Further Studies on Glycosides from the Leaves of *Tetrapanax papyriferum*

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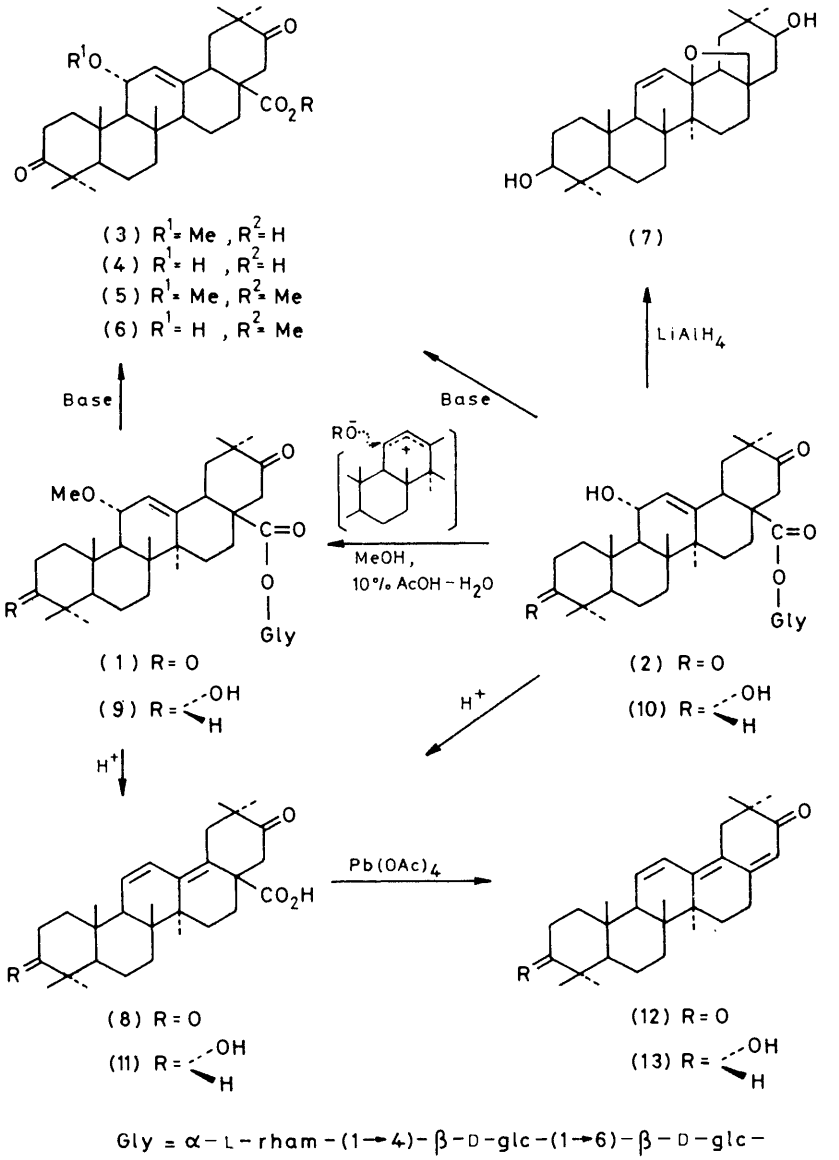
Papyrioside L-IIc, a glycoside from *Tetrapanax papyriferum*, was identified as 11α-hydroxy-3,21-dioxo-olean-12-en-28-oyl α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside (2). The previously described papyrioside L-IIa (1) is an artifact, produced from (2) during the extraction with methanol. The minor glycosides L-IIb and L-IId were assigned as 3α-hydroxy-11α-methoxy-21-oxo-olean-12-en-28-oyl and 3α,11α-dihydroxy-21-oxo-olean-12-en-28-oyl α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside [(9) and (10) respectively] by a ^{13}C n.m.r. analysis.

In the previous paper,[1] we described the isolation and structural elucidation of papyrioside L-IIa (1), isolated from the methanolic extracts of the leaves of *Tetrapanax papyriferum* (Araliaceae). This paper reports studies on several new glycosides from the same source.

The major glycoside fraction (L-II) was repeatedly chromatographed on silica gel to afford two major glycosides, papyrioside L-IIa (1) and L-IIc (2), and two minor glycosides, papyrioside L-IIb (9) and L-IId (10).



Structure of Papyrioside L-IIc (2).—The glycoside (1) was hydrolysed with 1% aqueous sodium hydroxide to yield the parent sapogenin, propapyriogenin A_1 (3). Propapyriogenin A_1 (3), $C_{31}H_{46}O_5$, exhibits a strong broad absorption at 1 700 cm^{-1} in the i.r. spectrum, no u.v. absorption above 210 nm, ^1H n.m.r. signals for an olefinic proton at δ 5.62 (d, *J* 4 Hz), methoxy-protons at δ 3.27, and an 11β proton geminal to 11α-OMe at δ 3.90 (dd, *J* 8 and 4 Hz), and a negative Cotton effect ($[\theta]_{224}$ — 9 900), supporting the structure (3), 11α-methoxy-3,21-dioxo-olean-12-en-28-oic acid, for propapyriogenin A_1. On the other hand, papyrioside L-IIc (2) was treated in the same manner to afford propapyriogenin A_2 (4). Propapyriogenin A_2 (4), $C_{30}H_{44}O_5$, exhibits similar i.r. and u.v. spectra to those of (3), an olefinic proton at δ 5.86 (d, *J* 4 Hz), a proton geminal to the hydroxy-group at δ 4.50 (dd, *J* 8 and 4 Hz), and no -OMe protons in the ^1H n.m.r. spectrum, and a negative Cotton effect ($[\theta]_{223}$ — 7 300). These spectral data suggested the presence of the 11α-hydroxy-group and we have assigned structure (4), 11α-hydroxy-3,21-dioxo-olean-12-en-28-oic acid, for propapyriogenin A_2. Furthermore, basic hydrolysis of glycosides (1) and (2) in methanol gave the methyl esters (5) and (6), respectively ($\nu_{max.}$ 1 733 cm^{-1}). Reduction of compound (2) with $LiAlH_4$ gave a complex mixture of triterpenes, from which only one compound (7), $C_{30}H_{48}O_3$, was isolated in a crystalline form in *ca.* 20% yield. This compound was assigned structure (7) on the basis of its ^1H n.m.r. spectrum,[2] [δ 3.50 (dd, *J* 10 and 7 Hz, 3α-H), 5.64 (dd, *J* 10 and 3 Hz, 12-H), 6.00 (d, *J* 1p Hz, 11-H), 3.83 (dd, *J* 11 and 6 Hz, 21α-H), and 3.43 and 3.74 (2 H, ABq, *J* 7 Hz, 28-H_2)].

In contrast, reduction of (1) gave two major crystalline compounds containing an 11-OMe group.[1] These experiments show that under the reaction conditions, the allylic hydroxy-group at C-11 is probably converted into an aluminate salt, which would be the effective leaving group. Acidic hydrolysis of the glycoside (2) gave papyriogenin A (8),[3,*] and D-glucose and L-rhamnose as sugar components (molar ratio 2 : 1), suggesting the structural similarity of (2) to (1). The final structural identification of (2) was carried out by a ^{13}C n.m.r. study of (1) and (2). The ^{13}C n.m.r. signals of the sugar moieties were almost identical for the two compounds; the assignments are summarized in the Table and show the considerable differences in chemical shifts around C-11. Consequently, papyrioside L-IIc is identified as 11α-hydroxy-3,21-dioxo-olean-12-en-28-oyl α-L-rhamnopyranosyl-(1 ⟶ 4)-β-D-glucopyranosyl-(1 ⟶ 6)-β-D-glucopyranoside (2).

This evidence strongly suggested that (1) might be an artifact derived from (2) during the extraction procedure with methanol.[4] To prove this, fresh leaves were extracted with ethanol following the same procedure to give a very small amount of ethoxylated glycoside and (2) as the major glycoside. A kinetic study was also carried out. Compound (2) was left in methanol with 10% aqueous acetic acid to give 50% † of (1) after 2 h and 100% after 2 days. On the other hand, if (2) was left in ethanol with 10% aqueous acetic acid, only 10% of the 11α-ethoxy-compound was obtained after 2 h and 50% after 2 days. This may be explained by the fact that methanolic acetic acid is more polar than ethanolic acetic acid, and being more acidic, may lead to a faster rate for the formation of an allylic cation as a rate-controlling step.

^{13}C Chemical shifts (δ in p.p.m. from Me_4Si; solvent C_5D_5N) [a]

	(1)	(2)	(9)	(10)
C-1	34.7	34.7	34.6	34.7
2	40.5	41.6	26.5	26.5
3	216.1	216.5	75.3	75.2
4	47.7	47.8	38.8	38.9
5	55.6	55.8	49.2	49.4
6	19.9	20.0	19.2	19.0
7	32.9	33.3	30.0	33.3
8	38.1	38.1	38.1	38.1
9	52.1	55.0	53.2	56.4
10	43.1	43.2	43.6	43.8
11	76.1	66.9	76.0	66.6
12	123.8	129.5	123.5	129.3
13	146.1	142.9	146.5	143.3
14	42.1	42.1	42.1	42.0
15	28.2	28.0	28.2	28.2
16	25.4	25.6	25.4	25.8
17	45.4	45.3	45.5	45.3
18	40.9	40.8	40.8	40.6
19	46.2	46.2	46.3	46.3
20	50.8	50.8	50.9	50.9
21	211.9	212.0	212.0	212.1
22	47.2	46.7	47.8	47.8
23	26.6	26.7	29.6	29.5
24	21.6	21.6	22.8	22.8
25	16.5	16.3	17.4	17.1
26	18.8	18.7	18.8	18.7
27	25.4	25.6	25.4	25.8
28	173.9	173.9	174.0	174.0
29	24.6	24.5	24.7	24.6
30	25.1	25.2	25.1	25.0
-OMe	54.4		54.4	
1	96.1	96.1	96.1	96.1
2	73.8	73.8	73.9	73.9
Glc. 3	78.4	78.4	78.5	78.4
4	70.7	70.7	70.7	70.9
5	76.1	76.4	76.4	76.4
6	69.4	69.3	69.4	69.4
1	105.0	104.8	105.0	104.9
2	75.2	75.2	75.3	75.2
Glc. 3	76.4	76.4	76.4	76.4
4	78.4	78.0	78.0	78.0
5	77.1	77.1	77.1	77.1
6	61.3	61.2	61.1	61.4
1	102.7	102.7	102.7	102.7
2	72.4	72.6	72.5	72.5
Rham 3	72.4	72.6	72.5	72.5
4	73.8	73.8	73.9	73.9
5	70.3	70.2	70.4	70.3
6	18.4	18.4	18.5	18.4

[a] Measured at 25 °C with a JEOL JNM-PFT 100 spectrometer at 25.15 MHz; computer-limited resolution ±0.10 p.p.m.

Structures of the minor Glycosides, Papyrioside L-IIb (9) *and L-IId* (10).—The glycosides (9) and (10) were separated in *ca.* 90% purity by chromatography on silica gel; pure compounds were obtained by repeated h.p.l.c. using a Zorbax ODS column. The glycosides exhibit similar spectroscopic properties to those of (1)

* In a previous paper,[1] we reported the $[\alpha]_D$ value of papyriogenin A to be −11.3; this value should be −113.0.

† Ratios of two compounds were determined on t.l.c. with a t.l.c. scanner (Shimadzu CS-900).

and (2), but with slight differences in the carbonyl region of the i.r. spectrum. Acidic hydrolysis of the minor pair gave a new triterpene, papyriogenin C (11), and D-glucose and L-rhamnose as sugar components (molar ratio 2 : 1). Papyriogenin C, $C_{30}H_{44}O_4$, is assigned structure (11) on the following evidence. Treatment of (8) with lead tetra-acetate [5] gave a pale yellow compound (12), $C_{29}H_{40}O_2$, which showed no carboxylic absorption in the i.r. spectrum [checked by addition of $NHEt_2$], a strong u.v. absorption at 338 nm (conjugated triene ketone system), a newly observed olefinic singlet at δ 5.60 in the ^{1}H n.m.r. spectrum, and a parent peak at *m/e* 420 in the mass spectrum. From these data, the structure of the oxidation product was determined to be 28-noroleana-11,13(18),17(22)-triene-3,21-dione (12), obtained by the oxidative decarboxylation of (8). A similar reaction was observed when papyriogenin C (11) was treated with lead tetra-acetate to give a compound (13). Compound (13), $C_{29}H_{42}O_2$, exhibits a strong u.v. absorption at 340 nm and an olefinic singlet at δ 5.61 and an extra H–C(–OH)– proton at δ 3.44 [br s, $W_{\frac{1}{2}}$ 6 Hz; shifted to δ 4.62 (br s, $W_{\frac{1}{2}}$ 6 Hz) by acetylation] in the ^{1}H n.m.r. spectrum. From these data, the structure of (13) was determined to be 3α-hydroxy-28-noroleana-11,13(18),17(22)-trien-21-one. On the other hand, oxidation of the methyl ester of (11) with chromic oxide–pyridine gave the methyl ester of (8), suggesting the presence of the 3-OH group in compound (11), and the coupling feature of the signal assigned to the proton on C-3 indicated the axial configuration (α) of the hydroxy-group. Thus the structure of papyriogenin C (11) was determined to be 3α-hydroxy-21-oxo-oleana-11,13(18)-dien-28-oic acid. These data suggested that the carbonyl group in the major glycosides was replaced by the hydroxy-group in the minor glycosides. To confirm this conclusion and to determine the total structures of (9) and (11), ^{13}C n.m.r. spectra of the four glycosides were recorded and assigned. ^{13}C N.m.r. signals for the carbonyl carbons at C-3 [δ 216.1 (1) and 216.5 (2)] were shifted to high field [δ 75.3 (9) and 75.2 (10)] and a complete similarity of the sugar moieties was observed. Consequently, papyriosides L-IIb (9) and L-IId (10) were identified as 3α-hydroxy-11α-methoxy-21-oxo-olean-12-en-28-oyl and 3α,11α-dihydroxy-21-oxo-olean-12-en-28-oyl α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside, respectively. The glycoside (9) may be an artifact of (10).

EXPERIMENTAL

M.p.s were measured with a Yamagimoto micro-apparatus. Unless otherwise stated, u.v. spectra were recorded for solutions in ethanol, optical rotations for solutions in ethanol, c.d. data for solutions in methanol, i.r. spectra for KBr discs, and n.m.r. spectra for solutions in deuteriochloroform.

Isolation of Papyrioside-L-IIb (9), *L-IIc* (2), *and L-IId* (10).—In a previous paper,[1] we described the isolation of papyrioside L-IIa (1) from the dried leaves of *Tetrapanax papyriferum* (1 kg). In the same way, papyrioside L-IIc (2) (2.86 g) was obtained as a white powder, together with crude papyrioside L-IIb (9) (154 mg) and papyrioside L-IId (10) (449 mg). L-IIb (9) and L-IId (10) were rechromatographed on silica gel [solvent, lower layer of $CHCl_3$–MeOH–H_2O (70 : 23 : 7)] to afford L-IIb (9) (86.4 mg) and L-IId (10) (48.6 mg) in *ca.* 90% purity (^{13}C n.m.r.). Samples for analysis were obtained by h.p.l.c. [Shimadzu LC-2 instrument; Zorbax ODS (2.1 mm × 25 cm) column; mobile phase, methanol–water (6 : 4); temperature, ambient; flow rate: 0.2 ml min^{-1}; pressure, 215 kg cm^{-2}; detector, Shimadzu SPD-1; u.v., 215 nm].

Papyrioside L-IIc (2) had m.p. 188—191°; $[\alpha]_D$ −47.1° (*c* 0.10); c.d. $[\theta]_{225}$ − 3 600; δ[$CDCl_3$–CD_3OD (1 : 1) + CF_3CO_2H] 5.67 (1 H, d, *J* 4 Hz, 12-H), 5.44 (1 H, d, *J* 7 Hz, anomeric proton of ester glycoside glucose), 4.88 (1 H, s, anomeric proton of rhamnose), and 4.35 (1 H, d, *J* 8 Hz, anomeric proton of glucose) (Found: C, 57.9; H, 7.6. $C_{48}H_{74}O_{19}$,$2H_2O$ requires C, 58.15; H, 7.9%).

Papyrioside L-IIb (9) had m.p. 178—182°; $[\alpha]_D$ −37.8° (*c* 0.27); c.d. $[\theta]_{221}$ − 4 200; $\nu_{max.}$ 3 400, 2 920, 1 735, 1 698, 1 630, and 1 070 cm^{-1}; δ[$CDCl_3$–CD_3OD (2.5 : 1)] 5.62 (1 H, d, *J* 4 Hz, olefinic 12-H), 5.43 (1 H, d, *J* 7 Hz, anomeric proton of ester glycoside glucose), 4.88 (1 H, s, anomeric proton of rhamnose), 4.33 (1 H, d, *J* 7 Hz, anomeric proton of glucose), and 3.26 (3 H, s, 11α-OMe) (Found: C, 57.7; H, 8.1. $C_{49}H_{78}O_{19}$,$3H_2O$ requires C, 57.4; H, 8.25%).

Papyrioside L-IId (10) had m.p. 185—190°; $[\alpha]_D$ −39.3° (*c* 0.15); c.d. $[\theta]_{222}$ − 1 700; $\nu_{max.}$ 3 400, 2 920, 1 740, 1 700, 1 640, and 1 065 cm^{-1}; δ[$CDCl_3$–CD_3OD (2.5 : 1)] 5.45br (2 H, s, olefinic 12-H and anomeric proton of ester glycoside glucose) and 4.89 (1 H, s, anomeric proton of rhamnose) (Found: C, 56.2; H, 8.1. $C_{48}H_{76}O_{19}\cdot 4H_2O$ requires C, 56.0; H, 8.25%).

Basic Hydrolysis of Papyrioside L-IIa (1) *and L-IIc* (2).—(*a*) L-IIa (1) (300 mg) was dissolved in 1% aqueous sodium hydroxide (10 ml) and the solution heated under reflux for 20 min. The solution was diluted with water, neutralized with acetic acid, and extracted with ether. The extract was evaporated and the residue crystallized from ether–benzene to afford *propapyriogenin* A_1 (3) (117 mg), m.p. 142—145°; $[\alpha]_D$ −30.0: (*c* 0.10); c.d. $[\theta]_{224}$ − 9 900; $\nu_{max.}$ 2 950 and 1 700br cm^{-1}; δ 8.50br (1 H, s, 28-COH), 5.62 (1 H, d, *J* 4 Hz, 12-H), 3.90 (1 H, dd, *J* 8 and 4 Hz, 11-H), 3.27 (3 H, s, 11α-OMe), 1.26 (3 H, s), 1.20 (3 H, s), 1.10 (3 H, s), 1.05 (3 H, s), 1.02 (6 H, s), and 0.82 (3 H, s) (Found: C, 72.0; H, 9.0. $C_{31}H_{46}O_5\cdot H_2O$ requires C, 72.05; H, 9.35%).

(*b*) L-IIc (2) (180 mg) was hydrolysed with 1% aqueous sodium hydroxide and worked up as in (*a*) to give *propapyriogenin* A_2 (4) (40 mg), m.p. 169—170°; $[\alpha]_D$ −20.0° (*c* 0.10); c.d. $[\theta]_{224}$ − 7 300; $\nu_{max.}$ 2 950 and 1 700br cm^{-1}; δ([$^2H_5$]pyridine) 6.75br (1 H, s, 28-CO_2H), 5.86 (1 H, d, *J* 4 Hz, 12-H), 4.50 (1 H, dd, *J* 8 and 4 Hz, 11-H), 3.68 (1 H, dd, *J* 13 and 5 Hz, 18-H), 1.32 (3 H, s), 1.22 (3 H, s), 1.16 (6 H, s), and 1.08 (9 H, s) (Found: C, 72.6; H, 8.65. $C_{30}H_{44}O_5\cdot 0.5H_2O$ requires C, 73.0; H, 9.1%).

(*c*) L-IIa (1) (500 mg) was dissolved in 2% aqueous sodium hydroxide in methanol (10 ml) and heated under reflux for 1 h. The solution was diluted with water, neutralized with acetic acid, and extracted with ether. The extract was evaporated and the residue was chromatographed on silica gel (solvent, $CHCl_3$–MeOH 100 : 1) to afford *methyl* 11α-*methoxy*-3,21-*dioxo-olean*-12-*en*-28-*oate* (5) (112 mg) as prisms, m.p. 82—84° (from ether–benzene);

c.d. $[\theta]_{223}$ − 9 800; $\nu_{max.}$ 1 733, 1 705sh, and 1 698 cm^{-1}; δ 5.66 (1 H, d, *J* 4 Hz, 12-H), 3.90 (1 H, dd, *J* 8 and 4 Hz, 11-H), 3.72 (3 H, s, 28-CO_2Me), 3.40 (1 H, dd, *J* 14 and 5 Hz, 18-H), 3.30 (3 H, s, 11α-OMe), 1.25 (3 H, s), 1.23 (3 H, s), 1.15 (3 H, s), 1.10 (3 H, s), 1.07 (6 H, s), and 0.82 (3 H, s) (Found: C, 74.8; H, 9.5. $C_{32}H_{48}O_5$ requires C, 75.0; H, 9.45%).

(*d*) L-IIc (2) (90 mg) was treated with 2% aqueous sodium hydroxide and worked up as in (*c*) to afford the methyl ester, *methyl* 11α-*hydroxy*-3,21-*dioxo-olean*-12-*en*-28-*oate* (6) (20 mg), as prisms, m.p. 85—90° (from ether–benzene); c.d. $[\theta]_{223}$ − 7 100; $\nu_{max.}$ 3 430, 1 733, 1 705, and 1 696 cm^{-1}; δ 5.52 (1 H, d, *J* 4 Hz, 12-H), 4.30 (1 H, dd, *J*8 and 4 Hz, 11-H), 3.71 (3 H, s, 28-CO_2Me), 3.36 (1 H, dd, *J* 14 and 5 Hz, 18-H), 1.28 (3 H, s), 1.23 (3 H, s), 1.18 (3 H, s), 1.10 (3 H, s), 1.07 (3 H, s), 1.03 (3 H, s), and 0.83 (3 H, s) (Found: C, 73.85; H, 9.45. $C_{31}H_{46}O_5 \cdot 0.5H_2O$ requires C, 73.35; H, 9.35%).

Reduction of Papyrioside L-IIc (2) *with Lithium Aluminium Hydride*.—A mixture of L-IIc (2) (500 mg) and $LiAlH_4$ (270 mg) in tetrahydrofuran (80 ml) was set aside overnight. Excess of the reagent was decomposed with water and the mixture was extracted with ether. The extract was dried (Na_2SO_4) and evaporated, and the residue (70 mg) was chromatographed on silica gel [benzene–ethyl acetate (1 : 1) as eluant] to afford 13β,28-*epoxy*-3β,21β-*dihydroxyolean*-11-*ene* (7), m.p. 255—257° (Found: C, 75.35; H, 10.65. $C_{30}H_{48}O_3,H_2O$ requires C, 75.95; H, 10.55%). The diacetate crystallised from methanol as prisms, m.p. 258—262°; $\nu_{max.}$ 2 940 and 1 755 cm^{-1}; δ 5.88 (1 H, d, *J* 10 Hz, 11-H), 5.40 (1 H, dd, *J* 10 and 3 Hz, 12-H), 4.87 (1 H, dd, *J* 11 and 6 Hz, 21α-H), 4.50 (1 H, dd, *J* 10 and 7 Hz, 3α-H), 3.71, 3.32 (2 H, AB q, *J* 7 Hz, 28-H_2), 2.05 (9 H, s, OAc), 1.09 (3 H, s), 0.94 (12 H, s), and 0.86 (6 H, s), (Found: C, 74.55; H, 9.7. $C_{34}H_{52}O_5 \cdot 0.5H_2O$ requires C, 74.3; H, 9.65%).

Acidic Hydrolysis of Papyrioside L-IIc (2), *L-IIb* (9), *and L-IId* (10).—(*a*) L-IIc (2) (10 mg) was dissolved in dioxan (1 ml), 2N-sulphuric acid (2 ml), and water (1 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 (4 mg) was crystallized with aqueous methanol to afford papyriogenin A (8). The aqueous layer of the hydrolysate was neutralized with ion-exchange resin (IR-45) and evaporated. Trimethylsilylation followed by g.l.c. [2% OV-1 on Chromosorb W (60—80 mesh)] showed the presence of D-glucose and L-rhamnose (molar ratio 2 : 1).

(*b*) L-IIb (9) (6 mg) was hydrolysed and worked up as in (*a*) to give papyriogenin C (11) (2 mg) and D-glucose and L-rhamnose as sugar components (molar ratio 2 : 1). *Papyriogenin C* (11) was obtained from methanol–water as prisms, m.p. 230—231°; $[\alpha]_D$ −188.4° (*c* 0.064); c.d. $[\theta]_{275}$ − 12 500; $\lambda_{max.}$ 243sh and 252 mn (ε 15 000); $\nu_{max.}$ 3 440, 1 725, 1 710, and 1 630 cm^{-1}; *m/e* 468 (M^+), 450, and 422; δ 6.46 (1 H, dd, *J* 10 and 3 Hz, 12-H), 5.78 (1 H, d, *J* 11 Hz, 11-H), 3.46br (1 H, s, $W_{\frac{1}{2}}$ 6 Hz, 3-H), 1.11 (3 H, s), 1.07 (3 H, s), 1.05 (3 H, s), 0.97 (3 H, s), 0.95 (3 H, s), 0.86 (3 H, s), and 0.80 (3 H, s) (Found: C, 76.7; H, 9.4. $C_{30}H_{44}O_4$ requires C, 76.9; H, 9.45%).

(*c*) L-IId (10) (24 mg) was hydrolysed and worked up as in (*a*) to give papyriogenin C (11) (8.5 mg) and D-glucose and L-rhamnose as sugar components (molar ratio 2 : 1).

Oxidative Decarboxylation of Papyriogenin A (8) *and Papyriogenin C* (11).—(*a*) Papyriogenin A (8) (200 mg) and lead tetra-acetate (1.0 g) were dissolved in benzene (50 ml) and refluxed under nitrogen. After 2 min, the red solution decolourized, and after 20 min, the mixture was poured into aqueous ferrous sulphate and extracted with ether; the ether layer was washed with water, aqueous sodium carbonate, and water, dried (Na_2SO_4), and concentrated. The residue (165 mg) was chromatographed on silica gel (solvent, benzene–acetone (40 : 1) to afford pure 28-*noroleana*-11,13(18),17(22)-*triene*-2,31-*dione* (12) (125 mg), m.p. 127—131°; $\nu_{max.}$ 2 920, 2 850, 1 702, 1 630, and 1 605 cm^{-1}; $\lambda_{max.}$ 338 nm (ε 1.7 × 10^4); δ 6.56 (1 H, dd, *J* 10 and 3 Hz, 12-H), 5.98 (1 H, d, *J* 10 Hz, 11-H), 5.61 (1 H, s, 22-H), 1.12 (6 H, s), 1.07 (9 H, s), 1.03 (3 H, s), and 0.85 (3 H, s); (*m/e*) 420 (M^+) (Found: C, 81.1; H, 9.45. $C_{29}H_{40}O_2 \cdot 0.5H_2O$ requires C, 81.1; H, 9.6%).

(*b*) Papyriogenin C (11) (8.2 mg) was treated and worked up as in (*a*) to give 3α-*hydroxy*-28-*norolean*-11,13(18),-17(22)-*trien*-21-*one* (13) (6.7 mg), m.p. 255—257°; $\lambda_{max.}$ 340 nm (ε 45 800); $\nu_{max.}$ 3 450, 2 940, 2 550, 1 655sh, 1 647, 1 590, and 1 580 cm^{-1}; *m/e* 422 (M^+) and 404; δ 6.50 (1 H, dd, *J* 10 and 3 Hz, 12-H), 6.01 (1 H, d, *J* 10 Hz, 11-H), 5.61 (1 H, s, 22-H), 3.44br (1 H, s, $W_{1/2}$ 6 Hz, 3-H), 1.12 (3 H, s), 1.06 (3 H, s), 1.03 (3 H, s), 0.98 (3 H, s), 0.95 (3 H, s), 0.86 (3 H, s), and 0.80 (3 H, s) (Found: C, 82.35; H, 10.0. $C_{29}H_{42}O_2$ requires C, 82.4; H, 10.0%).

Treatment of Papyriogenin C (11) *with Chromic Oxide–Pyridine*.—Papyriogenin C (11) (20 mg) in methanol was methylated with diazomethane in ether. To a stirred solution of chromic oxide (0.8 g) in pyridine (5 ml), the methyl ester in pyridine was added. The mixture was stirred for 2 h at room temperature, then diluted with water and extracted with ether. The organic layer was washed with water and evaporated. The residue (8.8 mg) was crystallized from methanol to give the *methyl ester* (1.9 mg) of papyriogenin A (8) as prisms, m.p. 165—167°; $\nu_{max.}$ 2 950, 2 860, 1 728, 1 708, and 1 630 cm^{-1}; δ 6.52 (1 H, dd, *J* 11 and 2 Hz, 12-H), 5.74 (1 H, d, *J* 11 Hz, 11-H), and 3.68 (3 H, s) (Found: C, 77.2; H, 9.05. $C_{31}H_{46}O_4$ requires C, 77.45; H, 9.9%).

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