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PARTIAL METHYLATION OF METHYL GLYCOSIDES

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We have previously studied the partial methylation of methyl β-D-xylopyranoside by various methods [1]. At the present time in view of the use of micropreparative gas–liquid chromatography (GLC) for separating the methyl ethers of methyl β-xylopyranoside from the mixtures formed in the partial methylation of methyl β-xylopyranoside [2], it appeared of interest to expand the possibilities of the method. With this aim, we have performed a partial methylation of a number of methyl glycosides by Purdie's method [3]. Using standard mixtures of methyl ethers it has been shown that the amounts of the individual methyl ethers are proportional to the areas of the peaks, and therefore no calibration coefficients were used.

On the partial methylation of the two anomers of methyl D-xylopyranoside, the monomethyl ether fraction contains all the possible derivatives, with the 2-O-methyl ether in predominating amount, which shows the high relative reactivity of the hydroxyl at C_2 (Tables 1 and 2). On the partial methylation of methyl β-xylopyranoside, the dimethyl ether fraction contains practically no 3,4-di-O-methyl ether, while it is formed in appreciable amounts from the methyl α-xylopyranoside. On partial methylation of the anomers of methyl L-arabinopyranoside (Tables 3 and 4), a considerable difference is observed in the amounts of monomethyl ethers; the 2-O-methyl ether predominates, its proportion reaching 50% in the

TABLE 1. Partial Methylation of Methyl α-D-Xylopyranoside

Reaction time, min	Initial glycoside, %	Methyl ether, %						
		2	3	4	2,3	2,4	3,4	2,3,4
5	91,9	3,5	2,4	2,2	—	—	—	—
10	89,5	4,4	3,4	2,7	—	—	—	—
20	75,6	9,8	7,9	5,5	0,3	0,6	0,3	—
30	60,9	15,9	12,3	7,7	0,8	1,6	0,8	—
45	44,0	26,9	16,3	8,9	1,1	2,0	0,8	—
60	23,9	27,6	21,7	8,4	5,8	8,8	3,4	0,4
90	11,7	27,8	21,0	5,0	12,7	12,7	7,0	2,1
120	7,5	28,9	21,2	4,0	13,5	14,7	5,9	4,3
180	4,3	25,5	17,8	2,4	20,0	16,3	8,5	5,2
240	3,3	22,6	17,4	2,0	19,8	17,7	7,4	9,8

TABLE 2. Partial Methylation of Methyl β-D-Xylopyranoside

Reaction time, min	Initial glucoside, %	Methyl ether, %						
		2	3	4	2,3	2,4	3,3	2,3,4
5	66,2	11,5	9,3	13,0	—	—	—	—
10	37,5	19,1	14,4	16,4	1,0	11,6	—	—
20	25,7	24,6	18,6	21,7	—	9,3	—	—
30	13,9	26,3	20,1	18,2	2,7	18,8	—	—
45	5,8	24,9	18,4	13,3	6,0	31,6	—	—
60	3,1	19,9	18,1	10,8	8,3	37,2	0,1	2,5
90	2,3	15,2	14,4	4,4	12,1	45,6	0,4	5,6
120	1,8	12,0	10,1	2,5	13,8	45,5	—	14,3

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TABLE 3. Partial Methylation of Methyl α-L-Arabinopyranoside

Reaction time, min	Initial glycoside, %	Methyl ether, %						
		2	3	4	2,3	2,4	3,4	2,3,4
5	94,9	2,4	1,8	0,9	—	—	—	—
10	89,4	5,3	3,5	1,8	—	—	—	—
20	79,0	10,0	8,0	2,6	0,1	0,2	0,1	—
30	63,0	17,6	13,0	4,9	0,3	0,7	0,5	—
45	44,6	27,6	18,3	3,9	1,7	2,4	1,4	0,1
60	33,7	32,1	21,4	2,3	4,1	3,5	2,3	0,6
90	14,5	40,3	25,1	0,9	9,3	5,4	3,4	1,1
120	9,7	40,5	24,1	0,3	13,6	6,0	3,7	2,1
180	4,8	35,9	19,9	0,4	21,0	7,8	3,9	6,3
240	3,7	31,0	18,6	0,3	26,4	8,2	4,2	7,6

TABLE 4. Partial Methylation of Methyl β-L-Arabinopyranoside

Reaction time, min	Initial glycosides, %	Methyl ether, %						
		2	3	4	2,3	2,4	3,4	2, 3, 4
5	93,2	5,1	1,7	—	—	—	—	—
10	83,2	13,3	3,4	—	—	—	—	—
20	40,5	39,1	9,7	—	6,8	3,9	—	—
30	18,5	50,4	13,9	—	10,7	6,3	—	0,2
45	3,1	45,7	16,0	—	22,2	11,7	—	1,3
60	0,4	44,4	11,3	—	26,3	14,9	—	2,7
90	—	37,1	11,2	—	29,1	17,3	—	5,3
120	—	34,5	11,0	—	32,0	17,2	—	5,3
180	—	32,7	11,0	—	32,1	18,8	—	5,4
240	—	27,8	11,1	—	37,1	18,9	—	6,1

TABLE 5. Partial Methylation of Methyl α-D-Lyxopyranoside

Reaction time, min	Initial glycoside, %	Methyl ether, %						
		2	3	4	2,3	2, 4	3,4	2,3,4
5	94,2	1,6	2,3	1,9	—	—	—	—
10	81,7	4,3	6,2	6,0	0,6	0,8	0,4	—
20	71,8	7,5	9,3	9,3	0,6	1,0	0,5	—
30	61,5	8,6	12,5	12,5	1,4	2,1	1,3	0,1
45	46,7	11,9	16,1	15,5	2,4	3,9	3,0	0,5
60	40,4	12,2	16,3	15,8	4,0	5,3	4,0	2,0
90	32,9	11,7	16,0	15,5	5,4	7,2	7,3	4,0
120	27,7	12,3	16,6	17,0	6,2	7,7	7,9	4,6
180	26,7	12,1	16,9	16,1	6,4	8,1	8,9	4,8
240	23,8	12,5	16,3	15,8	6,8	9,1	9,4	6,3

case of methyl β-arabinopyranoside. In the products of the methylation of the methyl α-arabinoside the amounts of the 4-O-methyl ether is small, and in the methylation of the β-arabinoside it is not formed at all. The methylation of the β-arabinoside does not give any of the 3,4-di-O-methyl ether either, and the dimethyl ether fraction contains mainly the 2,3-di-O-methyl compound, which is due to the low relative reactivity of the hydroxyl at C_4. On the partial methylation of methyl α-D-lyxopyranoside (Table 5), the mono- and dimethyl ether fractions contain practically equal amounts of the isomers, which shows an only slight difference in the relative reactivity of the three hydroxyls. Methylation of methyl α-L-rhamnopyranoside (Table 6) takes place more slowly, and only the 3-O-methyl ether is formed in appreciable amounts.

As can be seen from the Tables given, on partial methylation by Purdie's method almost all the possible methyl ethers are formed, which enables the mixtures obtained in this way to be used for isolating the individual methyl ethers by micropreparative GLC [2] in the form of acetates.

EXPERIMENTAL

Partial Methylation. A solution of 0.1 g of the methyl glycoside in 4 ml of absolute methanol (in the case of methyl β-xyloside, in 2 ml of absolute methanol) was treated with silver oxide (0.7 g) and methyl iodide (0.38 ml) and the mixture was stirred with a magnetic stirrer at room temperature in the dark. After pre-

TABLE 6. Partial Methylation of Methyl α-L-Rhamnopyranoside

Reaction time, min	Initial glycoside, %	Methyl ether, %						
		2	3	4	2,3	2,4	3,4	2,3,4
5	94,7	1,5	2,5	1,3	—	—	—	—
10	93,4	1,9	3,3	1,4	—	—	—	—
20	80,3	5,9	8,8	4,8	0,1	0,1	—	—
30	74,7	6,9	12,5	5,3	0,3	0,2	0,1	—
45	64,1	8,9	17,7	6,9	1.4	0,7	0,3	—
60	55,8	11,2	21,0	8,2	2,3	1,1	0,4	—
90	49,8	11,6	24,2	8,2	3.8	1,8	0,6	—
120	45,4	12,6	24,9	8,9	5,2	2,0	0,9	0,1
180	42,4	12,4	26,5	8,8	5,6	2,9	1,2	0,2
240	40,7	12,8	26,4	9,1	6,7	2,7	1,3	0,3

TABLE 7. Relative Retention Times of the Methyl Esters and GLC Conditions

Initial glycoside	Methyl ether							Glycoside acetate	Stationary phase and temperature
	2	3	4	2,3	2,4	3,4	2,3,4		
β-Xyl	1,17	1,33	1,28	0,81	1,00 (15,7 min)	0,93	0,39	1,50	15% BDS* 100° $\xrightarrow{4°}$ 225°
α-Xyl	1,39	1,00 (6,2min)	1,16	0,38	0,74	0,26	0,10	2,29	3% QF—1† 145°
β-Ara	1,36	1,00 (9.8 min)	1,18	0,45	0,65	0,78	0,24	1,95	15% BDS* 160°
α-Ara	1,00 (10 min)	1,14	1,22	0,44	0,50	0,84	0,26	1,62	3% QF—1† 125° $\xrightarrow{3°}$ 225
α-Lyx	1,50	1,00 (6,4 min)	1,34	0,62	0,67	0,38	0,22	2,10	3% QF—1† 140° $\xrightarrow{2°}$ 225
α-Rha	1,43	1,00 (9,2 min)	1,30	0,74	0,67	0,20	0,15	1,91	3% QF—1† 125° $\xrightarrow{2°}$ 225

*Steel columns (1 m×3 mm)
†Glass columns (1.5 m × 4 mm)

determined intervals of time, 0.1 ml samples were taken, and they were diluted with methanol, filtered, and evaporated. The resulting mixtures of methylated compounds were acetylated with acetic anhydride in pyridine, the acetates were isolated, and they were used in the form of chloroform solutions of GLC analysis.

GLC Analysis. The GLC of the products of the partial methylation of methyl β-xyloside was performed on a "Tsvet 2-65" instrument, the products of the partial methylation of methyl β-arabinoside were chromatographed on a "Tsvet-4-67" instrument, and the products of the partial methylation of the other glycosides were subjected to GLC on a Pye Unicam series 104 instrument (England).

Chromosorb W (60-80 mesh) was used as the support. The retention times of the methyl ethers and the working conditions are given in Table 7.

The methyl ethers of the methyl glycosides were identified by comparison with authentic samples by means of GLC and mass spectrometry [4]. The areas of the peaks were found by the usual method. The relative error was 3-10%.

SUMMARY

The partial methylation of methyl xylo-, arabino-, lyxo- and rhamnopyranosides by Purdie's method has been studied; it is possible to use the results obtained for the isolation of individual methyl ethers by micropreparative GLC.

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THE XYLAN OF THE STEMS OF THE HERB Phleum pratense

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Phleum pratense (timothy) is a fodder cereal grass which is distinguished by a high yield, for which reason it is widely used in agriculture [1]. The structure of the polysaccharides of this raw material, like that of a number of other grasses, has been studied little [2-4].

We have investigated the chemical composition and structure of the xylan of Phleum pratense, this forming the main part of its hemicellulose.

The carbohydrates of the stem of this grass include 28.20% of readily hydrolyzable polysaccharides (RHPs) and 39.57% of difficultly hydrolyable polysaccharides (DHPs), together with 17.18% of lignin, 0.76% of total nitrogen, and 6% of ash.

A hydrolyzate of the RHP contained 59.90% of xylose, 13.36% of arabinose and mannose, which are difficult to separate, 13.05% of glucose, 2.31% of lactose, and 11.48% of uronic acids, which shows the predominance of xylan among the polysaccharides of the hemicelluloses.

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