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Note

Derivatives of 5-deoxy-5-seleno-D-xylose

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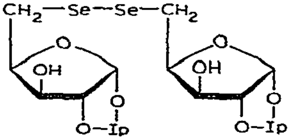
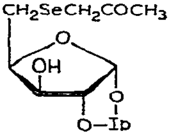
Methanolysis of 5,5′-diselenobis(5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose) (**1**) gave a mixture of anomeric glycosides as the main product[1]. Treatment of this mixture with acetone, copper sulfate, and sulfuric acid gave a totally unexpected result. The reaction product consisted of a major component and several minor products. The major component was separated by chromatography and was a crystalline compound. I.r. spectroscopy showed the presence of a hydroxyl and a carbonyl group. N.m.r. spectroscopy indicated the presence of the furanose ring and an isopropylidene group. Two singlets were also present in the spectrum, and their integration and position suggested the presence of an acetonyl group. Mass spectrometry showed a probable molecular ion at *m/e* 310 and the presence of one atom of selenium per molecule (from the intensities of the peaks containing ^{78}Se and ^{80}Se, *ca.* 1:2). A possible structure for this compound is that of 5-acetonylseleno-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**2**). Further confirmation of this structure was obtained by reductive removal of selenium from **2** with Raney nickel which gave 5-deoxy-1,2-*O*-isopropylidene-D-xylofuranose[2]. Also, reexamination of the n.m.r. spectrum of **1** in alkaline deuterium oxide showed that the two singlets associated with the acetonyl group collapsed as expected. Treatment of **1** with acetone in the presence of acid slowly formed the same compound **2**. Compounds of the type $ArSeCH_2COCH_3$ have been synthesized[3] from the corresponding selenolyl bromide (ArSeBr) with potassium thiocyanate in acetone. Treatment of **1** with bromine gave the corresponding selenolyl bromide which was treated without purification with potassium thiocyanate in acetone. The reaction product was identical with compound **2**. The action of acetone and sulfuric acid on another diselenide, 5,5′-diselenobis(methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside)[4] was also investigated. The reaction proceeded more slowly, but the resulting product was shown to have a structure of the same type as that of **2**.



1



2

EXPERIMENTAL

Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Column chromatography was performed on silica gel (60–200 mesh). I.r. spectra were determined on a Perkin–Elmer 700 spectrophotometer and n.m.r. spectra on a Varian T-60 spectrometer, chemical shifts being recorded in p.p.m. units with tetramethylsilane as the internal standard. Mass spectra were determined with a Hitachi–Perkin–Elmer RMU-7 mass spectrometer. Evaporations were conducted under diminished pressure at a bath temperature below 50°.

*5,5'-Diselenobis(methyl 5-deoxy-α,β-*D*-xylofuranoside)* (**3**). — A solution of 5,5'-diselenobis(5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose) (**1**, 1.5 g) in 1% methanolic hydrogen chloride (60 ml) was heated under reflux for 45 min and then neutralized with lead carbonate, filtered, and evaporated to a syrup (1.5 g). This was applied to a column of silica gel with 1:4 methanol–benzene as the eluent to give a chromatographically homogeneous syrup (0.84 g); n.m.r. (deuterium oxide) showed the presence of an anomeric mixture of glycosides (α- to β-anomer ratio, 4:5).

Anal. Calc. for $C_{12}H_{22}O_8Se_2$: C, 31.85; H, 4.87. Found: C, 31.82; H, 4.90.

*5-Acetonylseleno-5-deoxy-1,2-O-isopropylidene-α-*D*-xylofuranose* (**2**). — *From* **3**. A mixture of **3**, acetone (40 ml), anhydrous copper sulfate (4 0 g), and sulfuric acid (0.05 ml) was stirred overnight at room temperature. The suspension was filtered, the filtrate neutralized with calcium hydroxide, filtered, and evaporated to a syrup (1 35 g). This was applied to a column of silica gel with 3:37 methanol–benzene as the eluent to give a crystalline compound (0.68 g), which was recrystallized from ethyl acetate–petroleum ether (40–60°), m.p. 102–103°; $[\alpha]_D^{20}$ −17° (*c* 1.21, chloroform); i.r. data: $\nu_{max}^{CHCl_3}$ 3350 (OH), 1685 cm^{-1} (C=O); n.m.r. data (chloroform-*d*): δ 1.37 (6-proton doublet, *J* 12.0 Hz, CMe_2, 2.37 (3-proton singlet, $-CH_2COCH_3$), 2.68–3.02 (3-proton complex), 3.33 (2-proton singlet, $-CH_2COCH_3$), 4.05–4.35 (2-proton complex), 4.51 (1-proton doublet, *J* 4.0 Hz, H-2), 5.86 (1-proton doublet, *J* 4.0 Hz, H-1); addition of 10% potassium hydroxide in deuterium oxide caused the collapse of the signals at δ 2.37 and 3.33; m.s: 310 (308) (M^+), 295 (293) ($M^+ - CH_3$); 252 (250) ($M^+ - 58$).

Anal. Calc. for $C_{11}H_{18}O_5Se$: C, 42.52; H, 5.83. Found: C, 42.58; H, 5.86.

From **1**. (*a*) A mixture of **1** (1.5 g), acetone (60 ml), anhydrous copper sulfate (6.0 g), and sulfuric acid (0.08 ml) was stirred for 6 days at room temperature. The suspension was treated as just described and gave a partly crystalline product which crystallized from ethyl acetate–petroleum ether (40–60°) and from dilute ethanol to give unchanged **1** (0.50 g). The mother liquor from the first crystallization was evaporated to give **2** (0.85 g) as just described, m.p. 102–103° (after recrystallization).

(*b*). A 10% solution of bromine in dry chloroform (3.2 ml) was slowly added to a cooled (ice) solution of **1** (1.0 g) in dry chloroform (10 ml). After approximately 5 min a solid separated, the reaction mixture was kept for a further 15 min and then was diluted with dry petroleum ether (40–60°, 50 ml). The solid was filtered off, washed with petroleum ether, and added without purification to dry acetone (50 ml) and potassium thiocyanate (5.0 g). The mixture was stirred overnight at room temperature and then evaporated, and the residue extracted with chloroform and water. The chloroform phase was evaporated to give a solid (1.0 g). Crystallization from ethyl acetate–petroleum ether (40–60°) gave a solid, m.p. 102–103°, identical to the compound just described.

Removal of selenium from **2**. — Compound **2** (0.50 g), ethanol (25 ml), and Raney nickel (*ca.* 5 g) were heated under reflux with stirring overnight. The reaction mixture was filtered and the nickel repeatedly washed with hot ethanol. The filtrate was evaporated to a syrup (0.20 g) which crystallized from petroleum ether (40–60°) to give crystals, m.p. 67° (unchanged on admixture with 5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose[2]).

*Action of acetone on 5,5'-diselenobis(methyl 5-deoxy-1,2-*O*-isopropylidene-β-D-ribofuranoside).* — The diselenide[4] (1.0 g), acetone (40 ml), anhydrous copper sulfate (4.0 g), and sulfuric acid (0.05 ml) were stirred for 7 days at room temperature. The reaction mixture was treated as just described to give a syrup (1.10 g). This was applied to a column of silica gel which was eluted with 1:39 methanol–benzene to give a homogeneous syrup (0.62 g) $[\alpha]_D^{18}$ −44° (*c* 4.4, chloroform); i.r. datum: ν_{max}^{film} 1695 cm^{-1} (C=O); n.m.r. data (chloroform-*d*): δ 1.42 (6-proton doublet, *J* 9.0 Hz, CMe$_2$), 2.36 (3-proton singlet, $-CH_2COCH_3$), 2.64–2.87 (2-proton complex), 3.30 (2-proton singlet, $-CH_2COCH_3$), 3.38 (3-proton singlet, OMe), 3.92–4.53 (1-proton complex), 4.66 (2-proton singlet), 4.96 (1-proton singlet, H-1); m.s.: 324 (322) (M^+), 309 (307) ($M^+ - 15$), 292 (290) ($M^+ - CH_3OH$).

Anal. Calc. for $C_{12}H_{20}O_5Se$: C, 44.59, H, 6.19. Found: C, 44.43, H, 6.18.

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