THIN-LAYER CHROMATOGRAPHY OF SOME STRONGLY ADSORBED AMINES ON NON-BOUND ALUMINA PLATES

E. A. MISTRYUKOV

Institute of Organic chemistry, U.S.S.R. Academy of Science, Moscow (U.S.S.R.)

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Thin-layer (or column) chromatography of basic compounds such as secondary or primary amines on alumina presents great difficulties because of the strong adsorption affinity of the N-H group. Even solvents of great elution power do not give compact spots or zones on chromatograms. Moreover, it was noticed that these solvents (alcohols and lower ketones) were somewhat inferior to less polar mixtures, since solvents miscible with water enhance adsorption through the increase of adsorbent activity by dehydration. The obvious solution is the introduction of water into such solvent systems; in some instances, in fact (see below), addition of water does improve the results considerably and produces very compact spots. Another approach is to try to use competitive adsorption of some lower amines which are components of the elution system. Generally speaking, any amine may be used for the purpose but the solvent systems containing ammonia proved most effective. The effect of lower aliphatic amines is similar but their application is not so practicable for thin-layer chromatography because of too slow desorption. This slow desorption produces a coloured background on detection, especially by iodine vapour–U.V. technique,

TABLE I

No.	Compound	R_F values in					
		S_1	S_2	S_3	S_4	S_5	S_6
1	*trans*-Decahydroquinoline (I)	0.75 (c)	—	—	0.63 (c)	0.74 (c)	0.25 (et
2	*cis*-Decahydroquinoline (II)	0.64 (c)	—	—	0.63 (c)	0.74 (c)	0.27 (e)
3	4-Hydroxy-I (m.p. 130°)	0.50 (c)	0.17 (c)	—	—	0.34 (c)	—
4	4-Hydroxy-I (m.p. 170°)	0.45 (c)	0.14 (e)	—	—	0.31 (c)	—
5	4-Hydroxy-II (m.p. of HCl salt 261°)	0.55 (c)	0.26 (e)	—	—	0.39 (c)	—
6	4-Hydroxy-II (m.p. of HCl salt 201°)	0.30 (c)	0.14 (e)	—	—	0.22 (c)	—
7	4-Chloro-I (m.p. 92°)	—	—	—	0.71 (c)	—	0.40 (e)
8	4-Keto-I	—	—	0.61 (c)	—	—	—
9	4-Benzoyloxy-I (m.p. of HCl salt 276°)	—	0.82 (c)	—	—	0.78 (c)	0.33 (e)
10	4-Acetoxy-I (m.p. 86°)	0.76 (c)	0.54 (c)	—	—	0.70 (c)	—
11	4-Acetoxy-I (m.p. of HCl salt 249°)	0.64 (c)	0.16 (e)	—	—	0.62 (c)	—
12	4-Acetoxy-II (m.p. of HCl salt 193°)	0.79 (c)	0.13 (e)	—	—	0.72 (c)	—
13	4-Acetoxy-II (m.p. of HCl salt 258°)	0.59 (c)	0.14 (e)	—	—	0.64 (c)	—
14	7-Hydroxy-I (?) (m.p. of HCl salt 282°)	0.48 (e)	0.2 (et)	—	—	0.23 (c)	—
15	7-Hydroxy-I (?)	0.32 (e)	—	—	—	—	—
16	O-Acetate of No. 14	—	0.67 (c)	—	—	0.67 (c)	0.20 (e)
17	N-Acetate of No. 14	—	0.58 (c)	—	—	—	—

(continued on p. 31

TABLE I (*continued*)

No.	Compound	R_F values in					
		S_1	S_2	S_3	S_4	S_5	S_6
18	$\Delta^{8,8a}$-Octahydroquinolone-4	0.81 (c)	0.63 (c)	—	0.11 (c)	—	—
19	(1)-*cis*-Perhydropyrindine (III)	0.66 (e)	—	—	—	0.52 (c)	—
20	4-Keto-III	—	0.73 (c)	0.56 (c)	—	0.70 (c)	—
21	4-Hydroxy-III (m.p. 117°)	—	0.35 (e)	—	0.30 (c)	0.42 (c)	—
22	4-Hydroxy-III	—	0.21 (e)	—	0.20 (e)	0.35 (c)	—
23	N-Acetyl-4-acetoxy-III	—	—	0.53 (c)	—	0.69 (c)	—
24	N-Acetyl-4-hydroxy-III (m.p. 117°)	—	—	0.40 (c)	0.15 (e)	0.46 (c)	—
25	N-Benzoyl-4-hydroxy-III (m.p. 193°)	—	—	0.51 (c)	—	0.52 (c)	—
26	N-Benzoyl-4-hydroxy-III (m.p. 153°)	—	—	0.41 (c)	—	0.49 (c)	—
27	4-Hydroxy-3-methylpiperidine	0.42 (e)	0.1 (et)	—	—	—	—
28	Piperidine	—	—	0.2 (et)	—	0.55 (c)	—
29	Pyrrolidine	—	—	0.2 (et)	—	0.53 (c)	—
30	Morpholine	—	—	0.27 (et)	—	0.57 (c)	—
31	Cyclohexylamine	—	—	0.42 (et)	—	0.59 (c)	—
32	Benzylamine	—	—	0.67 (c)	—	0.64 (c)	—
33	Ethanolamine	—	—	0.2 (et)	—	0.14 (et)	—
34	Ethylenediamine	—	—	0.2 (et)	—	0.17 (et)	—

and masks the spots. Table I gives the R_F values of some nitrogen compounds on chromatograms with non-bound alumina[1], activity III, in the following solvent systems: S_1 = acetone–methanol–water (8:2:1); S_2 = methyl ethyl ketone–water (15:1); S_3 = acetone–heptane (1:1); S_4 = chloroform–NH_3 (saturated at 22°); S_5 = chloroform/NH_3–96% ethyl alcohol (30:1); S_6 = chloroform/NH_3–benzene (1:1). The type of spot is marked in Table I as follows: c = compact (round or almost so); e = elongated; et = elongated with a tail.

For reference purposes, R_F values of some N-acyl derivatives are given. All R_F values for S_3 not marked in the table are of the order 0.1–0.2 (et). Exclusion of water from S_2 lowers the R_F values and leads to tail formation, *e.g.*, for compound No. 18, the R_F value drops from 0.63 for S_2 to 0.1–0.2 (et) for dry methyl ethyl ketone. The content of alcohol in the NH_3-type systems is of great importance for the separation of geometrical isomers, *i.e.* compounds Nos. 21–22 can be distinguished in S_4 but they give practically the same R_F values in chloroform/NH_3–methanol (15:2, R_F 0.79), or isopropanol/NH_3 (satd.)–heptane (1:1, R_F 0.53), or *n*-butanol/NH_3 (satd.) (R_F 0.9).

SUMMARY

Solvent systems for the thin-layer chromatography of some strongly adsorbed amines on alumina plates are described.

REFERENCE

[1] E. A. MISTRYUKOV, *Collection Czech. Chem. Commun.*, 26 (1961) 2071.