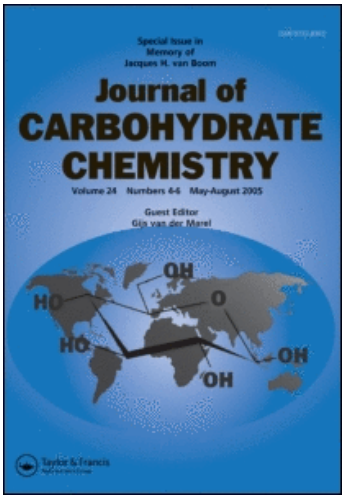

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CHEMICAL OXIDATION OF ISOMALTULOSE AND METHYL ISOMALTULOSIDES

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CHEMICAL OXIDATION OF ISOMALTULOSE AND METHYL ISOMALTULOSIDES

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ABSTRACT

The comparative chemical oxidation of isomaltulose and methyl isomaltuloside is described using TEMPO or Pt catalysts.

INTRODUCTION

Polycarboxylates derived from polyhydroxy compounds are interesting industrial targets as cation-sequestering agents.[1–3] The transformation of disaccharides by selective oxidation of primary hydroxyl groups without cleavage of the C—O acetal or/and C—C ring bonds can be achieved by heterogeneous catalysis over platinum with oxygen,[4–9] in homogeneous medium using the TEMPO/NaOCl/NaBr system, [10–19] or by electrocatalysis.[20, 21] Sonocatalysis of the TEMPO-mediated oxidation in the case of sucrose suppresses the need for NaBr as co-catalyst.[22] Some reducing disaccharides derived biochemically from sucrose, such as isomaltulose and trehalulose, have been also oxidized with hydrogen peroxide to yield carboxymethyl α-D-glucopyranoside in a one-step process.[23] This paper summarizes our results on a comparison between the use of a

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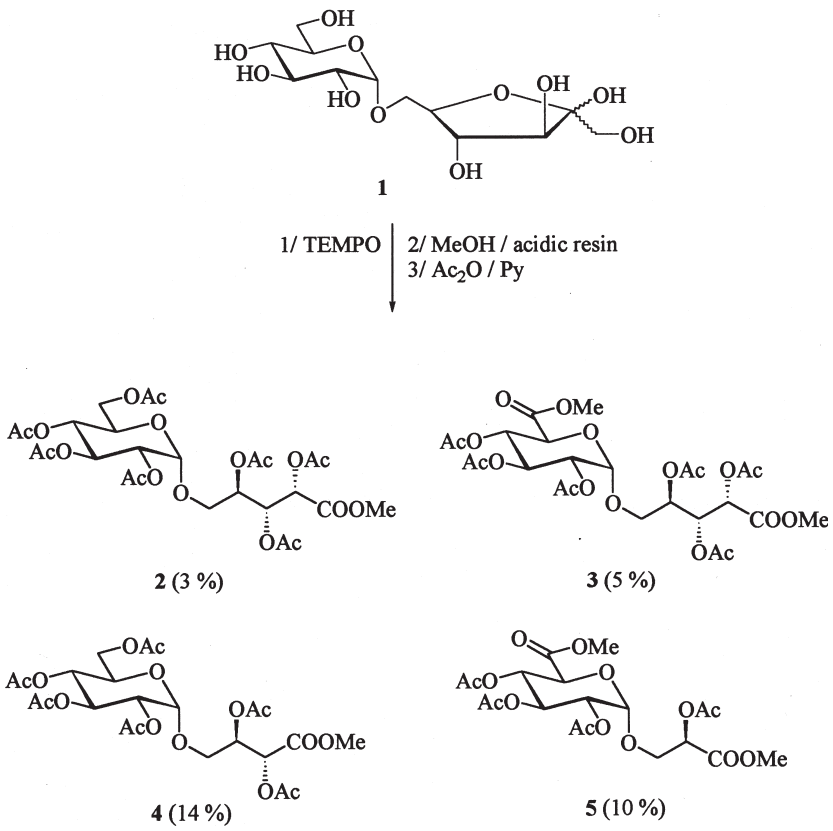
TEMPO/NaOCl system versus catalytic oxidation over Pt for the oxidation of isomaltulose and methyl isomaltuloside.

RESULTS

The reducing isomaltulose **1** (Scheme1) and non-reducing methyl isomaltuloside **6** (Scheme 2) were oxidized using TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy) or Pt catalysts. The formation of carboxylic acids was followed by measurement of the quantity of NaOH required to maintain the pH at 10.5.

For both oxidation procedures, overoxidation is observed for isomaltulose **1** and methyl isomaltuloside **6** (Fig. 1 and 2), but the oxidation process is significantly slower for isomaltuloside than for isomaltulose.

Stopping the oxidation of **1** after addition of 2 equivalents of NaOH for 1 equivalent of **1** gave a mixture composed of four oxidized compounds and 20 % of non transformed isomaltulose **1**. Oxidation products were separated and easily identified by NMR 2D $^{1}H/^{13}C$ as their methyl ester/*O*-acetyl derivatives 2–5.



Scheme 1.

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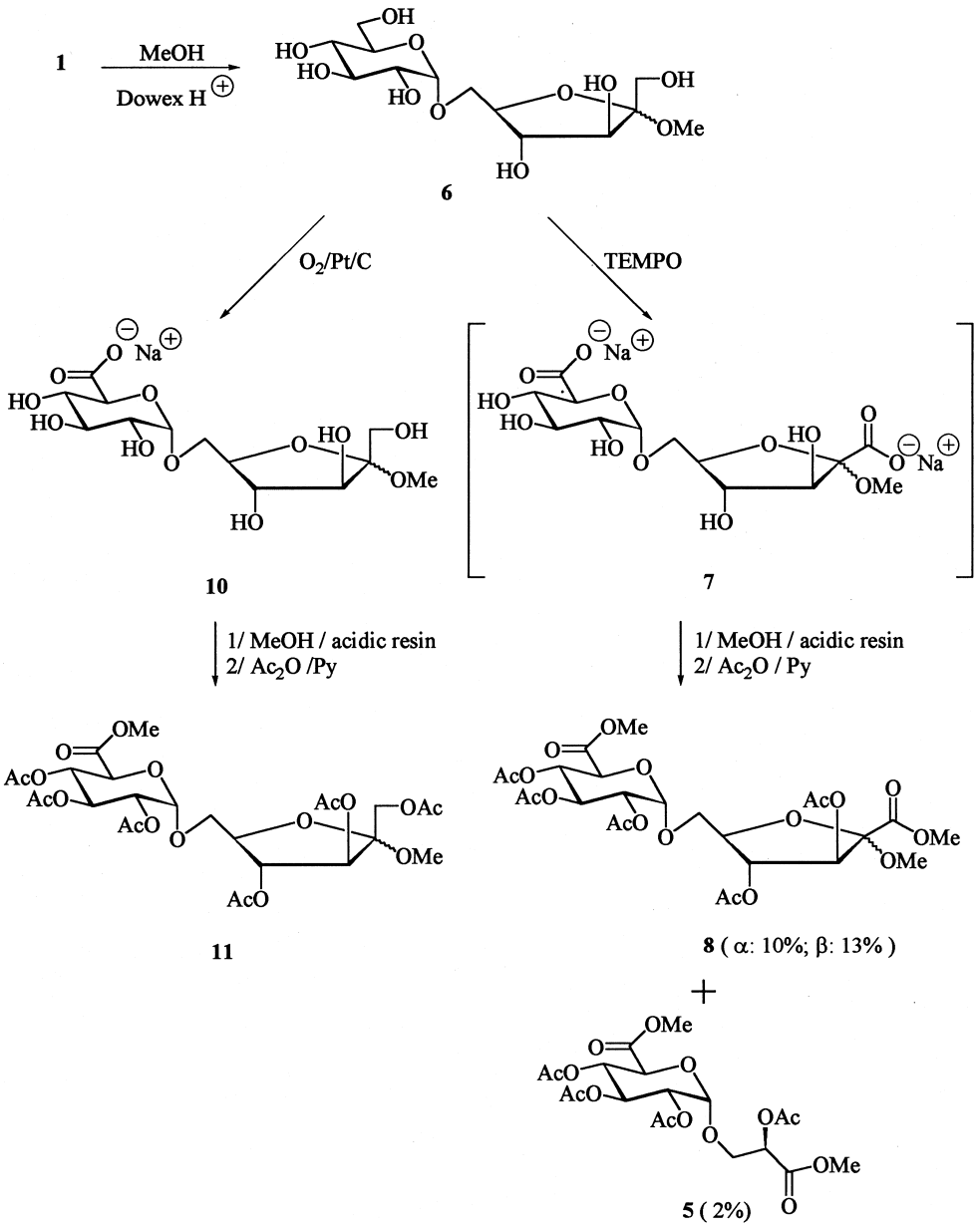

Scheme 2.

The oxidation of **1** by TEMPO/NaOCl confirms the poor selectivity of this reagent as observed with monosaccharides or oligosaccharides having a cyclic hemiacetal as terminal unit[16, 18] for the oxidation of primary hydroxyl groups into carboxylic acids and underscores the fast glycol cleavage of C—C bonds on a reducing furanosic chain.[17] The selectivity remains limited in comparison with the reported oxidation process[7–9] with O_2/Pt/KOH.

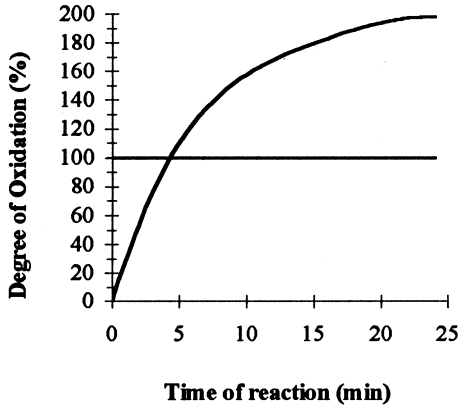

Figure 1. Oxidation of isomaltulose 1 at constant pH 10.5 and measured by amount of sodium hydroxide added. The degree of oxidation is expressed as the number of mmol of sodium hydroxide consumed per mmol of primary alcohol groups present.

Isomaltulose was converted quantitatively into methyl isomaltuloside **6** (α : β = 57/43) with MeOH/Dowex 50H$^+$ and this mixture of anomers was submitted to the same TEMPO/NaOCl oxidation conditions. The oxidation of **6** is slower than for **1** (Fig. 2) and not selective in comparison to sucrose.[22] The sole identified products were the sodium dicarboxylic salts **7** identified under the form of esters **8** (23 %) and a low yield degradation product characterized as the ester **5** in low yield (Scheme 2).

In contrast the O_2/Pt oxidation of methyl isomaltuloside **6** is regioselective and yields the mono-oxidized acid **10** (80 % yield) which was characterized as the methyl ester/*O*-acetylated compound **1** by ^{13}C NMR.

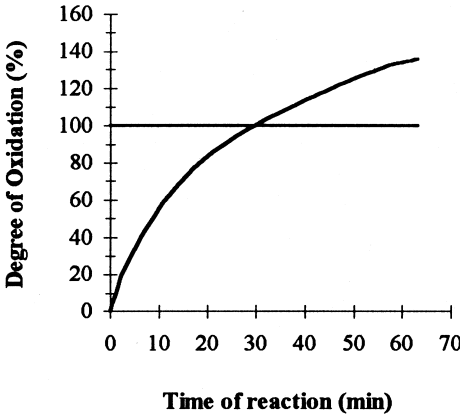

Figure 2. Oxidation of methyl isomaltuloside **6** at constant pH 10.5 and measured by amount of sodium hydroxyde added. The degree of oxidation is expressed as the number of mmol of sodium hydroxide consumed per mmol of primary alcohol groups present.

CONCLUSION

In conclusion, compared to sucrose,[19–22] the degradation or selective oxidation of isomaltulose **1** and methyl isomaltuloside **6** can be partially controlled using TEMPO/NaOCl/NaBr or O_2/Pt system.

EXPERIMENTAL

Isomaltulose was kindly provided by Südzucker AG Company (Germany). The 200 MHz ^{1}H NMR, 50 MHz ^{13}C and 300 MHz ^{1}H NMR spectra were recorded with a Bruker AC 200 or AM 300 spectrometer with TMS as an internal standard. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Thin-layer chromatography (TLC) was carried out on plates coated with silica gel 60. Column chromatography was carried out on silica gel Si 60.

Methyl α and α + β isomaltuloside (6). To a suspension of isomaltulose **1** (5 g, 14.6 mmol) in dry methyl alcohol (80 mL) was added an ion exchange resin Dowex 50H$^+$ (2.5 g). The mixture was stirred at room temperature and the reaction was followed by thin-layer chromatography (acetonitrile/water/pyridine : 4.0/0.5/0.5). After filtration of the cooled mixture, the ion exchange resin was washed with methyl alcohol. The organic solutions were concentrated giving 5.1 g (14.3 mmol) of product **6** as a white solid, a portion of which (0.460 g) was chromatographed and afforded pure **6**α (0.127 g) and the anomeric mixture **6** α+ β (0.320 g). **6**α : $[\alpha]_D^{25}$ + 122° (*c* 1.8, EtOH); ^{1}H NMR (300 MHz, D_2O): δ 3.32 (s, 3H, OCH_3), 3.42(dd, 1H, $J_{3',4'} = J_{4',5'}$ 9.4 Hz, H-4′), 3.55 (dd, 1H, $J_{1',2'}$ = 3.7Hz, $J_{2',3'}$ = 9.9, H-2′), 3.67 (m, 1H, H-6′a), 3.69 (m, 1H, H-5′), 3.72 (m, 1H, H-6a), 3.74 (dd, 1H, H-3′), 3.77 (d, 1H, $J_{1a,1b}$ = 12.1, H-1a), 3.82 (m, 1H, H-6′b), 3.88 (d, 1H, H-1b), 3.98 (m, 1H, H-6b), 4.10 (m, 3H, H-3, H-4, H-5), 4.95 (d, 1H, H-1′); ^{13}C NMR (75 MHz, D_2O): δ 48.8 (OCH_3), 58.1 (C-1), 61.0 (C-6′), 67.4 (C-6), 70.0 (C-4′), 71.9 (C-2′), 72.5 (C-5′), 73.6 (C-3′), 77.9 (C-4), 80.3 (C-5), 82.6 (C-3), 99.2 (C-1′), 109.1 (C-2); **6**β: ^{13}C NMR (75 MHz, D_2O): δ 49.6 (OCH_3), 60.3 (C-1), 60.9 (C-6′), 69.4 (C-6), 70.0 (C-4′), 71.8 (C-2′), 72.6 (C-5′), 73.5 (C-3′), 75.7 (C-4), 77.1 (C-3), 79.8 (C-5), 98.9 (C-1′), 104.5 (C-2).

Anal. Calcd for $C_{13}H_{24}O_{11}$: α+ β (356.33): C, 43.82; H, 6.79. Found: C,44.18; H, 7.08.

Oxidation of isomaltulose 1 and methyl isomaltuloside 6 with TEMPO/NaOCl. To isomaltulose **1** (5.3 g, 15.5 mmol) or methyl isomaltuloside **6** (5.5 g, 15.5 mmol) dissolved in water (400 mL) cooled at 2°C were added NaBr (1.27 g, 12.4 mmol) and TEMPO (0.035 g, 0.23 mmol). This solution was maintained at pH 10.5 by addition of (0.5N) NaOH and oxidized at 2°C with a solution of NaOCl (35 mL, 93 mmol) at 12.5% at pH equal to 10, as controlled by addition of (2N) HCl solution. The reaction was quenched by adding ethyl alcohol (10 mL) and then neutralized with 2N HCl. After evaporation of water at 20°C in vacuo, the new product, containing about 70% salt, was analyzed by NMR.

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Oxidation of methyl isomaltuloside 6 with Pt/C, O_2. A methyl isomaltuloside (2.87 g, 8.1 mmol) aqueous solution (100 mL) was poured into a three-neck round bottom flask charged with 3 g of Pt/C (5%) previously activated with hydrogen. The mixture was vigorously stirred at 60°C while the pH was maintained at 9 with 0.1N $NaHCO_3$ addition. The reaction was followed with ^{13}C NMR taking aliquots (5 mL) which were filtered and dried. After 110 h, the mixture was filtered and the solution was concentrated. The crude product was analyzed by ^{13}C NMR showing signals corresponding to both **10** α and β. **10**α: ^{13}C NMR (75 MHz, D_2O): δ 48.9 (OCH_3), 58.2 (C-1), 67.6 (C-6), 71.7, 72.5, 72.8, 73.5 (C-2′, C-3′, C-4′, C-5′), 77.8 (C-4), 80.4 (C-5), 82.5 (C-3), 99.2 (C-1′), 109.0 (C-2), 177.1 CO_2Na); **10**β: ^{13}C NMR (75MHz, D_2O): δ 51.4 (OCH_3), 61.1 (C-1), 69.8 (C-6), 98.7 (C-1′), 104.5 (C-2), 177.1 (C-6′).

Esterification and acetylation of crude product from TEMPO/NaOCl. Crude product (4.5 g) containing about 4.3 mmol of organic compound were ground up and suspended in a mixture of dry methyl alcohol (40 mL) and methyl orthoformate (3 mL, 27.4 mmol). The mixture was stirred for 15 min and then dried Amberlite IR-120 (H^+) ion exchange resin (1 g) was added. The mixture was stirred at room temperature for 72 h, then filtered and neutralized with solid $NaHCO_3$. After filtration, the solvent was evaporated under vacuum and the residue was chromatographed (dichloromethane/acetone/methyl alcohol: 65/20/15). The first fraction corresponding to the methyl esters was acetylated with an excess of acetic anhydride and pyridine, the mixture was concentrated to a syrup and then chromatographed (petroleum ether, ethyl acetate: 4/1).

From isomaltulose (1.5 g, 4.33 mmol) the following products were successively obtained, **5** (0.2 g, 0.42 mmol, 10%), **4** (0.3 g, 0.59 mmol, 14%), **3** (0.12 g, 0.2 mmol, 5%) and **2** (0.8 g, 0.13 mmol,3%).

Methyl-2,3,4-tri-*O*-acetyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-D-arabinonate (2). $[\alpha]_D^{25}$ +105.3°(*c* 5.4, $CHCl_3$) lit[24] +110.8°(*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 2.02, 2.04, 2.07, 2.09, 2.10, 2.11, 2.17 (7s, 21H, —$OCOCH_3$), 3.75 (1s, 3H, —CO_2CH_3), 3.77 (m, 2H, H-5a, H-5b), 3.98 (ddd, 1H, $J_{4',5'}$ = 10.3Hz, $J_{5',6'a}$ = 2.2Hz, $J_{5'6'b}$ = 4.4Hz, H-5′), 4.08 (dd, 1H, $J_{6'a,6'b}$ = 12.4Hz, H-6′a), 4.25 (dd, 1H, H-6′b), 5.08 (dd, 1H, $J_{3',4'}$ = 9.8Hz, H-4′), 5.10 (d, 1H, H-1′), 5.20 (m, 1H, H-4), 5.30 (d, 1H, $J_{2,3}$ = 2.2Hz, H-2), 5.44 (dd, 1H, H-3′), 5.63 (dd, 1H, $J_{3,4}$ = 8.9Hz, H-3) similar to literature data;[24] ^{13}C NMR (75MHz, $CDCl_3$): δ 20.8, 20.9, 21.0, 21.1 (—$OCOCH_3$), 53.2 (—CO_2CH_3), 62.0 (C-6′), 66.2 (C-5), 68.0 (C-5′), 68.7 (C-4′), 68.8 (C-4), 69.6 (C-3), 70.0 (C-2), 70.2 (C-3′), 71.0 (C-2′), 96.0 (C-1′), 167.9 (—CO_2CH_3), 169.6, 169.7, 170.0, 170.4, 170.7, 171.0 (—$OCOCH_3$).

Methyl-2,3,4-tri-*O*-acetyl-5-*O*-[methyl(2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl)uronate]-D-arabinonate (3). $[\alpha]_D^{25}$ +92.4°(*c* 5.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 2.02, 2.03, 2.04, 2.10, 2.11 (6s, 18H, —$OCOCH_3$), 3.67, 3.68 (2s,6H, —CO_2CH_3), 3.70 (m, 2H, H-5), 4.20 (d, 1H, $J_{4',5'}$ = 10.1Hz, H-5′),

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4.79 (dd, 1H, $J_{2',3'}$ = 10.1Hz, H-2′), 5.07 (dd, 1H, $J_{3',4'}$ = 9.9Hz, H-4′), 5.11 (d, 1H, $J_{1',2'}$ = 3.6Hz, H-1′), 5.15 (m, 1H, H-4), 5.19 (d, 1H, $J_{2,3}$ 1.9Hz, H-2), 5.41 (dd, 1H, H-3′), 5.54 (dd, 1H, $J_{3,4}$ = 8.9Hz, H-3); ^{13}C NMR (75MHz, $CDCl_3$): δ 20.8, 20.9, 21.0, 21.1 (—OCO*C*H_3), 53.2, 53.3 (—CO_2*C*H_3), 66.8 (C-5), 68.8 (C-5′ and C-4), 69.3 (C-3′), 69.5 (C-3), 69.8 (C-4′), 69.9 (C-2), 70.6 (C-2′), 96.4 (C-1′), 167.9, 168.2 (—*C*O_2CH_3), 169.5, 169.7, 169.9, 170.1, 170.4, 170.6 (—O*C*OCH$_3$).

Anal. Calcd for $C_{25}H_{34}O_{18}$ (622.55): C, 48.23; H, 5.50. Found: C, 48.05; H, 5.62.

Methyl-2,3-di-*O*-acetyl-4-*O*-(2, 3, 4, 6-tetra-*O*-acetyl-α-D-glucopyranosyl)-D-threonate (4). $[\alpha]_D^{25}$ +79.3°(*c* 3.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.01, 2.03, 2.08, 2.09, 2.12, 2.19 (6s, 18H, —OCOCH$_3$), 3.64 (dd, 1H, $J_{3,4a}$ = 7.3Hz, $J_{4a,4b}$ = 10.3Hz, H-4a), 3.81 (1s, 3H, —CO_2CH_3), 3.82 (dd, 1H, $J_{3,4b}$ = 5.3Hz, H-4b), 3.99 (ddd, 1H, $J_{4',5'}$ = 9.7Hz, $J_{5',6'a}$ = 2.2Hz, $J_{5',6'b}$ = 4.3Hz, H-5′), 4.11 (dd, 1H, $J_{6'a,6'b}$ = 12.4Hz, H-6′a), 4.25 (dd, 1H, H-6′b), 4.84 (dd, 1H, $J_{1',2'}$ = 3.7Hz, $J_{2',3'}$ =10.3Hz, H-2′), 5.06 (dd, 1H, $J_{3',4'}$ = 9.7Hz, H-4′), 5.10 (d, 1H, H-1′), 5.35 (d, 1H, $J_{2,3}$ = 3.4, H-2), 5.42 (dd, 1H, H-3′), 5.47 (dd, 1H, H-3); ^{13}C NMR (75MHz, $CDCl_3$): δ 20.9, 21.0, 21.1, 21.2 (—OCO*C*H_3), 53.2 (—CO_2*C*H_3), 62.0 (C-6′), 64.9 (C-4), 68.0 (C-5′), 68.7 (C-4′), 70.1 (C-3′), 70.4 (C-3), 70.9 (C-2′ and C-2), 96.3 (C-1′), 167,3 (—*C*O_2CH_3), 169.9, 170.0, 170.3, 170.4, 170.9, 171.0 (—O*C*OCH$_3$).

Anal. Calcd for $C_{26}H_{36}O_{18}$ (564.5): C, 48.94; H, 5.71. Found: C, 48.40; H, 5.71.

Methyl- 2-*O*-acetyl-3-*O*-[methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl) uronate]-D-glycerate (5). $[\alpha]_D^{25}$ +105.6°(*c* 2.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03, 2.10, 2.17 (4s,12H, 4-OCOCH$_3$), 3.75, 3.80 (2s, 6H, 2-CO_2CH_3), 3.94 (dd, 1H, $J_{2,3a}$ 4.7Hz, $J_{3a,3b}$=12.1Hz, H-3a), 4.13 (dd, 1H, $J_{2,3b}$ = 2.7Hz, H-3b), 4.33 (d, 1H, $J_{4',5'}$ = 10.1Hz, H-5′), 4.83 (dd, 1H, $J_{1',2'}$ = 3.7Hz, $J_{2',3'}$ = 10.0Hz, H-2′), 5.14 (dd, 1H, $J_{3',4'}$ = 9.8Hz, H-4′), 5.24 (dd, 1H, H-2), 5.35 (d, 1H, H-1′), 5.5 (dd, 1H, H-3′); ^{13}C NMR (75MHz, $CDCl_3$): δ 20.2, 20.3, 20.4, 20.5 (—OCO*C*H_3), 52.5, 52.7 (—CO_2*C*H_3), 66.6 (C-3), 68.2 (C-5′), 68.6 (C-3′), 69.4 (C-4′), 70.1 (C-2′), 71.5 (C-2), 95.9 (C-1′), 167.3, 167.7 (—*C*O_2CH_3), 169.4, 169.7, 170.1 (—O*C*OCH$_3$).

From methyl isomaltulose (0.55 g, 1.57 mmol).First obtained by chromatography was compound **5** (0.14 g, 0.03 mmol, 2%) and then the mixture of **8** α+ β. With a second chromatography were isolated **8** α(0.98 g, 0.16 mmol, 10%) and **8**β (0.213 g, 0.21 mmol, 13%).

Methyl [methyl-3,4-di-*O*-acetyl-6-*O*-[methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl)uronate]-α-D-fructofuranosid]uronate (8α). $[\alpha]_D^{25}$ +87.7°(*c* 2.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02, 2.03, 2.06, 2.08, 2.13 (5s,15H, —OCOCH$_3$), 3.31 (s, 3H, OCH$_3$), 3.76, 3.78 (2s, 6H, —CO_2CH_3), 3.84 (dd, 1H, $J_{5,6a}$ = 3.6Hz, $J_{6a,6b}$ = 10.9Hz, H-6a), 4.04 (dd, 1H, $J_{5,6b}$ = 5.3Hz, H-6b), 4.19

(ddd, 1H, $J_{4,5}$ = 5.7Hz, H-5), 4.47 (d, 1H, $J_{4',5'}$ = 10.0Hz, H-5′), 4.92 (dd, 1H, $J_{1',2'}$ = 3.7Hz, $J_{2',3'}$ = 10.0Hz, H-2′), 5.04 (dd, 1H, $J_{3,4}$ = 2.3Hz, H-4), 5.17 (dd, 1H, $J_{3',4'}$ = 9.7Hz, H-4′), 5.28 (d, 1H, H-1′), 5.40 (d, 1H, H-3), 5.50 (dd, 1H, H-3′); ^{13}C NMR (75MHz, $CDCl_3$): δ 20.6, 20.7 (—OCO*C*H_3), 51.3 (OCH_3), 52.6, 52.8 (—CO_2*C*H_3), 67.4 (C-6), 68.3 (C-5′), 69.3 (C-3′), 69.6 (C-4′), 70.3 (C-2′), 77.1 (C-4), 80.9 (C-5), 81.4 (C-3), 96.0 (C-1′), 106.7 (C-2).

Methyl [methyl-3,4-di-*O*-acetyl-6-*O*-[methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl)uronate]-β-D-fructofuranosid]uronate (8β). $[\alpha]_D^{25}$ +61.4°(*c* 1.4, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.0–2.1 (5s,15H, —OCOCH_3), 3.8 (s, 3H, OCH_3), 3.5, 3.7 (2s, 6H, —CO_2CH_3), 3.76 (m, 1H, H-6a), 3.89 (dd, 1H, $J_{5,6b}$ = 6Hz, H-6b), 4.29 (ddd, 1H, H-5), 4.46 (d, 1H, $J_{4',5'}$ = 10.1Hz, H-5′), 4.89 (dd, 1H, $J_{1',2'}$ = 3.7Hz, $J_{2',3'}$ = 10.2Hz, H-2′), 5.16 (dd, 1H, $J_{3',4'}$ = 9.6Hz, H-4′), 5.18 (d, 1H, H-1′), 5.48 (m, 2H, H-3, H-4), 5.51 (dd, 1H, H-3′); ^{13}C NMR (75MHz, $CDCl_3$): δ 20.5, 20.6, 20.7 (—OCO*C*H_3), 51.7 (OCH_3), 52.8, 53.0 (—CO_2*C*H_3), 68.5 (C-5′), 69.1 (C-3′), 69.3 (C-6), 69.5 (C-4′), 70.4 (C-2′), 74.7 (C-4), 78.0 (C-5), 78.3 (C-3), 96.1 (C-1′), 101.08 (C-2).

Anal. Calcd for $C_{25}H_{34}O_{18}$ (622.55): C, 48.23; H, 5.50. Found: C, 48.62; H, 5.49.

Crude product from Pt/C/O_2 oxidation. Crude product (2.86 g, 4.69 mmol) from oxidation was purified as before giving a mixture of the esterified compounds (2.18 g) which, after dissolving in methyl alcohol, was chromatographed (dichloromethane/acetone/methyl alcohol: 65/20/15). A portion of the esterified product (96 mg, 0.25 mmol) was acetylated with acetic anhydride and pyridine. After evaporation, the residue was chromatographed giving a part of **11**α pure (15 mg, 0.02 mmol), **11** α+ β (54 mg, 0.08 mmol) and **11**β pure (25 mg, 0.04 mmol).

Methyl-1,3,4-tri-*O*-acetyl-6-*O*-[methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl)uronate]-α-D-fructofuranoside (11α). $[\alpha]_D^{25}$ +75.0°(*c* 0.8, $CHCl_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.5- 20.8 (—OCO*C*H_3), 48.8 (OCH_3), 52.9 (—CO_2*C*H_3), 58.2 (C-1), 68.2 (CH), 68.3 (C-6), 69.3 (CH),69.6 (CH), 70.5 (CH), 76.3 (CH), 78.4 (CH), 79.8 (CH), 95.9 (C-1′), 106.2 (C-2), 168.1 (*C*O_2CH_3), 169.0–170.5 (O*C*OCH_3).

Methyl-1,3,4-tri-*O*-acetyl-6-*O*-[methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl)uronate]-β-D-fructofuranoside (11β). $[\alpha]_D^{25}$ +52.3°(*c* 1.3, $CHCl_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.5–20.8 (—OCO*C*H_3), 49.9 (OCH_3), 52.8 (—CO_2*C*H_3), 62.4 (C-1), 68.4 (CH), 69.1 (C-6), 69.5 (CH), 69.7 (CH), 70.4 (CH), 75.7 (CH), 78.0 (CH), 80.7 (CH), 96.1 (C-1′), 103.0 (C-2), 168.0 (*C*O_2CH_3), 169.0–170.5 (O*C*OCH_3).

Anal. Calcd for $C_{26}H_{34}O_{18}$ (636.55): C, 49.21; H, 5.50. Found: C, 49.30; H, 5.51.

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