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Separation of some methyl O-methyl-D-xylofuranosides by gas chromatography. II

The separation of methyl O-methyl-D-xylofuranosides, which may be formed by methanolysis of a methylated polysaccharide that contains D-xylopyranose as a structural unit, has been described[1]. We now describe the separation of the remaining theoretically possible methyl O-methyl-D-xylofuranosides in which, in contrast to those described previously[1], the C-5 hydroxyl group is methylated. These compounds may be encountered in the structural analysis of substances that contain D-xylofuranose as a structural unit.

Experimental

Apparatus. The instruments used were a Hewlett-Packard Research Chromatograph, Model 5750 G, and a Carlo Erba Fractovap, Model GT 200, both with a dual column system and a dual flame ionization detector. Relative retention times were taken from the record of a Hewlett-Packard Integrator, Model 3370 A.

Operating conditions. Gas chromatography was carried out on the following columns.

(A) 6 ft. × 1/4 in. (O.D.), packed with 5% XE-60 (Hewlett-Packard) on Embacel AW, 60–70 mesh (May and Baker), flow-rate 39 ml/min, temperature programmed over the range 100–220° (10°/min).

(B) 6 ft. × 1/8 in. (O.D.), packed with 3% ECNSS-M (Applied Science Laboratories) on 80–100 mesh Chromaton N AW DMCS (Lachema, Brno), flow-rate 25 ml/min, temperature programmed over the range 100–210° (4°/min).

(C) 6 ft. × 1/4 in. (O.D.), packed with 10% diethylene glycol succinate on 60–80 mesh Chromosorb W Silanizatto (Carlo Erba), flow-rate 29 ml/min, temperature programmed over the range 100–200° (8°/min).

(D) 6 ft. × 1/4 in. (O.D.), packed with 10% Carbowax 20M–terephthalic acid (Hewlett-Packard) on 60–75 mesh Chromaton N AW DMCS (Lachema, Brno), flow-rate 29 ml/min, temperature programmed over the range 100–240° (8°/min). Nitrogen was used as the carrier gas throughout.

Derivatives. Methyl O-methyl-D-xylofuranosides were prepared by using known procedures[2–4].

Results and discussion

This paper is an extension of our previous work[1] to the remaining theoretically possible methyl O-methyl-D-xylofuranosides. The purpose of the work was to ascertain whether BISHOP's rules[5] for the order of elution generally accepted for methyl O-methylglycopyranosides was also valid for the complete series of methyl O-methyl-D-xylofuranosides.

In Table I the retention times of the compounds of the present study relative to that of methyl 2,3,4-tri-O-methyl-β-D-xylopyranoside, on four liquid phases of different polarity, are presented. It can be seen from the data in Table I that column B gives an excellent separation of the substances under investigation. It is worth mentioning, however, that when we tried to repeat the separation of methyl O-methyl-D-xylofuranosides in which the C-5 hydroxyl group was unsubstituted on

TABLE I

RELATIVE RETENTION TIMES OF METHYL O-METHYL-D-XYLOFURANOSIDES

Methyl glycoside	*Column*			
	A	*B*	*C*	*D*
2,3,4-Tri-O-methyl-β-D-xylopyranoside	1.00[a]	1.00[b]	1.00[c]	1.00[d]
2,3,5-Tri-O-methyl-β-D-xylofuranoside	1.20	1.50	1.16	1.14
2,3,5-Tri-O-methyl-α-D-xylofuranoside	1.27	1.70	1.24	1.21
3,5-Di-O-methyl-α-D-xylofuranoside	1.28	1.93	1.40	1.30
2,5-Di-O-methyl-β-D-xylofuranoside	1.48	2.37	1.53	1.41
2,5-Di-O-methyl-α-D-xylofuranoside	1.71	3.29	1.80	1.61
5-O-Methyl-α-D-xylofuranoside	1.84	4.08	2.20	1.82
3,5-Di-O-methyl-β-D-xylofuranoside	1.96	4.23	2.13	1.79
5-O-Methyl-β-D-xylofuranoside	2.27	5.62	3.18	2.11

[a] 4.87 min.
[b] 2.86 min.
[c] 8.03 min.
[d] 7.86 min.

column B, in contrast to out previous findings[1], two of the compounds in the mixture were not separated. Methyl 2-O-methyl-α-D-xylofuranoside and methyl 3-O-methyl-β-d-xylofuranoside were eluted as a single peak, though the newly prepared column B had approximately the same number of theoretical plates as the "aged" one used previously[1]. Our attention was focused, therefore, on finding the stationary phase and the operating conditions under which these two compounds would be satisfactorily separated and which, at the same time, would be the most suitable for the sepa-

TABLE II

RELATIVE RETENTION TIMES OF ALL THE THEORETICALLY POSSIBLE METHYL O-METHYL-D-XYLOFURANOSIDES ON COLUMN A

Methyl glycoside	*Temperature programmed, 100–220° (10°/min)*	*Isothermal conditions, 160°*
2,3,4-Tri-O-methyl-β-D-xylopyranoside	1.00[a]	1.00[b]
2,3,5-Tri-O-methyl-β-D-xylofuranoside	1.20	1.31
2,3,5-Tri-O-methyl-α-D-xylofuranoside	1.27	1.45
3,5-Di-O-Methyl-α-D-xylofuranoside	1.28	1.53
2,5-Di-O-Methyl-β-D-xylofuranoside	1.48	2.05
2,3-Di-O-Methyl-β-D-xylofuranoside	1.55	2.31
2,3-Di-O-methyl-α-D-xylofuranoside	1.64	2.64
2,5-Di-O-methyl-α-D-xylofuranoside	1.71	2.95
3-O-methyl-α-D-xylofuranoside	1.72	3.06
2-O-methyl-β-D-xylofuranoside	1.84	3.72
5-O-methyl-α-D-xylofuranoside	1.84	3.75
3,5-Di-O-methyl-β-D-xylofuranoside	1.96	4.59
5-O-Methyl-β-D-xylofuranoside	2.27	8.16
2-O-Methyl-α-D-xylofuranoside	2.28	8.21
3-O-Methyl-β-D-xylofuranoside	2.35	9.43

[a] 4.87 min.
[b] 1.55 min.

ration of all the theoretically possible methyl O-methyl-D-xylofuranosides. The best results were obtained by using column A.

Relative retention times of all the theoretically possible methyl O-methyl-D-xylofuranosides relative to that of methyl 2,3,4-tri-O-methyl-β-D-xylopyranoside are presented in Table II. It can be seen that the use of temperature programming does not give satisfactory separation. On the other hand, under isothermal conditions the separation of the majority of the components is very good. We believe that on a capillary column all the theoretically possible methyl O-methyl-D-xylofuranosides could be separated.

From the data presented in Tables I and II, it can be seen that BISHOP's rule[5] for the order of elution of methyl O-methylglycopyranosides can be extended, without exception, to all the theoretically possible methyl O-methyl-D-xylofuranosides.

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