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## Note

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# The 2,3-*O*-isopropylidene-1,5-*O*-methylene and 1,5-*O*-methylene derivatives of β-D-ribofuranose

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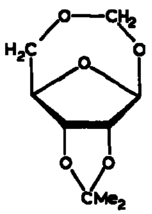
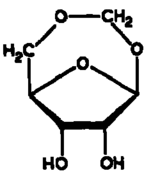
The acid-catalysed reaction of monosaccharides with acetone under thermodynamic control usually gives one or mainly one *O*-isopropylidene derivative[1,2]. Ribose is an exception and yields as many as four derivatives[3]. On acetonation of ribose in our laboratory, it was observed that, in the presence of formaldehyde, these acetals were replaced by a single, new compound. The identification of this compound and a product obtained from it by selective hydrolysis is now reported.

Treatment of D-ribose with acetone–sulphuric acid in the presence of slightly more than 1 equiv. of formaldehyde gave a crystalline product (**1**) in good yield. The mass spectrum showed that **1** was an *O*-isopropylidene-*O*-methylene derivative, and the spectrum was very similar to that from 1,5-anhydro-2,3-*O*-isopropylidene-β-D-ribofuranose[4] except for an additional peak at *m/z* 187 ($M^+ -$ Me). The chemical shift (112.32 p.p.m.) of the isopropylidene acetal carbon resonance in the $^{13}$C-n.m.r. spectrum of **1** is characteristic[5,6] of C-2 in a 2,2-dimethyl-1,3-dioxolane group *cis*-fused to a furanose ring. The $^{1}$H-n.m.r. coupling constants are almost the same as those repored[7] for 1,5:2,3-di-*O*-isopropylidene-β-D-ribofuranose, indicating **1** to be 2,3-*O*-isopropylidene-1,5-*O*-methylene-β-D-ribofuranose.

Treatment of **1** with aqueous acetic acid gave, as the major product, 1,5-*O*-methylene-β-D-ribofuranose (**2**), which was isolated by chromatography. The $^{13}$C-n.m.r. spectrum of **2** showed that the methylene group was intact, and the $^{1}$H-n.m.r. spectrum showed coupling constants not very different from those in the



**1**



**2**

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spectrum of **1** with additional coupling due to HO-2,3. Treatment of **2** with acetone–copper sulphate regenerated **1**.

## EXPERIMENTAL

*General methods.* — G.l.c. was performed on a Perkin–Elmer F-11 gas chromatograph, equipped with a flame-ionisation detector and a glass column (6 ft × 2 mm i.d.) filled with OV-225 (3%) on Supelcoport 100/120; temperature programme, 4°/min from 90°→150°. E.i. (70 eV)-mass spectra were obtained using a Micromass 12 F instrument with an ion-source temperature of 200° and an accelerating voltage of 4 kV. N.m.r. spectra were recorded with a Jeol JNM GX-270 spectrometer. T.l.c. was performed on Silica Gel G with chloroform–methanol (15:1) and detection with diphenylamine–aniline–phosphoric acid[8].

*2,3-O-Isopropylidene-1,5-O-methylene-β-D-ribofuranose* (**1**). — D-Ribose (1.2 g) was stirred with acetone (100 mL) for a few min, and acetone (50 mL) containing conc. sulphuric acid (3 mL) and aqueous 37% formaldehyde (0.75 mL) was then added. The stirring was continued for 2 h, the solution was neutralised with solid sodium hydrogencarbonate, filtered, and concentrated under reduced pressure, and the residue was partitioned between hexane (150 mL) and water (10 mL). The hexane layer was extracted with water (10 mL), the combined aqueous solutions were extracted with hexane (6 × 25 mL), and the combined hexane solutions (300 mL) were dried ($Na_2SO_4$). A single compound was detected by g.l.c. ($T$ 8.2 min) and t.l.c. ($R_F$ 0.80). The hexane solution was filtered and concentrated to a small volume, from which **1** crystallised (1.32 g, 82%), m.p. 114–116°, $[\alpha]_D^{20}$ −17° ($c$ 2, chloroform). N.m.r. data ($CDCl_3$): $^1H$ (270 MHz), $\delta$ 1.32 (s, 3 H, Me), 1.49 (s, 3 H, Me), 3.52 (dd, 1 H, H-5), 3.93 (d, 1 H, H-5′), 4.53 (d, 1 H, H-4), 4.62, 4.66 (2 d, 2 H, H-2,3), 4.73, 4.99 (2 d, 2 H, $OCH_2O$), 5.48 (s, 1 H, H-1); $J_{1,2}$ ~0, $J_{2,3}$ 5.86, $J_{3,4}$ ~0, $J_{4,5}$ 2.2, $J_{4,5'}$ ~0, $J_{5,5'}$ 12.5, and $J_{OCH_2O}$ 7 Hz; $^{13}C$, $\delta$ 112.32 ($CMe_2$), 105.54 (C-1), 91.95 ($OCH_2O$), 88.36, 87.61, 81.72 (C-2,3,4), 72.31 (C-5), 26.34, 24.80 (2 $CH_3$). Mass spectrum: $m/z$ 187 (45%), 157 (27), 114 (5), 101 (5), 86 (8), 85 (21), 81 (6), 73 (8), 71 (10), 69 (34), 68 (45), 59 (48), 57 (43), 43 (100).

*Anal.* Calc. for $C_9H_{14}O_5$: C, 53.5; H, 7.0. Found: C, 53.6; H, 7.0.

*1,5-O-Methylene-β-D-ribofuranose* (**2**). — A solution of **1** (0.4 g) in aqueous 70% acetic acid (10 mL) was kept for 4 h at 65–70°. T.l.c. then revealed a product with $R_F$ 0.2 in addition to D-ribose and **1**. The solution was concentrated under reduced presure at 40°, the residue was partitioned between chloroform (10 mL) and water (10 mL), the aqueous solution was concentrated under reduced pressure, and the residue was extracted with chloroform–methanol (4:1, 8 mL). The extract was added to a column (12 × 2 cm) of silica gel and eluted with chloroform–methanol (6:1, 50–70 mL) to give **2** (90 mg, 28%), m.p. 125–128°, $[\alpha]_D^{20}$ −13° ($c$ 1, methanol). N.m.r. data ($CDCl_3$): $^1H$, $\delta$ 2.54, 2.60 (2 d, 2 H, HO-2,3), 3.57 (dd, 1 H, H-5), 3.92 (d, 1 H, H-5′), 4.17 (t, 1 H, H-2), 4.37 (t, 1 H, H-4), 4.46 (m, 1 H, H-3), 4.81, 4.91 (2 d, 2 H, $OCH_2O$), 5.37 (s, 1 H, H-1); $J_{1,2}$ ~0, $J_{2,HO-2}$ 5.8, $J_{2,3}$ 5.5, $J_{3,HO-3}$ 6.6, $J_{3,4}$ 1, $J_{4,5}$ 2.2, $J_{4,5'}$ ~0, $J_{5,5'}$ 12.5, $J_{OCH_2O}$ 7.3 Hz; $^{13}C$, δ 106.99 (C-1), 90.96 ($OCH_2O$), 89.77 (C-4), 77.90, 72.21 (C-2,3), 71.38 (C-5).

*Anal.* Calc. for $C_6H_{10}O_5$: C, 44.4; H, 6.2. Found: C, 44.7; H, 6.4.

Treatment of a small amount of **2** with acetone (10 mL) and copper sulphate for 30 min gave, after filtration of the solution and evaporation of the acetone, **1**, m.p. 117°.

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