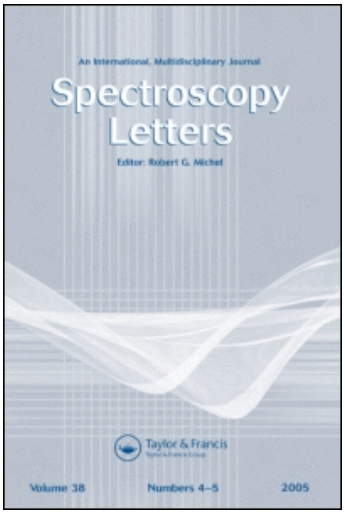

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SYNTHESIS AND SPECTROSCOPIC ELUCIDATION OF SOME SELECTIVELY PROTECTED TREHALOSE TYPE DISACCHARIDE BY 2D-NMR SPECTRA

Key words: Galacto-galacto trehalose analogues, selective de-*O*-acetylation and benzoylation.

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ABSTRACT

The selectively acylated trehalose type disaccharide **2** was prepared from the corresponding ditriflate derivative **1** *via* the inversion of configuration at C-4,4' positions. Cleavage of the transient protecting group (*O*-acetyl) from **2** furnished partially blocked disaccharides (**3** and **4**) capable of chain extension at position 4 or positions 4 and 4', respectively. Acetal and ketal formation of the synthetic galacto-galacto trehalose (**5**) yielded compounds **6** and **7**, respectively. The regioselective benzoylation of **7** gave **8** which has a free hydroxyl groups at positions 2 and 2'.

A detailed NMR analyses [^{1}H,^{13}C,^{13}C-^{1}H correlation, and 2D ^{1}H-^{1}H correlation experiments (COSY)] were used and discussed for the structural elucidation of the trehalose analogues **2, 3, 6** and **8.**

INTRODUCTION

Derivatives of the trehalose type disaccharides suitable for use as "standard building blocks" in chemical oligosaccharide synthesis are of continuing interest in this laboratory[1-3]. Previously, we have described the preparation of α-**D**-glucopyranosyl α-**D**-galactopyranoside[1], α-**D**-galacto-pyranosyl α-**D**-galactopyranoside[2], and their corresponding partially protected trehalose analogues[3]. Wessel and co-workers[4-7] synthesized 2,3,6-tri-*O*-benzyl-α-**D**-glucopyranosyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-**D**-glucopyranoside, which was used as trehalose glycosyl acceptor in multistep reactions.

In the present paper we describe the synthesis and spectroscopic structural elucidation of some partially acylated galacto-galacto trehalose analogues to serve as precursors for chain extension at different positions.

RESULTS AND DISCUSSION

In continuation of a program directed toward the synthesis of partially protected trehalose type disaccharide, the key intermediate 2,3,6-tri-*O*-benzoyl-4-*O*-trifluoromethylsulfonyl-α-**D**-glucopyranosyl 2,3,6-tri-*O*-benzoyl-4-*O*-trifluoromethylsulfonyl-α-**D**-glucopyranoside (**1**)[2] was used for the synthesis of galacto-galacto trehalose derivatives (**2-8**).

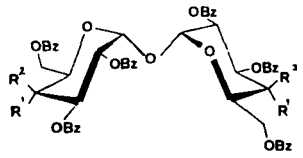
Inversion of configuration at C-4 in 4-sulfonates of α-**D**-gluco-pyranosides presumably through an S_N2 displacement-reaction, was found largely dependent on the nature of the leaving group and on the solvent used[8-13]. However, 4-methanesulfonate[8-11], 4-(*p*-toluenesulfonate[12]) and 4-

(*p*-bromobenzenesulfonate[13]) were examiaed in different solvents as potential leaving-groups, but the desired product was not always obtained in satisfactory yield. Recently, Bundle and co-workers reported[14] the displacement of the methanesulfonate group by acetate in the presence of crown ether in *N,N*-dimethylformamide at high temperature. Accordingly, in the present work, treatment of **1** with anhydrous potassium acetate in the presence of dicyclohexano-18-crown-6 in *N,N*-dimethylformamide at ambient temperature afforded 4-*O*-acetyl-2,3,6-tri-*O*-benzoyl-α-**D**-galactopyranosyl 4-*O*-acetyl-2,3,6-tri-*O*-benzoyl-α-**D**-galactopyranoside (**2**) in 80% yield (scheme I).

The structure of the symmetrical galacto-galacto trehalose derivative **2** was proved through a study of the ^{1}H NMR, decoupling experiments, 2D ^{1}H-^{1}H correlation experiment (COSY), attached proton test (APT), and ^{13}C-^{1}H correlation experiment. The ability of high resolution NMR spectroscopy to provide information about the structural details is firmly established.

The ^{1}H NMR spectrum shown in Figure 1 is characterized by a multiplet at δ 8.05-7.10 corresponding to 30 aromatic protons, two doublet of doublets appeared at δ 6.03 and 5.83 with four protons intensity, and two doublets centered at δ 5.77 and 5.74 correspond to four protons. A broad triplet at δ 4.44, which is attributed to the H-5,5', a doublet of quartets at δ 3.95 with four protons intensity due to the two methylene groups and a singlet at δ 2.10 due to the two acetyl methyl groups.

Since this spectrum is rather complex, it necessitated decoupling experiments for associating signals with their respective protons, especially those of H-2,2' and H-3,3' (Figure 1). On irradiation at δ 6.03, the pattern of the doublet of doublets at δ 5.83 changed to a doublet with a small splitting (H-2,2'), and collapsed the doublet at δ 5.74 into a singlet (H-



1 R^1 = OTf , R^2 = R^3 = H

2 R^1 = H , R^2 = R^3 = OAc

3 R^1 = H , R^2 = OH , R^3 = OAc

4 R^1 = H , R^2 = R^3 = OH

SCHEME I

4,4'), this indicated that the resonance at δ 6.03 is H-3,3'. Irradiation of the H-5,5' signal at δ 4.44 simplified the doublet of quartets at δ 3.95 into a clean quartet (H-$6_{a,b}$,$6'_{a,b}$). Finally on irradiation at H-$6_{a,b}$,$6'_{a,b}$ pattern, the broad triplet at δ 4.44 changed to a singlet (H-5,5').

A further elucidation of the structure of compound **2** was accomplished by the use of a COSY experiment (Figure 2). Commencing from the resonance for H-4,4', the chemical shifts of the other ^{1}H resonances were established by tracing of connectivities *via* the cross-peaks on the COSY contour map. The results were in agreement with the interpretation concluded from the decoupling experiments.

An additional manifestation of the structure of compound **2** was its ^{13}C NMR spectrum, which revealed a signal at δ 170.10 due to the carbonyl carbon of the acetate groups, a multiplet at δ 166.05-165.95 correspond to the carbonyl carbon of the benzoate groups, and an aromatic multiplet appeared at δ 134.50-128.00. The signal at δ 93.32 is attributed to the anomeric carbons (C-1,1') having an α-configuration, while the rest of the sugar ring carbons appeared at δ 68.63-61.78, and

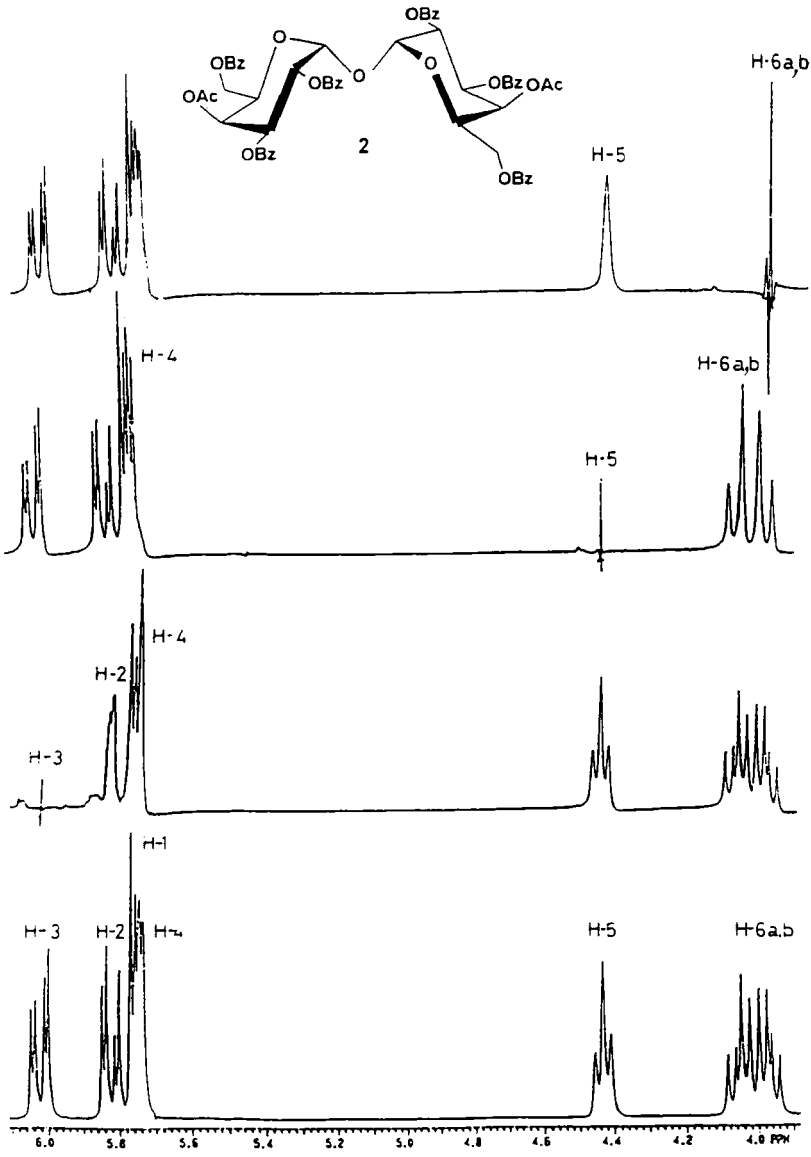
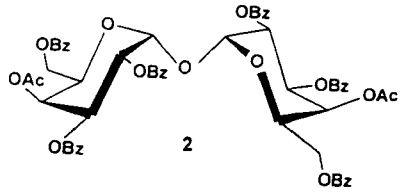


FIG. 1 : ^{1}H NMR spectrum and decoupling experiments on compound 2 .



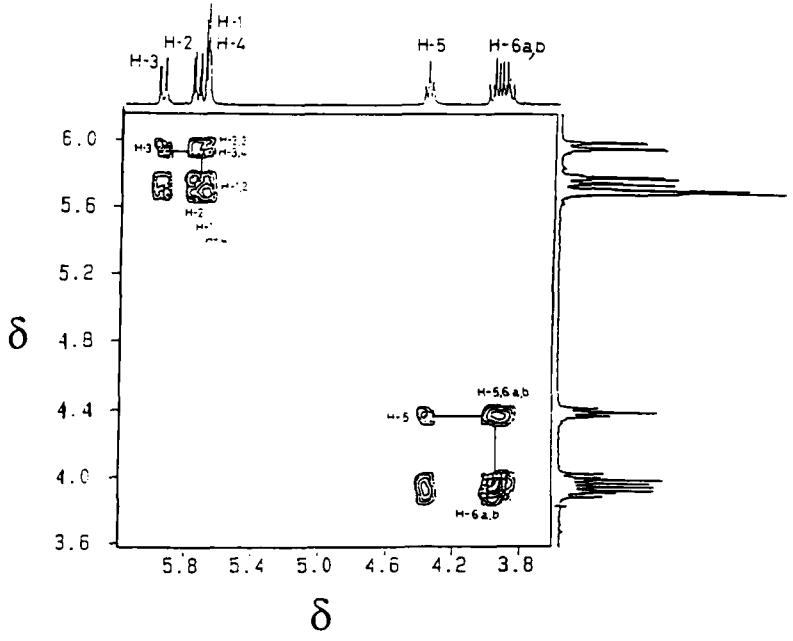


FIG. 2 : COSY contour plot of the region 6.0 - 3.6 ppm for compound 2.

that at δ 20.71 corresponds to the two methyl groups. The APT chart revealed inverted peak at δ 61.78 due to C-6,6'.

Uncertainty in several assignments was resolved by application of ^{13}C-^{1}H shift-correlated spectroscopy (Figure 3). The ^{1}H resonances assigned for compound **2** were then compared with the ^{13}C-^{1}H correlation

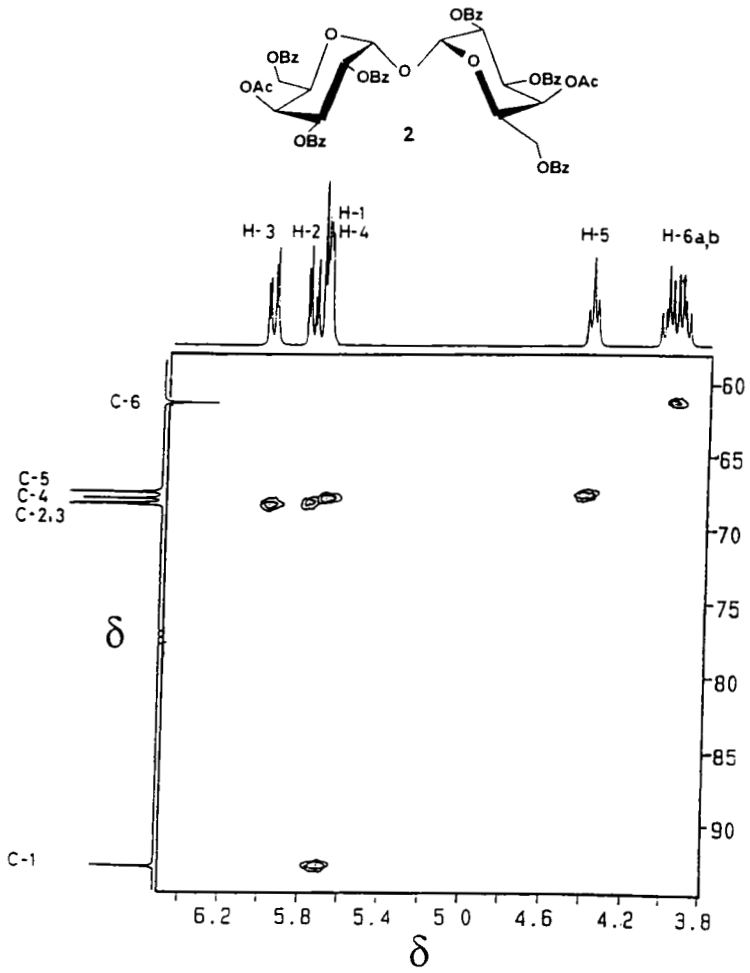


FIG. 3 : ^{1}H - ^{13}C shift correlation map of the spectral region F_1 (6.4 - 3.8 ppm) and F_2 (90 - 60 ppm) for compound 2.

data which revealed that C-3,3' centered at δ 68.63, C-2,2' at δ 68.56, while C-4,4' and C-5,5' appeared at δ 68.26 and 67.83, respectively.

The selective de-*O*-acetylation of the diacetate derivative **2** using methanolic hydrogen chloride in chloroform[15] furnished a $\sim$ 6 : 1 mixture of the 4-*O*-acetyl-2,3,6-tri-*O*-benzoyl-α-**D**-galactopyranosyl 2,3,6-tri-*O*-benzoyl-α-**D**-galactopyranoside (**3**) having free hydroxyl group at position 4 only, and the diol derivative **4** (Scheme I). Separation by column chromatography on silica gel (see experimental) gave the two products in 80% and 12% yield, respectively.

The ^{1}H NMR spectra (Figures 4,5) of the non-symmetrical trehalose type disaccharide **3** resemble the features of both diacetate derivative **2** and the diol **4**. A remarkable feature of the ^{1}H NMR spectrum (Figure 4, 500 MHz) of **3** is similar to that of **2** with an additional signals: A doublet of doublets with small and large splitting at δ 5.91 correspond to H-2^{II}, a doublet of doublets at δ 5.84 due to H-3^{II}, and a doublet at δ 5.69 (J 3.5 Hz) which is attributed to the anomeric proton (H-1)^{II}. A broad doublet centered at δ 4.30 with small spacing correspond to H-4^{II}. The high field shift of the H-4^{II} signal, indicating that the galactose moiety^{II} has a free hydroxyl group at position 4. Also the ^{1}H NMR spectrum (Figure 5, 600 MHz) showed a broad triplet at δ 4.27 with one proton intensity due to H-5^{II}, and a multiplet at δ 4.26-4.06 corrspond to H-6$_{a,b}^{II}$. A broad singlet at δ 2.51, undergoes deuterium exchange, is ascribed to a hydroxyl group at position 4.

An additional support for the proposed structure **3** was achieved through a study of ^{13}C-^{1}H shift-correlated spectrum (Figure 6). The ^{1}H resonances assigned for **3** were compared with the ^{13}C-^{1}H correlation data, which revealed that the C-1^{II} and C-1^{I} appeared at δ 94.40 and 94.00, respectively, and the methylene carbons centered at δ 64.60 and 63.50.

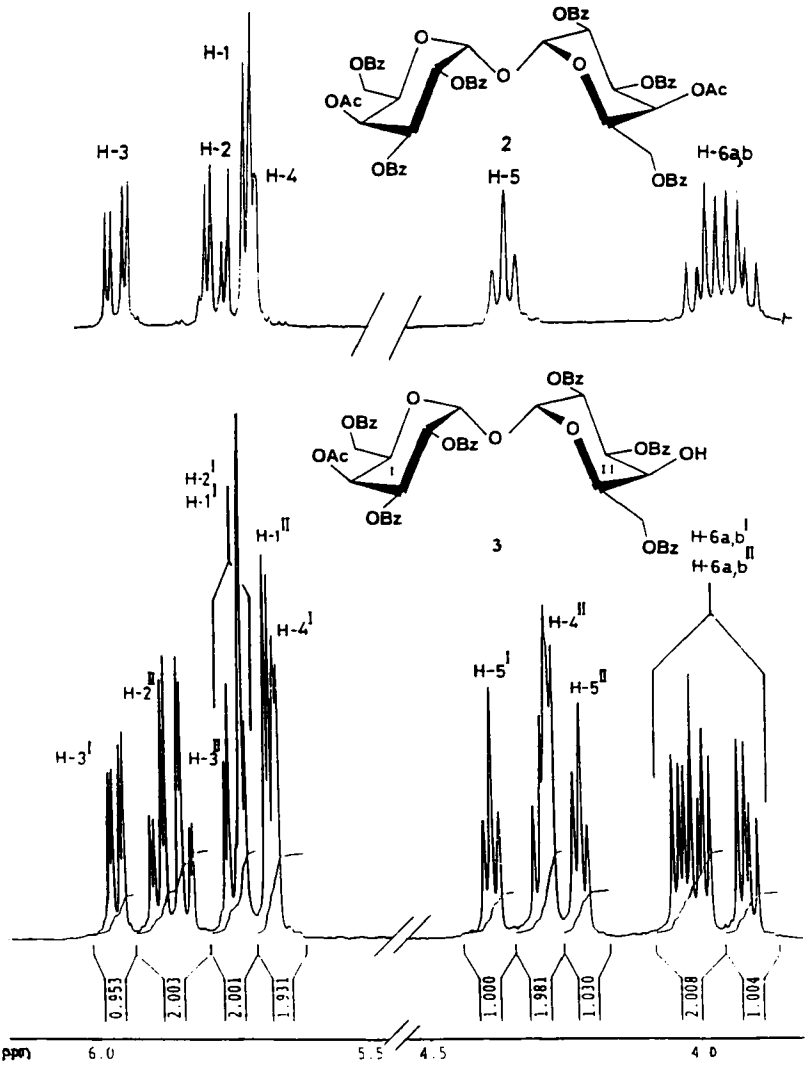


FIG. 4 : A comparison of ^{1}H NMR spectrum for compounds 2 and 3 .

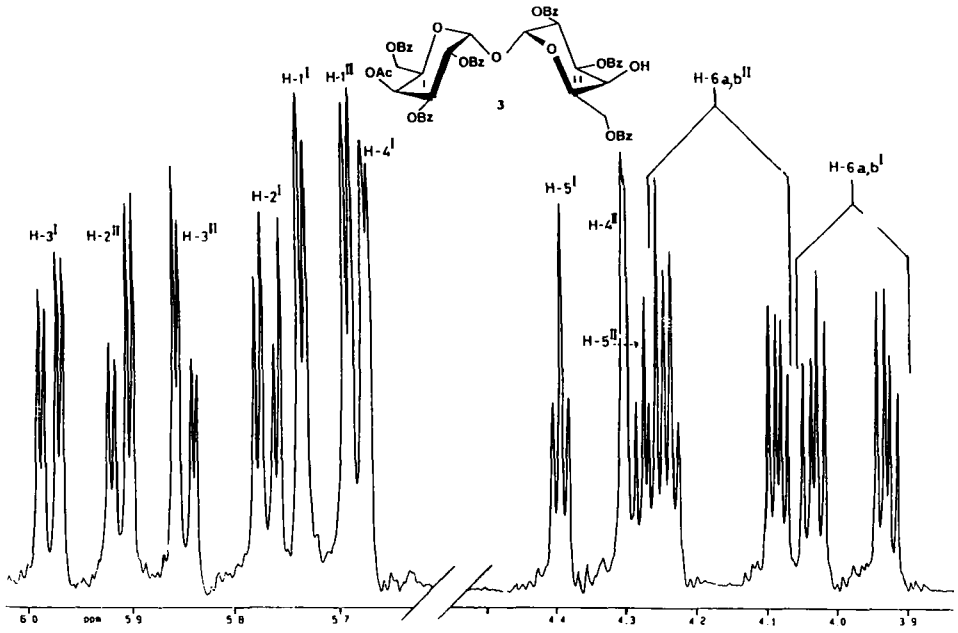


FIG. 5 : ^{1}H NMR spectrum for compound 3 .

The rest of the sugar ring carbons appeared at δ 73.00-69.30 (see experimental).

Characterization of the non-symmetrical trehalose type disaccharide 3 by FABMS.- Compound **3** was analysed by FABMS in the positive-ion mode, which gave a protonated molecular ion at m/z 1009 and $[M+Na]^+$ at m/z 1031 together with a major fragment ion at m/z 991 $[M+H^+-H_2O]$. Fragment ion peaks at m/z 517 (Y_1) and 475 (Y_2), which were identical to the predicted fragment ion peaks from the proposed structure (Figure 7), were also observed. Moreover, the diol derivative 2,3,6-tri-*O*-benzoyl-α-**D**-galactopyranosyl 2,3,6-tri-*O*-benzoyl-α-**D**-galactopyranoside (**4**) was isolated in 12% yield (Scheme I), which was identical in $[\alpha]_D$, ^{1}H and ^{13}C NMR with that prepared by Nashed et.al[2].

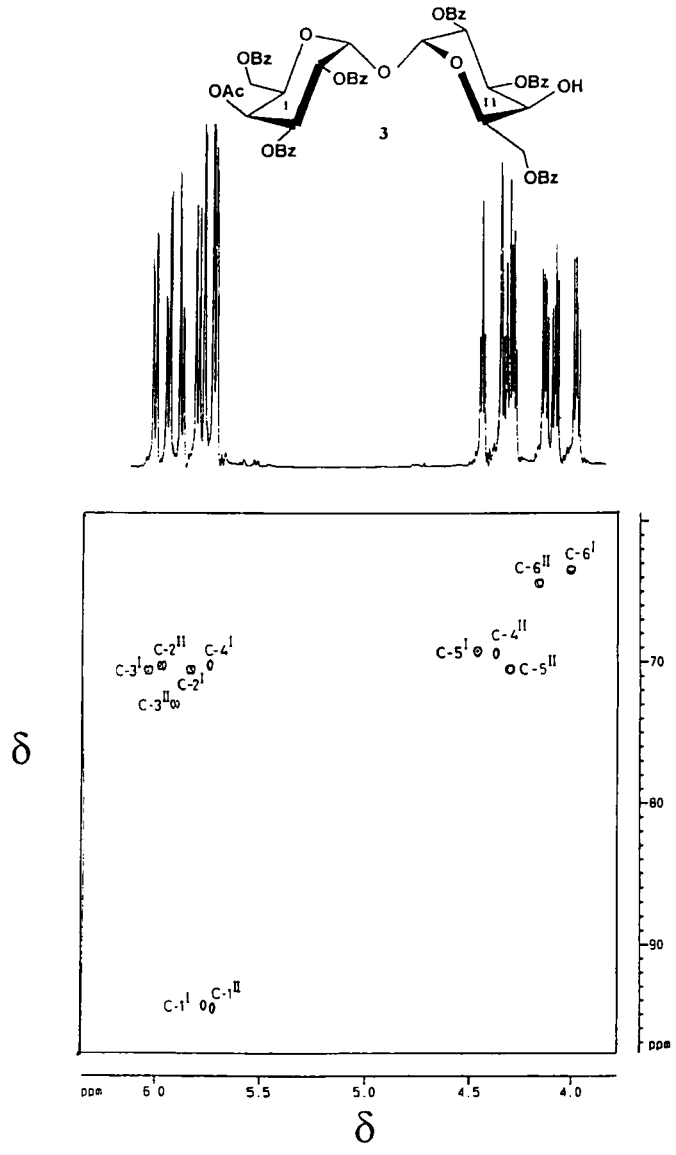


FIG. 6 : ^{1}H-^{13}C shift correlation map of the spectral region F_1 (6.0-4.0 ppm) and F_2 (97-60 ppm) for compound 3 .

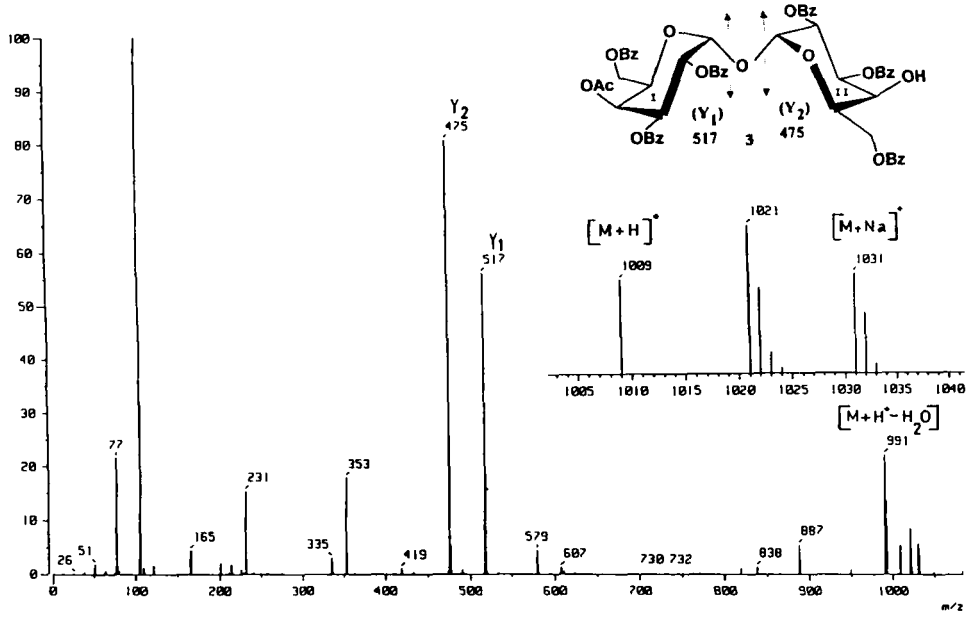
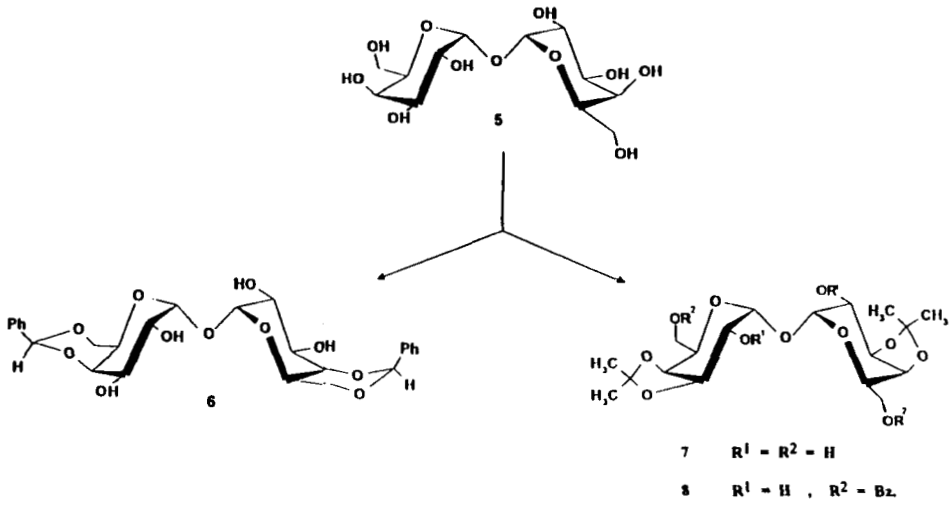


FIG. 7 : Fragment ions obtained by FABMS in the positive-ion mode of compound 3.

As reported in a previous papers[2,16,17], α-**D**-galactopyranosyl α-**D**-galactopyranoside (**5**) is readily made from the corresponding α,α-trehalose *via* the inversion of configuration at C-4,4' positions. In this connection it was interesting to prepare the dibenzylidene derivative **6**, which can be used as a precursor for the synthesis of the azide derivative and other partially protected galacto-galacto trehalose analogues. The dibenzylidene formation of **5** yielded 4,6-*O*-benzylidene-α-**D**-galactopyranosyl 4,6-*O*-benzylidene-α-**D**-galactopyranoside (**6**) in 54% yield (scheme II).

^{1}H NMR spectrum of **6** exhibited an aromatic multiplet at δ 7.50-7.30 equivalent to 10 protons, a siglet at δ 5.56 which corresponds to the



SCHEME II

methine hydrogens, a doublet at δ 5.00 with a small coupling constant ($J_{1,2}$ 3.3 Hz)due to H-1,1', and a broad doublet at δ 4.14 with small spacing attributable to H-4,4'. These signals are consistent with the assigned structure.

A further evidence for the proposed structure was achieved through a study of the ^{13}C NMR spectrum (Figure 8), which revealed amultiplet signals at δ 129.00-126.50 corresponding to the aromatic carbons. The methine carbons appear at δ 100.03, while the signal at δ 95.31 corresponds to anomeric carbons. The APT chart exhibited inverted peak at δ 68.98 due to C-6,6'.

The selective benzoylation of 3,4-*O*-isopropylidene-α-**D**-galacto-pyranosyl 3,4-*O*-isopropylidene-α-**D**-galactopyranoside (7)[3] was accomplished with *N*-benzoylimidazole[18] to give 6-*O*-benzoyl-3,4-*O*-isopropylidene-α-**D**-galactopyranosyl 6-*O*-benzoyl-3,4-*O*-isopropylidene-

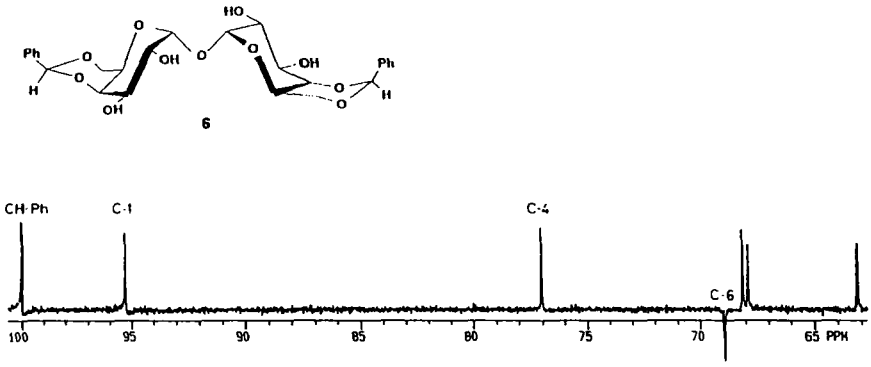


FIG. 8 : Attached proton test on compound 6.

α-**D**-galactopyranoside (**8**) (scheme II). It is interesting to mention here that the reaction of compound **7** with benzoyl chloride in pyridine at low temperature was examined. The desired product **8** was not always obtained in satisfactory yield and was contaminated with 2,2'-and 2,6'-dibenzoate derivative.

The characterization of compound **8** was primarily achieved through a study of its ^{1}H NMR spectrum, which revealed an aromatic multiplet at δ 8.04-7.27 with a 10 proton intensity and a doublet at δ 5.30 with small coupling constant due to anomeric protons. It was clear that the H-6,6' resonances had moved downfield to δ 4.54-4.29. This change indicated that the primary hydroxyl groups were protected by the benzoyl groups. Moreover, a multiplet at δ 4.05-3.95 is attributed to H-2,2' and a broad singlet signal at δ 3.30 corresponds to two protons and undergoes deuterium exchange, is ascribed to a two hydroxyl groups at 2,2' positions. Finally the signals attributed to the dioxolane methyl groups appeared at δ 1.45 and 1.38.

A further elucidation of the structure of compound **8** is obtained through a study of the 2D ^1H-^1H correlation experiment (COSY) (Figure 9). The chemical shift for H-1,1' resonance was traced easily on the ^1H NMR spectrum. Commencing from H-1,1' pattern, the chemical shifts of the rest of the sugar protons were established by tracing the connectivities *via* the cross-peaks.

EXPERIMENTAL

General methods.- Instrumental and chromatographic procedures were as described in earlier papers of this series [1-3].

***4-O-Acetyl-2,3,6-tri-O-benzoyl-α-D-galactopyranosyl 4-O-acetyl-2,3,6-tri-O-benzoyl-α-D-galactopyranoside* (2).**- To a solution of 2,3,6-tri-*O*-benzoyl-4-*O*-trifluoromethylsulfonyl-α-**D**-glucopyranosyl 2,3,6-tri-*O*-benzoyl-4-*O*-trifluoromethylsulfonyl-α-**D**-glucopyranoside (**1**) (17.4 g, 14.1 mmol) in dry *N,N*-dimethylformamide (25 mL), dicyclohexano-18-crown-6 (2.1 g, 0.4 molar equiv.) and anhydrous potassium acetate (9.68 g, 7.0 molar equiv.) were added. The suspension was stirred at room temperature overnight. When t.l.c. (9:1 toluene-ethyl acetate) showed the absence of the starting material, the reaction mixture was diluted with dichloromethane, washed with water thrice, and concentrated. The residue was purified on a column of silica gel (19:1 cholorform-acetone) to furnish(11.9 g, 80%) of the pure title compound **2** as an amorphous solid; $[\alpha]_D$ + 193°, $[\alpha]_{436}$ + 405° (*c* 1.61, chloroform); ^1H NMR. ($CDCl_3$) : δ 8.05-7.10 (m, 30H, Ph-*H*), 6.03 (dd, 2H, *J* 3.3, 10.7 Hz, *H*-2,2' or *H*-3,3'), 5.83 (dd, 2H, *J* 3.6, 10.6 Hz, H-2,2' or H-3.3') 5.77(d, 2H, *J* 3.7 Hz, *H*-1,1'), 5.74 (d, 2H, *J* 3.3 Hz, *H*-4,4'), 4.44 (bt, 2H, *H*-5,5'), 3.95 (dq, 4H, *J* 13.0Hz, *H*-$6_{a,b}$,$6'_{a,b}$), and 2.10 (s, 6H, 2COCH_3); decoupling: δ 5.74 (dd, 2H, $J_{3,4}$ 3.3, ~ 1 Hz; → bs, *J* ~ 1 Hz on irradiation at 6.03, *H*-4,4'), 5.83 (dd, 2H, $J_{1,2}$ 3.6Hz,

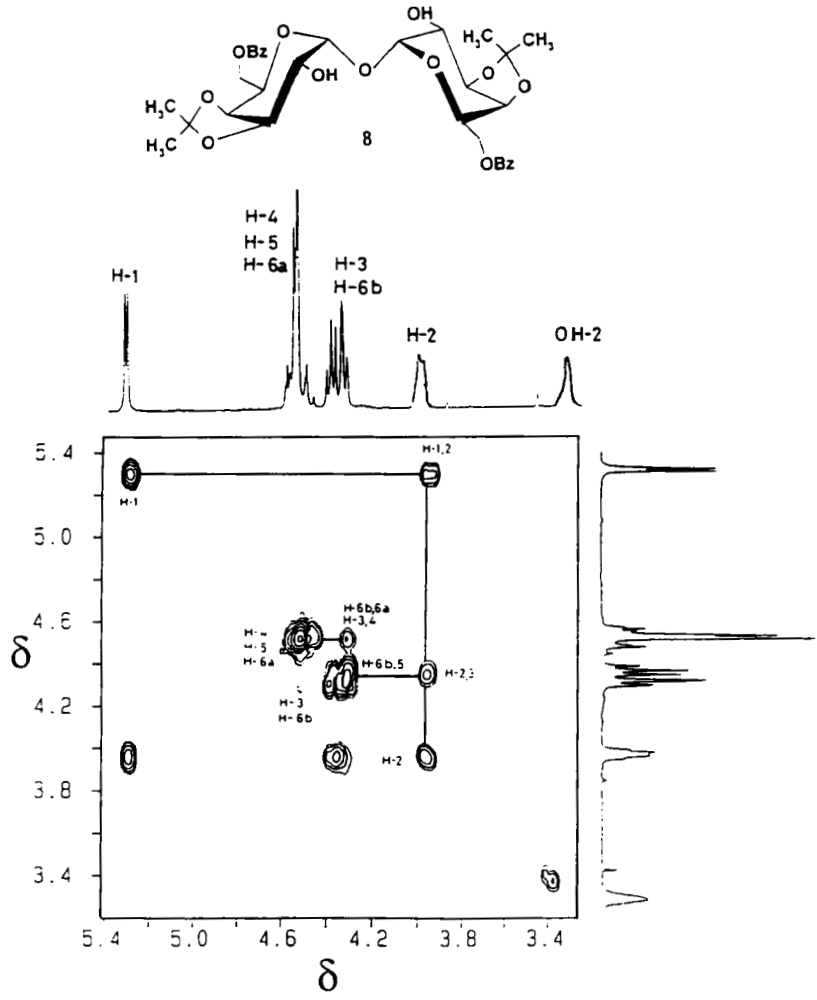


FIG. 9 : COSY contour plot of the region 5.4 - 3.4 ppm for compound 8.

$J_{2,3}$ 10.6Hz; → d, $J_{1,2}$ 3.6 Hz on irradiation at 6.03,→ d, $J_{2,3}$ 10.6 Hz on irradiation at 5.77,*H*-2'), 3.95 (dq, 4H → q on irradiation at 4.44, $2CH_2$), and 4.44 (bt, 2H → s on irradiation at 3.95, *H*-5,5'); ^{13}C NMR ($CDCl_3$):δ 170.10 ($2COCH_3$), 166.05-165.95 (6*C*O-Ph), 134.50-128.00 (aromatic carbons), 93.32 (C-1,1'), 68.63 (C-3,3'), 68.56 (C-2,2'), 68.26 (C-4,4'), 67.83 (C-5,5'), 61.78 (C-6,6'), and 20.71 ($2CH_3$); positive-ion LSIMS: m/z 1051.1 $(M+H)^+$; negative-ion LSIMS :m/z 1096.0 $(M+NO_2)^-$, and 1202.9 (M+*m*-NBA)$^-$.

Anal. Calcd. for $C_{58}H_{50}O_{19}$(1051.03): C, 66.28; H, 4.76. Found: C, 66.06; H, 5.22.

***4-O-Acetyl 2,3,6-tri-O-benzoyl-α-D-galactopyranosyl 2,3,6-tri-O-benzoyl-α-D-galactopyranoside* (3).-** A solution of compound **2** (1.1 g, 1 mmol) in chloroform (5 mL) was treated with methanolic hydrogen chloride [prepared by addition of acetyl chloride (0.2 mL) to dry methanol (5 mL) at 0°C] at room temperature. When t.l.c. (19:1 chloroform-acetone) showed a major and a minor component, the non-symmetric (**3**) and the symmetric component (**4**), respectively. The reaction mixture was diluted with chloroform (25 mL), washed sequentially with potassium hydrogencarbonate solution, water, dried over anhydrous sodium sulphate and concentrated to give a crude syrupy product, chromatography of the syrup on a column of silica gel (chloroform) to separate the product into its components. The major component, eluted first, furnished 0.81 g (80%) of the pure title compound **3** as a glass; ^1H NMR (600 MHz) ($CDCl_3$): δ 8.02-7.25 (m, 30H, Ph-*H*), 5.97(dd, 1H, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.5 Hz, *H*-3^I), 5.91 (dd, 1H, $J_{1,2}$ 3.5 Hz, $J_{2,3}$10.5 Hz, *H*-2^{II}), 5.84 (dd, 1H, $J_{2,3}$10.5 Hz, $J_{3,4}$3.0 Hz, *H*-3^{II}), 5.77 (dd, 1H, $J_{1,2}$ 3.5Hz, $J_{2,3}$ 10.0 Hz, *H*-2^I), 5.73 (d, 1H, $J_{1,2}$ 3.5 Hz, *H*-1^I), 5.69 (d, 1H, $J_{1,2}$ 3.5 Hz, *H*-1^{II}), 5.67 (d, 1H, $J_{3,4}$ 3.5Hz,

H-4^{I}), 4.39 (t, 1H, *H*-5^{I}), 4.30 (d, 1H, $J_{3,4}$ 3.0 Hz, *H*-4^{II}), 4.27 (t, 1H, *J*6.5 Hz, *H*-5^{II}), 4.26-4.06 (dq, 2H, $J_{5,6a}$ 6.0 Hz, $J_{5,6b}$ 7.0 Hz, *J*12.0 Hz, *H*-6$_a^{II}$, 6$_b^{II}$), 4.05-3.91(dq, 2H, $J_{5,6a}$ 7.0 Hz, *J*11.5 Hz, *H*-6$_a^{I}$, 6$_b^{I}$), 2.51 (bs, 1H, O*H*-4), 2.15 (s, 3H, CH_3CO); ^{13}C NMR ($CDCl_3$) : δ 94.40 (C-1^{II}), 94.00 (C-1^{I}), 73.00 (C-3^{II}), 71.70 (C-3^{I}), 71.10 (C-2^{I}), 70.80 (C-5^{II}), 70.70 (C-2^{II}), 70.60 (C-4^{I}), 69.80 (C-4^{II}), 69.30 (C-5^{I}), 64.60 (C-6^{II}) and 63.50 (C-6^{I}); positive-ion LSIMS: m/z 1009 $(M+H)^+$ and 1031 $(M+Na)^+$. The second eluted from the column was the minor component 2,3,6-tri-*O*-benzoyl-α-**D**-galactopyranosyl 2,3,6-tri-*O*-benzoyl-α-**D**-galactopyranoside **(4)** (120mg, 12%) as a syrup having ($[\alpha]_D$, and ^{1}H, ^{13}C NMR) which are agreement with our values[2].

***4,6-O-Benzylidene-α-D-galactopyranosyl 4,6-O-benzylidene-α-D-galactopyranoside* (6).-** With stirring, fused anhydrous zinc chloride (1.0 g) was quickly added to freshly distilled benzaldehyde (5 mL). After 15 minutes, α-**D**-galactopyranosyl α-**D**-galactopyranoside **(5)** (0.85 g, 2.5 mmol) was added and the stirring was continued overnight at ambient temperature. The syrupy mass obtained was poured into a separatory funnel containing ammonium cholride solution (15 mL) and petroleum ether (15 mL). The mixture was vigorously shaken, whereupon a crystalline solid started to precipitate. This was collected by filtration, washed with water, and dried overnight in air. The dry product was crystallized from ethanol to furnish the title compound **6** (0.7 g, 54.4%) as white crystals; m.p. 219-222°C; ^{1}H NMR (DMSO-d_6): δ 7.50-7.30 (m, 10H, Ph-*H*), 5.56 (s, 2H, C*H*-ph), 5.00 (d, 2H, $J_{1,2}$ 3.3 Hz, *H*-1,1'), 4.83 (d, 2H, *J* 6.9 Hz, D_2O-exchangeable, O*H*-2,2' or 3,3'), 4.80 (d, 2H, *J* 6.5 Hz, D_2O-exchangeable, O*H*-3,3' or 2,2'), 4.14 (d, 2H, $J_{3,4}$ 2.6 Hz, *H*-4,4'), and 4.04-3.70 (m, 10H, suger C*H* and CH_2); ^{13}C NMR (DMSO-d_6): δ 129.00-

126.50 (aromatic carbons), 100.03 (2*C*H-Ph), 95.31 (C-1,1'), 77.07 (C-4,4'), 68,98 (C-6,6'), 68.16, 67.92, and 63.17 (rest of suger carbons); positive-ion LSIMS: m/z 519.3 $(M+H)^+$, 611.3 $(M+H+92)^+$, and 703.3 $(M+H+184)^+$; negative-ion LSIMS: m/z 517.2 $(M-H)^-$, 609.2 $(M-H+92)^-$, and 701.2 $(M-H+184)^-$.

Anal. Calcd. for $C_{26}H_{30}O_{11}$(518.52):C, 60.23; H, 5.83. Found:C, 60.42; H, 6.04.

6-O-Benzoyl-3,4-O-isopropylidene-α-D-galactopyranosyl 6-O-Benzoyl-3,4-O-isopropylidene-α-D-galactopyranoside (**8**).- To a solution of imidazole (0.58 g, 8.5 mmol) in absolute chloroform (25 mL), benzoyl choride (0.5 mL, 4.3 mmol) was added slowly with stirring at room temperature. After 10 minutes, 3,4-*O*-isopropylidene-α-**D**-galactopyranosyl 3,4-*O*-isopropylidene-α-**D**-galactopyranoside (**7**) (0.72 g, 1.7 mmol) was added. The reaction mixture was heated under reflux 3.5 hours, whereupon t.l.c. (1:1 toluene-ethyl acetate) indicated that the reaction was complete. The mixture was evaporated under reduced pressure, and then toluene was evaporated from the residue several times. The residue when purified on a column of silica gel (19:1 chloroform-methanol) furnished 0.54 g (50%) of the pure title compound (**8**) as a syrup; $[\alpha]_D$ + 99.3°, $[\alpha]_{578}$+ 104°, $[\alpha]_{546}$ + 118°, $[\alpha]_{436}$ + 196°, $[\alpha]_{365}$ + 298°, (*c* 0.4, chloroform); ^{1}H NMR ($CDCl_3$) : δ 8.04-7.27 (m, 10H, Ph-*H*), 5.30 (d, 2H, $J_{1,2}$ 3.7 Hz, *H*-1,1'), 4.54-4.43 (m, 6H, *H*-4,4', *H*-5,5', and *H*-6_a,$6'_a$), 4.38-4.29 (m, 4H, *H*-3,3'and *H*-6_b,$6'_b$), 4.05-3.95 (m, 2H, *H*-2,2'), 3.30(bs, 2H, D_2O-exchangeable, O*H*-2,2'), and 1.45, 1.38 [2s, 12H, 2C(CH_3)$_2$]; ^{13}C NMR ($CDCl_3$) : δ 166.50 (2*C*O-Ph), 134.00-128.70 (aromatic carbons), 110.55 [2*C*(CH_3)$_2$], 93.05 (C-1,1'), 75.73, 73.37, 69.03, 67.92, 64.66 (C-6,6'), and 27.89, 26.16 [2C(CH_3)$_2$].

Anal. Calcd. for $C_{32}H_{38}O_{13}$(630.05): C, 60.95; H, 6.07. Found: C, 61.05; H, 6.25.

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