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Note

Application of thin-layer chromatography in the resolution of mixtures of isomeric mono- and di-aryl thioureas, thiazoles and thiazolines

It has been reported earlier[1] that equimolecular mixtures of a few isomeric mono- and di-aryl thioureas, thiazoles and thiazolines are separated into their components by thin-layer chromatography (TLC) in at least six solvent systems. In this work, an attempt has been made to separate a greater number of mixtures of isomeric thioureas, thiazoles and thiazolines more satisfactorily using a large number of solvent systems. A further eleven solvent systems, including both polar and non-polar types, have been used with success for completely resolving these isomeric mixtures.

Experimental

An adjustable Desaga TLC applicator was used, and the adsorbent was Silica Gel G (E. Merck) according to Stahl for TLC. The well cleaned glass plates were

TABLE I

R_F VALUES OF ISOMERIC MONO- AND *sym*-DI-ARYL THIOUREAS IN VARIOUS SOLVENT SYSTEMS

No.	*Compound*	*Solvent system*[a]							
		A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
		Time of development (min)							
		20	*25*	*30*	*12*	*15*	*35*	*30*	*35*
1	*p*-Carboxyphenylthiourea	0.80	0.05	0.06	0.12	0.03	0.05	0.06	
2	*o*-Carboxyphenylthiourea	0.97	0.27	0.29	0.83	0.14	0.73	0.88	
3	*p*-Chlorophenylthiourea	0.80							
4	*o*-Chlorophenylthiourea	0.97							
5	*p*-Nitrophenylthiourea		0.27	0.30	0.80	0.45			
6	*m*-Nitrophenylthiourea		0.19	0.10	0.78	0.05			
7	*o*-Nitrophenylthiourea		0.55	0.49	0.90	0.33			
8	*Sym*-di-*o*-carboxyphenylthiourea	0.95	0.16	0.14	0.80	0.43	0.78	0.81	0.88
9	*Sym*-di-*p*-carboxyphenylthiourea	0.37	0.03	0.02	0.26	0.03	0.21	0.20	0.39
10	*Sym*-di-*o*-nitrophenylthiourea		0.52	0.22	0.89		0.87	0.84	
11	*Sym*-di-*m*-nitrophenylthiourea		0.70	0.39	0.70		0.62	0.77	
12	*Sym*-di-*p*-nitrophenylthiourea		0.13	0.12	0.80		0.64	0.67	
13	*Sym*-di-*o*-tolylthiourea					0.48			
14	*Sym*-di-*m*-tolylthiourea					0.65			
15	*Sym*-di-*p*-tolylthiourea					0.69			
16	*Sym*-di-*m*-chlorophenylthiourea								0.97
17	*Sym*-di-*p*-chlorophenylthiourea								0.71

[a] Solvents: A = water–ethylene glycol (90:10); B = petroleum ether (40–60°)–diethyl ether (50:50); C = petroleum ether (60–80°)–chloroform (50:50); D = benzene–acetone (50:50); E = benzene–chloroform (50:50); F = benzene–isobutanol (60:40); G = benzene–amyl alcohol (60:40); and H = benzene–methanol (50:50).

coated with the adsorbent to a thickness of 250 μ and the developing time varied from 12 to 35 min, depending on the nature of the solvent. The plates were developed by the ascending technique inside air-tight glass chambers that had previously been well saturated with the solvent vapour. The operating temperature was 24–25° and the relative humidity of the atmosphere was 60–65%. After the development was completed, the plates were dried so as to evaporate the solvent and then the spots were made visible by spraying the plates with various reagents[1,2].

The following equimolecular mixtures were successfully separated on TLC plates in various solvent systems as shown in Tables I and II: *o*- and *p*-carboxyphenylthioureas; *o*- and *p*-chlorophenylthioureas; *o*-, *m*- and *p*-nitrophenylthioureas; *sym*-di-*m*- and -*p*-chlorophenylthioureas; *sym*-di-*o*- and -*p*-carboxyphenylthioureas; *sym*-di-*o*-, -*m*- and -*p*-nitrophenylthioureas; *sym*-di-*o*-, -*m*- and -*p*-tolylthioureas;

TABLE II

R_F VALUES OF ISOMERIC THIAZOLES AND THIAZOLINES IN VARIOUS SOLVENT SYSTEMS

No.	*Compound*	*Solvent system*					
		B	*C*	*F*	*J*	*K*	*L*
		Time of development (min)					
		25	*30*	*35*	*30*	*25*	*30*
1	2-*o*-Carboxyphenylamino-4-methylthiazole	0.86	0.88	0.91	0.83	0.92	0.81
2	2-*p*-Carboxyphenylamino-4-methylthiazole	0.24	0.27	0.32	0.23	0.43	0.22
3	2-*α*-Naphthylamino-4-methylthiazole	0.77	0.43	0.82	0.40	0.71	0.41
4	2-*β*-Naphthylamino-4-methylthiazole	0.60	0.28	0.68	0.22	0.49	0.23
5	2-*o*-Nitrophenylamino-4-methylthiazole	0.19	0.18				0.21
6	2-*m*-Nitrophenylamino-4-methylthiazole	0.77	0.71				0.75
7	2-*p*-Nitrophenylamino-4-methylthiazole	0.79	0.76				0.81
8	2-*o*-Chlorophenylamino-4-methylthiazole	0.23	0.24		0.26	0.65	0.25
9	2-*m*-Chlorophenylamino-4-methylthiazole	0.70	0.73		0.71	0.92	0.71
10	2-*p*-Chlorophenylamino-4-methylthiazole	0.71	0.79		0.76	0.95	0.75
11	2-*o*-Carboxyphenylimino-3-*o*-carboxyphenyl-4-phenyl-Δ^4-thiazoline	0.18	0.20	0.28	0.15	0.26	0.18
12	2-*p*-Carboxyphenylimino-3-*p*-carboxyphenyl-4-phenyl-Δ^4-thiazoline	0.64	0.69	0.86	0.59	0.76	0.62
13	2-*α*-Naphthylimino-3-*α*-naphthyl-4-phenyl-Δ^4-thiazoline	0.76	0.25	0.86	0.20	0.50	0.40
14	2-*β*-Naphthylimino-3-*β*-naphthyl-4-phenyl-Δ^4-thiazoline	0.58	0.90	0.62	0.80	0.31	0.64
15	2-*o*-Nitrophenylimino-3-*o*-nitrophenyl-4-phenyl-Δ^4-thiazoline	0.55	0.67	0.60	0.45		0.69
16	2-*p*-Nitrophenylimino-3-*p*-nitrophenyl-4-phenyl-Δ^4-thiazoline	0.40	0.44	0.82	0.26		0.50
17	2-*o*-Chlorophenylimino-3-*o*-chlorophenyl-4-phenyl-Δ^4-thiazoline	0.70	0.73	0.61	0.60	0.80	0.73
18	2-*m*-Chlorophenylimino-3-*m*-chlorophenyl-4-phenyl-Δ^4-thiazoline	0.82	0.93	0.79	0.75	0.61	0.88
19	2-*p*-Chlorophenylimino-3-*p*-chlorophenyl-4-phenyl-Δ^4-thiazoline	0.89	0.94	0.85	0.78	0.60	0.90

[a] Solvents: B = petroleum ether (40–60°)–ether (50:50); C = petroleum ether (60–80°)–chloroform (50:50); F = benzene–isobutanol (60:40); J = petroleum ether (40–60°)–benzene (50:50); K = petroleum ether (40–60°)–methanol (90:10); and L = petroleum ether (40–60°)–benzene (20:80).

2-*o*- and -*p*-carboxyphenylamino-4-methylthiazoles; 2-α- and -β-naphthylamino-4-methylthiazoles; 2-*o*-, -*m*- and -*p*-nitrophenylamino-4-methylthiazoles; 2-*o*-, -*m*- and *p*-chlorophenylamino-4-methylthiazoles; 2-*o*- and -*p*-carboxyphenylimino-3-*o*- and -*p*-carboxyphenyl-4-phenyl-Δ^4-thiazolines; 2-α- and -β-naphthylimino-3-α- and β-naphthyl-4-phenyl-Δ^4-thiazolines; 2-*o* and -*p*-nitrophenylimino-3-*o*- and -*p*-nitrophenyl-4-phenyl-Δ^4-thiazolines; 2-*o*-, -*m*- and -*p*-chlorophenylimino-3-*o*-, -*m*- and -*p*-chlorophenyl-4-phenyl-Δ^4-thiazolines.

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