Journal of Chromatography, 90 (1974) 399–401

CHROM. 7246

Notes

The differentiation of anomeric configuration and ring size in aryl ribosides by thin-layer and preparative layer chromatography

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(Received October 8th, 1973)

Of the large number of acids that have been used as catalysts in the synthesis of O- and S-glycosides, tin(IV) chloride is considered to be the most convenient[1–5]. However, as the reaction leads to the formation of a mixture of anomeric isomers, it is necessary to find an efficient method of separation. It has been shown that the application of classical methods for this purpose failed, and the only satisfactory results were achieved by chromatography[6]. In addition, the use of thin-layer chromatography (TLC) enables the course of the formation of the glycosides to be controlled and allows corresponding isomers to be obtained on a preparative scale. In this paper, we report the application of TLC and preparative layer chromatography (PLC) in the resolution of isomeric ribose aryl O- and S-triacetylglycosides, which otherwise are subject to serious crystallization difficulties when isolated from a crude reaction mixture.

EXPERIMENTAL

For TLC and PLC, 20×20 and 25×45 cm plates were used, respectively. The adsorption layer (0.2 mm) was prepared from a slurry of silica gel HF_{254} (Merck, Darmstadt, G.F.R.) and methanol. The plates were air dried and activated at 100° for 1 h before use. The separated spots were identified in UV light or by spraying with sulphuric acid followed by heating at 110°.

RESULTS AND DISCUSSION

It was found that the use of the mobile phases generally recommended for the separation of phenyl O- and S-glycopyranosides was unsuccessful with the corresponding anomeric aryl ribosides. On the basis of our investigations, it was possible to establish the conditions for the separation of four pairs of acetylated ribose glycosides. The best results were obtained when the following two-component systems with chloroform or benzene as the major component were used:

S_1 = chloroform–diethyl ether (9:1)
S_2 = chloroform–ethyl acetate (9:1)
S_3 = benzene–ethyl acetate (7:3).

TABLE I

SEPARATION OF ACETYLATED ANOMERIC RIBOSE GLYCOSIDES USING MOBILE PHASES S_1, S_2 AND S_3

No.	*Compound*	R_{RTA}*		
		S_1	S_2	S_3
1	Tetra-O-acetyl-β-D-ribofuranose	1.00	1.00	1.00
2	Phenyltri-O-acetyl-α-D-ribofuranoside	1.31	1.28	1.28
3	Phenyltri-O-acetyl-β-D-ribofuranoside	1.52	1.47	1.28
4	Phenyltri-O-acetyl-α-D-thioribofuranoside	1.50	1.39	1.38
5	Phenyltri-O-acetyl-β-D-thioribofuranoside	1.50	1.39	1.28
6	Tetra-O-acetyl-β-D-ribopyranose	1.00	1.00	1.00
7	Phenyltri-O-acetyl-α-D-ribopyranoside	1.34	1.37	1.37
8	Phenyltri-O-acetyl-β-D-ribopyranoside	1.58	1.50	1.26
9	Phenyltri-O-acetyl-α-D-thioribopyranoside	1.49	1.42	1.42
10	Phenyltri-O-acetyl-β-D-thioribopyranoside	1.67	1.56	1.32

* The R_{RTA} values indicated represent the mobilities of the aryl glycosides compared with that of ribose tetraacetate as a standard.

It is evident from the results in Table I that systems S_1 and S_2 exhibit different properties to those of system S_3 as regards specificity towards the anomers and the resolving power. By using system S_1 or S_2, the resolutions of anomers of phenyl ribofuranoside and ribopyranoside and also phenyl thioribopyranoside were achieved. System S_3, however, also enabled the anomers of phenyl thioribofuranoside to be separated.

The utility of these three mobile phases in separating the compounds listed in Table I can be summarized as follows.

System S_1 was used with success to resolve compounds 2 and 3, 7 and 8, 9 and 10 but failed with a mixture of 4 and 5. The β-anomers always had higher R_{RTA} values than those of the α-anomers. With system S_2, the results obtained were similar to those of system S_1. System S_3 showed weaker resolving properties than those of systems S_1 and S_2, but it can still be used for the separation of all α-anomers from β-anomers, except for compounds 2 and 3. In all instances, when using this solvent composition a faster migration of α-anomers than those of the corresponding β-anomers was observed.

Although the applied synthesis furnished only a mixture of α- and β-anomers with no admixture of isomers with different ring sizes, we were able also to demonstrate the possibility of using system S_1 or S_2 to resolve some furanoside–pyranoside mixtures, as shown in Table II.

TABLE II

SEPARATION OF ISOMERS WITH DIFFERENT RING SIZES

No.	*Compound*	R_F	
		S_1	S_2
10	Phenyltri-O-acetyl-β-D-thioribopyranoside	0.87	0.93
5	Phenyltri-O-acetyl-β-D-thioribofuranoside	0.79	0.85

Preparative-scale resolution of anomers

The differences between the R_F values of anomeric ribose glycosides are large enough for their separation to be successfully achieved in a 40-cm path length (Fig. 1). On a 25×45 cm plate, it was possible to resolve up to 0.5 g of an anomeric mixture. On a preparative scale, the best results for all anomeric pairs were obtained when system S_2 was used, except for the mixture of isomers 2 and 3, for which only system S_3 proved to be suitable.

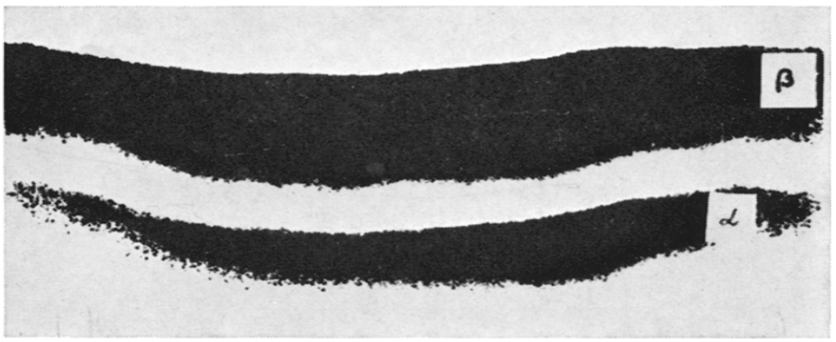

Fig. 1. Preparative chromatogram of a mixture of anomers of phenyl ribofuranoside.

ACKNOWLEDGEMENT

The research described in this paper was carried out as a part of Project No. 3.1.03 of the Polish Academy of Sciences.

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