

REVIEW

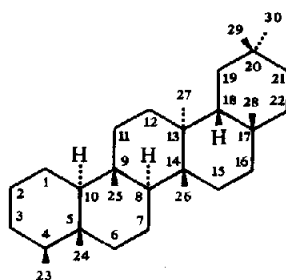
FRIEDELIN AND ASSOCIATED TRITERPENOID^{*}R. FRANK CHANDLER[†] and SHIRLEY N. HOOPER

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Key Word Index—D: A-friedelooleanane; friedelan-3-one; friedelin; friedelane; friedelanols; pentacyclic triterpenes; occurrence; properties.

Abstract—The literature is reviewed for the natural occurrence of the pentacyclic triterpenes, friedelin and the epimeric 3-friedelanols. A summary of the literature relating to the structure elucidation, physical properties, synthesis and biosynthesis of these friedelane derivatives is presented. Compounds possessing the same carbon skeleton (D: A-friedelooleanane) and occurring with at least one of the above friedelane derivatives are also tabulated.



1 Friedelane (D: A-Friedelooleanane)

Fig. 1. Skeleton and numbering of the friedelanols.

The scientific literature on friedelin, the 3-keto-derivative of the hydrocarbon, friedelane (Fig. 1), and related compounds (Table 1) is widely scattered; only limited information is available in the various general reviews on pentacyclic triterpenes.

White [1] summarized the data on structure determination of friedelin and some of its derivatives. Extensive tables of melting points[§], derivatives, and some

indication of plant source are available in the review by Halsall and Alpin [2]. Elsevier [3] covers all aspects until 1946 and structures until 1952. Kulshreshtha *et al.* [4] present a survey of the occurrence and structures of triterpenoids for the period 1963-70. However there are few listings for friedelin-related compounds. The only comprehensive review with friedelin as the focus is provided by Sainsbury [5]. Although his article lists only 73 sources of friedelin, it also documents the associated occurrence of the epimeric 3-friedelanols and other triterpenes.

Friedel [6], according to Karrer [7], first isolated friedelin; however, a much earlier reference is provided by Elsevier [3] to Chevreul [8] who obtained a substance from cork which he called 'cerine'. In 1899 Istrati and Ostrogovich [9] showed that cerine was composed of two substances, one they named friedelin in honor of their friend Friedel and the other cerin.

By 1935, Drake and Jacobsen [10] had repeated the isolation of friedelin and cerin, determined their molecular weights and empirical formulae and proven a common skeleton. Drake, working with Shrader [11] and Haskins [12], presented evidence that friedelin contained a ketone and that cerin was a hydroxyketone. The ensuing years saw numerous reports on studies of friedelin, with chemists preparing derivatives, attempting to trace biosynthetic intermediates and trying to synthesize friedelin.

Efforts to elucidate the structure and conformation were based initially on the preparation of derivatives and their comparison with known compounds [13-15]. Most modern physical methods were yet to be developed, but Drake and Wolfe [16] investigated the surface films formed by friedelin and cerin, and Lander and Svrbely [17] studied the structure of friedelin using the dipole moments of cerin, friedelin and various isomers. The

^{*} This review covers all articles listed in *Chem. Abstr.* up to and including Vol. 88, No. 22, 1978.

[†] To whom inquiries should be directed.

[§] For the more common physical properties the reader is also referred to standard works such as: (1965 *et seq.*) *Dictionary of Organic Compounds*, 4th edn. and supplements, Eyre and Spottiswoode, London; Devon, T. K. and Scott, A. I. (1972) *Handbook of Naturally Occurring Compounds*, Vol. II, Academic Press, New York; Newman, A. A. (ed.) (1972) *Chemistry of Terpenes and Triterpenoids*, Academic Press, London or (1976) *The Merck Index*, Merck, Rahway.

Table 1. Names and structures of friedelanes*

No.	Name†	Type and location of functional groups on friedelane‡						Seco
		C=C	OH	C=O	CHO	CO ₂ H	—O—	
1	Friedelane							
2	Friedelin			3				
3	Friedelan-3 α -ol		3 α					
4	Friedelan-3 β -ol		3 β					
5	Canophyllal		3 β		28			
6	Canophyllic acid		3 β			28		
7	Canophyllol		3 β , 28					
8	Cerin		2 α	3				
9	3,21-Dihydroxyfriedelan-25-oic acid		3 ξ , 21 ξ			25		
10	3,4-Epoxyfriedelane						3 α , 4 α	
11	Friedelan-1,3-dion-24-al			1, 3	24			
12	Friedelan-3,21-dion-25-al			3, 21	25			
13	Friedelan-1,3-dione			1, 3				
14	Friedelan-2,3-dione			2, 3				
15	Friedelan-3,21-dione			3, 21				
16	Friedelan-1,3-dion-24-oic acid			1, 3		24		
17	Friedelan-1,3-dion-24-ol		24	1, 3				
18	Friedelan-3-on-25-al			3	25			
19	Friedel-2-ene	2						
20	Friedel-3-ene	3						
21	Friedel-1-en-3-one	1		3				
22	7 α -Hydroxyfriedelan-1,3-dione		7 α	1, 3				
23	25-Hydroxyfriedelan-3,21-dione		25	3, 21				
24	21 β -Hydroxyfriedelan-3-on-25-al		21 β	3	25			
25	21 α -Hydroxyfriedelan-3-one		21 α	3				
26	21 β -Hydroxyfriedelan-3-one		21 β	3				
27	25-Hydroxyfriedelan-3-one		25	3				
28	21 α -Hydroxyfriedel-4(23)-en-3-one	4(23)	21 α	3				
29	Octandrolal		3 α		29			
30	Octandrollic acid		3 α			29		
31	Octandrolol		3 α , 29					
32	Octandronal			3	29			
33	Octandronic acid			3		29		
34	Octandronol		29	3				
35	25,26-Oxido-friedel-1,3-dione			1, 3			25 β , 26 β	
36	Pachysandiol A		2 α , 3 β					
37	Pachysandiol B		3 β , 16 ξ					
38	Pachysantriol		2 α , 3 β , 16 ξ					
39	Pachysonol		16 ξ	3				
40	Putranjic acid		2			3		3, 4
41	Putranjivadione			3, 7				
42	Putranjivic acid	4(23)				3		3, 4
43	Roxburgholone		3 α	7				
44	Roxburghonic acid			3		25		
45	Trichadenal		3 β		26			
46	Trichadenic acid A		3 α			26		
47	Trichadenic acid B		3 β			26		
48	Trichodonic acid			3		26		

* See Table 2 for occurrence and citations.

† Names used are those of the literature.

‡ See Fig. 1 for basic structure and numbering system.

latter paper contains an early reference to friedelan-3 α -ol.

In 1944 and 1949 Ruzicka and co-workers [18, 19] published the results of their attempts to derive the structure of friedelin by chemical means. However, it was not until 1955 that two groups (Dutler, Jeger and Ruzicka [20], and Corey and Ursprung [21, 22]), working independently, arrived at the accepted structure as a result of dehydrogenation studies and the isomerization of friedel-3-ene to olean-13(18)-ene. The structure

was confirmed independently by Brownlie and co-workers [23–25] and Ourisson and co-workers [26]. Further studies of the friedelin-oleanene rearrangement continued with attempts to isolate the intermediate compounds [27–31].

After the structure of friedelin was established, studies were done, notably by Djerassi and co-workers [32, 33], to determine the configuration using optical rotary dispersion. A crystallographic study of friedelin was

carried out by Rogers and Thomas [34] who reported that the unit cell contained four molecules, the formula indicated was $C_{30}H_{50}O$ and the crystals were orthorhombic. Further studies concluded that there were two possible conformations, the quasi-all-chair and the chair:chair:chair:boat:boat [35]. More recently, the crystal structure and conformation of friedelan-3 β -ol have been reported and confirmed the latter conformation [36].

Isolation procedures have been refined with the development of chromatography and its application to natural products. Stevenson and Kane [37, 38] reported a convenient isolation procedure for obtaining friedelin and related compounds from cork-board by-products.

Further details on column chromatography in the isolation and purification of triterpenes, including friedelin and related compounds, have been reported by Cambie and Parnell [39] and Sengupta and Mukherjee [40].

Several publications deal with TLC of pentacyclic triterpenes. Information regarding solvent systems, detection reagents and R_f values is available [41–43]. Increased efficiency in separating compounds of a given class is obtained on plates impregnated with silver nitrate as described by Fisher and Hertel [44] and by Barua *et al.* [45].

GLC of pentacyclic triterpenes utilizing a variety of column packing materials has been reported. Thus, Ikan and Gottlieb [46] obtained good results with the trimethylsilyl derivatives of triterpenes on a nitrile silicone phase, XE-60. Fokina and Belova [47] reported the use of SE-30, while Ikekawa *et al.* [48] compared results on a variety of columns.

Spectroscopic methods have also been applied to the study of triterpenes. Ourisson and Takahashi [49] published the IR spectrum of friedelin and Cole *et al.* [50] reported the spectrum of friedelan-3 α -ol. Solvent effects in IR spectroscopy were reported by Oganessian *et al.* [51] and Brooks *et al.* [52].

The development of NMR spectroscopy and mass spectrometry (MS) resulted in a series of papers reporting, first, the spectra obtained with known compounds, and then, the attempts to correlate this knowledge with the spectra of compounds of undetermined structures. Djerassi and co-workers [53–55] were responsible for much of the general application of MS to triterpenes, including friedelin, while Courtney *et al.* [56, 57], Hunech and Tummler [58], and Hirota *et al.* [59] considered the problem of friedelin-related derivatives.

Shamma *et al.* [60] published NMR spectra of a series of triterpenoid derivatives with correlations between spectra and structure as did Djerassi [54]. The value of NMR in structure elucidation was increased with the application of solvent induced shifts [61] and the development of shift reagents [62, 63], the use of ^{13}C NMR [64–66], and the application of homonuclear INDOR spectroscopy [67, 68].

The utility of combining NMR spectroscopy and MS in the determination of friedelin-related compounds is well demonstrated by two series of papers. Kikuchi and co-workers [69–72] isolated friedelin-type components from *Pachysandra terminalis* and formulated the structures based on the spectroscopic evidence of the compounds and their derivatives. The other series, by Courtney and co-workers, dealt with a number of

carbonyl, hydroxycarbonyl and polyhydroxy friedelanols isolated from *Siphonodon australe* [28, 29, 73–76].

A series of papers by Stevenson and his co-workers [77–79] explored the reactions of friedelin and friedelane with bromine and with *n*-bromosuccinimide. Takyuki *et al.* [80] and Shoppe and Johnson [81] provided interesting comments on yields in these preparations. Stevenson and co-workers [82–84] went on to investigate the effects of ultraviolet light on reactions involving friedelin and its derivatives.

Many Japanese workers were involved in the preparation of a wide variety of compounds using friedelin as the starting material [85], and varying the reaction conditions [86, 87] and/or employing irradiation [88–91]. Thus, 2-oxo-3-oxa-friedelane [92], epoxyfriedelane [93, 94], friedelan-3-on-24-al [95], 5 α -ethyl-10 β -(carbomethoxymethyl)-des-A-friedelone [96], 3 β -friedelanol, 3 α -friedelanol [97, 98], 3,4-seco-3-norfriedelan-2-al [99], 4-epifriedelin, 4-epishione [100, 101], and some nitrogen-containing friedelanols [102] were prepared. A one step synthesis of putranjivic acid from friedelin by photochemical oxidation in benzene under oxygen was also accomplished [103].

In addition, other workers employed a wide variety of techniques and reactions to explore the structure and reactivity of friedelin and related compounds. Among these were the reduction of cerin oxime [104]; the preparation of epimeric 3-amino friedelanols [105]; the acid catalysed rearrangement of the 3-friedelene into 13(18)-oleanene [31]; conformation studies of oxotriterpenes using circular dichroism [106, 107]; and surveys of the possible rearrangements leading to friedelin-type compounds [108, 109].

The biosynthesis of triterpenes has been reviewed by Rees and Goodwin [110] and discussed by Sengupta [111].

The chemical synthesis of friedelin starts with a more available triterpene such as amyryl [112] or with a readily available tetracyclic triterpene [113], or attacks the problem through the stereo-specific synthesis of intermediates [114, 115]. A total synthesis of friedelin was reported in 31 steps and 0.3% yield [116].

Finally, the use of friedelin or friedelin-type compounds has been considered for treatment of cancer of the bladder [117], convulsions, inflammation [118], topical ulcers, rheumatic inflammation, fever and dysentery [119]. Friedelin has also been found to have an 'antifeedant' activity upon some insects [120].

The natural occurrence of friedelin and the 3-friedelanols is extensive. Friedelin has been reported in many of the higher plants and in algae [121, 122], lichens [123, 124], mosses [125, 126], peat [42, 43, 46, 127, 128], coal [129–134], and mineral wax [135]. It has also been reported in swine [136] and epifriedelinol has been found in microorganisms [137]. Finally, a word of caution, the finding of friedelin in a study of polyhydroxylated neutral aglucons [138] was attributed to the cork stoppers used in the extraction!

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Table 2. Occurrence of friedelin, the friedelanols and associated friedelanones*

Plant	Part used	Friedelanones identified†				References
		2‡	3§	4	Others	
<i>Abroma augusta</i>	bark, roots	+				146, 147
<i>Acer amoenum</i>	leaves	+				148
<i>Acokanthera spectabilis</i>	various parts	+				120, 149, 150
<i>Actinodaphne augustifolia</i>	leaves	+				151
<i>Aesculus hippocastanum</i>	seed oil	+				152
<i>Ageratum conyzoides</i>	plant material	+				153
<i>Ageratum houstonianum</i>	plant material	+		+		153
<i>Alangium lamarckii</i>	leaves	+				154
<i>Albizzia lebeck</i>	bark	+				155
<i>Alectoria ochroleuca</i>	whole plant	+				123
<i>Alectryon excelsum</i>	bark	+		E		156
<i>Aleurites montana</i>	bark	+				157
<i>Antidesma buniuz</i>	leaves, stems	+				158
<i>Antirrhoea chinensis</i>	leaves	+		+		159
<i>Aporosa chinensis</i>	leaves, stems	+		+		160
<i>Argyrea speciosa</i>	leaves			E		161
<i>Argyrea populifolia</i>	fruit	+		+		162
<i>Arundinaria chino</i>	rhizomes	+				163
<i>Arundinarieae</i> ¶	whole plant	+		E		164
<i>Arundinella hirta</i>	herb	+				163
<i>Arundo donax</i>	leaves	+				165
<i>Asclepias tuberosa</i>	leaves	+				166
<i>Aster baccharoides</i>	leaves	+				167
<i>Aster baccharoides</i>	stems	+		+		167
<i>Aster scaber</i>	roots	+		+		168
<i>Aster tataricus</i>	roots	+		E		5, 169
<i>Atalantia monophylla</i>	leaves	+		E		170
<i>Athrixia pinilolia</i>	roots	+		E		171
<i>Avicennia officinalis</i>	aerial parts	+				172
<i>Baccaurea sapida</i>	bark	+		E		173
<i>Baccharis salicifolia</i>	whole plant	+		+		174
<i>Balanops australiana</i>	bark	+	+	+	8	175, 176
<i>Bischofia javanica</i>	bark	+		E**		177
<i>Bischofia trifoliata</i>	leaves, stems	+	+	+		178
<i>Bridelia micrantha</i>	bark	+		E		179
<i>Bridelia monoica</i>	leaves, stems	+		+		180
<i>Bridelia stipularis</i>	bark	+				181
<i>Bromus rigidus</i>	culms, blades	+				163
<i>Brosimum</i> ¶ (Takini bark)	bark	+				182
<i>Byrsonima verbascifolia</i>	bark	+				183
<i>Cacalia bulbifera</i>	whole plant	+				184
<i>Calophyllum apetalum</i>	bark	+				185
<i>Calophyllum brasiliense</i>	not stated††	+				186
<i>Calophyllum cordato-oblongum</i>	bark, wood	+				187
<i>Calophyllum cuneifolium</i>	bark	+				188
<i>Calophyllum inophyllum</i>	bark	+		+		185, 189
<i>Calophyllum inophyllum</i>	leaves	+			5-7	190
<i>Calophyllum thwaitesii</i>	bark	+				191
<i>Calophyllum tomentosum</i>	bark	+		+		185
<i>Cannabis sativa</i>	root	+		E		192, 193
<i>Canscora decussata</i>	aerial parts	+		+		194
<i>Canscora decussata</i>	roots	+		E		195
<i>Caraipa densiflora</i>	wood	+				196
<i>Carapa obovata</i>	bark, leaves	+				197
<i>Caryocar brasiliense</i>	leaves	+	+			198
<i>Castanopus concinna</i>	leaves, stems	+		+	7	199, 200
<i>Castanopus cuspidata</i>	leaves	+	+	+		199, 200
<i>Castanopus cuspidata</i>	stems	+	+	+		200
<i>Castanopus cuspidata</i> var. <i>sieboldii</i>	bark	+				5, 201
<i>Castanopsis eyrei</i>	leaves, stems	+		+		199, 200, 202
<i>Castanopsis fabri</i>	leaves	+		+		199, 200
<i>Castanopsis fabri</i>	stems	+		+	14	200
<i>Castanopsis fissa</i>	leaves, stems	+		+		199, 200
<i>Castanopsis hickelii</i>	leaves, stems	+		+		199, 200
<i>Castanopsis lamontii</i>	leaves	+		+		203
<i>Castanopsis lamontii</i>	stems	+		+	7, 10	203

Table 2.—continued

Plant	Part used	2‡	Friedelanes identified†			References
			3§	4	Others	
<i>Ceratopetalum apetalum</i>	bark	+		E		204
<i>Cetruria crispa</i>	whole plant	+				123
<i>Cetruria cucullata</i>	whole plant	+				123
<i>Cetruria delisei</i>	whole plant	+				123
<i>Cetruria islandica</i>	whole plant	+				123
<i>Cetruria nivalis</i>	whole plant	+		E	8	123, 124
<i>Choisya ternata</i>	leaves	+				205
<i>Citrus aurantium</i> var. <i>sinensis</i>	oil from peel	+				206
<i>Citrus paradisi</i>	oil from peel	+				207
<i>Cladonia alpestris</i>	whole plant	+				123
<i>Claoxylon polot</i>	leaves	+				208
<i>Clerodendron trichotomum</i>	bark	+				201
<i>Clusia rosea</i>	plant material	+	+	+		209
<i>Coix lacryma-jobi</i>	herb	+				163
<i>Colletia hystrix</i>	not stated††	+				210
<i>Colletia spinosa</i>	not stated††	+				210
<i>Conocephalum conicum</i>	not stated††	+				211
<i>Cuphea balsamona</i>	not stated††	+				212
<i>Cynanchum vincetoxicum</i>	not stated††	+				213
<i>Cynodon dactylon</i>	herb	+				163
<i>Dalbergia volubilis</i>	wood chips	+				214
<i>Dichrostachys cinerea</i>	bark, roots	+		+		215, 216
<i>Diospyros buxifolia</i>	leaves, stems	+		E		217
<i>Diospyros kaki</i>	flowers	+				218
<i>Elaeocarpus hookerianus</i>	wood	+				39
<i>Elephantopus scaber</i>	plant material			E		219
<i>Erica arborea</i>	not stated††	+				220
<i>Erythrospermum zeylanicum</i>	bark	+				221
<i>Eugenia fruticosa</i>	bark	+		E		222
<i>Eugenia jambolana</i>	stem bark	+		E		223, 224
<i>Eugenia wallichii</i>	bark	+		E		222
<i>Euonymus alata</i>	leaves	+		E		225
<i>Euonymus japonica</i>	leaves	+	+	E		226
<i>Euonymus radicans</i>	leaves		+			226
<i>Euphorbia antiquorum</i>	stems		+	+		227–229
<i>Euphorbia azureum</i>	leaves, stems			E		230
<i>Euphorbia hirta</i>	plant material	+				231
<i>Euphorbia hirta</i>	stems	+				232
<i>Euphorbia longana</i>	leaves			E		233
<i>Euphorbia nerifolia</i>	leaves		+	+		234
<i>Euphorbia nerifolia</i>	stems		+			234
<i>Festuca parvigluma</i>	herb	+				163
<i>Ficus bengalensis</i>	leaves	+				235
<i>Ficus nitida</i>	leaves	+		E		236
<i>Flotowia dicanthoides</i>	not stated††	+	+			237
<i>Fluggea microcarpa</i>	bark	+	+			238
<i>Fluggea virosa</i>	leaves	+	+			208
<i>Fluggea virosa</i>	stems	+		+		208
<i>Frullania tamarisci</i>	not stated††	+				239
<i>Fucus evanescens</i>	whole plant	+				122
<i>Grewia asiatica</i>	stem bark	+				240
<i>Glochidion macrophyllum</i>	leaves, stems	+		+		241
<i>Glochidion puberum</i>	leaves, stems	+		+		242
<i>Glycosmis mauritiana</i>	leaves, stems	+				151
<i>Gauzuma tomentosa</i>	bark	+				243
<i>Guazuma tomentosa</i>	leaves		+	**	+	244
<i>Gymnocolea inflata</i> ††	whole plant		+	+		126
<i>Gymnosporia wallichiana</i>	whole plant	+				246
<i>Haplopappus angustifolius</i>	not stated††	+		E		247
<i>Haplopappus foliosus</i>	not stated††	+		E		247
<i>Haplopappus heterophyllus</i> §§	not stated††	+	+			248
<i>Hemarthria sibirica</i>	herb	+				163
<i>Heimerocallis longituba</i>	roots	+				249
<i>Heterophragma adenophyllum</i>	fruit	+				250
<i>Holcus lanatus</i>	herb	+				163
<i>Holoptelea integrifolia</i>	leaves	+		+		251
<i>Hydnocarpus octandra</i>	fruit, wood	+				252

Table 2. continued

Plant	Part used	Friedelanes identified†				References
		2‡	3§	4	Others	
<i>Hydnocarpus octandra</i>	bark	+	+	+	29, 34, 46, 47**	252
<i>Hypserpa nitida</i>	leaves	+				253
<i>Imperata cylindrica</i>	culms, blades	+				163, 254
<i>Inula helenium</i>	oil from root	+				255
<i>Iresine pringlei</i>	ground stem, leaves	+				256
<i>Kalanchoe spathulata</i>	flowers	+				257
<i>Kielmeyera rosea</i>	branches	+				258
<i>Legnephora moorei</i>	whole plant	+				259
<i>Lithocarpus attenuata</i>	leaves	+		+	36	260
<i>Lithocarpus attenuata</i>	stems	+		—		260
<i>Lithocarpus cornea</i>	leaves, stems	+		—		260, 261
<i>Lithocarpus elizabethae</i>	leaves, stems	+		—		260
<i>Lithocarpus glabra</i>	leaves, stems	+		+		260, 261
<i>Lithocarpus haipinii</i>	leaves	+		+	7	260
<i>Lithocarpus haipinii</i>	stems	+		+		260
<i>Lithocarpus hancei</i>	leaves	+		+		260, 261
<i>Lithocarpus hancei</i>	stems	+		+	36	260
<i>Lithocarpus harlandi</i>	leaves	+		+	36	260, 261
<i>Lithocarpus harlandi</i>	stems	+		+		260, 261
<i>Lithocarpus irwinii</i>	leaves	+		+	14, 36	260, 262
<i>Lithocarpus irwinii</i>	stems	+		+		260, 262
<i>Lithocarpus litchioides</i>	leaves	+		+	36	260, 262
<i>Lithocarpus litchioides</i>	stems	+				260, 262
<i>Lithocarpus polystachya</i>	leaves, stems	+		+		260, 261, 263
<i>Lophatherum gracile</i>	culms, blades	+				163
<i>Lophopetalum rigidum</i>	bark	+				264
<i>Macaranga tanarius</i>	stems	+		+	20	265
<i>Madhuca huynhceae</i>	bark	+				266
<i>Madhuca nerifolia</i>	bark, wood	+				267
<i>Mallotus paniculatus</i>	leaves	+		+		160
<i>Mangifera indica</i>	roots	+				268
<i>Maytenus heterophylla</i>	bark	+		E		269
<i>Melaleuca leucadendron</i>	leaves, stems	+				270
<i>Melanolepis multiglandulosa</i>	not stated††	+				271
<i>Microstegium vimineum</i>	herb	+				163
<i>Mikania cordata</i>	roots	+		E		272, 273
<i>Milletia dielsiana</i>	leaves	+		+		274
<i>Milletia nitida</i>	leaves	+		+		274
<i>Milletia pachycarpa</i>	leaves	—		+		274
<i>Mimosa rubicaulis</i>	roots	+				275
<i>Miscanthus sacchariflorus</i>	culms, blades	+				163
<i>Miscanthus sinensis</i>	culms, blades	+				163
<i>Monostroma nitidum</i>	whole plant	+				121
<i>Nephelium litchi</i>	bark	+				276
<i>Notonia grandiflora</i>	leaves	+				277
<i>Olearia paniculata</i>	bark, roots	—		E		39, 278
<i>Olearia paniculata</i>	leaves	+				39
<i>Ophiorrhiza japonica</i>	whole plant	+				279
<i>Opismensus undulatifolius</i>	herb	+				163
<i>Opuntia vulgaris</i>	whole plant		+			280
<i>Orixa japonica</i>	leaves	+				281
<i>Pachysandra terminalis</i>	not stated††	+		E	36–39	35, 69–72, 282–285
<i>Paederia foetida</i>	not stated††	+				286
<i>Pedilanthus calcaratus</i>	whole plant	+				231
<i>Pedilanthus tehuacanus</i>	whole plant	+				231
<i>Pedilanthus tithymaloides</i>	not stated†‡	+		— **		287
<i>Phacelurus latifolius</i>	culms, blades	+				163
<i>Photina glabra</i>	leaves			E		288
<i>Phyllanthus reticulatus</i>	leaves	+				289
<i>Phyllanthus reticulatus</i>	stems	+		+	25, 28	289
<i>Phyllostachys heterocycla</i>	culms, wax	+				163
<i>Pinus roxburghii</i>	bark	+				290
<i>Pinus serotina</i>	bark	+		E		291
<i>Piper aurantiacum</i>	seeds	+		E		292
<i>Pleurostylia africana</i>	leaves	+		E		269
<i>Poa annua</i>	herb		+			163

Table 2.--continued

Plant	Part used	Friedelanes identified†				References
		2‡	3§	4	Others	
<i>Poa sphondylodes</i>	herb	+				163
<i>Polygonum plebejum</i>	flowers			E		293
<i>Prunus lusitanica</i>	leaves	+				294
<i>Prunus nepalensis</i>	bark	+				295
<i>Prunus turfosa</i>	bark	+		E		5
<i>Pterospermum acerifolium</i>	flowers		+	+		296
<i>Punica granatum</i>	bark	+				297
<i>Putranjiva roxburghii</i>	bark	+	+		40, 41, 43	40, 298–303
<i>Putranjiva roxburghii</i>	leaves				42, 44	299, 302, 304–306
<i>Putranjiva roxburghii</i>	root bark	+			41–43	307
<i>Pyrus communis</i>	bark	+		E		308
<i>Pyrus lanata</i>	leaves, bark	+				309
<i>Pyrus malus</i>	bark	+		E		310
<i>Pyrus pashia</i>	bark, leaves	+				311
<i>Pyrus pashia</i>	stems	+				151
<i>Pyrus sikkimensis</i>	whole plant	+				312
<i>Quercus</i> †	bark	+	+			313, 314
<i>Quercus acuta</i>	leaves	+	+			315
<i>Quercus acutissima</i>	pollen	+				316
<i>Quercus bambusaefolia</i>	leaves	+	+	+		317
<i>Quercus bambusaefolia</i>	stems	+		+		318
<i>Quercus championi</i>	leaves	+	+	E		319
<i>Quercus championi</i>	stems	+		+		318
<i>Quercus gilva</i>	leaves	+	+	**	+	315
<i>Quercus glauca</i>	leaves	+		+		267, 315, 320, 321
<i>Quercus ilex</i>	heart wood	+				322
<i>Quercus incana</i>	stem bark	+				323
<i>Quercus lanceaefolia</i>	stem bark	+			5, 7	324
<i>Quercus myrsinaefolia</i>	leaves	+	+	+		315, 317
<i>Quercus myrsinaefolia</i>	stems	+		+		318
<i>Quercus pachyphylla</i>	plant material	+			7	325
<i>Quercus petraea</i>	bark	+	+			326
<i>Quercus phillyracoides</i>	leaves	+	+			315
<i>Quercus robur</i>	bark	+	+			323, 327
<i>Quercus semicarpifolia</i>	bark	+				328
<i>Quercus sessilifolia</i>	leaves	+	+			315
<i>Quercus stenophylla</i>	leaves, branches	+	+	E		315, 329, 330
<i>Quercus suber</i>	cork wax	+			8	331
<i>Quercus suber</i>	see also 'cork'					—
<i>Raupellia grata</i>	whole plant	+		E		332
<i>Rhododendron adamsii</i>	defoliated shoots	+				333
<i>Rhododendron arboreum</i>	leaves	+				334
<i>Rhododendron aureum</i>	defoliated shoots	+				333
<i>Rhododendron barbatum</i>	leaves			E		334
<i>Rhododendron campanulatum</i>	leaves	+		E		334, 335
<i>Rhododendron championae</i>	leaves			E		336
<i>Rhododendron cinnamomeum</i>	leaves	+		E		337
<i>Rhododendron colletianum</i>	not stated††	+				338
<i>Rhododendron cucasicum</i>	stems, leaves	+		E		47
<i>Rhododendron dahuricum</i>	defoliated shoots	+				333
<i>Rhododendron decipiens</i>	leaves	+				339
<i>Rhododendron degronianum</i>	leaves	+		E		340
<i>Rhododendron falconeri</i>	leaves	+				334
<i>Rhododendron ferrugineum</i>	not stated††	+		E		341
<i>Rhododendron grande</i>	bark, leaves	+				342, 343
<i>Rhododendron hodgsonii</i>	not stated††	+				344
<i>Rhododendron kotschyi</i>	defoliated shoots	+				333
<i>Rhododendron luteum</i>	defoliated shoots	+				333
<i>Rhododendron metternichii</i>	leaves	+		E		345
<i>Rhododendron mucronulatum</i>	defoliated shoots	+				333
<i>Rhododendron nilagiricum</i>	leaves			E		346
<i>Rhododendron niveum</i>	leaves	+		E		151, 347
<i>Rhododendron ponticum</i>	leaves	+				348, 349
<i>Rhododendron reticulatum</i>	leaves	+		E		350
<i>Rhododendron schlippenbachii</i>	defoliated shoots	+				333
<i>Rhododendron westlandii</i>	not stated††	+		E		143, 351
<i>Rhodomyrtus tomentosa</i>	not stated††	+				352

Table 2.—continued

Plant	Part used	Friedelanes identified†				References
		2‡	3§	4	Others	
<i>Saccharum spontaneum</i>	culms, blades	+				163
<i>Salacia fruticosa</i>	root bark	+			21, 32, 34	353
<i>Salacia prinoides</i>	root bark	+			11, 13, 16, 17, 21, 22, 35	354–359
<i>Salix japonica</i>	bark	+		E		201, 360
<i>Salvia glutinosa</i>	gum exudate	+				361
<i>Sapium sebiferum</i>	leaves	+				362
<i>Sarcostemma viminalis</i>	whole plant	+				363, 364
<i>Saussurea lappa</i>	root oil	+				365
<i>Scolopia crenata</i>	not stated††	+				366
<i>Scolopia schieberi</i>	bark, wood	+				221
<i>Secamone afzelli</i>	roots	+				367
<i>Setaria chondrachne</i>	grains	+				163
<i>Severinia buxifolia</i>	leaves	+				368
<i>Siphonodon australe</i>	bark	+			9, 12, 15, 18, 23–27	28, 29, 57, 73, 76, 107
<i>Sorghum japonicum</i>	grains	+				163
<i>Spatholobus roxburghii</i>	beans	+				369
<i>Spireae formosana</i>	not stated††	+				370
<i>Stachytarpheta indica</i>	leaves	+				119
<i>Stereocaulon paschale</i>	whole plant	+				123
<i>Syzygium cordatum</i>	bark, sapwood	+		E		371
<i>Talguena quinquenervis</i>	not stated††	+				210
<i>Tillandsia usneoides</i>	whole plant	+				125
<i>Trevoa trinervis</i>	not stated††	+				210
<i>Trichadenia zeylanica</i>	bark, wood		++		45**, 46, 47**, 48	372, 373
<i>Tripetaleia paniculata</i>	leaves, flowers			E		374, 375
<i>Tripetaleia paniculata</i>	wood	+		E		375, 376
<i>Ulmus campestris</i>	bark	+				377
<i>Undaria pinnatifida</i>	not stated††	+				378
<i>Vaccinium bracteatum</i>	flowers	+				379
<i>Vaccinium bracteatum</i>	leaves	+		E		380
<i>Vaccinium membranaceum</i>	roots				20	381
<i>Vaccinium membranaceum</i>	cork	+			15, 19, 20	382
<i>Vaccinium uliginosum</i>	leaves	+				383
<i>Vanillosmopsis erythropappa</i>	not stated††	+	+			384
<i>Vincetoxicum</i> *	herb	+				363
<i>Viola odorata</i>	leaves	+				385
<i>Viola odorata</i>	wax	+		+		386
<i>Vitex trifolia</i>	leaves	+				387
<i>Vitadina australis</i>	whole plant	+		E		388
<i>Zea mays</i>	herb	+				163
<i>Zelkova serrata</i>	bark	+				201
<i>Zoysia tenuifolia</i>	herb	+	+			163
Coal		+	+	+		129–132, 134
Cork [presumably <i>Quercus suber</i> (389)]		+			8, 14 19, 20	3, 6, 8–10, 25, 37, 105, 138, 382
Mineral wax		+		+		135
Peat		+		+, E		43, 127, 128, 133

* This includes only those friedelane derivatives that were reported in association with friedelin and/or one or both of the epimeric 3-friedelanols. Additional D: A-friedeloolenane derivatives are known [e.g. 107, 139–141] but these have not been reported in the presence of friedelin or the 3-friedelanols. Similarly, there are additional sources for some of the compounds found in Tables 1 and 2 which are devoid of friedelin and the 3-friedelanols [e.g. 142–145].

† The numbers refer to the structures illustrated in Fig. 1 and Table 1.

‡ Friedelin (friedelan-3-one).

§ Friedelan-3 α -ol (friedelinol, friedelanol).

|| Friedelan-3 β -ol (epifriedelinol, epifriedelanol). As there is some confusion in the literature regarding the usage of the prefix 'epi-', we have chosen to distinguish between the reported occurrence of 'epifriedelanol' (E) and 'friedelan-3 β -ol' (+).

* Further details regarding the genus and species are not provided in the literature cited.

** Reported present as the alcohol and/or the acetates.

†† 'Not stated' indicates that the plant part used was not stated in the literature cited.

‡‡ Friedelin has been identified in additional liverworts, but the plants were not specified in the available literature [245].

§§ Also known as *Isocoma wrightii*.

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