## Monitoring of carbohydrate reactions by thin-layer chromatography

Since the introduction of thin-layer chromatography (t.l.c.) by STAHL AND KATTENBACK[1] this technique has been applied to a wide variety of compounds. Typical uses in the carbohydrate field have been for the separation of free sugars[1], acetates[2], benzyl ethers[3] and methyl ethers[4–6]. In the majority of cases the method has been used analytically rather than as a means of following the course of a reaction although such applications have been suggested[2] and used[7,8].

This note is concerned with the facile monitoring of a wide variety of carbohydrate reactions (Table I) and in particular the displacement of tosyl groups by nu-

TABLE I

T.L.C. DATA FROM SOME TYPICAL CARBOHYDRATE REACTIONS

| *Reactant* | *Product*[a] | $R_F$ | *Solvent*[b] |
|---|---|---|---|
| 1,6-Anhydro-β-maltose | 6′-O-trityl | 0.3 | B–W |
| 1,6-Anhydro-β-maltose | 5 unidentified tosyl derivatives | | B–W |
| Penta-O-acetyl-1,6-anhydro-6′-O-trityl-β-maltose | detritylated | 0.04 | |
| | R* | 0.58 | |
| | (tritanol) | 0.75 | E–T |
| 2,2′,3,3′,4′-Penta-O-acetyl-1,6-anhydro-β-maltose | 6′-O-tosyl | 0.22 | E–T |
| Penta-O-acetyl-1,6-anhydro-6′-O-tosyl-β-maltose | 6′-iodo | | |
| | 6′-azido | | |
| | 6′-thioacetate | 0.3 | E–T |
| Penta-O-acetyl-1,6-anhydro-6′-deoxy-β-maltose | β-heptaacetate | 0.39 | |
| | α-heptaacetate | 0.35 | E–T |
| Penta-O-acetyl-6′-S-acetyl-1,6-anhydro-β-maltose | β-heptaacetate | 0.39 | |
| | α-heptaacetate | 0.35 | E–T |
| Hexa-O-acetyl-1,6-anhydro-β-maltose | β-octaacetate | 0.37 | |
| | α-octaacetate | 0.34 | |
| | R* | 0.24 | E–T |
| Benzyl β-maltoside | 4′,6′-benzylidene | | |
| | R* | 0.60 | B–W |
| D-Glucose | diethyl dithioacetal | 0.50 | |
| | R* | 0.00 | B–W |
| 2,3:5,6-Diisopropylidene-D-glucose diethyl acetal 4-*p*-nitrobenzoate | (*a*) 4-OH | 0.33 | |
| | (*b*) 4-OMe | 0.45 | |
| | R* | 0.53 | E–T |
| Methyl α-D-glucopyranoside | 4,6-benzylidene | 0.59 | |
| | R* | 0.06 | B–W |
| Methyl 4,6-O-benzylidene-2,3-di-O-methyl-α-D-glucoside | methyl 2,3-di-O-methyl-α-D-glucoside | 0.33 | B–W |
| Methyl α-D-mannoside | methyl 2,3-isopropylidene-α-D-mannoside | 0.57 | |
| | R* | 0.06 | B–W |
| 1,2:5,6-Diisopropylidene-D-glucose | 1,2-monoisopropylidene-D-glucofuranose | 0.50 | |
| | R* | 0.70 | B–W |
| 3-O-(2,3,4-Tri-O-acetyl-D-xylosyl)-β-1,2:5,6-diisopropylidene-D-glucose | 3-O-(2,3,4-tri-O-acetyl-D-xylosyl)-β-1,2-isopropylidene-D-glucofuranose | 0.67 | |
| | R* | 0.78 | B–W |

[a] R* = unchanged reactant.
[b] B–W = butanone–water azeotrope; E–T = diethyl ether–toluene (2:1).

cleophiles and the opening of 1,6-anhydro rings by acetolysis[9]. The ease with which this latter reaction may be followed has permitted the use of this method for the removal of a variety of blocking groups at the reducing position[10].

Fig. 1a shows a typical nucleophilic displacement of tosylate by thiolacetate in dimethylformamide at 100° and demonstrates that the reaction was complete in 20 min. Fig. 1b indicates that acetolysis of a 1,6-anhydro ring occurred rapidly to give equal amounts of the $\alpha$ and $\beta$ acetates, followed by a slow anomerization to the equilibrium mixture in which the $\alpha$-form predominated. The good resolution obtained in one development suggests that diethyl ether–toluene may be a superior solvent for the resolution of some carbohydrate acetates. Fig. 1c represents the partial hydrolysis of a diisopropylidene derivative[8] using 75 % acetic acid at 45°.

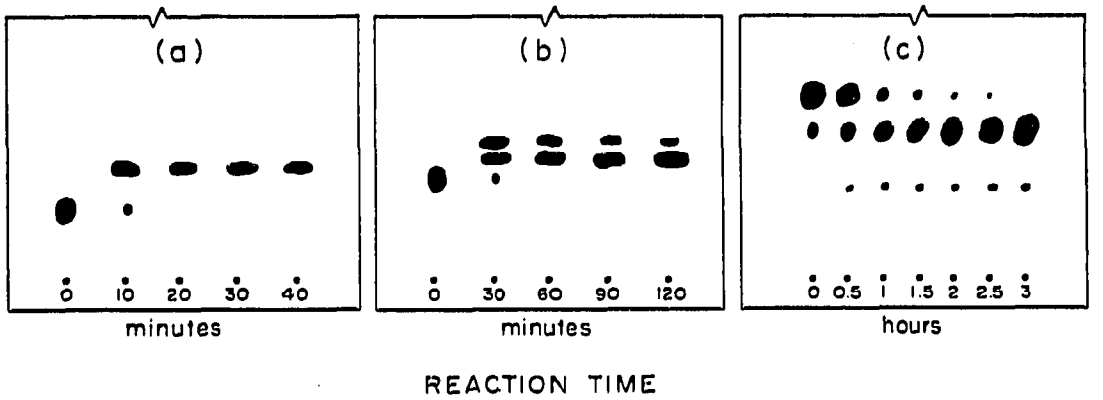


Fig. 1. (a) Reaction of penta-O-acetyl-6′-O-tosyl-1,6-anhydro-$\beta$-maltose with potassium thiolacetate; (b) Acetolysis of penta-O-acetyl-6′-S-acetyl-1,6-anhydro-$\beta$-maltose; (c) Partial hydrolysis of 3-O-(2,3,4-tri-O-acetyl-D-xylosyl)-$\beta$-1,2,5,6-diisopropylidene-D-glucose.

Chromatograms were run on silica gel using either 2:1 diethyl ether–toluene[4] or butanone–water azeotrope[5] as solvents. These solvents may be used with a wide variety of compounds. The plates were either 10 × 15 cm or microscope slides[11]. Slides may be developed within 5 min which, with their low cost and ease of preparation, makes them attractive for routine analyses and student use. Only when the slides were lightly loaded did the resolution approach that of the conventional plate. Since in many reactions the reactant and product differ greatly in mobility (Table I) this is a minor disadvantage.

*Experimental*

Standard plates 10 × 15 cm or microscope slides were coated with an aqueous slurry of silica gel (Camag D5) and dried at 110° for 2 h. The plates and slides were stored open to the atmosphere at room temperature. Slides may be coated by spraying in which case it is convenient to prepare the silica gel with approximately 20 % more water than when the spreading technique is used.

Samples were removed from the reaction mixtures and spotted directly onto the plates using glass capillaries. No interference was observed from solutions containing zinc chloride (benzylidene formation) but for acidic solutions such as the acetolysis mixture $Ac_2O$–AcOH–$H_2SO_4$ (70:30:1) a spot of pyridine was put on the origin before and after the sample. The plates were developed in tanks lined with filter-paper

and glass-stoppered weighing bottles were found very convenient for the microscope slides. Plates took 30–50 min for development while slides required only one-tenth as long.

Plates were sprayed with concentrated sulphuric acid and heated at 150°. Tosylates were identified by spraying with 1 % diphenylamine in ethanol and viewing in the ultraviolet[12] before overspraying with sulphuric acid.

$R_F$ values should be treated only as a guide and when possible standard samples should be run concurrently. Standards must be applied in the same solvent as that in which the reaction is being carried out. Traces of reaction solvent may greatly influence the rate of movement of compounds especially in the low polarity solvent (E–T).

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## Dünnschicht-Chromatographie von Aminen

Die bifunktionellen Verbindungen der Tabelle I zeigen dünnschicht-chromatographisch an den 3 geprüften Adsorptionsmitteln* ein unterschiedliches Verhalten.

*Kieselgel*

Bei Kieselgel bleiben die 3 Aminoalkohole in der Nähe des Startpunkts, was mit einer salzartigen Bindung an den sauren Si–OH-Gruppen[1] zusammenhängt. Der höhere $R_F$-Wert von Äthylenglykol entspricht der schwächeren Wasserstoffbrückenbindung[2].

* Kieselgel Woelm DC, Magnesiumsilikat Woelm DC, Aluminiumoxid Woelm neutral DC.