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TRITERPENOIDS OF THE GRAMINEAE

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Abstract—The distribution of triterpenes was studied in 56 species of the Gramineae and their wide occurrence confirmed. Twenty-eight triterpenes were identified and triterpene methyl ethers, especially those of fernane and arborane groups, were found to be characteristic constituents of this family. Some chemotaxonomic observations are also discussed.

INTRODUCTION

THE GRAMINEAE is the largest family of the Monocotyledoneae and contains about 10,000 species grouped in about 600 genera; 98 genera and 310 species are reported from Japan.[1] Since many plants in this family are utilized for food and forage, their chemistry has been extensively studied. Lower terpenes, phenethylamine, indole and pyrrolizidine alkaloids, flavonoids and other polyphenols, and some glycosides have been reported in this family.[2]

With regard to the triterpenoids, the following compounds have been characterized in the grasses: dihydro-β-sitosteryl ferulate;[3a] gramisterol, citrostadienol and γ-dihydrositosterol;[3b,3c] avenacin;[4] and β-cycloorystenol, 24-methylenecycloartenol, cycloartenol, and their ferulates.[5] The first two examples of a pentacyclic triterpenoid with a methoxyl group at 3β-position, namely miliacin (germanicol methyl ether) (XIX) from *Panicum miliaceum* L. and *Syntherisma sanguinalis* Dulac. var. *ciliaris* Honda and crusgallin (sawamilletin, taraxerol methyl ether) (XXI) from *Echinochloa crus-gallis* L., were reported and their structures elucidated.[6,7] From the rhizomes of *Imperata cylindrica* Beauv. var. *koenigii* Durand et Schinz, arundoin (fern-9(11)-en-3β-ol methyl ether) (III) and cylindrin (isoarborinol methyl

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[2] R. HEGNAUER, *Chemotaxonomie der Pflanzen*, Band 2, p. 156, Birkhäuser Verlag, Basel (1963).

[3] (a) T. TAMURA, N. SAKAEYA and T. MATSUMOTO, *Nippon Kagaku Zasshi* **79**, 1011 (1958); (b) T. TAMURA, T. HIBINO, K. YOKOYAMA and T. MATSUMOTO, *Nippon Kagaku Zasshi* **80**, 215 (1959); T. TAMURA, T. TAKESHIMA and T. MATSUMOTO, *Abura Kagaku* **11**, 215 (1962); T. TAMURA, A. MIURA and T. MATSUMOTO, *Abura Kagaku* **11**, 415 (1962); (c) G. OSSKE and K. SCHREIBER, *Tetrahedron* **21**, 1559 (1965).

[4] H. J. BURKHARDT, J. V. MEIZEL and H. K. MICHELL, *Biochem.* **3**, 424, 426 (1964).

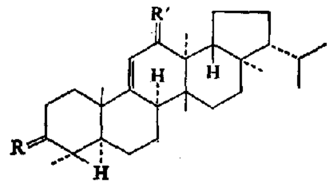
[5] S. YOSHIDA, R. TAKASAKI and H. SUEYOSHI, *Yakugaku Zasshi* **76**, 1335 (1956); G. OHTA and M. SCHIMIZU *Chem. Pharm. Bull. Tokyo* **5**, 36, 40 (1957); G. OHTA and M. SCHIMIZU, *Chem. Pharm. Bull. Tokyo* **6**, 325 (1958), G. OHTA, *Chem. Pharm. Bull. Tokyo* **8**, 5, 9 (1960), M. SHIMIZU and G. OHTA, *Chem. Pharm. Bull. Tokyo* **8**, 108 (1960).

[6] H. ITO, *J. Fac. Agri. Hokkaido Univ.* **37**, 1 (1934).

[7] T. OHARA and S. ABE, *Nippon Kagaku Zasshi* **80**, 677 (1959); S. ABE and T. OHARA, *Nippon Kagaku Zasshi* **80**, 1487 (1959); S. ABE, *Nippon Kagaku Zasshi* **80**, 1491 (1959)· N. SUGIYAMA and S. ABE, *Nippon Kagaku Zasshi* **82**, 1051 (1961); S. ABE, *Nippon Kagaku Zasshi* **82**, 1054, 1057 (1961).

CHART 1.

(Arabic numerals after the names of compounds refer to the plants listed in Table 1.)



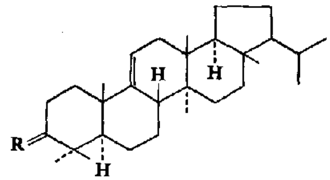
(I) R: OH, H R′: H_2 Fernenol
10, 29, 31, 32, 42, 44, 45, 47, 49

(II) R: H, OH R′: H_2 Fern-9(11)-en-3α-ol
31, 46, 47

(III) R: OCH_3, H R′: H_2 Arundoin
9, 11, 13, 15, 20, 22, 23, 24, 26, 28, 29, 31, 32, 44, 45, 47, 58

(IV) R: = O R′: H_2 Fernenone
31

(V) R: OCH_3, H R′: O 12-Oxoarundoin
31



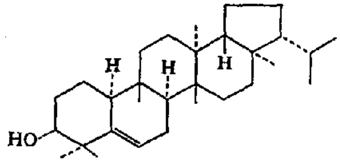
(VI) R: OH, H Isoarborinol
29, 33, 35, 39, 42, 44, 45, 46, 47, 49, 52, 55

(VII) R: OCH_3, H Cylindrin
5, 9, 13, 15, 20, 22, 23, 24, 25, 26, 29, 35, 42, 43, 44, 45, 47, 48, 52, 58

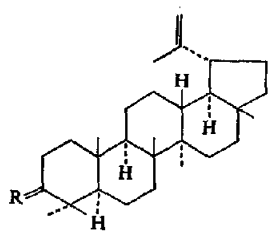
(VIII) R: = O Arborinone
44

(IX) R: H, OH Arborinol
44, 47

(X) R: H, OCH_3 Arborinol methyl ether
15, 44, 47



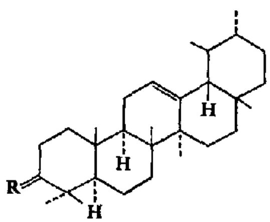
(XI) Simiarenol
45



(XII) R: OH, H Lupeol
17, 59

(XIII) R: OCH_3, H Lupeol methyl ether
37

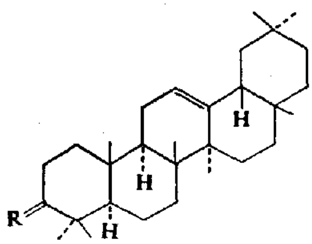
(XIV) R: = O Lupenone
59



(XV) R: OH, H α-Amyrin
5

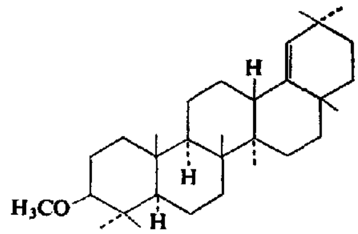
(XVI) R: OCH_3, H α-Amyrin methyl ether
26

CHART 1—*Continued.*

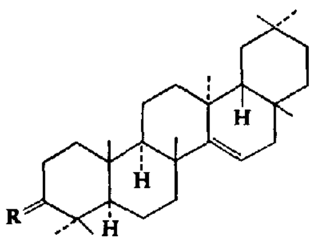


(XVII) R: OH / H — β-Amyrin
5, 10, 12, 17, 18, 19, 26, 28, 30, 36, 40, 43, 52, 57, 59

(XVIII) R: OCH_3 / H — β-Amyrin methyl ether
26



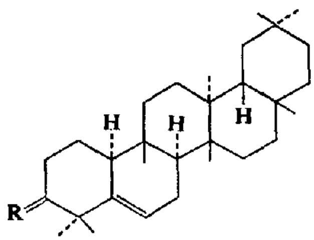
(XIX) Miliacin
7, 27, 36, 37, 46



(XX) R: OH / H — Taraxerol
18, 22, 48, 51

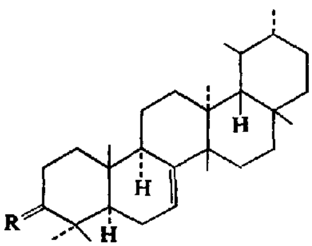
(XXI) R: OCH_3 / H — Crusgallin
30, 34, 48, 51

(XXII) R: =O — Taraxerone
18



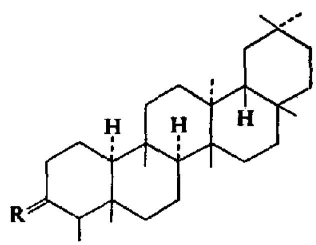
(XXIII) R: OH / H — Glutinol
51, 52

(XXIV) R: =O — Glutinone
10, 13, 52



(XXV) R: OH / H — Bauerenol
21

(XXVI) R: =O — Bauerenone
21



(XXVII) R: H / OH — Friedelinol
8, 21

(XXVIII) R: =O — Friedelin
2, 6, 10, 16, 20, 22, 28, 32, 35, 39, 43, 44, 46, 48, 49, 51, 52, 54, 55, 57, 58, 59

ether) (VII) were isolated together with fernenol (I), isoarborinol (VI), and simiarenol (XI) and their structures were established.[8]

These findings led us to study further the distribution of triterpenes in the Gramineae. We have so far examined 56 species[9] in 14 tribes (Table 1: classification according to Engler).[10] In this paper, the cumulative results so far obtained[9] will be reported and discussed from the chemotaxonomic point of view. During this work, α-amyrin methyl ether (XVI), β-amyrin methyl ether (XVIII), and arundoin (III) were isolated from *Cortaderia* spp.[11a, 11b] and arundoin (III) and crusgallin (XXI) from *Saccharum officinarum* L.[11c]

RESULTS

Since there exist some limitations in the identification of these compounds by chromatographic and spectral methods without isolation, rather large amounts of plant material were extracted with hexane and the unsaponifiable matter from the extract was further analyzed as shown in the Experimental. The compounds isolated in crystalline forms were compared with the authentic samples by TLC, GLC, i.r. and m.p. and identified.[9a–9g]

The results thus obtained are shown in Table 1 and 28 triterpenes identified in the course of study are shown in Chart 1, with the numbers referring to the plant names given in Table 1. Of these, fern-9(11)-en-3α-ol (II) from herbs of *Zoysia matrella** (31),[9g] arborinol methyl ether (X) from culms and blades of *Imperata cylindrica* var. *koenigii* (44),[9f] and lupeol methyl ether (XIII) from culms and blades of *Paspalum dilatatum* (37),[9e] were new compounds and their structures were elucidated.[9a–9h] Fern-9(11)-3-one (IV) and 12-oxoarundoin (V) from *Zoysia matrella* (31)[9e] and bauerenone (XXVI) from *Cortaderia argenta* (21)[9c] were isolated for the first time as natural products. Physical constants of these compounds are shown in Table 2.

Now three new triterpene methyl ethers (V, X, XIII) have been added[9h] to the known six compounds.[6–8, 11]

Besides these compounds, twelve triterpenoids or steroids shown in Table 1 were isolated but, due to the scarcity of the samples, have not yet been identified. All the plants so far examined contain the same mixture of phytosterols, namely β-sitosterol, campesterol, and stigmasterol with β-sitosterol as the major component.

For identification and checking purity, thin-layer and gas chromatography were employed. The conditions have already been reported.[9a] Since 15 different triterpene methyl ethers are now available, the retention times of these compounds are compared in Table 3. The results agree with those reported previously.[11c, 12]

* Author name omitted, cf. Table 1.

[8] T. OHMOTO, K. NISHIMOTO, M. ITO and S. NATORI, *Chem. Pharm. Bull. Tokyo* **13**, 224 (1965); K. NISHIMOTO, M. ITO, S. NATORI and T. OHMOTO, *Tetrahedron Letters* 2245 (1965), K. NISHIMOTO, M. ITO, S. NATORI and T. OHMOTO, *Chem. Pharm. Bull. Tokyo* **14**, 97 (1966), K. NISHIMOTO, M. ITO, S. NATORI and T. OHMOTO, *Tetrahedron* **24**, 735 (1968).

[9] (a) T. OHMOTO, *Shoyakugaku Zasshi* **20**, 67 (1966); (b) T. OHMOTO, *Shoyakugaku Zasshi* **21**, 115 (1967); (c) T. OHMOTO, *Shoyakugaku Zasshi* **21**, 120 (1967); (d) T. OHMOTO, T. NIKAIDO and K. NAKADAI, *Shoyakugaku Zasshi* **22**, 110 (1968); (e) T. OHMOTO, *Yakugaku Zasshi* **89**, 814 (1969); (f) T. OHMOTO, *Yakugaku Zasshi* **89**, 1682 (1969). (g) T. OHMOTO, T. NIKAIDO, K. NAKADAI and E. TOHYAMA, *Yakugaku Zasshi* **90**, 390 (1970); (h) T. OHMOTO and S. NATORI, *Chem. Commun.* 601 (1969).

[10] A. ENGLER, *Syllabus der Pflanzenfamilien*, Vol. II, p. 561, Borntraeger, Berlin (1964).

[11] (a) M. MARTIN-SMITH, G. SUBRAMANIAN and H. E. CONNOR, *Phytochem.* **6**, 559 (1967); (b) T. A. BRYCE, G. EGLINTON, R. H. HAMILTON, M. MARTIN-SMITH and G. SUBRAMANIAN, *Phytochem.* **6**, 727 (1967); (c) T. A. BRYCE, M. MARTIN-SMITH, G. OSSKE, K. SCHREIBER and G. SUBRAMANIAN, *Tetrahedron* **23**, 1283 (1967)

[12] M. IKEKAWA, S. NATORI, H. ITOKAWA, S. TOBINAGA and M. MATSUI, *Chem. Pharm. Bull. Tokyo* **13**, 316 (1965); N. IKEKAWA, S. NATORI, H. AGETA, K. IWATA and M. MATSUI, *Chem. Pharm. Bull. Tokyo* **13**, 320 (1965).

TABLE 1. TRITERPENOIDS OF THE GRAMINEAE

Tribe	Species (Japanese name)	Part used	Reference	Triterpenoid identified	M.p. of unidentified substance
1 Poeae	*Beckmannia syzigachne* Fernald (Kazunokogusa)	Grains	9c		
2 Poeae	*Bromus catharticus* Vahl. (Inumugi)	Grains	9c		
3 Poeae	*Bromus rigidus* Roth (Higenagasuzumenotyahiki)	Culms and blades	9c	XXVIII	
4 Poeae	*Dactylis glomerata* L. (Kamogaya)	Grains	9c		
5 Poeae	*Festuca arundinacea* Schreb. (Oniusinokegusa)	Culms and blades	9f	VII, XV, XVII	
6 Poeae	*Festuca parvigluma* Steud. (Tobosigara)	Herbs	9d	XXVIII	
7 Poeae	*Glyceria acutiflora* Torr. (Mutuoregusa)	Herbs	9d	XIX	
8 Poeae	*Poa annua* L. (Suzumenokatabira)	Herbs	9c	XXVII	
9 Poeae	*Poa pratensis* L. (Nagahagusa)	Herbs	9d	III, VII	
10 Poeae	*Poa sphondylodes* Trin. (Itigotunagi)	Herbs	9f	I, III, XVII, XXIV, XXVIII	
11 Triticeae	*Agropyron tsukushiense* Ohwi var. *transiens* Ohwi (Kamozigusa)	Culms and blades	9c		
12 Triticeae	*Elymus mollis* Trin. (Tenkigusa)	Herbs	9b	XVII	
13 Aveneae	*Agrostis alba* L. (Konukagusa)	Culms and blades	9d	III, VII, XXIV	
14 Aveneae	*Avena fatua* L. (Karasumugi)	Grains	9g		
15 Aveneae	*Calamagrostis epigeios* Roth (Yamaawa)	Culms and blades	9d	I, III, VII, X, XV	
16 Aveneae	*Holcus lanatus* L. (Siragegaya)	Herbs	9g	XXVIII	155*
17 Arundineae	*Arundo donax* L. (Dantiku)	Blades	9a	XII, XVII	
18 Arundineae	*Phragmites communis* Trin. (Yosi)	Herbs	9c	XVII, XX, XXII	
19 Arundineae	*Phragmites japonica* Steud. (Turuyosi)	Herbs	9d	XVII	
20 Arundinelleae	*Arundinella hirta* C. Tanaka (Todasiba)	Herbs	9b	III, VII, XXVIII	
21 Arundinelleae	*Cortaderia argenta* Stapf (Siroganeyosi)	Culms and blades	9c	XXV, XXVI	
22 Arundinelleae	*Lophatherum gracile* Brongn. (Sasakusa)	Culms and blades	9f	III, VII, XX, XXVIII	
23 Arundinelleae	*Lophatherum gracile* Brongn.	Rhizomes	9f	III, VII	
24 Phalarideae	*Alopecurus aequalis* Sobal. var. *amurensis* Ohwi (Suzumenoteppo)	Herbs	9d	VII	
25 Phalarideae	*Pharlaris arundinacea* L. (Kusayosi)	Culms and blades	9g	III, VII	
26 Eragrosteae	*Eragrostis curvula* Ness (Sinadaresuzumegaya)	Culms and blades	9d	III, VII, XVI, XVII, XVIII	198,† 284‡
27 Eragrosteae	*Eragrostis ferruginea* Beauv. (Kazekusa)	Culms and blades	9d	XVIII, XIX	
28 Chlorideae	*Cynodon dactylon* L. (Gyoogisiba)	Herbs	9b, 9e	III, XXVIII	
29 Zoysieae	*Zoysia japonica* Steud. (Siba)	Herbs	9a	I, III, VI, VII	
30 Zoysieae	*Zoysia macrostachya* Franch. et Savat (Onisiba)	Herbs	9b	XVII, XXI	
31 Zoysieae	*Zoysia matrella* Merr. (Harisiba)	Herbs	9b, 9e, 9g	I, II, III, IV, V	

TABLE 1—*Continued*

	Tribe	Species (Japanese name)	Part used	Reference	Triterpenoid identified	M.p. of unidentified substance
32	Zoysieae	*Zoysia tenuifolia* Willd. (Kooraisiba)	Herbs	9b	I, III, XXVII, XXVIII	
33	Oryzeae	*Oryza sativa* L. (Ine)	Herbs	9g	III, VI, VII	
34	Paniceae	*Echinochloa crusgalli* Beauv. var. *crus-galli* L. (Inubie)	Grains	9a	XXI	
35	Paniceae	*Oplismenus undulatifolius* Romer et Schultes (Tizimizasa)	Herbs	9c	VI, VII, XXVIII	
36	Paniceae	*Panicum dichotomiflorum* Michx. (Ookusakibi)	Culms and blades	9g	XVII, XIX	
37	Paniceae	*Paspalum dilatatum* Poir. (Simasuzumenohie)	Culms and blades	9e	XIII, XIX	276§
38	Paniceae	*Pennisetum alopecuroides* Spreng. (Tikarasiba)	Grains	9a		
39	Paniceae	*Setaria chondrachne* Honda (Inuawa)	Grains	9f	VI, XXVIII	
40	Paniceae	*Setaria faberi* Herrm. (Akinoenokorogusa)	Grains	9a	XVII	
41	Paniceae	*Setaria italica* P. Beauv. (Awa)	Grains	9a		245‖
42	Andropogoneae	*Arthraxon hispidus* Makino (Kobunagusa)	Culms and blades	9c	I, VI, VII	
43	Andropogoneae	*Hemarthria sibirica* Ohwi (Usinosippei)	Herbs	9e	VII, XVII, XXVIII	224¶, 190** 288††
44	Andropogoneae	*Imperata cylindrica* Beauv. var. *koenigii* Durand et Schinz (Tigaya)	Culms and blades	9f	I, III, VI, VII, VIII, IX, X, XXVIII	
45	Andropogoneae	*Imperata cylindrica* Beauv. var. *koenigii* Durand et Schinz (Tigaya)	Rhizomes	8	I, III, VI, VII, XI	
46	Andropogoneae	*Microstegium vimineum* A. Comus (Himeasiboso)	Herbs	9b	II, VI, XIX, XXVIII	
47	Andropogoneae	*Miscanthus floridulus* Warb. (Tokiwasusuki)	Culms and blades	9f	I, II, III, VI, VII, IX, X	
48	Andropogoneae	*Miscanthus sacchariflorus* Benth. (Ogi)	Culms and blades	9e	VII, XX, XXI, XXVIII	
49	Andropogoneae	*Miscanthus sinensis* Anderss. (Susuki)	Culms and blades	9e	I, VI, XXVIII	
50	Andropogoneae	*Miscanthus sinensis* Anderss. (Susuki)	Rhizomes	9a		111‡‡
51	Andropogoneae	*Phacelurus latifolius* Ohwi (Aiasi)	Culms and blades	9c	XX, XXI, XXIII, XXVIII	
52	Andropogoneae	*Saccharum spontaneum* L. var. *arenicola* Ohwi (Waseobana)	Culms and blades	9e	VI, VII, XXIII, XXIV, XXVIII	Ac 249§§
53	Andropogoneae	*Sorghum halepense* Persoon (Seibanmorokosi)	Culms and blades	9b	XVII	
54	Andropogoneae	*Sorghum japonicum* Roshevitz (Morokosi)	Grains	9a	XXVIII	291‖‖
55	Maydeae	*Coix lacryma-jobi* L. (Zyuzudama)	Herbs	9a, 9e	VI, XXVIII	
56	Maydeae	*Coix lacryma-jabi* L. var. *ma-yuen* Stapf. (Hatomugi)	Blades	9a		
57	Maydeae	*Zea mays* L. (Toomorokosi)	Herbs	9e	XVII, XXVIII	Ac 174¶¶
58	Arundinarieae	*Arundinaria chino* Makino (Azumanezasa)	Rhizomes	9g	III, VII, XXVIII	
59	Arundinarieae	*Phyllostachys heterocycla* Mitf. var. *pubescens* Ohwi (Moosootiku)	Culms and wax	9a, 9e	XII, XIV, XVII, XXVIII	

Ac: acetate. Some physical data of these compounds are shown in footnotes.

* I.r. 3400, 2925, 1655, 1600, 1450, 1370, 1068, 1038, 997, 830, 796 cm^{-1}.
† $C_{30}H_{50}O$ (M^+, 426), i.r. 3520, 2960, 1635, 1463, 1392, 922, 910 cm^{-1}.
‡ $C_{30}H_{48}O$ (M^+, 424), i.r. 2890, 1697, 1440, 1375, 1113, 1077, 1055, 827, 765 cm^{-1}.
§ I.r. 2850, 1687, 1437, 1365, 821, 763, 706 cm^{-1}.
‖ I.r. 2850, 1698, 1450, 1384, 833 cm^{-1}.
¶ $C_{31}H_{52}O$ (M^+, 440), $(\alpha)_D^{21}$ +3·93 ($CHCl_3$), i.r. 2930, 1623, 1444, 1381, 1366, 1183, 1119, 1095, 982, 812 cm^{-1}. NMR 4·60 (1 H, t), 6·66 (3 H, s), 7·45 (1 H, m).
** I.r. 2960, 2870, 1455, 1380, 1366, 1050, 986, 953, 910 cm^{-1}.
†† I.r. 3500, 1450, 1392, 1364, 1054, 1027, 1011, 918, 854, 772 cm^{-1}.
‡‡ I.r. 1698, 833 cm^{-1}.
§§ $C_{32}H_{52}O_2$ (M^+ 468).
‖‖ I.r. 3510, 1700, 785 cm^{-1}.
¶¶ I.r. 2930, 2842, 1722, 1450, 1367, 1246, 1032, 981, 916, 831, 788 cm^{-1}.

TABLE 2. PHYSICAL PROPERTIES OF NEW TRITERPENES

	m.p.	$[\alpha]_D(CHCl_3)$	I.r. cm^{-1}	NMR
Fern-9(11)-en-3α-ol (II)	223–224°	$[\alpha]_D^{30}$ −10·7	3340 (—OH) 1635, 862, 813 (>C=CH—)	4·71 (1H, m, >C=*CH*—) 6·64 (1H, m, *H*—C(|)--OH)
Fernenone (IV)	206–207°	$[\alpha]_D^{23}$ −39·4	1695 (>C=O) 1637, 811, 790 (>C=CH—)	*
12-Oxoarundoin (V)	291°	$[\alpha]_D^{23}$ −5·2	1660, 1607, 870 (>C=CH—C(|)=O) 1190, 1104 (—OCH$_3$)	†
Arborinol methyl ether (X)	285°	$[\alpha]_D^{15}$ +11·5	1606, 807, 793 (>C=CH—) 1200, 1109 (—OCH$_3$)	4·73 (1H, m, >C=*CH*—) 6·68 (3H, s, —OC*H*$_3$) 7·14 (1H, m, *H*—C(|)--OCH$_3$)
Lupeol methyl ether (XIII)	250–251°	$[\alpha]_D^{23}$ +35·6	1620, 874 (H$_2$C=C(|)—CH$_3$) 1182, 1103 (—OCH$_3$)	5·35 (2H, m, *H*$_2$C=C(|)—CH$_3$) 6·67 (3H, s, —OCH$_3$) 7·44 (1H, m, *H*--C(|)—OCH$_3$) 8·32 (3H, br. s, H$_2$C=C(|)—C*H*$_3$)
Bauerenone (XXVI)	242–244°		1702 (>C=O) 838, 826, 814 (>C=CH—)	

* Mass 424 (M^+), 409 (M—CH$_3$), 257 (base peak) *m/e*.
† U.v. λ_{max}^{hexane} 238 nm (ϵ 12500).

TABLE 3. RELATIVE RETENTION TIMES OF TRITERPENE METHYL ETHERS*

Compound	Type of nucleus	Position of double bond	Relative Rt†
Crusgallin (XXI)	Oleanane	14	2·45
Isomiliacin[7]	Oleanane	13 (18)	2·54
Miliacin (XIX)	Oleanane	18	2·65
β-Amyrin methyl ether (XVIII)	Oleanane	12	2·68
Glutinol methyl ether[9c]	Oleanane	5	2·90
Lupeol methyl ether (XIII)	Lupane	20 (29)	2·65
α-Amyrin methyl ether (XVI)	Ursane	12	2·76
Bauerenol methyl ether[11c]	Ursane	7	3·45
3α-Methoxy-fern-9(11)-ene[9g]	Hopane	14	3·04
3β-Methoxy-fern-8-ene[8]	Hopane	8	3·26
Arundoin (III)	Hopane	9 (11)	3·40
Neomotiol methyl ether‡	Hopane	12	3·93
12-Ketoarundoin (V)	Hopane	9 (11)	5·93
Arborinol methyl ether (X)	Arborane	9 (11)	3·34
Cylindrin (VII)	Arborane	9 (11)	3·67

* Hitachi Model K-54 Gas Chromatograph; hydrogen flame detector; column: stainless steel column, 100 cm × 3 mm, 1·5% SE-30 on Chromosorb W, 60–80 mesh; carrier gas, N_2, 80 ml/min; injection temp., 310°; column temp., 260°; chart speed, 10 mm/min.

† 5α-Cholestane, 1·00.

‡ See Experimental.

DISCUSSION

Although the triterpene content of grasses are rather low (the highest is 0·036%, crusgallin (XXI) from *Phacelurus latifolius* (51)) 48 of 56 species examined have been proved to contain pentacyclic triterpenoids. Of 28 triterpenes, ten (XVII–XXIV, XXVII, XXVIII) belong to the oleanane series, six (I–V, XI) to the hopane, five (VI–X) to the arborane, four (XV, XVI, XXV, XXVI) to the ursane and three (XII–XIV) to the lupane series (Chart 1). Compounds such as taraxerene, friedelene, fernene, arborene and bauerene derivatives, are quite common (19 compounds) and are characteristic triterpenoids in this family.

Since the analyses have been confined to the unsaponifiable fraction of hexane extracts, some polar compounds, such as polyhydroxy and acidic compounds and those in glycosidic forms, might have been missed. Although tetracyclic triterpenes have been isolated from rice bran oil,[5] we have no evidence for their presence in any of the plants here studied.

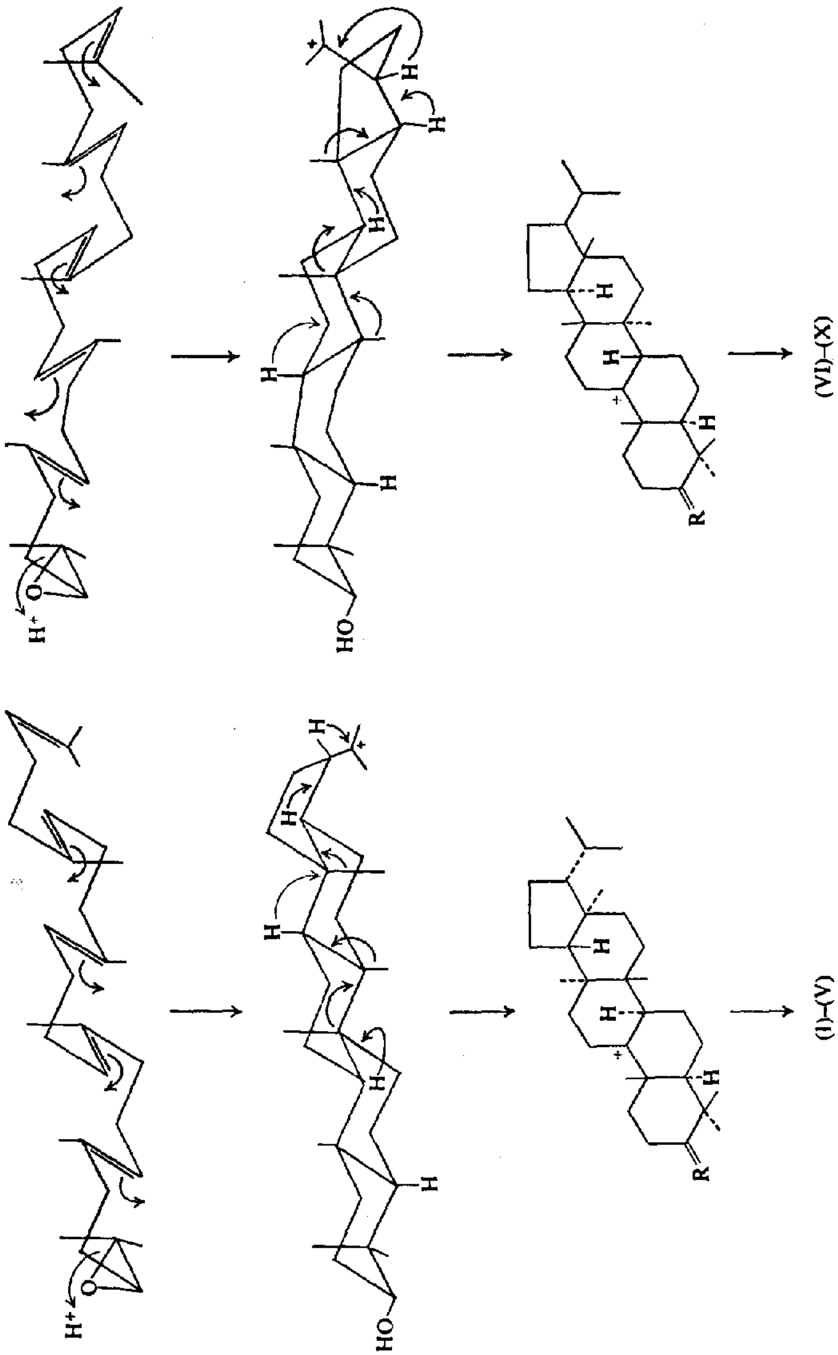
Friedelin (XXVIII) is distributed most widely and has been isolated from 22 species. Cylindrin (VII) and arundoin (III) are also widespread, occurring in 20 and 18 plants respectively.

Hopanes, such as fern-9(11)-ene derivatives, have proved to be the especial constituents of ferns.[13] Although fernene derivatives have been isolated from several higher plants,[14] the first example in higher plants was arundoin (III) from *Imperata cylindrica* var. *koenigii* (45).[8] Now fern-9(11)-ene derivatives (I–V), especially fernenol (I) and arundoin (II), have been proved to occur widely (21 species) in the family.

[13] G. BERTI and F. BOTTARI, *Progress in Phytochemistry* (edited by L. REINHOLD and Y. LIWSCHITZ), Vol. 1, p. 645, Interscience, London (1968).

[14] (a) R. T. APLIN, H. R. ARTHUR and W. H. HUI, *J. Chem. Soc.* (c) 1251 (1966); (b) S. NAKAMURA, T. YAMADA, H. WADA, Y. INOUE, T. GOTO and Y. HIRATA, *Tetrahedron Letters* 2017 (1965); *Nihon Kagaku Zasshi* **86**, 1308, 1310, 1315 (1965); H. WADA, G. GOTA and Y. HIRATA, *Tetrahedron Letters* 3461 (1966); (c) S. K. KUNDU, A. CHATTERJEE and A. S. RAO, *Tetrahedron Letters* 1043 (1966).

CHART 2.



Arbor-9(11)-ene derivatives are the newest group of triterpenes[8,15] and three compounds (VI, VIII, IX) have been isolated from the Rubiaceae and Rutaceae.[16] Cylindrin (VII), the fourth natural product of this group and the first from this family, was isolated by us from *Imperata cylindrica* var. *koenigii* (45) and its structure established.[8,15,16] Now the wide occurrence (25 species) of the five arborane derivatives (VI–X), which are the only known natural products of this group, has been established.

Fern-9(11)-ene and arbor-(11)-ene have the same configuration at 3, 5 and 10 positions and are enantiomeric at 8, 13, 14, 17, 18 and 21 positions. The difference is assumed to arise from chair and boat conformations of the ring B at the initial stage of cyclization of squalene or equivalent (Chart 2).[8] Thus, the coexistence of both series of compounds in 15 plant species is of biogenetic interest. From *Imperata cylindrica* var. *koenigii* (44) and *Miscanthus floridulus* (47) the complete sets of the two series (I, III, VI, VII, IX, X) have been isolated.

As anticipated, nine triterpene methyl ethers (III, V, VII, X, XIII, XVI, XVIII, XIX, XXI) were proved to occur widely in the Gramineae and have been isolated from 31 species belonging to 14 tribes. Triterpene methyl ethers are otherwise rather uncommon, having only been found elsewhere in the Pinaceae and Burseraceae.[17] Thus the wide occurrence of the methyl ethers is assumed to be the most significant triterpene character in this family. Of 31 species containing the methyl ethers, 25 plants are perennial and the higher distribution in perennial than in annual plants, along with their seasonal variations,[9a] might suggest some physiological function in the plants.

Finally, some correlations with the tribal, generic and species classification will be mentioned. All the four species of Zoysieae (29–32) contain triterpene methyl ethers (III, V, VII, XXI), in which crusgallin (XXI) is the chief component of *Zoysia macrostachya* (30), growing on sandy sea-shore, while arundoin (III) is the chief constituent of the other three (29, 31, 32), growing inland. Eleven species of Paniceae (34–41), including three studied previously,[6,7] have so far been examined and the presence of the methyl ethers (XIX, XXI) of oleanane series in six species (34, 36, 37 and Refs. 6, 7) has been demonstrated. *Oplismenus undulatifolius* (35) is assumed to be an exceptional case, since it contains cylindrin (VII). By contrast, plants of the Andropogoneae (42–54) generally contain fernene and arborene derivatives, such as arundoin (III) and cylindrin (VII), the presence of which in eight out of eleven species (42–50, 52) was confirmed.

Five species of the genus *Cortaderia* were studied and three indigenous to New Zealand proved to contain triterpene methyl ethers (III, XVI, XVIII), while two others from South America lacked these compounds.[11a,11b] *Cortaderia argenta* (21), naturalized from South America, does not contain the methyl ethers but contains bauerenol (XXV) and bauerenone (XXVI) instead. *Lophatherum gracile* (22), once grouped in Tribe Centotheraceae,[18] is not described in the Syllabus.[10] Since it contains arundoin (III) and cylindrin (VII), it has been tentatively placed (Table 1) in Arundinelleae from the similarity of its constituents with other members of this group. *Setaria chondrachne* (39) is a perennial plant with rhizomes and thus differs from other *Setaria* species (34–41). However, it has been proved to contain iso-

[15] O. Kennard, L. R. Sanseverino, H. Vorbrüggen and C. Djerassi, *Tetrahedron Letters* 3433 (1965); O. Kennard, L. R. di Sanseverino and J. S. Ralett, *Tetrahedron* **23**, 131 (1967).

[16] H. Vorbrüggen, S. C. Pakrashi and C. Djerassi, *Ann.* **688**, 57 (1963); W. H. Hui and C. N. Lam, *Phytochem.* 4, 333 (1965).

[17] S. Uyeo, J. Okada, S. Matsunaga and J. W. Rowe, *Tetrahedron* **24**, 2859 (1968); J. W. Rowe and C. L. Bower, *Tetrahedron Letters* 2745 (1965); A. F. Thomas and B. Willhalm, *Tetrahedron Letters* 3177 (1964); J. P. Kutney, I. H. Rogers and J. W. Rowe, *Tetrahedron* **25**, 3731 (1969).

[18] H. N. Ridley, *Natural Flora of the Malay Peninsula*, Vol. 3, p. 122, L. Reeve, London (1907).

arborinol (VI) and fridelin (XXVIII) as *Oplismenus undulatifolius* (35) in the same tribe does. In the genus *Miscanthus* (47–50) in Andropogoneae the similarty of *M. sinensis* (49, 50) and *M. floridulus* (47) and their difference from *M. sacchariflorus* (48) in leaf anatomy has been reported;[19] however, distinct differences were not observed in the triterpenoid constituents.

Although the plants so far examined are rather small in number in such a large family, the results suggest that some triterpenes are characteristic of the family. However, the data do not seem to contribute much to the taxonomy within the Gramineae, because the same compounds are rather widely distributed.

EXPERIMENTAL

Materials

Most of the plant materials were collected at Narashino, Chiba, in May–October, 1964–1968. For further information on the materials, see Ref. 9a–9g.

General Procedure for Extraction and Separation

Dried and cut material (10–50 kg) was extracted with boiling hexane and the extract, after evaporation of the solvent, was saponified with 5% EtOH–KOH. The unsaponifiable matter was extracted with ether and chromatographed on alumina or silica-gel columns employing hexane, benzene, $CHCl_3$, or their mixtures as eluant. For further separation of triterpene alcohols and phytosterols, mixtures were acetylated and separated by the chromatography. Further details and the modifications of the separation procedure are given in preceding papers.[9a–9g]

Thin-layer Chromatography

Silica-gel G and Wako-gel B-5 were employed for the absorbent and hexane–benzene (1:1) was used for development. For detection, the plates were sprayed with 10% H_2SO_4 and heated at 110° for 5–10 min.

Gas Chromatography

See Table 3.

Neomotiol Methyl Ether

Neomotiol (neohop-12-en-3β-ol)[14b] (16 mg) was dissolved in benzene (4 ml) and, after the addition of K (20 mg), boiled for 2 hr. After cooling, MeI (0·5 ml) was added and boiled for 2 hr. EtOH (0·2 ml) and water (8 ml) were added to the reaction mixture, which was extracted with benzene. The extract was washed, dried and evaporated. The residue was chromatographed and recrystallized from hexane to colorless needles of m.p. 230–231°, i.r. ν_{KBr} cm^{-1}: 1626, 1183, 1103, 1055, 1045, 898, 827, 785.

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[19] Y. N. LEE, *Shokubutsu Kenkyu Zasshi* 39, 115 (1964).