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Constituents of the Fruit of *Pseudopanax arboreum* (Araliaceae)

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Abstract

Saponification and methylation of the acidic fraction of an extract of the fruit of the New Zealand tree *Pseudopanax arboreum* has led to the isolation of a series of ring-A substituted and ring-A seco triterpenoids possessing oleanane or ursane skeletons. These include methyl 3-oxo-24-norurs-12-en-28-oate (1), dimethyl 4-oxo-3,24-dinor-2,3-secours-12-ene-2,28-dioate (7), methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10), the ε-lactone of 23-hydroxy-4,17-dimethoxycarbonyl-2,3-secours-12-en-2-oic acid (15), trimethyl 24-nor-2,3-secours-12-ene-2,3,28-trioate (20), methyl 2-hydroxy-3-oxo-24-noroleana-1,4,12-trien-28-oate (26), and methyl 2-hydroxy-3-oxo-24-norursa-1,4,12-trien-28-oate (27) whose parent acids have not hitherto been obtained as natural products. Other compounds are methyl 2α,3α-dihydroxyolean-12-en-28-oate (9), methyl 2α,3α-dihydroxyurs-12-en-28-oate (23), methyl asiatate (24), methyl arjunolate (13), the methoxy artefact (12), and the aryl-substituted methyl cinnamates (28), (29), (30) and (31). Neutral constituents include the esters (1), (9) and (10), stigmasterol and the sesquiterpene spathulenol (32).

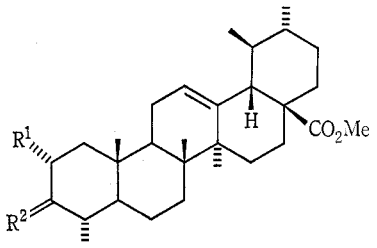
Introduction

During an examination of New Zealand dicotyledons for triterpenoids it was observed[1] that the fruit of the tree *Pseudopanax arboreum* (Murr.) Philipson[2] [syn. *Neopanax arboreum* (Murr.) Allan] (fam. Araliaceae) appeared to be a rich source of triterpenoid acids. Initial extracts on a small scale[3] gave a mixture of acids which after chromatography of their methyl esters on alumina afforded an unsaturated keto ester, m.p. 145–149°, which appeared to be new. Other than the isolation of palmitic acid no further work was carried out at the time but we now report the results of a more comprehensive examination of the constituents of the fruit.

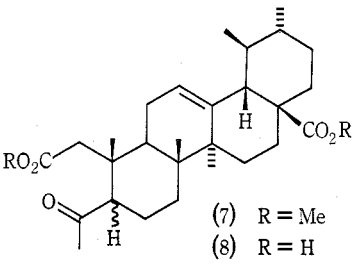
Discussion

Extraction of the dried fruit with methanol and saponification of the concentrate with methanolic potassium hydroxide afforded acidic and neutral fractions. Chromatography of the methylated acidic fraction on alumina and repeated chromatography of non-characterized material on silica gel afforded a series of ring-A substituted or ring-A seco triterpenoid methyl esters (1), (7), (9), (10), (15), (20), (23), (26,) (27) and (12) and the aryl-substituted methyl cinnamates (28), (29), (30) and (31). In addition, a mixture of methyl asiatate (24) and methyl arjunolate (13) was also obtained but the fraction could not be separated into its components or induced to crystallize.

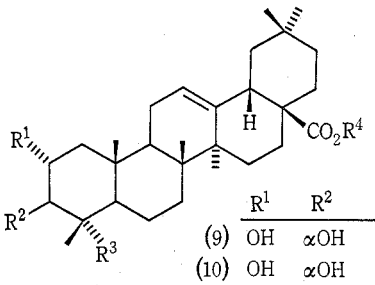
[1] Cambie, R. C., Cain, B. F., and La Roche, S., *N. Z. J. Sci.*, 1961, **4**, 604.
[2] Philipson, W. R., *N. Z. J. Bot.*, 1965, **3**, 333.
[3] Cambie, R. C., and Parnell, J. C., *N. Z. J. Sci.*, 1970, **13**, 108.



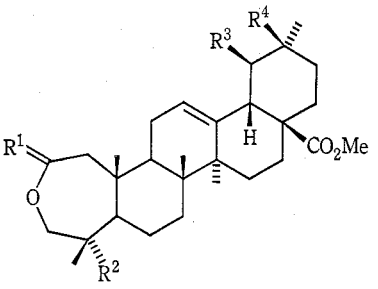
	R^1	R^2
(1)	H	O
(2)	H	αOH,βH
(3)	H	βOH,αH
(4)	Br	O
(5)	Br	βOH,αH
(6)	Br	αOH,βH



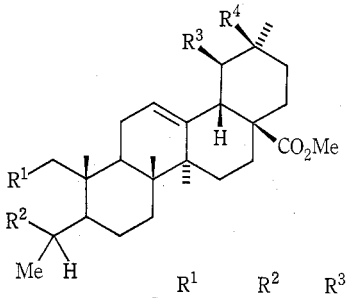
(7) R = Me
(8) R = H



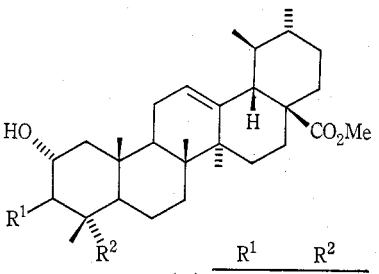
	R^1	R^2	R^3	R^4
(9)	OH	αOH	Me	Me
(10)	OH	αOH	CH_2OH	Me
(11)	OH	αOH	Me	H
(12)	OMe	αOAc	CH_2OAc	Me
(13)	OH	βOH	CH_2OH	Me
(14)	H	H	Me	Me



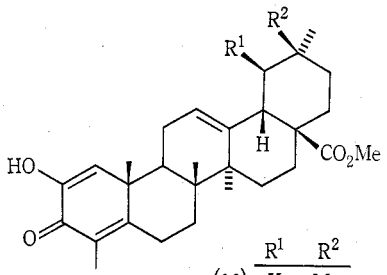
	R^1	R^2	R^3	R^4
(15)	O	CO_2Me	Me	H
(16)	αOH,βH	CHO	H	Me
(17)	O	CO_2Me	H	Me
(18)	O	CHO	H	Me
(19)	O	CO_2H	H	Me



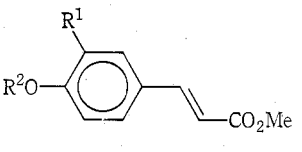
	R^1	R^2	R^3	R^4
(20)	CO_2Me	CO_2Me	Me	H
(21)	CHO	CHO	Me	H
(22)	CO_2H	CHO	H	Me



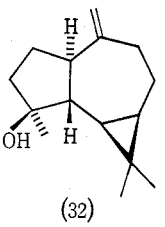
	R^1	R^2
(23)	αOH	Me
(24)	βOH	CH_2OH
(25)	βOMe	CH_2OH



	R^1	R^2
(26)	H	Me
(27)	Me	H



	R^1	R^2
(28)	OH	Me
(29)	OMe	Me
(30)	OMe	H
(31)	H	Ac

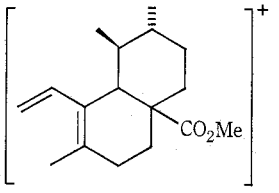


(32)

Compounds identified as methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10), methyl 3-oxo-24-norurs-12-en-28-oate (1), methyl 2α,3α-dihydroxyolean-12-en-28-oate (9), stigmasterol and the sesquiterpene spathulenol (32)[4] were isolated from the neutral fraction.

Methyl 3-oxo-24-norurs-12-en-28-oate (1), m.p. 212–215°, $[\alpha]_D^{20}$ +104°, was identical with an authentic sample prepared from methyl asiatate (24).[5] It was further characterized as its oxime, m.p. 202–204°, and by reduction with sodium borohydride which yielded the C 3α and C 3β alcohols (2) and (3). Although the corresponding oleanane derivative, methyl hedragonate, occurs naturally[6] this is the first report of the isolation of the analogous ursane derivative from natural sources.

Dimethyl 4-oxo-3,24-dinor-2,3-secours-12-ene-2,28-dioate (7), m.p. 148–150°, $[\alpha]_D^{20}$ +85°, was identified as the keto ester isolated in the preliminary investigation,[3] and is a compound not previously obtained from natural sources. The i.r. spectrum indicated the presence of ester (1730 cm^{-1}) and keto (1710 cm^{-1}) groups and a trisubstituted double bond (830 cm^{-1}), while the n.m.r. spectrum showed the presence of five methyl groups [δ 0·81, 0·85–0·95 (2), 1·07, and 1·10], a methyl keto group (δ 2·24), two methyl ester groups (δ 3·61, 3·66), and a single olefinic proton (δ 5·30). Mass spectral examination showed a molecular weight of 486·3351 in agreement with the formula $C_{30}H_{46}O_5$ obtained from elementary analysis. Abundant ions in the mass spectrum at *m/e* 262 and 203 corresponded to ions *a* and *b*, suggesting that



a *b*

fragmentation was occurring in a manner typical of urs-12-enes or olean-12-enes with a C 17 methoxycarbonyl group.[7,8] Other peaks characteristic of the system were observed at *m/e* 249, 189 and 133.[8,9] The appearance in the n.m.r. spectrum of two secondary methyl signals with second order perturbation[8] (δ 0·85–0·95) and of the allylic C 18β hydrogen as a doublet at δ 2·20[10,11] indicated that the compound belonged to the ursane series. Hydrolysis with methanolic potassium hydroxide gave a diacid (8) which, like the parent diester, gave positive Brady's and iodoform tests. While not proved, structure (7) would appear to be the most likely for the diester from the above evidence.

[4] Bowyer, R. C., and Jefferies, P. R., *Chem. Ind.* (London), 1963, 1245.
[5] Polonsky, J., and Zylber, M. J., *Bull. Soc. Chim. Fr.*, 1961, 1586.
[6] Eade, R. A., Hunt, K., Simes, J. J. H., and Stern, W., *Aust. J. Chem.*, 1969, **22**, 2703.
[7] Budzikiewicz, H., Wilson, J. M., and Djerassi, C., *J. Amer. Chem. Soc.*, 1963, **85**, 3688.
[8] Karliner, J., and Djerassi, C., *J. Org. Chem.*, 1966, **31**, 1945.
[9] Pelletier, S. W., Adityachaudhury, N., Tomaz, M., Reynolds, J. J., and Mechoulam, R., *J. Org. Chem.*, 1965, **30**, 4234.
[10] Cheung, H. T., and Williamson, D. G., *Tetrahedron*, 1969, **25**, 119.
[11] Cheung, H. T., and Yan, T. C., *Aust. J. Chem.*, 1972, **25**, 2003; *Chem. Commun.*, 1970, 369.

2α,3α-Dihydroxyolean-12-en-28-oic acid (11) has recently been isolated from natural sources for the first time.[11] Literature[11–13] melting points and optical rotations for methyl 2α,3α-dihydroxyolean-12-en-28-oate (9) not only vary but the 2α,3α- and 2β,3β-dihydroxy compounds were originally assigned incorrectly.[12] N.m.r. data for the sample, m.p. 277–280°, $[\alpha]_D$ +55°, isolated from *P. arboreum* agreed with that published for the 2α,3α isomer[10,11] and the compound differed from an authentic sample of the 2β,3β isomer. The structure was supported by i.r. and mass spectral data and was confirmed by formation of a diacetate, a 2,3-acetonide (33), and by oxidation to a diosphenol (36) which after Wolff–Kishner reduction and re-esterification afforded methyl olean-12-en-28-oate (14).[14]

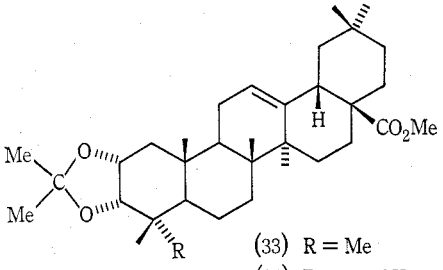
Methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10), m.p. 263–268°, $[\alpha]_D^{20}$ +43°, or its corresponding acid has not hitherto been isolated from natural sources. From its i.r., n.m.r. and mass spectral parameters the compound was clearly a trihydroxy triterpenoid monoester belonging to the methyl olean-12-en-28-oate series. The hydroxy groups appeared to be in the C 2, C 3 and C 23 positions which are commonly substituted in triols of this series but the compound was not identical with any known compounds, e.g. bayogenin or methyl arjunolate (13).

In addition to a triacetate and a 3,23-methylenedioxy derivative (37) the triol readily formed a mixture of two isopropylidene derivatives which were separated by dry column chromatography[15] on deactivated silica gel. The major compound possessed a secondary hydroxy group (3570, 3440 and 1030 cm^{-1}) and was identified as the 2α-hydroxy 3α,23-acetonide (38). Oxidation gave a keto acetonide (39) which exhibited a positive Cotton effect in the o.r.d. curve as expected for a C 2 ketone. Acetylation of the hydroxyacetonide (38) gave a monoacetate (40). While the magnitude of the molecular rotation difference (+74·4°) associated with acetylation was somewhat smaller than that expected (+143·8°) for acetylation of a 2α-hydroxy compound in the oleanane series[16] the positive value was incompatible with a 2β-hydroxy compound for which a negative value would be expected. Further support for the assignment of an α-configuration and thus an equatorial conformation for the hydroxy group at C 2 was obtained from the n.m.r. spectrum of the monoacetate. The signal of the C 2 proton occurred as a broad multiplet at δ 5·17 whose breadth ($W_{h/2}$ 20 Hz) indicated the presence of at least two couplings of *c.* 8 Hz. As pointed out by Glen and coworkers[16] this can only occur when the proton at C 2 occupies an axial conformation allowing axial–axial interaction with the C 3 proton and an axial C 1 proton.

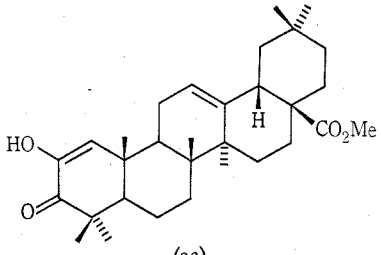
The minor acetonide possessed a primary hydroxy group and was identified as the 23-hydroxy-2α,3α-acetonide (34). Doublets at δ 3·33 and 3·80 (*J* 12 Hz) in the n.m.r. spectrum were consistent with an equatorial CH_2OH group at C 4.[17] Oxidation of the acetonide (34) with Collins reagent[18] gave an aldehyde (35) which on Wolff–

[12] Tschesche, R., Henckel, E., and Snatzke, G., *Justus Liebigs Ann. Chem.*, 1964, **676**, 175.
[13] Djerassi, C., Thomas, D. B., Livingston, A. L., and Thompson, C. R., *J. Amer. Chem. Soc.*, 1957, **79**, 5292; Brieskorn, C. H., and Zweyrohn, G., *Pharmazie*, 1970, **25**, 488.
[14] Djerassi, C., Henry, J. A., Lemin, A. J., and Rios, T., *Chem. Ind.* (London), 1955, 1520; Djerassi, C., Henry, J. A., Lemin, A. J., Rios, T., and Thomas, G. H., *J. Amer. Chem. Soc.*, 1956, 3783.
[15] Loev, B., and Goodman, M. M., *Chem. Ind.* (London), 1967, 2026.
[16] Glen, A. T., Lawrie, W., McLean, J., and El-Garby Younes, M., *J. Chem. Soc. C.*, 1967, 510.
[17] Gaudemer, A., Polonsky, J., and Wenkert, E., *Bull. Soc. Chim. Fr.*, 1964, 407.
[18] Ratcliffe, R., and Rodehorst, R., *J. Org. Chem.*, 1970, **35**, 4000.

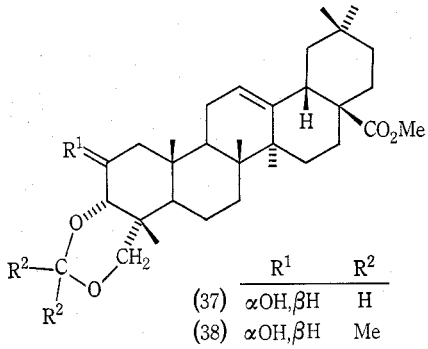
Kishner reduction and re-esterification afforded methyl 2α,3α-isopropylidene-dioxyolean-12-en-28-oate (33), identical with that from methyl 2α,3α-dihydroxyolean-12-en-28-oate (9), thereby confirming the structure of the triol (10). Treatment of the triol (10) with sodium metaperiodate afforded the hemiacetal (16) previously obtained by Eade *et al.*[6] from the action of periodic acid on bayogenin methyl ether and by Sasaki *et al.*[19] from methyl arjunolate (13).



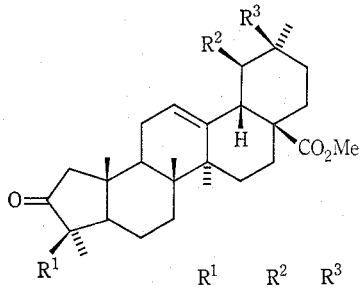
(33) R = Me
(34) R = CH_2OH
(35) R = CHO



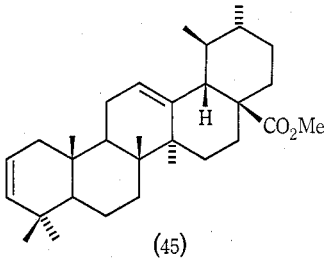
(36)



	R^1	R^2
(37)	αOH,βH	H
(38)	αOH,βH	Me
(39)	O	Me
(40)	αOAc,βH	Me



	R^1	R^2	R^3
(41)	H	H	Me
(42)	CHO	H	Me
(43)	CO_2Me	Me	H
(44)	H	Me	H



(45)

The physical constants, m.p. 228–232°, $[\alpha]_D^{20}$ +126°, of a further ester from the fruit which was formulated as the ε-lactone of 23-hydroxy-4,17-dimethoxycarbonyl-2,3-secours-12-en-2-oic acid (15), appeared to be in agreement with those, m.p. 234–236°,

[19] Sasaki, S., Chiang, H. C., Habaguchi, K., Hsü, H-Y., and Nakanishi, K., *Bull. Chem. Soc. Jap.*, 1966, **39**, 1816.

$[\alpha]_D$ +117°, described by Brewis and Halsall[20] for the same compound and with those m.p. 232–234° described by Singh and Rastogi[21] for a methylated product derived from methyl asiatate (24). To ensure that the isolated compound did not have an oleanane skeleton, the ε-lactone of 23-hydroxy-4,17-dimethoxycarbonyl-2,3-secoolean-12-en-2-oic acid (17) was synthesized from the previously isolated methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10). The keto acetonide (39) prepared from the triol (10) (see above) was hydrolysed with acetic acid and oxidized with sodium meta-periodate to yield the lactone aldehyde (18) which was then oxidized to the acid (19) with potassium permanganate in aqueous acetone. The acid was methylated with diazomethane to yield the lactone ester (17), m.p. 258–261°, $[\alpha]_D^{20}$ +131°. As expected, this compound exhibited spectra similar to those of the isolated compound but the two were not identical and the differences were consistent with one having an ursane skeleton and the other an oleanane skeleton.

Only a small quantity of trimethyl 2,3-seco-24-norurs-12-ene-2,3,28-trioate (20), m.p. 149–152°, $[\alpha]_D^{20}$ +74°, was isolated from the fruit and its structure was initially assigned on the basis of its spectral data. Thus, its i.r. spectrum showed three ester peaks (1740, 1733 and 1727 cm^{-1}) and trisubstituted double bond absorption (850 cm^{-1}) while its n.m.r. spectrum showed the presence of three secondary methyl groups (δ 0·85–1·0, 1·13) and three tertiary methyl groups (δ 0·78, 0·93, 1·09). The n.m.r. spectrum confirmed the presence of three methyl ester groups (δ 3·60, 3·60, 3·67) and a single olefinic proton (δ 5·30) and from the chemical shift of the C 18β proton (δ 2·20) indicated an ursane skeleton. Fragments in the mass spectrum were consistent with the formulation of the compound as a 2,3-seco-Δ^{12}-triterpenoid trimethyl ester.

It was considered that the trimethyl ester (20) may have arisen by ring opening and loss of formaldehyde from the lactone ester (15) during saponification of the original extract. Such a facile loss of formaldehyde by a retro-aldol reaction could be expected from Barton and de Mayo's[22] conversion of methyl hederagonate into methyl hedragonate with dilute base. A corresponding sequence was therefore investigated for the oleanane series. However, treatment of the lactone aldehyde (18) with base did not yield the expected acidic product (22) but afforded a five-membered-ring ketone which was assigned the structure (41). This neutral product presumably arises from ring opening of the lactone in the usual manner, loss of formaldehyde, and then subsequent cyclization of the anion in a Dieckmann reaction to yield the β-keto aldehyde (42) which cleaves under the basic conditions to yield the ketone (41). In a similar fashion the lactone ester (17) also afforded the ketone (41) after prolonged treatment with base. No trace of the oleanane analogue of the compound (20) could be detected in the reaction products after methylation and it would thus appear that the trimethyl ester (20) is not produced from the lactone ester (15) under the conditions of isolation.

In an attempt to correlate the structures of the ketone (1) and the ring-A opened compound (20), the ketone was oxidized with chromic acid. The acidic material was methylated with diazomethane and purified by preparative t.l.c. to give a low yield of the compound (20). The majority of the material underwent further oxidation,

[20] Brewis, S., and Halsall, T. G., *Chem. Commun.*, 1970, 891.
[21] Singh, B., and Rastogi, R. P., *Phytochemistry*, 1969, **8**, 917.
[22] Barton, D. H. R., and de Mayo, P., *J. Chem. Soc.*, 1954, 887.

in particular oxidation at the allylic C 11 position. All attempts to oxidize the ketone (1) with potassium permanganate under basic, neutral or acidic conditions yielded no acidic products and starting material was recovered.

In a further attempt to improve the yield of the ring-A seco compound (20) by initial functionalization of ring A at the C 2 position, the ketone (1) was treated with bromine in acetic acid to yield methyl 2α-bromo-3-oxo-24-norurs-12-en-28-oate (4). However, attempts to solvolyse the bromine atom with silver acetate were unsuccessful, the bromide (4) being stable to these conditions and also to treatment with base. This result was unexpected in view of the apparent ease of hydrolysis of the corresponding 2α-bromo ketone in the steroid series.[23] Treatment of the bromo derivative (4) with sodium borohydride afforded the epimeric bromo alcohols (5) and (6) which were separated by preparative t.l.c. The mixture of bromo alcohols was converted into a mixture of epimeric hydroxy acetates with silver acetate and the latter was hydrolysed to give a mixture of diols which were oxidized with sodium metaperiodate. The crude product which contained mainly the dialdehyde (21) was oxidized with potassium permanganate to the diacid which after methylation with diazomethane and purification by preparative t.l.c. afforded the ester (20), thus confirming its structure.

For cross reference purposes the ester (20) was converted into the ursane analogue of the five-membered-ring ketone (41) previously prepared from the compounds (17) and (18). Cyclization of the ester (20) with potassium t-butoxide gave the β-keto ester (43) which cleaved under the reaction conditions to give the ketone (44) directly.

A further product m.p. 195–197°, $[\alpha]_D^{20}$ +50°, obtained from the mother liquors of the diol (9), was identified as methyl 2α,3α-dihydroxyurs-12-en-28-oate (23). The ester has recently been isolated from a methylated acidic fraction of the leaves of *Prunus serotina* and *P. lusitanica*[24] and prior to this prepared as a mixture with the 2β,3β isomer by osmylation of methyl ursa-2,12-dien-28-oate (45).[16] Its i.r. spectrum indicated the presence of hydroxyl (3500 cm^{-1}) and ester (1730 cm^{-1}) groups and the presence of three peaks in both the 1392–1355 cm^{-1} region and the 1330–1236 cm^{-1} region for the spectrum recorded in pyridine indicated an ursane derivative.[25] The n.m.r. spectrum showed the presence of one olefinic proton (δ 5·30) and one methyl ester group (δ 3·62). The appearance of the allylic C 18β proton signal as a doublet at δ 2·24 confirmed that the compound belonged to the ursane series.[11] Mass spectral examination indicated a molecular weight of 486 in agreement with the formula $C_{31}H_{50}O_4$ while abundant ions at *m/e* 262, 203, 189 and 133 were those expected for a methyl urs-12-en-28-oate derivative.

In order to confirm the structure of methyl 2α,3α-dihydroxyurs-12-en-28-oate (23) an attempt was made to prepare an authentic sample of the compound. Treatment of methyl ursa-2,12-dien-28-oate (45)[26] with osmium tetroxide gave a mixture of 2α,3α and 2β,3β diols. As previously reported[16] these were not easily separated. However, as experienced in the oleanane series[13] the predominant product was methyl 2α,3α-dihydroxyurs-12-en-28-oate (23) which was contaminated with only a

[23] Evans, D. E., de Paulet, A. C., Shoppee, C. W., and Winternitz, F., *J. Chem. Soc.*, 1957, 1451.
[24] Biessels, H. W. A., van der Kerk-van Hoof, A. C., Kettenes-van den Bosch, J. J., and Salemink, C. A., *Phytochemistry*, 1974, **13**, 203.
[25] Snatzke, G., Lampert, F., and Tschesche, R., *Tetrahedron*, 1962, **18**, 1417.
[26] Salle, N. E., *Suom. Kemistilehti B*, 1956, **29**, 175.

small amount of the 2β,3β isomer. Direct comparison showed that the major product was identical with the material isolated from the fruit of *P. arboreum*.

The non-crystalline mixture of methyl 2-hydroxy-3-oxo-24-noroleana-1,4,12-trien-28-oate (26) and methyl 2-hydroxy-3-oxo-24-norursa-1,4,12-trien-28-oate (27) from the fruit possessed spectral parameters which were similar to those of the diosphenol (36) obtained by oxidation of methyl 2α,3α-dihydroxyolean-12-en-28-oate. All attempts to separate the compounds were unsuccessful and in the absence of analytical data the identifications can only be regarded as tentative. In the case of the non-crystalline mixture of methyl asiatate (24) and methyl arjunolate (13) obtained from the fruit, spectral comparison with a *c.* 1 : 1 mixture of authentic samples indicated their identity.

During rechromatography of fractions containing methyl 2α,3α-dihydroxyolean-12-en-28-oate (9) a product was isolated which could not be induced to crystallize. However, acetylation afforded a product which was identified as methyl 3α,23-diacetoxy-2α-methoxyolean-12-en-28-oate (12) and which was subsequently prepared in low yield by methylation and then acetylation of methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10). The compound (12) is undoubtedly an artefact arising from monomethylation of the triol (10) during esterification of the acidic material. A similar compound (25) has been prepared by monomethylation of methyl asiatate (24) under these conditions.[5,27]

Experimental

Melting points are uncorrected. I.r. spectra were recorded with Perkin–Elmer 237 or 337 spectrophotometers and unless otherwise stated are for chloroform solutions. U.v. spectra were recorded for ethanolic solutions with a Unicam SP 800A spectrophotometer. N.m.r. spectra were measured with Varian T60 or HA100 spectrometers, tetramethylsilane being the internal reference and deuterochloroform the solvent. High-resolution mass spectra were determined on an AEI MS-9 instrument and low resolution spectra on a Varian CH-7 spectrometer using a direct insertion probe. Optical rotations and o.r.d. data are for chloroform solutions and were obtained with a Jasco ORD/UV-5 instrument. Alumina for column chromatography was P. Spence type H material and silica gel for column chromatography was Kieselgel S (Riedel de Haan). T.l.c. was conducted with plates coated (0·25 mm) with Kieselgel DG (Riedel de Haan) and preparative t.l.c. on plates coated (1 mm) with Kieselgel $PF_{254+366}$ (Merck).

Extraction of the Fruit

The dried fruit (12·5 kg) of *Pseudopanax arboreum* was extracted (Soxhlet) with methanol for 60 h and the extract was concentrated to a thick syrup. Approximately half of the extract was heated under reflux with 2M methanolic potassium hydroxide for 2 h and the cooled solution was diluted with water and extracted with ether.

Isolation of the neutral constituents.—The ether extract was concentrated and the neutral residue (158 g) was triturated with benzene to give methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10) (10 g).

A portion (60 g) of the benzene-soluble neutrals was chromatographed on alumina (1·3 kg). Elution with benzene gave waxes and solids of low melting point (15 g) which were not examined further. Continued elution with benzene gave methyl 3-oxo-24-norurs-12-en-28-oate (1) (0·10 g). Elution with ether gave an oil which was purified by Kugelrohr distillation at 100°/1 mm (90% pure by g.l.c.) and by preparative t.l.c. to give spathulenol (32) (0·10 g). Further elution with ether gave stigmasterol (0·70 g). Elution with ethyl acetate gave methyl 2α,3α-dihydroxyolean-12-en-28-oate (9) (0·10 g) while elution with ethyl acetate–methanol (9 : 1) gave methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10) (3·0 g).

[27] Polonsky, J., *Bull. Soc. Chim. Fr.*, 1952, 649.

Isolation of the acidic constituents.—The alkaline layer was acidified with 2M sulphuric acid and extracted with ether to give an acidic fraction (550 g). A portion (320 g) was methylated with an excess of an ethereal solution of diazomethane and the bulk of the methylated acids (259 g) were chromatographed on alumina (3·8 kg). Successive elution with benzene gave oils, solids of low melting point (2·4 g), methyl 3-oxo-24-norurs-12-en-28-oate (1) (2·5 g) and dimethyl 4-oxo-3,24-dinor-2,3-secours-12-ene-2,28-dioate (7) (0·10 g). Elution with ethyl acetate gave methyl 2α,3α-dihydroxyolean-12-en-28-oate (9) (0·21 g), methyl isoferulate (28) (2·0 g), and then the ε-lactone of 4,17-dimethoxycarbonyl-23-hydroxy-2,3-secoolean-12-en-2-oic acid (15) (45 mg). Elution with ethyl acetate–methanol (9 : 1) gave methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10) (5·3 g) and then a non-crystalline mixture (*c.* 5 g) of methyl asiatate (24) and methyl arjunolate (13).

Uncharacterized material (9·0 g) eluted from the previous column with benzene and ether, was rechromatographed on silica gel (200 g). Successive elution with benzene gave methyl 3-oxo-24-norurs-12-en-28-oate (1) (0·8 g), trimethyl 2,3-seco-24-norurs-12-ene-2,3,28-trioate (20) (75 mg), methyl 3,4-dimethoxycinnamate (29) (65 mg) and dimethyl 4-oxo-3,24-dinor-2,3-secours-12-ene-2,28-dioate (7) (0·18 g).

Uncharacterized material (20 g) eluted from the original column with ethyl acetate, was repeatedly rechromatographed on silica gel using benzene–chloroform (1 : 1) and ether–hexane (1 : 1) as the eluents. This afforded methyl 2α,3α-dihydroxyolean-12-en-28-oate (9) (0·70 g), methyl 2α,3α-dihydroxyurs-12-en-28-oate (23) (1·0 g), and a non-crystalline mixture (*c.* 2 g) of methyl 2-hydroxy-3-oxo-24-noroleana-1,4,12-trien-28-oate (26) and methyl 2-hydroxy-3-oxo-24-norursa-1,4,12-trien-28-oate (27). A further non-crystalline fraction was acetylated with acetic anhydride–pyridine to give crystalline methyl 3α,23-diacetoxy-2α-methoxyolean-12-en-28-oate (12) (0·44 g).

Mother liquors from fractions which gave methyl isoferulate were extracted with saturated sodium hydrogen carbonate solution. Acidification of the extract gave isoferulic acid (0·24 g). The remaining material was extracted with 3M potassium hydroxide solution and the phenolic material was acetylated with acetic anhydride–pyridine. Crystallization from methanol gave acetylisoferulate (2·0 g). Material (*c.* 5 g) in the crystallization mother liquors was purified by preparative t.l.c. using carbon tetrachloride–acetone (9 : 1) to yield three fractions. The most polar fraction gave methyl acetylisoferulate (1·95 g) while the least polar fraction gave methyl acetyl-*trans*-*p*-coumarate (31) (45 mg). *trans*-*p*-Coumaric acid (0·1 g) was obtained by hydrolysis of the crystallization mother liquors of the acetoxy ester (31). The intermediate fraction gave methyl acetylferulate (0·47 g).

Methyl 3-Oxo-24-norurs-12-en-28-oate (1)

Methyl 3-oxo-24-norurs-12-en-28-oate crystallized from acetone as needles, m.p. and mixed m.p. 212–215°, $[\alpha]_D^{20}$ +104° (*c*, 0·70) (lit.[5] 210–213°, $[\alpha]_D$ +93°) [Found: C, 79·2; H, 10·3; O, 10·4; $M^{+\cdot}$, 454·3446 (mass spectrum). Calc. for $C_{30}H_{46}O_3$: C, 79·2; H, 10·2; O, 10·6%; mol. wt, 454·3447]. λ_{max} 215 nm (ε 1435); ν_{max} (KBr) 1732 (CO_2Me), 1705 (CO) and 830 cm^{-1} (C=C); n.m.r.: δ 0·84 (s, 26-Me), 0·80–0·90 (m, 29-, 30-Me), 0·99 (d, *J* 6 Hz, 23-Me), 1·06 (s, 25-Me), 1·12 (s, 27-Me), 2·20 (d, *J* 10 Hz, C 18–H), 2·39 (q, *J* 6 Hz, $J_{4,5}$ *c.* 0 Hz, C 4–H), 3·61 (s, CO_2Me) and 5·24 (m, C 12–H); mass spectrum: *m/e* 439 (M − Me), 395 (M − CO_2Me), 379 (439 − HCO_2Me), 262 (M − $C_{13}H_{20}O$), 233 (262 − C_2H_5), 203 (262 − CO_2Me), 189 and 133 (203 − C_5H_{10}).

The oxime crystallized from aqueous ethanol as needles, m.p. 202–204°. The *ethylene acetal* crystallized from methanol as needles, m.p. 232–235°, $[\alpha]_D^{20}$ +95·5° (*c*, 1·0) (Found: C, 77·1; H, 10·1. $C_{32}H_{50}O_4$ requires C, 77·1; H, 10·1%).

Borohydride Reduction of Methyl 3-Oxo-24-norurs-12-en-28-oate

A cooled solution of methyl 3-oxo-24-norurs-12-en-28-oate (1) (0·10 g) in methanol (80 ml) was treated with sodium borohydride (12 mg) and the solution was stirred at 0° for 2 h. The solvent was evaporated under reduced pressure to a volume of *c.* 10 ml and the mixture was then diluted with water and extracted with ether. The extracts were dried and evaporated to give a solid which was chromatographed on alumina (15 g).

Benzene–ether (50 : 1) eluted *methyl 3α-hydroxy-24-norurs-12-en-28-oate* (2) (24 mg), which crystallized from acetone–methanol as needles, m.p. 255–257°, $[\alpha]_D^{20}$ +69° (*c*, 0·7) (Found: C, 78·5; H, 10·5. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%). λ_{max} 215 nm (ε 1995); ν_{max} (Nujol) 3520 (OH) and 1715 cm^{-1} (CO_2Me); n.m.r.: δ 0·80 (s, 26-Me), 0·90–1·00 (m, 23-, 29-, 30-Me), 0·95 (s,

25-Me), 1·11 (s, 27-Me), 2·20 (d, *J* 10 Hz, C18–H), 3·64 (s, CO_2Me), 3·7–3·9 (m, $W_{h/2}$ 6 Hz, C3β–H) and 5·30 (m, C12–H).

Benzene–ether (20 : 1) eluted *methyl 3β-hydroxy-24-norurs-12-en-28-oate* (3) (40 mg) which crystallized from hexane as needles, m.p. 174–175°, or as prisms, m.p. 182–185°, $[\alpha]_D^{20}$ +90° (*c*, 1·08) (Found: C, 79·1; H, 11·0. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%). λ_{max} 214 nm (ε 2190); ν_{max} (Nujol) 3300–3100 (OH), 1730 (CO_2Me) and 1035 cm^{-1} (OH); n.m.r.: δ 0·78 (s, 26-Me), 0·90 (m, 25-, 29-, 30-Me), 0·97 (d, *J* 7 Hz, 23 Me), 1·08 (s, 27-Me), 2·20 (d, *J* 10 Hz, C18–H), 3·08 (ddd, *J* 10, 9·2, 5·4 Hz, C3α–H), 3·61 (s, CO_2Me) and 5·30 (m, C12–H).

The *acetate* of the 3β-alcohol crystallized from hexane as leaflets, m.p. 201–204°, $[\alpha]_D^{20}$ +100° (*c*, 1·19) (Found: C, 77·0; H, 10·3. $C_{32}H_{50}O_4$ requires C, 77·1; H, 10·1%). λ_{max} 211 nm (ε 2510); ν_{max} (Nujol) 1735 (OAc) and 1722 cm^{-1} (CO_2Me); n.m.r.: δ 0·78 (s, 26-Me), 0·85–0·95 (m, 23-, 25-, 29-, 30-Me), 1·07 (s, 27 Me), 2·03 (s, C3–OAc), 3·61 (s, CO_2Me), 4·35 (ddd, *J* 10·5, 9·8, 5·4 Hz, C3α–H) and 5·25 (m, C12–H).

Dimethyl 4-Oxo-3,24-dinor-2,3-secours-12-ene-2,28-dioate (7)

Dimethyl 4-oxo-3,24-dinor-2,3-secours-12-ene-2,28-dioate crystallized from methanol as prisms, m.p. 148–152°, $[\alpha]_D^{20}$ +85° (*c*, 1·29) [Found: C, 74·3; H, 9·5; O, 16·7; $M^{+\bullet}$, 486·3351 (mass spectrum). $C_{30}H_{46}O_5$ requires C, 74·0; H, 9·5; O, 16·5%; mol. wt, 486·3345]. λ_{max} 217 nm (ε 1190); ν_{max} (KBr) 1730 (CO_2Me) and 1710 cm^{-1} (CO); n.m.r.: δ 0·81 (s, 26-Me), 0·85–0·95 (m, 29-, 30-Me), 1·07 (s, 25-Me), 1·10 (s, 27-Me), 2·20 (d, *J* 10 Hz, C18–H), 2·24 (s, COMe), 2·7–3·2 (m, C5–H), 3·61 (s, C28–CO_2Me), 3·66 (s, C2–CO_2Me) and 5·30 (m, C12–H); mass spectrum: *m/e* 454 ($M-CH_3OH$), 262 ($M-C_{13}H_{20}O_3$), 249 ($M-C_{14}H_{21}O_3$), 237 ($M-C_{16}H_{25}O_2$), 205 ($237-CH_3OH$), 203 ($262-CO_2Me$), 163 ($205-C_2H_2O$ and $M-C_{19}H_{31}O_4$) and 133 ($203-C_5H_{10}$).

4-Oxo-3,24-dinor-2,3-secours-12-ene-2,28-dioic Acid (8)

The keto ester (7) (25 mg) was heated under reflux with 5% methanolic potassium hydroxide for 1 h. The mixture was diluted with water and acidified to give *4-oxo-3,24-dinor-2,3-secours-12-ene-2,28-dioic acid* which crystallized from methanol as needles (15 mg), m.p. 195–196° with shrinking at 187° (Found: C, 73·4; H, 8·7. $C_{28}H_{42}O_5$ requires C, 73·3; H, 9·2%). ν_{max} (KBr) 3400, 2800–2600 (CO_2H), 1724 (CO_2H), 1706 (COMe), 1612 (C=C) and 815 cm^{-1} (C=C).

Methyl 2α,3α-Dihydroxyolean-12-en-28-oate (9)

Methyl 2α,3α-dihydroxyolean-12-en-28-oate crystallized from chloroform–methanol as needles, m.p. 277–280°, $[\alpha]_D^{20}$ +55° (*c*, 0·55) (lit.[11] 296–299°, $[\alpha]_D$ +58°; lit.[12] 276–284°; lit.[13] 276–284°) [Found: C, 75·9; H, 10·3; O, 13·4; $M^{+\bullet}$, 486·3715 (mass spectrum). Calc. for $C_{31}H_{50}O_4$: C, 76·5; H, 10·4; O, 13·2%; mol. wt, 486·3709]. λ_{max} 214 nm (ε 1835); ν_{max} (KBr) 3520sh (OH), 3380 (OH), 1730 (CO_2Me), 1660 (C=C), 1200 (CO_2Me), 1030 (OH) and 820 cm^{-1} (C=C); n.m.r.: δ 0·70 (s, 26-Me), 0·85 (s, 24-Me), 0·91 (s, 29-, 30-Me), 0·95 (s, 25-Me), 1·01 (s, 23-Me), 1·13 (s, 27-Me), 2·85 (dd, J_{AX+BX} 18 Hz, C18–H), 3·60 (s, CO_2Me), 4·85 (s, C2,3–OH) and 5·30 (m, C12–H); mass spectrum: *m/e* 471 (M−Me), 426, 262 ($M-C_{14}H_{24}O_2$), 249 ($M-C_{15}H_{25}O_2$), 223 ($M-C_{17}H_{27}O_2$), 203 ($262-CO_2Me$), 189 and 133 ($203-C_5H_{10}$).

The *diacetate*, prepared with acetic anhydride–pyridine (100°, 1 h), was obtained as a gum, $[\alpha]_D^{20}$ +19° (*c*, 2·78) (Found: C, 73·0; H, 9·5; O, 17·4. $C_{35}H_{54}O_6$ requires C, 73·6; H, 9·5; O, 16·8%). λ_{max} 222 nm (ε 6300); ν_{max} (film) 1745 (OAc), 1725 (CO_2Me), 1650 (C=C), 1250 (OAc) and 880 cm^{-1} (C=C); n.m.r.: δ 0·72 (s, 26-Me), 0·90 (s, 23-Me), 0·92 (s, 29-, 30-Me), 0·98 (s, 24-Me), 1·03 (s, 25-Me), 1·13 (s, 27-Me), 1·95, 2·13 (2s, OAc), 3·60 (s, CO_2Me), 4·97 (d, *J* 3 Hz, C3–H), 5·20 (m, $W_{h/2}$ 18 Hz, C2–H) and 5·30 (m, C12–H).

Methyl 2-Hydroxy-3-oxooleana-1,12-dien-28-oate (36)

A solution of the dihydroxy ester (9) (0·25 g) in purified dichloromethane (2 ml) was added to a stirred solution of chromium trioxide (0·6 g) in pyridine (0·95 g) and purified dichloromethane (15 ml). The mixture was stirred for 15 min, decanted from an insoluble residue and extracted with ether. The ether extracts were washed with 5% sodium hydroxide, 5% hydrochloric acid and saturated sodium hydrogen carbonate solutions, and dried to give methyl 2-hydroxy-3-oxooleana-

1,12-dien-28-oate as a gum (0·20 g), which was purified further by preparative t.l.c. λ_{max} 273 nm (ε 4200), (EtOH–KOH) 315 nm (3430), (EtOH–HCl) 273 (5800); ν_{max} 3448 (OH), 1721 (CO_2Me), 1670 (conjugated CO) and 1640 cm^{-1} (C=C); n.m.r.: δ 0·80 (s, 26-Me), 0·90, 0·94, 1·03–1·12 (2s and m, 23-, 24-, 25-, 29-, 30-Me), 1·14 (s, 27-Me), 2·85 (dd, J_{AX+BX} 18 Hz, C18–H), 3·62 (s, CO_2Me), 5·30 (m, C12–H), 5·90 (br s, OH) and 6·35 (s, C1–H).

Wolff–Kishner Reduction of Methyl 2-Hydroxy-3-oxooleana-2,12-dien-28-oate

The diosphenol (36) (0·15 g) in ethanol (1 ml) was heated under reflux with 95% hydrazine hydrate (2·5 ml) in diethylene glycol (3 ml) for 2 h. Potassium hydroxide (1·0 g) was added, solvent and water were removed, and the mixture was heated under reflux at 195–200° for 4 h. The cooled mixture was acidified with 2M sulphuric acid and extracted with ether. The product was re-esterified with an excess of an ethereal solution of diazomethane and purified by preparative t.l.c. to give methyl olean-12-en-28-oate (14) which crystallized from ethanol as fine needles (50 mg), m.p. 164–167°, $[\alpha]_D^{20}$ +85° (*c*, 0·5) (lit.[14] 166–168°, $[\alpha]_D$ +84°). The n.m.r. spectrum was identical with that recorded.

Methyl 2α,3α-Isopropylidenedioxyolean-12-en-28-oate (33)

A solution of the dihydroxy ester (9) (0·50 g) in dry acetone (25 ml) was treated with 70% perchloric acid (0·5 ml) and the mixture was stirred at 20° until the reaction was complete (30 min, t.l.c.). The product was purified by preparative t.l.c. to give methyl 2α,3α-isopropylidenedioxyolean-12-en-28-oate (0·48 g) which crystallized from acetone as needles, m.p. 237–239° (lit.[11] 235–239°), $[\alpha]_D^{20}$ +94° (*c*, 1·03) (Found: C, 77·5; H, 10·4. Calc. for $C_{34}H_{54}O_4$: C, 77·5; H, 10·3%). λ_{max} 211 nm (ε 2775); ν_{max} 1725 (CO_2Me), and 1160, 1119, 1048, 870, 860 cm^{-1} (isopropylidenedioxy); n.m.r.: δ 0·72 (s, 26-Me), 0·90, 0·91, 1·08 (3s, 24-, 25-, 29-, 30-Me), 1·15 (s, 27-Me), 1·32, 1·47 (2s, isopropylidene Me_2), 2·87 (dd, J_{AX+BX} 18 Hz, C18–H), 3·64 (s, CO_2Me), 3·68 (d, *J* 5 Hz, C3–H), 4·18 (ddd, *J* 5, 4, 10 Hz, C2–H) and 5·33 (m, C12–H).

Methyl 2α,3α,23-Trihydroxyolean-12-en-28-oate (10)

Methyl 2α,3α,23-trihydroxyolean-12-en-28-oate crystallized from ethanol as needles, m.p. 263–268°, $[\alpha]_D^{20}$ +43° (*c*, 0·40) [Found: C, 73·3; H, 10·1; O, 16·6; $M^{+\bullet}$, 502·3651 (mass spectrum). $C_{31}H_{50}O_5$,0·5EtOH requires C, 73·2; H, 10·2; O, 16·7%. $C_{31}H_{50}O_5$ requires mol. wt 502·3658]. λ_{max} 212 nm (ε 2200); ν_{max} (Nujol) 3420 (OH), 1715 (CO_2Me), 1260 (OH), 1166 (ester), 1045 (primary and secondary OH) and 820 cm^{-1} (C=C); n.m.r. (pyridine): δ 0·90 (br s, 24-, 26-, 29-, 30-Me), 1·08 (s, 27-Me), 2·85 (dd, J_{AX+BX} 18 Hz, C18–H), 3·35 (d, *J* 3 Hz, C3–H), 3·70 (s, CO_2Me), 3·90 (m, C2–H), 3·70, 4·18 (2d, *J* 9 Hz, CH_2OH), 4·92 (s, C2,3,23–OH) and 5·38 (m, C12–H); mass spectrum: *m/e* 487 (M−Me), 484 (M−H_2O), 469 (M−Me−H_2O), 466 (M−2H_2O), 262 (M−$C_{14}H_{24}O_3$), 249 (M−$C_{15}H_{25}O_3$), 203 (262−CO_2Me), 189 and 133 (203−C_5H_{10}).

The *triacetate*, prepared with acetic anhydride–pyridine (100°, 1 h), was obtained as a gum, $[\alpha]_D^{20}$ +37° (*c*, 1·16) (Found: C, 70·1; H, 9·0; O, 20·8. $C_{37}H_{56}O_8$ requires C, 70·7; H, 9·0; O, 20·4%). λ_{max} 218 nm (ε 1100); ν_{max} 1750 (OAc), 1730 (CO_2Me), 1660 (C=C) and 825 cm^{-1} (C=C); n.m.r.: δ 0·74 (s, 26-Me), 0·91 (s, 24-Me), 0·92 (s, 29, 30-Me), 1·10 (s, 25-Me), 1·12 (s, 27-Me), 1·95, 1·98, 2·03 (3s, C2,3,23–OAc), 2·85 (dd, J_{AX+BX} 18 Hz, C18–H), 3·62 (s, CO_2Me), 3·68, 4·08 (2d, *J* 10 Hz, CH_2OAc), 5·02–5·26 (m, C2,3–H) and 5·30 (m, C12–H).

2α,3α,23,28-Tetrahydroxyolean-12-ene

The triol (10) was heated under reflux with an excess of lithium aluminium hydride in tetrahydrofuran for 15 min. Workup in the normal manner gave *2α,3α,23,28-tetrahydroxyolean-12-ene* which crystallized from ethanol as needles, m.p. 267–270° (Found: C, 75·8; H, 10·6. $C_{30}H_{50}O_4$ requires C, 75·9; H, 10·6%).

Acetonides of Methyl 2α,3α,23-Trihydroxyolean-12-en-28-oate

A mixture of the triol (10) (10 g) and 70% perchloric acid (10 ml) in dry acetone (500 ml) was stirred at 20° for 2 h. T.l.c. (benzene–acetone, 9 : 1) indicated the presence of two products. The mixture was chromatographed (dry column[15]) on silica gel deactivated with 12% water and 5%

benzene–acetone (9 : 1). Elution with benzene–acetone (9 : 1) separated the products which were further purified by preparative t.l.c.

The more polar compound crystallized from acetone to give *methyl 2α-hydroxy-3α,23-isopropylidenedioxyolean-12-en-28-oate* (38) (7·2 g) as needles, m.p. 219–221°, $[\alpha]_D^{20}$ +52° (*c*, 0·76) (Found: C, 75·3; H, 9·9. $C_{34}H_{54}O_5$ requires C, 75·2; H, 10·0%). λ_{max} 212 nm (ε 2600); ν_{max} 3570, 3440 (OH), 1720 (CO_2Me), 1252, 1030 (secondary OH), and 1112, 1060, 843 cm^{-1} (isopropylidenedioxy); n.m.r.: δ 0·75 (s, 26-Me), 0·75, 0·90, 0·93, 0·98 (4s, 24-, 25-, 29-, 30-Me), 1·17 (s, 27-Me), 1·42 (s, isopropylidene Me_2), 2·85 (dd, J_{AX+BX} 18 Hz, C18–H), 3·60 (s, CO_2Me), 3·77 (d, *J* 3 Hz, C3–H), 3·80 (m, C2–H), 3·28, 3·65 (2d, *J* 12 Hz, C23–H_2) and 5·26 (m, C12–H).

The less polar compound crystallized from acetone to give *methyl 23-hydroxy-2α,3α-isopropylidenedioxyolean-12-en-28-oate* (34) (1·7 g) as needles, m.p. 138–140°, $[\alpha]_D^{20}$ +94° (*c*, 0·65) (Found: C, 75·3; H, 10·6. $C_{34}H_{54}O_5$ requires C, 75·2; H, 10·0%). λ_{max} 212 nm (ε 2350); ν_{max} 3500 (OH), 1300, 1035 (primary OH), and 1160, 1115, 1070, 850 cm^{-1} (isopropylidenedioxy); n.m.r.: δ 0·73 (s, 26-Me), 0·83, 0·93 (2s, 24-, 25-, 29-, 30-Me), 1·17 (s, 27-Me), 1·33, 1·48 (2s, isopropylidene Me_2), 2·85 (dd, J_{AX+BX} 18 Hz, C18–H), 3·47 (s, CH_2OH), 3·64 (s, CO_2Me), 3·85 (d, *J* 4 Hz, C3–H), 4·23 (m, C2–H) and 5·33 (m, C12–H).

Methyl 2-Oxo-3α,23-isopropylidenedioxyolean-12-en-28-oate (39)

The 3α,23-acetonide (38) (0·50 g) and a mixture of chromium trioxide (6·0 g) and pyridine (9·5 g) in acid-washed dichloromethane (150 ml) was stirred at 20° for 30 min. The solution was decanted from a tarry residue which was washed with ether (200 ml). The combined organic solutions were washed with 5% aqueous sodium hydroxide, 5% hydrochloric acid, 5% sodium hydrogen carbonate and saturated sodium chloride solutions and the solvent was removed from the dried solution. Purification by preparative t.l.c. gave *methyl 2-oxo-3α,23-isopropylidenedioxyolean-12-en-28-oate* which crystallized from acetone as needles, m.p. 186–193°, $[\alpha]_D^{20}$ +102° (*c*, 0·33) (Found: C, 75·7; H, 9·8. $C_{34}H_{52}O_5$ requires C, 75·5; H, 9·7%). λ_{max} 212 nm (ε 3570); ν_{max} 1720 (CO_2Me), 1710 (CO), and 1160, 1112, 1060, 840 cm^{-1} (isopropylidenedioxy); n.m.r.: δ 0·72 (s, 26-Me), 0·77, 0·93, 0·93, 0·95 (4s, 24-, 25-, 29-, 30-Me), 1·18 (s, 27-Me), 1·45 (s, isopropylidene Me_2), 2·85 (dd, J_{AX+BX} 18 Hz, C18–H), 3·37, 3·82 (2d, *J* 12 Hz, C23–H_2), 3·64 (s, CO_2Me), 3·78 (s, C3–H) and 5·30 (m, C12–H); o.r.d. (*c*, 0·33 in $CHCl_3$) $[\phi]_{589}^{20}$ +520°, $[\phi]_{400}$ +1305°, $[\phi]_{328}$ +4350° and $[\phi]_{290}$ +675°.

Methyl 2α-Acetoxy-3α,23-isopropylidenedioxyolean-12-en-28-oate (40)

The acetonide (38) (0·50 g) was acetylated with acetic anhydride (2 ml) and pyridine (4 ml) at 20° for 12 h. Workup and purification of the product by preparative t.l.c. gave *methyl 2α-acetoxy-3α,23-isopropylidenedioxyolean-12-en-28-oate* which crystallized from methanol as needles, m.p. 193–195°, $[\alpha]_D^{20}$ +61° (*c*, 0·85) (Found: C, 73·9; H, 9·9. $C_{36}H_{56}O_6$ requires C, 73·9; H, 9·7%). λ_{max} 212 (ε 2680); ν_{max} 1725 (br, OAc and CO_2Me), and 1120, 1067, 855 cm^{-1} (isopropylidenedioxy); n.m.r.: δ 0·75 (s, 26-Me), 0·80, 0·90, 0·95, 1·07 (4s, 24-, 25-, 29-, 30-Me), 1·18 (s, 27-Me), 1·43 (s, isopropylidene Me_2), 2·07 (s, OAc), 2·85 (dd, J_{AX+BX} 18 Hz, C18 H), 3·30, 3·70 (2d, *J* 12 Hz, C23–H_2), 3·86 (d, *J* 3 Hz, C3–H), 5·17 (m, $W_{h/2}$ 20 Hz, C2–H) and 5·33 (m, C12–H).

Methyl 23-Oxo-2α,3α-isopropylidenedioxyolean-12-en-28-oate (35)

The 2α,3α-acetonide (38) (1·0 g) was oxidized with Collins reagent[19] as above. Workup gave *methyl 23-oxo-2α,3α-isopropylidenedioxyolean-12-en-28-oate* (85%) which crystallized from methanol as needles, m.p. 206–212° (Found: C, 75·8; H, 9·5. $C_{34}H_{52}O_5$ requires C, 75·5; H, 9·7%). ν_{max} 2720 (CHO), 1730 (CO_2Me), and 1720 cm^{-1} (CHO); n.m.r.: δ 0·77 (s, 26-Me), 0·92, 0·92, 0·95, 1·13 (4s, 24-, 25-, 29-, 30-Me), 1·18 (s, 27-Me), 1·24, 1·48 (2s, isopropylidene Me_2), 2·85 (dd, J_{AX+BX} 18 Hz, C18–H), 3·63 (s, CO_2Me), 3·87 (d, *J* 4 Hz, C3–H), 4·27 (m, C2–H), 5·33 (m, C12–H) and 9·50 (s, CHO).

Wolff–Kishner Reduction of Methyl 23-Oxo-2α,3α-isopropylidenedioxyolean-12-en-28-oate

The aldehyde (35) (35 mg) was heated under reflux with 2·5 ml of a solution prepared from *N,N*-dimethylhydrazine (1·06 g) and dry ethanol (50 ml), until no starting material remained (72 h, t.l.c.). The solution was concentrated under reduced pressure, treated with 2·5 ml of a solution prepared from hydrazine (0·28 g) in dry ethanol (25 ml), and heated under reflux for 48 h. The latter

treatment was repeated and the mixture was poured into water and extracted with ether. Workup gave the hydrazone which was heated under reflux with resublimed potassium t-butoxide (0·25 g) in sodium-dried toluene (2·5 ml) for 6 h. The mixture was added to dilute hydrochloric acid and extracted with ether. Workup gave a product which was methylated with diazomethane. Preparative t.l.c. gave methyl 2α,3α-isopropylidenedioxyolean-12-en-28-oate (33) (19 mg, 56%) which crystallized from acetone as needles, m.p. and mixed m.p. 237–239° (identical i.r. spectrum).

Methyl 2α-Hydroxy-3α,23-methylenedioxyolean-12-en-28-oate (*37*)

A suspension of the triol (10) (0·10 g) and paraformaldehyde (50 mg) in benzene (10 ml) was stirred and warmed with a crystal of *p*-toluenesulphonic acid until the triol had dissolved. The solution was cooled, washed with water, dried, and concentrated to yield a product which was purified by preparative t.l.c. Crystallization from methanol gave *methyl 2α-hydroxy-3α,23-methylenedioxyolean-12-en-28-oate* (90 mg) as needles, m.p. 248–250° (Found: C, 74·7; H, 9·9. $C_{32}H_{50}O_5$ requires C, 74·7; H, 9·8%). ν_{max} (Nujol) 3250 (OH), 1730 (CO_2Me), 1165, and 1040 cm^{-1} (OH); n.m.r.: δ 0·70 (s, 26-Me), 0·73, 0·93, 0·93, 0·98 (4s, 24-, 25-, 29-, 30-Me), 1·17 (s, 27-Me), 2·90 (m, C18–H), 2·97 (d, *J* 12 Hz, C23–H), 3·62 (s, CO_2Me), 3·49 (d, *J* 3 Hz, C3β–H), 4·05 (m, C2β–H), 4·00 (d, *J* 12 Hz, C23–H), 4·64, 5·50 (2d, *J* 6 Hz, OCH_2O) and 5·30 (m, C12–H); mass spectrum: *m/e* 514 ($M^{+\cdot}$), 499 (M − Me), 262 ($M-C_{15}H_{24}O_3$), 203 ($262-CO_2Me$), 189 and 133 ($203-C_5H_{10}$).

ε-Hemiacetal of Methyl 23-Hydroxy-2,3-dioxo-2,3-secoolean-12-en-28-oate (*16*)

A solution of methyl 2α,3α,23-trihydroxyolean-12-en-28-oate (10) (0·10 g) in acetic acid (16 ml) was treated with sodium metaperiodate (40 mg) in water (4 ml). The solution was kept in the dark for 15 h, diluted with water and extracted with chloroform. The extract was worked up to yield the ε-hemiacetal of methyl 23-hydroxy-2,3-dioxo-2,3-secoolean-12-en-28-oate which crystallized from ethanol as needles (68 mg, 69%), m.p. *c.* 200° (dec.), $[\alpha]_D^{20}$ +132° (*c*, 0·90) (lit.[6] 206–207°, $[\alpha]_D^{16}$ +142°; lit.[19] 200–201°, $[\alpha]_D$ +191·8°). ν_{max} (Nujol) 3540 (OH), 2720 (CHO), and 1725 cm^{-1} (CO_2Me and CHO); n.m.r.: δ 0·81 (s, 26-Me), 0·93 (s, 29-, 30-Me), 0·98, 1·07 (2s, 24-, 25-Me), 1·13 (s, 27-Me), 2·90 (dd, J_{AX+BX} 18·5 Hz, C18–H), 3·62 (s, CO_2Me), 3·66 (d, *J* 14 Hz, C23α–H), 3·88 (s, OH), 3·97 (d, *J* 14 Hz, C23β–H), 5·12 (dd, *J* 9·5, 5 Hz, C2–H), 5·30 (m, C12–H) and 9·98 (s, CHO).

ε-Lactone of 23-Hydroxy-4,17-dimethoxycarbonyl-2,3-secours-12-en-2-oic Acid (*15*)

The ε-lactone of 23-hydroxy-4,17-dimethoxycarbonyl-2,3-secours-12-en-2-oic acid crystallized from acetone as needles, m.p. 228–232°, $[\alpha]_D^{20}$ +126° (*c*, 1·36) (lit.[20] 234–236°, $[\alpha]_D$ +117°,[21] 232–234°) [Found: C, 72·6; H, 9·2; O, 18·2; $M^{+\cdot}$, 528·3457 (mass spectrum). Calc. for $C_{32}H_{48}O_6$: C, 72·7; H, 9·2; O, 18·2%; mol. wt, 528·3450]. λ_{max} 215 nm (ε 1450); ν_{max} (KBr) 1750 (lactone), 1725 (CO_2Me), 1660 (C=C), and 825 cm^{-1} (C=C); n.m.r.: δ 0·83 (s, 26-Me), 0·92 (m, 29-, 30-Me), 1·00 (s, 25-Me), 1·04 (s, 27-Me), 1·35 (s, 24-Me), 2·23 (d, *J* 11 Hz, C18–H), 2·63 (s, C1–H_2), 3·59 (s, C28–CO_2Me), 3·68 (s, C3–CO_2Me), 3·98 (d, *J* 13 Hz, C23α–H), 4·58 (d, *J* 13 Hz, C23β–H) and 5·28 (m, C12–H); mass spectrum: *m/e* 513 (M − Me), 469 ($M-CO_2Me$), 262 ($M-C_{15}H_{22}O_4$), 249 ($M-C_{16}H_{23}O_4$), 203 ($262-CO_2Me$), 189 and 133 ($203-C_5H_{10}$).

ε-Lactone of 23-Hydroxy-17-methoxycarbonyl-3-oxo-2,3-secoolean-12-en-2-oic Acid (*18*)

A solution of the keto acetonide (39) (0·30 g) was warmed with glacial acetic acid (35 ml) and then treated with a solution of sodium metaperiodate (0·13 g) in water (10 ml). The mixture was kept in the dark at 20° for 24 h, diluted with water and extracted with chloroform. The extract was washed with water, dried and evaporated to yield a product which was triturated with ether. *17-Methoxycarbonyl-3-oxo-2,3-secoolean-12-ene-2,23-lactone* (0·23 g, 83%) crystallized from methanol as needles, m.p. 192–210° (dec.), $[\alpha]_D^{22}$ +118° (*c*, 0·64) (Found: C, 74·6; H, 9·1. $C_{31}H_{46}O_5$ requires C, 74·7; H, 9·3%). λ_{max} 214 nm (ε 2040); ν_{max} (Nujol) 1740 (lactone) 2725 (CHO), 1725 (CO_2Me), and 1705 cm^{-1} (CO); n.m.r.: δ 0·81 (s, 26-Me), 0·95 (m, 29-, 30-Me), 1·01 (s, 25-Me), 1·16 (s, 27-Me), 1·21 (s, 24-Me), 2·65 (s, C1–H_2), 2·90 (dd, J_{AX+BX} 18 Hz, C18–H), 3·64 (s, CO_2Me), 4·06 (d, *J* 13·5 Hz, C23α–H), 4·50 (d, *J* 13·5 Hz, C23β–H), 5·30 (m, C12–H), and 9·85 (s, CHO); mass spectrum: *m/e* 498 ($M^{+\cdot}$), 439 ($M-CO_2Me$), 262 ($M-C_{14}H_{20}O_3$), 203 ($262-CO_2Me$), 189 and 133 ($203-C_5H_{10}$).

ε-Lactone of 23-Hydroxy-4,17-dimethoxycarbonyl-2,3-secoolean-12-en-2-oic Acid (17)

A solution of the aldehydo lactone (18) (0·10 g) in acetone (20 ml) containing a few drops of water was heated under reflux while potassium permanganate (25 mg) was added in small portions. Refluxing was continued until the permanganate colour disappeared (*c.* 10 min) and the mixture was then poured into water, acidified with concentrated hydrochloric acid (2 ml), and extracted with ether. Workup gave the crude acid (19) which was methylated with diazomethane to yield *4,17-dimethoxycarbonyl-2,3-secoolean-12-ene-2,23-lactone* which crystallized from methanol as needles (71 mg, 67%), m.p. 258–261°, $[\alpha]_D^{20}$ +131° (*c*, 2·17) (Found: C, 73·0; H, 9·1. $C_{32}H_{48}O_6$ requires C, 72·7; H, 9·2%). λ_{max} 219 (ε 1070) and 250 nm (309); ν_{max} (Nujol) 1740 (lactone), 1737 (CO_2Me) and 1730 cm^{-1} (CO_2Me); n.m.r.: δ 0·81 (s, 26-Me), 0·93 (s, 29, 30-Me), 1·00 (s, 25-Me), 1·14 (s, 27-Me), 1·35 (s, 24-Me), 2·61 (s, C1–H_2), 2·90 (dd, J_{AX+BX} 16 Hz, C18–H), 3·62 (s, C28 CO_2Me), 3·69 (s, C3–CO_2Me), 3·98 (d, *J* 13·5 Hz, C23α–H), 4·61 (d, *J* 13·5 Hz, C23β–H) and 5·30 (m, C12–H).

Trimethyl 2,3-Seco-24-norurs-12-ene-2,3,28-trioate (20)

Trimethyl 2,3-seco-24-norurs-12-ene-2,3,28-trioate crystallized from methanol as needles, m.p. 149–152°, $[\alpha]_D^{20}$ +74° (*c*, 0·41) (Found: C, 72·5; H, 9·3. $C_{32}H_{48}O_6$ requires C, 72·7; H, 9·2%). ν_{max} (KBr) 1740 (CO_2Me), 1733 (CO_2Me), 1727 (CO_2Me) and 840 cm^{-1} (trisubstituted C=C); n.m.r.: δ 0·78 (s, 26-Me), 0·85–1·0 (m, 29-, 30-Me), 0·93 (s, 25-Me), 1·09 (s, 27-Me), 1·13 (d, *J* 6·5 Hz, 23-Me), 2·20 (d, *J* 10 Hz, C18–H), 2·33 (d, *J* 2 Hz, C1–H_2), 2·76 (q, $J_{3,4}$ 6·5 Hz, $J_{4,5} \approx 0$ Hz, C4–H), 3·60 (s, C2 or 3, 28 CO_2Me), 3·67 (s, C2 or 3 CO_2Me), and 5·30 (m, C12–H); mass spectrum: *m/e* 528 ($M^{+\cdot}$), 262 ($M-C_{15}H_{22}O_4$), 203 (262 − CO_2Me), 189 and 133 (203 − C_5H_{10}).

Methyl 3-Oxo-1,24-dinorolean-12-en-28-oate (41)

(i) A mixture of the aldehyde lactone (18) (70 mg) in methanol (28 ml) and potassium hydroxide (1·5 g) in water (12 ml) was stirred at 20° for 20 h, acidified, and then extracted with ether. Workup and purification by preparative t.l.c. (benzene) gave *methyl 3-oxo-1,24-dinorolean-12-en-28-oate* (28 mg, 46%) which crystallized from methanol as needles, m.p. 173–174°, $[\alpha]_D^{20}$ +178° (*c*, 0·32) (Found: C, 78·9; H, 10·1. $C_{29}H_{44}O_3$ requires C, 79·0; H, 10·1%). λ_{max} 214 nm (ε 2200); ν_{max} (KBr) 1735 (CO_2Me) and 1730 cm^{-1} (CO); n.m.r.: δ 0·84 (s, 26-Me), 0·95 (s, 25-, 29-, 30-Me), 1·03 (d, *J* 7 Hz, 23-Me), 1·21 (s, 27-Me), 2·90 (dd, J_{AX+BX} 18 Hz, C18–H), 3·64 (s, CO_2Me), and 5·30 (m, C12–H); mass spectrum: *m/e* 440 ($M^{+\cdot}$), 425 (M − Me), 381 (M − CO_2Me), 262 ($M-C_{12}H_{18}O$), 203 (262 − CO_2Me), 189 and 133 (203 − C_5H_{10}); o.r.d. (*c*, 0·32 in $CHCl_3$) $[\phi]_{589}^{20}$ +790°, $[\phi]_{400}$ +2740°, $[\phi]_{326}$ +16,400° $[\phi]_{304}$ 0° and $[\phi]_{280}$ −1052°.

(ii) A mixture of the lactone (17) (20 mg) in methanol (20 ml) and potassium hydroxide (1·0 g) in water (4 ml) was stirred with occasional warming on a steam bath for 4 days. The mixture was worked up as in (i), re-esterified with diazomethane, and purified by preparative t.l.c. to yield starting material (10 mg) and methyl 3-oxo-1,24-dinorolean-12-en-28-oate (6 mg), m.p. and mixed m.p. 173–174° (identical i.r. spectrum).

Oxidation of Methyl 3-Oxo-24-norurs-12-en-28-oate

A solution of the ketone (1) (0·20 g) in acetic acid (10 ml) was treated with chromium trioxide (70 mg) and sulphuric acid (1 ml) in acetic acid (5 ml). The mixture was kept at 0° for 30 min, diluted with water, and extracted with chloroform. Workup gave a residue which was dissolved in ether and extracted with 3M sodium hydroxide solution. The acidic material was methylated with an ethereal solution of diazomethane and purified by preparative t.l.c. to yield trimethyl 2,3-seco-24-norurs-12-ene-2,3,28-trioate (20) which crystallized from methanol as needles (4 mg), m.p. and mixed m.p. 147–150° (identical i.r. spectrum).

Most of the oxidation product was neutral and appeared to be composed mainly of the 11-oxo derivative but was not investigated further. Oxidation of the ketone (1) with a limited amount of chromic acid failed to improve the yield of the ester (20).

Methyl 2α-Bromo-3-oxo-24-norurs-12-en-28-oate (4)

A solution of methyl 3-oxo-24-norurs-12-en-28-oate (1) (0·50 g) in acetic acid (50 ml) was shaken with bromine (0·20 g) in acetic acid (20 ml) for 3 min. Water was added and the product was

crystallized from methanol to yield *methyl 2α-bromo-3-oxo-24-norurs-12-en-28-oate* (0·40 g, 67%) as needles, m.p. 163–164° (dec.), $[\alpha]_D^{20}$ +72° (*c*, 0·22) (Found: C, 67·6; H, 8·5; Br, 15·2. $C_{30}H_{45}BrO_3$ requires C, 67·5; H, 8·5; Br, 15·0%). λ_{max} 215 nm (ε 2140); ν_{max} (Nujol) 1745 (CO_2Me) and 1730 cm^{-1} (CO); n.m.r.: δ 0·84 (s, 26-Me), 0·85–0·95 (m, 29-, 30-Me), 1·08 (s, 25-Me), 1·14 (d, *J* 7 Hz, 23-Me), 1·23 (s, 27-Me), 2·66 (q, *J* 7 Hz, C4–H), 3·62 (s, CO_2Me), 4·82 (dd, *J* 13, 6 Hz, C2β–H), and 5·30 (m, C12–H); mass spectrum: *m/e* 534/532 ($M^{+\cdot}$), 452 (M − HBr), 393 (452 − CO_2Me), 262 (M − $C_{13}H_{19}OBr$), 203 (262 − CO_2Me), 189 and 133 (203 − C_5H_{10}).

Borohydride Reduction of the Bromo Ketone (4)

Sodium borohydride (30 mg) was added to a stirred solution of methyl 2α-bromo-3-oxo-24-norurs-12-en-28-oate (0·24 g) in methanol (25 ml). The mixture was kept at 20° for 5 min, diluted with water, and filtered to yield a mixture of axial and equatorial alcohols (5) and (6) which was purified by preparative t.l.c. (benzene–hexane, 1 : 1). The less polar product, methyl 2α-bromo-3α-hydroxy-24-norurs-12-en-28-oate (5), was obtained as an oil (0·10 g) which could not be induced to crystallize. $[\alpha]_D^{20}$ +42° (*c*, 1·07); ν_{max} 3560 (OH) and 1720 cm^{-1} (CO_2Me); n.m.r.: δ 0·77 (s, 26-Me), 0·90–1·02 (m, 23-, 25-, 29-, 30-Me), 1·10 (s, 27-Me), 2·17 (s, OH), 2·25 (d, *J* 10 Hz, C18–H), 3·61 (s, CO_2Me), 3·83 (m, $W_{h/2}$ 5·6 Hz, C3β–H), 4·53 (ddd, *J* 11·6, 6·2, 2·6 Hz, C2β–H) and 5·30 (m, C12–H).

Conversion of the Bromohydrins (5) and (6) into the Trimethyl Ester (20)

The mixture of bromohydrins (5) and (6) (0·10 g) in acetic acid (10 ml) was stirred with silver acetate (35 mg) at 100–110° for 2 h. The mixture was cooled, diluted with water and extracted with chloroform. Workup gave a residue which was dissolved in methanol (10 ml) and warmed on a steam bath with potassium hydroxide (0·20 g) in water (1 ml) for 1 h. The cooled mixture was diluted with water and extracted with ether. Workup gave a mixture of diols which was dissolved in acetic acid (16 ml) and treated with sodium metaperiodate (40 mg) in water (4 ml) at 20° for 5 days. The mixture was diluted with water, extracted with chloroform and the extract was worked up to yield the crude dialdehyde (21) which was dissolved in acetone (5 ml) containing a drop of water and heated under reflux while potassium permanganate (50 mg) was added in small portions. After 10 min the mixture was poured into water, acidified with concentrated hydrochloric acid (2 ml) and extracted with ether. Workup gave a product which was methylated with an excess of an ethereal solution of diazomethane. Purification by preparative t.l.c. gave trimethyl 2,3-seco-24-norurs-12-ene-2,3,28-trioate (20) (27 mg) which crystallized from methanol as needles, m.p. and mixed m.p. 149–152° (identical i.r. and n.m.r. spectra).

Methyl 3-Oxo-1,24-dinorurs-12-en-28-oate (44)

A solution of the trimethyl ester (20) (24 mg) in dry benzene (30 ml) was heated under reflux with freshly sublimed potassium t-butoxide (15 mg) for 5 h. The solvent was removed and the residue was retreated with a fresh portion of potassium t-butoxide (15 mg) in dry benzene (30 ml) for a further 6 h. Water (2 ml) was added and the mixture was stirred at 20° for 24 h. The organic phase was separated, dried and evaporated to yield a product which was purified by preparative t.l.c. Crystallization from methanol gave *methyl 3-oxo-1,24-dinorurs-12-en-28-oate* (8 mg) as needles, m.p. 162–164° (Found: C, 79·0; H, 10·2. $C_{29}H_{44}O_3$ requires C, 79·0; H, 10·1%). ν_{max} (KBr) 1735 (CO_2Me) and 1725 cm^{-1} (CO).

Methyl 2α,3α-Dihydroxyurs-12-en-28-oate (23)

Methyl 2α,3α-dihydroxyurs-12-en-28-oate crystallized from methanol as needles, m.p. 195–197°, $[\alpha]_D^{20}$ +50° (*c*, 1·0) (Found: C, 76·3; H, 10·6. $C_{31}H_{50}O_4$ requires C, 76·5; H, 10·4%). λ_{max} 214 nm (ε 2000); ν_{max} (KBr) 3500 (OH), 3385 (OH), 1730 (CO_2Me), 1035, 990 (OH) and 830 cm^{-1} (C=C), (0·5% in pyridine) 1390, 1380, 1360, 1308, 1276, and 1236 cm^{-1} (ursane skeleton); n.m.r.: δ 0·73 (s, 26-Me), 0·85 (s, 24-Me), 0·95 (m, 29-, 30-Me), 0·95 (s, 25-Me), 1·01 (s, 23-Me), 1·10 (s, 27-Me), 2·14 (s, C2,3–OH), 2·24 (d, *J* 11 Hz, C18–H), 3·44 (d, *J* 3 Hz, C3β–H), 3·62 (s, CO_2Me), 4·05 (m, C2β–H) and 5·30 (m, C12–H); mass spectrum: *m/e* 486 ($M^{+\cdot}$), 471 (M − Me), 468 (M − H_2O), 453 (M − Me − H_2O), 435 (M − Me − $2H_2O$), 426 (M − HCO_2Me), 262 (M − $C_{14}H_{24}O_2$), 203 (262 − CO_2Me), 189 and 133 (203 − C_5H_{10}).

Osmylation of Methyl Ursa-2,12-dien-28-oate

A solution of methyl ursa-2,12-dien-28-oate (45)[26,28] (0·20 g) in dioxan (10 ml) was treated with osmium tetroxide (0·40 g) at 20° for 10 days. A saturated solution of sodium metabisulphite (5 ml) was added and the mixture was worked up to give an oil which contained two components. The major product possessed identical R_F value to that of the dihydroxy ester (23) and the i.r. and n.m.r. spectra were almost identical.

Methyl 2-Hydroxy-3-oxo-24-noroleana-1,4,12-trien-28-oate (26) and Methyl 2-Hydroxy-3-oxo-24-norursa-1,4,12-trien-28-oate (27)

The non-crystalline mixture of diosphenols had ν_{max} 3430 (OH), 1720 (CO_2Me), and 1625 cm^{-1} (conj. dienone); n.m.r.: δ 0·80–1·07 (m, methyls), 1·31 (s, C4–Me), 2·22 (d, J 10 Hz, C18–H of (27)), 2·80 (m, C18–H of (26)), 3·65 (s, CO_2Me), 5·36 (m, C12–H), 6·30 (s, C1–H) and 6·50 (br s, OH, exchanged with D_2O).

Methyl 3α,23-Diacetoxy-2α-methoxyolean-12-en-28-oate (12)

Methyl 3α,23-diacetoxy-2α-methoxyolean-12-en-28-oate crystallized from methanol as needles, m.p. 184–188°, $[\alpha]_D^{20}$ +52° (c, 1·02) (Found: C, 71·7; H, 9·4. $C_{36}H_{56}O_7$ requires C, 72·0; H, 9·4%). λ_{max} 216 nm (ε 1520); ν_{max} 1745 (OAc), 1730 (OAc), and 1720 cm^{-1} (CO_2Me); n.m.r.: δ 0·73 (s, 26-Me), 0·90, 0·93 (2s, 29-, 30-Me), 1·04 (s, 24-, 25-Me), 1·17 (s, 27-Me), 2·03 (s, C3α,23–OAc), 2·89 (dd, J 14,5 Hz, C18–H), 3·33 (s, C2–OMe), 3·3–3·7 (m, C2β–H), 3·62 (s, CO_2Me), 3·72 (d, J 11 Hz, C23–H), 4·07 (d, J 11 Hz, C23–H) and 5·2–5·4 (m, C3,12–H).

Conversion of the Triol (10) into the Methoxy Diacetate (12)

A solution of the triol (10) (0·50 g) in ethanol (30 ml) was treated with an excess of an ethereal solution of diazomethane at 0° for 4 h. The solvent and excess of diazomethane were removed and the residue was crystallized from ethanol to yield starting material (0·35 g). Material in the mother liquors was acetylated with acetic anhydride–pyridine (20°, 12 h) and the product was purified by preparative t.l.c. to yield methyl 3α,23-diacetoxy-2α-methoxyolean-12-en-28-oate (12) (37 mg) which crystallized from methanol as needles, m.p. and mixed m.p. 184–188° (identical i.r. and n.m.r. spectra).

Methyl Isoferulate (28)

Methyl isoferulate crystallized from hexane as prisms or leaflets, m.p. 78–79° (Found: C, 63·5; H, 5·9. Calc. for $C_{11}H_{12}O_4$: C, 63·5; H, 5·8%). λ_{max} 219 (ε 16220), 235sh (12300), 244 (14130), 297 (18200) and 328 nm (20890); ν_{max} (Nujol) 3500–3300 (OH), 1688 (conjugated CO_2Me), and 972 cm^{-1} (C=C); n.m.r.: δ 3·78 (s, CO_2Me), 3·91 (s, ArOMe), 5·80 (s, OH), 6·25 (d, J 16 Hz, CH=CHCO$_2$R), 6·7–7·3 (m, ArH), and 7·60 (d, J 16 Hz, ArCH=CH); acetate, leaflets (from benzene–hexane), m.p. 116–117° (lit.[29] 116°) (Found: C, 62·1; H, 5·8. Calc. for $C_{13}H_{14}O_5$: C, 62·4; H, 5·6%) (correct i.r. and n.m.r. spectra); isoferulic acid, m.p. and m.m.p. 226–227° (lit.[30] 224–225°).

Methyl 3,4-Dimethoxycinnamate (29)

Methyl 3,4-dimethoxycinnamate crystallized from hexane as needles, m.p. 63–64°, or prisms, m.p. and m.m.p. 68–70° (lit.[31] plates, 63–64°, prisms, 67–68°). λ_{max} 218 (ε 10230), 238 (10230), 296 (13180) and 324 nm (17380); ν_{max} (KBr) 1690 (conjugated CO_2Me) and 980 cm^{-1} (C=C); n.m.r.: δ 3·83 (s, CO_2Me), 3·91 (s, ArOMe), 6·28 (d, J 16·4 Hz, CH=CHCO$_2$R), 6·7–7·3 (m, ArH) and 7·62 (d, ArCH=CH); 3,4-dimethoxycinnamic acid, m.p. 181–182·5° (lit.[32] 178–182°).

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Methyl Acetylferulate

Methyl acetylferulate crystallized from methanol as leaflets, m.p. 120–122° (lit.[29] 122°). ν_{max} (Nujol) 1760 (OAc), 1715 (conjugated CO_2Me) and 982 cm^{-1} (C=C); n.m.r.: δ 2·32 (s, OAc), 3·81 (s, CO_2Me), 3·87 (s, ArOMe), 6·36 (d, *J* 16 Hz, CH=CHCO$_2$R), 7·0–7·3 (m, ArH), and 7·69 (d, *J* 16 Hz, ArCH=CH); methyl ferulate, m.p. 65° (lit.[33] 65°); ferulic acid, m.p. 170–171° (lit.[34] 167–169°).

Methyl Acetyl-p-*coumarate* (*31*)

Methyl acetyl-*p*-coumarate crystallized from methanol as plates, m.p. 81–82° (lit.[35] 82–83°). N.m.r.: δ 2·33 (s, OAc), 3·83 (s, CO_2Me), 6·38 (d, *J* 16 Hz, CH=CHCO$_2$R), 7·13, 7·55 (2d, *J* 7·5 Hz, ArH), and 7·68 (d, *J* 16 Hz, ArCH=CH).

Spathulenol (*32*)

Spathulenol was obtained as an oil [Found: $M^{+\cdot}$, 220·1833 (mass spectrum). $C_{15}H_{24}O$ requires mol. wt 220·1827]. ν_{max} (film) 3605 (OH), 3080 (OH), 1635 (C=C), and 885 cm^{-1} (C=C); n.m.r.: δ 0·60 (m, C6,7–H), 1·07 (s, *gem*–Me_2), 1·30 (s, C4–Me), and 4·70 (s, C=CH_2); mass spectrum: *m/e* 205 (M − CH_3) and 177 (M − C_3H_7 or 205 − C_2H_3). Ozonolysis gave a ketol, ν_{max} 3400 (OH) and 1690 cm^{-1} (cyclopentanone); n.m.r.: δ 0·60 (m, C6,7–H), 1·03, 1·13 (2s, *gem*–Me_2), and 1·30 (s, C4–Me); negative Cotton effect curve. The 3,5-dinitrobenzoate[4] had m.p. and mixed m.p. 145–147°.

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