Carbohydrate Research, 76 (1979) 101–108

SYNTHESIS OF GLYCOSYL ESTERS OF OLEANOLIC ACID

SEIICHI TAKABE, TADAHIRO TAKEDA, AND YUKIO OGIHARA
Faculty of Pharmaceutical Sciences, Nagoya City University, Nagoya (Japan)
(Received August 16th, 1978; accepted for publication in revised form, January 2nd, 1979)

ABSTRACT

The trisaccharide, *O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose has been prepared by two different routes.

Condensation of this trisaccharide with oleanolic acid afforded the corresponding 1,2-*trans* glycosyl ester. Some other glycosyl esters of oleanolic acid were also prepared by the same method.

INTRODUCTION

Our previous paper[1] on the components of the leaves of *Tetrapanax papyriferum* reported the isolation of a new triterpenoid glycoside, 11α-methoxy-3,21-dioxo-olean-12-en-18-oyl α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (papyrioside, L-IIa), from the methanolic extracts. We now report the synthesis of glycosyl esters of oleanolic acid as model compounds for study of the biosynthesis of papyrioside and related compounds.

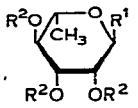
The trisaccharide *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranose is found as the glycon in several kinds of saponin[2,3]. Even though much effort has been expended on synthetic methods for glycosyl esters[4], reports on the synthesis of triterpene glycosides are rare.

RESULTS AND DISCUSSION

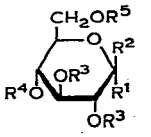
Two reasonable routes (*A* and *B*) were employed for synthesis of the aforementioned trisaccharide. The synthetic route *A* is illustrated in Chart I. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide[5] (**2**) reacted with 1,2,3,6-tetra-*O*-benzoyl-α-D-glucose[6] (**3**) in 1:1 benzene–nitromethane for 44 h at 60° to give 1,2,3,6-tetra-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-α-D-glucopyranose (**6**).

The bromide **7**, obtained conventionally from **6**, was condensed with 1,2,3,4-tetra-*O*-acetyl-β-D-glucose (**5**) in toluene by using mercuric cyanide to afford the trisaccharide **9**, *O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose, in 25% yield; m.p. 115–117°, $[\alpha]_D^{22}$ +82.4°. The same trisaccharide was also synthesized

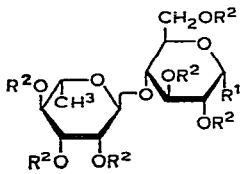
Route *A*: 2 + 3 ⟶ 6, 7 + 5 ⟶ 9
Route *B*: 4 + 5 ⟶ 8, 2 + 8 ⟶ 9



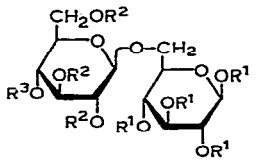
1 R^1 = OBz, R^2 = Bz
2 R^1 = Br, R^2 = Bz



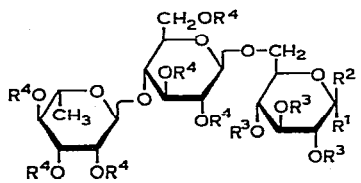
3 R^1 = OBz, R^3 = R^5 = Bz, R^2 = R^4 = H
4 R^1 = Br, R^3 = R^5 = Bz, R^2 = R^4 = H
5 R^2 = OAc, R^3 = R^4 = Ac, R^1 = R^5 = H



6 R^1 = OBz, R^2 = Bz
7 R^1 = Br, R^2 = Bz



8 R^1 = Ac, R^2 = Bz, R^3 = H



9 R^1 = H, R^2 = OAc, R^3 = Ac, R^4 = Bz
10 R^1 = Br, R^2 = H, R^3 = Ac, R^4 = Bz

Chart I

via route *B*. 2,3,6-Tri-*O*-benzoyl-α-D-glucopyranosyl bromide (**4**) was treated with compound **5** in the presence of mercuric cyanide to give disaccharide **8**. The trisaccharide was obtained in 60% yield by coupling **8** with **2** under the conditions used for the disaccharide synthesis. The trisaccharides obtained by the two routes were identical in all respects.

The latter method gave far superior yields. Permethylation of **9** followed by deacylation and methanolysis gave three methylated sugars. These were identified by g.l.c. as the methyl pyranosides of 2,3,4-tri-*O*-methylrhamnose, and 2,3,4-tri-*O*-methyl- and 2,3,6-tri-*O*-methylglucose, as already described[1].

The alditol acetate resulting from deacylation and borohydride reduction of compound **8** showed, in its ^{1}H-n.m.r. spectrum, an anomeric proton signal at δ 4.50 (d, J = 8 Hz), which was assigned to the β-D-glucopyranosyl group. The ^{13}C-chemical shift (δ 100.5) of the anomeric C-1′ atom in compound **9** corroborated the assigned β-D configuration, as the chemical shifts for the non-reducing anomeric carbon atom and the reducing anomeric carbon are 98.8 and 91.6 p.p.m., respectively.

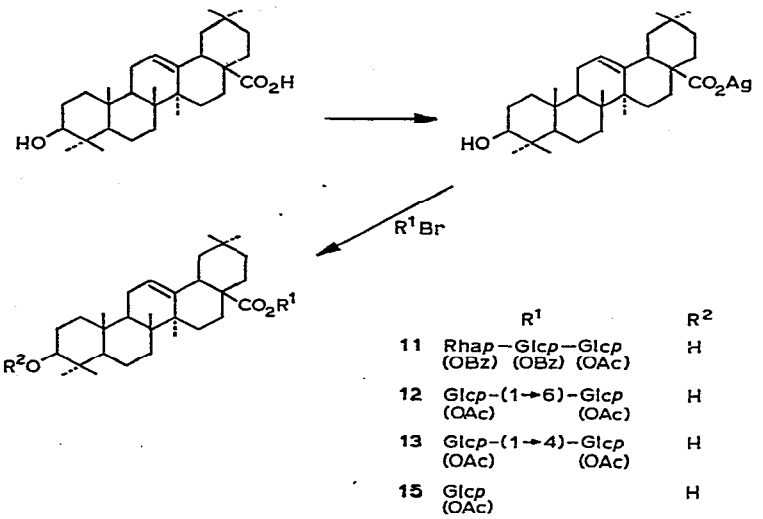
The presence of the β-D-glucopyranosyl group at O-4′ and O-6 of compound

9 deshields C-4′ by ~8.0 p.p.m., and C-6 by 4.8 p.p.m., as compared with β-gentiobiose octaacetate and β-glucose pentaacetate, respectively.

These results indicate that no migration occurred during glycosidation. Therefore, the trisaccharide must indeed, as expected from the mode of synthesis, possess structure **9**.

For synthesis of glycosyl esters, the general procedures employed were similar to those reported by Wulff[7]. The synthetic route is shown in Chart II. The trisaccharide bromide **10** reacted with silver oleanolate (prepared by Wulff's procedure) in benzene solution to give the corresponding 1,2-*trans*-D-glycosyl ester **11**, m.p. 143–145°, $[\alpha]_D^{22}$ +79.2°. in 31% yield.

The other glycosyl esters were obtained by the same method. As may be seen from Table I, ester-linked, anomeric proton signals are observed at low field (5.79 p.p.m.) with a spacing of 8 Hz.



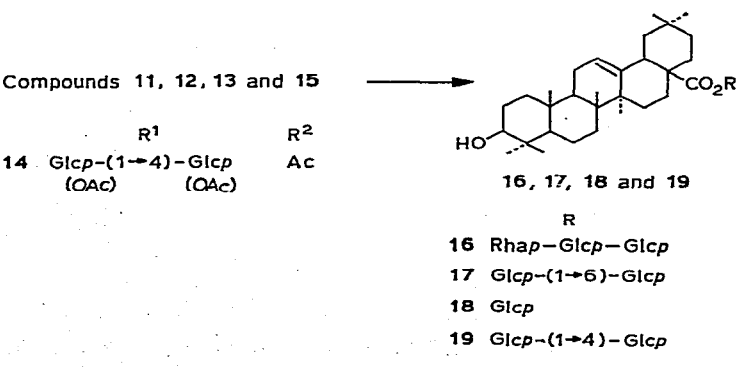


Chart II

TABLE I

PHYSICAL DATA FOR COMPOUNDS **11–15**

Compound	*M.p. (deg.)*	$[\alpha]_D$ *(deg.)*	^{1}*H-n.m.r. data*
11	143–145	+79.2	5.79 (d, *J* 8 Hz, H-1) 5.22 (s, H-1″) 4.36 (d, *J* 8 Hz, H-1′)
12	251–252	+25.2	5.62 (d, *J* 8 Hz, H-1) 4.58 (d, *J* 8 Hz, H-1′)
13	123–126	+28.0	5.57 (d, *J* 8 Hz, H-1) 4.54 (d, *J* 8 Hz, H-1′)
14	140–142	+74.0	5.51 (d, *J* 8 Hz, H-1) 4.48 (d, *J* 8 Hz, H-1′)
15	175–178	+40.8	5.62 (d, *J* 8 Hz)

Furthermore, to establish whether the glycon was attached to the carboxyl or the 3-hydroxyl group of oleanolic acid, compound **13** was acetylated with acetic anhydride–pyridine at room temperature to give compound **14**. In the ^{1}H-n.m.r. spectrum of **14**, an acetyl signal shows increased intensity and the signal for H-3 (at δ 3.23) is shifted to lower field as compared with the corresponding signals of **13**, indicating the formation of an ester linkage between carbohydrate and oleanolic acid.

Saponification of **11** with methanolic potassium carbonate[8] gave quantitatively the oleanolic acid trisaccharide ester **16**, *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl oleanolate, m.p. 190–193°, $[\alpha]_D^{24}$ +17.5°. From **15**, **13**, and **12**, the oleanolic glucosyl ester **18**, cellobiosyl ester **19**, and gentiobiosyl ester **17** were similarly obtained.

Characteristic data for each of these glycosides are shown in Table II. In the ^{1}H-n.m.r. spectrum of **16**, the anomeric-proton signals appear at 5.32 (d, *J* 8 Hz),

TABLE II

PHYSICAL DATA FOR COMPOUNDS **16–19**

Compound	*M.p. (deg.)*	$[M]_D \times 10^{-2}$ *(deg.)*	$-\Delta[M]_D$[a] *(deg.)*	^{1}*H-N.m.r. data*
16	190–193	+162.1	−120.2	5.32 (d, *J* 8 Hz, H-1) 4.84 (s, H-1″) 4.38 (d, *J* 8 Hz, H-1′)
17	177–179	+282.3	−70.0	5.31 (d, *J* 8 Hz, H-1) 4.30 (d, *J* 8 Hz, H-1′)
18	229–231	+352.3		5.36 (d, *J* 8 Hz, H-1)
19	220–223	+249.6		5.41 (d, *J* 8 Hz, H-1) 4.43 (d, *J* 8 Hz, H-1′)

[a]The following $[M]_D \times 10^{-2}$ values were used: methyl α-L-rhamnopyranoside, −111°; methyl β-L-rhamnopyranoside, +170°; methyl β-D-glucopyranoside, −66°; methyl α-D-glucopyranoside, +309°; Oleanolic acid, +379.8°.

4.38 (d, *J* 8 Hz), and 4.84 (s), and are assigned respectively to those of ester-linked β-D-glucopyranose ($^4C_1$ conformation), β-D-glucopyranose ($^4C_1$ conformation), and α-L-rhamnopyranose ($^1C_4$ conformation). These conformational analyses are also supported by application of Klyne's rule[9] (see Table II).

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto micro-apparatus and are uncorrected. The ^{1}H-n.m.r. spectra were recorded on a JNM MH-100 spectrometer with tetramethylsilane as the internal standard; abbreviations used: s = singlet; d, doublet; dd, doublet of doublets; t, triplet; and m, multiplet. I.r. spectra were recorded with a JASCO-IRA-2 spectrometer and optical rotations with a JASCO DIP-2 spectrometer. Thin-layer chromatography was conducted on pre-coated silica gel plates (Merck GF-254) and column chromatography on silica gel (Kanto 100 mesh, Merck Kieselgel 60).

Materials. — 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide[5], 1,2,3,6-tetra-*O*-benzoyl-α-D-glucopyranose, 2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl bromide[6], 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose[10], and the acetylated glycosyl bromides of D-glucose[11], gentiobiose[12], and cellobiose were synthesized by well established procedures.

*1,2,3,6-Tetra-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-α-D-glucopyranose* (**6**). — A solution of the α-bromide **2** (1.80 g, 3.35 mmol) in 1:1 benzene–nitromethane (10 mL) was added to a mixture of compound **3** (2.0 g, 3.35 mmol), mercuric cyanide (0.87 g), and Drierite (1.0 g) in the same solvent (30 mL). After stirring for 26 h at 60°, 0.9 g of **2** was added and the mixture was stirred for an additional 18 h at 60°. The mixture was then cooled and washed successively with saturated aqueous sodium hydrogencarbonate, saturated aqueous sodium chloride, and water, dried (sodium sulfate), and evaporated to dryness. The residue was chromatographed on silica gel with 15:1 benzene–ethyl acetate as the developing solvent. The major fraction eluted (1.9 g) was crystallized from chloroform–ethanol (48.1%) as colorless needles, m.p. 108–110°, $[\alpha]_D^{22}$ +84° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 0.83 (3 H, d, *J* 7 Hz), 5.65 (1 H, s, H-1′), 5.78 (1 H, dd, *J* 10 and 4 Hz, H-2), 6.29 (1 H, t, *J* 10 Hz, H-3), 6.81 (1 H, d, *J* 4 Hz, H-1), and 7.18–8.27 (35 H, m, arom.).

Anal. Calc. for $C_{61}H_{50}O_{17}$: C, 69.44; H, 4.78. Found: C, 69.30; H, 4.72.

*2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-α-D-glucopyranosyl bromide* (**7**). — A solution of compound **6** (1.7 g) in acetic acid (20 mL) saturated with hydrogen bromide was kept for 24 h at 0°. After dilution with chloroform (40 mL) and chilling with ice, the solution was washed with water (3 times) and saturated aqueous sodium hydrogencarbonate and evaporated to dryness. The residue was chromatographed on silica gel with 20:1 benzene–ethyl acetate to give a syrup that was crystallized from diethyl ether–ethanol; yield 0.99 g (61%), m.p. 120–122°; ^{1}H-n.m.r. ($CDCl_3$): δ 0.83 (3 H, d, *J* 7 Hz), 5.62 (1 H, s, H-1′), 5.75 (1 H,

dd, *J* 10 and 4 Hz, H-2), 6.20 (1 H, t, *J* 10 Hz, H-3), 6.76 (1 H, d, *J* 4 Hz, H-1), and 7.12–8.12 (30 H, m, arom.).

*1,2,3,4-Tetra-*O*-acetyl-6-*O*-(2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**8**). — Compound **5** (1.5 g, 4.3 mmol) was condensed with compound **4** (2.4 g, 4.3 mmol) as in the preceding reaction. The title compound (**8**) was obtained as colorless prisms (2.25 g, 63.6%), m.p. 158–160°, $[\alpha]_D^{22}$ +54.4° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): 1.93, 1.95, 1.98, 1.99 (each 3 H, s, OAc), 3.60–4.00 (5 H, m, loss of 1 H on D_2O exchange), 4.60–4.92 (5 H, m), 4.66 (1 H, d, *J* 8 Hz, H-1′), 5.18 (1 H, t, *J* 10 Hz, H-3), 5.47 (2 H, m), and 5.63 (1 H, d, *J* 8 Hz, H-1).

Anal. Calc. for $C_{41}H_{42}O_{18}$: C, 59.85; H, 5.15. Found: C, 59.64; H, 4.97.

O-*(2,3,4,6-Tetra-*O*-acetyl-β-*D*-glucopyranosyl)-(1→6)-1,2,3,4,5-penta-*O*-acetyl-*D*-glucitol.* — Compound **8** (40 mg) was *O*-deacylated with triethylamine (0.3 mL) in 50% aqueous methanol (3 mL) and, after removal of the solvents, the residue (25 mg) was reduced with sodium borohydride (10 mg) in water (5 mL) for 3 h at room temperature. After treatment with Dowex 50 (H^+) resin and evaporation, boric acid was removed by repeated evaporation of methanol from the residue. The product was treated with 1:1 acetic anhydride–pyridine (2 mL) for 12 h at room temperature. Examination of the residue $[\alpha]_D^{22}$ +9.33° (*c* 1.5, chloroform) by ^{1}H-n.m.r. after conventional processing showed the presence of a doublet at δ 4.50 (d, *J* 8 Hz, H-1).

O-*(2,3,4-Tri-*O*-benzoyl-α-*L*-rhamnopyranosyl)-(1→4)-O-(2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranosyl)-(1→6)-1,2,3,4-tetra-*O*-acetyl-β-*D*-glucopyranose* (**9**). — (*A*) To a solution (20 mL) of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose **5** (0.7 g, 2 mmol), mercuric cyanide (0.52 g), and Drierite was added compound **7** (2.0 g, 2 mmol) in toluene during 0.5 h. The solution was stirred for 62 h at 60°, cooled to room temperature, and washed successively with saturated aqueous sodium hydrogencarbonate, saturated sodium chloride, and water, dried (sodium sulfate), and evaporated. Chromatography of the residue on silica gel gave a major fraction (0.85 g).

Recrystallization from ethanol gave 0.65 g (25.2%) of colorless prisms, m.p. 115–117°, $[\alpha]_D^{24}$ +82.4° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$); 1.78 (3 H, d, *J* 7 Hz), 1.94 (6 H, s 2 OAc), 1.98, 2.01 (each 3 H, s, OAc), 4.40 (1 H, d, *J* 8 Hz, H-1′), 5.62 (1 H, s, H-1″), 5.74 (1 H, d, *J* 8 Hz, H-1), and 7.10–8.17 (30 H, m, arom.); ^{13}C-n.m.r. ($CDCl_3$); 17.1 (C-6″), 62.5 (C-6′), 67.3 (C-6), 67.8 (C-5″), 68.6 (C-4), 69.5 (C-3′), 70.4 (C-2), 71.2, 71.3, 72.2 (C-2′, C-2″, C-3″, these assignments may be interchanged), 72.7 (C-3), 73.6, 73.8 (C-5 or C-5′), 74.3 (C-4″), 76.6 (C-4′), 91.6 (C-1), 98.8 (C-1″), and 100.5 (C-1′).

Anal. Calc. for $C_{68}H_{64}O_{25}H_2O$: C, 62.86; H, 5.12. Found: C, 62.58; H, 4.97.

(*B*) A solution of compound **2** (0.192 g) was added to a solution (8 mL) in nitromethane of 1,2,3,4-tetra-*O*-acetyl-6-*O*-(2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranose (**8**, 0.33 g) containing mercuric cyanide (0.093 g) and Drierite. The mixture was stirred under dry argon for 5 h at 60°. Conventional processing gave a colorless powder, yield 0.3 g (58.4%).

*Per-*O*-methylation and methanolysis of compound* **9**. — The *O*-deacylated com-

pound **9** (50 mg) was methylated in *N,N*-dimethylformamide (2 mL) with silver oxide (200 mg) and methyl iodide (1 mL) for 72 h according to the method of Kuhn. The precipitate was filtered off, and the filtrate was diluted with water and extracted with chloroform. After evaporation, the residue was boiled in 5% methanolic hydrochloric acid for 5 h under reflux. The mixture was made neutral with silver carbonate, filtered, and the filtrate 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.

O-(*2,3,4-Tri*-O-*benzoyl*-α-L-*rhamnopyranosyl*)-(1→4)-O-(*2,3,6-tri*-O-*benzoyl*-β-D-*glucopyranosyl*)-(1→6)-*1,2,3,4-tetra*-O-*acetyl*-β-D-*glucopyranosyl bromide* (**10**). — To a solution (6 mL) of compound **9** (0.4 g) in chloroform was added 2 mL of hydrogen bromide in acetic acid, and the mixture was kept for 3 h at 0°. Conventional isolation gave an amorphous powder (0.3 g, 74%), m.p. 111–113°, $[\alpha]_D^{24}$ +98.5° (*c* 0.4, chloroform); ^{1}H-n.m.r. ($CDCl_3$): 4.49 (1 H, d, *J* 8 Hz, H-1′), 5.58 (1 H, s, H-1″), and 5.63 (1 H, d, *J* 4 Hz, H-1).

2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl oleanolate* (**15**). — A solution of tetra-*O*-acetyl-α-D-glucopyranosyl bromide (0.2 g) in benzene (3 mL) was added dropwise to a suspension of silver oleanolate (0.18 g) and the mixture was stirred for 22 h at room temperature, filtered to remove the unreacted silver salt and silver bromide, and the filtrate evaporated. The residue was chromatographed on a column of silica gel with 15:1 benzene–ethyl acetate to give a syrup that was crystallized from methanol to give 0.1 g of **15** (39.8% on the basis of silver oleanolate).

Anal. Calc. for $C_{44}H_{66}O_{12} \cdot 0.5\,H_2O$: C, 66.39; H, 8.48. Found: C, 66.35; H, 8.78.

Hepta-O-*acetyl*-β-D-*gentiobiosyl oleanolate* (**12**). — To a suspension of the silver salt (0.13 g) in benzene was added a solution of hepta-*O*-acetylgentiobiosyl bromide (0.07 g) and the mixture was stirred for 17 h at room temperature. Isolation gave a colorless, amorphous powder; yield 20.2%. Data are given in Table I.

Anal. Calc. for $C_{56}H_{82}O_{20} \cdot 2\,H_2O$: C, 60.53; H, 7.80. Found: C, 60.44; H, 7.31.

Hepta-O-*acetyl*-β-*cellobiosyl oleanolate* (**13**). — Treatment of per-*O*-acetylcellobiosyl bromide (0.75 g) and the silver salt (0.3 g) as just described gave **13** as an amorphous powder (0.3 g, 52.4%). Data are given in Table I.

Anal. Calc. for $C_{56}H_{82}O_{20} \cdot H_2O$: C, 61.52; H, 7.74, Found: C, 61.15; H, 7.53.

Hepta-O-*acetyl*-β-D-*cellobiosyl 3*-O-*acetyl-oleanolate* (**14**). — Compound **13** was acetylated with pyridine and acetic anhydride to give compound **14** quantitatively.

Anal. Calc. for $C_{58}H_{84}O_{21} \cdot H_2O$: C, 61.36; H, 7.64, Found: C, 61.56; H, 7.56.

O-(*2,3,4-Tri*-O-*benzoyl*-α-L-*rhamnopyranosyl*)-(1→4)-O-(*2,3,6-tri*-O-*benzoyl*-β-D-*glucopyranosyl*)-(1→6)-*1,2,3,4-tetra*-O-*acetyl*-β-D-*glucopyranosyl oleanolate* (**11**). — A solution of **10** (0.4 g) in benzene (7 mL) was added to a suspension of silver oleanolate (0.22 g) in dry benzene (3 mL), and the mixture was stirred for 40 h at room temperature. Isolation as before gave 0.2 g of compound **11** (31%); ^{13}C-n.m.r. ($CDCl_3$) of the sugar component: 17.1 (C-6″), 72.5 (C-6′), 67.2 (C-6), 67.8 (C-5″), 68.9 (C-4), 69.5 (C-3′), 70.1 (C-2), 71.1, 71.4, 72.2 (C-2′, C-2″, C-3″, these assignments

may be interchanged), 72.8 (C-3), 73.7, 73.8 (C-5 or C-5'), 74.5 (C-4''), 76.8 (C-4'), 91.6 (C-1), 98.8 (C-1''), and 100.4 (C-1'). Further data are shown in Table I.

Anal. Calc. for $C_{96}H_{108}O_{26}$: C, 68.72; H, 6.49, Found: C, 68.39; H, 6.38.

O-α-L-*Rhamnopyranosyl*-(1→4)-O-β-D-*glucopyranosyl*-(1→6)-β-D-*glucopyranosyl oleanolate* (**16**). — A solution (7 mL) of compound **11** (0.05 g) in methanolic sodium carbonate was stirred for 5 h at room temperature. The mixture was passed through a column of ion-exchange resin (Amberlite IR-120B, H^+) with methanol as solvent. The syrup obtained was treated with diethyl ether to afford a powder, m.p. 190–193°, $[\alpha]_D^{24}$ +17.5° (*c* 0.4, methanol). Data are given in Table II.

Anal. Calc. for $C_{48}H_{78}O_{17} \cdot 2\,H_2O$: C, 59.86; H, 8.58. Found: C, 59.95; H, 8.17.

Deprotection of the oleanolic acid glycosyl esters **12**, **13**, *and* **15**. — Compounds **12**, **13**, and **15** were treated as described for the synthesis of **16** to give **17**, **19**, and **18** quantitatively.

O-β-D-*Glucopyranosyl*-(1→6)-β-D-*glucopyranosyl oleanolate* (**17**) had m.p. 177–179°, $[\alpha]_D^{22}$ +36.2° (*c* 0.4, methanol).

Anal. Calc. for $C_{42}H_{68}O_{13} \cdot 2\,H_2O$: C, 61.74; H, 8.88. Found: C, 61.55; H, 8.87.

β-D-*Glucopyranosyl oleanolate* (**18**) had m.p. 229–231°, $[\alpha]_D^{22}$ +57.0° (*c* 0.2, methanol).

Anal. Calc. for $C_{36}H_{58}O_8 \cdot H_2O$: C, 67.89; H, 9.50. Found: C, 67.58; H, 9.13.

O-β-D-*Glucopyranosyl*-(1→4)-β-D-*glucopyranosyl oleanolate* (**19**) had m.p. 220–223°, $[\alpha]_D^{22}$ +32.0° (*c* 0.5, methanol).

Anal. Calc. for $C_{42}H_{68}O_{13} \cdot 2\,H_2O$: C, 61.74; H, 8.88. Found: C, 61.74; H, 8.41.

ACKNOWLEDGMENTS

We thank Miss T. Ito for the ^{1}H-n.m.r. spectral measurements and Misses M. Ishiguro and S. Iwauchi for the microanalyses.

REFERENCES

1 M. TAKAI, S. AMAGAYA, AND Y. OGIHARA, *J. Chem. Soc., Perkin Trans. 1*, (1977) 1801–1806.
2 G. M. FROLOVA AND YU. S. OVODOV, *Chem. Abstr.*, 76 (1972) 59965.
3 N. K. KOCHETKOV AND A. J. KHORLIN, *Arzneimittelforsch.*, 16 (1966) 101.
4 T. OGAWA, M. NOZAKI, AND M. MATSUI, *Carbohydr. Res.*, 60 (1978) c7.
5 R. K. NESS, H. G. FLETCHER, JR., AND C. S. HUDSON, *J. Am. Chem. Soc.*, 73 (1951) 296–300.
6 J. F. BATEY, C. BULLOCK, E. O'BRIEN, AND J. M. WILLIAMS, *Carbohydr. Res.*, 43 (1975) 43–50.
7 G. WULFF, W. KRÜGER, AND G. RÖHLE, *Chem. Ber.*, 104 (1971) 1387–1396.
8 T. KONISHI, A. TADA, AND O. TANAKA, *Chem. Pharm. Bull.*, 26 (1978) 668–670.
9 W. KLYNE, *Biochem. J.*, 47 (1950) 41.
10 R. L. WHISTLER, L. W. DONER, AND M. KOSIK, *Methods Carbohydr. Chem.*, 6 (1972) 411–412.
11 R. U. LEMIEUX, *Methods Carbohydr. Chem.*, 2 (1963) 221–222.
12 K. TAKIURA, S. HONDA, T. ENDO, AND K. KAKEHI, *Chem. Pharm. Bull.*, 24 (1972) 438–442.