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Note

Argentation chromatography of some stilbene derivatives

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Following the discovery[1] that silver ions can form complexes with olefinic double bonds, this effect has found widespread application in the column and thin-layer chromatographic (TLC) separation of a great number and different kinds of compounds; *e.g.* fatty acid methyl esters[2–5], glyceride mixtures[6], terpenes[7–9], olefin-paraffin separation[10], α,β-unsaturated acids[11], unsaturated β-lactams[12], 3- and 4-substituted styrenes[13] and allylic–propenylic pairs of benzene derivatives[14]. As the technique of the high-performance liquid chromatography (HPLC) has advanced, many successful applications of "argentation chromatography" have been described both on straight phase (silica gel impregnated with silver salt) and reversed phase (chemically bonded C_8 or C_{18} phase plus eluent containing silver ion); *e.g.* for unsaturated aliphatic compounds[15,16], vitamin D[17] and prostaglandins[18].

The successful separations hitherto performed by the argentation method were based on the difference in co-ordinative bond strength between the silver ion and the olefinic double bond, because of either the different numbers or the different steric hindrance (substitutional, positional or geometrical isomerism) of the double bonds in the compounds separated. Exceptions were styrenes containing different substituents in 3 and 4 positions, where differences in electron density of olefinic bonds were responsible for different R_F values[13].

This paper deals with the separation of some stilbene type compounds into their *cis* and *trans* isomers by means of TLC and HPLC (Table I). Examination of the structures of compounds I–VII shows that there is no steric difference in the vicinity of the olefinic bond. The only difference between the olefinic bonds of the *Z* and *E* isomers is the electron density, as one of the two phenyl groups in the *trans* position (and thus causing a conjugation effect) has either substituent X (*E*) or a hydrogen atom (*Z*) in the *para* position.

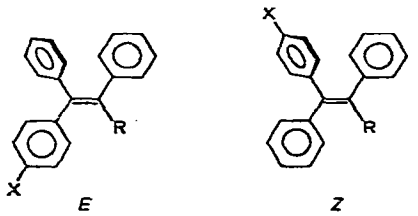
EXPERIMENTAL

TLC plates (20 × 20 cm; layer thickness, 300 μm) were made of silica gel HF_{254} (Merck, Darmstadt, G.F.R.) suspended in distilled water or 2% silver nitrate solution (5%, w/w, impregnation) by a Camag spreader. Layers were dried overnight at room temperature and used thereafter. All developments were done in an unsaturated chamber. Detection was performed either by examination under 254 nm UV light or spraying with aqueous sulphuric acid–$KMnO_4$.

TABLE I

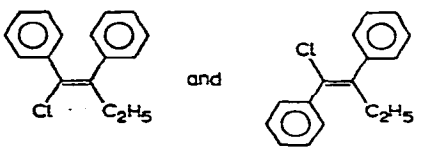
SUMMARY OF EXPERIMENTAL DATA

Structures of I–VII:



E *Z*

Structure of VIII:



Compound	*hR_F values on 5% $AgNO_3$ impregnated silica gel TLC*	*Retention time (min:sec)*					*X*	*R*
		Straight-phase HPLC on 5% $AgNO_3$ Partisil 10	*Reversed-phase HPLC*					
			Methanol–water (200:50)		*Acetonitrile–water (200:80)*			
				+5% $AgNO_3$		*+10% $AgNO_3$*		
I	18	1:39	12:16	8:30	10:45	11:45	F	C_2H_5
	9	3:00	12:58	9:13	11:08	12:13		
II	22	1:29	18:00	11:40	14:13	15:40	Cl	C_2H_5
	12	2:38		12:20				
III	21	1:33	19:55	12:42	15:08	16:45	Br	C_2H_5
	11	2:44		13:17				
IV	0	—	12:05	8:15	9:52	10:46	OCH_3	C_2H_5
V	0	—	5:55	4:35	4:50	4:58	OH	C_2H_5
			6:05	4:52	5:22	5:34		
VI	18	1:47	—	—	—	—	F	CH_3
	9	2:58						
VII	22	1:32	—	—	—	—	F	n-C_4H_9
	11	2:44						
VIII	25	w	7:26	6:05	7:09	7:36		
			8:28	6:52	7:55	8:28		

All solvents and silver nitrate used were analytical grade (Reanal, Budapest, Hungary). Partisil 10 was obtained from Whatman (Clifton, N.J., U.S.A.), and RP-8 (5 μm) from Merck.

HPLC experiments were performed on a Varian 8500 type LC system consisting of an 8500 type pump worked at 60 ml/h, septumless stop-flow injector, and Variscan UV absorbance detector (used at 254 nm). A 250 × 2.1 mm stainless-steel column, slurry packed with a suspension of Partisil 10 impregnated with 5% (w/w) silver nitrate in ethyl acetate, was used for straight-phase argentation chromatography, and a 180 × 4.0 mm column slurry packed with RP-8 (5 μm) was used for the reversed-phase mode.

RESULTS AND DISCUSSION

TLC on silica gel gave no satisfactory separation. Therefore silver nitrate impregnation was applied which resulted in excellent separations of I–III, VI and VII (Fig. 1). The method fails for compound VIII, even though the steric difference between the *cis* and *trans* isomers is very pronounced.

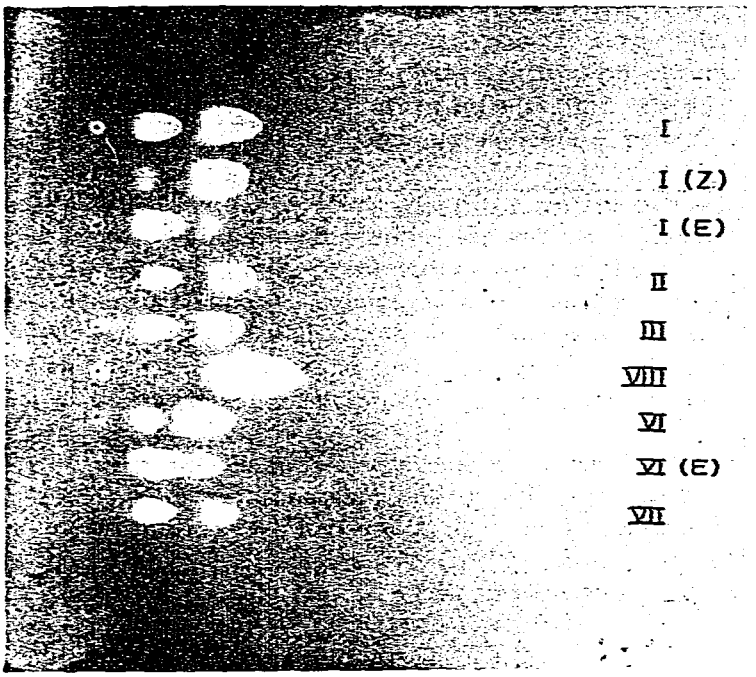


Fig. 1. Separation of stilbene derivates on silica gel impregnated with 5% silver nitrate. Eluents, heptane–benzene (90:5); relative humidity, 31% at 23°. Compound numbers relate to Table I.

Fig. 2. Separation of compounds I. II and III into their isomers on 2.1 × 250 mm Partisil 10 (5% $AgNO_3$) column.

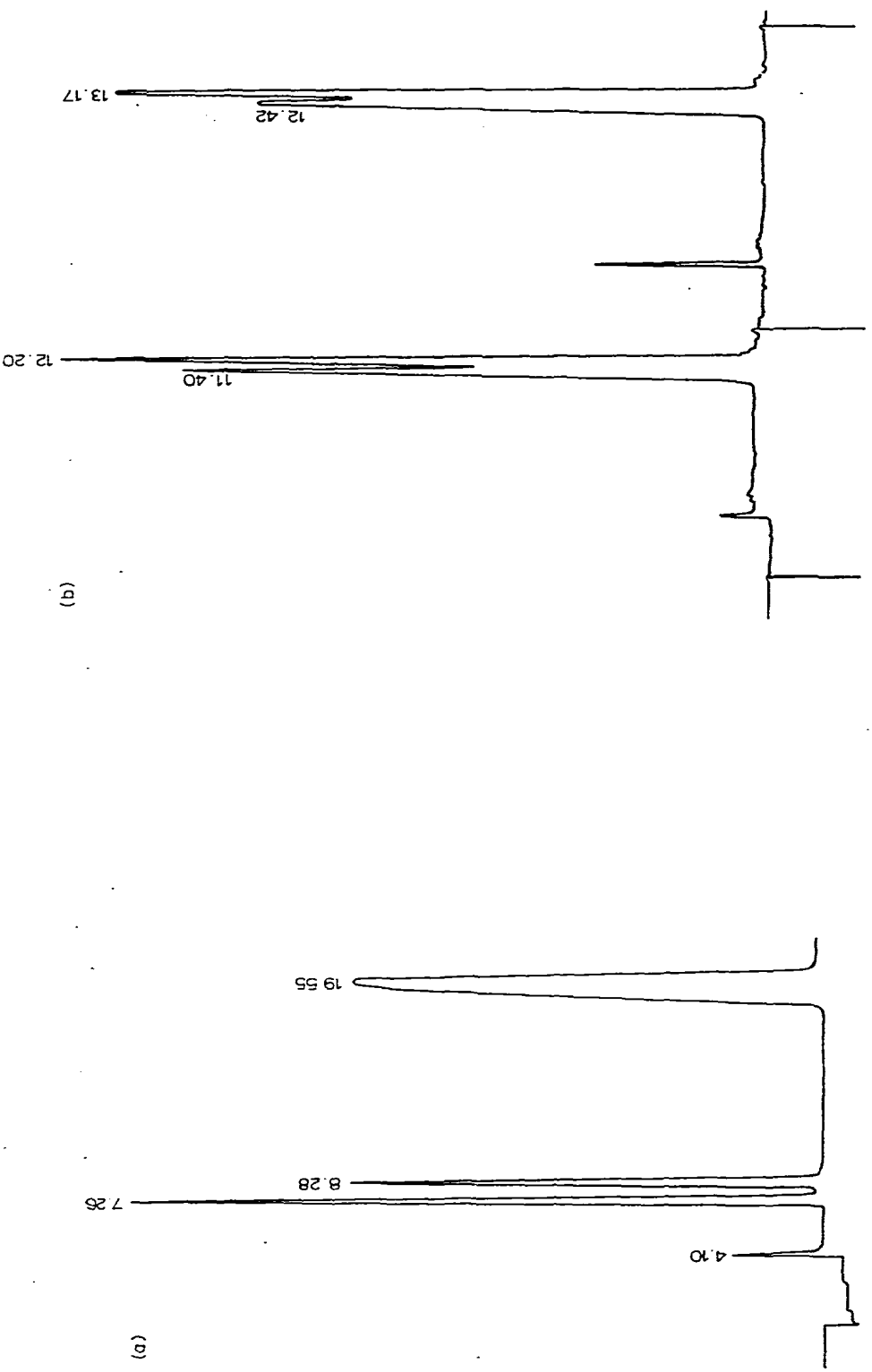


Fig. 3. Reversed-phase chromatography. (a) Eluent: methanol–water (200:50). Well-separated peaks of compound VIII and the broad peak of compound III can be seen. (b) Eluent: methanol–5% aqueous silver nitrate solution (200:50). The isomers of compounds II and III are evident in the chromatogram.

Similar results were obtained using straight-phase argentation HPLC (HPLC on silicagel was as ineffective as simple TLC); the eluent was heptane–diethyl ether (250:0.8) (Fig. 2). The isomers of compound I were identified by ^1H nuclear magnetic resonance spectroscopy[19], and those of compounds II–VII by structural analogy with compound I. Thus spots with higher R_F values and peaks of shorter retention time are assigned *Z* structure.

In each case that the separation occurred, it was possible to differentiate the *E* and *Z* isomers, but retentions were affected very slightly by the nature of the X and R substituents when straight-phase argentation chromatography (TLC or HPLC) was used. Thus it seemed worthwhile to find whether reversed-phase argentation HPLC had any advantage or supplementary power. For packing material RP-8 (5 μm) was used.

When methanol–water (200:50) was used as eluent, the peaks of compounds I and V were split, showing initial separations, the peaks of compounds II and III were single but broad, presumably owing to the presence of two isomers, whereas compound VIII gave two baseline separated peaks (Fig. 3a). When the water in the eluent was replaced with 5% silver nitrate solution, the peaks of compounds II and III were also split, proving the presence of two isomers (Fig. 3b). Retentions were markedly shortened by the presence of silver ion, owing to complexation taking place in the mobile phase.

When the eluent was acetonitrile–water (200:80) the isomers of compounds V and VIII were well separated but the others gave single sharp peaks with exception of compound I, which had a shoulder-type separation. Unexpectedly, when the water in the eluent was replaced with even 10% silver nitrate solution, the silver ion had no effect on the selectivity and increased retentions times by 5–10%.

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