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Note

Identification of a [6-*O*-(hydroxypropyl)-D-glucosyl]-D-glucose as a faecal metabolite of *O*-(hydroxypropyl)starch in the rat

D. C. LEEGWATER

Central Institute for Nutrition and Food Research TNO, Zeist (The Netherlands)

AND J. W. MARSMAN

Institute for Organic Chemistry TNO, Utrecht (The Netherlands)

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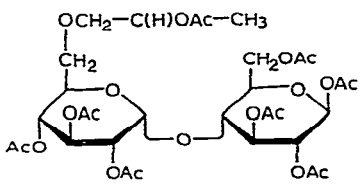
Recently, we reported[1,2] on the isolation and identification of a [2-*O*-(2-hydroxypropyl)-D-glucosyl]-D-glucose as the major faecal metabolite in rats of *O*-(hydroxypropyl)starches having a degree of substitution <0.11.

We now describe the identification of a further *O*-(hydroxypropyl)-D-glucosyl-D-glucose. The compound was isolated as its amorphous, β-anomeric peracetate (**1**) in a yield of ~2% from the acetylated, faecal metabolites by repeated column chromatography on silicic acid as reported earlier[1]. In the final purification, 10-mm (i.d.) columns packed with 8 g of adsorbent were used. The R_F value of **1** was slightly larger than that of the peracetate of the major metabolite (**2**).



1

The structure of **1** was elucidated by p.m.r. analysis (100 MHz, 70°) of a solution in chloroform-*d*. The integral was in fair agreement with that expected for a monohydroxypropyl-D-glucosyl-D-glucose octa-acetate, *viz.* 3 protons at τ 8.81 for the methyl group of the acetoxypropyloxy moiety, 24 protons at τ 7.8–8.1 for the acetyl methyl groups, and 18 protons in the low-field portion (expected: 17 protons). In accordance with this assignment, characteristic peaks at *m/e* 677, 389, 331, and 101 were present in the mass spectrum of **1** (*cf.* Ref. 1).

The expanded, low-field portion of the spectrum is shown in Fig. 1. The assignments are based on comparison of the p.m.r. data of **1** with those of β-maltose octa-acetate[1], supported by the results of spin-decoupling and spin-tickling experiments in which the doublet of the methyl group of the acetoxypropyloxy moiety

(τ 8.81), the doublet of the β-anomeric proton (τ 4.28, J 7.8 Hz) of the reducing D-glucopyranose moiety, and the doublet of the α-anomeric proton (τ 4.67, J 4.0 Hz) of the non-reducing D-glucopyranose moiety were taken as starting points.

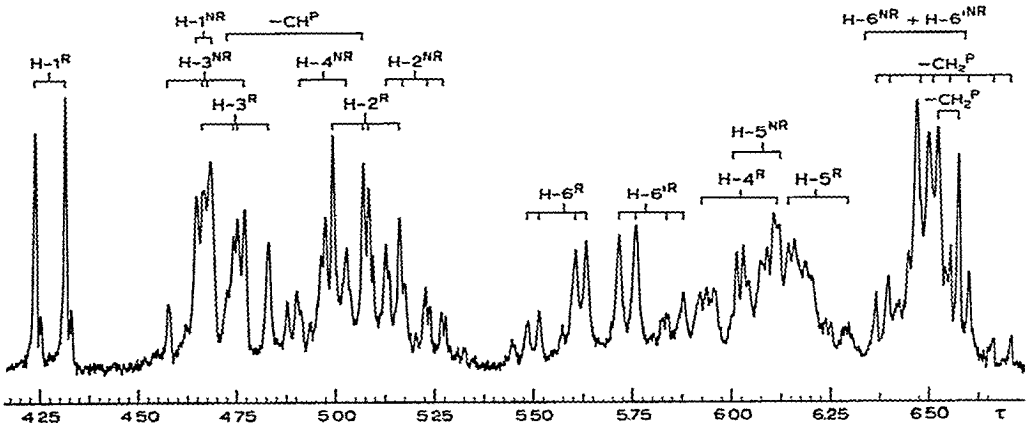


Fig. 1. Expanded low-field portion of the 100-MHz spectrum of **1** in chloroform-*d* at 70°. The protons of the reducing and non-reducing D-glucopyranose moieties and those of the acetoxypropyloxy moiety are designated by the suffixes R, NR, and P, respectively.

The chemical shifts of the methine proton of the acetoxypropyloxy group (τ 4.9) and the methylene protons of this moiety (centred at τ 6.5 and giving rise to a double pair of quartets) were consistent with an ether function of the type R–O–CH_2–C(H)OAc–CH_3, indicating that **1** is a 2-hydroxypropyl derivative (*cf.* Ref. 1).

With the exception of the methylene protons at C-6 of the non-reducing D-glucopyranose moiety which absorbed at τ 6.5, the chemical shifts of the protons of both the reducing and the non-reducing D-glucopyranose moieties agreed (within 0.06 p.p.m.) with those reported for the corresponding protons of β-maltose octa-acetate[1]. The presence of the signals for the C-6 protons at τ 6.5 was established by decoupling experiments; a detailed analysis was not feasible because the signals remained, for the greater part, concealed by the signals of the methylene protons of the acetoxypropyloxy moiety.

Since only the protons at C-6 of the non-reducing D-glucopyranose moiety absorbed at a considerably (~0.65 p.p.m.) higher field, and also because their shift was as expected for a methylene group in an ether function, it was concluded that the acetoxypropyloxy group was attached to this carbon atom*. Thus **1** was identified as 4-*O*-[6-*O*-(2-hydroxypropyl)-α-D-glucopyranosyl]-D-glucopyranose octa-acetate.

As noted above, the methylene protons of the acetoxypropyloxy moiety gave rise to a double pair of quartets. Doubled signals were also observed for H-2 and H-4

*The presence of peaks at 360, 301, and 300 in the mass spectrum of **1** provided further evidence that the acetoxypropyl group is attached to the non-reducing moiety (*cf.* Ref. 1).

of the non-reducing moiety and for most of the other protons after addition of the paramagnetic shift reagent[3] $Eu(FOD)_3$. This indicates that **1**, just like **2**, is a mixture of *S* and *R* diastereoisomers (*cf.* Ref. 1).

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