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## Note

### Gas chromatographic determination of some methyl $\alpha$ -D-glucopyranoside pentyloxymethyl ethers

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In previous work<sup>1-6</sup> we discussed the synthesis and properties of non-ionic surfactants having sucrose or glucose as the hydrophilic part of the surfactant molecule and an alkyloxymethyl group as the hydrophobic part. Thin-layer chromatography<sup>7,8</sup> was used to determine the relative proportions of the mono-, di- and tri-substituted derivatives. However, the proportions of the individual positional isomers were not determined.

The aim of this work was to determine the chromatographic conditions for separating the positional isomers of methyl mono-O-pentyloxymethyl- $\alpha$ -D-glucopyranoside and methyl di-O-pentyloxymethyl- $\alpha$ -D-glucopyranoside, the main products in the reaction of methyl  $\alpha$ -D-glucopyranoside with pentyloxymethyl chloride.

## EXPERIMENTAL

### *Materials*

The products from the reaction of methyl  $\alpha$ -D-glucopyranoside with pentyloxymethyl chloride, the standard isomers of methyl mono-O-pentyloxymethyl- $\alpha$ -D-glucopyranoside having a pentyloxymethyl group at the 2, 3, 4 or 6 positions and a mixture of the positional isomers of methyl di-O-pentyloxymethyl- $\alpha$ -D-glucopyranoside, were obtained in our laboratory. Methyl  $\alpha$ -D-glucopyranoside (Fluka, Buchs, Switzerland) was used as substrate.

The products were analysed as their trimethylsilyl derivatives. A mixture of anhydrous pyridine, hexamethyldisilazane and trimethylchlorosilane (9:3:1) was used as solvent.

### *Chromatographic separation*

A Jeol 1100 TFP gas chromatograph equipped with a flame-ionization detector and coupled with a Takeda Riken TR-2215A electronic integrator was used. For the separation, glass columns (2 m  $\times$  3 mm I.D.) were used with SE-30, OV-1, OV-17 and OV-25 (3%) as the liquid phases. Gas-Chrom Q (80-100 mesh) was used as the support. Helium was used as the carrier gas with a flow-rate of 1 cm<sup>3</sup>/sec. The detector and injector temperatures were 555  $\pm$  2 and 565  $\pm$  5°K, respectively. The column temperature was raised from 453 to 533°K at a rate of 2°K/min.

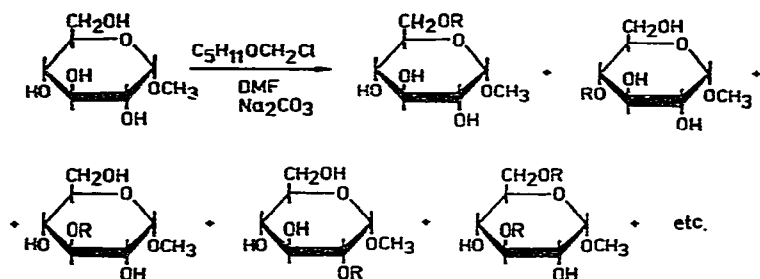


Fig. 1. Reaction scheme.

## RESULTS AND DISCUSSION

In the reaction of methyl  $\alpha$ -D-glucopyranoside with pentyloxymethyl chloride the products may contain four different positional monoether isomers, six diether isomers, four triether isomers and one tetraether (Fig. 1).

When columns having OV-17 or OV-25 semi-polar phases were used we did not separate all the monoisomers: the isomers having a pentyloxymethyl group at

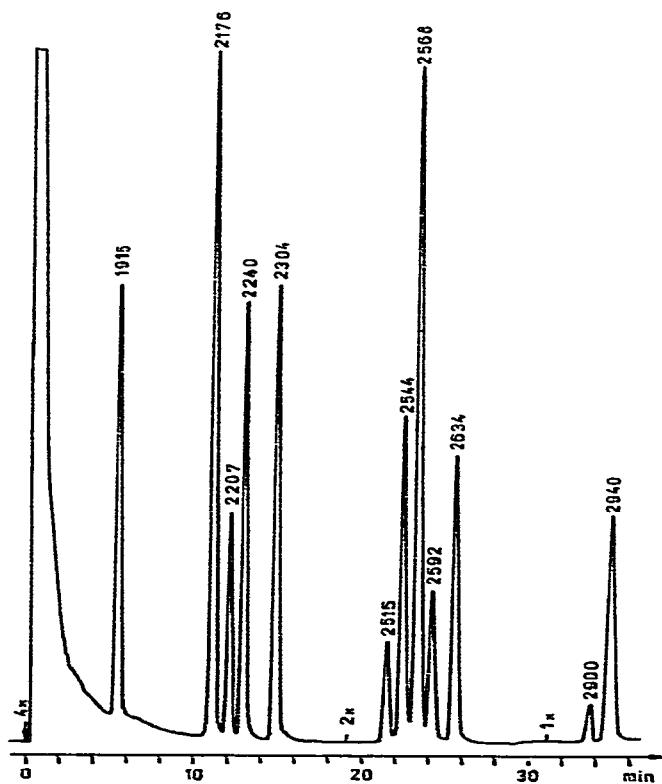
Fig. 2. Chromatogram of methyl  $\alpha$ -D-glucopyranoside pentyloxymethyl ethers.

TABLE I

RETENTION INDICES OF METHYL  $\alpha$ -D-GLUCOPYRANOSIDE PENTYLOXYMETHYL ETHERS MEASURED FOR TRIMETHYLSILYL ETHERS

<i>Compound</i>	<i>Isomer</i>	<i>Retention index</i>
Methyl $\alpha$ -D-glucopyranose		1915
Monoether	3-O-	2176
	4-O-	2207
	2-O-	2249
	6-O-	2304
Diether	3,4-O-	2515
	2,3-O- + 2,4-O-	2544
	3,6-O-	2568
	4,6-O-	2592
	2,6-O-	2634
Tri- and tetraethers	Tri- and tetraethers	2900
		2942

positions 2 and 4 eluted together. Similarly, we obtained only four partly separated peaks for the diether.

When columns having SE-30 or OV-1 phases were used we separated all four isomers of the monoether and all four isomers of the diether. Only methyl 2,3-di-O-pentyloxymethyl- $\alpha$ -D-glucopyranoside and methyl 2,4-di-O-pentyloxymethyl- $\alpha$ -D-glucopyranoside eluted together as one single peak. A somewhat better separation was obtained for the SE-30 phase (Fig. 2).

TABLE II

COMPOSITION OF THE REACTION PRODUCTS

Temperature, 320°K; N,N-dimethylformamide used as solvent. Product A = methyl  $\alpha$ -D-glucopyranoside-pentyloxymethyl chloride (2:1, mole/mole); product B = methyl  $\alpha$ -D-glucopyranoside-pentyloxymethyl chloride = (1:2, mole/mole).

<i>Compound</i>	<i>Isomer</i>	<i>Content (%)</i>	
		<i>Product A</i>	<i>Product B</i>
Monoether	3-O-	33.5	22.9
	4-O-	9.8	4.8
	2-O-	17.8	8.8
	6-O-	22.3	11.2
Diether	3,4-O-	0.9	2.1
	2,3-O- + 2,4-O-	3.2	8.0
	3,6-O-	6.6	18.8
	4,6-O-	1.5	4.7
	2,6-O-	4.4	11.8
Tri- and tetraethers		—	6.9

The first five peaks were identified by comparison with standard samples of methyl  $\alpha$ -D-glucopyranoside and methyl mono-O-pentyloxymethyl- $\alpha$ -D-glucopyranosides. Successive isomers of the diether were identified by comparison of the chromatograms (*i.e.* of the retention indices of the separated components) of the products obtained separately from four different positional isomers of the monoether. The isomers of the tri- and tetraethers were not considered.

The values of the retention indices for the separated isomers of the mono- and diethers are given in Table I. The values of the retention indices depend upon the position of the pentyloxymethyl group, especially when positions 3 and 6 are considered. The range of the retention indices, both for the mono- and diethers, is *ca.* 120–130, the smallest differences being observed for isomers substituted at the 3-, 4- or 2-positions (25–30 units).

For the separated mono- and diethers, the relative molar response is *ca.* 1 (this was checked and the error of such an assumption found to be less than 5%). The proportions of the different isomers of the mono- and diethers in two exemplary products are given in Table II.

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