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PREPARATION OF SOME ACYLATED D-*arabino*-HEXOPYRANOSULOSES AND 4-DEOXY-D-*glycero*-HEX-3-ENOPYRANOSULOSES*

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ABSTRACT

Oxidation of 1,3,4,6-tetra-*O*-benzoyl-α- and β-D-glucopyranose gave the tetra-*O*-benzoyl-α- and -β-D-*arabino*-hexopyranosuloses (**3α** and **β**), from which benzoic acid was readily eliminated to give the anomeric tri-*O*-benzoyl-4-deoxy-D-*glycero*-hex-3-enopyranosuloses (**4α** and **β**). The anomeric 1-*O*-acetyl-tri-*O*-benzoyl-D-*arabino*-hexopyranosuloses (**7α** and **β**) were obtained as very unstable syrups which readily lost benzoic acid. Treatment of tetra-*O*-benzoyl-2-*O*-benzyl-D-glucopyranose (**1**) with hydrogen bromide gave 3,4,6-tri-*O*-benzoyl-α-D-glucopyranosyl bromide (**5**) in one step.

INTRODUCTION

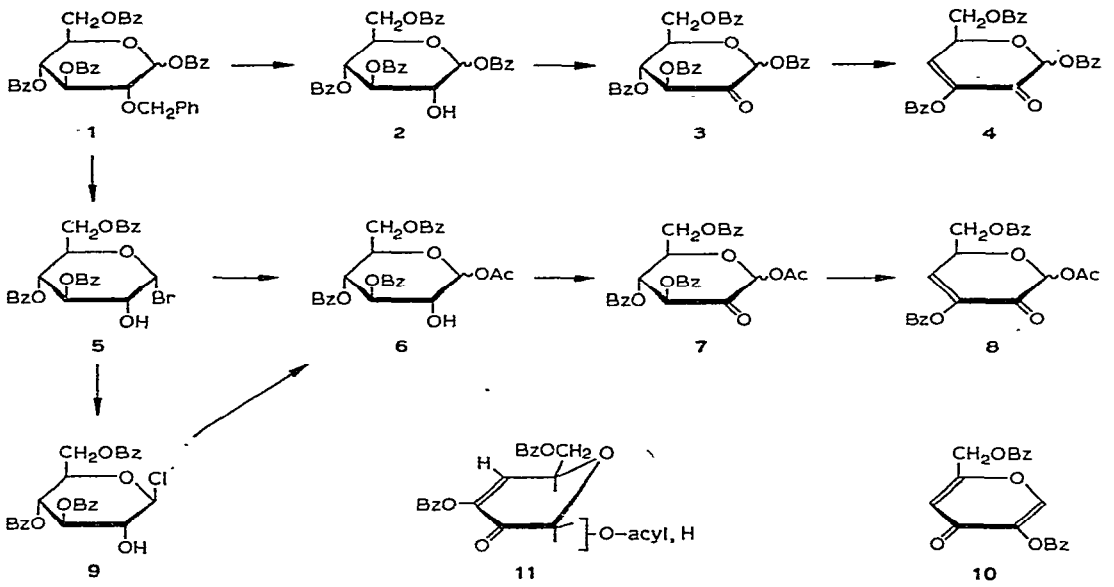
Maurer and Petsch studied the reaction of 1,5-anhydrotetra-*O*-benzoyl-D-*arabino*-hex-1-enitol with chlorine[1] and, by hydrolysis of the crude chlorination product, obtained a compound which they assumed was tetra-*O*-benzoyl-D-*arabino*-hexopyranosulose (**3**). Treatment of the chlorination product with sodium acetate yielded a compound assumed[1] to be the corresponding 1-acetate (**7**). Chittenden confirmed the latter result[2]. However, we have not been able to obtain **3** or **7** by the procedures described by Maurer and Petsch, and we therefore decided to prepare these compounds by oxidation of the corresponding 2-hydroxy compounds **2** and **6**.

RESULTS AND DISCUSSION

Benzoylation of 2-*O*-benzyl-D-glucose at low temperature gave mainly the α-tetrabenzoate **1α**, whereas benzoylation at higher temperature yielded **1β**. Catalytic hydrogenolysis of **1α** and **1β** gave good yields of 1,3,4,6-tetra-*O*-benzoyl-α- and -β-D-glucopyranose (**2**), respectively. These products were subsequently oxidized with a catalytic amount of ruthenium dioxide and potassium periodate[3]. By this procedure, **2α** gave the 2-ulose **3α**, which was contaminated with a hydrated product as seen from

*Dedicated to Dr. Horace S. Isbell, in honour of his 75th birthday.

an n.m.r. spectrum. After removal of the water over phosphorus pentaoxide, pure **3α** was obtained as a syrup.



Oxidation of **2β** gave a crystalline, partially hydrated 2-ulose **3β**. Recrystallization gave **3β** in low yield, while the 3,4-unsaturated ketone **4β** could be isolated from the mother liquor. When crude **3β** was heated in benzene with aqueous sodium hydrogen carbonate, pure, crystalline **4β** was obtained.

That acylated hexopyranosuloses undergo elimination readily has been shown in several cases. Thus, Overend and co-workers[4] oxidized methyl 3,4,6-tri-*O*-benzoyl-α-D-glucopyranoside with ruthenium tetraoxide to the 2-ulose, from which benzoic acid was eliminated on column chromatography. Oxidation of 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose with methyl sulfoxide resulted in formation of di-*O*-acetylkojic acid[2]. Similar results were obtained by Lichtenthaler[5].

The α-compound **3α**, although more stable than **3β**, also lost benzoic acid on treatment with aqueous sodium hydrogen carbonate to give pure **4α**. Both anomers of **4** lost a further equivalent of benzoic acid when treated with pyridine at 40° to give di-*O*-benzoylkojic acid (**10**).

Treatment of **1α** with hydrogen bromide in carbon tetrachloride resulted in both debenzylation and replacement of the 1-*O*-benzoyl group, and thus gave 3,4,6-tri-*O*-benzoyl-α-D-glucopyranosyl bromide (**5**) in good yield. This product served as a starting material for the preparation of the 1-acetates.

Treatment of **5** with silver acetate gave 1-*O*-acetyl-3,4,6-tri-*O*-benzoyl-β-D-glucopyranose (**6β**). In order to obtain **6α**, it was necessary to prepare a β-halide. Treatment of **5** with freshly prepared silver chloride gave the β-chloride **9** as a rather unstable product which, on treatment with silver acetate[6], yielded **6α**.

TABLE I

PROTON CHEMICAL SHIFTS (p.p.m.) IN DEUTERIOCHLOROFORM AND COUPLING CONSTANTS (Hz) OF HEXOPYRANOSULOSES AND OF RELATED COMPOUNDS

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*
1α	6.74	4.05	6.15	5.66	4.3———		———4.9
	$J_{1,2}$ 3.8	$J_{2,3}$ 10.0	$J_{3,4}$ 9.8				
1β	6.24	4.06	5.9	5.7	4.2———		———4.7
	$J_{1,2}$ 7.8	$J_{2,3}$ 8	$J_{3,4}$ 9				
2α	6.67	4.28	6.0	5.7	4.0———		———4.7
	$J_{1,2}$ 4.0	$J_{2,3}$ 9.6	$J_{3,4}$ 9.6				
2β	6.15	4.16	5.65———	———5.9	4.35	4.64	4.48
	$J_{1,2}$ 8.0				$J_{5,6}$ 3	$J_{5,6'}$ 4.5	$J_{6,6'}$ 11.8
3α	6.5		6.27	6.07	4.94	4.72	4.55
			$J_{3,4}$ 10.0	$J_{4,5}$ 10.5	$J_{5,6}$ 2.8	$J_{5,6'}$ 4.25	$J_{6,6'}$ 12.2
3β	6.7		6.3	6.06	4.5———		———5.0
			$J_{3,4}$ 9.5	$J_{4,5}$ 9.5			
4α	6.62			7.02	5.31	4.7	4.55
				$J_{4,5}$ 1.8	$J_{5,6}$ 4.6	$J_{5,6'}$ 5.2	$J_{6,6'}$ 11.4
4β	6.67			7.03	5.24	4.66	
				$J_{4,5}$ 3.2	$J_{5,6}$ 5.8	$J_{5,6'}$ 6.3	
5α	6.7	4.0	5.7———	———6.0	4.4———		———4.9
	$J_{1,2}$ 3.8	$J_{2,3}$ 9					
6α	6.38	4.2	5.5———	———5.9	~4.4	4.6	4.4
					$J_{5,6}$ 4.5	$J_{5,6'}$ 4	$J_{6,6'}$ 13
6β	5.86	3.95	5.5———	———5.7	4.2	4.6	4.4
	$J_{1,2}$ 8	$J_{2,3}$ 9			$J_{5,6}$ 3.2	$J_{5,6'}$ 4.5	$J_{6,6'}$ 12
7α	6.26		6.2	6.02	4.86	4.73	4.53
			$J_{3,4}$ 10	$J_{4,5}$ 10	$J_{5,6}$ 3	$J_{5,6'}$ 4.5	$J_{6,6'}$ 12.5
7β	6.35		6.13	5.95	4.28	4.5———	———4.8
			$J_{3,4}$ 10	$J_{4,5}$ 10			
8α	6.40			6.96	5.27	4.71	4.54
				$J_{4,5}$ 1.8	$J_{5,6}$ 5.0	$J_{5,6'}$ 5.4	$J_{6,6'}$ 11.7
8β	6.40			6.97	5.20	4.75	4.60
				$J_{4,5}$ 3.2	$J_{5,6}$ 6	$J_{5,6'}$ 6	$J_{6,6'}$ 12

Oxidation of **6α** and **6β** with ruthenium tetraoxide gave the anomeric 1-*O*-acetyl-3,4,6-tri-*O*-benzoyl-D-*arabino*-hexopyranosuloses (**7α** and **7β**). These compounds were very unstable and could not be obtained completely pure; their n.m.r. spectra (Table I) were, however, in agreement with the assigned structures. On standing, or on treatment with sodium hydrogen carbonate, both **7α** and **7β** lost benzoic acid to give the 3,4-unsaturated products (**8α** and **8β**).

The p.m.r. spectra (Table I) of the 3,4-unsaturated ketones **4** and **8** showed $J_{4,5}$ values of 1.8 Hz for the α anomers and 3.2 Hz for the β anomers. This is in agreement with previous results[7] and confirms the anomeric structures. Anet[8] has proposed that anomeric pairs of 3,4-unsaturated ketones both adopt the same conformation (**11**), in which H-5 is pseudo-axial. In Table II, ^{13}C-n.m.r. data of a number of compounds are given, and it is seen that $^1J_{C-1,H-1}$ is large (178 and 180 Hz) for the α anomers **4α** and **8α**, whereas it is smaller (172 and 173 Hz, respectively) for **4β** and **8β**. This is in agreement with previous results[9], if all four compounds have conformation **11**. The equatorial H-1 of the α anomers will be close to the lone-pair electrons of the ring-oxygen atom, giving a large $^1J_{C-1,H-1}$ value. In the β anomers, H-1 is axial, and the coupling constant is therefore smaller.

TABLE II

^{13}C CHEMICAL SHIFTS (p.p.m. RELATIVE TO Me_4Si) AND $^1J_{C-1,H-1}$ VALUES OF HEXOPYRANOSULOSES

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	$^1J_{C-1,H-1}$ (*Hz*)
3α	91.5	190.3	75.7	70.6	69.6	62.0	181
3β	92.3	191.3	77.1	71.0	74.3	63.2	168
4α	90.4	180.3	141.8	~133[a]	69.0	64.6	178
4β	90.8	181.2	142.5	~133[a]	71.3	65.6	172
7α	91	190	75	70.2	69.7	61.9	180
8α	90.3	181.1	142.4	~133[a]	69.1	64.8	180
8β	90.5	181.2	143.1	~133[a]	71.7	65.7	173

[a]This signal is found together with the C-1 carbon atom of the benzoyl groups.

From the present work, it is concluded that the acylated osones **3** and **7** can be prepared, but that they undergo elimination very easily to give the 3,4-unsaturated ketones **4** and **8**. A study of the paper[1] by Maurer and Petsch shows that the conditions under which they prepared the products, to which they ascribed structures **3** and **7**, were such that these compounds would not be stable. From the data given by Maurer and Petsch, it seems likely that their "tetrabenzoate" was in fact **4α**. The compound which they believed to be **7**, and which Chittenden[2] also claimed to have prepared, is probably impure **8**. Further details will be published later.

EXPERIMENTAL

Melting points are uncorrected. For thin-layer chromatography (t.l.c.), Silica Gel PF_{254} (Merck) was used; preparative t.l.c. was conducted with 1-mm layers on 20×40 cm plates. Compounds were detected with u.v. light. P.m.r. spectra were recorded with Varian A-60 and HA-100 instruments, with tetramethylsilane as the internal reference. ^{13}C-n.m.r. spectra were measured as previously described[9].

Tetra-O-benzoyl-2-O-benzyl-α-D-glucopyranose (**1α**). — A mixture of pyridine (60 ml) and benzoyl chloride (20 ml) was stirred and cooled to 0°. 2-*O*-Benzyl-D-glucose[10] (7.0 g) was then added during 45 min at ~0°, and the mixture was kept at room temperature overnight. It was then diluted with dichloromethane, washed with water, dilute sulfuric acid, and aqueous sodium hydrogen carbonate, dried, and concentrated. The residue (15 g) was crystallized from ethanol (~200 ml) to give 10.2 g (57%) of **1α**, m.p. 117–118°, $[\alpha]_D^{23}$ +46.0° (*c* 2.2, chloroform).

Anal. Calc. for $C_{41}H_{34}O_{10}$: C, 71.72; H, 4.99. Found: C, 71.35; H, 5.05.

Tetra-O-benzoyl-2-O-benzyl-β-D-glucopyranose (**1β**). — A solution of 2-*O*-benzyl-D-glucose (1.04 g) in pyridine (10 ml) was heated to 70° for 1 h. It was then cooled in ice, and benzoyl chloride (3.0 ml) was added during 5 min. The mixture was kept overnight and worked up as described above. The crude product (2.53 g) was crystallized from dichloromethane–pentane to give 1.4 g (53%) of **1β**, m.p. 167–171°. An additional recrystallization gave the pure product, m.p. 170–171°, $[\alpha]_D^{25}$ +2.8° (*c* 3.0, chloroform).

Anal. Found: C, 71.90; H, 5.33.

The material in the mother liquor consisted of almost pure **1α**, as shown by an n.m.r. spectrum. Crystallization from ethanol gave 0.76 g (29%) of **1α**, m.p. 115–117°.

The structures of **1α** and **1β** were further confirmed through their n.m.r. spectra (Table I).

1,3,4,6-Tetra-O-benzoyl-α-D-glucopyranose (**2α**). — A solution of **1α** (1.0 g) in *p*-dioxane (8.0 ml) was hydrogenated with palladium oxide (150 mg) and hydrogen for ~14 h at room temperature and 1 atm. pressure. Filtration through activated carbon and evaporation gave a syrup which appeared to be pure [t.l.c. and n.m.r. spectra (Table I)]. Since the product underwent acyl migration very easily, further purification was not possible.

1,3,4,6-Tetra-O-benzoyl-β-D-glucopyranose (**2β**). — This compound was prepared, in the same manner as for **2α**, by hydrogenolysis of **1β**. Recrystallisation from chloroform–pentane gave **2β** (71%), m.p. 188–189°, $[\alpha]_D^{23}$ +7.07° (*c* 2.6, chloroform). N.m.r. data are recorded in Table I.

Anal. Calc. for $C_{34}H_{28}O_{10}$: C, 68.46; H, 4.73. Found: C, 68.60; H, 4.84.

3,4,6-Tri-O-benzoyl-α-D-glucopyranosyl bromide (**5**). — The 2-*O*-benzyl derivative **1α** (12.0 g) was suspended in tetrachloromethane (10 ml), which was then removed *in vacuo*. This was repeated twice, leaving **1α** as a syrup which would be completely dissolved in 10 ml of tetrachloromethane. A stream of hydrogen bromide was passed through the solution for 1.5 h, and the mixture was kept for 20 h at room temperature.

The crystalline precipitate was filtered off and recrystallized from dichloromethane–pentane to give 2.45 g (25%) of **5**, m.p. 155–157°. The combined mother liquors were evaporated, and the residue was dissolved in tetrachloromethane (5 ml) and treated with hydrogen bromide as described above. This gave an additional 4.9 g (51%) of recrystallized **5**, m.p. 153–155°. Recrystallization from chloroform–pentane gave pure **5**, m.p. 157–158°, $[\alpha]_D^{23}$ +126.8° (*c* 2.7, chloroform). N.m.r. data are shown in Table I.

Anal. Calc. for $C_{27}H_{23}BrO_8$: C, 58.39; H, 4.18. Found: C, 58.22; H, 4.07.

*3,4,6-Tri-*O*-benzoyl-β-*D*-glucopyranosyl chloride* (**9**). — The bromide **5** (2.0 g) was dissolved in anhydrous acetonitrile (35 ml), and silver chloride (freshly prepared from 5.0 g of silver nitrate, and washed with methanol, ether, and acetonitrile) was added together with Drierite. The mixture was stirred for 2 h at room temperature, and the silver salts were removed by filtration through activated carbon. The solvent was removed, and a solution of the residue in dichloromethane was filtered through activated carbon and concentrated to give a syrup (1.69 g, 92%). An n.m.r. spectrum (Table I) showed that the product was mainly the β-chloride **9** mixed with a small proportion of the α-chloride; the bromide **5** was not present. The syrup was crystallized from ether–pentane to give 1.0 g of crude **9**, m.p. 127–130°, which also contained some α-chloride. The β-chloride **9** anomerizes to the α-chloride on storage or on recrystallization, and it was therefore not obtained completely pure.

*1-*O*-Acetyl-3,4,6-tri-*O*-benzoyl-α-*D*-glucopyranose* (**6α**). — A solution of **9** (202 mg) in glacial acetic acid (5.0 ml) was stirred with silver acetate (400 mg) for 6 h at room temperature[6]. Filtration through activated carbon and evaporation gave a syrup (230 mg) which was dissolved in ether (5 ml). Cooling to −20° for 2 days gave 85 mg (41%) of **6α**, m.p. 149–150°, $[\alpha]_D^{23}$ +70.4° (*c* 2, chloroform). N.m.r. data are given in Table I.

Anal. Calc. for $C_{29}H_{26}O_{10}$: C, 65.16; H, 4.90. Found: C, 65.00; H, 5.03.

Concentration of the mother liquor and cooling gave an additional 41 mg of **6α**, m.p. 149–150°, bringing the total yield to 61%. The preparation of **6α** is difficult because of the instability of the β-chloride **9**. If **9** contained too much α-chloride, pure **6α** could not be obtained by crystallization, and attempts to purify it by t.l.c. led to acyl migration.

*1-*O*-Acetyl-3,4,6-tri-*O*-benzoyl-β-*D*-glucopyranose* (**6β**). — A solution of the bromide **5** (3.36 g) in acetonitrile (60 ml) was stirred with silver acetate (14 g) for 3 h at room temperature. The mixture was filtered through activated carbon and concentrated; the residue was dissolved in dichloromethane and again filtered through carbon. Removal of the solvent gave 2.35 g (73%) of **6β**, m.p. 168–169°. Recrystallization from ethanol gave the pure product, m.p. 170–171°, $[\alpha]_D^{25}$ −2.14° (*c* 2.9, chloroform). N.m.r. data are shown in Table I.

Anal. Found: C, 65.06; H, 5.00.

*1,3,4,6-Tetra-*O*-benzoyl-α-*D*-arabino-hexopyranosulose* (**3α**). — To a mixture of dichloromethane (6 ml) and water (6 ml) was added **2α** (477 mg), potassium periodate (200 mg), sodium hydrogen carbonate (50 mg), and ruthenium dioxide (50 mg). The mixture was stirred vigorously at room temperature and, after 1 and 3 h, additional

portions of potassium periodate (200 mg) and sodium hydrogen carbonate (50 mg) were added. After 4 h, the mixture turned yellow (RuO_4), and t.l.c. (benzene–ether, 8:2) showed that the starting material was no longer present. Excess 2-propanol was then added and, after 10 min, the mixture was filtered through carbon. The aqueous phase was extracted three times with chloroform, and the combined extracts were washed with water, dried, and evaporated to give a syrup (472 mg). The product was purified by preparative t.l.c. (benzene–ether, 8:2) to give 268 mg (57%) of **3α**, which was partially hydrated as seen from an n.m.r. spectrum. The product was dried for 48 h over phosphorous pentaoxide *in vacuo* to give pure **3α**, $[\alpha]_D^{25}$ +37.1° (*c* 1.1, chloroform).

Anal. Calc. for $C_{34}H_{26}O_{10}$: C, 68.68; H, 4.41. Found: C, 68.32; H, 4.44.

1,3,4,6-Tetra-O-*benzoyl*-β-D-arabino-*hexopyranosulose* (**3β**). — This compound was prepared, as described above, by oxidation of **2β** (1.05 g). The n.m.r. spectra (Table I) of the product (843 mg) showed that it contained a small amount of **4β** and ~50% of the hydrate of **3β**. The residue crystallized when the solvent was evaporated. Recrystallization from chloroform–pentane gave 210 mg of a product with m.p. 105–125° which, as seen from an n.m.r. spectrum (Table I), was mainly hydrated **3β**. When the $CDCl_3$ solution was kept for a few h, water was eliminated, and an n.m.r. spectrum then showed that the ketoform **3β** was formed. The product was dissolved in chloroform, the solution was kept for 2 h, and pentane was then added. This gave 123 mg (12%) of product with m.p. 122–126°. The product, when recrystallized again and dried over P_2O_5, had m.p. 127–129°, $[\alpha]_D^{23}$ −9.3° (*c* 1.0, chloroform).

Anal. Found: C, 68.11; H, 4.56.

1,3,6-Tri-O-*benzoyl-4-deoxy*-β-D-glycero-*hex-3-enopyranosulose* (**4β**). — Crude **3β** (416 mg) was stirred with benzene (10 ml), water (0.3 ml), and sodium hydrogen carbonate (100 mg) for 1.5 h at 80°. The solid was then filtered off and washed with dichloromethane, and the solution was dried and evaporated. The residue (321 mg, 80%) was crystallized twice from ethanol to give **4β**, m.p. 103–105°, $[\alpha]_D^{23}$ −75.0° (*c* 2.3, chloroform).

Anal. Calc. for $C_{27}H_{20}O_8$: C, 68.64; H, 4.27. Found: C, 68.60; H, 4.33.

1,3,6-Tri-O-*benzoyl-4-deoxy*-α-D-glycero-*hex-3-enopyranosulose* (**4α**). — This compound was prepared from **3α** (250 mg), as described for **3β**. The crude product (115 mg, 58%) was recrystallized from ethanol to give **4α**, m.p. 126.5–127°, $[\alpha]_D^{25}$ +2.69° (*c* 1.6, chloroform).

Anal. Found: C, 68.49; H, 4.40.

1-O-*Acetyl-3,4,6-tri*-O-*benzoyl*-α-D-arabino-*hexopyranosulose* (**7α**). — A solution of **6α** (270 mg) in dichloromethane (3 ml) and water (3 ml) was oxidized, as described above, with ruthenium dioxide (50 mg) and potassium periodate (230 mg) in the presence of sodium hydrogen carbonate (60 mg). The reaction was monitored by t.l.c. (ether–pentane, 2:1), and work-up after 3 h gave 210 mg of **7α** as a syrup which was too unstable to be purified. The n.m.r. spectrum (Table I) was obtained after **7α** had been dried *in vacuo* over P_2O_5.

1-O-*Acetyl-3,4,6-tri*-O-*benzoyl*-β-D-arabino-*hexopyranosulose* (**7β**). — This com-

pound was prepared by oxidation of **6β** (1.096 g), as described for **6α**, to give a syrup (778 mg). An n.m.r. spectrum, obtained after **7β** had been dried over P_2O_5, showed that the product contained a trace of the unsaturated ketone **8β**. When kept in dichloromethane solution, the product slowly deposited crystals of **8β**.

*1-O-Acetyl-3,6-di-O-benzoyl-4-deoxy-α-*D-glycero-*hex-3-enopyranosulose* (**8α**). — A solution of **7α** (190 mg) in benzene (5.0 ml) was boiled with water (0.1 ml) and sodium hydrogen carbonate (100 mg) for 1 h. The mixture was then dried ($MgSO_4$), filtered, and evaporated to give 123 mg (82%) of **8α** which crystallized. After recrystallization from ethanol, the product (50 mg, 33%) had m.p. 137–138° $[\alpha]_D^{23}$ −34.7° (*c* 0.8, chloroform).

Anal. Calc. for $C_{22}H_{18}O_8$: C, 64.39; H, 4.42. Found: C, 64.18; H, 4.62.

*1-O-Acetyl-3,6-di-O-benzoyl-4-deoxy-β-*D-glycero-*hex-3-enopyranosulose* (**8β**). — This compound was prepared from **7β**, as described for **7α**. When crystallized from dichloromethane–pentane, **8β** had m.p. 147–148°, $[\alpha]_D$ −60.8° (*c* 3, chloroform).

Anal. Found: C, 64.20; H, 4.60.

Di-O-benzoylkojic acid (**10**). — A solution of **4β** (115 mg) in pyridine (3 ml) was kept at 60° for 1 h. It was then diluted with dichloromethane, washed with 1.5M sulfuric acid and aqueous sodium hydrogen carbonate, and dried, and the solvent evaporated. The residue (43 mg, 50%) gave an n.m.r. spectrum which was identical with that of pure **10**. Crystallization from ethanol gave 30 mg of **10**, m.p. 130–132°; lit.[1] m.p. 136°. A mixture melting-point with authentic **10** gave no depression.

The α anomer **4α**, when treated with pyridine in the same manner, also gave **10**.

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