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Note

Acetonation of methyl β-maltoside with 2-methoxypropene

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The acid-catalysed acetonation of carbohydrates with 2-methoxypropene[1–4] and 2,2-dimethoxypropane[5–8] yields acetals that are different from those obtained under the usual thermodynamic conditions[9]. The nature of the products of acetonation with 2-methoxypropene depends on the conditions. Thus, the products of the reaction of benzyl β-lactoside depend on the time of the reaction, the catalyst, and the temperature[3]. Some of these new acetals are useful for synthesis, as demonstrated by the one-pot synthesis of the chiral receptor benzyl 3′,4′-*O*-isopropylidene-6,6′-*O*-(3,6,9-trioxaundecane-1,11-diyl)-β-lactoside[3] from benzyl 3′,4′-*O*-isopropylidene-β-lactoside. We now report on the acetonation of methyl β-maltoside[10] (**1**) with 2-methoxypropene as part of a program on the synthesis of compounds containing the maltose unit. The acetonation of maltose with 2-methoxypropene[11] and with 2,2-dimethoxypropane[6] has been investigated.

Reaction of **1** with 3.7 mol. equiv. of 2-methoxypropene for 20 min at 0° in the presence of pyridinium toluene-*p*-sulfonate gave a mixture from which the methyl 6-*O*-(methoxydimethyl)methyl (**2**, 14%), 6′-*O*-(methoxydimethyl)methyl (**3**, 23%), and 6,6′-di-*O*-(methoxydimethyl)methyl (**4**, 27%) derivatives of methyl β-maltoside were isolated by column chromatography. The ^{13}C-n.m.r. spectra of **2**–**4** (Table I) contained signals for methyl, methoxyl, and acetal carbons. Acetylation of **4** gave **6**, but acetylation of **2** and **3** gave mixtures containing methyl hepta-*O*-acetyl-β-maltoside, among other products, as a consequence of mixed acetal cleavage. The ^{1}H-n.m.r. spectrum of **6** accorded with the structure proposed, and that of the acetylation mixture of **2** could be partially analysed and established **5** as the major product. The composition of the reaction mixture rapidly changed (t.l.c.) with time and, after several hours, the t.l.c. pattern was very similar to that observed when a more active catalyst (toluene-*p*-sulfonic acid) and higher temperature (ambient) were used. Under the latter conditions, the main products which could be isolated after reaction of 1 h were methyl 4′,6′-*O*-isopropylidene-β-maltoside (**7**, 24%) and methyl 4′,6′-*O*-isopropylidene-6-*O*-(methoxydimethyl)methyl-β-maltoside (**8**,

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TABLE I

^{13}C-N.M.R. SHIFTS FOR ACETALS (SOLVENT, PYRIDINE-d_5)

Compound	*Acetal carbons*	*Acetal methoxyl carbons*	*Methyl carbons*
2	100.1	48.1	24.6, 24.5
3	100.2	48.4	24.5 (×2)
4	100.4, 100.3	48.6, 48.5	25.1, 24.9 (×3)
7	99.6		29.6, 19.4
8	100.3, 99.6	48.3	29.6, 24.8, 24.6 19.4
11	99.7, 99.5		29.5, 27.4, 24.7 19.3
12[a]	100.1, 99.8 98.6	48.5	29.1, 27.0 (×2) 24.4 (×3), 19.2

[a]Solvent $CDCl_3$.

11%). The ^{13}C-n.m.r. spectra of **7** and **8** contained signals for the gem-dimethyl groups of the dioxane ring[12], and that of **8** contained signals for methoxyl and methyl groups of a mixed acetal (Table I). Conventional acetylation of **7** and **8** gave **9** and **10**, respectively, the ^{1}H-n.m.r. spectra of which accorded with the structures proposed.

An excess of reagent (5.2 equiv.) and longer reaction time (20 h) with **1** resulted in the isolation of methyl 3,2′:4′,6′-di-*O*-isopropylidene-β-maltoside (**11**, 32%) and methyl 3,2′:4′,6′-di-*O*-isopropylidene-6-*O*-(methoxydimethyl)methyl-β-maltoside (**12**, 33%), besides **7** and **8**. The ^{13}C-n.m.r. spectra of **11** and **12** contained signals for the methyl groups in six-[12] and eight-membered[3] rings, and that of **12** contained signals for the methoxyl and methyl groups of a mixed acetal. Acetylation of **11** and **12** gave **13** and **14**, respectively, the ^{1}H-n.m.r. spectra of which accorded with the structures proposed.

The above results support the postulate that 2-methoxypropene reacts initially with the more reactive[13–15] primary hydroxyl groups to give the equilibrium mixture of the mixed acetals **2–4**, each of which then cyclises irreversibly. The six-membered 4′,6′-*O*-isopropylidene acetals **7** and **8** may be formed easily from **3** and **4**, whereas cyclisation of the mixed acetals at C-6 in **2** and **4** is precluded. The eight-membered 3,2′-cyclic acetals **11** and **12** may be formed from non-isolated, slowly formed 3- or 2′-mixed acetals.

The reaction of **1** with 2,2-dimethoxypropane under the conditions reported for maltose[6] gave, after 3 h, **7** (23%), **8** (10%), **11** (25%), and **12** (11%).

The utility of this acetonation reaction in synthesis was demonstrated by the easy preparation of the diol **16** as a synthon for maltose-derived chiral macrocyclic compounds. Conventional benzylation of **11** gave **15**, which was submitted to selective acidic hydrolysis to give 60% of **16**. Acetylation of **16** gave **17**, the ^{1}H-n.m.r. spectra of which accorded with the structure proposed.

EXPERIMENTAL

General methods. — Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. T.l.c. was performed on Silica Gel GF_{254} (Merck) with detection by charring with sulfuric acid. Column chromatography was performed on silica gel (Merck 70–230). ^{1}H-N.m.r. spectra were recorded with a Varian XL-300 (300 MHz) or Bruker AM-200 (200 MHz) spectrometer, and ^{13}C-n.m.r. spectra with a Bruker AM-200 (50 MHz) or WP-80 (20 MHz) spectrometer. Optical rotations were determined with a Perkin–Elmer 141 polarimeter.

Acetonation of methyl β-maltoside (**1**) *with 2-methoxypropene.* — (*a*) Treatment of **1** (2 g, 5.62 mmol) in *N*,*N*-dimethylformamide (7.5 mL) with 2-methoxypropene (1.88 mL, 20.79 mmol) in the presence of pyridinium toluene-*p*-sulfonate (42 mg) at 0°, under argon, for 20 min gave, after neutralization with Na_2CO_3 and concentration, a residue, column chromatography (5:1 chloroform–methanol) of which followed by further column chromatography (8:1 chloroform–methanol) afforded **4** (0.75 g, 27%), **3** (0.56 g, 23%), and **2** (0.34 g, 14%).

Methyl 6,6′-di-*O*-(methoxydimethyl)methyl-β-maltoside* (**4**) had m.p. 77–79°, $[\alpha]_D$ +42° (*c* 0.99, methanol). N.m.r. data (pyridine-d_5): ^{1}H (200 MHz), δ 5.92 (d, 1 H, $J_{1',2'}$ 3.2 Hz, H-1′), 4.84 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.84, 3.61, and 3.59 (3 s, each 3 H, 3 OMe), 1.76 and 1.70 (2 s, each 3 H, 2 Me), and 1.67 (s, 6 H, 2 Me); ^{13}C (50 MHz), δ 105.2 and 103.1 (C-1,1′), 100.4 and 100.3 (2 *C*Me_2OMe), 82.0, 77.7, 75.6, 75.1, 74.6, 74.4, 73.6, 71.4, 61.1 (double intensity, C-6,6′), 56.7 (OMe), 48.6 and 48.5 (2 OMe), 25.1 (Me), and 24.9 (3 Me).

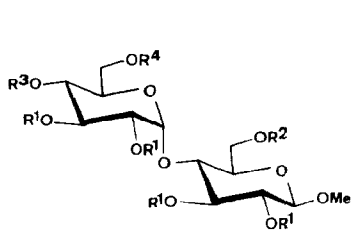
The penta-acetate* (**6**) of **4** had m.p. 116–118°, $[\alpha]_D$ +47° (*c* 0.52, chloroform). ^{1}H-N.m.r. data (200 MHz, $CDCl_3$): δ 5.26 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1′), 5.23 (t, 1 H, $J_{2',3'} \approx J_{3',4'} \approx$ 9.7 Hz, H-3′), 5.11 (t, 1 H, $J_{2,3} \approx J_{3,4} \approx$ 9.3 Hz, H-3), 4.96 (t, 1 H, $J_{4',5'} \approx$ 9.7 Hz, H-4′), 4.69 (dd, 1 H, $J_{1,2}$ 7.8 Hz, H-2), 4.67 (dd, 1 H, H-2′), 4.29 (d, 1 H, H-1), 3.32, 3.09, and 3.02 (3 s, each 3 H, 3 OMe), 1.90, 1.87, and 1.86 (3 s, each 3 H, 3 Ac), 1.85 (s, 6 H, 2 Ac), 1.21 (s, 6 H, 2 Me), 1.19 and 1.16 (2 s, each 3 H, 2 Me).

Methyl 6′-*O*-(methoxydimethyl)methyl-β-maltoside (**3**) was an unstable syrup. ^{13}C-N.m.r. data (50 MHz, pyridine-d_5): δ 105.4 and 103.1 (C-1,1′), 100.2 (*C*Me_2OMe), 56.6 (OMe), 48.4 (OMe), and 24.5 (2 Me).

Methyl 6-*O*-(methoxydimethyl)methyl-β-maltoside (**2**) was an unstable syrup. ^{13}C-N.m.r. data (50 MHz, pyridine-d_5): δ 104.8 and 103.0 (C-1,1′), 100.1 (*C*Me_2OMe), 81.3, 77.6, 75.0, 74.7 (double intensity), 74.1 (double intensity), 71.2, 62.1 and 61.0 (C-6,6′), 56.3 (OMe), 48.1 (OMe), 24.6 and 24.5 (2 Me).

(*b*) A solution of **1** (0.75 g, 2.11 mmol) in *N*,*N*-dimethylformamide (7.5 mL) was treated with 2-methoxypropene (0.71 mL, 7.81 mmol) in the presence of toluene-*p*-sulfonic acid (16 mg) at room temperature, under argon, for 1 h to give, after neutralization (Na_2CO_3) and concentration, a residue, column chromato-

*Satisfactory elemental analyses for **4** and **6** could not be obtained.



1 $R^1 = R^2 = R^3 = R^4 = H$

2 $R^1 = R^3 = R^4 = H$, $R^2 = CMe_2OMe$

3 $R^1 = R^2 = R^3 = H$, $R^4 = CMe_2OMe$

4 $R^1 = R^3 = H$, $R^2 = R^4 = CMe_2OMe$

5 $R^1 = R^3 = R^4 = Ac$, $R^2 = CMe_2OMe$

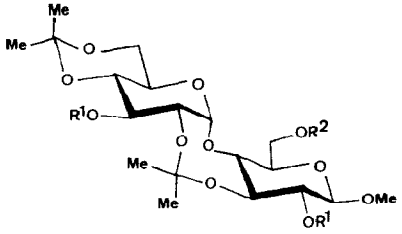
6 $R^1 = R^3 = Ac$, $R^2 = R^4 = CMe_2OMe$

7 $R^1 = R^2 = H$, $R^3, R^4 = CMe_2$

8 $R^1 = H$, $R^2 = CMe_2OMe$, $R^3, R^4 = CMe_2$

9 $R^1 = R^2 = Ac$, $R^3, R^4 = CMe_2$

10 $R^1 = Ac$, $R^2 = CMe_2OMe$, $R^3, R^4 = CMe_2$

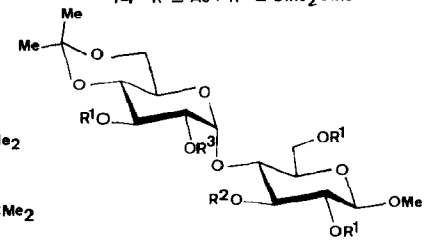


11 $R^1 = R^2 = H$

12 $R^1 = H$, $R^2 = CMe_2OMe$

13 $R^1 = R^2 = Ac$

14 $R^1 = Ac$, $R^2 = CMe_2OMe$



15 $R^1 = Bzl$, $R^2, R^3 = CMe_2$

16 $R^1 = Bzl$, $R^2 = R^3 = H$

17 $R^1 = Bzl$, $R^2 = R^3 = Ac$

graphy of which (ethyl acetate) gave **8** and **7**. Further column chromatography (7:1 chloroform–methanol) gave **8** (0.11 g, 11%) and 7 (0.20 g, 24%).

Methyl 4′,6′-*O*-isopropylidene-6-*O*-(methoxydimethyl)methyl-β-maltoside (**8**) had m.p. 90–92°, $[\alpha]_D$ +35° (*c* 0.49, methanol). ^{13}C-N.m.r. data (20 MHz, pyridine-d_5): δ 105.2 and 103.3 (C-1,1′), 100.3 and 99.6 (acetal C), 81.8, 77.9, 75.2, 74.8 (double intensity), 74.4, 72.0, 65.3, 63.0 and 61.0 (C-6,6′), 56,5 (OMe), 48.3 (OMe), 29.6, 24.8, 24.6, and 19.4 (4 Me).

Anal. Calc. for $C_{20}H_{36}O_{12}$: C, 51.27; H, 7.74. Found: C, 51.16; H, 8.00.

The tetra-acetate (**10**) of **8** had m.p. 152–155°, $[\alpha]_D$ +17.5° (*c* 0.26, chloroform). ^{1}H-N.m.r. data (300 MHz, $CDCl_3$): δ 5.35 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′), 5.31 (t, 1 H, $J_{2',3'} \approx J_{3',4'} \approx 9.5$ Hz, H-3′), 5.24 (t, 1 H, $J_{2,3} \approx J_{3,4} \approx 9.4$ Hz, H-3), 4.82 (dd, 1 H, $J_{1,2}$ 8.0 Hz, H-2), 4.76 (dd, 1 H, H-2′), 4.42 (d, 1 H, H-1), 4.06 (t, 1 H, $J_{4,5} \approx 9.4$ Hz, H-4), 3.47 and 3.26 (2 s, each 3 H, 2 OMe), 2.05 (s, 6 H, 2 Ac), 2.02 and 2.00 (2 s, each 3 H, 2 Ac), 1.46, 1.40, 1.38, and 1.35 (4 s, each 3 H, 4 Me).

Anal. Calc. for $C_{28}H_{44}O_{16}$: C, 52.82; H, 6.97. Found: C, 53.22; H, 7.35.

Methyl 4′,6′-*O*-isopropylidene-β-maltoside (**7**) had m.p. 110–112°, $[\alpha]_D$ +51° (*c* 0.51, methanol). ^{13}C-N.m.r. data (20 MHz, pyridine-d_5): δ 105.4 and 103.3 (C-1,1′), 99.6 (CMe_2), 81.3, 77.7, 76.3, 75.1, 74.9, 74.5, 72.1, 65.4, 62.9 and 61.8 (C-6,6′), 56.7 (OMe), 29.6 and 19.4 (2 Me).

Anal. Calc. for $C_{16}H_{28}O_{11}$: C, 48.48; H, 7.12. Found: C, 48.53; H, 7.23.

The penta-acetate (**9**) of **7** had m.p. 150–152°, $[\alpha]_D$ +37° (*c* 0.49, chloroform). ^{1}H-N.m.r. data (300 MHz, $CDCl_3$): δ 5.31 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1'), 5.28 (t, 1 H, $J_{2',3'} \approx J_{3',4'} \approx 9.5$ Hz, H-3'), 5.25 (t, 1 H, $J_{2,3} \approx J_{3,4} \approx 9.2$ Hz, H-3), 4.82 (dd, 1 H, H-2'), 4.81 (dd, 1 H, $J_{1,2}$ 7.9 Hz, H-2), 4.54 (dd, 1 H, $J_{5,6a}$ 2.6, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.44 (d, 1 H, H-1), 4.25 (dd, 1 H, $J_{5,6b}$ 3.8 Hz, H-6b), 4.00 (t, 1 H, $J_{4,5} \approx 9.2$ Hz, H-4), 3.49 (s, 3 H, OMe), 2.13 (s, 3 H, Ac), 2.04 (s, 6 H, 2 Ac), 2.03 and 2.00 (2 s, each 3 H, 2 Ac), 1.45 and 1.37 (2 s, each 3 H, 2 Me).

Anal. Calc. for $C_{26}H_{38}O_{16}$: C, 51.48; H, 6.31. Found: C, 51.78; H, 6.59.

(*c*) Treatment of **1** (3 g, 8.43 mmol) in *N,N*-dimethylformamide (30 mL) with 2-methoxypropene (3.95 mL, 43.84 mmol) in the presence of toluene-*p*-sulfonic acid (60 mg) at room temperature, under argon, for 20 h gave, after neutralization (Na_2CO_3) and concentration, a residue, column chromatography (hexane, 1:1 ethyl acetate–hexane, ethyl acetate) of which gave **12** and **11** as syrups.

Methyl 3,2':4',6'-di-*O*-isopropylidene-6-*O*-(methoxydimethyl)methyl-β-maltoside (**12**) solidified on washing with ethyl acetate, to give a white powder (1.20 g 33%), m.p. 175–176°, $[\alpha]_D$ +25° (*c* 0.49, methanol). ^{13}C-N.m.r. data (20 MHz, $CDCl_3$): δ 104.0 and 101.9 (C-1,1'), 100.1, 99.8 and 98.6 (acetal C), 79.4, 76.3, 74.3, 73.8, 73.1, 72.1, 70.4, 63.9, 62.4 and 60.3 (C-6,6'), 57.0 (OMe), 48.5 (OMe), 29.1 and 27.0 (2 Me), 24.4 (3 Me), and 19.2 (Me).

Anal. Calc. for $C_{23}H_{40}O_{12}$: C, 54.32; H, 7.93. Found: C, 54.58; H, 8.20.

The diacetate (**14**) of **12** had m.p. 70–73°, $[\alpha]_D$ +1.5° (*c* 0.53, chloroform). ^{1}H-N.m.r. data (300 MHz, $CDCl_3$): δ 5.48 (dd, 1 H, $J_{1',2'}$ 3.8 Hz, H-1'), 5.24 (t, 1 H, $J_{2',3'} \approx J_{3',4'} \approx 9.3$ Hz, H-3'), 4.78 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 10.1 Hz, H-2), 4.32 (d, 1 H, H-1), 3.47 and 3.22 (2 s, each 3 H, 2 OMe), 2.065 and 2.060 (2 s, each 3 H, 2 Ac), 1.45, 1.41, and 1.37 (3 s, each 3 H, 3 Me), 1.35 (s, 6 H, 2 Me), and 1.25 (s, 3 H, Me).

Anal. Calc. for $C_{27}H_{44}O_{14}$: C, 54.72; H, 7.48. Found: C, 54.52; H, 7.39.

Methyl 3,2':4',6'-di-*O*-isopropylidene-β-maltoside (**11**) solidified on washing with ethyl acetate and hexane, to afford material (0.90 g, 32%) having m.p. 149–150°, $[\alpha]_D$ +22° (*c* 0.51, methanol), ^{13}C-N.m.r. data (20 MHz, pyridine-d_5): δ 105.4 and 102.0 (C-1,1'), 99.7 and 99.5 (2 CMe_2), 80.1, 77.7, 75.7, 75.2, 74.4, 72.4, 70.5, 64.6, 62.8 and 61.9 (C-6,6'), 56.8 (OMe), 29.5, 27.4, 24.7, and 19.3 (4 Me).

Anal. Calc. for $C_{19}H_{32}O_{11}$: C, 52.29; H, 7.39. Found: C, 52.50; H, 7.70.

The triacetate (**13**) of **11** had m.p. 197–200° $[\alpha]_D$ +3.3° (*c* 0.49, chloroform). ^{1}H-N.m.r. data (300 MHz, $CDCl_3$): δ 5.46 (d, 1 H, $J_{1',2'}$ 3.9 Hz, H-1'), 5.23 (t, 1 H, $J_{2',3'} \approx J_{3',4'} \approx 9.4$ Hz, H-3'), 4.79 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 10.1 Hz, H-2), 4.41 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.33 (d, 1 H, H-1), 4.30 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 3.96 (dd, 1 H, $J_{3,4}$ 8.6 Hz, H-3), 3.77 (dd, 1 H, H-2'), 3.48 (s, 3 H, OMe), 2.09 (s, 3 H, Ac), 2.07 (s, 6 H, 2 Ac), 1.45, 1.40, 1.37, and 1.25 (4 s, each 3 H, 4 Me).

Anal. Calc. for $C_{25}H_{38}O_{14}$: C, 53.38; H, 6.81. Found: C, 54.07; H, 7.30.

Acetonation of 1 with 2,2-dimethoxypropane. — A solution of **1** (0.40 g, 1.12 mmol) in *N,N*-dimethylformamide (4 mL) was treated with 2,2-dimethoxypropane (1.2 mL, 9.74 mmol) in the presence of toluene-*p*-sulfonic acid (4 mg) for 3 h at 80°, to give, after neutralization (Na_2CO_3) and concentration, a residue, column

chromatography (hexane, 1:1 ethyl acetate–hexane, ethyl acetate) of which gave **12** (60 mg, 11%), **11** (120 mg, 25%), **8** (50 mg, 10%), and **7** (100 mg, 23%).

*Methyl 2,6,3′-tri-O-benzyl-3,2′:4′,6′-di-O-isopropylidene-β-maltoside (**15**).* — A mixture of **11** (54 mg, 0.12 mmol), *N,N*-dimethylformamide (0.5 mL), sodium hydride (28 mg, 1.09 mmol), and benzyl bromide (0.14 mL, 1.14 mmol) was stirred for 2 h at room temperature. Methanol (5 mL) and water (10 mL) were added, the mixture was extracted with ether (2 x 30 mL), and the combined extracts were dried (Na_2SO_4) and concentrated. Column chromatography (1:4 ethyl acetate–hexane) of the syrupy residue gave **15** (78 mg, 90%), as a syrup, $[\alpha]_D$ +14.5° (*c* 0.24, chloroform). N.m.r. data (C_6D_6): ^{1}H (200 MHz), δ 5.22 (d, 1 H, $J_{1',2'}$ 3.3 Hz, H-1′), 3.87 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.02 (s, 3 H, OMe), 1.21, 1.15, 1.05, and 0.99 (4 s, each 3 H, 4 Me); ^{13}C (20 MHz), 105.4 and 101.7 (C-1,1′), 99.5 (2 *C*Me$_2$), 80.2, 79.0, 76.3, 74.8, 74.6, 74.2, 73.8, 69.8, 64.4 and 62.9 (C-6,6′), 56.5 (OMe), 29.5, 27.1, 24.4, and 19.2 (4 Me).

Anal. Calc. for $C_{40}H_{50}O_{11}$: C, 67.97; H, 7.13. Found: C, 68.03; H, 7.34.

*Methyl 2,6,3′-tri-O-benzyl-4′,6′-O-isopropylidene-β-maltoside (**16**).* — A solution of **15** (0.27 g, 0.38 mmol) in ethanol (25 mL) was stirred with pyridinium toluene-*p*-sulfonate (65 mg) for 7 h at room temperature, then neutralized (Na_2CO_3), and concentrated. Column chromatography (1:2 ethyl acetate–hexane) of the syrupy residue afforded **16** (0.16 g, 60%), as a syrup, $[\alpha]_D$ +27° (*c* 0.56, chloroform). N.m.r. data ($CDCl_3$): ^{1}H (200 MHz), δ 5.10 (d, 1 H, $J_{1',2'}$ 1.9 Hz, H-1′), 4.29 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.55 (s, 3 H, OMe), 1.46 and 1.41 (2 s, each 3 H, 2 Me); ^{13}C (50 MHz), 138.7, 138.5 and 138.1 (C-ipso), 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6 (aromatic), 104.3 and 101.9 (C-1,1′), 99.4 (*C*Me$_2$), 64.6 and 62.4 (C-6,6′), 57.0 (OMe), 29.1 and 19.1 (2 Me).

Anal. Calc. for $C_{37}H_{46}O_{11}$: C, 66.65; H, 6.95. Found: C, 65.86; H, 7.29.

The diacetate **17** of **16** was a syrup, $[\alpha]_D$ +55° (*c* 0.40, chloroform). ^{1}H-N.m.r. data (300 MHz, $CDCl_3$): δ 5.25 (d, 1 H, $J_{1',2'}$ 4.3 Hz, H-1′), 5.22 (t, 1 H, $J_{2,3} \approx J_{3,4} \approx$ 9.4 Hz, H-3), 4.79 (dd, 1 H, $J_{2',3'}$ 8.2 Hz, H-2′), 4.37 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.97 (t, 1 H, $J_{4,5} \approx$ 9.1 Hz, H-4), 3.57 (s, 3 H, OMe), 3.26 (dd, 1 H, H-2), 2.04 and 1.85 (2 s, each 3 H, 2 Ac), 1.47 and 1.43 (2 s, each 3 H, 2 Me).

Anal. Calc. for $C_{41}H_{50}O_{13}$: C, 65.59; H, 6.71. Found: C, 65.52; H, 6.92.

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