

CHROM. 5231

Thin-layer chromatography of anomeric aryltetra-O-acetyl-D-glucopyranosides

Generally glycosidation reactions result in the formation of acylated glycosides which are subsequently deacylated to free glycosides¹⁻⁸. These glycosidation reactions are not very stereospecific and usually lead to a mixture of anomeric glycoside acylates in various proportions^{5,9,10}. In several cases the more abundant anomer separates out from an alcoholic solution of the clarified reaction products and the anomeric purity of the crystalline product is judged from its optical rotation.

Thin-layer chromatography can provide more direct visual criterion for judging the anomeric purity, if applied to these compounds. BOSE AND INGLE⁵ have reported the use of TLC in identifying the presence of 40% phenyltetra-O-acetyl- α -D-glucoside under the conditions which were prescribed by LEMIEUX AND SHYLUK¹¹ for the exclusive preparation of the corresponding β -anomer.

When both the anomers are available it has been often possible to differentiate between their anomeric configurations by means of the optical rotation, mass, infrared or proton magnetic resonance spectra¹²⁻¹⁷. TLC has been found to give comparable results in differentiating the anomeric configurations depending upon their mobilities. This note records the TLC of the anomeric pairs of aryltetra-O-acetyl-D-glucopyranosides.

Experimental

Thin-layer plates 20 × 20 cm of silica gel were prepared from a slurry of silica gel (25 g) and water (50 ml). Before use the plates were air dried and heated at 110° for 1 h. Other details of the experimental procedure are included in Table I.

TABLE I
SUMMARY OF EXPERIMENTAL PROCEDURE FOR TLC

Sorbent ^a	Silica Gel G (Merck)
Mobile phase ^b	Methyl ethyl ketone-petroleum ether 40-60° (1:3)
Development	Ascending, in a saturated chamber, height of run 15 cm; at the ambient temperature.
Detection	Concentrated sulphuric acid was used as spray reagent. On heating at 110° black spots develop against a white background.

^a TLC grade silica gel made by N.C.L. Poona, India, also worked well.

^b Other suitable mobile phases are: (1) acetone-petroleum ether (1:3); (2) ethyl acetate-benzene (2:7).

Results and discussion

Seven anomeric pairs of aryltetra-O-acetyl-D-glucopyranosides were prepared by using stannic chloride, penta-O-acetyl- β -D-glucopyranose and various phenols¹⁰. Their R_f values are listed in Table II.

From the data in Table II it is obvious that the two anomers of a pair of the aryl-

TABLE II

RELATIVE MOBILITIES OF THE ANOMERIC ARYLTETRA-O-ACETYL-D-GLUCOPYRANOSIDES

 R_f values represent mobilities of compounds against that of penta-O-acetyl- β -D-glucopyranose.

Compound	R_f
1 Penta-O-acetyl- β -D-glucopyranose	1.00
2 Phenyltetra-O-acetyl- β -D-glucopyranoside	1.40
3 Phenyltetra-O-acetyl- α -D-glucopyranoside	1.76
4 4-Chlorophenyltetra-O-acetyl- β -D-glucopyranoside	1.52
5 4-Chlorophenyltetra-O-acetyl- α -D-glucopyranoside	2.00
6 2-Chlorophenyltetra-O-acetyl- β -D-glucopyranoside	1.20
7 2-Chlorophenyltetra-O-acetyl- α -D-glucopyranoside	1.48
8 4-Nitrophenyltetra-O-acetyl- β -D-glucopyranoside	1.04
9 4-Nitrophenyltetra-O-acetyl- α -D-glucopyranoside	1.50
10 2-Methylphenyltetra-O-acetyl- β -D-glucopyranoside	1.17
11 2-Methylphenyltetra-O-acetyl- α -D-glucopyranoside	1.58
12 4-Methylphenyltetra-O-acetyl- β -D-glucopyranoside	1.17
13 4-Methylphenyltetra-O-acetyl- α -D-glucopyranoside	1.73
14 4-Phenylphenyltetra-O-acetyl- β -D-glucopyranoside	1.04
15 4-Phenylphenyltetra-O-acetyl- α -D-glucopyranoside	1.35

tetra-O-acetyl-D-glucopyranosides can easily be differentiated on the basis of their R_f values and irrespective of the nature of the aglucone, the α -anomer always moved faster than the corresponding β -anomer, thus providing a simple method for judging the anomeric configuration¹⁶.

The experimental data shows that TLC is applicable in this case in its simplest form, therefore, this technique has proved a convenient laboratory practice for monitoring glucosidation reactions. Beside the qualitative application, this technique was found useful in preparative separation of a desired glucoside acetate when fractional crystallisation failed to separate it out of the mixture of reaction products. 2-Chlorophenyltetra-O-acetyl- α -D-glucopyranoside and 2-methylphenyltetra-O-acetyl- α -D-glucopyranoside were recovered in this way¹⁶.

During the synthesis of the aryltetra-O-acetyl- α -D-glycopyranosides extensive recourse was made to TLC. TLC monitoring of the reactions of phenol, penta-O-acetyl- β -D-glucopyranose and stannic chloride in benzene helped in the optimization of two sets of reaction parameters for the preparation of phenyltetra-O-acetyl- α -D-glycopyranoside as well as that of the corresponding β -anomer simply by changing the dilution of benzene¹⁶. Lastly, the application of this technique appears to be promising for the other series of glycosides having a difference in their aglycone or glycone fragment.

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Dünnschichtchromatographischer Nachweis von Jodidverunreinigungen in aromatischen Aminosäuren auf Zweischichtenplatten

Bei Dünnschichtchromatographie aromatischer Aminosäuren, speziell von Jodaminosäuren auf Kieselgel- oder Zelluloseplatten mit Verunreinigungen an anorganischen Jodiden, läuft das Jodid normalerweise unter Schwanzbildung kurz hinter der Laufmittelfront mit. Dadurch wird in den für Zellulose gebräuchlichen Laufmitteln: Methanol-Ammoniak bzw. Aceton-Essigsäure z.B. der Nachweis von Tyrosin erschwert. Dieses Problem kann auf einfache Weise umgangen werden, indem man Zweischichtenplatten mit einem basischen Anionenaustauscher als untere und Zellulose als obere Schicht verwendet und mit Essigsäure chromatographiert. Mit einem dazu speziell hergestellten Streichgerät wurde der Schichtträger mit einer 4 cm breiten Schicht aus DEAE/MN 300 Zellulose und darüber mit einer 16 cm breiten Zellulose MN 300-Schicht beschichtet. Die Probe wurde in der Austauscherschicht 2-2,5 cm vom unteren Rand aufgetragen. Bei lipidhaltigem Material kann dem wässrigen Laufmittel ein neutrales Netzmittel zugesetzt werden. Die Chromatographie erfolgt mit 5 N-Essigsäure. Die Laufstrecke beträgt insgesamt etwa 14 cm. Fig. 1 zeigt den Vergleich einer Chromatographie von Kaliumjodid, Tyrosin, Dijodtyrosin und Thyroxin auf einer Zweischichten- und einer Zelluloseplatte im gleichen Laufmittel. Angefärbt wird mit dem Reagenz nach GMELIN UND VIRTANEN^{1, 2}.

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