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REVIEW

THE TRITERPENOIDS*

PUSHPA PANT and R. P. RASTOGI
Central Drug Research Institute, Lucknow, India

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Key Word Index—Triterpenoids; pentacyclic triterpenes; tetracyclic triterpenes; vascular plants; fungi; distribution; identification.

Abstract—The literature on the identification and distribution of penta- and tetracyclic triterpenoids in vascular plants and fungi is reviewed for the period 1971–1977.

The chemistry and distribution of triterpenoids in the plant kingdom have been excellently surveyed by Boiteau *et al.* [1] and in a number of other subsequent reviews, of which the last one by Kulshreshtha *et al.* [2] covered the literature up to 1970. The present review comprises of a survey of the advances in the last seven years (from 1971 to 1977) in the field of triterpenoids but excludes saponins and their genins which have been covered elsewhere [3].

ANALYTICAL TECHNIQUES

A colour reaction [4] has been reported to differentiate triterpenes from steroids based on heating with CCl_3CO_2H which produces temperature-dependent characteristic colours. A study of the IR spectra of 18α-H and 18β-H olean-12-ene derivatives [5] showed that 18β-H compounds with an axial COOMe at C-20 absorbed at 1165 and 1090 cm^{-1}, while the 18α-H epimers absorbed at 1117 cm^{-1}. The 18β-H compound with an axial CH_2OH at C-20 absorbed at 1210–1205 cm^{-1}, whereas the 18α-H epimers absorbed at 1193–1189 cm^{-1}. The ursolic acid content of cranberries was determined by IR at solution concentrations of 4×10^{-4} to 2.4×10^{-3} percent [6]. The UV spectra of pentacyclic triterpenoids in sulfuric acid showed a characteristic absorption maximum at 310 nm regardless of the substituents present [7]. The hypsochromic shift in the UV spectrum associated with the 18β to 18α transformation, observed in the case of α-boswellic acid, has been proposed as a diagnostic technique in conformational analysis [8].

GLC of triterpenoids has been reviewed [9]. The relative retention times of tetracyclic triterpenes (e.g. lanostane, cycloartane, tirucallane) and pentacyclic triterpenes (e.g. ursane and oleanane, modified oleananes [taraxerane, glutinane], friedelane and lupane) were examined and relationships between structure and retention time have been discussed [10]. The GLC mobilities of 20 triterpenoids of *Rhododendron* were determined on SE-30 [11]. It has been shown that the relative retention volumes of triterpenoids increase in the series alcohol < ketone < acetate on QF-1 and SE-30 phases; diols have higher retention volumes than monohydric triterpenoids. Trimethylsilyl derivatives of triterpene diols were found to be chromatographically more mobile on the QF-1 phase than in SE-30. Mixtures of alcohols and the corresponding ketones (e.g. simmiarenol and simmiarenone), or mixtures of their trimethylsilyl derivatives, could be separated only on the QF-1 phase [12]. GLC separations of esters of triterpene alcohols with lower and higher fatty acids as well as their trimethylsilyl ethers have been studied. Esters of monols with higher fatty acids (lauric, myristic and palmitic acids) were separated on an OV-101 column while the monol esters with lower fatty acids (acetic and butyric acids) and trimethylsilyl ethers were separated on an OV-17 column. These separations have also allowed the quantitative determination of most of the triterpene monols [13].

The GLC mobilities of 52 triterpenoids have been tested and the OV-17 phase was found to be best for analysis of methylated triterpenoid acids. The retention time on OV-17 decreased in the order acetates > free triterpenoids > trimethylsilyl ester derivatives. The retention time of ketones was less than that of such alcohols as taraxerone or simmiarenone and somewhat higher than that of friedelin. Epimeric mixtures were not separated either on OV-17 or SE-30 phases. The retention times of triterpenoids with OH groups did not differ when either the OV-17 or SE-30 phases were used [14].

Methods are described for GLC separation of the oxidation (SeO_2) products of triterpene pentacyclic alcohols such as α-amyrin from lupeol and of triterpene diols, their acetates and oxidation products. Thus, triterpene monols and diols from *Calendula officinalis*, were acetylated and then oxidized by SeO_2, and triterpene alcohol acetates were prepared. The GLC analysis was performed on OV-17 and the relative retention times (cholesterol as standard) were recorded [15].

The application of NMR techniques like INDOR, lanthanide shift reagents and ^{13}C NMR have become more frequent. The chemical shifts of the Me groups of tetrahymanol and tetrahymanone were assigned on the basis of the analysis of their 100 MHz spectra [16]. In cycloartane triterpenes, a paramagnetic displacement of the chemical shifts of the 30, 31-methyls was caused by the 3-oxo group of strong magnetic anisotropy. The effect

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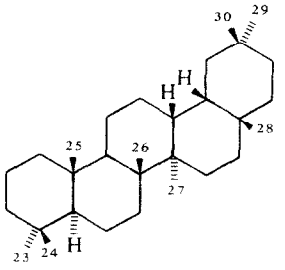
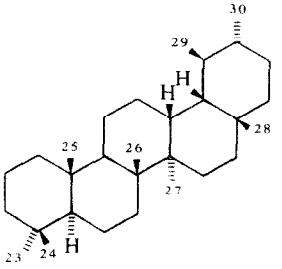
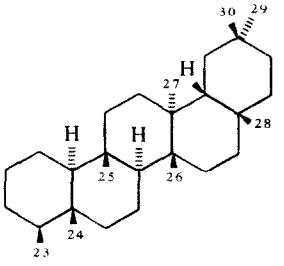


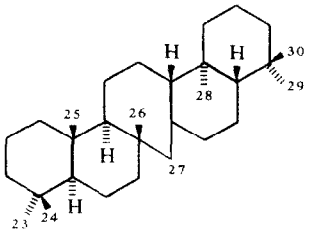
Oleanane (I)



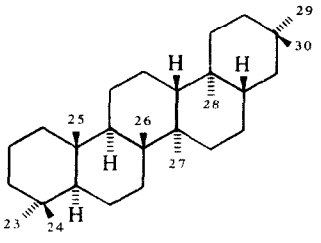
Ursane (II)



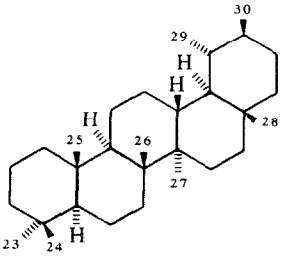
Friedelane (III)



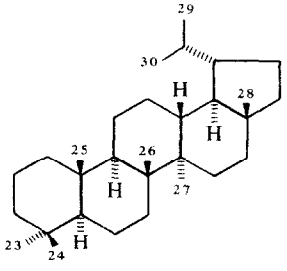
Serratane (IV)



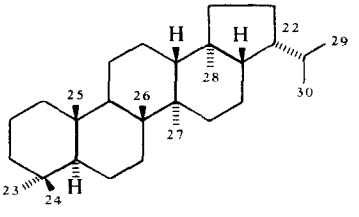
Stictane (V)



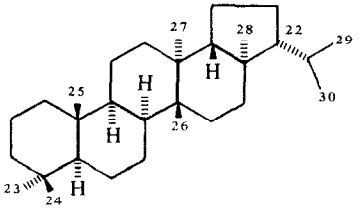
ψ-Taraxasterane (VI)



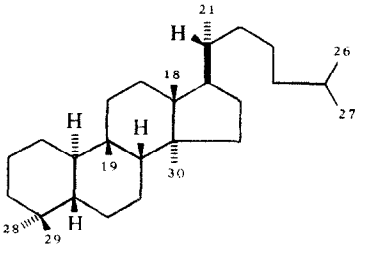
Lupane (VII)



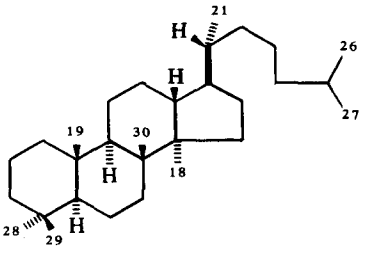
Hopane (VIII)



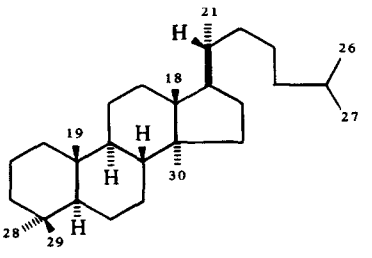
Fernane (IX)



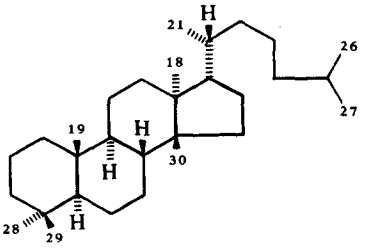
Cucurbitane (X)



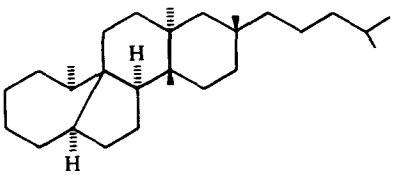
Dammarane (**XI**)



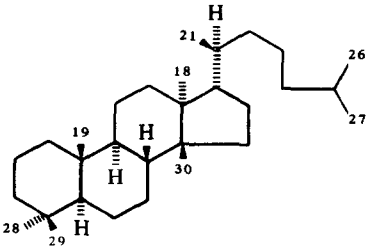
Lanostane (**XII**)



Euphane (**XIII**)



Halimane (**XIV**)



Tirucallane (**XV**)

of the substituents on the chemical shifts of 18-Me and 32-Me was found to be additive, and the para- or diamagnetic displacements induced by groups like 12-oxo, 12-OH, 12-OAc, 15-oxo, 15-OH and 15-OAc, were found to be useful in the differentiation between these methyls; the former resonating at a lower field than the latter [17].

The Me resonances in the ^{1}H NMR spectra of 19 olean-18-ene derivatives have been assigned [18]. Introduction of a substituent in the 3-position caused a shift in the resonances of the Me groups at the 23-, 24-, 25-positions. Similarly, introduction of an 11β-OH had a substantial effect on the resonances of the Me at the 25- and 26-positions; the methyls at the 29- and 30-positions showed up as a double intensity signal at 0.94 ppm, characteristic of these compounds. A study of the ^{1}H NMR spectra of methyl melaleucicate derivatives variously substituted at C-3 has been made whereby the 25-Me signal could be distinguished from those of the geminal 23,24-methyls [19].

The ^{1}H NMR spectra of olean-12-ene and the derivatives in pyridine were comparable in the magnitude of the chemical shifts to those obtained in benzene; hence it was concluded that pyridine may be substituted as a solvent for those triterpenes which were slightly soluble in benzene [20].

INDOR studies have been carried out with friedelin derivatives [21, 22]. The lanthanide shift reagent Eu(dpm)$_3$ has been used to characterize the methyls of triterpenoids [23–25]. The β-amyrin spectrum in the presence of this reagent showed that the 29-Me experienced more shielding than the 30-Me [26]. As a result of ^{1}H NMR spectral analysis of ursene derivatives in the presence of Eu(dpm)$_3$, it was shown that the pseudocontact shifts of bifunctional triterpenes could be calculated as the sum of the corresponding shifts of the two corresponding monofunctional compounds [27]. The use of Eu(fod)$_3$ allowed complete assignment of the 8 Me signals of urs-12-ene and evaluation of the effect of substituents on C-3, C-11 and C-17 on the Me signals [28]. The Eu(fod)$_3$ spectra of 12 triterpenoids related to urs-12-ene are reported. All the Me resonances were assigned for ursolic acid derivatives and the corresponding 3-*epi* series. The shielding effects of substituents on the Me resonances were found to be additive [29]. The Me groups of methyl ursolate, methyl oleanolate and their acetates were unambiguously assigned by nuclear overhauser effect (NOE) measurements in lanthanide-induced NMR spectra [30].

^{13}C NMR studies of tetracyclic and pentacyclic triterpenes have been carried out [31–35]. ^{13}C NMR of olean- and urs-12-enes were assigned by using single frequency

off-resonance decoupling techniques and chemical shift values [36, 37]. Extensive use of partially relaxed Fourier transform (PRFT) ^{13}C NMR has been made in structure elucidation of pristimerin and tingenins [38]. The ^{13}C NMR signals of the saikogenins E–G and the corresponding olean-12-enes were assigned in $CDCl_3$; the effects of C-16 hydroxylation on ^{13}C chemical shifts reflected the difference in D-ring conformation, which was an ordinary chair in the 16α- and 16β-hydroxyolean-12-enes, but which adopted a slightly deformed configuration in the saikogenins [39].

Mass spectral fragmentation patterns are described for dammarane compounds having C-3, C-6 and/or C-12 substituents and various side chain configurations. The main fragmentation mechanisms involved side chain decomposition and C-ring cleavage [40]. Through extensive deuterium labelling of the steroid nucleus, the electron impact induced fragmentation of ring D in lanostane (and 14α-methyl cholestane) has been elucidated in order to provide a secure basis for the interpretation of the MS of tetracyclic triterpenes [41]. The characteristic fragmentation patterns of shionane and friedelane derivatives have been described by high resolution mass spectroscopy [42]. The MS of three glycyrrhetic acid derivatives having modified ring A and two unsaturated nitrile derivatives from ring A *seco*-β-amyrin and glycyrrhetic acid were studied [43]. Except for the nitrile derivative from glycyrrhetic acid, the others showed Diels–Alder fragmentation arising from the double bond in ring C as well as special fragmentation patterns from the cleavage of the α and β carbon bonds adjacent to the existing C=N or C=O groups in ring A. The glycyrrhetic derived products showed yet another mode of fragmentation across ring B involving McLafferty rearrangement and cleavage of the C-7, 8 bond. Suitable mechanisms have been proposed to rationalize the formation of these ions.

The fragmentation of eighteen 20-β, 28-epoxy-18α, 19β-H ursane derivatives, containing in their ring E an oxabicyclo[2,2,2]octane or oxabicyclo[2,2,1]heptane system, has been studied. The cleavage always took place in ring E but the cleavage of ring D was found to be dependent on the substitution at C-21 and C-22 [44]. The basic type of molecular ion fragmentation of twelve 12-oxolupanes is a retro-Diels–Alder cleavage of the enol form occurring in ring C to form characteristic fragments containing rings D and E. These ions may serve for the detection of a 12-oxo group. Thus it was shown that the second oxygen function in thurberine was not in position 12 as originally proposed [45]. A study of the MS of 3,4(A)-*seco* triterpenoids has shown that fragments $[M-43]^+$, $[M-81]^+$ and $[M-87]^+$ were characteristic of the 3,4(A)-*seco* system [46].

A series of mono and dicarbonyl derivatives of pentacyclic triterpenic alcohols were investigated by ORD and CD in order to determine the usefulness of these methods in allocating the position of OH groups in the molecule [47]. Slight interaction of the carbonyl groups in urs-12-ene-3,16 dione and 18α-, 19β-urs-20-ene-3,12 dione and a stronger interaction in lup-20(30)-ene-3,12 dione and olean-12-ene-3,21 dione were found by approximation of the ORD and CD curves by the method of linear combination of normal ORD and CD curves for mono carbonyl (3-keto) analogs [48]. CD has also been used in determining the stereochemistry of carboxyacetylquercinic acid and its congeners with lanosterol [49]. The CD of triterpene tertiary carboxylic acids having a COOH group in a potentially hindered situation has been studied [50] at −10 to −180°. It was found that the magnitude of $\Delta\varepsilon$ increased with decreasing temperature and the average change for 17 β-carboxylic acids of the oleanene and ursene series was of the order of −25%. For 17 β-carboxylic acids of lup-20(30)-en series it was about −16%. These values were a rough measure of the conformational freedom of the COOH group in a particular structural situation.

The final word on stereochemistry, however, comes from X-ray crystallography. The chemical structures of a number of triterpenoids, e.g. cyclograndisolide and its 23-epimer [51, 52] a 2,3-*seco*-ursene lactone from dammar resin [53], abieslactone [54], pristimern [55] pachysandiol B and pachysonal [56, 57], baccharis oxide [58], tingenone [59], echinocystic acid diacetate [60], methyl meristotropate [61] and tetrahymanol hemihydrate [62], have been confirmed by this method.

TABULATION OF DATA

The triterpenoids isolated and identified during the period under review have been listed under the plants in which they occur in Table 1. The triterpenes obtained from other sources are given in Table 2. As mentioned earlier, this tabulation excludes *tetranor*-triterpenoids, saponins and their genins.

Table 1. Distribution of triterpenoids in the plant kingdom

Plant	Family	Substance	mp (°)	Basic skeleton	Groups	Ref.
Mycophyta						
(a) Fungi						
Cladosporium sp.	Dematiaceae	Viridominic acid A	151–5	XII	3α,7β-OH,6α-OAc,11-oxo, $\Delta^{17,24}$,21-COOH	63
		Viridominic acid B	—	XII	3α,7β,12α-OH,6α-OAc, $\Delta^{17,24}$,21-COOH	
Fomes officinalis	Polyporaceae	Substance I	188	XII	3β,6β-OH,22-oxo,$\Delta^{8(9)}$, 22,23,24,25,26,27-hexa*nor*	64
		3-Oxodehydro-sulfurenic acid	173–5	XII	3-Oxo,15α-OH,$\Delta^{7(8),9(11),24}$, 21-COOH	
F. senex	Polyporaceae	Senexonol	117	XII	3-Oxo-22-OH,31-*nor*,$\Delta^{8,24}$	65
		Senexdione	108–10	XII	3,22-Oxo,31-*nor*,$\Delta^{8,24}$	
		Oxidosenexone	223–5	XII	3-Oxo,31-*nor*,Δ^{8},22→25-epoxy	
		Senexdiolic acid	273–6	XII	3β,22-OH,$\Delta^{8,24}$,30-COOH	

Table 1—*continued*

Plant	Family	Substance	mp (°)	Basic skeleton	Groups	Ref.
Inonotus obliquus	Polyporaceae	Ionotodiol (=obliquol)	190	XII	3β,22-OH,$\Delta^{8(9)}$	66
Trametes odorata	Polyporaceae	—	—	XII	3β,15α-OH,$\Delta^{8,24}$,21,27-COOH	67
(b) Lichens						
Lobaria retigera group	Stictaceae	Retigeric acid A	296–9	VIII	2α,3β-OH,$\Delta^{9(11)}$,23-COOH	68
L. isidiosa (Mull. Arg.) Vain		Retigeric acid B	>268	VIII	2α,3β-OH,$\Delta^{9(11)}$,23,25-COOH	
Lobaria retigera		Retigeradiol		V	3β,22α-OH	69
Parmelia leucotyliza	Physciaceae	Isoleucotylin	266–8	VIII	6α,16β,22-OH	70
Pyxine endochrysina	Physciaceae	Methyl pyxinate	288	VIII	3β,22-OH,30-COOMe	71
		Methyl-3, acetyl pyxinate	255	VIII	3β-OAc,22-OH,30-COOMe	
Sticta coronata	Stictaceae	Substance I	276	V	2α,3β,22α-OH	72
		Substance II	274	V	2α,3β,22α-OAc	
		Substance III	231	V	2α,3β-OAc,22α-OH	
		Substance IV	215	V	2α-OAc,3β,22α-OH	
		Substance V	227	V	3β-OAc,2α,22α-OH	
		Substance VI	263	V	2α,3β-OAc,22-Oxo	
		Substance VII	283	V	3β,22α-OH	
		Substance VIII	281–3	V	3β,22α-OAc	
		Substance IX	243	V	3β-OAc,22α-OH	
		Substance X	216	V	3-Oxo,22α-OH	
S. mougeotiana var. *dissecta*		Substance I	230	VIII	6α,7α,22-OH	73
		Substance II	198	VIII	6α-OAc,7α,22-OH	
		Substance III	198	VIII	6α,22-OH,7α-OAc	
		Substance IV	216	VIII	11β,22-OH	
Xanthoria resendei	Teloschistaceae	Substance I	268–70	IX	3β-OH,22α-OAc,$\Delta^{9(11)}$	74
		Substance II	208	IX	3β,12α-OH,$\Delta^{9(11)}$	
		Substance III	250	IX	3,12-Oxo,$\Delta^{9(11)}$	
Pteridophyta						
(a) Lycopods						
Lycopodium clavatum	Lycopodiaceae	16-Oxoserratriol	—	IV	16-Oxo,3β,21α,24-OH,Δ^{14}	75
		16-Oxolycoclavanol	—	IV	16-Oxo,3α,21β,24-OH,Δ^{14}	
		Lycocryptol	—	IV	3β,21α,22α,24-OH,Δ^{14}	
		21-Epilycocryptol	—	IV	3β,21β,22α,24-OH,Δ^{14}	
		Diepilycocryptol	—	IV	3α,21β,22α,24-OH,Δ^{14}	
		Lyclaninol	—	IV	3α,21β,20β,24-OH,Δ^{14}	
		Lyclanitin	—	IV	3α,21β,20β,22α,24-OH,Δ^{14}	
		16-Oxolyclanitin	—	IV	16-Oxo,3α,21β,20β,22α,24-OH,Δ^{14}	
		Lycernuic acid A	—	IV	3β,21β-OH,Δ^{14},24-COOH	
		Lycernuic acid B	—	IV	3β,21β,22α-OH,Δ^{14},24-COOH	
L. phlegmaria		Phlegmanol F	254–60	IV	3β,21α,22α-OAc,14β-OH	76
L. serratum		Serratriol	235	IV	3β,21α,24-OH,Δ^{14}	77
(b) Ferns						
Cheilanthes longissima	Polypodiaceae	—	—	IX	3-Oxo,$\Delta^{9(11)}$	78
C. marantae		I	238–42	VIII	6β,22-OH	79
Pleopeltis farinosa	Polypodiaceae	—	137	XI	24-Me,$\Delta^{12,25}$	80
Polypodium feullei	Polypodiaceae	Feullene	—	VIII	16-Oxo,22-OAc,Δ^{12}	81
P. juglandifolium		I	241	IX	6α-OH,$\Delta^{9(11)}$	82
		III	186		20β-OH,$\Delta^{9(11)}$	
		V	120–22	XII	3β-OH,24,24-Me,Δ^{25}, 9,19-cyclo(9β)	
		VII	241	VIII	29-OH	
Gymnospermae						
Abies grandis	Pinaceae	Cyclograndisolide	191–3	XII	3α-OMe,9,19-cyclo(9β),Δ^{24}, 23(*R*)→26-lactone	83
		Epicyclograndisolide	194	XII	3α-OMe,9,19-cyclo(9β),Δ^{24}, 23(*S*)→26-lactone	
Abies mariesii	Pinaceae	Abies lactone	252	XII	3α-OMe,$\Delta^{7,28}$,9β-H, 23(*R*)→26-lactone	84
Pinus monticola	Pinaceae	Methoxylanostenediol	193	XII	3β-OMe,24,25-OH,$\Delta^{9(11)}$	85

Table 1—*continued*

Plant	Family	Substance	mp (°)	Basic skeleton	Groups	Ref.
Angiospermae						
(a) Monocotyledoneae						
Ananas comosus var. *cayenne*	Bromeliaceae	Ananasic acid	194–97	**XII**	3β,11α,15α-OH,Δ^{24},26-COOH,9,19-cyclo(9β)	86
Chionochloa sp.	Gramineae	Cycloartenol methyl ether	118–20	**XII**	3β-OMe,9,19-cyclo(9β),Δ^{24}	87
		Parkeol methyl ether	140–2	**XII**	3β-OMe,$\Delta^{9(11),24}$	
Cymbopogan citratus	Gramineae	Cymbopogone	262–5	R*	3-Oxo,D:A friedoursane	88
		Cymbopogonol	191–3	R	3β-OH,D:A friedours,$\Delta^{4(23)}$	89
(b) Dicotyledoneae						
Aglaia odorata	Meliaceae	Aglaiondiol	125–7	**XI**	3β,25-OH,24-Oxo,Δ^{20}	90
		Aglaitriol	185–7	**XI**	3β,24-25-OH,24(*S*),Δ^{20}	
		Isoaglaitriol	165–7	**XI**	3β,24,25-OH,24(*R*),Δ^{20}	
Alangium lamarckii	Alangiaceae	Alangidiol	224	R	3β,18-OH,18α-B′:A′-*neo*gammacerane	91
		Isoalangidiol	224	R	3α isomer of above	
A. villosum		Isodeoxyemmolactone	189	**VII**	A(1),28-bis*nor*,$\Delta^{2,17,20(29)}$, 27→16α-lactone	92
Alnus serrulatoides	Betulaceae	Alnuserrudiolone	—	**XI**	3-Oxo,12β,20β-OH,Δ^{24}	93
		Alnuseric acid	—	**XI**	3,4-*seco*,3-COOH,$\Delta^{4(28)}$, 20→24-epoxy	94
		Alnuselide	—	**XI**	3,4-*seco*,$\Delta^{4(28)}$,3→11-lactone, 20→24-epoxy,24-Me	95
		Alnuserol	—	**XI**	3-Oxo,11α-OH,20→24-epoxy	96
Alphitonia macrocarpa	Rhamnaceae	Alphitexolide	—	**VII**	A(1)-*nor*,2-COOH,3-(4′-OMe-benzoyl)oxy,$\Delta^{20(29)}$,19→28β-lactone	97
Arnica montana	Compositae	Arnidiol†	—	**VI**	3β,16β-OH,$\Delta^{20(30)}$	98
		Faradiol†	—	**VI**	3β,16β-OH,$\Delta^{20(21)}$	
Astilbe thunbergii var. *congests*	Saxifragaceae	Astilbic acid	208	**I**	3β,6β-OH,Δ^{12},27-COOH	99
Baccharis halimifolia	Compositae	Baccharis oxide	148	**XIV**	3→10-epoxy,Δ^{21}	100
Barbacenia bicolor	Velloziaceae	I	152–4	**XI**	3β,20(*R*)-OH,Δ^{24}	101
		II	99–102	**XI**	3-Oxo,20(*R*)-OH,Δ^{24}	
Barringtonia acutangula	Barringtoniaceae	Barrinic acid	120–3 (acetate)	**I**	2α,3β,19α-OH,Δ^{12},23,28-COOH	102
Betula costata	Betulaceae	—	—	**XI**	3α,12β,17α,25-OH,20→24-epoxy	103
		I	—	**XI**	3α,17α,20-OH,Δ^{24}	104
		II	—	**XI**	3α,12β,17α,25-OH,20→24-epoxy	
B. latifolia		Betulafolianediol	—	**XI**	3α,25-OH,20(*R*)→24(*S*)-epoxy	105
B. platyphylla Sukatchev var. *japonica*		Betulafolientriol oxide	237–40	**XI**	3α,12β,25-OH,20(*S*)→24(*R*)-epoxy	106
B. platyphylla Sukatchev var. *mandshurica*		Betulafolienpentaol	203	**XI**	3α,12β,17,20,25-OH,Δ^{23}	107
B. utilis		Karachic acid	—	**I**	6α-OAc,Δ^{12},28-COOH	108
Bosistoa euodiformis	**Rutaceae**	Bosistoin	225	**XII**	3β-OMe,25-Me,$\Delta^{9(11),24}$	109
Bryonia dioica	Cucurbitaceae	Cucurbitacin S	75	**X**	2,16α-OH,3,11,23-Oxo,$\Delta^{1,5}$, 22α→25β-epoxy	110
Bursera arida	Burseraceae	Benulin	281–3	**VII**	3α-OH,$\Delta^{20(29)}$,28-COOH, 3→25-epoxy	111
Carbralea eichleriana	Meliaceae	Eichlerianic acid	109–11 (Me ester)	**XI**	3,4-*seco*,$\Delta^{4,28}$,3-COOH,25-OH,20(*S*)→24(*R*)-epoxy	112
		Eichleria lactone	126 (Me ester)	**XI**	3,4-*seco*,$\Delta^{4,28}$,3-COOH, 20→24-lactone 25,26,27-tri*nor*	
C. polytricha		Cabraleadiol	175	**XI**	3α,25-OH,20(*S*)→24(*S*)-epoxy	113
		Cabraleone	160		3-Oxo,25-OH,20(*S*)→24(*S*)-epoxy	
Calendula officinalis	Compositae	Ursadiol	240–2	**II**	3β,21α-OH,Δ^{12}	114
		—	244–50	**II**	3,16,21-OH,Δ^{12}	

Table 1—*continued*

Plant	Family	Substance	mp (°)	Basic skeleton	Groups	Ref.
Canthium dicoccum	Rubiaceae	3-Epibetulin	215	VII	3α,28-OH,$\Delta^{20(29)}$	115
Castanopsis lamontii	Fagaceae		187–9	I	3-Oxo,15α-OH,Δ^{12}	116
Castanopsis sp. (six)		—	189–91	VIII	3α-OH,$\Delta^{17(21)}$	117
Catha cassinoides	Celastraceae	Iguesterin	—	III	2-Oxo,3-OH, $\Delta^{1(10),3,5,7,20}$	118
Celastrus paniculatus	Celastraceae	Paniculatadiol	—	I	3β,29-OH	119
Celtis laevigata	Ulmaceae	Moretenol	225	VIII	3β-OH,$\Delta^{22(30)}$	120
Centaurea squarrosa	Compositae	Substance I	—	II	3β-OH,$\Delta^{20(30)}$	121
Cimicifuga acerina	Ranunculaceae	Cimigol	—	XII	3β,25-OH,9,19-cyclo(9β), 16β→23,16α→24-epoxy	122
C. simplex						
C. japonica						
C. acerina		25-*O*-Methylisodahurinol	—	XII	3β,24-OH,25-OMe,15-oxo, 16→23-epoxy,(24*R*)	123
C. simplex		Dahurinol	—	XII	3β,24,25-OH,15-oxo,16→23-epoxy, (24*R*)	
		Dehydroxydahurinol	—	XII	3β,24-OH,15-oxo,16→23-epoxy,(24*S*)	
		Isodahurinol	—	XII	3β,24,25-OH,15-oxo,16→23-epoxy,(24*S*)	
Citrullus colocynthis	Cucurbitaceae	Citrullonol	—	U	3-OH,11-oxo,$\Delta^{5,16,20(22),25}$ 16,24-cyclo	124
Claoxylon polot	Euphorbiaceae	—	262	VII	3β-OAc,20-oxo,30-*nor*	125
Clausena pentaphylla	Rutaceae	*O*-Methylclausenol	182–4	XII	3β-OMe,23,24,24-Me,$\Delta^{9(11),25}$	126
Clethra barbinervis	Clethraceae	Barbinervic acid	298	II	3α,19α,24-OH,Δ^{12},28-COOH	127
Cucurbita lundelliana	Cucurbitaceae	Isomultiflorenone	—	R	3-Oxo,D:C friedoolean,$\Delta^{8(9)}$	128
Datisca glomerata	Cucurbitaceae	Datiscacin	208–12	X	2β,16α,25-OH,3,22-oxo,20β-OAc,$\Delta^{1,5,23}$	129
Datura innoxia	Solanaceae	Daturadiol	260	I	3β,6β-OH,Δ^{12}	130
		Daturaolone	276–9	I	3-Oxo,6β-OH,Δ^{12}	
Ecaballium elaterium	Cucurbitaceae	Anhydro-22-deoxo-3-*epi*-isocucurbitacin D	265–7	X	3α,20β-OH,2,11-oxo,$\Delta^{5,24}$, 16α→23-epoxy	131
		Hexanorcucurbitacin I	Amorph	X	2β,16α-OH,3,11,20-oxo,-$\Delta^{1,5}$,22,23,24,25,26,27-hexa*nor*	
		Hexanor 16-deoxy-ene cucurbitacin 0	230–3	X	2β,3β-OH,11,20-oxo,$\Delta^{5,16}$, 22,23,24,25,26,27-hexa*nor*	
Echinodontium tsugicola	Echinodontiaceae	Substance I	225–7	XII	3-Oxo,22β-OAc,Δ^{24},16→23-epoxy	132
		Substance II	186	XII	3-Oxo,22β-OH,$\Delta^{8,24}$,16→23-epoxy	
		Substance III	230	XII	3α-OH,22β-OAc,$\Delta^{8,24}$,16→23-epoxy	
		Substance IV	232	XII	3α,22β-OH,$\Delta^{8,24}$,16→23-epoxy	
		Substance V	194	XII	3α-OH,$\Delta^{8,24}$,16→23-epoxy	
		Substance VI	194	XII	3β-OH,$\Delta^{8,24}$,16→23-epoxy	
		Substance VII	182	XII	3-Oxo,$\Delta^{8,24}$,16→23-epoxy	
Entandrophragma cyclindricum	Meliaceae	Sapelin C	243–6	R	3-Oxo,7α,23,25-OH,21 → 24-epoxy,apo-tirucall-1,14-ene	133
		Sapelin D	243	R	3α,7α,23,25-OH,21 → 24-epoxy,apo-tirucall-14-ene	
		Sapelin E	239–41	R	3-Oxo,7α,23,24-OH,21→25-epoxy.apotirucall-1,14-ene	
		Sapelin F	210–2	XV	3α,21,23,24,25-OH,Δ^{7}	
Euonymus tingens	Celastraceae	Tingenone	182	III	2,21-Oxo,3-OH, $\Delta^{1(10),3,5,7}$,24,29-bis*nor*	134
		Hydroxytingenone	—	III	20-OH tingenone	
Euphorbia corollata	Euphorbiaceae	Corollatadiol	193–5	XII	3β,24ξ-OH,24-Me,$\Delta^{8(9),25}$	135
E. nerifolia		—	312–4	R	1-Oxo,D:B friedoolean,$\Delta^{5(10)}$	136
E. pulcherrima		Pulcherrol	—	I	Stereoisomer of β-amyrin	137
E. royleana		Epitaraxerol	259	R	3α-OH,D friedoolean,Δ^{14}	138
Fouquieria splendens	Fouquierolaceae	Fouquierol	163–5	X	3β,20,24ξ-OH,Δ^{25}	139
		Isofouquierol	108	X	3β,20,25-OH,Δ^{23}	
Gardenia latifolia	Rubiaceae	3-Episiaresinolic acid	288 (Me ester)	I	3α,19α-OH,Δ^{12},28-COOH	140

Table 1—*continued*

Plant	Family	Substance	mp (°)	Basic skeleton	Groups	Ref.
Glochidion eriocarpum	Euphorbiaceae	Glochidol	201–3	VII	3β-OH,$\Delta^{1,20(29)}$	141
G. macrophyllum		—	209–13	VII	3α,23-OH,$\Delta^{20(29)}$	142
G. multiloculare		Glochilocudiol	235	VII	1α,3β-OH,$\Delta^{20(29)}$	143
Glycyrhiza macedonica	Leguminosae	Macedonic acid	—	I	3β,21α-OH,$\Delta^{11,13(18)}$,29-COOH	144
		Isomacedonic acid	—	I	3β,21α-OH,$\Delta^{9(11),12}$,29-COOH	
Harpullia pendula	**Sapindaceae**	Harpullone	302–4	I	3-Oxo,15α,16α,22α,28-OH,Δ^{12}	145
Holoptelea integrifolia	Ulmaceae	—	294–6 (Me ester)	I	2α,3α-OH,Δ^{12},28-COOH	146
Hydnocarpus octandra	Flacourtiaceae	Octandrolal	318	III	3α-OH,29-CHO	147
		Octandrolol	—	III	3α-OH,29-CH_2OH	
		Octandrolic acid	—	III	3α-OH,29-COOH	
		Octandronal	—	III	3-Oxo,29-CHO	
		Octandronol	—	III	3-Oxo,29-CH_2OH	
		Octandronic acid	—	III	3-Oxo,29-COOH	
Jacaranda caucana	**Bignoniaceae**	Jacoumaric acid	297 (Me ester)	II	2α-OH,3β-(4′ OH cinnamoyl) oxy,Δ^{12}	148
Jatropha macrorhiza	Euphorbiaceae	Acetylaleuritolic acid	298	R	3β-OAc,D-friedoolean,Δ^{14}, 28-COOH	149
Kadsura japonica	Schisandraceae	Kadsuric acid	—	XII	3,4-*seco*,$\Delta^{9(11),4(28),24}$,3,26-COOH	150
Lantana camara	Verbenaceae	Lantanolic acid	306–9	I	3α-OH,3→25-epoxy,Δ^{12},28-COOH	151
		Lantic acid	256–9	II	3α-OH,3→25-epoxy,Δ^{12},28-COOH	152
		Lantadene A	137–9 (Me ester)	I	3-Oxo,22β-(angeloyl)oxy, Δ^{12},28-COOH	153
		Lantadene B	233–5	I	3-Oxo,22β-(dimethyl acryloyl)oxy,Δ^{12},28-COOH	
		—	200–5	I	3-Oxo,24-OH,Δ^{12},28-COOH	
		Lantabetulic acid	280–2	VII	3α-OH,$\Delta^{20(29)}$,28-COOH, 3→25-epoxy	
		Lantanilic acid	277–9	I	3α-OH,Δ^{12},28-COOH,22β-(dimethyl acryloyl)oxy,3→25-epoxy	154, 155
		Lantanolic acid	—	I	3α-OH,Δ^{12},28-COOH,3→25-epoxy	
Lemaireocereus thurberi	Cactaceae	Thurberin	218	VII	3β,16β-OH,$\Delta^{20(29)}$	156
Lithocarpus cornea	Fagaceae	I	298	R	3β,29-OH,D-friedo-olean,Δ^{14}	157
		II	271	R	3β,29-OAc,D-friedo-olean,Δ^{14}	
		III	263	R	3-Oxo,29-OH,D-friedo-olean,Δ^{14}	
		IV	198	R	3-Oxo,29-OAc,D-friedo-olean,Δ^{14}	
		V	214	VIII	3-Oxo,22-OH,21α-H	
		VI	259–61	R	3-Oxo,14α-OH,D-friedo-olean	
		VII	269	R	3β,14α-OH,D-friedo-olean	
		VIII	214	VII	3β,27-OH,$\Delta^{20(29)}$	
L. irwinii *L. litchiodides*		Lithocarpic lactone	319	III	2,3-seco,2→3-lactone	158
L. polystachya		I	224	VII	3-Oxo,20-OH	159
		II	227–9	VII	3β-OAc,29-CHO	
		III	237–9	VII	3β,29-OH	
Litsea tomentosa	Lauraceae	Litsomentol	218	X	3β,5α-OH,Δ^{24}	160
Lyonia ovalifolia var. *elliptica*	Ericaceae	—	—	I	2α-OAc,3-(4′OH,*trans* cinnamoyl)oxy,Δ^{12},28-COOMe	161
Mallotus paniculatis	Euphorbiaceae	—	274	VIII	3,22-Oxo,29-*nor*,21α-H	162
M. hookerianus			342–7	II	3-Oxo,Δ^{12},27,28-COOH	
			262–8	II	3β,28-OH,Δ^{12},27-COOH	

Table 1—*continued*

Plant	Family	Substance	mp (°)	Basic skeleton	Groups	Ref.
M. repandus		I	385	II	3β-OH,12β→28-lactone,13α-H	163
		II	240–2	II	3β-OBz,12β→28-lactone,13α-H	
		III	319–21	II	3α-OH,12β→28-lactone,13α-H	
M. stananthus		Mallotin	190	XII	3α-OH,24,24-Me,$\Delta^{7,25}$	164
Maytenus dispermus	Celastraceae	Dispermoquinone	—	III	2,7-Oxo,$\Delta^{1(10),3,5}$,30-COOMe	165
M. ilicitfolia		Maitenin	228	III	2-Oxo,3-OH,$\Delta^{1(10),3,5,7}$,24-*nor*,?-oxo	166
M. senegalsis		Maytenonic acid	262	III	3-Oxo,29-COOH	167
Melia azedarach	Meliaceae	Methyl kulonate	107	XIII	3-Oxo,16β-OH,$\Delta^{7,24}$,21-COOMe,20(*R*)	168
Melianthus comosus	Melianthaceae	—	—	I	3β-OH,27-(3′,4′OH,*trans*-cinnamoyl)oxy,Δ^{12},28-COOH	169
Mesua myrtifolia	Guttiferae	Myrtifolic acid	259	R	3α-OH,D:C friedo-urs, Δ^{7},28-COOH	170
Mimusops littoralis	Sapotaceae	I	—	I	3β-(Caproyl)oxy,Δ^{12}	171
		II	—	R	3β-(Lignoceroyl)oxy,D-friedo-olean,Δ^{14}	
Myroxylon balsamum	Leguminosae	—	190	I	3-Oxo,6β-OH,Δ^{12},28-COOH	172
		20*R*,24-Ocotillone	204	XI	3-Oxo,25-OH,20(*R*)→24ξ-epoxy	173
Neolitsea pulchella	Lauraceae	Substance I	214–7	XII	3β-OMe,24,24-Me,$\Delta^{9(11),25}$	174
		Substance II	168–71	XII	3-Oxo,24,24-Me,$\Delta^{9(11),25}$	
		Substance III	272–5	XII	3β-OMe,24ξ-OH,24,25-Me,$\Delta^{9(11)}$	
		Substance IV	248–50	XII	3β,24ξ-OMe,24,25-Me,$\Delta^{9(11)}$	175
		Substance V	178–81	XII	3-Oxo,24ξ-OMe,24,25-Me,$\Delta^{9(11)}$	
Olea europea	Oleaceae	Substance I	—	I	2α,3β-OH,Δ^{12},28-COOMe	176
		Substance II	183	I	3β-OH,$\Delta^{13(18)}$,28-COOMe	
Parthenium argentatus	Compositae	Argentatine A	—	XII	3-Oxo,16,25-OH,9,19-cyclo-(9β),20(*R*)→24(*S*)-epoxy	177
		Argentatine B	—	XII	3-Oxo,25-OH,9,19-cyclo-(9β),16→23-epoxy,24-Me	
		Argentatine C	—	XII	3-Oxo,16,23,24-OH,9,19-cyclo(9β),24-Me	
P. incanum		Incaniline	—	XII	3-Oxo,16,25-OH,Δ^{8},20→24-epoxy,30-*nor*,17 ξ-H	178
Pachysandra terminalis	Buxaceae	Pachysonol	278–80	III	3-Oxo,16α-OH	179
		Pachysantriol	—	III	2α,3β,16β-OH	180
Pertya robusta	Compositae	*O*-Methylpertyol	223	XII	3β-OMe, 24-(=CH_2),25-ethyl,	181
Phytolacca americana	Phytolaccaceae	Phytolaccagenic acid	—	I	3β,23-OH,Δ^{12},28-COOH,-30-COOMe	182
P. esculenta		Esculentic acid	>360	I	3β,23-OH,Δ^{12},28,30-COOH	183
Phitolacca rivinoides		—	230–5	I	3β-OH,30β-COOMe,Δ^{12},28-COOH	184
Planchonia careya	Barringtoniaceae	- -	274–6	I	3-Oxo,16α,21β,22α,28-OH,Δ^{12}	185
Plenckia polpunea	Celastraceae	Polpunonic acid	—	III	3-Oxo,30-COOH	186
Polyalthia oliveri	Annonaceae	Polycarpol‡	173	XII	3β,15α-OH,$\Delta^{7,9(11),24}$	187
Prunus lusitanica	Rosaceae	—	196–8 (Me ester)	II	2α,3α-OH,Δ^{12},28-COOH	188
P. serotina						
Pterocarpus santalinus	Leguminosae	—	234	VII	2α,3β-OH,$\Delta^{20(29)}$	189
Putranjiva roxburghii	Euphorbiaceae	Roxburghonic acid	>340	III	3-Oxo,25-COOH	190
Quercus bombusaefolia	Fagaceae	I	247	R	3-Oxo,D-friedo-olean,$\Delta^{1,14}$	191
Q. championi		II	231–4	R	3β,16α-OH,D-friedo-olean,Δ^{14}	
Q. myrsinaefolia		III	209–11	VIII	3β,22-OH,21α-H	
		IV	194	XII	3β-OH,24,25-Me,$\Delta^{9(11),23}$	
		V	209	XII	3β-OAc,24,25-Me,$\Delta^{9,(11),23}$	
		VI	146	XII	3-Oxo,24,25-Me,$\Delta^{9(11),23}$	
Q. gilva			—	XII	3β-OAc,24,24-Me,$\Delta^{9(11),25}$	192
Q. glauca		Cyclobalanone	187–90	XII	3-Oxo,9,19-cyclo(9β),24,24-Me,Δ^{25}	193, 194

Table 1—*continued*

Plant	Family	Substance	mp (°)	Basic skeleton	Groups	Ref.
Rhododendron collettianum *R. macrophyllum*	Ericaceae	Dendropanoxide (=Campanulin)	—	R	D:B friedo-olean,3→10-oxide	195, 196, 197
Rhodomyrtus tomentosa	Myrtaceae	R_4	243–46	VIII	3β-OH,30-CHO,$\Delta^{22(29)}$	198
		R_5	287–89	I	3β-OAc,12-oxo,13→28-lactone	
Salacia macrosperma	Celastraceae	Salacia quinonemethide	203–5	III	2,21-Oxo,3-OH,-$\Delta^{1(10),3,5,7,9(11)}$,30-COOMe,11-Me,12-*nor*	199
S. prinoides		Compound P	280–3	III	1,3-Oxo	200
		Compound Q	303–5	III	1,3-Oxo,24-CHO	
		Compound S	305–10	III	1,3-Oxo,7α-OH	
		Compound T	285–7	III	1,3-Oxo,24-CH_2OH	
		Compound U	330–5	III	1,3-Oxo,24-COOH	
		Compound B	290–5	III	1,3-Oxo,7→24-epoxy	201
		Compound R	300	III	1,3-Oxo,25→26-epoxy	202
Salvia broussoneti	Labiatae	Anagadiol	212–4	I	1β,3β-OH,$\Delta^{18(19)}$	203
S. horminum		—	228	I	2β,3β-OH,$\Delta^{13(18)}$	204
S. virgata		Virgatic acid	226–8	I	1-Oxo,3β-OAc,Δ^{12},28-COOH	205
Sandorium indicum	Meliaceae	Bryononic acid	244	R	3-Oxo,D:C friedo-olean, Δ^{8},29-COOH	206
Schinus molle	Anacardiaceae	—	—	XIII	3-Oxo,21-CHO,$\Delta^{8,24}$,26-COOMe	207
		-	-	XIII	3-Oxo,$\Delta^{8,24}$,26-COOMe	
S. terebenthifolius		Bauerenone	240	R	3-Oxo,D:C friedo-urs,Δ^{7}	208
		Terebenthifolic acid	270	R	3-Oxo,D:C friedo-urs, Δ^{7},28-COOH	
Schizandra nigra	Magnoliaceae	Nigranoic acid	—	XII	3,4-*seco*,$\Delta^{4(28),24}$,9,19-cyclo(9β),3,26-COOH	209
Scoparia dulcis	Scrophulariaceae	Ifflaionic acid§	265–7	II	3-Oxo,Δ^{12},30-COOH	210
Shorea acuminata	Dipterocarpaceae	—	296–9 (Me ester)	I	2α,3α-OH,Δ^{12},28-COOH	211
Simarouba amara	Simaroubaceae	Triterpene 2	154	XV	3-Oxo,20-CHO,$\Delta^{7,24}$	
		Triterpene 3	115	XV	3-Oxo,$\Delta^{7,24}$	
Suriana maritima	Surianaceae	Surianol	173	XII	3β,4α-OH,9,19-cyclo(9β),24-(=CH_2),28-29-bis*nor*	213
Swietenia mahagoni	Meliaceae	Cyclomahogenol	151	XII	3β,16β-OH,9,19-cyclo (9β),Δ^{24}	214
		Cycloswietenol	123	XII	3β-OH,9,19-cyclo(9β),22-Me,Δ^{20}	215
Terminalia sericea	Combretaceae	Sericic acid	282	I	2α,3β,19α,24-OH,Δ^{12},28-COOH	216
Thea sinensis (Tea seed)	Theaceae	—	—	XIII	3β-OH,$\Delta^{7,24}$	217
Trechadenia zeylanica	Flacourtiaceae	Trechadenic acid A	292–3	III	3α-OH,26-COOH	218
		Acetyltrechadenic acid A	251	III	3α-OAc,26-COOH	
		Acetyltrechadenic acid B	261	III	3β-OAc,26-COOH	
		Trechadonic acid	245	III	3-Oxo,26-COOH	
		Trichadenal	300	III	3β-OH,26-CHO	219
		O-acetyltrichadenal	246	III	3β-OAc, 26-CHO	
Trevoa trinervis	Rhamnaceae	Trevoagenin A	—	XII	25,30-OH,16-oxo,20→24-epoxy	220
		Trevoagenin B	—	XII	Isomer of trevoagenin A	
Trichosantes palmata	Cucurbitaceae	Cyclotrichosantol	143	R	4α,14α-dimethyl,24-ethyl,9,19-cyclocholest-25-ene-3β-ol	221
Vernonia fasciculata	Compositae	—	—	R	3β-OAc,D:C friedo-olean,$\Delta^{8(9)}$	222
Xanthoxylum rhetsa	Rutaceae	Xanthoxylone	230	I	7-Oxo,Δ^{12}	223
Xylosma velutina	Flacourtiaceae	Velutinic acid	290	III	3-Oxo,21α-OH,28-COOH	224

* 'R' denotes rearranged structure and 'U' denotes unknown structure.
† These are also present in *Tussilago farfara* (Compositae) [98].
‡ Also isolated from *Meiocarpidium lapidotum* Engl. & Diels. (Annonaceae) [187].
§ Also isolated from *Flindersia* sp. [228].

Table 2. Triterpenoids from miscellaneous sources

Source	Family	Substance	mp (°)	Basic skeleton	Groups	Ref.
Acetobacter xylinum	—	Tetrahydroxy bacteriohopane	—	VIII	22-$CH_3CH_2CH_2CH(OH)CH(OH)CH_2OH$	224, 225
		Methyl tetrahydroxy bacteriohopane	—	VIII	3-Me,22-$CH_3CH_2CH_2$-$CH(OH)CH(OH)CH_2OH$	226
Green River shale (Eocene, 60×10^6 years old)	—	Tetrahymanol	313	R	3α-OH gammacerane	227

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