Separation of 2,4-dinitrophenylosazones of vicinal dicarbonyls into classes by thin-layer chromatography

Several chromatographic methods have recently been reported for separation of 2,4-dinitrophenylosazones[1,2]. The method described by SCHWARTZ[2] provides a clue to carbonyl class by the color of developing bands on the partition column, but if the bands contain more than one class, it is difficult to ascertain the composition of such mixtures. The purpose of this communication is to describe a thin-layer chromatographic (TLC) procedure that affords separation of DNP-osazones into classes. Application of the procedure in conjunction with either of the aforementioned column partition procedures provides valuable clues to the identity of the DNP-osazones.

Two coatings were employed for preparing thin-layer plates: SeaSorb 43–Silica Gel G (1:1) and SeaSorb 43–Celite (anal. grade)–calcium sulfate (10:8.5:1.5). The mixtures were slurried with approximately 1.75 volumes of distilled water and coated onto plates (5 × 20 cm) in a 250 μ layer. The coated plates were dried in an oven at 110° for 2–12 h. Two solvent systems were used for separation of the DNP-osazones into classes: (a) benzene saturated with ethanolamine–8 % methanol, and (b) chloroform–tetrahydrofuran–methanol (15:4:1). Development of the chromatograms was carried out in 600 ml beakers covered with a polyvinyl sheet, as described by LIBBEY AND DAY[3].

Fig. 1 illustrates movement of the DNP-osazones, using the benzene–ethanol-

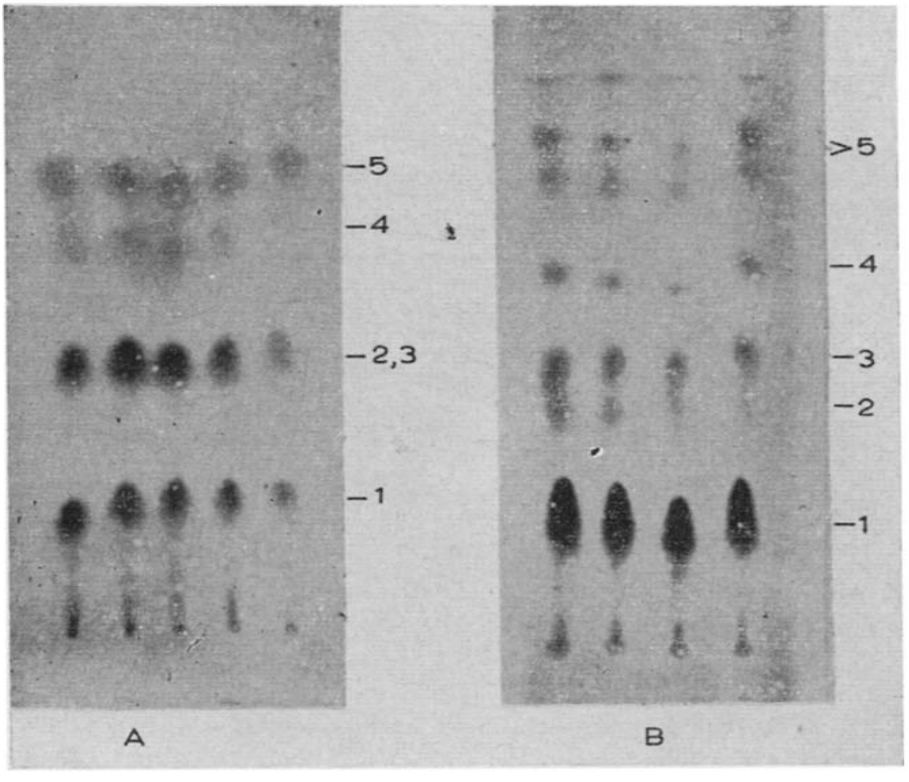

Fig. 1. Thin-layer chromatograms of DNP-osazones of vicinal dicarbonyls. Solvent: benzene saturated with ethanolamine–8 % methanol. Plate A coated with SeaSorb 43–Silica Gel G (1:1); plate B coated with SeaSorb 43–Celite (anal. grade)–calcium sulfate (10:8.5:1.5). 1 = glyoxal; 2 = methylglyoxal; 3 = C_4–C_7 α-ketoalkanals; 4 = diacetyl; 5 = C_6 and C_7 2,3-diketones.

amine–methanol system. The first members of each dicarbonyl class behave differently from the remaining members of the homologous series. It will be noted that the osazones of diacetyl, glyoxal, and in certain instances, methylglyoxal, travel at a slower rate than the remaining homologs. Similar behavior has been reported on class separations of the DNP-hydrazones of monocarbonyls[4,5]. The colors of DNP-osazone spots on the TLC plates are indicative of their class: α-ketoalkanals exhibit blue color, glyoxal is blue to purple, and diketones are blue-green. The spots representing the vicinal dicarbonyl derivatives will fade after removal from the developing chamber, but the color can be intensified by spraying with 10% ethanolic KOH.

Freshly-prepared plates, dried 2 h in the oven, show maximum resolving power.

The only non-vicinal dicarbonyl osazone available in our laboratory was that of hexa-2,5-dione. This compound failed to migrate from the baseline when developed in the benzene solvent system.

This investigation was supported by P.H.S. research grant No. EF-00182 from the National Institutes of Health, Division of Environmental Engineering and Food Protection.

Department of Food Science and Technology,
Oregon State University, Corvallis, Oreg. (U.S.A.)

WILLIAM Y. COBB

[1] E. A. CORBIN, *Anal. Chem.*, 34 (1962) 1244.
[2] D. P. SCHWARTZ, *J. Chromatog.*, 9 (1962) 187.
[3] L. M. LIBBEY AND E. A. DAY, *J. Chromatog.*, 14 (1964) 273.
[4] A. GADDIS AND R. ELLIS, *Anal. Chem.*, 31 (1959) 870.
[5] D. P. SCHWARTZ, O. W. PARKS AND M. KEENEY, *Anal. Chem.*, 34 (1962) 669.

Received October 15th, 1963

J. Chromatog., 14 (1964) 512–513

Dünnschicht-chromatographische Bestimmungen von Zuckern und Zuckeralkoholen auf Magnesiumsilikat

Magnesiumsilikat kann man nicht nur in der Säule[1], sondern auch auf Dünnschichtplatten[2] zur Chromatographie von Zuckern verwenden. Mit den Laufmitteln *n*-Propanol–Wasser–Chloroform (6:2:1) und *n*-Propanol–Wasser–Methyläthylketon (2:1:1) liess sich eine Reihe von Zuckern, Zuckeralkoholen und Glykolen gut identifizieren und trennen.

Die Untersuchungen wurden auf die Laufmittel *n*-Propanol–Wasser (5:5) und *n*-Propanol–Wasser–*n*-Propylamin (5:3:2) ausgedehnt. Tabelle I enthält die R_F-Werte, die unter Anwendung von je 2.5 γ bzw. bei nicht reduzierenden Zuckern und Zuckeralkoholen von je 5 γ in 0.001 ml wässriger Lösung ermittelt wurden.

Ersetzt man in dem Gemisch *n*-Propanol–Wasser (5:5) 40% des Wassers durch *n*-Propylamin, müsste man einen Abfall der R_F-Werte erwarten, da *n*-Propylamin in der eluotropen Reihe über dem Wasser stehen dürfte. Wie man der Tabelle I entnehmen kann, tritt der erwartete Abfall jedoch nur bei den untersuchten Ketosen,