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GAS CHROMATOGRAPHIC BEHAVIOUR OF HYDROXYNAPHTHALENES AND DERIVATIVES ON LIQUID CRYSTAL STATIONARY PHASES

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SUMMARY

The gas chromatographic separation of α- and β-naphthols and some dihydroxynaphthalenes on a column of liquid crystal is compared with those on conventional packed columns. Use of the acyl derivatives of such compounds led to improved resolution on the mesomeric phase. The liquid crystal substrate shows high and constant relative molar responses especially at low concentration levels.

INTRODUCTION

Due to their widespread usage, phenolic compounds are often observed in waste effluent. Many substituted phenols have been found to be toxic to fish and other aquatic life. It is therefore desirable or necessary to identify the individual compounds present in ground-water, sea-water and in other natural or anthropogenic sources. Colorimetry with 4-aminoantipyrene is widely used for analysis of total phenols[1]. However, this method cannot differentiate between substituted phenols or be used for determining *para*-substituted phenols. The most rapid and convenient technique for separating and determining mixtures of phenols is gas–liquid chromatography (GLC)[2–5] and more recently high-performance liquid chromatography (HPLC)[6–10].

In our laboratory we are evaluating the chromatographic analysis of phenolic compounds in water, and now describe the GLC separations of mono- and dihydroxynaphthalenes on a liquid crystal column. Liquid crystals form a state of matter intermediate between crystalline solids and isotropic liquids[11]. The unusual solvent properties of such crystals have lead to their use as stationary phases in GC. The first practical demonstrations of this were presented by Kelker[12,13] and Dewar and Schroeder[14,15]. Several liquid crystalline phases have been employed, and our earlier papers[16–18] have described the synthesis and the chromatographic properties, as stationary phases, of some naphthalene diesters having a relative large mesomeric range.

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EXPERIMENTAL

Apparatus

The gas chromatograph was a C. Erba Fractovap GT equipped with a flame ionization detector (FID) coupled to a Shimadzu CR-1A integrator. Mass spectra were recorded with a LKB 9000 gas chromatograph–mass spectrometer at 70 eV.

Chromatographic conditions

For the GLC separations three glass columns were used: A, 1.5% OV-17 on Gas-Chrom Z (80–100 mesh), 3 m × 3 mm I.D.; B, 15% 2,6-naphthalene-bis-*p*-*n*-heptyloxycinnamate on Chromosorb W AW (80–100 mesh), 1 m × 3 mm I.D.; C, 1.5% OV-225 on Gas-Chrom Q (100–120 mesh), 2 m × 2 mm I.D.

The liquid crystal stationary phase (B) was prepared as reported previously[17]. It was recrystallized several times to constant transition temperatures. The mesomeric range, determined with a Leitz Wetzlar polarizing microscope and a Perkin-Elmer DSC 1B differential calorimeter, is as follows:

$$\text{solid} \xrightarrow{158^\circ\text{C}} \text{liquid crystal} \xrightarrow{291^\circ\text{C}} \text{isotropic}$$

Column B was heated to a few degrees above the mesophase–isotropic liquid transition temperature, with carrier gas flowing, and held for 1 h at this temperature before cooling to the temperature chosen for analysis. This heating–cooling cycle was repeated each time the column was reused.

Derivatization of naphthols

The acyl derivatives were prepared as reported by Coutts *et al.*[19,20] for the direct acetylation of phenols in environmental water samples.

To 10 μmol of naphthols in 10 ml solvent (water–methanol, 9:1, v/v) were added 0.5 g $NaHCO_3$ (excess); upon complete dissolution, 500 μl of the proper anhydride were added and the reaction vessel shaken vigorously until the evolution of carbon dioxide had ceased. The solution had a final pH of 8. It was extracted twice with 3 ml volumes of methylene chloride, the combined extracts were concentrated and a 5-μl sample injected into the gas chromatograph.

Pivaloyl and benzoyl derivatives were prepared in benzene solution in the presence of pyridine because the respective anhydrides are scarcely soluble in aqueous media.

Mass spectra

The derivatives were positively identified by gas chromatography–mass spectrometry (GC–MS), *m/e* (percentage relative abundance):

α-Naphthyl acetate: 186 (13), 145 (13), 144 (100), 116 (19), 115 (29)
β-Naphthyl acetate: 186 (10), 145 (9), 144 (100), 116 (13), 115 (25)
α-Naphthyl propionate: 200 (6), 144 (100), 115 (22), 57 (37), 44 (27)
β-Naphthyl propionate: 200 (7), 144 (100), 115 (16), 57 (33), 44 (19)
α-Naphthyl pivalate: 228 (11), 144 (100), 115 (21), 85 (13), 57 (79)
β-Naphthyl pivalate: 228 (17), 144 (78), 115 (21), 85 (19), 57 (100)

α-Naphthyl benzoate: 248 (10), 115 (9), 106 (10), 105 (100), 77 (35)
β-Naphthyl benzoate: 248 (11), 115 (6), 106 (8), 105 (100), 77 (34)

RESULTS AND DISCUSSION

Table I reports the retention data of mono- and dihydroxynaphthalenes on OV-17, liquid crystal and OV-225 columns. The separation of α- and β-naphthol is complete on both the mesomeric and the polar conventional phase OV-225; no separation is obtained on the OV-17 column.

Although there is overlapping between some isomers, with the dihydroxynaphthalenes the resolution obtained on the liquid crystal column was generally better than on the conventional columns. However, the quantitative analysis of phenolic compounds at trace levels in water is usually hampered by their poor GLC characteristics and the low efficiency of extraction with organic solvents. Derivatization with various reagents may reduce tailing, increase sensitivity, enhance the solvent extraction and improve MS characteristics.

In order to optimize the analysis of such compounds we have studied the acyl derivatives because of their simple and efficient derivatization in aqueous media[19,20].

Fig. 1 compares the separation of α- and β-naphthols and of their derivatives on the liquid crystal phase. The resolution is improved by the acylation, increasing

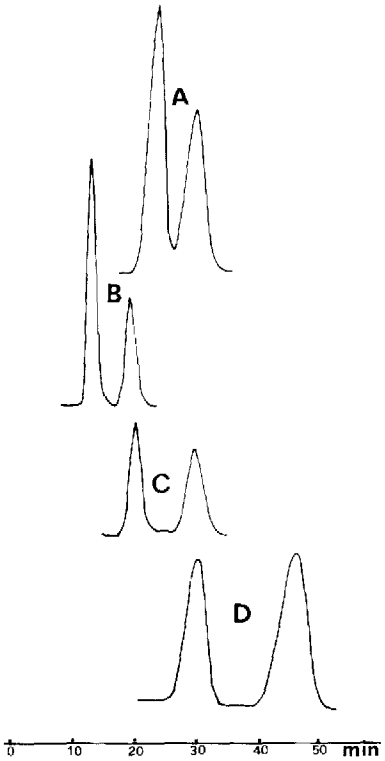

Fig. 1. Separation of α- and β-naphthols and some derivatives on the liquid crystal column. A, α- and β-naphthols (160°C); B, α- and β-naphthyl acetate (170°C); C, α- and β-naphthyl propionate (170°C); D, α- and β-naphthyl benzoate (225°C).

TABLE I

RETENTION DATA OF MONO- AND DIHYDROXYNAPHTHALENES

Compound	*Column A*		*Column B*		*Column C*	
	Retention time (min)	*Temperature (°C)*	*Retention time (min)*	*Temperature (°C)*	*Retention time (min)*	*Temperature (°C)*
α-Naphthol	8.65	190	23.25	160	11.92	180
β-Naphthol	9.02	190	29.54	160	13.72	180
1,3-Dihydroxynaphthalene	9.84	220	27.21	220	12.86	240
2,3-Dihydroxynaphthalene	8.26	220	20.21	220	–*	240
1,5-Dihydroxynaphthalene	9.64	220	22.49	220	11.50	240
1,6-Dihydroxynaphthalene	9.98	220	25.85	220	12.93	240
2,6-Dihydroxynaphthalene	10.91	220	27.72	220	13.56	240
1,7-Dihydroxynaphthalene	10.89	220	25.46	220	12.15	240
2,7-Dihydroxynaphthalene	10.57	220	32.65	220	14.91	240

* Not eluted.

TABLE II

RETENTION DATA OF HYDROXYNAPHTHALENE DERIVATIVES

Compound	*Column A*				*Column B*				*Column C*			
	Retention time (min)	*Temp. (°C)*	α	*R*	*Retention time (min)*	*Temp. (°C)*	α	*R*	*Retention time (min)*	*Temp. (°C)*	α	*R*
α-Naphthyl acetate	10.55	190	1.05	0.66	13.52	170	1.43	6.46	7.35	190	1.01	0.60
β-Naphthyl acetate	11.15				19.34				7.39			
α-Naphthyl propionate	10.61	210	1.03	0.52	20.21	170	1.46	7.82	9.46	190	1.02	0.40
β-Naphthyl propionate	10.95				29.60				9.59			
α-Naphthyl pivalate	11.75	210	1.01	0.25	23.30	170	1.28	6.38	7.00	190	1.03	0.35
β-Naphthyl pivalate	11.95				30.00				7.19			
α-Naphthyl benzoate	36.23	220	1.11	2.71	30.94	225	1.50	8.89	10.13	240	1.11	1.00
β-Naphthyl benzoate	40.30				46.51				11.28			
1,7-Naphthyl-diacetate	17.30	230	1.09	1.30	30.38	180	1.76	18.64	10.39	215	1.12	1.23
2,7-Naphthyl-diacetate	19.00				53.69				12.04			
1,7-Naphthyl-dipropionate	13.39	250	1.27	4.53	28.83	200	1.72	17.53	15.17	215	1.23	2.44
2,7-Naphthyl-dipropionate	17.02				49.87				19.19			
1,7-Naphthyl-dipivalate	14.73	250	1.28	5.02	21.22	200	1.55	13.92	12.98	215	1.41	3.37
2,7-Naphthyl-dipivalate	19.00				33.06				18.12			

with the chain length of the acyl group; the presence of a benzene ring (benzoyl derivative) also has a positive effect because of the aromatic nature of the stationary phase.

Table II shows the retention data of α- and β-naphthol derivatives together with the derivatives of a pair of dihydroxynaphthalenes. The separation on the mesomeric phase is clearly enhanced in comparison with traditional phases; benzoyl and propionyl derivatives appear to be the most useful but, considering the possibility of direct derivatization in aqueous solution, the propionyl ester seems to be the best derivative for the analysis of naphthol compounds on the mesomeric phase.

The second aspect of GLC analysis that we studied is the suitability of the liquid crystal column for quantitation. Fig. 2 illustrates the response curves for α-naphthol and the corresponding naphthyl propionate on liquid crystal and conventional columns. The constant relative molar responses (RMR) on mesomeric and OV-225 phases indicate good chromatographic behaviour. Moreover, this form of presentation emphasizes adsorptive losses during chromatography with the OV-17 column, particularly for small samples.

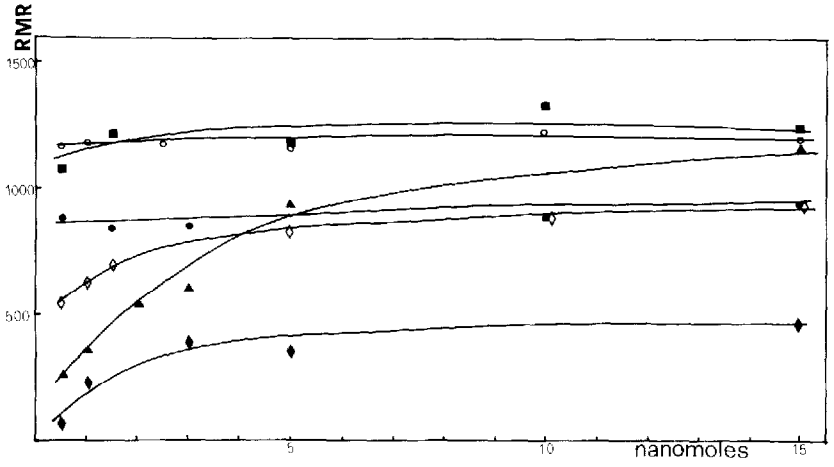

Fig. 2. RMR[21] on FID of α-naphthol on OV-17 at 200°C (◆), on liquid crystals at 170°C (●) and on OV-225 at 175°C (◇), and of α-naphthyl propionate on OV-17 at 200°C (▲), on liquid crystals at 190°C (○) and on OV-225 at 180°C (■). The values are relative to heptane.

The acyl derivative exhibits an obviously greater FID response than the underivatized naphthol.

To summarize, the investigated polar mesomeric phase is well suited for selective separations of hydroxynaphthalenes and particularly for their derivatives, allowing better peak resolution and good response with a FID.

ACKNOWLEDGEMENT

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