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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.

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### 1. Introduction

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

### 2. The squalene group

Sapelenins G 1–J 4 are further anti-inflammatory squalene derivatives from the bark of Cameroonian *Entandrophragma cylindricum*.<sup>9</sup> The highly oxidised squalene derivative 5 has been isolated from Peruvian *Protium subserratum*.<sup>10</sup> 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.<sup>11</sup> The mechanism of triterpene biosynthesis in *Botryococcus braunii* has been reviewed.<sup>12</sup>

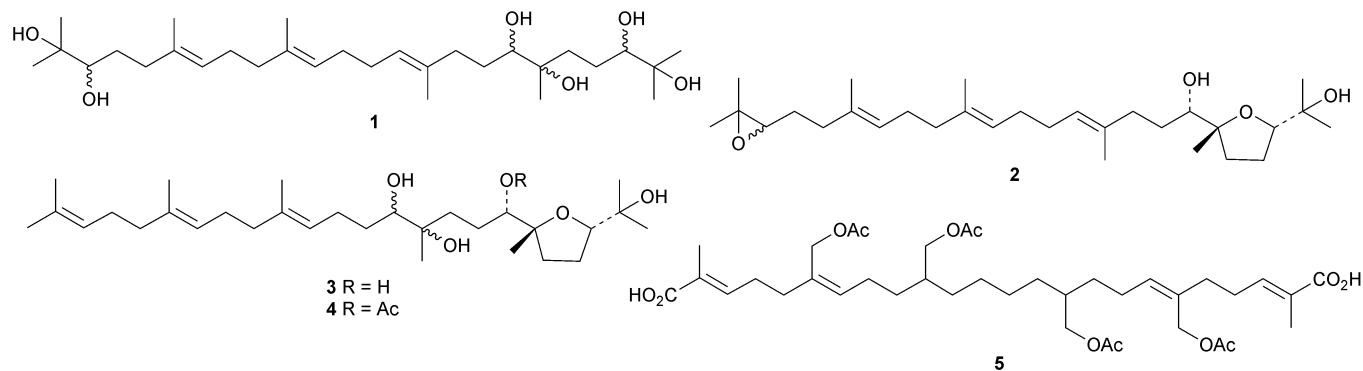
### 3. The lanostane group

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*.<sup>15</sup> The tetraterpenes abiestetranes A 11 and B 12, from *Abies fabri*,<sup>16</sup> and abibalsamins A 13 and B 14, from the oleoresin of *Abies balsamea*,<sup>17</sup> appear to have arisen by Diels–alder cycloadditions of rearranged lanostanes with the monoterpene  $\beta$ -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*.<sup>18</sup> 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*.<sup>19</sup> The tetranor derivative 22 and the 3,4-secolanostane 23 have been found in *Abies holophylla*.<sup>20</sup>

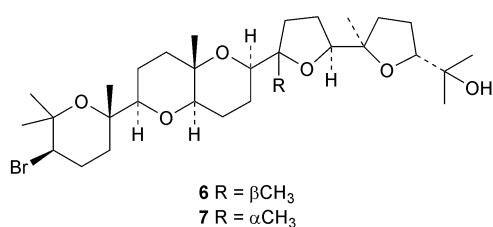
Pseudoferic acids A 24, B 25 and C 26 are interesting new 16,24-cyclised lanostanes from *Pseudolarix kaempferi*.<sup>21</sup> The stems of *Schisandra glaucescens* contain the ring A-cleaved lanostanes schiglausins A 27–H 34, together with the intact derivatives schiglausins I 35 and J 36.<sup>22</sup> 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*.<sup>23</sup> Kadcoocitones A 51 and B 52 are unusual rearranged lanostane derivatives from *Kadsura coccinea* where they occur with kadcoocitone C 53, whose structure was confirmed by X-ray analysis.<sup>24</sup> Secococcinic acids G 54–K 58 are further constituents of *Kadsura coccinea*.<sup>25</sup> Three esters 59–61 of 3-epidehydrotumulolic acid have been obtained from *Wolfiporia extensa*.<sup>26</sup> Other new lanostanes include lanosta-5,15-dien-3 $\alpha$ -ol 62 from *Arctium lappa*<sup>27</sup> and inonotsuoxodiols B 63 and C 64, epoxyinonotsudiol 65 and methoxyinonotsutriol 66 from *Inonotus obliquus*.<sup>28</sup>

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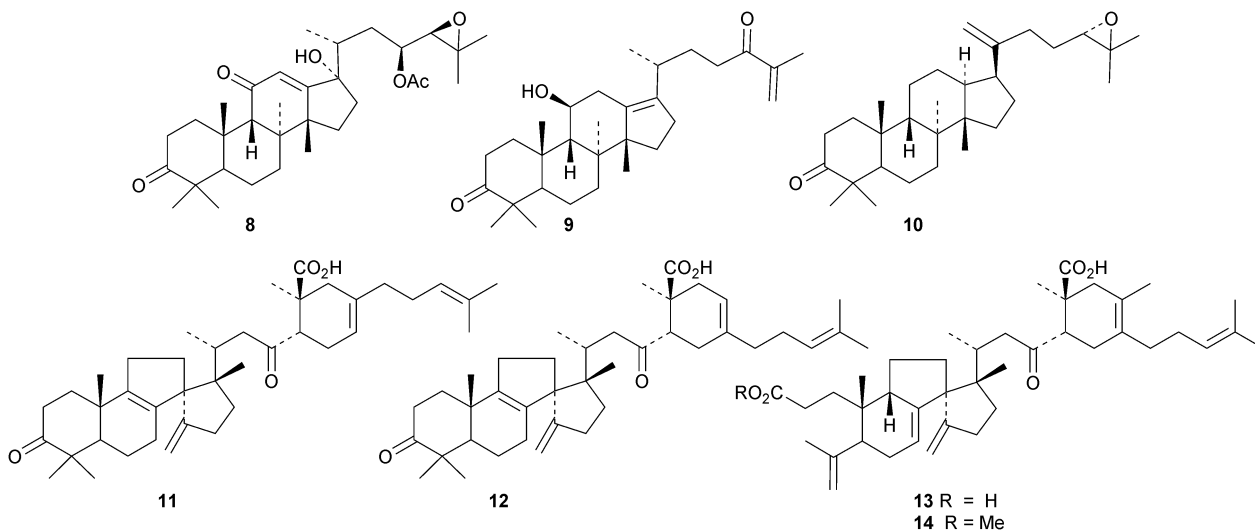


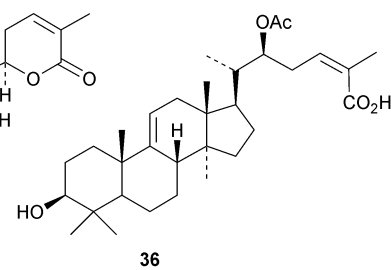
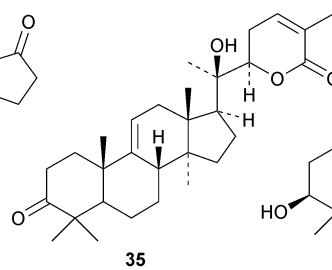
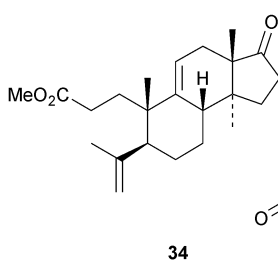
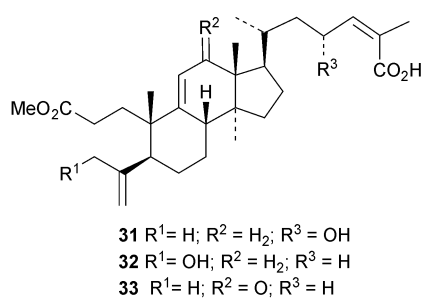
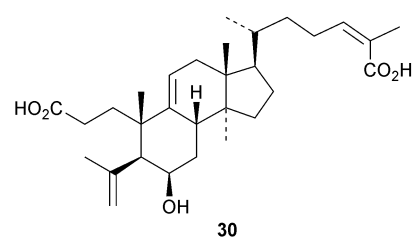
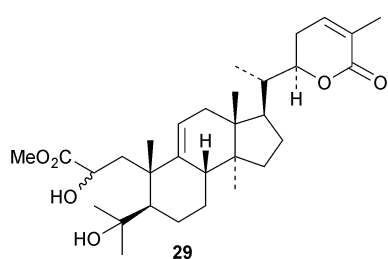
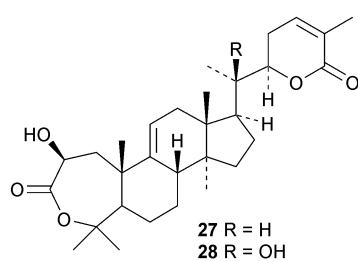
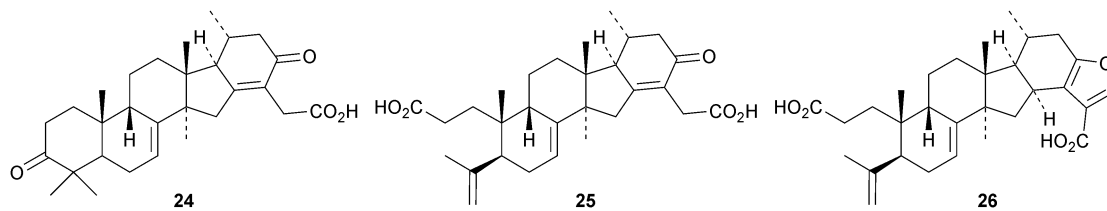
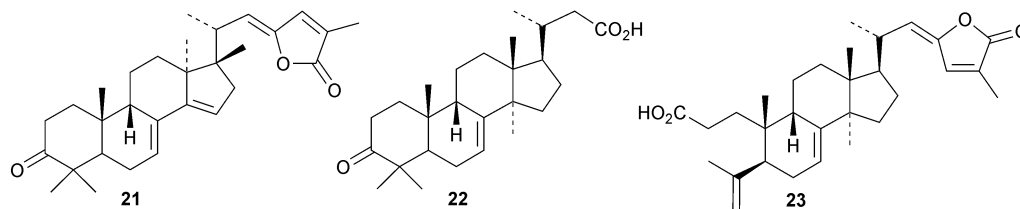
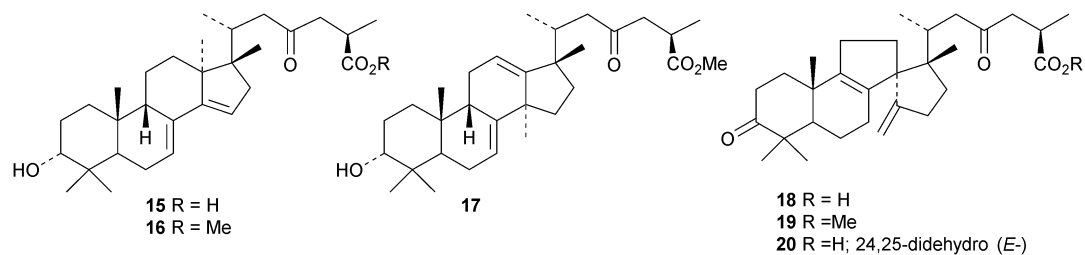
Sarasinosides N–R are 30-norlanostane glycosides from the sponge *Lypastrotethya* sp. with the new genins **67**, **68**, **69** and the 30-nor-18(13 → 14)-abeo-derivative **70**.<sup>29</sup> Scillanostaside F, with the new genin **71**, and scillanostaside G, with a known tetra-norlanostane genin, have been isolated from the bulbs of *Scilla scilloides*.<sup>30</sup>

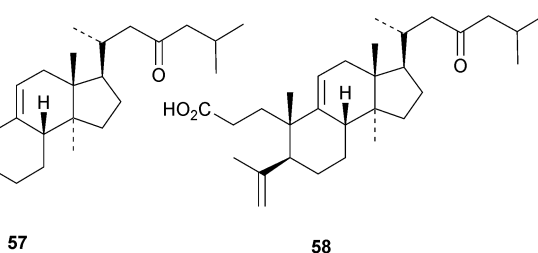
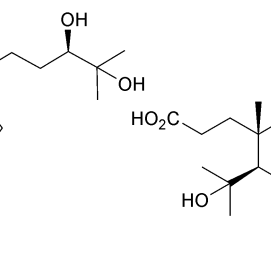
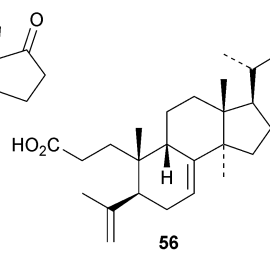
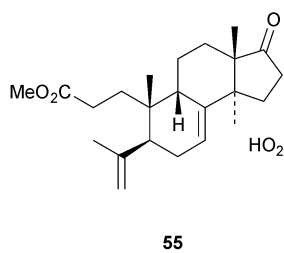
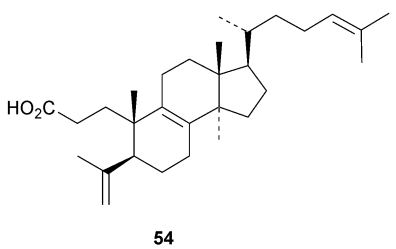
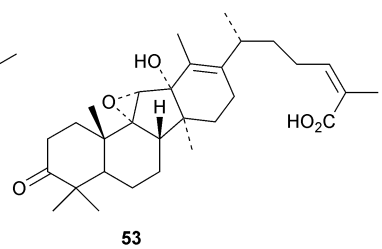
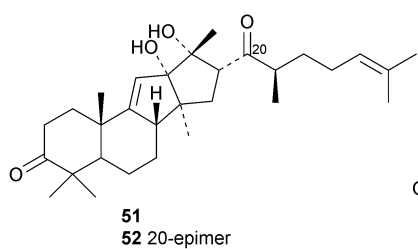
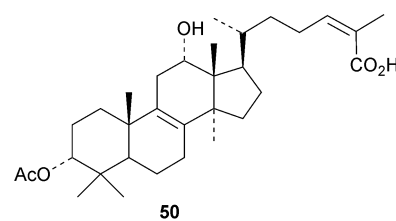
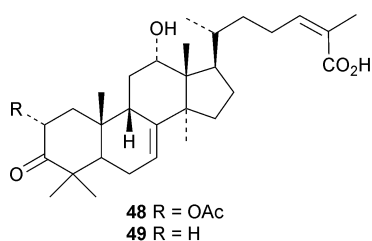
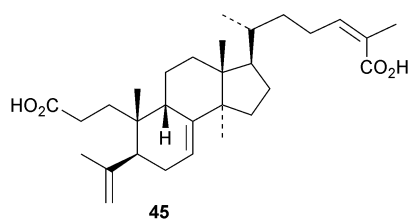
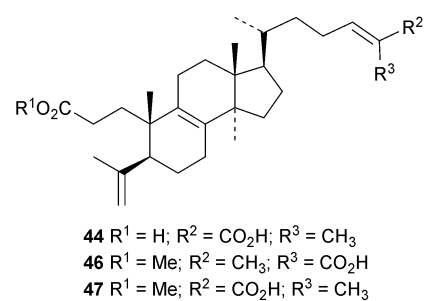
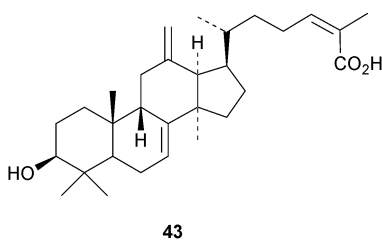
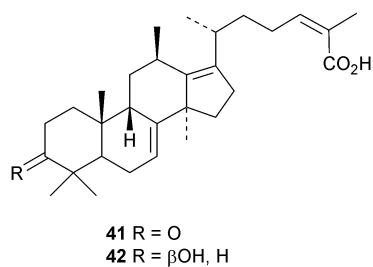
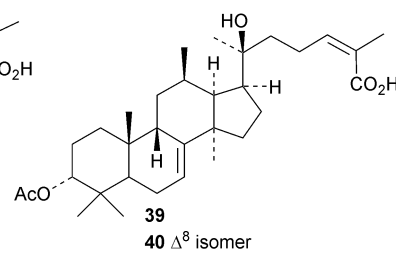
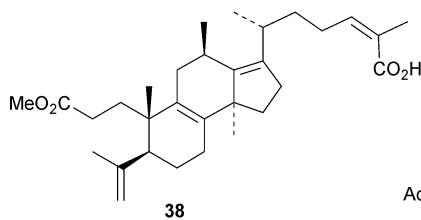
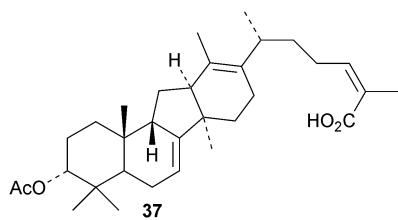


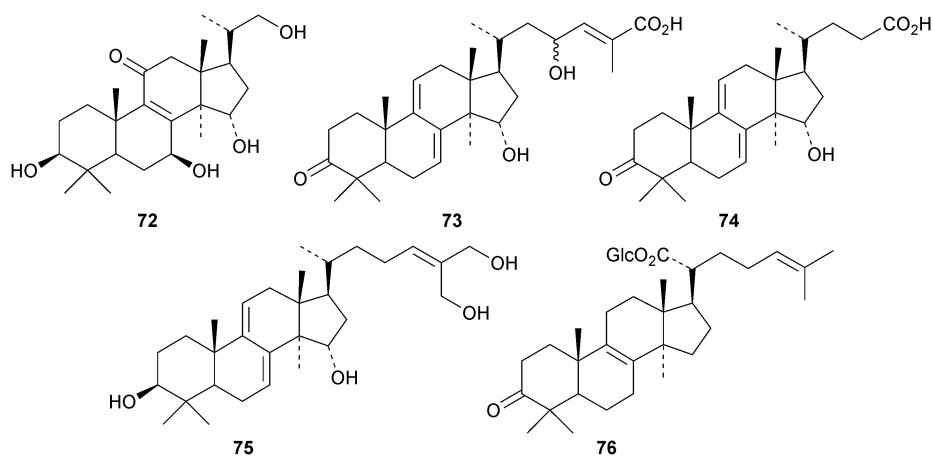
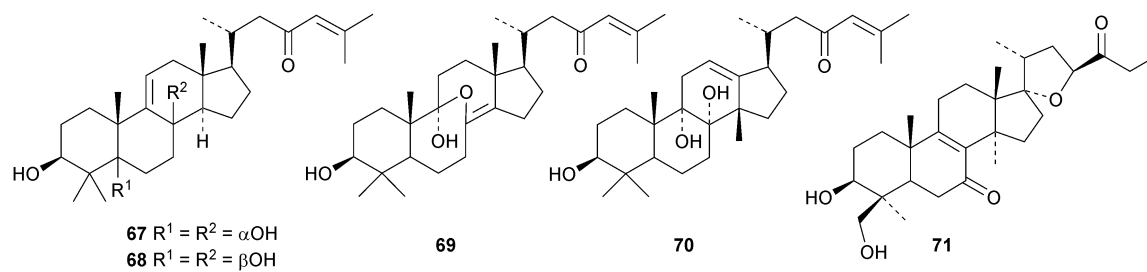
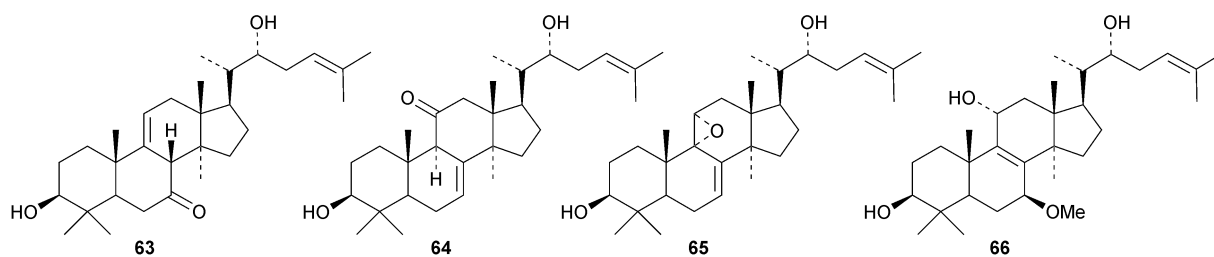
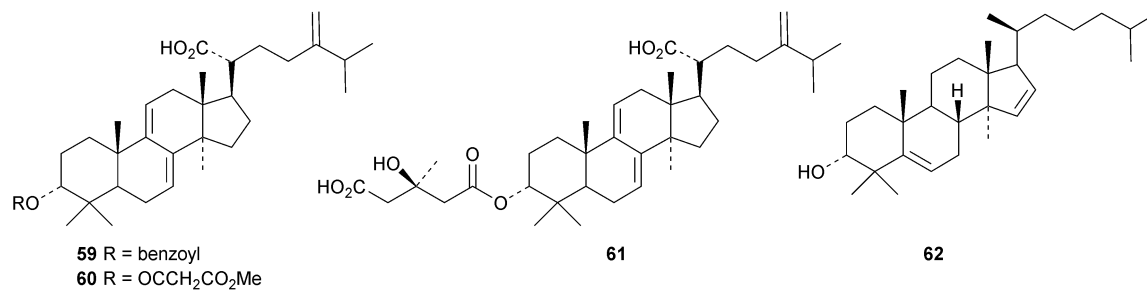
New compounds from *Ganoderma sinense* include the pentanor derivative ganosineniol A **72**, ganoderic acids J<sub>c</sub> **73** and J<sub>d</sub> **74**, ganodermatetraol **75**, the glucosyl ester ganosinoside A **76** with a known genin, ganolucidic acid  $\gamma_a$  **77**, ganolucidate F **78**,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

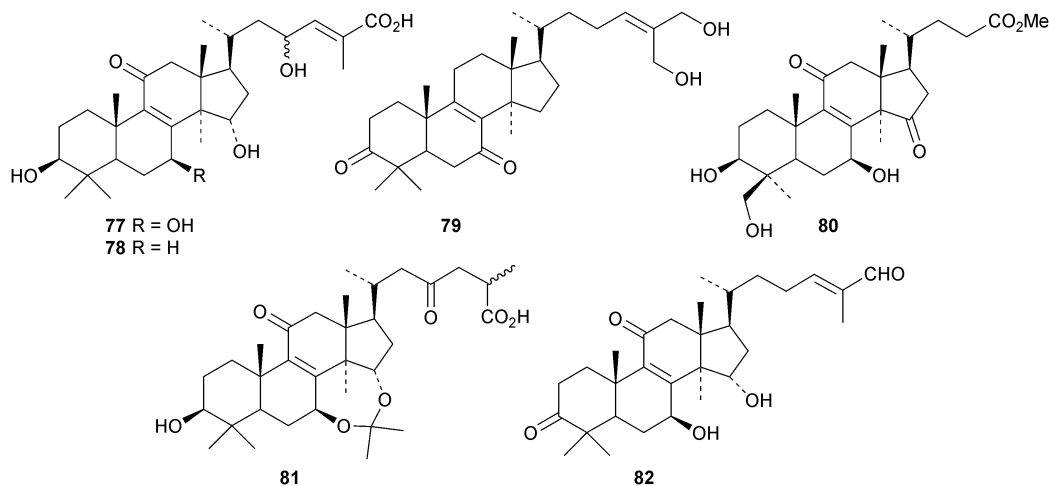
Astraodoric acids A **83**–D **86** are metabolites of the mushroom *Astraeus odoratus*.<sup>29</sup> The structure of astraodoric acid B **84** was confirmed by X-ray analysis. The structure of astrakurkulol **87**, from the Indian edible mushroom *Astraeus hygrometricus*, was also confirmed by X-ray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









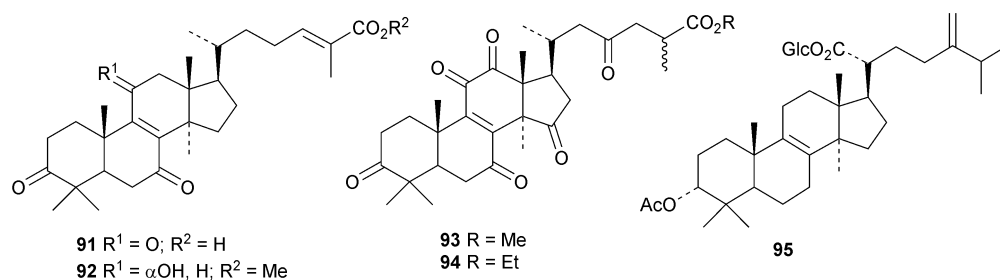
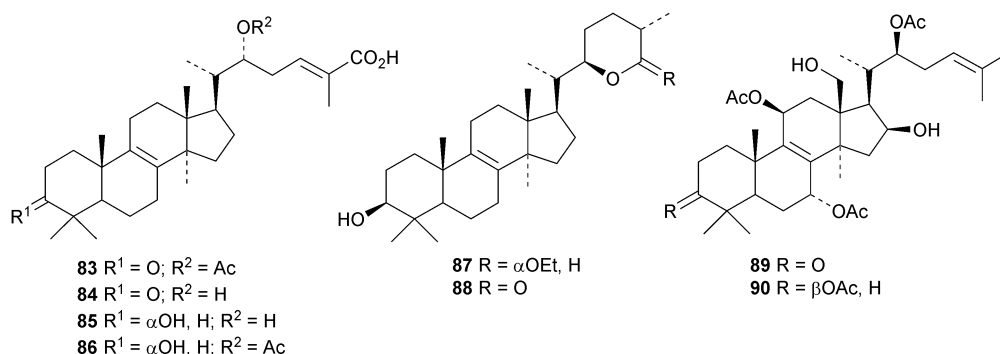


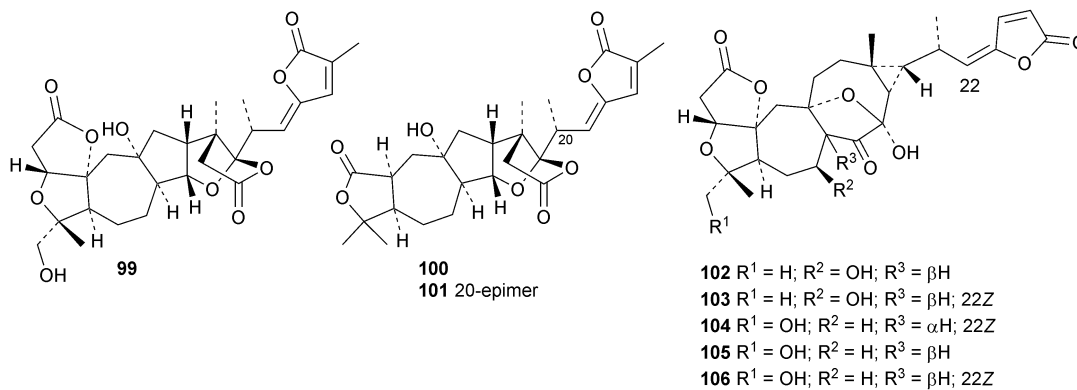
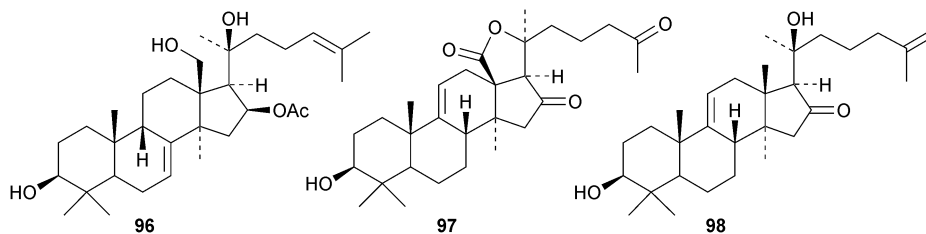
reported from *Coprinus cinereus*.<sup>38</sup> Other fungal metabolites include **91–94** from *Antrodia camphorate*<sup>39</sup> and formitoside K **95**, a glucoside with a new genin, from *Fomitopsis nigra*.<sup>40</sup>

Cucumarioside A8 is a lanostane saponin with the new genin **96** from the sea cucumber *Eupentacta fraudatrix*.<sup>41</sup> The sea cucumber *Apostichopus japonicus* is the source of several saponins, 26-*nor*-25-oxoholotoxin A<sub>1</sub> with the new genin **97** and

holototoxins D–G.<sup>42</sup> Holototoxins F and G have the new genin **98** while the genins of D and E are known. Cucumariosides B<sub>1</sub> and B<sub>2</sub><sup>43</sup> and cucumariosides H<sub>2</sub>, H<sub>3</sub> and H<sub>4</sub>,<sup>44</sup> from *Eupentacta fraudatrix*, all have known genins. Holostane saponins and their biological activity have been reviewed.<sup>45</sup>

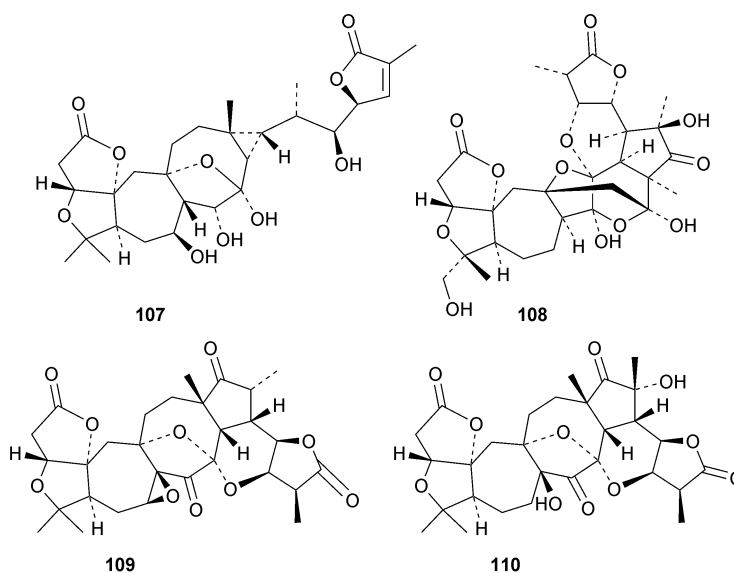
Interesting new structures continue to appear from *Schisandra* species. Schilancitrilactones A **99**, B **100** and C **101**

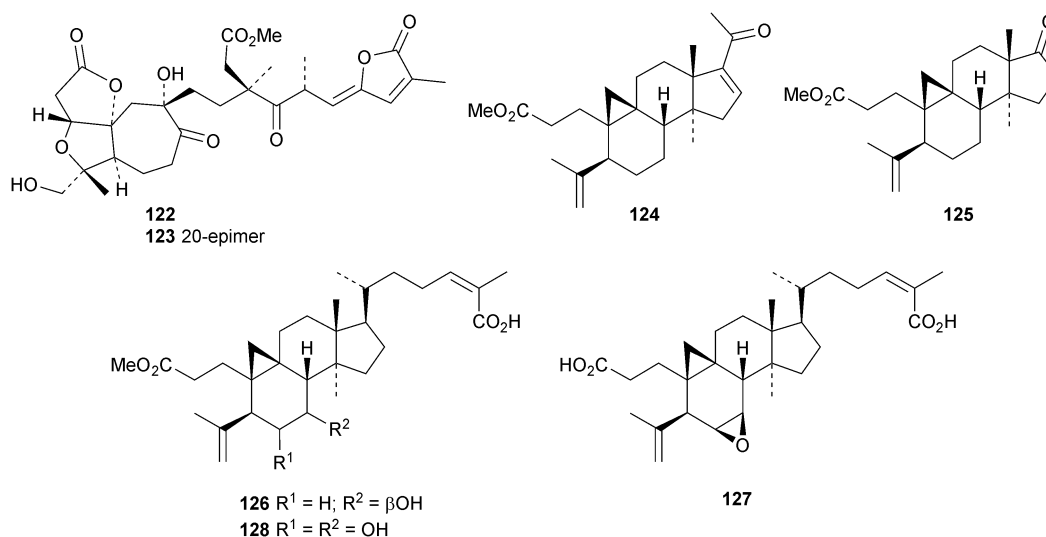
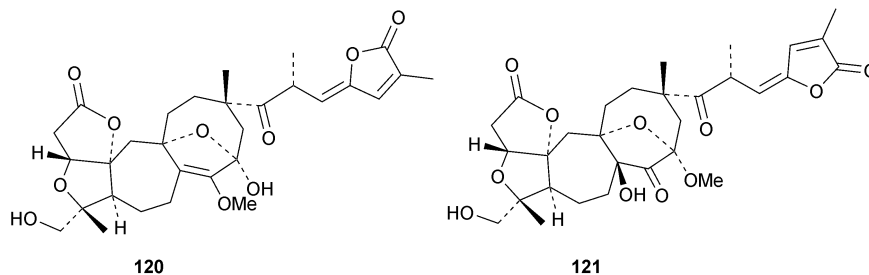
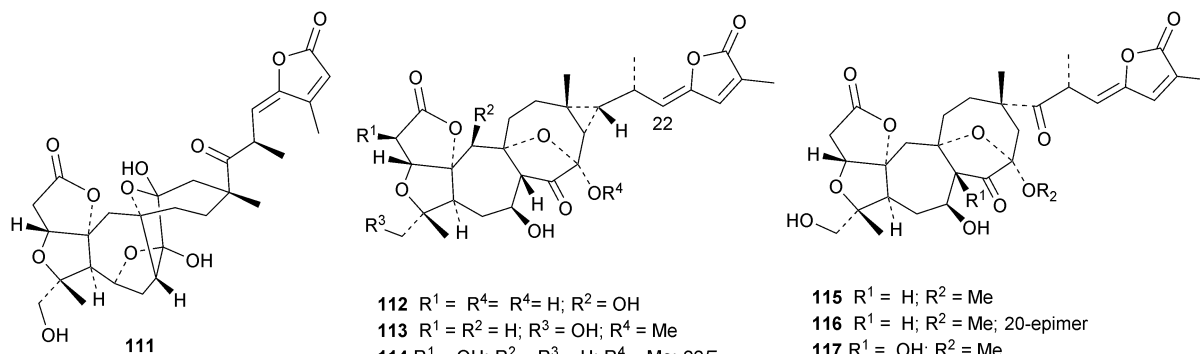




have been reported from *Schisandra lancifolia*.<sup>46</sup> The structures of all the schilancitrilactones were confirmed by X-ray analyses. New structures from *Schisandra sphenanthera* include preschisanartanins E **102**–J **107** and sphenadilactones D **108**–F **110**.<sup>47</sup> Isoschicagenin 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*.<sup>48</sup> Schiglausins K **124**–O **128** are simple ring A-cleaved cycloartanes from *Schisandra glaucescens*.<sup>49</sup>



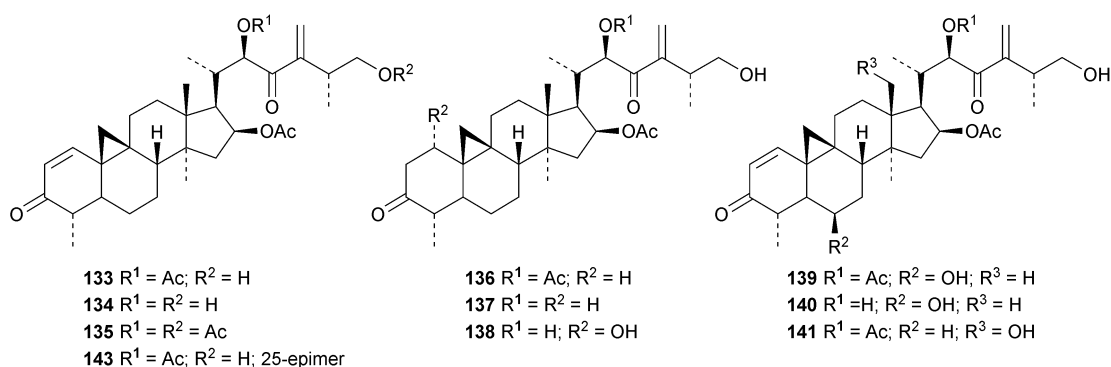
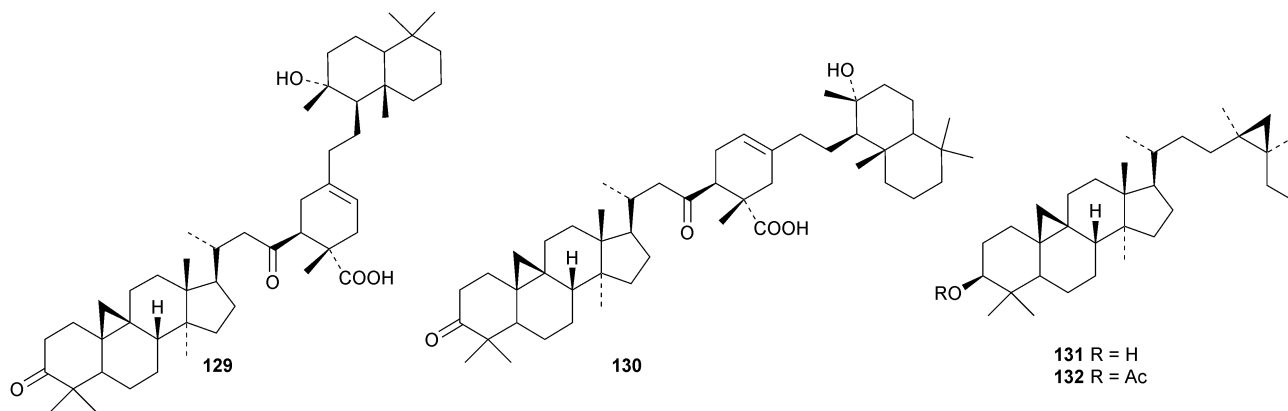


An interesting approach to the “dereplication, residual complexity and rational naming” of the *Actea* triterpenoids has the potential to be applied to other groups of natural products with the same inherent problems.<sup>50</sup> Pseudolaridimers A **129** and

B **130**, from *Pseudolarix amabilis*, appear to have arisen by a Diels–Alder reaction involving a cycloartane and a labdane.<sup>51</sup> The structure of **129** was confirmed by an X-ray analysis of the corresponding methyl ester. The cycloartanes lygodipenoids A

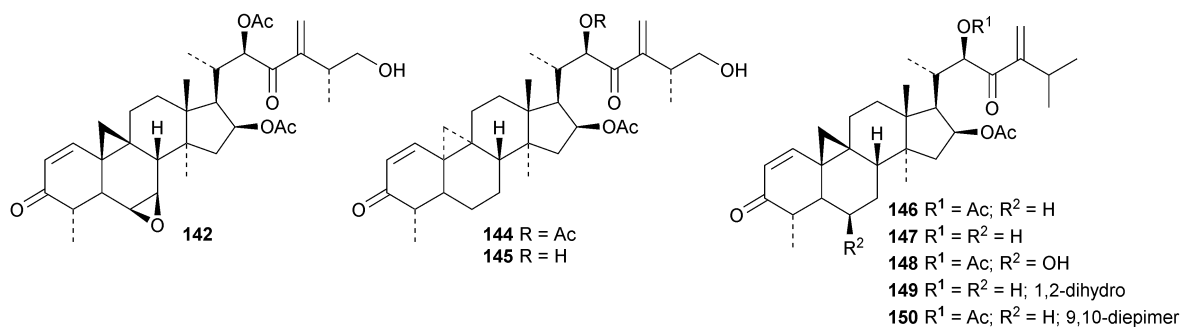


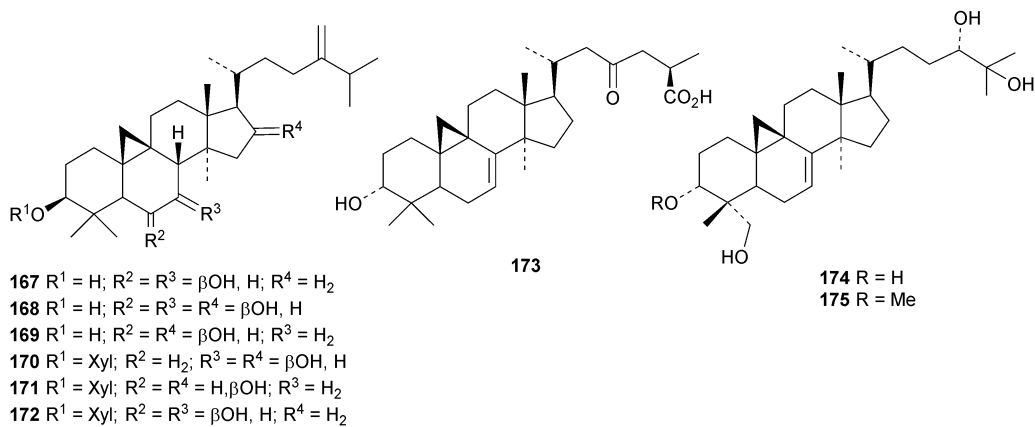
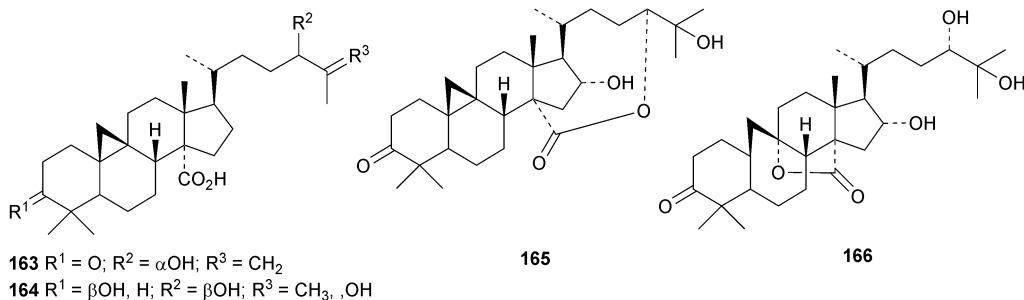
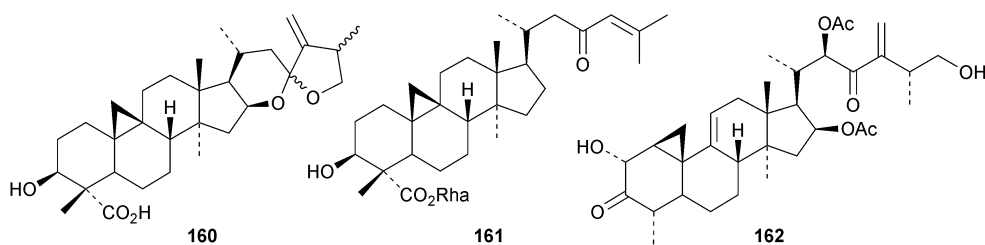
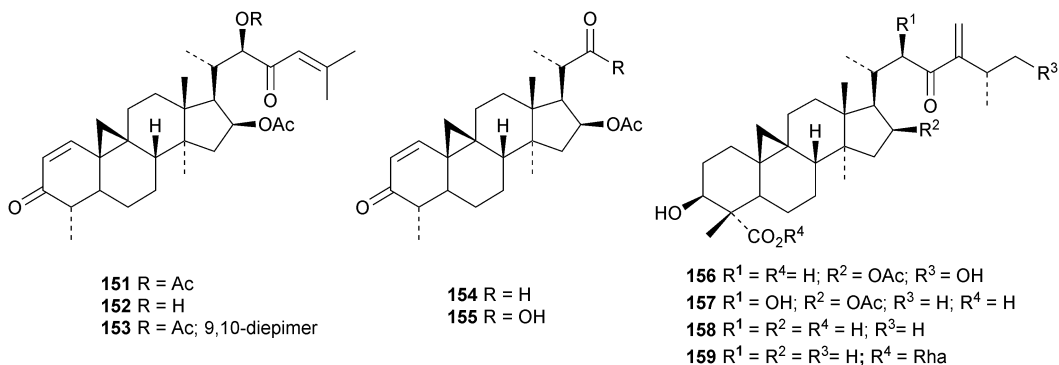


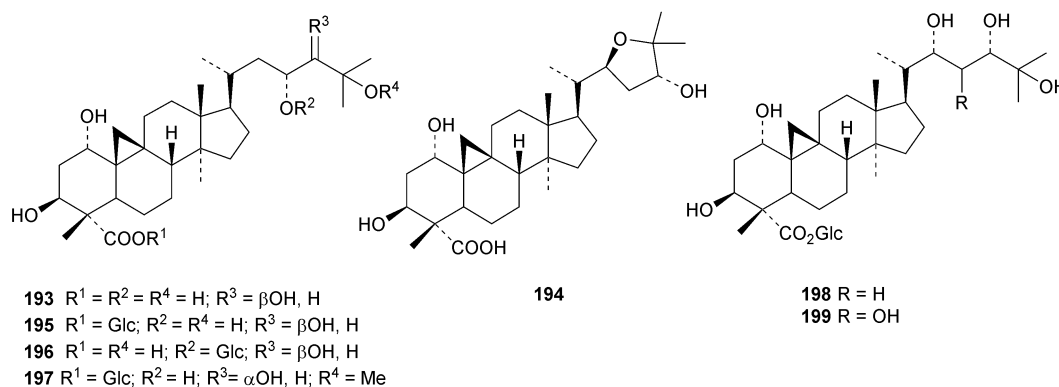
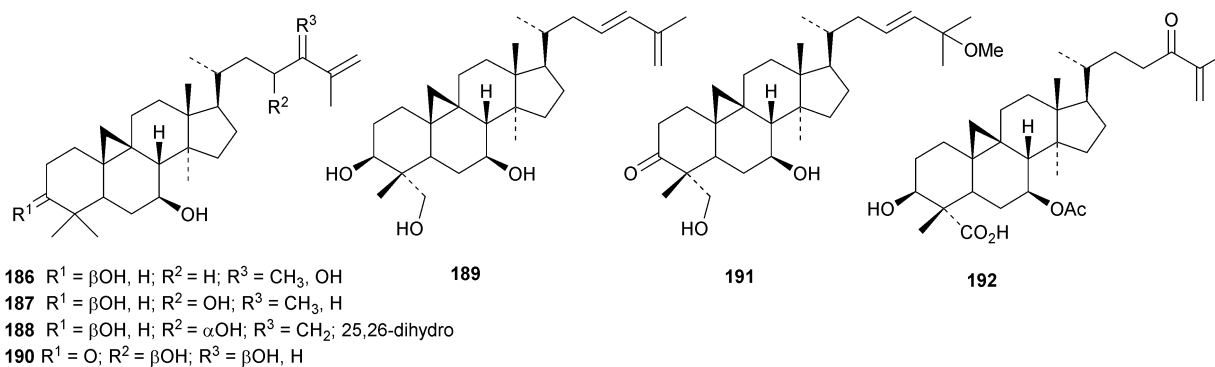
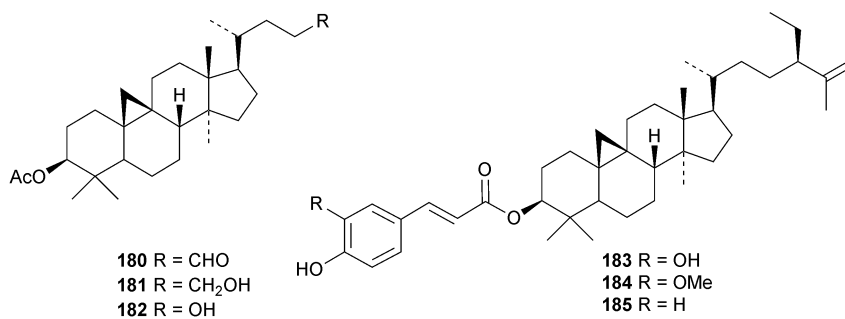
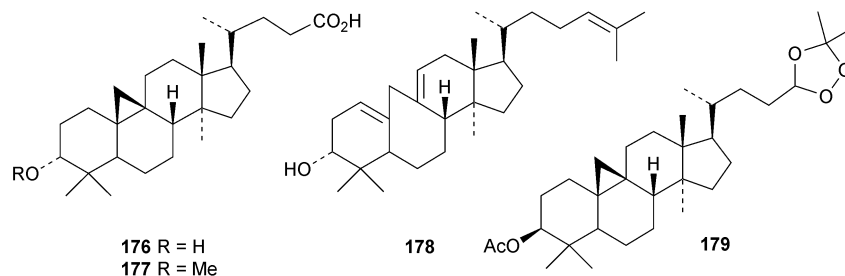


131 and B 132, from *Lygodium japonicum*, have an additional cyclopropane in their side chains.<sup>52</sup> Thirty new cycloartane proteasome inhibitors 133–162 have been reported from *Neoboutonia melleri*.<sup>53</sup> An interesting UV light-induced inversion of the configurations at C-9 and C-10 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*.<sup>54</sup> Compounds 167–172 are new cycloartanes from the leaves of *Homonoia riparia*.<sup>55</sup> Neoabiestrines G 173–I 175 have been

reported from *Abies recurvata*.<sup>18</sup> 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*,<sup>20</sup> rotundusolide C 178 from the rhizomes of *Cyperus rotundus*,<sup>56</sup> 179–182 from the aerial parts of *Atemisia lagocephala*,<sup>57</sup> three esters 183–185 of cyclomargenol from *Krameria pauciflora*,<sup>58</sup> euphonerins A 186–G 192 from the leaves of *Euphorbia nerifolia*,<sup>59</sup> cycloccidentallic acids A 193 and B 194 and the related saponins cycloccidalisides I 195–V 199 from



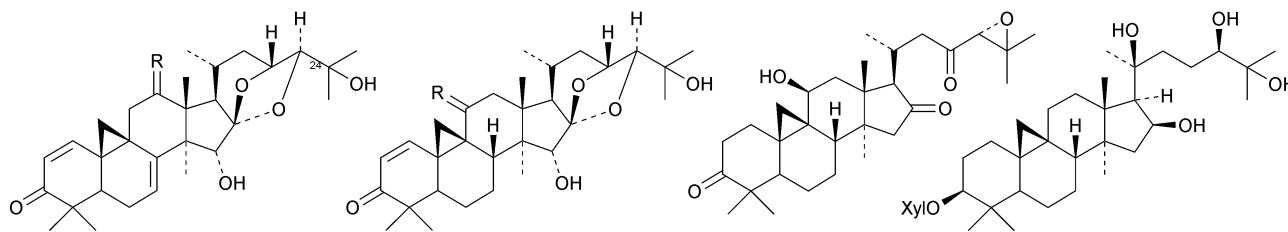
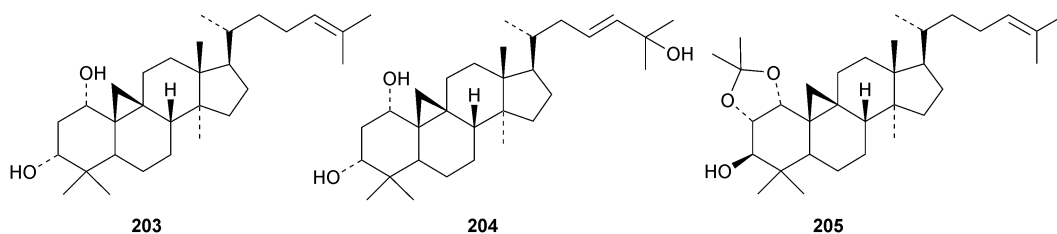
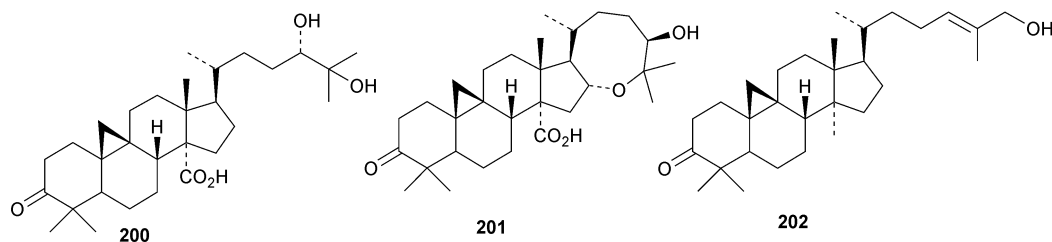




*Cassia occidentalis*,<sup>60</sup> glaucartanoic acids A **200** and B **201** from the fruit of *Caloncoba glauca*<sup>61</sup> and **202** from the leaves of *Aglaia exima*.<sup>62</sup> Compounds **203**, **204** and the acetone **205**, a likely artefact, have been obtained from the resin of *Commiphora opobalsamum*.<sup>63</sup> 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**.<sup>64</sup> 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*.<sup>65</sup> Other new compounds include the galactopyranosides **221–223**, all with new genins, from the roots



**206** R = O

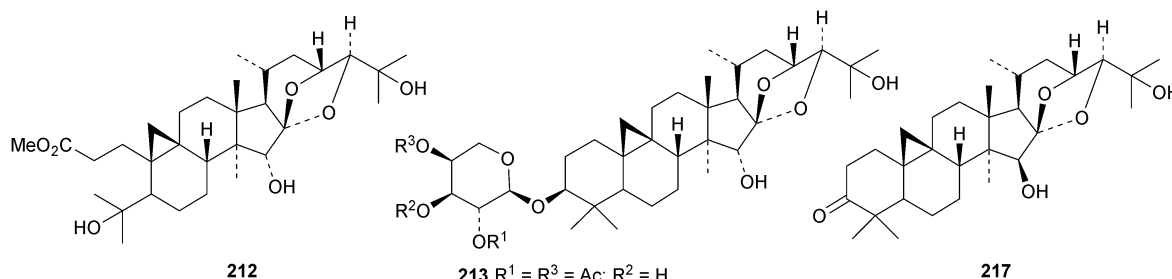
**210** R = H<sub>2</sub>; 7,8β-dihydro; 24-*epi*

**207** R = O

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

**209**

**211**



**213** R<sup>1</sup> = R<sup>3</sup> = Ac; R<sup>2</sup> = H

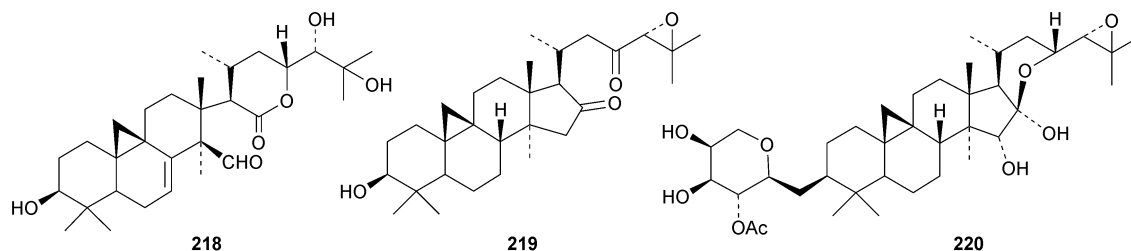
**214** R<sup>1</sup> = H; R<sup>2</sup> = R<sup>3</sup> = Ac

**215** R<sup>1</sup> = R<sup>2</sup> = H; R<sup>3</sup> = Ac

**216** R<sup>1</sup> = R<sup>3</sup> = H; R<sup>2</sup> = Ac; 25,26-anhydro

**217**



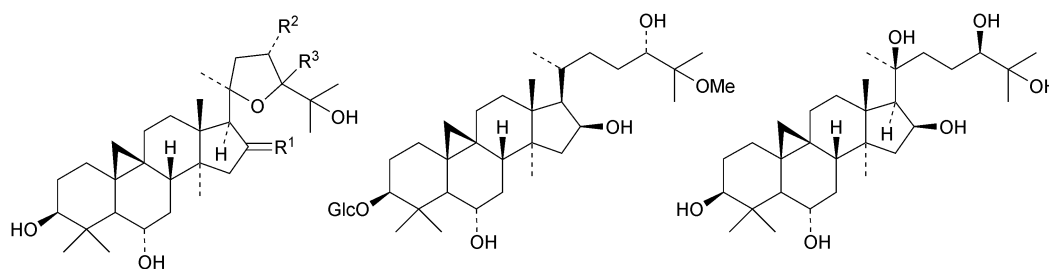
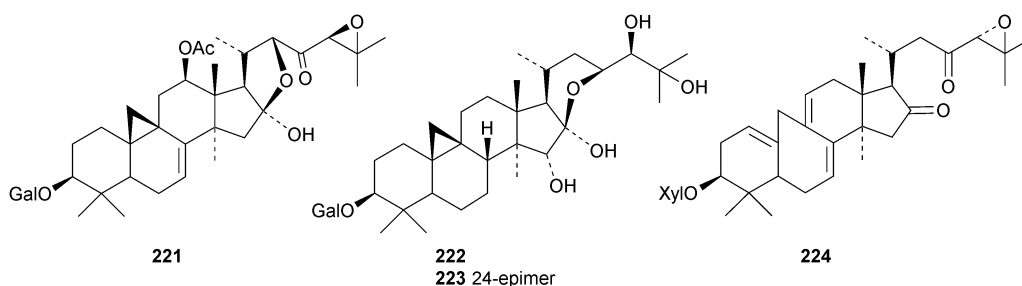


of *Cimicifuga simplex*<sup>66</sup> and isocimipodocarpaside **224** from *Cimicifuga racemosa*.<sup>67</sup>

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

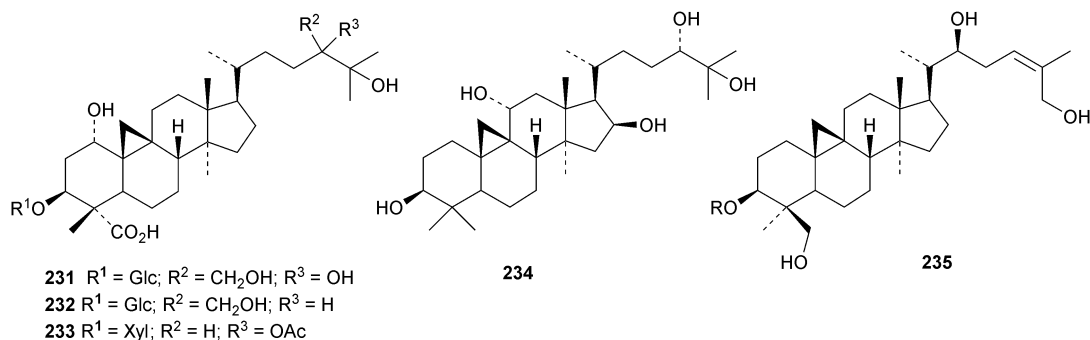
*Astragalus hareftae*,<sup>78</sup> neoastragaloside **I** from *Astragalus membranaceus*<sup>79</sup> and unnamed saponins from *Astragalus erinaceus*.<sup>80</sup>

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



- 225** R<sup>1</sup> =  $\beta$ O<sub>2</sub>CCH<sub>2</sub>OH, H; R<sup>2</sup> = H; R<sup>3</sup> =  $\alpha$ H  
**226** R<sup>1</sup> =  $\beta$ O<sub>2</sub>CCH<sub>2</sub>OH, H; R<sup>2</sup> = OH; R<sup>3</sup> =  $\alpha$ H  
**227** R<sup>1</sup> = O; R<sup>2</sup> = H; R<sup>3</sup> =  $\alpha$ H  
**228** R<sup>1</sup> =  $\beta$ OH, H; R<sup>2</sup> = H; R<sup>3</sup> =  $\beta$ H



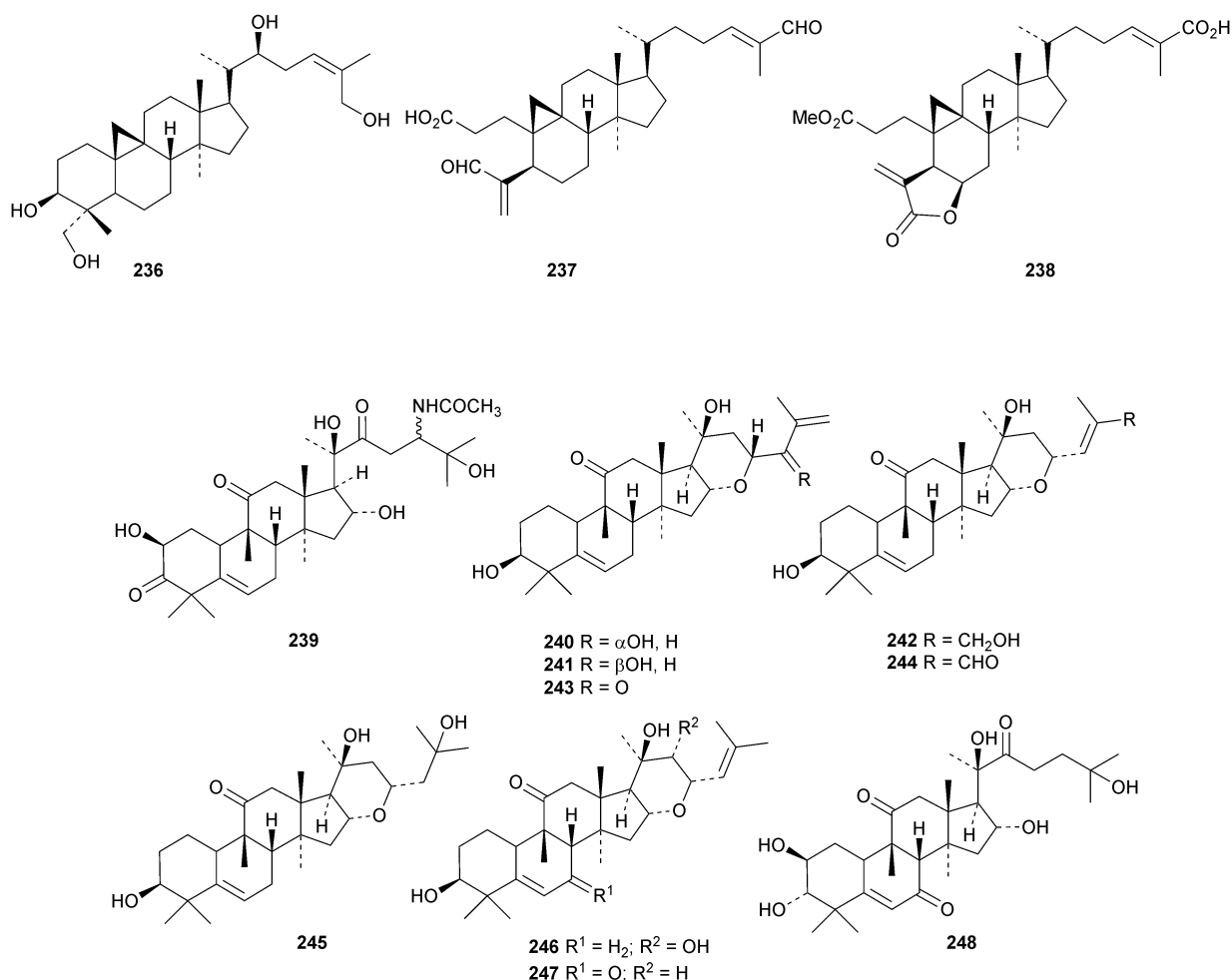


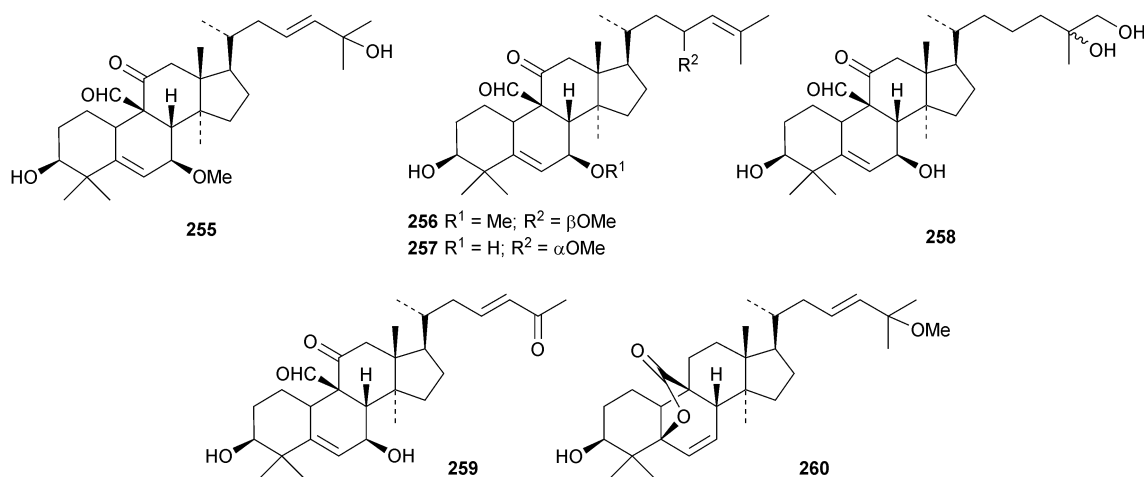
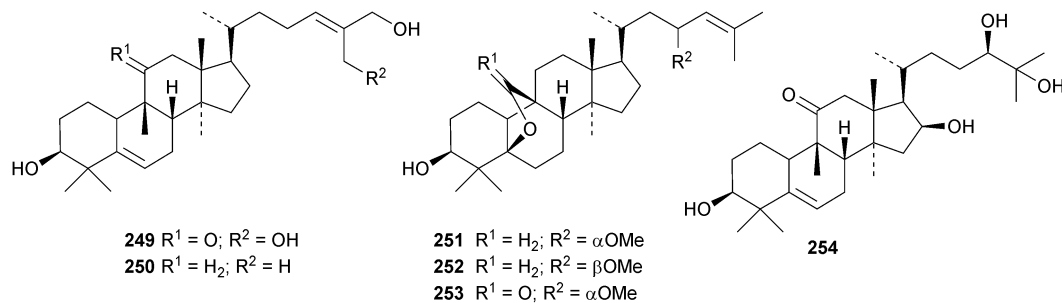
cucurbitacins and bottle gourd toxicity,<sup>90</sup> medicinally important plants of the Cucurbitaceae<sup>91</sup> and the anticancer activity of the cucurbitacins.<sup>92,93</sup>

#### 4. The dammarane group

A review of ginsenoside derivatives and their antitumour activity has been published.<sup>94</sup> New saponins from the stems and leaves of *Panax ginseng* include ginsenosides Rh<sub>14</sub>–Rh<sub>17</sub> with the new

genins **264** (Rh<sub>15</sub>) and **265** (Rh<sub>17</sub>)<sup>95</sup> and ginsenosides Rh<sub>18</sub>–Rh<sub>20</sub>.<sup>96</sup> The new genin **266** of ginsenoside Rh<sub>18</sub> was also isolated together with the dammarane **267**.<sup>96</sup> Two new saponins of 20S-protopanaxatriol have also been found in *Panax ginseng* together with the dammarane **268**.<sup>97</sup> The biological activity of an artefact **269** from the acid hydrolysate of *Panax ginseng* has been investigated.<sup>98</sup> The hexanordammarane saponin, ginsenoside R<sub>10</sub> **270**, has been isolated from the stems and leaves of *Panax quinquefolium*.<sup>99</sup>

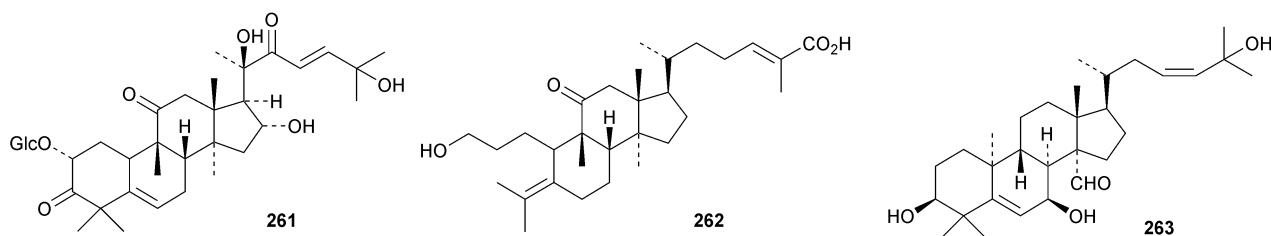


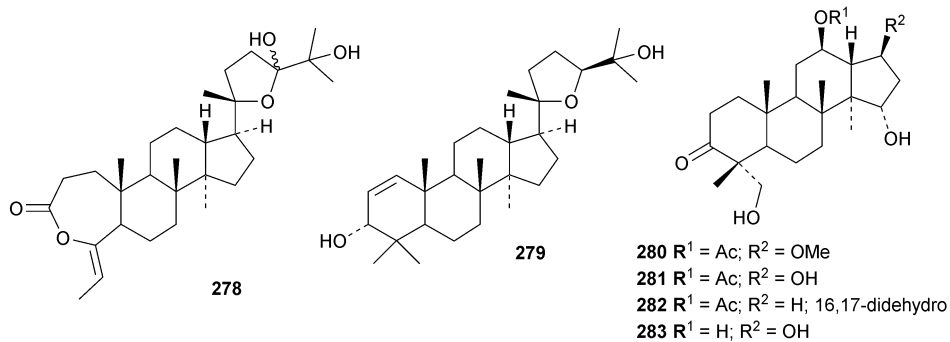
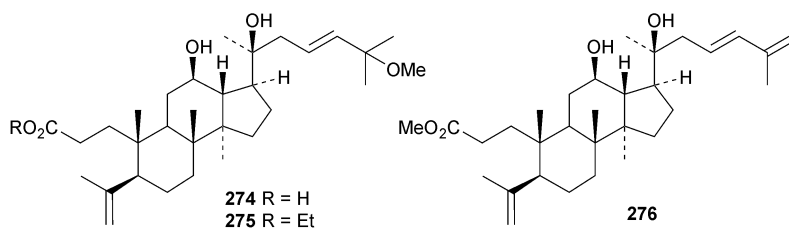
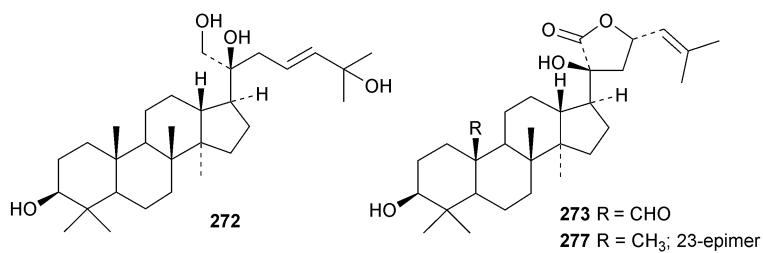
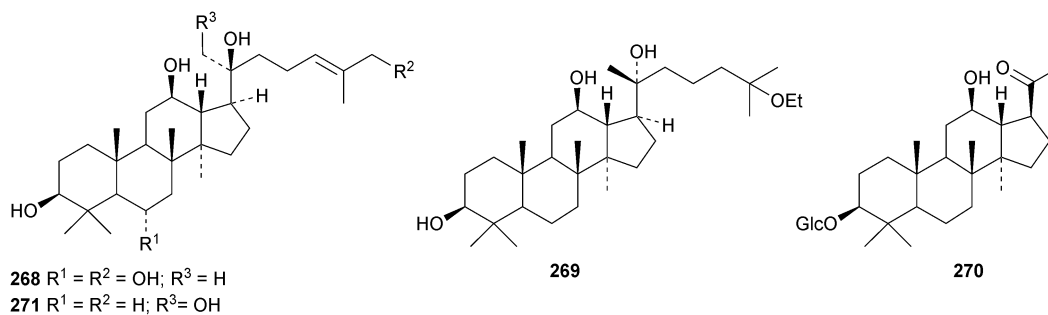
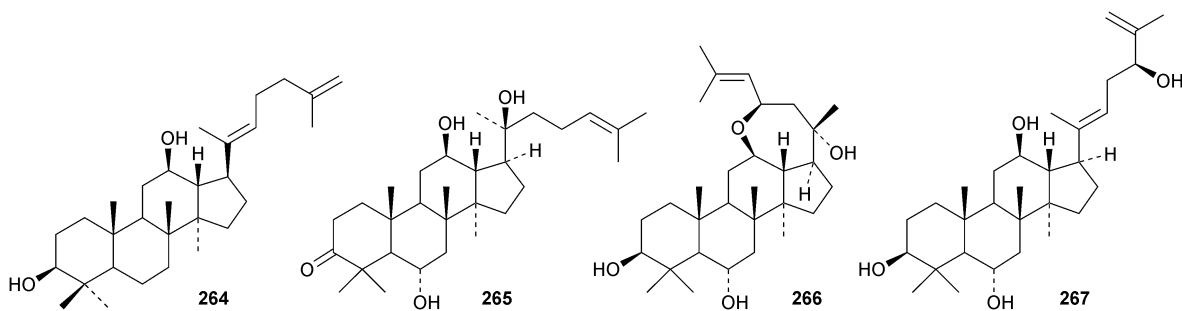


Saponins with the new genins 271 and 272 (ref. 100) and 273 (ref. 101) have been isolated from *Gynostemma pentaphyllum*. Cyclocariosides D–G, with the new genins 274 and 275, cyclocarioside H, with a known genin, and the dammarane cyclocarin A 276 are constituents of the leaves of *Cyclocarya paliurus*.<sup>102</sup> Dammarane saponins with known genins have been

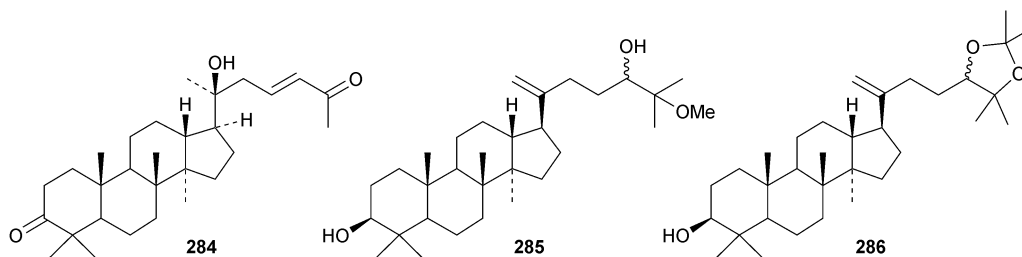
isolated from the roots of *Machilus yaoshansis*.<sup>103</sup> This paper also reports a revision the C-23 configuration of *Gynostemma pentaphylla* saponins as in 277.

New dammaranes include the rearranged aglione 278 and aglione E 279 from the bark of *Aglaia smithii*,<sup>104</sup> the *nor*-derivatives 280–283 from *Dysoxylum hainanense*,<sup>105</sup> the



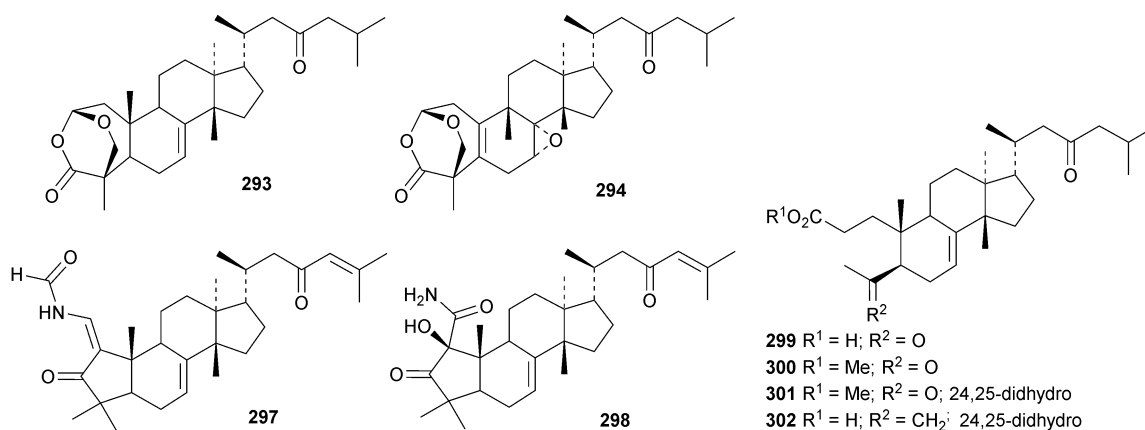
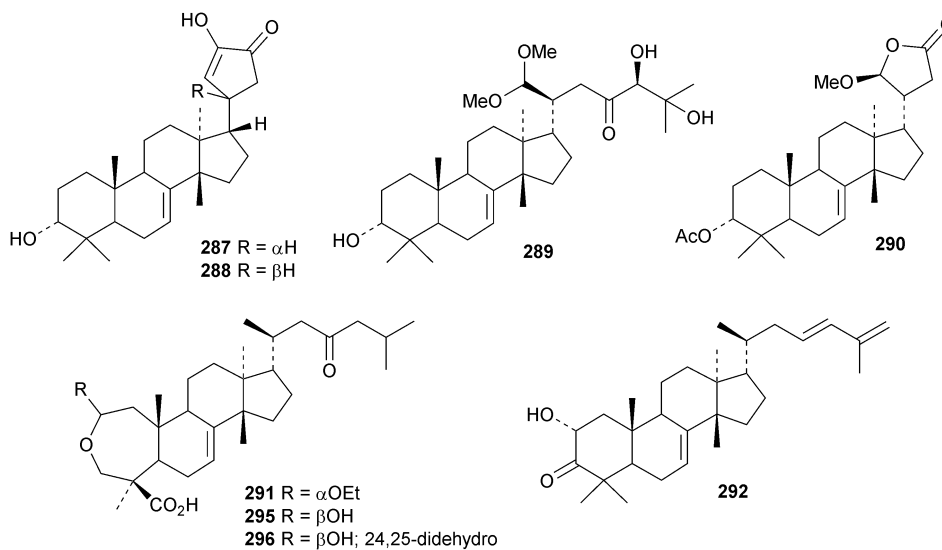


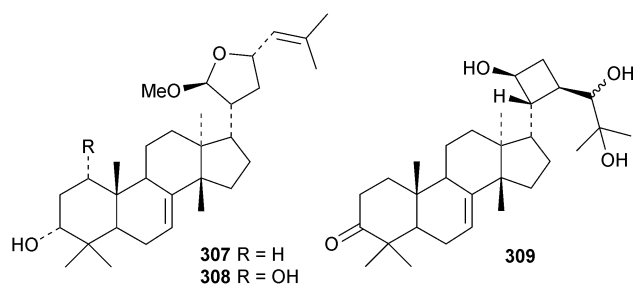
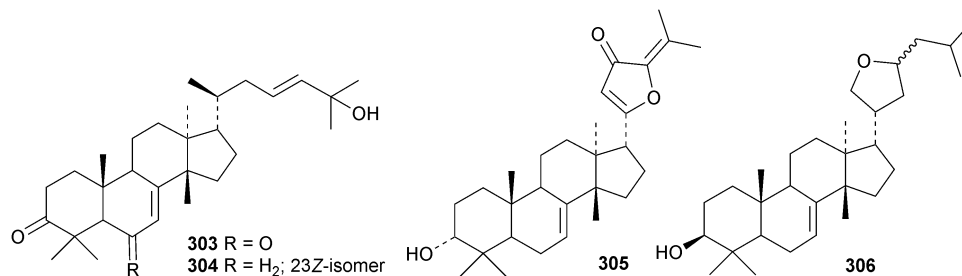




27-nor-derivative **284** from *Dipterocarpus obtusifolius*<sup>106</sup> and the two probable artefacts **285** and **286** from the leaves of *Aglaia odorata*.<sup>15</sup>

Novel dammarane saponins with known genins include acerbosides A and B from *Hovenia acerba*,<sup>107</sup> chikusetsusaponins FK<sub>1</sub>–FK<sub>7</sub>, FH<sub>1</sub>, FH<sub>2</sub>, FM and FT<sub>1</sub>–FT<sub>4</sub> from *Panax japonicus*,<sup>108,109</sup> gypenbiosides A and B from *Gynostemma*

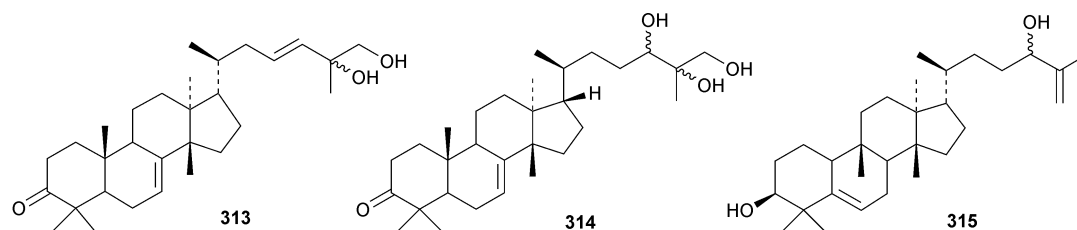
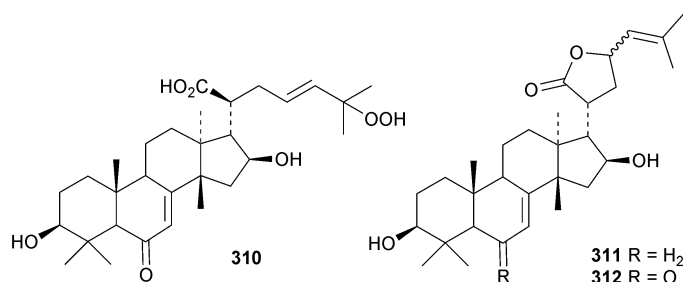


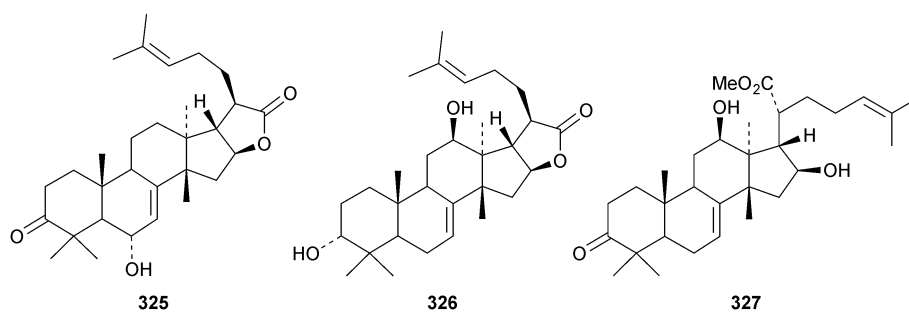
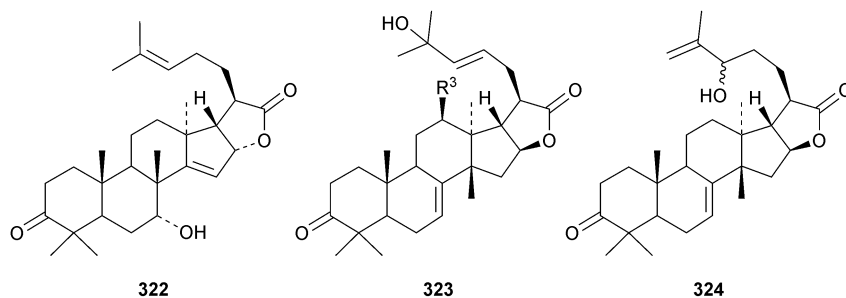
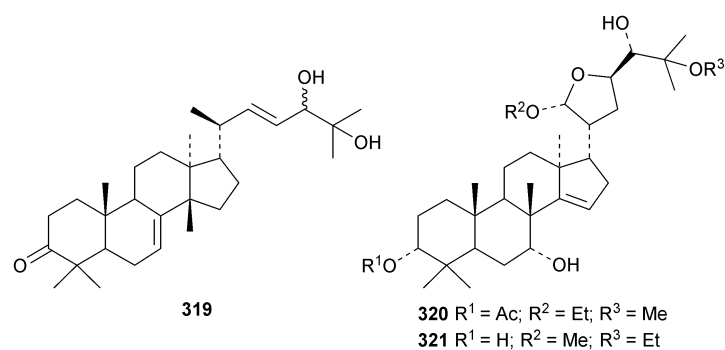
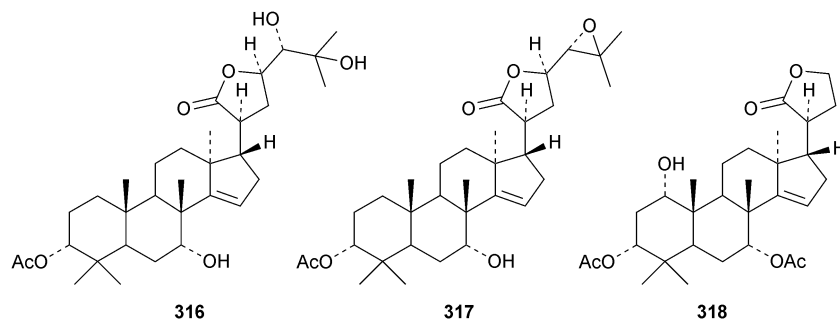


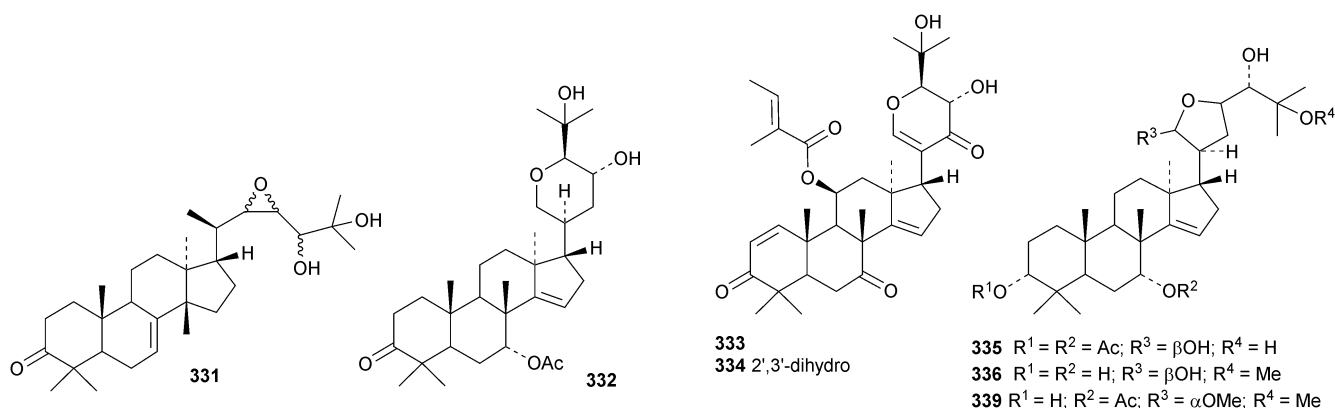
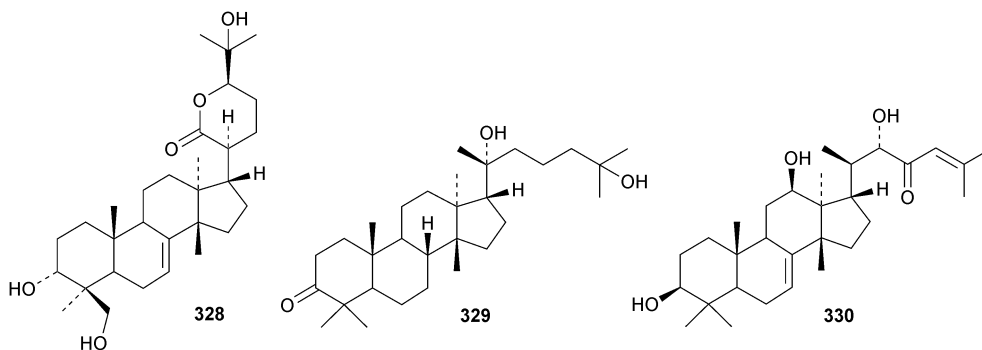
*pentaphyllum*,<sup>110</sup> 20*R*-pseudoginsenoside F<sub>11</sub> (ref. 111) and quinquenosides Ja and Jb<sup>112</sup> from *Panax quinquefolium*.

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**.<sup>114</sup> Compounds **287** and **288** were originally named apha-granins A and B, names used by the authors for previous compounds. Their names have been changed to apha-graones A and B.<sup>115</sup> Two further derivatives **291** and **292** were obtained from the leaves and twigs of *Aphanamixis grandifolia*.<sup>116</sup> Some of these compounds clearly incorporate the extraction solvent. Aphanamgrandins A **293**–**302** constitute a series of 2,3-*seco*- and 3,4-*seco*-tirucallanes from the stems of *Aphanamixis grandifolia*.<sup>117</sup> 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*,<sup>118</sup> ixoroid **306** from the flowers of *Ixora coccinea*,<sup>119</sup> **307** and **308** from the stem bark of *Araliopsis synopsis*,<sup>120</sup> capulin **309** from *Capuronianthus mahafalensis*,<sup>121</sup> **310**–**312** from the stem bark of *Melia toosendan*,<sup>122</sup> dysohainanin F **313** from *Dysoxylum hainanense*<sup>123</sup> and







24,25,26-trihydroxytirucall-7-en-3-one **314** from *Salacia hainanensis*.<sup>124</sup> The 19(10 → 9)-abeotirucallane **315** has been reported from *Euphorbia mellifera*.<sup>125</sup>

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**.<sup>128</sup> The apotirucallane **332** was also isolated from *Dysoxylum hainanense* and named dysohainanin E.<sup>123</sup> Other new apotirucallanes include piscidinones A **333** and B **334** from *Walsura trifoliata*,<sup>129</sup> agladorals A **335**–E **339** from *Aglaia odorata* var. *microphyllina*<sup>130</sup> and trichostemonate **340** from the roots of *Walsura trichostemon*.<sup>131</sup> The structure of **340** was confirmed by X-ray analysis. Toonaciliatavarins A **341**–H **348** are constituents of *Toona ciliata*.<sup>132</sup>

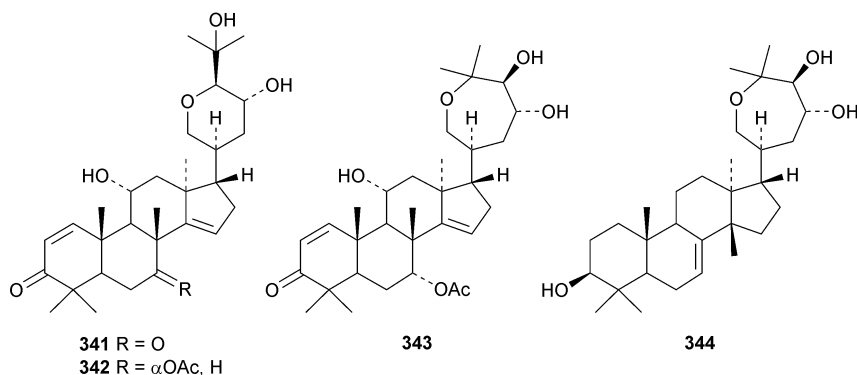
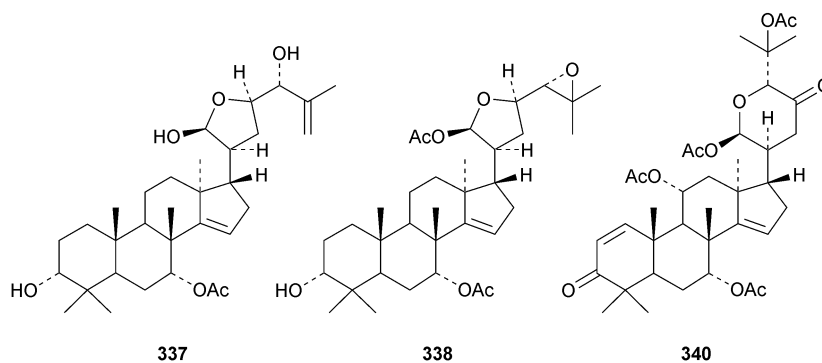
#### 4.1 Tetranortriterpenoids

A review of the structures and biological activities of limonoids from *Cipadessa* species has been published.<sup>133</sup> Walsucochinoids

A **349** and B **350** are rearranged limonoids, with an aromatic ring D, from *Walsura cochinchinensis*.<sup>134</sup> Andhraxylocarpins A **351**, B **352**, C **353** and E **354** are new skeletal types from *Xylocarpus granatum*.<sup>135</sup> 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.<sup>136</sup> 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*.<sup>137</sup> Other new structural types include citriolide A **366** from the seeds of *Citrus reticulata*,<sup>138</sup> aphanamixoid A **367** from *Aphanamixis polystachya*<sup>139</sup> and chukrasones A **368** and B **369** from *Chukrasia tabularis*.<sup>140</sup> The structure of aphanamixoid A **367** was confirmed by X-ray analysis. It was accompanied in the extract by aphanamixoid B **370**.

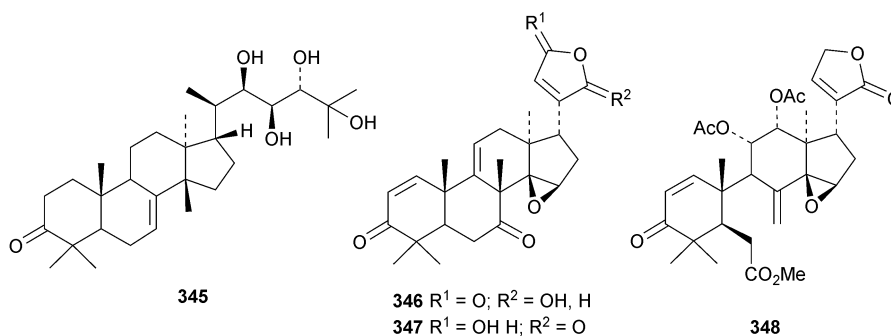
Toonayunnanins A **371**–L **382** constitute a group of assorted limonoids from the leaves of *Toona ciliata* var. *yunnanensis*.<sup>141</sup> Toonayunnanin I **378** is the same as toonaciliatin P, published in 2011. Another group of compounds, toonaciliatones B **383**–F

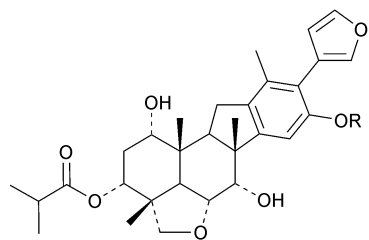




387, has been obtained from the seeds of *Toona ciliata*.<sup>142</sup> Meliatoosenins E 388, F 389, I 390, J 391, L 392–N 394 and P 395–S 398 are new compounds from the fruit of *Melia toosendan*.<sup>143</sup> Meliatoosenins G, H, K and O, claimed as new compounds, have all been published previously.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

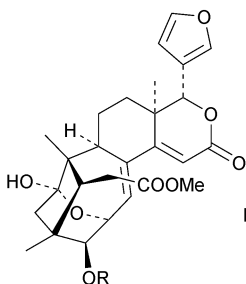
The ring A-cleaved compounds, aphanalides A 414–H 421, have been reported from the fruit of *Aphanamixis polystachya*.<sup>147</sup> The structures of aphanalides A 414 and C 416 were confirmed by X-ray analyses. Aphanagranins A 422–D 425 are constituents of *Aphanamixis grandifolia*.<sup>148</sup> Other 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.<sup>123</sup> 6-O-Deacetylseverinolide 445 is a constituent of *Atalantia buxifolia*.<sup>151</sup>





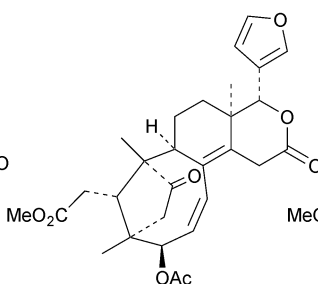
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350 R = H; 3-deacyl; 3-tigloyl

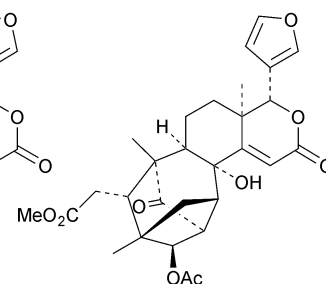


351 R = tigloyl

352 R = Ac

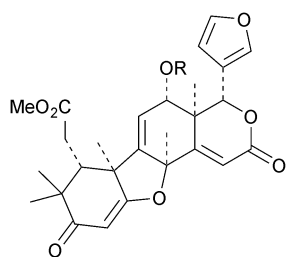


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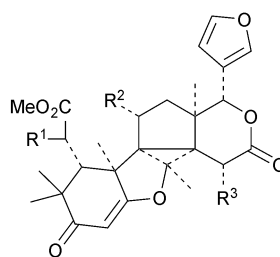
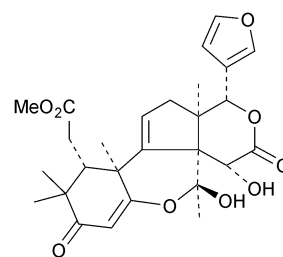
354 R = Ac

355 R = tigloyl

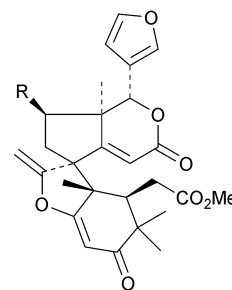


356 R = H

357 R = Ac

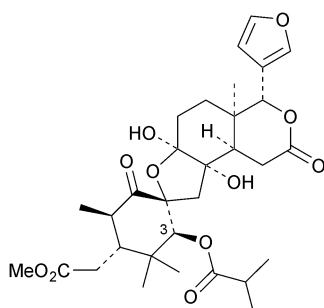
358 R<sup>1</sup> = R<sup>2</sup> = H; R<sup>3</sup> = OH359 R<sup>1</sup> = R<sup>3</sup> = OH; R<sup>2</sup> = H360 R<sup>1</sup> = OH; R<sup>2</sup> = OAc; R<sup>3</sup> = H

361



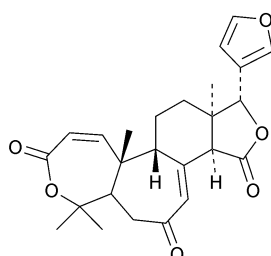
362 R = H

363 R = OH

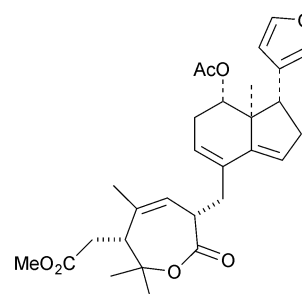


364

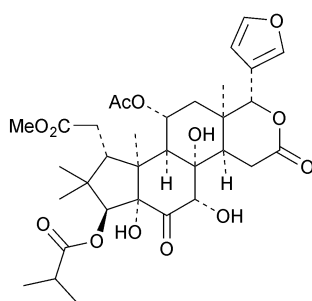
365 3-deacyl; 3-tigloyl



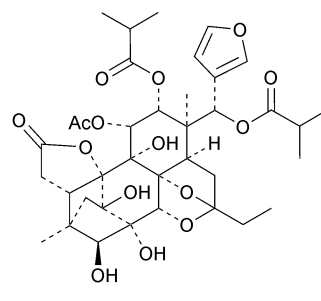
366



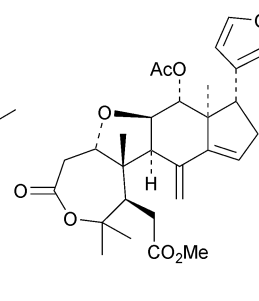
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368

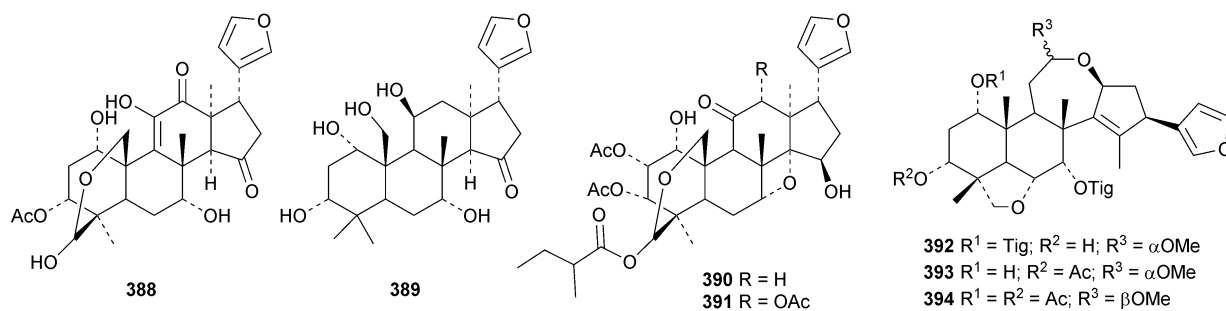
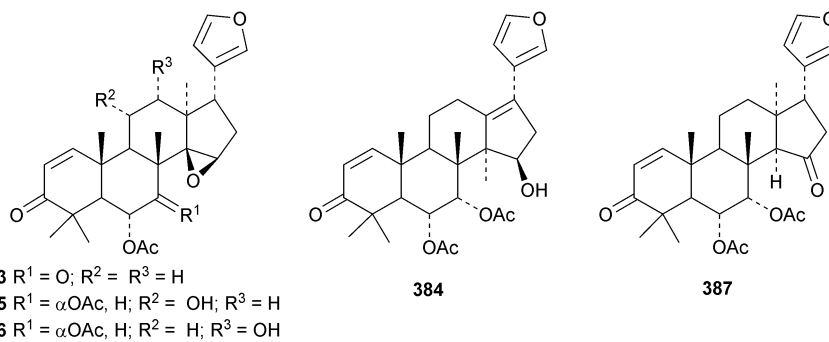
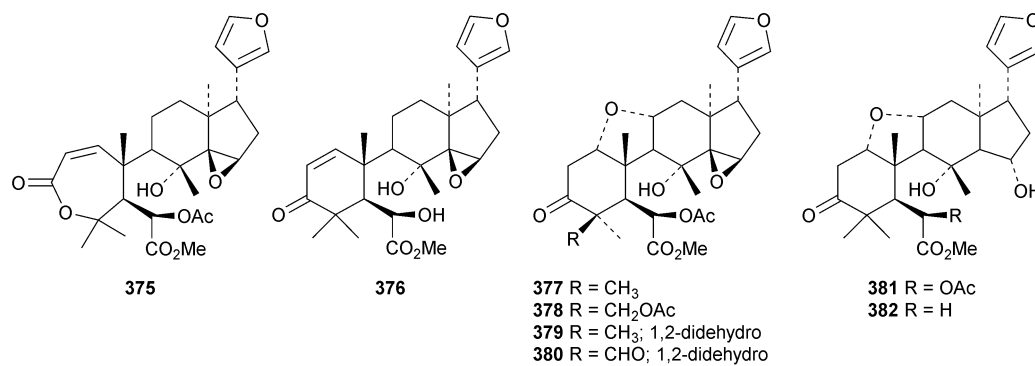
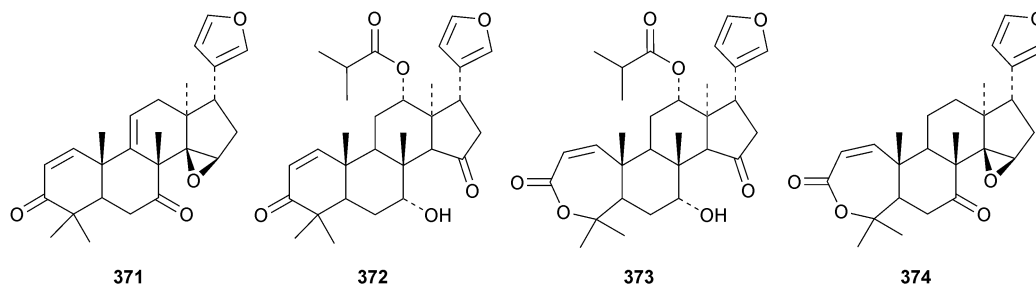


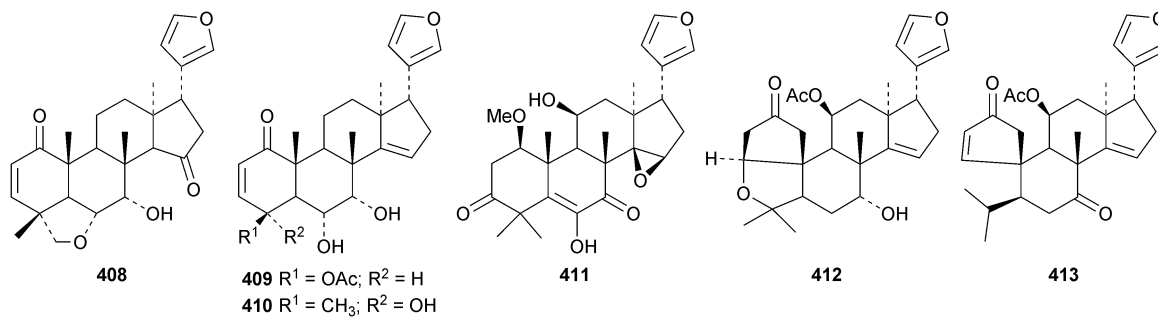
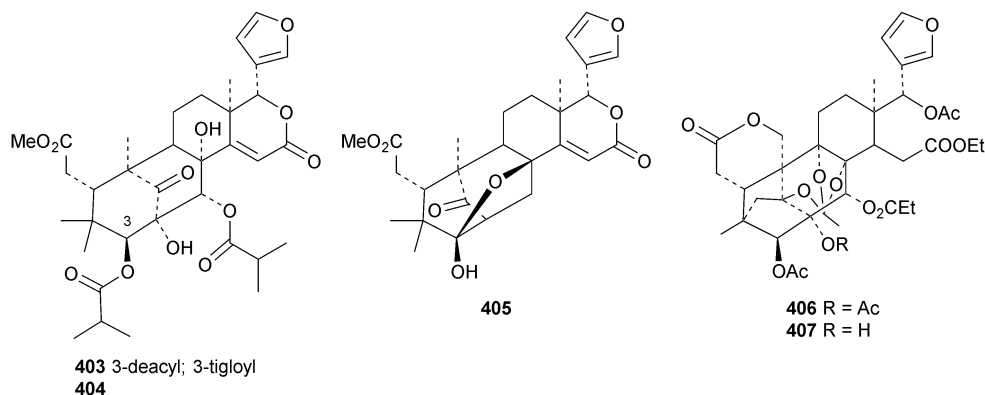
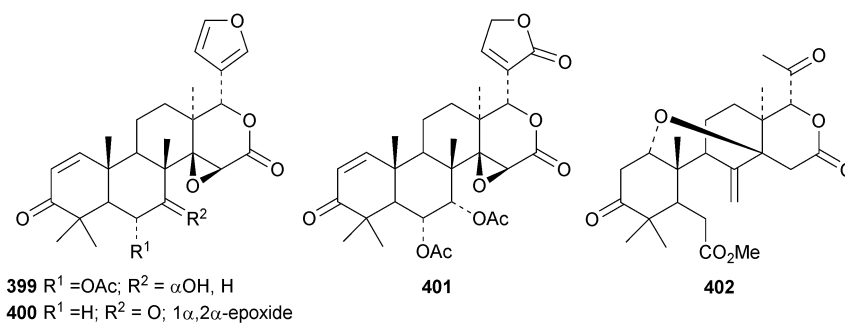
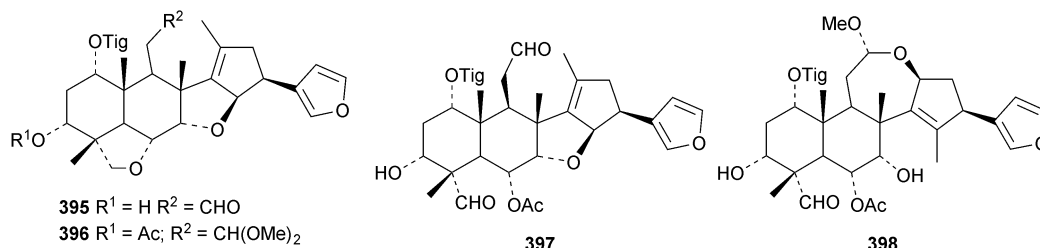
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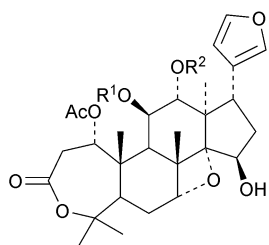
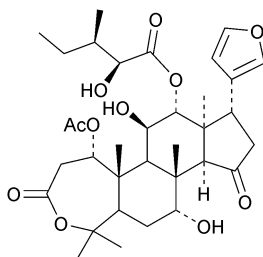
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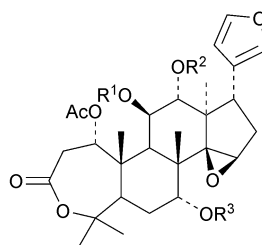
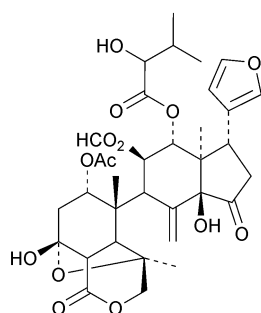




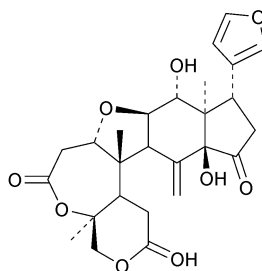


414 R<sup>1</sup> = HCO; R<sup>2</sup> = Me<sub>2</sub>CHCH<sub>2</sub>CO415 R<sup>1</sup> = H; R<sup>2</sup> = Me<sub>2</sub>CHCH<sub>2</sub>CO416 R<sup>1</sup> = H; R<sup>2</sup> = Et(Me)CHCH(OH)CO422 R<sup>1</sup> = R<sup>2</sup> = H

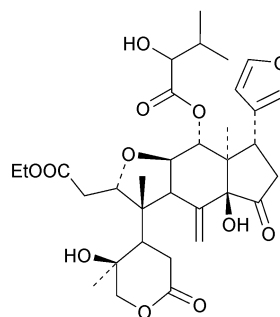
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418 R<sup>1</sup> = H; R<sup>2</sup> = Et(Me)CHCH(OH)CO; R<sup>3</sup> = H419 R<sup>1</sup> = H; R<sup>2</sup> = Et(Me)CHCH(OH)CO; R<sup>3</sup> = Ac420 R<sup>1</sup> = HCO; R<sup>2</sup> = Et(Me)CHCH(OH)CO; R<sup>3</sup> = H421 R<sup>1</sup> = HCO; R<sup>2</sup> = Me<sub>2</sub>CHCH<sub>2</sub>CO; R<sup>3</sup> = H

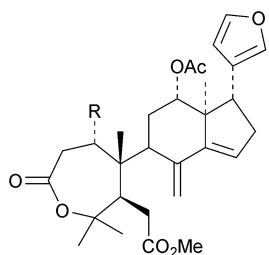
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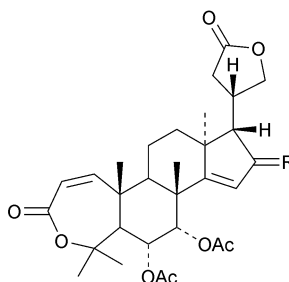


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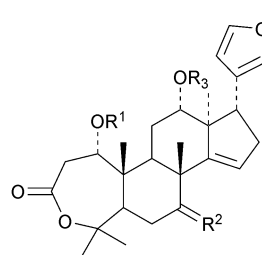
426 R = OAc

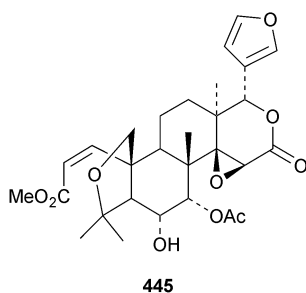
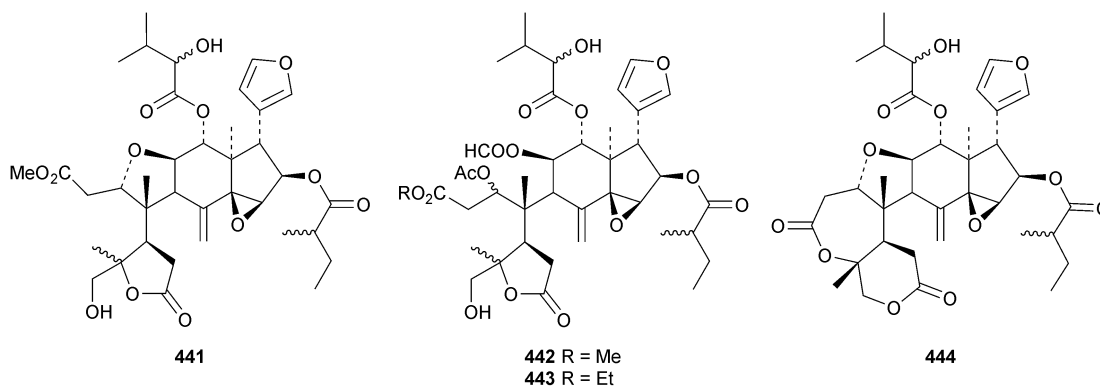
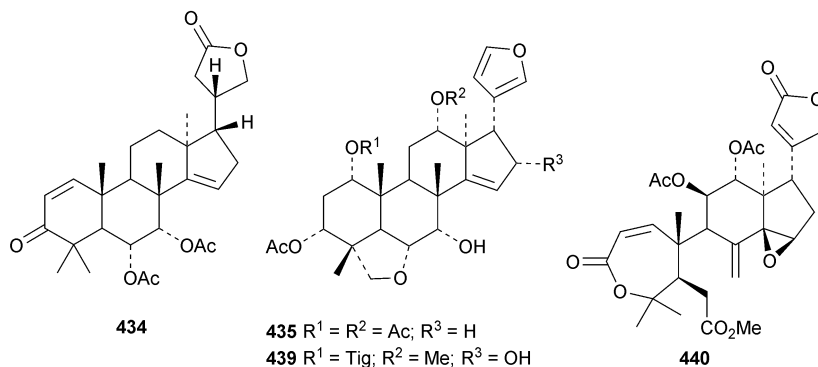
427 R = H; 1,2-didehydro

428 R = H<sub>2</sub>; 14β,15β-epoxide429 R = H<sub>2</sub>

430 R = O

431 R = βOOH, H

432 R<sup>1</sup> = R<sup>3</sup> = Ac; R<sup>2</sup> = O433 R<sup>1</sup> = R<sup>3</sup> = Ac; R<sup>2</sup> = αOH, H436 R<sup>1</sup> = Ac; R<sup>2</sup> = αOAc, H; R<sup>3</sup> = Et(Me)CHCH(OH)CO437 R<sup>1</sup> = R<sup>3</sup> = Ac; R<sup>2</sup> = αOAc, H438 R<sup>1</sup> = R<sup>3</sup> = Ac; R<sup>2</sup> = αOTig, H



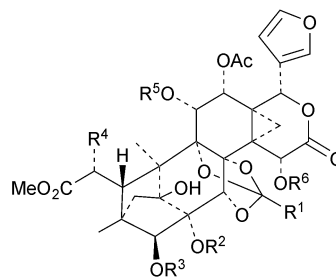
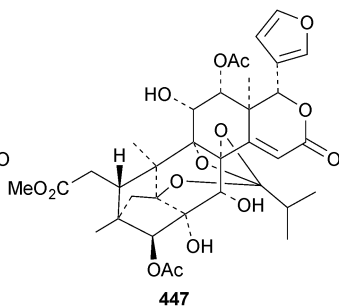
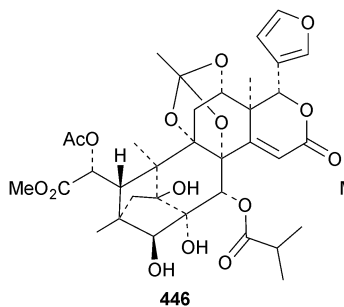
The seemingly unending flow of phragmalin/busein derivatives and variants continues and is matched only by the proliferation of confusing trivial names. These points are well illustrated by *Chukrasia tabularis* and *Chukrasia tabularis* var. *velutina*, the sources of chubularisins A 446–R 463,<sup>152</sup> chuktabrins C 464–J 471 and chuktubararins U 472–X 475,<sup>153</sup> tabulalins G 476–I 478,<sup>154</sup> chukvelutins D 479–F 481 (ref. 155) and R310B8 482 and velutinalides A 483 and B 484.<sup>156</sup>

Chabularisin O 460 is the same as chuktubarin 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*.<sup>157</sup> Other new compounds in this group include hisomicines D 494 and E 495 from *Chisocheton ceramicus*,<sup>158</sup> malayanines A 496 and B 497 from *Chisocheton erythrocarpus*,<sup>159</sup> senegalensins A 498–C 500 from *Khaya senegalensis*,<sup>160</sup> kotschyins D 501–H 505 from *Pseudocedrela kotschy*,<sup>161</sup> soymidins A 506 and B 507 from *Soymida febrifuga*<sup>162</sup> and swietenin J 508 from *Swietenia macrophylla*.<sup>163</sup> Five new mexicanolide derivatives, heytrijunolides A 509–E 513, have been obtained from *Heynea trijuga*.<sup>164</sup> Mollucensins R 514–Y 521 are new mexicanolide and phragmalin derivatives from the seeds of *Xylocarpus moluccensis*.<sup>165</sup>

## 4.2 Quassinoids

The compounds isolated from *Brucea javanica* and their pharmacology have been reviewed.<sup>166</sup> 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



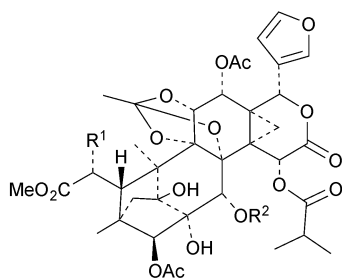


**449**  $R^1 = \text{Me}; R^2 = \text{EtCO}; R^3 = \text{Ac}; R^4 = R^5 = \text{H}; R^6 = \text{iPrCO}$

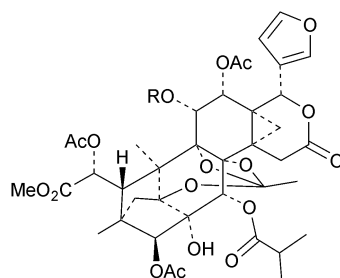
**450**  $R^1 = \text{Me}; R^2 = \text{iPrCO}; R^3 = \text{Ac}; R^4 = R^5 = \text{H}; R^6 = \text{iPrCO}$

**451**  $R^1 = \text{iPr}; R^2 = R^5 = R^6 = \text{H}; R^3 = \text{Ac}; R^4 = \text{OAc}$

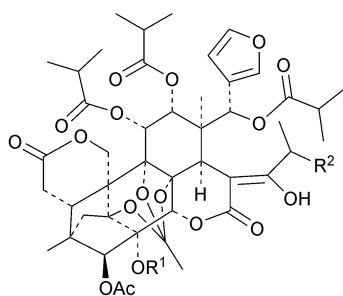
**452**  $R^1 = \text{iPr}; R^2 = \text{H}; R^3 = \text{Ac}; R^4 = \text{OAc}; R^5 = R^6 = \text{Ac}$



**454**  $R^1 = \text{H}; R^2 = \text{EtCO}$

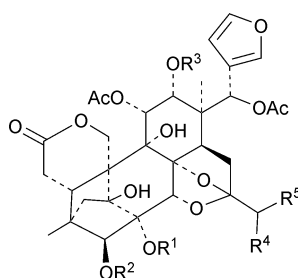


**456**  $R = \text{H}$



**458**  $R^1 = \text{Ac}; R^2 = \text{CH}_3$

**459**  $R^1 = \text{Ac}; R^2 = \text{H}$

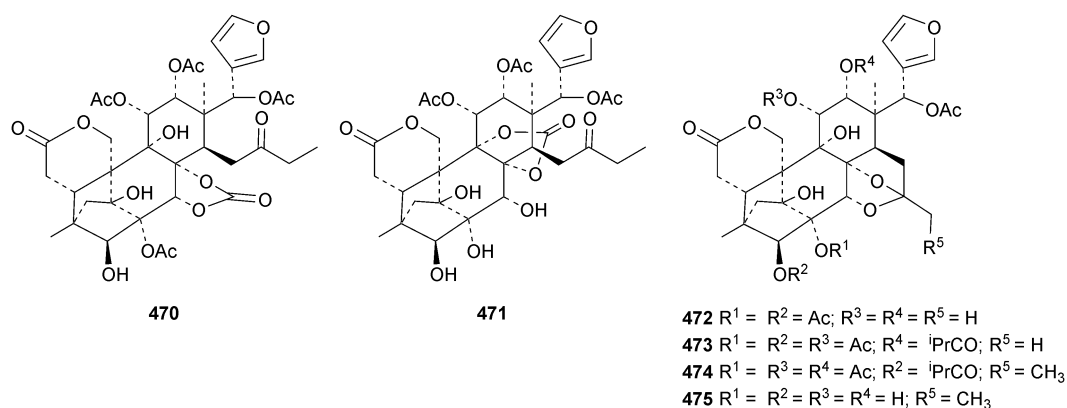
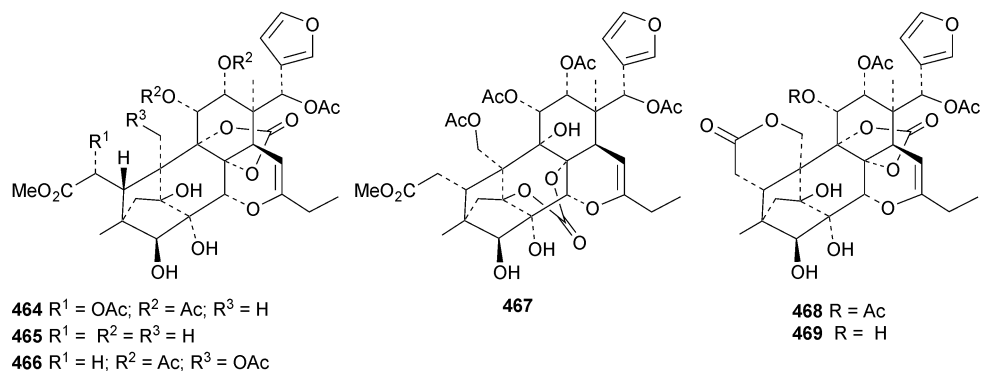


**461**  $R^1 = \text{H}; R^2 = \text{Ac}; R^3 = \text{EtCO}; R^4 = \text{Me}; R^5 = \text{H}$

**462**  $R^1 = \text{Ac}; R^2 = \text{H}; R^3 = \text{iPrCO}; R^4 = \text{Me}; R^5 = \text{H}$

**463**  $R^1 = \text{H}; R^2 = \text{Ac}; R^3 = \text{Ac}; R^4 = \text{Me}; R^5 = \text{Me}$

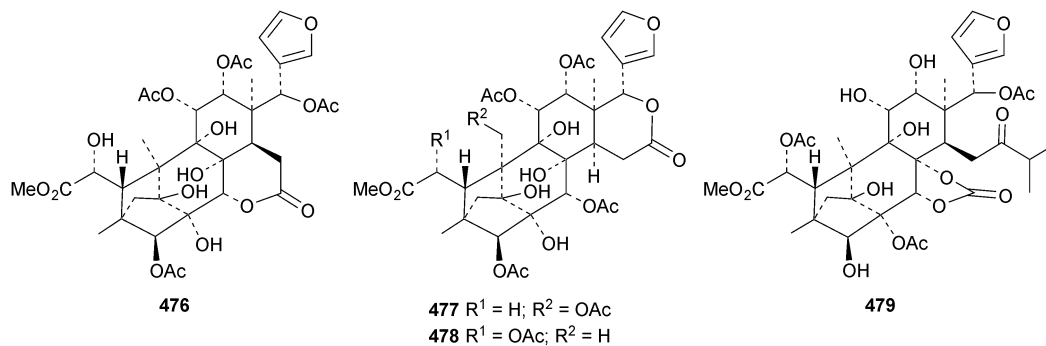


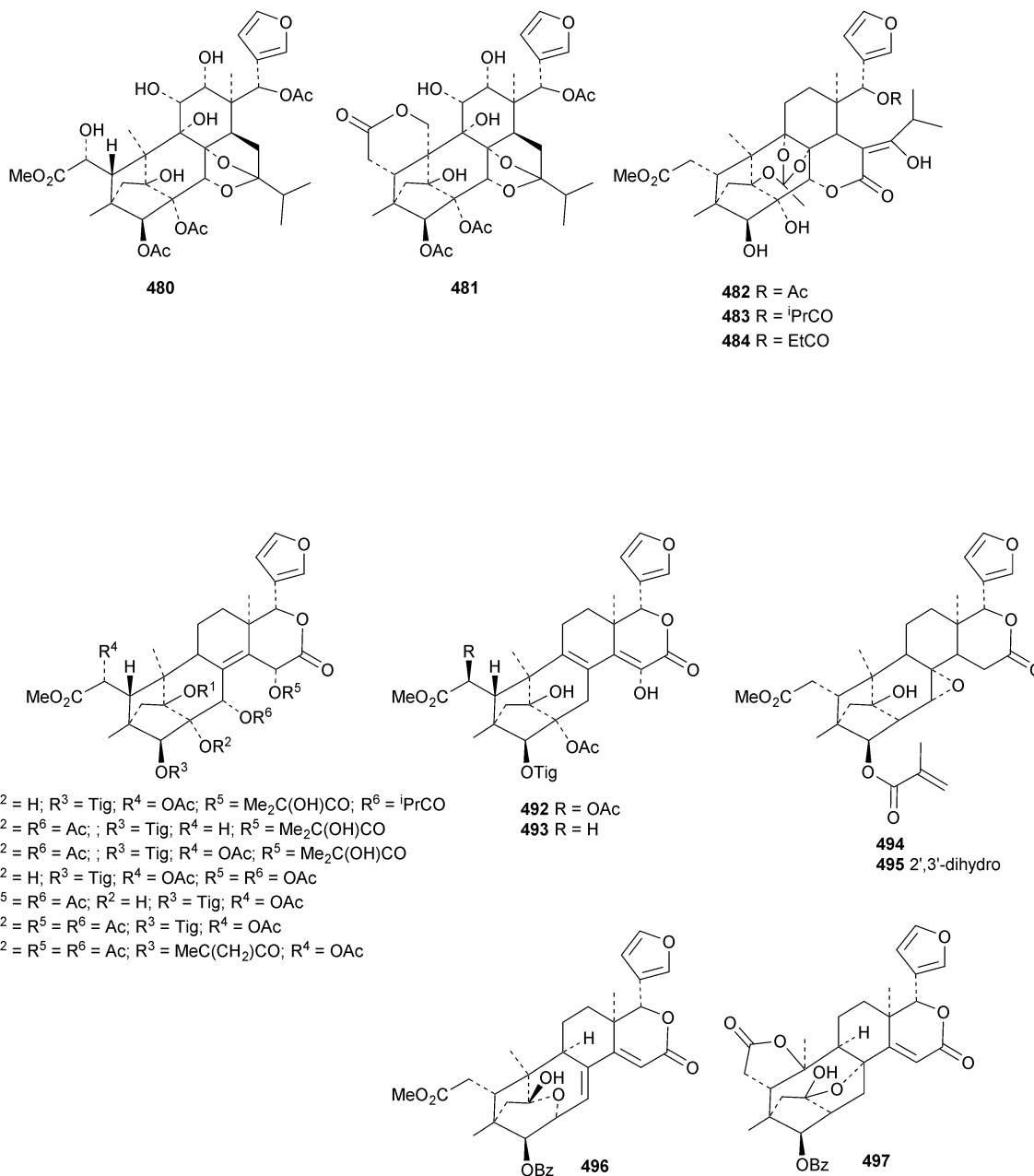


seeds of *Brucea javanica*.<sup>167</sup> Other new quassinoids include picrasin K 528 from *Quassin amara*<sup>168</sup> and odyendanol 529 from the fruit of *Odyendyca gabonensis*.<sup>169</sup>

## 5. The lupane group

Reviews covering the sources and biological properties of betulinic acid<sup>170</sup> and the antineoplastic effects of lupeol<sup>171</sup> have



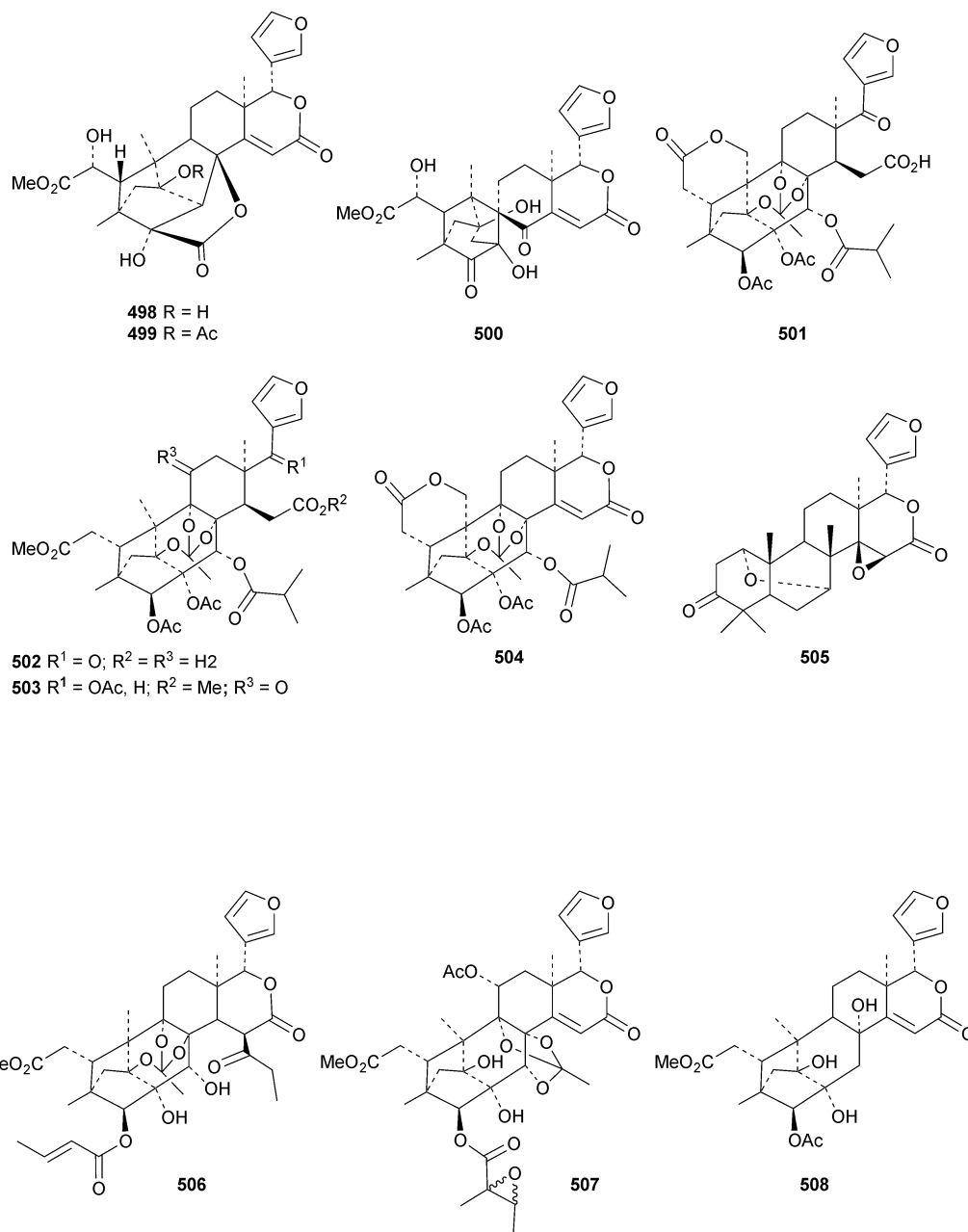


appeared. The 3,4-secolupane derivatives acanthosessiligenins I 530 and II 531 and acanthosessiliosides A 532–F 537 have been isolated from the fruit of *Acanthopanax sessiliflorus*.<sup>172</sup> The 17,18-secolupane 538 has been found in the roots of *Taraxacum platycarpum* together with 3 $\beta$ -acetoxyilup-18-en-21-one 539, the neolupane derivatives 540–542 and the migrated lupane 543.<sup>173</sup> Lup-20(29)-ene-2 $\beta$ ,3 $\beta$ -diol 544 is a constituent of *Salacia hainanensis*<sup>124</sup> and the related ketones 545 and 546 have been found in *Fagus hayatae*.<sup>174</sup> Other simple lupane derivatives include glochitriol 547 from *Glochidion lanceolarium*,<sup>175</sup> bengalensinone

548 from *Ficus bengalensis*,<sup>176</sup> 3 $\beta$ -hydroxylupane-28,29-dioic acid 549 from *Aglaia duperreana*<sup>177</sup> and the norlupane derivatives 550, 551 and 552 from *Dipterocarpus obtusifolius*.<sup>106</sup>

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



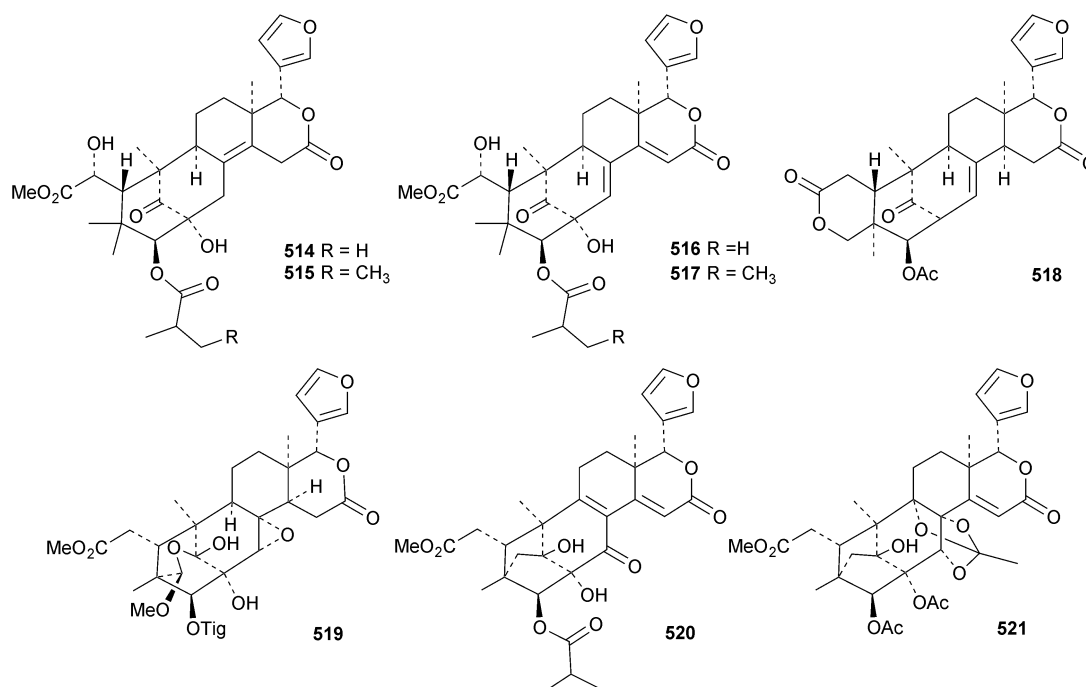
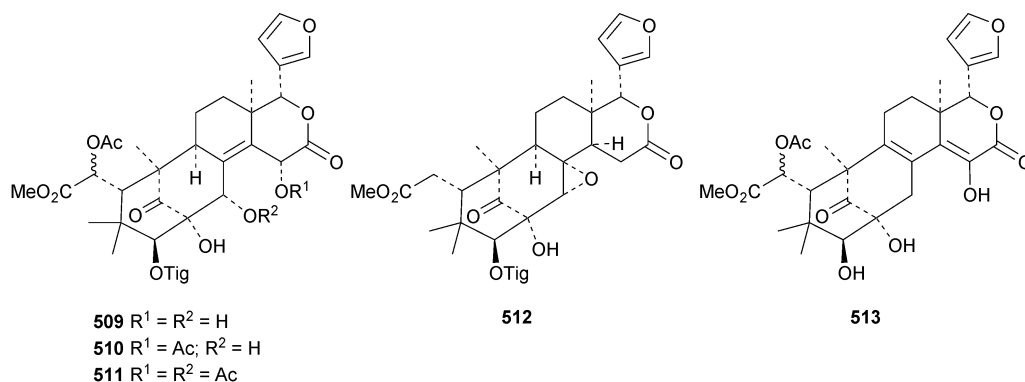


Oleanderocioic acid **554**, a lupane ester with the unusual *cis*-4-acetylcinnamic acid, is claimed to be a constituent of *Nerium oleander*.<sup>183</sup> Other new lupane esters include the nonanoyl ester of lupeol **555** from *Dorstenia harmsiana*,<sup>184</sup> kurramanoic acid **556** from *Nepeta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

## 6. The oleanane group

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



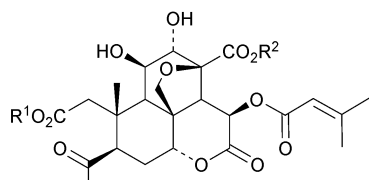
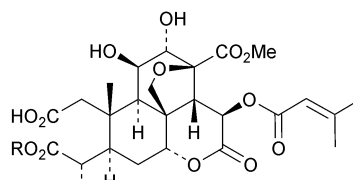


566, from *Pyrenacantha kaurabassana*, has the unusual  $18\alpha H$ -configuration.<sup>193</sup> Zizimauritic acids A 567, B 568 and C 569 are ring-A contracted 20,21-secooleanane derivatives from *Ziziphus mauritiana*.<sup>194</sup> The zizimauritic acids also have the  $18\alpha H$ -configuration. A ring-E contracted oleanane derivative 570 has been isolated from the bark of *Diospyros decandra*.<sup>195</sup> Platycodonoids A 571 and B 572 are 28-noroleanane derivatives from the roots of *Platycodon grandiflorum*.<sup>196</sup> 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*.<sup>197</sup> Further noroleanane derivatives include

30-noroleanolic acid 576 from *Olea europea*,<sup>198</sup> the 24,30-dinor derivatives 577 and 578 and the 24-nor compounds 579 and 580 from the roots of *Paeonia emodi*<sup>199</sup> and 581 from *Pilea cavaleriei*.<sup>200</sup> 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.<sup>201</sup>

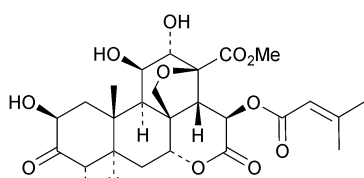
Several olean-18-ene derivatives have been identified including olean-18-ene- $1\beta,2\alpha,3\beta$ -triol 588 from *Salvia atropatana*,<sup>202</sup> 589–596 from *Cassine xylocarpa*, 597 from *Maytenus jelskii*,<sup>203</sup> olean-18-ene- $1\alpha,3\beta$ -diol 598 from *Juglans sinensis*<sup>204</sup> and  $2\alpha,3\alpha,24$ -trihydroxyolean-18-en-28-oic acid 599 from



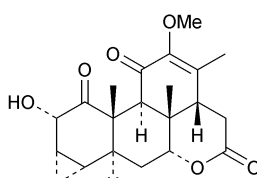
522 R<sup>1</sup> = H; R<sup>2</sup> = Me523 R<sup>1</sup> = R<sup>2</sup> = H524 R<sup>1</sup> = R<sup>2</sup> = Me

525 R = H

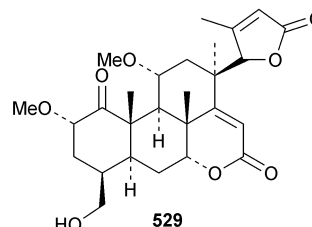
526 R = Me



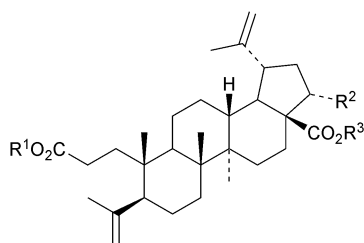
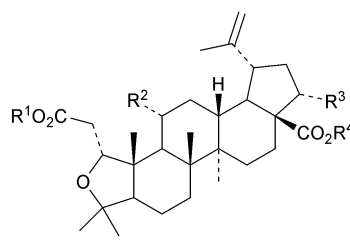
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528



529

530 R<sup>1</sup> = Me; R<sup>2</sup> = OH; R<sup>3</sup> = H531 R<sup>1</sup> = R<sup>2</sup> = H; R<sup>3</sup> = Glc532 R<sup>1</sup> = Me; R<sup>2</sup> = OH; R<sup>3</sup> = R<sup>4</sup> = H533 R<sup>1</sup> = Me; R<sup>2</sup> = OH; R<sup>3</sup> = H; R<sup>4</sup> = Glc534 R<sup>1</sup> = Me; R<sup>2</sup> = R<sup>3</sup> = OH; R<sup>4</sup> = Glc535 R<sup>1</sup> = Glc; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H536 R<sup>1</sup> = R<sup>2</sup> = H; R<sup>3</sup> = OH; R<sup>4</sup> = Glc

*Eucalyptus exserta*.<sup>205</sup> 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**.<sup>206</sup> Other new simple oleanane derivatives include pseuderranic acid **604** from *Pseuderanthemum carruthersii*,<sup>207</sup> punicaone **605** from *Punica granatum*,<sup>208</sup> turformosinic acid **606** from *Turpinia formosana*,<sup>209</sup> 3 $\beta$ ,23,28-trihydroxyolean-12-en-11-one **607** from *Aster yomena*,<sup>210</sup> 3 $\alpha$ ,29-dihydroxyolean-12-ene-23,28-dioic acid **608** from *Schefflera farinosa*,<sup>211</sup> oleana-9(11),12-diene-1 $\beta$ ,3 $\beta$ -diol **609** from *Salvia xanthocheila*,<sup>212</sup> 1-*epi*-castanopsol **610** from *Simira glaziovii*,<sup>213</sup> the 29,22-olide **611** from *Celastrus orbiculatus*<sup>214</sup> and the epoxy aldehyde **612** from *Tetraena mongolica*.<sup>215</sup>

New oleanane esters include the caffeoyl derivatives **613–615**, from *Tetraena mongolica*,<sup>215</sup> the coumaroyl ester **616** from *Rubia schumanniana*,<sup>216</sup> the feruloyl ester **617** from *Saniculiphyllum guangxiense*,<sup>85</sup> the palmitates **618** from *Anemone rivularis*,<sup>217</sup> **619** from *Barringtonia asiatica*<sup>218</sup> and **620** from *Lobelia sessilifolia*.<sup>219</sup> Four esters **621–624** of the 19(18  $\rightarrow$  17)-*abeo*-28-

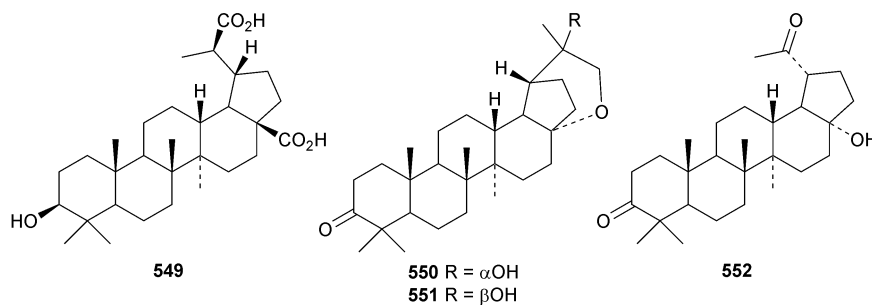
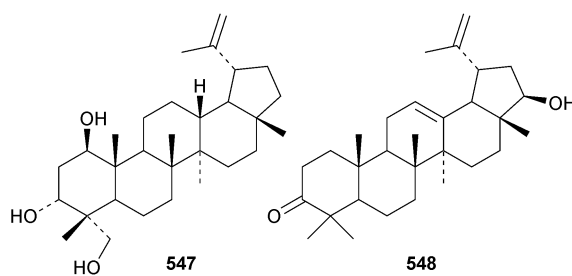
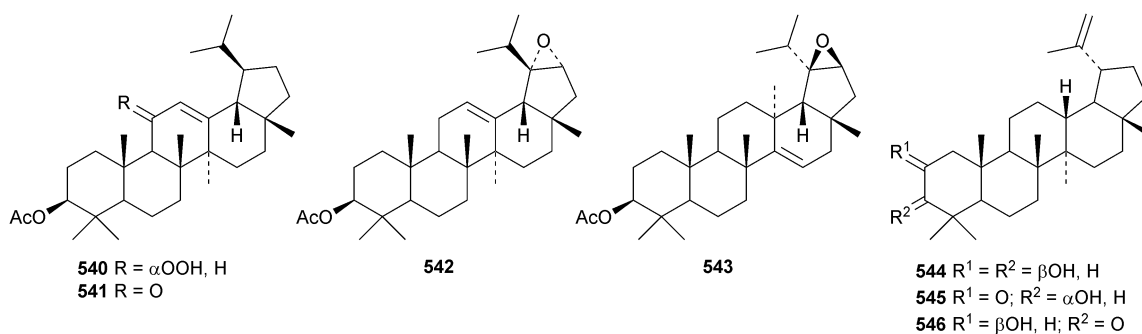
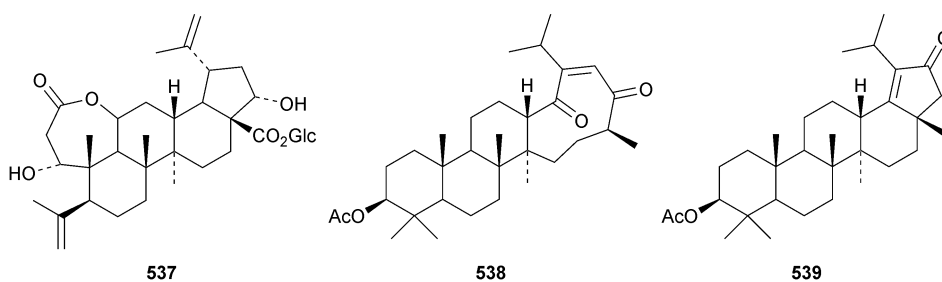
noroleanane phlomstetraol B have been isolated from *Leonurus heterophyllum*.<sup>220</sup>

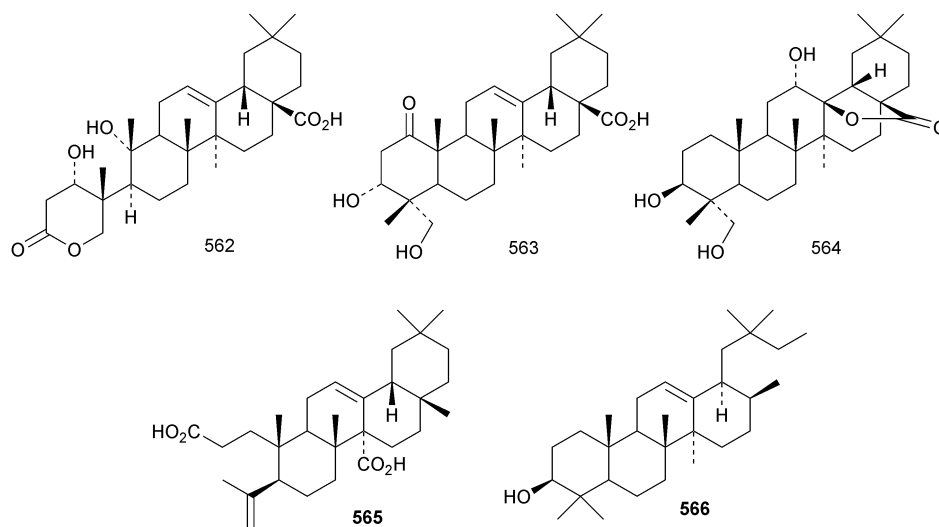
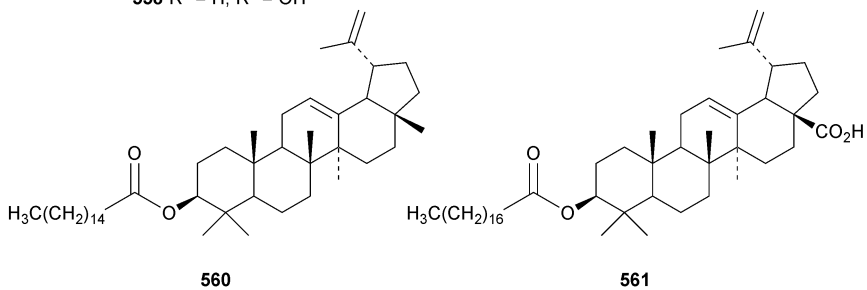
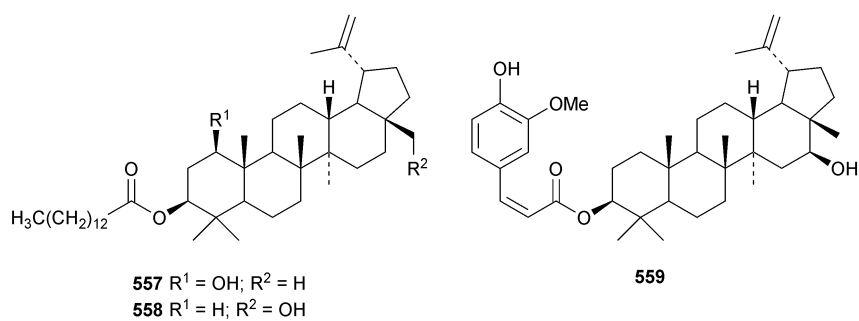
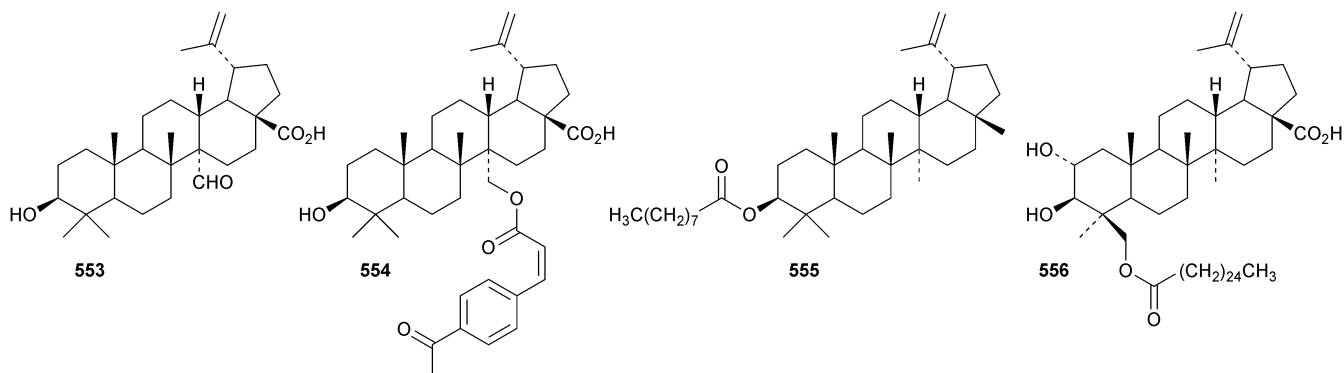
Two oleanane saponins, with the new genin olean-12-ene-2 $\beta$ ,15 $\alpha$ ,23-triol **625**, have been isolated from *Ammannia auriculata*.<sup>221</sup> Antoniosides E–J are oleanane saponins from *Antonia ovata*.<sup>222</sup> Antoniosides E–H have new genins that are esters of olean-12-ene-3 $\beta$ ,15 $\alpha$ ,16 $\alpha$ ,21 $\beta$ ,22 $\alpha$ ,23,28-heptol **626**. Sorbifoliasides G–J, from *Xanthoceras sorbifolia*, have known genins and sorbifoliaside K has the new genin oleana-12,15-diene-3 $\beta$ ,21 $\beta$ ,22 $\alpha$ ,28-tetrol **627**.<sup>223</sup> A variety of new 30-noroleanane genins, **628–631**, are included in akemisaponins A–K from *Akebia trifoliata*.<sup>224</sup> Two saponins from *Camellia japonica* have been assigned the names camelliosides E and F that have been used previously.<sup>225</sup> Camellioside E has the new genin 28-norolean-12-ene-3 $\beta$ ,16 $\alpha$ ,17 $\beta$ -triol **632**. Four saponins have been isolated from *Astragalus angustifolius* including the new genin olean-12-ene-3 $\beta$ ,21 $\beta$ ,22 $\alpha$ ,24,29-pentol **633**.<sup>68</sup>

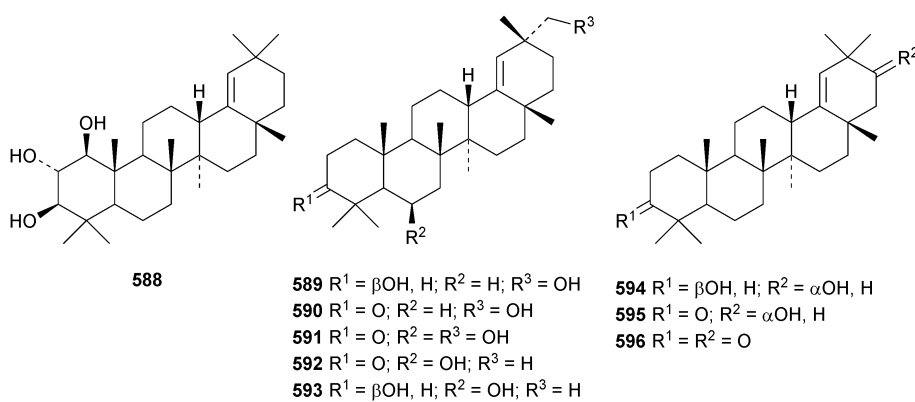
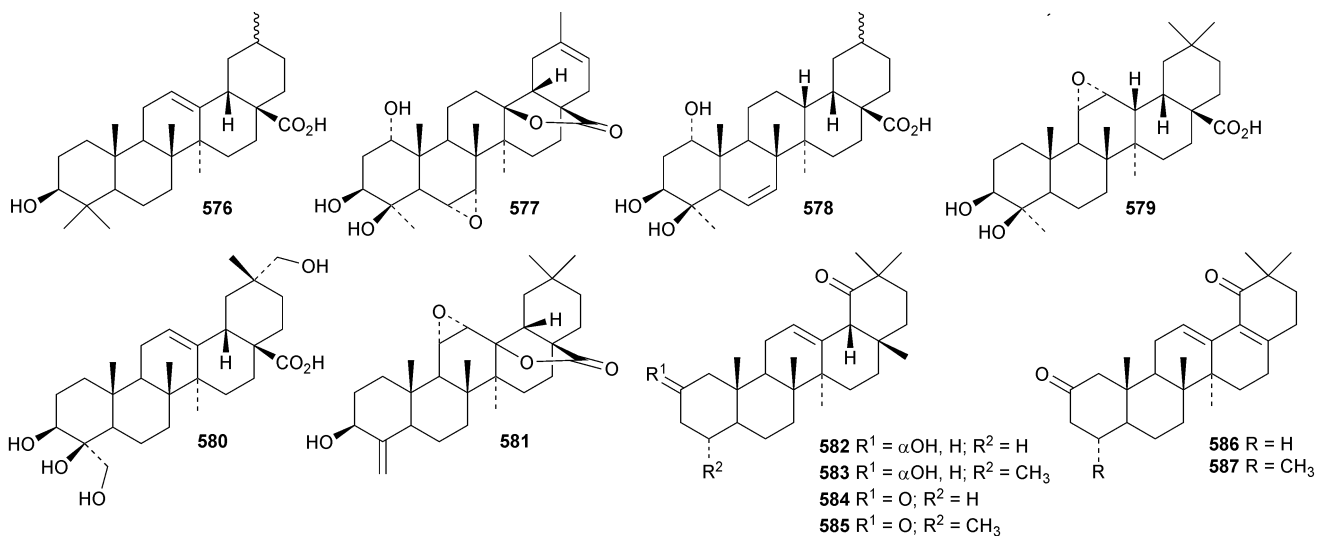
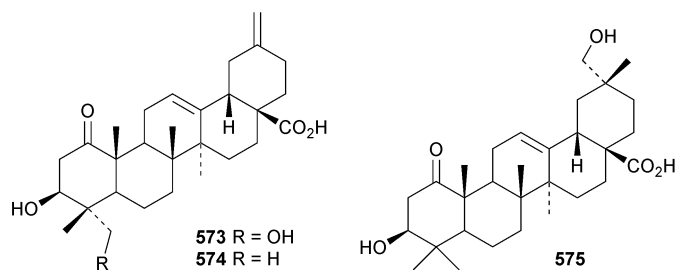
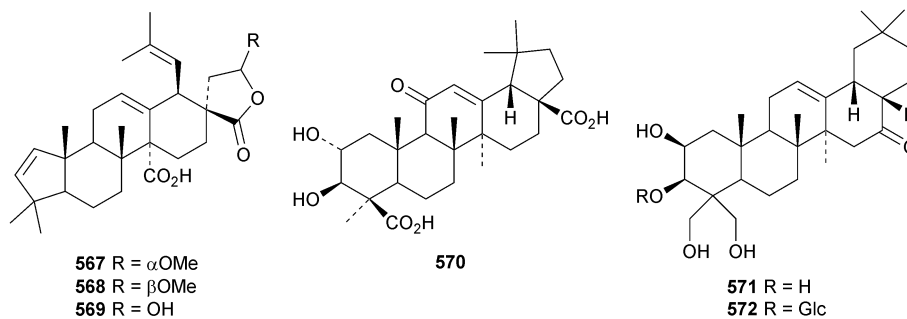
New oleanane saponins with known genins that have been assigned trivial names are listed in Table 1.

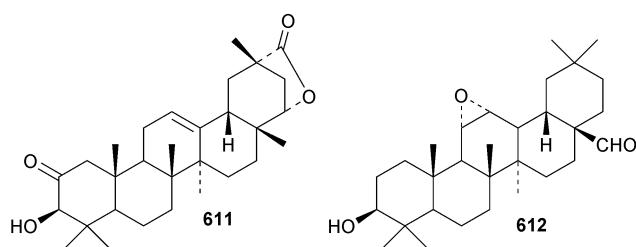
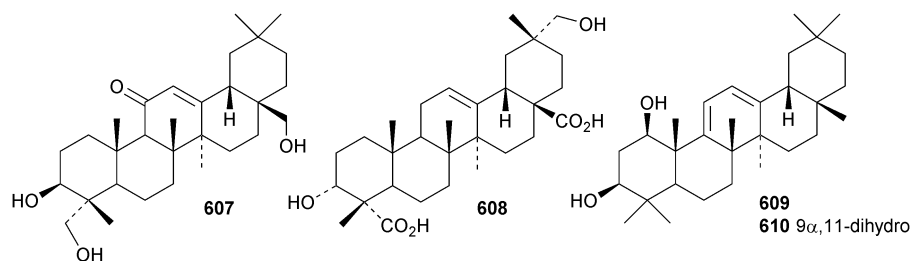
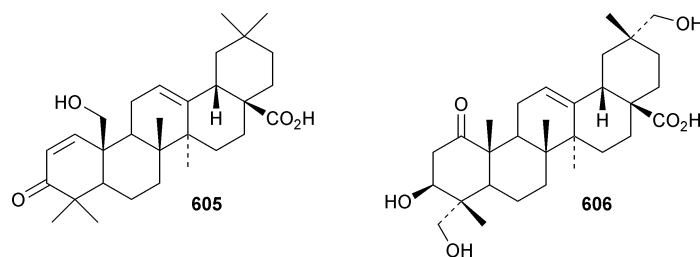
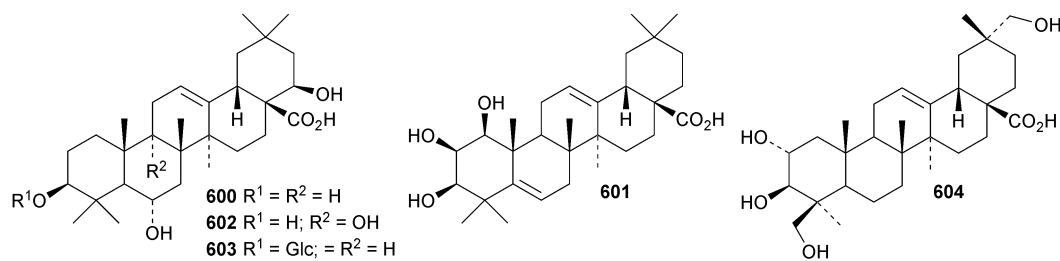
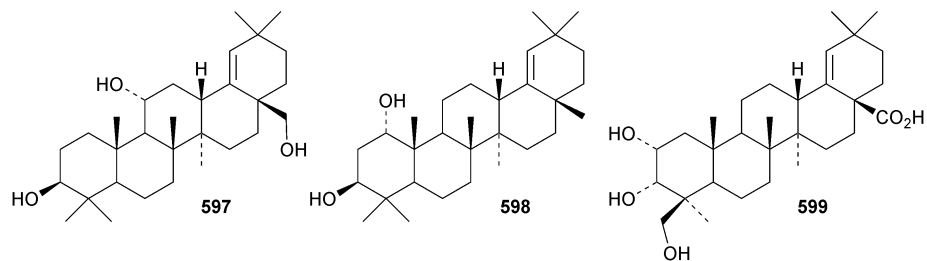


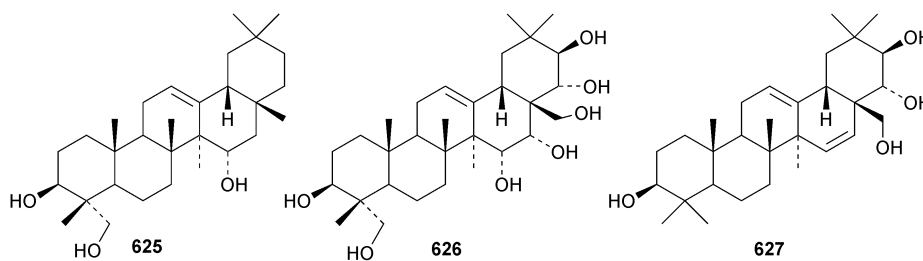
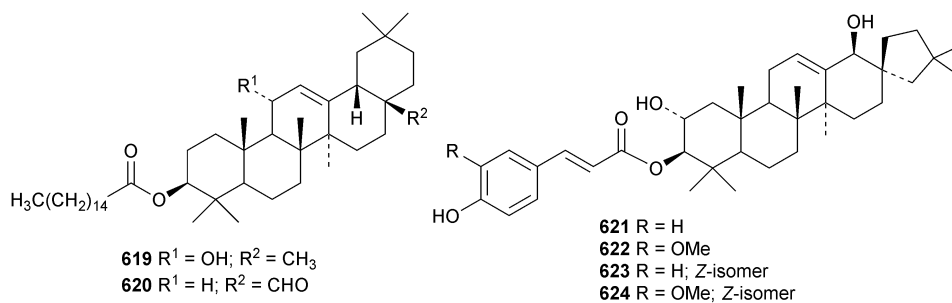
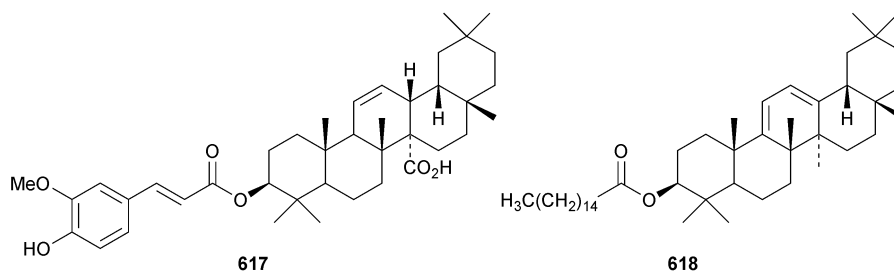
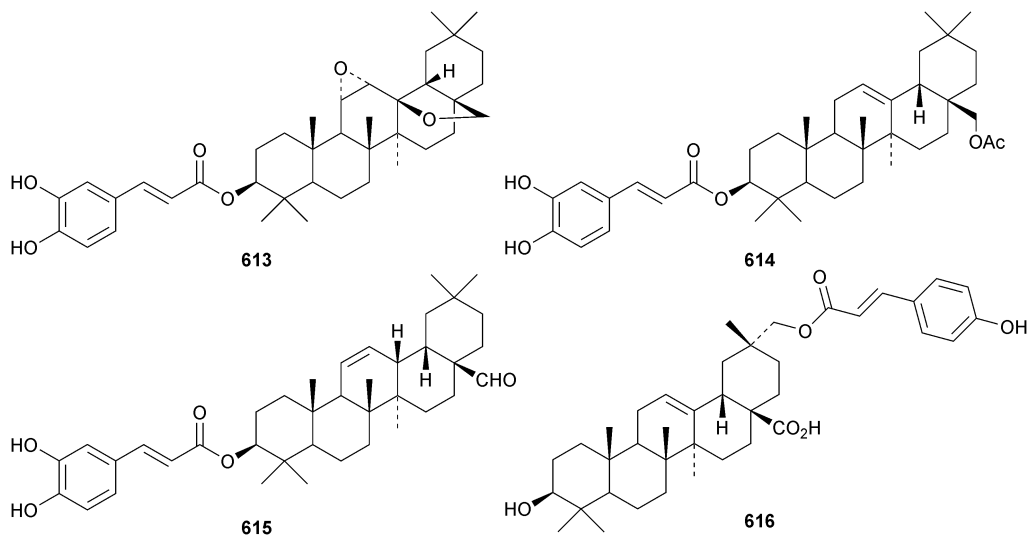












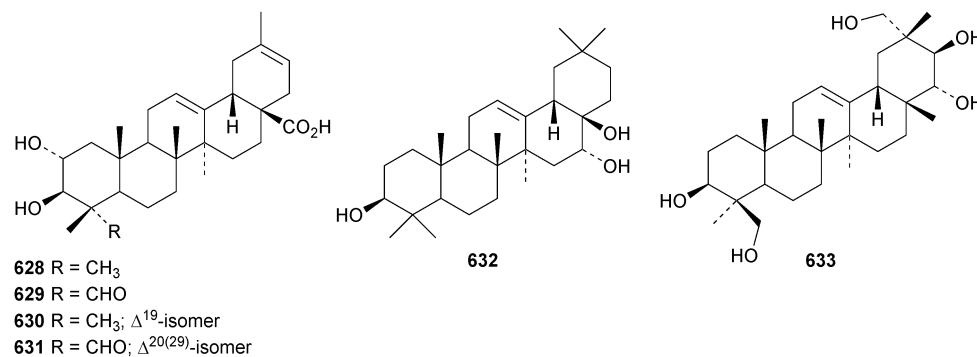


Table 1

Trivial name	Plant species	Ref.
Aesculosides G1–G16	<i>Aesculus glabra</i>	226
Afrocyclamins A and B	<i>Cyclamen africanum</i>	227
Anemonerivulariside A	<i>Anemone rivularis</i>	228
Asperosaponins A–C	<i>Dipsacus Asper</i>	229
Besylvosides I–VI	<i>Aegilops geniculata</i>	230
Bigeloviis A and B	<i>Salicornia bigelovii</i>	231
Bodinosides C and D	<i>Elsholtzia bodinieri</i>	232
Bonarienosides A–E	<i>Hydrocotyle bonariensis</i>	233
Bunkakasaponin F	<i>Xanthoceras sorbifolia</i>	234
Centelloside D	<i>Centella asiatica</i>	235
Chakasaponin IV	<i>Camellia sinensis</i>	236
Dumortierinoside A methyl ester	<i>Isolatocereus dumortieri</i>	237
Elmalienosides A–C	<i>Cephalaria elmaliensis</i>	238
Entadosides A–D	<i>Entada phaseoloides</i>	239
Gardenisides A–C	<i>Gardenia jasminoides</i>	240
Guaianin P	<i>Guaiacum officinale</i>	241
Gummososide A, gummososide A methyl ester	<i>Stenocereus alamosensis</i>	237
Hareftoside E	<i>Astragalus hareftae</i>	78
Hederifoliosides A–E	<i>Cyclamen hederifolium</i>	242
Ilexsaponins D–F	<i>Ilex pubescens</i>	243
Ilexsaponin D (duplicate name)	<i>Ilex pubescens</i>	244
Kalopanaxsaponins L and M	<i>Kalopanax pictus</i>	245
Lobatosides L and M	<i>Actinostemma lobatum</i>	246
Lonicacanthoides IV and V	<i>Lonicera macranthoides</i>	247
Mimengosides H and I	<i>Buddleja lindleyana</i>	248
Oleiferasaponin A <sub>1</sub>	<i>Camellia oleifera</i>	249
Paviosides A–H	<i>Aesculus pavia</i>	250
Pleurosaponins A–K	<i>Pleurospermum kamschaticum</i>	251
Polygalasaponins LI–LIII	<i>Polygala japonica</i>	252
Raddeanosides R <sub>20</sub> –R <sub>22</sub>	<i>Anemone raddeana</i>	253
Sanchakasaponins A–D	<i>Camellia japonica</i>	254
Sanchakasaponins E–H	<i>Camellia japonica</i>	255
Sandrosaponin XI	<i>Ferula hermonis</i>	256
Seneciapittosides A and B	<i>Pittosporum senacia</i>	257
Silenoviscoside F	<i>Silene viscidula</i>	258
Sorbifoliasides A–F	<i>Xanthoceras sorbifolia</i>	234
Teaseedsaponins A–L	<i>Camellia sinensis</i>	259
Treleaseside A	<i>Stenocereus eruca</i>	180

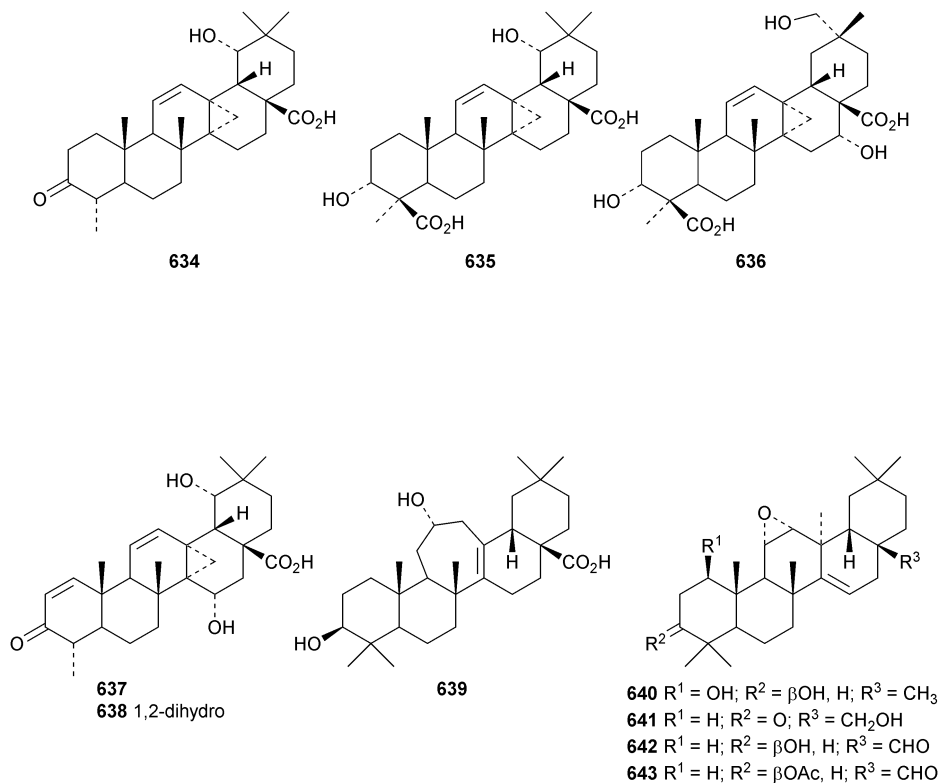
The sources of new oleanane saponins with known genins that have not been assigned trivial names are listed in Table 2.

Pachanosides I1 and D1 are pachanane saponins with known genins from *Isolatocereus dumortieri*.<sup>237</sup> 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.<sup>291</sup> The donellanic acids are accompanied by two

Table 2

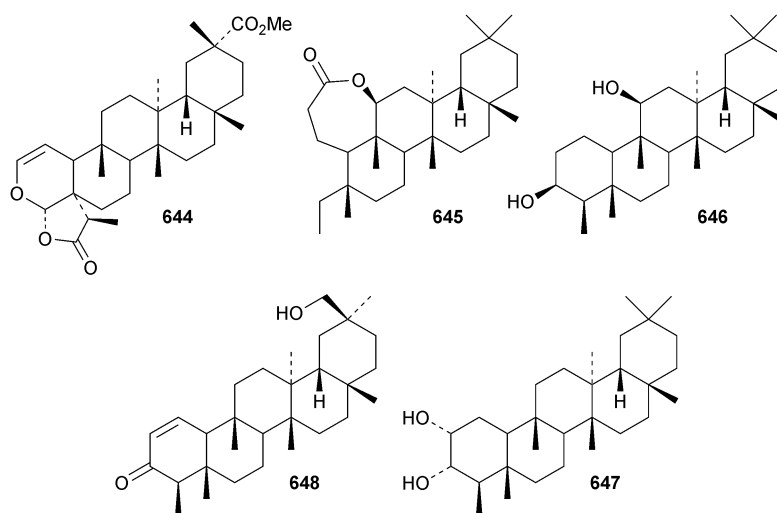
Plant species	Ref.
<i>Abrus precatorius</i>	260
<i>Abuta grandifolia</i>	261
<i>Acanthopanax senticosus</i>	262
<i>Acanthophyllum gypsophiloides</i>	263
<i>Alhagi maurorum</i>	264
<i>Anemone amurensis</i>	265
<i>Aralia elata</i>	266
<i>Aralia taibaiensis</i>	267
<i>Ardisia gigantifolia</i>	268
<i>Callicarpa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

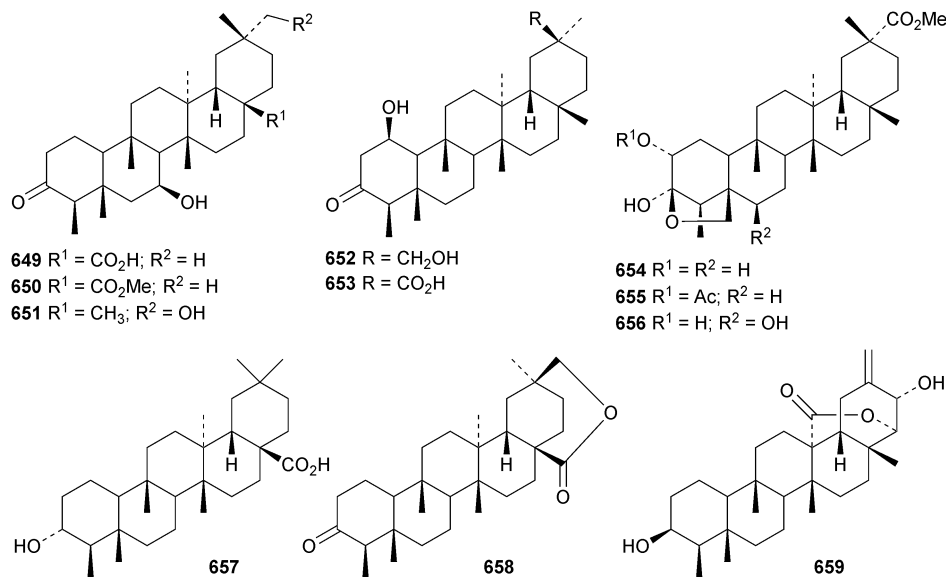




further 13,17-cyclized compounds that have been assigned the tentative structures **637** and **638**. Ilelic acid B **639** is a rearranged oleanane with a seven-membered C-ring from *Ilex latifolia*.<sup>292</sup> Four taraxerane derivatives **640–643** have been identified in *Saussurea graminea*.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

Cassinolide **644**, from *Cassine xylocarpa*, is a 2,3-secofriedelan-3,24-olide derivative.<sup>294</sup> *Maytenus robusta* is the source of the 3,4-secofriedelan-3,11 $\beta$ -olide **645** (ref. 295) and friedelane-3 $\beta$ ,11 $\beta$ -diol **646**.<sup>296</sup> Reissantadiol, from *Reisantia grahamii*, has been identified as friedelane-2 $\alpha$ ,3 $\alpha$ -diol **647**.<sup>297</sup>

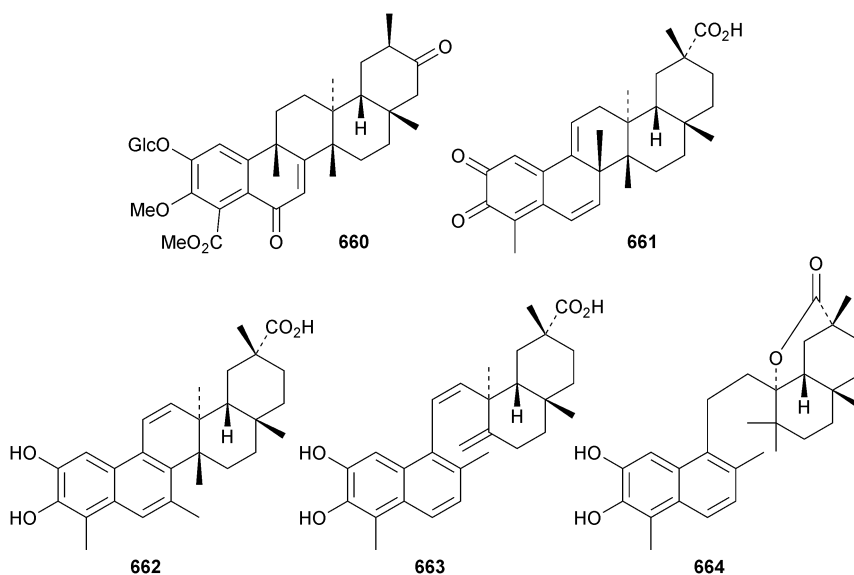




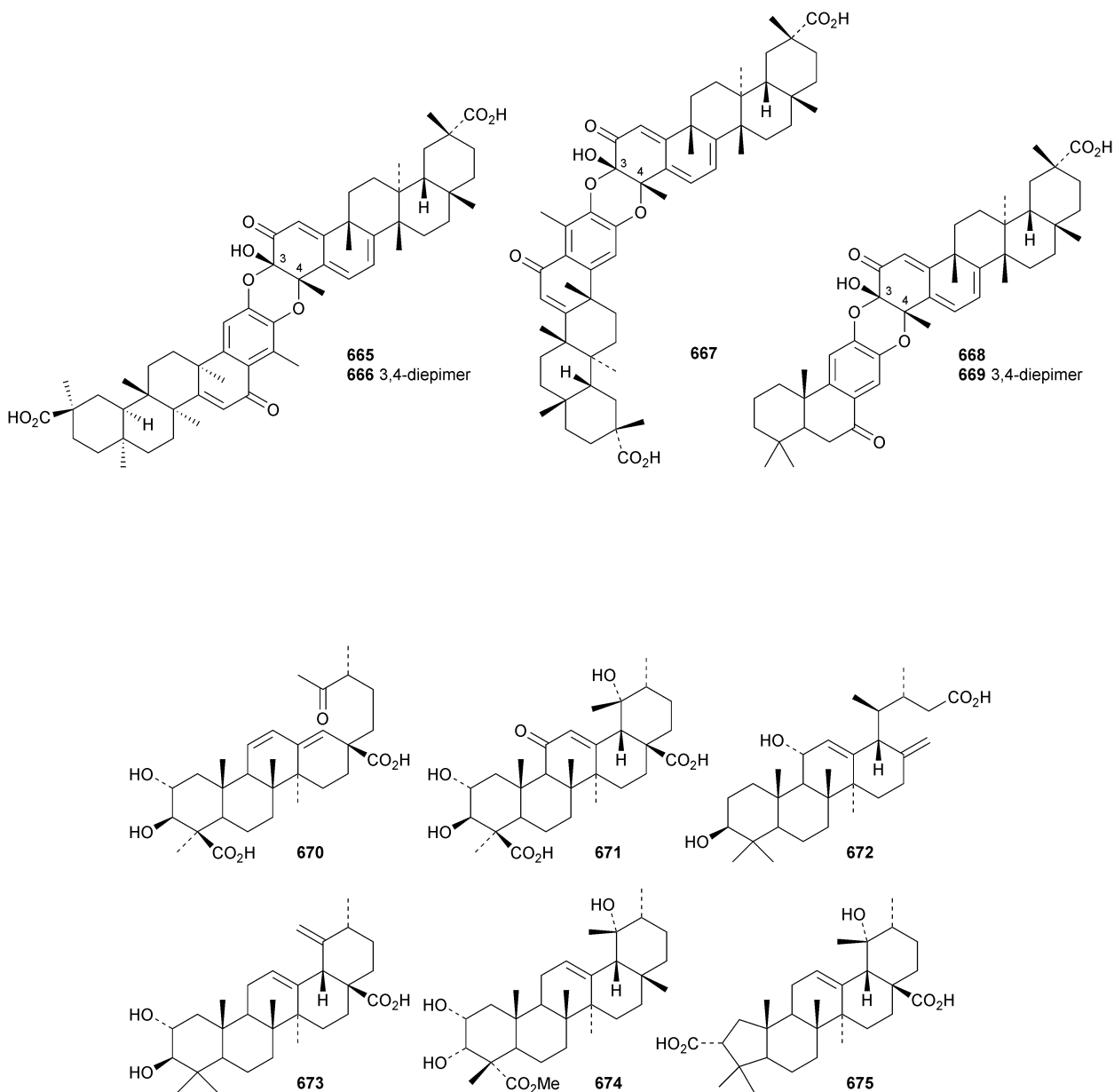
Other simple friedelane triterpenoids include 30-hydroxyfriedel-1-en-3-one **648** from *Salacia hainanensis*,<sup>124</sup> **649–653** from *Celastrus vulcanicola* and **654–658** from *Maytenus jelskii*<sup>298</sup> and glaucalactone **659** from *Caloncoba glauca*.<sup>61</sup>

A review of the pharmacology of celastrol, a norfriedelane derivative, has been published.<sup>299</sup> Hypoglaside A **660** is a dinorfriedelane glucoside from *Tryperygium hypoglaucum*.<sup>300</sup> *Celastrus orbiculatus* is the source of a range of norfriedelane and methyl-migrated derivatives.<sup>301</sup> 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 A $\alpha$  **665** and A $\beta$  **666** and isocelastrolines A $\alpha$  **667**, together with celastrolines B $\alpha$  **668** and B $\beta$  **669** that have a linkage to a podocarpane derivative.







## 7. The ursane group

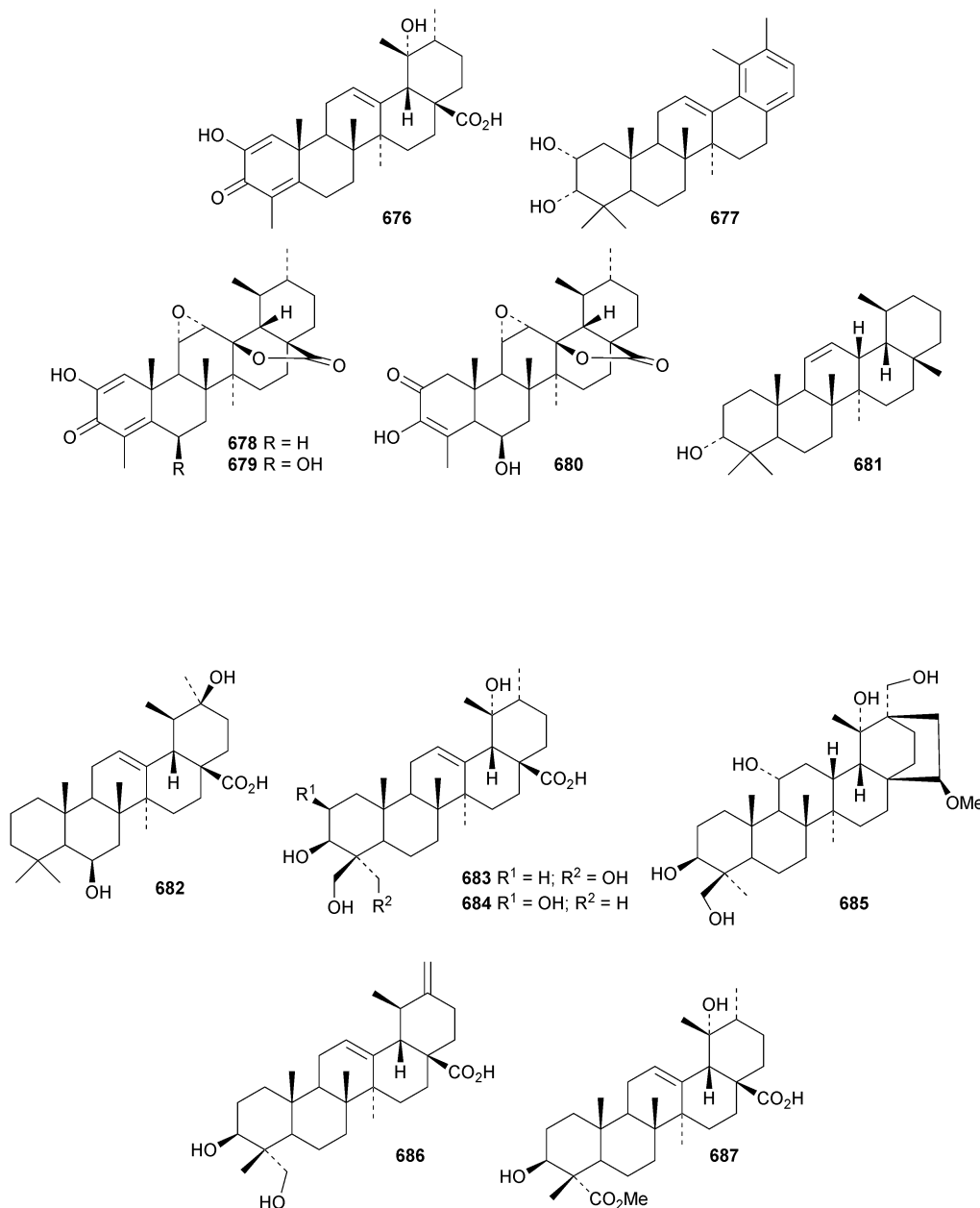
Ursane triterpenoids have shown potential as anticancer drugs.<sup>302</sup> Reviews on the anticancer activities of ursolic acid<sup>303</sup> and acetyl-11-keto- $\beta$ -boswellic acid (AKBA)<sup>304</sup> have been published.

The 18,19-secoursane derivative **670** has been isolated from the bark of *Diospyros decandra* together with **671**.<sup>195</sup> The 17,22-*seco* derivative **672** has been found in both *Salvia palaestina* and *Salvia syriaca*.<sup>305</sup> Euscaphic acids J **673**, K **674** and L **675** have been isolated from *Euscaphis japonica*.<sup>197</sup> 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.<sup>306</sup> Further 24-norursanes include ulmoidol A **678** from *Eucommia ulmoides*<sup>307</sup> and the related compounds **679** and **680** from *Dipsacus chinensis*.<sup>308</sup> 30-Norurs-11-en-3 $\alpha$ -ol **681** has been identified in the roots of *Alhagi camelorum*.<sup>309</sup>

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



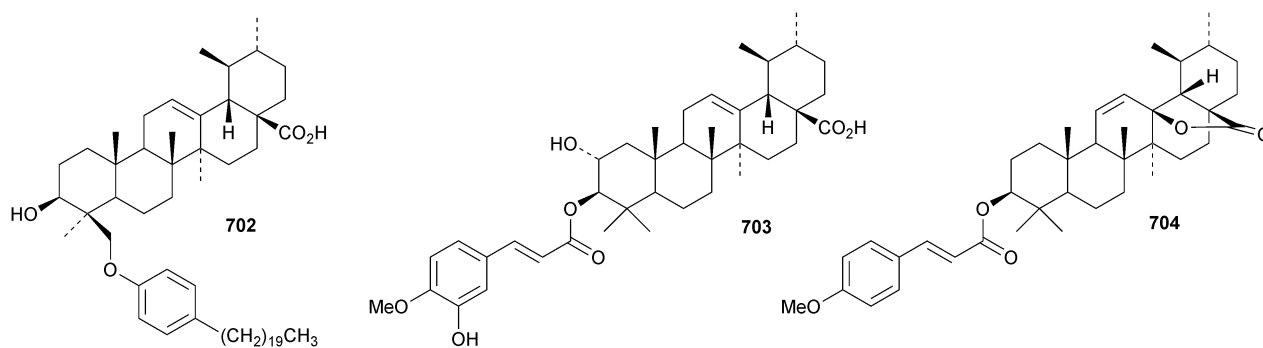
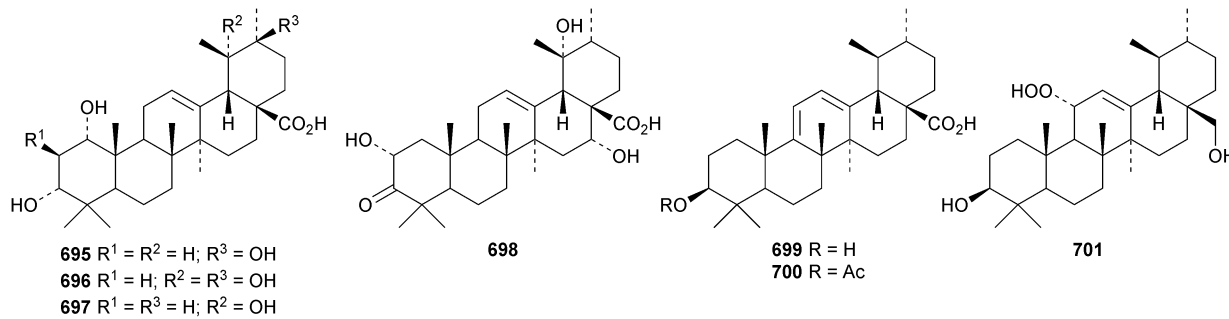
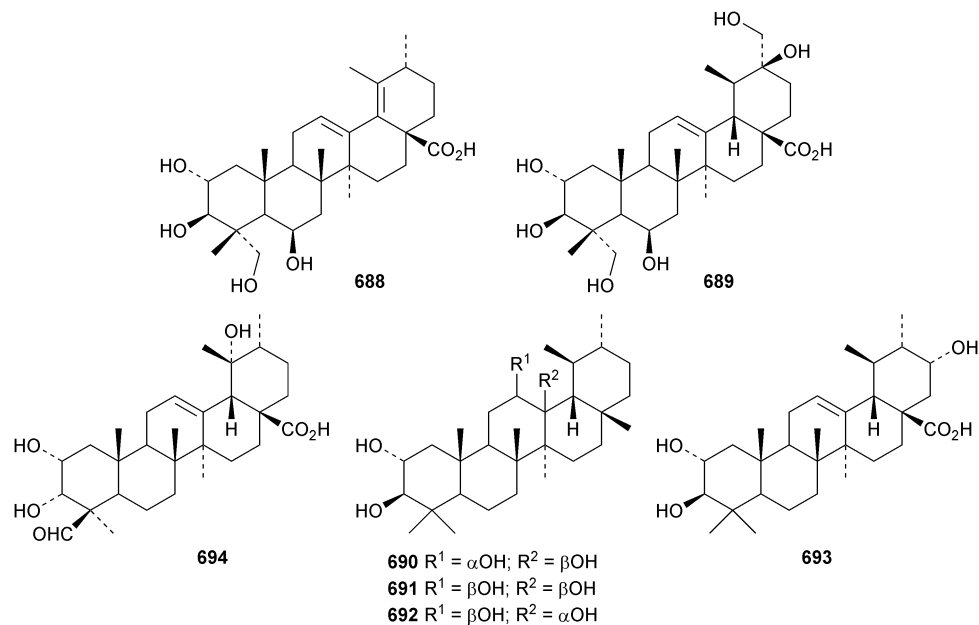


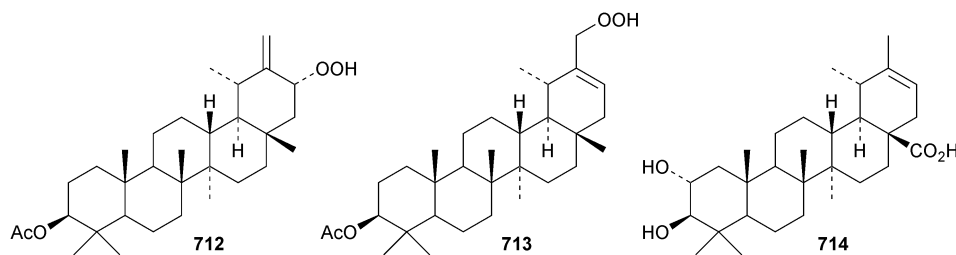
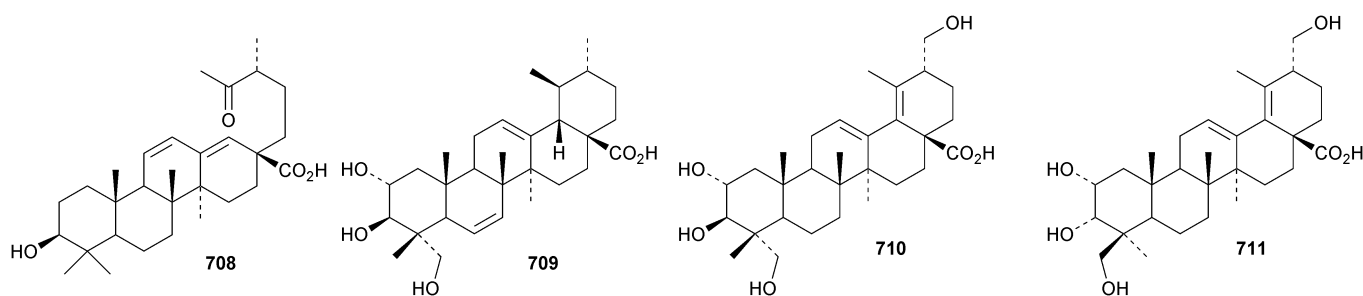
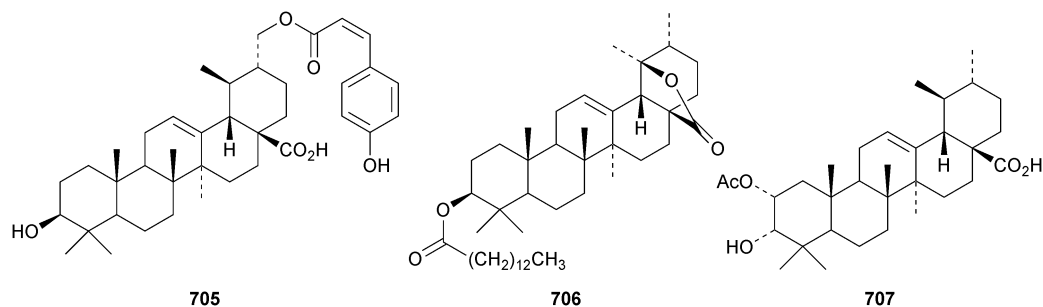
from *Rhododendron brachycarpum*,<sup>312</sup> uncariursanic acid **687** from *Uncaria macrophylla*,<sup>313</sup> 2 $\alpha$ ,3 $\beta$ ,6 $\beta$ ,23-tetrahydroyursa-12,18-dien-28-oic acid **688** from *Kadsura marmorata*,<sup>314</sup> 2 $\alpha$ ,3 $\beta$ ,6 $\beta$ ,20 $\beta$ ,23,30-hexahydroxyurs-12-en-28-oic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

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

Sanguiside A is an ursane saponin from *Sanguisorba officinalis* with the new 18,19-*seco*-ursane genin **708**.<sup>323</sup> 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*.<sup>324</sup>







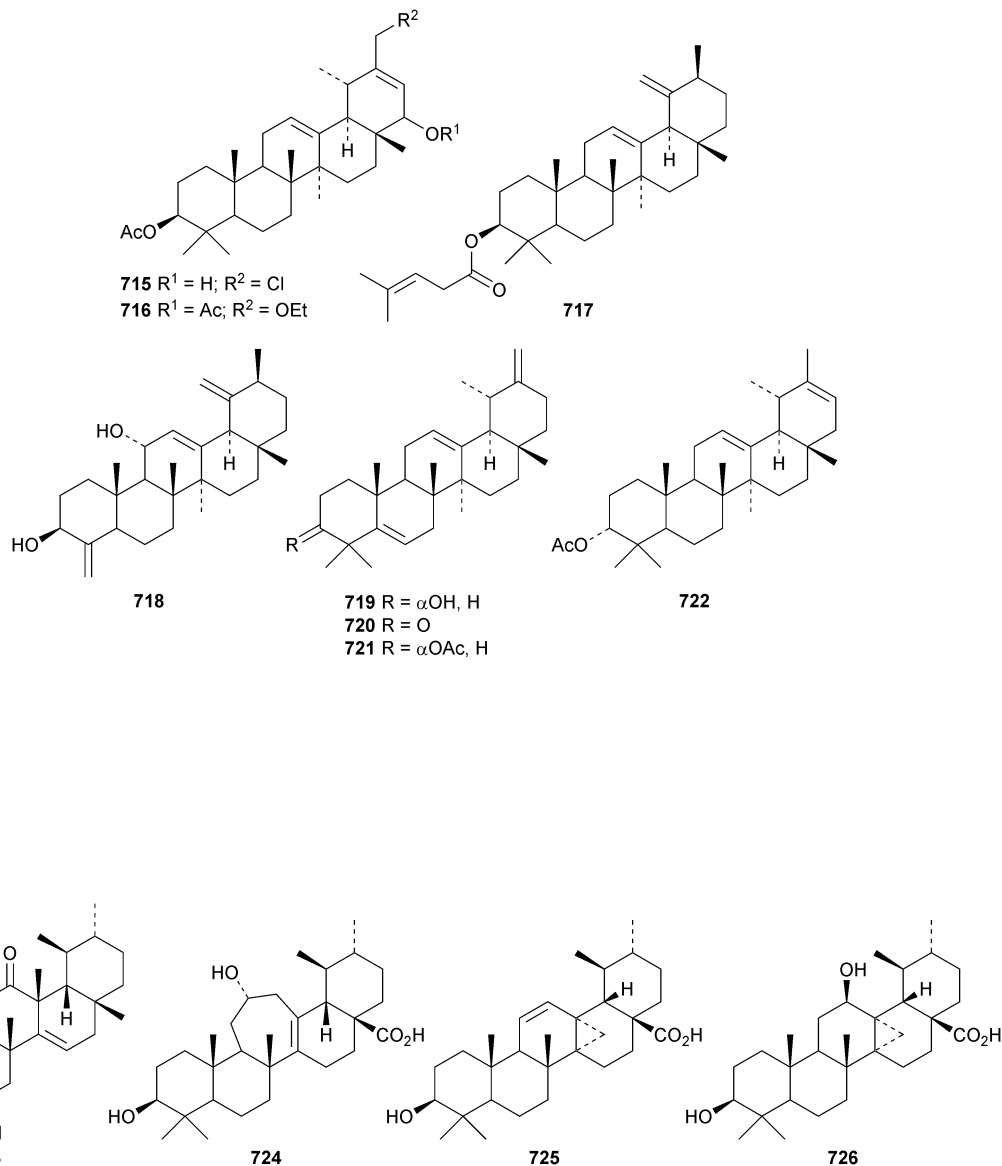
Ursane saponins with known genins include asphorins A and B from *Asphodelus tenuifolius*,<sup>325</sup> asprellanosides A and B from *Ilex asprella*,<sup>326</sup> elasticoside from *Ficus elastica*,<sup>327</sup> ilekudinichosides F and G from *Ilex kudincha*,<sup>328</sup> ilemaminosides A and B from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

The taraxastane hydroperoxide derivatives 712 and 713 have been isolated from the roots of *Taraxacum platycarpum*.<sup>173</sup> Psi-guanin A, which is 2 $\alpha$ ,3 $\beta$ -dihydroxytaraxast-20-en-28-oic acid

714, has been found in the leaves of *Psidium guajava*.<sup>315</sup> Other new taraxastane derivatives include chlorotolpidiol 715 and tolpidiol A 716 from *Tolpis proustii* and *Tolpis lagopoda*,<sup>320</sup> pergularines A 717 and B 718 from *Pergularia tomentosa*<sup>333</sup> and calotropoceryl A 719, calotropocerylone A 720 and calotropoceryl acetates A 721 and B 722 from *Calotropis procera*.<sup>334</sup> Two taraxastane saponins with known genins have been found in the roots of *Ilex pubescens*.<sup>335</sup>

The 27(14  $\rightarrow$  13)-abeo-urs-14-enone derivative 723, from *Rubia schumanniana*, has the unusual  $\beta$ -configuration for the migrated methyl.<sup>216</sup> The rearranged ursanes ilelic acids A 724, C





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

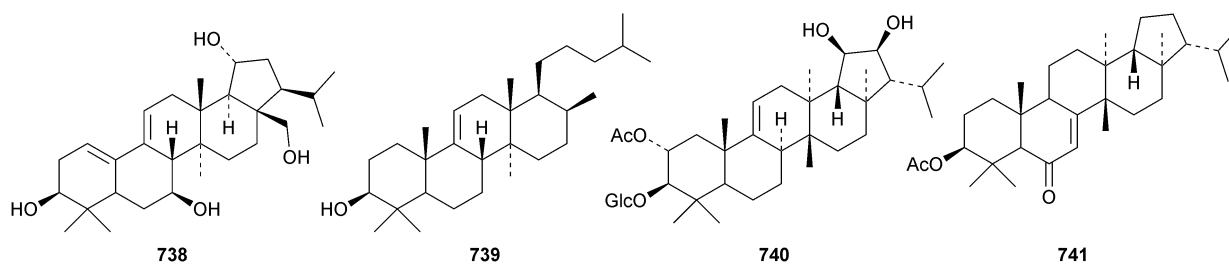
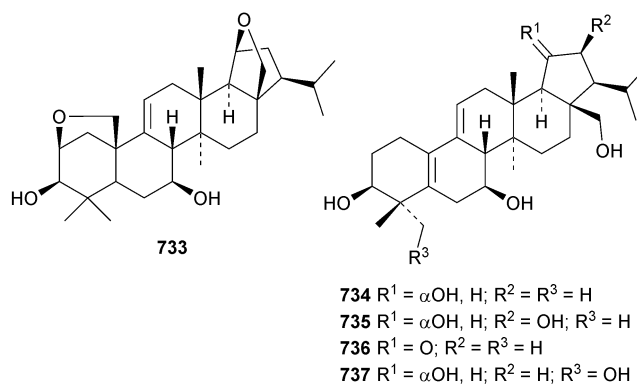
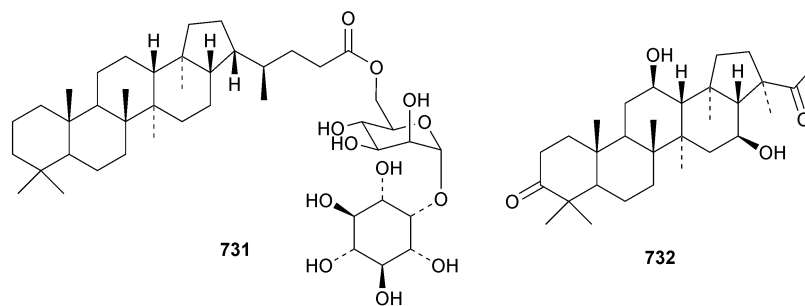
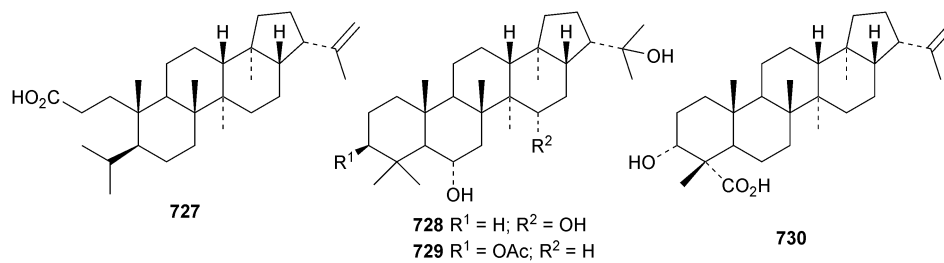
## 8. The hopane group

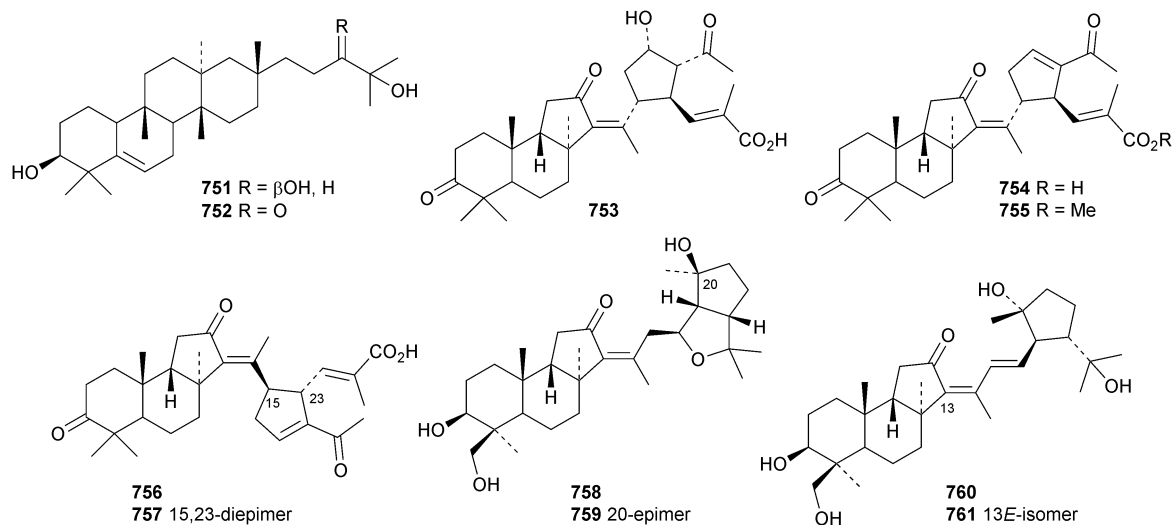
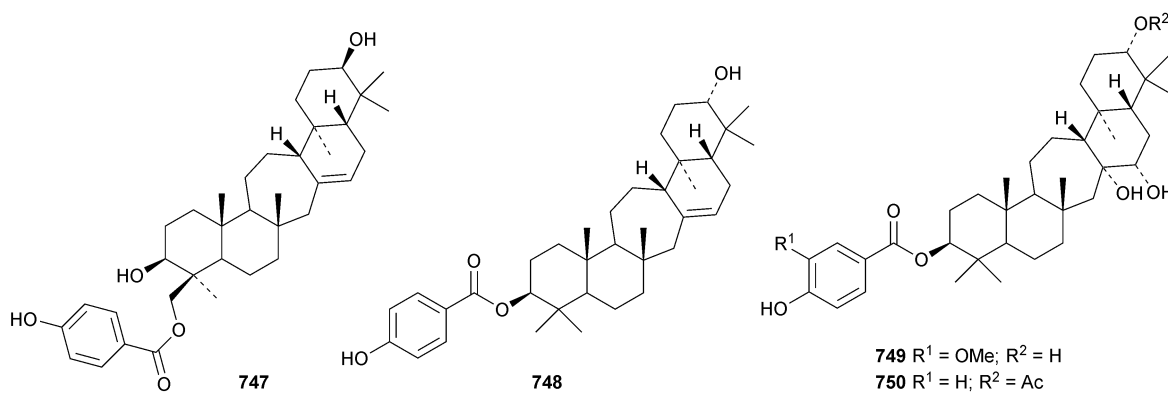
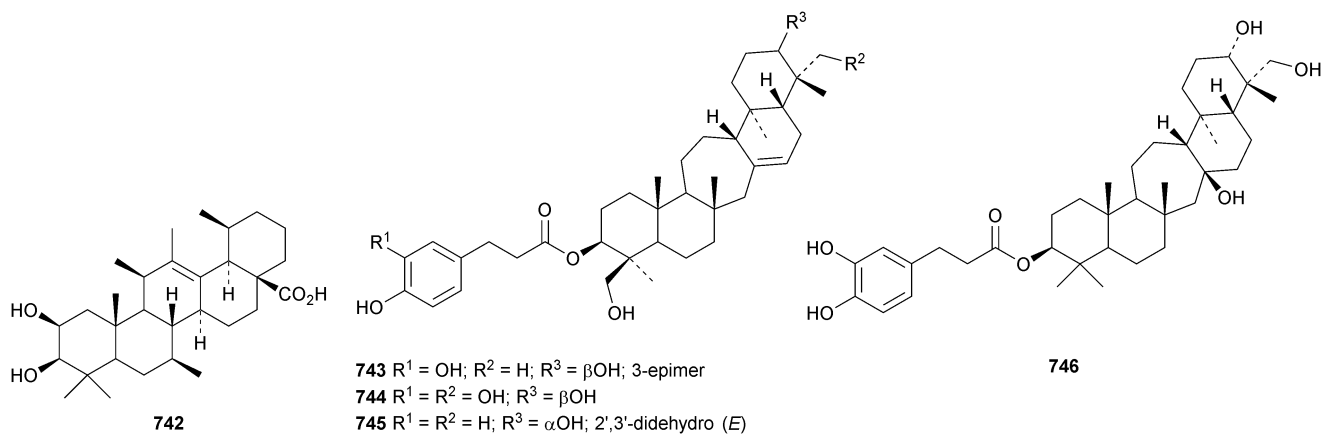
3,4-Secohop-22(29)-en-3-oic acid 727 has been isolated from *Maytenus robusta*.<sup>295</sup> The scale insect pathogenic fungus *Aschersonia calendulina* is the source of two hopane metabolites 728 and 729.<sup>336</sup> The leaves of *Hybanthus austro-caledonicus* produce 3-epiwoodwardinic acid 730.<sup>337</sup> Plakohopanoic acid 731, a C<sub>32</sub> hopanoic acid, has been isolated from the sponge *Plakortis cf. lita*.<sup>338</sup> The structure of plakohopanoic acid 731 implies that it is of bacterial origin. This is the first example of a biologically produced C<sub>32</sub> hopanoic acid. Such

acids were considered to only be geohopanoic acids formed by abiotic degradation of bacteriohopanoic acids. Oppositifolone 732, from *Glinus oppositifolius*, has a 29(22 → 21)-abeo-hopane skeleton and is the 3-ketone of spergulagenin A.<sup>339</sup>

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







## 9. Miscellaneous compounds

The unlikely structure **742** has been proposed for erucaic acid from *Sonchus eruca*.<sup>344</sup> 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*).<sup>346</sup> The D:B-friedobaccharane derivatives leonatriol **751** and the corresponding ketone leonatriolone **752** have been isolated from *Cassine xylocarpa* and *Celastrus vulcanicola*, respectively.<sup>294</sup> Globostellets J **753**–**S 761**, from the marine sponge *Rhabdastrella globostellata*, are isomalabaricanes with cyclopentane side chains.<sup>347</sup>

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