The Reaction of Ammonia with Acylated Disaccharides. VIII. Octa-*O*-benzoylmaltose and Benzoyl Derivatives of Maltose

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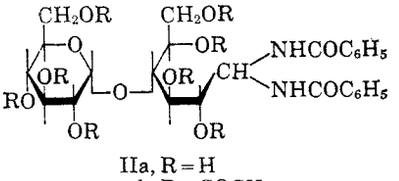
Octa-*O*-benzoyl-β-maltose (I) was prepared and its reaction with methanolic ammonia produced 4-*O*-α-D-glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol (IIa), maltose (III), 6-*O*-benzoylmaltose (IV), and *N*-benzoylmaltosylamine (Va) isolated as its heptaacetate Vb. The structures of IIa and IV were established. Octa-*O*-benzoyl-α-maltose (VI) and 6-*O*-benzoylmaltitol (VII) were obtained, respectively, by benzoylation and by reduction of IV. Enzymatic hydrolysis of IV gave 6-*O*-benzoyl-D-glucose (XII); 6-*O*-benzoyl-D-glucitol (XIII) was obtained by reduction of XII.

The purpose of the present work was to evaluate the stereochemical factors which influence the reaction of ammonia on disaccharide benzoates and to compare the course of the reaction with analogous experiments previously recorded in mono-[1] and disaccharides.[2,3] The reaction of octa-*O*-benzoyl-β-maltose with methanolic ammonia is described in this paper.

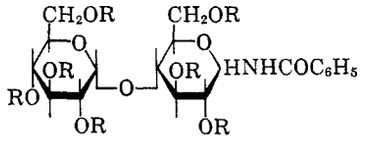
The benzoates of maltose reported in the literature are a hepta-*O*-benzoyl and a penta-*O*-benzoylmaltose, obtained by Skraup and Panormow[4] by benzoylation of the sugar with benzoyl chloride and sodium hydroxide. Benzoylation with benzoyl chloride and pyridine gave octa-*O*-benzoyl-β-maltose (I) which was ammonolyzed with methanolic ammonia. Chromatography of the reaction products on a cellulose column gave 20.8% of 4-*O*-α-D-glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol (IIa), 37.8% of maltose (III), and 31.6% of 6-*O*-benzoylmaltose (IV). Acetylation of some of the chromatographic fractions afforded hepta-*O*-acetyl-*N*-benzoylmaltosylamine (Vb) in a yield corresponding to 0.1% of free *N*-benzoylmaltosylamine (Va).

Octa-*O*-acetyl-4-*O*-α-D-glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol (IIb) was obtained by acetylation of 4-*O*-α-D-glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol (IIa). The formation of an octaacetate and the uptake of 4 moles of sodium metaperiodate with formation of 1 mole of formaldehyde from IIa, indicated the acyclic structure of the nitrogenated moiety of the molecule.



IIa, R = H
b, R = $COCH_3$

The *N*-benzoylmaltosylamine must have the pyranose structure Va, since the hydroxyl group at C-4 is blocked by the glycosidic linkage and the substance was obtained as a heptaacetate (Vb).



Va, R = H
b, R = $COCH_3$

The structure of 6-*O*-benzoylmaltose (IV) was demonstrated by methylation and hydrolysis, in which 2,3,-4,6-tetra-*O*-methyl-D-glucose (IX), 2,3,6-tri-*O*-methyl-D-glucose (X), and 2,3-di-*O*-methyl-D-glucose (XI) were obtained. Compound XI was identified by its specific rotation and by oxidation with sodium metaperiodate. The 2,3-di-*O*-methyl-D-glucitol, obtained by reduction of XI with sodium borohydride, was also oxidized. Both substances consumed 1.9 moles of sodium metaperiodate and produced 0.9 mole of formaldehyde. The formation of X is attributed to partial debenzoylation of the 6-*O*-benzoylmaltose during the methylation reaction. The nearly quantitative relationship of IX to the sum of X and XI showed that the *O*-benzoyl group must have been present in the reducing moiety of the disaccharide. The formation of 2,3-di-*O*-methyl-D-glucose and 2,3,4,6-tetra-*O*-methyl-D-glucose can be explained only by supposing that position C-6 of the reducing moiety is blocked. They can not be formed from 6′-*O*-benzoylmaltose.

6-*O*-Benzoylmaltose (IV) was also oxidized with sodium metaperiodate in order to establish that the C-6 benzoyl group had not migrated during methylation. This oxidation took up 3.9 moles of sodium metaperiodate and did not produce formaldehyde. 6-*O*-Benzoylmaltitol (VII) and maltitol (VIII) were prepared by reduction of IV and III with sodium borohydride and were oxidized in parallel experiments to confirm the former results; VII took up 4.2 moles of sodium metaperiodate and produced 1 mole of formaldehyde and VIII took up 4.9 moles of oxidant and produced 2 moles of formaldehyde. This agrees with a blocked C-6 position in VII, as it gave only 1 mole of formaldehyde.

Enzymatic hydrolysis of 6-*O*-benzoylmaltose (IV) produced 6-*O*-benzoyl-D-glucose (XII) and reduction of the last product gave 6-*O*-benzoyl-D-glucitol (XIII); the structures of both substances were confirmed by periodate oxidation. The benzoylation of 6-*O*-benzoylmaltose (IV) produced octa-*O*-benzoyl-α-maltose (VI). The formation of the octabenzoate with the α configuration is attributed to a steric effect due to the benzoyl group at C-6 in IV, which would lead to the formation

(1) V. Deulofeu, *et al.*, *J. Org. Chem.*, **17**, 1087, 1093, 1097 (1952); **22**, 802 (1957); **24**, 180 (1959).

(2) J. O. Deferrari, I. M. E. Thiel, and R. A. Cadenas, *ibid.*, **30**, 3053 (1965).

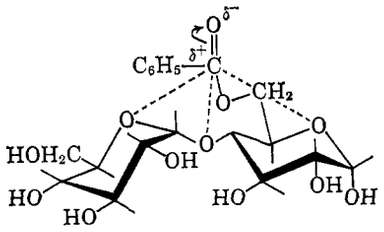
(3) J. O. Deferrari and R. A. Cadenas, *ibid.*, **28**, 1070 (1963); R. A. Cadenas and J. O. Deferrari, *ibid.*, **28**, 1072, 2613 (1963).

(4) H. Skraup, *Monatsh.*, **10**, 398 (1889); A. Panormow, *J. Russl. Chem. Gesellsch.*, 375 (1891) (I); *Chem. Zentr.*, 853 (1891) (II); *Ber. Referate*, **24**, 971 (1891).

of the α anomer, while the absence of this benzoyl group leads to the β anomer.

To establish the anomeric character of both benzoates, anomerization was carried out with zinc chloride and benzoic acid, adapting the technique of Ness, Fletcher, and Hudson.[5] The β anomer was obtained from octa-*O*-benzoyl-α-maltose. The same technique was unsuccessful with octa-*O*-benzoyl-β-maltose, but, using zinc chloride and benzoic anhydride, the α anomer was obtained.

The benzoyl group in 6-*O*-benzoylmaltose is very resistant to ammonolysis. It was eliminated completely only after 15 days, while the benzoyl group of 6-*O*-benzoylmaltitol (VII) was eliminated after 2 days, when treated with methanolic ammonia. The stability of the 6-*O*-benzoyl group could be attributed to an interaction of the carbon atom of the carbonyl group with the oxygen atoms of the pyranose rings and with that of the glycosidic linkage, as shown in structure IV. The 6-*O*-benzoyl group is the only one for which



IV

such interactions could be observed in Stuart-type molecular models of disaccharides. These interactions are absent in the monosaccharide benzoates,[1] which are rapidly ammonolyzed and did not give 6-*O*-benzoyl derivatives. In disaccharides, the interaction shown in IV would fix the steric position of the benzoyl group, thus shielding it against attack by ammonia; if this interaction is lacking, the benzoyl group could adopt a more accesible position and would be eliminated as rapidly as the other benzoyl groups. Stabilization would depend on the combined influence of the three oxygen atoms mentioned above, as the 6-*O*-benzoyl group is eliminated more rapidly if any one of them is absent, as, for example, in 6-*O*-benzoylmaltitol (2 days), 6-*O*-benzoylcellobiitol (6 hr), 6-*O*-benzoylglucose (2 hr), and 6-*O*-benzoyl-D-glucitol (2 hr). The examination of Stuart-type models of 6-*O*-benzoylcellobiose, which was obtained with 6.6% yield and was completely ammonolyzed after 7 days, showed that, if the benzoyl group occupies an equidistant position from the three considered oxygen atoms, it is less hindered in face of the attack by ammonia than in an equidistant position in the 6-*O*-benzoylmaltose molecule.

6-*O*-Acetyl derivatives have not been isolated in the ammonolysis of octa-*O*-acetyl disaccharides[3] carried out under the experimental conditions described in this paper. The 6-*O*-acetyl group would present the same interactions as were pointed out for the 6-*O*-benzoate, but their effect would be negligible, since the acetyl group is more reactive and smaller than the benzoyl group and therefore more accessible to nucleophilic attack by ammonia.

(5) R. K. Ness, H. G. Fletcher, and C. S. Hudson, *J. Am. Chem. Soc.*, **72**, 2200 (1950).

In the case of octa-*O*-benzoylmaltose the described stabilizing interactions could also be present prior to ammonolysis; nearly 70% of the C-6 benzoyl group is, however, eliminated in 24 hr. This suggests either that steric compression might weaken this interaction in the octabenzoate, or that the presence of free hydroxyl groups might have an important stabilizing effect after elimination of the other benzoyl groups.

The infrared spectra of 6-*O*-benzoylmaltose (IV) and 6-*O*-benzoylmaltitol (VII) showed a strong absorption at 1700–1710 cm^{-1} which confirmed the existence of the carbonyl group in both substances and precluded the possibility of the benzoyl group's participation in an ortho ester structure, which could have explained its stability. The shift of the carbonyl absorption from 1725 to 1735 cm^{-1} observed in octa-*O*-benzoyl-β-maltose suggested that it was involved in some interaction. Similar shifts have been observed in some alkaloids[6] and in other natural products[7] and have been attributed to interaction of a carbonyl group with nitrogen atoms and to hydrogen bonding, respectively. The shift of the carbonyl absorption observed in 6-*O*-benzoylmaltose (IV) and 6-*O*-benzoylcellobiose could be attributed to the interactions postulated in structure IV or to hydrogen bonding. The latter possibility would seem to be supported by the absorption of the carbonyl group in solid 6-*O*-benzoyl-D-glucose (XII), 6-*O*-benzoyl-D-glucitol (XIII), 6-*O*-benzoylmaltitol (VII), and 6-*O*-benzoylcellobiitol, which exhibited a similar shift. The rapid ammonolysis of these compounds, in which the combined interactions postulated in structure IV are impossible, would point out that provided the same hydrogen bonding persisted in methanolic solution, it would not be a decisive factor in the stabilization of the benzoyl group in 6-*O*-benzoylmaltose.

Deulofeu, *et al.*,[8] studied the participation of benzoyl groups at different positions in glucose and found that the contribution of the C-4 benzoyl group (0.82 mole/mole) is the highest observed in the formation of 1,1-bis(benzamido)-1-deoxy-D-glucitol. In accordance with this, the yields of nitrogenated sugar derivatives could be expected to be less in the disaccharide field, because C-4 is involved in the glycosidic linkage. The yield of 7.8% of 4-*O*-β-D-glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol[2] is as low as could be expected. The high yield, 20.8% of 4-*O*-α-D-glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol (IIa), could be attributed to a different participation of benzoyl groups of the reducing moiety of maltose with reference to that observed in glucose, or to a probable participation of the benzoyl groups of the nonreducing moiety due to the α-glycosidic configuration of the maltose molecule.

Experimental Section

A 16% methanolic solution of ammonia was used. Paper chromatography was carried out on Whatman No. 1 paper, using 1-butanol–ethanol–water (5:1:4, v/v, top layer) as developing solvent. The spray reagents used were (a) silver nitrate–

(6) F. A. L. Anet and L. Marion, *Can. J. Chem.*, **32**, 452 (1954); N. J. Leonard and M. Oki, *J. Am. Chem. Soc.*, **76**, 3463 (1954).

(7) A. F. McInnes, S. Yoshida, and G. H. N. Towers, *Tetrahedron*, **21**, 2939 (1965).

(8) E. G. Gros, M. A. Ondetti, J. F. Sproviero, V. Deulofeu, and J. O. Deferrari, *J. Org. Chem.*, **27**, 924 (1962).

sodium methoxide[9] and (b) aniline hydrogen phthalate.[10] Thin layer chromatography was performed on silicic acid–starch plates,[11] developed with benzene–ethyl acetate (95:5, v/v). The spots were observed by spraying with reagent a and heating at 110° for 15–30 min. Melting points are not corrected.

Octa-*O*-benzoyl-β-maltose (I) by Benzoylation of Maltose.—Maltose (25 g, 0.073 mole), mp 120–122°, was suspended in 250 ml of pyridine and 100 ml (0.84 mole) of benzoyl chloride was added in portions shaking the mixture vigorously and keeping it in a water bath at 0°. After standing for 4 days at room temperature it was heated for 4 hr at 60° and 3 hr at 100°. The reaction mixture was poured into ice–water and the syrup obtained was washed until it gave a pulverized solid. The yield was 81 g (94%) of an amorphous substance of mp 170–180°. Crystallized three times from acetone–methanol (1:3), it gave prisms of mp 190–192°, $[\alpha]^{21}D$ +67.6° (*c* 1.0, chloroform), and was homogeneous by thin layer chromatography.

Anal. Calcd for $C_{68}H_{54}O_{19}$: C, 69.48; H, 4.64. Found (for a sample dried at 140° and 1 mm): C, 69.60: H, 4.74.

Reaction of Octa-*O*-benzoyl-β-maltose (I) with Methanolic Ammonia. A. Isolation of 4-*O*-α-D-Glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol (IIa).—Compound I (40 g) was suspended in 1000 ml of methanolic ammonia and dissolved by shaking for 7 hr. After standing for 24 hr at room temperature the solution was evaporated to dryness and the residue was extracted with six 100-ml portions of ethyl acetate. Dissolving the residue in 600 ml of hot isopropyl alcohol, 0.66 g of IIa crystallized; it was a nonreducing substance of R_f 0.34 which after three crystallizations from methanol gave needles of mp 225–226°, $[\alpha]^{22}D$ +42.6° (*c* 1.15, pyridine).

Anal. Calcd for $C_{26}H_{34}N_2O_{12}$: C, 55.12; H, 6.05; N, 4.94. Found (for a sample dried at 120° and 1 mm): C, 54.85; H, 6.02; N, 4.85.

The mother liquors of the crystallization of IIa were evaporated and chromatographed on a 68 × 4.5 cm cellulose column, loaded with water-saturated butanol, and developed with butanol saturated with water. Fractions (90) of 25 ml each were collected. Fractions 27–41 gave upon evaporation and crystallization from isopropyl alcohol 2.68 g of IIa. By chromatography of fractions 42–90 (as described under C), another 0.68 g of IIa was obtained (total yield 4.02 g, 20.8%).

B. Isolation of Maltose (III).—By washing the cellulose column with methanol and water and evaporation of the combined washings, 2.77 g of III was obtained, which was crystallized four times from water–ethanol (2:8) and gave mp 124–126°, $[\alpha]^{21}D$ +109° (10 min) → +131° (final value) (*c* 1.08, water). By chromatography of fractions 42–90 (as described under C), another 1.62 g of III was obtained (total yield 4.40 g, 37.8%).

C. Isolation of 6-*O*-Benzoylmaltose (IV).—Fractions 42–90 formed by mixtures of the reaction products and obtained as described under A were chromatographed as before, collecting 105 fractions of 25 ml each. Evaporation of fractions 47–65 gave 4.81 g (31.6%) of IV, which after four crystallizations from methanol–ethyl acetate (1:2) gave a reducing product of R_f 0.30, as needles of mp 140–141°, $[\alpha]^{26}D$ +130.0° (5 min) → +105.8° (96 hr) (*c* 0.96, water).

Anal. Calcd for $C_{19}H_{26}O_{12}$: C, 51.12; H, 5.87. Found (for a sample dried at 110° and 1 mm): C, 51.14; H, 6.27.

Evaporation of fractions 34–46 gave 0.68 g of IIa; fractions 90–105 and washings of the column gave 1.62 g of III.

D. Isolation of *N*-Benzoylmaltosylamine (Va) as Hepta-*O*-acetyl-*N*-benzoylmaltosylamine (Vb).—Chromatography using Whatman 3MM paper of fractions 10–24 obtained as described under C, gave 0.023 g of a syrup which was acetylated with 2 ml of a (1:1) solution of acetic anhydride in pyridine. The syrup obtained (0.040 g) was purified three times by precipitation from its ethanolic solution. It gave 0.023 g of Vb as a syrup which when dried at 64° and 1 mm had $[\alpha]^{18}D$ +115.8° (*c* 1.2, chloroform), corresponding to 0.1% yield of free *N*-benzoylmaltoyslamine (Va).

Anal. Calcd for $C_{33}H_{41}NO_{18}.H_2O$: C, 52.31; H, 5.72; N, 1.85. Found (for a sample dried at 64° and 1 mm): C, 52.30; H, 5.94; N, 2.14.

Octa-*O*-acetyl-4-*O*-α-D-glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol (IIb).—Compound IIa (120 mg) was acetylated with 6 ml of a (1:1) solution of acetic anhydride in pyridine; the mixture was kept for 24 hr at room temperature, then heated 30 min at 60° and evaporated to dryness in a vacuum desiccator over sulfuric acid and sodium hydroxide. Recrystallization from ethanol gave 0.15 g (74%) of IIb as needles, which after three crystallization from ethanol had mp 130–131°, $[\alpha]^{21}D$ +31.9° (*c* 0.79, chloroform).

Anal. Calcd for $C_{42}H_{50}N_2O_{20}$: C, 55.87; H, 5.58; N, 3.10. Found (for a sample dried at 110° and 1 mm): C, 55.62; H, 5.78; N, 3.23.

Octa-*O*-benzoyl-α-maltose (VI) from 6-*O*-Benzoylmaltose (IV).—Compound IV (50 mg, 0.0001 mole) was dissolved in 4 ml of pyridine and 2 ml of benzoyl chloride was added. The mixture was kept 14 hr at room temperature, and heated for 3 hr at 60° and 2 hr at 100°; it was cooled and poured into 50 ml of ice–water and washed with water until it gave a pulverized solid. Dissolved in hot acetone–methanol (1:2) it gave upon cooling 0.122 g (93%) of VI as an amorphous solid which after four similar purifications had mp 130–133°, $[\alpha]^{23}D$ +137.2° (*c* 0.98, chloroform).

Anal. Calcd for $C_{68}H_{54}O_{19}$: C, 69.48; H, 4.64. Found (for a sample dried at 110° and 1 mm): C, 69.66; H, 4.89.

Octa-*O*-benzoyl-β-maltose (I) by Anomerization of VI.—Anhydrous zinc chloride (0.32 g) and 0.65 g of benzoic acid were melted at 140° in a stoppered test tube; 0.65 g of VI was added and the mixture was heated for 1 hr at 140°, then cooled, and dissolved in pyridine. The dark solution was poured into 100 ml of water and extracted with three 50-ml portions of chloroform; the chloroform solution was washed with 1 *N* sulfuric acid, a saturated sodium hydrogen carbonate solution, and finally with water. The solution was dried with anhydrous magnesium sulfate, and evaporated to dryness, and the residue was crystallized eight times from acetone–methanol (1:1); it gave 0.22 g (33.8%) of I, $[\alpha]^{20}D$ +68.2° (*c* 1.1, chloroform).

Octa-*O*-benzoyl-α-maltose (VI) by Anomerization of I.—The above technique applied to I only gave the starting material. Anomerization was carried out using benzoic anhydride instead of benzoic acid, as follows: in a stoppered test tube 2.6 g of anhydrous zinc chloride and 5.3 g of benzoic anhydride were melted at 140°; 5.3 g of I was added and the mixture was heated for 15 min at 140° and for 2 hr at 100°; then it was cooled and dissolved in pyridine; the solution was poured into 200 ml of water and extracted with four 50-ml portions of chloroform; and the chloroform solution was washed with 1 *N* sulfuric acid, a saturated sodium hydrogen carbonate solution, and finally with water, dried with anhydrous magnesium sulfate, and evaporated to dryness. The residue, purified by dissolution in hot acetone–methanol (1:2) and cooling, gave an amorphous solid of $[\alpha]^{24}D$ +112°, which after two purifications as described gave 0.093 g (1.7%) of VI as an amorphous substance of mp 132–133°, $[\alpha]^{23}D$ +136.8° (*c* 0.88, chloroform). From the mother liquors 3.56 g of $[\alpha]D$ +115° were obtained, for which a 67% concentration of α anomer was calculated; the total anomerization yield was 46.7%.

Methylation of 6-*O*-Benzoylmaltose (IV) and Isolation of Its Hydrolysis Products.—Compound IV (500 mg) was dissolved in 25 ml of dimethylformamide and shaken with 20 ml of methyl iodide and 3.5 g of barium oxide during 24 hr. The mixture was filtered, then 200 ml of chloroform was added, and the chloroform solution was washed with 1 *N* sulfuric acid, a saturated sodium hydrogen carbonate solution, and water; it was dried with anhydrous magnesium sulfate and evaporated to dryness. The syrup obtained was dissolved in 15 ml of a 0.07% solution of sodium methoxide in methanol, which was neutralized with 1 *N* sulfuric acid after 4 days. The reaction mixture was heated with 15 ml of 1 *N* sulfuric acid for 6 hr at 100°. The sulfuric acid was neutralized with barium carbonate, filtered, and evaporated. The syrup obtained (0.43 g) was chromatographed on a 62 × by 2.8 cm cellulose column, loaded with water-saturated butanol, and eluted with butanol saturated with water, collecting 100 fractions of 100 ml each. Evaporation of fractions 30–35 gave 0.082 g of 2,3,4,6-tetra-*O*-methyl-D-glucose (IX) of $[\alpha]^{18}D$ +87.2° (final value) (*c* 1.30, water) (lit.[12] $[\alpha]D$ +92°). Evaporation of fractions 40–54 gave 0.040 g of 2,3,6-tri-*O*-methyl-D-glucose (X) of $[\alpha]^{18}D$ +69.4° (final value) (*c* 1.23, water) (lit.[13] $[\alpha]D$ +70°) and fractions 60–82 gave 0.042 g of 2,3-di-*O*-methyl-

(9) R. A. Cadenas and J. O. Deferrari, *Analyst*, **86**, 132 (1961).
(10) M. Patridge, *Nature*, **164**, 443 (1949).
(11) J. O. Deferrari, R. M. de Lederkremer, B. Matsuhiro, and J. F. Sproviero, *J. Chromatog.*, **9**, 283 (1962).
(12) J. C. Irvine and J. W. H. Oldham, *J. Chem. Soc.*, **119**, 1744 (1921).
(13) J. C. Irvine and E. L. Hirst, *ibid.*, **121**, 1231 (1922); J. C. Irvine and R. P. McGlynn, *J. Am. Chem. Soc.*, **54**, 356 (1932).

D-glucose (XI) of $[\alpha]^{22}D$ +48.5° (*c* 1.2, acetone) (lit.[14] $[\alpha]D$ +48.3°).

6-*O*-Benzoylmaltitol (VII) by Reduction of IV.—Compound IV (350 mg) dissolved in 5 ml of water was reduced by a solution of 58.8 mg of sodium borohydride in 3 ml of water during 3 hr. Zeo Karb 225 sulfonic resin was added to destroy the excess of reducing substance and to eliminate sodium ions. The solution was filtered and evaporated several times with methanol; the product was purified by dissolution in absolute ethanol, cooling to −10°, and decantation of the supernatant solution; 0.314 g (89.7%) of VII was obtained as an amorphous substance, which, after three further purifications as described and drying at 60° and 0.001 mm, had $[\alpha]^{26}D$ +84° (*c* 1.2, water).

Anal. Calcd for $C_{19}H_{28}O_{12}$: C, 50.89; H, 6.29. Found (for a sample dried at 60° and 0.001 mm): C, 50.65; H, 6.54.

Maltitol (VIII) by Reduction of III.—Compound VIII was obtained by borohydride reduction of III as described above, in 84% yield, and had $[\alpha]^{25}D$ +104.2° (*c* 0.87, water) (lit.[15] $[\alpha]D$ +90° and [16] $[\alpha]D$ +103°).

Isolation of 6-*O*-Benzoyl-D-glucose (XII) by Enzymatic Hydrolysis of IV.—Compound IV (350 mg) was incubated with 0.076 g of maltase (Nutritional Biochemical), in 103 ml of potassium phosphate buffer (pH 6.8, 0.05 *M*) at 30–35° for 8 hr. The solution was evaporated under vacuum and the residue was chromatographed on an 41.5 × 1.8 cm cellulose column, loaded, and eluted with 1-butanol–water (100:15, v/v), collecting 50 fractions of 25 ml each. Fractions 2–9 gave upon evaporation 0.163 g (73%) of XII, which, after two purifications by dissolution in hot methanol, precipitation by cooling, and decantation of the supernatant solution, gave a reducing syrup of R_f 0.66, which when dried at 64° and 0.001 mm, had $[\alpha]^{24}D$ +48.2° (5 min) → +45.0° (24 hr) (*c* 1.05, water) [lit.[17] $[\alpha]D$ +45.76° (10 min) → +44.57° (24 hr) (water)].

Fractions 13–30 gave upon evaporation 0.135 g (96%) of glucose of $[\alpha]^{28}D$ +52° (equilibrium).

6-*O*-Benzoyl-D-glucitol (XIII) by Reduction of XII.—Compound XII (45 mg) dissolved in 1 ml of water was reduced with 0.013 g of sodium borohydride in 1 ml of water for 3 hr, and worked as described for the preparation of VII; 0.043 g of XIII was obtained and purified by chromatography on a 12.5 × 1.8 cm cellulose column, loaded, and eluted with 1-butanol–water (100:15, v/v), collecting 25 fractions of 10 ml each. Fraction 3 gave by evaporation 28.8 mg (79%) of XIII, which when crystallized from methanol gave a nonreducing product of R_f 0.66, as needles of mp 141–143°, $[\alpha]^{29}D$ +18.2° (*c* 0.42, water).

Anal. Calcd for $C_{13}H_{18}O_7$: C, 54.53; H, 6.33. Found (for a sample dried at 64° and 0.001 mm): C, 54.28; H, 6.45.

Sodium Metaperiodate Oxidations.—The spectrophotometric technique was applied, measuring the sodium metaperiodate uptake with a Beckman DU spectrophotometer at 222.5 mμ[18] and the formaldehyde produced at 570 mμ.[19] Oxidations were carried out on samples of 2–6 mg dissolved in 3–4 ml of metaperiodate solution, containing 10 moles in excess over the calculated amount; the reaction mixtures were kept at 26° during oxidation. The results are shown in Table I.

Ammonolysis of some 6-*O*-Benzoyl Sugars.—6-*O*-Benzoyl sugars (1.5–3 mg) were dissolved in methanolic ammonia (0.5–1 ml); samples were chromatographed and developed with reagents a and b. Disappearance times for the corresponding spots are as follows: 6-*O*-benzoylmaltose (IV), 15 days; 6-*O*-benzoylmaltitol (VII), 2 days; 6-*O*-benzoylcellobiose,[2] 7 days; 6-*O*-benzoylcellobiitol, 6 hr; 6-*O*-benzoyl-D-glucose (XII), 2 hr; and 6-*O*-benzoyl-D-glucitol (XIII), 2 hr.

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(15) P. Karrer and J. Büchi, *Helv. Chim. Acta*, **20**, 86 (1937).
(16) M. L. Wolfrom and T. S. Gardner, *J. Am. Chem. Soc.*, **62**, 2553 (1940).
(17) E. Fischer and H. Noth, *Ber.*, **51**, 330 (1918).
(18) C. E. Crouthamel, H. V. Meek, D. S. Martin, and C. V. Banks, *J. Am. Chem. Soc.*, **71**, 3031 (1949).
(19) D. A. MacFadyen, *J. Biol. Chem.*, **158**, 107 (1945).

TABLE I

SODIUM METAPERIODATE OXIDATIONS

Time, hr	$NaIO_4$, moles	Formaldehyde, moles
A. 6-*O*-Benzoylmaltose (IV)[a]		
0.5	1.9	0
2	3.5	0
6	3.9	0
9.5	3.9	0
B. 6-*O*-Benzoylmaltitol (VII)[a]		
0.5	1.0	1.0
2	2.4	1.0
6	3.4	1.0
24	4.2	1.0
C. Maltitol (VIII)[a]		
0.5	2.8	1.8
2	4.4	2.0
9.5	4.9	2.0
24	4.9	2.0
D. 2,3-Di-*O*-methyl-D-glucose (XI)[b]		
1	0.7	0.5
9	1.7	0.8
27	1.9	0.8
77	1.9	0.8
E. 2,3-Di-*O*-methyl-D-glucitol[b,c]		
2	1.1	0.7
8	1.3	0.8
27	1.8	0.8
77	1.9	0.8
F. 4-*O*-α-D-Glucopyranosyl-1,1-bis(benzamido)-1-deoxy-D-glucitol (IIa)[d]		
2	1.6	0.8
6	3.2	1.0
10	4.0	1.0
14	4.0	1.0
G. 6-*O*-Benzoyl-D-glucose (XII)[a]		
0.5	2.1	0
2	3.0	0
4	3.0	0
H. 6-*O*-Benzoyl-D-glucitol (XIII)[e]		
0.5	3.5	1.0
1	3.9	1.0
6.5	4.0	1.0

[a] Overoxidation was not observed after 34 hr. [b] Carried out at pH 1. [c] 2,3-Di-*O*-methyl-D-glucose (2 mg) was reduced with sodium borohydride (4 mg); the excess of reducing agent was destroyed with formic acid and the pH adjusted to 1; the oxidation was carried out as described above. [d] Carried out at 0°; overoxidation began after 15 hr and at 70 hr 9 moles of $NaIO_4$ was consumed and formaldehyde concentration was diminished. (Other oxidations were carried out at different temperatures and at different pH values, but no constancy of values was obtained because of strong overoxidation.) [e] Overoxidation was observed after 24 hr.

Infrared Absorption Spectra of Some Benzoylated Products.—The infrared spectra were determined with a Perkin-Elmer infrared spectrophotometer Model 21 and carbonyl absorption is indicated as follows: (a) in potassium bromides, octa-*O*-benzoyl-β-maltose (I) 1725–1735 cm^{-1}, 6-*O*-benzoylmaltose (IV) 1700–1710 cm^{-1}, 6-*O*-benzoyl-D-glucitol (XIII) 1695–1698 cm^{-1}; (b) as a film, 6-*O*-benzoylmaltitol (VII) 1700–1715 cm^{-1}, 6-*O*-benzoylcellobiose 1700–1715 cm^{-1}, 6-*O*-benzoylcellobiitol 1698–1710 cm^{-1}, 6-*O*-benzoyl-D-glucose (XII) 1695–1710 cm^{-1}.