Selective Oxidation of Oleanane Triterpenoids

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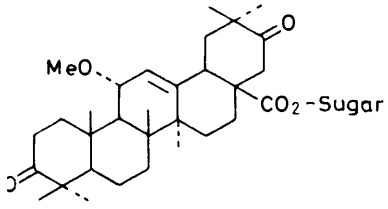
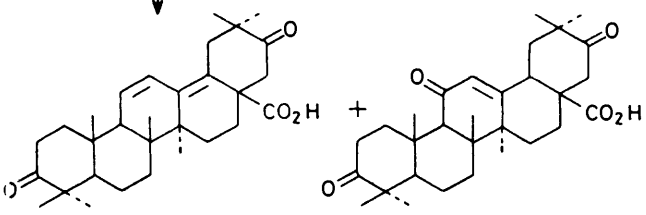
Reagent A (exact composition unknown) was obtained from a mixture of CrO_3, pyridine, and Bu^nOH saturated with water. The reaction of the oleanane triterpenoid glycosides (1), (4), and (5) with reagent A gave 11-oxo-compounds (3) and (6), which indicated that this reagent is useful for the oxidation of an allyl alcohol and an allyl ether. On the other hand, the reaction of oleanane triterpenoids (11), (13), (14), and (15) with reagent A gave 16-oxo-derivatives (9), (16), (17), and (18), while compounds (19) and (22) with this reagent gave 21-oxo-derivatives (24) and (25). Reagent A is also very useful for the selective oxidation of 16- and 21-axial hydroxy-groups.

A PREVIOUS paper of ours [1] has described the oxidation of the glycoside (1) with chromium trioxide–pyridine followed by acidic hydrolysis to give the diene (2) and 3,11,21-trioxo-olean-12-en-28-oic acid (3). It seemed strange that the methoxy-group was oxidized to a carbonyl group by chromic trioxide–pyridine. However a model



Papyrioside L-IIa
(1)



Papyriogenin A
(2)

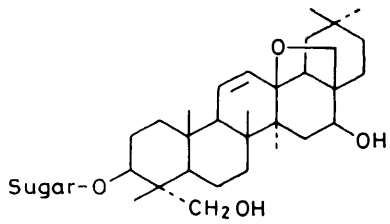
(3)

experiment revealed the formation of the carbonyl group during the acidic treatment of the n-butanolic extract of the reaction mixture. This paper describes the preparation of the reagent A, suggested by the above results, and its application to some oleanane triterpenoids.

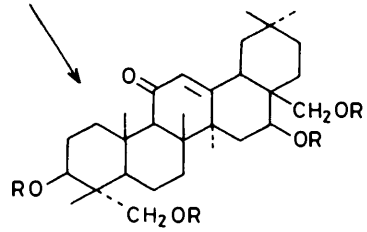
RESULTS AND DISCUSSION

Preparation of Reagent A.—A mixture of CrO_3, pyridine and Bu^nOH saturated with water were kept at room temperature for a day. The mixture was concentrated under reduced pressure and the resultant precipitate was filtered off, washed with water and $CHCl_3$, and dried under reduced pressure to afford a brown powder, termed reagent A.

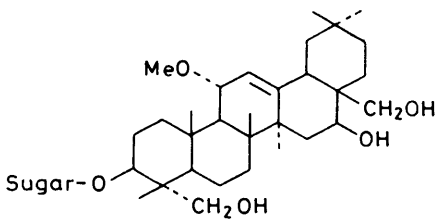
Some Reactions on the Oleanane Triterpenoids.—The reaction of the glycoside (1) with reagent A followed by acidic treatment gave the diene (2) and 3,11,21-trioxo-olean-12-en-28-oic acid (3). On the other hand, the reaction of saikosaponin a (4) [2] and b_3 (5) [3] with an allyl ether group with reagent A gave the same 11-keto-derivative (6), the structure of which was determined on the basis of its ^1H n.m.r. spectrum [δ 5.56 (1 H, s, 12-H)]. From these experiments, reagent A was found to be useful for the oxidation of an allyl alcohol or an allyl



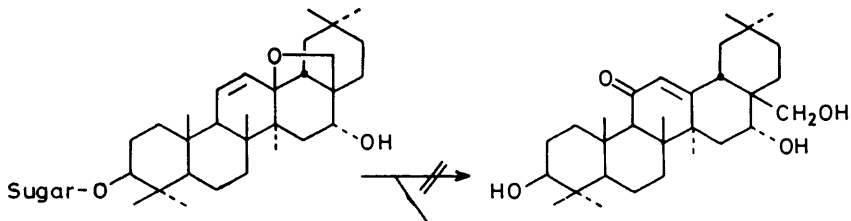
Saikosaponin a
(4)



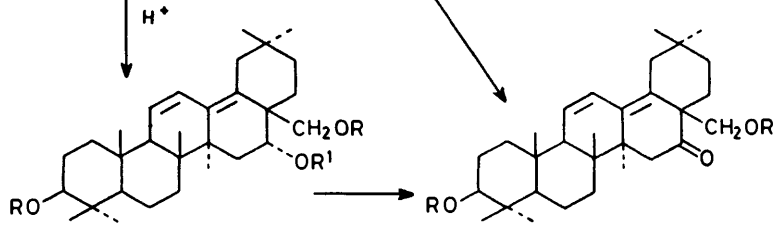
(6) R = H
(6a) R = Ac



Saikosaponin b_3
(5)



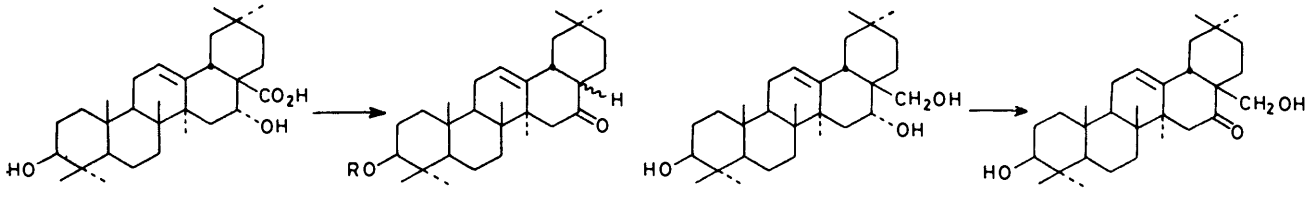
Rotundioside F (7) (8)



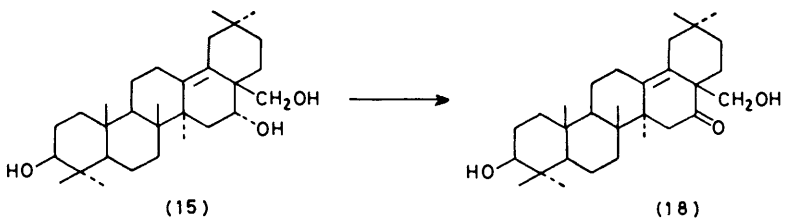
Rotundiogenin B

(11) R = R1 = H
(11a) R = R1 = Ac
(12) R = Ac, R1 = H

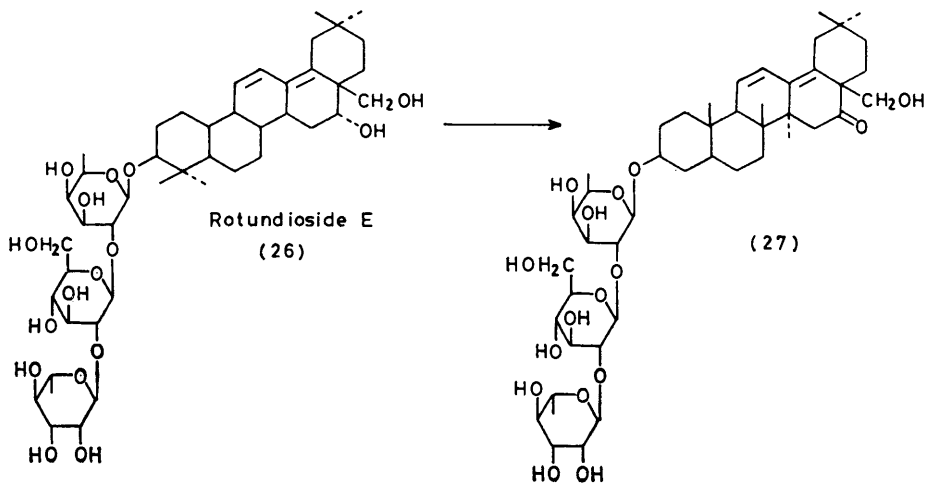
(9) R = H
(10) R = Ac



(13) (16) R = H
(16a) R = Ac
(14) (17)

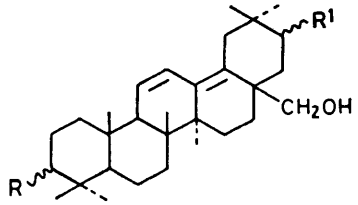


(15) (18)

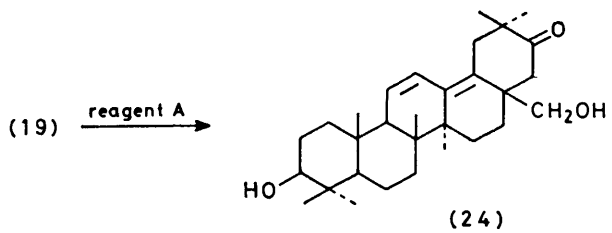


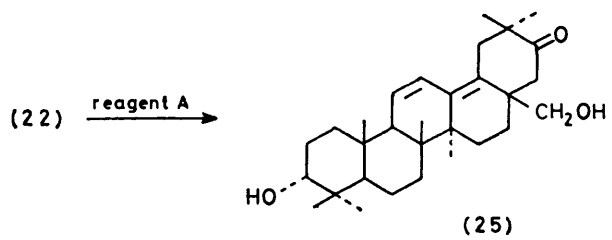
Rotundioside E (26) (27)

ether group to an αβ-unsaturated ketone without affecting the other hydroxy-groups. Rotundioside F (7) [4] (isolated from the leaves of *Bupleurum rotundifolium* L.), which has an allyl ether group, when treated with reagent A gave not the expected 11-oxo-olean-12-en-3β,16α,28-triol (8) but the 16-oxo-oleana-11,13(18)-diene-3β,28-diol (9). The structure (9) was deduced from the following chemical and spectroscopic evidence. Compound (9), $C_{30}H_{46}O_3$, exhibits a broad OH absorption and sharp band at 1 688 cm^{-1}, indicative of a carbonyl group, in the i.r. spectrum, and ^1H n.m.r. signals for two olefinic protons (AB quartet, δ 5.71 and 6.50, *J* 11 Hz) on a disubstituted double bond and three easily identified protons next to oxygens (3α-H: δ 3.22, dd, *J* 9 and 8 Hz; 28-CH_2: δ 3.63 and 3.95, AB quartet, *J* 11 Hz). Compound (9) was then treated with acetic anhydride–pyridine to give the diacetate (10),[5] which was identified by comparison with an authentic sample prepared from rotundiogenin B (11) [4] *via* rotundiogenin B diacetate (12). It is interesting that the selective oxidation of the 16α-hydroxy-group (axial) was achieved without affecting the other hydroxy-groups. The reaction of other oleanane triterpenoids with 16α-hydroxy-group, *i.e.* compounds (11), (13), (14), and (15), with reagent A were then examined [solvent, dioxan–2N-H_2SO_4 (1 : 1); reflux for 30 min]. Rotundiogenin B (11) gave a 90% yield of 16-oxo-oleana-11,13(18)-diene-3β,28-diol (9) as a single product. Echinocystic acid (13), isolated from the fresh leaves of *Bupleurum rotundifolium* L., reacted with reagent A to afford a mixture of two stereoisomeric 16-keto-derivatives (16), which were isomeric at C-17 based on g.l.c. analysis of the acetates (16a) [6] (α : β = 1 : 3). Primulagenin A (14), derived from echinocystic acid (13), was treated with reagent A to give the 16-keto-derivative (17) only. The dihydro-rotundiogenin B (15), derived by catalytic reduction of rotundiogenin B (11), was treated with reagent A to give an 85% yield of 16-oxo-olean-13(18)-ene-3β,28-diol (18) as a single product. Thus the 16α-hydroxy-group (axial) is selectively oxidized to a ketone function in some oleanane triterpenoids. On the other hand, when the known papyriogenin A (2) and C (21) were reduced with lithium aluminium hydride,[7] compounds (19) and (20) [3β,21β,28- and 3β,21α,28-trihydroxyoleana-11,13(18)-diene] were obtained from (2) and compounds (22) and (23) [3α,21β,28- and 3α,21α,28-trihydroxyoleana-11,13(18)-diene] were obtained from (21). Compounds (19) and (22) have a 21α-axial hydroxy-group, compounds (22) and (23) a 3α-axial hydroxy-group. The reaction of reagent A with compounds (19), (20), (22), and (23) was then examined to clarify the selective oxidation of axial hydroxy-groups at C-3 and C-21. Reagent A with compounds (19) and (22) gave 21-oxo-derivatives (24) and (25), but compounds (20) and (23) were recovered unchanged. The structures of the 21-oxo-derivatives (24) and (25) were assigned on the basis of ^1H n.m.r. analysis. This indicated that reagent A was also useful for the selective oxidation of a 21-axial-hydroxy-group. The selective oxidation of the 16- and 21-axial hydroxy-groups with reagent A seems to be influenced by the presence of a C-28 hydroxy-group. To a solution of rotundioside E (26) [4] in dioxan–2N-H_2SO_4 was added reagent A and the total mixture was stirred at room temperature for 15 h. This reaction gave a 79% yield of the 28-hydroxy-16-oxo-oleana-11,13(18)-dien-3β-yl α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl-(1→2)-β-D-fucopyranoside (27), the structure of which was confirmed mainly by ^{13}C n.m.r. analysis. The ^{13}C n.m.r. signal for C-16 at δ 67.7 of compound (26) shifted to low field [δ 214.8 in (27)] due to carbonyl formation and a complete identity in the sugar moieties of both compounds was observed. The signal assignments were fairly straightforward by comparison of its ^{13}C n.m.r. spectrum with that of the mother compound (9) and literature data of saikogenins [8,9] (Table).



	R	R1
(2)	=O	=O
(21)	---OH(ax)	=O
(19)	—OH(eq)	—OH(ax)
(20)	—OH(eq)	---OH(eq)
(22)	---OH(ax)	—OH(ax)
(23)	---OH(ax)	---OH(eq)





(20) reagent A → recovery

(23) reagent A → recovery

^{13}C *Chemical* shifts (δ from $SiMe_4$; solvent C_5D_5N)

	(11) [a]	(11a)	(26) [a]	(27)	(9)	(10)
C-1	39.0 [b]	(37.9)	39.1 [b]	38.4 [b]	38.5 [b]	(37.9)
2	28.1	(23.4)	26.6	26.4	27.9	(23.4)
3	78.0	(80.7)	89.6	89.3	77.9	(80.6)
4	39.5	(37.9)	39.9	39.7	39.4	(37.9)
5	55.4	(55.0)	55.6	54.2	54.3	(54.8)
6	18.9	(18.2)	18.9	18.4	18.6	(18.1)
7	32.6 [c]	(32.2)	32.6 [c]	32.8	32.8	(32.1)
8	41.1 [d]	(41.0)	41.1 [d]	40.2	40.3	(40.0)
9	53.9	(53.4)	53.9	53.8	54.0	(53.4)
10	37.0	(36.5)	36.6	36.6	37.0	(36.6)
11	126.2	(126.9)	126.2	127.5	127.5	(127.6)
12	126.2	(125.3)	126.2	124.8	124.9	(124.5)
13	136.1	(136.8)	136.0	136.5	136.6	(136.6)
14	41.9 [d]	(41.4)	41.9 [d]	47.3	47.3	(46.9)
15	31.9 [c]	(28.7)	31.9 [c]	45.6	45.7	(44.7)
16	67.7	(71.1)	67.7	214.8	214.7	(213.9)
17	45.3	(40.9)	45.3	55.1	55.0	(50.8)
18	133.1	(129.3)	133.1	133.3	133.4	(131.2)
19	38.6 [b]	(38.3)	38.5 [b]	38.2 [b]	38.2 [b]	(37.9)
20	32.6	(32.2)	32.6	33.4	33.4	(33.5)
21	35.5	(34.4)	35.6	35.2	35.2	(34.9)
22	24.5	(24.3)	24.5	27.4	27.4	(27.2)
23	28.5	(27.8)	28.2	28.0	28.5	(27.8)
24	16.0	(16.1)	16.3	16.2	16.0	(16.2)
25	18.4 [e]	(18.2)	18.3 [e]	18.0 [e]	18.1 [e]	(18.0)
26	17.3 [e]	(16.9)	17.4 [e]	17.1 [e]	17.2 [e]	(17.0)
27	21.9	(20.9)	21.8	22.0	22.1	(21.8)
28	64.7	(65.4)	64.8	65.8	65.8	(65.9)
29	25.1	(24.6)	25.1	24.0	24.0	(23.8)
30	32.6	(32.2)	32.6	32.2	32.2	(32.5)
Fucose 1			105.3	105.1		
Fucose 2			78.0	78.0		
Fucose 3			76.2	76.1		
Fucose 4			72.8	72.8		
Fucose 5			70.9	70.8		
Fucose 6			17.4	17.3		
Glucose 1			101.8 [f]	101.7 [f]		
Glucose 2			79.5	79.3		
Glucose 3			77.2	76.9		
Glucose 4			72.8	72.7		
Glucose 5			77.2	77.2		
Glucose 6			63.3	63.3		
Rhamnose 1			102.2 [f]	102.0 [f]		
Rhamnose 2			72.8	72.4		
Rhamnose 3			72.8	72.7		
Rhamnose 4			74.3	74.2		
Rhamnose 5			69.5	69.4		
Rhamnose 6			18.7	18.9		

[a] The assignments of these signals have been revised: *cf.* ref. 4. [b-f] Assignments may be reversed in each vertical column. Peracetates of (9) and (11) (in parentheses) in $CDCl_3$.

In conclusion, reagent A is found to be very useful for the selective oxidation of an allyl alcohol, an allyl ether, and 16- and 21-axial hydroxy-groups. The composition of this reagent is under investigation.

EXPERIMENTAL

M.p.s were measured with a Yanagimoto micro-apparatus. Unless otherwise stated, optical rotation were measured on solutions in chloroform, i.r. spectra on KBr discs, and ^1H n.m.r. spectra on solutions in deuteriochloroform. ^1H N.m.r. spectra were recorded using a JEOL Model JNM-MH-100 spectrometer, employing $SiMe_4$ as an internal standard, and ^{13}C n.m.r. spectra on a JEOL Model JNM-FX-100 spectrometer on [$^2H_5$]pyridine solutions containing $SiMe_4$ as internal reference, in 5-mm spinning tubes at room temperature.

Preparation of Reagent A.—A mixture of CrO_3 (500mg), pyridine (30 ml), and n-butyl alcohol saturated with water (250 ml) was kept at room temperature for one day. The mixture was concentrated under reduced pressure and the residue washed with water and chloroform, then dried under reduced pressure to give the reagent A (520 mg) as a brown powder. Reagent A is soluble only in sulphuric acid, and is insoluble in acetone, chloroform, pyridine, ether, and water; $\nu_{max.}$ (KBr) 3 380, 1 607, 1 485, 1 445, 1 218, 1 153, 1 068, 1 045, 1 015, 905, 800, 693, 640, and 510 cm^{-1}; $\lambda_{max.}$ (2N-H_2SO_4) 255.5 (ε 10 400) nm (Found: C, 26.55; H, 2.9; N, 6.05; O, 17.9. $C_{10}H_{14}Cr_4N_2O_5$ requires C, 26.65; H, 3.1; N, 6.2; O, 17.8%).

Reaction of the Oleanane Triterpenoid Glycosides (1), (4), *and* (5) *with Reagent A.*—(*a*) To a stirred solution of reagent A (200 mg) in dioxan (2 ml) and 2N-H_2SO_4 (2 ml), papyrioside L-IIa (1 200 mg) in dioxan (1 ml) was added. The mixture was refluxed for 30 min, then diluted with water and extracted with ether. The ether layer was washed with water and evaporated and the residue was chromatographed on silica gel to give papyriogenin A (40 mg) and 3,11,21-trioxo-olean-12-en-28-oic acid (3) (90 mg), m.p. 251—254 °C (Found: C, 76.85; H, 9.55. $C_{30}H_{44}O_4$ requires C, 76.9; H, 9.45%), identical with an authentic specimen [1] (mixed m.p., t.l.c., and ^1H n.m.r. spectrum).

(*b*) Saikosaponin a (4) (70 mg) and saikosaponin b_3 (5) (100 mg) were worked up as in (*a*) and the reaction mixture was purified by preparative t.l.c. to afford 11-oxo-oleana-12-en-3β,16β,23,28-tetraol (6) (12 mg), not crystalline; δ ($CDCl_3$–CD_3OD) 0.74 (3 H, s), 0.96 (6 H, s), 1.19 (6 H, s), 1.50 (3 H, s), 3.20—3.88 (6 H, m), and 5.56 (1 H, s). Compound (6) (10 mg) was acetylated in the usual way to afford the tetra-acetate (6a) (12 mg), not crystalline; δ 0.87 (3 H, s), 0.96 (6H, s), 1.20 (6 H, s), 1.51 (3 H, s), 3.72 (1 H, d, *J* 11 Hz), 3.92 (2 H, d, *J* 11 Hz), 4.18 (1 H, d, *J* 11 Hz), 4.82 (1 H, t, *J* 8 Hz), 5.60 (1 H, dd, *J* 10 and 6 Hz), and 5.65 (1 H, s).

Reaction of Rotundioside F (7) *with Reagent A.*—Rotundioside F (7) (250 mg) was treated with reagent A as above and the reaction mixture was purified by column chromatography to give compound (9) (80 mg, 64%) as colourless needles from benzene, m.p. 213—216 °C, $[\alpha]_D$ −15.5° (*c* 0.32); $\nu_{max.}$ 3 450 and 1 688 cm^{-1}; *m/e* 454 (M^+); δ ($CDCl_3$–CD_3OD) 0.76 (3 H, s), 0.79 (3 H, s), 0.92 (3 H, s), 0.94 (3 H, s), 0.95 (3 H, s), 1.01 (6 H, s), 3.22 (1 H, t, *J* 8 Hz), 3.63 (1 H, d, *J* 11 Hz), 3.95 (1 H, d, *J* 11 Hz), 5.71 (1 H, d, *J* 11 Hz), and 6.50 (1 H, dd, *J* 11 and 3 Hz) (Found: C, 77.7; H, 10.1. $C_{30}H_{46}O_3 \cdot 0.5H_2O$ requires C, 77.7; H, 10.2%); compound (9) (20 mg) was acetylated in the usual way to give the diacetate (10) (22 mg), m.p. 247—250 °C; δ 3.93 (1 H, d, *J* 11 Hz), 4.53 (1 H, dd, *J* 9 and 8 Hz), 4.70 (1 H, d, *J* 11 Hz), 5.72 (1 H, d, *J* 10 Hz), and 6.49 (1 H, dd, *J* 10 and 3 Hz) (Found: C, 75.65; H, 9.5. $C_{34}H_{50}O_5$ requires C, 75.8; H, 9.35%), identical with an authentic specimen [10] (mixed m.p., and i.r. and n.m.r. spectra).

Reaction of the Oleanane Triterpenoids (11) *and* (13)—(15) *with reagent A.*—(*a*) Rotundiogenin B (11) (100 mg) and reagent A (100 mg) were dissolved in dioxan (2 ml) and 2N-H_2SO_4 (2 ml), and refluxed for 30 min. The solution was extracted with ether and treated as usual to afford 16-oxo-oleana-11,13(18)-diene-3β, 28-diol (9) (91 mg, 90%), identical with compound (9) obtained as above (t.l.c. and n.m.r. spectrum).

(*b*) Echinocystic acid (13) (92 mg) was worked up as in (*a*) and the product was chromatographed on silica gel [benzene–acetone (10 : 1)] to afford 3β-hydroxy-16-oxo-28-noroolean-12-ene [6] (16) (maragenin I) (40 mg, 48%). Compound (16) was recrystallized from methanol, m.p. 207—209 °C, $[\alpha]_D$ +32.1° (*c* 0.12); $\nu_{max.}$ 3 470 and 1 693 cm^{-1}; *m/e* 426 (M^+),

218, and 190; δ 3.20 (1 H, t, *J* 8 Hz), and 5.44 (1 H, pseudo-triplet, *J* 4 Hz) (Found: C, 81.85; H, 10.9. $C_{29}H_{46}O_2$ requires C, 81.65; 10.85%). Acetylation of compound (16) (34 mg) gave a stereoisomeric mixture of the monoacetates (16a) (38 mg). The monoacetates (16a) were not crystalline; δ 2.08 (3 H, s), 4.56 (1 H, t, *J* 8 Hz) and 5.54 (1 H, t, *J* 4 Hz); g.l.c. [0.5% SE-30 on Chromosorb W (60-80 mesh)] showed the presence of the 17α- and 17β-isomers.

(*c*) Primulagenin A (14) (50 mg) was worked up as in (*a*) and the product was chromatographed on silica gel [$CHCl_3$–MeOH (30 : 1)] to afford 16-oxo-oleana-12-ene-3β,28-diol (17) (29 mg, 58%) as a colourless powder (from MeOH–H_2O), m.p. 211—213 °C, $[\alpha]_D$ +18.2° (*c* 0.22); $\nu_{max.}$ 3 410 and 1 698 cm^{-1}; *m/e* 456 (M^+), 248 and 208; δ 0.80 (3 H, s), 0.88 (6 H, s), 0.95 (3 H, s), 1.00 (3 H, s), 1.03 (3 H, s), 1.22 (3 H, s), 3.19 (1 H, dd, *J* 8 and 9 Hz), 3.40 (1 H, d, *J* 11 Hz), 3.94 (1 H, d, *J* 11 Hz), and 5.48 (1 H, br s, $W_{\frac{1}{2}}$ 7 Hz) (Found: C, 77.2; H, 10.5. $C_{30}H_{48}O_3 \cdot 0.5H_2O$ requires C, 77.35; H, 10.6%).

(*d*) *Synthesis of dihydrorotundiogenin B* (15). Rotundiogenin B (150 mg) was dissolved in glacial acetic acid (5 ml) and shaken with PtO_2 (100 mg) under an atmosphere of H_2 for 2 h. The catalyst was filtered off and the filtrate was evaporated *in vacuo*. Recrystallization of the residue from MeOH–H_2O afforded as a colourless powder (120 mg) the dihydro-derivative, olean-13(18)-ene-3β,16α-28-triol (15), m.p. 228—231 °C; δ ($CDCl_3$–CD_3OD) 0.77 (6 H, s), 0.86 (3 H, s), 0.97 (9 H, s), 1.24 (3 H, s), 3.14 (1 H, t, *J* 8 Hz), 3.40 (1 H, d, *J* 11 Hz), 3.90 (1 H, d, *J* 11 Hz), and 3.96 (1 H, t, *J* 3 Hz) (Found: C, 75.3; H, 11.0. $C_{30}H_{50}O_3 \cdot H_2O$ requires C, 75.6; H, 11.0%). This was acetylated with acetic anhydride–pyridine to give the triacetate; δ 0.80 (3 H, s), 0.84 (3 H, s), 0.87 (6 H, s), 0.90 (3 H, s), 0.96 (3 H, s), 1.26 (3 H, s), 2.06 (9 H, s), 3.96 (1 H, d, *J* 11 Hz), 4.23 (1 H, d, *J* 11 Hz), 4.49 (1 H, dd, *J* 9 and 8 Hz), and 5.12 (1 H, t, *J* 3 Hz).

Dihydrorotundiogenin B (15) (80 mg) was worked up as in (*a*) and the product was chromatographed on silica gel to afford 16-oxo-olean-13(18)-ene-3β-28-diol (18)(68 mg, 85%) as colourless crystals from benzene, m.p. 227—230 °C, $[\alpha]_D$ −91.7° (*c* 0.12); $\nu_{max.}$ 3 450 and 1 685 cm^{-1}; *m/e* 426, 424, and 203 (100%); δ 0.71 (3 H, s), 0.76 (3 H, s), 0.89 (3 H, s), 0.96 (3 H, s), 0.98 (3 H, s), 1.00 (3 H, s), 1.11 (3 H, s), 3.19 (1 H, dd, *J* 9 and 8 Hz), 3.63 (1 H, d, *J* 11 Hz), and 3.85 (1 H, d, *J* 11 Hz) (Found: C, 78.65; H, 10.9. $C_{30}H_{48}O_3$ requires C, 78.9; H, 10.6%).

Reaction of the Oleanane Triterpenoids (19), (20), (22), *and* (23) *with Reagent A*.—(*a*) Compound (19) (53 mg), derived from papyriogenin A (2) by reduction with lithium aluminium hydride, and reagent A (60 mg) were dissolved in dioxan (2 ml) and 2N-H_2SO_4 (2 ml), and refluxed for 1 h. The solution was extracted with ether, treated as usual, and the product purified by preparative t.l.c. [$CHCl_3$–MeOH (10 : 1)] to afford 21-oxo-oleana-11,13(18)-diene-3β,28-diol (24) (25 mg, 47%) as colourless crystals from MeOH, m.p. 250—251 °C; $[\alpha]_D$ −37.2° (*c* 0.54); $\nu_{max.}$ (KBr) 3 420 and 1 704 cm^{-1}; δ 0.75 (3 H, s), 0.79 (3 H, s), 0.92 (3 H, s), 1.01 (3 H, s), 1.08 (3 H, s), 1.10 (3 H, s), 3.26 (1 H, dd, *J* 8 and 7 Hz), 3.52 (2 H, s), 5.72 (1 H, d, *J* 10 Hz), and 6.52 (1 H, dd, *J* 10 and 3 Hz) (Found: C, 78.1; H, 10.25. $C_{30}H_{46}O_3 \cdot 0.5H_2O$ requires C, 77.7; H, 10.2%). It was acetylated in the usual way to give the diacetate; $[\alpha]_D$ −65.0° (*c* 0.40); δ 0.72 (3 H, s), 0.89 (6 H, s), 0.96 (3 H, s), 1.04 (3 H, s), 1.08 (3 H, s), 1.12 (3 H, s), 2.08 (6 H, s), 3.98 (1 H, d, *J* 12 Hz), 4.18 (1 H, d, *J* 12 Hz), 4.57 (1 H, dd, *J* 8 and 7 Hz), 5.79 (1 H, d, *J* 10 Hz), and 6.53 (1 H, dd, *J* 10 and 3 Hz).

(*b*) Compound (22) (92 mg), derived from papyriogenin C (21) by reduction with lithium aluminium hydride, and reagent A (100 mg) were worked up as in (*a*) and the product chromatographed on silica gel [benzene–acetone (15 : 1)] to give 21-oxo-oleana-11,13(18)-diene-3α,28-diol (25) (44 mg, 49%) as colourless needles from MeOH, m.p. 246—248 °C; $[\alpha]_D$ −26.8° (*c* 0.82); $\nu_{max.}$ (KBr) 3 430 and 1 700 cm^{-1}; δ (C_5D_5N) 0.82 (3 H, s), 0.90 (3 H, s), 0.99 (6 H, s), 1.11 (3 H, s), 1.16 (3 H, s), 1.18 (3 H, s), 3.63 (1 H, br s, $W_{\frac{1}{2}}$ 7 Hz), 3.80 (2 H, s), 5.87 (1 H, d, *J* 10 Hz), and 6.65 (1 H, dd, *J* 10 and 3 Hz) (Found: C, 78.2; H, 10.55. $C_{30}H_{46}O_3 \cdot 0.5H_2O$ requires C, 77.7; H, 10.2%). It was acetylated in the usual way to give the diacetate; δ 0.78 (3 H, s), 0.88 (3 H, s), 0.91 (3 H, s), 0.95 (3 H, s), 1.09 (3 H, s), 1.12 (3 H, s), 1.28 (3 H, s), 2.08 (3 H, s), 2.11 (3 H, s), 3.94 (1 H, d, *J* 11 Hz), 4.16 (1 H, d, *J* 11 Hz), and 4.72 (1 H, br s, $W_{\frac{1}{2}}$ 7 Hz).

(*c*) Compound (20) (54 mg) was worked up as in (*a*); the product was identical with starting material (t.l.c. and n.m.r. spectrum).

(*d*) Compound (23) (150 mg) was worked up as in (*a*); the product was identical with starting material (t.l.c., i.r. and n.m.r. spectra).

Reaction of Rotundioside E (26) *with Reagent A at Room Temperature*.—Rotundioside E (26, 66 mg) and reagent A (70 mg) were dissolved in dioxan (3 ml) and 2N-H_2SO_4 (2 ml) and stirred at room temperature for 15 h. The solution was extracted with n-butyl alcohol and treated as usual to afford 16-oxo-rotundioside E (27) (52 mg, 79%). Compound (27) was recrystallized from aqueous methanol as a white powder, m.p. 240—243 °C, $[\alpha]_D$ −67.0° (*c* 1.0 in pyridine); δ (C_5D_5N) 6.63 (1 H, d, *J* 10 Hz), 5.61 (1 H, d, *J* 10 Hz), 6.31 (1 H, br s, anomeric proton of rhamnose), 4.52 (1 H, d, *J* 8 Hz, anomeric proton of glucose), and 4.00 (1 H, d, *J* 7 Hz, anomeric proton of fucose) (Found: C, 63.55; H, 8.4. $C_{48}H_{76}O_{16}$ requires C, 63.4; H, 8.45%).

We thank Professor S. Nishibe and Mr. A. Sakushima, Higashi Nihon University, for mass spectra.

[0/1920 *Received*, 12*th December*, 1980]

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