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Note

Gas chromatographic investigation of the *exo* and *endo* isomers of dioxolane ring benzylidene acetals of some carbohydrates

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Benzylidene derivatives play an important role in synthetic carbohydrate chemistry, and their importance was enhanced by the recent observation of the stereoselective opening of the benzylidene ring by hydrogenolysis to give excellent yields of hydroxybenzyl ethers[1]. In the 4,6-O-benzylidene hexopyranoside derivatives the direction of ring opening is determined by the bulk of the C-3 substituent. In the dioxolane derivatives formed on *cis* axial–equatorial hydroxyl groups, the decisive factor is the steric position of the phenyl group[2]. The hydroxybenzyl ethers obtained upon hydrogenolysis have several advantages that make them suitable derivatives for the synthesis of oligosaccharides, as the benzyl group can be removed selectively by hydrogenation whereas it is stable to both basic and slightly acidic media[3].

Because of the very small differences between the R_F values of these isomers, thin-layer and column chromatographic methods are not always suitable for following the course of the reaction and determining the relative proportions of the isomers. According to Baggett *et al.*[4], the ratio and the absolute configurations of the *exo* and *endo* isomers can be determined by proton magnetic resonance spectroscopy, the benzylidene C*H* proton of the *exo* isomers resonating at a lower field than that of the *endo* isomers. We have found[5] that the configuration of the isomers can also be determined by ^{13}C nuclear magnetic resonance (NMR) spectroscopy, as the acetal carbon of the *endo* isomers resonates 1.3–1.5 ppm lower than that of the *exo* isomers. Both methods require, however, considerable amounts of compounds. With this in mind, we developed a gas chromatographic procedure for the separation of the stereoisomers of the dioxolane ring benzylidene acetals of carbohydrates.

A comparison of the results of the gas chromatographic investigations and the NMR data shows that of the compounds studied by us the *endo* isomers have shorter retention times than the corresponding *exo* isomers. This observation makes possible the identification of the isomers in a reaction mixture even prior to isolation or NMR investigations. It is suggested that the greater mobility of the *endo* isomers is caused by their more compact structure compared with elongated *exo* isomers.

As the molar response factors of the isomers are identical, the molar percentage composition of the mixtures was obtained directly. For a comparison, benzyl, allyl and acetyl derivatives of dioxolane benzylidene derivatives of some carbohydrates were also studied.

EXPERIMENTAL

All gas chromatographic investigations were made on a Hewlett-Packard 5830A gas chromatograph fitted with a flame-ionization detector. The experimental conditions were as follows: column temperature 180°, rate of heating 5°/min; column temperature 200°, rate of heating 2.5°/min; column temperature 220°, rate of heating 2.5°/min; column temperature 250°, rate of heating 2.5°/min; column temperature 275°, rate of heating 2.5°/min; column temperature 300°. At the final temperature, isothermal investigations were made.

TABLE I

RELATIVE RETENTION TIMES OF *ENDO* AND *EXO* ISOMERS

	Conditions	*Column*	*Relative retention time*		*Retention time of exo isomer (min)*
			Endo	*Exo*	
Benzyl 3,4-O-benzylidene-β-D-arabinopyranoside	3	A	0.897	1.0	5.85
	3	B	0.911	1.0	8.28
	4	C	0.913	1.0	5.49
Benzyl 2-O-benzyl-3,4-O-benzylidene-β-D-arabinopyranoside	3	A	0.952	1.0	14.97
	6	C	0.950	1.0	4.04
	4	A	0.844	1.0	8.01
Benzyl 2-O-allyl-3,4-O-benzylidene-β-D-arabinopyranoside	5	A	0.911	1.0	2.92
Phenyl 3,4-O-benzylidene-β-D-fucopyranoside	3	A	0.899	1.0	5.27
	3	B	0.905	1.0	7.72
	4	C	0.910	1.0	5.13
Benzyl 2,3-O-benzylidene-α-L-rhamnopyranoside	3	A	0.911	1.0	4.81
	4	C	0.932	1.0	5.01
Benzyl 4-O-acetyl-2,3-O-benzylidene-α-L-rhamnopyranoside	3	A	0.943	1.0	7.83
Benzyl 4-O-benzyl-2,3-O-benzylidene-α-L-rhamnopyranoside	4	A	0 947	1.0	8.19
Methyl 2,3-O-benzylidene-α-L-rhamnopyranoside	1	A	0.874	1.0	3.73
Methyl 4-O-acetyl-2,3-O-benzylidene-α-L-rhamnopyranoside	1	A	0.912	1.0	4.75
Benzyl 2,6-di-O-methyl-3,4-O-benzylidene-β-D-galactopyranoside	4	A	0.890	1.0	2.98
Benzyl 2,6-di-O-benzyl-3,4-O-benzylidene-β-D-galactopyranoside	4	A	0.945	1.0	18.69
Benzyl 2,3;4,6-di-O-benzylidene-α-D-mannopyranoside	5	A	0.884	1.0	6.05
1,2;4,6-di-O-benzylidene-α-D-glucopyranose	3	A	0.854	1.0	8.49
	4	A	0.811	1.0	4.87
3-O-acetyl-1,2;4,6-di-O-benzylidene-α-D-glucopyranose	3	A	0.883	1.0	7.17

The following experimental conditions were kept constant at the values indicated: first isothermal period 1 min; injection temperature 300°; detector temperature 350°; carrier gas (nitrogen) flow-rate 20 ml/min.

The following columns were used:

(A) 10% UCW 982 on Chromosorb W, AW DMCS, 80–100 mesh, stainless-steel column, 2 ft. × 2.16 mm I.D.

(B) 10% OV-1 on Chromosorb W, AW, 80–100 mesh, stainless-steel column, 6 ft. × 2.16 mm I.D.

(C) 20% SE-30 on Gas-Chrom Q, 80–100 mesh, stainless-steel column, 4 ft. × 2.16 mm I.D.

RESULTS

The results are given in Table I.

For each *exo–endo* pair, the *exo* isomer was selected as a standard to obtain the relative retention time of the corresponding *endo* isomer. It is apparent from Table I that the benzylidene derivatives containing a free hydroxyl group are well separated, the difference in the relative retention times being approximately 0.1. The separation of the acetylated derivatives was smaller, although it was adequate for quantitative determinations. The isomers of the benzyl derivatives are only partially resolved: the difference in the relative retention times is approximately 0.05, which permits identification only. The low volatility of these compounds, which is due to their high molecular weight, was compensated for by the high initial temperatures.

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