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Selective Benzoylation of 1,6-Anhydro-4′,6′-O-benzylidene-β-maltose[1]

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Selective benzoylation of 1,6-anhydro-4′, 6′-O-benzylidene-β-maltose (**1**), using 2 molar equivalents of benzoyl chloride in pyridine at *ca.* −10°, yielded five benzoates which were designated **2** to **6** in order of decreasing *Rf* value on TLC. After column chromatography on silica gel, compounds **2** to **6** were separated as the 2,2′,3,3′-tetrabenzoate (**2**, 1.2%), 2,2′,3′-tribenzoate (**3**, 2.8%), 2,2′-dibenzoate (**4**, 9%), 2′,3′-dibenzoate (**5**, 7.3%), and 2′-benzoate (**6**, 48%), respectively. Thus, the order of reactivities of the secondary hydroxyl groups in **1** is 2′>2,3′>3. Compound **3** to **6** have potential value in the chemical modification of maltose or the synthesis of maltose-containing oligosaccharides.

In studies of chemical modifications of reducing disaccharides, 1,6-anhydro derivatives of β-lactose, cellobiose, and maltose are useful starting materials.[3] In part I of this series, benzylidenation of 1,6-anhydro-β-maltose was reported to yield 1,6-anhydro-4′,6′-O-benzylidene-β-maltose (**1**). Compound **1** contains only unblocked secondary hydroxyl groups of which those in the reducing moiety are *trans*-diaxial and those in the non-reducing are *trans*-diequatorial. Therefore, the reactions of **1** are of potential interest in relation to obtaining intermediates for the selective modifications of particular secondary hydroxyl groups in maltose. We now report on the partial benzoylation of **1** and discuss about the order of reactivities of the secondary hydroxyl groups in **1**.

Benzoylation of **1** with 2 molar equivalents of benzoyl chloride in pyridine at *ca.* −10° gave five products which were identified by thin-layer chromatography (TLC) on silica gel. The products were designated **2** to **6** in order of decreasing *Rf* value; **6** preponderated. Product **2** to **6** were isolated by column chromatography on silica gel.

Compound **2** was obtained in 1.2% yield, and was identified as 1,6-anhydro-2,2′,3,3′-tetra-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**2**) by comparison with an authentic sample.[1]

Compound **3**, isolated in 2.8% yield, gave a crystalline acetate (**7**, 90%) by acetylation. In the nuclear magnetic resonance (NMR) spectrum the signal for acetyl protons appeared at τ 8.03 as a singlet. From the ratio of acetyl protons to total protons, **7** was identified as a mono-O-acetyl-tri-O-benzoyl derivative of **1**.

Methylation of **3** with diazomethane-boron trifluoride etherate, a reagent which does not cause acyl migration,[4] yielded a crystalline tri-O-benzoyl-mono-O-methyl derivative (**8**, 49%) of **1** as indicated by NMR spectral and elemental analytical data. The location of the methyl group in **8** was determined as follows. Debenzylidenation of **8** by palladium-catalysed hydrogenolysis and successive debenzoylation of the resulting amorphous powder with methanolic sodium methoxide afforded an amorphous powder, which when hydrolyzed with dilute sulfuric

1) This paper forms Part II of the series entitled "Chemical Modifications of Maltose"; Part I: M. Mori, M. Haga, and S. Tejima, *Chem. Parm. Bull.* (Tokyo), **23**, 1480 (1975).

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3) S. Tejima, *Carbohyd. Res.*, **20**, 123 (1971); S. Tejima and Y. Okamori, *Chem. Pharm. Bull.* (Tokyo), **20**, 2036 (1972); S. Tejima and T. Chiba, *ibid.*, **21**, 546 (1973); Y. Okamori, M. Haga, and S. Tejima, *ibid.*, **21**, 2538 (1973); T. Chiba, M. Haga, and S. Tejima, *ibid.*, **22**, 398 (1974); M. Mori, M. Haga, and S. Tejima, *ibid.*, **22**, 1331 (1974); T. Chiba, M. Haga, and S. Tejima, *ibid.*, **23**, 1283 (1975).

4) J.O. Deferrari, E.G. Gros, and I.M.E. Thiel, "Methods in Carbohydrate Chemistry," Vol. 6, Academic Press, New York and London, 1972, p. 365.

acid gave glucose and 3-O-methylglucose, identified by paper partition chromatography (PPC). Therefore, the methyl group in **8** was shown to be located either at C-3 or C-3′ in **1**. In order to determine the exact position, periodate consumption and formic acid formation in debenzylidenated and debenzoylated product (**9**) of **8** were investigated. Compound **9** consumed *ca.* 2 moles of sodium metaperiodate with concomitant formation of *ca.* 1 mole of formic acid. Thus, **3**, **7**, **8**, and **9** were assigned the structures 1,6-anhydro-2,2′,3′-tri-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**3**), 3-O-acetyl-1,6-anhydro-2,2′,3′-tri-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**7**), 1,6-anhydro-2,2′,3′-tri-O-benzoyl-4′,6′-O-benzylidene-3-O-methyl-β-maltose (**8**), and 1,6-anhydro-3-O-methyl-β-maltose (**9**), respectively.

Compound **4**, isolated in 9% yield, gave a crystalline acetate (**10**) by acetylation. In the NMR spectrum the signal for acetyl protons appeared at τ 8.01 and 8.03 as each singlets. From the ratio of acetyl to total protons, **10**, was identified as a di-O-acetyl-di-O-benzoyl derivative of **1**. Methylation of **4** as described above gave a crystalline di-O-benzoyl-di-O-methyl derivative (**11**, 55%) of **1** as indicated by NMR spectral and elemental analytical data.

Determination of position of the methyl groups in **11** was performed as described above for **8**. Namely, after debenzylidenation, debenzoylation, and acid hydrolysis, 3-O-methylglucose was identified by PPC as the sole component monosaccharide. Therefore, the methyl groups in **11** were shown to be located at C-3 and C-3′ in maltose. Thus, the following structures were assigned; 1,6-anhydro-2,2′-di-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**4**), 3,3′-di-O-acetyl-1,6-anhydro-2,2′-di-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**10**), and 1,6-anhydro-2,2′-di-O-benzoyl-4′,6′-O-benzylidene-3,3′-di-O-methyl-β-maltose (**11**).

Further structural assignment was performed as follows. Debenzylidenation of **4** afforded 1,6-anhydro-2,2′-di-O-benzoyl-β-maltose (**12**) as an amorphous powder. Compound **12** consumed *ca.* 1 mole of sodium metaperiodate with no concomitant formation of formic acid.

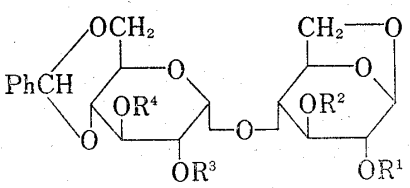
Compound **5**, isolated in 7.3% yield, gave a crystalline diacetate (**13**, 87%) and a crystalline dimethyl ether (**14**, 42%). By using procedures similar to those described for **8** and **11**, glucose and 2,3-di-O-methylglucose were determined to the component monosaccharides in **14**. Therefore, the methyl groups in **14** were shown to be located either at C-2 and C-3, or, C-2′ and C-3′ in **1**. While, debenzylidenation product (**15**) of **5** consumed *ca.* 1 mole of sodium metaperiodate with no concomitant formation of formic acid. Thus, the following structures were assigned; 1,6-anhydro-2′,3′-di-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**5**), 2,3-di-O-acetyl-1,6-anhydro-2′,3′-di-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**13**), 1,6-anhydro-2′,3′-di-O-benzoyl-4′,6′-O-benzylidene-2,3-di-O-methyl-β-maltose (**14**), and 1,6-anhydro-2′,3′-di-O-benzoyl-β-maltose (**15**).

Compound **6**, the major product (48%) in the selective benzoylation, was an amorphous powder which yielded a crystalline triacetate (**16**, 88%) and a crystalline trimethyl ether (**17**, 69%). Using the procedures described above, 3-O-methylglucose and 2,3-di-O-methylglucose were identified to the component monosaccharides in **17**. Therefore, the methyls in **17** were shown to be located at either C-2, C-3, and C-3′, or, C-2′, C-3′, and C-3 in **1**. While, debenzylidenation product (**18**) of **6** consumed *ca.* 2 moles of sodium metaperiodate with no concomitant formation of formic acid. Thus, the structures 1,6-anhydro-2′-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**6**), 2,3,3′-tri-O-acetyl-1,6-anhydro-2′-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**16**), 1,6-anhydro-2′-O-benzoyl-4′,6′-O-benzylidene-2,3,3′-tri-O-methyl-β-maltose (**17**), and 1,6-anhydro-2′-O-benzoyl-β-maltose (**18**) were assigned.

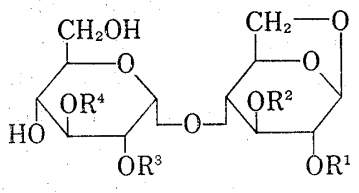
The yields of **2**—**6** suggest that the reactivity of the hydroxyl groups in **1** is 2′-OH$>$ 2-OH, 3′-OH$>$ 3-OH. It was not possible to determine the order of 2-OH and 3′-OH by this selective benzoylation.

Thus, in **1**, 2′-OH has the highest reactivity. According to the recent report from this laboratory,[5] selective benzoylation of 1,6-anhydro-4′,6′-O-benzylidene-β-lactose (**19**) under

5) T. Chiba, M. Haga, and S. Tejima, *Carbohyd. Res.*, **45**, 11 (1975).



	R^1	R^2	R^3	R^4
1:	H	H	H	H
2:	Bz	Bz	Bz	Bz
3:	Bz	H	Bz	Bz
4:	Bz	H	Bz	H
5:	H	H	Bz	Bz
6:	H	H	Bz	H
7:	Bz	Ac	Bz	Bz
8:	Bz	Me	Bz	Bz
10:	Bz	Ac	Bz	Ac
11:	Bz	Me	Bz	Me
13:	Ac	Ac	Bz	Bz
14:	Me	Me	Bz	Bz
16:	Ac	Ac	Bz	Ac
17:	Me	Me	Bz	Me



	R^1	R^2	R^3	R^4
9:	H	Me	H	H
12:	Bz	H	Bz	H
15:	H	H	Bz	Bz
18:	H	H	Bz	H

Ph=phenyl
Ac=acetyl
Bz=benzoyl
Me=methyl

Chart 1

almost the same conditions, as described for the corresponding maltose derivative, yielded 2,2′,3,3′-tetrabenzoate (3%), 2,3,3′-tribenzoate (11%), 2,2′,3′-tribenzoate (5%), 2,3′-dibenzoate (major, 30%), and 3′-benzoate (22%). In addition, one molar benzoylation of 2,3′-dibenzoate afforded 2,2′,3,3′-tetrabenzoate (15%), 2,3,3′-tribenzoate (56%), 2,2′,3′-tribenzoate (8%), and unreacted 2,3′-dibenzoate (5%), respectively. Therefore, in **19**, the order of reactivity of the secondary hydroxyl groups is 3′>2>3>2′. Thus, the 2′-OH has the lowest reactivity.

The reverse order in reactivity at C-2′ in lactose and maltose derivatives may be attributed to the different steric circumstances in **1** and **19**. Molecular models suggest that because the conformation of the galactose moiety in **19** is fixed by the 1,3-dioxane ring, the bulky 1,6-anhydro-β-glucosidic residue strongly hinders 2′-OH. While in **1**, the 1,6-anhydro-α-glucosidic residue is not shown to be located providing steric hindrance at 2′-OH.

It is noteworthy to describe that the lowest reactivity at 3-OH in maltose and lactose. Hodge, *et al.*[6] showed that selective acetylation of maltose afforded the heptaacetate having 3-OH unsubstituted. Deferrari, *et al.* reported isolation of heptabenzoate having 3-OH unsubstituted, together with octabenzoate, by benzoylation of maltose[7] or lactose.[8] This paper adds another example of the lowest reactivity of 3-OH in maltose derivative. However, in this case, the effect may be attributed to the presence of the 1,6-anhydro-β-ring in the reducing moiety having 1C conformation.

According to the literature,[9] equatorially-oriented secondary hydroxyl groups in pyranoid rings tend to be esterified more readily than the axial groups. In selective benzoylation of secondary hydroxyl group of *myo*-inositol derivative, the same result has been reported by Suami, *et al.*[10] Therefore, prior to this experiment, the authors expected that preferential formation of 2′,3′-dibenzoate (**5**) should occur by selective benzoylation of **1** using 2 molar

6) W.E. Dick, Jr., B.G. Baker, and J.E. Hodge, *Carbohyd. Res.*, **6**, 52 (1968).
7) I.M.E. Thiel, J.O. Deferrari, and R.A. Cadenas, *Ann. Chem.*, **723**, 192 (1969).
8) I.M. Vazquez, I.M.E. Thiel, and J.O. Deferrari, *Carbohyd. Res.*, **26**, 351 (1973).
9) R.J. Ferrier and P.M. Collins, "Monosaccharide Chemistry," Penguin Books Ltd, Harmondsworth Middlesex, England, 1972, p. 211.
10) T. Suami, F.W. Lichtenthaler, and S. Ogawa, *Bull. Chem. Soc. Japan*, **39**, 170 (1966).

equivalent of benzoyl chloride. However, contrary to our expectation, 2′-monobenzoate (**6**) was the major product (48%) with a low yield (7.3%) of **5**.

Recently, other reports[11] have suggested that the factors governing the relative reactivities of hydroxyl groups are not at present sufficiently known and other factors, besides conformational effects, were invoked to explain the preferential reactivity sequence. Therefore, further accumulation of data is required to discuss the reactivities of hydroxyl groups in disaccharides.

Experimental

Melting points are uncorrected. Solutions were concentrated *in vacuo* in a rotary evaporator at $<40°$. Optical rotations were measured in a 0.5 dm cell with a Yanagimoto OR-10 automatic polarimeter. Infrared (IR) spectra were recorded for Nujol mulls with a Jasco IRA-2 spectrometer. NMR spectra were recorded at 100 MHz with a Jeol JNM-MH-100 spectrometer for solution in $CDCl_3$ (internal Me_4Si). Chemical shifts are given on the τ scale. TLC was performed on Silica Gel GF_{254} (Merck) activated at 110° using (A) 9:1 (v/v) CH_2Cl_2–acetone, (B) 1:1 CH_2Cl_2–acetone, and (C) 3:1 ether–benzene. Detection was effected with H_2SO_4 or ultraviolet(UV) light (short wave length). Column chromatography was performed on Wakogel C-200 (Wako Pure Chemical Industries Ltd., Osaka) (1 g of sample per 20 g of adsorbent). PPC was performed on Toyo Filter Paper No. 50 (Toyo Roshi Kaisha, Ltd., Tokyo) by the ascending method[12] using 6:4:3 (v/v) BuOH–pyridine–H_2O and detection with (A) Tollens' reagent[13] and (B) aniline hydrogen phthalate.[14]

Selective Benzoylation of 1,6-Anhydro-4′,6′-O-benzylidene-β-maltose (1)——To a chilled solution of **1**[1] (2 g, 4.85 mmole) in dry pyridine (15 ml), benzoyl chloride (1.4 g, 9.96 mmole) was added dropwise with stirring at *ca.* −10°, and the stirring was continued, with the exclusion of moisture, for 1 hr. The mixture was stored overnight at 5°, then the mixture was poured into ice-water (150 ml), and extracted with CH_2Cl_2 (40 ml × 2). The combined extracts were washed with ice-cold dil. H_2SO_4 (100 ml × 3), saturated aq. $NaHCO_3$ (100 ml × 2), and water (100 ml × 2), dried over anhydrous Na_2SO_4, and concentrated to dryness. The resulting sirup (2.4 g) contained five components, *Rf* 0.74, 0.42, 0.32, 0.22, and 0.11 (major) (TLC, solvent A). Elution of the mixture from silica gel column with CH_2Cl_2 (100 ml), and 30:1 (v/v) (200 ml), 20:1 (600 ml), and 10:1 (300 ml) of CH_2Cl_2–acetone gave the following products (**2**—**6**).

The component having *Rf* 0.74 crystallized from EtOH–AcOEt (0.05 g, 1.2%) as white prisms, mp 197—200°, which was indistinguishable from 1,6-anhydro-2,2′,3,3′-tetra-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**2**) by mixed mp and TLC.

The component (0.1 g, 2.8%) having *Rf* 0.42 was 1,6-anhydro-2,2′,3′-tri-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**3**), which was an amorphous powder, $[\alpha]_D^{23}+69.1°$ ($c=1.98$, $CHCl_3$). TLC: *Rf* 0.42 (solvent A) and 0.68 (C). IR ν_{max} 3480 cm^{-1} (OH). *Anal.* Calcd. for $C_{40}H_{36}O_{13}$: C, 66.29; H, 5.01. Found: C, 66.03; H, 5.07.

The component having *Rf* 0.32 crystallized from EtOH (0.27 g, 9%), mp 185—187°, $[\alpha]_D^{26}+56.2°$ ($c=0.88$, $CHCl_3$), which was 1,6-anhydro-2,2′-di-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**4**). TLC: *Rf* 0.32 (solvent A) and 0.50 (C). IR ν_{max} 3420 cm^{-1} (OH). *Anal.* Calcd. for $C_{33}H_{32}O_{12}$, C, 63.87; H, 5.20. Found: C, 63.66; H, 5.03.

The component having *Rf* 0.22 crystallized from MeOH as white needles (0.22 g, 7.3%), mp 228—230°, $[\alpha]_D^{22}+65.1°$ ($c=1.85$, $CHCl_3$), which was **1,6-anhydro-2′,3′-di-O-benzoyl-4′,6′-O-benzylidene-β-maltose (5)**. TLC: *Rf* 0.22 (solvent A) and 0.27 (C). IR ν_{max} 3380 cm^{-1} (OH). *Anal.* Calcd. for $C_{33}H_{32}O_{12}$: C, 63.87; H, 5.20. Found: C, 63.62; H, 4.98.

The component (1.2 g, 48%) having *Rf* 0.11 was 1,6-anhydro-2′-O-benzoyl-4′,6′-O-benzylidene-β-maltose (**6**), which was an amorphous powder, $[\alpha]_D^{25}+64.2°$ ($c=1.96$, $CHCl_3$). TLC: *Rf* 0.11 (solvent A) and 0.23 (C). IR ν_{max} 3420 cm^{-1} (OH). *Anal.* Calcd. for $C_{26}H_{28}O_{11}$: C, 60.46; H, 5.46. Found: C, 60.17; H, 5.56.

3-O-Acetyl-1,6-anhydro-2,2′,3′-tri-O-benzoyl-4′,6′-O-benzylidene-β-maltose (7)——To an ice-cold solution of **3** (80 mg) in dry pyridine (1 ml), Ac_2O (1 ml) was added dropwise. The mixture was stored overnight at room temperature, and concentrated to dryness by repeated co-distillation with EtOH and toluene. Elution of the product from silica gel column with 30:1 (v/v) CH_2Cl_2–acetone gave an amorphous powder (76 mg, 90%), which crystallized from EtOH. Recrystallization from iso-PrOH gave white needles, mp 115—117°, $[\alpha]_D^{27}+74.7°$ ($c=0.93$, $CHCl_3$). NMR (τ): 1.80—2.25 (6H, m, *o*-H of 3PhCO), 2.71—3.01 (14H, m, *m*- and *p*-H of 3PhCO and $C_6\underline{H}_5CH$), 4.49 (1H, s, PhC<u>H</u>), 8.03 (3H, s, AcO). TLC: *Rf* 0.66 (solvent A) and 0.51 (C). *Anal.* Calcd. for $C_{42}H_{38}O_{14}$: C, 65.79; H, 5.00. Found: C, 65.49; H, 4.79.

1,6-Anhydro-2,2′,3′-tri-O-benzoyl-4′,6′-O-benzylidene-3-O-methyl-β-maltose (8)——To a solution of **3** (350 mg) in dry CH_2Cl_2 (40 ml) maintained at 0°, boron trifluoride etherate (2 drops) was added followed by a

11) J. Staněk, Jr., P. Chuchvalec, K. Čapec, K. Kefurt, and J. Jarý, *Carbohyd. Res.*, **36**, 273 (1974); M.E. Chacon-Fuertes and M. Martin-Lomas, *ibid.*, **42**, C4-C5 (1975).
12) M. Ueda, *Yakugaku Zasshi*, **90**, 1332 (1970).
13) W.E. Travelyan, D.P. Procter, and J.S. Harrison, *Nature*, **166**, 444 (1950).
14) S.M. Partridge, *Nature*, **164**, 443 (1949).

solution of diazomethane[15] in CH_2Cl_2 until a faint yellow color persisted. After 30 min at 0°, the mixture was stored overnight at room temperature, then filtered, and washed successively with saturated aq. $NaHCO_3$ and water, dried ($CaCl_2$), and evaporated to dryness. Elution of the product from silica gel column with 30:1 (v/v) CH_2Cl_2–acetone gave an amorphous powder (180 mg, 49%) which crystallized from EtOH. Recrystallization from EtOH gave white needles, mp 140—142°, $[\alpha]_D^{26}$+74.5° (c=1.52, $CHCl_3$). NMR (τ): 1.76—2.18 (6H, m, o-H of 3PhCO), 2.46—2.84 (14H, m, m- and p-H of 3PhCO and $C_6\underline{H}_5CH$), 4.44 (1H, s, PhC$\underline{H}$), 6.79 (3H, s, $C\underline{H}_3O$). TLC: Rf 0.70 (solvent A) and 0.64 (C). *Anal.* Calcd. for $C_{41}H_{38}O_{13}$: C, 66.66; H, 5.18. Found: C, 66.68; H, 5.02.

Identification of the Component Monosaccharides in 8——To a suspension of **8** (50 mg) in dry MeOH (10 ml), Pd catalyst[16] freshly prepared from $PdCl_2$ (30 mg) was added, and the mixture was hydrogenated with stirring at room temperature under atmospheric pressure. The mixture was filtered, and concentrated to dryness. Elution of the product from silica gel column with 10:1 (v/v) CH_2Cl_2–acetone gave an amorphous powder. To a solution of this powder in MeOH (1 ml), methanolic sodium methoxide (0.1 M, 0.1 ml) was added at room temperature and the mixture was stirred under exclusion of moisture for 3 hr; debenzoylation was monitored by TLC. Dry Amberlite IR-120 (H^+) resin was added, the suspension was stirred for 30 min, then filtered, concentrated, and a solution of sirupy residue in 0.5 M H_2SO_4 (8 ml) was kept at 95° for 6 hr. The hydrolyzate was neutralized with $BaCO_3$, filtered, and, after treatment with charcoal, concentrated to a thin sirup, in which glucose (Rf 0.40) and 3-O-methylglucose[17] (Rf 0.59) were identified by PPC.

1,6-Anhydro-3-O-methyl-β-maltose (9)——Debenzylidenation of **8** (180 mg) as described above gave a chromatographically homogeneous amorphous powder (135 mg, 90%), $[\alpha]_D^{22}$+116° (c=1, $CHCl_3$). TLC: Rf 0.61 (solvent B). Sequential debenzoylation of the product with methanolic sodium methoxide as described above afforded **9** as an amorphous powder, $[\alpha]_D^{20}$+74.6° (c=0.54, MeOH).

Periodate consumption[18] (mole) of **9** (28 mg in H_2O) at room temperature was as follows: 1.01 (0.5 hr), 1.42 (1 hr), 1.58 (4 hr), 1.60 (24 hr), and 1.74 (44 hr, constant) with concomitant formation of 0.84 mole of formic acid.

3,3′-Di-O-acetyl-1,6-anhydro-2,2′-di-O-benzoyl-4′,6′-O-benzylidene-β-maltose (10)——Acetylation of **4** (100 mg) as described above for **7** gave **10** (80 mg, 70%), mp 113—115° (from iso-PrOH), $[\alpha]_D^{27}$+87° (c=0.95, $CHCl_3$). NMR (τ): 1.82—2.13 (4H, m, o-H of 2PhCO), 2.51—2.84 (11H, m, m- and p-H of 2PhCO and $C_6\underline{H}_5$-CH), 8.01, 8.03 (each 3H, s, 2AcO). TLC: Rf 0.65 (solvent A) and 0.53 (C). *Anal.* Calcd. for $C_{37}H_{36}O_{14}$: C, 63.06; H, 5.15. Found: C, 63.21; H, 5.33.

1,6-Anhydro-2,2′-di-O-benzoyl-4′,6′-O-benzylidene-3,3′-di-O-methyl-β-maltose (11)——To a chilled mixture of **4** (130 mg) in dry CH_2Cl_2 (15 ml) and boron trifluoride etherate (1 drop) a solution of diazomethane in CH_2Cl_2 was added at 0° until a faint yellow color persisted. The mixture was processed, as described above for **8**, to afford sirupy **11** (75 mg, 55%) which crystallized from MeOH. Recrystallization from MeOH gave white needles, mp 126—128°, $[\alpha]_D^{23}$+71.2° (c=0.76, $CHCl_3$). NMR (τ): 1.73—2.12 (4H, m, o-H of 2PhCO), 2.36—2.64 (11H, m, m- and p-H of 2PhCO and $C_6\underline{H}_5CH$), 6.55, 6.74 (each 3H, s, 2C$\underline{H}_3$O). TLC: Rf 0.66 (solvent A) and 0.64 (C). *Anal.* Calcd. for $C_{35}H_{36}O_{12}$: C, 64.81; H, 5.59. Found: C, 65.03; H, 5.89.

Identification of the Component Monosaccharides in 11——Treatment of **11** as described for **8**, gave 3-O-methylglucose (Rf 0.59) as the sole component which was identified by PPC.

1,6-Anhydro-2,2′-di-O-benzoyl-β-maltose (12)——Debenzylidenation of **4** (200 mg) as described above for **3** gave an amorphous powder (160 mg, 93%), $[\alpha]_D^{16}$+120.5° (c=1.39, MeOH). TLC: Rf 0.28 (solvent B).

Periodate consumption (mole) of **12** (57 mg in 30% aq. MeOH) at room temperature was as follows: 0.10 (1 hr), 0.35 (2 hr), 0.53 (4 hr), 1.15 (8 hr), and 1.20 (24 hr, constant); no concomitant formation of formic acid was observed for 48 hr.

2,3-Di-O-acetyl-1,6-anhydro-2′,3′-di-O-benzoyl-4′,6′-O-benzylidene-β-maltose (13)——Acetylation of **5** (70 mg), as described above for **7** gave **13** (70 mg, 87%), mp 109—111° (from iso-PrOH), $[\alpha]_D^{26}$+46.1° (c=0.79, $CHCl_3$). NMR (τ): 2.00—2.10 (4H, m, o-H of 2PhCO), 2.52—2.76 (11H, m, m- and p-H of 2PhCO and $C_6\underline{H}_5$-CH), 4.44 (1H, s, PhC$\underline{H}$), 8.02, 8.08 (each 3H, s, 2AcO). TLC: Rf 0.62 (solvent A) and 0.61 (C). *Anal.* Calcd. for $C_{37}H_{36}O_{14}$: C, 63.06; H, 5.15. Found: C, 63.33; H, 5.34.

1,6-Anhydro-2′,3′-di-O-benzoyl-4′,6′-O-benzylidene-2,3-di-O-methyl-β-maltose (14)——To a chilled mixture of **5** (150 mg) in dry CH_2Cl_2 (15 ml) and boron trifluoride etherate (1 drop) a solution of diazomethane in CH_2Cl_2 was added at 0° until a faint yellow color persisted. The mixture was processed as described for **8** to afford sirupy **14** (65 mg, 42%). Recrystallization from MeOH gave white needles, mp 189—191°, $[\alpha]_D^{24}$ +59.6° (c=0.8, $CHCl_3$). NMR (τ): 1.94—2.02 (4H, m, o-H of 2PhCO), 2.48—2.72 (11H, m, m- and p-H of 2PhCO and $C_6\underline{H}_5CH$), 4.42 (1H, s, PhC$\underline{H}$), 6.82 (6H, s, 2C$\underline{H}_3$O). TLC: Rf 0.61 (solvent A) and 0.62 (C). *Anal.* Calcd. for $C_{35}H_{36}O_{12}$: C, 64.81; H, 5.59. Found: C, 64.53; H, 5.33.

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Identification of the Component Monosaccharides in 14——Treatment of **14**, as described above for **8**, gave glucose (*Rf* 0.40) and 2,3-di-O-methylglucose[19] (*Rf* 0.70) which identified by PPC.

1,6-Anhydro-2′,3′-di-O-benzoyl-β-maltose (15)——Debenzylidenation of **5** (140 mg), as described above for **3**, gave an amorphous powder (110 mg, 92%), $[\alpha]_D^{20}+100°$ ($c=1$, MeOH). TLC: *Rf* 0.29 (solvent B).

Periodate consumption (mole) of **15** (65 mg in 30% aq. MeOH) at room temperature was as follows: 0.35 (0.5 hr), 0.38 (1 hr), 0.42 (4 hr), and 0.92 (24 hr, constant); no concomitant formation of formic acid was observed for 48 hr.

2,3,3′-Tri-O-acetyl-1,6-anhydro-2′-O-benzoyl-4′,6′-O-benzylidene-β-maltose (16)——Acetylation of **6** (130 mg), as described for **7**, gave **16** (140 mg, 88%) as an amorphous powder which crystallized from EtOH. Recrystallization from EtOH gave white needles, mp 110—112°, $[\alpha]_D^{28}+48.1°$ ($c=1.18$, $CHCl_3$). NMR (τ): 1,92—2. (2H, m, *o*-H of PhCO), 2.42—2.74 (8H, m, *m*- and *p*-H of PhCO and $C_6\underline{H}_5CH$), 4.47 (1H, s, PhC<u>H</u>), 8.02 (6H, s, 2AcO), 8.11 (3H, s, AcO). TLC: *Rf* 0.59 (solvent A) and 0.54 (C). *Anal.* Calcd. for $C_{32}H_{34}O_{14}$: C, 59.81; H, 5.33. Found: C, 59.40; H, 5.12.

1,6-Anhydro-2′-O-benzoyl-4′,6′-O-benzylidene-2,3,3′-tri-O-methyl-β-maltose (17)——To a chilled mixture of **6** (200 mg) in dry CH_2Cl_2 (20 ml) and boron trifluoride etherate (1 drop) a solution of diazomethane in CH_2Cl_2 was added at 0° until a faint yellow color persisted. The mixture was processed as described above for **8** to afford a sirup (150 mg, 69%). Recrystallization from EtOH gave **17** as white needles, mp 105—106°, $[\alpha]_D^{17}+65.5°$ ($c=0.84$, $CHCl_3$). NMR (τ): 1.86—1.94 (2H, m, *o*-H of PhCO), 2.44—2.80 (8H, m, *m*- and *p*-H of PhCO and $C_6\underline{H}_5CH$), 4.43 (1H, s, PhC<u>H</u>), 6.38, 6.81, 6.93 (each 3H, s, 3C<u>H</u>$_3$O). TLC: *Rf* 0.63 (solvent A) and 0.64 (C). *Anal.* Calcd. for $C_{29}H_{34}O_{11}$: C, 62.36; H, 6.14. Found: C, 62.42; H, 5.70.

Identification of the Component Monosaccharides in 17——Treatment of **17**, as described above for **8**, gave 3-O-methylglucose (*Rf* 0.58) and 2,3-di-O-methylglucose (*Rf* 0.70) which were identified by PPC.

1,6-Anhydro-2′-O-benzoyl-β-maltose (18)——Debenzylidenation of **6** (170 mg), as described above for **3**, gave an amorphous powder (170 mg, 82%), which crystallized from AcOEt as white needles, mp 176—177°, $[\alpha]_D^{18}+86°$ (c=1.3, H_2O). TLC: *Rf* 0.10 (solvent B). *Anal.* Calcd. for $C_{19}H_{24}O_{11}$: C, 53.27; H, 5.65. Found: C, 52.99; H, 5.62.

Periodate consumption (mole) of **18** (65 mg in H_2O) at room temperature was as follows: 0.41 (0.5 hr), 0.65 (1 hr), 1.30 (2 hr), 1.80 (4 hr), and 2.25 (24 hr, constant); no concomitant formation of formic acid was observed for 48 hr.

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