A New Triterpenoid Glycoside from the Leaves of *Tetrapanax papyriferum*

By **Makoto Takai, Sakae Amagaya, and Yukio Ogihara,*** Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabedori, Mizuhoku, Nagoya 467, Japan

A new triterpenoid glycoside isolated from the leaves of *Tetrapanax papyriferum* by using droplet counter-current chromatography and silica gel column chromatography was identified as 11α-methoxy-3,21-dioxo-olean-12-en-28-oyl α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside.

Tetrapanax papyriferum (Araliaceae, Japanese name Kamiyatsude) has been used as a material for paper production. We have investigated the glycosides from the leaves and now describe the identification of the major glycoside.

The crude glycoside fraction from the methanolic extracts was subjected to droplet counter-current chromatography [1] to afford a main glycoside fraction (L-II). This was separated by silica gel column chromatography to give a pure glycoside, papyrioside L-IIa (1).

Acidic hydrolysis of the glycoside (1) gave a major genin, papyriogenin A (2), a minor genin, papyriogenin B (3), and D-glucose and L-rhamnose as sugar components (molar ratio 2 : 1). Alkaline hydrolysis of the glycoside (1) also gave papyriogenin A, and an oligosaccharide; this indicated that the sugar components are linked to the genin by an ester bond.

Papyriogenin A (2), $C_{30}H_{42}O_4$, exhibits two carbonyl (1 700 and 1 685 cm^{-1}) and one carboxylic (1 735 cm^{-1}) absorption in i.r. spectrum, strong u.v. absorption at 247, 252, and 262 nm characteristic of a heteroannular diene, and ^1H n.m.r. signals for two olefinic protons (AB quartet, δ 5.72 and 6.50, J 12 Hz) on a disubstituted

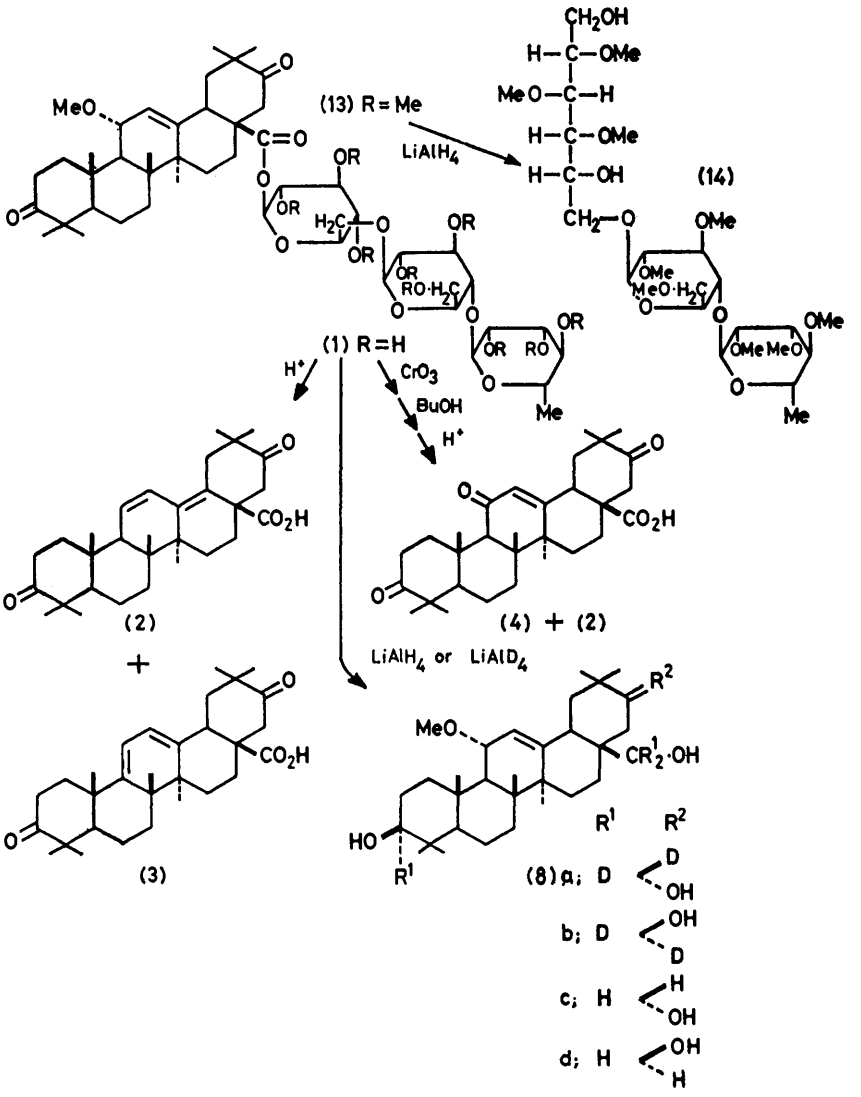
[1] T. Tanimura, J. J. Pisano, Y. Ito, and R. L. Bowman, *Science*, 1970, **169**, 54.

double bond. These results and biogenetic considerations suggest that the genin (2) is a derivative of oleana-11,13(18)-dien-3-one. To clarify the positions of the oxo- and carboxy-groups, *X*-ray analysis of the genin (2) was carried out, and the results indicated that this material was 3,21-dioxo-oleana-11,13(18)-dien-28-oic acid.[2]

Papyriogenin B (3) is isomeric with papyriogenin A. The ^{1}H n.m.r. spectrum showed two olefinic protons [δ 5.60 (s)] and u.v. absorption at 287 nm indicated a homoannular diene system; the compound was therefore identified as 3,21-dioxo-oleana-9(11),12-dien-28-oic acid.

The fact that acidic hydrolysis gave the homoannular diene (3) as well as the heteroannular diene (2) suggests the existence of an 11-oxygen function in the original glycoside, which shows only end absorption in the u.v. spectrum.

Oxidation of the glycoside (1) with chromic oxide–pyridine followed by acidic hydrolysis gave the diene (2) and 3,11,21-trioxo-olean-12-en-28-oic acid (4) [δ 5.80 (s), $\nu_{max.}$ 1 650 cm^{-1}, $\lambda_{max.}$ 250 nm]. The structure (4) was confirmed by the following experiments. Hydrogenation[3] of (4) over Adams catalyst gave the dihydroxy-acid (5) as a mixture of stereoisomers, which, without purification, was oxidized with chromic oxide–pyridine to 11-deoxy-derivative (6). Compound (6) was reduced by the Huang-Minlon method to give olean-12-en-28-oic acid (7), identical with an authentic sample derived from oleanolic acid *via* 3-oxo-olean-12-en-28-oic acid.[4] The fact that we could obtain (4) by oxidation of the glycoside (1), misled us into thinking that the original sapogenin was 3,21-dioxo-11-hydroxy-olean-12-en-28-oic acid.



To clarify the configuration at the 11-position, the glycoside (1) was reduced with lithium aluminium deuteride. In the n.m.r. spectrum of the reduction products (8a and b), the 11-H signal could be identified

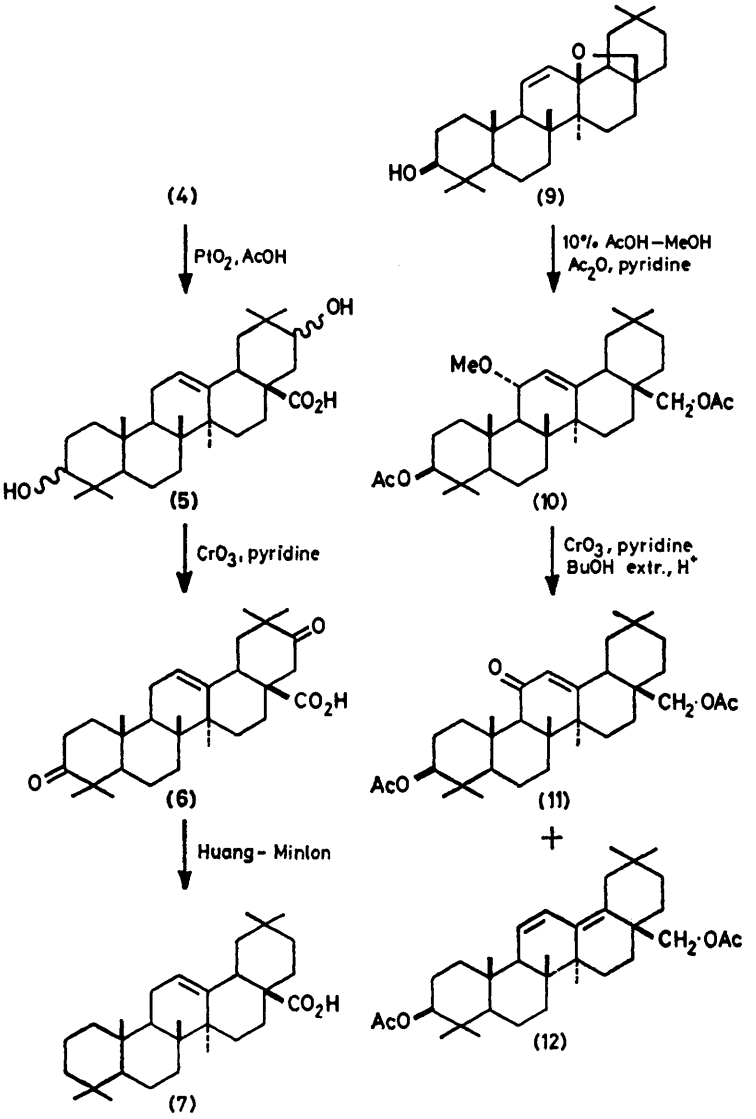
[2] S. Amagaya, M. Takai, Y. Ogihara, and Y. Iitaka, *J.C.S. Chem. Comm.*, 1975, 991.

[3] J. H. Beynon, K. S. Sharples, and F. S. Spring, *J. Chem. Soc.*, 1938, 1233.

[4] J. Karlnier and C. Djerassi, *J. Org. Chem.*, 1966, **31**, 1945.

at δ 3.86 (dd, *J* 10 and 3.5 Hz), and assigned to a β-axial proton.[5] When lithium aluminium hydride was used the products (8c and d) gave confused signals in the region δ 3.2—4.0; moreover one methoxy-signal appeared at δ 3.29. Thus the reduction products are not the expected olean-12-ene-3β,11α,21,28-tetraols but the 11α-methoxyolean-12-ene-3β,21,28-triols. C.d. data of the products (8c and d) show negative Cotton effects ($[\theta]_{214}$ −16 600) in accord with the data of Scott *et al.*[6]

group arose during acidic hydrolysis of the reaction mixture containing the oxidizing agents. When 3β,28-diacetoxy-11α-methoxyolean-12-ene (10), prepared from 13β,28-epoxy-3β-hydroxyolean-11-ene (9) [7] by treatment with acid in methanol,[8] was treated with chromic oxide–pyridine, no oxidation occurred. However when an n-butanolic extract of the reaction mixture was hydrolysed, 3β,28-diacetoxyolean-12-en-11-one (12) and 3β,28-diacetoxyoleana-11,13(18)-diene (12) [9] were obtained.



The presence of an 11α-methoxy-group in the original glycoside was supported by ^{13}C n.m.r. data [δ 54.1 (q)] and a negative Cotton effect ($[\theta]_{221}$ −7 800).

It seemed strange that the methoxy-group was oxidized to a carbonyl group by chromic oxide–pyridine. However a model experiment revealed that the carbonyl

During the acidic hydrolysis, the colour of the mixture changed from brown to green. It is apparent that the n-butanolic extract contained the oxidizing agents. Compounds (2) and (4) were also obtained by treatment of the glycoside (1) with chromic oxide–sulphuric acid.

The permethylated derivative (13) of papyrioside L-IIa gave on methanolysis three kinds of methylated

[5] D. H. R. Barton, E. F. Lier, and J. F. McGhie, *J. Chem. Soc.* (*C*), 1968, 1031.
[6] A. I. Scott and A. D. Wrixon, *Tetrahedron*, 1971, **27**, 4787.
[7] I. Kitagawa, K. Kitazawa, and I. Yoshioka, *Tetrahedron*, 1972, **28**, 907.
[8] A. Shimaoka, S. Seo, and H. Minato, *J.C.S. Perkin I*, 1975, 2043.
[9] D. H. R. Barton and N. J. Holness, *J. Chem. Soc.*, 1952, 78.

sugar. They were identified by g.l.c. as methyl pyranosides of 2,3,4-tri-*O*-methylrhamnose and 2,3,4-tri-*O*-methyl- and 2,3,6-tri-*O*-methyl-glucose.

Reduction of compound (13) with lithium aluminium hydride provided a colourless syrup (14), methanolysis of which gave two kinds of methylated sugar identified by g.l.c. as methyl pyranosides of 2,3,4-tri-*O*-methylrhamnose and 2,3,6-tri-*O*-methylglucose. The mass spectrum of compound (14) exhibits the molecular ion (*m/e* 616) and a peak due to a terminal permethylated methylpentose residue (*m/e* 189). In the n.m.r. spectrum of (14) the anomeric proton signals appear at δ 4.31 (d, *J* 7 Hz) and 4.93 (s), and are assigned respectively to those of β-D-glucopyranose ($^4C_1$ conformation) and rhamnopyranose (assumed to be of the L-series with α-linkage, in the $^1C_4$ conformation). Therefore compound (14) is 2,3,4-tri-*O*-methyl-α-L-rhamnopyranosyl-(1 → 4)-2,3,6-tri-*O*-methyl-β-D-glucopyranosyl-(1 → 6)-2,3,4-tri-*O*-methyl-D-sorbitol, $[\alpha]_D$ −33°.[10] In the n.m.r. spectrum of the glycoside (1) [$CDCl_3$–CD_3OD (1 : 1) containing one drop of CF_3CO_2H)][11] the anomeric proton signals appear at δ 5.47 (d, *J* 8 Hz), 4.38 (d, *J* 7 Hz), and 4.93 (s), and are assigned respectively to those of an ester-linked β-D-glucopyranose ($^4C_1$ conformation), β-D-glucopyranose, and α-L-rhamnopyranose. Consequently the glycoside (1) is identified as 11α-methoxy-3,21-dioxo-olean-12-en-28-oyl α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside.

The presence of the 11α-methoxy-group suggests that (1) might be an artefact formed during extraction by methanol; this possibility is under investigation.

EXPERIMENTAL

M.p.s were measured with a Yanagimoto micro-apparatus. Unless otherwise stated, u.v. spectra were taken for solutions in ethanol, optical rotations for solution in chloroform, c.d. data for solutions in methanol, and n.m.r. spectra for solutions in deuteriochloroform.

Isolation of Papyrioside L-IIa (1).—The dried leaves of *Tetrapanax papyriferum* (1 kg) were extracted with methanol. The extracts were diluted with water and then extracted with ether. The aqueous layer was extracted with n-butanol. The n-butanolic extract was evaporated and the residue dissolved in a minimal amount of methanol and poured into ether with stirring. The precipitate (crude saponins) was filtered off (91 g) and subjected to droplet counter-current chromatography [10 g in the solvent system $CHCl_3$–MeOH–H_2O (35 : 65 : 40); moving phase, upper layer; stationary phase, lower layer; number of glass tubes 250 (2.5 × 600 mm)]. In one fraction 10 g of eluted moving phase were collected, and from tubes 36—65 2.5 g of saponins (L-II) were obtained. The saponins L-II (5 g) were chromatographed on silica gel [solvent, lower layer of $CHCl_3$–MeOH–H_2O (70 : 23 : 7)] to afford pure *papyrioside L-IIa* (1) (1.25 g) as a white powder, m.p. 183—188°, $[\alpha]_D$ −39° (*c* 0.82), $[\theta]_{221}$ −7 800, δ_H [$CDCl_3$–CD_3OD (1 : 1) + CF_3CO_2H] 5.65 (1 H, d, *J* 3.5 Hz, olefinic 12-H), 5.47 (1 H, d, *J* 8 Hz, anomeric proton of ester glycoside glucose), 4.93 (1 H, s, anomeric proton of rhamnose), and 4.38 (1 H, d, *J* 7 Hz, anomeric proton of glucose), δ_C ([$^2H_5$]pyridine) 54.1 (11α-OMe), 96.1 (anomeric carbon of ester glycoside glucose), 102.7 (anomeric carbon of rhamnose), 104.8 (anomeric carbon of glucose), 123.8 (C-12), 146.1 (C-13), 173.9 (C-28), 211.9 (C-21), 216.1 (C-13), and 78.0 (C-11) (Found: C, 58.55; H, 8.05. $C_{49}H_{76}O_{19},2H_2O$ requires C, 58.55; H, 8.0%).

Acidic Hydrolysis of Papyrioside L-IIa.—Papyrioside L-IIa (1 g) was dissolved in dioxan (10 ml), 2N-sulphuric acid (20 ml), and water (10 ml) and heated under reflux for 5 h. The solution was diluted with water and extracted with ether. The extract was evaporated and the residue (390 mg) was crystallized from aqueous methanol to afford papyriogenin A (2) (170 mg). The mother liquor was subjected to preparative t.l.c. to give papyriogenin B (38 mg). The aqueous layer of the hydrolysate was neutralized with ion-exchange resin (IR-45) and evaporated. Trimethylsilylation followed by g.l.c. [20% OV-1 on Chromosorb W (60—80 mesh)] showed the presence of glucose and rhamnose.

Papyriogenin A (2) was obtained from methanol–water as prisms, m.p. 262—264°, $[\alpha]_D$ −11.3° (*c* 16.7), $\nu_{max.}$ (KBr) 1 730, 1 700, and 1 685 cm^{-1}, $\lambda_{max.}$ 247, 252 (ε 33 000), and 262 nm, δ 0.82 (3 H, s), 1.02 (15 H, s), 1.06 (6 H, s), 5.72 (1 H, d, *J* 12 Hz, 11-H), and 6.50 (1 H, dd, *J* 12 and 3 Hz, 12-H) (Found: C, 77.0; H, 9.35. $C_{30}H_{42}O_4$ requires C, 77.2; H, 9.05%).

Papyriogenin B (3) was obtained from methanol–water as prisms, m.p. 259—262°, $[\alpha]_D$ +19.6° (*c* 10), $\nu_{max.}$ (KBr) 1 730, 1 700br, and 1 600 cm^{-1}, $\lambda_{max.}$ 287 nm (ε 4 500), δ 1.02 (3 H, s), 1.05 (6 H, s), 1.08 (3 H, s), 1.13 (3 H, s), 1.25 (3 H, s), 1.32 (3 H, s), and 5.68 (2 H, s, 11- and 12-H) (Found: C, 75.9; H, 9.1. $C_{30}H_{42}O_4,0.5H_2O$ requires C, 75.8; H, 9.05%).

Treatment of the Glycoside (1) *with Chromic Oxide–Pyridine followed by Acidic Hydrolysis.*—To a stirred solution of chromic oxide (1.2 g) in pyridine (40 ml), papyrioside L-IIa (500 mg) in pyridine was added. The mixture was stirred for 2 h at room temperature, then diluted with water and extracted with n-butanol. The organic layer was washed with water and evaporated and the residue was hydrolysed in N-sulphuric acid in dioxan for 3 h at 110°. After dilution with water, the mixture was extracted with ether. The ether layer was washed with water and dried (Na_2SO_4) and separated by preparative t.l.c. to give papyriogenin A (2) (50 mg) and 3,11,21-*trioxo-olean*-12-*en*-28-*oic acid* (4) (60 mg), obtained from methanol as prisms, m.p. 252—255°, $\nu_{max.}$ (KBr) 1 724, 1 705, 1 685, and 1 650 cm^{-1}, $\lambda_{max.}$ 252 nm (ε 12 000), δ 0.98, 1.04, 1.07, 1.10, 1.23, 1.30, and 1.38 (each 3 H, s), and 5.80 (1 H, s, 12-H) (Found: C, 74.65; H, 9.1. $C_{30}H_{42}O_5$ requires C, 74.65; H, 8.75%).

Conversion of the Acid (4) *into Olean*-12-*en*-28-*oic Acid* (7).—A suspension of the acid (4) (50 mg) and platinum oxide (50 mg) in acetic acid was stirred for 5 h under hydrogen. The catalyst was filtered off and the filtrate evaporated to afford a colourless powder (5). The product (5), a mixture of epimeric 3,21-dihydroxyolean-12-en-28-oic acids, was dissolved in pyridine and added to the solution of chromic oxide (50 mg) in pyridine (2 ml). The solution was stirred

[10] R. Higuchi and T. Kawasaki, *Chem. and Pharm. Bull. (Japan)*, 1972, **20**, 2143.

[11] K. Miyahara and Y. Kawasaki, *Chem. and Pharm. Bull. (Japan)*, 1974, **22** 1407.

for 2 h, diluted with water, and extracted with ether. The extract was washed with water and evaporated to give 3,21-*dioxo-olean*-12-*en*-28-*oic acid* (6) (25 mg), prisms from methanol, m.p. 264—266°, $[\alpha]_D$ +45° (*c* 0.2), $\nu_{max.}$ ($CHCl_3$) 1 715sh, 1 700, and 1 685sh cm^{-1}, δ 0.80 (3 H, s), 1.05 (9 H, s), 1.06 (3 H, s), 1.13 (3 H, s), 1.27 (3 H, s), and 5.52br (1 H, s) (Found: C, 73.6; H, 9.15. $C_{30}H_{44}O_4,H_2O$ requires C, 74.05; H, 9.55%).

The acid (6) (16 mg) and 100% hydrazine hydrate (0.2 ml) in diethylene glycol (1 ml) and ethanol (1 ml) were heated under reflux for 1 h under nitrogen. After addition of potassium hydroxide pellets (0.1 g) and heating under reflux for an additional 0.5 h, the condenser was removed and the mixture was warmed slowly until an internal temperature of 195 °C was attained. The condenser was replaced and the mixture was maintained at 195—205° for 4 h, under nitrogen. After cooling to room temperature, the solution was poured into dilute hydrochloric acid and extracted with ether. Evaporation of the extract afforded olean-12-en-28-oic acid (7) (13 mg), m.p. 266—269° (from methanol), $[\alpha]_D$ +46° (*c* 0.26), $\nu_{max.}$ ($CHCl_3$) 1 690 cm^{-1}, δ 0.76 (3 H, s), 0.87 (3 H, s), 0.94 (9 H, s), 1.15 (3 H, s), and 5.35br (1 H, s) (Found: C, 81.55; H, 11.0. Calc. for $C_{30}H_{48}O_2$: C, 81.55; H, 11.0%), identical with an authentic specimen (mixed m.p., $[\alpha]_D$, and i.r. and n.m.r. spectra).

Reduction of the Glycoside (1) *with Lithium Aluminium Deuteride*.—A mixture of the glycoside (1) (100 mg) and $LiAlD_4$ (50 mg) in tetrahydrofuran (10 ml) was set aside overnight. The excess of reagent was decomposed with water and the mixture was extracted with ether. The extract was dried (Na_2SO_4) and evaporated and the residue was chromatographed on silica gel [benzene–ethyl acetate (1 : 1)] into 11α-methoxy[3α,21β-$^2H_2$]olean-12-ene-3β,21α,28-triol (8a) (10 mg) and 11α-methoxy[3α,21α-$^2H_2$]olean-12-ene-3β,21β,28-triol (8b) (14 mg), identified by comparison of R_F values with (8c) and (8d), respectively [δ 3.86 (1 H, dd, *J* 10 and 3.5 Hz) and 3.29 (3 H, s)].

Reduction of the Glycoside (1) *with Lithium Aluminium Hydride*.—Papyrioside L-IIa (1) (500 mg) was reduced with $LiAlH_4$ and the products were chromatographed as above to afford 11α-*methoxyolean*-12-*ene*-3β,21α,28-*triol* (8c) (60 mg), prisms from methanol, m.p. 239—242°, c.d. $[\theta]_{214}$ −16 000, δ ([$^2H_5$]pyridine) 1.00 (3 H, s), 1.04 (3 H, s), 1.10 (3 H, s), 1.17 (3 H, s), 1.23 (3 H, s), 1.43 (3 H, s), 3.26 (3 H, s), 3.42 (1 H, t, *J* 9 Hz, 3α-H), 3.65 (2 H, ABq, 28-H_2), 3.89 (1 H, s, 21β-H), and 5.50 (1 H, d, *J* 3.5 Hz, 12-H) (Found: C, 73.3; H, 10.35. $C_{31}H_{52}O_4,H_2O$ requires C, 73.45; H, 10.45%), and the 3β,21β,28-*triol* (8d) (70 mg), prisms from methanol, m.p. 239—242°, c.d. $[\theta]_{214}$ −16 000, δ ([$^2H_5$]pyridine) 1.00 (3 H, s), 1.06 (3 H, s), 1.09 (3 H, s), 1.22 (3 H, s), 1.25 (3 H, s), 1.37 (3 H, s), 3.27 (3 H, s), 3.45 (1 H, t, *J* 9 Hz, 3α-H), 3.66 (2 H, ABq, 28-H_2), 3.8—3.95 (2 H, m, 11β- and 21α-H), and 5.50 (1 H, d, *J* 3.5 Hz, 12-H) (Found: C, 74.25; H, 10.9. $C_{31}H_{52}O_4,0.5H_2O$ requires C, 74.8; H, 10.75%).

3β,28-*Diacetoxy*-11α-*methoxyolean*-12-*ene* (10).—13β,28-Epoxyolean-11-en-3β-ol (165 mg) was dissolved in 10% acetic acid in methanol (30 ml) and left for 6 h at room temperature. The solution was neutralized with 10% sodium carbonate and extracted with ethyl acetate. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel [benzene–ethyl acetate (1 : 1)] to afford starting material (50 mg) and 3β,28-dihydroxy-11α-methoxyolean-12-ene (57 mg). This oily compound was acetylated (acetic anhydride–pyridine) to afford 3β,28-diacetoxy-11α-methoxy-olean-12-ene (10) (28 mg), needles, m.p. 147—149° (from methanol), δ 0.88 (6 H, s), 0.91 (6 H, s), 1.00 (3 H, s), 1.07 (3 H, s), 1.25 (3 H, s), 2.05 (6 H, s, OAc × 2), 3.21 (3 H, s, OMe), 3.63, 3.75, 3.95, and 4.07 (2 H, ABq, 28-H_2), and 3.85 (1 H, dd, *J* 10 and 3 Hz, 11β-H) (Found: C, 75.2; H, 10.15. Calc. for $C_{35}H_{56}O_5$: C, 75.5; H, 10.15%).

Treatment of the Diacetate (10) *with Chromic Oxide–Pyridine*.—To a stirred solution of chromic oxide (15 mg) in pyridine (0.5 ml), a solution of the diacetate (10) (14 mg) in pyridine (0.5 ml) was added. The mixture was stirred for 2 h at room temperature. Water was added and the mixture was extracted with ether. The organic layer was washed with water, dried, and evaporated. The residue was identical with starting material (t.l.c. and n.m.r. spectrum).

Treatment of the Diacetate (10) *with Chromic Oxide–Pyridine followed by Acidic Hydrolysis*.—To a stirred solution of chromic oxide (30 mg) in pyridine (1 ml), a solution of the diacetate (10) (30 mg) in pyridine (1 ml) was added. The mixture was poured into water and extracted with n-butanol, and the extract was washed with water and evaporated. The residue was heated in sulphuric acid in dioxan at 110 °C for 30 min, then diluted with water and extracted with ether. The extract was evaporated and the residue was separated by preparative t.l.c. [benzene–acetone (10 : 1)] to afford 3β,28-*diacetoxyolean*-12-*en*-11-*one* (11) (10 mg), prisms, m.p. 200—203°, $[\alpha]_D$ +37° (*c* 0.40), $\nu_{max.}$ ($CHCl_3$) 1 720 and 1 655 cm^{-1}, $\lambda_{max.}$ 250 nm (ε 14 000), δ 0.86 (6 H, s), 0.90 (3 H, s), 1.11 (3 H, s), 1.13 (3 H, s), 2.03 (6 H, s, OAc × 2), 3.61, 3.73, 3.99, and 4.01 (2 H, ABq, 28-H_2), 4.49 (1 H, t, *J* 9 Hz, 3α-H), and 5.55 (1 H, s, 12-H) (Found: C, 75.3; H, 9.9. $C_{34}H_{52}O_5$ requires C, 75.5; H, 9.7%), and 3β,28-diacetoxyoleana-11,13(18)-diene (12) [9] (10 mg), prisms, m.p. 217—220°, $[\alpha]_D$ +91° (*c* 0.15), $\lambda_{max.}$ ($CHCl_3$) 243, 252 (ε 31 000), and 261 nm, δ 0.72 (3 H, s), 0.78 (3 H, s), 0.86 (6 H, s), 0.92 (3 H, s), 0.96 (3 H, s, 2.04 (6 H, s), 3.93, 4.04, 4.12, and 4.23 (2 H, ABq, 28-H_2), 4.50 (1 H, t, *J* 9 Hz, 3α-H), 5.57 (1 H, d, *J* 11 Hz, 11-H), and 6.40 (1 H, dd, *J* 11 and 3 Hz, 12-H) (Found: C, 77.6; H, 10.15. Calc. for $C_{34}H_{52}O_4$: C, 77.8; H, 10.0%).

Treatment of the Glycoside (1) *with Chromic Oxide–Sulphuric Acid*.—A mixture of papyrioside L-IIa (40 mg) and chromic oxide (20 mg) in dioxan (4 ml), 2N-sulphuric acid (8 ml), and water (4 ml) was refluxed for 30 min. After dilution with water, the mixture was extracted with ether, and the extract was evaporated. The residue was separated by preparative t.l.c. to give papyriogenin A (2) (3 mg) and 3,11,21-trioxo-olean-12-en-28-oic acid (4) (9 mg).

Per-O-*methylpapyrioside L-IIa* (13).—Papyrioside L-IIa (530 mg) was methylated in dimethylformamide (6 ml) with silver oxide (2 g) and methyl iodide (6 ml) for 72 h according to the Kuhn method. The precipitate was filtered off, and the filtrate was diluted with water and extracted with chloroform. The residue was then passed through a silica gel column [hexane–ethyl acetate (1 : 1)] to give *per*-O-*methylpapyrioside L-IIa* (13) (390 mg), white powder, m.p. 110—113°, $[\alpha]_D$ −49° (*c* 0.82) (Found: C, 63.35; H, 8.9. $C_{58}H_{94}O_{19}$ requires C, 63.6; H, 8.65%).

Methanolysis of Per-O-*methylpapyrioside L-IIa* (13).—Compound (13) was refluxed in methanolic 5% hydrochloric acid for 3 h. The mixture was neutralized with silver carbonate, filtered, and evaporated. The residue was examined by g.l.c. [10% DEGS on Chromosorb W (60—80 mesh)]; three methylated sugars were detected and

identified as methyl pyranosides of 2,3,4-tri-*O*-methylrhamnose and 2,3,4-tri-*O*-methyl- and 2,3,6-tri-*O*-methylglucose by comparison with synthetic samples.

Reduction of the Permethylated Derivative (13) *with Lithium Aluminium Hydride*.—A solution of compound (13) (100 mg) and $LiAlH_4$ (50 mg) in tetrahydrofuran (10 ml) was refluxed for 3 h. The excess of reagent was decomposed with water and the mixture was acidified with 2N-sulphuric acid (to dissolve the white precipitate) and extracted with ether and then chloroform. Evaporation of the chloroform layer gave, as a syrup, 2,3,4-tri-*O*-methyl-α-L-rhamnopyranosyl-(1 ⟶ 4)-2,3,4-tri-*O*-methyl-β-D-glycopyranosyl-(1 ⟶ 4)-2,3,4-tri-*O*-methyl-β-D-glucopyranosyl-(1 ⟶ 6)-2,3,4-tri-*O*-methyl-D-sorbitol (14) (44 mg), $[\alpha]_D$ −33° (*c* 0.88), *m/e* 616 (M^+, $C_{27}H_{52}O_{15}^+$) and 189 ($C_9H_{17}O_4^+$), δ 1.28 (3 H, d, *J* 7 Hz, 6-CH_3 of rhamnose), 4.31 (1 H, d, *J* 7 Hz, anomeric proton of glucose), and 4.93 (1 H, s, anomeric proton of rhamnose).

Methanolysis of the Trisaccharide (14).—Compound (14) was methanolysed as for compound (13). Methyl pyranosides of 2,3,4-tri-*O*-methylrhamnose and 2,3,6-tri-*O*-methylglucose were detected on g.l.c.

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