Routes to Substituted Methyl β-Maltosides[1]

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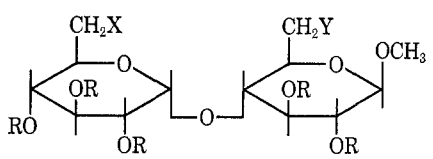
Reaction of methyl β-maltoside (**1**) with *p*-toluenesulfonyl (tosyl) chloride in a 1:1.1 molar ratio gave 28% of the 6,6′-ditosylate (**2a**) (isolated as an ethanolate **2b**), 18% of the 6′-tosylate (**3**), and 1% of the 6-tosylate (**4**). Acetylation of **2a** (or **2b**), **3**, and **4** produced the corresponding peracetates **5**, **6**, and **7**, which on treatment with sodium iodide in acetone were converted to 6,6′-dideoxy-6,6′-diiodo acetate (**8**), 6′-deoxy-6′-iodo acetate (**9**), and 6-deoxy-6-iodo acetate (**10**), respectively. Catalytic hydrogenolysis of the iodo acetates **8**, **9**, and **10** gave the corresponding deoxy acetyl maltosides **11**, **12**, and **13**. Reaction of methyl 2,2′,3,3′,4′-penta-*O*-acetyl-6,6′-di-*O*-*p*-tolylsulfonyl-β-maltoside (**5**) with sodium iodide in a 1:1 molar ratio produced methyl 2,2′,3,3′,4′-penta-*O*-acetyl-6-deoxy-6-iodo-6′-*O*-*p*-tolylsulfonyl-β-maltoside (**14**) as the major iodo product. Structures were assigned on the basis of catalytic hydrogenolysis of **14** to the related 6-deoxy-6′-tosylate (**15**), which on treatment with sodium hydroxide gave methyl 3′,6′-anhydro-6-deoxy-β-maltoside (**16**). Structures were also assigned by nmr evidence that located the C_5-CH_3 doublet for the α anomer in a higher field than the β anomer in a 6-deoxypyranoside.

Many studies during the past 5 years have reported on the hydrolytic behavior of substituted and unsubstituted glycosides in dilute acid solution.[3] Little work, however, has been done on disaccharides. We wished to determine the effect of substitution on the rate of hydrolysis of the 1′-4 glycosidic bonds of methyl β-maltoside, since we felt that results could be extrapolated to starch. Alteration of substituents in the 6 position was known to affect the rate of hydrolysis of glycopyranosides.[3d] Consequently, we undertook the synthesis of 6,6′-mono- and disubstituted derivatives of methyl β-maltoside and report here the details leading to the syntheses of these derivatives (Table I).

TABLE I
COMPOUNDS INVESTIGATED[a]



Compd no.	R	X	Y
1	H	OH	OH·H_2O
2a	H	OTs	OTs
2b	H	OTs	OTs·C_2H_5OH
3	H	OTs	OH
4	H	OH	OTs
5	Ac	OTs	OTs
6	Ac	OTs	OAc
7	Ac	OAc	OTs
8	Ac	I	I
9	Ac	I	OAc
10	Ac	OAc	I
11	Ac	H	H
12	Ac	H	OAc
13	Ac	OAc	H
14	Ac	OTs	I
15	Ac	OTs	H
17	Ac	OBz	H

[a] Ac, acetyl; Ts, *p*-tolylsulfonyl; Bz, benzoyl.

Wolfrom and Koizumi,[4] using maltose and trityl chloride, isolated the three 6,6′-di- and monosubstituted trityl derivatives. Because the procedure envisioned for transforming these 6,6′-trityl derivatives to the related maltosyl sulfonate derivatives was multistepped, a direct reaction of methyl β-maltoside to form the sulfonates was deemed more convenient. Preferential reaction at a primary hydroxyl group by *p*-toluenesulfonyl (tosyl) chloride was known[5] and had been used previously to synthesize methyl 6,6′-di*O*-*p*-tolysulfonyl-β-maltoside.[6] The related 6,6′-dimethanesulfonate had been prepared by Newth, *et al.*[7] For convenience tosyl chloride was selected as the reagent of choice for entry into the series.

After work-up and recrystallization, a 6,6′-ditosylate derivative was obtained in 28% yield when tosyl chloride and methyl β-maltoside (**1**) were allowed to react in a 1.1:1 molar ratio. Both nmr spectroscopy and chemical analysis[8] established that this ditosylate contained 1 mol of ethanol of crystallization. Consequently, the ditosylate was methyl 6,6′-di-*O*-*p*-tolylsulfonyl-β-maltoside monoethanolate (**2b**). Our results on this ditosyloxymaltoside differed from those reported[6] in that the ethanol of crystallization was not previously indicated.

By column chromatography[9] and acetylation, 18% of **6** and 1% of **4** were obtained. This result was in accord with the expected influence of steric hindrance. The ratio of 6′- to 6-tosyl substitution agreed with results reported for analogous tritylation.[10]

The corresponding iodides of **2a**, **3**, and **4** were produced in over 90% yield with excess sodium iodide in acetone following acetylation of the substrates (Figure 1B). Without acetylation these iodide displacements resulted in a large number of spots on tlc plates and the desired products were isolated in low yield (<20%). The iodo acetates **8**, **9**, and **10** were, in turn, catalytically hydrogenolyzed to produce **11**, **12**, and **13** (Figure 1B).

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(2) This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) (a) T. E. Timell, *Can. J. Chem.*, **42**, 1456 (1964); (b) R. J. Ferrier, L. R. Hatton, and W. G. Overend, *Carbohyd. Res.*, **8**, 56 (1968); (c) M. D. Saunders and T. E. Timell, *ibid.*, **6**, 12 (1968); (d) T. E. Timell, W. Enterman, F. Spencer, and E. J. Soltes, *Can. J. Chem.*, **43**, 2296 (1965); (e) M. S. Feather and J. F. Harris, *J. Org. Chem.*, **30**, 153 (1965); (f) J. T. Edward, *Chem. Ind. (London)*, 1102 (1955).

(4) M. L. Wolfrom and K. Koizumi, *J. Org. Chem.*, **32**, 656 (1967).

(5) D. H. Ball and F. W. Parrish, *Advan. Carbohyd. Chem.*, **23**, 240 (1968); **24**, 139 (1969).

(6) M. L. Wolfrom, Y.-L. Hung, P. Chakravarty, G. U. Yuen, and D. Horton, *J. Org. Chem.*, **31**, 2227 (1966).

(7) F. H. Newth, S. D. Nicholas, F. Smith, and L. F. Wiggins, *J. Chem. Soc.*, 2552 (1949).

(8) In ref 6 an incorrect chemical formula was used to calculate the analytical values.

(9) B. Loev and M. M. Goodman, *Chem. Ind. (London)*, 2026 (1967).

(10) In ref 4 some conflict exists between values reported in the abstract and those given in the experimental section. We believe this error to be typographical.

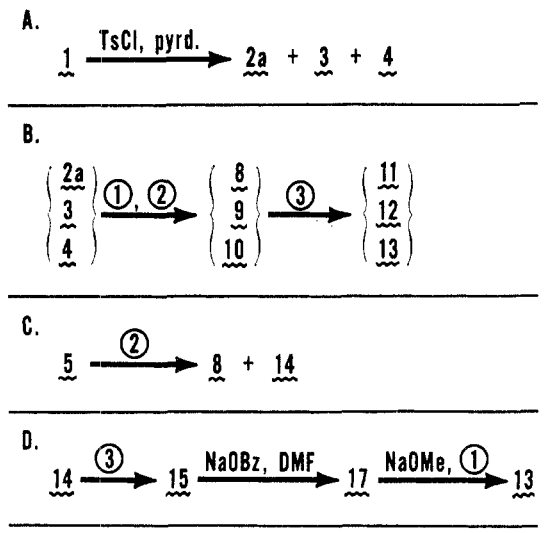

Figure 1.—Reaction sequences: ① = Ac_2O, pyridine; ② = NaI, refluxing acetone; ③ = H_2, Pd–C, KOH; pyrd. = pyridine; DMF = N,N-dimethylformamide.

Proof of structure of the three deoxy sugars **11–13** was obtained in two ways. The first was a new nmr correlation method,[1,11] which held that, for C-6-deoxypyranosides, the doublet for the C-5 methyl was always located at higher field for the α anomer than the doublet for the β anomer. Examples are given in Table II. Thus **11** had two doublets: δ 1.16 for the C-5′ methyl and 1.39 for the C-5 methyl. The doublet at δ 1.15 in the spectrum of **12** was indicative of the C-5′ methyl. The doublet at δ 1.39 in the spectrum of **13** corresponded to the C-5 methyl (Figure 2).

TABLE II

C_5-CH_3 RESONANCE PEAK IN ANOMERIC 6-DEOXYPYRANOSIDES

	Anomer			
Compd	α	J, Hz	β	J, Hz
6-Deoxy-L-mannose	1.60	6	1.65	6
Methyl 6-deoxy-L-mannoside	1.26	6	1.28	6
Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-L-mannoside	1.20	6	1.28	6
6-Deoxy-D-galactose	1.19	7	1.22	7
Methyl 2,3,4-tri-*O*-acetyl-6-deoxy D-galactoside	1.13	6	1.21	6

The second proof of structure was established by chemical conversions, generally known to give unrearranged products[5] that are observed when **5** was treated with sodium iodide in a 1:1 molar ratio. Preferential displacement of the 6-*O*-tosyl group gave the products shown in Figure 1C. Catalytic hydrogenolysis of **14** gave **15**, which had a doublet for the C-5 methyl at δ 1.34. Compound **15** was converted to **13** by the sequence shown in Figure 1D. Reaction of **15** with ethanolic sodium hydroxide (Figure 3) gave methyl 3′,6′-anhydro-6-deoxy-β-maltoside (**16**) as the only product (~90%). Compound **16**, having the C-5 methyl doublet at δ 1.39, was oxidized by sodium metaperiodate with an uptake to 1.06 equiv of periodate per mol of anhydro substrate. The only other possible structure that could have consumed 1 mol equiv of periodate was methyl 3′,6-anhydro-6′-deoxy-β-maltoside. Such eight-membered anhydro rings are not known to occur by base elimination of tosylate groups in carbohydrates;[7] it is unlikely that an eight-membered ring would be formed in as high yield as found. Any other anhydro structure would have consumed 2 mol equiv of sodium metaperiodate.

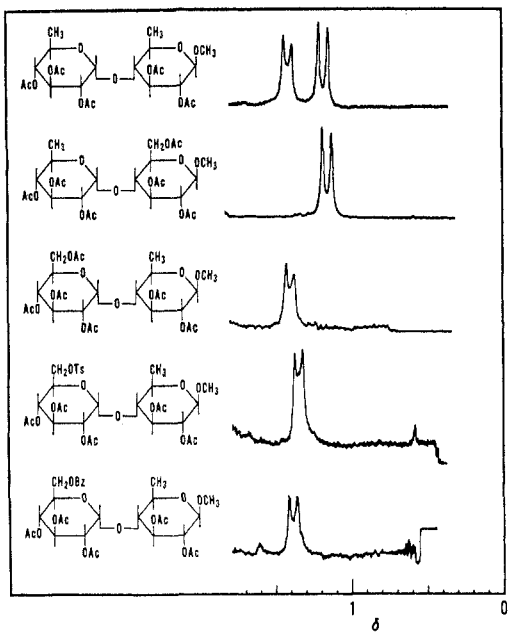

Figure 2.—Nmr spectra (100 MHz) in chloroform-*d* with internal tetramethylsilane.

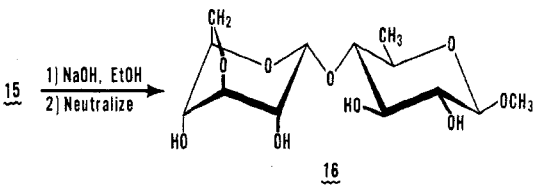

Figure 3.—3′,6′-Anhydro formation.

Partial tosylation of **1** and partial tritylation of maltose[4] and benzyl β-maltoside[12] resulted in a 6′ derivative. This difference in reactivity of the two primary hydroxyl groups, 6 and 6′, was attributed to a steric effect. Although considerations of the steric accessibility would have predicted that the 6′-tosylate to be more reactive than the 6-tosylate, the latter proved to be more reactive in the partial displacement of the 6,6′-ditosylate **5** by sodium iodide. Dutton and Slessor[13] report their attempts were unsuccessful at selective tosylation of the primary hydroxyl group in benzyl 4′,6′-*O*-benzylidene-β-maltoside.

Little systematic work has been carried out on the selective sulfonation of disaccharides and on the displacement reactions of these sulfonyl disaccharides. The present investigations show that reactions usually classed as typical with monosaccharides become altered when applied to disaccharides.

(11) H. B. Sinclair and R. T. Sleeter, *Tetrahedron Lett.*, 833 (1970).

(12) B. Helferich and W. Speicher, *Justus Liebigs Ann. Chem.*, **579**, 106 (1953).

(13) G. G. S. Dutton and K. N. Slessor, *Can. J. Chem.*, **44**, 1069 (1966).

Experimental Section

Tlc was performed on silica gel G[14] with air-equilibrated plates of 0.25-mm thickness. For unacetylated compounds benzene:absolute ethanol 2:1 (v/v) was used; for acetylated compounds, toluene:methanol 50:1 (v/v). The spots were detected by spraying with 5% ethanolic sulfuric acid and heating until charred. Uv spectra were measured with a Cary Model 14 spectrophotometer. Ir spectra were determined as KBr pellets with a Perkin-Elmer Model 621 spectrophotometer. Nmr spectra were obtained with a Varian Model HA-100 spectrometer. The chemical shifts were measured in chloroform-*d* unless otherwise specified and were compared against internal tetramethylsilane. Melting points of samples of capillary tubes was measured on a Mel-Temp apparatus. All analytical samples were dried in the presence of sodium hydroxide and sulfuric acid at room temperature and at 1–10 mm vacuum for 24–48 hr unless otherwise specified. Acetylations were carried out in dry pyridine with excess acetic anhydride for 16 hr at room temperature.

Methyl β-Maltoside Monohydrate (1).—The procedure of Newth, *et al.*,[7] was followed for the preparation of the title compound in 27.4% overall yield: mp 108–111°, $[\alpha]^{22.3}D$ +77.5° (*c* 1.65, chloroform) (lit.[7] mp 110–111°, $[\alpha]^{19}D$ +81°).

Methyl 2,2′,3,3′,4′-Penta-*O*-acetyl-6,6′-di-*O*-*p*-tolylsulfonyl-β-maltoside (5).—Tosyl chloride (5.34 g, 28 mmol) was added to a solution of dry **1** (4.76 g, 13.3 mmol) in dry pyridine (50 ml). The reaction mixture was kept 3 hr at −10° and 16 hr at 5°, when acetic anhydride (20 ml) was added to acetylate. Partitioning the mixture between water (~500 ml) and chloroform (three 50-ml portions) gave after evaporating the chloroform a solid, which on dissolving in boiling ethanol and cooling deposited crystalline **5** (6.8 g, 59%): mp 186–189°; $\lambda_{max}^{95\%\ EtOH}$ 263 nm (ε 1240); $[\alpha]^{23}D$ +60.4° (*c* 1.63, chloroform); λ_{max}^{KBr} 1752 (acetate), 1355, 1157 cm^{-1} (sulfonate); nmr δ 7.86–7.24 (m, aryl, 8 H), 5.40–3.40 (m, maltoside, 14 H), 3.30 (s, –OCH_3, 3 H), 2.42 (s, aryl–CH_3, 6 H), and 1.96 (s, –OAc, 15 H).

Anal. Calcd for $C_{37}H_{46}O_{20}S_2$: C, 50.80; H, 5.30; S, 7.33. Found: C, 50.69; H, 5.52; S, 7.42.

Methyl 6,6′-di-*O*-*p*-Tolylsulfonyl-β-maltoside (2a) and Its Ethanolate (2b).—The procedure for the tosylation was the same as for **5**. The mixture was vacuum concentrated (bath temperature <40°) to a syrup that was partitioned between water (200 ml) and chloroform (four 200-ml portions). Drying and concentrating the organic extract yielded a solid that was recrystallized four times from ethanol to give **2b**, 4.95 g (56%); mp 120–121;[15] nmr δ 7.85–7.11 (m, aryl, 8 H), 5.14–2.82 (m, maltoside H, OH, CH_2, 22 H), 2.55 (s, aryl–CH_3, 6 H), 1.18 (t, CH_3 of ethanol, 3 H); $\lambda_{max}^{95\%\ EtOH}$ 262.5 nm (ε 1189); λ_{max}^{KBr} 3430 (OH), 1358, 1176 cm^{-1} (sulfonate); $[\alpha]^{22}D$ +46.3° (*c* 1.76, chloroform).

Anal. Calcd for $C_{29}H_{42}O_{16}S_2$: C, 49.00; H, 5.96; S, 9.02. Found: C, 48.82; H, 5.88; S, 9.00.

Heating **2b** at 78° and 2 Torr for 7 hr gave **2a**, mp 123–124° (lit.[6] mp 124–126°).

Anal. Calcd for $C_{27}H_{36}O_{15}S_2$: C, 48.78; H, 5.46; S, 9.65. Found: C, 48.74; H, 5.73; S, 9.49.

Methyl 6-*O*-*p*-Tolylsulfonyl-β-maltoside (4) and Methyl 6′-*O*-*p*-Tolylsulfonyl-β-maltoside (3).—Dry **1** (4.78 g, 13.4 mmol) and tosyl chloride (2.81 g, 14.7 mmol) were allowed to react in dry pyridine (50 ml) as in the preparation of **5** but at −10° for 48 hr. Concentration of the mixture under aspirator pressure (bath temperature <50°), followed by addition of absolute ethanol (~50 ml), and two similar concentrations resulted in a yellow syrup, which was dissolved in absolute ethanol (20 ml) and divided in half. Each half was treated as follows: silica gel (15 g, Davison Grade 12, Mesh 28–200) was deactivated by adding sufficient 95% ethanol to cover the solid and after cooling, the ethanolic reaction solution was added, and the mixture was swirled and then concentrated under aspirator pressure to a dry mass which was rendered free flowing and dry column[9] chromatographed on silica gel G (200 g, 4 × 40 cm) using benzene:absolute ethanol 2:1 (v/v) as the developing solvent. The elution order was polytosyl substituted maltoside (which were not examined), **2b**, **3**, and **4**.

The front-running monosubstituted product **3** was obtained as a syrup, which could not be crystallized; it was characterized as a crystalline acetate (see below).

The slow-running monosubstituted product **4** was crystallized (seed crystals were obtained from the last fractions containing **4**). Recrystallization from 95% ethanol gave crystalline **4** (1%): mp 154–155° dec; λ_{max}^{KBr} 3400 (OH), 1355, 1154 cm^{-1} (sulfonate); $\lambda_{max}^{95\%\ EtOH}$ 262 nm (ε 521); nmr (25% in DMSO-*d*) δ 7.82–7.32 (m, aryl, 4 H), 5.58–2.12 (m, maltoside-H-OH, 23 H), and 2.39 (s, aryl–CH_3, 3 H).

An average yield of methyl 6,6′-di-*O*-*p*-toluenesulfonyl-β-maltoside for five reactions was 24.0%.

Methyl 2,2′,3,3′,4′,6-Hexa-*O*-acetyl-6′-*O*-*p*-tolylsulfonyl-β-maltoside (6).—Crude **3** was acetylated and worked up in the usual manner by partitioning between water and chloroform. Removal of the chloroform left a syrup that on dissolving in a minimum amount of hot ethanol and cooling deposited crystalline **6**: mp 143–144°; λ_{max}^{KBr} 1750 (acetate), 1372, 1174 cm^{-1} (sulfonate); $\lambda_{max}^{95\%\ EtOH}$ 262 nm (ε 578); $[\alpha]^{23}D$ +55.3° (*c* 5.128, chloroform); nmr δ 7.84–7.26 (m, aryl, 4 H), 5.40–3.50 (m, maltoside, 14 H), 3.45 (s, –OCH_3, 3 H), 2.43 (s, aryl CH_3, 3 H), and 2.23–1.90 (4 s, –OAc, 18 H).

Anal. Calcd for $C_{32}H_{42}O_{19}S$: C, 50.39; H, 5.55; S, 4.20. Found: C, 49.98; H, 5.48; S, 4.21.

The average yield (calculated on the basis of methyl β-maltoside monohydrate) in five runs was 17.4%.

Methyl 2,2′,3,3′,4′-Penta-*O*-acetyl-6,6′-dideoxy-6,6′-diiodo-β-maltoside (8).—Compound **5** (4.011 g, 4.58 mmol), sodium iodide (3.75 g, 25 mmol), and acetone (60 ml) were heated to reflux under anhydrous conditions. Tlc monitoring with toluene:methanol 50:1 (v/v) easily revealed the progress of the displacement from **5** to methyl 2,2′,3,3′,4′-penta-*O*-acetyl-6-deoxy-6-iodo-6′-*O*-*p*-tolylsulfonyl-β-maltoside to **8** as spots with increasing R_f values. When monitoring revealed the displacement was complete (~4–5 days), the mixture was transferred with water (50 ml) and chloroform (50 ml) to a separatory funnel and extracted with two additional 50-ml portions of chloroform. The combined extracts were dried and concentrated to crude crystalline **8**. Recrystallization from absolute ethanol gave pure **8**, 3.58 g (98%): mp 196–197°; positive Beilstein halogen test; λ_{max}^{KBr} 1755, 1245 cm^{-1} (acetate); $[\alpha]^{24}D$ +48.2° (*c* 7.63, chloroform); nmr δ 5.46–3.00 (m, maltoside, 14 H), 3.51 (s, –OCH_3, 3 H), and 2.10–1.90 (4 s, –OAc, 15 H).

Anal. Calcd for $C_{23}H_{32}I_2O_{14}$: C, 35.13; H, 4.10. Found: C, 34.79; H, 4.21.

Methyl 2,2′,3,3′,4′-Penta-*O*-acetyl-6-deoxy-6-iodo-6′-*O*-*p*-tolylsulfonyl-β-maltoside (14).—Sodium iodide (0.180 g, 1.2 mmol), **5** (0.965 g, 1.1 mmol), and acetone (15 ml) were heated to reflux under anhydrous conditions for 2 days. On removal of the acetone a solid remained. Trituration of this solid with boiling absolute ethanol (~60 ml) left undissolved nearly pure **14**; an additional recrystallization from ethanol gave **14**, 0.197 g (21%): mp 203–204°; λ_{max}^{KBr} 1350, 1240 (acetate), 1361, 1172 cm^{-1} (sulfonate); $\lambda_{max}^{95\%\ EtOH}$ 252 nm (ε 970); positive Beilstein halogen test; nmr δ 7.84–7.24 (m, aryl, 4 H), 5.46–3.12 (m, maltoside, 14 H), 3.49 (s, –OCH_3, 3 H), 2.44 (s, aryl–CH_3, 3 H), 1.99 and 1.97 (s, OAc, 15 H); $[\alpha]^{24.0}D$ +50.1° (*c* 2.565, chloroform).

Reworking the mother liquor followed by trituration increased the yield to 28%. In boiling absolute ethanol the solubility of **14** is 1 g/250 ml, qualitatively much less soluble than **5** or **7**.

Anal. Calcd for $C_{30}H_{39}IO_{17}S$: C, 43.38; H, 4.73. Found: C, 43.60; H, 5.08.

Methyl 2,2′,3,3′,4′,6-Hexa-*O*-acetyl-6′-deoxy-6′-iodo-β-maltoside (9).—We used the same procedure employed to prepare **8** with **6** (4.09 g, 5.38 mmol), sodium iodide (4.3 g, 28 mmol), and acetone (80 ml). Recrystallization from absolute ethanol gave **9**: 3.80 g (98%); mp 170–171°; $[\alpha]^{24.0}D$ +52.4° (*c* 5.815, chloroform); λ_{max}^{KBr} 1753, 1230 cm^{-1} (acetate); nmr δ 5.46–3.00 (m, maltoside, 14 H), 3.45 (s, –OCH_3, 3 H), 2.12 and 2.06–1.97 (4 s, –OAc, 18 H).

Anal. Calcd for $C_{25}H_{35}IO_{16}$: C, 41.80; H, 4.91. Found: C, 41.89; H, 4.99.

Methyl 2,2′,3,3′,4′,6′-Hexa-*O*-acetyl-6-deoxy-6-iodo-β-maltoside (10).—Compound **4** (310 mg, 0.6 mmol) was acetylated with acetic anhydride (5 ml) in dry pyridine (5 ml) and worked up in the usual manner by partitioning between water and chloroform. Removal of the chloroform left syrupy **7**, which could not

(14) The mention of firm names or trade products does not imply an endorsement or recommendation by the Department of Agriculture over other firms or similar products not mentioned.

(15) At first the small difference in melting point between **2a** and **2b** was attributed to a trace impurity. However, a consistently low per cent of sulfur after each crystallization resulted in the conclusion this compound was an ethanolate, which nmr spectroscopy confirmed.

be crystallized. Syrupy **7**, sodium iodide (0.27 g, 1.8 mmol), and acetone (10 ml) were heated to reflux for 4 days, and worked up according to the procedure employed to prepare **8**. Recrystallization from absolute ethanol gave **10**, 0.228 g (52%): mp 129–130°; λ_{max}^{KBr} 1750, 1238 cm^{-1} (acetate); nmr δ 5.47–3.16 (m, maltoside, 14 H), 3.49 (s, –OCH$_3$, 3 H), 2.08 and 2.03–1.90 (4, s, –OAc, 18 H).

Anal. Calcd for $C_{25}H_{35}IO_{16}$: C, 41.80; H, 4.91. Found: C, 41.59; H, 5.09.

Methyl 2,2′,3,3′,4′-Penta-*O*-acetyl-6,6′-dideoxy-β-maltoside (11).—Compound **8** (0.502 g, 0.63 mmol) was added to a mixture of potassium hydroxide (0.147 g, 2.54 mmol), 5% Pd–C (0.202 g), and methanol (50 ml), pressured to 50 psi with hydrogen, and mechanically shaken at room temperature for 7 hr. After separation of the catalyst by filtration, the methanolic solution was concentrated to leave a syrup, which was acetylated. Work-up and recrystallization from ethanol gave **11**: mp 186–187°; $[\alpha]^{24}D$ +50.0° (*c* 3.04, chloroform); λ_{max}^{KBr} 1350, 1242 cm^{-1} (acetate); nmr δ 5.44–3.36 (m, maltoside-ring, 10 H), 3.46 (s, –OCH$_3$, 3 H), 2.10–1.93 (3 s, –OAc, 15 H), 1.16 (d, J = 6.2 cps, C5′–CH$_3$, 3 H), and 1.39 (d, J = 6 cps, C$_5$–CH$_3$, 3 H).

Anal. Calcd for $C_{23}H_{34}O_{14}$: C, 51.68; H, 6.41. Found: C, 51.30; H, 6.45.

Methyl 2,2′,3,3′,4′,6-Hexa-*O*-acetyl-6′-deoxy-β-maltoside (12).—Compound **9** (0.504 g, 0.70 mmol) was hydrogenolyzed according to the procedure given for **11**. Recrystallization from absolute ethanol deposited **12**, 0.340 g (82%); mp 176–177°; λ_{max}^{KBr} 1750, 1232 cm^{-1} (acetate); nmr δ 5.39–3.52 (m, maltoside-ring, 10 H), 3.43 (s, –OCH$_3$, 3 H), 2.09, 2.04–1.88 (4 s, –OAc, 18 H), 1.15 (d, J = 6 cps, C5′–CH$_3$, 3 H).

Anal. Calcd for $C_{25}H_{36}O_{16}$: C, 50.68; H, 6.12. Found: C, 50.78; H, 6.24.

Methyl 2,2′,3,3′,4′,6′-Hexa-*O*-acetyl-6-deoxy-β-maltoside (13).—Compound **10** (89 mg, 0.121 mmol) was hydrogenolyzed according to the procedure for **11**. Recrystallization gave **13**: 12 mg (17%); mp 120–121°; λ_{max}^{KBr} 1350, 1240 cm^{-1} (acetate); nmr δ 5.45–3.30 (m, maltoside-ring, 10 H), 3.46 (s, –OCH$_3$, 3 H), 2.06, 2.04–1.90 (3 s, –OAc, 18 H), 1.39 (d, J = 6 cps, C-5–CH$_3$, 3 H).

Methyl 2,2′,3,3′,4′-Penta-*O*-acetyl-6-deoxy-6′-*O*-*p*-tolylsulfonyl-β-maltoside (15).—Compound **14** (113.3 mg, 0.136 mmol) was hydrogenolyzed following the procedure for **11** for 2.5 hr. Recrystallization from absolute ethanol gave **15**, 54 mg (57%): mp 143–144°; $\lambda_{max}^{95\% EtOH}$ 262 nm (ϵ 579); λ_{max}^{KBr} 1750, 1240 (acetate), 1372, 1174 cm^{-1} (sulfonate); $[\alpha]^{23}D$ +43.2° (*c* 2.37, chloroform); nmr δ 7.84–7.20 (m, aryl, 4 H), 5.42–3.20 (m, maltoside, 10 H), 3.43 (s, –OCH$_3$, 3 H), 2.43 (s, aryl-CH$_3$, 3 H), 2.02–1.80 (3 s, –OAc, 15 H), 1.34 (d, J = 5 cps, C-5–CH$_3$, 3 H).

Anal. Calcd for $C_{30}H_{40}O_{17}S$: C, 51.14; H, 5.72. Found: C, 50.71; H, 6.01.

Methyl 2,2′,3,3′,4′-Penta-*O*-acetyl-6′-*O*-benzoyl-6-deoxy-β-maltoside (17).—Compound **15** (53 mg, 0.075 mmol) and sodium benzoate (23.5 mg, 0.15 mmol) were heated to 100 ± 1° with stirring in anhydrous N,N-dimethylformamide (30 ml) for 16 hr. After vacuum concentrating (bath temperature <70°) the reaction mixture, it was extracted with chloroform. Removal of the chloroform and recrystallization from ethanol gave **17**: 41 mg (83%); mp 196–197°; λ_{max}^{KBr} 1750, 1246 (acetate), 1735, 1280, 1125 cm^{-1} (benzoate); nmr δ 8.19–7.24 (m, aryl, 5 H), 5.49–3.30 (m, maltoside, 10 H), 3.43 (s, –OCH$_3$, 3 H), 2.20–1.84 (3 s, –OAc, 15 H), 1.39 (d, J = 5 cps, C-5–CH$_3$, 3 H).

Anal. Calcd for $C_{30}H_{38}O_{16}$: C, 55.05; H, 5.85. Found: C, 55.26; H, 6.23.

Conversion of 17 to 13.—Compound **17** (20.4 mg, 0.031 mmol) was dissolved in dry methanol (30 ml) and a few granules of sodium–lead alloy (J. T. Baker Chemical Co., "dri-Na") were added. After the solution was held 48 hr at room temperature, methanol was removed from it and the resulting syrup covered with anhydrous pyridine (~5 ml) and acetic anhydride (~5 ml). Work-up in the usual manner gave a product whose nmr spectrum was identical with **13**.

Methyl 3′,6′-Anhydro-6-deoxy-β-maltoside (16).—Compound **15** (200 mg, 0.284 mmol) was dissolved in a mixture of ethanol (5 ml) and 1 *N* sodium hydroxide (0.2 ml) and heated to 60° for 3.5 hr. After diluting with an equal volume of water, the solution was adjusted to pH 7.10 with 0.1 *N* hydrochloric acid and concentrated to a dry solid. Dry silica gel G column (100 g, 4 × 21 cm) chromatography developed with benzene:absolute ethanol 2:1 (v/v) gave only one compound, a yellowish oil (81.5 mg, 90%), which could not be rendered crystalline. An nmr spectrum established that the tosyl group was absent, a glycosidic methoxyl was present, a C-5 methyl proton resonance was present, and the proton integral was consistent with the title compound: nmr δ 5.36–2.95 (m, maltoside H-OH, 14 H), 3.50 (s, –OCH$_3$, 3 H), 1.38 (d, J = 5 cps, C-5–CH$_3$, 3 H).

Periodate Oxidation of 16.—A weighed amount of **16** (~1–5 mg) when oxidized by the procedure of Dixon and Lipkin[16] consumed 1.06 mol equiv after 24 hr. Methyl α-D-glucopyranoside and methyl α-L-rhamnopyranoside when oxidized under the identical conditions consumed 1.95 and 1.98 mol equiv, respectively.

Registry No.—**2b**, 25787-29-5; **4**, 25834-66-6; **5**, 25787-30-8; **6**, 25834-67-7; **8**, 25787-31-9; **9**, 25834-68-8; **10**, 25787-32-0; **11**, 25787-33-1; **12**, 25787-34-2; **13**, 25787-35-3; **14**, 25787-36-4; **15**, 25787-37-5; **16**, 25787-38-6; **17**, 25787-39-7.

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(16) J. S. Dixon and P. Lipkin, *Anal. Chem.*, **26**, 1092 (1954).