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Short Communication

Use of three molecularly toroid phases for the gas chromatography of some volatile oil constituents, and comparison with liquid crystal phases

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ABSTRACT

A commercially available capillary, "Chiraldex-A-DA" and two 24-crown-8-ethers in packed columns, have been used in the gas chromatographic examination of some volatile oil constituents. They lose some selective-retaining properties at high temperatures. These molecular toroid phases show a characteristic elution sequence for aromatics: cuminal–anethole–safrole–thymol, different to liquid crystals. The Chiraldex and dicyclohexanocrown exhibit good retention of geraniol and caryophyllene; whereas the more polar dibenzocrown shows poor geraniol and good estragole retention, compared to other solutes.

INTRODUCTION

We have previously utilised liquid crystal substances as stationary phases for study by gas chromatography of volatile oil constituents in packed columns [1–4] and a commercially available capillary [2]. These phases could be used below [1,3] and above [2] their nematic or chiral nematic [4] temperature ranges. As these results should have been influenced by the molecular shapes of the solutes studied (in contrast to conventional stationary phases) it was of interest to investigate the effect of some molecularly toroid (ring) phases, which should respond in a different way to solute molecule shapes.

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Crown (cyclic) ethers are one source of molecular rings, every third atom of which is oxygen; for example, eight ether bonds joining two-carbon units into a 24 (atom)-crown-8 (ether). Their properties can be influenced by including, on opposite sides of the ring, cyclic C_6 benzene or cyclohexane ring systems to form dibenzo- or dicyclohexano-crowns (see Fig. 1). The first crown ethers used for gas chromatography almost ten years ago by Ono [5] for dichlorophenols were the 18-crown-6s of smaller size. More recently, Ayyangar *et al.* [6] studied substituted aromatics both on this smaller dibenzo-18-crown-6, and on the two larger 24-crown-8 ethers. They found that on the larger crowns "nitrochlorobenzene and dimethylphenol isomers are separated very well", and as these two ethers are liquids well below the melting point of the 18-crown (which is about 153°C [6]) they were chosen for this study, along with the commercially available capillary to-

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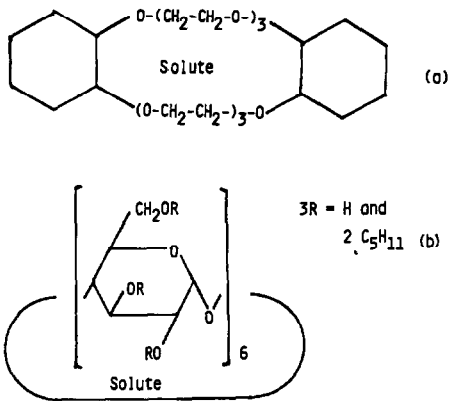

Fig. 1. Formulae of toroid phases used. (a) 24-Crown-8-ethers, with left and right hexagonal rings either dicyclohexano or dibenzo structure. (b) Chiraldex-A-DA.

roid phase "Chiraldex-A-DA". This lattermost consists of a di-O-pentylated α-cyclodextrin [7] and so retains an unsubstituted hydroxyl-group on each of its six α-glucose units which form a 30-atom ring (see Fig. 1). It is claimed to have a "hydrophobic surface" and "show pronounced selectivity differences based on the size, shape and functionality of the analyte" which "applies to both aromatic and nonaromatic enantiomers" with the warning that there is "critical temperature dependence for enantioselectivity" [7]. α-Cyclodextrin has the smallest cyclodextrin-ring system, and so is closest to the crown ether size.

Modified cyclodextrins in capillaries have been used recently to resolve enantiomers of terpene hydrocarbons by Konig *et al.* [8], but with fully tri-O-pentylated larger cyclodextrins. They have also been used in dilute mixture in polysiloxanes as stationary phases for mono- and sesqui-terpene hydrocarbons [9], which obviously leaves their contribution confused.

EXPERIMENTAL

Apparatus

For the capillary studies a Hewlett-Packard 5790A gas chromatograph was used, fitted with a flame ionisation detector, capillary control unit and splitter injection port in split mode. A Hewlett-Packard 3380A integrator/recorder was attached. For the packed column work a Pye-Unicam GCD gas chromatograph was used, fitted with a flame ionisation detector. A Pye wide-range amplifier and Hewlett-Packard 3390A integrator/recorder were attached.

A "Chiraldex-A-DA" capillary was used (Advanced Separation Technologies, Whippany, NJ, USA), 10 m × 0.25 mm I.D., only heated to 140°C or below at about 8°C min^{-1} and cooled slowly by switching the oven off. The injection port was maintained above 200°C. Helium was the mobile phase at 1.6 ml min^{-1}.

The packed columns were of glass, 1.5 m × 2 mm I.D. containing 3% (w/w) of the crown-ether on Chromosorb W AW, 80–100 mesh, prepared as in ref. 2, where details of the liquid crystal packed columns and capillary are also given. A high load 10% (w/w) crown ether column yielded very slowly emerging peaks, and was rejected, although used by Ayyangar *et al.* [6]. Reasonably high temperatures were needed.

Operating conditions are given in Table I, observing the GCD oven temperatures with a Technoterm 7300 probe. Nitrogen was the mobile phase for the packed columns at the high flow-rate of 40 ml min^{-1}.

Materials and methods

Di-benzo-24-crown-8 and di-cyclohexano-24-crown-8 were from Aldrich. Sources of solutes for injection are given in refs. 2–4. Injections were made from a microsyringe which had been filled, then "emptied".

RESULTS AND DISCUSSION

The polartity of the toroid phases was evaluated as before [4]. At 120° on Chiraldex-A-DA, 2-octyne emerged considerably after *n*-butanol and pyridine, indicating a very low polarity phase. In contrast, the dibenzo-crown ether released octyne together with butanol, well ahead of pyridine, typical of a quite polar phase. The dicyclohexano-crown ether had octyne eluting just ahead of pyridine, after butanol, indicating intermediate polarity; between the other two phases.

Once again, relative retention times to linalol were calculated, after subtracting holdup times [4], and were compared to results on liquid crystal phases obtained before. Average results are given in

TABLE I

RELATIVE RETENTION TIMES (LINALOL = 1.00) ON TOROIDAL AND LIQUID CRYSTAL PHASE COLUMNS

Average results. Values in italics are out of descending sequence, and could be shifted up or down the Table as indicated by their suffix arrows to the position of their abbreviation (G, etc.) Mobile phase details for toroids in this text, and for liquid crystals in refs. 1–4. Capillary shown by "cap" and packed column by "pac".

Solute	Gas chromatographic phases, used at various temperatures (°C), with liquid crystal condition shown											
	"Chiraldex-A-DA" cap			Dicyclohexano-crown pac		Dibenzo-crown pac		"MPMS" cap nematic [2]	$(MBT)_2$ pac		Cholesteryl acetate pac	
									Melted super-cool [1–3]	Unmelted	Chiral nematic [4]	Isotropic
	110	125	140	155	170	155	170	150	150	150	115	155
Thymol			10.00	10.51	9.00	10.75	9.18	A 6.20	A 6.60	4.71		5.65[a] Y
Geraniol (G)	4.60	4.04	*3.64*↓	*3.33*↓	*3.08*↓	*3.52*↓	*3.27*↓	*2.58*↓	*4.27*↓	3.85		2.40[a]↓
Safrole (S)	4.17	3.99	3.82	3.63 G	3.56	5.01	4.82	5.21	*4.58*↓	*2.67*↓		*3.48*↓
Anethole (A)	4.03	3.91	3.72 G	3.29	3.20 G	4.82	4.55	*7.60*↑	*8.26*↑	3.53		3.82
Caryophyllene (Y)	3.77	3.75	3.61	3.12	3.04	*2.43*↓	*2.52*↓	*3.26*↓	*2.18*↓	*2.87*↓		*5.08*[a]↑ S
Cuminal	3.25	3.28	3.22	2.69	2.68	4.30 G	4.21 GY	5.21 YG	5.01 SG	3.30 YS	2.79	2.69 G
α-Terpineol (T)	2.29	2.24	2.18	1.96	1.94	*2.30*↓	*2.32*↓	*2.54*↓	*2.43*↓	1.94	2.21	2.13
Estragole	2.03	2.05	2.04	1.86 P	1.84	2.44 YT P	2.42 T	3.03 T	2.83 TY P	1.70	2.02	1.97
γ-Terpinene	0.44			0.48		0.45			0.53	0.44	0.65 P	0.72 P
Cineole (N)	0.44			0.41		0.43			*0.41*↓	0.44 P	*0.46*↓	*0.58*↓
Limonene	0.39			0.40		0.37			0.49	0.40	0.54	0.63
p-Cymene (P)	0.38			*0.48*↑		*0.50*↑			*0.53*↑	*0.43*↑	*0.57*↑	*0.66*↑
α-Terpinene	0.32			0.36		0.35			0.43 N	0.38	0.48 N	0.59 N
α-Pinene	0.20			0.21		0.24			0.23	0.23	0.24	0.33

[a] New results, not in ref. 4.

Table I, and draw on some previous work [1–4], with some new observations included.

On all toroid phases the relative retention times of the linear aromatic estragole are almost constant despite column temperature changes. Two of these phases also show this near constancy for the branched side-chain aromatic cuminal, and the cyclic terpenoid α-terpineol. However, all three phases behave most distinctively at lower temperatures, losing some of their geraniol- or estragole-retaining property at 140°C for Chiraldex, and at 170°C for the crown-ethers. These are approaching maximum usable temperatures for the crowns [6], whilst higher temperatures for the Chiraldex might alter its character [7]. Under the conditions used, the Chiraldex capillary gave no sign of enantiomer resolution with racemic linalol or carvone.

All three toroid phases show the following elution sequence for this set of aromatics: cuminal (first)–anethole–safrole–thymol (long last). Thus

safrole is not ahead of anethole, as it is on liquid crystal phases [2,4]. On these, anethole is often last and safrole first, except for cholesteryl acetate [4]. The acyclic terpenoid geraniol is a variable amongst this aromatic set, being strongly retained on the low polarity Chiraldex capillary at lower temperatures (after safrole), and also at lower temperature on the intermediate polarity dicyclohexano-crown (but less strongly, ahead of safrole). This is unlike conventional phases. In contrast, its lack of affinity for the aromatic nature of dibenzo-crown sees geraniol emerge ahead of the aromatic solute set. The liquid crystal unmelted aromatic bis(methoxybenzylidineanilbitoluidine) [$(MBT)_2$] also strongly retains geraniol, whereas isotropic terpenoidal cholesteryl acetate shows low affinity for it. These results are the reverse of what might be expected, but neither phase is in the nematic state. The "MPMS" multiaromatic liquid crystal capillary also shows a logical lack of affinity for geraniol, as does melted $(MBT)_2$.

A trio of mixed solutes, earlier than the aromatic set, shown on the lower polarity toroids Chiraldex and dicyclohexano-crown is: estragole–α-terpineol–caryophyllene (last); as it is also on unmelted $(MBT)_2$, isotropic cholesteryl acetate and nematic bis(methoxybenzilidineanilchloroaniline) [$(MBCA)_2$] [2]. This three-solute sequence is reversed on melted, supercooled $(MBT)_2$ [2] as the aromatic nature of the phase has become apparent by strongly retaining the aromatic estragole. The polar dibenzo-crown's aromaticity also delays estragole till last at 155°C. The non-polar large cyclic sesquiterpene hydrocarbon caryophyllene thus exhibits reasonable affinity for the Chiraldex and dicyclohexano-crown, appropriate strong retention on cholesteryl acetate, but little holdup on melted aromatics $(MBT)_2$ and azoxydiphenetole [2].

The Chiraldex capillary at 125°C or less thus shows similar responses in respect of good geraniol and caryophyllene retention to packed columns of dicyclohexano-24-crown-8 at 155°C and to unmelted $(MBT)_2$, although the capillary gives better chromatograms, or course. The six alcohol groups remaining in the Chiraldex-A-DA ring molecule (despite each sugar unit having dialkyl substituents) probably help to retain primary alcohols like geraniol, but not tertiary alcohols like α-terpineol. The packed column of dibenzo-24-crown-8-ether shows similar responses in respect of good estragole and poor geraniol retention to the "MPMS" liquid crystal capillary, and the latter is naturally the one to use, except for monoterpene hydrocarbons.

With regard to cyclic monoterpene hydrocarbons and substances of similar short retention times, the Chiraldex capillary cannot resolve cineole from γ-terpinene, nor limonene from *p*-cymene. Of the crown ethers these separations are surprisingly better on the polar dibenzo-crown as other overlaps appear on dicyclohexano-crown. A feature of both crown ethers is their strong affinity for *p*-cymene. This aromatic is also strongly retained by melted $(MBT)_2$ [10] and surprisingly well by isotropic cholesteryl acetate [4]. However, these two phases show low affinity for cineole, unlike the toroids.

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