

CHROM. 3503

Thin-layer chromatography of 3-methyl-2-benzothiazolone hydrazone derivatives of aliphatic aldehydes

Published methods for the identification of carbonyls by thin-layer chromatography (TLC) mostly employ the separation of 2,4-dinitrophenylhydrazone derivatives although methods utilizing azine derivatives have been described¹⁻⁴.

Aliphatic aldehydes form azine compounds with 3-methyl-2-benzothiazolone hydrazone (MBTH)⁵. These azines in turn form blue dyes by oxidative coupling with another molecule of MBTH⁵. A method employing these reactions for the determination of total aliphatic aldehydes in air pollution studies has been described⁶.

These two reactions also afford a method for the identification of aliphatic aldehydes, by the TLC separation of the azine derivatives on Silica Gel G. Subsequent visualisation on the TLC plate is accomplished by spraying with a solution of MBTH under oxidising conditions, to form the blue dyestuff.

Experimental

Apparatus and reagents. Merck precoated TLC plates with a layer thickness of 0.25 mm of Silica Gel G were used throughout the investigation. 3-Methyl-2-benzothiazolone hydrazone hydrochloride was obtained from Aldrich Chemical Co., Milwaukee, U.S.A.

Preparation of azines. Azine derivatives of C₁ to C₈ aliphatic aldehydes were prepared by the method of HÜNIG AND FRITSCH⁵ and were recrystallised from ethanol or cyclohexane.

Plate preparation. The Merck precoated Silica Gel G plates were heated in a drying oven for one hour at 110°, then stored in a desiccator until use.

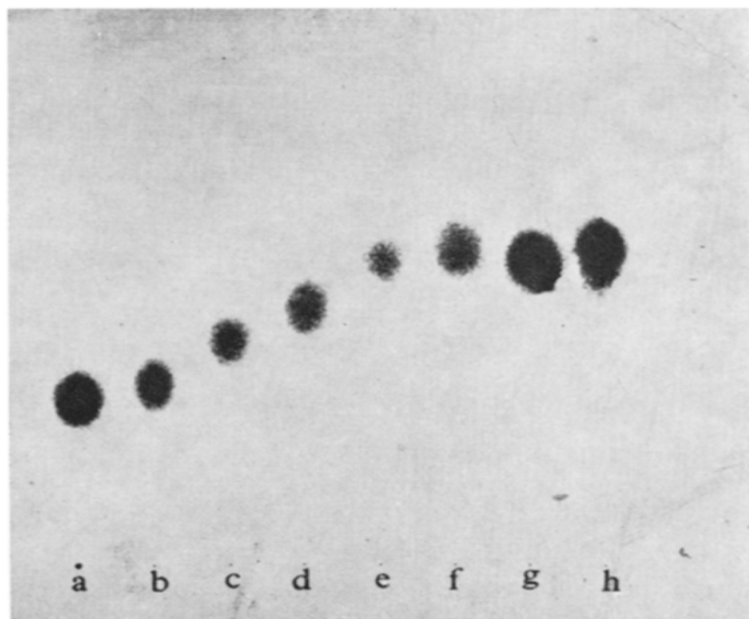


Fig. 1. Thin-layer chromatogram of MBTH derivatives of C₁-C₈ aliphatic aldehydes on Silica Gel G. Solvent: light petroleum (b.p. 30-40°)-ethyl acetate-acetic acid (88:10:2). MBTH derivatives from: (a) formaldehyde; (b) acetaldehyde; (c) propionaldehyde; (d) butyraldehyde; (e) 2-methylbutyraldehyde; (f) hexyl aldehyde; (g) heptyl aldehyde; (h) octyl aldehyde.

Thin-layer chromatography. Chloroform solutions (2 μ l, concentration 5 mg/ml) of the MBTH azine derivatives were applied to a start line 2 cm from the bottom of the plate. The plate was developed with a solvent system of light petroleum (b.p. 30–40°)–ethyl acetate–acetic acid (88:10:2), after 1 h prior equilibration of the spotted plate in a tank, the atmosphere of which was saturated with solvent vapour.

After the solvent front had advanced 15 cm from the start line, the plate was removed from the tank and allowed to dry by evaporation. The separated azines were made visible by spraying with an ethanol solution containing 0.2% MBTH hydrochloride, 0.2% ferric chloride and 0.5% hydrochloric acid.

TABLE I

R_F VALUES OF MBTH AZINE DERIVATIVES OF C_1 TO C_8 ALIPHATIC ALDEHYDES

MBTH azine derivative of	R_F
Formaldehyde	0.29
Acetaldehyde	0.32
Propionaldehyde	0.38
Butyraldehyde	0.43
2-Methylbutyraldehyde	0.47
Hexyl aldehyde	0.52
Heptyl aldehyde	0.48
Octyl aldehyde	0.49

Results and discussion

The separation of the azine derivatives of C_1 to C_8 aliphatic aldehydes is shown in Fig. 1 and the corresponding R_F values in Table I.

Incomplete resolution of the C_1 and C_2 aldehyde derivatives and of the C_5 to C_8 derivatives was obtained. The other derivatives were satisfactorily separated.

The colour obtained with all the separated azines upon spraying with the spray reagent was stable for several hours, however, considerable fading occurred after 24 h. The colour could be regenerated by respraying.

Ketones also react with MBTH, however they do not form the blue dyestuff by coupling with more MBTH. Thus aldehydes can be separated and identified in the presence of ketones.

*Air Pollution Control Branch,
New South Wales Department of Public Health,
Sydney, New South Wales (Australia)*

FREDERICK C. HUNT

- 1 R. BRANDT, J. C. KOUINES AND N. D. CHERONIS, *Microchem. J.*, 6 (1962) 519.
- 2 R. BRANDT, J. C. KOUINES AND N. D. CHERONIS, *J. Chromatog.*, 12 (1963) 380.
- 3 L. H. KLEMM, C. E. KLOPFENSTEIN AND H. P. KELLY, *J. Chromatog.*, 23 (1966) 428.
- 4 E. D. BARBER, *J. Chromatog.*, 27 (1967) 398.
- 5 S. HÜNIG AND K. H. FRITSCH, *Ann. Chem.*, 609 (1957) 172.
- 6 E. SAWICKI, T. R. HAUSER, T. W. STANLEY AND W. ELBERT, *Anal. Chem.*, 33 (1961) 93.

Received March 11th, 1968