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Note

Thin-layer chromatography of chlorinated guaiacols

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In a previous paper¹ we discussed the thin-layer chromatography (TLC) of guaiacol and six chlorinated guaiacols on silica gel with 40 different solvent systems. In that study dichloromethane-benzene-methanol (60:30:10) and acetone were recommended for group separation, whereas light petroleum (b.p. 40-60°C)-ethyl acetate (70:30) and dichloromethane-chloroform (90:10) were shown to be suitable for separation of the individual compounds by one-dimensional TLC.

The work described here was undertaken to synthesize nine new chlorinated guaiacols, study their characteristic colour reactions on the TLC plate, determine the R_F values with different solvent systems and finally calculate the standard deviations¹ and the relative differences^{1,2} in the R_F values in order to select the most suitable solvent systems for particular separations.

EXPERIMENTAL

Samples

The compounds used (see Fig. 1) were 4-chloroguaiacol (I), 3-chloroguaiacol (II), 6-chloroguaiacol (III), 3,6-dichloroguaiacol (IV), 3,4-dichloroguaiacol (V), 5,6-dichloroguaiacol (VI), 3,4,5-trichloroguaiacol (VII) and a mixture (1:1) of 3,4,6-trichloroguaiacol and 3,5,6-trichloroguaiacol (VIII).

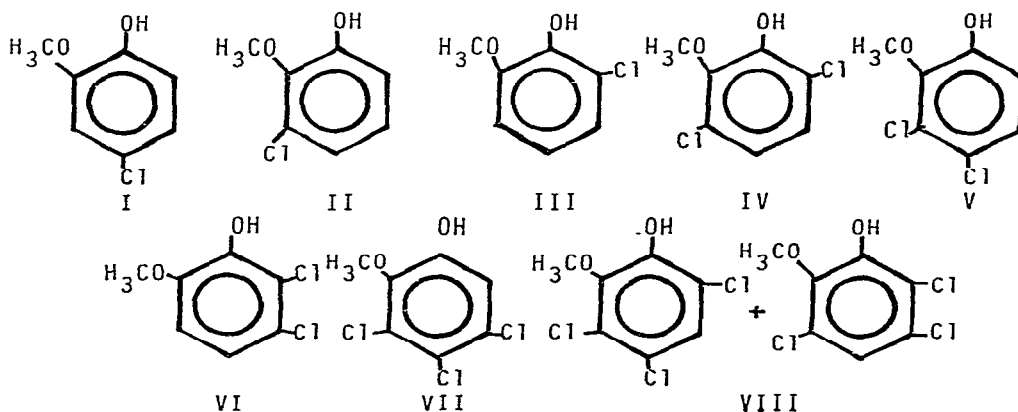


Fig. 1. Structures of 4-chloroguaiacol (I), 3-chloroguaiacol (II), 6-chloroguaiacol (III), 3,6-dichloroguaiacol (IV), 3,4-dichloroguaiacol (V), 5,6-dichloroguaiacol (VI), 3,4,5-trichloroguaiacol (VII) and a mixture (1:1) of 3,4,6-trichloroguaiacol and 3,5,6-trichloroguaiacol (VIII).

dichloroguaiacol (VI), 3,4,5-trichloroguaiacol (VII) and a mixture (*ca.* 1:1) of 3,4,6-trichloroguaiacol and 3,5,6-trichloroguaiacol (VIII). All compounds were synthesized using limited methylation of the corresponding chlorinated catechols according to the method of Vickery *et al.*³. They were purified by silica gel column chromatography (eluent: dichloromethane). The structures were confirmed by infrared (IR), ¹H nuclear magnetic resonance (NMR), ¹³C NMR and mass spectroscopy (MS). The purity of the compounds was checked by glass capillary gas chromatography.

Apparatus and methods

A 0.5% solution of each guaiacol in dichloromethane was prepared. Two microlitres of I–VII and 4 μ l of VIII were spotted 1.5 cm from the bottom of the plate to the concentrating zone with spot intervals of 1 cm. Other conditions and apparatus were as presented in ref. 1. A 2% solution of 3,5-dichloro-*p*-benzoquinonechlorimine in toluene⁴ was used for spot detection.

Solvent systems

A preliminary screening of eight solvents or solvent mixtures was undertaken. The compositions (v/v) of these were as follows:

- (1) dichloromethane
- (2) chloroform
- (3) dichloromethane–chloroform (90:10)
- (4) light petroleum (b.p. 40–60°C)–diethyl ether (70:30)
- (5) light petroleum (b.p. 40–60°C)–ethyl acetate (70:30)
- (6) acetone
- (7) dichloromethane–benzene–methanol (60:30:10)
- (8) dichloromethane–ethyl acetate–acetic acid (80:15:5)

TABLE I

CHARACTERISTIC COLOUR REACTIONS OF CHLORINATED GUAIACOLS

Plates were sprayed after different times with a 2% solution of 3,5-dichloro-*p*-benzoquinonechlorimine in toluene and the colours of the spots were compared after different times. Amount of each compound applied: 10 μ g.

Compound	Neutral developing solvent			Acidic developing solvent		
	1 h	24 h	10 days	1 h	24 h	10 days
I	Brown	Brown	Brown	Orange-brown	Brown	Brown
II	Violet-blue	Violet-blue	Light violet-blue	Light yellow	Light violet	Violet-blue
III	Blue	Brown	Orange-brown	Orange-brown	Brown	Orange-brown
IV	Blue-green	Violet-blue	Violet	Violet-grey	Violet	Violet
V	Light yellow	Greenish grey	Light violet	Light yellow	Light yellow	Light violet
VI	Blue	Red-brown	Red-brown	Red-brown	Red-brown	Red-brown
VII	Light yellow	Light violet	Light violet	Light yellow	Light yellow	Light violet
VIII*	Violet	Violet	Violet	Light yellow	Violet	Violet

* Only one spot was observed.

RESULTS AND DISCUSSION

Colour reactions

The characteristic colour reactions of compounds I–VIII are shown in Table I. With neutral solvent systems (1–7) and 1 h after spraying, different colours for almost all spots were observed. The colour reactions of the 3-chloro-substituted guaiacols were clearly different from those of the others: after 10 days the spots of II, IV, V, VII and VIII were violet-based and those of the other compounds studied were brownish. In addition, II, V and VII were coloured much more slowly and for these compounds only light colours were observed.

Using the acidic solvent system (8) and 1 h after spraying, the spots of 3-chloro-substituted guaiacols (except IV, see Table I) were yellowish and those of the other compounds studied were brownish. Compounds II, IV, V, VII and VIII (especially V and VII) gave much slower and weaker colour reactions and their final colours after 10 days were violet-based, whereas those of I, III and VI were brownish.

R_F values

The R_F values of the spots were measured with an accuracy of better than 0.03. All runs were carried out three times and the average R_F values were calculated. The results are presented in Table II.

TABLE II

R_F VALUES OF CHLORINATED GUAIACOLS ON A SILICA GEL G 60 LAYER WITH DIFFERENT SOLVENT SYSTEMS

Solvent system	Compound								Standard deviation of R_F	Development time (min)
	I	II	III	IV	V	VI	VII	VIII*		
1	0.38	0.25	0.40	0.33	0.25	0.43	0.29	0.35	0.062	30
2	0.45	0.37	0.48	0.43	0.35	0.46	0.34	0.42	0.053	35
3	0.36	0.25	0.38	0.32	0.28	0.41	0.28	0.34	0.055	30
4	0.18	0.21	0.18	0.26	0.17	0.12	0.16	0.22	0.042	30
5	0.34	0.39	0.34	0.46	0.35	0.26	0.35	0.43	0.062	30
6	0.64	0.63	0.63	0.65	0.64	0.63	0.63	0.63	0.009	25
7	0.57	0.54	0.58	0.58	0.53	0.57	0.54	0.57	0.020	30
8	0.68	0.68	0.70	0.72	0.66	0.69	0.68	0.72	0.021	45

* Only one spot was observed.

All these solvent systems (1–8) have previously¹ been used for selecting the most suitable solvent systems for particular separations of guaiacol and six chlorinated guaiacols. Under the present experimental conditions with solvent system 3 the R_F value of 5-chloroguaiacol in the three runs was less than 0.03 units smaller than the corresponding value presented in ref. 1. Hence we conclude that the present results are comparable with those obtained previously.

Standard deviations, s , of the R_F values (see ref. 1) and relative differences, x , between R_F values (see refs. 1 and 2) of I–VIII in each run were calculated to estimate the separation power of each solvent system. Additional information on the separation of the components was obtained from x_{ij} matrixes and \bar{x} and Σx values (see Table III).

TABLE III

RELATIVE DIFFERENCES, x , BETWEEN R_F VALUES OF GUAIACOLS ON SILICA GEL G 60 WITH SELECTED SOLVENT SYSTEMS

Each value of x is calculated by dividing the difference of two R_F values by their average. The averages, \bar{x} , and sums, Σx , of x for each run are also given.

Solvent system	x values								Average, \bar{x}	Sum, Σx
	I	II	III	IV	V	VI	VII	VIII		
1	I	0.413	0.051	0.141	0.269	0.123	0.269	0.082	0.222	6.218
	II		0.462	0.276	0.148	0.529	0.148	0.333		
	III			0.192	0.319	0.072	0.319	0.133		
	IV				0.129	0.263	0.129	0.059		
	V					0.389	0.000	0.188		
	VI						0.389	0.205		
	VII							0.188		
2	I	0.195	0.065	0.045	0.250	0.022	0.278	0.069	0.156	4.371
	II		0.259	0.150	0.056	0.217	0.085	0.127		
	III			0.110	0.313	0.043	0.341	0.133		
	IV				0.205	0.067	0.234	0.023		
	V					0.272	0.029	0.182		
	VI						0.300	0.090		
	VII							0.211		
3	I	0.361	0.054	0.118	0.250	0.130	0.250	0.057	0.206	5.762
	II		0.413	0.246	0.113	0.485	0.113	0.305		
	III			0.171	0.303	0.076	0.303	0.111		
	IV				0.133	0.247	0.133	0.061		
	V					0.377	0.000	0.194		
	VI						0.377	0.187		
	VII							0.194		
4	I	0.154	0.000	0.364	0.057	0.400	0.118	0.200	0.269	7.523
	II		0.154	0.213	0.211	0.545	0.270	0.047		
	III			0.364	0.057	0.400	0.118	0.200		
	IV				0.419	0.737	0.476	0.167		
	V					0.345	0.061	0.256		
	VI						0.286	0.588		
	VII							0.316		
5	I	0.137	0.000	0.300	0.029	0.267	0.029	0.234	0.198	5.531
	II		0.137	0.165	0.108	0.400	0.108	0.098		
	III			0.300	0.029	0.267	0.029	0.234		
	IV				0.272	0.556	0.272	0.067		
	V					0.295	0.000	0.205		
	VI						0.295	0.493		
	VII							0.205		
6	I	0.016	0.016	0.016	0.000	0.016	0.016	0.016	0.012	0.347
	II		0.000	0.031	0.016	0.000	0.000	0.000		
	III			0.031	0.016	0.000	0.000	0.000		
	IV				0.016	0.031	0.031	0.031		
	V					0.016	0.016	0.016		
	VI						0.000	0.000		
	VII							0.000		

The following conclusions can be made from Tables II and III. With all solvent systems studied, 3,4,6-trichloroguaiacol and 3,5,6-trichloroguaiacol had the same R_F values (see Table II). The use of chloroform (2) always resulted in x_{ij} values which

were different from zero and also in relatively high s , \bar{x} and Σx values. Thus this solvent is recommended for the separation of I–VIII by one-dimensional TLC. Solvent systems 1, 3, 4 and 5 give one (or two) x_{ij} values which differ from zero (see Table III) and large s , \bar{x} and Σx values. Hence, these solvent systems could be used only as the first stage in a two-dimensional TLC procedure in which the final separation of I, III, V and VII is carried out with an another solvent system. The highest \bar{x} and Σx values were observed for solvent system 4. However, the value of s is relatively small (0.042) and one x_{ij} value is equal to zero. Thus, dichloromethane (system 1) or dichloromethane–chloroform (90:10) (system 3) could be applied as with system 4 to the separation of I–VIII by two-dimensional TLC. Finally, solvent system 6 (acetone) gives almost identical R_F values (0.63–0.65) and the smallest s , \bar{x} and Σx values. Hence it is the best solvent system for group separation of I–VIII.

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REFERENCES

- 1 J. Knuutinen and J. Paasivirta, *J. Chromatogr.*, 194 (1980) 55.
- 2 M. A. Sattar and J. Paasivirta, *J. Chromatogr.*, 189 (1980) 73.
- 3 E. H. Vickery, L. F. Pahler and E. J. Eisenbraun, *J. Org. Chem.*, 44 (1979) 4444.
- 4 J. M. Bobbit, *Thin-Layer Chromatography*, Chapman & Hall, London, 1964, p. 92.