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SYNTHESIS OF MELEZITOSE DERIVATIVES

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*The reactivity of melezitose hydroxyls is studied during tritylation in pyridine. Some novel derivatives of melezitose are prepared. An acetyl is transferred from the 4- to the 6-position after detritylation of **3** and **4**. The structures of the products are proved by elemental analysis; ^1H, ^{13}C, and $^1H—^1H$ COSY NMR spectra; IR spectra; and fast-atom bombardment mass spectrometry.*

Key words: melezitose hydroxyls, oligosaccharide, *Alhagi pseudalhagi* Desv.

Melezitose is a natural trisaccharide formed in leaves of the leguminous plant *Alhagi pseudalhagi* Desv. as a white secretion. This oligosaccharide possesses unique physiological activity and is used in Chinese medicine [1]. Our goal was to investigate the reactivity of various melezitose hydroxyls and the ability to protect selectively its primary hydroxyls.

We selected triphenylmethylchloride (TrCl) as the reagent. The resulting products were acetylated by acetic anhydride. Triphenylmethylchloride is known to protect more selectively primary hydroxyls in carbohydrates whereas acetic anhydride is less selective. Melezitose has 11 hydroxyls including 4 primary ones. The main products for a TrCl:melezitose ratio of 2:1 were **2** and **3**. According to elemental analysis, **2** contains two trityl groups whereas **3** has only one trityl substituent. It was previously reported [2-4] that the reactivity of the 1′-OH in the fructose ring is lower than that of the other primary hydroxyls whereas the 6′-OH is more reactive in saccharose and oligosaccharides containing a saccharose, for example, rafinose [5]. We found that the trityl of **3** is located in the 6′-position by comparing these groups with starting melezitose using ^1H and ^{13}C NMR spectra, IR spectra, and mass spectrometry.

Thus, we propose structures for the synthesized melezitose derivatives. Compound **2** is 6,6′-di-O-trityl-2,3,4,1′,4′,2″,3″,4″,6″-nona-O-acetylmelezitose; **3**, 6′-O-trityl-2,3,4,6,1′,4′,2″,3″,4″,6″-deca-O-acetylmelezitose. Increasing the TrCl:melezitose ratio to 4:1 produced **5**: 6,6′,6″-tri-O-trityl-2,3,4,1′,4′,2″,3″,4″-octa-O-acetylmelezitose. This indicates that only three hydroxyls of the four primary ones are tritylated. The sterically more hindered 1′-OH is not alkylated. Furthermore, we observed another product **4** that contains only one trityl. The structure of **4** was proved using fast-atom bombardment mass spectrometry. Compound **4** differs from **3** by the location of the trityl. In **4** it is located in the glucose 6-position whereas in **3** it is in the 6′-position of fructose.

Thus, tritylation of melezitose shows that not all primary hydroxyls have the same reactivity. The most reactive is that in the 6′-position of fructose; the least reactive, in the 1′-position of fructose. This is due to the greater steric hindrance.

It should be noted that 4- and 4′-acetyls migrate to the 6- and 6′-positions after removal of trityl protection from the 6- or 6′-position of acetylated melezitose on heating in acidic solution. Such migration is well known [6]. The mixture was heated in acidic solution until the acetyl had migrated completely from the 4- to the 6-position because of difficulty in separating **8** and **9**.

The ^1H NMR spectra of **2** and **3** exhibit chemical shifts for H-1′ that are shifted to strong field and are located in the same region as other protons of the carbohydrates owing to the effect of the acetyls. The $^1H—^1H$ COSY spectra give $\delta_{H\text{-}1}$ = 5.85 ppm and $J_{1,2}$ = 3.78 Hz (**2**) and $\delta_{H\text{-}1}$ = 5.84 ppm and $J_{1,2}$ = 3.93 Hz (**3**). Protecting groups in glucopyranoses shift the signal for the fructofuranoside C-2′ to weak field in the ^{13}C NMR [7]. We also observed that the OTr group shields the neighboring C more strongly than OAc. Therefore, its signal is shifted to strong field by 2-3 ppm.

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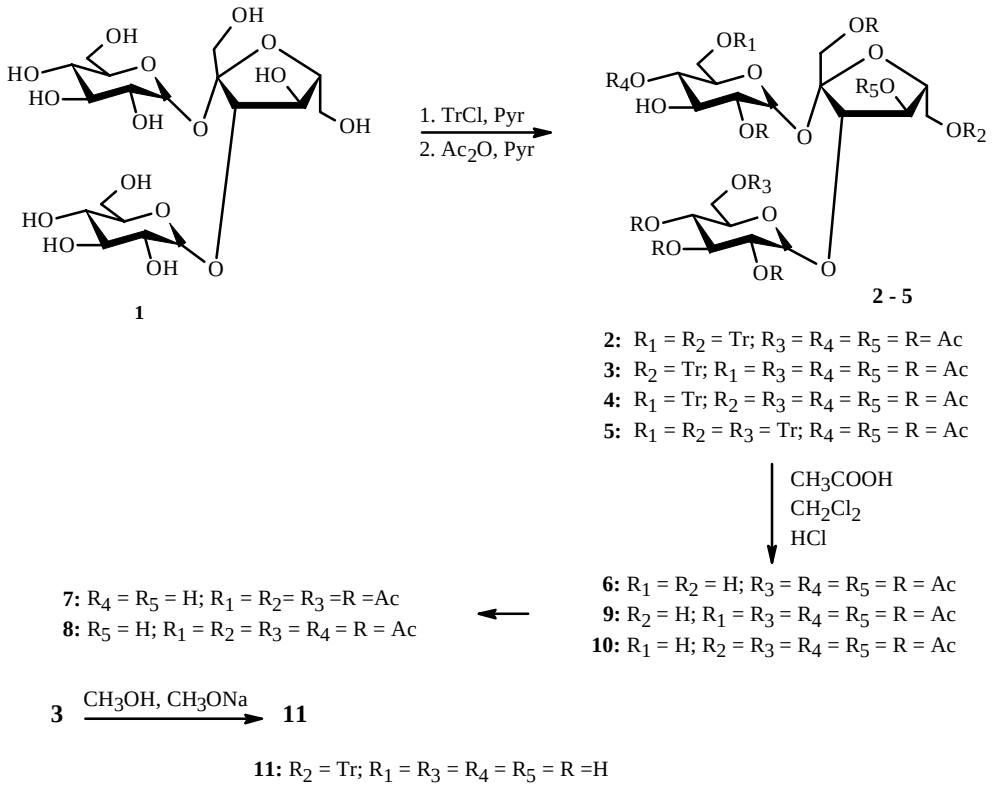

EXPERIMENTAL

The syntheses were carried out in absolute solvents. TLC used GF-254 (China) plates. The solvent systems were: benzene:acetone (7:1, A), diethylether:petroleum ether (6:1, B; 3:1, C), ethylacetate:diethylether (2:3, D), ethylacetate:petroleum ether (2:1, E; 1:1.5, F), and chloroform:methanol (2:1, G). Melting points were measured on a Yanaco MP-S3 (Japan) heating stage. Optical activity was determined on a Perkin—Elmer 241 MC instrument. Elemental analysis was performed using automated MT-3 and Perkin—Elmer 2400 analyzers. IR spectra were recorded on a Perkin—Elmer-325 instrument (KBr); NMR, on Bruker AX 400 (^{1}H, 400 MHz; ^{13}C, 103.6 MHz) and Bruker AC 80 (^{1}H, 80 MHz; ^{13}C, 20.1 MHz) spectrometers using $CDCl_3$ or D_2O solvents and TMS internal standard. Mass spectra were measured in a VG-ZAB-HS instrument at scan limits 2000-200 amu with scan rate 20 s/d and accelerating potential 8 kV. Accelerated Ar ions were used to bombard a $HSCH_2$–CH(OH)–CH_2OH + NaCl + LiCl matrix containing the analyte.

Preparation of Melezitose (1) from a Mixture of Natural *Alhagi pseudalhagi* Desv. A mixture of raw material (200 g) was soaked in hot water (80-90°C) for 30 min and filtered. The filtrate was treated with alcohol until the solution became cloudy and was left for 2-3 h. The gummy substance was removed. Ethanol (95%) was added until a precipitate appeared. The solid was filtered off and recrystallized from H_2O—C_2H_5OH, mp 159-160°C, $[\alpha]_D^{25}$ +86.1° (*c* 1, H_2O).

6,6′-Di-O-triphenylmethyl-2,3,4,1′,4′,2″,3″,4″,6″-nona-O-acetylmelezitose (2) and 6′-O-Triphenylmethyl-2,3,4,1′,4′,2″,3″,4″,6″-deca-O-acetylmelezitose (3). Anhydrous melezitose (5 g, 10 mmole) and TrCl (6 g, 22 mmole) were dissolved in absolute pyridine (125 mL), stirred for 18 h at 65°C, cooled to room temperature, treated with acetic anhydride (100 mL), stirred for 24 h at room temperature (~25°C), treated with icewater containing HCl (1%), and filtered. The solid was dissolved in $CHCl_3$ (150 mL), washed with water, and dried over Na_2SO_4. The solvent was removed in vacuo. The products were separated over a silica-gel column using diethylether:petroleum ether (1:1 and 6:1) to afford a white powder (**2**) and colorless syrup (**3**).

Compound 2. White crystals (from $CHCl_3$—CH_3OH), 1.3 g (9.6%), mp 178-180°C, R_f 0.54 (A), 0.39 (B), 0.25 (C), $[\alpha]_D^{25}$ +118° (*c* 0.1, $CHCl_3$). Found (%): C 64.84, H 5.77. $C_{74}H_{78}O_{25}$. Calc. (%): C 64.98, H 5.75. IR spectrum (KBr,

ν, cm $^{-1}$): 1751 (C=O), 1648, 1490 (Ar).

^{1}H NMR spectrum ($CDCl_3$, δ, ppm, J/Hz): 7.42~7.22 (m, 30H, Ar-H), 5.85 (dd, 1H, $J_{1,2}$ = 3.78, H-1), 5.77 (dd, 1H, $J_{1'',2}$ = 4.09, H-1″), 5.45 (m, 1H, H-3″), 5.39 (m, 1H, H-4′), 5.36 (dd, 1H, $J_{3,4}$ = 9.46, H-3), 5.20 (dd, 1H, $J_{4,5}$ = 8.29, H-4), 4.96 (dd, 1H, $J_{4''-5''}$ = 4.49, H-4″), 4.92 (dd, 1H, $J_{2'',3''}$ = 4.25, H-2″), 4.85 (dd, 1H, $J_{2,3}$ = 7.98, H-2), 4.49 (dd, 1H, $J_{3',4'}$ = 5.91, H-3′), 4.33 (dd, 1H, $J_{5,6a}$ = 2.0, $J_{5,6b}$ = 4.60, H-5), 4.30 (m, 1H, H-6b′), 4.28 (m, 1H, H-5″), 4.16 (dd, 1H, $J_{6a,6b}$ = 8.03, H-6b), 4.02 (m, 1H, H-6a″), 4.00 (m, 1H, H-5′), 3.95 (dd, 1H, $J_{6a,6b}$ = 8.03, H-6a), 3.83 (m, 1H, H-6b′), 3.73 (m, 1H, H-6a′), 3.30 (dd, 1H, $J_{1a',1b'}$ = 8.04, H-1b′), 3.13 (dd, 1H, $J_{1a',1b'}$ = 8.04, H-1a′), 2.15~1.90 (27H, 9CH_3CO).

^{13}C NMR spectrum: 170.9, 170.6, 170.4, 170.3, 170.1, 169.7, 169.5, 169.3, 169.1 (C=O), 143.6, 129.8, 129.1, 128.9, 128.7, 128.2, 127.9, 127.7, 127.5, 127.1 (Ar-C), 101.8 (C-2′), 97.5 (C-1″), 92.8 (C-1), 88.4 (C-3′), 87.4 (C-5′), 76.6 (C-4′), 75.4 (C-2″), 74.1 (C-2), 73.9 (C-3″), 73.5 (C-3), 73.4 (C-4″), 72.6 (C-4), 72.3 (C-5″), 71.8 (C-5), 70.2 (C-6″), 64.1 (C-1′), 63.4 (C-6′), 62.4 (C-6), 20.7 (CH_3CO).

Mass spectrum (FAB), *m/z* (I_{rel}, %): 1366 [M$^+$] (7), 1019 (7), 242 (100).

Compound 3. Colorless syrup, 3.1 g (26.8%), R_f 0.28 (A), 0.17 (B), $[\alpha]_D^{25}$ +22.6° (*c* 1, $CHCl_3$). Found (%): C 58.38, H 5.69. $C_{57}H_{66}O_{26}$. Calc. (%): C 58.64, H 5.70. IR spectrum (KBr, ν, cm^{-1}): 1754 (C=O), 1493 (Ar).

^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 7.43~7.22 (m, 15H, Ar-H), 5.84 (dd, 1H, $J_{1,2}$ = 3.93, H-1), 5.79 (dd, 1H, $J_{1'',2''}$ = 3.76, H-1″), 5.58 (m, 1H, H-4′), 5.38 (m, 1H, H-3), 5.34 (m, 1H, H-3″), 5.19 (m, 1H, H-4″), 5.16 (m, 1H, H-4), 4.96 (t, 1H, $J_{2'',3''}$ = 4.56, H-2″), 4.92 (t, 1H, $J_{2,3}$ = 3.96, H-2), 4.49 (dd, 1H, $J_{3',4'}$ = 6.81, H-3′), 4.37 (m, 2H, H-5, H-5″), 4.29 (m, 2H, H-6b, H-6b″), 4.09 (m, 1H, H-5′), 3.99 (m, 1H, H-6b′), 3.95 (m, 2H, H-6a, H-6a″), 3.75 (m, 1H, H-6a′), 3.55 (dd, 1H, $J_{1a',1b'}$ = 7.72, H-1b′), 3.34 (dd, 1H, $J_{1a',1b'}$ = 7.72, H-1a′), 2.13~1.92 (30H, 10CH_3CO).

^{13}C NMR: 170.7, 170.5, 170.3, 169.9, 169.6, 169.4, 169.2 (C=O), 143.8, 129.9, 129.3, 128.9, 128.6, 128.4, 127.9, 127.7, 127.6, 127.3 (Ar-C), 101.7 (C-2′), 97.6 (C-1″), 92.9 (C-1), 88.4 (C-3′), 87.5 (C-5′), 76.7 (C-4′), 75.6 (C-2″), 74.2 (C-2), 73.9 (C-3″), 73.7 (C-3), 73.5 (C-4″), 72.8 (C-4), 72.6 (C-5″), 71.9 (C-5), 70.1 (C-6″), 64.1 (C-1′), 62.9 (C-6′), 61.3 (C-6), 20.6 (CH_3CO). Mass spectrum (FAB), *m/z* (I_{rel}, %): 1166 [M$^+$] (9), 1090 [M - C_6H_5] (35), 819 (7), 471 (7), 331 (100).

6-O-Triphenylmethyl-2,3,4,1′,4′,6′,2″,3″,4″,6″-deca-O-acetylmelezitose (4) and 6,6′,6″-Tri-O-triphenylmethyl-2,3,4,1′,4′,2″,3″,4″-octa-O-acetylmelezitose (5). Compounds **2**, **3**, **4** and **5** were prepared analogously from anhydrous melezitose (5 g, 10 mmole) and TrCl (13 g, 44 mmole).

Compound 4. Colorless syrup, 1.9 g (16.4%), R_f 0.27 (A), 0.16 (B). Found (%): C 58.47, H 5.57. $C_{57}H_{66}O_{26}$. Calc. (%): C 58.64, H 5.70. IR spectrum (KBr, ν, cm^{-1}): 1753 (C=O), 1498 (Ar).

^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 7.40-7.25 (m, 15H, Ar-H), 5.80 (dd, 1H, $J_{1,2}$ = 3.89, H-1), 5.78 (dd, 1H, $J_{1'',2''}$ = 3.76, H-1″), 5.56 (dd, 1H, $J_{4',5'}$ = 7.21, H-4′), 5.35 (dd, 1H, $J_{3,4}$ = 9.18, H-3), 5.31 (m, 1H, H-3″), 5.15 (dd, 1H, $J_{3'',4''}$ = 3.57, H-4″), 5.12 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.18, H-4), 4.95 (dd, 1H, $J_{2'',3''}$ = 3.24, H-2″), 4.91 (dd, 1H, $J_{2,3}$ = 3.78, H-2), 4.49 (dd, 1H, $J_{3',4'}$ = 6.78, H-3′), 4.38 (m, 1H, H-5″), 4.29 (m, 1H, H-5′), 4.27 (m, 1H, H-6b″), 4.24 (m, 1H, H-5), 4.17 (m, 1H, H-6b′), 4.00 (m, 1H, H-6a″), 3.97 (m, 1H, H-6a′), 3.77 (m, 1H, H-6b), 3.65 (m, 1H, H-6a), 3.57 (dd, 1H, $J_{1a',1b'}$ = 8.04, H-1b′), 3.33 (dd, 1H, $J_{1a'-1b'}$ = 8.04, H-1a′), 2.15-1.97 (30H, 10CH_3CO).

^{13}C NMR: 170.6, 170.4, 170.2, 169.8, 169.6, 169.3, 169.1 (C=O), 143.8, 129.9, 129.3, 128.9, 128.7, 128.5, 127.9, 127.8, 127.5, 127.2 (Ar-C), 102.3 (C-2′), 98.1 (C-1″), 92.9 (C-1), 88.1 (C-3′), 87.3 (C-5′), 76.6 (C-4′), 75.4 (C-2″), 74.1 (C-2), 73.8 (C-3″), 73.6 (C-3), 73.3 (C-4″), 72.6 (C-4), 72.4 (C-5″), 71.8 (C-5), 70.1 (C-6″), 64.3 (C-1′), 62.8 (C-6′), 62.5 (C-6), 20.8 (CH_3CO).

Mass spectrum (FAB), *m/z* (I_{rel}, %): 1166 [M]$^+$ (10), 1090 [M - C_6H_5]$^+$ (30), 531 (16), 331 (100).

Compound 5. Colorless syrup, 5.3 g (34.2%), R_f 0.65 (A), $[\alpha]_D^{25}$ +91.3° (*c* 0.1, $CHCl_3$). Found (%): C 70.50, H 6.02. $C_{91}H_{90}O_{24}$. Calc. (%): C 69.72, H 5.79. IR spectrum (KBr, ν, cm^{-1}): 1745 (C=O), 1600, 1490 (Ar).

^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 7.43~7.20 (m, 45H, Ar-H), 5.66 (dd, 1H, $J_{1,2}$ = 3.67, H-1), 5.65 (dd, 1H, $J_{1'',2''}$ = 3.62, H-1″), 5.41 (dd, 1H, $J_{3',4'}$ = 5.94, H-3′), 5.38 (m, 2H, H-3, H-3″), 4.99 (m, 2H, H-4, H-4″), 4.86 (m, 2H, H-2, H-2″), 4.51 (dd, 1H, $J_{4',5'}$ = 6.34, H-4′), 4.29 (m, 2H, H-5, H-5″), 4.01 (m, 1H, H-6b′), 3.86 (m, 4H, H-6, H-6″), 3.82 (m, 1H, H-5′), 3.74 (m, 1H, H-6a′), 3.32 (dd, 1H, $J_{1a',1b'}$ = 8.04, H-1b′), 3.15 (dd, 1H, $J_{1a',1b'}$ = 8.04, H-1a′), 2.15~1.90 (24H, 8CH_3CO).

^{13}C NMR: 171.1, 170.9, 170.6, 170.3, 170.2, 169.8, 169.6, 169.2, 168.9 (C=O), 143.7, 129.9, 129.2, 128.9, 128.8, 128.3, 127.9, 127.7, 127.3, 126.7 (Ar-C), 101.9 (C-2′), 95.6 (C-1″), 92.8 (C-1), 89.0 (C-3′), 87.1 (C-5′), 76.4 (C-4′), 75.3 (C-2″), 74.1 (C-2), 73.8 (C-3″), 73.5 (C-3), 73.3 (C-4″), 72.4 (C-4), 72.1 (C-5″), 71.5 (C-5), 70.1 (C-1′), 63.4 (C-6″), 63.0 (C-6′), 62.2 (C-6), 20.7 (CH_3CO).

2,3,4,1′,4′,2″,3″,4″,6″-Nona-O-acetylmelezitose (6). Compound **2** (4.5 g, 3.3 mmole) was dissolved in CH_2Cl_2

(40 mL), treated with glacial acetic acid (40 mL) and conc. HCl (0.8 mL), and stirred for 1.5 h on an icewater bath. The course of the reaction was monitored using TLC and system E. The mixture was neutralized with saturated $NaHCO_3$ solution, washed with water, dried over Na_2SO_4, evaporated in vacuo, and separated on a silica-gel column by elution with ethylacetate:petroleum ether (1:1 and 2:1) to afford **6** as a syrup.

Compound 6. Colorless syrup, 1.9 g (73%), R_f 0.29 (D), 0.11 (E), $[\alpha]_D^{25}$ +101° (*c* 0.1, $CHCl_3$). Found (%): C 49.46, H 5.70. $C_{36}H_{50}O_{25}$. Calc. (%): C 48.96, H 5.71. IR spectrum (KBr, ν, cm^{-1}): 3524 (6,6′-OH), 1743 (C=O).

^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 5.76 (dd, 1H, $J_{1,2}$ = 5.68, H-1), 5.67 (dd, 1H, $J_{1'',2''}$ = 3.34, H-1″), 5.57 (dd, 1H, $J_{3'',4''}$ = 12.7, H-3″), 5.39 (dd, 1H, $J_{4',5'}$ = 10.35, H-4′), 5.37 (m, 1H, H-3), 5.29 (dd, 1H, $J_{4,5}$ = 8.36, H-4), 4.98 (dd, 1H, $J_{4'',5''}$ = 5.34, H-4″), 4.75 (dd, 1H, $J_{2'',3''}$ = 5.68, H-2″), 4.45 (dd, 1H, $J_{2,3}$ = 4.10, H-2), 4.49 (dd, 1H, $J_{3',4'}$ = 8.21, H-3′), 4.34 (m, 1H, H-5), 4.31 (m, 1H, H-6b″), 4.29 (m, 1H, H-5″), 4.09 (m, 1H, H-6a″), 4.06 (dd, 1H, $J_{6a,6b}$ = 10.0, H-6b), 3.91 (m, 1H, H-5′), 3.82 (m, 1H, H-6b′), 3.78 (dd, 1H, $J_{6a,6b}$ = 10.0, H-6a), 3.71 (m, 1H, H-6a′), 3.65 (dd, 1H, $J_{1a',1b'}$ = 6.01, H-1b′), 3.61 (dd, 1H, $J_{1a',1b'}$ = 6.01, H-1a′), 2.15~1.90 (27H, 9CH_3CO).

Mass spectrum (FAB), *m/z* (I_{rel}, %): 905 $[M + Na]^+$ (100), 889 $[M + Li]^+$ (100), 863 $[M + Na - CH_2CO]^+$ (25), 847 [M + Li - CH_2CO] (28).

2,3,6,1′,6′,2″,3″,4″,6″-Nona-O-acetylmelezitose (7). Compound **6** (0.5 g, 0.6 mmole) was dissolved in benzene (10 mL), treated with glacial acetic acid (3 mL), heated on an oil bath until boiling, and stirred for 16 h. The course of the reaction was monitored using TLC (system D). The solution was evaporated in vacuo. The product was separated by chromatography on silica-gel plates (system D) to afford **7** as a colorless syrup.

Compound 7. Colorless syrup, 0.38 g (76%), R_f 0.41 (D), 0.19 (E), $[\alpha]_D^{25}$ +71° (*c* 0.1, $CHCl_3$). Found (%): C 49.80, H 5.70. $C_{36}H_{50}O_{25}$. Calc. (%): C 48.96, H 5.71. IR spectrum (KBr, ν, cm^{-1}): 3422 (4,4′-OH), 1750.6 (C=O).

^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 5.74 (dd, 1H, $J_{1,2}$ = 4.58, H-1), 5.61 (dd, 1H, $J_{1'',2''}$ = 3.32, H-1″), 5.47 (m, 1H, H-3″), 5.36 (m, 1H, H-3), 4.96 (dd, 1H, $J_{4'',5''}$ = 4.49, H-4″), 4.92 (dd, 1H, $J_{2'',3''}$ = 5.25, H-2″), 4.85 (dd, 1H, $J_{2,3}$ = 3.78, H-2), 4.52 (dd, 1H, $J_{3',4'}$ = 5.91, H-3′), 4.40 (m, 1H, H-4′), 4.32 (m, 1H, H-5), 4.30 (m, 1H, H-6b″), 4.28 (m, 1H, H-5″), 4.21 (m, 1H, H-6b), 4.05 (m, 1H, H-6b′), 4.02 (m, 1H, H-6a″), 4.00 (m, 1H, H-6a), 3.96 (m, 1H, H-6a′), 3.83 (m, 1H, H-5′), 3.58 (m, 1H, H-4), 3.33 (dd, 1H, $J_{1a',1b'}$ = 6.50, H-1b′), 3.18 (dd, 1H, $J_{1a',1b'}$ = 6.50, H-1a′), 2.32~2.02 (27H, 9CH_3CO).

^{13}C NMR: 170.9, 170.6, 170.4, 170.2, 170.1, 169.6, 169.3, 169.1, 168.9 (C=O), 102.3 (C-2′), 97.3 (C-1″), 92.8 (C-1), 89.9 (C-3′), 82.3 (C-5′), 76.2 (C-4′), 75.3 (C-2″), 74.1 (C-2), 73.6 (C-3″), 73.4 (C-3), 73.2 (C-4″), 72.4 (C-4), 72.2 (C-5″), 71.7 (C-5), 70.0 (C-6″), 63.9 (C-1′), 62.3 (C-6′), 61.2 (C-6), 20.6 (CH_3CO).

Mass spectrum (FAB), *m/z* (I_{rel}, %): 905 $[M + Na]^+$ (100), 889 $[M + Li]^+$ (91), 863 $[M + Na - CH_2CO]^+$ (23), 847 [M + Li - CH_2CO] (30), 289 (6), 228 (12).

2,3,4,6,1′,6′,2″,3″,4″,6″-Deca-O-acetylmelezitose (8). A mixture of **8** and **9** [for **9**, R_f = 0.49 (D) and 0.17 (F)] was prepared analogously from **3** (5 g, 4.3 mmole). The mixture (0.5 g) was dissolved in benzene (10 mL), treated with glacial acetic acid (3 mL), heated on a bath until boiling, and stirred for 36 h. The course of the reaction was monitored using TLC. The solution was evaporated in vacuo. The solid was separated by chromatography on silica-gel plates (system D) to afford **8** as a colorless syrup.

Compound 8. Colorless syrup, 0.34 g (68%), R_f 0.57 (D), 0.25 (F), $[\alpha]_D^{25}$ +106° (*c* 0.1, $CHCl_3$). Found (%): C 49.13, H 5.62. $C_{38}H_{52}O_{26}$. Calc. (%): C 49.34, H 5.67. IR spectrum (KBr, ν, cm^{-1}): 3528 (4′-OH), 1751 (C=O).

^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 5.71 (dd, 1H, $J_{1,2}$ = 3.55, H-1), 5.63 (dd, 1H, $J_{1'',2''}$ = 3.80, H-1″), 5.57 (m, 1H, H-3″), 5.39 (dd, 1H, $J_{3,4}$ = 7.48, H-3), 5.28 (m, 1H, H-4), 5.26 (m, 1H, H-4″), 4.98 (m, 1H, H-2″), 4.94 (m, 1H, H-2), 4.74 (dd, 1H, $J_{3',4'}$ = 3.87, H-3′), 4.43 (m, 1H, H-5), 4.41 (m, 1H, H-6b″), 4.40 (m, 1H, H-4′), 4.37 (m, 1H, H-5"), 4.34 (m, 1H, H-6a″), 4.28 (m, 1H, H-6b), 4.05 (m, 1H, H-5′), 4.11 (dd, 1H, $J_{6a',6b'}$ = 11.87, H-6b′), 4.04 (m, 1H, H-6a), 3.92 (dd, 1H, $J_{6a',6b'}$ = 11.87, H-6a′), 3.57 (m, 1H, H-1b′), 3.43 (m, 1H, H-1a′), 2.13~1.92 (30H, 10CH_3CO).

^{13}C NMR: 171.9, 171.5, 170.7, 170.2, 170.1, 169.9, 169.7 (C=O), 102.4 (C-2′), 97.8 (C-1″), 93.0 (C-1), 88.5 (C-3′), 87.7 (C-5′), 75.7 (C-2″), 74.6 (C-2), 74.3 (C-4′), 73.9 (C-3″), 73.7 (C-3), 73.5 (C-4″), 72.8 (C-4), 72.6 (C-5″), 71.9 (C-5), 70.5 (C-6″), 64.2 (C-1′), 63.0 (C-6′), 61.5 (C-6), 20.6 (CH_3CO).

Mass spectrum (FAB), *m/z* (I_{rel}, %): 947 $[M + Na]^+$ (5), 931 $[M + Li]^+$ (21), 331 (7), 289 (9), 229 (18), 169 (60).

2,3,4,1′,4′,6′,2″,3″,4″,6″-Deca-O-acetylmelezitose (10) was prepared analogously from **4**.

Compound 10. Colorless syrup, 1.8 g (69%), R_f 0.41 (D), $[\alpha]_D^{25}$ +134 (*c* 0.1, $CHCl_3$). Found (%): C 49.55, H 5.65. $C_{38}H_{52}O_{26}$. Calc. (%): C 49.34, H 5.67. IR spectrum (KBr, ν, cm^{-1}): 3450 (6-OH), 1735 (C=O).

^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 5.81 (dd, 1H, $J_{1,2}$ = 3.89, H-1), 5.79 (dd, 1H, $J_{1'',2''}$ = 3.78, H-1″), 5.56 (dd, 1H,

$J_{4',5'}$ = 7.71, H-4′), 5.33 (m, 1H, H-3), 5.30 (m, 1H, H-3″), 5.16 (dd, 1H, $J_{4'',5''}$ = 3.57, H-4″), 5.11 (dd, 1H, $J_{4,5}$ = 9.18, H-4), 4.94 (dd, 1H, $J_{2'',3''}$ = 3.24, H-2″), 4.90 (dd, 1H, $J_{2,3}$ = 3.78, H-2), 4.49 (dd, 1H, $J_{3',4'}$ = 6.12, H-3′), 4.39 (m, 1H, H-5″), 4.28 (m, 1H, H-5′), 4.26 (m, 1H, H-6b″), 4.24 (m, 1H, H-5), 4.18 (m, 1H, H-6b′), 4.08 (m, 1H, H-6b), 3.99 (m, 1H, H-6a″), 3.97 (m, 1H, H-6a′), 3.76 (m, 1H, H-6a), 3.60 (dd, 1H, $J_{1a',1b'}$ = 9.82, H-1b′), 3.36 (dd, 1H, $J_{1a',1b'}$ = 9.82, H-1a′), 2.13~2.04 (30H, 10CH_3CO).

^{13}C NMR: 171.8, 171.5, 170.6, 170.2, 170.1, 169.8, 169.4 (C=O), 101.1 (C-2′), 97.4 (C-1″), 92.6 (C-1), 88.1 (C-3′), 87.4 (C-5'), 75.4 (C-2″), 74.4 (C-2), 74.2 (C-4′), 73.7 (C-3″), 73.5 (C-3), 73.3 (C-4″), 72.6 (C-4), 72.3 (C-5″), 71.5 (C-5), 70.2 (C-6″), 64.0 (C-1′), 63.1 (C-6′), 61.0 (C-6), 20.7 (CH_3CO).

Mass spectrum (FAB), *m/z* (I_{rel}, %): 931 $[M + Li]^+$ (100), 625 [619 + Li - H] (7.67).

6′-O-Triphenylmethylmelezitose (11). Sodium (small amount) was added to absolute methanol (15 mL) until the pH was 9. Compound **3** (0.5 g) was added at room temperature. The mixture was stirred for 2 h, neutralized with glacial acetic acid, evaporated in vacuo, and separated on a silica-gel column with elution by $CHCl_3$:CH_3OH (4:1) to afford **11** as a colorless syrup.

Compound 11. Colorless syrup, 0.26 g (82%), R_f 0.25 (G), 0.36 (H), $[\alpha]_D^{25}$ +65° (*c* 0.1, H_2O). Found (%): C 59.48, H 6.22. $C_{37}H_{46}O_{16}$. Calc. (%): C 59.51, H 6.21. IR spectrum (KBr, ν, cm^{-1}): 3425 (-OH), 1633, 1491 (Ar).

^{1}H NMR (D_2O, δ): 5.45 (dd, 1H, $J_{1,2}$ = 3.80, H-1), 5.18 (dd, 1H, $J_{1'',2''}$ = 3.78, H-1″), 4.32 (dd, 1H, $J_{3',4'}$ = 7.60, H-3′), 4.30 (dd, 1H, $J_{3',4'}$ = 7.60, $J_{4',5'}$ = 8.0, H-4′), 3.94 (dd, 1H, $J_{5,6a}$ = 2.20, $J_{5,6b}$ = 4.80, H-5), 3.93 (dd, 1H, $J_{5'',6a''}$ = 2.20, $J_{5'',6b''}$ = 4.80, H-5″), 3.91 (dd, 1H, $J_{4',5'}$ = 8.0, H-5′), 3.90 (dd, 1H, $J_{5,6b}$ = 4.80, H-6b), 3.86 (dd, 1H, $J_{5',6b'}$ = 4.80, H-6b″), 3.81 (dd, 1H, $J_{1a',1b'}$ = 12.0, H-1b′), 3.79 (dd, 1H, $J_{6a'',6b''}$ = 12.2, H-6a″), 3.78 (dd, 1H, $J_{6a,6b}$ = 12.2, H-6a), 3.75 (dd, 1H, $J_{2'',3''}$ = 10.0, $J_{3'',4''}$ = 9.0, H-3″), 3.67 (dd, 1H, $J_{2,3}$ = 10.0, $J_{3,4}$ = 8.80, H-3), 3.65 (dd, 1H, $J_{1a',1b'}$ = 12.0, H-1a′), 3.58 (dd, 1H, $J_{1'',2''}$ = 3.80, $J_{2'',3''}$ = 10.0, H-2″), 3.56 (dd, 1H, $J_{1,2}$ = 3.80, $J_{2,3}$ = 10.0, H-2), 3.53 (m, 2H, H-6a′, H-6b′), 3.45 (dd, 1H, $J_{3'',4''}$ = 9.0, $J_{4'',5''}$ = 10.2, H-4″), 3.44 (dd, 1H, $J_{3,4}$ = 8.80, $J_{4,5}$ = 10.2, H-4).

^{13}C NMR: 104.8 (C-2′), 101.0 (C-1″), 92.7 (C-1), 84.3 (C-3′), 78.4 (C-5′), 74.6 (C-4′), 74.1 (C-2″), 73.8 (C-2), 73.2 (C-3″), 72.5 (C-3), 71.9 (C-4″), 70.6 (C-4), 70.3 (C-5″), 70.0 (C-5), 63.2 (C-6″), 62.4 (C-1′), 61.4 (C-6), 60.4 (C-6′).

Mass spectrum (FAB), *m/z* (I_{rel}, %): 769 $[M + Na]^+$ (10), 753 $[M + Li]^+$ (9), 243 $[Tr]^+$ (100), 77 $[C_6H_6]^+$ (20).

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