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Triterpenoids

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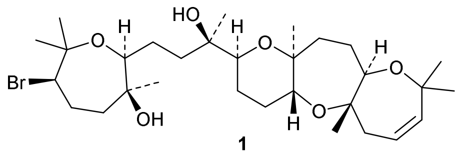
This review covers the isolation and structure determination of triterpenoids reported during 2013 including squalene derivatives, lanostanes, holostanes, cycloartanes, cucurbitanes, dammaranes, euphanes, tirucallanes, tetranortriterpenoids, quassinoids, lupanes, oleananes, friedelanes, ursanes, hopanes, serratanes, isomalabaricanes and saponins; 349 references are cited.

1. Introduction

The anticancer activities of triterpenoids and their saponins have been extensively reviewed.[1-8] Other activities such as the antidiabetic properties[9, 10] and neuropharmacological effects[11] of triterpenoids have also been covered. Surveys of triterpenoids from *Albizia*,[12] *Aphanamixis*,[13] *Boswellia*,[14] *Calendula*,[15] *Clinopodium*,[16] *Lonicera*,[17] *Schefflera*,[18] and *Toona*[19] species and *Argania spinosa*,[20] *Olea europea*,[21] and *Platycodon grandiflorum*,[22] have appeared. There is interest in the production of triterpenoids with cell and tissue cultures[23] and enhancing saponin production by cell and gene engineering.[24] The biological roles of triterpenoid saponins in plants have been reviewed.[25]

2. The squalene group

The synthesis of armatol A, from the red alga *Chondria armata*, has led to the revision of the relative and absolute configuration to **1**.[26] The configurations of the other compounds in this series, armatols B – F have also been revised and a biosynthetic pathway to the armatols from squalene has been proposed.



1

3. The lanostane group

Streptoseolactone **2**, a protostane derivative from the marine-derived actinomycete *Streptomyces seoulensis*, shows neuraminidase inhibition activity.[27] The structures and biological activities of natural protostane and fusidane triterpenoids have been reviewed.[28]

The following lanostane derivatives have been reported from *Ganoderma* species: 16α,26-dihydroxylanosta-8,24*E*-dien-3-one **3** from the fruiting bodies of *Ganoderma hainanense*,[29] ethyl lucidenate A **4**[30] and the ganoderic acid **5**[31] from *Ganoderma lucidum*, ganorbiformins A **6** - G **12** from cultures of *Ganoderma orbiforme*,[32] lucidones D **13** – G **16**, ganoderesins A **17** and B **18** and 7-oxoganoderic acids Z_2 **19** and Z_3 **20** from *Ganoderma resinaceum*,[33] the related compounds **21** - **23** from the fruiting bodies of *Ganoderma tropicum*[34] and tsugaric acids D **24** and E **25** from *Ganoderma tsugae*.[35] Three new lanostanes **26** - **28** have been isolated from the fungus *Ceriporia lacerata* (associated with *Acanthaster planci*).[36] The lanostane **26** has also been isolated from another strain of *Ceriporia lacerata* (an endophytic fungus of *Huperzia serrata*) together with compound **29**.[37] Other lanostane derivatives include the two pentanorlanostanes curvalarols A **30** and B **31** from the soil fungus *Curvularia borreriae*,[38] the oxalate esters **32** and **33** from the fungus *Perenniporia maackiae*,[39] fasciculols J **34** - M **37** from the mushroom *Naematoloma fasciculare*[40] and

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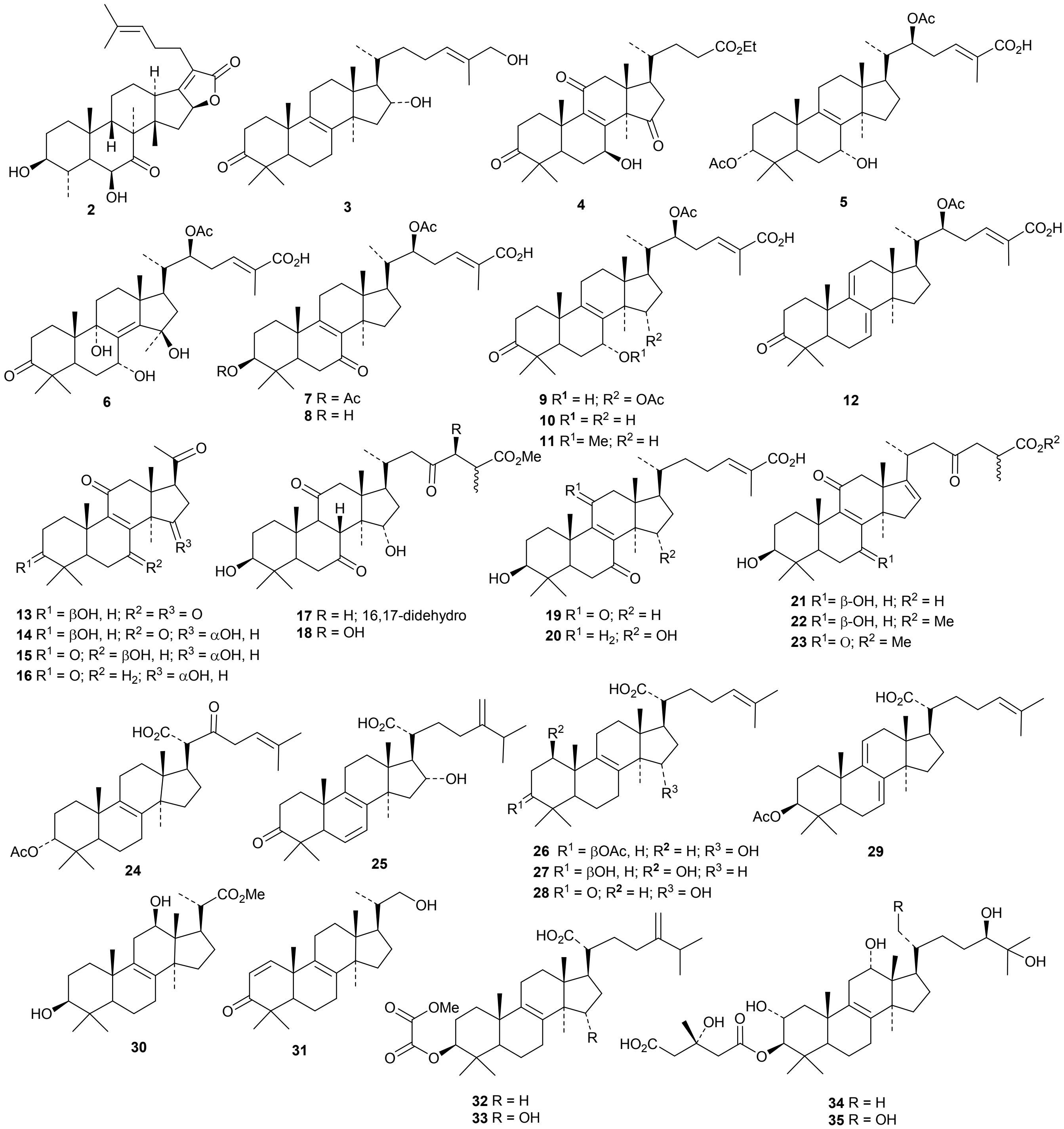
terresterol **38** from the oomycete *Saprolegnia terrestris*.[41] 15-*O*-Acetylganolucidate A **39** and the tetraketo-acid **40** have been isolated from *Antrodia camphorata* together with the ethyl esters of the known lucidenic acids A and F.[42]

The structure **41**, originally proposed for a lanostane from *Wyethia mollis*, has been revised to **42** on the basis of an X-ray crystallographic analysis.[43] Other simple lanostanes include klainedoxalanostenone **43** from the stem bark of *Klainedoxa gabonensis*,[44] moruslanosteryl acetate **44** from the stem bark



2 **3** **4** **5**

6

7 R = Ac
8 R = H

9 R^1 = H; R^2 = OAc
10 R^1 = R^2 = H
11 R^1= Me; R^2 = H

12

13 R^1 = βOH, H; R^2 = R^3 = O
14 R^1 = βOH, H; R^2 = O; R^3 = αOH, H
15 R^1 = O; R^2 = βOH, H; R^3 = αOH, H
16 R^1 = O; R^2 = H_2; R^3 = αOH, H

17 R = H; 16,17-didehydro
18 R = OH

19 R^1 = O; R^2 = H
20 R^1 = H_2; R^2 = OH

21 R^1= β-OH, H; R^2 = H
22 R^1= β-OH, H; R^2 = Me
23 R^1= O; R^2 = Me

24 **25**

26 R^1 = βOAc, H; R^2 = H; R^3 = OH
27 R^1 = βOH, H; R^2 = OH; R^3 = H
28 R^1 = O; R^2 = H; R^3 = OH

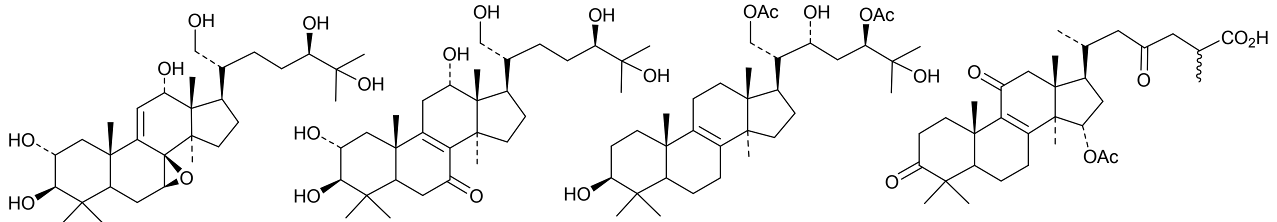
29

30 **31**

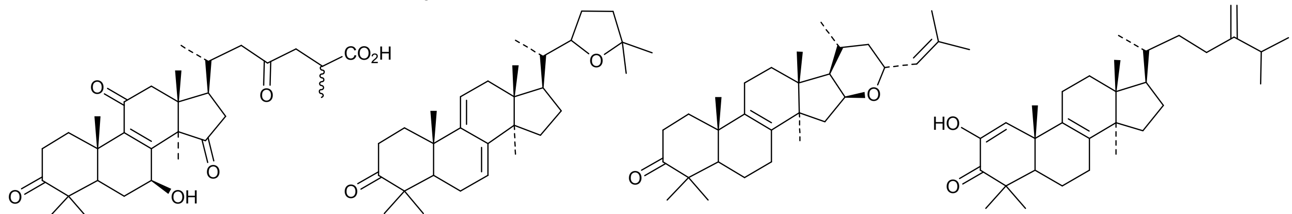
32 R = H
33 R = OH

34 R = H
35 R = OH

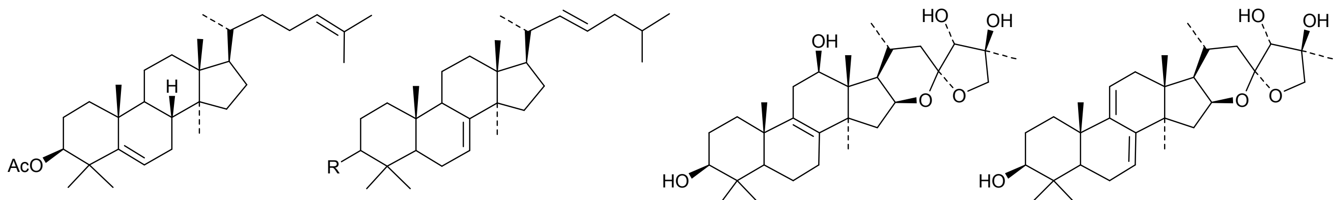
of *Morus alba*,[45] conyzagenins A **45** and B **46** from *Conyza canadensis*,[46] the spiroacetals yunnanterpenes D **47** and E **48** from *Cimicifuga yunnanensis*[47] and the unusual 3β-hydroxylanosta-8,17(20)-diene-22-carboxylic acid **49** from a crown gall induced on *Eucalyptus tereticornis*.[48] Structure **50** has been proposed for turpetholanostenol from the roots of *Operculina turpethum*.[49] Two other compounds, **51** and **52**, from this source, have been assigned unlikely structures with a Δ^5-7α,3α -hemiacetal.Further rearranged lanostane derivatives have been isolated from *Abies* species. These



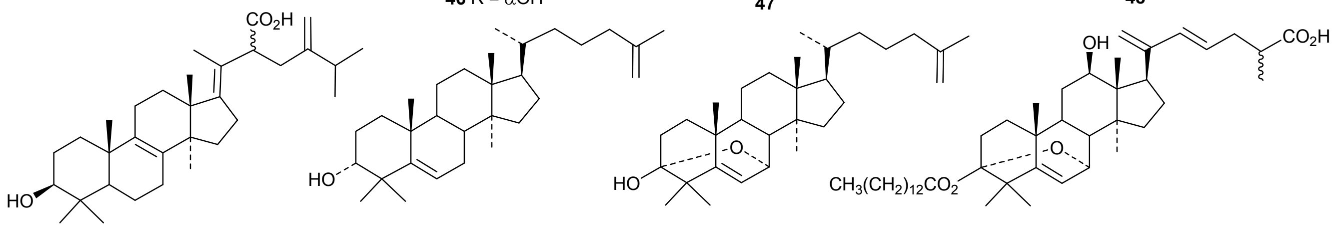
36 **37** **38** **39**



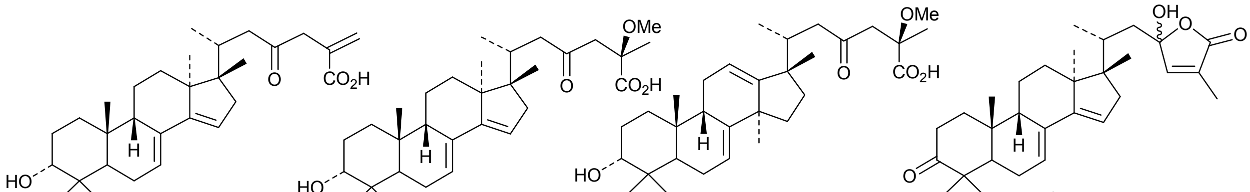
40 **41** **42** **43**



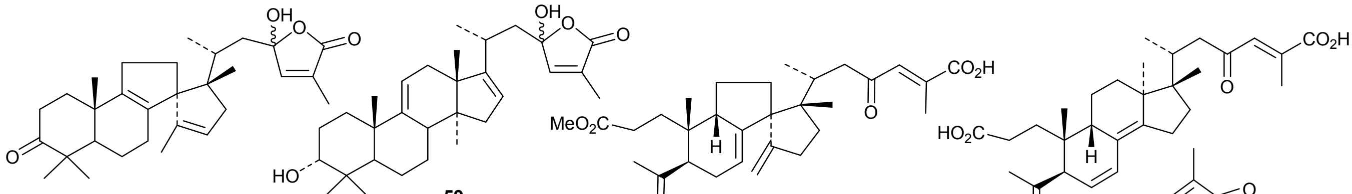
44 **45** R = βOH **46** R = αOH **47** **48**



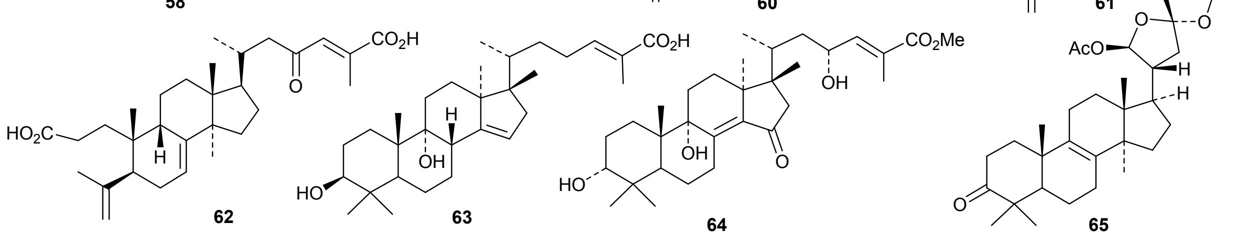
49 **50** **51** **52**



53 **54** **55** **56** **57** Δ^8



58 **59** **60** **61**

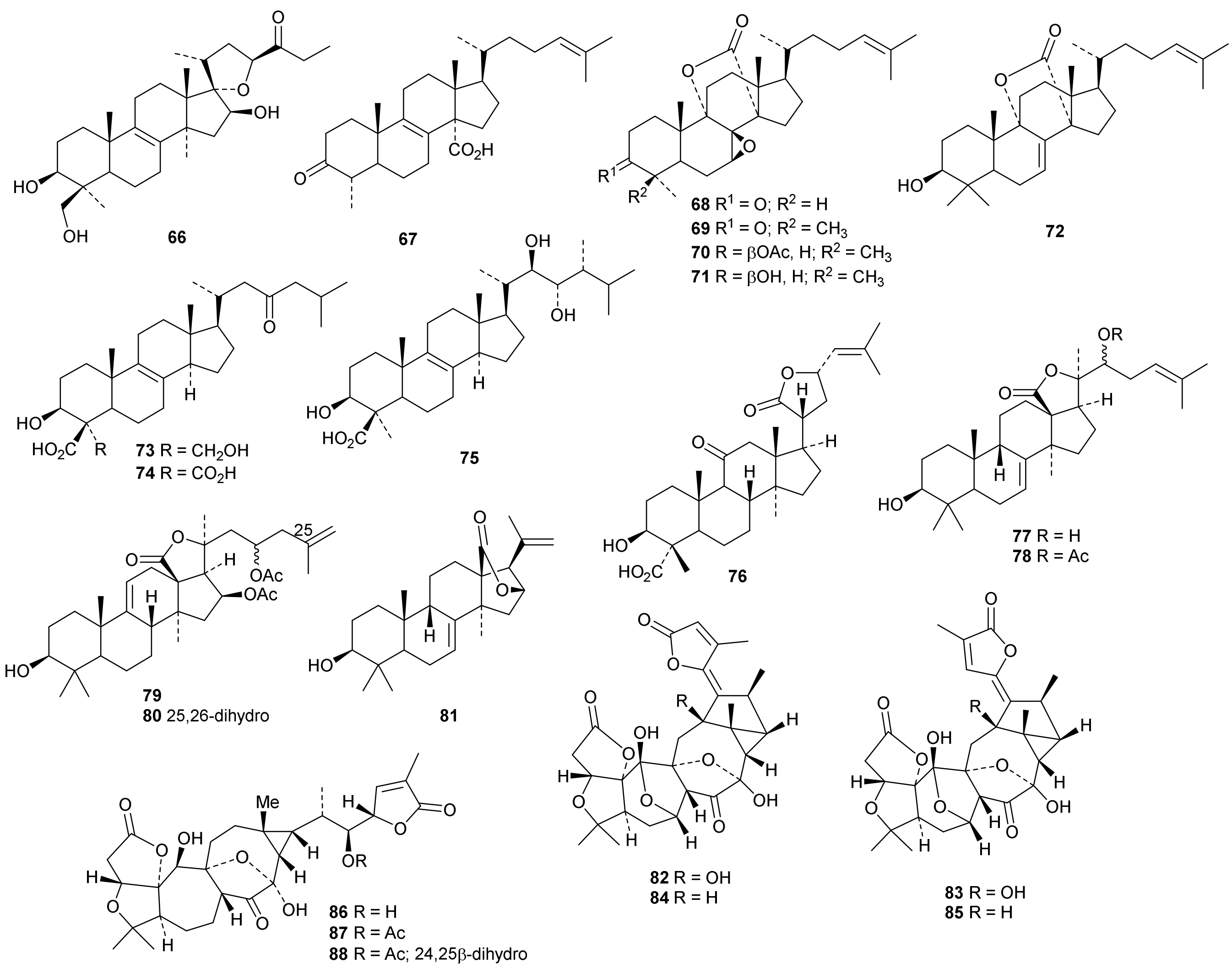


62 **63** **64** **65**

include compounds **53** - **58** from *Abies sibirica* and the unrearranged lanostanes **59**,[50] the methyl ester **60** of the known abiesonic acid and the *E*-isomer **61** of sibiric acid, together with the ring-A cleaved derivative **62**, from the oleoresin of *Abies balsamea*.[51] The friedolanostane (mariesane) derivatives garcihombronanes K **63** and L **64** have been found in the twigs of *Garcinia hombroniana*.[52] Omphalocarpoidone **65** is a constituent of the wood of *Tridesmostemon omphalocarpoides*.[53] Scillanostasides H - L are new glycosides from the bulbs of *Scilla scilloides*.[54] Scillanostasides I and J have the new genin **66**.

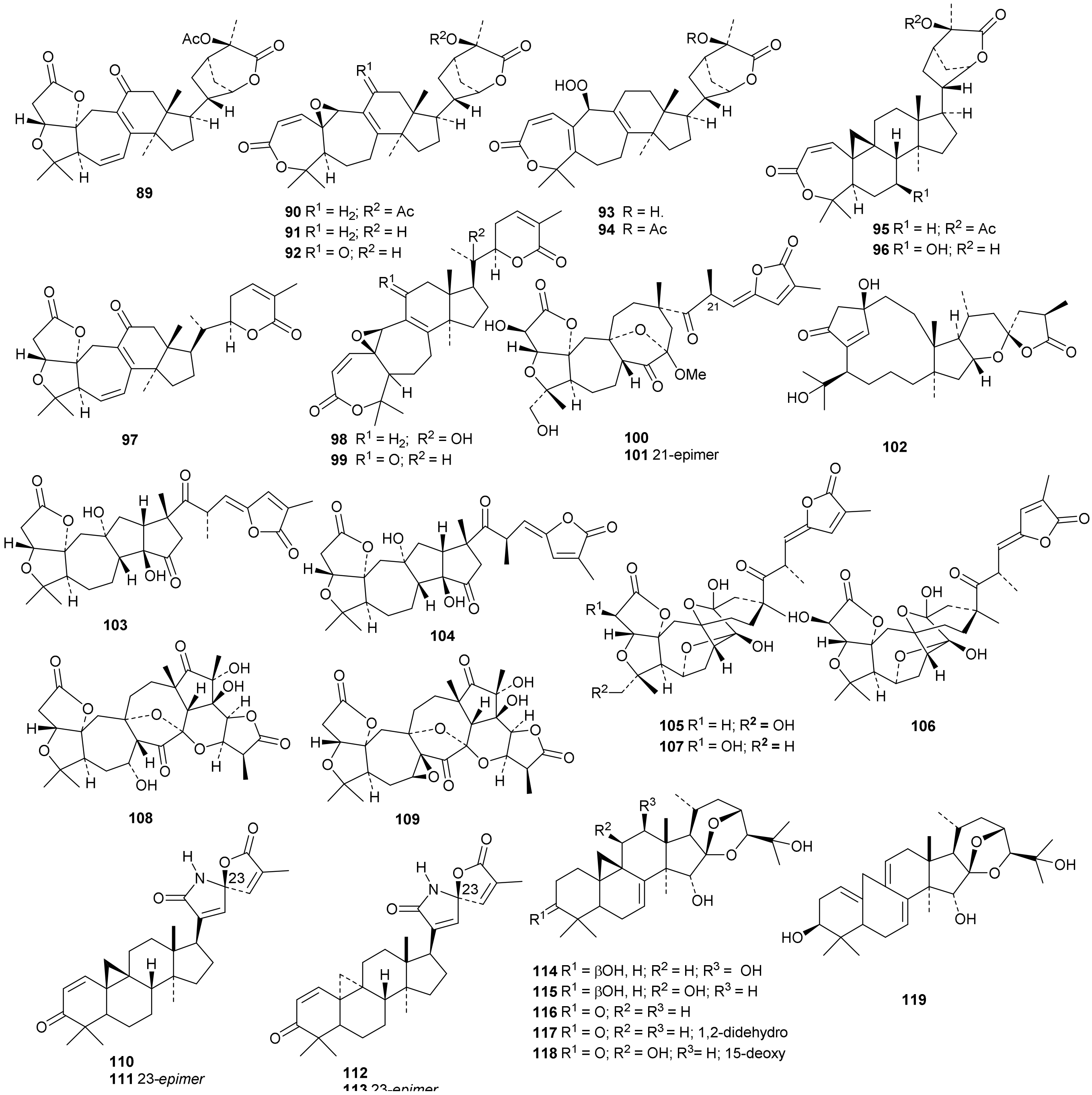
The 29-norlanostane derivatives 29-norpenasterone **67** and **68** have been isolated from a marine sponge of the genus *Penares* together with the lanostanes **69** - **72**.[55] The structure of the 29-nor compound **68** was confirmed by X-ray crystallographic analysis. Urabosides A and B and ulososide F are new glycosides from the marine sponge *Ectyoplasia ferox*.[56] Urabosides A and B have the new 30-norlanostane genins **73** and **74**, respectively. The genin **75** of ulososide F is known but its side chain stereochemistry has been revised. A glycosyl ester from *Artemisia absinthium* has the new genin **76**.[57]

Several new sea cucumber holostane glycosides have been isolated. Typicosides A_1, A_2, B_1, C_1 and C_2 are from *Actinocucumis typica*.[58] Typicoside A_1 has a known genin while the others have the new genins **77** (C_1) and **78** (A_2, B and C_2). Cladolosides B_1, B_2, C, C_1, C_2 and D from *Cladolabes schmeltzii* have the new genins **79** (B_2, C and D) and **80** (B_1 and C_1) while C_2 has a known genin.[59] Cucumariosides I_1, I_3 and I_4[60] and I_2[61] are from *Eupentacta fraudatrix*. Only cucumarioside I_4 has a new genin **81** with a pentanor side chain. Turquetoside A from *Staurocucumis turqueti*[62] and eleganoside A from *Gelsemium elegans*[63] have known genins.



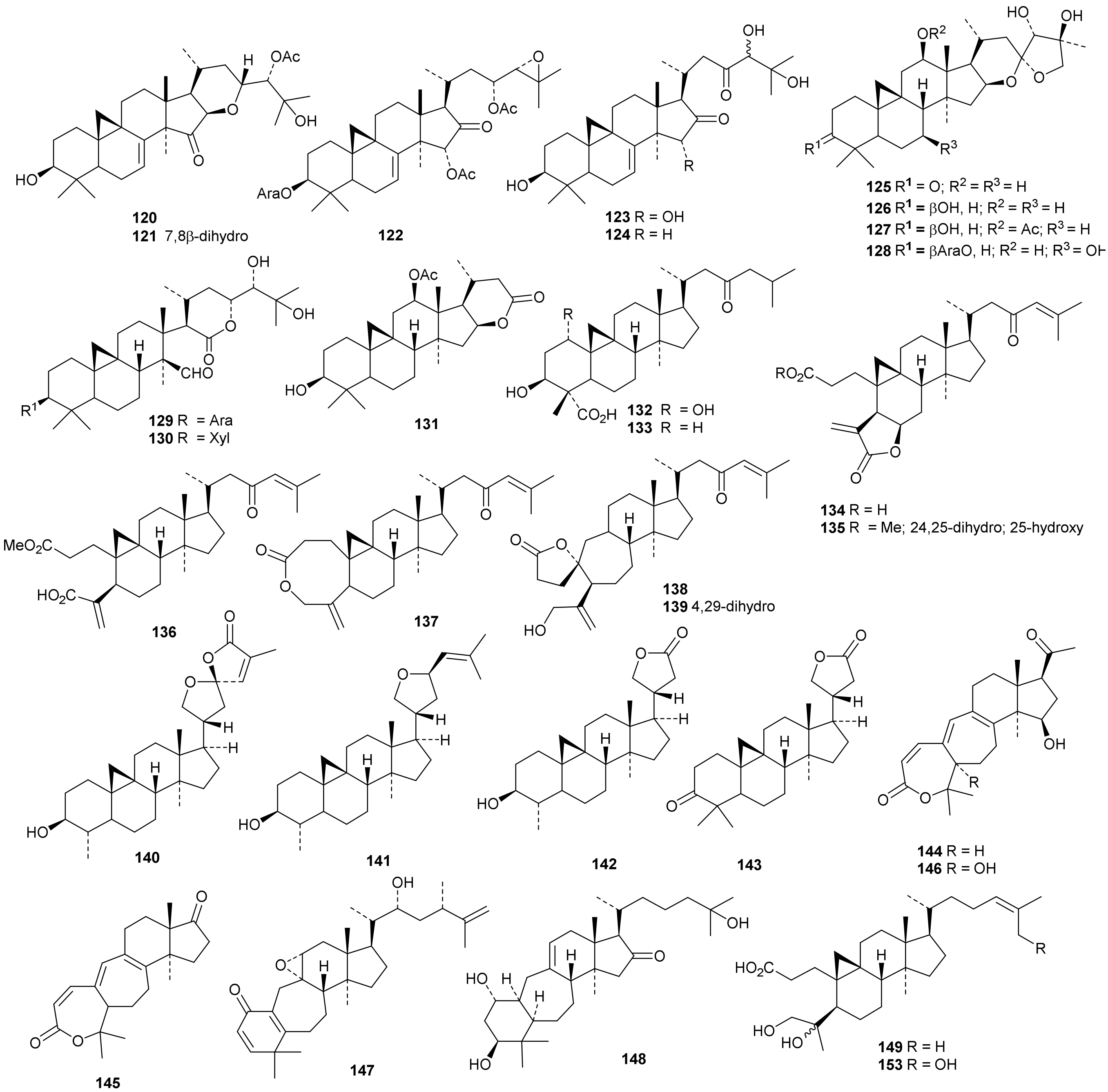
Several new skeletal types have been reported from *Schisandra* and related species. Lancolides A **82** - D **85**, from *Schisandra lancifolia*, are accompanied by preschisanartanin O **86**.[64] The structures of **82**, **83**, **85** and **86** were all confirmed by X-ray crystallographic analyses. The related schilancidilactones V **87** and W **88** are from the fruit of *Schisandra wilsoniana*.[65] Schinchinenins A **89** - H **96** and schinchinenlactones A **97** - C **99** have been reported from the leaves and stems of *Schisandra chinensis*.[66] The structure of schinchinenin A **89** was confirmed by X-ray crystallographic analysis. Further constituents from the stems of *Schisandra chinensis* include schisdilactones H **100** and I **101**.[67] Pseudolarenone **102**, from *Pseudolarix amabilis*, has an unusual bicyclo[8.2.1]tridecane core.[68] Other new *Schisandra* compounds include schisarisanlactones A **103** and B **104** from the fruit of *Schisandra arisanensis*[69] and schicagenins D **105** - F **107** and negleschidilactones A **108** and B **109** from the stems of *Schisandra neglecta.*[70]

Kleinhospitines A **110** -D **113**, cycloartanes with spiro-nitrogen containing side chains, have been isolated from *Kleinhovia hospita*.[71] The Chinese medicine Shengma (*Cimicifuga dahurica*) is a rich source of cimigenol derivatives and related cycloartanes **114 - 122**.[72] Only three of the new



saponins, heracleifolinosides A - F, from *Cimicifuga heracleifolia*, have new genins **123** (A and C) and **124**. (B).[73] The aerial parts of *Cimicifuga yunnanensis* produce an interesting range of metabolites which include cycloartanes yunnanterpenes A **125** -C **127** and F **128**, the cleaved cycloartanes 15,16-secocimiterpenes A **129** and B **130** and the tetranor-derivative cimilactone C **131**.[47] The structures of yunnanterpene A **125** and 15,16-secocimiterpene A **129** were confirmed by X-ray crystallographic analyses. Carinatins A **132** - H **139** are new compounds from the leaves and twigs of *Gardenia carinata*.[74] *Aphanamixis grandifolia* is the source of aphagrandinoids A **140** - D **143**.[75]

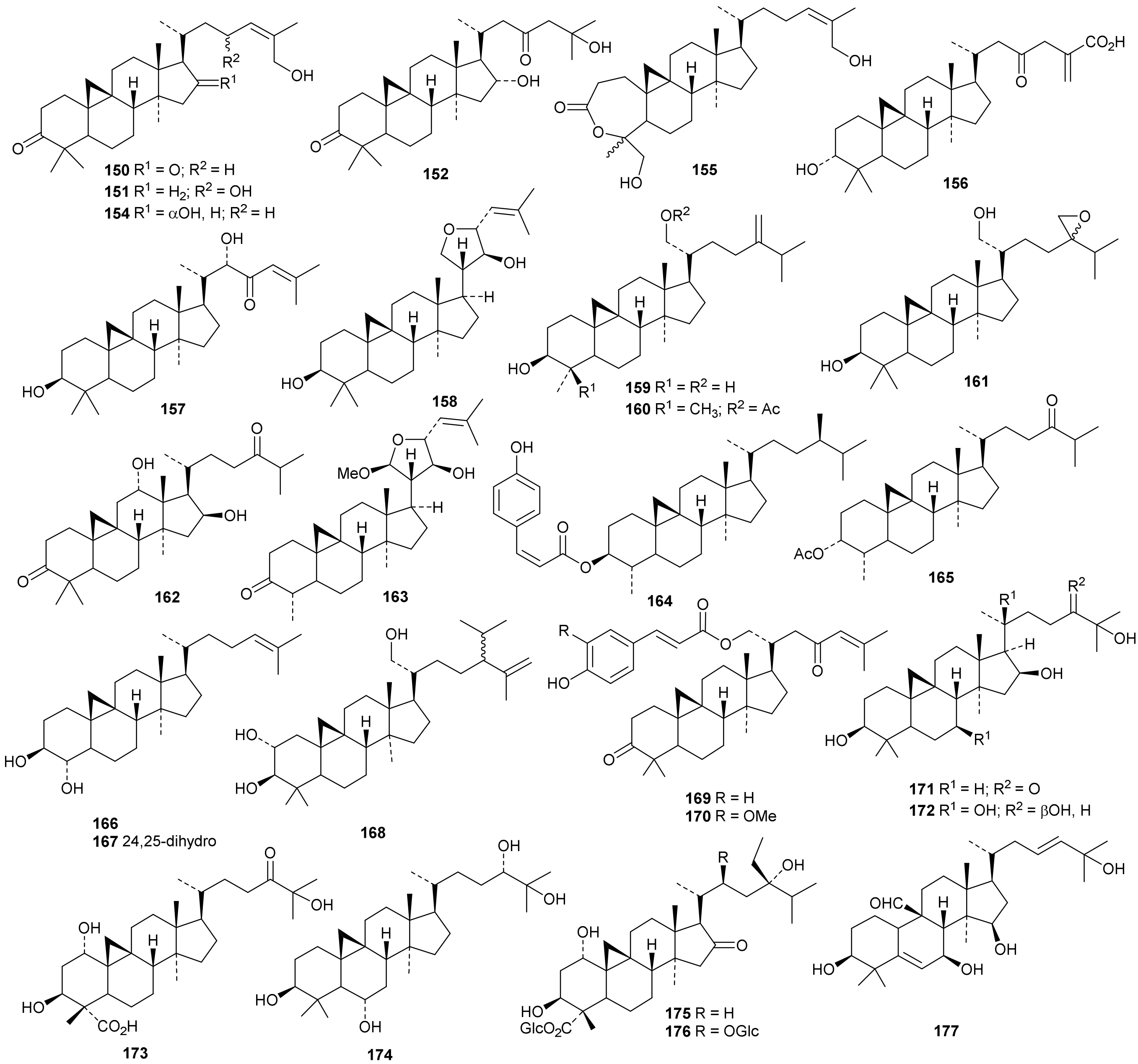
New 9,10-cleaved cycloartanes include cattienoids A **144** - C **146** from the mushroom *Tomophagus cattienensis*,[76] balansinone **147** from the leaves and twigs of *Casearia balansae*[77] and compound **148** from the goat willow *Salix caprea*.[78] Seven new cycloartane derivatives are reported from *Gardenia gummifera* resin with the trivial names gummiferartanes 1 **149** – 5 **153**, 8 **154** and 9 **155**.[79]



Other new cycloartanes reported this year include 3α-hydroxy-23-oxocycloart-25(27)-en-26-oic acid **156** from the oleoresin of *Abies balsamea,*[51] perviridisinols A **157** - C **159** from *Aglaia perviridis*,[80] compounds **160** and **161** from *Dasymaschalon dasymaschalum,*[81] 12α,16β-dihydroxycycloartane-3,24-dione **162** from *Curculigo orchioides* whose structure was confirmed by X-ray crystallographic analysis,[82] odoratanone A **163** from *Aglaia odorata*,[63] the *Z*-coumaroyl ester of dihydrocycloeucalenol **164** from *Nervilia fordii*,[83] the acetate **165** from the stems and leaves of *Quercus variabilis*,[84] the 28,29-dinorcycloartane **166** and its 24,25-dihydro-derivative **167** from *Marcetia latifolia*,[85] annonaretin A **168** from the leaves of *Annona reticulata*[86] and esters **169** and **170** from *Trichilia connaroides*.[87]

Tareciliosides N - S are cycloartane saponins from *Tarenna gracilipes*.[88] Tareciliosides N and S have the new genins **171** and **172**, respectively. The others have known genins. Further saponins from *Nervilia fordii* include nervisides D - H, of which only G and H have a new genin **173**.[89] Agroastragaloside V is a saponin with a new genin **174** from *Astragalus membranaceous*.[90] Cyclopassiflosides XII **175** and XIII **176**, from *Passiflora edulis*, also have new genins.[91] Cycloartane saponins with known genins include cycloasgenin C 3-*O*-β-D-xylopyranoside from *Astragalus mucidus*[92] and cyclolehmanoside C from *Astragalus lehmannianus*[93] and saponins from *Astragalus halicacabus*,[94] *Beesia calthaefolia*[95] and *Thalictrum fortunei*.[96]

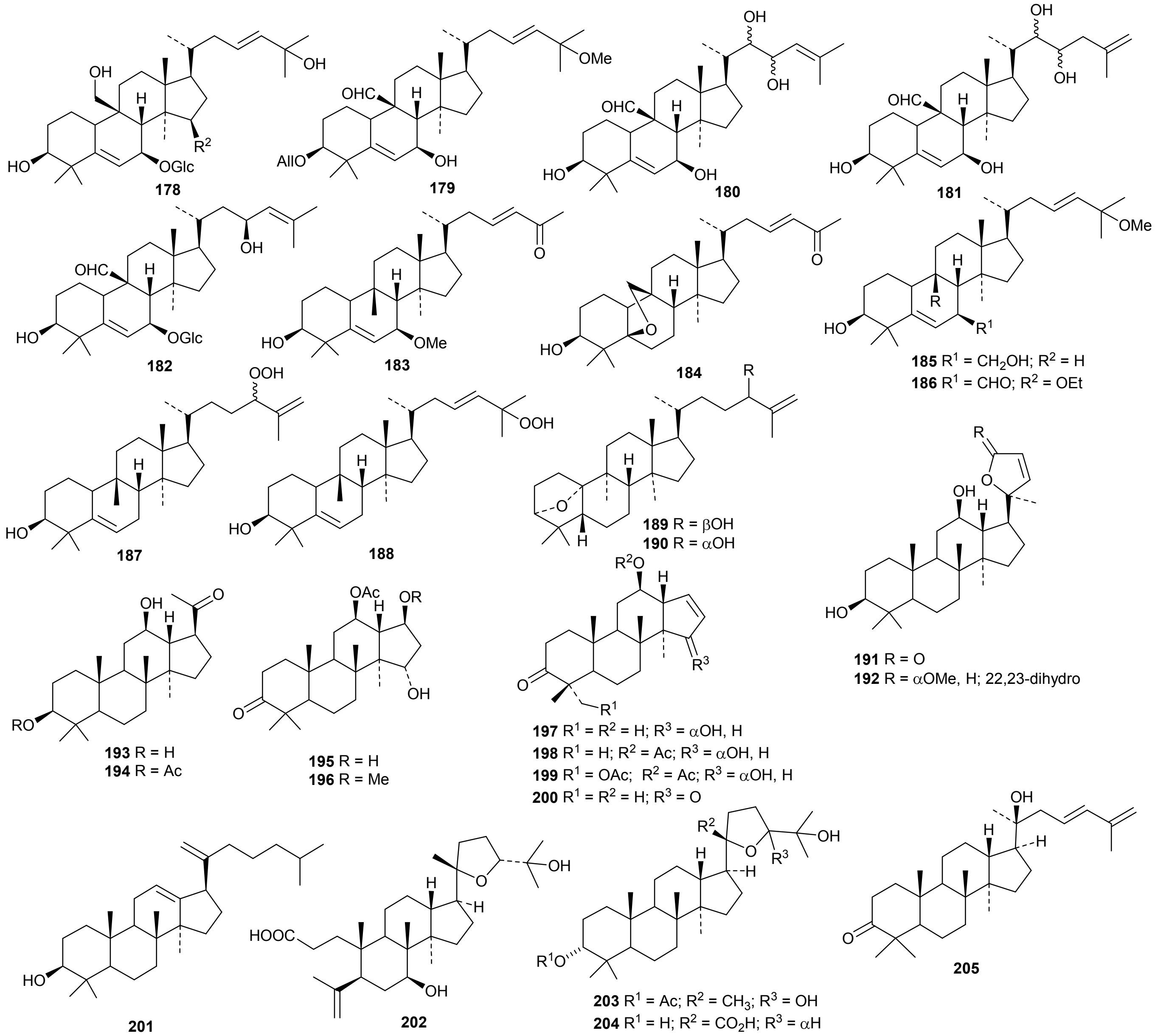
A review of the pharmacological activities of cucurbitane triterpenoids, particularly the anticancer activities of kuguacin J, from *Momordica charantia,* has been published.[97] New cucurbitane derivatives include compounds **177** - **182** from



Momordica charantia,[98] the 27-nor-derivatives **183** and **184** from the fruit of *Momordica charantia* var. *abbreviata* [99] and compounds **185** and **186** from the fruit pulp of *Momordica charantia*.[100] The hydroperoxides **187** and **188** have been reported from the seeds of watermelon *Citrullus lanatus*.[101] The stereochemistry at C-9 reported for 3,10-epoxides **189** and **190**, from the dried fruit of *Vitex negundo,* seems unusual.[102] Datiscosides I - O are cucurbitane glycosides with known genins from *Datisca glomerata*.[103]

4. The dammarane group

An interesting group of nordammaranes **191** - **197** has been isolated from *Viburnum mongolicum*.[104] Three nordammaranes **198** - **200** have also been obtained from *Dysoxylum hainanense*.[105] Other dammaranes include ixorene **201** from the leaves of *Ixora coccinea*,[106] the ring A-cleaved derivative **202** from the leaves of *Dysoxylum grande*,[107] 3-acetylaglinin C **203** from the leaves of *Aglaia odorata*,[108] mauritic acid **204** from the roots of *Mauritia flexuosa,*[109] altissimanin C **205** from *Ailanthus altissima*[110] and the 25,26,27-trinordammarane **206** from the dried fruit of *Forsythia koreana*.[111]

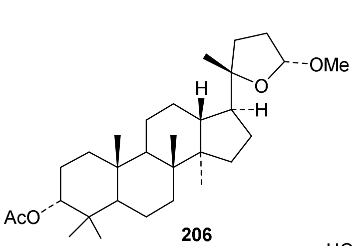


Hodulosides XI and XII are new saponins from the seeds of *Hovenia trichocarpa*.[112] They both have the new genin 20,26-epoxypseudojujubogenin **207**. Several new saponins, combretasides A - G, have been found in *Combretum inflatum*.[113] There are four new genins **208** (A and B), **209** (C and D), **210** (E and F) and **211** (G). Two new saponins from *Gymnostemma pentaphyllum* have the new genins **212** and **213**.[114] Hydrolysis of the total *Gymnostemma pentaphyllum* saponins afforded three new compounds, gypensapogenins E **214** - G **216**.[115] The structure of gypensapogenin E **214** was confirmed by X-ray crystallographic analysis.

The saponins of *Panax* species continue to attract attention. Sanchirhinoside D, with the new genin **217**, was obtained from *Panax notoginseng*.[116] Hydrolysis of the saponin from the leaves and stem of *Panax notoginseng* afforded notoginsengaglycone MPD **218**.[117] Hydrolysis of the total ginsenosides of *Panax ginseng* gave the new compound **219** whose structure was confirmed by X-ray crystallographic analysis.[118] Three ginsenosides Rh_{10}, Rg_{11} and 12-*O*-glucoginsenoside Rh_4 have been isolated from the heat-processed roots of *Panax ginseng*.[119] Only ginsenoside Rg_{11} has a new genin **220**. The arabinoside **221** was also isolated from the heat-processed roots of *Panax ginseng*.[120] The leaves and stems of *Panax quinquefolium* afforded pseudoginsenoside RT_6 **222** and its genin pseudoginsengenin R_1 **223**.[121] Heptdamoside A is a dammarane saponin from *Schefflera heptaphylla* with the new genin 3β,6α,20*S*,26-tetrahydroxy-24*E*-dammaren-12-one **224**.[122]

Dammarane saponins with known genins include chikusetsusaponins LM_3 – LM_6[123] and VIII[124] from *Panax japonicas*, ginsenjilinol[125] and 20*R*-ginsenoside Rf[126] from *Panax ginseng*, jujubosides I – IV from *Ziziphus jujuba*,[127] a different jujuboside I[128] and jujuboside A_2[129] from *Zizyphus jujuba* var. *spinosa*, sanchirhinosides A_1 – A_6 and B from *Panax notoginseng*,[130] quinquefolosides Ld and Le from *Panax quinquefolium*,[131] and unnamed saponins from *Panax notoginseng*.[116, 132]

The unusual structure **225** of aphanamgrandiol A, a rearranged tirucallane derivative from *Aphanamixis grandifolia*, has been confirmed by X-ray crystallographic analysis.[133] Two 19(10→9)-abeo derivatives, tiliacols A **226** and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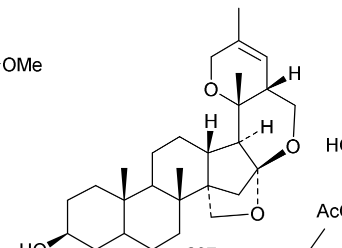
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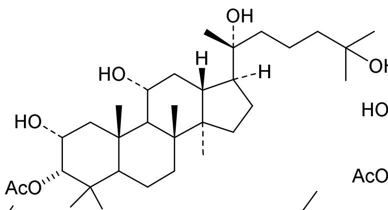
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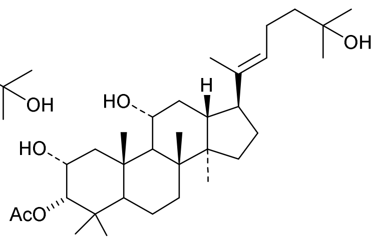
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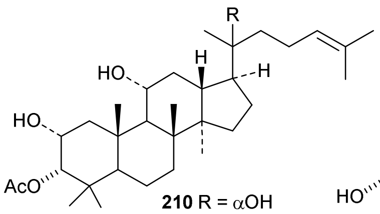
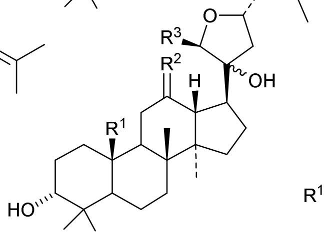
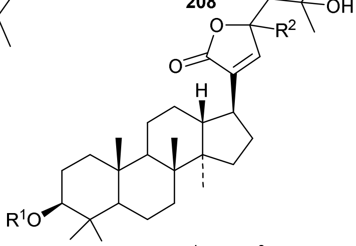
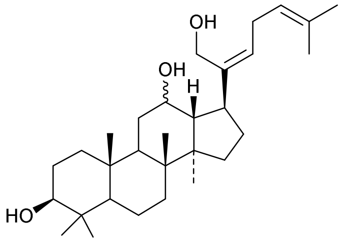

210 R = αOH
211 R = βOH


212 R^1 = CH_3; R^2 = O; R^3 = OMe
213 R^1 = CHO; R^2 = H_2; R^3 = H


214 R^1 = H; R^2 = αH
215 R^1 = H; R^2 = βH
216 R^1 = Ac; R^2 = αH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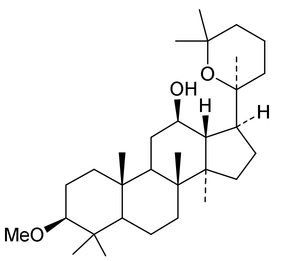
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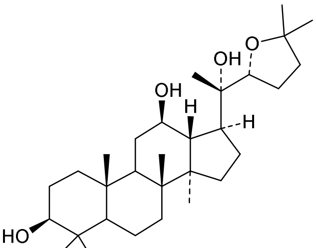
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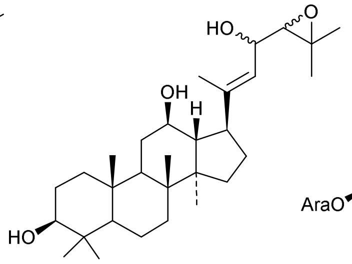
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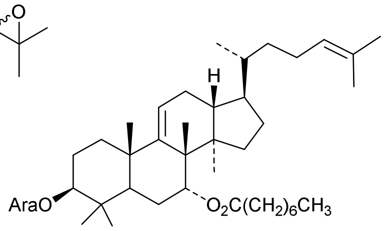
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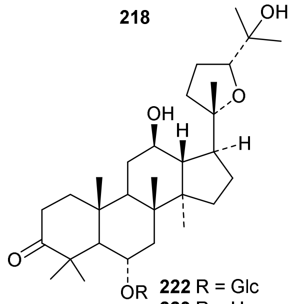
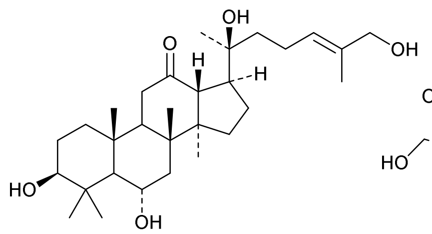

222 R = Glc
223 R = H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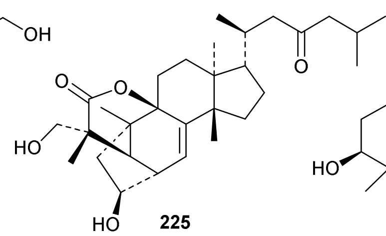
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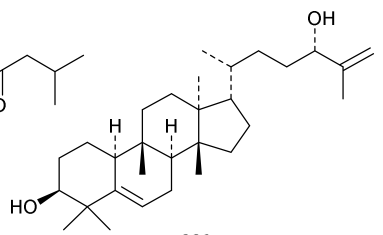
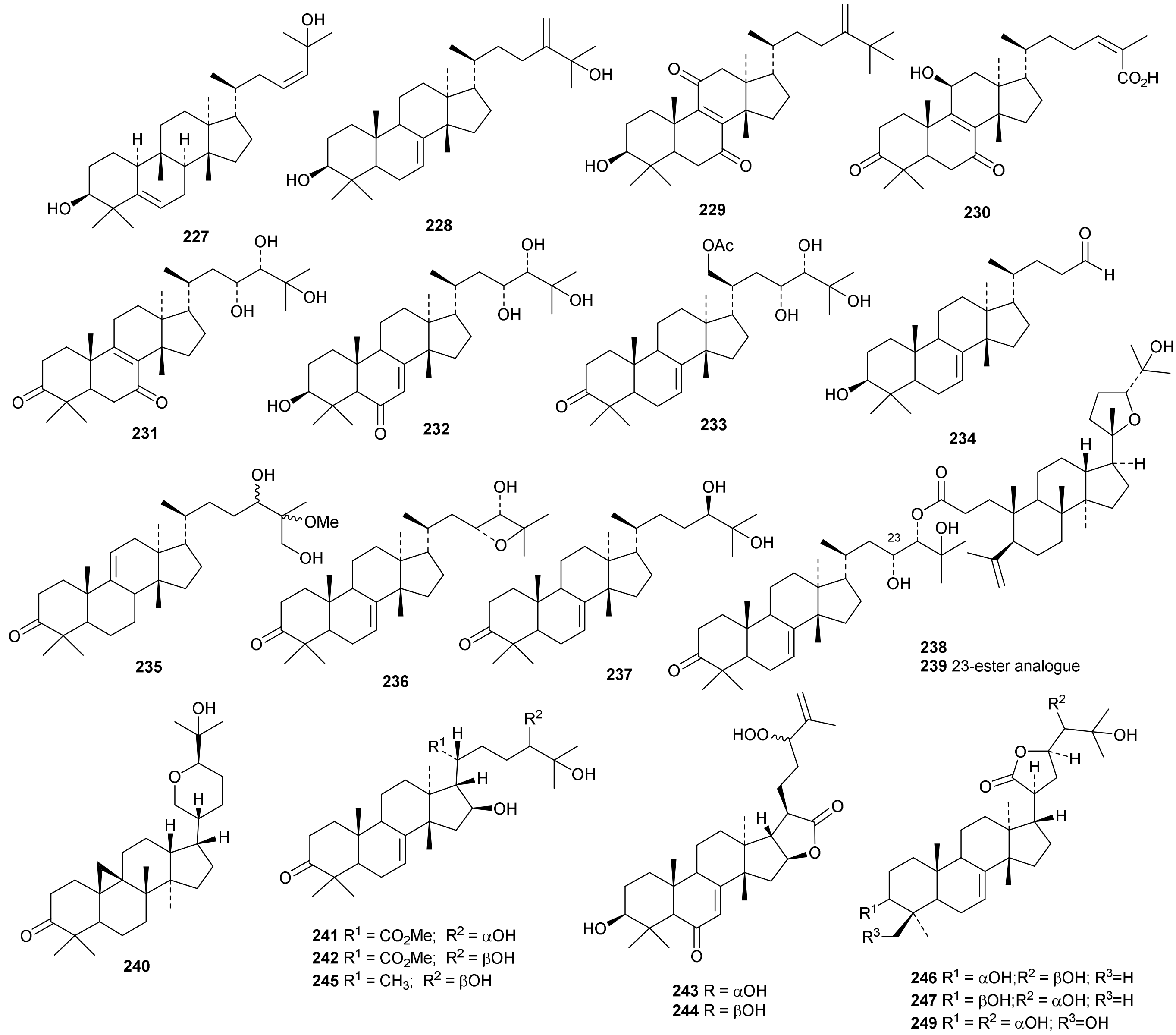
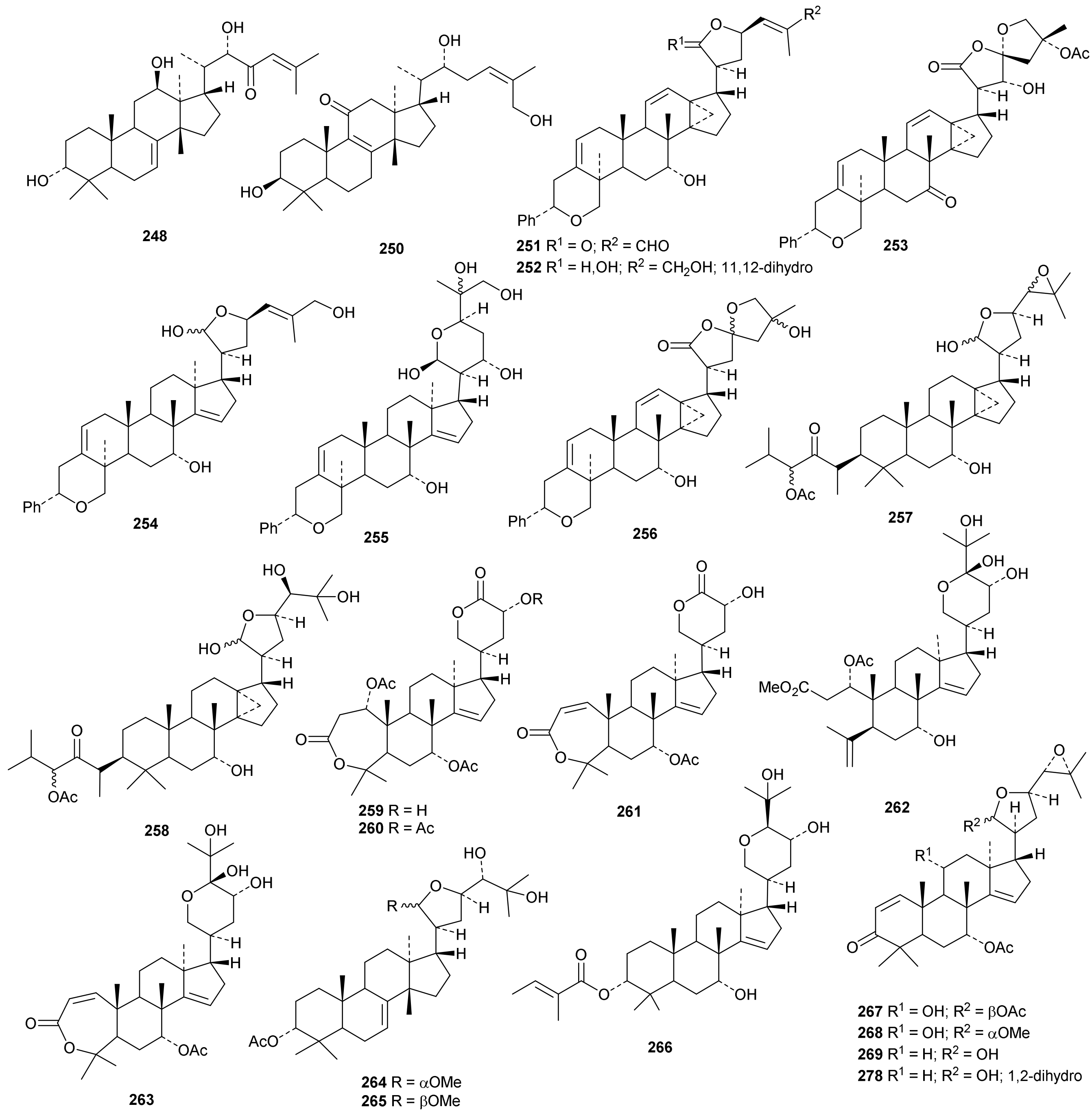

226

B **227**, have been reported from the semi-mangrove plant *Hibiscus tiliaceus*.[134] Aquilacallanes A **228** and B **229** are tirucallane derivatives from the leaves of *Aquilaria sinensis.*[135] Aquilacallane B **229** has an extra methyl group at C-25. Other new tirucallanes include **230** from resin of *Pistacia lentiscus*,[136] brumollisols A **231** - C **233** from the stems of *Brucea mollis*,[137] the trinor-derivative sikkimenoid F **234** from the aerial parts of *Euphorbia sikkimensis*[138] and compound **235** from the roots of *Salacia hainanensis*.[139] The bark of *Ailanthus altissima* (the "Tree of Heaven") is the source of the tirucallane derivatives altissimanins A **236**, B **237**, D **238** and E **239**.[110] Altissimanins D **238** and E **239** are 24- and 23-esters of the known tirucallane piscidinol A with the secodammarane shoreic acid. Hirtinone **240**, from *Trichilia hirta* is described as a cycloartane but is actually a 9,19-cycloeuphane derivative.[140] Further compounds from the stem of *Melia toosendan* include the euphanes meliasenins S **241** - W **245** and the tirucallane meliasenin X **246**.[141] The names meliasenins S and T have already been used. The 3,24-diepimer of meliasenin X, cochinchinoid K **247**, together with 3-epimesendanin S **248** have been reported from *Walsura cochinchinensis.*[142] The structure of cochinchinoid K **247** was confirmed by X-ray analysis. The related mesendanin M **249** has been found in *Melia azedarach*.[143] The euphane **250** is a metabolite of the endophytic fungus *Phomopsis chimonanthi* isolated from *Tamarix chinensis*.[144]



Dichapetalins N **251**, O **252** - R **255** and S **256** have been obtained from *Dichapetalum mombuttense*, *Dichapetalum zenkeri* and *Dichapetalum leucosia*, repectively.[145] Dysoxylumglabretols A **257** and B **258** were isolated from *Dysoxylum mollissimum* as mixtures of 21-epimers.[146] Dictamins A **259** - C **261** are trinorapotirucallanes from *Dictamnus dasycarpus*.[147] The structure of dictamin A **259** was confirmed by X-ray crystallographic analysis. The fruit of *Aphanamixis polystachya* is the source of the apotirucallanes polystanins A **262** and B **263** and the tirucallanes polystanins C **264** and D **265**.[148] 3-Tigloylsapelin D **266** is a further apotirucallane constituent of the fruit of *Melia azedarach*.[149]
The twigs of *Brucea javanica* proved to be a rich source of apotirucallanes, yielding fourteen new compounds, brujavanones A **267** - N **280**.[150] During this work the structure of bruceajavanin C was revised to its C-21 epimer **281**. Other



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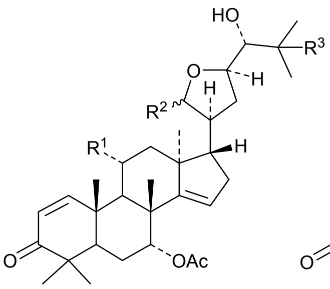
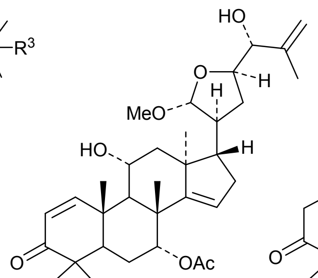
new compounds in this series include feroniellides C **282** - E **284** from *Feroniella lucida*,[151] lepidotrichilins A **285** and B **286** from *Trichilia lepidota*,[152] polystanin E **287** from the fruit of *Aphanamixis grandifolia,*[153] **288**, **289** and dihydrosapelin E acetate **290** from *Turraea pubescens*[154] and azadirahemiacetal **291** from *Azadirachta indica*.[155]

4.1 Tetranortriterpenoids

Interesting new tetranortriterpenoid skeletal types continue to appear. Thaixylomolin A **292** has a 6,7-cleaved skeleton while thaixylomolins B **293** and C **294** both incorporate a pyridine ring.[156] They are constituents of *Xylocarpus moluccensis*. The structure of harperforatin **295**, from *Harrisonia perforata*, was confirmed by X-ray crystallographic analysis.[157] It was accompanied by harperfolide **296**. New trijugin-related derivatives include cipatrijugins G **297** and H **298** from *Cipadessa cinerascens*,[158] compound **299**, also named cipatrijugin G, and also from *Cipadessa cinerascens*,[159] and trijugins I **300** and J **301** from *Trichilia connaroides*.[160]

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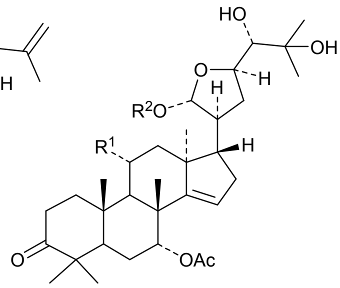
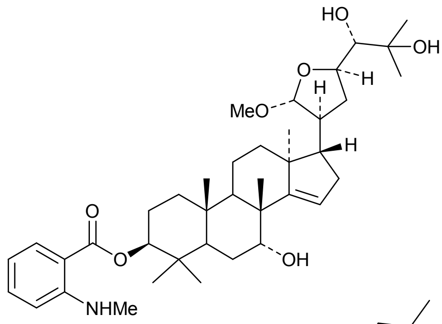


279 $R^1 = O_2C(CH_2)_4CH_3$; R^2 = Me
280 R^1 = H; R^2 = Et



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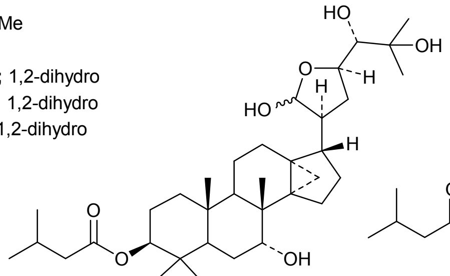
270 $R^1 = R^3$ = OH; R^2 = βOMe
271 $R^1 = R^3$ = OH; R^2 = βOH
272 R^1 = OH; R^2 = αOMe; R^3 = OMe
274 R^1 = H; R^2 = αOMe; R^3 = OH
275 R^1 = H; R^2 = αOMe; R^3 = OH; 1,2-dihydro
276 R^1 = H; R^2 = βOMe; R^3 = OH; 1,2-dihydro
277 R^1 = H; R^2 = αOH; R^3 = OH; 1,2-dihydro
281 $R^1 = R^3$ = OH; R^2 = αOMe



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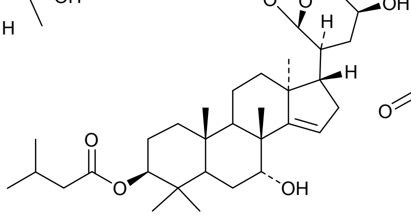

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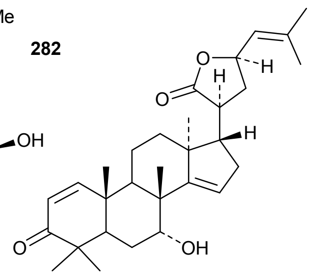
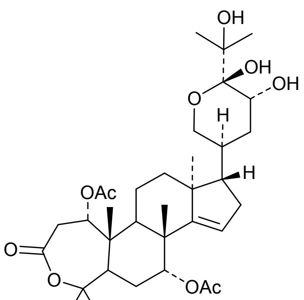


285
286 1,2-dihydro



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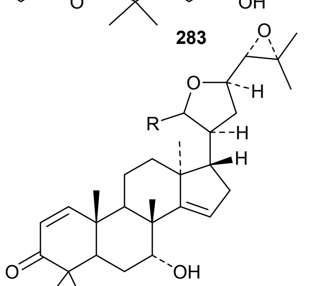
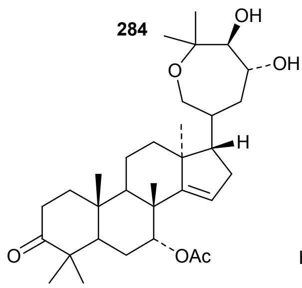


288 R = βOMe
289 R = αOMe; 1,2-dihydro



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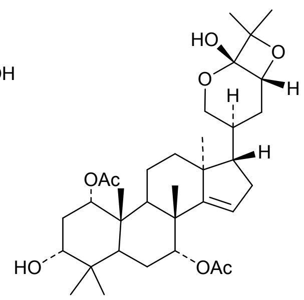

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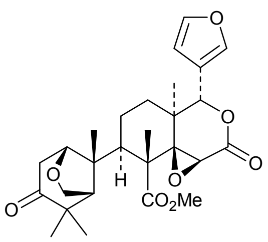

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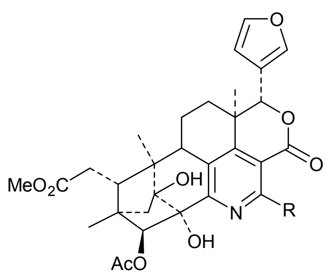
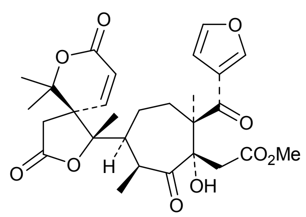


293 R = Me
294 R = ^{i}Pr



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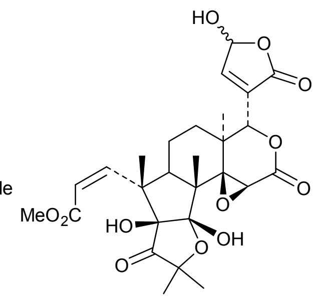

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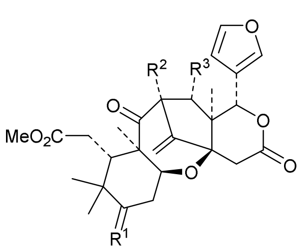
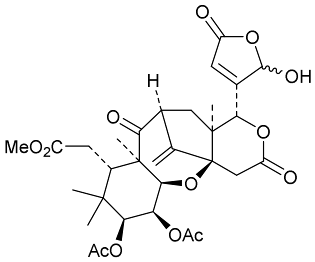
Cipaferens A **302** - D **305** are constituents of the leaves of *Cipadessa baccifera*.[161] Phyllanthoids A **306** and B **307** are two C,D-rearranged derivatives from *Phyllanthus cochinchinensis*.[162] The structure of phyllanthoid A **306** was confirmed by X-ray crystallographic analysis.

Ten limonoids, cochinchinoids A **308** - J **317** have been reported from *Walsura cochinchinensis*.[142] The structure of cochinchinoid A **308** was confirmed by X-ray analysis. Rubescins A **318** - C **320** are constituents of *Trichilia rubescens*.[163] The limonoids mesendanins K **321** and L **322** have been isolated from *Melia azedarach*.[143] Extraction of the kernels of *Azadirachta indica* afforded the new compounds **323**, **324** and azadiralactone **325**.[155]

X-Ray crystallographic analysis established the 21*S*-configuration of evorubodinin **326** (21-*O*-methyllimonexic acid) from *Euodia rutaecarpa* var. *bodinieri*.[164] The ring A cleaved limonoids aphanalides I **327** -M **331** have been isolated from



297 R^1 = O; R^2 = OH; R^3 = H
298 R^1 =βOAc, H; R^2 = H; R^3 = OH



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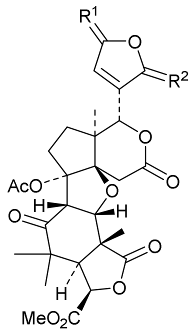
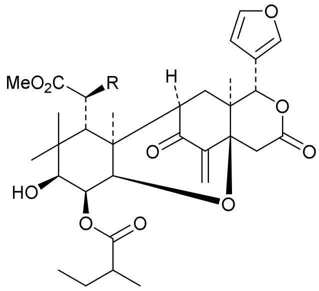
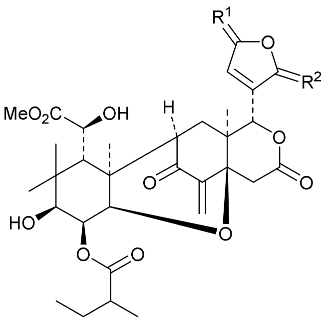


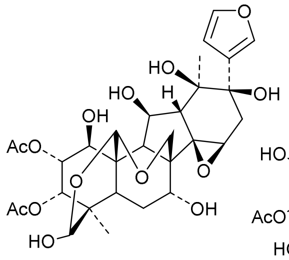
300 R^1 = O; R^2 = OH, H
301 R^1 = OMe, H; R^2 = O



302 R = H
303 R = OH



304 R^1 = OH, H; R^2 = O
305 R^1 = O; R^2 = OH, H



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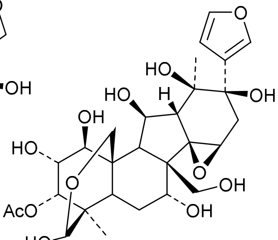

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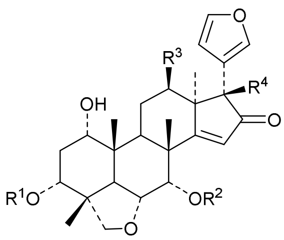
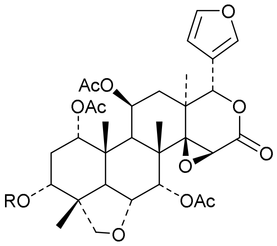
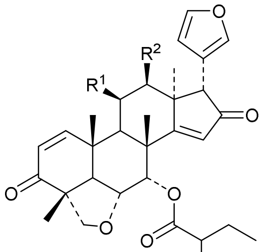


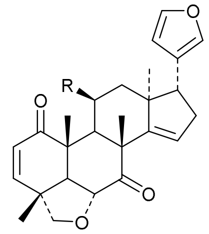
308 R^1 = R^2 = 2*R*-methylbutanoyl; R^3 = H; R^4 = OH
309 R^1 = R^2 = 2*S*-methylbutanoyl; R^3 = H; R^4 = OH
310 R^1 = R^2 = tigloyl; R^3 = R^4 = H
311 R^1 = tigloyl; R^2 = 2-methylbutanoyl; R^3 = OAc; R^4 = H



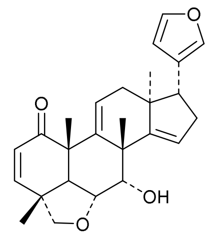
312 R = tigloyl
313 R = 2*R*-methylbutanoyl
314 R = 2*S*-mrthylbutanoyl



315 R^1 = OAc; R^2 = H
316 R^1 = H; R^2 = OAc
317 R^1 = H; R^2 = OAc; 1,2-dihydro



318 R = H; 5,6-didehydro
320 R = OAc



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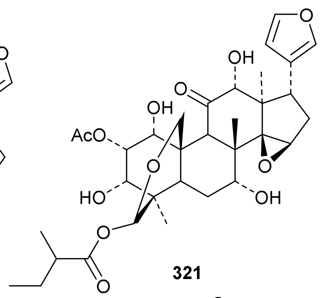

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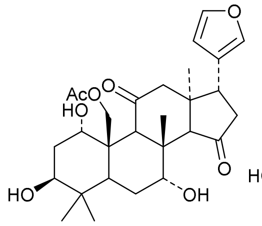

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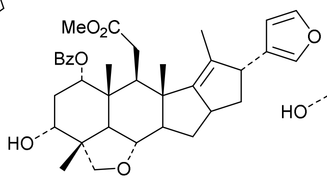

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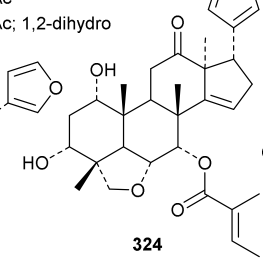

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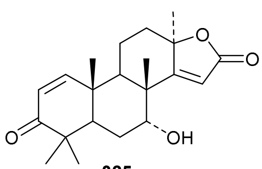

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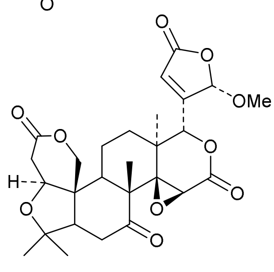

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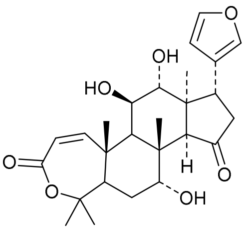
the fruit of *Aphanamixis grandifolia*.[153] The structure of aphanalide I **327** was confirmed by X-ray crystallographic analysis. Other compounds from this source include the rearranged aphagranols A **332** and B **333**[165] and aphanamolides C **334** and D **335**.[166] Toonins A **336** and B **337** are new constituents of the roots of *Toona sinensis*.[167] *Sandoricum koetjape* is the source the cleaved limonoids sanjecumins A **338** and B **339**.[168] Andirolide S **340** is a related ring-cleaved limonoid from the flowers of *Carapa guianensis* together with the intact limonoid andirolide Q **341** and the defuro-derivative andirlide R **342**.[169]

Various limonoids, turrapubins A **343** - K **353** have been obtained from *Turraea pubescens*.[154] More ring C-cleaved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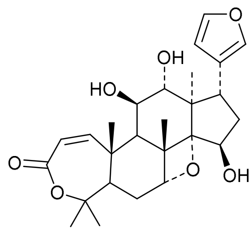
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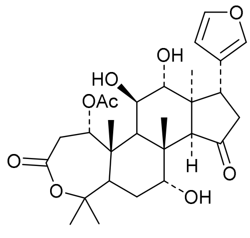
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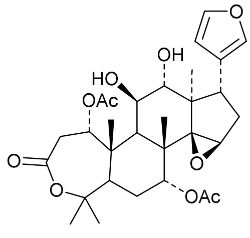
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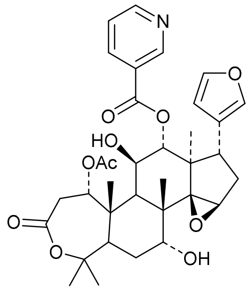
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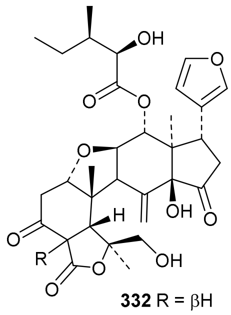
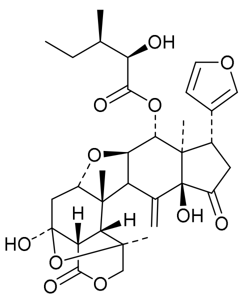

332 R = βH
333 R = αH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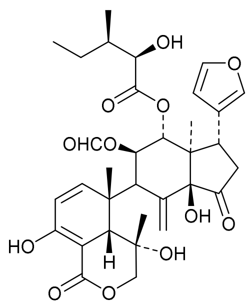
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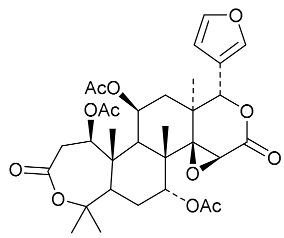
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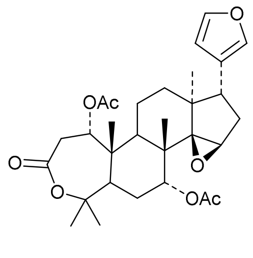
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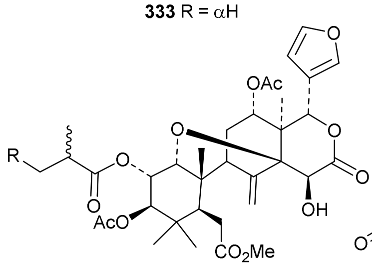
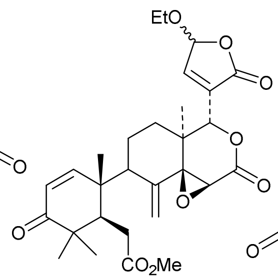

338 R = CH_3
339 R = H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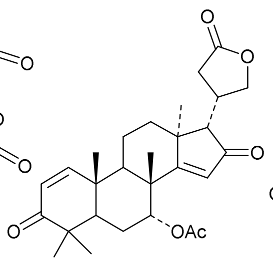
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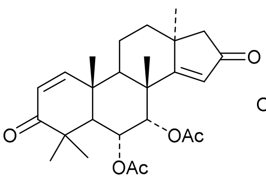
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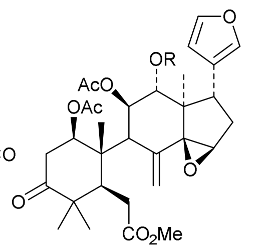
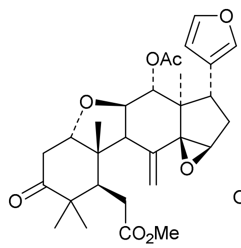

343 R = Ac
344 R = methypropanoyl
345 R = 2-methylbutanoyl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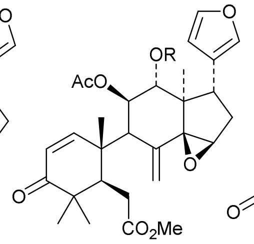
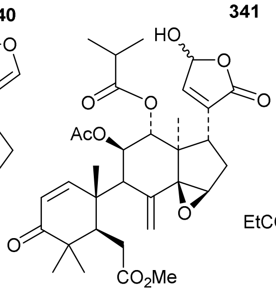

347 R = H
348 R = methypropanoyl
349 R = 2-methylbutanoyl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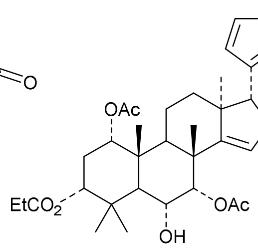
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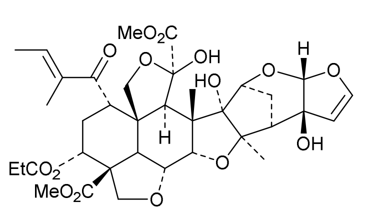
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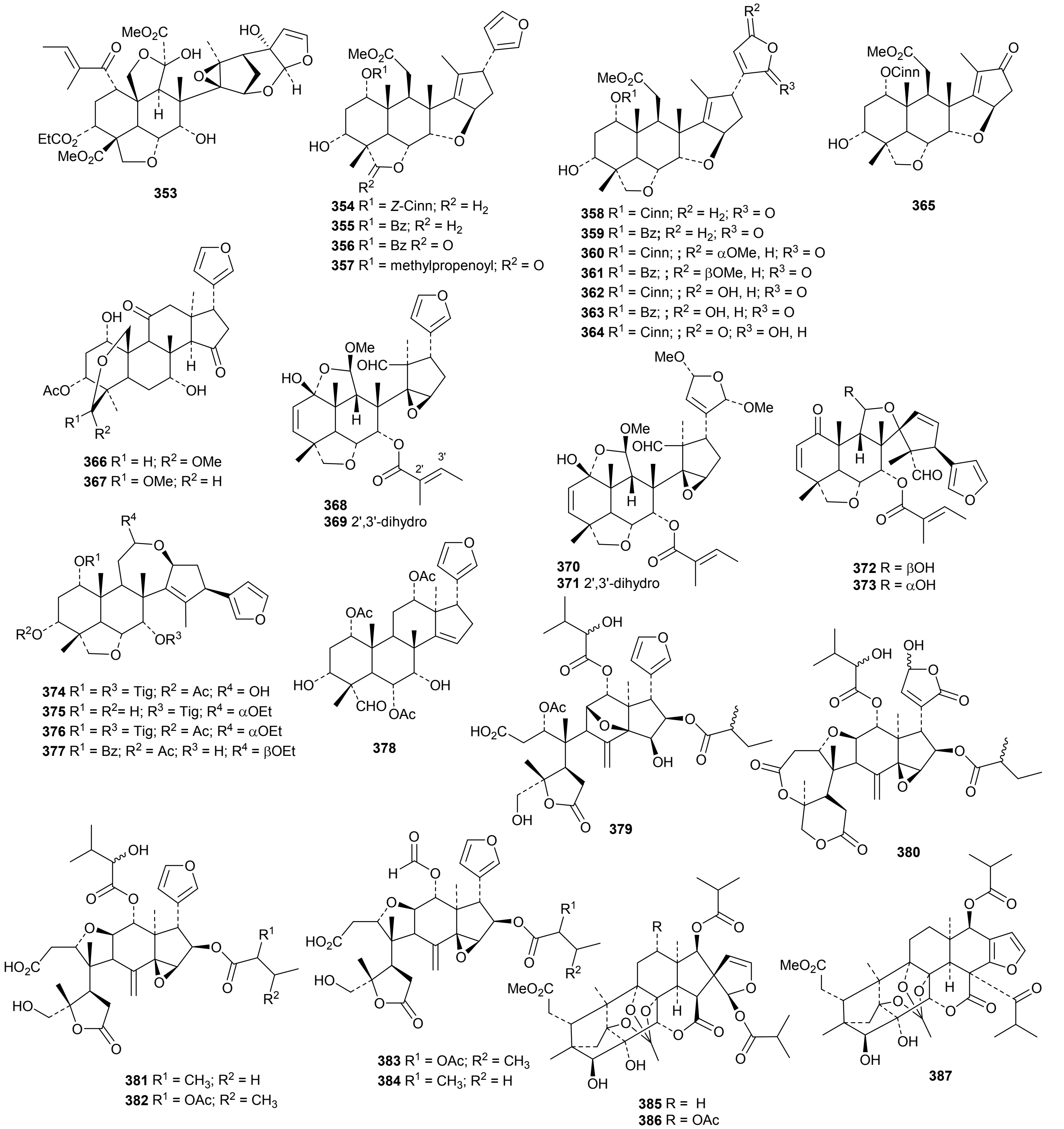
derivatives **354** - **365**, accompanied by the intact limonoids **366** and **367**, have been reported from the fruit of *Melia azedarach*.[170] The name ohchininolide has been assigned to **358**. Compound **355** has also been isolated from kernals of *Azadirachta indica*.[155] Other ring C-cleaved constituents include walsogynes B **368**- G **373** from *Walsura chrysogyne*[171] and toosendalinin **374**,[172] isolated as an epimeric mixture, and the nimbolinin derivatives **375** - **377**,[173] together with compound **378**, from the fruit of *Melia toosendan*. *Dysoxylum mollissimum* is the source of the AB-cleaved limonoids dysoxylumasins A **379** - F **384**.[174]

The phragmalin derivatives chukfuransins A **385** - D **388**,



353

354 R^1 = *Z*-Cinn; R^2 = H_2
355 R^1 = Bz; R^2 = H_2
356 R^1 = Bz R^2 = O
357 R^1 = methylpropenoyl; R^2 = O

358 R^1 = Cinn; R^2 = H_2; R^3 = O
359 R^1 = Bz; R^2 = H_2; R^3 = O
360 R^1 = Cinn; ; R^2 = αOMe, H; R^3 = O
361 R^1 = Bz; ; R^2 = βOMe, H; R^3 = O
362 R^1 = Cinn; ; R^2 = OH, H; R^3 = O
363 R^1 = Bz; ; R^2 = OH, H; R^3 = O
364 R^1 = Cinn; ; R^2 = O; R^3 = OH, H

365

366 R^1 = H; R^2 = OMe
367 R^1 = OMe; R^2 = H

368
369 2',3'-dihydro

370
371 2',3'-dihydro

372 R = βOH
373 R = αOH

374 R^1 = R^3 = Tig; R^2 = Ac; R^4 = OH
375 R^1 = R^2= H; R^3 = Tig; R^4 = αOEt
376 R^1 = R^3 = Tig; R^2 = Ac; R^4 = αOEt
377 R^1 = Bz; R^2 = Ac; R^3 = H; R^4 = βOEt

378

379

380

381 R^1 = CH_3; R^2 = H
382 R^1 = OAc; R^2 = CH_3

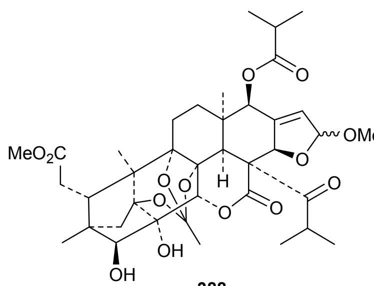
383 R^1 = OAc; R^2 = CH_3
384 R^1 = CH_3; R^2 = H

385 R = H
386 R = OAc

387

from *Chukrasia tabularis*,[175] and guianolides A **389** and B **390**, from *Carapa guianensis*,[176] all have novel features involving cyclisations of the furan ring. The structures of chukfuranisins A **385** and C **387** and of guianolide A **389** were all confirmed by X-ray crystallographic analyses. Andirolides T **391** - V **393** are further constituents of the flowers of *Carapa guianensis*.[169] Twenty new mexicanolide derivatives, trichinenlides A **394** - T **413**, have been isolated from *Trichilia sinensis*.[177] Secotrichagmalin A **414** and trichanolides A, B, C **415**, D **416** and E **417** have been reported from *Trichilia connaroides*.[160] Trichanolides A and B are identical to trichinenlides I **402** and D **397**, respectively. The structure of trichanolide A was confirmed by X-ray crystallographic analysis.

1,2-Cleaved derivatives include trichilitons G **418** and H **419** from *Trichilia connaroides*[87] and deacetyl-2α-methoxykhayanolide E **420** and kigelianolide **421** from *Kigelia africana*.[178] The structure of deacetyl-2α-methoxykhayanolide E **420** was confirmed by X-ray analysis.



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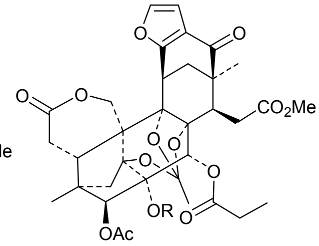
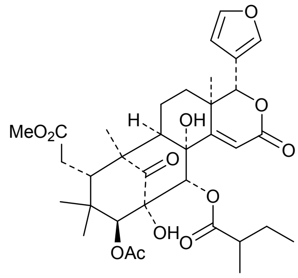


389 R = Ac
390 R = H



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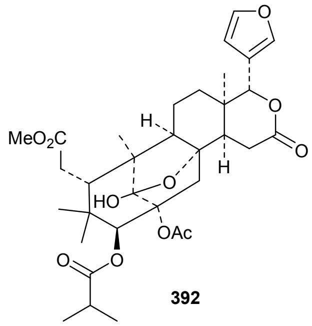

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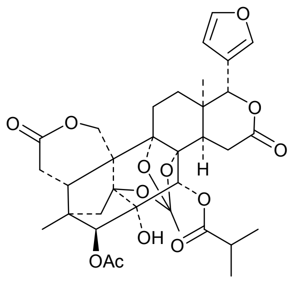

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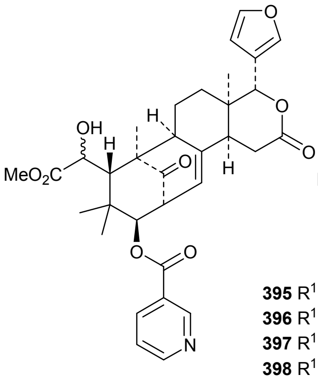

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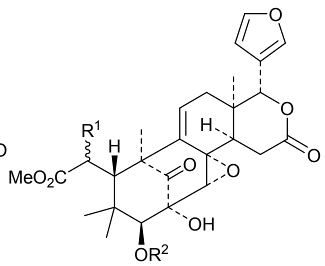
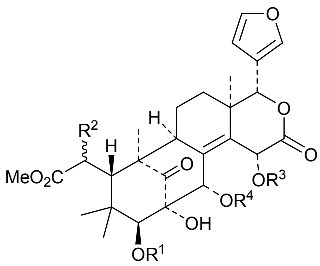
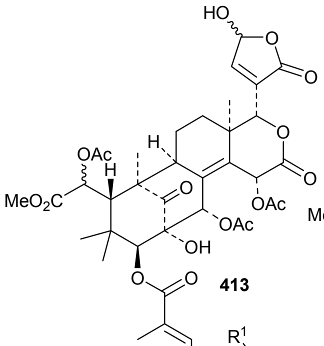


395 R^1 = 2*E*-butenoyl; R^2 = H
396 R^1 = 2*E*-butenoyl; R^2 = OH
397 R^1 = Tig; R^2 = H
398 R^1 = Tig; R^2 = OH
399 R^1 = Nic; R^2 = H; 9α,11-dihydro
400 R^1 = Nic; R^2 = OAc; 9α,11-dihydro
401 R^1 = 2*E*-butenoyl; R^2 = OH; 9α,11-dihydro
402 R^1 = Tig; R^2 = H; 9α,11α-epoxide
403 R^1 = 2*E*-butenoyl; R^2 = H; 9α,11α-epoxide
404 R^1 = Tig; R^2 = OH; 9α,11α-epoxide



405 R^1 = Tig; R^2 = H; R^3 = R^4 = Ac
406 R^1 = Tig; R^2 = OAc; R^3 = H; R^4 = Ac
407 R^1 = Tig; R^2 = R^3 = H; R^4 = Ac
408 R^1 = 2*E*-butenoyl; R^2 = OAc; R^3 = R^4 = Ac
409 R^1 = 2-methylbutanoyl; R^2 = OAc; R^3 = R^4 = Ac
410 R^1 = Tig; R^2 = R^3 = H; R^4 = 2-methylpropanoyl
411 R^1 = R^3 = Tig; R^2 = OAc; R^4 = Ac
412 R^1 = R^3 = Tig; R^2 = H; R^4 = Ac



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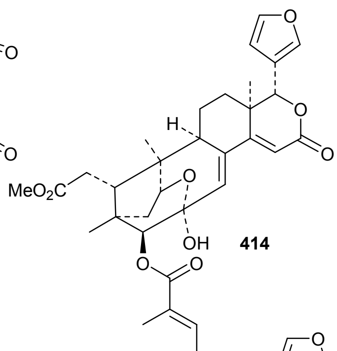

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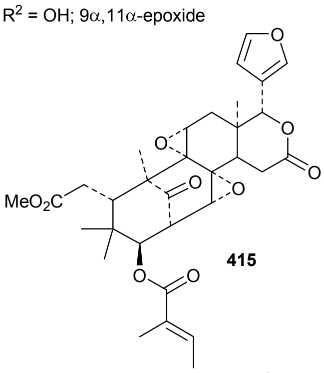
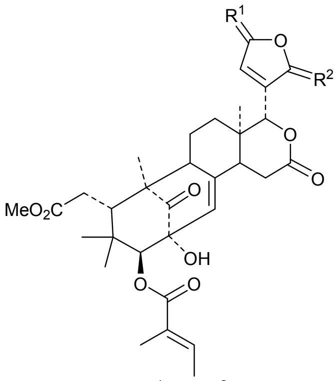
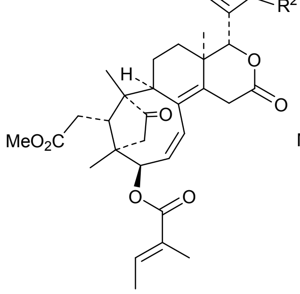


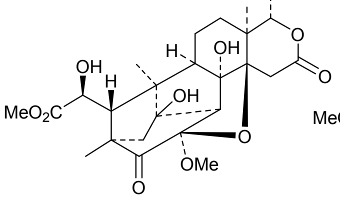
415



416 R^1 = O; R^2 = OH, H
417 R^1 = OH, H; R^2 = O



418 R^1 = OH, H; R^2 = O
419 R^1 = O; R^2 = OH, H



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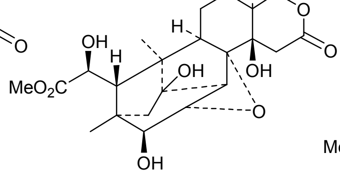

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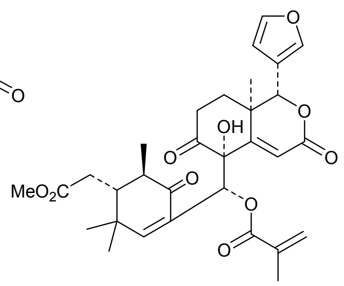

422

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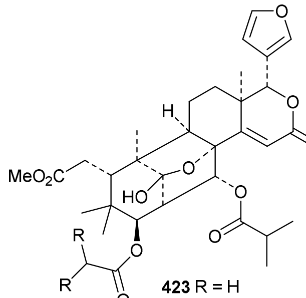
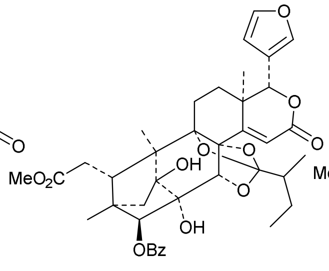
New derivatives from *Xylocarpus granatum* include xylomexicanins C **422** and D **423**,[179] xylogranins A **424** and B **425**.[180] and granatumins I **426**, J **427** and K **428** (accompanied by granatumin H which is a known compound).[181] Other related derivatives include 11α-hydroxyswietephragmin B **429** from *Swietenia mahogani* (accompanied by swietephragmins H and I which are known compounds),[182] chukvelutilide G **430** and chukrasin F **431** from *Chukrasia tabularis* var. *velutina*,[183] thaixylomolins D **432** - F **434** from *Xylocarpus moluccensis*[184] Khayaseneganins A **435** - H **442** are further constituents of *Khaya senegalensis*.[185]

4.2 Quassinoids

There is little activity in the quassinoid field. Bruceine M **443** has been isolated from the fruit of *Brucea javanica* [186] and altissinols A **444** and B **445** from *Ailanthus altissima*.[187] Altissinol B **445** is not a new compound and was identified as 13,18- didehydroexcelsin in 1980.[188]



423 R = H
424 R = CH_3



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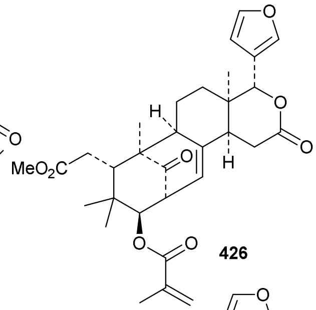

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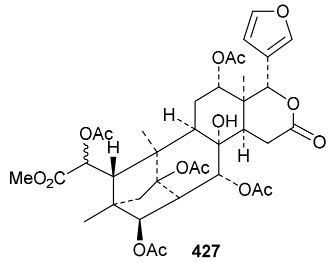

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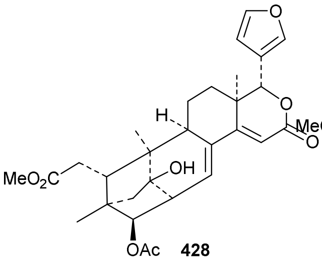

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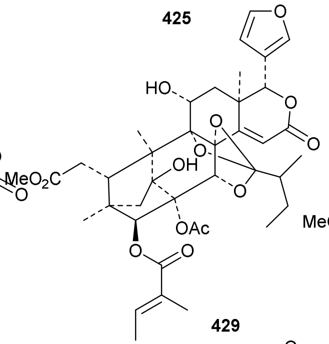

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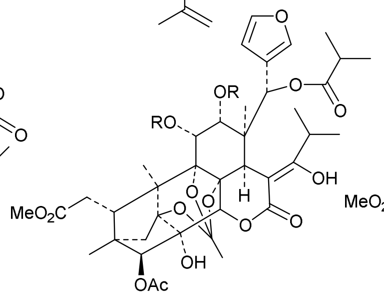

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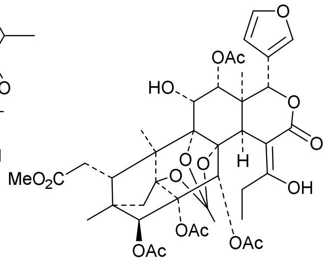

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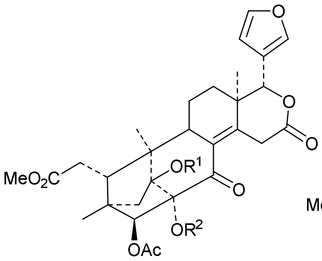
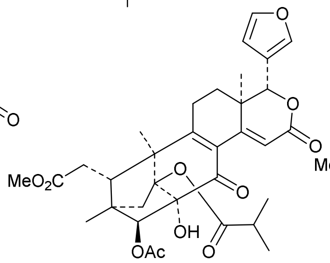


432 R^1 = Tig; R^2 = H
433 R^1 = H R^2 = 2-methylpropanoyl



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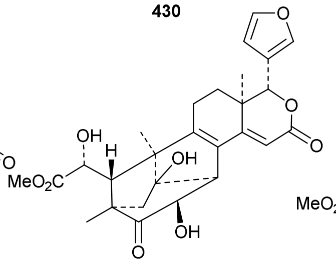

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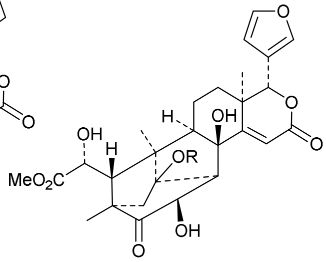
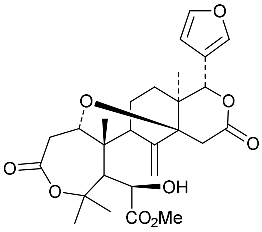


436 R = H
437 R = Ac



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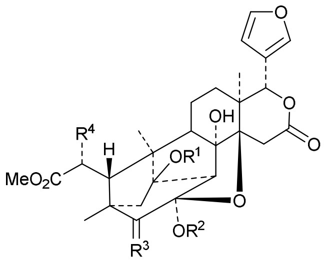
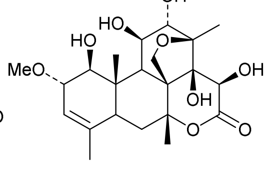


439 R^1 = R^2 = H; R^3 = βOH, H; R^4 = OH
440 R^1 = R^4 = H; R^2 = Me; R^3 = βOH, H
441 R^1 = H; R^2 = Me; R^3 = O; R^4 = OH
442 R^1 = Ac; R^2 = Me; R^3 = O; R^4 = OH



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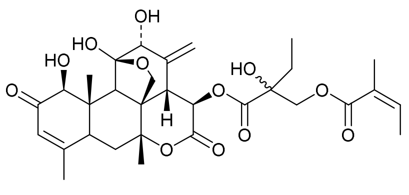

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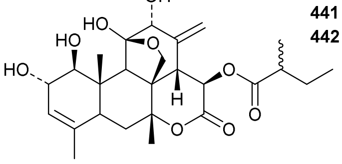

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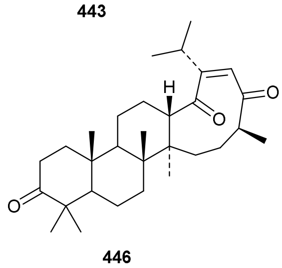

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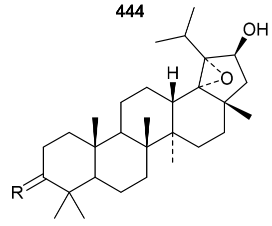


447 R = βOAc, H
448 R = O

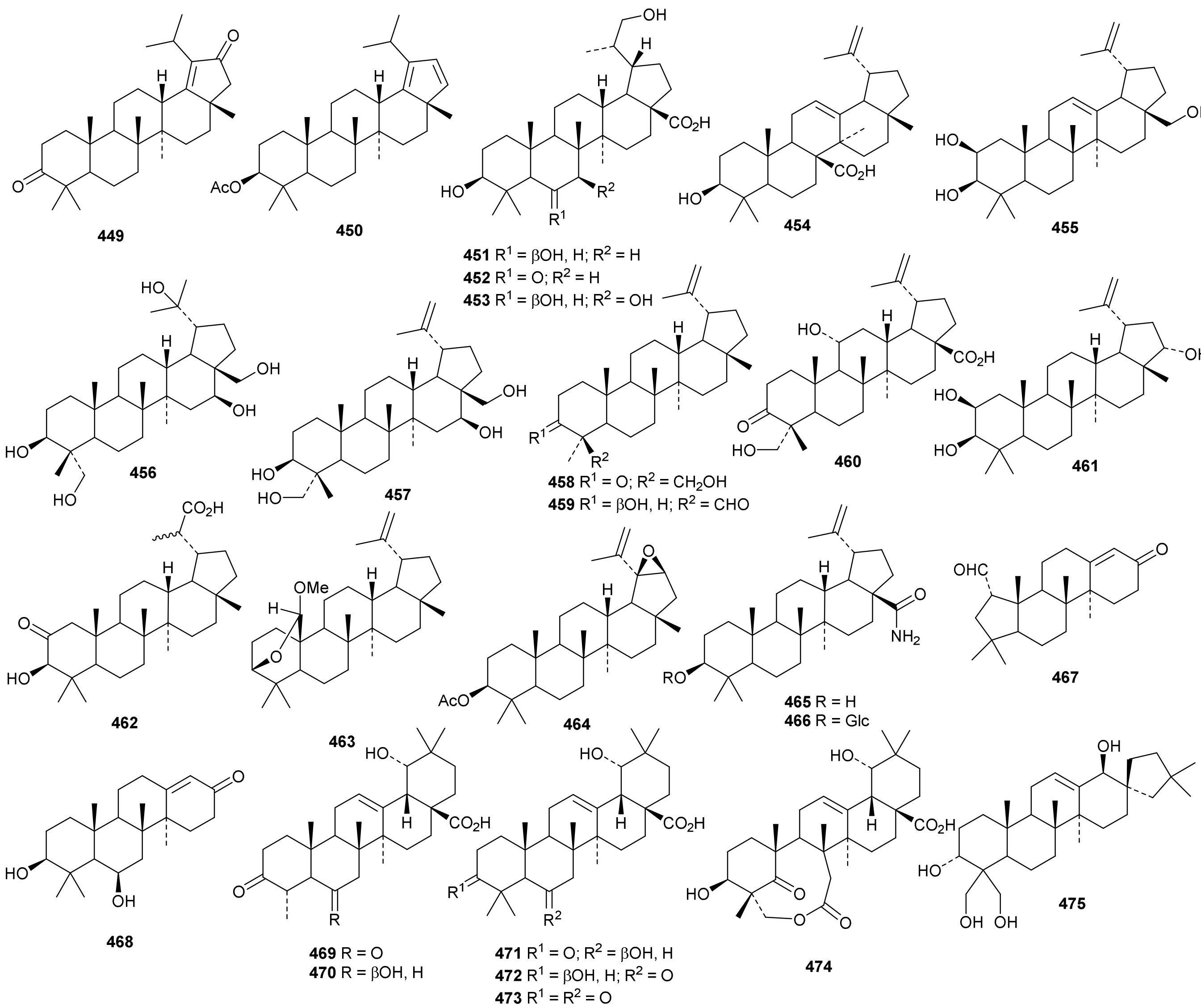
5. The lupane group

A review presenting spectral data of natural lupane triterpenoids has been published with a view to helping analysis of new structures.[189] The anti-HIV activity of betulinic acid and its derivatives have been covered in a short review.[190] Officinatrione **446**, with an unusual 17,18-secolupane skeleton, was isolated from *Taraxacum officinale* where it occurs with four intact lupanes **447** – **450**.[191] The structure of officinatrione **446** was confirmed by X-ray analysis. The structures of three compounds from *Saprosma merrillii* were originally assigned as ursane derivatives.[192] However it was later established that they were the lupane derivatives **451** – **453** by the X-ray analysis of **453**.[193] Moruslupenoic acid B **454**, from the stem bark of *Morus alba*, is 3β-hydroxy-12,20(29)-lupadien-26-oic acid where it co-occurs with the well-known 3β-hydroxy20(29)lupen-28-oic acid which has been named as moruslupenoic acid A.[45] Actinidin A **455**, from *Actinidia deliciosa*, has been identified as 12,20(29)-lupadiene-2β,3β,28-triol.[194] Other simple lupane derivatives include lupane-3β,16β,20,23,28-pentol **456**[195] and 20(29)-lupene-3β,16β,23,28-tetrol **457**[196] from *Gymnema sylvestre*, 24-hydroxy-20(29) lupen-3-one **458** and 3β-hydroxy-20(29)-lupen-24-al **459** from *Ilex cornuta*, 11α,23-dihydroxy-3-oxo-20(29)-lupen-28-oic acid **460** from *Acanthopanax trifoliatus*,[197] 20(29) lupene-2β,3β,22α-triol **461** and 3β-hydroxy-2-oxo-29-lupanoic acid **462** from the roots of *Salacia hainanensis*,[139] the acetal **463** from *Siphonodon celastrineus*,[198] the 19,21-epoxide **464** from *Abelmoscus esculentus*[199] and the decanoyl ester of lupeol from *Cadaba farinosa*.[200]

Betulinic amide **465** and its 3-*O*-β-D-glucopyranoside **466** have been isolated from *Rhododendron lepidotum*.[201] New lupane saponins with known genins include the 28-*O*-β-D-glucopyranosyl ester of platanic acid from *Tetracera scandens*,[202] lonimacranthoside A_1 from *Lonicera macranthoides*[203] and ryobusaponins E – G from *Clethra barbinervis*[204] and unnamed saponins from *Lonicera macranthoides*[205] and *Pulsatilla chinensis*.[206]

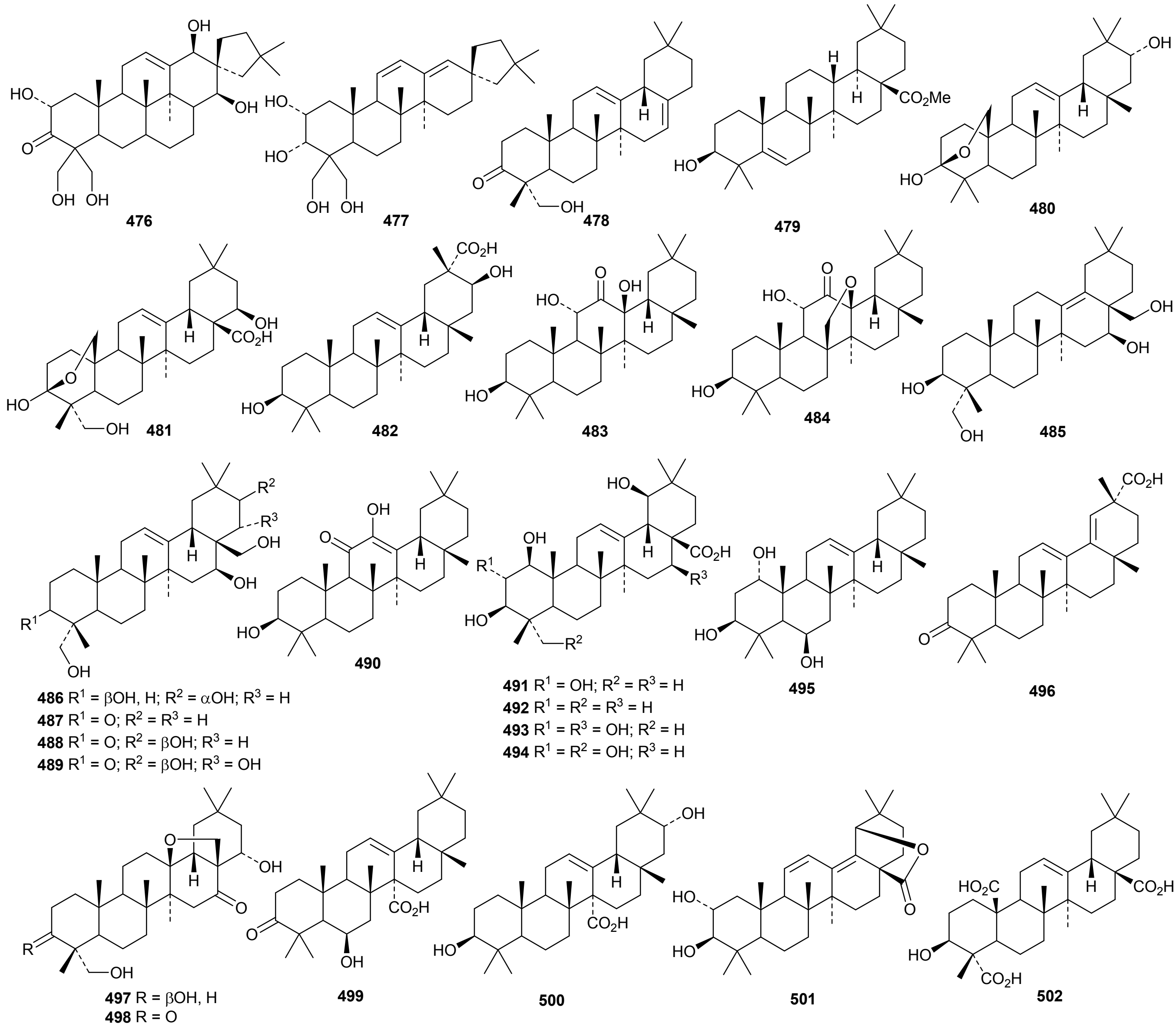
6. The oleanane group

Teydealdehyde **467**, from *Nepeta teydea*,[207] has a contracted ring A and lacks ring E and the related laevigatone A **468** has been found in *Uncaria laevigata* where it occurs with the 24-

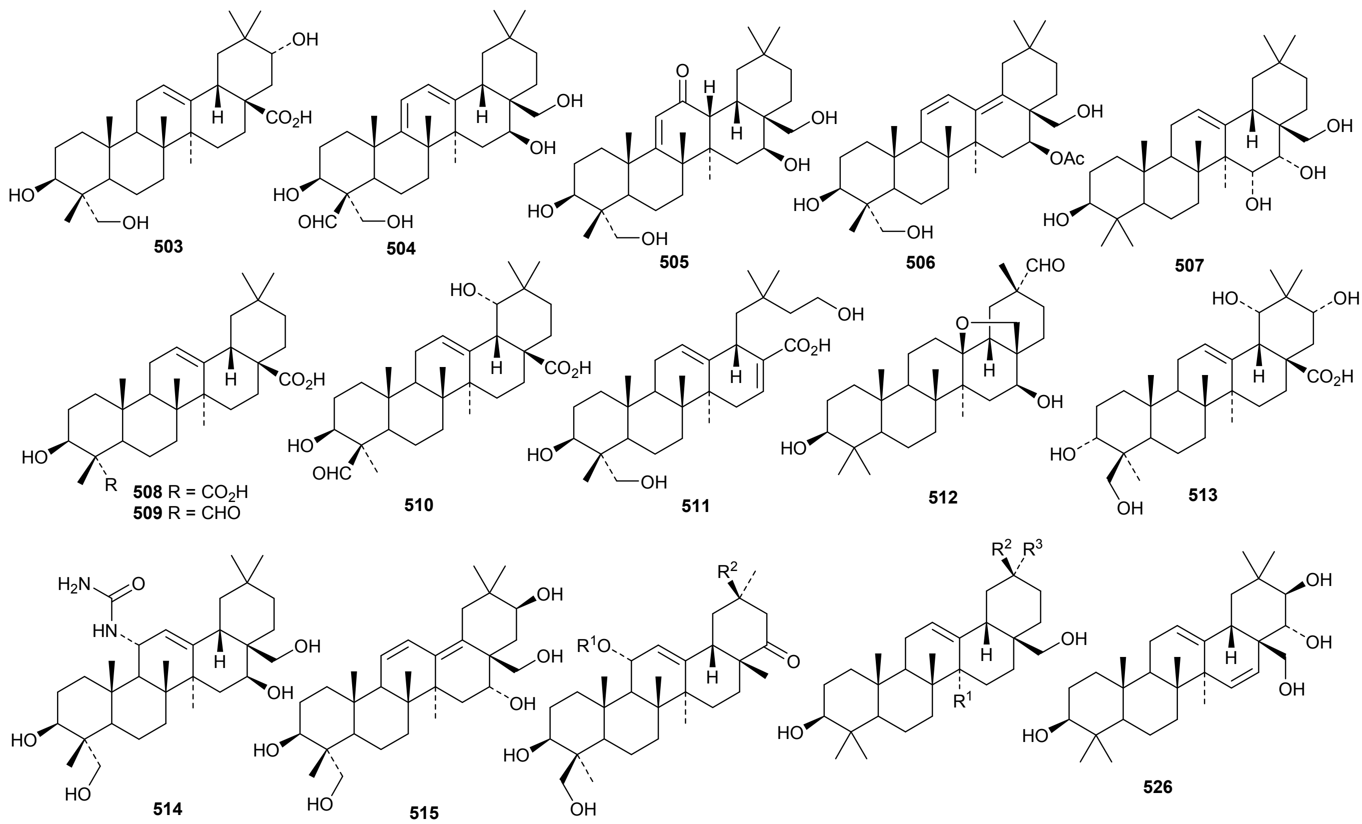


noroleananes **469** and **470** and the intact oleanane derivatives **471** – **473**.[208] The oleanane **471** has also been isolated from*Uncaria sessilifructus* and named as uncarilic acid together with the 5,6-seco derivative secouncarilic acid **474**.[209] The19(18→17)-abeo-28-noroleanane derivatives stewartiisins A **475** – C **477** have been isolated from *Phlomis stewartii*.[210] Sambucasan A **478** is a 28-nor-12,16-oleanadiene from *Sambucus williamsii*.[211] Alstoprenyol **479**, from *Alstonia scholaris*, has been reported to have the unusual 18α-configuration.[212] Xyloketal **480** is a hemiacetal derivative from *Cassine xylocarpa*[213] and a related hemiacetal **481** has been found in *Lantana montevidensis*.[214] 3β,21β-Dihydroxy-12-oleanen-29-oic acid **482**, from *Maytenus royleanus*, has been named ficusonic acid.[215] Japanese fermented tea (*Camellia sinsensis* leaves) is the source of two oleanan-12-one derivatives **483** and **484**.[216] Other new simple oleanane derivatives include 13(18)-oleanene-3β,16β,23,28-tetrol **485** and four related 12-oleanene derivatives **486** – **489** from *Gymnema sylvestre*,[196] 3β,12-dihydroxy-12-oleanen-11-one **490** from *Siphonodon celastrineus*,[198] 1β,2α,3β,19β-tetrahydroxy-12-oleanen-28-oic acid **491** and the related compounds **492** – **494** from *Euphorbia sieboldiana*,[217] 12-oleanene-1α,3β,6β-triol **495** from *Vernicia fordia*,[218] 3-oxo-12,18-oleanadien-29-oic acid **496** from *Limnophila indica*,[219] the 13,28-epoxides **497** and **498** from *Lysimachia parvifolia*,[220] the 12-oleanen-27-oic acids **499** and **500** from *Chrysosplenium carnosum*[221] and 2α,3β-dihydroxy-11,13(18)-oleanadien-28,19β-olide **501** from *Rhaphiolepis indica* var. *tashiroi*.[222]

Celosins I and II, from *Celosia argentea*, are saponins with the new genin 3β-hydroxy-12-oleanene-23,25,28-trioic acid **502**.[223] Other oleanane saponins with new genins include



clematangoside B from *Clematis tangutica* with 3β,21α,23-trihydroxy-12-oleanen-28-oic acid **503**,[224] clinoposapanins A – C from *Clinopodium chinense* with the genins **504** – **506**, respectively,[225] gordonsaponins B and E from *Gordonia kwangensis* with the genin 12-oleanene-3β,15α,16α,28-tetrol **507**,[226] heptoleosides A and B from *Schefflera heptaphylla* with the genins **508** and **509** respectively,[122] ilexpublesnins L and M from *Ilex pubescens* with 3β,19α-hydroxy-12-oleanene-24,28-dioic acid **510**,[227] pittangretoside I from *Pittosporum angustifolium* with the 17,22-seco genin **511**,[228] psychotrianoside B from a *Psychotria* sp. with 13β,28-epoxy-3β,16β-dihydroxy-12-oleanen-29-al **512**,[229] ryobunin C from *Clethra barbinervis* with 3α,19α,21α,24-tetrahydroxy-12-oleanen-28-oic acid **513**,[230] saikosaponin w and 21β-hydroxysaikosaponin b_2 from *Bupleurum chinense* with the genins **514** and **515** respectively,[231] sarosiensins I – IV, VI and VII from *Trifolium medium* with the genins **516** – **520**,[232] saponins from *Genista ulicina* with the genins **521** – **525**,[233] and saponins from *Xanthoceras sorbifolia* with the genin 12,15-oleanadiene-3β,21β,22α,28-tetrol **526**.[234]



516 R^1 = H; R^2 = CO_2H
517 R^1 = H; R^2 = CH_2OH
518 R^1 = Me; R^2 = CH_2OH
519 R^1 = H; R^2 = CH_3
520 R^1 = Me; R^2 = CH_3

521 R^1 = R^2 = CH_2OH; R^3 = CH_3
522 R^1 = R^3 = CH_2OH; R^2 = CH_3
523 R^1 =CO_2H; R^2 = CH_3; R^3 = CH_2OH
524 R^1 = CH_2OH; R^2 = CH_3; R^3 = CO_2H
525 R^1 = H; R^2 = CH_3; R^3 = CH_2OH

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

Table 1

Trivial name	Plant species	Reference
2”- and 6”-*O*-acetylrandianins	*Nematostylis anthophylla*	235
6”-Acetylsaikosaponins b_1, b_3 and e	*Bupleurum chinense*	231
Achyranthosides B and D	*Achyranthes bidentata*	236
Aesculiosides C1 – C15	*Aesculus californica*	237
Assamicoside A	*Glochidion assamicum*	238
Caraganins A and B	*Caragana microphylla*	239
Chiococcasaponins III – V	*Chiococca alba*	240
Clematangosides A, C, D	*Clematis tangutica*	224
Clematochinenosides H – J	*Clematis chinensis*	241
Congmuyenosides C – E	*Aralia elata*	242
Cowpeasaponins I and II	*Vigna sinensis*	243
Cylindroside A	*Cylindrokelupha dalatensis*	244
Eryngiosides M and N	*Eryngium yuccifolium*	245

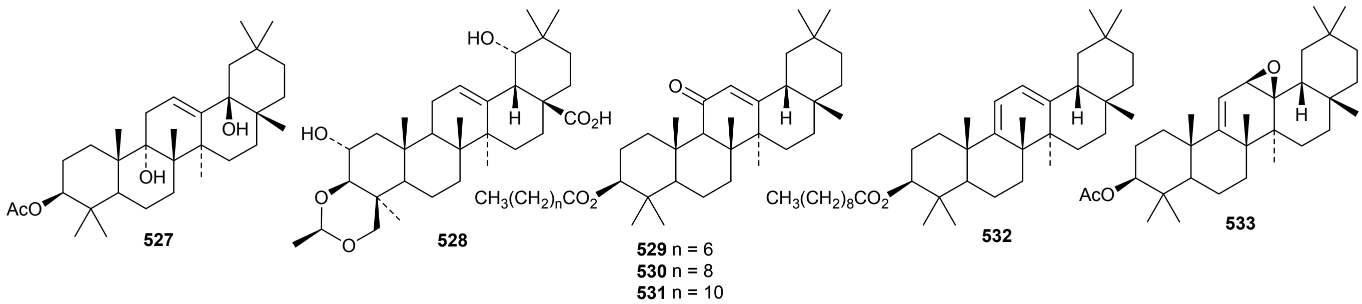
Gordonsaponins A, C, D, F – K	*Gordonia kwangsiensis*	226
Heptoleosides C and D	*Schefflera heptaphylla*	122
Kakkasaponins II and III	*Pueraria thomsonii*	246
Longicarposides A – I	*Gordonia longicarpa*	247
Mandshunosides C – E	*Clematis mandshurica*	248
Magnosides A and B	*Cybianthus magnus*	249
Neanoside A	*Neanotis wightiana*	250
Nebulosides A and B	*Gypsophila arrostii* var. *nebulosa*	251
Nummularoside	*Lysimchia nummularia*	252
Paritrisides A – F	*Paris polyphylla* var. *yunnanensis*	253
Patrinovilosides A and B	*Petrinia villosa*	254
Phaseoloidesides A – D	*Entada phaseoloides*	255
Piptadeniaoside	*Piptadeniastrum africanum*	256
Pittangretosides A – H	*Pittosporum angustifolium*	228
Platycodons A and B	*Platycodon grandiflorum*	257
Psychotrianosides A, C – G	*Psychotria* sp.	229
Pulsatilloside F	*Pulsatilla koreana*	258
Ryobusaponins A – D	*Clethra barbinervis*	204
Sarosiensin V	*Trifolium medium*	232
Sibiricasaponin E	*Polygala sibirica*	259
Soysaponins M1 – M3	*Glycine max*	260
Thyrsiloside A	*Lysimachia thyrsiflora*	252
Tomentosides A – C	*Anemone tomentosa*	261
Virgaureasaponins 4 – 6	*Solidago virgaurea*	262
Xanthohuskisides A and B	*Xanthoceras sorbifolia*	263

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

Table 2

Plant species	Reference
Anabasis setifera	264
Anemone raddeana	265
Anemone taipaiensis	266, 267
Aralia elata	268
Ardisia gigantifolia	269
Astragalus tauricolus	270
Benincasa hispida	271
Calliandra pulcherrima	272
Clematis lasiandra	273
Clematis tangutica	274
Gypsophila trichotoma	275, 276
Ilex cornuta	277
Lonicera macranthoides	205
Lysimachia parvifolia	220
Pittospermum verticillatum ssp. *verticillatum*	278
Pulsatilla chinensis	279
Ricinus communis	280
Sapindus mukorossi	281, 282
Saponaria officinalis	283
Sesbania vesicaria	284
Swartzia apetala var. *glabra*	285
Swertia yunnanensis	286
Trifolium hybridum	287
Xanthoceras sorbifolia	234, 288

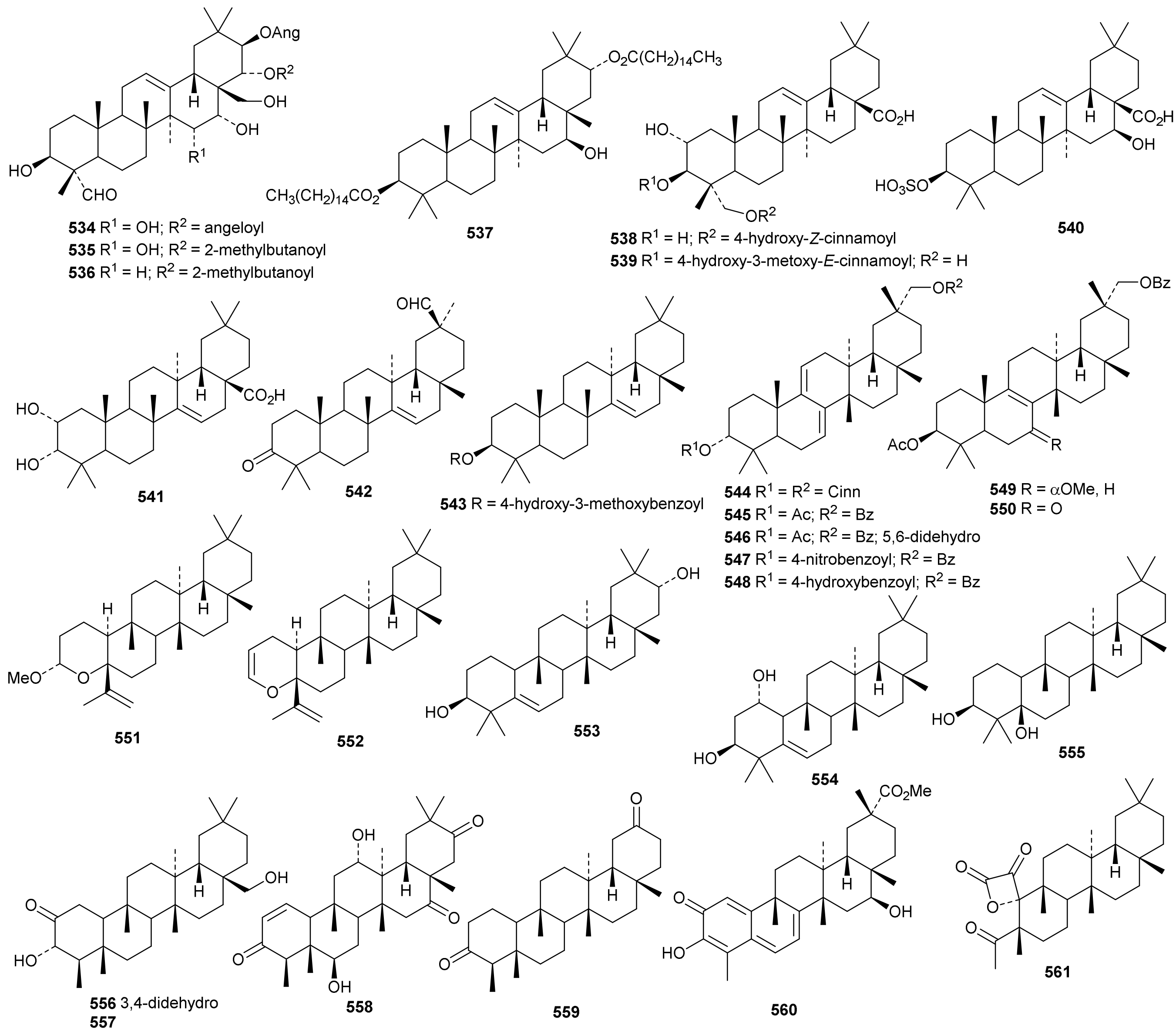
New oleanane esters include the tetraacetate of 12-oleanene-3β,16β,23,28-tetrol and three esters of 12-oleanene-3β,16β,21β,22α,23,28-hexol from *Gymnema sylvestre*,[195] and the 3-acetate of 12-oleanene-3β,9α,17β-triol **527** from *Abelmoschus exculentus.*[199] An acetaldehyde acetal **528** has been identified as a constituent of *Terminalia brownii*.[289] Several oleanane esters **529** – **533** have been isolated from *Dorstenia arifolia*.[290] Further new oleanane esters include the



angeloyl esters **534** – **536** from *Camellia oleifera*,[291] the dipalmitoyl ester **537** from *Chrysanthemum macrocarpum*,[292] the *cis*-coumaroyl ester **538** and the *trans*-feruloyl ester **539** from *Rhodomyrtus tomentosa*[293] and the 3-sulfate of **540** 3β,16β-dihydroxy-12-oleanen-28-oic acid from *Schefflera elegantissima*.[294]

Zenkeric acid **541**, a constituent of *Hypodaphnis zenkeri*, has been identified as 2α,3α-dihydroxy-14-taraxeren-28-oic acid.[295] 3-Oxo14-taraxeren-30-al **542** has been found in *Vitex trifolia* var. *simplicifolia*.[296] Microcisin **543**, the vanilloyl ester of taraxerol, has been isolated from the roots of *Microcos tomentosa*.[297] The dicinnamoyl ester **544** of karounidiol is a constituent of fruits of *Benicasa hispida*.[271] Three multiflorane esters **545** – **547**, including the *p*-nitrobenzoyl ester **547**, have been found in seeds of zucchini (*Cucurbita pepo*).[298] Related esters **548** – **550** have been isolated from pumpkin seeds (*Cucurbita maxima*).[299] Two related 3,4-secoglutinane derivatives torreyanoxane **551** and euphorbiane **552** have been isolated from *Torreya nucifera*[300] and *Euphorbia tirucalli*,[300] respectively. The structure of euphorbiane **552** was confirmed by X-ray analysis. Simple glutinane derivatives include 5-glutinene-3β,21α-diol **553** from *Celastrus vulcanicola*,[213] 5-glutinene-1α,3β-diol **554** from *Vernicia fordii*[218] and glutinane-3β,5β-diol **555** from *Rhaphiolepis indica* var. *tashiroi*.[222]

A review of naturally occurring friedelanes, isolated between 1977 and March 2011 has been published.[301] Ovalifolones A **556** and B **557**, from *Garcinia ovalifolia*,[302] and maytensifolone **558**, from *Maytenus distichophylla*,[303] are new friedelane derivatives. Phyllaembicone A **559**, isolated from the roots of *Phyllanthus emblica*, is 29,30-dinorfriedelane-3,20-dione.[304] 16β-Hydroxypristimerin **560** is a 24-norfriedlane quinine methide from *Maytenus salicifolia*.[305] Three ring-A cleaved norfriedelane derivatives named as norfriedelins A **561** - C **563** have been identified in *Malpighia emarginata*.[306] The structure of norfriedelin A **561**, containing an interesting α-keto-β-lactone, was confirmed by X-ray analysis. The 3-benzoyl

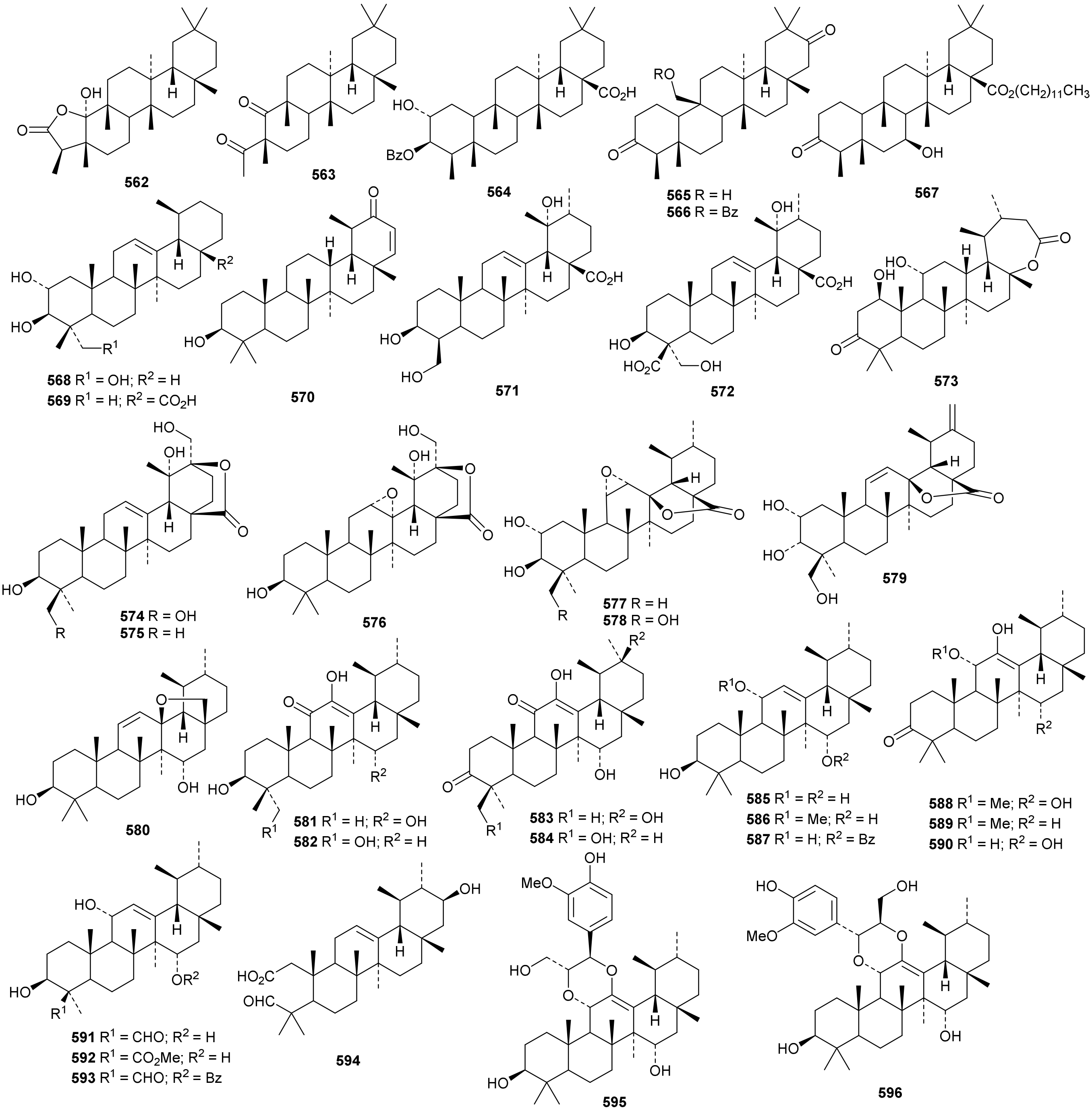


Ester **564** of pluricostatic acid has been found in *Trigonostemon xyphophylloides* [307] and 25-hydroxyfriedelane-3,21-dione **565** and its 25-benzoate **566** have been isolated from *Siphonodon celastrineus*.[198] The dodecyl ester **567** of 7β-hydroxy-3-oxofriedelan-28-oic acid has been found in *Pouzolzia indica*.[308]

7. The ursane group

The sources and pharmacological properties of ursolic acid have been reviewed.[309-311] The 30-nor ursane derivatives rubrajaleelol **568** and rubrajeelic acid **569** have been identified in *Plumeria rubra*.[312] A further 30-nor derivative 3β-hydroxy-30-nor-21-ursen-20-one **570** has been found in *Eupatorium fortunei*.[313] A 24-nor ursane derivative **571** together with 3β,19α-dihydroxy-12-ursene-24,28-dioic acid **572** have been isolated from *Emmenopterys henryi*.[314] Urmiensolide **573**, from *Salvia urmiensis*, is the first example of an E-ring ε-lactone.[315] The structure of urmiensolide **573** was confirmed by X-ray analysis. Gluinosalactones A **574**, B **575** and C **576** are 28,20-ursanolides isolated from the leaves of *Rehmannia glutinosa*.[316] Three 28,13-ursanolides **577** – **579** have been identified in *Isodon excisoides*.[317]

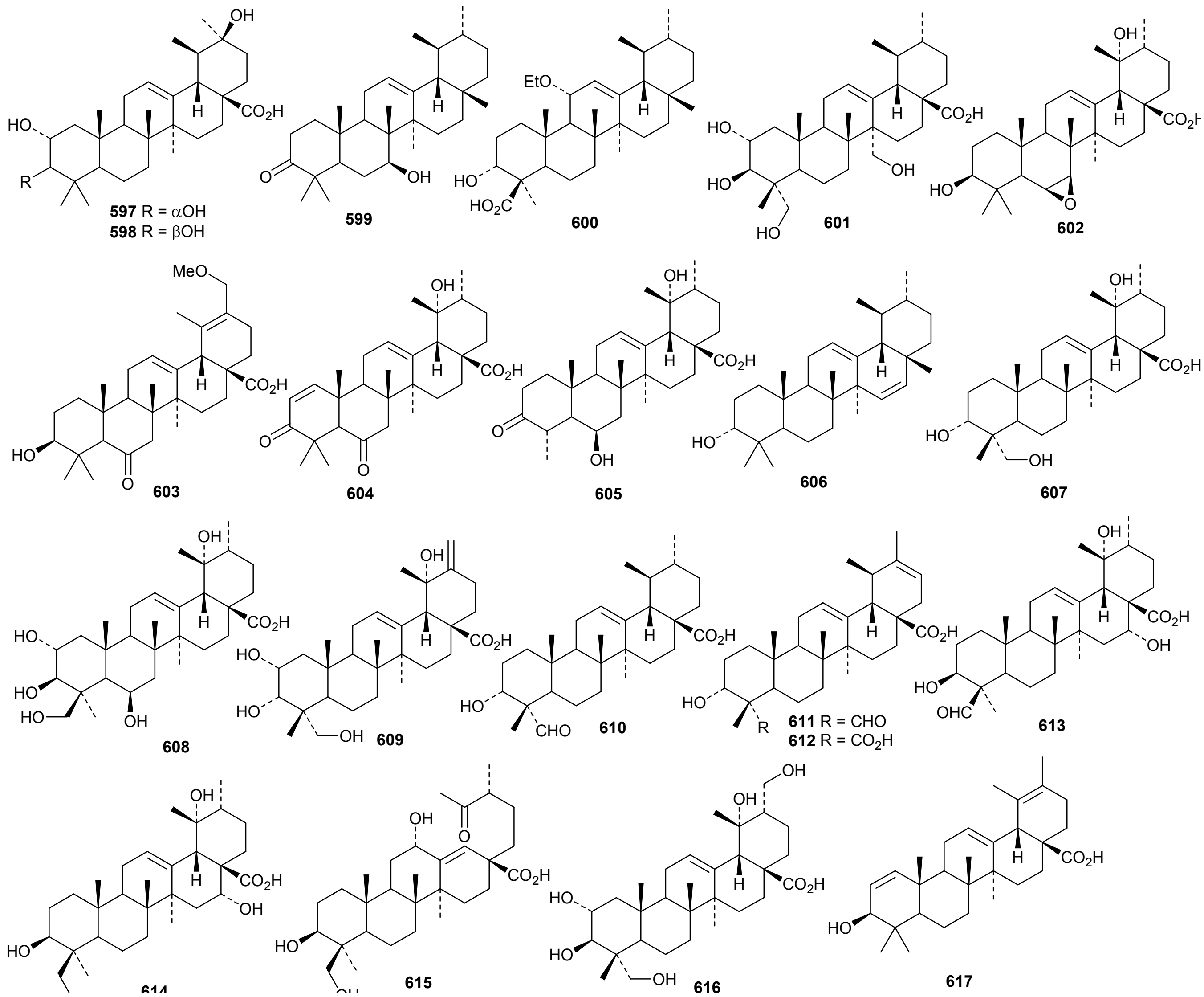
Seventeen ursane derivatives **580** – **596** have been isolated from *Siphonodon celastrineus* including the 2,3-seco aldehyde derivative **594** and two phenylpropanoid adducts **595** and



596.[198] Fulgic acids A **597** and B **598**, from *Potentilla fulgens*, have been identified as 2α,3α,20β-trihydroxy-12-ursen-28-oic acid and the 3β-epimer, respectively.[318] 6β-Hydroxy-12-ursen-3-one **599** a constituent of *Boswellia sacra*, has been named nizwanone and it is accompanied by 11α-ethoxy-β-boswellic acid **600** that is likely to be an isolation artefact.[319] Other new simple ursane derivatives include 2α,3β,23,27-tetrahydroxy-12-ursen-28-oic acid **601** from *Actinidia deliciosa*,[194] four derivatives **602** – **605** from *Uncaria laevigata*,[208] 12,15-ursadien-3α-ol **606** from *Croton bonplandianum*,[320] 4-*epi*-barbinervic acid **607** from *Verbena officinalis*,[321] 2α,3β,6β,19α,24-pentahydroxy-12-ursen-28-oic acid **608** from *Ludwigia hyssopifolia*[322] and 2α,3α,19α,23-tetrahydroxy-12,20(30)-ursadien-28-oic acid **609** from *Callicarpa nudiflora*.[323]

New ursane saponins with new genins include hepturosides A – C from *Schefflera heptaphylla* with the genins **610** – **612** respectively,[122] ilexpublesnins C and D from *Ilex pubescens* with 3β,19α-dihydroxy-24-oxo-12-ursen-28-oic acid **613**,[227] ryobunins A and B from *Clethra barbinervis* with 3α,16α,19α,24-tetrahydroxy-12-ursen-28-oic acid **614** and the 18,19-seco derivative **615** respectively,[230] a saponin from *Potentilla multicaulis* with the new genin 2α,3β,19α,23,30-pentahydroxy-12-ursen-28-oic acid **616**[324] and a saponin from *Asparagus racemosus* with 3β-hydroxy-1,12,19-ursatrien-28-oic acid **617**.[325]

Ursane saponins with known genins include actinidicoside from *Premna fulva*,[326] asprellanosides C – E from *Ilex asprella*,[327] heptursoside D from *Schefflera heptaphylla*,[122] ilexgenin A2[328] and ilexoside P[329] from *Ilex pubescens*, monepalosides M and N from *Morina nepalensis* var. *alba*,[330] sibiricasaponins A – D from *Polygala sibirica*[259] and ilexpuplesnins E and G – K from *Ilex pubescens*.[227] Unnamed saponins with known genins have been isolated from *Callicarpa nudiflora*,[323] *Ilex asprella*[331] and *Ilex cornuta*.[277]



Prunol **618**, from *Prunus cerasoides*, has been identified as an ester of ursolic acid with 2,3,6-trihydroxybenzoic acid.[332] Other new ursane esters include the 28-formate of 12-ursene-3β,28-diol and its 3-acetate derivative from *Ilex cornuta*,[333] the 6-acetate of ursane-3β,6β,19α-triol from *Astilbe chinensis*,[334] the 30-*cis*-*p*-coumaroyl ester of 3β,30-dihydroxy-12-ursen-28-oic acid from *Teucrium viscidum*,[335] the 2-*cis*-*p*-coumaroyl ester and the 2-*trans*-*p*-coumaroyl ester of 2α,3β,19α-trihydroxy-12-ursen-28-oic acid from *Prinsepia utilis*,[336] and four long-chain ursane esters **619** - **622** from *Dorstenia arifolia*. Alstoprenylene **623**, from *Alstonia scholaris*, has been reported to be a 24-norursane with the unusual 18α-stereochemistry.[212] Clerodendrumic acid **624**, from *Clerodendrum glabrum*, has also be reported with this stereochemistry.[337] The acetonide **625** is likely to be an artefact from chromatography of the extract of *Rhododendron hainanense*.[338]

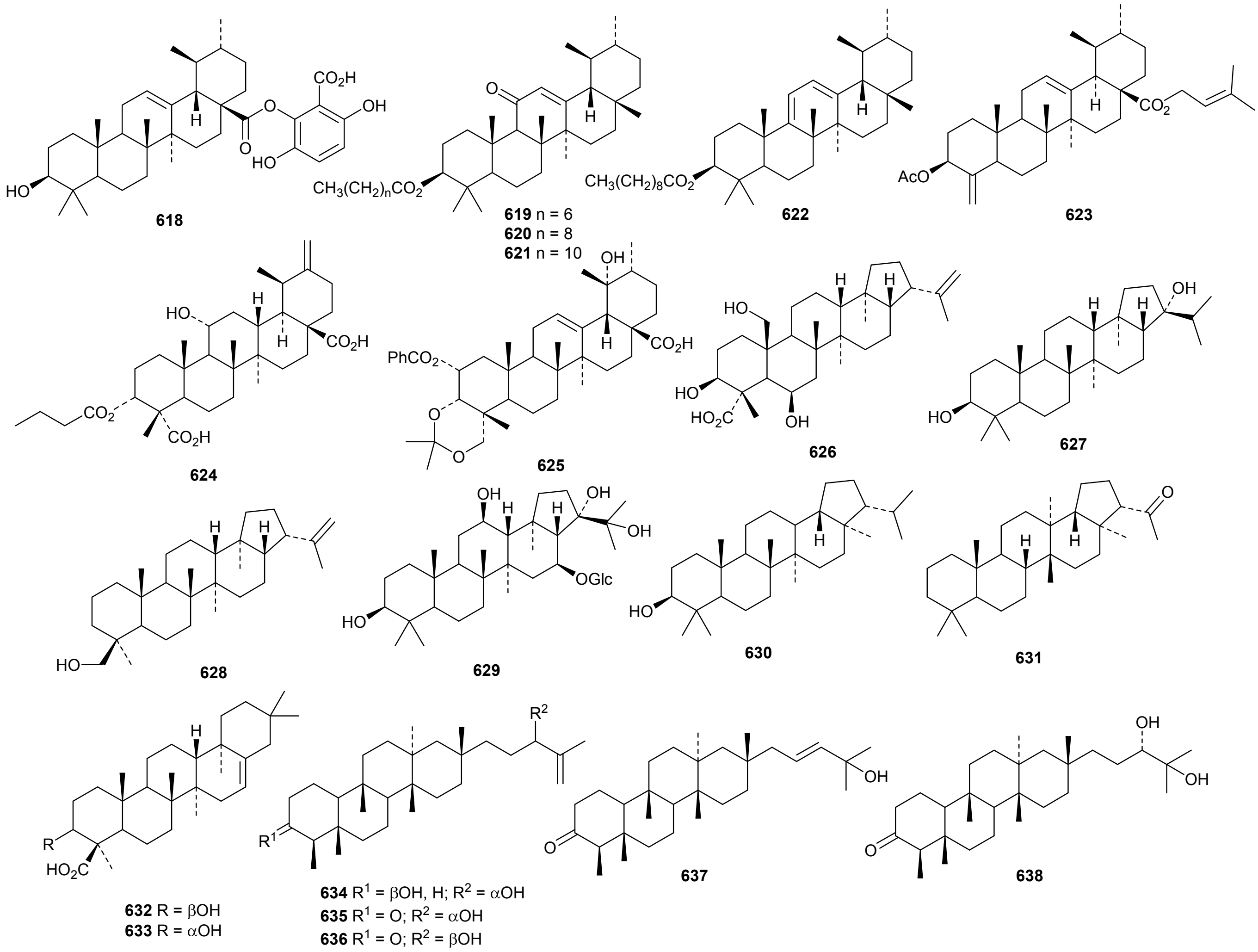
Ilexpublesnin F is a taraxastane saponin with a known genin from *Ilex pubescens*.[227] The 3-acetate of 12,20(30)-taraxastadiene-3β,11α,21α-triol has been isolated from *Echinops galalensis*.[339]

8. The hopane group

The structure of sonhafouonic acid **626**, from *Zehneria scabra camerunensis*, was confirmed by X-ray analysis as 3β,6β,25-trihydroxy-20(29)-hopen-23-oic acid.[340] Hopane-3β,21α-diol **627** has been isolated from the leaves of *Carissa carandas* and has been named carandinol.[341] *Humata tyermanni* is the source of 20(29)-hopen-24-ol **628**.[342] The new hopane saponin glinuside C **629**, from *Glinus oppositifolius*, has a new genin.[343] Dryocrassol xylopyranoside, with a known hopane genin, has been isolated from *Alsophila spinulosa*.[344] The migrated hopane derivatives capillirol B **630** (neophopane-3β-ol) and capillirone **631** (30-norfernan-22-one) have been identified in *Adiantum capillus-veneris*.[345]

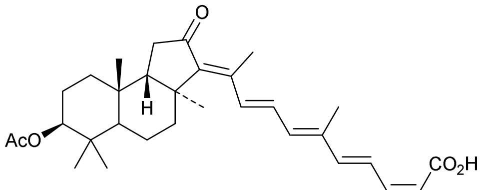
9. Miscellaneous compounds

Two chiratane triterpenoids, kouitchenoids A **632** and B **633** have been isolated from *Swertia kouitchensis*.[346] *Aster tataricus* is the source of the five shionane triterpenoids astataticusol A **634** and astataticusones A **635** – D **638**.[347]



Stellettin N **639**, from a sponge of the genus *Stelletta*, is an isomalabaricane triterpenoid that shows potent protein-tyrosine phosphatase 1B inhibition.[348]

Three tricyclic triterpenoids with unusual skeletons, kadcotriones A **640** - C **642**, have been isolated from *Kadsura coccinea*.[349] Biosynthetic pathways to the kadcotriones, from a common lanostane precursor, have been proposed. The biosynthesis of volvalerenol A **643**, from the roots of *Valeriana hardwickii*, is thought to involve head-to-tail linkages of two units of farnesyl diphosphate.[350]



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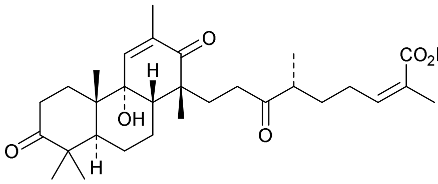

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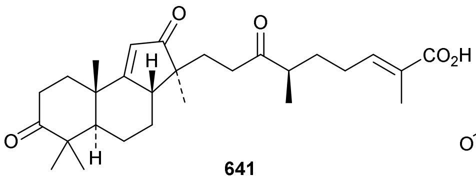

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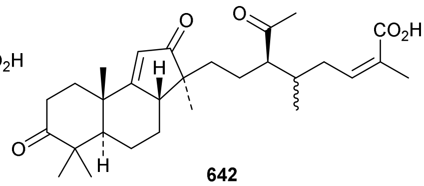

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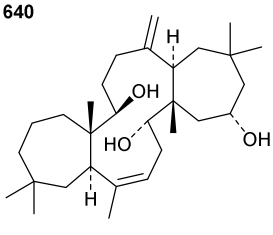

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