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MICROPREPARATIVE GAS—LIQUID CHROMATOGRAPHY OF THE PRODUCTS OF THE PARTIAL METHYLATION OF METHYL α-L-RHAMNOPYRANOSIDE

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In a preceding paper [1] we showed the applicability of preparative gas—liquid chromatography (GLC) to the production of the methyl ethers of methyl β-D-xylopyranoside. In the present paper we give the properties and describe the conditions for the production of individual acetates of methyl ethers of methyl α-L-rhamnopyranoside by preparative gas—liquid chromatography of the products of the partial methylation of methyl α-L-rhamnopyranoside.

Under analytical conditions in columns of QF-1 and butanediol succinate (BDS) a satisfactory separation of the acetates of the methyl ethers of methyl α-L-rhamnopyranoside is achieved. The results of preparative separation with the aid of GLC and the analytical figures for the methyl ethers obtained are given in Table 1. It must be mentioned that on the QF-1 column incomplete separation of the 2,3- and 2,4-di-O-methyl ethers is observed, and on the BDS column the 3- and 4-O-methyl ethers are poorly separated and they issue as one peak from a preparative BDS column. Consequently, the QF-1 column was used as an auxiliary column only for the separation of the 3- and 4-O-methyl ethers. The load on a two-meter column containing 10% of BDS (column A) did not exceed 300 mg of the mixture, while when a mixture of the acetates of the methyl ethers of methyl β-D-xylopyranoside were used overloading of the column set in when more than 600 mg of the mixture was applied [1]. The use of a three-meter column with 10% of BDS (column B) led to the partial separation of the 3- and 4-O-methyl ethers but not sufficiently to enable these components to be collected in the pure state. The efficiency of column B was 230 plates, while the efficiency of column A was 150 plates. At the same time, even the increase in the length of the column to 3 m (column B) did not permit the load to be increased to more than 400 mg without a serious loss of efficiency. Consequently, to obtain the 3- and 4-O-methyl ethers of methyl α-L-rhamnopyranoside we used two methods. The first method consisted in subjecting to periodate oxidation the product of the partial methylation by Purdie's method of methyl α-L-rhamnospyranoside with the highest content of 3-O-methyl ether (26%). All the components of the mixture obtained were separated well by preparative GLC on a BDS column.

The second method consisted in the use of a mixture of the 3- and 4-O-methyl ethers of the rhamnoside obtained by means of preparative GLC on a BDS column for preparative GLC on a QF-1 column. Complete separation of the 3- and 4-O-methyl ethers was observed with a load on the column of 100 mg of the mixture.

The methylation of methyl α-L-rhamnopyranoside by Kuhn's method with barium oxide in the final stages of the reaction led to an accumulation of the 2,3-di-O-methyl ether in the reaction mixture, and after methylation for 40 min the reaction mixture contained mainly the 2,3-di-O-methyl ether and the permethylated rhamnoside. This enabled the load on column B to be increased to 1.0 g of this mixture.

Analytical GLC demonstrated the chromatographic purity of all the methyl ethers separated. The results of elementary and functional analysis correspond to the theoretical figures. The total degree of extraction and the coefficient of chromatographic extraction were approximately 70 and 60%, respectively.

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TABLE 1. Yields and Characteristics of the Acetates of the Methyl Ethers of Methyl α-L-Rhamnoside Obtained by Partial Methylation Followed by Separation by Micropreparative GLC

Methyl ether	$T_{2,3}$-Rha*		mp, °C	$[\alpha]_D^{20}$ (in chloroform), deg	Yield by the following methods											
					Haworth			Purdie + HIO_4			Kuhn			mixture of 3- and 4-O-methyl ethers		
	BDs	QF-1			column A			column A			column B			column B		
					obtained		analysis, %	obtained		analysis, %	obtained		analysis, %	obtained		analysis, %
					mg	%		mg	%		mg	%		mg	%	
2, 3,4	0,21	0,15	Syrup	—58,1 (*c* 4,4)	24	8,0	18,7	1	0,3	0,5	233	23,3	49,0			
3,4	0,34	0,31	Syrup	—34,4 (*c* 3,3)	9	3,0	4,9	4	1,3	3,3						
2,4	0,76	0,85	Syrup	—47,4 (*c* 2,4)	34	11,3	18,9	13	4,3	8,0						
2,3	1,00	1,00	46—47	—54,6 (*c* 1,3)	33	11,0	20,4	26	8,7	15,4	258	25,8	51,0			
3	1,41	1,63	103—140	—27.5 (*c* 1,5)	32	10,7	6,8	130	43,3	72,8				30	30,0	49,1
4	1,56	2,49	Syrup	—41,3 (*c* 1,1)			7,0							31	31,0	50,9
2	2,25	2,56	73,5—74	—74,7 (*c* 3,9)	53	17,7	22,5									
Initial rhamnoside	3,23	3,20	88—89	—67,1 (*c* 4,3)	2	0,7	0,8									
	Total yield				187	62,4	100	174	57,9	100	491	49,1	100	61	61,0	

*Retention time given relative to the acetate of methyl 2,3-di-O-methyl-α-L-rhamnopyranoside.

EXPERIMENTAL

The acetates of the methyl ethers of methyl α-L-rhamnopyranoside were shown to be identical with authentic samples by the chromatographic—mass-spectrometric method [2].

Analytical GLC. A Pye Unicam 104 instrument fitted with a flame-ionization detector and a double spiral column (0.4 × 150 cm) was used for analytical purposes. The liquid phase was QF-1 (3%) on Gas-Chrom Q (100-120 mesh). The temperature of the thermostat was 150°C, and the rate of flow of argon 60 ml/min. In addition to this, we used a Tsvet-160 instrument fitted with a flame-ionization detector and with double U-shaped column (0.3 × 100 cm). The liquid phase used was BDS (10%) on Chromosorb W (100-120 mesh). The rate of flow of argon was 60 ml/min. The temperature of the thermostat was 140°C.

Preparative GLC. For preparative purposes we used a Tsvet-3-66 instrument with a preparative attachment fitted with a flame-ionization detector. The rate of flow of argon was 300 ml/min. We used U-shaped columns with an internal diameter of 1.5 cm: A — 2 m, 10% of BDS; B — 3 m, 10% of BDS; and C — 3 m, 3% of QF-1. The support for the BDS was Chromaton N (45-60 mesh) and for the QF-1 it was Chromosorb W (45-60 mesh). The temperature of the evaporator and of the collector was 300°C. As the collectors we used straight glass tubes 6 cm long and 0.5 cm in internal diameter having constrictions at the end and attached to penicillin bulbs. The mixture of acetates of methyl ethers was introduced into the chromatograph in the form of a concentrated solution in chloroform.

Measurements. Specific rotations were measured on a Perkin—Elmer M-141 instrument, using chloroform as solvent. The melting points were measured on a Boëtius instrument.

SUMMARY

A method has been developed for obtaining acetates of the methyl ethers of methyl α-L-rhamnopyranoside by the preparative gas—liquid chromatography of the products of the partial methylation of methyl α-L-rhamnopyranoside, and the properties of the compounds isolated have been described.

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