SELECTIVE ESTERIFICATION OF METHYL α-D-GLUCOPYRANOSIDE

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ABSTRACT

6-Monoesters of methyl α-D-glucopyranoside have been prepared by transesterification with methyl laurate, methyl palmitate, methyl stearate, and methyl benzoate, catalyzed by sodium methoxide in the absence of a solvent. The benzoylation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was separately performed with methyl benzoate and with benzoyl chloride, and the product distributions with the two reagents were compared; methyl 2-*O*-benzoyl-α-D-glucopyranoside and methyl 3-*O*-benzoyl-α-D-glucopyranoside were obtained by hydrolysis of the corresponding monobenzoates of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside. Methyl 4-*O*-benzoyl-α-D-glucopyranoside was prepared by ring-opening of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside with *N*-bromosuccinimide in the presence of water.

INTRODUCTION

During the past twenty years, methyl α-D-glucopyranoside (**1**) has become available in large quantity, and detailed studies have been made of its chemical reactions with a view to finding products having commercial value. As part of this program, we have examined the transesterification of **1** with some methyl esters to form mono-acyl derivatives of **1**. The products may have utility in food processing as emulsifiers, in detergents, and in the paint and varnish industries[1].

Selective esterification of **1** by base-catalyzed ester-interchange has been reported previously[2-4], but products so obtained were not well defined and were probably mixtures.

RESULTS AND DISCUSSION

Base-catalyzed ester-interchange, essentially as described by Wolff and Hill[4], has proved to be a rapid and simple method for the preparation in crystalline form of certain 6-*O*-acyl derivatives of **1**. Thus, by heating methyl benzoate, methyl laurate, methyl palmitate, or methyl stearate with 2–3 molar proportions of **1** in the presence of sodium methoxide for 15–30 min, at 200–230°, mixtures are obtained from

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which the crystalline 6-monoesters can readily be separated in yields of 30–40% (based on the methyl ester).

The major product prepared in this way from **1** and methyl palmitate had physical constants closely similar to those reported[5] for methyl 6-*O*-palmitoyl-α-D-glucopyranoside prepared by treating **1** with 1 equivalent of palmitoyl chloride. Esterification at the 6-hydroxyl group was also supported by the uptake of 2 molar proportions of periodate when the palmitic ester of the glycoside was oxidized by periodic acid in acetic acid containing 2–3% of water[6]. Consumption of the second mole of periodate was much slower than for **1**; this effect may be characteristic of **1** substituted at the 6-hydroxyl group[7]. The monopalmitate of **1** was benzoylated, and the crystalline product was identical with that obtained by treating methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside[8] with palmitoyl chloride. As benzoylating conditions do not promote acyl migration[9], the identity of these compounds prepared by the two different methods is additional evidence that the monopalmitate produced by ester interchange is the 6-palmitate of **1**.

Similarly, the crystalline monoesters of **1** produced from methyl benzoate, methyl laurate, or methyl stearate were shown to be 6-esters. These results support the generalization[10] that the primary hydroxyl group of methyl α-D-glycopyranoside is esterified more readily than its secondary hydroxyl groups.

Methyl 6-*O*-benzoyl-α-D-glucopyranoside (**8**) crystallizes from water as a monohydrate. The hydrate is converted into an anhydrous form by crystallization from ethanol. The 6-benzoate is soluble in chloroform, as well as in water; it shows little solubility in ether. These solubility characteristics make easy its separation from unreacted **1** and from higher esters formed during the reaction.

The solubility of the 6-benzoate in water may, in part, be responsible for the report by Lieser and Schweizer[11] that this compound could not be isolated after treating **1** with a deficiency (<2 molar proportions) of benzoyl chloride. We have shown that, on treating **1** with 0.5 molar proportion of benzoyl chloride in pyridine, at least 35–40% of the benzoyl chloride is used to form the 6-monobenzoate. This compound may be isolated by washing the water-quenched reaction-mixture with ether (to remove higher esters), removing pyridine by azeotropic distillation with water *in vacuo*, and neutralizing the pyridine hydrochloride remaining in the aqueous phase. The last step is critical, as pyridine hydrochloride appears to inhibit crystallization of the 6-benzoate. Concentration of the neutralized, aqueous solution gives the 6-benzoate monohydrate. After evaporation of the mother liquor to dryness, the residue may be extracted with chloroform to secure residual 6-benzoate free from unreacted **1**.

Esterification of **8** with 1 equivalent of benzoyl chloride in pyridine gave a mixture from which the major product was isolated in crystalline form by column chromatography on silica. This product had physical properties identical with those reported[11] for the 2,6-dibenzoate.

Similarly, the known[12] methyl 6-*O*-benzoyl-β-D-glucopyranoside was obtained from the reaction of methyl benzoate with methyl β-D-glucopyranoside. Periodate oxidation of this ester gave results identical with those obtained for the 6-esters already mentioned.

Methyl 2-*O*-benzoyl-α-D-glucopyranoside (**9**) and methyl 3-*O*-benzoyl-α-D-glucopyranoside (**10**) were prepared by interaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**11**) with benzoyl chloride or methyl benzoate. The known[13] monobenzoates of **11**, namely, methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**12**) and methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**13**) were isolated by column chromatography on silica gel, and **9** and **10**, which have not been described previously, were obtained on removing the acetal group.

The relative reactivity of the secondary hydroxyl groups of **11** depends[14] on the nature of the benzoylating agent. With benzoyl chloride and **11** at 0°, the yields of **12** and **13** were 24 and 6%, respectively, whereas, with benzoic anhydride at 20–30° or at 50°, the same products were obtained in yields of 12–13 and 22–25%, respectively[14]. Compounds **12** and **13** were obtained in yields of 59 and 9.8%, respectively, when the esterification with benzoyl chloride was performed at −20° by the procedure described by Long and coworkers[15] for sulfonylation. Comparison of our results with those of the Jeanlozes[14] shows that, at −20°, the selectivity for reaction of benzoyl chloride at O-2 of **11** is increased significantly over that at 0°; this observation was anticipated in the light of previous work on selective esterification[15]. Selectivity for O-2 was also observed, but was less pronounced, when transesterification between methyl benzoate and **11** was performed; compounds **12** and **13** were obtained in yields of 21 and 8.6%, respectively.

Compound **9** has m.p. 174–175°, identical with that reported by Lieser and Leckzyck[16] for a monobenzoate of **1**. These workers obtained their monobenzoate by removal of the xanthate group from the corresponding *S*-methyl dithiocarbonate, and assigned the benzoate group to C-2 or C-6; our establishing that this monobenzoate is **9** shows, indirectly, that the *S*-methyl dithiocarbonate of **1**, reported by the same workers, is the 6-substituted derivative. The structure of the last-named compound has since been established in a direct way[17].

To complete the set of monobenzoates of **1**, we undertook the preparation of methyl 4-*O*-benzoyl-α-D-glucopyranoside (**14**) by applying a procedure described by Hanessian[18] for the preparation of methyl 2-acetamido-4-*O*-benzoyl-2-deoxy-3-*O*-methyl-α-D-glucopyranoside. Ring-opening of **11** with *N*-bromosuccinimide in the presence of water afforded **14** in 25% yield, together with methyl 4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside[19] in 32% yield.

The specificities of fungal esterases with many of the above benzoic esters as substrates have been examined[20].

EXPERIMENTAL

General. — Methyl α-D-glucopyranoside (**1**) was freed of D-glucose by passage through Dowex 1 (OH^-) ion-exchange resin and subsequent recrystallization from methanol. Methyl laurate (Eastman Organic Chemicals), methyl palmitate, and methyl stearate (Matheson Coleman & Bell) were used as supplied. Column chromatography was performed on Brinkmann silica gel (0.05–0.2 mm) and on Woelm acid alumina, and thin-layer chromatography (t.l.c.) on Brinkmann silica gel GF_{254} with 45:5:3 (v/v) ethyl acetate–ethanol–water. Evaporations were performed below 40°. Melting points were determined with a Thomas–Hoover capillary melting-point apparatus, and optical rotations were measured with an ETL-NPL automatic polarimeter. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

Methyl 6-O-lauroyl-α-D-glucopyranoside (**2**). — Compound **1** (77.6 g, 0.4 mole), methyl laurate (44.6 g, 0.2 mole), and sodium methoxide (0.30 g) were heated in a round-bottomed flask contained in a Wood's metal bath and equipped with a stirrer and Dean–Stark trap. The mixture was heated for 45 min at 210–230°, methanol being collected in the trap. The mixture was cooled to 90°, and poured into a solution of acetic acid (0.4 ml) in water (800 ml) at 98°. On cooling to room temperature, a syrup separated from the aq. solution. The mixture was extracted with chloroform (3 x 100 ml), and the extracts were combined, dried (sodium sulfate), decolorized with carbon, filtered, and evaporated to a pale-yellow solid (61.8 g). Two recrystallizations from propyl ether gave pure **2** (26.8 g, 35.6% based on methyl laurate), m.p. 68–70°, $[\alpha]_D^{27}$ +69.5° (*c* 2.0, chloroform).

Anal. Calc. for $C_{19}H_{36}O_7$: C, 60.61; H, 9.64; saponification equivalent, 376. Found: C, 60.60; H, 9.58; saponification equivalent, 375.

Methyl 2,3,4-tri-O-benzoyl-6-O-lauroyl-α-D-glucopyranoside (**3**). — A solution of **2** (1.88 g, 5 mmoles) in dry pyridine (10 ml) was treated with benzoyl chloride (3 ml), and the mixture was kept for 45 min at 60°, cooled, and poured into cold water (100 ml). The solid **3** (2.2 g, 64%) that separated was removed by filtration, and recrystallized from methanol, m.p. 53–55°, $[\alpha]_D^{26}$ +87.7° (*c* 1.0, pyridine).

Anal. Calc. for $C_{40}H_{48}O_{10}$: C, 69.75; H, 7.03. Found: C, 69.71; H, 7.05.

Compound **3** was also obtained when a solution of methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside[8] (3.8 g, 7.5 mmoles) in pyridine (20 ml) was treated with lauroyl chloride (2.74 g, 12.5 mmoles) for 45 min at 60°. The cooled mixture was poured into cold water (100 ml), and the syrup that separated solidified after standing for 5 days in water. The solid **3** (4.8 g, 93%) was recrystallized from methanol, m.p. 50–52° and mixed m.p. (with product obtained from **1**) 51.5–53.5°, $[\alpha]_D^{26}$ +85.2° (*c* 1.0, pyridine).

Anal. Calc. for $C_{40}H_{48}O_{10}$: C, 69.75; H, 7.03. Found: C, 69.78; H, 7.11.

Methyl 6-O-palmitoyl-α-D-glucopyranoside (**4**). — In a manner similar to that used for **2**, methyl palmitate (27.0 g, 0.1 mole), **1** (38.8 g, 0.2 mole), and sodium methoxide (0.14 g) were fused, with stirring, at 235–250° for 30 min (when distillation of methanol ceased). The mixture was processed as described for **2**, to give a yellow solid (33 g). This material was stirred for 20 h at 27° with ethyl ether (80 ml), and insoluble monopalmitate (16 g, 37% based on methyl palmitate) was recovered by filtration. Recrystallization from ethyl ether or propyl ether gave pure **4**, m.p. 87°, $[\alpha]_D^{26}$ +64° (*c* 2.7, chloroform); lit.[5] m.p. 89–90°, $[\alpha]_D$ +61.5° (*c* 1.215, chloroform).

Anal. Calc. for $C_{23}H_{44}O_7$: C, 63.86; H, 10.25; saponification equivalent, 432. Found: C, 64.04; H, 10.32; saponification equivalent, 436.

The yield of **4** was 50% when a 3:1 mole ratio of **1** to methyl palmitate was used, and 16.5% from equimolar quantities of these reactants.

The filtrate from the ether extraction of the crude product was evaporated to dryness, giving a solid (16.2 g). Part of this material (500 mg) was dissolved in benzene (4 ml) and chromatographed on a column (15 × 1 cm) of Woelm acid alumina. The alumina was eluted successively with 200 ml each of benzene, ether, chloroform, and methanol. The benzene eluate contained methyl palmitate (50 mg, 10%), and the combined ether and chloroform eluates gave unidentified solid material (80 mg, 16%). The methanol eluate gave **4** (250 mg, 50%), m.p. 87°, $[\alpha]_D^{26}$ +62.9° (*c* 2.2, chloroform).

Column chromatography on silica gel of the filtrate from the ether extraction gave a similar distribution of products, **4** being eluted with ethyl acetate.

Methyl 2,3,4-tri-O-benzoyl-6-O-palmitoyl-α-D-glucopyranoside (**5**). — Compound **4** (433 g) was benzoylated as described for the preparation of **3** from **2**, to give **5** (0.55 g, 74%), m.p. 60.0–61.5° (methanol), $[\alpha]_D^{26}$ +80.8° (*c* 1.0, pyridine).

Anal. Calc. for $C_{44}H_{56}O_{10}$: C, 70.94; H, 7.58. Found: C, 71.00; H, 7.51.

Compound **5** was also obtained when a solution of methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (3.8 g, 7.5 mmoles) in pyridine (20 ml) was treated with palmitoyl chloride (3.43 g, 12.5 mmoles) as described for the lauric ester. Recrystallization from methanol gave **5** (4.8 g, 86%), m.p. 59.5–61.0° and mixed m.p. (with product obtained from **4**) 60.0–61.5°, $[\alpha]_D^{26}$ +80.1° (*c* 2.0, pyridine).

Methyl 6-O-stearoyl-α-D-glucopyranoside (**6**). — Compound **1** (18.8 g, 0.2 mole), methyl stearate (29.8 g, 0.1 mole), and sodium methoxide (0.15 g) were fused, with stirring, for 30 min at 230°. The mixture was cooled to 100° and poured into boiling water (400 ml) containing acetic acid (0.2 ml). After 16 h at 27°, the light-brown solid that had separated was removed by filtration, and the filtrate was discarded. The solid was dissolved in chloroform (200 ml), and the solution was dried (Drierite), decolorized, and evaporated, to give crude **6** as a white solid (26.5 g). Recrystallization from propyl ether gave pure **6** (18 g, 39% based on methyl stearate), m.p. 91.5°, $[\alpha]_D^{27}$ +58.0° (*c* 2.0, chloroform).

Anal. Calc. for $C_{25}H_{48}O_7$: C, 65.18; H, 10.50; saponification equivalent, 460. Found: C, 64.95; H, 10.53; saponification equivalent, 464.

Methyl 2,3,4-tri-O-benzoyl-6-O-stearoyl-α-D-glucopyranoside (**7**). — In the way described for benzoylation of **2**, compound **6** (921 mg, 2 mmoles) gave **7** (600 mg, 39%), m.p. 63–65° (isopropyl alcohol), $[\alpha]_D^{26}$ +78.0° (*c* 1.0, pyridine).

Anal. Calc. for $C_{46}H_{60}O_{10}$: C, 71.48; H, 7.83. Found: C, 71.68; H, 7.82.

Compound **7** was also obtained, in 38% yield, by treatment of methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside with stearoyl chloride in pyridine; it had m.p. 61–62° and mixed m.p. (with product obtained from **6**) 62.0–63.5°, $[\alpha]_D^{26}$ +77.7° (*c* 2.0, pyridine).

Anal. Calc. for $C_{46}H_{60}O_{10}$: C, 71.48; H, 7.83. Found: C, 71.30; H, 7.84.

Methyl 6-O-benzoyl-α-D-glucopyranoside (**8**). — Compound **1** (77.6 g, 0.4 mole), methyl benzoate (24.8 ml, 0.2 mole), and sodium methoxide (0.28 g) were heated, with stirring, in a flask equipped with a Dean–Stark trap for 1 h at 190–200° (bath temperature). The mixture was cooled to 100°, and poured into boiling water (800 ml) containing acetic acid (0.5 ml). The solution was concentrated to 200 ml, and, on standing overnight at 27°, crystals of **8** monohydrate (22.3 g, 35.3% based on methyl benzoate) were formed, m.p. 127.0–129.0° (with softening at 75°), $[\alpha]_D^{27}$ +102° (*c* 1.0, water).

Anal. Calc. for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.20; H, 6.34.

The aq. mother liquors were extracted with ether (3 × 100 ml), and extracts were combined, washed successively with cold 3% (w/v) sodium hydroxide (2 × 50 ml) and water (3 × 25 ml), dried (sodium sulfate), filtered, and evaporated to a syrup. The syrup was dissolved in chloroform (5 ml), and hexane was added until crystals began to form. The suspension was kept for 16 h at 27°, and the crystals were then removed by filtration and identified as methyl 2,6-di-O-benzoyl-α-D-glucopyranoside[21] (1.05 g, 2.6% based on methyl benzoate), m.p. 141.5–142.5°, $[\alpha]_D^{27}$ +77° (*c* 2.0, chloroform); lit.[21] m.p. 141–142°, $[\alpha]_D^{30}$ +75° (*c* 3.1, chloroform).

Anal. Calc. for $C_{21}H_{22}O_8$: C, 62.67; H, 5.51. Found: C, 62.59; H, 5.54.

The sodium hydroxide washings were combined, acidified with conc. hydrochloric acid, and extracted with ether (3 × 50 ml) to remove benzoic acid (0.9 g, m.p. 120.0–121.5°). The aqueous solutions from which higher benzoates and benzoic acid had been removed were evaporated to a syrup; this was extracted with boiling chloroform (3 × 100 ml), and, during the extraction, the syrup solidified. The solid material was filtered off, washed with chloroform, and air-dried to give unreacted **1** (50.0 g, 64.5% of starting material).

The chloroform extracts were combined, and evaporated to a dark-brown syrup which was dissolved in water (150 ml). The solution was decolorized and then kept at 27°, to give an additional crop of **8** monohydrate (3.2 g, 5.1% based on methyl benzoate), m.p. 130.0–131.5° (with softening at 80°). Recrystallization of the combined crops (25.5 g) of **8** monohydrate from ethanol gave anhydrous **8**, m.p. 131.0–132.5° (no softening), $[\alpha]_D^{27}$ +108° (*c* 1.2, water).

Anal. Calc. for $C_{14}H_{18}O_7$: C, 56.37; H, 6.08. Found: C, 56.50; H, 6.05.

Methyl 6-O-benzoyl-β-D-glucopyranoside. — This compound was prepared in 38% yield (based on methyl benzoate) in a manner identical to that used for **8**; m.p. 131–132°, $[\alpha]_D^{27}$ −24.2° (*c* 1.4, water).

Anal. Calc. for $C_{14}H_{18}O_7$: C, 56.37; H, 6.08. Found: C, 56.44; H, 6.10.

Methyl 2,6-di-O-benzoyl-α-D-glucopyranoside[21]. — Compound **8** (2.98 g, 10 mmoles), dry pyridine (20 ml), and benzoyl chloride (1.2 ml, 1 equiv) were kept for 1 h at −40°, 24 h at −20°, and 24 h at room temperature. Pyridine was then removed, and the mixture was fractionated on silica gel. Elution with chloroform gave methyl 2,6-di-*O*-benzoyl-α-D-glucopyranoside (2.09 g, 52%), m.p. 142–143° and mixed m.p. (with product obtained during preparation of **8**) 141.5–142.5°, $[\alpha]_D^{27}$ +77° (*c* 2.0, chloroform).

Anal. Calc. for $C_{21}H_{22}O_8$: C, 62.67; H, 5.51. Found: C, 62.70; H, 5.52.

Methyl 2-O-benzoyl-α-D-glucopyranoside (**9**) *and methyl 3-O-benzoyl-α-D-glucopyranoside* (**10**). — Treatment of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**11**) (7 g, 25 mmoles) in pyridine (50 ml) with benzoyl chloride (3.5 ml, 1.2 equiv) as described for the preparation of methyl 2,6-di-*O*-benzoyl-α-D-glucopyranoside gave a mixture which was fractionated on silica gel. Elution with 10, 20, and 40% ether in benzene gave methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (1.24 g, 10.2%), methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**12**) (5.67 g, 59%), and methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**13**) (0.94 g, 9.8%), respectively. These compounds had physical constants in agreement with those reported by the Jeanlozes[14]. Elution with 1:1 ether–ethyl acetate gave unchanged **11** (1.35 g, 19.4%).

Reaction of **11** (2.82 g, 10 mmoles), methyl benzoate (5 ml, 40 mmoles), and sodium methoxide (15 mg) for 45 min at 200°, followed by fractionation of the reaction mixture on silica gel, afforded methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (184 mg, 3.8% based on **11**), **12** (810 mg, 21%), **13** (332 mg, 8.6%), and unchanged **11** (1.86 g, 66%).

Hydrolysis of **12** and **13** (600 mg), respectively, in 75% aq. acetic acid (24 ml) for 1 h at 75° gave, respectively, **9** (440 mg, 95%), m.p. 174–175° (from chloroform), $[\alpha]_D^{24}$ +156° (*c* 1.1, ethanol); and **10** (449 mg, 97%), m.p. 78–79° (from propyl alcohol) $[\alpha]_D^{30}$ +127° (*c* 2.4, ethanol).

Anal. Calc. for $C_{14}H_{18}O_7$: C, 56.37; H, 6.08. Found for **9**: C, 56.45; H, 6.10. Found for **10**: C, 56.50; H, 6.11.

Methyl 4-O-benzoyl-α-D-glucopyranoside (**14**). — Compound **11** (2 g), *N*-bromosuccinimide (1.4 g), barium carbonate (4 g), water (0.25 ml), and carbon tetrachloride (100 ml) were heated under reflux for 1 h; examination by t.l.c. then indicated complete absence of **11**. The mixture was filtered, and fractionated on silica gel to give methyl 4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside[17] (809 mg, 32%) eluted with chloroform, m.p. 130–131°, $[\alpha]_D^{24}$ +116° (*c* 1.0, chloroform); and **14** (519 mg, 25%) eluted with ethyl acetate, m.p. 128–129° (propyl alcohol), $[\alpha]_D^{29}$ +116° (*c* 2.6, ethanol). The two products were clearly different in i.r. spectra and t.l.c. behavior.

Anal. Calc. for $C_{14}H_{18}O_7$: C, 56.37; H, 6.08. Found: C, 56.55; H, 6.10.

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