Short Communication

Structurally informative response patterns of some monoterpenoids found in volatile oils to gas chromatography on two commercial dipentylated cyclodextrin phases

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ABSTRACT

Gas chromatographic retention times relative to *n*-undecane at 100–150°C were plotted for various monoterpenoid alcohols or carbonyl compounds on two "Chiraldex" depentylated cyclodextrin phases. As the temperature was increased, the modified β-cyclodextrin ("B-DA") just showed all values decreasing. However, the α-cyclodextrin ("A-DA") exhibited distinctive solute patterns. 4- and 1-ols and aldehydes typically gave a decrease again, but 3-ols and 3-ones exhibited near constant values, whilst the relative retention times of 4-ones (especially bicyclic ones) increased. This smaller ring "Chiraldex" responded to the position of the polar group in the solute molecules, whilst the larger ring reacted to the rigid bulk of the molecules. Increases in results with change to the larger ring phase B-DA were over 70% at 125°C for bicyclics, exactly 28% at 150°C for three different dienes, and low or even negative for acyclic tepenoids like citral. Such results could indicate structural information about unidentified terpenoids.

INTRODUCTION

This author has recently used a toroid commercially available capillary gas chromatographic phase "Chiraldex-A-DA" to observe special responses by some volatile oil constituents [1], to assess its value for oil analysis [2], and in phase polarity studies [3]. It consists of modified α-cyclodextin with two-thirds of the hydroxyls on each of the ring of six α-glucose units pentylated; depicted in ref. 1. Its low polarity [3], although it still retains some polar hydroxyls, should make it appropriate for resolving various volatile oil constituents. These include a range of somewhat polar monoterpenoid alcohols and carbonyls, with their oxygen-containing function in various positions in their molecules. The molecular "fit" to the modified cyclodextrin of these various branched acyclic, monocyclic and bicyclic terpenoids as the phase temperature is changed, should be useful. It could indicate the oxygen-group position or other features in an unknown solute, and could suggest how the Chiraldex functions, if results are compared with those for unbranched alkanes, alcohols and aldehydes of similar retention times. Such deductions might be further assisted by comparing the results on the A-DA phase with those from the larger

molecular ring B-DA consisting of the same dipentylated modification, but of β-cyclodextrin and seven α-glucose units in a ring.

Volatile oils also contain terpene hydrocarbons and their enantiomers have been resolved by Konig et al. [4] using fully tri-pentylated β- and γ-cyclodextrins. They were also used in 1990 by Takeoka et al. [5] in diluted admixture with a polysiloxane (which leaves their contribution to separations confused) to resolve the terpene hydrocarbons of ginger oil, and the esters of grapefruit juice. Recently, monopentyl, dimethyl β-cyclodextrin diluted in polysiloxane was used by Bicchi et al. [6] to try to resolve ten pairs of

enantiomers including limonene and menthol. These, with α-pinene, fenchone, pulegone, borneol, α-terpineol and linalol were not better resolved by Schmalzing et al. [7] on trimethylated β-cyclodextrin when it was chemically bonded to a polysiloxane than on a mixture.

EXPERIMENTAL

Apparatus

A Hewlett-Packard 5790A gas chromatograph was used, fitted with a capillary control unit, and a splitter injection port and flame ionisation

TABLE I

RELATIVE RETENTION TIMES (n-UNDECANE = 1.00) ON CHIRALDEX-DA (DIPENTYL) CAPILLARIES WITH PERCENTAGE INCREASES ON CHANGING TO THE LARGER MOLECULAR RING

Average results. Percentage increase (inc) shown for solutes on changing from the smaller α- to the larger β-cyclodextrin modification. Helium holdup times on both phases 0.25–0.30 min.

Solute		Gas chromatographic phases, used at various temperatures (°C)								
		100			125			150		
		β	α	% inc	β	α	% inc	β	α	% inc
Isoborneol	I		3.46		7.78	3.45	125	6.35	3.33	91
Borneol	B		3.95		8.36	3.84	118	6.87	3.57	92
Thujone	T	3.17	1.08	193	2.69	1.24	117	2.52	1.36	85
Camphor	CM	4.55	1.67	172	4.01	1.86	116	3.84	2.04	88
α-Terpineol	α		3.65		6.96	3.47	101	5.78	3.19	81
4-Terpineol	4		2.83		5.26	2.85	85	4.54	2.88	58
Fenchone	F	2.11	0.98	115	2.02	1.16	74	2.00	1.29	55
Menthone	MN	3.16	1.59	99	2.80	1.73	62	2.65	1.85	43
Menthol	ML		3.87		5.92	3.73	59	4.71	3.33	41
Carvone	CV		3.48		5.30	3.54	50	4.53	3.54	28
Perillal	PE					6.57		7.59	5.95	28
Linalol	L	2.74	1.57	74	2.26	1.57	44	2.00	1.56	28
Pulegone	PU		2.69		3.83	2.77	38	3.56	2.84	25
Piperitone	PI		3.63		4.96	3.70	34	4.44	3.59	24
Citronellal	CA	2.60	1.82	43	2.26	1.81	25	2.15	1.79	20
Citronellol	CO				6.40	5.11	25	4.94	4.27	16
Geraniol	G				6.60	6.36	4	4.88	5.04	−3
n-Dodecane	DO	2.06	2.03	1.5	1.83	1.84	−0.5	1.70	1.73	−1.7
Citral	CT				5.27	5.93	−11	4.29	5.02	−14
n-Decanal	DA				2.96	3.78	−22	2.81	3.28	−14
n-Octanol	O	2.43	3.26	−25	2.01	2.75	−27	1.81	2.37	−24
n-Undecane retention time (min)		0.84	1.00		0.35	0.37		0.17	0.17	

detector both set at 235°C. A Hewlett-Packard 3380A recorder/integrator was attached.

The "Chiraldex-A-DA" and "B-DA" capillaries (from Advanced Separation Technologies, Whippany, NJ, USA) 10 m × 0.25 mm I.D. were heated and cooled at less than 10°C min^{-1} to preserve the phases. Helium was the mobile phase used at 1.5–2.0 ml min^{-1}, and as the "make-up" gas for the detector.

Materials and methods

Solutes used were obtained from various commercial sources including Aldrich, Allwest (Perth), BDH, Dragoco (Holzminden), Koch-Light, Sigma and T.C.I. (Tokyo). They are listed in Table I and their structures presented in Fig. 1. The formula numbering used in this figure is
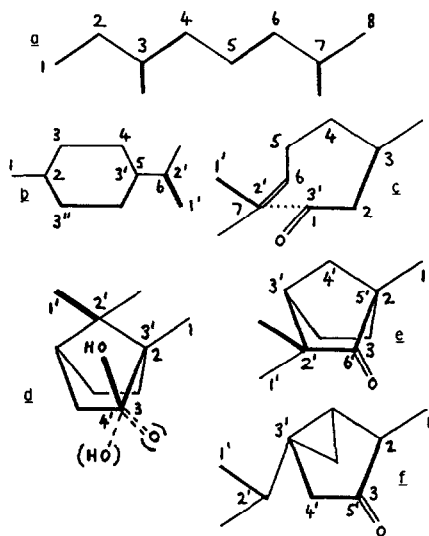

Fig. 1. Formulae of terpenoid solutes used. Their numbering does not necessarily conform to required chemical nomenclature. (a) Citral with 1-one and 2–3,6–7 diene. Citronellal with 1-one and 6–7 monoene (see also 1c). Citronellol with 1-ol and 6–7 monoene. Geraniol with 1-ol and 2–3,6–7 diene. Linalol with 3-ol and 1–2,6–7 diene. (b) Carvone with 3-one and 2–3″,1′–2′ diene. Menthol with 4-ol. Menthone with 4-one. Perillal with 1-one and 2–3,1′–2′ diene. Piperitone with 4-one and 2–3 monoene. Pulegone with 4-one and 2′–3′ monoene. α-Terpineol with 6-ol and 2–3 monoene. 4-Terpineol with 3′-ol and 2–3 monene. (c) Citronellal conformation, pseudo 3′-one. (d) Isoborneol (continuous lines). Borneol with 3-OH "down" instead of "up". Camphor with 3=O instead of OH. (e) Fenchone: 6′-one or 3-one. (f) Thujone; 5′-one or 3-one.

purely for the discussion in this paper, and is not intended to be correct in a conventional chemical sense. Thus aldehydes are considered as 1-ones, with 4-terpineol and linalol as 3-ols. Injections of traces of these solutes (strong alcoholic solutions of borneols, camphor and menthol) were made from a microsyringe which had been filled, then "emptied". Holdup times were deducted from observed retention times, and obtained by extrapolating to methane the times for n-heptane and n-hexane plotted on semi-logarithmic graph paper.

RESULTS AND DISCUSSION

Average results are given in Table I and mostly depicted in Fig. 2 as relative retention times to the inert n-undecane. A typical result for an unbranched non-polar substance can be expected from the next alkyl homologue n-dodecane. The plot of its retention relevant to undecane starts just above 2.0 and decreases, with temperature increase, towards 1.7 on both phases. The same typical decline (with different higher values, greatest on the α-ring phase) is shown by unbranched octanol and decanal; and also by the branched eight-carbon chains of geraniol (Fig. 2), citronellol and citral (main peak used of mixture), with geraniol giving similar values on both phases. We reported this response on conventional phases in 1970 [8]. These solutes are all 1-ols or 1-ones (Fig. 1a) and cyclic perillal is an example of the latter, with its aldehyde group at the opposite end of a rigid ring system to an isopropenyl chain. Unlike the modified α-cyclodextrin capillary the Chiraldex-B-DA showed all results (dashed lines) decreasing with increase in temperature, so there were no different patterns.

In contrast, on Chiraldex-A-DA 3-ols such as monocyclic 4-terpineol, isoborneol (at lower temperatures), and branched chain linalol, with the monocyclic 3-one carvone, show virtually no change, i.e. practically a horizontal plot over a temperature range. Surprisingly, this is also exhibited by the branched chain aldehyde citronellal on this smaller ring phase. Perhaps this solute flexes its molecules to adopt a conforma-

Fig. 2. Average relative retention times to n-undecane of monoterpenoids at three temperatures. Continuous lines, on Chiraldex-A-DA; dashed lines, on Chiraldex-B-DA. Abbreviations for solute identities in Table I.

tion making it a pseudo-3-one (Fig. 1c), unlike its comparable alcohol, citronellol? Citronellal exhibits surprisingly low retention for a C_{10} unsaturated aldehyde on other phases too [8–10] and so does not relate chromatographically to citronellol as citral does to geraniol.

Of the other alcohols studied on the smaller ring phase this leaves the monocyclic, 4-ol (from either end) menthol (Fig. 1b) behaving like the bicylic borneol which could also function as a 4-ol. They show a lesser decrease in relative retention times than the 1-ols. Isoborneol may behave like a 4-ol, and not a 3-ol, above 125°C, possibly due to the juxtaposition of its alcohol group to the paired methyls in the rigid molecule

(Fig. 1d). The chiral isomers borneol and isoborneol can be resolved on normal phases, and perhaps this 3 vs. 4-ol behaviour is involved?

Of the ketones considered, there is the group of monocyclic, 4-ones (from either end) pulegone and menthone, which show with piperitone (at lower temperatures) an increase in relative retention times on Chiraldex-A-DA with temperature rise. Other ketones examined were the bicyclics fenchone, thujone and camphor, which although obviously 3-ones, do not behave like carvone —they may actually function as higher number ketones (Fig. 1d, e, f), giving a larger continual increase. We previously observed this relative increase [8] on normal phases with isomenthone and camphor, but not with pulegone or piperitone. These increases are not shown on Chiraldex-B-DA.

A feature of changing to the larger ring phase was the over 70% increase in relative retention times at 125°C (over 50% increase at 150°C) given by the bicyclic saturated alcohols and ketones. For most the increase was over 115% at 125°C and the lower results for fenchone could be because it is behaving as a 6-one on this phase unlike the other bicylics. It is then like α-terpineol, functioning as a 6-ol. The larger β-cycodextrin molecular rings gave virtually no change in relative relention times compared to α- for the saturated linear hydrocarbon dodecane and surprisingly for the diene geraniol also (Table I and Fig. 2). They were thus effective in retaining bulky, rigid, bicyclic molecules, but less so with flexible, elongated acyclics.

Geraniol was different to two other branched unsaturated acyclics citronellol and citronellal. These monoenes both gave a low 25% increase at 125°C in relative retention times. In this respect, citronellal is mimicking its corresponding alcohol, but with much lower retention times. The diene citral is different again in showing a small decrease in relative retention times on changing from the α- to the β-phase, like the decreases shown by saturated unbranched n-decanal and n-octanol. Chiraldex-B-DA thus only shows more retention than A-DA (for acyclics relative to undecane) with the monoenes citronellol and citronellal, and not

with saturated substances, nor the dienes geraniol and citral. This monoene affinity is supported by the α- to β-phase increase of the two terpineols, which are greater than for the other monocyclics (Table I). However, the monoenes pulegone and piperitone gave only 25% increases at 150°C, compared to the 40% for the saturated 4-one menthone, and for menthol.

Three different dienes, cyclic and acyclic, gave exactly 28% increases (α- to β-phase) in relative relention times at 150°C. These were linalol, carvone and perillal. Thus the Chiraldex-B-DA can indicate the degree of unsaturation or bicyclic nature of solutes, compared to the oxygenation position selectivity of the A-DA phase. The latter phase appears to exhibit constant relative retention of monoterpenoid 3-ols and a 3-one, despite temperature increase. Possibly their polar groups fit about midway into the α-ring molecules, unlike 1-, 4-, and other oxygenated position terpenoids? Other mechanisms like simple partition and adsorption may influence various solutes to show alterations in relative retention. Nevertheless, some distinctive features can be noted for both compared to conventional phases. On Chiraldex-DA borneol is retained more strongly than carvone, and menthol more than pulegone —a preference for saturated alcohols is exhibited rather than unsaturated ketones.

In summary, the relative retention time effects to undecane observed for a limited number (18) of monoterpenoids are as follows.

(1) Chiraldex-A-DA, with temperature increase: fall in values suggest 1- or 4-ol or aldehyde; "constant" values suggest 3-ol or 3-one; or rise in values suggest 4-, 5- or 6-one. (*Note:* Some solutes behave atypically to their obvious polar group position).

(2) Chiraldex-B-DA results compared to above at 150°C: over 80% increase suggests bicyclic; below 80% to about 25% increase suggests monocyclic, with higher values possibly monoene; 28% increase suggests diene; or below 25% increase (or fall) suggests acyclic.

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