SYNTHESIS OF METHYL 2,6- AND 3,6-DIDEOXY-α-L-ARABINO-HEXOPYRANOSIDES AND METHYL 4,6-DIDEOXY-α-L-LYXO-HEXOPYRANOSIDE

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A convenient method of synthesizing methyl 2,6- and 3,6-dideoxy-α-L-arabino-hexopyranosides and of methyl 4,6-dideoxy-α-L-lyxo-hexopyranoside is proposed.

Deoxysugars are widespread in nature. Dideoxysugars, in particular, are present as components of cardiac glycosides, lipopolysaccharides, and antibiotics. In the study of the structure of lipopolysaccharides of Gram-negative microorganisms the necessity arises for authentic samples of 3,6-dideoxysugars. The known syntheses of deoxysugars have many stages, are laborious, and frequently require expensive reagents. The most convenient method of introducing a deoxy unit into a sugar molecule may be considered to be that proposed in recent years of the reduction of sugar esters by solvated electrons obtained on irradiating a mixture of hexamethylphosphorotriamide and water. Acetates and pivalates have been used successfully for these purposes [1]; at the same time, benzoates, formates and thiocarbonates give lower yields of reduction products [2].

In order to eliminate the multistage nature connected with the preliminary protection of the hydroxy groups, we have used an approach based on the partial deoxygenation of a methyl glycoside acetate and chromatography of the deoxysugars obtained. The differences in the chromatographic mobilities of the dideoxysugars obtained permitted the complete separation of the deoxygenation products of methyl α-L-rhamnopyranoside by column chromatography and the isolation in the individual state of methyl 2,6- and 3,6-dideoxy-α-L-arabino-hexopyranosides and methyl 4,6-dideoxy-α-L-lyxo-hexopyranoside. The total yield of methyl glycosides of the dideoxysugars was 40%. Identification, performed with the aid of ^{13}C NMR spectroscopy, agreed with that given previously [3].

EXPERIMENTAL

Melting points were measured on a Boetius instrument. Specific rotations were determined on a Perkin-Elmer M141 polarimeter. ^{13}C NMR spectra were obtained on a Bruker HZ-90E spectrometer. Chemical shifts are given in parts per million (ppm) and were measured relative to CH_3OH (δ = 49.6 ppm). D_2O was used as the solvent. TLC was conducted on silica gel L 5-40 μm (Chemapol) in the chloroform–methanol (95:5) system. Silica gel L 40-100 μm (Chemapol) was used for column chromatography.

Synthesis of Dideoxysugars. Methyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranoside (1.8 g) was dissolved in 180 ml of hexamethylphosphorotriamide (redistilled in vacuum at 80°C/2 mm Hg) and 5.5 ml of water, and the solution was irradiated in quartz test tubes (1.5 × 15 cm) with two OKN-11-M quartz irradiators for 12 h. The resulting solution was treated with 180 ml

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

Compound	C1	C2	C3	C4	C5	C6	OMe
Methyl 2,6-dideoxy-α-L-arabino-hexopyranoside	98,8	37,6	68,6	77,3	68,6	17,5	55,1
Methyl 3,6-dideoxy-α-L-arabino-hexopyranoside	100,3	68,9	34,3	70,3	67,5	17,5	55,2
Methyl 4,6-dideoxy-α-L-lyxo-hexopyranoside	100,2	68,4	65,8	35,3	65,8	20,7	55,2

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of water and was extracted three times with 360-ml portions of hexane. The extract obtained was filtered through a paper filter and was evaporated, and the residue was separated by chromatography on a column (1 × 30 cm) of silica gel in the hexane–ethyl acetate (95:5) system to eliminate degradation products and traces of hexametapol. The total yield of dideoxysugars was 0.59 g, R_f 0.42 in the hexane–ethyl acetate (1:1) system. The mixture of dideoxysugar acetates obtained (0.59 g) was dissolved in 6 ml of absolute methanol, and 0.2 ml of a 0.4 N solution of sodium methanolate in methanol was added. The mixture was kept at 60°C for 5 min (with TLC monitoring). The resulting solution was cooled, deionized with KU-2 ion-exchanger (H^+), and filtered and evaporated. The yield of syrupy product was 0.39 g. This mixture was deposited on a column (1 × 30 cm) containing silica gel and was eluted with the methanol–chloroform (1:50) system.

The following products were obtained as a result: Methyl 4,6-Dideoxy-α-L-lyxo-hexopyranoside. Yield 0.12 g (31.3%), R_f 0.24; mp 97-98°C, $[\alpha]_D^{20}$ −95.4° (c 0.6; methanol). According to the literature: mp 99-100.5°C, $[\alpha]_D^{20}$ −83° (chloroform) [3].

Methyl 2,6-Dideoxy-α-L-arabino-hexopyranoside. Yield 0.16 g (41%). R_f 0.21; syrup, $[\alpha]_D^{20}$ −170.5° (c 0.6; methanol). According to the literature: syrup, $[\alpha]_D^{23}$ −146° (acetone) [4].

Methyl 3,6-Dideoxy-α-L-arabino-hexopyranoside. Yield 0.06 g (15%) R_f 0.15; mp 85-86°C; $[\alpha]_D^{20}$ −143.8° (c 0.7; methanol). According to the literature: mp 82-84°C, $[\alpha]_D^{20}$ −127.7° (chloroform) [5].

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PHOSPHOLIPID COMPOSITION OF PROSTAGLANDIN EXTRACTS OF SOME MARINE INVERTEBRATES WITH DIFFERENT DEGREES OF PROSTAGLANDIN-LIKE ACTIVITY

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The qualitative and quantitative compositions of the phospholipids of eight species of marine invertebrates have been determined. A correlation has been shown between the amounts of particular phospholipids and the prostaglandin-like activities of the extracts. The activities of the extracts have been expressed quantitatively as a function of the set of phospholipids in them.

It is known that phospholipids (PhLs) are synergists of the prostaglandins (PGs) [1-3]. The creation of drugs is based upon this property of them both in the Soviet Union and abroad. In 1983, Japanese workers created an antitumoral drug consisting of a complex of PGs of group A with PhLs [4]. An improvement in the pharmacological action of PGE_1 on its inclusion into lipid microspheres containing egg PhLs has been shown [2, 5]. L. M. Braginsteva and her colleagues have proposed a drug consisting of PGE_2 and $PGF_{2\alpha}$ enriched with PhLs and with unsaturated fatty acids and tocopherol [6-8]. The capacity of the PGs for forming complexes with phosphatidylcholine (PhC) and cholesterol has been established [9].

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