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Short Communication

Comparison of two esterified γ-cyclodextrins with some other chirally selective gas chromatographic phases using volatile oil constituents

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Abstract

Twenty-six different volatile oil constituents were used as solutes to check some chirally selective gas chromatographic phases for similar behaviour. Some diverse monoterpenoids and aromatics gave almost the same relative retention times on three differently esterified γ-cyclodextrins. However, rigid molecular bicyclic monoterpenes yielded different results on the trifluoroacetyl ester phase, and caused a changed elution sequence. This phase was equivalent to the previously used propionyl ester for some solutes, with increase in values, when compared to an α-cyclodextrin ester phase, remaining over 100% for most bicyclics. The γ-cyclodextrin butyryl ester was equivalent to Chirasil-Val for several solutes, but not for some bicyclic terpenes and aromatics, and it did not give as good an analysis of patchouli oil sesquiterpenes.

1. Introduction

This author has previously compared the behaviour of various solutes found in volatile oils on sets of dipentylated cyclodextrins which were either esterified or unesterified (with the 3-OH remaining). Relative retention times, using the three cyclodextrin ring sizes [1–3] allowed deductions to be made concerning the chemical nature of each solute peak. Percentage increases in these values on changing to γ-unesterified cyclodextrin from the corresponding α-modification (both dipentylated) were very indicative of whether monoterpenoids were bicyclic, monocyclic or acyclic. These results were partly seen with the esterified cyclodextrins, although here a different ester was used on the α- and γ-rings, trifluoroacetyl and propionyl respectively [3]. The latter was used for its claimed temperature stability (the manufacturer's booklet [4] has to give directions for regenerating the trifluoroacetyl cyclodextrins after high-temperature "misuse"), "enhanced selectivity" and "increased sensitivity" [4]. In case this change of esterifying acid had influenced the observations, it was desirable to check what would occur using the γ-trifluoroacetate ester instead of the propionate dipentylated γ-cyclodextrin [3]. These phases were introduced in 1990 and subsequently [3] to resolve enantioners, but that is not the purpose of this work.

Besides this recently introduced γ-propionate phase, the manufacturers have provided γ-butyrylester cyclodextrin, which is "nonpolar and has temperature stability. It is considered a good alternative to the L-valine *tert.*-butylamide

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phase (Chirasil-Val, which has a methylpolysiloxane backbone and contains no cyclodextrin). The influence of the inclusion mechanism on selectivity is much reduced" [4]. A comparison of new observations on butyryl and trifluoroacetyl γ-(dipentylated) cyclodextrins with previous results on propionyl γ-cyclodextrin [3] and Chirasil-Val [5] would thus be interesting.

2. Experimental

2.1. Apparatus

A Hewlett-Packard 5790A gas chromatograph was used, fitted with a capillary control unit and a splitter injection port. This latter and the flame ionisation detector, were both used at 215°C. Helium was the mobile phase, used at 0.6–1.2 ml min^{-1}, and as "make-up" gas to the detector.

The Chiraldex modified cyclodextrin capillaries used were purchased from Advanced Separation Technologies (Whippany, NJ, USA) and were all 10 m × 0.25 mm I.D. with film thickness given as 0.125 μm ± 10%. They were G-TA (trifluoroacetyl, dipentyl, γ-cyclodextrin), and G-BP (butyryl, dipentyl, γ-cyclodextrin). The previously used [3] G-PN (propionyl, dipentyl, γ-cyclodextrin) and A-TA (trifluoroacetyl, dipentyl, α-cyclodextrin) were from the same supplier. The Chirasil-Val capillary [5] was from Alltech (Deerfield, IL, USA) and was 25 m × 0.25 mm I.D. with 0.16 μm film thickness. All capillaries were heated and cooled at less than 10°C min^{-1} to avoid damaging the phases.

2.2. Methods

Solutes from various commercial sources were used. Trace residues from an "emptied" syringe were injected. Holdup times, obtained by extrapolating to methane the retention times for *n*-heptane and *n*-hexane on semi-logarithmic graph paper, were deducted from observed retention times. Relative retention times to *n*-undecane or to linalol were calculated, having been found previously to be more significant for this work than retention indices [2]. These were very reproducible; for example, repeated determinations for cuminal and menthol on Chiraldex G-TA gave identical different relative retention times given in Table 1. Results for fenchone and some other solutes were ±0.02. Similarly, 4-terpineol and estragole on G-BP gave identical values shown in Table 2. Results for fenchone on this phase, and for some other solutes were ±0.01.

3. Results and discussion

Table 1 lists new results as relative retention times against *n*-undecane for the modified γ-cyclodextrins Chiraldex G-TA (trifluoracetyl ester) and G-BP (butyryl ester). They are compared with previous results on the propionyl ester G-PN and on the α-cyclodextrin trifluoracetyl ester A-TA. Some solutes give similar values on all three γ-ester phases at 125°C. These are the aromatics *p*-cymene, estragole and cuminal; the acyclic monoterpenoids myrcene, linalol, citronellal, (citral and citronellol on two phases); and the monocyclic hydrocarbons α-terpinene, limonene and γ-terpinene (columns 3, 5 and 7, Table 1). Estragole is distinctive in showing the lowest relative retention time (by a small amount) for the three γ-esters on G-TA, which usually has the highest values. Such are distinctively shown by the rigid molecular bicyclics α-pinene, camphene, cineole and fenchone. Three of these even appear earlier in the solute elution sequence from the other two phases. Their percentage increase in relative retention going from G-BP (usually the lowest values) to G-TA (usually the highest) ranges from 63–88% (column 6, Table 1). The other bicyclics, 3-carene and thujone, which has a rotatable three-carbon side-chain, give only 17 and 33% increase, respectively. These values are similar to those of the monocyclics menthone and 4-terpineol, respectively, which also have such a side-chain. "No" increase (less than ±8%) is shown by three monocyclic terpene hydrocarbons, three acyclic monoterpenoids;

Table 1
Relative retention times (*n*-undecane = 1.00) on esterified dipentyl cyclodextrin capillaries at three temperatures

Solute	Type[a]	Column No. in this table								
		3: Chiraldex G-TA at 125°C	4: % increase ← G-PN to TA (columns 3/5)	5: Chiraldex G-PN at 125°C (Ref. [3])	6: % increase G-PB to TA (columns 3/7)	7: Chiraldex G-BP at 125°C	8: Chiraldex G-BP at 110°C	9: Chiraldex G-BP at 140°C	10: Chiraldex A-TA at 125°C (Ref. [3])	11: % increase A- to G-TA (columns 3/10)
Piperitone	M	8.01	12	7.17					*3.60*[b]	122
Citronellol	N	6.75	3	6.54					*4.74*	42
Citral	N	6.66	5	6.33					6.03	10
Cuminal	A	6.53	−1	↑ *6.55*[b]				5.24	4.88	34
Menthol	M	6.13	11	5.54					3.59	71
4-Terpineol	M	5.01	14	4.39	30	3.85[c]	4.28	3.41	*2.77*	81
Estragole	A	3.65	−7	3.93	−3	3.75[c]	4.12	3.38	2.82	29
Fenchone	B	3.35	29	*2.59*	74	*1.93*[c]	*2.03*	*1.83*	*1.16*	189
Thujone	B	3.32	16	*2.85*	33	*2.49*[c]	*2.75*	*2.22*	*1.26*	163
Menthone	M	3.30	6	3.12	18	2.80[c]	3.08	2.52	*1.72*	92
Citronellal	N	2.45	−1	2.46	7	2.28[c]	2.48	2.08	1.77	38
Linalol	N	2.37	−2	2.42	6	2.24[c]	2.48	2.00	1.44	65
Cineole	B	2.07	49	1.39	88	1.10	*1.05*		0.76	172
Camphene	B	1.27	55	*0.82*	87	*0.68*	*0.62*		*0.42*	202
γ-Terpinene	M	1.17	3	1.14	5	1.11[c]	1.11	1.11	0.74	58
Limonene	M	1.07	8	0.99	8	0.99	0.92		0.67	60
3-Carene	B	1.03	13	0.91	17	0.88	0.80		0.59	75
p-Cymene	A	1.01	−3	↑ *1.04*	−2	↑ *1.03*	↑ *1.00*		↑ *0.68*	48
α-Terpinene	M	0.91	5	0.87	5	0.87	0.80		0.56	62
α-Pinene	B	0.88	38	*0.64*	63	*0.54*	*0.56*		*0.37*	138
Myrcene	N	0.71	6	0.67	6	0.67	0.63		0.43	65

Using γ-(G) or α-(A) cyclodextrins which are dipentylated with 3-0 esterified: trifluoroacetyl (-TA), butyryl (-BP) or propionyl (-PN).
[a] A = Aromatic; B = bicyclic; M = monocyclic; N = acyclic.
[b] Values in italics are not in the elution sequence from Chiraldex G-TA (lower, unless with upward pointing arrow).
[c] Estimated from columns 8 and 9.

Table 2
Relative retention times (linalol = 1.00) on butyryl-esterified dipentyl γ-cyclodextrin compared with those from Chirasil-Val [5] at two temperatures and with two other esterified dipentyl γ-cyclodextrins at a third temperature

Solute	Type[a]	Column No. in this table								
		3: Chiraldex G-BP at 110°C	4: % increase ← columns 3/5	5: Chirasil-Val at 110°C	6: Chiraldex G-BP at 140°C	7: % increase ← columns 6/8	8: Chirasil-Val at 140°C	9: Chiraldex G-BP at 125°C	10: Chiraldex G-PN at 125°C	11: Chiraldex G-TA at 125°C
Caryophyllene	B				4.25	19	3.56			
Anethole	A				3.01	27	2.36			
Cuminal	A				2.62	20	2.19		2.71	2.75
Isoborneol	B				2.47	43	*1.73*[b]			
α-Terpineol	M				2.11	9	1.94			
Camphor	B	1.82	55	*1.17*[b]	1.69	27	*1.33*			
4-Terpineol	M	1.71	4	1.65	1.70	6	1.61	1.71	1.81	2.11
Estragole	A	1.65	22	1.35	1.69	19	1.42	1.67	1.62	1.54
Thujone	B	1.10						1.11	1.18	1.40
Citronellal	N	1.01	3	0.98	1.04	−2	1.06	1.02	1.02	1.03
Fenchone	B	0.85	15	0.74	0.91	−2	0.89	0.86	↑ *1.07*[b]	↑ *1.41*[b]
γ-Terpinene	M	0.44	−2	0.45	0.56	4	0.54	0.49	0.47	0.49
Cineole	B	0.42	2	0.41				0.49	↑ *0.57*	↑ *0.87*
p-Cymene	A	0.40	3	0.39				0.46	0.43	0.43
Limonene	M	0.38	5	0.36				0.44	0.41	↑ *0.45*
3-Carene	B	0.32						0.39	0.38	0.43
Camphene	B	0.25						0.30	0.34	↑ *0.54*
α-Pinene	B	0.20						0.24	0.26	0.37

[a,b] See footnotes to Table 1.

and by two aromatics which give a slight decrease.

A purpose of this study was to compare the ester phases G-TA and G-PN. A number of solutes give almost the same relative retention times on both phases —"no" increase, as before (column 4, Table 1). This group now includes menthone, all five acyclics and all three aromatics. The four rigid bicyclics are again distinctive with the largest increases (PN to TA) of 29–55%, leaving five other cyclic monoterpenes exhibiting "in-between" increases of 11–16%. Thus G-PN is not equivalent to G-TA for all solutes, particularly rigid bicyclic molecules which presumably are able to form transient inclusion complexes with the TA phase, but not the PN. There are a few changes in solute elution sequence, too. The monoterpenoid bicyclics α-pinene, camphene, thujone and fenchone are delayed, relatively, on TA, whilst the aromatics *p*-cymene and cuminal elute relatively quicker (see Table 1).

Previously [3], results on the dipentylated γ-cyclodextrin ester G-PN were compared with those from the α-ester A-TA. Now comparing G-TA with A-TA (column 11, Table 1) there is still [3] over 100% increase in relative retention time for nearly all bicyclics (not 3-carene which falls in a group of cyclic and acyclic monoterpenes ranging from 58–92% increase). As before, the monocyclic piperitone (122%) is grouped with the bicyclics. Three terminally oxygenated acyclics continue to exhibit low increases (less than 45%), particularly citral. Three aromatics also give increases less than 50%.

A second intention of this study was to compare Chiraldex G-BP phase with Chirasil-Val. The results are given in Table 2 as relative retention times to linalol at two temperatures as before [5]. Values are virtually the same (±9%) for the acyclic citronellal, four monocyclics, the bicyclics cineole and fenchone (at 140°C) and the aromatic hydrocarbon *p*-cymene. Despite having an identical polarity rating by *c* value [6] of 0.46, which is "fairly low", the Chiraldex G-BP phase gives increases in relative retention time at 140°C of 19–43% for three bicyclics and 19–27% for three aromatics. Increases seen at 110°C are 15–55%. Thus this Chiraldex is not an exact alternative to Chirasil-Val for all solutes, including the sesquiterpene caryophyllene. At 130°C, the helium flowrate on G-BP was adjusted to yield an uncorrected retention time of 5.30 min for caryophyllene, as was obtained from Chirasil-Val [5]. Two other sesquiterpene hydrocarbons, longifolene and humulene, then emerged at 5.35 and 6.60 min, respectively, from G-BP (5.07 and 6.10 min from Chirasil-Val). Using the conditions previously determined for patchouli oil (8 min isothermally at 130°C, then programmed up at 5°C min^{-1}) gave an inferior chromatogram from Chiraldex G-BP, which could not be improved by changing the conditions. The pairs of sesquiterpenes α-patchoulene/seychellene and β-patchoulene/α-gurjunene would not resolve. Thus for this author's purpose, the phases were not equivalent.

Comparing columns 9–11 of Table 2, nearly half the solutes yield virtually constant relative retention times at 125°C on the three Chiraldex G ester phases. Where this is not so, they usually increase from G-BP to -PN to -TA. The rise is particularly seen on the lattermost with the bicyclic terpenoids. The aromatic estragole behaves in reverse fashion, as seen in Table 1.

The most significant fact from this work is that Chiraldex G-TA is valuable for indicating bicyclic terpenoids when relative retention times are compared to values from another γ-cyclodextrin ester phase, particularly G-BP. Increase relative to undecane of over 60% suggests a rigid bicyclic molecule. A slight decrease may indicate an aromatic solute.

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