Phytochemistry, 1972, Vol. 11, pp. 2369 to 2381. Pergamon Press. Printed in England.

REVIEW ARTICLE

THE TRITERPENOIDS*

M. JYOTI KULSHRESHTHA, D. K. KULSHRESHTHA and R. P. RASTOGI
Central Drug Research Institute, Lucknow, India

(*Received* 15 *June* 1971, *in revised form* 16 *November* 1971)

Key Word Index—Fungi; Lichens; Pteridophyta; Gymnospermae; Angiospermae; triterpenoids; review

INTRODUCTION

THE TERM 'triterpenoids' refers to a group of natural products containing thirty carbon atoms based on six isoprene units. This definition, though generally applicable, is by no means rigid, since several substances which contain more or less than thirty carbon atoms and also those which do not strictly follow the isoprene rule have been isolated and characterized as triterpenoids during the recent years. The invention of highly sophisticated physicochemical techniques and the contemporary developments in the biogenetic theories, have been mainly responsible for the isolation and identification of new unconventional type of triterpenoids.

Earlier surveys in this field have been made by Holtzem *et al.*,[1] White[2] and Halsall *et al.*[3] Recently the triterpenoid saponins and their sapogenins have been reviewed by Basu *et al.*[4] and Daloze[5] has dealt with current research in triterpenoid chemistry. This review, therefore, presents a survey of the triterpenoid field for the period 1963–70 excluding the triterpenoid saponins, their genins and their biogenesis which have already been covered.[4]

ANALYTICAL TECHNIQUES

TLC and GLC[6] permit quick detection and identification of triterpenoids. Recent developments in TLC, e.g. the impregnation of silica gel G with silver nitrate or a fluorescent indicator has enhanced its utility.[7]

IR, UV and to some extent even NMR spectroscopy are now used as routine techniques. Recent developments in NMR, namely the use of 100 Mc (and even 220 Mc) instruments, double resonance and deuterium labelling[8] have increased its potentiality as a tool for studying finer details of molecular structure. It is now possible to assign resonance positions to the methyl groups in triterpenoids and their derivatives belonging to all the major

* Communication No. 1652 from Central Drug Research Institute, Lucknow, India.

[1] H. HOLTZEM and M. STEINER, *Modern Methods of Plant Analysis* (edited by K. PAECH and M. V. TRACEY), Vol. 3, p. 58, Springer, Berlin (1955).
[2] D. E. WHITE, *Rev. Pure Appl. Chem.* **6,** 191 (1956).
[3] T. G. HALSALL and R. T. APLIN, *Progress in the Chemistry of Organic Natural Products* (edited by L. ZECHMEISTER), Vol. 22, p. 153, Springer, New York (1964).
[4] N. BASU and R. P. RASTOGI, *Phytochem.* **6,** 1249 (1967).
[5] D. DALOZE, *Ind. Chim. Belges* **32,** 413 (1967).
[6] T. TSUKAMOTO, A. YAGI, K. MIHASHI and Y. MORI, *Chem. Pharm. Bull.* **16,** 2123 (1968).
[7] J. G. KIRCHNER, *Thin-Layer Chromatography, Techniques of Organic Chemistry* (edited by E. S. PERRY and A. WEISSBERGER), Vol. 12, Interscience, New York (1967); F. FISCHER and R. HERTEL, *J. Chromatogr.* **38,** 274 (1968); A. N. STARATT, *Phytochem.* **8,** 795 (1969).
[8] J. KARLINER and C. DJERASSI, *J. Org. Chem.* **31,** 1945 (1966).

classes[9–20] (viz. euphane, isoeuphane, dammarane, lanostane, oleanane, ursane, lupane and hopane) and these assignments have been used for structure elucidation of unknown substances.[21] Shamma *et al.*[22] have studied the relationship between the NMR spectra and general structural features of pentacyclic triterpenes. Judicious use of spin–spin coupling has led to assignment of configuration to substituents in the triterpenoid molecule, for example, C-6 hydroxyl as α-equitorial in zeorinin[23] has been deduced on the basis of large J values for the C-6 methine multiplet. Rassat *et al.*[24] have reported an interesting observation that long range spin–spin interactions are possible between protons separated by four bonds provided their steric arrangement is 'M' shaped. Anisotropy of the functional groups also affects the chemical shift of the protons other than methyl groups. In the β-amyrin series, a lactone bridge from C-28 to C-21 results in the downfield shift of the Δ^{12} olefinic proton.[25] A method for the identification of protons on a carbon bearing a hydroxyl group through methylation which results in the upfield shift by 0·6 ppm,[26] has been reported as an alternative to acetylation. The fact that the protons lying in the region of high electron density tend to be deshielded in benzene solution, has been exploited in structure determination.[27] The configuration of the aldehyde groups located at 4-position in triterpenoids, has also been deduced from their chemical shifts.[28]

Mass spectrometry has some unique advantages over other physicochemical techniques. It has been found that, in general, the mode of fragmentation of triterpenoids is controlled by the position of double bonds (retro-Diels–Alder fragmentation) either originally present or generated by the elimination of water or acetic acid and, therefore, characteristic features appear in the MS which frequently allow the assignment of a given triterpene to one of the major classes. In addition, the location of functional groups can often be narrowed down by consideration of the fragmentation pattern.[29]

Deuterium labelling has frequently been used to confirm the proposed mode of fragmentation.[8] By a study of the cracking pattern, the deuterated friedelanones of *Siphonodon*

[9] J. C. MANI, *Ann. Chim.* **10,** 533 (1965).
[10] D. LAVIE, Y. SHVO and E. GLOTTER, *Tetrahedron* **19,** 2255 (1963).
[11] J. M. LEHN, *Bull. Soc. Chim. Fr.* 1832 (1962).
[12] A. I. COHEN, D. ROSENTHAL, G. W. KRAKOWER and J. FRIED, *Tetrahedron* **21,** 3171 (1965).
[13] B. TURSCH, R. SAVOIR and G. CHIURDOGLU, *Bull. Soc. Chim. Belges* **75,** 107 (1966); *Chem. Abs.* **64,** 19692 f (1966).
[14] R. SAVOIR, R. OTTINGER, B. TURSCH and G. CHIURDOGLU, *Bull. Soc. Chim. Belges* **76,** 335 (1967); *Chem. Abs.* **68,** 13200 u (1968).
[15] SHO ITO, M. KODAMA and M. SUNAGAWA, *Tetrahedron Letters* 3989 (1967).
[16] G. S. RICEA and G. RUSSO, *Gazz. Chim. Ital.* **98,** 602 (1968); *Chem. Abs.* **69,** 59438 b (1968).
[17] R. SAVOIR, R. OTTINGER, B. TURSCH and G. CHIURDOGLU, *Bull. Soc. Chim. Belges* **76,** 371 (1967); *Chem. Abs.* **68,** 73884 c (1968).
[18] J. M. LEHN and G. OURISSON, *Bull. Soc. Chim. Fr.* 1137 (1962).
[19] J. M. LEHN and A. VYSTRCIL, *Tetrahedron* **19,** 1733 (1963).
[20] H. T. CHEUNG and D. G. WILLIAMSON, *Tetrahedron* **25,** 119 (1969); S. ITO, M. KODAMA, M. SUNAGAWA, T. OBA and H. HIKINO, *Tetrahedron Letters* 2905 (1969).
[21] H. T. CHEUNG, CHI-SHUN-WONG and T. C. YAN, *Tetrahedron Letters* 5077 (1969).
[22] M. SHAMMA, R. E. GLICK and R. O. MUMMA, *J. Org. Chem.* **27,** 4512 (1962).
[23] S. HUNECK and J. M. LEHN, *Bull. Soc. Chim. Fr.* 1702 (1963).
[24] A. RASSAT, C. W. JEFFORD, J. M. LEHN and B. WAEGELL, *Tetrahedron Letters* 233 (1964).
[25] B. TURSCH, D. DALOZE, R. OTTINGER, J. REISSE and G. CHIURDOGLU, *Bull. Soc. Chim. Belges* **75,** 191 (1966); *Chem. Abs.* **65,** 5495 g (1966).
[26] C. R. NARAYANAN and K. N. IYER, *Tetrahedron Letters* 3741 (1965).
[27] R. G. WILSON and D. H. WILLIAMS, *Tetrahedron* **25,** 155 (1969).
[28] M. FETIZON, G. MOREAU and N. MOREAU, *Bull. Soc. Chim. Fr.* 3295 (1968).
[29] H. BUDZIKIEWICZ, J. M. WILSON and C. DJERASSI, *J. Am. Chem. Soc.* **85,** 3688 (1963); C. WUENSCHE and I. LOEW, *Tetrahedron* **22,** 189 (1966).

australe have been divided into two groups according to the position of the carbonyl function.[30]

The mass spectra of certain Δ^1-3-oxo and Δ^4-3-oxo triterpenes show a very prominent peak corresponding to ring A containing C-19 and C-6.[31] The fragmentation of the tetracyclic triterpenes of cucurbitacin group has been studied.[32] Bryogenin, the simplest member of this series, exhibited an intense peak at *m/e* 305, which has been assigned to fragment arising out of the cleavage of 7:8 C–C bond preceded by McLaferty rearrangement involving the participation of the 11-keto group and a hydrogen at C-1. Several tetracyclic triterpenes containing a 9:19 cyclopropane function,[33] as in cycloartenol, undergo two diagnostic fragmentations. The first is due to the loss of the side chain (R) to give a peak at M − R. The other involves the cleavage of either 9:10, 10:19, 6:7 or 9:10, 9:19, 5:6 linkages with rearrangement of an hydrogen atom. A different mechanism involving cleavage at 9:10, 9:19 and 5:6-bond has been proposed[34] but in either case the positive charge is retained by rings C and D. In the triterpenes related to serratenediol, characteristic fragmentation of the seven membered ring has been observed.[35] The MS of the dehydration products of β-amyrin and glycyrrhetic acid have been studied.[36]

The development of 'molecular mass spectrography' is another leap forward in this technique wherein negatively charged M-1 ions are formed by the addition of low energy electrons to the molecule followed by loss of 1H, usually without fragmentation, and allow an accurate determination of molecular weight up to 2000.[37] It has been reported[38] that the molecular mass spectra of zeorin, methyl ursolate, betulin, γ-onocerin, 3-friedelanol, and friedelin showed peaks corresponding to their MW, M or M-1, while the spectra of allobetula-2-ene, 2-onocerone and primulagenin A gave peak corresponding to values higher than M due to the addition of oxygen.

Circular dichroism, a complementary tool of ORD, has been used to determine the conformation of ring A in triterpenoids and the stereochemistry of OH group in ring A of cucurbitacin-α-ketols.[39–41] The negative Cotton effect of some triterpenoid ketones has been rationalized in terms of octant rule by assuming a skewed-boat conformation for ring A.[42] The configuration of C-19 acetyl group in 3β, 28-diacetoxy-30-norlupan-2-one has been shown to be α by direct comparison with the analogous derivatives of A-nor-5 α-cholestane.[43] In the unsaturated triterpene acids of oleanane and ursane series, the 28-carboxylic group has been shown to exist in solution in a syn-planar configuration with C_{16}–C_{17} bond.[44]

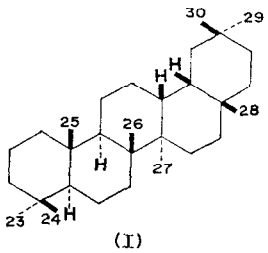
X-Ray crystallography is being increasingly employed for structural determinations of

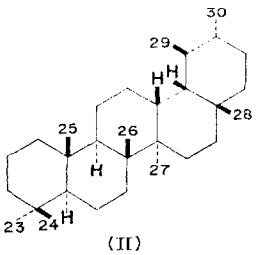
[30] J. L. COURTNEY and J. S. SHANNON, *Tetrahedron Letters* 13 (1963); J. S. SHANNON, C. C. MACDONALD and J. L. COURTNEY, *Tetrahedron Letters* 173 (1963).
[31] H. AUDIER, M. FETIZON and W. VETTER, *Bull. Soc. Chim. Fr.* 415 (1964).
[32] H. E. AUDIER and B. C. DAS, *Tetrahedron Letters* 2205 (1966).
[33] H. E. AUDIER, R. BEUGELMANS and B. C. DAS, *Tetrahedron Letters* 4341 (1966).
[34] R. T. APLIN and G. M. HORNBY, *J. Chem. Soc.* **B,** 1078 (1966).
[35] J. P. KUTNEY, G. EIGENDORF and I. H. ROGERS, *Tetrahedron* **25,** 3753 (1969).
[36] M. H. A. ELGAMAL, M. B. E. FAYEZ and T. R. KOMP, *Org. Mass Spectros.* **2,** 175 (1969).
[37] M. V. ARDENNE, K. STEINFELDER, R. TÜMMLER and K. SCHREIBER, *Experientia* **19,** 178 (1963).
[38] S. HUNECK and R. TÜMMLER, *J. Prakt. Chem.* **38,** 233 (1968).
[39] P. WITZ, H. HERRMANN, J. M. LEHN and G. OURISSON, *Bull. Soc. Chim. Fr.* 1101 (1963).
[40] G. SNATZKE, P. R. ENSLIN, C. W. HOLZAPFEL and K. B. NORTON, *J. Chem. Soc.* **C,** 972 (1967).
[41] G. SNATZKE and A. NISAR, *Ann. Chem.* **683,** 159 (1965).
[42] J. S. E. HOLKER and W. B. WHALLEY, *Proc. Chem. Soc.* 454 (1961); D. LAVIE, E. GLOTTER and Y. SHVO, *Israel J. Chem.* **1,** 409 (1963).
[43] F. FISCHER, P. PALITZSCH and S. HUNECK, *Z. Chem.* **7,** 458 (1967); *Chem. Abs.* **68,** 49815 n (1968).
[44] J. D. RENWICK, P. M. SCOPES and S. HUNECK, *J. Chem. Soc.* **C,** 2544 (1969).

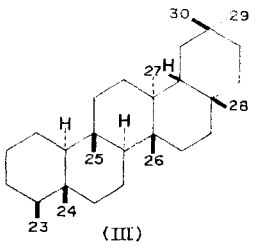
the unknown molecules. Thus, the structures of mexicanolide, arborinol, fusidic acid and the 17α-H configuration in the dammarane group have been determined by this means.[45–48]

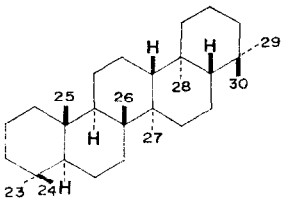
TABULATION OF DATA

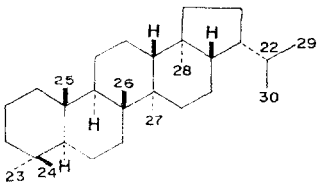
With a view to giving an overall picture of the various groups of triterpenoids present in individual species and to present the distribution of triterpenoids within higher taxa, the compounds characterised during the period under review, excluding genins and tetranortriterpenoids, are listed under the plants in which they occur in Table 1. Table 2 lists triterpenoids reported from other sources.

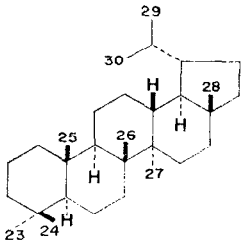

(I)

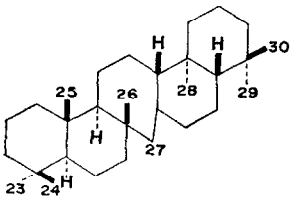

(II)

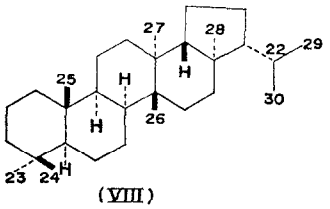

(III)

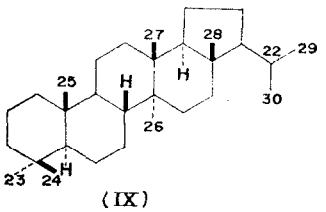

(IV)

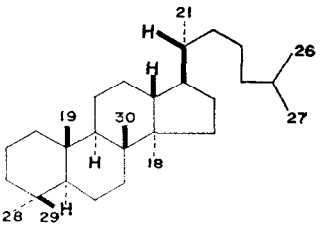

(V)

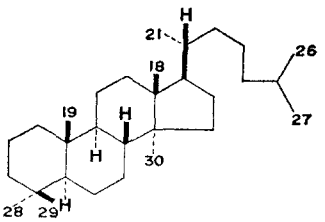

(VI)

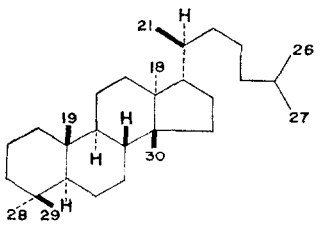

(VII)

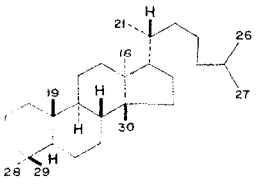

(VIII)

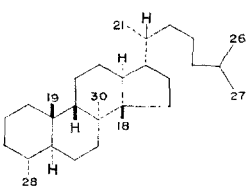

(IX)

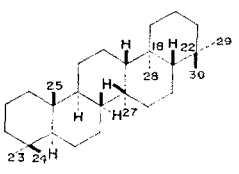

(X)

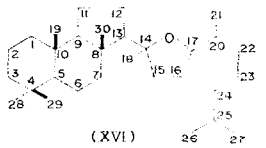

(XI)


(XII)


(XIII)


(XIV)


(XV)


(XVI)

[45] O. TANAKA, N. TANAKA, T. OHSAWA, Y. IITAKA and S. SHIBATA, *Tetrahedron Letters* 4235 (1968).
[46] S. A. ADEOYE and D. A. BEKEO, *Chem. Commun.* 301 (1965).
[47] A. COOPER, *Tetrahedron* **22**, 1379 (1966).
[48] O. KENNARD, L. RIVA DI SANSEVERINO, H. VORBRUGGEN and C. DJERASSI, *Tetrahedron Letters* 3433 (1965).

TABLE 1. DISTRIBUTION OF TRITERPENOIDS IN THE PLANT KINGDOM

Plant	Family	Substance	m.p.	Basic skeleton	Groups	Ref.
MYCOPHYTA						
(a) Fungi						
Cephalosporium acremonium	Stilbaceae (Moniliales)	Cephalosporin P_1	—	XIV	3α,7β-OH, 6α,16β-acetoxy $\Delta^{17(20),24}$, 21-COOH	49,50
		Monodeacetyl cephalosporin P_1	197	XIV	3α,6α,7β-OH, 16β acetoxy, $\Delta^{17(20),24}$, 21-COOH	51
C. caerulens		Helvolic acid	214	XIV	6β,16β-acetoxy, 3,7-oxo, $\Delta^{1,17(20),24}$, 21-COOH, (16,21-*cis*)	52,53
		Diol	—	XIV	3β-OH, 4β-CH_2OH, $\Delta^{17(20),24}$, (16,21-*cis*)	52
		Acid	119* (Me-ester)	XIV	16β-acetoxy,3-oxo, $\Delta^{1,17(20),24}$, 21-COOH, (16,21-*cis*)	54
		—	104	XIV	3β-OH, 4β-CH_3, $\Delta^{17(20),24}$, (16,21-*cis*)	55
		—	117	XIV	3β-OH, 4β-CH_3, $\Delta^{13(17),24}$, 24(*S*)	
C. lamellaecola		Fusidic acid	153* (Me-ester)	XIV	3α,11α-OH, 16β-acetoxy, $\Delta^{17(20),24}$, 21-COOH, (16,21-*cis*)	56
Fomes senex Nees & Mont	Polyporaceae	Senexonol	—	XI	6α-OH,3-oxo, $\Delta^{8(9),24}$, 29-*nor*	57
F. officinalis		Dehydroeburiconic acid	240	XI	3-oxo, 24-CH_2, $\Delta^{7(8),9(11)}$, 21-COOH	58
Fusidium coccineum	Moniliales	Fusidic acid	153* (Me-ester)	XIV	See above	59
		Didehydrofusidic acid	184	XIV	6β-acetoxy, 3,11-oxo, $\Delta^{17,(20),24}$, 21-COOH, (16-21-*cis*)	60
		Dehydrofusidic acid	193	XIV	11α-OH, 16β-acetoxy, 3-oxo, $\Delta^{17(20),24}$, 21-COOH (16,21-*cis*)	
Inonotus obliquus	Polyporaceae	Inotodiol	190	XI	3β,12β-OH, $\Delta^{8(9)}$	61
Poria cocos (Schw.) Wolf. (*-Pachyma hoelen Rumph.*)	Polyporaceae	3β-Hydroxy lanosta 7,9(11),24-triene 21-oic acid	142	XI	3β-OH, $\Delta^{7,9(11),24}$, 21-COOH	62
P. obliqua		Obliquol		XI	3β,12β-OH, $\Delta^{8(9),24}$	63
Trametes feei	Polyporaceae	6α-Hydroxypoly porenic acid C	222* (Me-seter)	XI	6α,16α-OH, 3-oxo, 24-CH_2, $\Delta^{7,9(11)}$, 21-COOH	64
(b) Lichens						
Cetraria nivalis (L.) Ach. *Lobaria retigera* (Bory) Trevis.	Parmeliaceae	$C_{30}H_{50}O_2$	221	U†	OH, C=O	65
L. subretigera Inum.	Stictaceae	Retigeradiol	272	R†	3β,19β-Dihydroxy-D-friedo-oleanane	66
Parmelia entotheiochroa Hue.	Parmeliaceae	Substance N_2	228	V	16β-Acetoxy, 22-OH	67
		Substance N_3	232	V	6α,16β-Acetoxy, 22-OH	
		Substance N_4	268	V	16β, 22-OH	
		Substance N_5	225	V	6α-Acetoxy, 16β, 22-OH	
		16β-*O*-Acetyl leucotylic acid	176* (Me-ester)	V	22-OH, 16β-acetoxy, 23-COOH	
		Substance N_1 $C_{30}H_{50}O$	258	U	C=O	
P. leucotyliza Nyl.	Physciaceae	Leucotylin	289	V	6α,16β,22-OH	67,68
		Zeorin	227	V	6α,22-OH, (21Hα)	
		Leucotylic acid	260	V	16β,22-OH, 23-COOH	69
Pyxine endochrysing Nyl.		Diacetylpyxinol	247	IX	12β-OH, 3β,25-acetoxy, 20(*S*) → 24(*R*)-epoxy	70,71
PTERIDOPHYTA						
Lycopods						
Lycopodium clavatum L.	Lycopodiaceae	Lycoclavanin	344	VII	3α,20β,21β,24-OH, 16-oxo	80,81
		Lycoclavanol	308	VII	3α,21β,24-OH, Δ^{14}	80,82
		Triterpenoid B_5	294	VII	3β,21α-OH, 16-oxo, Δ^{14}	83
		Triterpenoid B_3	300	VII	3β,21β-OH, 16-oxo, Δ^{14}	
		Triterpenoid B_4	318	VII	3α,21β-OH, 16-oxo, Δ^{14}	
		21-Episerratriol	230	VII	3β,21β,24-OH, Δ^{14}	84
		16-Oxolycoclavanol	—	VII	3α,21β,24-OH, 16-oxo, Δ^{14}	85
L. phlegmalia L.		Phlegmanol-A	300* (Acetate)	VII	3β(3,4-Dihydroxy phenyl proprionoxy), 21α-OH, Δ^{14}	86
L. serratum Thunb. var. *Thunbergii* Makino		Serratenediol	300	VII	3β,21α-OH, Δ^{14}	87
		Tohogenol	253	VII	3β,14β,21α-OH	88
		Tohogeninol	311	VII	3β,14β,21α,24-OH	
		Serratriol	335	VII	3β,21α,24-OH, Δ^{14}	82
		16-Oxoserratriol		VII	3β,21α,24-OH, 16-oxo, Δ^{14}	85
Ferns						
Adiantum capillus-veneris L.	Adiantaceae	21-Hydroxy-adiantone	—	V	21-OH, 22-oxo, 30-*nor*	72
		7-Fernene	208	VIII	$\Delta^{7(8)}$	73
		Adianene	190	R	E:B-Friedohop-5-one	74
		Filicene	228	R	E:A-Friedohop-5-ene	
		Hydroxyadiantone	270	V	21β-OH, 30-*nor*, 22-oxo	75
		Ketohakonanol	295	IV	22-OH, 30-*nor*, 21-oxo	
A. pedatum L. *A. monochlamys* Eaton.		Fernadiene	128	VIII	$\Delta^{7,9(11)}$	76
A. pedatum L.		Filicenal	272	R	E:A Friedohop-3-en-23-al	77
		Adipedatol	185	V	22-OH, 22 → 28-epoxy, 30-*nor*	
A. venustum G. Don		$C_{29}H_{48}O_2$	280–300	U	-OH, C=O	78
Cyathea taiwaniana	Cyatheaceae	$C_{30}H_{50}$	173	U	—	79

TABLE 1—*continued*

Plant	Family	Substance	m.p.	Basic skeleton	Groups	Ref.
Oleandra wallichii (Hook) Pr.	Oleandraceae	Wallichiene	196	V	$\Delta^{13(18)}$	89
		Wallichienene	210	V	$\Delta^{11,13(18)}$	
Polypodium vulgare L.	Polypodiaceae	17,21-Epoxy hopane	—	V	17 → 21-epoxy	72
		29-Nor cyclo-laudenol	139	XI	3β-OH, 9,19-cyclo, 29-*nor*, 24-CH_3, $\Delta^{25(26)}$	90
		29-Nor cyclo artenol	—	XI	3β-OH, 9,19-cyclo, 29-*nor*, Δ^{24}	72
GYMNOSPERMAE						
Picea sitchensis	Pinaceae	Compound A	307	VII	3β-OCH_3, 21β-OH, Δ^{14}	91,92
		Compound B	276	VII	3α-OCH_3, 21β-OH, Δ^{14}	
		Compound C	194	VII	3α-OCH_3, 21β-OH, Δ^{13}	91
		Compound B-methyl ether	—	VII	3α,21β-OCH_3, Δ^{14}	74
Pinnus banksiana Lamb.	Pinaceae	*O*-Methyl episerra-tenediol	—	VII	3β-OH,21β-OCH_3, Δ^{14}	93
P. lambertiana Dougl.		Compound II	319	VII	3β-OCH_3, 21α-OH, Δ^{14}	93,94
		Compound III	320	VII	3β,21α-OCH_3, Δ^{14}	
		Compound V	267	VII	3β-OCH_3, 21-oxo, Δ^{14}	91
		Compound VII	—	VII	3α,21β-OH, Δ^{14}	
		Compound IX	268	VII	3β-OH, 21-oxo, Δ^{14}	
P. banksiana Lamb. *P. lambertiana* Dougl. *P. taeda* L.		Episerratenediol	303	VII	3β,21β-OH, Δ^{14}	91,93,94
ANGIOSPERMAE						
(a) Monocotyledoneae						
Alisma plantago-aquatica L. var. *orientale* Samuels	Alismataceae	Alisol A‡	Amorph.	XIV	11β,23(*S*), 24(*R*), 25-OH, 3-oxo, $\Delta^{13(17)}$	95,96
		Alisol B‡	166	XIV	11β,23(ξ)-OH, 3-oxo, $\Delta^{13(17)}$, 24(ξ) → 25-epoxy	95,97
		Epialisol A	Amorph.	XIV	23 or 24 epimer of alisol A	95
		Alisol C monoacetate	232	XIV	11β-OH, 23(ξ)-acetoxy, 3,16-oxo, $\Delta^{13(17)}$ 24(ξ) → 25-epoxy	97
Copernicia cerifera Mart. (Carnauba wax)	Palmae	Carnaubadiol	167	IX	3β,20(ξ)-OH, $\Delta^{25(26)}$, 24(*R*)-CH_3	98
Imperata cylindrica P. Beauv. var. *media* Hubbard	Gramineae	Arundoin	235	VII	3β-OCH_3, $\Delta^{9(11)}$	99,100
		Fernenol	192	VII	3β-OH, $\Delta^{9(11)}$	100
		Cylindrin	269	IX	3β-OCH_3, $\Delta^{9(11)}$	100,101
		Arborinol methyl ether	284	IX	3α-OCH_3, $\Delta^{9(11)}$	102,103
Oryza santiva L.	Gramineae	Cyclobranol	156	XI	3β-OH, 9,19-cyclo, Δ^{24}, 24-CH_3	104
		Compound I	181	XI	3β,25-OH, 9,19 cyclo, Δ^{24}	105
		Compound II	109	XI	3β-OH, 25-OC_2H_5, 9,19-cyclo, Δ^{24}	106
		Compound III	151	XI	3β-OH,9, 19-cyclo, 24-OCH_3, 24-CH_3	
Paspalum dilatum Poir.	Gramineae	Lupeol methyl ether	250	VI	3β-OCH_3, $\Delta^{20(29)}$	102
Tillandsia usneoides L.	Bromeliaceae	Cycloarten 3,25-diol	200	XI	3β,25-OH, 9,19-cyclo, Δ^{23}	107 108
		Cycloarten-25-methoxy-3-ol	152* (Acetate)	XI	3β-OH, 25-OH_3, 9,19-cyclo, Δ^{23}	108
		Cycloarten-3-24-diol	184	XI	3β,24-OH,9, 19-cyclo, $\Delta^{25(26)}$	
		Cylcoarten-24-one	133* (Acetate)	XI	3β-OH, 24-oxo, 9,19-cyclo, $\Delta^{25(26)}$	
Zoysia matrella Merr.	Gramineae	Fernen-3-one	—	VIII	3-oxo, $\Delta^{9(11)}$	102
		12-Oxoarundoin	291	VIII	3β-OCH_3, 12-oxo, $\Delta^{9(11)}$	
		Fernen-3α-ol	—	VIII	3α-OH, $\Delta^{9(11)}$	109
Zea mays L.	Gramineae	Cyclosadol	121	XI	3β-OH, 9,19-cyclo, 24-CH_3, Δ^{23}	110
(b) Dicotyledoneae						
Aglaia odorata Lour.	Meliaceae	Aglaiol	113	X	3β-OH, $\Delta^{20(21)}$, 24(ξ) → 25 epoxy	111
Ailanthus malabarica D.C.	Simaroubaceae	Malabaricol	68	XVI	20(ξ)-OH, 3-oxo, Δ^{24}	112
		Epoxy malabaricol	143	XVI	25-OH, 3-oxo, 20(ξ) → 24(ξ) epoxy	
		Malabaricane diol	Amorph.	XVI	3,20-OH, Δ^{24}	
Alangium villosum (B1) Wang. var. *vitiense* (A. Gray) Bloemb.	Alangiaceae	22-Deoxyemmol-actone	226	R	A(1), 28-norlupa 2,16,20(29)-triene-27 → 18α-olide	113
Aleurites montana	Euphorbiaceae	Aleuritolic acid	241* (Me-ester)	R	3β-*O*-Acetyl D-friedoolean-14-en-28-oic acid	114
Allamanda cathartica L.	Apocynaceae	$C_{30}H_{48}O$	178	U	C=O	115
Alnus glutinose	Betulaceae	Alnus foliene-diolone	198	X	12β,20(*S*)-OH, 3-oxo, $\Delta^{25(26)}$	116
A. incana (L.) Vill.		Alnincanone	172	X	3-oxo,20(ξ) → 24(ξ)epoxy,24(ξ)-CH_3	117
Aphanamixis polystachya	Meliaceae	Aphanamixin	232	XII	21β-OH, 3-acetoxy, Δ^{7}, 21 → 23 and 24 → 25 epoxy	118

Wall (Parker) (*Amoora rohituka*)						
Aster tataricus L.	Compositae	Shionone	158	R	17α-(4′methyl-3′-pentenyl)-des-E, D:A-friedoolean-3-one	119,120 121
Barringtonia acutangula (L.) Gaertn.	Banringtonia-ceae	Tanginol	283	I	3β,6β,7β,16β,23,28-OH, Δ^{12}	122
		Acid-A		I	2,3,19-OH, Δ^{12}, 23,28-COOH	123
Betula pendula Roth.	Betulaceae	Folientriol	196	X	3α,12β,20(*S*)-OH, Δ^{24}	124
		Folientetrol	168	X	3α,12β,17α,20(*S*)-OH, Δ^{24}	
B. platyphylla Sukatchev. var. *Japonica* Hara.		Triterpene B	197	X	12β,20(*S*)-OH, 3-oxo, Δ^{24}	125
		Triterpene C	240	X	3α,12β,25-OH, 20(*S*) → 24(ξ)-epoxy	
Beyeria leschenaultii (D.C.) Bail.	Euphorbiaceae	Lup-20-en-3,16 diol	218	VI	3β,16β-OH, $\Delta^{20(29)}$	126
Brandegea bigelovii Cogn.	Cucurbitaceae	Cucurbitacin O	—	R	2α,3α,16α,20(ξ),25-Pentahydroxy-9β-methyl-10-*nor*-lanosta-5,23 dien-11,22-dione	127
		Cucurbitacin P	157, 211	R	2α,3α,16α,20(ξ),25-Pentahydroxy-9β-methyl-10-*nor*-lanosta-5-en-11,22-dione	
		Cucurbitacin Q	118–135 amorph.	R	2α,3α,16α,20(ξ)-Tetrahydroxy-25-*O*-acetyl-9β-methyl-10-*nor*-lanosta-5,23-dien-11,22-dione	
Bryonia dioica	Cucurbitaceae	Bryonolic acid	303	R	3β-Hydroxy D:C-friedoolean-8-en-29-oic acid	128
Calophyllum appetalum Willd. *C. tomentosum* T. Anders. (*C. elatum* Bedd.)	Guttiferae	Apetalactone	335d	III	28-OH, 3,4-*seco*, 4α → 3-lactone	129
C. inophyllum L.		Canophyllol	280	III	28-OH, 3-oxo	130
		Canophyllal	263	III	3-oxo, 28-CHO	
		Canophyllic acid	312	III	3β-OH, 28-COOH	
Canarium sp. (Elemi resin)	Burseraceae	—	109* (Me-ester)	XII	3-oxo, $\Delta^{8,24}$, 21-COOH	131
		—	149* (Me-ester)	XII	3α-OH, $\Delta^{8,24}$, 21-COOH	
		—	117* (Me-ester)	XII	3β-OH, $\Delta^{8,24}$, 21-COOH	
		—	147* (Me-ester)	XII	3α-OH, $\Delta^{7,24}$, 21-COOH	
Ceanothus americanus	Rhamnaceae	Ceanothic acid	344	R	2α-Carboxy-3β-hydroxy-A(1) norlup-20(29)-en-28-oic acid	132,133
Cedrela glaziovii	Meliaceae	Isoodoratol	251	XII	24-Epiodorotol	134,136
		Triterpene pentaol	215* (Acetonide acetate)	XII	3α,22(ξ),23(ξ),24(ξ),25-OH,(20ξ), Δ^{7}	137
C. odorata L.		Odoratone	230	XII	23β,24β-OH, 3-oxo, 22(*S*) → 25 epoxy, (20ξ), Δ^{7}	134,136, 138
		Odoratol‖	236	XII	3α,23β,24β-OH, 22(ξ) → 25 epoxy, (20ξ), Δ^{7}	134,136 138
Centella asiatica L.	Hydrocotyl-aceae	Brahmic acid§	290–93	II	2α,3β,6β-OH, Δ^{12}, 28-COOH	139
Chamaenerion angustifolium L.	Onagraceae	2α-Hydroxy ursolic acid	245	II	3β-OH, Δ^{12}, 28-COOH	141
Cimicifuga acerina	Ranuncul-aceae	25-*O*-Acetyl-cimigenol	193	XI	3β,15-OH, 25-acetoxy,9, 19-*cyclo*-(9β), 16 → 23, 16 → 24 epoxy	142,143
		Dehydroxy-15-*O*-methyl cimigenol	222	XI	15-OCH_3, 9, 19-cyclo, (9β), 16 → 23, 16 → 24 epoxy	
		15-*O*-Methyl cimigenol	199	XI	3β,25-OH, 15-OCH_3, 9, 19-*cyclo*-(9β),16 → 23, 16 → 24 epoxy	
		Cimicifugenol	118* (Acetate)	XI	3β-OH, 9,19-cyclo, $\Delta^{8(9),24}$	144
Commiphora pyracanthoides Engl.	Burseraceae	Commic acid A¶	200* (Me-ester)	II	2,3-OH/OCH_3, Δ^{12}, 23-COOH	145
		Commic acid B	239* (Me-ester)	II	3β-OH, Δ^{12}, 23-COOH	
Drybalanops aromatica Gaertn. F.	Diptero-carpaceae	11-Oxo-asiatic acid	253* (Acetonide)	II	2α,3β,23-OH, 11-oxo, Δ^{12}, 28-COOH	148
		Dryobalanolide	278* (Acetonide)	II	2α,3β,23-OH, Δ^{11}, 13β → 28 lactone	
		Dryobalanone	100	X	20(*S*), 21-OH, 3-oxo, Δ^{24}	149
Dryobalanops species (Kapur)		Kapurone	183	X	25-OH, 3-oxo, 20(*R*) → 24(ξ)-epoxy	150
		Kapurol	206	X	3β,25-OH, 20(*R*) → 24(ξ)-epoxy	
		Ocotillone	170	X	25-OH, 3-oxo, 20(*S*) → 24(ξ)epoxy	
		Futabanone	124	X	3-oxo, $\Delta^{25(26)}$, 20(*R*) → 24(ξ)epoxy	
		Dryobalanol	88	X	3β,20(*R*), 21-OH, Δ^{24}	
Emmenospermum alphitonioides F. Muell.	Rhamnaceae	Jingullic acid	179* (Me-ester)	R	A(1)norlup-20(29)-en-14-oic acid-28 → 19-olide	151
		22-Deoxyem-molactone	226	R	A(1), 28-norlupa2,16,20(29)-trien-27 → 28α-olide	113
Entandrophragma cylindricum Sprague.	Meliaceae	Sapelin A	216	XII	3α,23(*R*), 25-OH, Δ^{7}, 21 → 24(*R*)-epoxy	152
		Sapelin B	173	XII	3α,23(*S*), 24(*R*)-OH, Δ^{7}, 21 → 25-epoxy	

TABLE 1—*continued*

Plant	Family	Substance	m.p.	Basic skeleton	Groups	Ref.
Evodia fraxinifolia Hook. F.	Rutaceae	Triterpene alcohol	162	R	3β-Hydroxy-D:C-friedours-8(9)-ene	153
Flindersia bourjotiana	Flindersiaceae	Bourjotinolone A	176	XII	23(*R*), 25-OH, 3-oxo, 21 → 24(*R*)-epoxy	154
		Bourjotinolone B	202	XII	23(*R*), 24(*R*)-OH, 3-oxo, $\Delta^{25(26)}$	
		Bourjotinolone C	190	XII	25-Cl, 23(*R*), 24(*R*)-OH, 3-oxo, Δ^{7}	
		Bourjotone	151	XII	25,26,27-tris *nor*, 3,23-oxo, Δ^{7}	
Glochidion hohenackeri Bedd.	Euphorbiaceae	Glochidone	164	VI	3-oxo, $\Delta^{1.20(29)}$	155
		Glochidiol	253* (Diacetate)	VI	1β,3α-OH, $\Delta^{20(29)}$	
C. wrightii Benth.		Glochidonol	173	VI	1β-OH, 3-oxo, $\Delta^{20(29)}$	156
Glycyrrhiza echinata L.	Leguminosae	Echinatic acid	298	I	3β,16,21 or 22-OH, $\Delta^{9(11)12}$, 28-COOH	157
G. glabra L.	Leguminosae	Liquiritic acid	298	I	3β,11-oxo, Δ^{12}, 30-COOH	158,159
		24-Hydroxy-11-deoxy glycyrrhetic acid	263* (Me-ester)	I	3β,24-OH, Δ^{12}, 30-COOH	160
		Glycyrrhetol	252	I	3β,30-OH, 11-oxo, Δ^{12}	159,161
		24-Hydroxy glycyrrhetic acid	247* (Me-ester)	I	3β,24-OH, 11-oxo, Δ^{12}, 30-COOH	160
		21-Hydroxy isoglabrolide	304	I	3β,21α-OH, Δ^{12}, 29 → 18α-lactone	161
		Isoglabrolide	318	I	3β-OH, Δ^{12}, 29 → 18α-lactone	159,162
		Glabric acid	—	I	3β,26-OH, 3-oxo, Δ^{12}, 30-COOH	163
		Acid I	—	I	3β-OH, Δ^{12}, 30-COOH	159
		Compound A	239* (Me-ester)	U	OH, COOH	163
		Acid II	—	I	3β-OH, $\Delta^{11.13(18)}$, 30-COOH	159
		Glabrolide	—	I	3β-OH,11-oxo-, Δ^{12}, 30→22β-lactone	
		Deoxoglabrolide	—	I	3β-OH. Δ^{12},30 → 22β-lactone	
G. macedonica Boiss. et Orph.		Macedonic acid	340	I	3,19-OH, $\Delta^{11.13(18)}$, 17-COOH	164,165
Helichrysum italicum	Compositae	Ursololactone	252* (Acetate)	II	3β-OH, 28 → 13-lactone	166
Ilex rotunda Thunb.	Aquifoliaceae	Rotundic acid	257* (Me-ester)	II	3β,19α,23-CH, Δ^{12}, 28-COOH	167
Jasminum auriculatum Vahl.	Oleaceae	Jasminol	208	VI	28β-OH, $\Delta^{20(29)}$	168
Jatropha urens	Euphorbiaceae	Urensol, $C_{30}H_{50}O$	166	U	Δ	169
Khaya grandifoliola	Meliaceae	Grandifoliolenone	172* (Diacetate)	R	21 → 24-Epoxy, 23,25-dihydroxy, 7α-*O*-acetyl, 8β-methyl, 30-*nor* (13α,17βH), lanosta-1,14-dien-3-one	170
Lansium domesticum Jack.	Meliaceae	Lansic acid	182	XV	3:3,21,22-seco, $\Delta^{4(23)7(8)}$, $^{14(27)22(29)}$, 3,21-COOH	171,172
Lantana camara L.	Verbenaceae	Lantanolic acid $C_{30}H_{46}O_4$	306	U	Δ, COOH, cyclic hemiketal	173
Lippia rehmanni	Verbenaceae	22-Angeloyloxy oleanolic acid	296	I	3β-OH, 22β-angeloyloxy, Δ^{12}, 28-COOH	174
		22-Angeloyloxy-24-hydroxy oleanolic acid	294		3β,24-OH, 22β-angeloyloxy, Δ^{12}, 28-COOH	
Mangifera indica L.	Anacardiaceae	Hydroxymangiferonic acid	190	XI	27-OH, 9,19-cyclo, 3-oxo, Δ^{24}, 26-COOH	175
		Magiferolic acid	181	XI	3β-OH, 9,19-cyclo, Δ^{24}, 26-COOH	
		Substance II	166	XI	3β-OH, 9,19-cyclo, Δ^{24}, 24-CH_3, 26-CHO	176
		Substance III	154	XI	3β,26-OH, 9,19-cyclo, 24-CH_3	176,177
		Mangiferonic acid	187	XI	9,19-cyclo, 3-oxo, Δ^{24}, 26-COOH	178
		Isomangiferolic acid	168	XI	3α-OH, 9,19-cyclo, Δ^{24}, 26-COOH	
		Hydroxymangiferolic acid	201	XI	3β,27-OH, 9,91-cyclo. Δ^{24}, 26-COOH	
		Ambonic acid	149	XI	9,19-cyclo, 3-oxo, 24-CH_2, 26-COOH	179
		—	66–70	XI	3β-OH, 9,19-cyclo, Δ^{24},26-CHO	177
		—	—	XI	3′-Hydroxy-24′-methylene, 9′,19′-cyclo lanost-26′-yl, 3-oxo, 9,19-cyclo lanosta-24-methylene, 26-oate	
		Oleanolic aldehyde	168	I	3β-OH, Δ^{12}, 28-CHO	176
		Dammar-24-en-3β,20-diol	130	X	3β,20(*S*))-OH, Δ^{24}	177
Malus sylvestris Mill.	Rosaceae	Pomolic acid	301 d.	II	3β,19α-OH, Δ^{12}, 28-COOH	180
		Pomonic acid	204* (Me-ester)	II	19α-OH, 3-oxo, Δ^{12}, 28-COOH	
Melia azedarach L.	Meliaceae	Meliantriol	176	XII	3β,21,24(*R*), 25-OH, Δ^{7}, 21 → 23(*R*) epoxy	181
		Melianone	232	XII	21-OH, 3-oxo, Δ^{7}, 21 → 23(*R*), 24(*R*) → 25 epoxy	182
		Melianol	194	XII	3β,21-OH, Δ^{7}, 21 → 23(*R*), 24(*R*) → 25 epoxy	
		Kulinone	138	XIII	16β-OH, 3-oxo, $\Delta^{7,24}$	183,184
		Kulactone	163	XIII	3-oxo, $\Delta^{7,24}$, 21 → 16β lactone	184
		Kulolactone	Amorph.	XIII	3α-OH, $\Delta^{7,24}$, 21 → 16β-lactone	
	Meliaceae	Substance Ia	169* (Acetate)	R	3β,7α-Dihydroxy, 8β-methyl, 30-*nor* (13α 17β,H), 20(*S*) Lanosta-14(15),24-dien-21 → 23(*R*)-olide	185
Meristotropis triphylla *M. xanthoides*	Leguminosae	Meristotropic acid	358	I	3β-OH, 6-oxo, $\Delta^{11.13(18)}$, 29-COOH	186,187

Micromeria bethami Webb. et Berth. *M. species*	Labiatae	Micromeric acid	182* (Acetate Me-ester)	II	3β-OH, $\Delta^{12.20(30)}$, 28-COOH	146,147, 188
Mimusops hexandra Roxb.	Sapotaceae	Substance I $C_{30}H_{50}O_3$	263	U	—OH, COOH	189
		Substance II $C_{30}H_{50}O_4$	215	U	4-OH	
Neolitsea dealbota R. Br. Merr.	Lauraceae	Gycloneolitsin	169	XI	3β-OCH_3, 9,19-cyclo, 24,24-CH_3, Δ^{25}	190
N. pulchella (Meissn) Merr.	—	$C_{33}H_{56}O$	213	U	$-OCH_3$	191
Pachysandra terminalis Sieb. et Zucc.	Buxaceae	Pachysandiol B, $C_{30}H_{52}O_2$	262	U	2-OH	192
		Pachysandiol A	278	III	2α-3β-OH	
		Cerin	250	III	2α-OH, 3-oxo	192,193
Putranjiva roxburghii Wall.	Euphorbiaceae	Putranjivanonol $C_{30}H_{50}O_2$	312	U	-OH, C=O	194
		Putranjivadione	284	III	3,7-oxo	195
		Putranjic acid (Putric acid)	218	III	2-OH, 3,4 *seco*, 3-COOH	194,196
		Roxburgholone	312	III	3α-OH, 7-oxo	197
		Putranjivic acid**	177	III	3,4 *seco*, $\Delta^{4(23)}$, 3-COOH	198
Rhododendron folconeri Sm.	Ericaceae	Uvaol-3-acetate	—	II	28-OH, 3β-acetoxy, Δ^{12}	199
R. linearifolium Sieb. et Zucc.		Epigermanidiol	221	I	2α-3β-OH, $\Delta^{18(19)}$	200
		Germanidiol	275	I	2β,3β-OH, $\Delta^{18(19)}$	201
		Fernenediol	204	VIII	2α,3β-OH, $\Delta^{9(11)}$	200
		Motiol	218	VIII	3β-OH, $\Delta^{7(8)}$	201
		Motidiol	233	VIII	2β,3β-OH, $\Delta^{7(8)}$	
		Neomotiol	228	V	3β-OH, Δ^{12}	
		Neohopene)††				
		Adianenediol	279	R	2,3-Dihydroxy-E:B-friedohop-5-ene	
R. macrophyllum		D:B-Friedooleanan-3,5-oxide	203	R	3,5-Epoxy-D:B-friedooleanane	202
R. simiarum		Simiarenol	209	R	3β-Hydroxy-E:B-friedohop-5-ene	99,203
Ricinus communis L.	Euphorbiaceae	Compound II	237	VI	3β-OH, 30-*nor*, 20-oxo, $\Delta^{20(29)}$	204
Rubus fructicosus L.	Rosaceae	Rubitic acid	252	II	3β,6 or 7-OH, Δ^{12}, 28-COOH	205
R. moluccanus L.		Rubusic acid	—	I	3β,7α-OH, Δ^{12}, 28-COOH	206
Saussurea frolowii	Compositae	Sosyurol	212	U	*sec*.OH	207
Schinus terebinthefolius Radd.	Anacardiaceae	Schinol	145	XII	3α-OH, $\Delta^{7,24}$, 26-COOH	208,209
Shorea mecistopteryx Ridl.	Dipterocarpaceae	Shoreic acid	92* (Me-ester)	IX	25-OH, 2,3*seco*, 3-*nor*, $\Delta^{4(28)}$, 20(*S*) → 24(ξ)-epoxy, 2-COOH	210
Siphonodon australe Benth.	Siphonodontaceae	O_4 acid	334	III	3,21 or 22-oxo, 25-COOH	211
Thelocactus bicolor	Cactaceae	Eisacol $C_{30}H_{50}O_2$	—	U	*sec*. OH, *tert*. OH	212
Vateria indica L. (Dammar resin)	Dipterocarpaceae	Compound B	234	II	Δ^{12}, 2,3 *sec*, 3,28-$COOH_3$ 2 → 23-lactone	213
Vitex magapotamica (Spreng) Moldenke.	Verbenaceae	Triterpene I $C_{30}H_{50}O_8$	220	U	4-OH	214
Walsura tabulata	Meliaceae	Walsurenol	185	R	3β-Hydroxy-D:C-friedoolean-9(11)ene	215

* Denotes the m.p. of the derivative given below in the parenthesis.
† 'U' denotes unknown structure and 'R' denotes rearranged structure.
‡ Also present as monoacetate.
§ Same as madasiatic acid.[140] m.p. 248°.
‖ Identical with mexicanol, m.p. 236° from *Cedrela glaziovii*.[135]
¶ Probably an artefact; also present in *Micromeria* sp.[146,147]
** Also present as methyl ester, m.p. 132°.
†† Also present in *Adiantum* sp.[76]

[49] P. Oxley, *Chem. Commun.* 729 (1966).
[50] T. G. Halsall, E. R. H. Jones, G. Lowe and C. E. Newall, *Chem. Commun.* 685 (1966).
[51] T. S. Chou and E. J. Eisenbraum, *Tetrahedron Letters* 409 (1967).
[52] S. Okuda, Y. Sato, T. Hattori, H. Igarasjhi, T. Tsuchiya and N. Wasoda, *Tetrahedron Letters* 4769 (1968).
[53] S. Iwasaki, M. I. Sair, H. Igarachi and S. Okuda, *J. Chem. Soc.* **D**, 1119 (1970).
[54] S. Okuda, Y. Sato, T. Hattori and M. Wakabayashi, *Tetrahedron Letters* 4847 (1968).
[55] T. Hattori, H. Igarashi, S. Iwasaki and S. Okuda, *Tetrahedron Letters* 1023 (1969).

[56] K. ABILDGAARD, *Belg. Pat.* 619, 287 (24 Dec., 1962); *Chem. Abs.* **59,** P2133 (1963); W. O. GODTFREDSEN, W. V. DAEHNE, S. VANGEDAL, K. MARQUET, D. ARIGONI and A. MELERA, *Tetrahedron* **21,** 3505 (1965); A. COOPER, *Tetrahedron* **22,** 1379 (1966); A. COOPER and D. C. HODGKIN, *Tetrahedron* **23,** 909 (1967).
[57] A. K. BATLA and S. RANGASWAMI, *Ind. J. Chem.* **7,** 1063 (1969).
[58] K. E. SCHULTE, G. RUCKER and H. FACHMANN, *Tetrahedron Letters* 4833 (1967).
[59] W. O. GODTFREDSON, S. JAHNNEN, H. LORCK, K. ROHOLT and L. TYBRING, *Nature, Lond.* **193,** 987 (1962).
[60] LOEVENS KEMISKE FABRIK PRODUKTIONSAKTIESELSKAB. *Belg. Pat.* 636, 220 (2 Dec., 1963); *Chem. Abst.* **61** 16106 h (1964).
[61] R. S. LUDWICZAK and U. WRZECOINE, *Rocz. Chem.* **42,** 601 (1969); *Chem. Abs.* **71,** 50270 z (1969).
[62] A. KANEMOTSU and S. NATORI, *Chem. Pharm. Bull.* **18,** 779 (1970).
[63] L. B. KIER and W. S. BREY, JR., *J. Pharm. Sci.* **52,** 465 (1963).
[64] J. J. H. SIMES, M. WOOTTON, P. J. RALPH and J. T. PINHEY, *J. Chem. Soc.* **D,** 1150 (1969).
[65] T. BRUUN, *Acta Chem. Scand.* **23,** 3038 (1969).
[66] P. S. RAO and T. R. SESHADRI, *Indian J. Chem.* **6,** 398 (1968).
[67] I. YOSHIOKA, M. YAMAKI and I. KITAGAWA, *Chem. Pharm. Bull.* **14,** 804 (1966).
[68] I. YOSHIOKA, T. NAKANISHI and I. KITAGAWA, *Chem. Pharm. Bull.* **17,** 279 (1969); *idem. ibid.* **17,** 291 (1969).
[69] I. YOSHIOKA, T. NAKANISHI and E. TSUDA, *Tetrahedron Letters* 607 (1966).
[70] I. YOSHIOKA, H. YAMAUCHI and I. KITAGAWA, *Tetrahedron Letters* 4241 (1969).
[71] H. YAMAUCHI, T. FUGIWARA and K. TOMITA, *Tetrahedron Letters* 4245 (1969).
[72] G. BERTI, *Corsi Semin. Chim.* **11,** 65 (1968); *Chem. Abs.* **72,** 129386 w (1970).
[73] A. K. IWATA and S. NATORI, *Tetrahedron Letters* 3413 (1964).
[74] I. H. ROGERS and L. R. ROZOU, *Can. J. Chem.* **48,** 1021 (1970).
[75] H. AGETA, K. IWATA and Y. ARAI, *Tetrahedron Letters* 5679 (1966).
[76] H. AGETA, K. SHIOJIMA and Y. ARAL, *Chem. Commun.* 1105 (1968).
[77] H. AGETA and K. IWATA, *Tetrahedron Letters* 6069 (1966).
[78] S. RANGASWAMI and R. T. IYER, *Curr. Sci.* **36,** 83 (1967).
[79] TSUNG-HSING LIN and YAU-TANG LIN, *Hua Hsuch* 39 (1965); *Chem. Abs.* **63,** 7348 a (1965).
[80] Y. INUBUSHI, Y. TSUDA and T. SANO, *Yakugaku Zasshi* **82,** 1083 (1962).
[81] Y. TSUDA and T. FUGIMOTO, *J. Chem. Soc.* **D,** 260 (1970).
[82] Y. TSUDA, T. SANO, A. MORIMOTO and Y. INUBUSHI, *Tetrahedron Letters* 5933 (1966).
[83] Y. TSUDA and T. FUGIMOTO, *J. Chem. Soc.* **D,** 1042 (1969).
[84] Y. TSUDA and M. HATANAKA, *J. Chem. Soc.* **D,** 1040 (1969).
[85] Y. TSUDA, T. FUJIMOTO and K. KIMPARA, *J. Chem. Soc.* **D,** 261 (1970).
[86] Y. INUBUSHI, T. HARAYAMA, T. HIBINO and R. SOMANATHAN, *J. Chem. Soc.* **D,** 1118 (1970).
[87] Y. INUBUSHI, Y. TSUDA, B. ISHII, M. HOSOKAWA and T. SANO, *Yakugaku Zasshi* **82,** 1339 (1962); *Chem. Abs.* **59,** 678 h (1963); Y. INUBUSHI, T. SANO and Y. TSUDA, *Tetrahedron Letters* 1303 (1964); Y. INUBUSHI, Y. TSUDA, T. SANO, T. KONITA, S. SUZUKI, H. AGETA and Y. OTAKA, *Chem. Pharm. Bull.* **15,** 1153 (1967).
[88] T. SANO, Y. TSUDA and Y. INUBUSHI, *Tetrahedron* **26,** 2981 (1970).
[89] G. N. PANDEY and C. R. MITRA, *Tetrahedron Letters* 4683 (1967).
[90] G. BERTI, F. BOTTARI, B. MACCHIA, A. MARSILI, G. OURISSON and H. PIOTROWSKS, *Bull. Soc. Chim. Fr.* 2359 (1964).
[91] J. P. KUTNEY, I. H. ROGERS and J. W. ROWE, *Tetrahedron* **25,** 3731 (1969).
[92] J. P. KUTNEY and I. H. ROGERS, *Tetrahedron Letters* 761 (1968).
[93] J. W. ROWE, *Tetrahedron Letters* 2347 (1964).
[94] J. W. ROWE and C. L. BOWER, *Tetrahedron Letters* 2795 (1965).
[95] T. MURATA and M. SHINOHARA, *Tetrahedron Letters* 103 (1968).
[96] T. MURATA and M. MIYAMOTO, *Chem. Pharm. Bull.* **18,** 1354 (1970).
[97] T. MURATA, M. SHINOHARA and M. MIYAMIOTO, *Chem. Pharm. Bull.* **18,** 1369 (1970).
[98] C. S. BARNES, M. N. GALBRAITH, E. RITCHIE and W. C. TAYLOR, *Austral. J. Chem.* **18,** 1411 (1965).
[99] Ref. 3, p. 170.
[100] K. NISHIMOTO, M. ITO, S. NATORI and T. OHMOTO, *Chem. Pharm. Bull.* **14,** 97 (1966).
[101] T. OHMOTO, K. NISHIMOTO, M. ITO and S. NATORI, *Chem. Pharm. Bull.* **13,** 224 (1965).
[102] T. OHMOTO and S. NATORI, *J. Chem. Soc.* **D,** 601 (1969); T. OHMOTO, *Yakugaku Zasshi* **89,** 814 (1969).
[103] T. OHMOTO, *Yakugaku Zasshi* **89,** 1682 (1969).
[104] K. TACHIBANA, T. ENDO and T. MISUMI, *Jap. Pat.* 7007, 318 (Cl. 30 A 31); *Chem. Abs.* **73,** 4058 e (1970).
[105] T. ENDO, S. NAITO and Y. INABA, *Yakugaku zasshi* **19,** 298 (1970); *Chem. Abs.* **73,** 45627 h (1970).
[106] T. ENDO, S. NAITO and Y. INABA, *Yakugaku zasshi,* **19,** 302 (1970); *Chem. Abs.* **73,** 45628 j (1970).
[107] R. MCCRINDLE and C. DJERASSI, *Chem. Ind.* 1311 (1961).
[108] C. DJERASSI and R. MCCRINDLE, *J. Chem. Soc.* 4034 (1962).
[109] T. OHMOTO, T. NIKAIDO, K. NAKADAI and E. TOHYAMA, *Yakugaku Zasshi* **90,** 390 (1970); *Chem. Abs.* **73,** 53020 v (1970).
[110] H. PINHAS, *Bull. Soc. Chim. Fr.* 2037 (1969).

[111] D. SHIENGTHONG, A. VERASARN, P. NA NONGGAI-SUWANRATH and K. W. WARNHOFF, *Tetrahedron* **21,** 917 (1965).
[112] A. CHAWLA and SUKH DEV, *Tetrahedron Letters* 4837 (1967).
[113] M. B. BURBAGE and K. JEWERS, *J. Chem. Soc.* **D,** 814 (1970).
[114] D. R. MISRA and H. N. KHASTGIR, *J. Indian Chem. Soc.* **46,** 1063 (1969); *idem. Tetrahedron* **26,** 3017 (1970).
[115] N. C. GUPTA, B. SINGH and D. S. BHAKUNI, *Phytochem.* **8,** 791 (1969).
[116] F. G. FISCHER and N. SEILER, *Ann.* **644,** 162 (1961).
[117] A. A. RYABININ and L. G. MATYUKHINA, *Zh. Obshch. Khim.* **31,** 1033 (1961); *Chem. Abst.* **55,** 22501 h (1961); A. A. RYABININ, L. G. MATYUKHINA, I. A. SALTIKOVA, F. PATIL and G. OURISSON, *Bull. Soc. Chim. Fr.* 1089 (1968).
[118] A. CHATTERJI, A. B. KUNDU, T. CHAKRAVARTI and S. CHANDRASEKHARAN, *Tetrahedron* **26,** 1859 (1970).
[119] T. TAKAHASHI, Y. MORIYAMA, Y. TANAHASHI and G. OURISSON, *Tetrahedron Letters* 2991 (1967).
[120] T. TSUYUKI, T. HOSHINO, M. ITO and T. TAKAHASHI, *Bull. Soc. Chim. Fr.* 2895 (1968).
[121] Y. MORIYAMA, Y. TANAHASHI and T. TAKAHASHI, *Bull. Soc. Chim. Fr.* 2890 (1968).
[122] C. S. P. SASTRY and L. R. ROW, *Tetrahedron* **23,** 3837 (1967).
[123] A. K. BARUA, S. K. PAL and S. P. DUTTA, *Sci. Cult.* **34,** 259 (1968).
[124] F. G. FISCHER and N. SEILER, *Ann.* **644,** 146 (1961).
[125] M. NAGAI, N. TANAKA, S. ICHIKAWA and O. TANAKA, *Tetrahedron Letters* 4239 (1968).
[126] G. V. BADDELEY, A. J. BEALING, P. R. JEFFERIES and R. W. RETALLACK, *Austral. J. Chem.* **17,** 908 (1964).
[127] S. M. KUPCHAN, R. M. SMITH, Y. AYNELCHI and M. MASAO, *J. Org. Chem.* **35,** 2891 (1970).
[128] G. BIGLINO, L. CATTEL, O. CAPUTA and G. NOBILI, *Gazz. Chim. Ital.* **99,** 830 (1969); *idem. Ric. Sci.* **39,** 207 (1969); *Chem. Abs.* **72,** 111640 q (1970).
[129] T. R. GOVINDACHARI, D. PRAKASH and N. VISHVANATHAN, *J. Chem. Soc.* **C,** 1323 (1968).
[130] T. R. GOVINDACHARI, N. VISHWANATHAN, B. R. PAI, U. R. RAO and M. SRINIVASAN, *Tetrahedron* **23,** 1901 (1967).
[131] G. P. COTTERRELL, T. G. HALSALL and M. I. WRIGLESWORTH, *J. Chem. Soc.* **C,** 739 (1970).
[132] P. DE MAYO and A. N. STARRATT, *Tetrahedron Letters* 259 (1961).
[133] R. A. EADE, P. K. GRANT, M. J. A. MCGRATH, J. J. H. SIMES and M. WOOTTON, *Chem. Commun.* 1204 (1967).
[134] J. D. CONNOLLY, K. L. HANDA, R. MCCRINDLE and K. H. OVERTON, *J. Chem. Soc.* **C,** 2230 (1968).
[135] J. D. CONNOLLY, K. L. HANDA, R. MCCRINDLE and K. H. OVERTON, *Tetrahedron Letters* 3449 (1967).
[136] W. R. CHAN, H. L. HOLDER, G. SNATZKE, A. W. FEHLHABER and D. R. TAYLOR. *J. Chem. Soc.* **C,** 2485 (1968).
[137] J. D. CONNOLLY and K. L. HÄNDA, *J. Chem. Soc,* **C,** 2435 (1969).
[138] W. R. CHAN and D. R. TAYLOR, *Chem. Commun.* 548 (1967).
[139] BHAGIRATH SINGH and R. P. RASTOGI, *Phytochem.* **7,** 1385 (1968).
[140] H. PINHAS, *Bull. Soc. Chim. Fr.* 3592 (1969).
[141] A. T. GLEN, W. LAWRIE, J. MCLEAN and M. EL-GARBY YOUNES, *Chem. & Ind.* 1908 (1965).
[142] T. TAKEMOTO and G. KUSANO, *Yakugaku Zasshi* **89,** 954 (1969); *Chem. Abs.* **71,** 91696 m (1969).
[143] S. CORSANO and G. PIANCATELLI, *Gazz. Chim. Ital.* **99,** 1140 (1969); *Chem. Abs.* **72,** 90666 k (1970).
[144] T. TAKEMOTO, G. KUSANO and N. YAMAMOTO, *Yakugaku Zasshi* **90,** 68 (1970); *Chem. Abs.* **72,** 111644 u (1970).
[145] A. F. THOMAS and B. WILLHALM, *Tetrahedron Letters* 3177 (1964).
[146] J. B. BARRERA, J. L. B. FUNES, G. M. D. DE LA FUENTE and A. G. GONZALEZ, *Tetrahedron Letters* 4649 (1967).
[147] J. M. ARTEAGA, J. L. B. FUNES, B. M. FRAGA and A. G. GONZALEZ, *An. Quim.* **66,** 181 (1970); *Chem. Abs.* **73,** 95401 a (1970).
[148] H. T. CHEUNG and L. TOKES, *Tetrahedron Letters* 4363 (1968).
[149] H. T. CHEUNG, *Tetrahedron Letters* 2807 (1967); *idem. J. Chem. Soc.* **C,** 2686 (1968).
[150] Y. HIROSE, T. YANAGAWA and T. NAKATSUKA, *Nippon Mokuzai Gakkaishi* **14,** 59 (1968); *Chem. Abs.* **69,** 10582 e (1968); *idem. ibid.* **14,** 440 (1968); *Chem. Abs.* **70,** 106705 w (1969).
[151] R. A. EADE, J. ELLIS, P. HARPER and J. J. H. SIMES, *J. Chem. Soc.* **D,** 579 (1969).
[152] W. R. CHAN, D. R. TAYLOR and T. YEE, *J. Chem. Soc.* **C,** 311 (1970).
[153] S. K. TALPATRA, S. SEN GUPTA and B. TALPATRA, *Tetrahedron Letters* 5963 (1968).
[154] G. J. W. BREEN, E. RITCHIE, W. T. L. SIDWELL and W. C. TAYLOR, *Austral. J. Chem.* **19,** 455 (1966).
[155] A. K. GANGULY, T. R. GOVINDACHARI, P. A. MOHAMMED, A. D. RAHIMTULLA and N. VISHWANATHAN, *Tetrahedron* **22,** 1513 (1966); *idem. Bull. Nat. Inst. Sci. India* **77** (1968).
[156] W. H. HUI and M. L. FUNG, *J. Chem. Soc.* **C,** 1710 (1969).
[157] N. P. KIRYALOV and T. N. NAUGOLNAYA, *Zh. Obshch. Khim.* **33,** 700 (1963); N. P. KIRYALOV and V. F. BOGATKINA, *Khim. Prir. Soedin* **5,** 447 (1969); *Chem. Abs.* **72,** 67137 e (1970).
[158] L. CANONICA, G. RUSSO and E. BOMBARDELLI, *Gazz. Chim. Ital.* **96,** 833 (1966); *Chem. Abs.* **65,** 15436 f (1966).

[159] G. RUSSO, *Corsi Semin. Chim.* **11,** 20 (1968); *Chem. Abs.* **72,** 21799 u (1970).
[160] L. CANONICA, B. DANIELI, P. MANITTO, G. RUSSO and A. BONATI, *Gazz. Chim. Ital.* **97,** 1359 (1967); *Chem. Abs.* **68,** 49811 h (1968).
[161] L. CANONICA, B. DANIELI, P. MANITTO, G. RUSSO and E. BOMBARDELLI, *Gazz. Chim. Ital.* **97,** 1347 (1967); *Chem. Abs.* **68,** 49810 (1968).
[162] L. CANONICA, B. DANIELI, P. MANITTO and G. RUSSO, *Gazz. Chim. Ital.* **96,** 843 (1966); *Chem. Abs.* **65,** 15436 b (1966).
[163] M. H. A. ELGAMAL and M. B. E. FAYEZ, *Acta Chim. Budapest* **58,** 75 (1968); *Chem. Abs.* **7,** 29115 x (1969).
[164] N. P. KIRYALOV and T. N. NAUGOLNAYA, *Boiss et Orph. Zhurn. Obschei Khimi* **33,** 697 (1963).
[165] N. P. KIRYALOV, *Khim. Prir. Soedin.* **5,** 448 (1969); *Chem. Abs.* **72,** 67136 d (1970).
[166] G. ORZALESI, T. MENZETTI and V. BELLAVITA, *Boll. Chim. Farm.* **108,** 540 (1969); *Chem. Abs.* **72,** 121740 m (1970).
[167] T. OYAMA, H. AOYAMA and K. YAMADA, *Tetrahedron Letters* 4639 (1968).
[168] S. M. DESHPANDE and R. R. UPADHYAY, *Experientia* **26,** 10 (1970).
[169] A. X. DOMINGUEZ and G. R. V. RENGIFO, *Rev. Soc. Quim Mex.* **13,** 118 a (1969); *Chem. Abs.* **72,** 718 b (1970).
[170] J. D. CONOLLY and R. MCCRINDLE, *Chem. Commun.* 1193 (1967).
[171] A. K. KIANG, E. L. TAN, F. Y. LIM, K. HABAGUCHI and K. NAKANISHI, *Tetrahedron Letters* 3571 (1967).
[172] K. HABAGUCHI, M. WATANABE, Y. NAKADAIRA and K. NAKANISHI, *Tetrahedron Letters* 3731 (1968).
[173] A. K. BARUA, P. K. CHAKRAVARTY, S. P. DUTTA, D. K. MUKHERJEE and B. C. DAS, *Sci. Cult.* **32,** 456 (1966).
[174] L. A. P. ANDERSON, W. T. DE KOCK and P. R. ENSLIN, *J. S. African Chem. Inst.* **14,** 58 (1961); *Chem. Abs.* **57,** 15163 (1962).
[175] S. CORSANO and G. PIANCATELLI, *Ric. Sci. Rend. Sez.* **8,** 484 (1965); *Chem. Abs.* **63,** 18181 c (1965).
[176] S. CORSANO and E. MINCIONE, *Ric. Sci.* **37,** 370 (1967); *Chem. Abs.* **67,** 116988 r (1967).
[177] E. MINCIONI, C. IAVARONE and S. CORSANO, *Ric. Sci.* **38,** 537 (1968); *Chem. Abs.* **70,** 78191 c (1969).
[178] S. CORSANO and E. MINCIONE, *Ann. Chim.* **57,** 508 (1967).
[179] S. CORSANO and E. MINCIONE, *Ann. Chim.* **57,** 522 (1967).
[180] C. H. BRIESKORN and H. WUNDERER, *Chem. Ber.* **100,** 1252 (1967).
[181] D. LAVIE, M. K. JAIN and S. R. SHAPAN-GABRIELITH, *Chem. Commun.* 910 (1967).
[182] D. LAVIE, M. K. JAIN and I. KIRSON, *J. Chem. Soc.* **C,** 1347 (1967).
[183] F. C. CHANG and CHAO KUO CHIANG, *Chem. Commun.* 1158 (1968).
[184] F. C. CHANG and CHAO-KUO CHIANG, *Tetrahedron Letters* 891 (1969).
[185] D. LAVIE and E. C. LEVY, *Tetrahedron Letters* 3525 (1969).
[186] A. D. ZORINA, L. G. MATYUKHINA and A. A. RYABININ, *Khim. Prirodn. Soedin. Akad. Nauk uz. SSSR* **2,** 217 (1966); *Chem. Abs.* **65,** 17010 c (1966).
[187] N. P. KIR'YALOV and G. S. AMIROVA, *Khim. Prir. Soedin.* **4,** 87 (1968); *Chem. Abs.* **69,** 87231 x (1968).
[188] J. B. BARRERA, J. L. B. FUNES, G. M. DE LA FUENTE and A. GONZALEZ, *An. Quim.* **64,** 175 (1968); *Chem. Abs.* **69,** 19326 g (1968).
[189] C. R. MITRA and G. MISRA, *Phytochem.* **4,** 345 (1965).
[190] E. RITCHIE, R. G. SENIOR and W. C. TAYLOR, *Austral. J. Chem.* **22,** 2371 (1969).
[191] H. R. ARTHUR and S. N. LOO, *Tetrahedron Letters* 3767 (1967).
[192] T. KIKUSHI and T. TOYODA, *Tetrahedron Letters* 3181 (1967).
[193] E. J. COREY and J. J. URSPRUNG, *J. Am. Chem. Soc.* **78,** 5041 (1956).
[194] H. S. GARG and C. R. MITRA, *Phytochem.* **7,** 2053 (1968); *idem. Tetrahedron Letters* 231 (1969).
[195] P. SENGUPTA, A. K. CHAKRABORTY, A. M. DUFFIELD, L. J. DURHAM and C. DJERASSI, *Tetrahedron* **24,** 1205 (1968).
[196] G. R. CHOPRA, A. C. JAIN and T. R. SESHADRI, *Curr. Sci.* **38,** 101 (1969); *idem. Ind. J. Chem.* **8,** 401 (1970).
[197] P. SENGUPTA and J. MUKERJEE, *Tetrahedron* **24,** 6259 (1968).
[198] G. R. CHOPRA, A. C. JAIN and T. R. SASHADRI, *Ind. J. Chem.* **7,** 1179 (1969).
[199] P. SENGUPTA, A. K. DEY, J. MUKERJI, S. GHOSH and K. G. DAS, *J. Ind. Chem. Soc.* **46,** 775 (1969).
[200] H. WADA, G. GOTO, T. GOTO and Y. HIRATA, *Tetrahedron Letters* 3461 (1966).
[201] S. NAKAMURA, T. YAMADA, H. WADA, Y. INOUE, T. GOTO and Y. HIRATA, *Tetrahedron Letters* 2017 (1965).
[202] G. H. CONSTANTINE and J. H. BLOCK, *Phytochem.* **9,** 1659 (1970).
[203] R. T. APLIN, H. R. ARTHUR and W. H. HUI, *J. Chem. Soc.* **C,** 1251 (1966).
[204] M. J. THOMPSON and W. S. BOWERS, *Phytochem.* **7,** 845 (1968).
[205] S. N. GANGULY, *Chem. & Ind.* 869 (1970).
[206] A. K. BHATTACHARYA and H. K. DUTTA, *J. Ind. Chem. Soc.* **46,** 381 (1969).
[207] A. T. TROSHCHENKO and V. S. KOBRIN, *Khim. Priodn. Soedin. Akad. Nauk USSR*, 256 (1965); *Chem. Abs.* **64,** 3615 e (1966).

[208] K. K. KAISTHA and L. B. KIER, *J. Pharm. Sci.* **51,** 1136 (1962).
[209] L. B. KIER, J. M. LEHN and G. OURISSON, *Bull. Soc. Chim. Fr.* 911 (1963).
[210] J. P. LANTZ and E. R. WOLFF, *Bull. Soc. Chim. Fr.* 2131 (1968).
[211] J. L. COURTNEY and W. STERN, *Tetrahedron Letters* 3733 (1965).
[212] A. X. DOMINGUEZ, V. A. BARRAGAN, O. JOAQUIN, S. KRAUSE, LOTHAR, G. A. BROVO and G. J. MORALES, *Planta Med.* **16,** 458 (1968).
[213] S. BREWIS, T. G. HALSALL, H. R. HARRISON and O. J. R. HODDER, *J. Chem. Soc.* **D,** 891 (1970).
[214] R. HAENOEL, CH. LEUCKERT, H. RIMPLER and K. D. SCHAOF, *Phytochem.* **4,** 19 (1965).
[215] A. CHATTERJI, A. B. KUNDU, T. CHAKRAVARTY and S. CHANDRASEKHARAN, *Chem. Commun.* 418 (1968).

TABLE 2. MISCELLANEOUS SOURCES

Source	Family	Substance	m.p.	Basic skeleton	Groups	Ref.
Petroleum oil (Nigeria)		Triterpane E	260	R	1(10 → 5), abeo-3β-methyl-24β-*nor*-18α-oleanane	216
Tetrahymena pyriformis	Protozoon	Tetrahymanol	313	R	3α-Hydroxy D:B-5βH-friedooleanane	217

[216] I. R. HILLS, G. W. SMITH and E. V. WHITEHEAD, *Nature, Lond.* **219,** 243 (1968).
[217] F. B. MALLORY, J. T. GORDON and R. L. CONNER, *J. Am. Chem. Soc.* **85,** 1362 (1963).