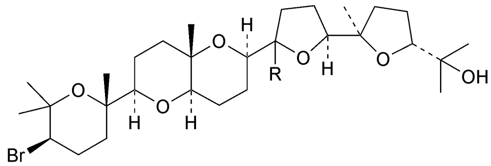
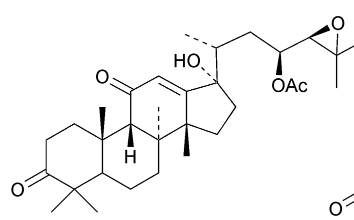
Sarasinosides N–R are 30-norlanostane glycosides from the sponge *Lypastrotethya* sp. with the new genins **67**, **68**, **69** and the 30-*nor*-18(13 → 14)-*abeo*-derivative **70**.[29] Scillanostaside F, with the new genin **71**, and scillanostaside G, with a known tetranorlanostane genin, have been isolated from the bulbs of *Scilla scilloides*.[30]


6 R = βCH$_3$
7 R = αCH$_3$

New compounds from *Ganoderma sinense* include the pentanor derivative ganosineniol A **72**, ganoderic acids J$_c$ **73** and J$_d$ **74**, ganodermatetraol **75**, the glucosyl ester ganosinoside A **76** with a known genin, ganolucidic acid γ$_a$ **77**, ganolucidate F **78**, ganoderiol J **79** and methyl lucidenate H$_a$ **80**.[31] Ganodermacetal **81** is an acetonide from *Ganoderma amboinense*[32] and lucialdehyde E **82** is a further compound from *Ganoderma lucidum*.[33] Reviews have appeared on the triterpenoids of *Ganoderma lucidum*[34,35] and lanostanes from fungi.[36]

Astraodoric acids A **83**–D **86** are metabolites of the mushroom *Astraeus odoratus*.[29] The structure of astraodoric acid B **84** was confirmed by X-ray analysis. The structure of astrakurkurol **87**, from the Indian edible mushroom *Astaeus hygrometricus*, was also confirmed by X-ray analysis.[37] The corresponding lactone, astrakurkurone **88**, was also obtained. Two highly acetylated lanostanes, coprinacins A **89** and B **90**, have been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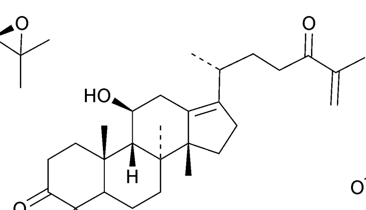
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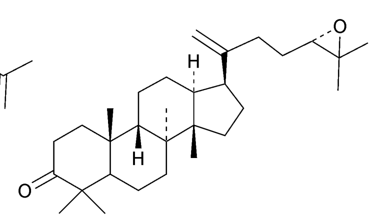
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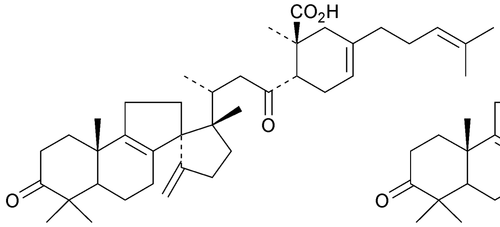
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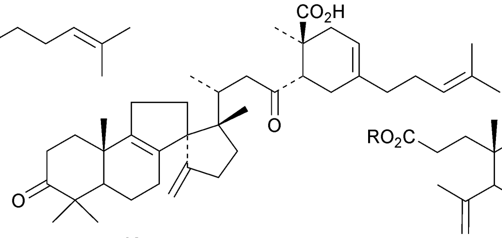
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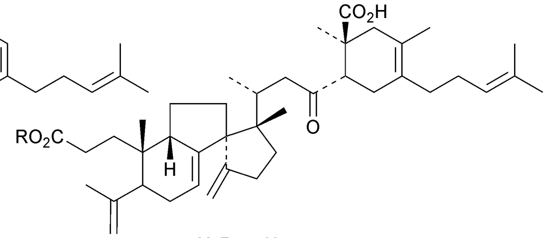
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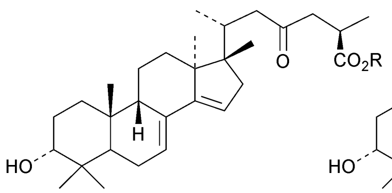
14 R = Me



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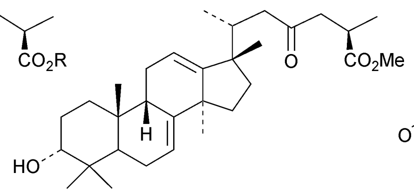
16 R = Me



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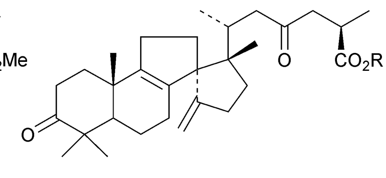
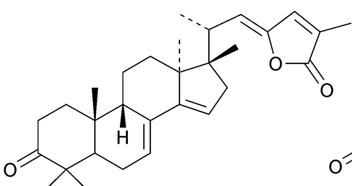


18 R = H
19 R =Me
20 R =H; 24,25-didehydro (*E*-)



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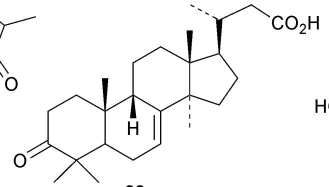

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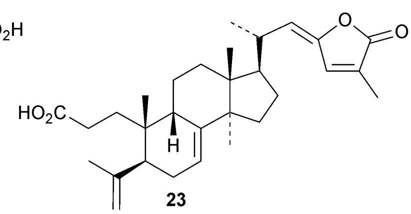

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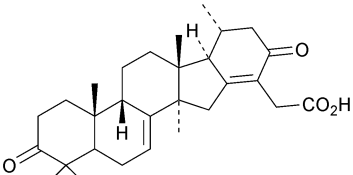

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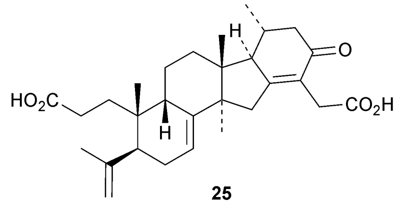

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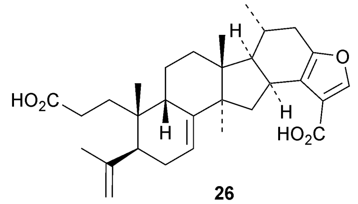

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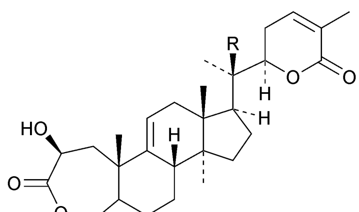
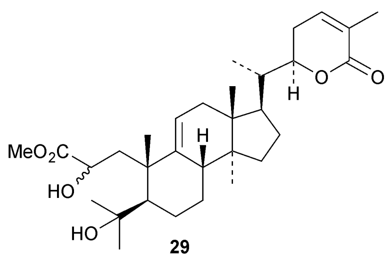


27 R = H
28 R = OH



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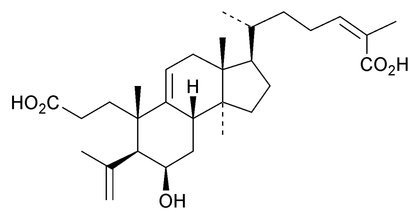

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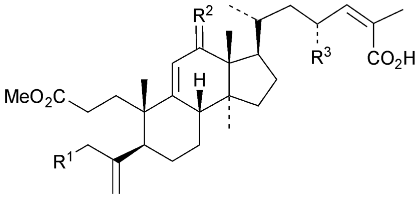
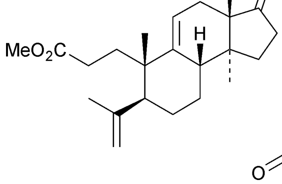


31 R^1= H; R^2 = H_2; R^3 = OH
32 R^1= OH; R^2 = H_2; R^3 = H
33 R^1= H; R^2 = O; R^3 = H



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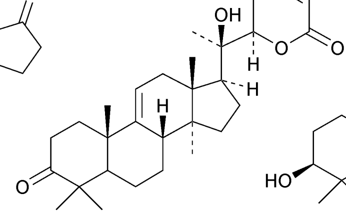

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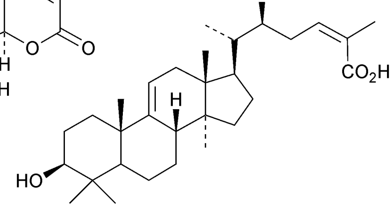

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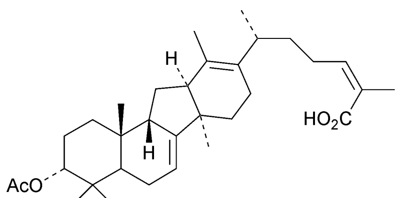
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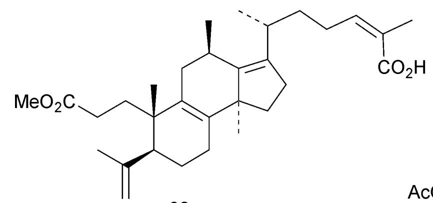
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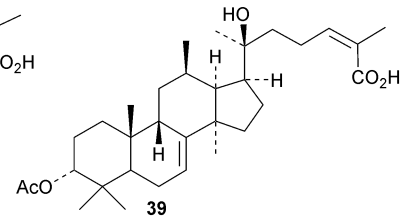
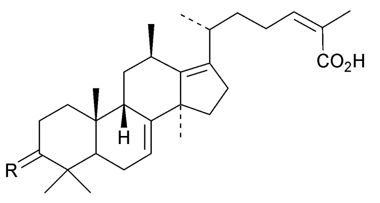
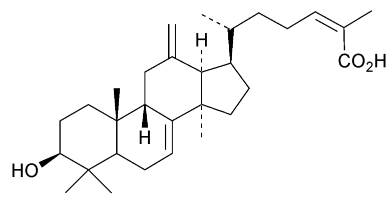

39
40 Δ^8 isomer


41 R = O
42 R = βOH, H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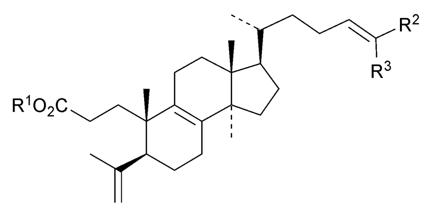
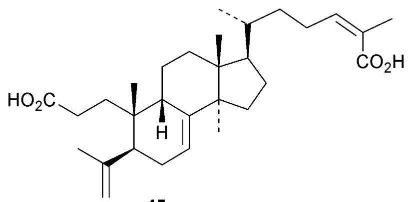

44 R^1 = H; R^2 = CO_2H; R^3 = CH_3
46 R^1 = Me; R^2 = CH_3; R^3 = CO_2H
47 R^1 = Me; R^2 = CO_2H; R^3 = CH_3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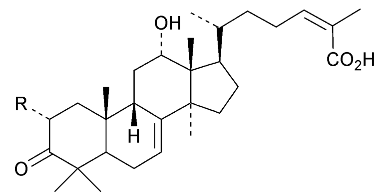
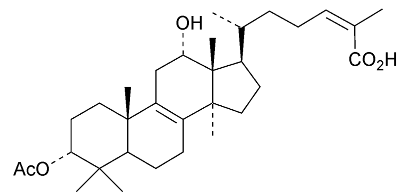

48 R = OAc
49 R = H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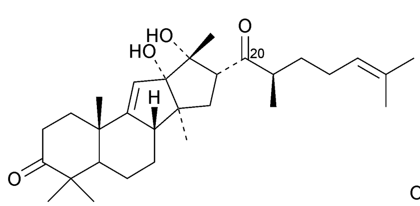
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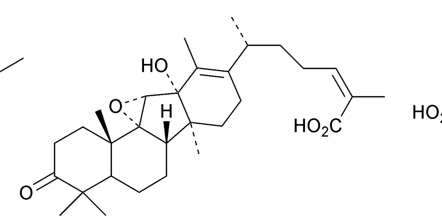
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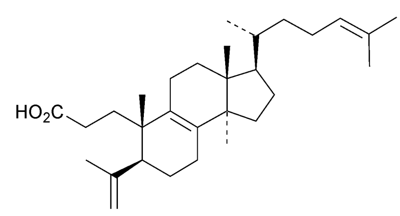
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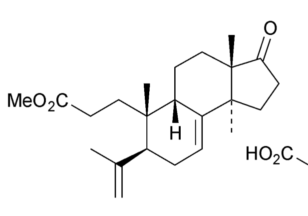
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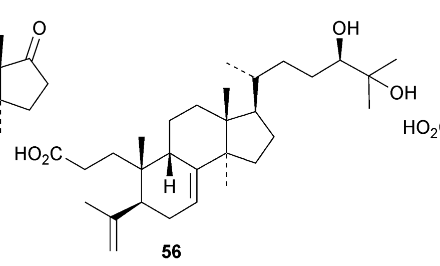
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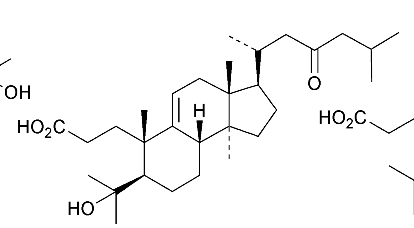
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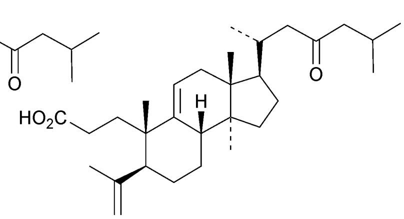
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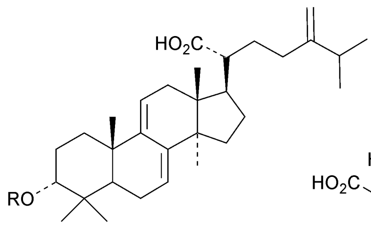
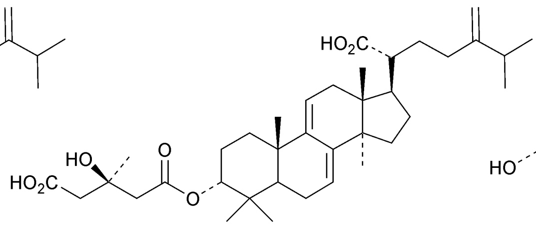


59 R = benzoyl
60 R = $OCCH_2CO_2Me$



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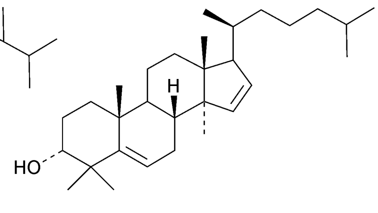

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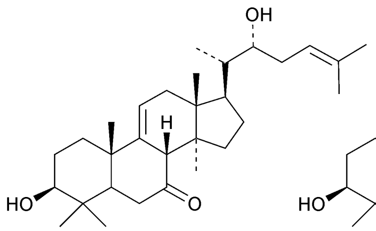

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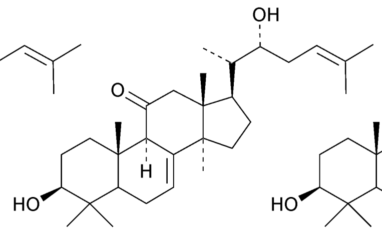

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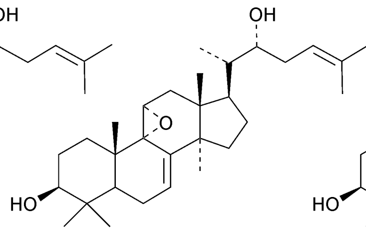

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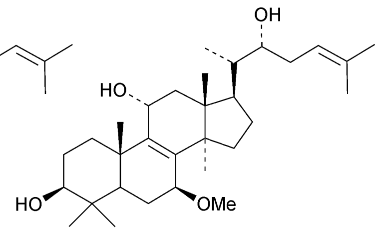

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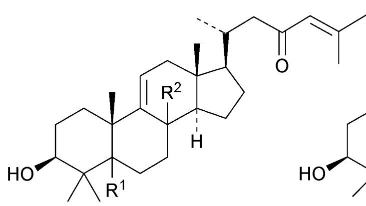
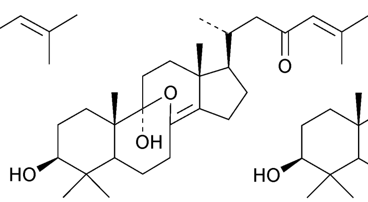


67 $R^1 = R^2 = \alpha OH$
68 $R^1 = R^2 = \beta OH$



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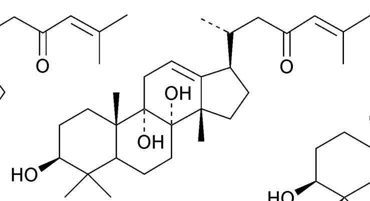

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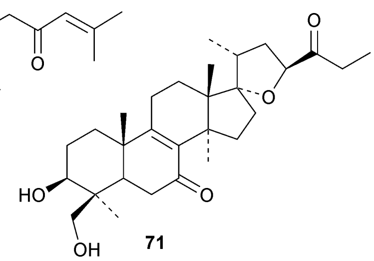

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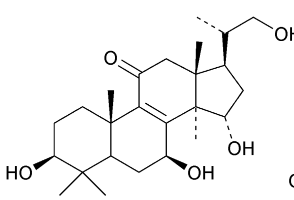

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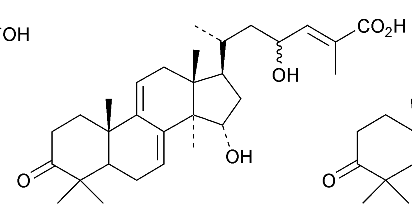

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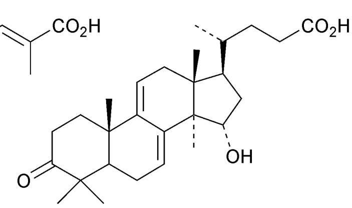

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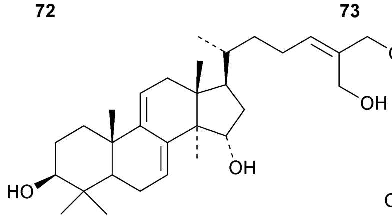

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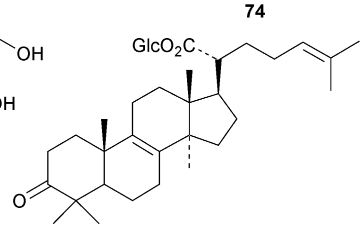

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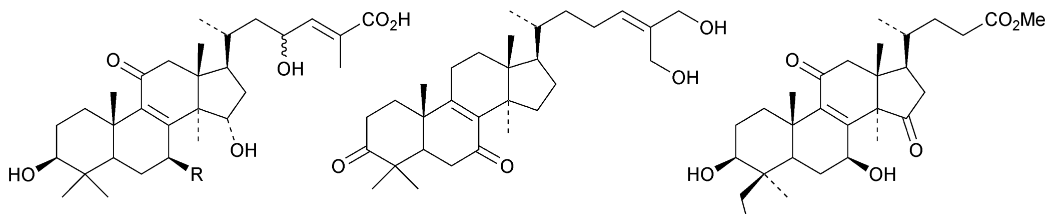
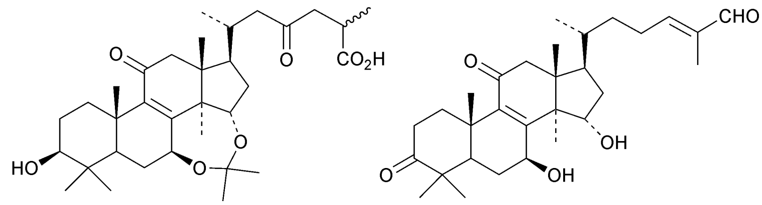


77 R = OH
78 R = H
79
80

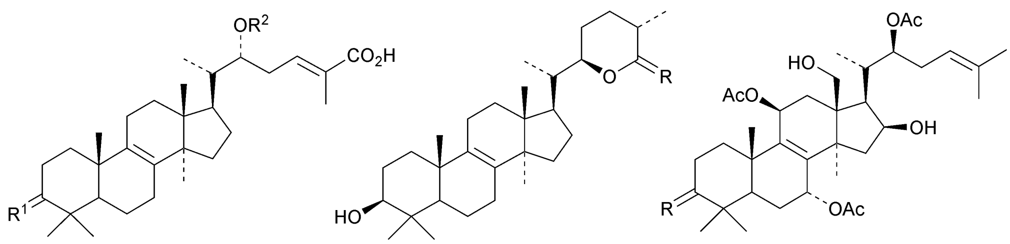


81
82

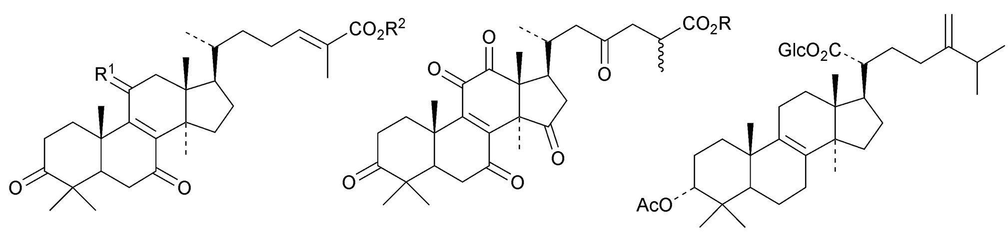
reported from *Coprinus cinereus*.[38] Other fungal metabolites include **91–94** from *Antrodia camphorate*[39] and formitoside K **95**, a glucoside with a new genin, from *Fomitopsis nigra*.[40]

Cucumarioside A8 is a lanostane saponin with the new genin **96** from the sea cucumber *Eupentacta fraudatrix*.[41] The sea cucumber *Apostichopus japonicus* is the source of several saponins, 26-*nor*-25-oxoholotoxin A_1 with the new genin **97** and holototoxins D–G.[42] Holototoxins F and G have the new genin **98** while the genins of D and E are known. Cucumariosides B_1 and B_2[43] and cucumariosides H_2, H_3 and H_4,[44] from *Eupentacta fraudatrix*, all have known genins. Holostane saponins and their biological activity have been reviewed.[45]

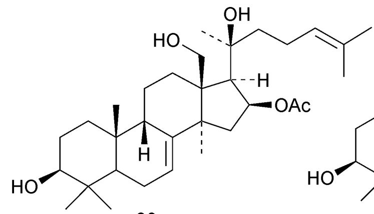
Interesting new structures continue to appear from *Schisandra* species. Schilancitrilactones A **99**, B **100** and C **101**



83 R^1 = O; R^2 = Ac
84 R^1 = O; R^2 = H
85 R^1 = αOH, H; R^2 = H
86 R^1 = αOH, H; R^2 = Ac
87 R = αOEt, H
88 R = O
89 R = O
90 R = βOAc, H



91 R^1 = O; R^2 = H
92 R^1 = αOH, H; R^2 = Me
93 R = Me
94 R = Et
95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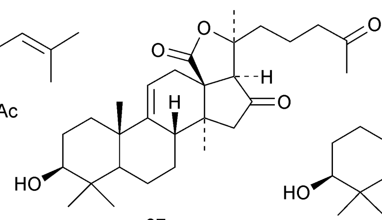
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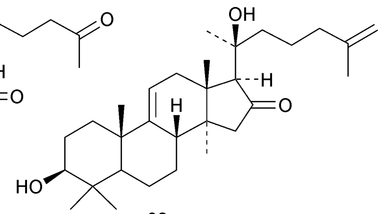
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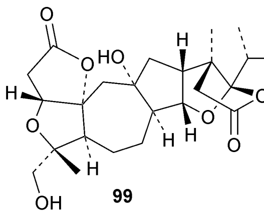
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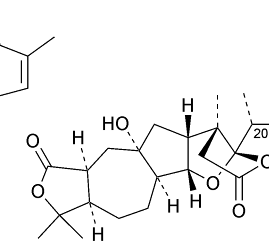
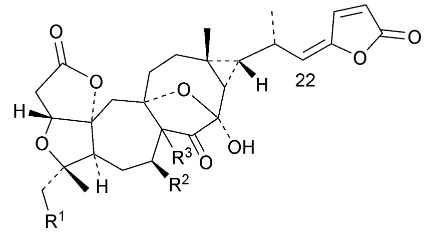
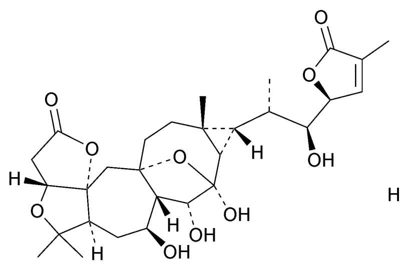

100
101 20-epimer


102 R^1 = H; R^2 = OH; R^3 = βH
103 R^1 = H; R^2 = OH; R^3 = βH; 22*Z*
104 R^1 = OH; R^2 = H; R^3 = αH; 22*Z*
105 R^1 = OH; R^2 = H; R^3 = βH
106 R^1 = OH; R^2 = H; R^3 = βH; 22*Z*

have been reported from *Schisandra lancifolia*.[46] The structures of all the schilancitrilactones were confirmed by X-ray analyses. New structures from *Schisandra sphenanthera* include preschisanartanins E **102**–J **107** and sphenadilactones D **108**–F **110**.[47] Isoschicagenin C **111**, preschisanartanins K **112**–M **114**, schisdilactones A **115**–G **121** and schinesdilactones A **122** and B **123** constitute an impressive array of new derivatives from *Schisandra chinensis*.[48] Schiglausins K **124**–O **128** are simple ring A-cleaved cycloartanes from *Schisandra glaucescens*.[49]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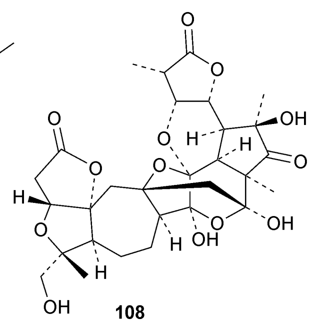
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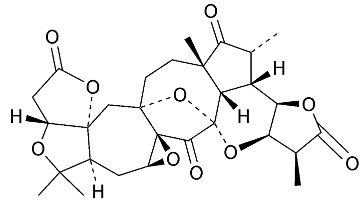
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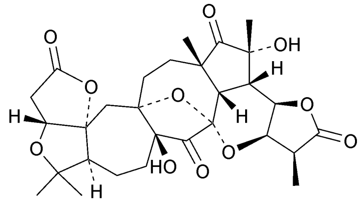
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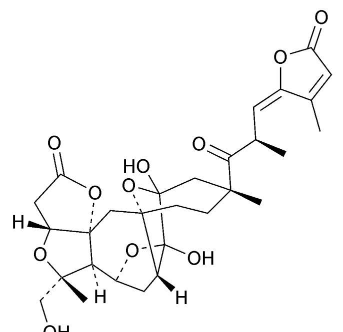

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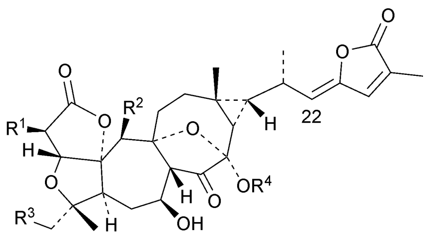
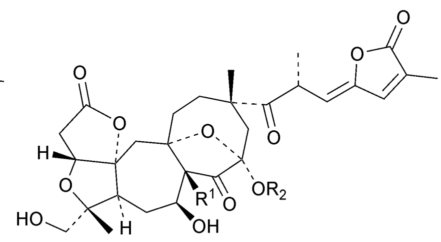
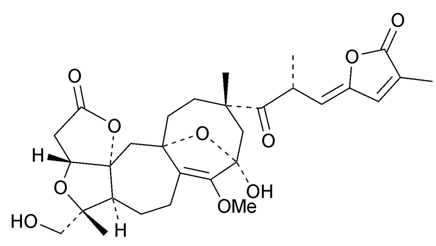


112 $R^1 = R^4 = R^4 = H$; $R^2 = OH$
113 $R^1 = R^2 = H$; $R^3 = OH$; $R^4 = Me$
114 $R^1 = OH$; $R^2 = R^3 = H$; $R^4 = Me$; 22*E*



115 $R^1 = H$; $R^2 = Me$
116 $R^1 = H$; $R^2 = Me$; 20-epimer
117 $R^1 = OH$; $R^2 = Me$
118 $R^1 = OH$; $R^2 = Me$; 20-epimer
119 $R^1 = R^2 = H$



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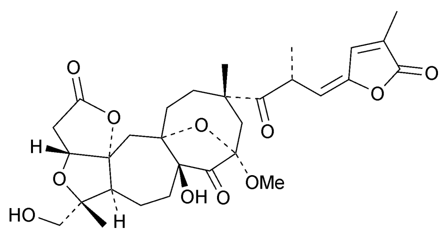

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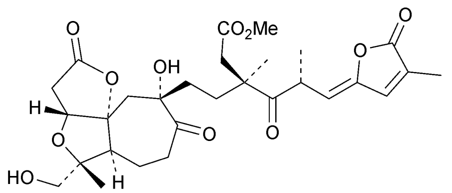
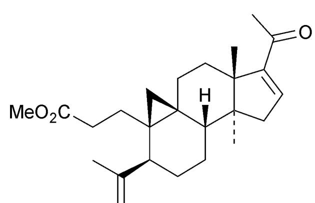


122
123 20-epimer



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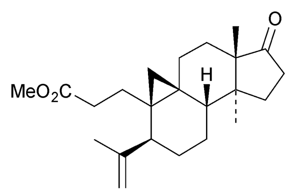

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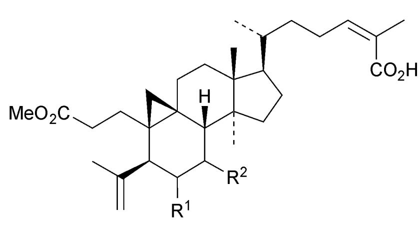
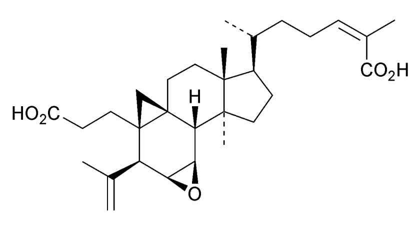
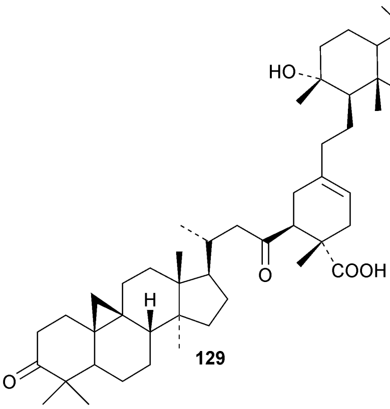


126 $R^1 = H$; $R^2 = \beta OH$
128 $R^1 = R^2 = OH$



127

An interesting approach to the "dereplication, residual complexity and rational naming" of the *Actea* triterpenoids has the potential to be applied to other groups of natural products with the same inherent problems.[50] Pseudolaridimers A **129** and B **130**, from *Pseudolarix amabilis*, appear to have arisen by a Diels–Alder reaction involving a cycloartane and a labdane.[51] The structure of **129** was confirmed by an X-ray analysis of the corresponding methyl ester. The cycloartanes lygodipenoids A



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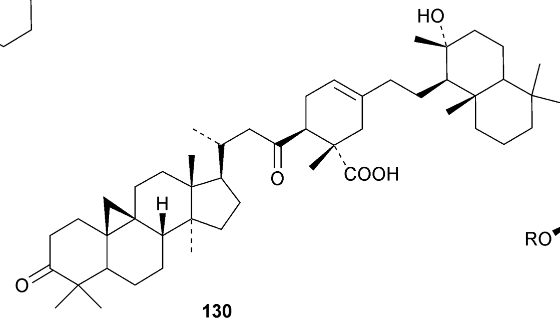

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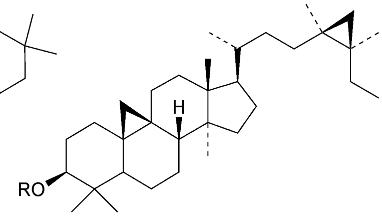
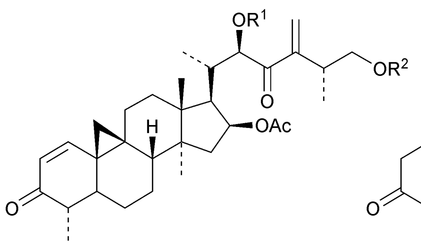
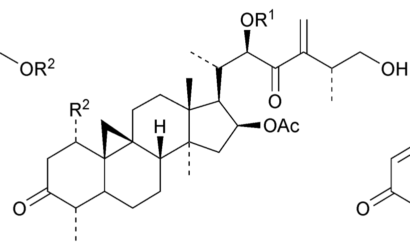


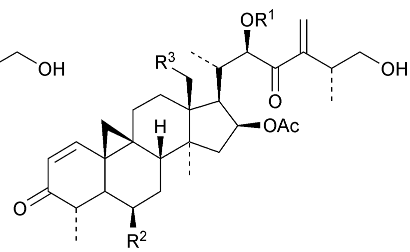
131 R = H
132 R = Ac



133 R¹ = Ac; R² = H
134 R¹ = R² = H
135 R¹ = R² = Ac
143 R¹ = Ac; R² = H; 25-epimer

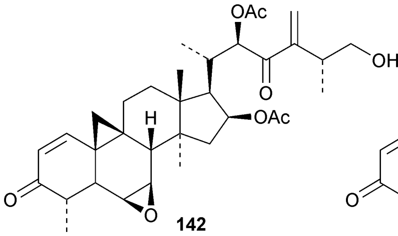


136 R¹ = Ac; R² = H
137 R¹ = R² = H
138 R¹ = H; R² = OH

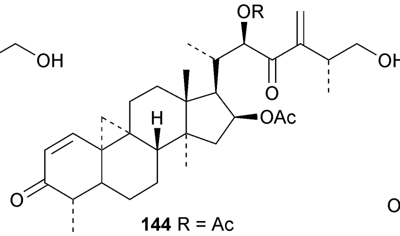


139 R¹ = Ac; R² = OH; R³ = H
140 R¹ =H; R² = OH; R³ = H
141 R¹ = Ac; R² = H; R³ = OH

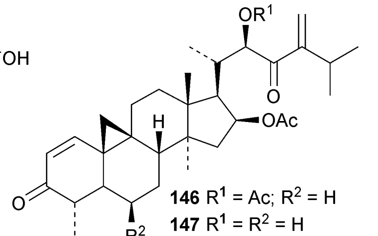
131 and B **132**, from *Lygodium japonicum*, have an additional cyclopropane in their side chains.[52] Thirty new cycloartane proteasome inhibitors **133–162** have been reported from *Neoboutonia melleri*.[53] An interesting UV light-induced inversion of the configurations at C-9 and C-10 was observed in this series. Caloncobic acids A **163** and B **164** and caloncobalactones A **165** and B **166** are constituents of the leaves of *Caloncoba glauca*.[54] Compounds **167–172** are new cycloartanes from the leaves of *Homonoia riparia*.[55] Neoabiestrines G **173**–I **175** have been reported from *Abies recurvata*.[18] The structure of neoabiestrine H **174** was confirmed by X-ray analysis. Other new cycloartanes include the trinor derivatives **176** and **177** from *Abies holophylla*,[20] rotundusolide C **178** from the rhizomes of *Cyperus rotundus*,[56] **179–182** from the aerial parts of *Atemisia lagocephala*,[57] three esters **183–185** of cyclomargenol from *Krameria pauciflora*,[58] euphonerins A **186**–G **192** from the leaves of *Euphorbia neriifolia*,[59] cycloccidentalic acids A **193** and B **194** and the related saponins cycloccidentalisides I **195**–V **199** from



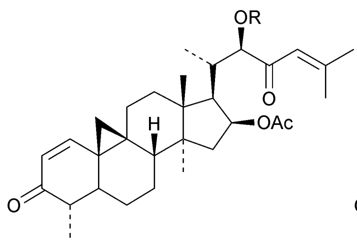
142



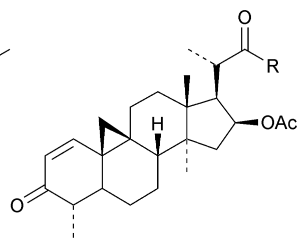
144 R = Ac
145 R = H



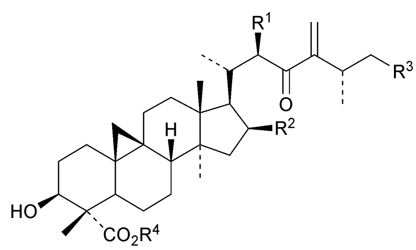
146 R¹ = Ac; R² = H
147 R¹ = R² = H
148 R¹ = Ac; R² = OH
149 R¹ = R² = H; 1,2-dihydro
150 R¹ = Ac; R² = H; 9,10-diepimer



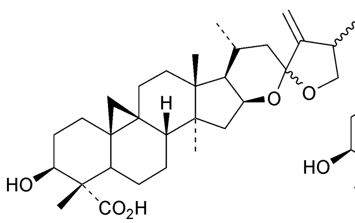
151 R = Ac
152 R = H
153 R = Ac; 9,10-diepimer



154 R = H
155 R = OH



156 $R^1 = R^4 = H$; R^2 = OAc; R^3 = OH
157 R^1 = OH; R^2 = OAc; R^3 = H; R^4 = H
158 $R^1 = R^2 = R^4 = H$; $R^3 = H$
159 $R^1 = R^2 = R^3 = H$; R^4 = Rha



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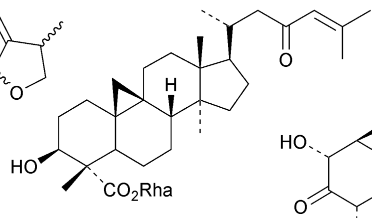

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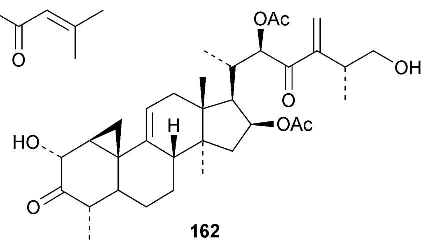

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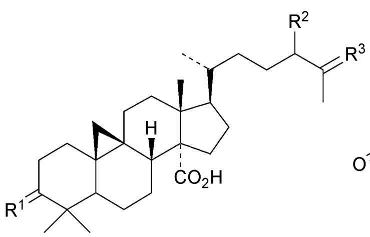
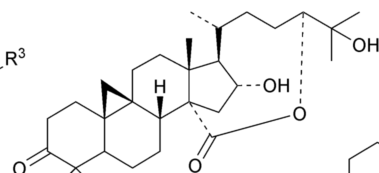


163 R^1 = O; $R^2 = \alpha$OH; $R^3 = CH_2$
164 $R^1 = \beta$OH, H; $R^2 = \beta$OH; $R^3 = CH_3$, ,OH



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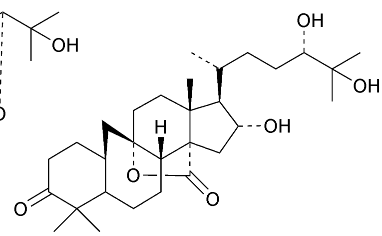

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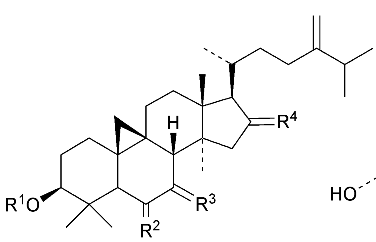
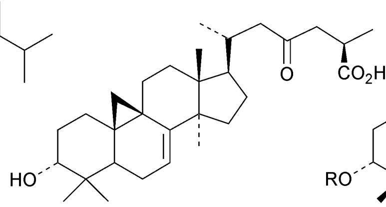


167 R^1 = H; $R^2 = R^3 = \beta$OH, H; $R^4 = H_2$
168 R^1 = H; $R^2 = R^3 = R^4 = \beta$OH, H
169 R^1 = H; $R^2 = R^4 = \beta$OH, H; $R^3 = H_2$
170 R^1 = Xyl; $R^2 = H_2$; $R^3 = R^4 = \beta$OH, H
171 R^1 = Xyl; $R^2 = R^4$ = H,βOH; $R^3 = H_2$
172 R^1 = Xyl; $R^2 = R^3 = \beta$OH, H; $R^4 = H_2$



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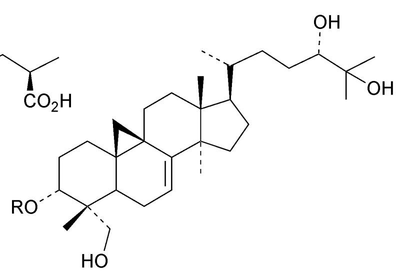
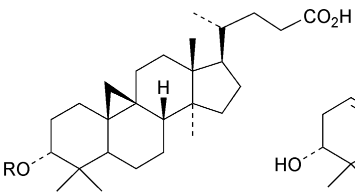
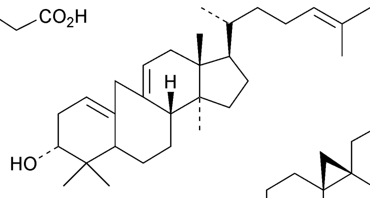


174 R = H
175 R = Me



176 R = H
177 R = Me



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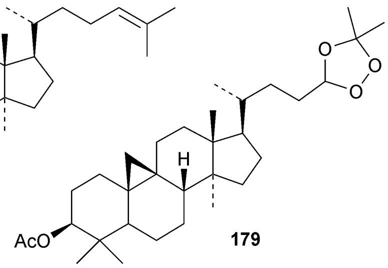

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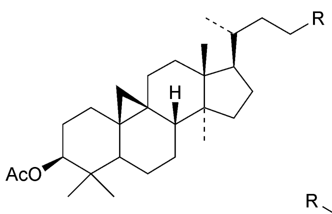
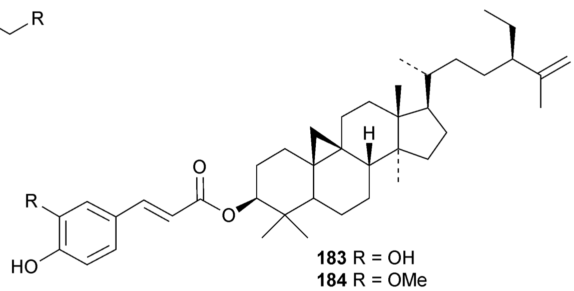
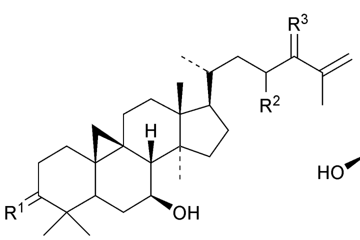


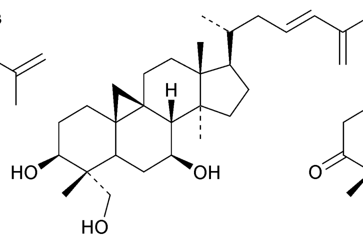
180 R = CHO
181 R = CH_2OH
182 R = OH



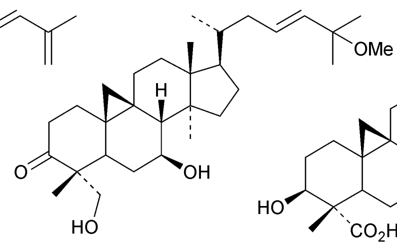
183 R = OH
184 R = OMe
185 R = H



186 R^1 = βOH, H; R^2 = H; R^3 = CH_3, OH
187 R^1 = βOH, H; R^2 = OH; R^3 = CH_3, H
188 R^1 = βOH, H; R^2 = αOH; R^3 = CH_2; 25,26-dihydro
190 R^1 = O; R^2 = βOH; R^3 = βOH, H



189



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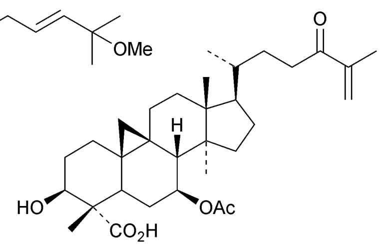

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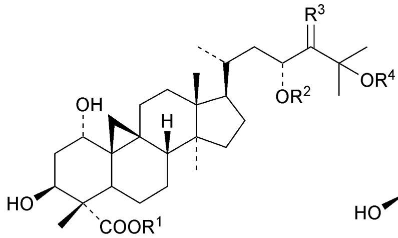
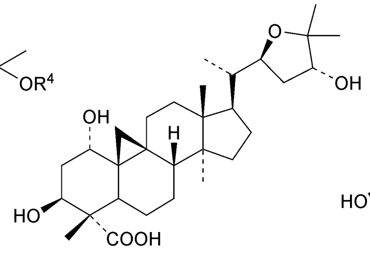


193 R^1 = R^2 = R^4 = H; R^3 = βOH, H
195 R^1 = Glc; R^2 = R^4 = H; R^3 = βOH, H
196 R^1 = R^4 = H; R^2 = Glc; R^3 = βOH, H
197 R^1 = Glc; R^2 = H; R^3= αOH, H; R^4 = Me



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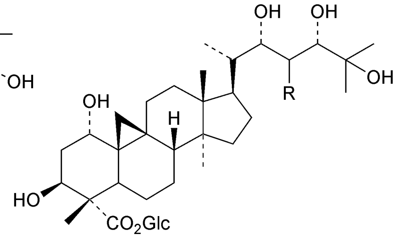
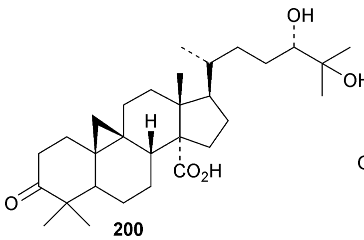


198 R = H
199 R = OH

Cassia occidentalis,[60] glaucartanoic acids A **200** and B **201** from the fruit of *Caloncoba glauca*[61] and **202** from the leaves of *Aglaia exima*.[62] Compounds **203**, **204** and the acetonide **205**, a likely artefact, have been obtained from the resin of *Commiphora opobalsamum*.[63] The structures of **203** and **205** were confirmed by X-ray analyses.

New cycloartanes continue to be isolated from *Cimicifuga* species. *Cimicifuga foetida* is the source of compounds **206–209** (ref. 70) and of 24-*epi*-cimigenol-3-one **210** and the xyloside foetinoside **211**.[64] The ring A-cleaved derivative **212**, the cimigenol arabinosides **213–215**, the 25-dehydrocimigenol arabinoside **216**, compounds **217–219** and the shengmanol arabinoside **220** have all been isolated from the roots of *Cimicifuga heracleifolia*.[65] Other new compounds include the galactopyranosides **221–223**, all with new genins, from the roots



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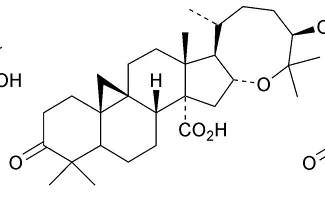

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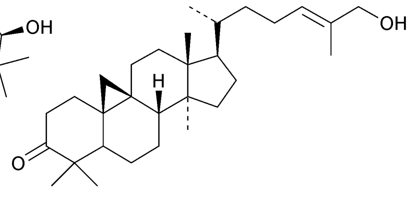

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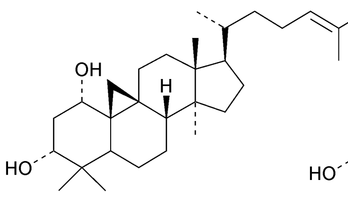

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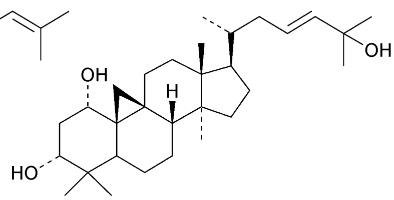

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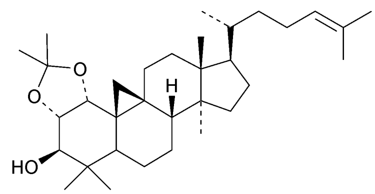

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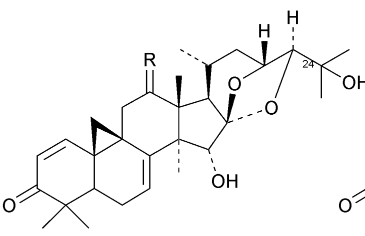
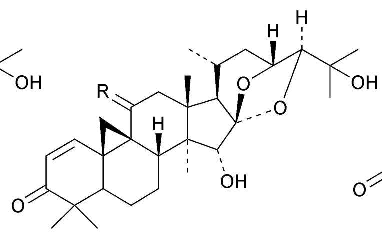
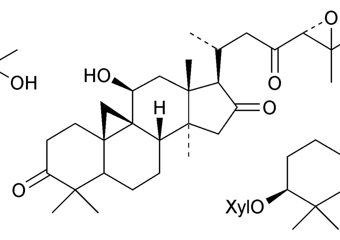


206 R = O
210 R = H_2; 7,8β-dihydro; 24-epimer



207 R = O
208 R = βOH, H; 7,8-didehydro; 1,2-dihydro



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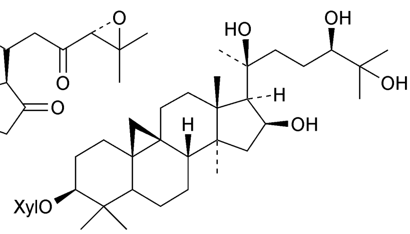

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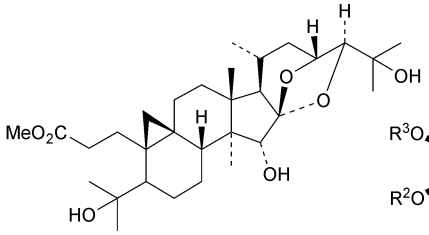

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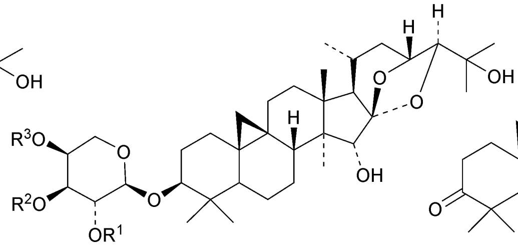
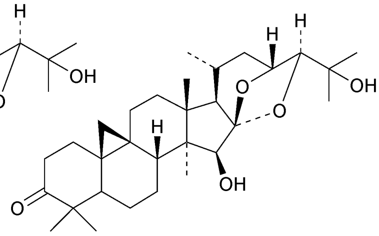


213 $R^1 = R^3$ = Ac; R^2 = H
214 R^1 = H; $R^2 = R^3$ = Ac
215 $R^1 = R^2$ = H; R^3 = Ac
216 $R^1 = R^3$ = H; R^2 = Ac; 25,26-anhydro



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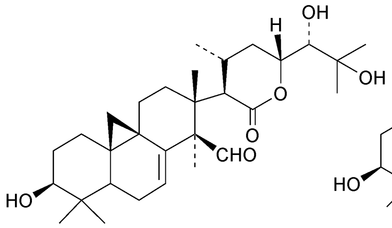

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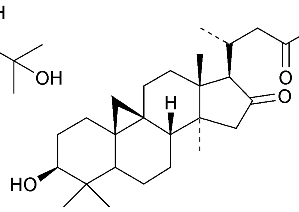

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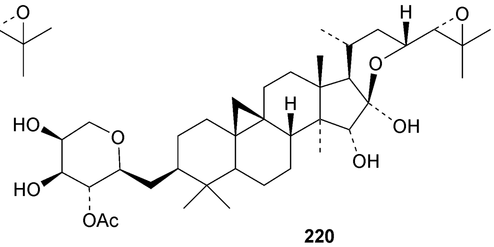
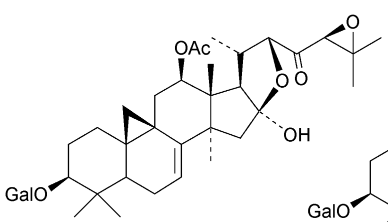


220

of *Cimicifuga simplex*[66] and isocimipodocarpaside **224** from *Cimicifuga racemosa*.[67]

Six cycloartane saponins with the new genins **225–228** have been obtained from *Astragalus angustifolius*.[68] Cycloquivinoside A **229** is a new saponin from *Astragalus chivensis*.[69] The new genin cycloartane-3β,6α,16β,20*S*,24*R*,25-hexol **230** has been identified in the saponins of *Astragalus stereocalyx*[70] and in saponins from *Astragalus schottianus*.[71] Nervisides A **231**–C **233**, from *Nervilia fordii*, all have new genins.[72] Other cycloartane saponins with new genins include curculigosaponins N and O from *Curculigo orchioides* with the genin **234** (ref. 73) and two saponins from *Thalictrum fortune* with the genins **235** and **236**.[74] The ring-A cleaved cycloartanes sootependial **237** and sootepenoic acid **238** have been isolated from the exudates of *Gardenia sootepensis*.[75] Novel cycloartane saponins with known genins include cycloascidoside from *Astragalus mucidus*,[76] cyclogaleginoside C from *Astragalus galegiformis* and cycloascauloside D from *Astragalus caucasicus*,[77] hareftosides A–D from *Astragalus hareftae*,[78] neoastragaloside I from *Astragalus membranaceus*[79] and unnamed saponins from *Astragalus erinaceus*.[80]

A new nitrogen-containing cucurbitane, endecaphyllacin C **239**, has been reported from the tubers of *Hemsleya endecaphylla*.[81] Eleaocarpucins A **240**–H **247** are 16,23-epoxy derivatives from *Eleaocarpus chinensis*.[82] The new cucurbitanes jinfushanencins A **248** and B **249** occur in the tubers of *Hemsleya penxianensis*, together with the glycosides jinfushanosides E–K.[83] Jinfushanoside K has the new genin **250.** Other new cucurbitanes include **251–253** from the fruit of *Momordica charantia*,[84] 10β-hydroxybryodulcosigenin **254** from *Saniculiphyllum guangxiense*,[85] six new compounds **255–260** from the leaves of *Momordica charantia*[86] and isoarvenin III **261** from the fruit of *Trichosanthes kirilowii*.[87] The 3,4-*seco*-cucurbitane **262** is a constituent of *Russula lepida* and *Russula amarissima*.[88] The unlikely 10α-methyl lanostane structure **263** has been proposed for a compound from *Momordica charantia*.[89] Perhaps the compound is a cucurbitane! Reviews have appeared on



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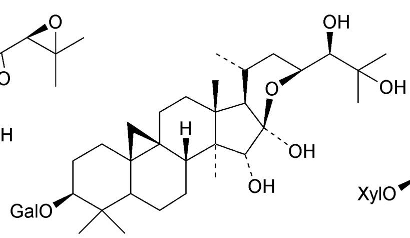
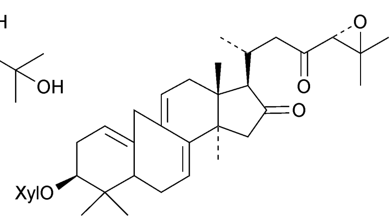


222
223 24-epimer



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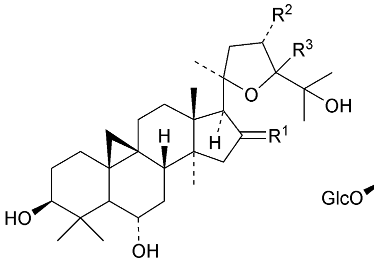
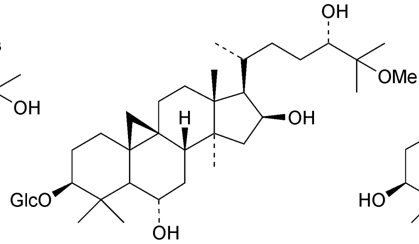


225 R^1 = βO_2CCH_2OH, H; R^2 = H; R^3 = αH
226 R^1 = βO_2CCH_2OH, H; R^2 = OH; R^3 = αH
227 R^1 = O; R^2 = H; R^3 = αH
228 R^1 = βOH, H; R^2 = H; R^3 = βH



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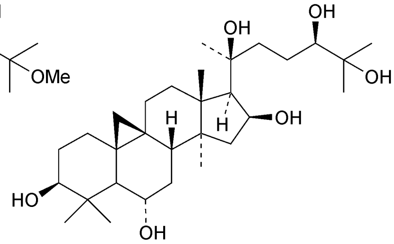

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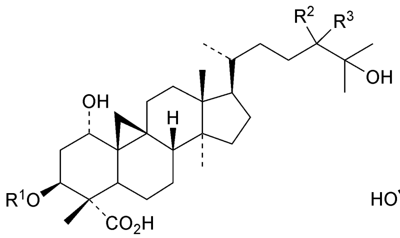
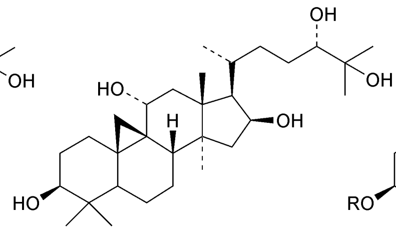


231 R^1 = Glc; R^2 = CH_2OH; R^3 = OH
232 R^1 = Glc; R^2 = CH_2OH; R^3 = H
233 R^1 = Xyl; R^2 = H; R^3 = OAc



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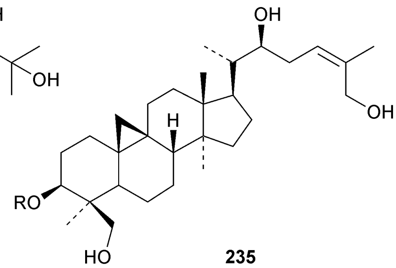
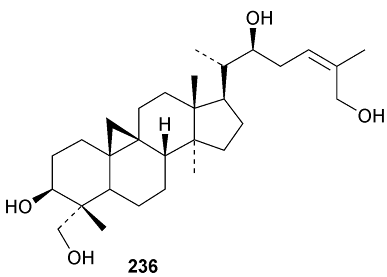


235

cucurbitacins and bottle gourd toxicity,[90] medicinally important plants of the Cucurbitaceae[91] and the anticancer activity of the cucurbitacins.[92,93]

4. The dammarane group

A review of ginsenoside derivatives and their antitumour activity has been published.[94] New saponins from the stems and leaves of *Panax ginseng* include ginsenosides Rh_{14}–Rh_{17} with the new genins **264** (Rh_{15}) and **265** (Rh_{17})[95] and ginsenosides Rh_{18}– Rh_{20}.[96] The new genin **266** of ginsenoside Rh_{18} was also isolated together with the dammarane **267**.[96] Two new saponins of 20*S*-protopanaxatriol have also been found in *Panax ginseng* together with the dammarane **268**.[97] The biological activity of an artefact **269** from the acid hydrolysate of *Panax ginseng* has been investigated.[98] The hexanordammarane saponin, ginsenoside R_{10} **270**, has been isolated from the stems and leaves of *Panax quinquefolium*.[99]



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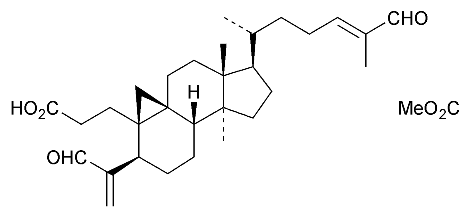

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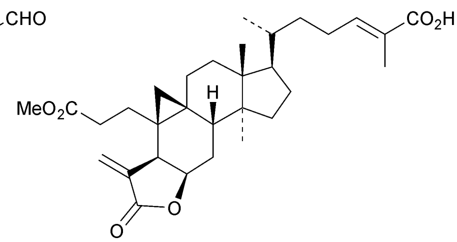

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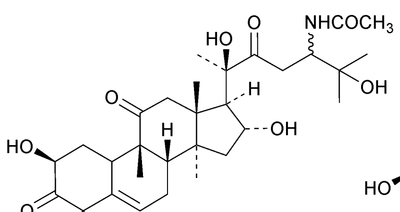

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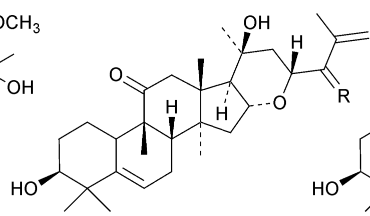
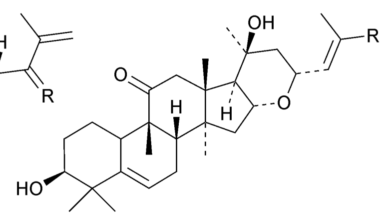
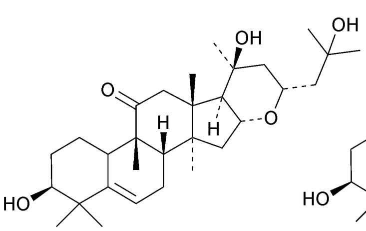


240 R = αOH, H
241 R = βOH, H
243 R = O



242 R = CH_2OH
244 R = CHO



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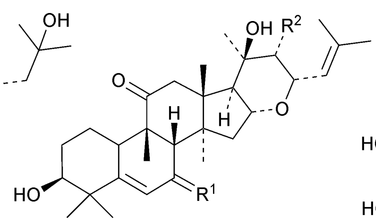
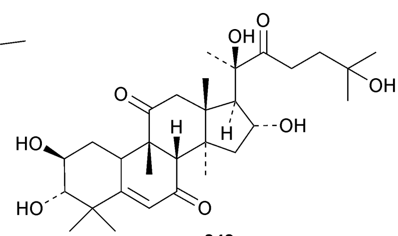


246 R^1 = H_2; R^2 = OH
247 R^1 = O; R^2 = H



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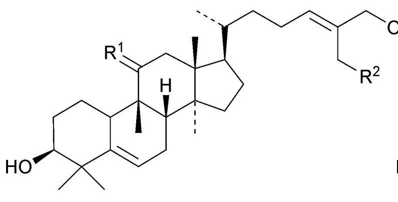
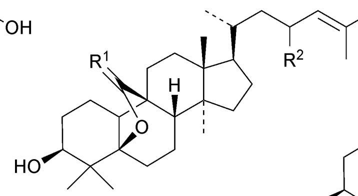
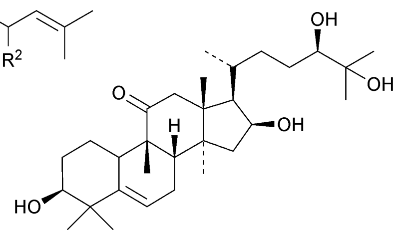


249 R^1 = O; R^2 = OH
250 R^1 = H_2; R^2 = H



251 R^1 = H_2; R^2 = αOMe
252 R^1 = H_2; R^2 = βOMe
253 R^1 = O; R^2 = αOMe



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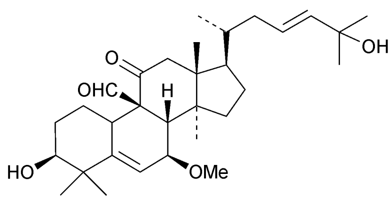

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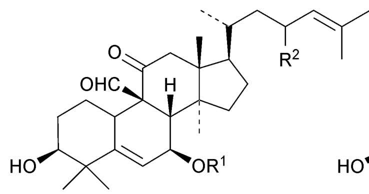
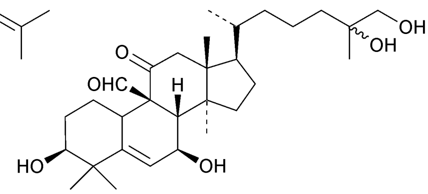


256 R^1 = Me; R^2 = βOMe
257 R^1 = H; R^2 = αOMe



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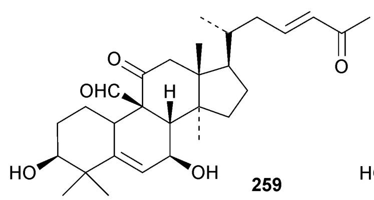

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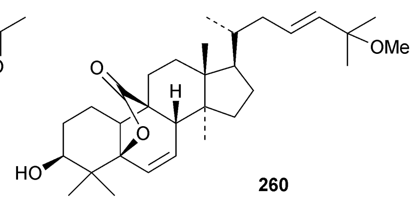
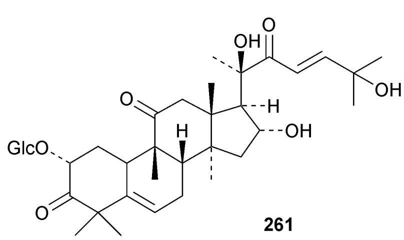


260

Saponins with the new genins **271** and **272** (ref. 100) and **273** (ref. 101) have been isolated from *Gynostemma pentaphyllum*. Cyclocariosides D–G, with the new genins **274** and **275**, cyclocarioside H, with a known genin, and the dammarane cyclocarin A **276** are constituents of the leaves of *Cyclocarya paliurus*.[102] Dammarane saponins with known genins have been isolated from the roots of *Machilus yaoshansis*.[103] This paper also reports a revision the C-23 configuration of *Gynostemma pentaphylla* saponins as in **277**.

New dammaranes include the rearranged aglinone **278** and aglinin E **279** from the bark of *Aglaia smithii*,[104] the *nor*-derivatives **280–283** from *Dysoxylum hainanense*,[105] the



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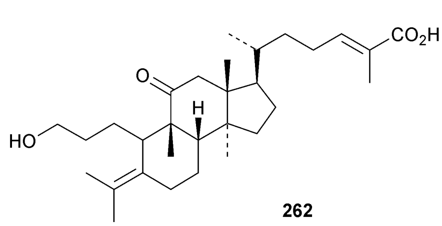

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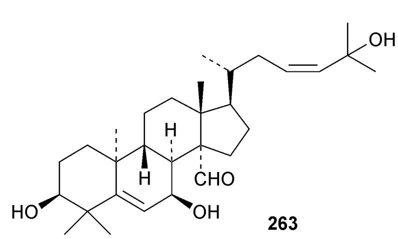

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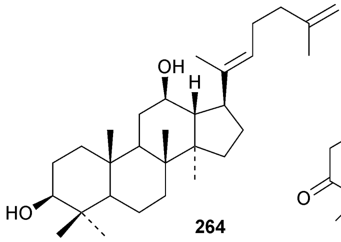
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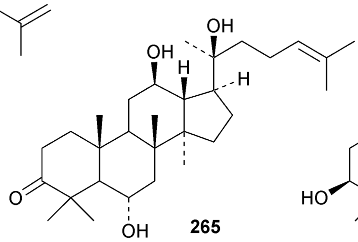
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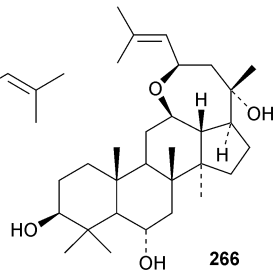
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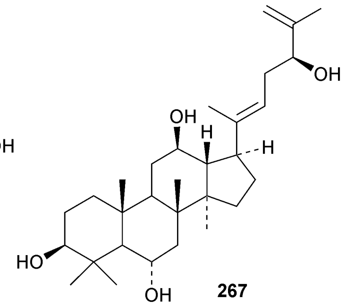
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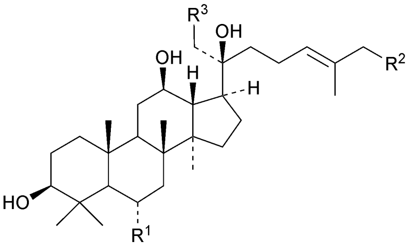
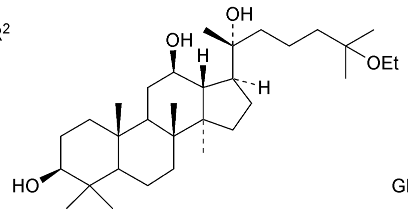

268 $R^1 = R^2 = OH; R^3 = H$
271 $R^1 = R^2 = H; R^3 = OH$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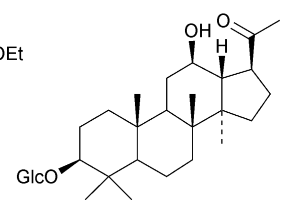
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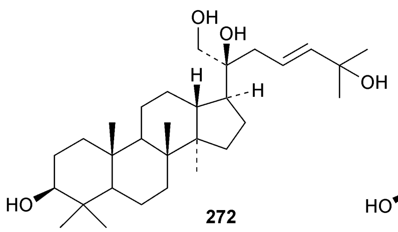
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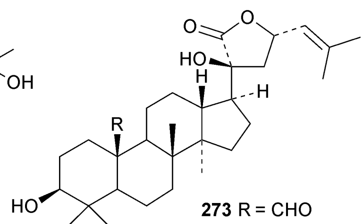
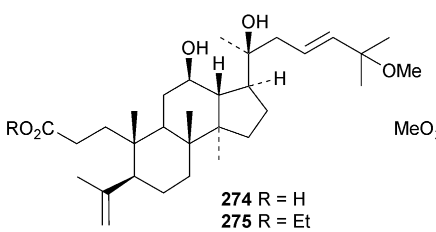
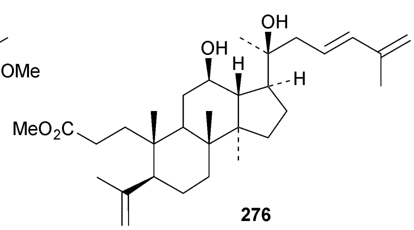

273 R = CHO
277 R = CH_3; 23-epimer


274 R = H
275 R = Et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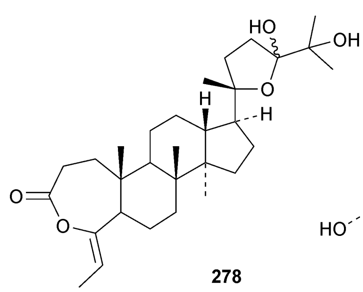
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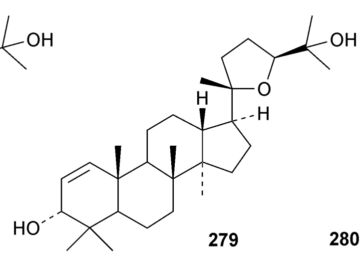
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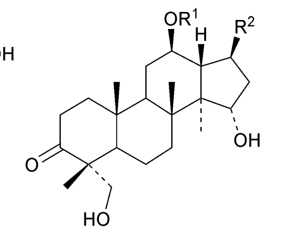
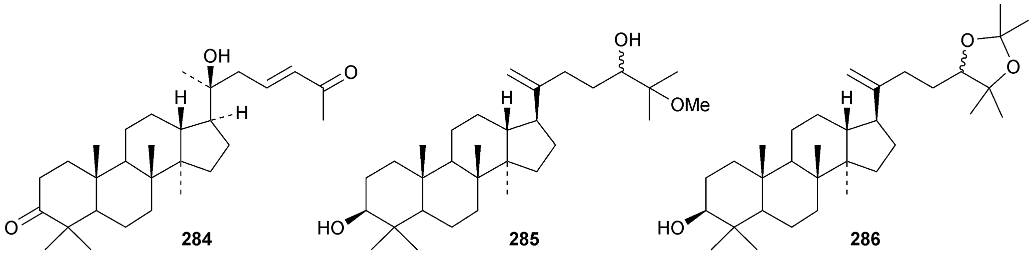
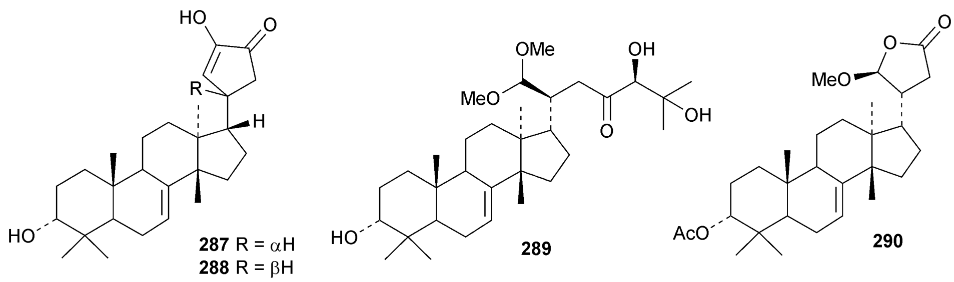

280 R^1 = Ac; R^2 = OMe
281 R^1 = Ac; R^2 = OH
282 R^1 = Ac; R^2 = H; 16,17-didehydro
283 R^1 = H; R^2 = OH



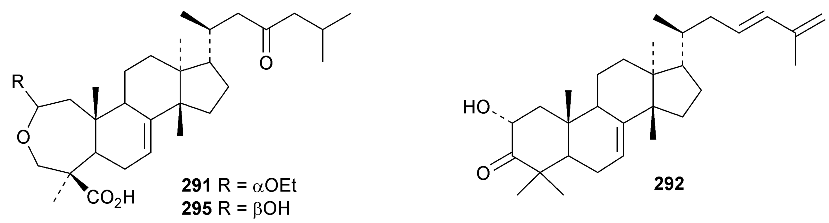
284 **285** **286**

27-*nor*-derivative **284** from *Dipterocarpus obtusifolius*[106] and the two probable artefacts **285** and **286** from the leaves of *Aglaia odorata*.[15]

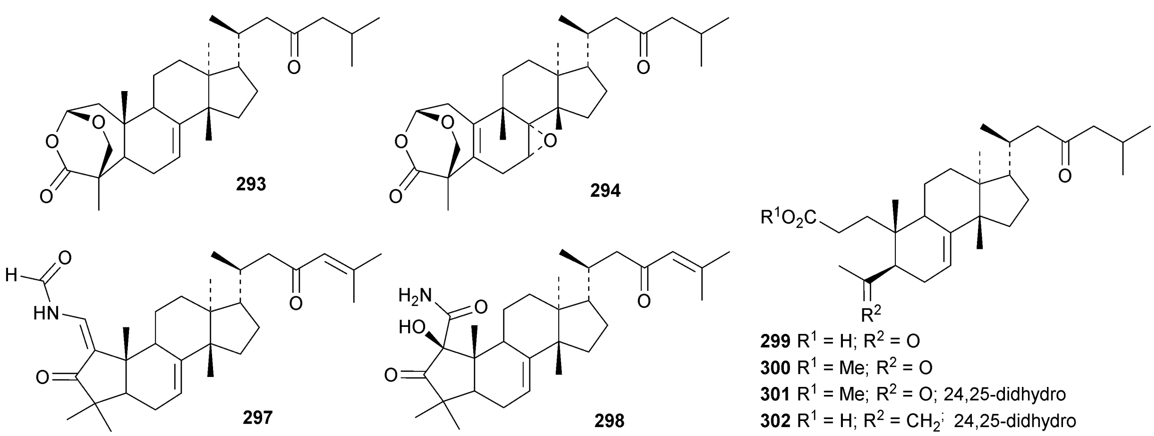
Novel dammarane saponins with known genins include acerbosides A and B from *Hovenia acerba*,[107] chikusetsusaponins FK_1–FK_7, FH_1, FH_2, FM and FT_1–FT_4 from *Panax japonicus*,[108,109] gypenbiosides A and B from *Gynostemma*



287 R = αH
288 R = βH
289
290

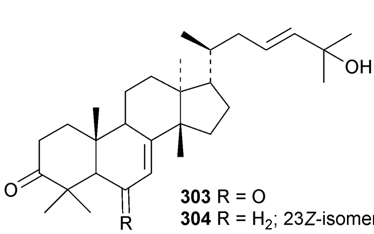


291 R = αOEt
295 R = βOH
296 R = βOH; 24,25-didehydro
292

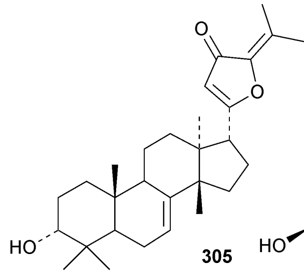


293 **294** **297** **298**

299 R^1 = H; R^2 = O
300 R^1 = Me; R^2 = O
301 R^1 = Me; R^2 = O; 24,25-didhydro
302 R^1 = H; R^2 = CH_2; 24,25-didhydro



303 R = O
304 R = H_2; 23*Z*-isomer



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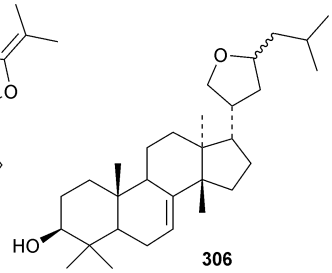

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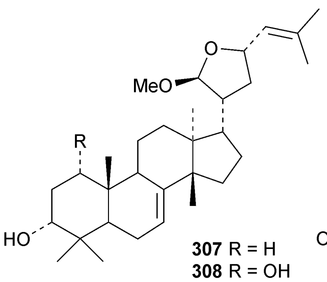
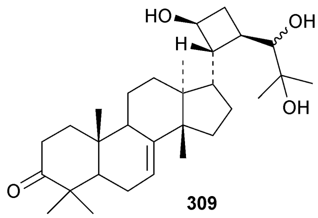


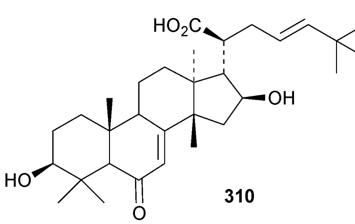
307 R = H
308 R = OH



309

pentaphyllum,[110] 20*R*-pseudoginsenoside F_{11} (ref. 111) and quinquenosides Ja and Jb[112] from *Panax quinquefolium*.

New compounds from the stem bark of *Aphanamixis grandifolia* include the tautomeric tirucallane cyclopentenones **287** and **288** (ref. 113) and the tirucallanes **289** and **290**.[114] Compounds **287** and **288** were originally named aphragranins A and B, names used by the authors for previous compounds. Their names have been changed to aphagraones A and B.[115] Two further derivatives **291** and **292** were obtained from the leaves and twigs of *Aphanamixis grandifolia*.[116] Some of these compounds clearly incorporate the extraction solvent. Aphanamgrandins A **293**–J **302** constitute a series of 2,3-*seco*- and 3,4-*seco*-tirucallanes from the stems of *Aphanamixis grandifolia*.[117] They were accompanied by the ring-A intact derivatives aphanamgrandin J **303** and the dienone **304**. The structures of aphanamgramins A **293** and B **294** were confirmed by X-ray analyses. Other new tirucallanes include the 21-*nor*-derivative dysoxylentin A **305** from *Dysoxylum lenticellatum*,[118] ixoroid **306** from the flowers of *Ixora coccinea*,[119] **307** and **308** from the stem bark of *Araliopsis synopsis*,[120] capulin **309** from *Capuronianthus mahafalensis*,[121] **310–312** from the stem bark of *Melia toosendan*,[122] dysohainanin F **313** from *Dysoxylum hainanense*[123] and



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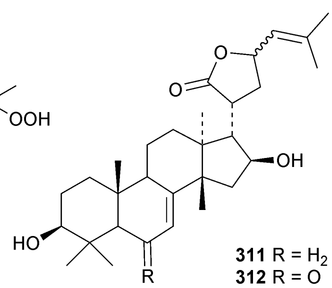
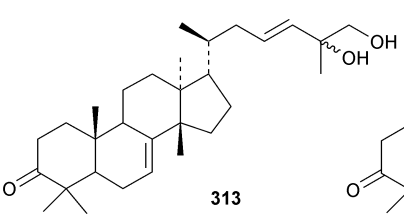


311 R = H_2
312 R = O



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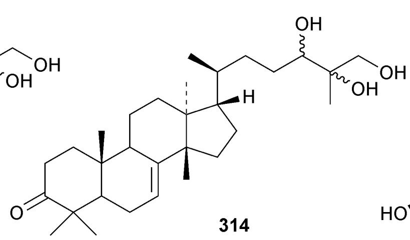

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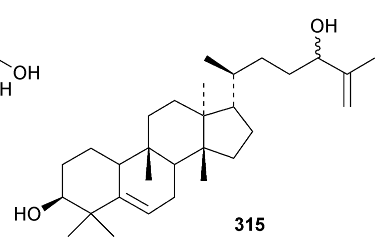

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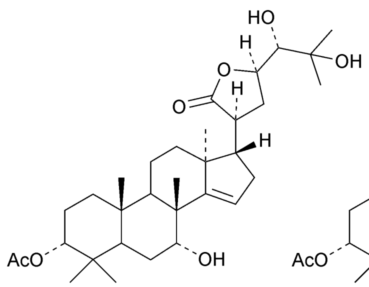

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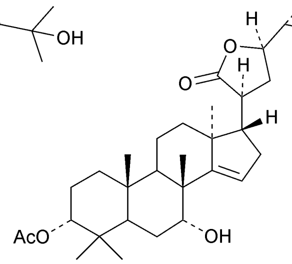

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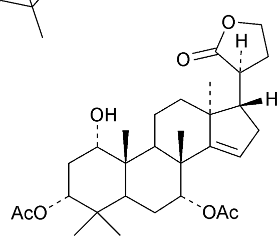

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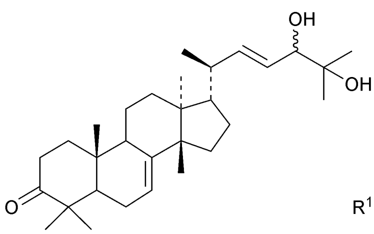

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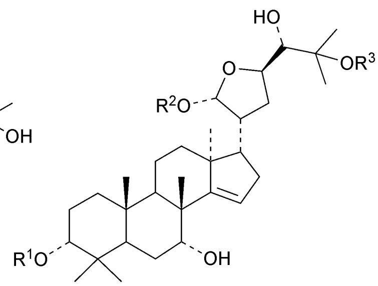
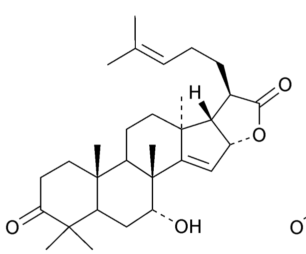


320 R^1 = Ac; R^2 = Et; R^3 = Me
321 R^1 = H; R^2 = Me; R^3 = Et



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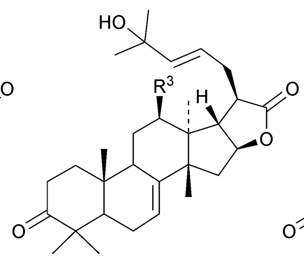

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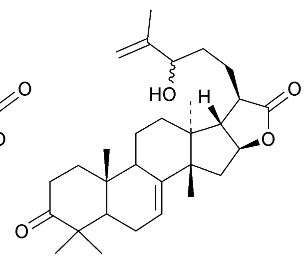

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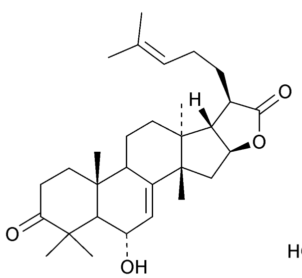

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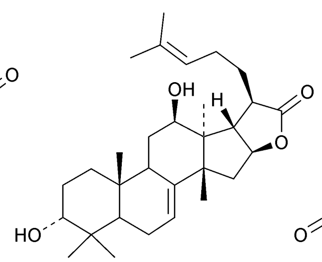

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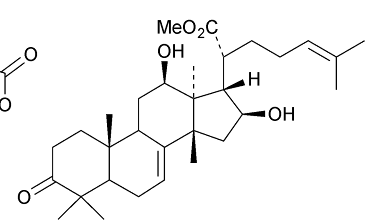

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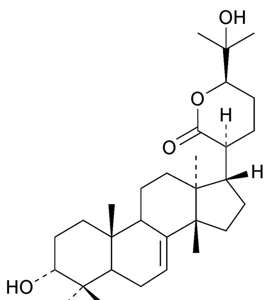
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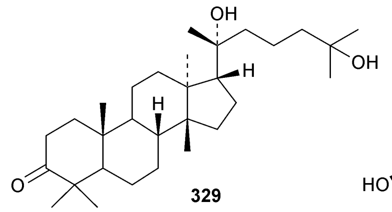
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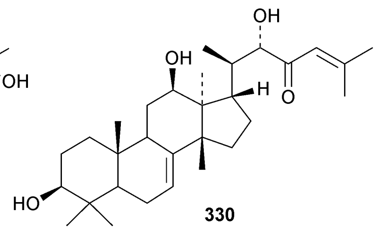
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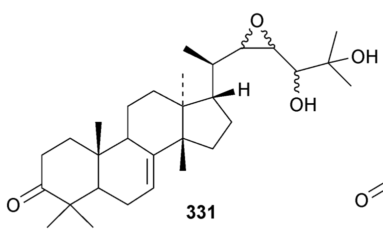
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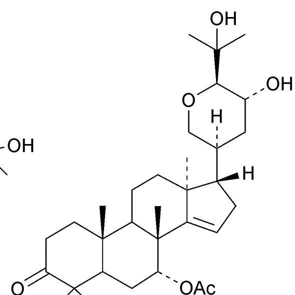
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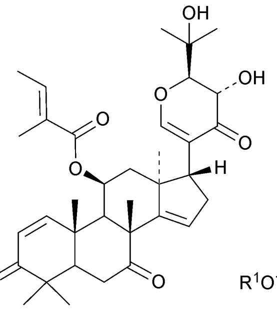
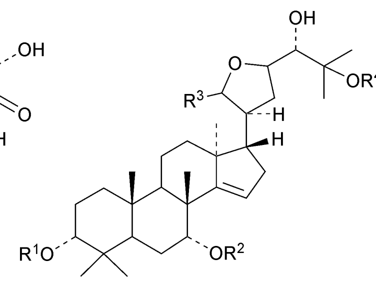

333
334 2',3'-dihydro


335 $R^1 = R^2 = Ac$; $R^3 = \beta OH$; $R^4 = H$
336 $R^1 = R^2 = H$; $R^3 = \beta OH$; $R^4 = Me$
339 $R^1 = H$; $R^2 = Ac$; $R^3 = \alpha OMe$; $R^4 = Me$

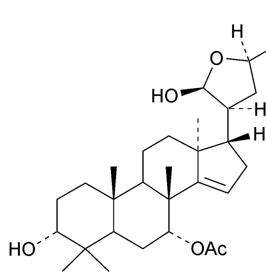
24,25,26-trihydroxytirucall-7-en-3-one **314** from *Salacia hainanensis*.[124] The 19(10 → 9)-*abeo*tirucallane **315** has been reported from *Euphorbia mellifera*.[125]

Chisiamols G **316** and H **317** (ref. 126) and chisopanins L **318**–O **321** (ref. 108 and 127) are new apotirucallanes from *Chisocheton paniculatus*. A series of compounds from the leaves and twigs of *Melia toosendan* includes the apoeuphane mesendanin K **322**, the euphanes mesendanins L **323**–P **327**, the tirucallanes mesendanins Q **328**–T **331** and the apotirucallane mesendanin U **332**.[128] The apotirucallane **332** was also isolated from *Dysoxylum hainanense* and named dysohainanin E.[123] Other new apotirucallanes include piscidinones A **333** and B **334** from *Walsura trifoliata*,[129] agladorals A **335**–E **339** from *Aglaia odorata* var. *microphyllina*[130] and trichostemonate **340** from the roots of *Walsura trichostemon*.[131] The structure of **340** was confirmed by X-ray analysis. Toonaciliatavarins A **341**–H **348** are constituents of *Toona ciliata*.[132]

4.1 Tetranortriterpenoids

A review of the structures and biological activities of limonoids from *Cipadessa* species has been published.[133] Walsucochinoids A **349** and B **350** are rearranged limonoids, with an aromatic ring D, from *Walsura cochinchinensis*.[134] Andhraxylocarpins A **351**, B **352**, C **353** and E **354** are new skeletal types from *Xylocarpus granatum*.[135] The structures of **349**, **351** and **353** were confirmed by X-ray analyses. Andhraxylocarpin D **355** is the same as chisomicin A, published in 2011. *Hortia oreadica* is the source of the interesting rearranged limonoids **356**–**363**, related to the known hortiolide A.[136] The structure of hortiolide C **358** was confirmed by X-ray analysis. The configurations at C-5 and C-10 of hortiolide E **362** and 12-hydroxyhortiolide E **363** are wrongly drawn in the paper. Carapanolides A **364** and B **365** are 9,10-*seco* mexicanolide derivatives from the seeds of *Carapa guianensis*.[137] Other new structural types include citriolide A **366** from the seeds of *Citrus reticulate*,[138] aphanamixoid A **367** from *Aphanamixis polystachya*[139] and chukrasones A **368** and B **369** from *Chukrasia tabularis*.[140] The structure of aphanamixoid A **367** was confirmed by X-ray analysis. It was accompanied in the extract by aphanamixoid B **370**.

Toonayunnanins A **371**–L **382** constitute a group of assorted limonoids from the leaves of *Toona ciliata* var. *yunnanensis*.[141] Toonayunnanin I **378** is the same as toonaciliatin P, published in 2011. Another group of compounds, toonaciliatones B **383**–F



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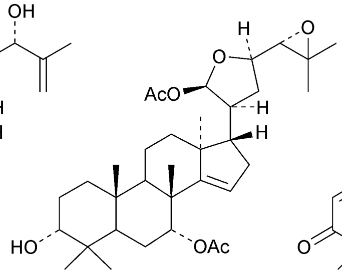

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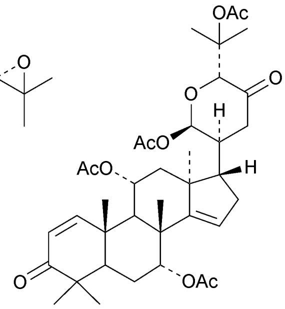

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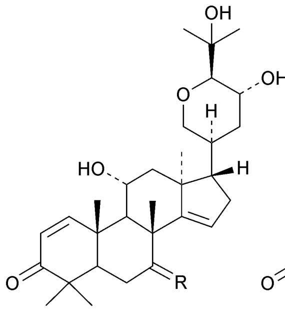
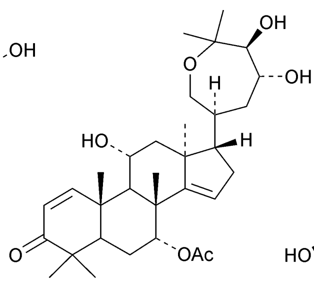


341 R = O
342 R = αOAc, H



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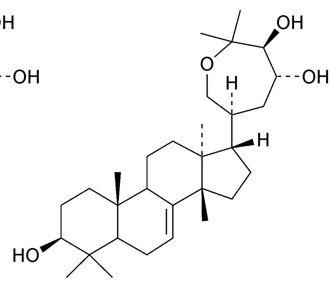
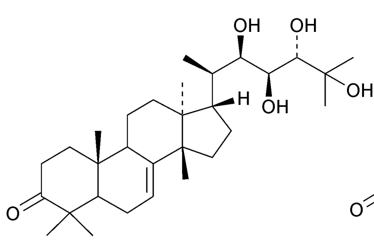


344

387, has been obtained from the seeds of *Toona ciliata*.[142] Meliatoosenins E **388**, F **389**, I **390**, J **391**, L **392**–N **394** and P **395**–S **398** are new compounds from the fruit of *Melia toosendan*.[143] Meliatoosenins G, H, K and O, claimed as new compounds, have all been published previously. Other new compounds include andirolides H **399**–P **407** from *Carapa guianensis* flowers,[144] ceramicines J **408**–L **410** from *Chisocheton ceramicus*[145] and walsuranins A **411**–C **413** from *Walsura yunnanensis*.[146]

The ring A-cleaved compounds, aphanalides A **414**–H **421**, have been reported from the fruit of *Aphanamixis polystachya*.[147] The structures of aphanalides A **414** and C **416** were confirmed by X-ray analyses. Aphanagranins A **422**–D **425** are constituents of *Aphanamixis grandifolia*.[148] Other species producing multiple new compounds include *Munronia unifoliata* with munronoids A **426**–J **435** (ref. 149) and K **436**–O **440** (ref. 150) and *Dysoxylum hainanense* with dysohainanins A **441**–D **444**.[123] 6-*O*-DeacetylsevErinolide **445** is a constituent of *Atalantia buxifolia*.[151]



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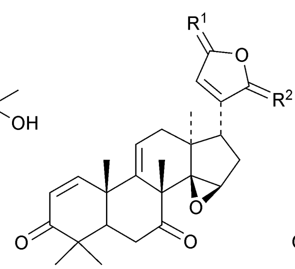
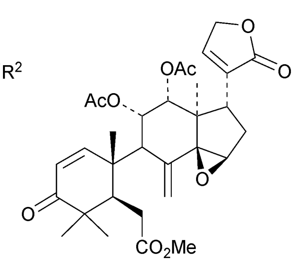


346 R^1 = O; R^2 = OH, H
347 R^1 = OH H; R^2 = O



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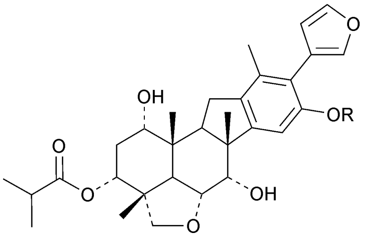
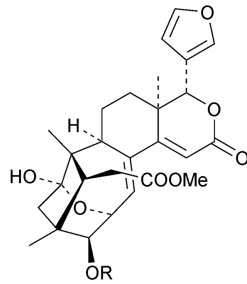
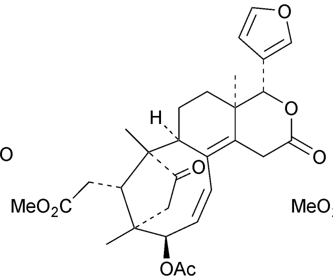


349 R = Me
350 R = H; 3-deacyl; 3-tigloyl



351 R = tigloyl
352 R = Ac



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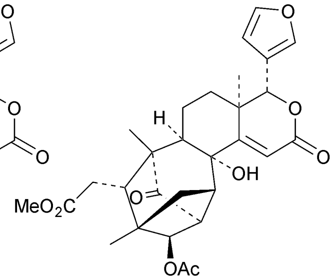
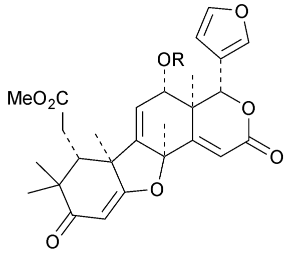
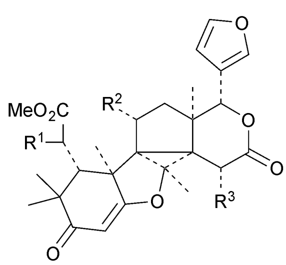


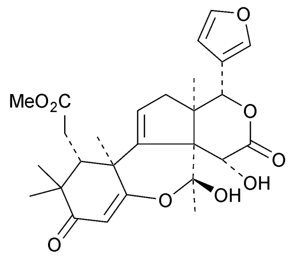
354 R = Ac
355 R = tigloyl



356 R = H
357 R = Ac



358 $R^1 = R^2 = H$; $R^3 = OH$
359 $R^1 = R^3 = OH$; $R^2 = H$
360 $R^1 = OH$; $R^2 = OAc$; $R^3 = H$



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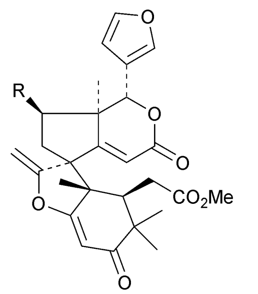
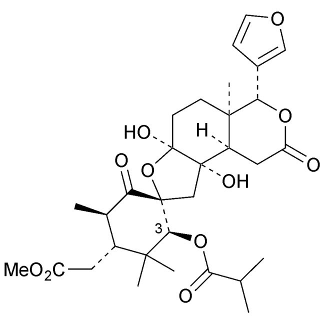
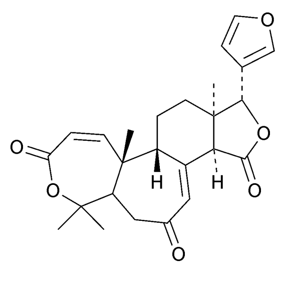


362 R = H
363 R = OH



364
365 3-deacyl; 3-tigloyl



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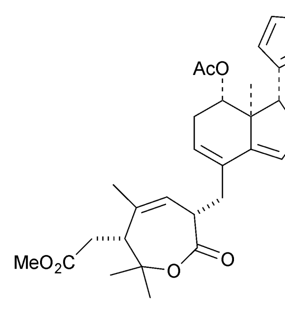

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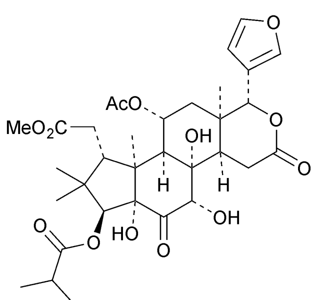

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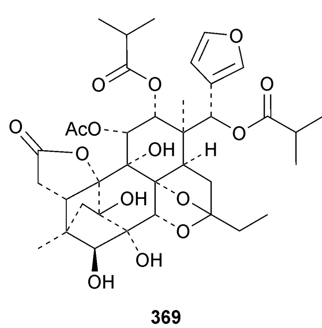

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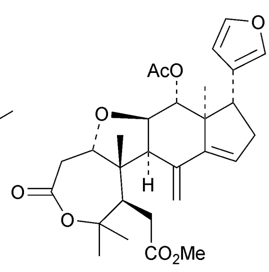

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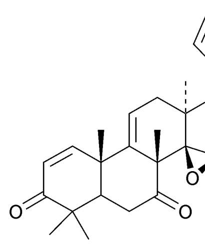

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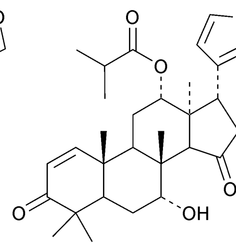

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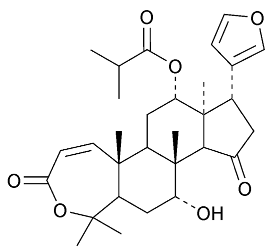

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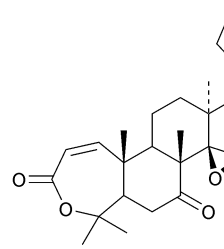

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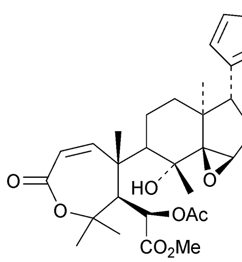

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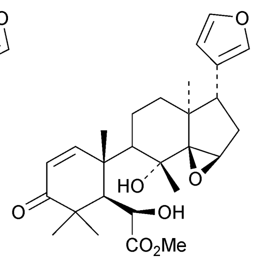

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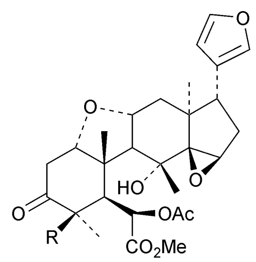
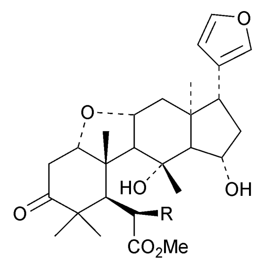
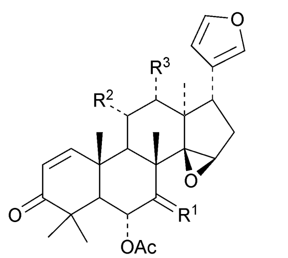


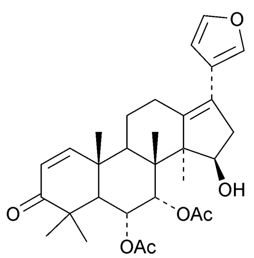
377 R = CH_3
378 R = CH_2OAc
379 R = CH_3; 1,2-didehydro
380 R = CHO; 1,2-didehydro



381 R = OAc
382 R = H



383 R^1 = O; R^2 = R^3 = H
385 R^1 = αOAc, H; R^2 = OH; R^3 = H
386 R^1 = αOAc, H; R^2 = H; R^3 = OH



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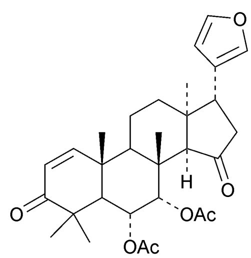

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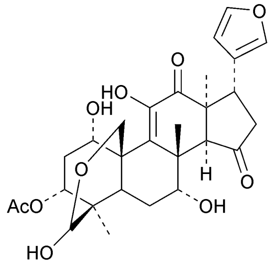

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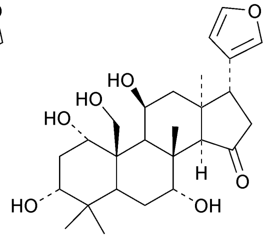
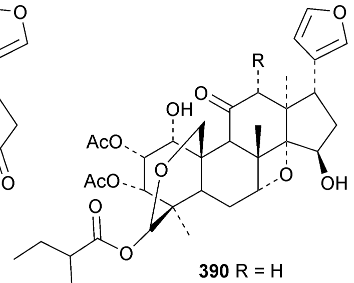
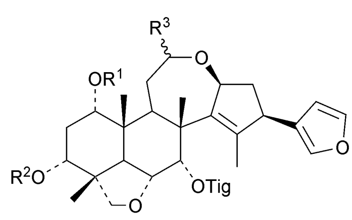


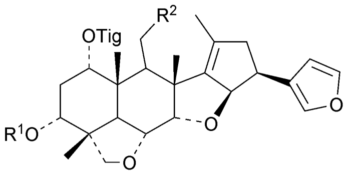
389



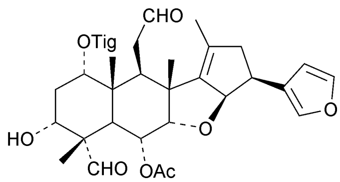
390 R = H
391 R = OAc



392 R^1 = Tig; R^2 = H; R^3 = αOMe
393 R^1 = H; R^2 = Ac; R^3 = αOMe
394 R^1 = R^2 = Ac; R^3 = βOMe



395 R^1 = H R^2 = CHO
396 R^1 = Ac; R^2 = $CH(OMe)_2$



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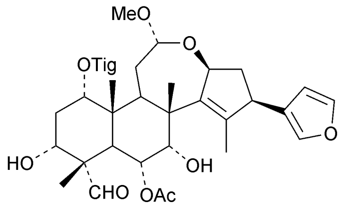

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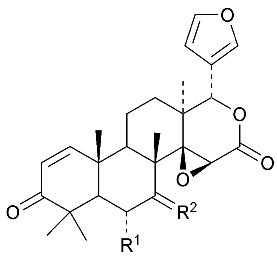
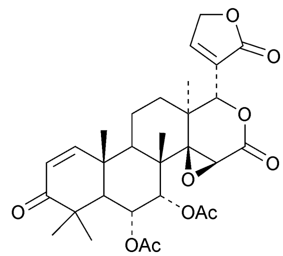


399 R^1 =OAc; R^2 = αOH, H
400 R^1 =H; R^2 = O; 1α,2α-epoxide



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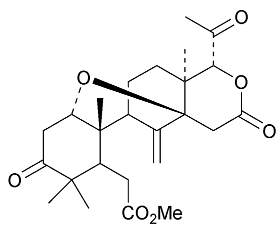

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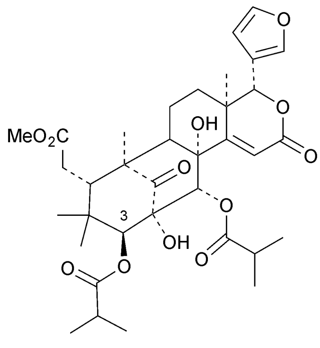
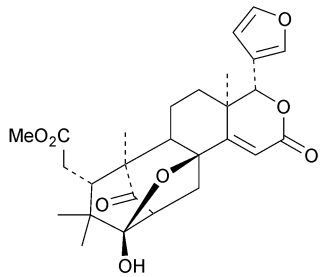


403 3-deacyl; 3-tigloyl
404



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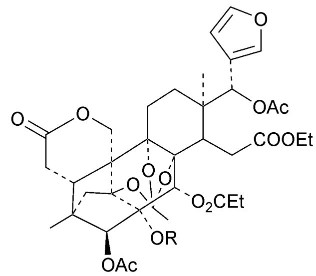
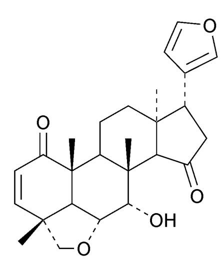


406 R = Ac
407 R = H



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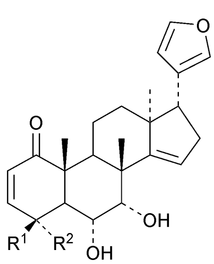
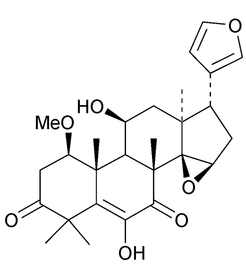


409 R^1 = OAc; R^2 = H
410 R^1 = CH_3; R^2 = OH



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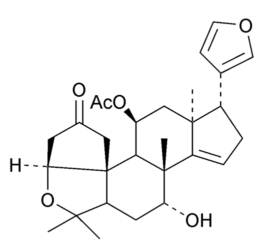

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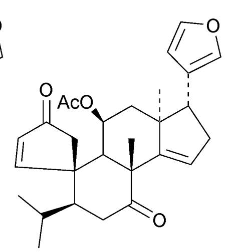

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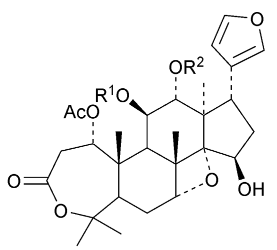
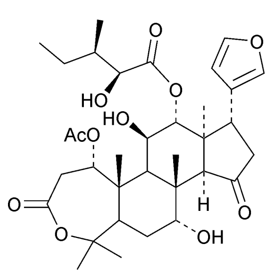


414 R^1 = HCO; R^2 = Me_2CHCH_2CO
415 R^1 = H; R^2 = Me_2CHCH_2CO
416 R^1 = H; R^2 = Et(Me)CHCH(OH)CO
422 R^1 = R^2 = H



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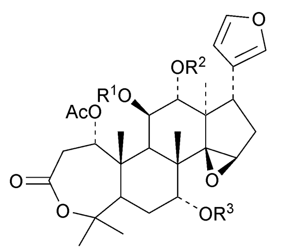
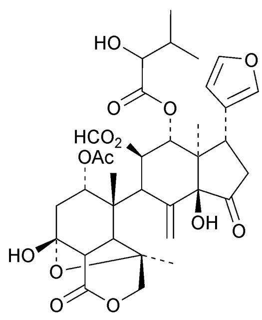


418 R^1 = H; R^2 = Et(Me)CHCH(OH)CO; R^3 = H
419 R^1 = H; R^2 = Et(Me)CHCH(OH)CO; R^3 = Ac
420 R^1 = HCO; R^2 = Et(Me)CHCH(OH)CO; R^3 = H
421 R^1 = HCO; R^2 = Me_2CHCH_2CO; R^3 = H



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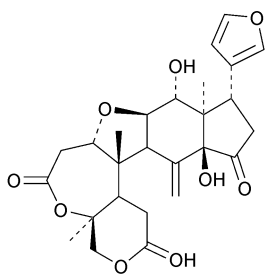

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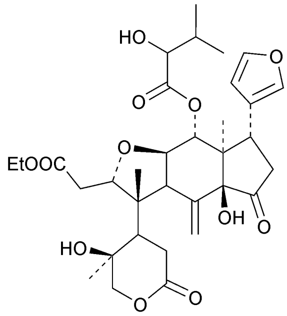

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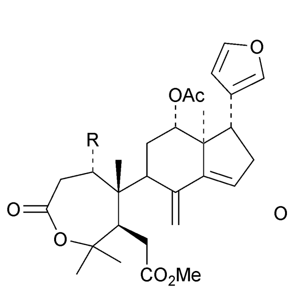
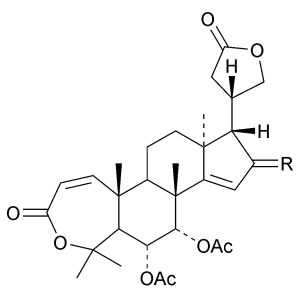
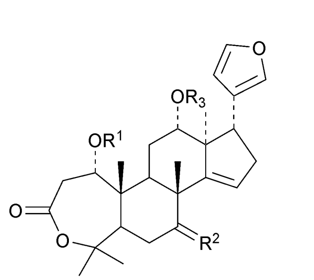


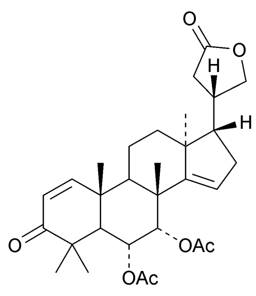
426 R = OAc
427 R = H; 1,2-didehydro



428 R = H_2; 14β,15β-epoxide
429 R = H_2
430 R = O
431 R = βOOH, H



432 R^1 = R^3 = Ac; R^2 = O
433 R^1 = R^3 = Ac; R^2 = αOH, H
436 R^1 = Ac; R^2 = αOAc, H; R^3 = Et(Me)CHCH(OH)CO
437 R^1 = R^3 = Ac; R^2 = αOAc, H
438 R^1 = R^3 = Ac; R^2 = αOTig, H



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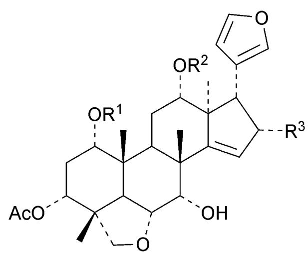
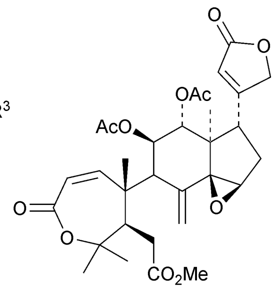


435 $R^1 = R^2 = Ac; R^3 = H$
439 $R^1 = Tig; R^2 = Me; R^3 = OH$



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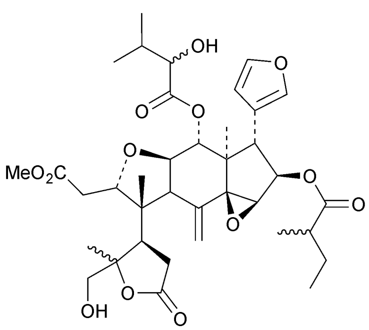

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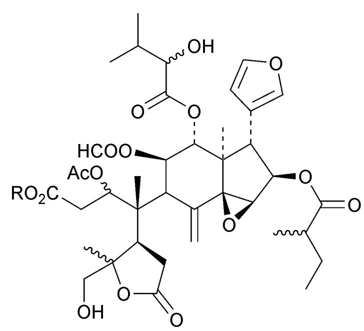
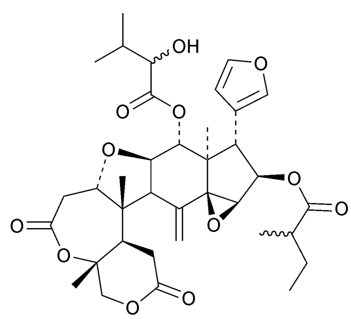


442 R = Me
443 R = Et



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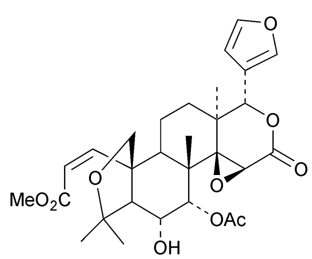
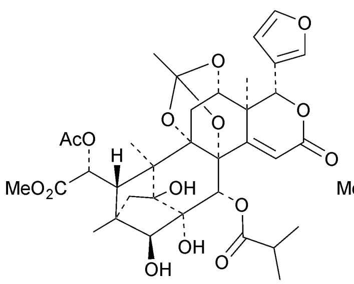


445

The seemingly unending flow of phragmalin/bussein derivatives and variants continues and is matched only by the proliferation of confusing trivial names. These points are well illustrated by *Chukrasia tabularis* and *Chukrasia tabularis* var. *velutina*, the sources of chubularisins A **446**–R **463**,[152] chuktabrins C **464**–J **471** and chuktabularins U **472**–X **475**,[153] tabulalins G **476**–I **478**,[154] chukvelutins D **479**–F **481** (ref. 155) and R310B8 **482** and velutinalides A **483** and B **484**.[156] Chabularisin O **460** is the same as chuktabularin V **474**. The structure of chuktabrin C **464** was confirmed by X-ray analysis. Heytrijumalins A **485**–I **493** have been isolated from the twigs and leaves of *Heynea trijuga*.[157] Other new compounds in this group include hisomicines D **494** and E **495** from *Chisocheton ceramicus*,[158] malayanines A **496** and B **497** from *Chisocheton erythrocarpus*,[159] senegalensions A **498**–C **500** from *Khaya senegalensis*,[160] kotschyins D **501**–H **505** from *Pseudocedrela kotschyi*,[161] soymidins A **506** and B **507** from *Soymida febrifuga*[162] and swietenin J **508** from *Swietenia macrophylla*.[163] Five new mexicanolide derivatives, heytrijunolides A **509**–E **513**, have been obtained from *Heynea trijuga*.[164] Mollucensins R **514**–Y **521** are new mexicanolide and phragmalin derivatives from the seeds of *Xylocarpus moluccensis*.[165]

4.2 Quassinoids

The compounds isolated from *Brucea javanica* and their pharmacology have been reviewed.[166] Bruceanic acids E **522** and F **523**, buruceanic acid E methyl ester **524**, javanic acids A **525** and B **526** and javanicolide H **527** are new compounds from the



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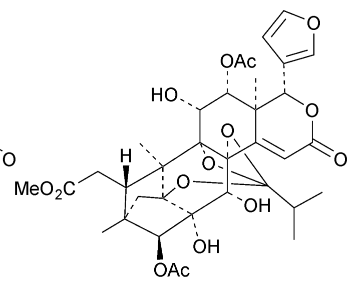
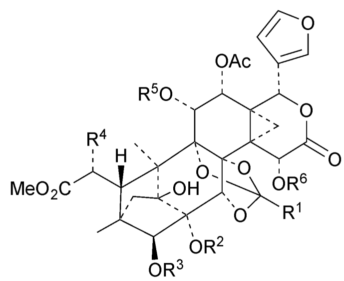
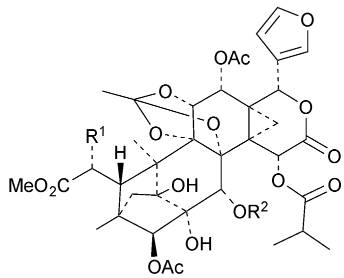


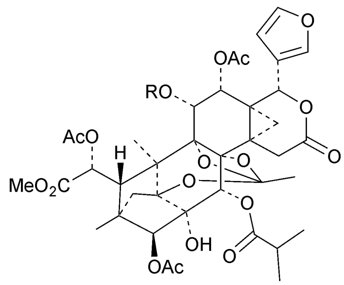
447



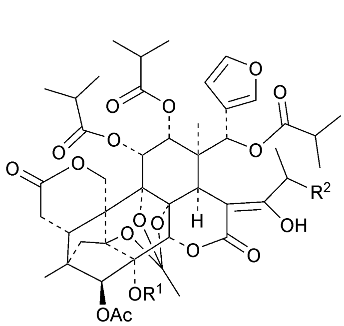
448 R^1 = Et; R^2 = R^3 = R^4 = H; R^5 = Ac; R^6 = ^{i}PrCO
449 R^1 = Me; R^2 = EtCO; R^3 = Ac; R^4 = R^5 = H; R^6 = ^{i}PrCO
450 R^1 = Me; R^2 = ^{i}PrCO; R^3 = Ac; R^4 = R^5 = H; R^6 = ^{i}PrCO
451 R^1 = ^{i}Pr; R^2 = R^5 = R^6 = H; R^3 = Ac; R^4 = OAc
452 R^1 = ^{i}Pr; R^2 = H; R^3 = Ac; R^4 = OAc; ; R^5 = R^6 = Ac



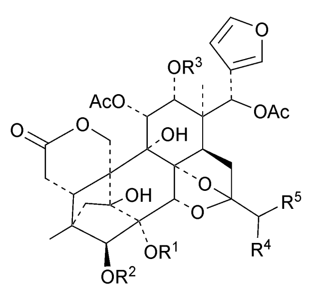
453 R^1 = OAc; R^2 = ^{i}PrCO
454 R^1 = H; R^2 = EtCO



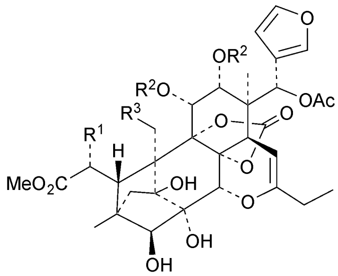
455 R = Ac
456 R = H



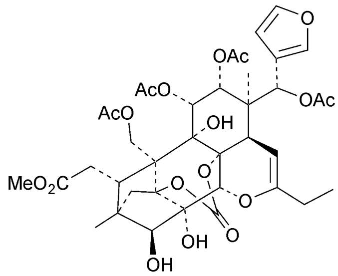
457 R^1 = H; R^2 = CH_3
458 R^1 = Ac; R^2 = CH_3
459 R^1 = Ac; R^2 = H



460 R^1 = R^2 = Ac; R^3 = ^{i}PrCO; R^4 = R^5 = H
461 R^1 = H; R^2 = Ac; R^3 = EtCO; R^4 = Me; R^5 = H
462 R^1 = Ac; R^2 = H; R^3 = ^{i}PrCO; R^4 = Me; R^5 = H
463 R^1 = H; R^2 = Ac; R^3 = Ac; R^4 = Me; R^5 = Me



464 R^1 = OAc; R^2 = Ac; R^3 = H
465 R^1 = R^2 = R^3 = H
466 R^1 = H; R^2 = Ac; R^3 = OAc



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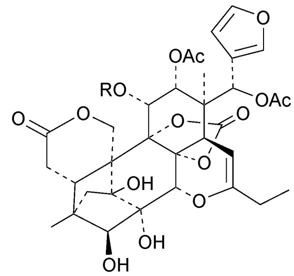
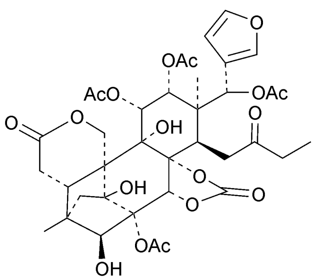


468 R = Ac
469 R = H



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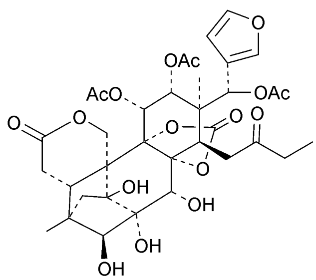

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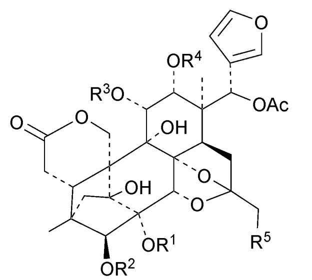
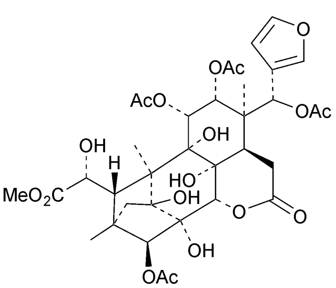


472 R^1 = R^2 = Ac; R^3 = R^4 = R^5 = H
473 R^1 = R^2 = R^3 = Ac; R^4 = ^{i}PrCO; R^5 = H
474 R^1 = R^3 = R^4 = Ac; R^2 = ^{i}PrCO; R^5 = CH_3
475 R^1 = R^2 = R^3 = R^4 = H; R^5 = CH_3

seeds of *Brucea javanica*.[167] Other new quassinoids include picrasin K **528** from *Quassin amara*[168] and odyendanol **529** from the fruit of *Odyendyea gabonensis*.[169]

5. The lupane group

Reviews covering the sources and biological properties of betulinic acid[170] and the antineoplastic effects of lupeol[171] have



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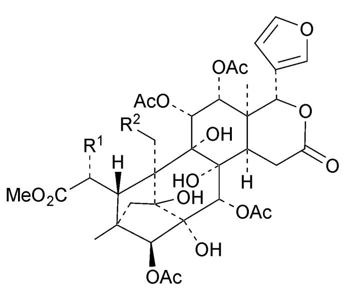
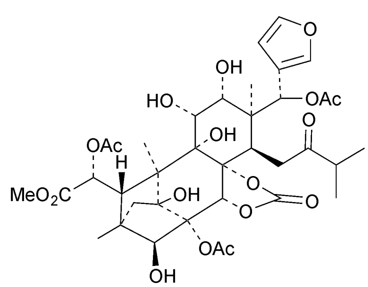


477 R^1 = H; R^2 = OAc
478 R^1 = OAc; R^2 = H



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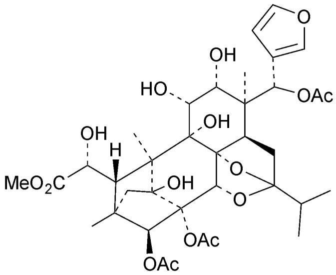

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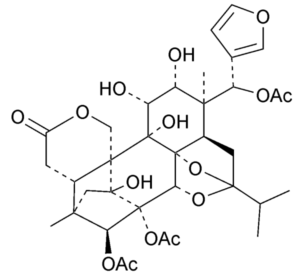

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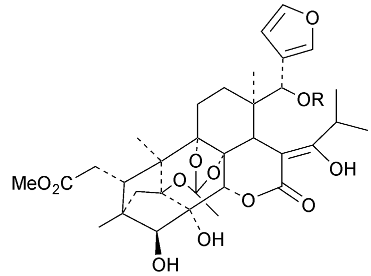
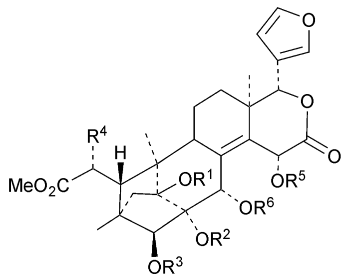
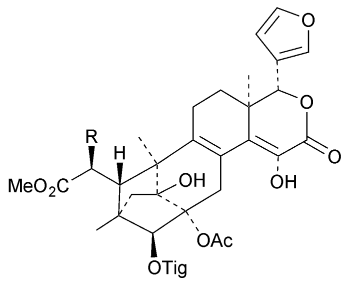


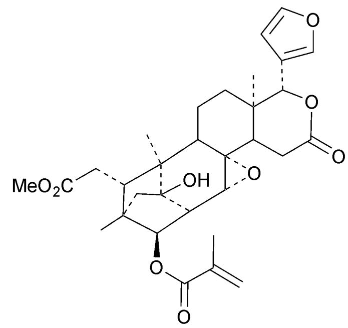
482 R = Ac
483 R = ^{i}PrCO
484 R = EtCO



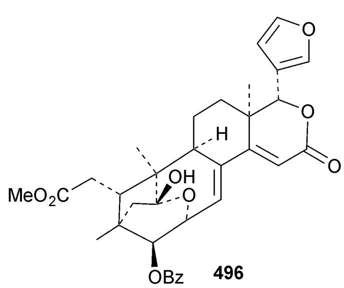
485 $R^1 = R^2 = H$; R^3 = Tig; R^4 = OAc; R^5 = $Me_2C(OH)CO$; R^6 = ^{i}PrCO
486 $R^1 = R^2 = R^6$ = Ac; ; R^3 = Tig; R^4 = H; R^5 = $Me_2C(OH)CO$
487 $R^1 = R^2 = R^6$ = Ac; ; R^3 = Tig; R^4 = OAc; R^5 = $Me_2C(OH)CO$
488 $R^1 = R^2 = H$; R^3 = Tig; R^4 = OAc; $R^5 = R^6$ = OAc
489 $R^1 = R^5 = R^6$ = Ac; R^2 = H; R^3 = Tig; R^4 = OAc
490 $R^1 = R^2 = R^5 = R^6$ = Ac; R^3 = Tig; R^4 = OAc
491 $R^1 = R^2 = R^5 = R^6$ = Ac; R^3 = $MeC(CH_2)CO$; R^4 = OAc



492 R = OAc
493 R = H



494
495 2',3'-dihydro



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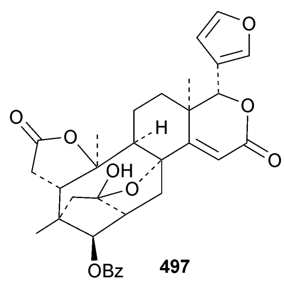
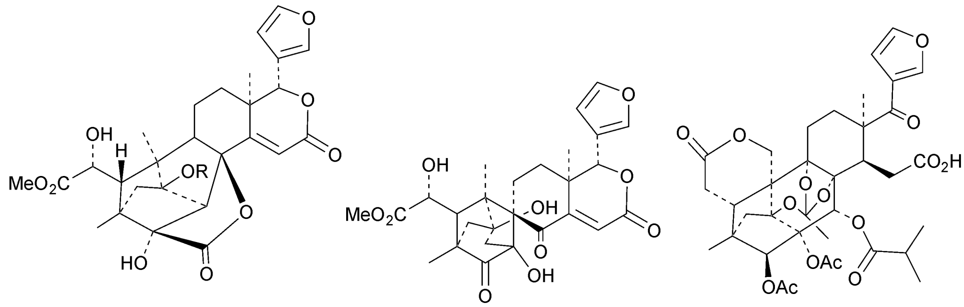


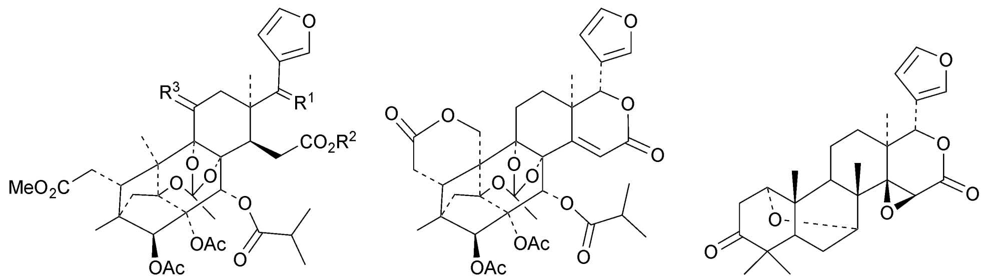
497

appeared. The 3,4-secolupane derivatives acanthosessiligenins I **530** and II **531** and acanthosessiliosides A **532**–F **537** have been isolated from the fruit of *Acanthopanax sessiliflorus*.[172] The 17,18-secolupane **538** has been found in the roots of *Taraxacum platycarpum* together with 3β-acetoxylup-18-en-21-one **539**, the neolupane derivatives **540–542** and the migrated lupane **543**.[173] Lup-20(29)-ene-2β,3β-diol **544** is a constituent of *Salacia hainanensis*[124] and the related ketones **545** and **546** have be found in *Fagus hayatae*.[174] Other simple lupane derivatives include glochitriol **547** from *Glochidion lanceolarium*,[175] bengalensinone **548** from *Ficus bengalensis*,[176] 3β-hydroxylupane-28,29-dioic acid **549** from *Aglaia duperreana*[177] and the norlupane derivatives **550**, **551** and **552** from *Dipterocarpus obtusifolius*.[106]

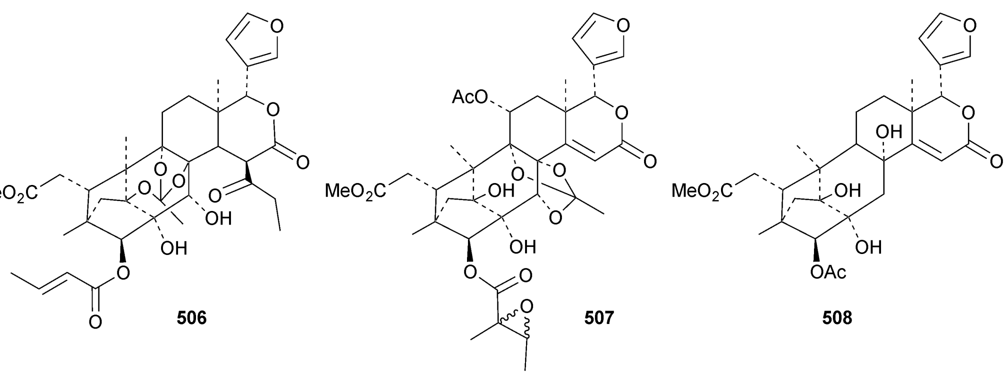
Two lupane saponins with the new genin **553** have been isolated from *Schefflera venulosa*.[178] New lupane saponins with known genins include ilekudinchoside E from *Ilex kudincha*,[179] stellatosides C, D and E, the methyl esters of stellatosides B and C and thurberoside A from *Stenocereus eruca*[180] and unnamed saponins from *Liquidambar formosana*[181] and *Cichorium intybus*.[182]



498 R = H
499 R = Ac
500
501



502 R^1 = O; R^2 = R^3 = H2
503 R^1 = OAc, H; R^2 = Me; R^3 = O
504
505



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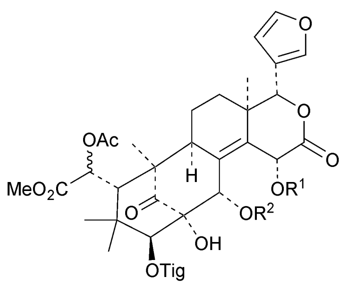
508

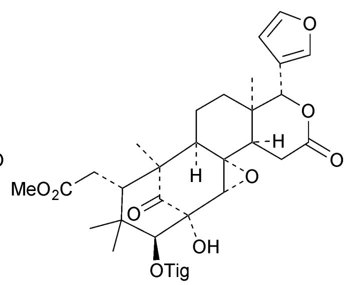
Oleanderocioic acid **554**, a lupane ester with the unusual *cis*-4-acetylcinnamic acid, is claimed to be a constituent of *Nerium oleander*.[183] Other new lupane esters include the nonanoyl ester of lupeol **555** from *Dorstenia harmsiana*,[184] kurramanoic acid **556** from *Nepeta clarkei*,[185] the myristoyl esters **557** from *Glochidion wrightii*[186] and **558** from *Sinocalamus affinis*,[187] the *cis*-feruloyl ester **559** from *Panax ginseng*,[188] the palmitoyl ester **560** from *Cichorium intybus*[182] and the stearoyl ester **561** from *Ocimum sanctum*.[189]

6. The oleanane group

Reviews have appeared on the origins, biosynthesis and biological activity of oleanolic acid[190] and the beneficial effects of arjunolic acid in type 1 diabetes.[191] *Fagus hayatae* is the source of the 1,10-secooleanane derivative **562** where it is found with 3α,23-dihydroxy-3-oxoolean-12-en-28-oic acid **563** and 3β,12α,23-trihydroxyoleanan-28,13β-olide **564**.[174] Sentulic acid from *Sandoricum koetjape* has been identified as 3,4-secooleana-4(23),12-diene-3,27-dioic acid **565**.[192] The 17,22-secooleanenol



509 $R^1 = R^2 = H$
510 $R^1 = Ac$; $R^2 = H$
511 $R^1 = R^2 = Ac$



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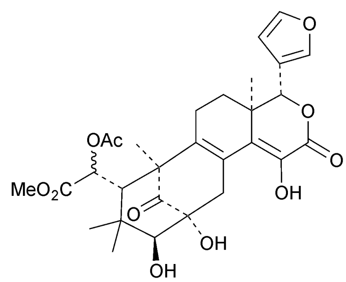

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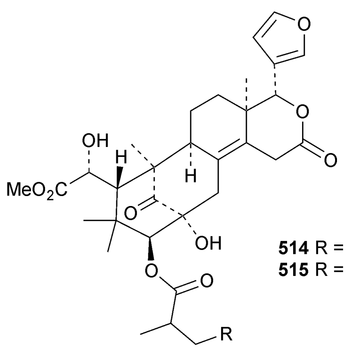
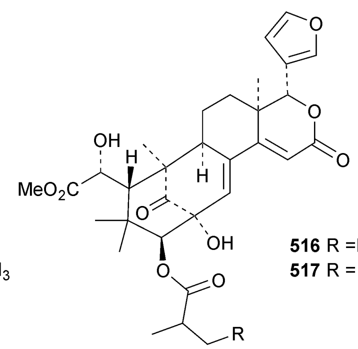
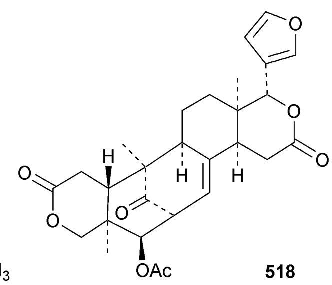


514 R = H
515 R = CH_3



516 R =H
517 R = CH_3



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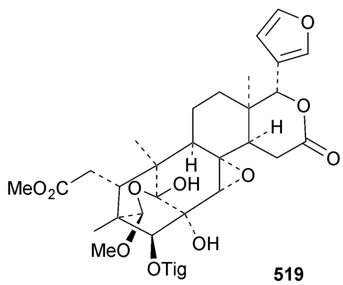

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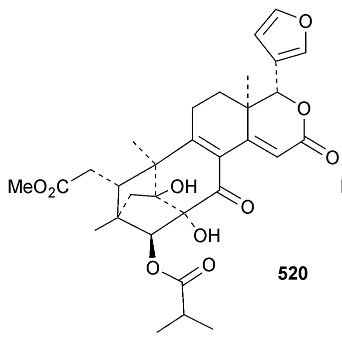

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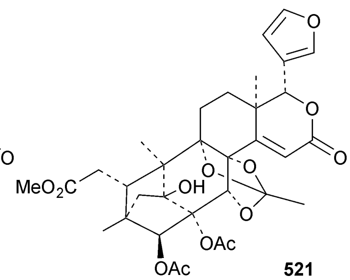
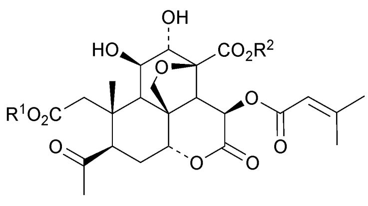


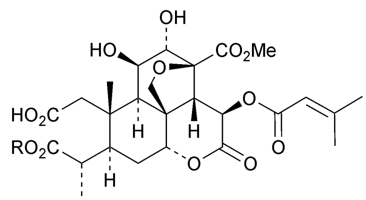
521

566, from *Pyrenacantha kaurabassana*, has the unusual 18α*H*-configuration.[193] Zizimauritic acids A **567**, B **568** and C **569** are ring-A contracted 20,21-secooleanane derivatives from *Ziziphus mauritiana*.[194] The zizimauritic acids also have the 18α*H*-configuration. A ring-E contracted oleanane derivative **570** has been isolated from the bark of *Diospyros decandra*.[195] Platycodonoids A **571** and B **572** are 28-noroleanane derivatives from the roots of *Platycodon grandiflorum*.[196] The 30-*nor* derivatives euscaphic acids G **573** and H **574**, together with their likely precursor euscaphic acid I **575**, are present in *Euscaphis japonica*.[197] Further noroleanane derivatives include 30-noroleanolic acid **576** from *Olea europea*,[198] the 24,30-dinor derivatives **577** and **578** and the 24-*nor* compounds **579** and **580** from the roots of *Paeonia emodi*[199] and **581** from *Pilea cavaleriei*.[200] A 4900 year old oak wood sample found in a freshwater sediment has produced six noroleanane derivatives **582–587** all lacking oxygenation at C-3.[201]

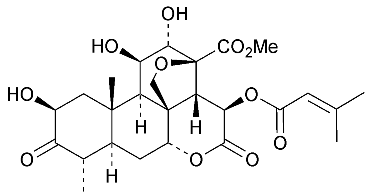
Several olean-18-ene derivatives have been identified including olean-18-ene-1β,2α,3β-triol **588** from *Salvia atropatana*,[202] **589–596** from *Cassine xylocarpa*, **597** from *Maytenus jelskii*,[203] olean-18-ene-1α,3β-diol **598** from *Juglans sinensis*[204] and 2α,3α,24-trihydroxyolean-18-en-28-oic acid **599** from



522 R^1 = H; R^2 = Me
523 R^1 = R^2 = H
524 R^1 = R^2 = Me



525 R = H
526 R = Me



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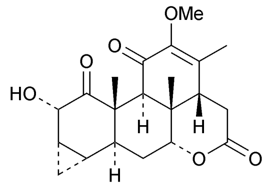

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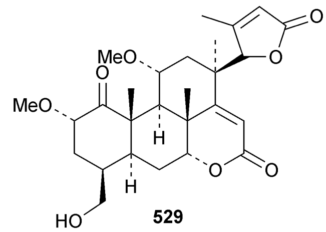

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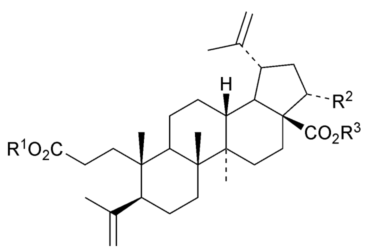
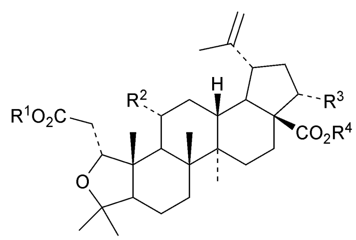


530 R^1 = Me; R^2 = OH; R^3 = H
531 R^1 = R^2 = H; R^3 = Glc



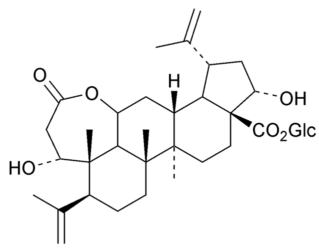
532 R^1 = Me; R^2 = OH; R^3 = R^4 = H
533 R^1 = Me; R^2 = OH; R^3 = H; R^4 = Glc
534 R^1 = Me; R^2 = R^3 = OH; R^4 = Glc
535 R^1 = Glc; R^2 = R^3 = R^4 = H
536 R^1 = R^2 = H; R^3 = OH; R^4 = Glc

Eucalyptus exserta.[205] The stem bark of *Terminalia arjuna* is the source of oleaterminaloic acids A **600**, B **601** and C **602** together with the 3-glucoside oleaterminalide **603**.[206] Other new simple oleanane derivatives include pseuderanic acid **604** from *Pseuderanthemum carruthersii*,[207] punicaone **605** from *Punica granatum*,[208] turformosinic acid **606** from *Turpinia formosana*,[209] 3β,23,28-trihydroxyolean-12-en-11-one **607** from *Aster yomena*,[210] 3α,29-dihydroxyolean-12-ene-23,28-dioic acid **608** from *Schefflera farinosa*,[211] oleana-9(11),12-diene-1β,3β-diol **609** from *Salvia xanthocheila*,[212] 1-*epi*-castanopsol **610** from *Simira glaziovii*,[213] the 29,22-olide **611** from *Celastrus orbiculatus*[214] and the epoxy aldehyde **612** from *Tetraena mongolica*.[215]

New oleanane esters include the caffeoyl derivatives **613–615**, from *Tetraena mongolica*,[215] the coumaroyl ester **616** from *Rubia schumanniana*,[216] the ferruloyl ester **617** from *Saniculiphyllum guangxiense*,[85] the palmitates **618** from *Anemone rivularis*,[217] **619** from *Barringtonia asiatica*[218] and **620** from *Lobelia sessilifolia*.[219] Four esters **621–624** of the 19(18 → 17)-*abeo*-28-noroleanane phlomstetraol B have been isolated from *Leonurus heterophyllus*.[220]

Two oleanane saponins, with the new genin olean-12-ene2β,15α,23-triol **625**, have been isolated from *Ammannia auriculata*.[221] Antoniosides E–J are oleanane saponins from *Antonia ovata*.[222] Antioniosides E–H have new genins that are esters of olean-12-ene-3β,15α,16α,21β,22α,23,28-heptol **626**. Sorbifoliasides G–J, from *Xanthoceras sorbifolia*, have known genins and sorbifoliaside K has the new genin oleana-12,15-diene-3β,21β,22α,28-tetrol **627**.[223] A variety of new 30-nor-oleanane genins, **628–631**, are included in akemisaponins A–K from *Akebia trifoliate*.[224] Two saponins from *Camellia japonica* have been assigned the names camelliosides E and F that have been used previously.[225] Camellioside E has the new genin 28-norolean-12-ene-3β,16α,17β-triol **632**. Four saponins have been isolated from *Astragallus angustifolius* including the new genin olean-12-ene-3β,21β,22α,24,29-pentol **633**.[68]

New oleanane saponins with known genins that have been assigned trivial names are listed in Table 1.



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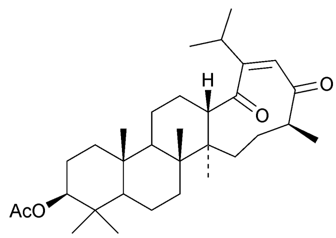

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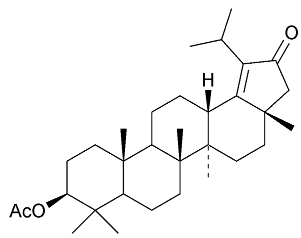

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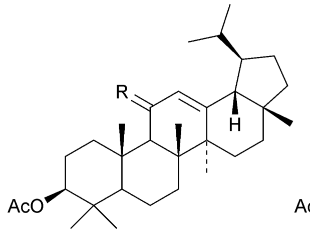
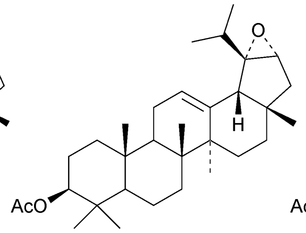


540 R = αOOH, H
541 R = O



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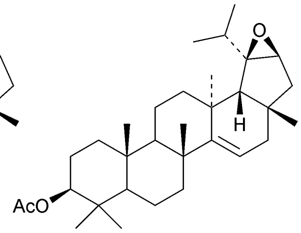

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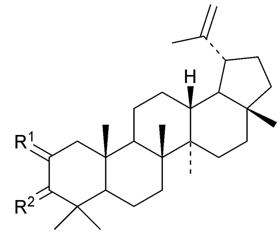
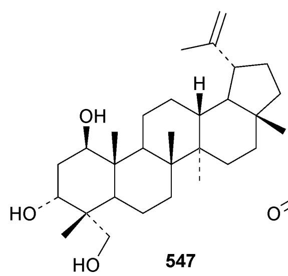


544 $R^1 = R^2$ = βOH, H
545 R^1 = O; R^2 = αOH, H
546 R^1 = βOH, H; R^2 = O



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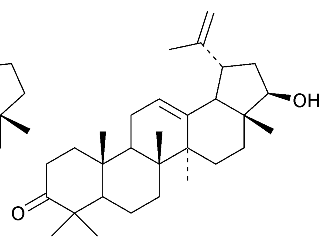

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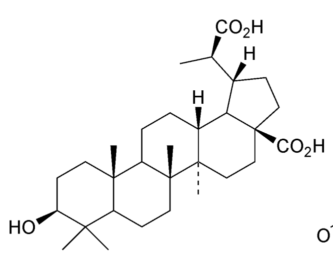

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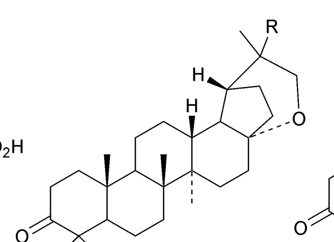
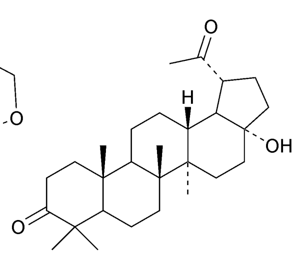


550 R = αOH
551 R = βOH



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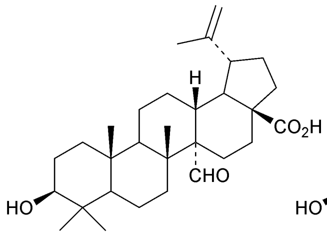
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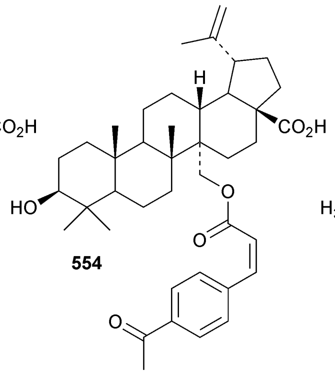
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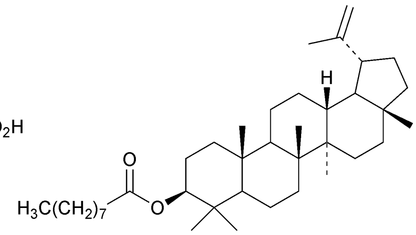
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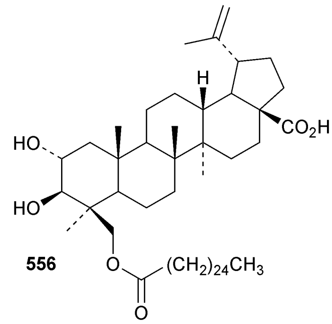
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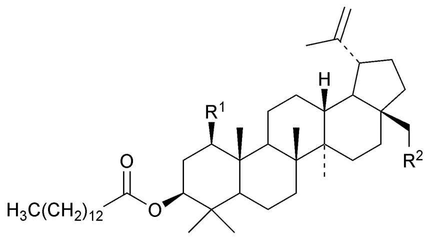
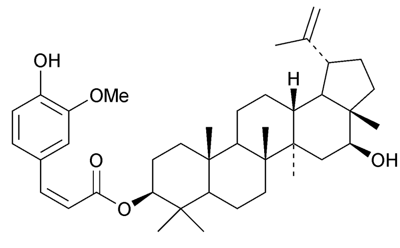

557 R^1 = OH; R^2 = H
558 R^1 = H; R^2 = OH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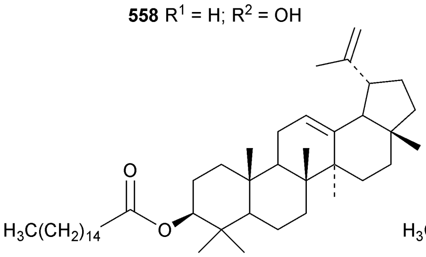
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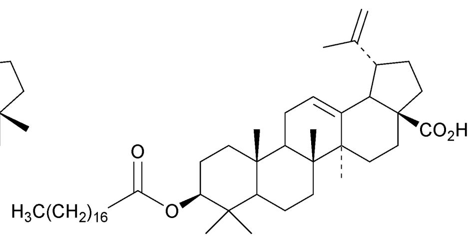
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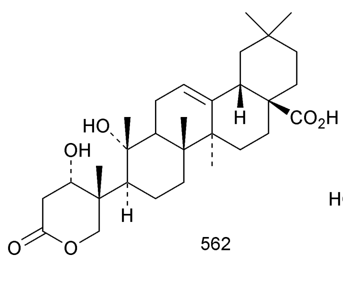
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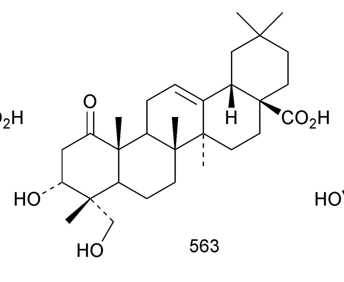
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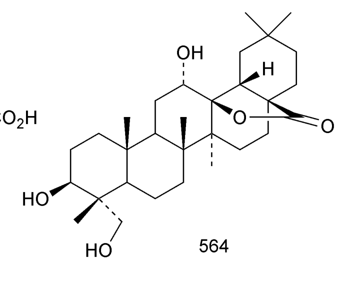
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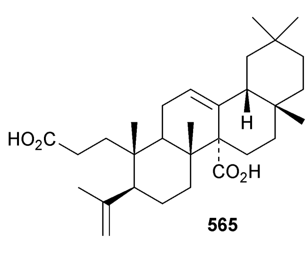
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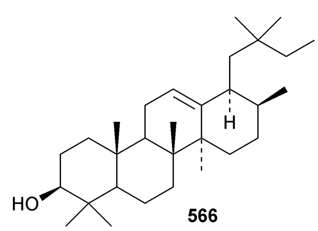
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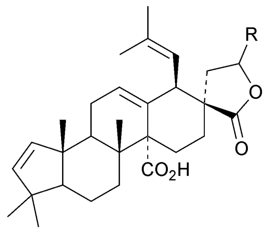
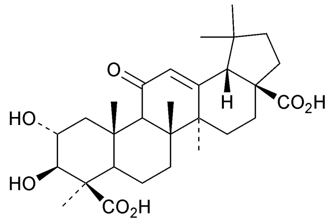

567 R = αOMe
568 R = βOMe
569 R = OH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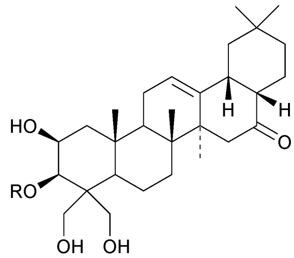
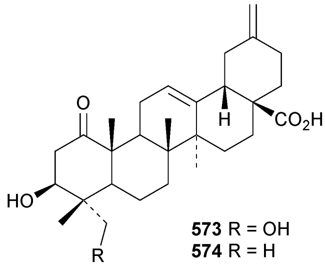
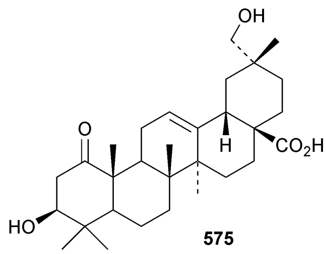

571 R = H
572 R = Glc


573 R = OH
574 R = H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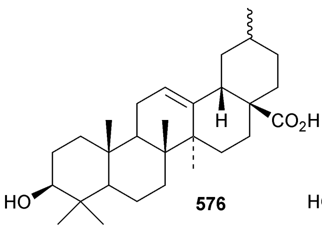
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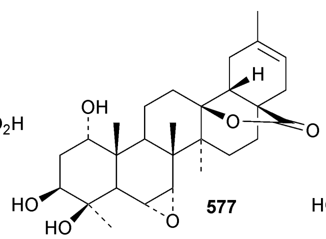
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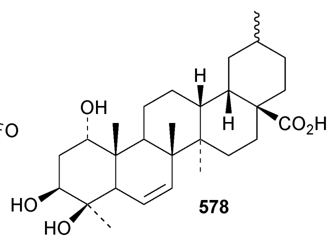
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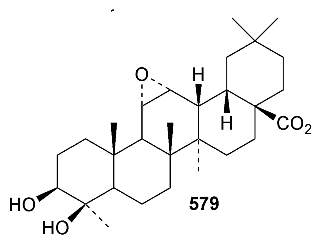
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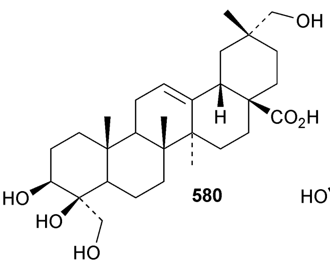
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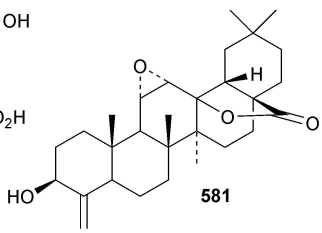
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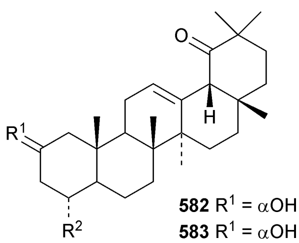
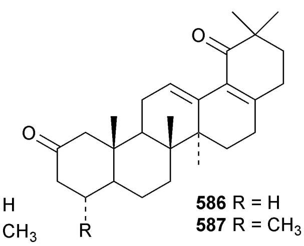
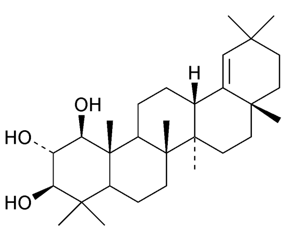

582 R^1 = αOH, H; R^2 = H
583 R^1 = αOH, H; R^2 = CH_3
584 R^1 = O; R^2 = H
585 R^1 = O; R^2 = CH_3


586 R = H
587 R = CH_3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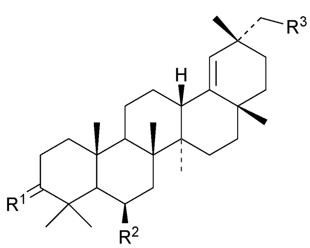
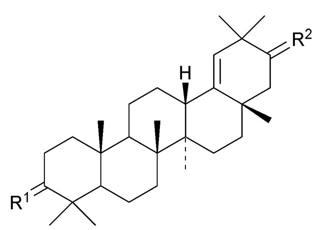
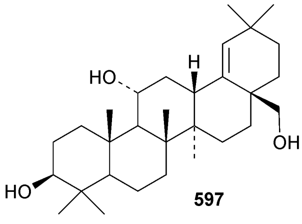

589 R^1 = βOH, H; R^2 = H; R^3 = OH
590 R^1 = O; R^2 = H; R^3 = OH
591 R^1 = O; R^2 = R^3 = OH
592 R^1 = O; R^2 = OH; R^3 = H
593 R^1 = βOH, H; R^2 = OH; R^3 = H


594 R^1 = βOH, H; R^2 = αOH, H
595 R^1 = O; R^2 = αOH, H
596 R^1 = R^2 = O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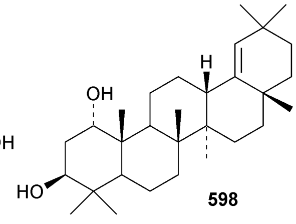
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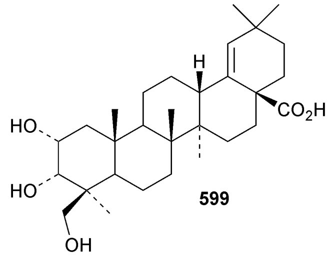
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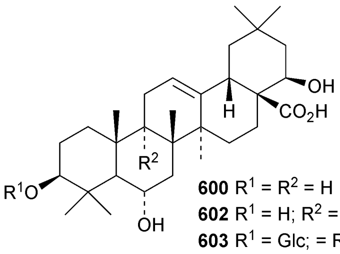
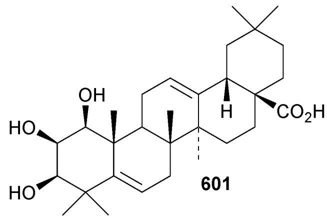

600 $R^1 = R^2 = H$
602 $R^1 = H$; $R^2 = OH$
603 R^1 = Glc; = $R^2 = H$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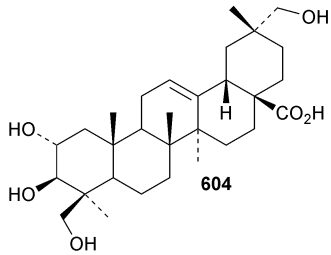
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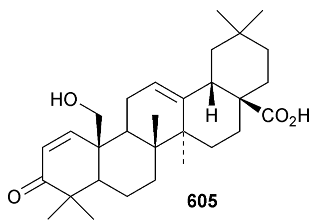
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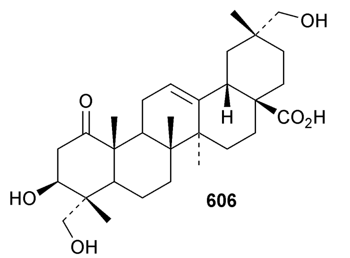
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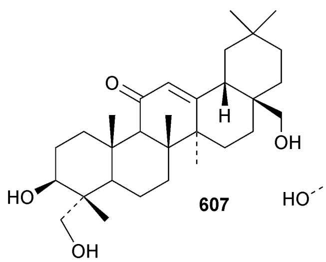
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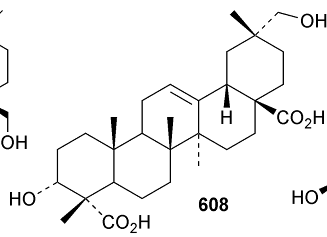
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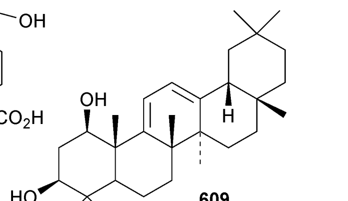
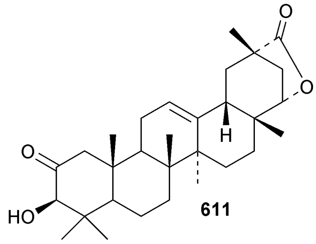

609
610 9α,11-dihydro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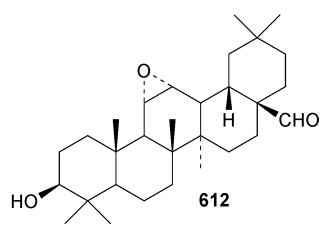
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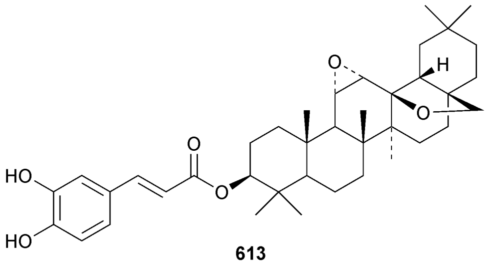

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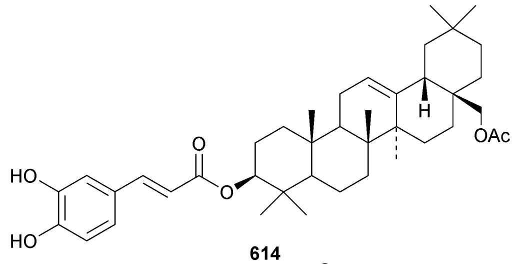

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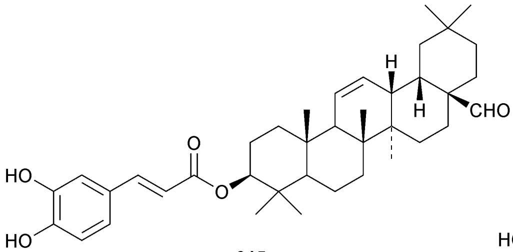

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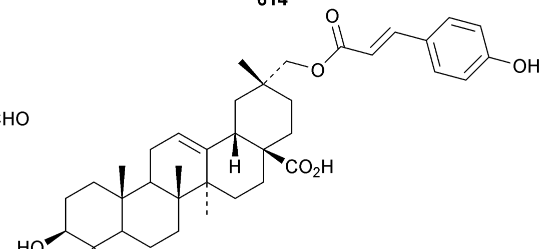

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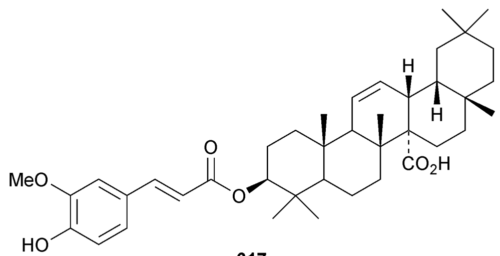

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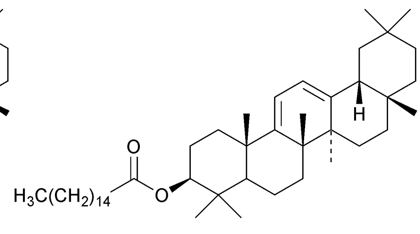

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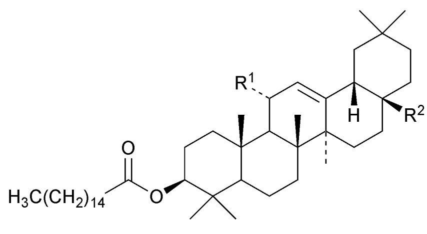
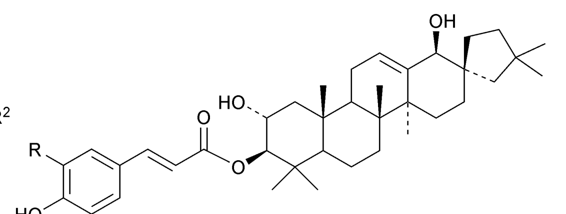
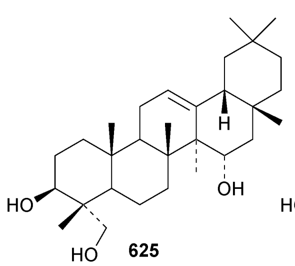


619 R^1 = OH; R^2 = CH_3
620 R^1 = H; R^2 = CHO



621 R = H
622 R = OMe
623 R = H; *Z*-isomer
624 R = OMe; *Z*-isomer



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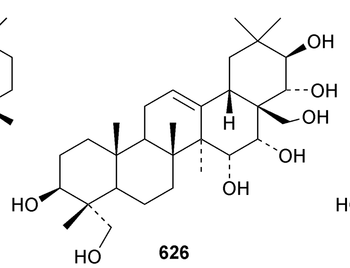

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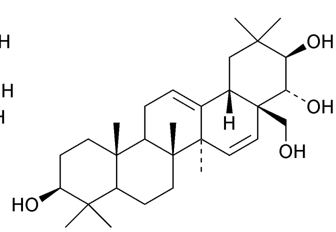

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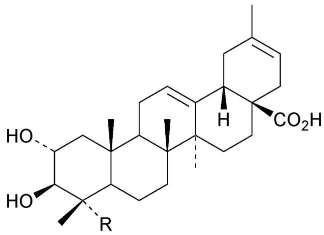
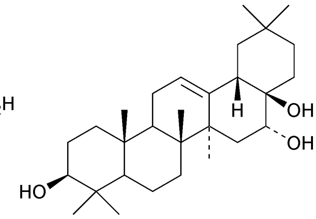


628 R = CH_3
629 R = CHO
630 R = CH_3; Δ^{19}-isomer
631 R = CHO; $\Delta^{20(29)}$-isomer



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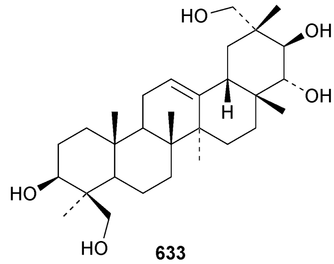


633

Table 1

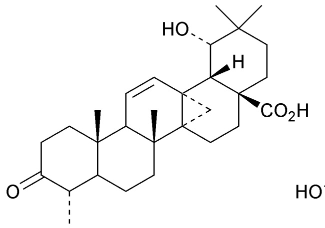
Trivial name	Plant species	Ref.
Aesculiosides G1–G16	*Aesculus glabra*	226
Afrocyclamins A and B	*Cyclamen africanum*	227
Anemonerivulariside A	*Anemone rivularis*	228
Asperosaponins A–C	*Dipsacus Asper*	229
Besylvosides I–VI	*Aegilops geniculata*	230
Bigeloviis A and B	*Salicornia bigelovii*	231
Bodiniosides C and D	*Elsholtzia bodinieri*	232
Bonarienosides A–E	*Hydrocotyle bonariensis*	233
Bunkankasaponin F	*Xanthoceras sorbifolia*	234
Centelloside D	*Centella asiatica*	235
Chakasaponin IV	*Camellia sinensis*	236
Dumortierinoside A methyl ester	*Isolatocereus dumortieri*	237
Elmalienosides A–C	*Cephalaria elmaliensis*	238
Entadosides A–D	*Entada phaseoloides*	239
Gardenisides A–C	*Gardenia jasminoides*	240
Guaianin P	*Guaiacum officinale*	241
Gummososide A, gummososide A methyl ester	*Stenocereus alamosensis*	237
Hareftoside E	*Astragalus hareftae*	78
Hederifoliosides A–E	*Cyclamen hederifolium*	242
Ilexsaponins D–F	*Ilex pubescens*	243
Ilexsaponin D (duplicate name)	*Ilex pubescens*	244
Kalopanaxsaponins L and M	*Kalopanax pictus*	245
Lobatosides L and M	*Actinostemma lobatum*	246
Lonimacranthoides IV and V	*Lonicera macranthoides*	247
Mimengosides H and I	*Buddleja lindleyana*	248
Oleiferasaponin A_1	*Camellia oleifera*	249
Paviosides A–H	*Aesculus pavia*	250
Pleurosaponins A–K	*Pleurospermum kamtschaticum*	251
Polygalasaponins LI–LIII	*Polygala japonica*	252
Raddeanosides R_{20}–R_{22}	*Anemone raddeana*	253
Sanchakasaponins A–D	*Camellia japonica*	254
Sanchakasaponins E–H	*Camellia japonica*	255
Sandrosaponin XI	*Ferula hermonis*	256
Senaciapittosides A and B	*Pittosporum senacia*	257
Silenoviscoside F	*Silene viscidula*	258
Sorbifoliasides A–F	*Xanthoceras sorbifolia*	234
Teaseedsaponins A–L	*Camellia sinensis*	259
Treleaseside A	*Stenocereus eruca*	180

The sources of new oleanane saponins with known genins that have not been assigned trivial names are listed in Table 2.

Pachanosides I1 and D1 are pachanane saponins with known genins from *Isolatocereus dumortieri*.[237] The structures of the 13,27-cyclized oleananes donellanic acids A **634**, B **635** and C **636**, from *Donella ubanguiensis*, were all established by X-ray analyses.[291] The donellanic acids are accompanied by two

Table 2

Plant species	Ref.
Abrus precatorius	260
Abuta grandifolia	261
Acanthopanax senticosus	262
Acanthophyllum gypsophiloides	263
Alhagi maurorum	264
Anemone amurensis	265
Aralia elata	266
Aralia taibaiensis	267
Ardisia gigantifolia	268
Callicarpa integerrima	269
Chenopodium foliosum	270
Clematis argentilucida	271 and 272
Cyperus rotundus	273
Dizygotheca elegantissima	274
Eragrostis tef	275
Grangea maderaspatana	276
Gymnema sylvestre	277
Gymnocladus chinensis	278
Gypsophila trichotoma	279
Kalopanax pictus	245
Kalopanax septemlobus	280
Maesa lanceolata	281
Patrinia scabiosifolia	282
Pometia pinnata	283
Salicornia europaea	284
Salicornia herbacea	285
Samanea saman	286
Sideroxylon obtusifolium	287
Tarenna grevei	288
Wedelia chinensis	289
Xanthoceras sorbifolia	290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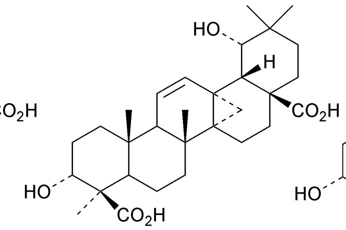
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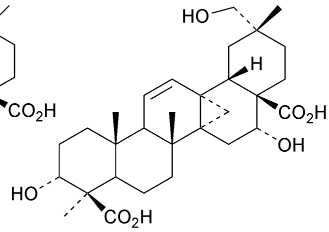
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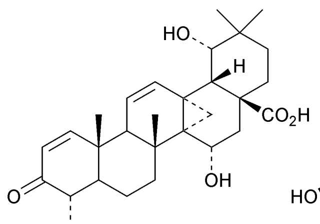
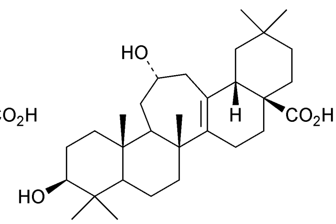

637
638 1,2-dihydro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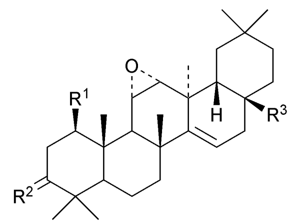
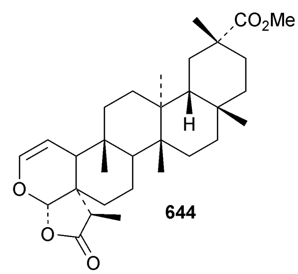

640 R^1 = OH; R^2 = βOH, H; R^3 = CH_3
641 R^1 = H; R^2 = O; R^3 = CH_2OH
642 R^1 = H; R^2 = βOH, H; R^3 = CHO
643 R^1 = H; R^2 = βOAc, H; R^3 = CHO

further 13,17-cyclized compounds that have been assigned the tentative structures **637** and **638**. Ilelic acid B **639** is a rearranged oleanane with a seven-membered C-ring from *Ilex latifolia*.[292] Four taraxerane derivatives **640–643** have been identified in *Saussurea graminea*.[293]

Cassinolide **644**, from *Cassine xylocarpa*, is a 2,3-secofriedelan-3,24-olide derivative.[294] *Maytenus robusta* is the source of the 3,4-secofriedelan-3,11β-olide **645** (ref. 295) and friedelane-3β,11β-diol **646**.[296] Reissantiadiol, from *Reisantia grahamii*, has been identified as friedelane-2α,3α-diol **647**.[297]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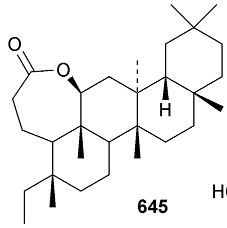
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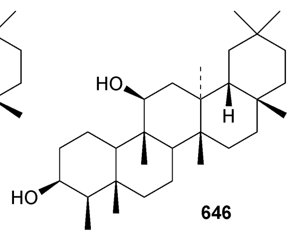
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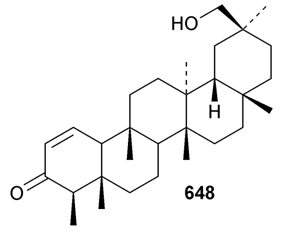
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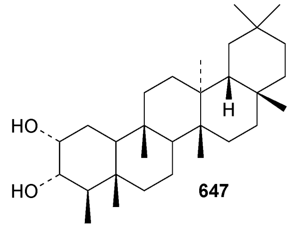
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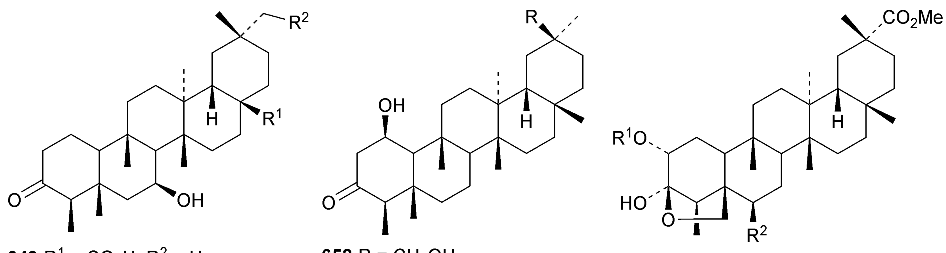
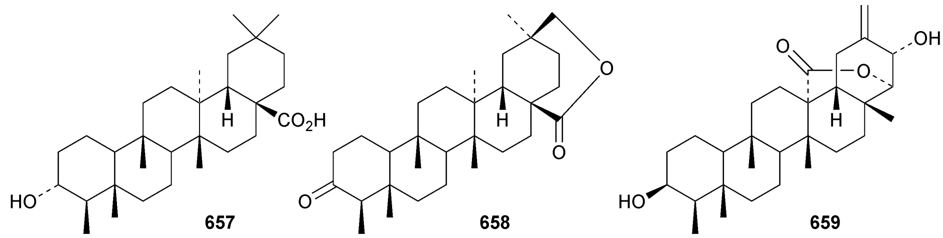


649 $R^1 = CO_2H$; $R^2 = H$
650 $R^1 = CO_2Me$; $R^2 = H$
651 $R^1 = CH_3$; $R^2 = OH$

652 $R = CH_2OH$
653 $R = CO_2H$

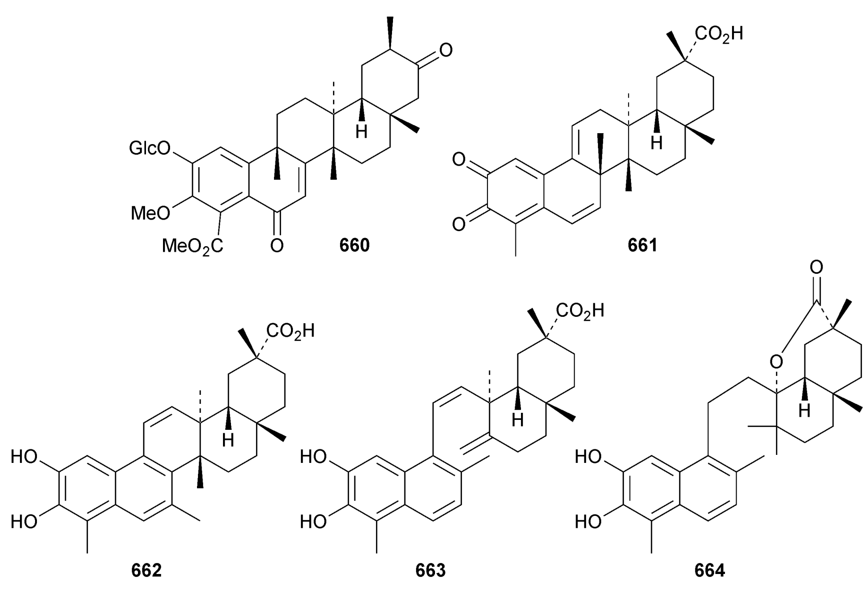
654 $R^1 = R^2 = H$
655 $R^1 = Ac$; $R^2 = H$
656 $R^1 = H$; $R^2 = OH$



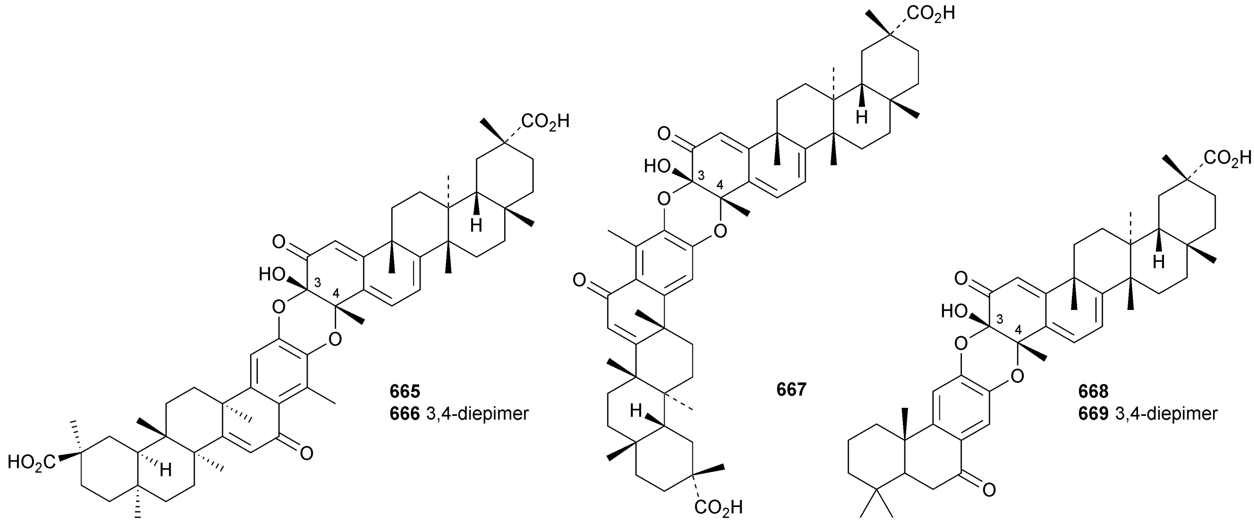
657 **658** **659**

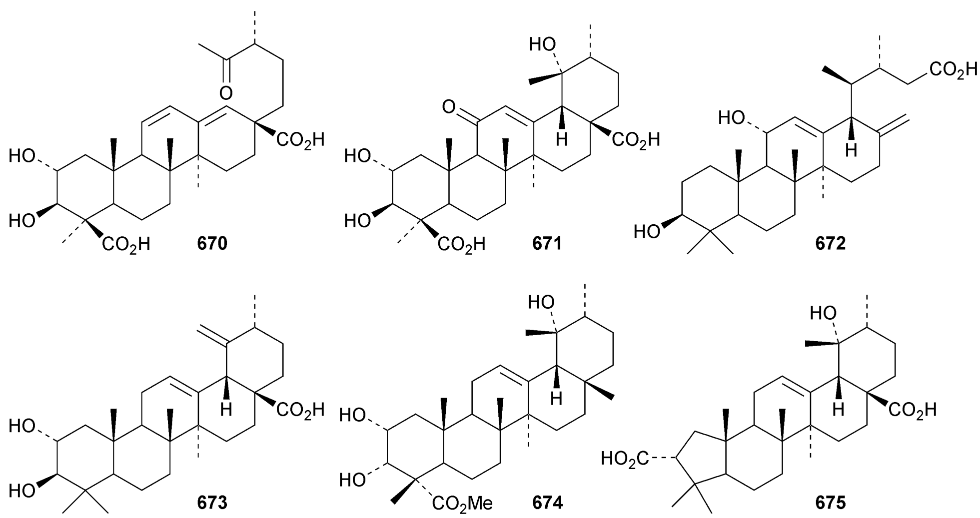
Other simple friedelane triterpenoids include 30-hydroxyfriedel-1-en-3-one **648** from *Salacia hainanensis*,[124] **649–653** from *Celastrus vulcanicola* and **654–658** from *Maytenus jelskii*[298] and glaucalactone **659** from *Caloncoba glauca*.[61]

A review of the pharmacology of celastrol, a norfriedlane derivative, has been published.[299] Hypoglaside A **660** is a dinorfriedelane glucoside from *Tryperygium hypoglaucum*.[300] *Celastrus orbiculatus* is the source of a range of norfriedelane and methyl-migrated derivatives.[301] The 25(9 → 8)-*abeo* norfriedelane **661** and the 25(9 → 7)-*abeo* derivative **662** are accompanied by the 8,14-*seco* compounds **663** and **664**. A biosynthetic pathway to these rearranged friedelane derivatives has been proposed. Also present in *Celastrus orbiculatus* are the "dimeric" norfriedelanes celastrolines Aα **665** and Aβ **666** and isocelastroline Aα **667**, together with celastrolines Bα **668** and Bβ **669** that have a linkage to a podocarpane derivative.



660 **661** **662** **663** **664**



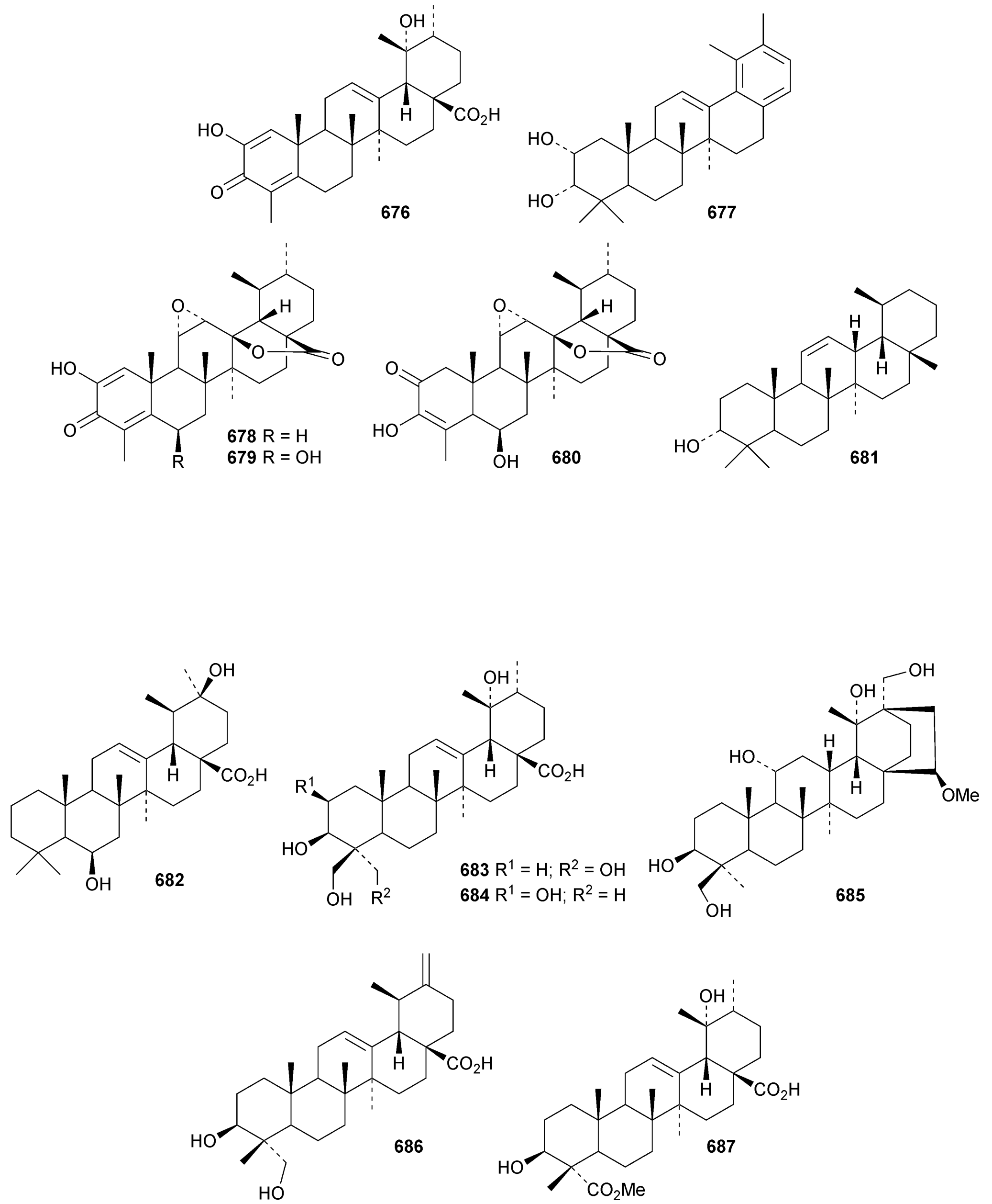


7. The ursane group

Ursane triterpenoids have shown potential as anticancer drugs.[302] Reviews on the anticancer activities of ursolic acid[303] and acetyl-11-keto-β-boswellic acid (AKBA)[304] have been published.

The 18,19-secoursane derivative **670** has been isolated from the bark of *Diospyros decandra* together with **671**.[195] The 17,22-*seco* derivative **672** has been found in both *Salvia palaestina* and *Salvia syriaca*.[305] Euscaphic acids J **673**, K **674** and L **675** have been isolated from *Euscaphis japonica*.[197] Euscaphic acid L **675** has a contracted ring-A. Negundonorins A **676** and B **677**, from *Vitex negundo*, are 24-nor and 28-noruranes, respectively.[306] Further 24-norursanes include ulmoidol A **678** from *Eucommia ulmoides*[307] and the related compounds **679** and **680** from *Dipsacus chinensis*.[308] 30-Norurs-11-en-3α-ol **681** has been identified in the roots of *Alhagi camelorum*.[309]

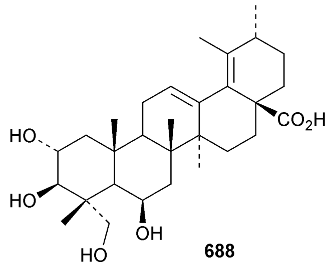
6β,20β-Dihydroxyurs-12-en-28-oic acid **682**, from leaves of *Psidium guajava*, is unusual as it lacks oxygenation at C-3.[310] The structure of 3β,19α,23,24-tetrahydroxyurs-12-en-28-oic acid **683**, from *Nauclea officinalis*, was confirmed by X-ray analysis.[311] It is accompanied by the corresponding 2β,3β,19α,24-tetrahydroxy compound **684**. Further simple ursane derivatives include the acetal **685** from *Juglans sinensis*,[204] rhododendric acid A **686**



from *Rhododendron brachycarpum*,[312] uncariursanic acid **687** from *Uncaria macrophylla*,[313] 2α,3β,6β,23-tetrahydroxyursa-12,18-dien-28-oic acid **688** from *Kadsura marmorata*,[314] 2α,3β,6β,20β,23,30-hexahydroxyurs-12-en-28-oic acid **689** and psiguanins B **690**, C **691** and D **692** from *Psidium guajava*,[315] the 2α,3β,21α-trihydroxy derivative **693** and the 24-aldehyde **694** from *Berberis koreana*,[316] the 1α,3α-dihydroxy derivatives **695–697** from *Euphorbia kansuensis*,[317] the 3-ketone **698** from *Albizzia lebbeck*,[318] loxanic acid **699** and its acetate **700** from *Eucalyptus loxophleba*[319] and tolpidiol B **701** from *Tolpis proustii* and *Tolpis lagopoda*.[320]

Kirmanoic acid **702**, from *Nepeta clarkei*, is an unusual alkylphenyl ether.[185] New ursane esters include the isoferuloyl ester **703** from *Eucalyptus exserta*,[205] ehretiolide **704** from *Ehretia longifolia*,[321] the 30-*cis*-coumaryl ester **705** from *Rubia schumanniana*,[216] 3β-tetradecanoyloxyurs-12-en-28,19β-olide **706** from *Lysimachia clethroides*[322] and 3-*epi*-cecropic acid **707** from *Dipterocarpus obtusifolius*.[106]

Sanguisoside A is an ursane saponin from *Sanguisorba officinalis* with the new 18,19-*seco*-ursane genin **708**.[323] Centelloside E from *Centella asiatica* has the new genin **709** (ref. 235) and the genins **710** and **711** are present in saponins from *Actinidia valvata*.[324]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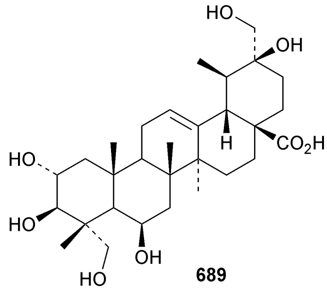
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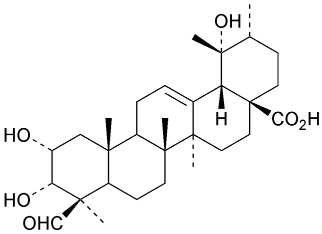
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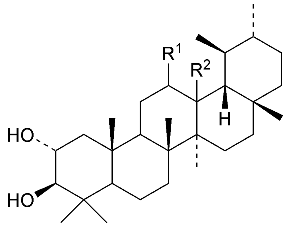
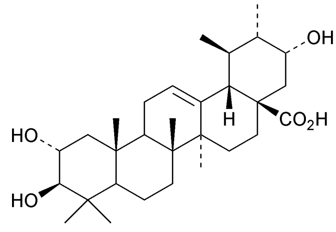

690 R^1 = αOH; R^2 = βOH
691 R^1 = βOH; R^2 = βOH
692 R^1 = βOH; R^2 = αOH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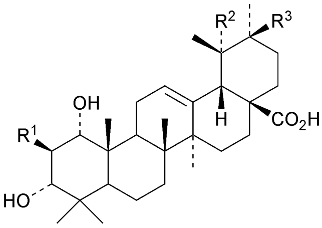
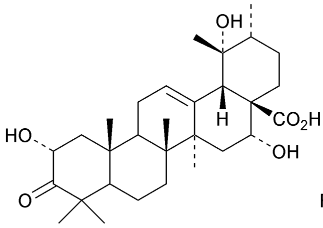

695 $R^1 = R^2$ = H; R^3 = OH
696 R^1 = H; $R^2 = R^3$ = OH
697 $R^1 = R^3$ = H; R^2 = OH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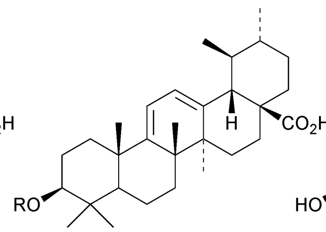
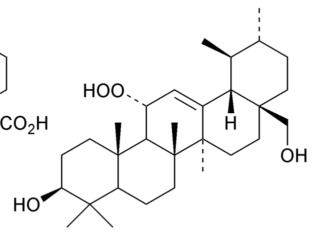

699 R = H
700 R = Ac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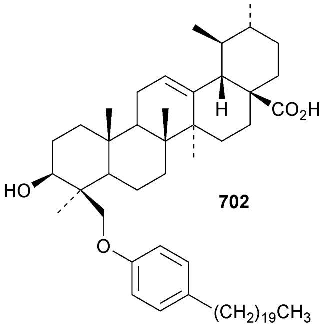
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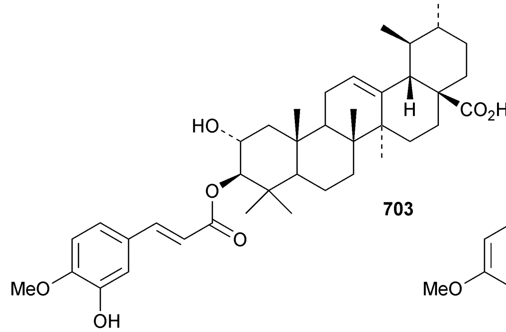
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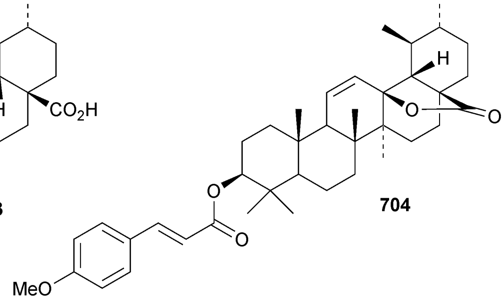
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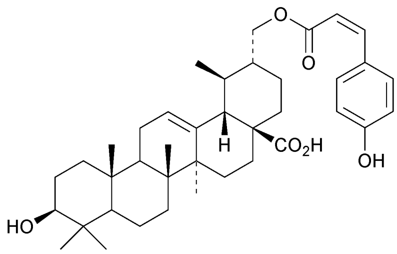
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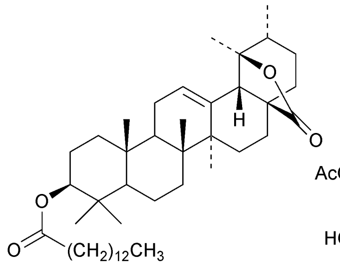
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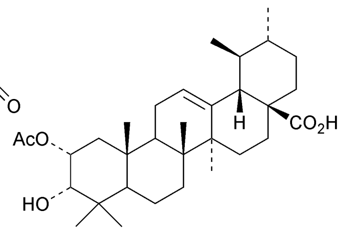
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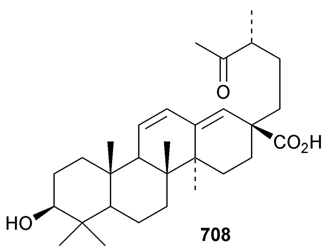
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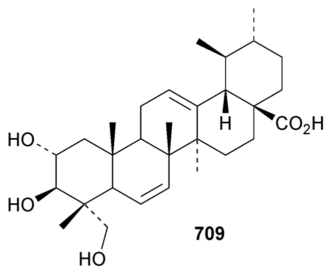
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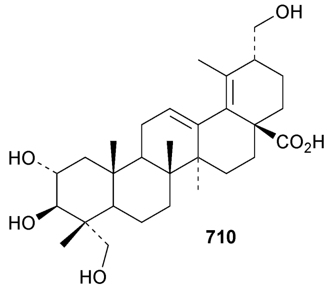
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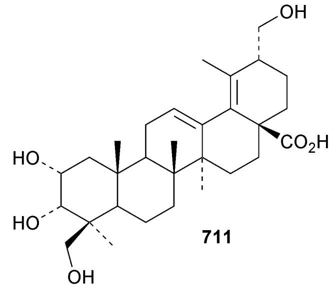
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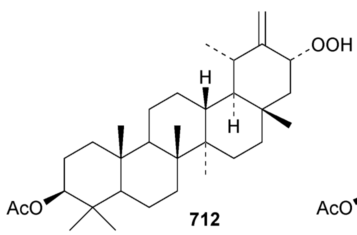
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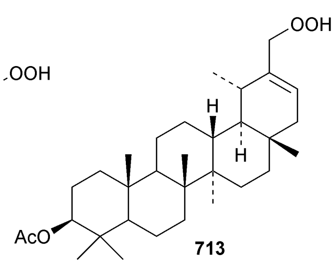
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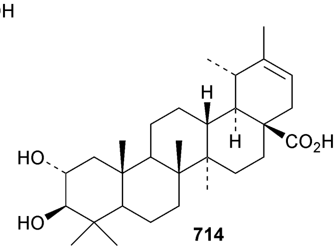
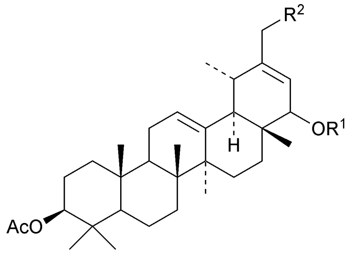

714

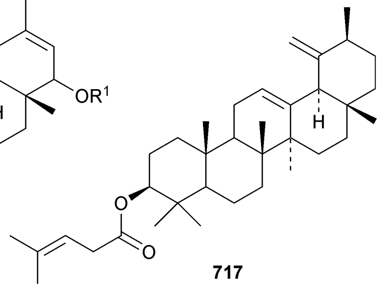
Ursane saponins with known genins include asphorins A and B from *Asphodelus tenuifolius*,[325] asprellanosides A and B from *Ilex asprella*,[326] elasticoside from *Ficus elastica*,[327] ilekudinchosides F and G from *Ilex kudincha*,[328] ilemaminosides A and B from *Ilex mamillata*,[329] ilexasosides A–H from *Ilex asprella*,[330] phillyriside A from *Stenocereus eruca*,[180] and unnamed saponins from *Diospyros decandra*,[195] *Juglans sinensis*,[204] *Lantana camara*[331] and *Psidium guajava*.[332]

The taraxastane hydroperoxide derivatives **712** and **713** have been isolated from the roots of *Taraxacum platycarpum*.[173] Psiguanin A, which is 2α,3β-dihydroxytaraxast-20-en-28-oic acid **714**, has been found in the leaves of *Psidium guajava*.[315] Other new taraxastane derivatives include chlorotolpidiol **715** and tolpidiol A **716** from *Tolpis proustii* and *Tolpis lagopoda*,[320] pergularines A **717** and B **718** from *Pergularia tomentosa*[333] and calotroprocerol A **719**, calotroprocerone A **720** and calotroproceryl acetates A **721** and B **722** from *Calotropis procera*.[334] Two taraxastane saponins with known genins have been found in the roots of *Ilex pubescens*.[335]

The 27(14 → 13)-*abeo*-urs-14-enone derivative **723**, from *Rubia schumanniana*, has the unusual β-configuration for the migrated methyl.[216] The rearranged ursanes ilelic acids A **724**, C



715 R^1 = H; R^2 = Cl
716 R^1 = Ac; R^2 = OEt



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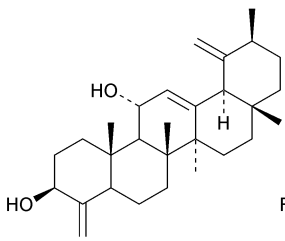

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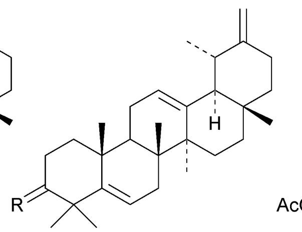
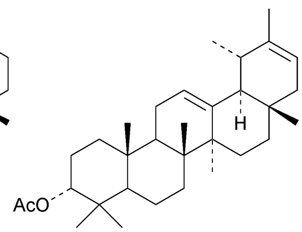


719 R = αOH, H
720 R = O
721 R = αOAc, H



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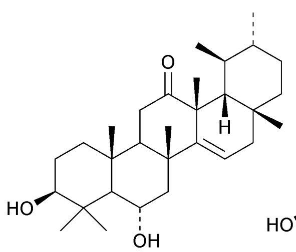

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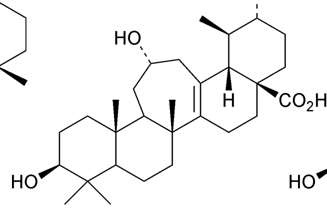

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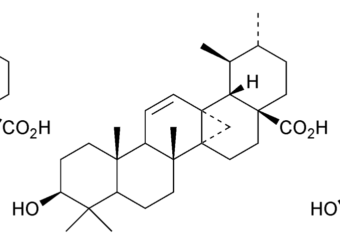

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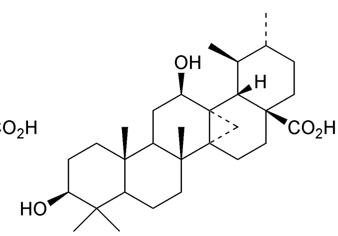


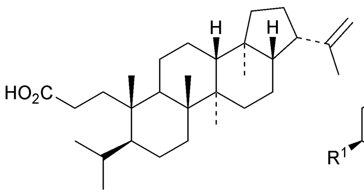
726

725 and D **726** have been isolated from *Ilex latifolia*.[292] The structure of ilelic acid D **726** was confirmed by X-ray analysis.

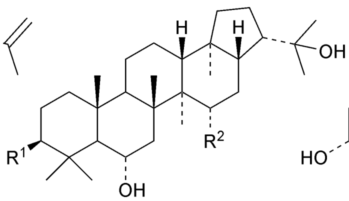
8. The hopane group

3,4-Secohop-22(29)-en-3-oic acid **727** has been isolated from *Maytenus robusta*.[295] The scale insect pathogenic fungus *Aschersonia calendulina* is the source of two hopane metabolites **728** and **729**.[336] The leaves of *Hybanthus austro-caledonicus* produce 3-epiwoodwardinic acid **730**.[337] Plakohopanoid **731**, a C_{32} hopanoid ester of a manosyl myoinostol, has been isolated from the sponge *Plakortis cf. lita*.[338] The structure of plakohopanoid **731** implies that it is of bacterial origin. This is the first example of a biologically produced C_{32} hopanoic acid. Such acids were considered to only be geohopanoids formed by abiotic degradation of bacteriohopanoids. Oppositifolone **732**, from *Glinus oppositifolius*, has a 29(22 → 21)-*abeo*-hopane skeleton and is the 3-ketone of spergulagenin A.[339]

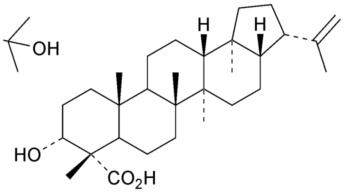
Pteroxygonumnol **733**, from the roots of *Pteroxygonum giraldii*, has been identified as 2β,25 : 19β,28-diepoxyarborin-9(11)-ene-3β,7β-diol.[340] Five 25-norarborinane derivatives **734–738** have been isolated from bamboo stems, *Sinocalamus affinis*.[187] The structure of **734** was confirmed by X-ray analysis. *Atalantia retusa* is the source of the 17,21-*seco*-arborane derivative retusinol **739**.[341] Peniciside **740** is a fernane metabolite of *Penicillium* sp.169[342] and 3β-acetoxyfern-7-en-6-one **741** is a constituent of *Scorzonera latifolia*.[343]



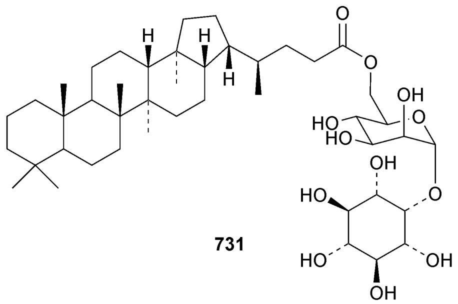
727



728 R[1] = H; R[2] = OH
729 R[1] = OAc; R[2] = H



730



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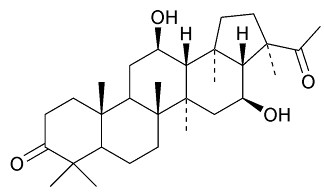
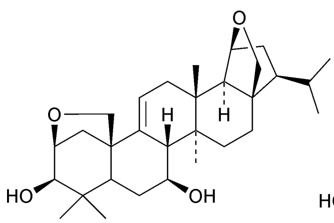


732



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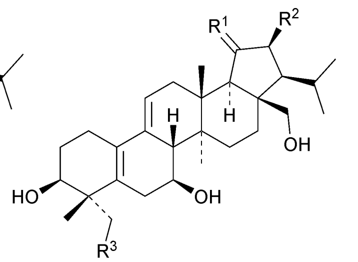
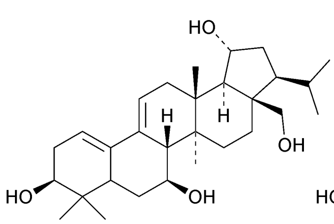


734 R[1] = αOH, H; R[2] = R[3] = H
735 R[1] = αOH, H; R[2] = OH; R[3] = H
736 R[1] = O; R[2] = R[3] = H
737 R[1] = αOH, H; R[2] = H; R[3] = OH



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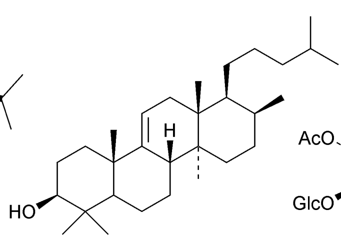

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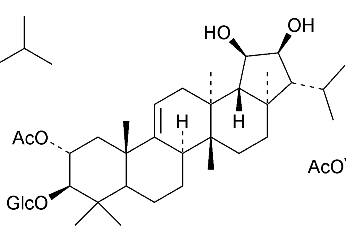

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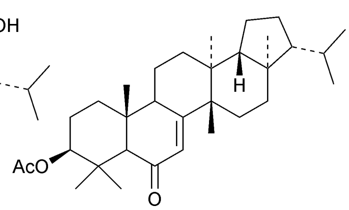

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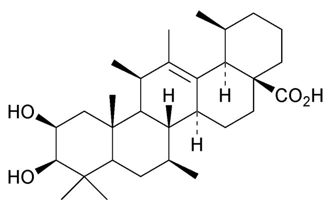

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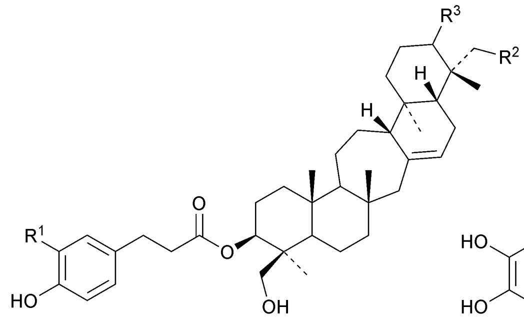
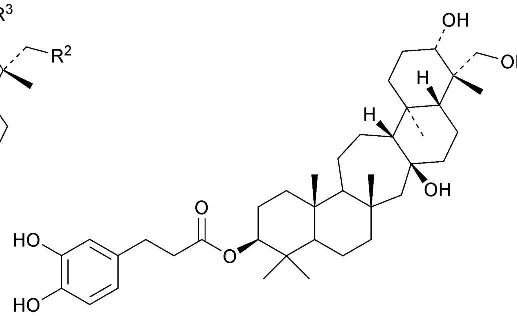


743 R^1 = OH; R^2 = H; R^3 = βOH; 3-epimer
744 R^1 = R^2 = OH; R^3 = βOH
745 R^1 = R^2 = H; R^3 = αOH; 2',3'-didehydro (*E*)



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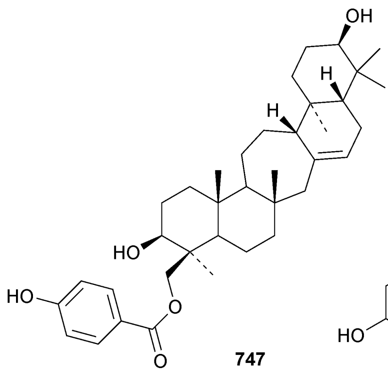

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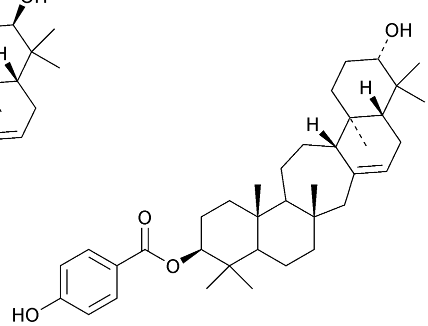
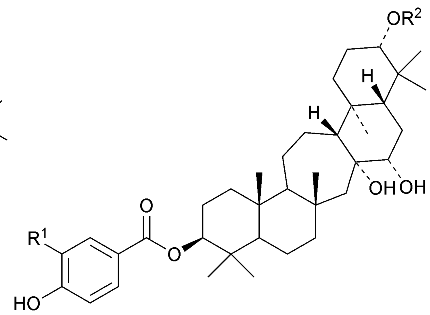
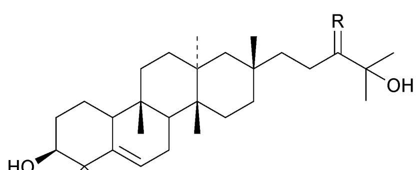


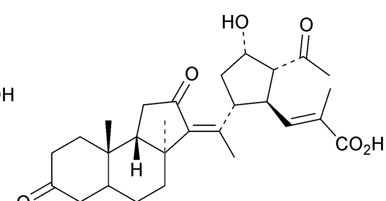
748



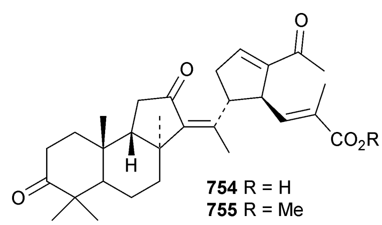
749 R^1 = OMe; R^2 = H
750 R^1 = H; R^2 = Ac



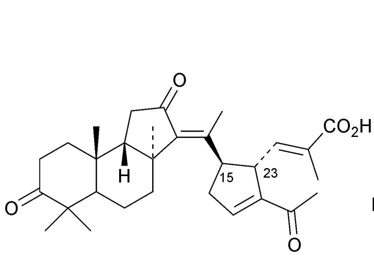
751 R = βOH, H
752 R = O



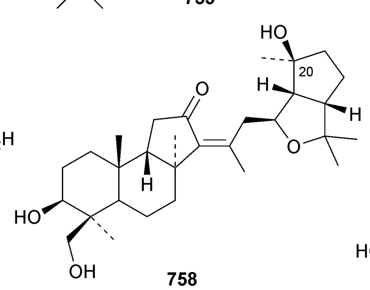
753



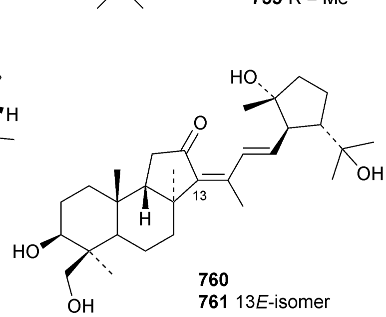
754 R = H
755 R = Me



756
757 15,23-diepimer



758
759 20-epimer



760
761 13*E*-isomer

9. Miscellaneous compounds

The unlikely structure **742** has been proposed for erucaoic acid from *Sonchus eruca*.[344] The club moss *Lycopodium phlegmaria* is the source of the serratane esters lycophlegmariols A **743**–D **746** (ref. 345) and four esters **747–750** have been found in *Palhinhaea cernua* (syn. *Lycopodium cernuum*).[346] The D:B-friedobaccharane derivatives leonatriol **751** and the corresponding ketone leonatriolone **752** have been isolated from *Cassine xylocarpa* and *Celastrus vulcanicola*, respectively.[294] Globostelletins J **753**–S **761**, from the marine sponge *Rhabdastrella globostellata*, are isomalabaricanes with cyclopentane side chains.[347]

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