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Synthesis of Methyl 3-*O*-(3,6-Dideoxy-α-D-*xylo*-hexopyranosyl)-α-D-mannopyranoside

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The synthesis of methyl 3-*O*-(3,6-dideoxy-α-D-*xylo*-hexopyranosyl)-α-D-mannopyranoside, required for immunological studies of *Salmonella*, is described. The glycosylation was performed by means of the Helferich procedure and the influence of a *p*-nitrobenzoyl group or a non-participating benzyl group in the 2-position in the 3,6-dideoxyhexosyl bromide used, was investigated.

The disaccharide unit 3-*O*-α-abequopyranosyl-α-D-mannopyranosyl (3-*O*-(3,6-dideoxy-α-D-*xylo*-hexopyranosyl)-α-D-mannopyranosyl) corresponds to the *Salmonella* O-factor 4,[1] which when covalently linked to a protein would provide an antigen of immunological interest.[2] Its methyl glycoside (title compound) is of interest as an O-4 inhibitor and was required for immunological studies. In these studies we have explored two different pathways to the title substance; the more efficient of these has subsequently been used in the synthesis of *p*-isothiocyanatophenyl 3-*O*-abequopyranosyl-α-D-mannopyranoside, which can be covalently linked to suitable proteins. For these exploratory studies we chose the methyl rather than the *p*-isothiocyanatophenyl mannoside, since the former is the more readily accessible. In addition, the products of glycosylation using the methyl mannoside aglycone described in this work are more readily purified and identified than those from the corresponding *p*-isothiocyanato mannoside aglycone described in Ref. 11.

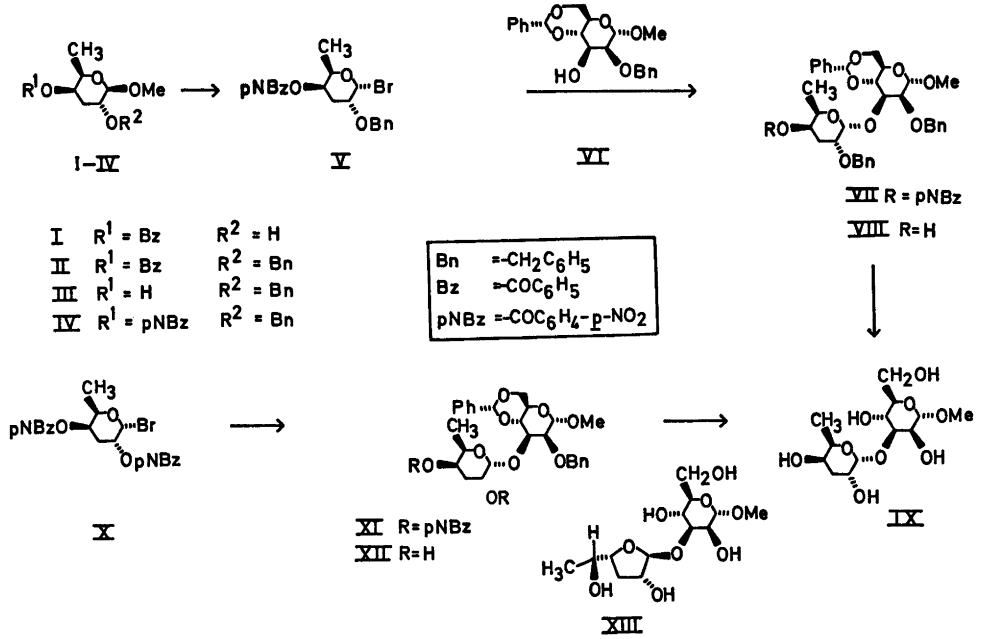
Fucopyranosyl bromides containing a non-participating benzyl group in the 2-position are useful for the synthesis of α-D- (α-L-) fucopyranosides[3] and we thus anticipated that abequopyranosyl bromides benzylated in the 2-position would give similar results. We have previously obtained methyl 4-*O*-benzoyl-β-abequopyranoside from methyl β-D-fucopyranoside *via* treatment of the 3,4-*O*-benzylidene acetal with *N*-bromosuccinimide[4] and hydrogenation of the resulting 3-bromo compound.[5] Benzylation of the remaining free 2-position of methyl 4-*O*-benzoyl-β-abequopyranoside is most efficiently carried out using benzyl trifluoromethanesulfonate.[6]

The glycosylation of a 2,4-di-*O*-acylabequosyl halide offers a more direct route, providing the yield of the desired α-abequopyranoside is high enough. A *p*-nitrobenzoyl group in the axial position in fucopyranosyl halides containing a non-participating benzyl group in the 2-position has previously been shown to favour the formation of α-glycosides.[3,7] In 2,4-di-*O*-*p*-nitrobenzoylabequosyl bromide, a potential precursor for α-abequopyranosides, competing participation from the 2-position might, however, interfere and give a β-glycopyranoside. Indeed, 2,4-di-*O*-*p*-nitrobenzoyl-3,6-dideoxy-D-*ribo*-hexopyranosyl bromide, with an equatorial group in the 4-position yields the β-glycoside exclusively.[8] In the present work, however, the controlling influence of the axial 4-*O*-*p*-nitrobenzoyl group in the 2,4-di-*O*-*p*-nitrobenzoylabequosyl bromide is indicated by the fact that the α-pyranoside was the major product.

Methyl 4-*O*-benzoyl-β-abequoside (I)[5] was benzylated with benzyl trifluoromethanesulfonate;[6] the 2-*O*-benzyl ether II was obtained in 51 % yield. Removal of the benzoyl group in II afforded the hydroxy compound III in 85 % yield and acylation of III with *p*-nitrobenzoyl

chloride afforded the 4-*O*-*p*-nitrobenzoate IV in 87 % yield. Treatment of the abequoside IV with hydrogen bromide in dichloromethane afforded the crude bromide V, used directly in the next step. Condensation of the bromide V with methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside [9] (VI) in nitromethane-benzene using mercury(II) cyanide as promotor [10] afforded, after chromatographic purification, the α-linked disaccharide derivative VII in 37 % yield. Debenzoylation of VII afforded the disaccharide derivative VIII in 87 % yield, the latter was converted into the title disaccharide IX in 90 % yield by catalytic hydrogenation.

In the alternative synthesis, 2,4-di-*O*-*p*-nitrobenzoyl-α-abequosyl bromide (X), prepared as described in Ref. 11, was condensed with the above mannoside VI in nitromethane-benzene using mercury(II) cyanide as promotor.[10] Chromatographic purification afforded the disaccharide derivative XI in 34 % yield. Debenzoylation of XI afforded XII in 87 % yield. The latter was hydrogenated to IX in 93 % yield. The final product IX was identical to that produced in the first-mentioned synthesis. A minor component isolated from the reaction mixture was shown to be methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(3,6-dideoxy-2,5-di-*O*-*p*-nitrobenzoyl-β-D-*xylo*-hexofuranosyl)-α-D-mannopyranoside and was converted into methyl 3-*O*-(3,6-dideoxy-β-D-*xylo*-hexofuranosyl)-α-D-mannopyranoside (XIII) by debenzoylation followed by hydrogenation. Hydrolysis of the disaccharide and conversion into the per-acetylated alditols produced abequitol and mannitol acetates. From the methylation analysis [12,13] (GLC-MS), 1,4-di-*O*-acetyl-2,5-di-*O*-methylabequitol and 1,3,5-tri-*O*-acetyl-2,4,6-tri-*O*-methylmannitol were identified. These findings show the presence of an abequosyl-mannosyl disaccharide containing a furanosidic abequose moiety. NMR and optical rotation established a β-linkage. The β-furanoside is presumably formed from the 3,6-dideoxy-2,5-di-*O*-*p*-nitrobenzoyl-D-*xylo*-hexofuranosyl bromide present as a by-product of the treatment of methyl 3,6-dideoxy-*p*-nitrobenzoyl-α-D-*xylo*-hexopyranoside with hydrogen bromide in dichloromethane. Similar rearrangements have been observed by Bock and Pedersen in the treatment of acetylated methyl glycopyranosides with hydrogen bromide in acetic acid.[14]



The NMR assignments given in the experimental part were, where necessary, corroborated by spin decoupling experiments. Thus, the signal given by the anomeric proton of the abequosyl unit in the disaccharide derivative VII was assigned as follows: Irradiation at the H-3, H-3′ frequency (abequose residue) caused a simplification of the signals at δ 3.7 and those at δ 5.00–5.16. From chemical shift considerations the former of these is due to H-2, attached to benzyloxy carbon and the latter to H-4, attached to *p*-nitrobenzoyloxy carbon. This was confirmed by irradiating the H-6 doublet at δ 1.05, locating the H-5 signal of the abequose unit and then irradiating at the H-5 frequency. Since H-2 (abequose unit) had the same resonance frequency as H-5, this irradiation caused both simplification in the H-4 signal and collapse of the H-1 doublet into a singlet. Irradiation at the H-1 resonance frequency conversely caused a simplification of the H-2 signal. The coupling constant of the H-1 (abequose) doublet of 4 Hz indicates an α-linkage to the mannose unit.

EXPERIMENTAL

General methods were the same as those reported in a recent paper [15] and in Ref. 11, respectively.

Methyl 4-O-benzoyl-2-O-benzyl-3,6-dideoxy-β-D-xylo-hexopyranoside (II). Trifluoromethanesulfonic anhydride (0.55 ml) was dissolved in anhydrous dichloromethane (2 ml) and cooled to −60 °C. A solution of benzyl alcohol (0.44 ml) and 2,6-lutidine (0.44 ml) in anhydrous dichloromethane (3 ml) was added at this temperature. After 30 min, a solution of methyl 4-*O*-benzoyl-3,6-dideoxy-β-D-*xylo*-hexopyranoside (I) (300 mg) and 2,6-lutidine (0.27 ml) in anhydrous dichloromethane (2 ml) was added during 30 min at −60 °C. The reaction mixture was allowed to stand for 60 h at this temperature. TLC (toluene–ethyl acetate, 4:1) showed the presence of starting material and a faster-moving component (II) The reaction mixture was diluted with dichloromethane and washed with water. The organic layer was dried over sodium sulfate, filtered and concentrated. The two components were separated by column chromatography on silica gel to yield chromatographically pure II (205 mg) $[\alpha]_D$ +4° (chloroform). 60 MHz NMR ($CDCl_3$): δ 1.25 (3 H, d, $J_{5,6}$ 7 Hz, H-6), 1.5–2.7 (2 H, m, H-3, H-3′), 3.62 (3 H, s, methoxyl protons), 4.38 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 4.63, 4.83 (2 H, AB spectrum, $J_{H,H}$ 12 Hz, benzylic protons), 5.10–5.24 (1 H, m, H-4), 7.1–7.4 (8 H, m) and 8.0–8.2 (2 H, m, aromatic protons).

Methyl 2-O-benzyl-3,6-dideoxy-β-D-xylo-hexopyranoside (III). The above product II (200 mg) in methanol (50 ml) containing barium oxide (150 mg) was refluxed for 30 min. The mixture was neutralized with solid carbon dioxide and concentrated. The residue was taken up in ethyl acetate (50 ml) and filtered. The filtrate was concentrated to a syrup which was purified by silica gel column chromatography (toluene–ethyl acetate, 4:1) to yield chromatographically pure III (120 mg) $[\alpha]_D$ −23° (chloroform). The material crystallized from diethyl ether, m.p. 84–85 °C. (Found: C 66.5; H 7.87. $C_{14}H_{20}O_4$ requires: C 66.6; H 7.99.) 60 MHz NMR: δ 1.26 (3 H, d, $J_{5,6}$ 7 Hz, H-6), 1.5–2.5 (3 H, m, H-3, H-3′, OH), 3.57 (3 H, s, methoxyl protons), 4.30 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 4.63, 4.80 (2 H, AB spectrum, $J_{H,H}$ 12 Hz, benzylic protons), 7.33 (5 H, aromatic protons).

Methyl 2-O-benzyl-3,6-dideoxy-4-O-p-nitrobenzoyl-β-D-xylo-hexopyranoside (IV). The benzyl ether III (110 mg) was dissolved in pyridine (15 ml) and cooled to 0 °C. *p*-Nitrobenzoyl chloride (110 mg) in pyridine (5 ml) was added with stirring. The reaction mixture was kept at room temperature for 4 h. Ice-water was added and the mixture extracted with chloroform. The organic layer was washed with water, dried over sodium sulfate and concentrated to a syrup which was purified by silica gel column chromatography (toluene–ethyl acetate, 3:2) to yield chromatographically pure IV (155 mg $[\alpha]_D$ +50° (chloroform). 60 MHz NMR ($CDCl_3$) δ 1.26 (3 H, d, $J_{5,6}$ 7 Hz, H-6), 1.4–2.7 (2 H, m, H-3, H-3′), 3.62 (3 H, s, methoxyl protons), 4.42 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 4.64, 4.86 (2 H, AB spectrum, $J_{H,H}$ 12 Hz, benzylic protons), 5.13–5.30 (1 H, m, H-4), 7.30 (5 H) and 8.25 (4 H), aromatic protons.

2-O-Benzyl-3,6-dideoxy-4-O-p-nitrobenzoyl-α-D-xylo-hexopyranosyl bromide (V). A solution of the glycoside IV (160 mg) in dichloromethane (10 ml) was cooled to −20 °C. A saturated solution of hydrogen bromide in dichloromethane (10 ml) was added at −20 °C. The reaction was monitored by TLC (toluene–ethyl acetate, 4:1). After 30 min at −20 °C, the solution was concentrated and used immediately in the next reaction step, $[\alpha]_D$ +137° (chloroform). 60 MHz NMR ($CDCl_3$): δ 6.74 (1 H, $J_{1,2}$ 4 Hz, H-1.

Methyl-2-O-benzyl-3-O-(2-O-benzyl-3,6-dideoxy-4-O-p-nitrobenzoyl-α-D-xylo-hexopyranosyl)-4,6-benzylidene-α-D-mannopyranoside (VII). A solution of methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (VI) [9] (160 mg) in nitromethane–benzene (1:1, 8 ml) was boiled until 2.5 ml solvent had distilled off. The solution was cooled to room temperature. Mercury(II) cyanide (140 mg) and the hexosyl bromide V (prepared from 160 mg glycoside IV) dissolved in dry dichloromethane, were

added during 5 min. The mixture was stirred at room temperature under nitrogen for 16 h and then diluted with toluene. The solution was washed with water, saturated aqueous sodium hydrogen carbonate and finally water, dried over sodium sulfate, filtered and concentrated to a syrup. Silica gel column chromatography (toluene – ethyl acetate, 4:1) yielded chromatographically homogeneous VII (120 mg), R_F 0.63, TLC in the same solvent, $[\alpha]_D$ +129° (chloroform). (Found: C 66.4; H 5.98; N 1.82. $C_{41}H_{43}O_{12}$ requires: C 66.4; H 5.84; N 1.89) 100 MHz NMR ($CDCl_3$): δ 1.05 (3 H, d, $J_{5,6}$ 7 Hz, H-6, abequose residue), 2.0 – 2.3 (2 H, m, H-3, H-3′, abequose residue), 3.43 (3 H, s, methoxyl protons), 4.80 (3 H, s, benzylic protons and H-1, mannose residue), 5.00 – 5.16 (1 H, m, H-4), 5.42 (1 H, d, $J_{1,2}$ 4 Hz, H-1, abequose residue), 5.46 (1 H, s, benzylidene proton), 6.9 – 7.5 (15 H, aromatic protons), 8.05 and 8.19 (2 H each, each d, each $J_{H,H}$ 8 Hz, *p*-nitrobenzoyl protons).

*Methyl-2-*O*-benzyl-3-*O*-(2-*O*-benzyl-3,6-dideoxy-*α*-*D*-xylo-hexopyranosyl)-4,6-*O*-benzylidene-*α*-*D*-mannopyranoside (VIII).* The above disaccharide derivative VII (50 mg) in methanol (25 ml) containing barium oxide (50 mg) was refluxed for 30 min. The mixture was neutralized with solid carbon dioxide and concentrated. The residue was taken up in ethyl acetate and filtered. The filtrate was concentrated to a syrup which was purified by silica gel column chromatography (toluene – ethyl acetate, 1:1) to yield chromatographically pure VIII (35 mg) $[\alpha]_D$ +94° (chloroform). 60 MHz NMR ($CDCl_3$): δ 1.11 (3 H, d, $J_{5,6}$ 7 Hz, H-6, abequose residue), 1.4 – 1.6 (3 H, m, H-3, H-3′ and OH), 3.42 (3 H, s, methoxyl protons), 4.83 (3 H, s, benzyl protons and H-1, mannose residue), 5.40 (1 H, d, $J_{1,2}$ 4 Hz, H-1, abequose residue), 5.47 (1 H, s, benzylidene proton), 7.0 – 7.5 (15 H, aromatic protons).

*Methyl-3-*O*-(3,6-dideoxy-*α*-*D*-xylo-hexopyranosyl)-*α*-*D*-mannopyranoside (IX).* (a) From VIII: The above disaccharide derivative XIII (30 mg) was hydrogenated at room temperature and atmospheric pressure in ethanol using a catalytic amount of 10 % palladium on carbon. After 5 h, the catalyst was removed by filtration and the filtrate concentrated to a chromatographically pure syrup, IX (14 mg), $[\alpha]_D$ +103° (water). 100 MHz NMR (D_2O): δ 1.14 (3 H, d, $J_{5,6}$ 7 Hz, H-6), 1.86 – 2.12 (2 H, m, H-3, H-3′), 3.42 (3 H, s, methoxyl protons) 4.75 (1 H, d, $J_{1,2}$ 1.5 Hz, H-1, mannose residue), 5.06 (1 H, d, $J_{1,2}$ 4 Hz, H-1, abequose residue). An aliquot of IX was converted into the corresponding pentaacetate with acetic anhydride and pyridine. (Found for IX pentaacetate: C 51.4; H 6.24. $C_{23}H_{34}O_{14}$ requires: C 51.7; H 6.41). An aliquot of IX was hydrolyzed with 0.25 M aqueous sulfuric acid for 12 h at 100 °C. The hydrolyzate was reduced with sodium borohydride and the mixture of alditols was fully acetylated.[16] GLC-MS showed the presence of two components, indistinguishable from abequitol tetraacetate and mannitol hexaacetate, respectively. Another aliquot of IX was methylated with dimethylsulfinyl anion and iodomethane in dimethyl sulfoxide.[12] The product was hydrolyzed, reduced with sodium borohydride and the alditols converted into their per-acetates.[16] The alditol acetates thus obtained were indistinguishable by GLC-MS [13] from 1,5-di-*O*-acetyl-2,4-di-*O*-methylabequitol and 1,3,5-tri-O-acetyl-2,4,6-tri-*O*-methyl-mannitol, respectively.

(b) From XII (see below): Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(3,6-dideoxy-*α*-*D*-*xylo*-hexopyranosyl)-*α*-*D*-mannopyranoside (XI) (70 mg) was hydrogenated and worked up as described above under (a). Chromatographically pure IX (42 mg) was obtained, $[\alpha]_D$ +95° (water), with NMR data identical to those found for IX. Hydrolysis and conversion to the corresponding alditol acetates [15] of an aliquot of the material (see above) afforded abequitol and mannitol acetates. Likewise, methylation analysis [12,13] yielded the same methylated alditol acetates as described above under (a). Conversion of IX obtained from both routes into the fully trimethylsilylated products gave materials with identical data on both GLC and MS.

Methyl 2-O-*benzyl-4,6-*O*-benzylidene-3-*O*-(3-6-dideoxy-2,4-di-*O*-p-nitrobenzoyl-*α*-*D*-xylo-hexopyranosyl-*α*-*D*-mannopyranoside (XI).* A solution of the mannoside VI (312 mg) in nitromethane – benzene (1:1, 12.4 ml) was boiled until 3.7 ml solvent had distilled off. The solution was cooled to room temperature. Mercury(II) cyanide (360 mg) and 3,6-dideoxy-2,4-di-*O*-*p*-nitrobenzoyl-*α*-*D*-*xylo*-hexopyranosyl bromide (X) (prepared from 400 mg methyl 3,6-dideoxy-2,4-di-*O*-*p*-nitrobenzoyl-*α*-*D*-*xylo*-hexopyranoside [17] and used immediately) in dry dichloromethane (2 ml) were added. After stirring at room temperature for 24 h the mixture was diluted with toluene and the solution washed with water, saturated aqueous sodium hydrogen carbonate and finally water. The solution was dried over sodium sulfate, filtered and concentrated to a syrup. Silica gel column chromatography (toluene – ethyl acetate, 8:1) yielded chromatographically pure XI (230 mg), R_F 0.34, TLC in the same solvent. The material crystallized from diethyl ether – light petroleum, m.p. 105 – 108 °C, $[\alpha]_D$ +90° (chloroform). (Found: C 61.3; H 5.19; N 3.40. $C_{41}H_{40}O_{15}N_2$ requires: C 61.5; H 5.04; N 3.50.) 100 MHz NMR ($CDCl_3$): δ 1.16 (3 H, d, $J_{5,6}$ 7 Hz, H-6), abequose residue), 2.1 – 2.7 (2 H, m, H-3, H-3′, abequose residue), 3.44 (3 H, s, methoxyl protons), 7.0 – 8.4 (18 H, m, aromatic protons).

*Methyl-2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(3,6-dideoxy-*α*-*D*-xylo-hexopyranosyl)-*α*-*D*-mannopyranoside (XII).* The above disaccharide derivative XI (220 mg) in methanol (50 ml) containing barium oxide (100 mg) was debenzo-

ylated and worked up as described above for VIII. Purification by silica gel column chromatography (toluene–ethyl acetate, 3:2) afforded chromatographically pure XII (138 mg) $[\alpha]_D$ +29° (chloroform). 100 MHz NMR: δ 1.09 (3 H, d, $J_{5,6}$ 7 Hz, H-6, abequose residue), 1.6–2.5 (4 H, m, H-3, H-3′, OH, abequose residue), 3.34 (3 H, s, methoxyl), 4.70 (3 H, s, H-1, mannose residue and benzyl protons), 5.02 (1 H, d, $J_{1,2}$ 4 Hz, H-1, abequose residue), 5.58 (1 H, benzylidene proton), 7.2–7.5 (10 H, m, aromatic protons).

*Methyl 3-O-(3,6-dideoxy-β-*D*-xylo-hexofuranosyl)-α-*D*-mannopyranoside (XIII).* A minor component with R_F 0.30 (TLC, toluene–ethyl acetate, 8:1) was obtained in the preparation of XI (above). This material, presumably, methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(3,6-dideoxy-2,5-di-*O*-*p*-nitrobenzoyl-β-D-*xylo*-hexofuranosyl)-α-D-mannopyranoside was debenzoylated and the product hydrogenated as described above for VIII and IX, respectively. The product (XIII) had $[\alpha]_D$ +3° (water). 100 MHz NMR (D_2O): δ 1.23 (3 H, d, $J_{5,6}$ 7 Hz, H-6, abequose residue), 1.64 (1 H, J 3.0, 6.9 and 15.5 Hz, H-3, abequose residue), 2.53 (1 H, J 6.9, 8.6 and 15.5 Hz, H-3′, abequose residue), 3.48 (3 H, s, methoxyl protons), 4.85 (1 H, d, $J_{1,2}$ 1.5 Hz, H-1, mannose residue), 5.21 (1 H, s, $J_{1,2}=0$ Hz, H-1, abequose residue). An aliquot of XIII was hydrolyzed and converted into the corresponding alditol acetates. These were shown to be indistinguishable from abequitol and mannitol acetates by GLC-MS. Another aliquot was subjected to methylation analysis as described above and yielded 1,4-di-*O*-acetyl-2,5-di-*O*-methylabequitol and 1,3,5-tri-*O*-acetyl-2,4,6-tri-*O*-methylmannitol, respectively. On GLC 1,4-di-*O*-acetyl-2,5-di-*O*-methylabequitol had a relative retention time of 0.31 (1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylglucitol, $r=1$) as compared to that of 0.32 for 1,5-di-*O*-acetyl-2,4-di-*O*-methylabequitol (column: 3 % ECNSS-M on Gas-Chrom Q). Pertinent mass spectral peaks: *m/e* (rel. intensity): 43(65), 59(100), 69(7), 97(20), 101(8), 117(8), 129(20), 189(2).

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