SYNTHESIS OF METHYL 2,6-DIDEOXY-β-D-ARABINO-, 3,6-DIDEOXY-β-D-RIBO-, AND 4,6-DIDEOXY-β-D-XYLO-HEXOPYRANOSIDES

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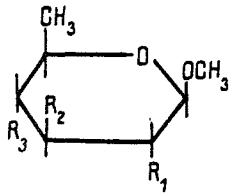
A convenient method is proposed for the synthesis of methyl 1,6-dideoxy-β-D-arabino-, 3,6-dideoxy-β-D-ribo-, and 4,6,dideoxy-β-D-xylo-hexopyranosides by the partial deoxygenation ofmethyl β-D-quinovopyranoside followed by liquid chromatography of the dideoxysugars.

We have recently proposed a simple method [1] for obtaining a series of dideoxysugars by the partial deoxygenation of methyl α-L-rhamnopyranoside acetate, followed by the separation of the compounds obtained. In connection with the demand for samples of a number of authentic sugars in the structural study of lipopolysaccharides, a similar approach has been used for the synthesis of the dideoxysugars named in the title, which were obtained by the partial reduction of methyl 6-deoxy-β-D-glucopyranoside acetate (V) with a total yield of 55% and were separated by liquid chromatography.



I. $R_1=R_2=R_3=OH$
II. $R_1=H$; $R_2=R_3=OH$
III. $R_1=R_3=OH$; $R_2=H$
IV. $R_1=R_2=OH$; $R_3=H$
V. $R_1=R_2=R_3=AcO$
VI. $R_1=H$; $R_2=R_3=AcO$
VII. $R_1=R_3=AcO$; $R_2=H$
VIII. $R_1=R_2=AcO$; $R_3=H$

The partial deoxygenation of the methyl β-D-quinovopyranoside acetate (V) and the isolation of the reaction products were carried out as described previously [1], with the exception of the fact that water was added to the reaction mixture constantly during the reaction. This prevented the formation of degradation products and led to a higher yield of dideoxysaccharides. However, the presence of more than 5% of water in the reaction mixture is undesirable, since it retards the reaction and may practically stop it. The concentration of the initial acetate can be brought to 2% without an appreciable increase in the amount of decomposition products. Monitoring of the separation was carried out by TLC and GLC.

The dideoxysugars obtained were identified by ^{13}C NMR spectroscopy. The ^{13}C chemical shifts of compounds (I)-(IV) given in a review [2] practically coincided with those that we obtained.

EXPERIMENTAL

Melting points were determined on a Boëtius instrument, and specific optical rotations on a Perkin-Elmer M141 automatic polarimeter. The ^{13}C NMR spectra were obtained on a Bruker HX-90E spectrometer. Chemical shifts are given in parts per million (ppm) and were measured relative to TMS (0, ppm). Methanol was selected as internal standard (δ_C 49.6). The solvent was D_2O. TLC was conducted on silica gel L 5-40 μm (Chemapol).

For the separation of the dideoxysugars we used the chloroform–methanol (95:5) system, and for separating their acetates the ethyl acetate–hexane (1:1) system. For column chromatography we used silica gel L 40-100 μm (Chemapol). GLC was conducted on a Tsvet-106 instrument fitted with a flame-ionization detector and a double column with 1.5% of NPGS on Chromaton N-AW-HMDS (0.125-0.160 mm, Chemapol). The rate of flow of argon was 60 ml/min. The temperature of the thermostat was 160°C.

Acetylation. The deoxysugars were acetylated with acetic anhydride in pyridine. The ratio between the monosaccharide, acetic anhydride, and pyridine in equivalents was 1:2.5:4.

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TABLE 1. ^{13}C NMR Chemical Shifts of the Deoxysugars

Compound	C-1	C-2	C-3	C-4	C-5	C-6	MeO–
I	103,9	74,1	76,3	75,7	72,6	17,3	57,8
II	101,2	39,1	77,1	70,8	72,6	17,6	57,1
III	106,0	68,6	39,0	70,4	76,4	17,3	57,5
IV	104,2	75,6	71,2	40,6	69,2	20,5	57,6

The mixture was kept at 20°C for 10 h and was then diluted with a tenfold volume of cold water and, after 20 min, it was extracted twice with an equal volume of chloroform. The combined chloroform extract was washed with 2 N HCl and with saturated sodium bicarbonate solution and was filtered through a paper filter and evaporated.

Deacetylation. A solution of deoxysugar acetate in absolute methanol (10 ml per 1 g) at 20°C was treated with a 0.4 N solution of sodium methanolate in an amount of 0.03 equivalent of sodium methanolate to 1 equivalent of acetate. The mixture was kept at 60°C for 5 min (with monitoring by TLC). The solution was cooled, deionized with KU-2 cation-exchange resin (H^+), filtered, and evaporated.

Methyl 2,3,4-Tri-O-acetyl-6-deoxy-β-D-glucopyranoside (V). With stirring at 60°C, N-bromosuccinimide (12.1 g, 68 mmole) was added over 0.5 h to a solution of methyl β-D-glucopyranoside [3] (6.5 g, 34 mmole) and triphenylphosphine (17.8 g, 68 mmole) in a mixture of dimethylformamide (65 ml) and toluene (65 ml), and heating was continued for another 0.5 h. The mixture was cooled, poured into chloroform (400 ml), and extracted with water (2 × 200 ml). The aqueous extracts were combined and were evaporated in vacuum, and the residue was acetylated. The syrup obtained after acetylation was purified on a column of silica gel with elution by hexane–ethyl acetate (95:5).

The yield of methyl 2,3,4-tri-O-acetyl-6-bromo-6-deoxy-β-D-glucopyranoside was 6.6 g (51.2%), mp 115-116°c, $[\alpha]_D^{20}$ −6.5° (c 0.5; chloroform). According to the literature [4]: mp 117-118°C, $[\alpha]_D^{20}$ −3.9° (chloroform). The product obtained (3.8 g, 10 mmole) was dissolved in ethanol (100 ml) containing triethylamine (1.5 g, 15 mmole) and 10% Pd/C (1 g) and was hydrogenated at room temperature for 48 h. The solution was filtered, and the filtrate was evaporated in vacuum to a syrup, which was purified on a column of silica gel with elution by the hexane–ethyl acetate (9:1) system. The yield of the quinovoside acetate (V) was 2.2 g (73%), mp 96-97°C, $[\alpha]_D^{20}$ −7.0° (c 0.6; chloroform), R_f 0.42, R_T 2.75. According to the literature [5]: mp 94-100°c, $[\alpha]_D^{20}$ −20.2° (alcohol). After deacetylation, methyl 6-deoxy-β-D-glucopyranoside (I) was obtained. mp 132-133°C, $[\alpha]_D^{20}$ −39.7° (c 0.8; methanol). According to the literature [6]: mp 130-131°c, $[\alpha]_D^{20}$ −42° (water).

Partial Deoxygenation. The methyl 2,3,4-tri-O-acetyl-6-deoxy-β-D-glucopyranoside (V) (1.4 g) in hexamethylphosphorotriamide (70 ml) containing 3.5 ml (5%) of water was irradiated in quartz test-tubes (1.5 × 15 cm) with two OKN-11-M quartz irradiators for 10 h, 1.05-ml portions of water being added to the reaction mixture after every 2 h. The resulting solution was treated with 70 ml of water and was extracted with hexane (3 × 150 ml). The extract so obtained was filtered through a paper filter, and the filtrate was evaporated to a syrup, which was chromatographed on a column (1 × 30 cm) of silica gel in the hexane–ethyl acetate (95:5) system.

This gave methyl 3,4-di-O-acetyl-2,6-dideoxy-β-D-arabino-hexopyranoside (VI). Yield 0.06 g (5.3%), R_f 0.59, R_T 0.71. Deacetylation led to methyl 2,6-dideoxy-β-D-arabino-hexapyranoside (II), syrup, $[\alpha]_D^{20}$ −47.3° (c 0.7; chloroform), R_f 0.25, R_T 1.33. According to the literature [7]: $[\alpha]_D^{20}$ + 63.0° (methanol) for the L-enantiomer.

The yield of the combined acetates of methyl 3,6-dideoxy-β-D-ribo- and 4,6-dideoxy-β-D-xylo-hexopyranosides was 0.56 g (49.6%), 0.21 g (15%) of the initial methyl 6-deoxy-β-D-glucopyranoside acetate (V) being recovered. The mixture of dideoxysugar acetates (VI) and (VIII) was deacetylated and the products were chromatographed on a column (1 × 30 cm) of silica gel in the chloroform–methanol (95:5) system. This gave methyl 4,6-dideoxy-β-D-xylo-hexopyranoside (IV). Yield 0.17 g (46%), mp 103-104°c, $[\alpha]_D^{20}$ −60.4° (c 1.2; chloroform), R_f 0.31, R_T 0.31, R_T 0.58. According to the literature [8]: mp 104-105°C, $[\alpha]_D^{20}$ −55.8° (water). The methyl 2,3-di-O-acetyl-4,6-dideoxy-β-D-xylo-hexopyranoside (VIII) had R_f 0.54, R_T 0.79.

Methyl 3,6-dideoxy-β-D-ribo-hexopyranoside (III). Yield 0.09 g (24%), mp 50-51°C, $[\alpha]_D^{20}$ −58.8° (c 2.4; chloroform), R_f 0.22, R_T 1.08. According to the literature [9]: mp 51-53°C, $[\alpha]_D$ −64° (water). Methyl 2,4-di-O-acetyl-3,6-dideoxy-β-D-ribo-hexopyranoside (VII) had R_f 0.56, R_T 1.00 (6.9 min).

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HYDROXY ACIDS OF THE RESERVE LIPIDS OF Galeopsis bifida

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The structures of fatty monohydroxy acids of the lipids of the seeds of Galeopsis bifida Boenn. have been studied by the methods of chromatographic, spectral, and chemical analysis. (31) Acids with chain lengths of from 14 to 20 carbon atoms, with from 0 to 3 double bonds, and with the hydrolyls in positions characteristic for the products of the direct hydroxylation and the lipoxygenase and photosensitized oxidation of unsaturated fatty acids were detected. Of them, the 13-OH-9Z, 11E-17:2, the 15-OH-9, 12-18:2, the 16-OH-9, 12-18:2, and 17-OH-11, 14-20:2 acids were new, while this is the first time that the 15-OH-9Z, 12Z, 16E-18:3 acid has been described as a natural compound. The behavior of the TMS derivatives of the hydroxy acids on a polyester phase in GLC is discussed.

We have previously detected epoxy-, oxo-, and hydroxyacyldiacylglycerols with a complex set of oxygenated acyls in the lipids of the seeds of Galeopsis bifida Boenn. (family Lamiaceae) [1], and their detailed analysis has permitted the revelation of new fatty oxo acids [2] and epoxy acids [3]. Of the monohydroxy acids (HAs) of the hydroxyacyldiacylglycerols (H-TAGs) we succeeded in identifying two isomeric 12(9)-hydroxyoctadeca-9Z(12Z)-enoic and two isomeric 9(13)-hydroxyoctadeca-10E, 12Z(9Z-11E)-dienoic acids [1]. In the present paper we give the results of a further study of the composition and structure of the HAs of the reserve lipids of G. bifida and discuss possible routes of their biosynthesis.

The H-TAGs were isolated from the total lipids by a combination of CC and TLC, and their mild alkaline hydrolysis gave a mixture of unsubstituted and hydroxylated fatty acids. This mixture, in the form of methyl esters (MEs), was separated by preparative TLC into the MEs of unsubstituted acids and two fraction of HAMEs. The first fraction (1, R_f 0.56, 0.8% of the weight of the total lipids) consisted of isomeric saturated, monoenoic, and dienoic acids, and the second fraction (2, R_f 0.54, 1.5%) of isomeric dienoic and trienoic HAs. The ratio of the weights of the three fractions was 4.7:1.28:1.0 and corresponded to the structure of the initial H-TAGs with one residue of unoxidized and two residues of

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