RELATIVE RETENTION TIMES OF CHLORINATED TERPENES

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Introduction

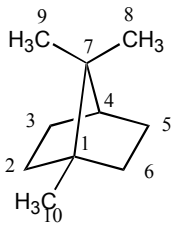
The aim of present study is to summarize available data on GC retention times for various chlorinated terpenes, synthesized in our laboratory. Such information should be helpful in identification of "unknown" Toxaphene congeners, still appearing in environmental samples. Additionally we would like to demonstrate the reliability of our approach for prediction of retention times based on the structure of a congener[1].

Materials and Methods

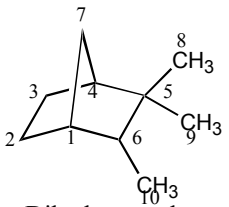
All compounds were prepared by chlorination of lower chlorinated terpenes (2-exo,10-Dichlorobornane, 2,10,10-Trichlorobornane, 2,10-Dichlorocamphene, etc), followed by fractionation on silica gel with hexane as eluent[2-5]. As a rule, several successive crystallizations from different solvents were a way to final purification. Relative retention times were determined against 2,2,5,5,8,9,9,10,10-Nonachlorobornane(Parl #62). This compound was chosen because, according to our experience, it has no significant coeluters on GC. GC conditions were as follows : GC-Varian3700, inj. – Gerstel split/splitless at 250^{o}C, column – DB-5(app. 50m), Det. – ECD(at 300^{o}C), carrier gas – nitrogen, make-up – nitrogen. Pr.: 160 ^{o}C(2 min) - 20 ^{o}C/min - 280 ^{o}C(10 min) Purge 1.00-1.90 min. Several mixtures of chlorinated terpenes, each including 2,2,5,5,8,9,9,10,10-NCB, were prepared in order to achieve well-resolved chromatograms. The most important congeners were included into more than one mixture to obtain more reliable RRTs, and to make sure RRTs do not change in course of the study.

Results and Discussion

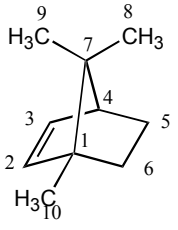
Retention times for 67 compounds are given in Table 1. Compounds are grouped by their carbon skeleton structure and number of chlorine atoms in molecule. The structures of terpenes and numbering of carbon atoms, used in this work are shown below :



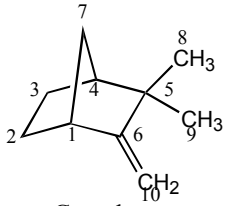
Bornane



Dihydrocamphene



Bornene



Camphene

Table 1. Polychloroterpenes. Relative retention times.

#	Chemical name	Historical name(s)	RRT
1	2-exo,5-endo,9,9,10-PeCB		0.6887
2	2-exo,3-endo,6-exo,8,9,10-HxCB	Hx-Sed	0.7667
3	2,2,5,5,10,10-HxCB		0.7181
4	2-endo,3-exo,6-exo,8,9,10-HxCB		0.7791
5	2-exo,3-endo,5-exo,9,9,10,10-HpCB	Tox7	0.7639
6	2-exo,5,5,9,9,10,10-HpCB		0.7756
7	2-endo,3-exo,5-endo,6-exo,8,9,10-HpCB	Hp-Sed	0.7875
8	2,2,5,5,10,10,10-HpCB		0.7921
9	2-exo,3-endo,5-exo,8,9,10,10-HpCB		0.8319
10	2-exo,5,5,8,9,10,10-HpCB		0.8359
11	2,2,5,5,8,9,10-HpCB		0.8423
12	2,2,5-endo,6-exo,8,9,10-HpCB	Tox B, Parl32	0.8432
13	2-exo,3-endo,6-exo,8,9,10,10-HpCB		0.8468
14	2-exo,3-endo,5-exo,6-exo,8,9,10-HpCB		0.8472
15	2-exo,3-exo,5-endo,8,9,10,10-HpCB		0.8621
16	2-exo,3-endo,6-endo,8,9,10,10-HpCB		0.8592
17	2-exo,5-exo,6-endo,8,9,10,10-HpCB		0.8757
18	2,2,5-exo,8,9,10,10-HpCB		0.8765
19	2-endo,3-exo,5-endo,6-exo,8,8,10,10-OCB	T2, Parl26	0.8161
20	2-endo,3-exo,5-endo,6-exo,8,8,9,10-OCB		0.8282
21	2,2,5,5,9,9,10,10-OCB	Parl38	0.8689
22	2,2,3-exo,5-endo,6-exo,8,9,10-OCB	3-exo-Cl-B, Parl39	0.8799
23	2-endo,3-exo,5-endo,6-exo,8,9,10,10-OCB	Parl40	0.8825
24	2-exo,3-endo,5-exo,8,9,9,10,10-OCB	Parl41	0.8857
25	2,2,5-endo,6-exo,8,8,9,10-OCB	8-Cl-B, Parl42a	0.8918
26	2,2,5-endo,6-exo,8,9,9,10-OCB	9-Cl-B, Parl42b	0.8918
27	2-exo,5,5,8,9,9,10,10-OCB	Parl44	0.8986
28	2,2,5-endo,6-exo,8,9,10,10-OCB	10-Cl-B	0.9232
29	2,2,5,5,8,9,10,10-OCB	Parl51	0.9347
30	2-endo,3-exo,6-exo,8,8,9,10,10-OCB		0.9388
31	2,2,5,5,6-exo,8,9,10-OCB	5-exo-Cl-B	0.9438

32	2,2,3-exo,6-exo,8,9,10,10-OCB		0.9451
33	2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-NCB	T12, $ToxA_c$, Parl50	0.9239
34	2-exo,3,3,5-exo,6-endo,9,9,10,10-NCB		0.9262
35	2,2,3-exo,5,5,9,9,10,10-NCB		0.9394
36	2,2,3-exo,5-endo,6-exo,8,9,10,10-NCB	3-exo,10-Cl_2-B	0.9575
37	2-exo,3,3,5-exo,6-endo,8,9,10,10-NCB		0.9575
38	2,2,5-endo,6-exo,8,8,9,10,10-NCB	8,10-Cl_2-B, Parl56	0.9618
39	2,2,3-exo,5,5,8,9,10,10-NCB	ToxC, Parl58	0.9719
40	2,2,5-endo,6-exo,8,9,9,10,10-NCB	9,10-Cl_2-B, Parl59	0.9770
41	2,2,5,5,8,9,9,10,10-NCB	Parl62	1.0000
42	2,2,3-exo,5-endo,6-exo,8,9,9,10,10-DCB		1.0458
43	2-exo,3,3,5-exo,6-endo,8,9,9,10,10-DCB		1.0892
44	2-exo,3,3,6,6,8,8,9,10,10-DCB	Parl69	1.1133
45	2,2,3-exo,5,5,8,9,9,10,10-DCB		1.1163
46	5-endo,6-exo,8,9,10-PeCB-en		0.6550
47	2,6-exo,9,9,10,10-HxCB-en *		0.6567
48	5,5,9,9,10,10-HxCB-en		0.6867
49	5,5,8,9,10,10-HxCB-en		0.7110
50	2,5-endo,8,9,10,10-HxCB-en		0.7439
51	2,5,5,9,9,10,10-HpCB-en		0.7433
52	2,5-endo,6-exo,8,9,10,10-HpCB-en		0.7588
53	2,5,5,8,9,10,10-HpCB-en		0.7733
54	5,5,8,9,9,10,10-HpCB-en		0.7756
55	3,5-exo,6-endo,8,9,10,10-HpCB-en		0.7881
56	3,5-exo,6-endo,8,9,9,10,10-OCB-en		0.8458
57	2,5-endo,6-exo,8,9,9,10,10-OCB-en		0.8637
58	2,5,5,8,9,9,10,10-OCB-en		0.8711
59	2-exo,3,3,6-exo,8,10,10-HpCDHC *		0.8066
60	2,2,3-exo,6-exo,8,10,10-HpCDHC		0.8335
61	2,2,3-exo,6-exo,8,8,10,10-OCDHC		0.9313
62	2,2,3-exo,6-exo,8,9,10,10-OCDHC *		0.9422
63	2-exo,3-endo,6-exo,8,8,9,10,10-OCDHC *		0.9752
64	2,2,3-exo,6-exo,8,8,9,10,10-NCDHC *		1.0248
65	2,2,3-exo,6-exo,8,9,9,10,10-NCDHC *		1.0374
66	2,2,3-exo,6-endo,8,8,9,10,10-NCDHC *		1.0416
67	2,2,3-exo,8,8,9,10-HpCC	Parl #25	0.8073

* - minor elements of structure are not confirmed yet

In general, RRTs for the chlorobornanes are in good accordance with the rules, reported by us previously[1)]. However, the following notes should be made :

- Retention order is the same, despite the changes in GC conditions for all but three chlorobornanes, compounds #17,18(the most polar heptachlorobornanes) and #21(one of the least polar octachlorobornanes).

- For isomers, GC retention order is similar to their elution order on silicagel/hexane column.
- Predicted RRT for compound #10 (under different GC conditions[1]), 0.8452, is only 1.2% different from the experimental value – 0.8359. Estimated RRT under GC conditions, used in this work – 0.8348, is much closer, in fact this difference in RRTs corresponds to less than 1 second difference in retention times !
- Our approach is proved to be very useful in identification of compounds of a given structure and their isolation on prep-scale. Particularly, in order to isolate recently reportend persistent compounds #2(Hx-Sed), 7(Hp-Sed)[6] and 20(major OCB in biota[7]) we have estimated their RRTs – 0.7668, 0.7901 and 0.8361. These values are very close to experimental ones, and it allowed us to identify the target compounds, to optimize the mixtures for separation and to isolate successfully sufficient amounts of each congener.
- For chlorobornanes, there is significant overlapping of retention times for congeners with different extent of chlorination. Such overlapping has not been observed for chlorodihydrocamphenes, and, obviously, is not so common for chlorobornenes.
- Compounds #30 and #33 represent a unique pair. The first has longer retention time, despite the fact it is a product of formal abstraction of chlorine from 5-endo position of #33 !

Table 2. Relative retention times of chlorobornanes as function of substitution pattern in six-membered ring and in methyl groups.

	8,9,10	9,9,10,10	8,9,9,10	8,9,10,10	8,9,9,10,10
2-exo,3-endo,5-exo		0.7639		0.8319	0.8857
2-exo,5,5		0.7756		0.8359	0.8956
2-exo,3-endo,6-exo	0.7667			0.8468	
2-exo,3-endo,6-endo				0.8592	
2-exo,3-exo,5-endo				0.8621	
2-exo,5-exo,6-endo	0.7791			0.8757	0.9388
2,2,5-exo				0.8765	
2-exo,3-endo,5-exo,6-endo	0.7875	0.8161	0.8282	0.8825	0.9239
2-exo,3-endo,6,6	0.8432		0.8918	0.9232	0.9618
2,2,5,5	0.8423	0.8689		0.9347	1.0000
2-exo,3-endo,5-exo,6-exo	0.8472				
2,2,3-exo,6-exo				0.9451	
2,2,3-exo,5-endo,6-exo	0.8799			0.9575	1.0458
2-exo,3,3,5-exo,6-endo		0.9262		0.9575	1.0892
2,2,5,5,6-exo	0.9438				1.1133
2,2,3-exo,5,5		0.9394		0.9719	1.1163

Acknowledgements
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References

1. Nikiforov V, Tribulovich V, Bolshakov S; *Organohalogen Compounds* **1996**, 28, 355-358
2. Tribulovich V, Nikiforov V, Karavan V, Miltsov S, Bolshakov S; *Organohalogen Compounds* **1994**, 19, 97-101
3. Nikiforov V, Tribulovich V, Karavan V; *Organohalogen Compounds* **1995**, 26, 379-382
4. Tribulovich V, Nikiforov V, Bolshakov S; *Organohalogen Compounds* **1996**, 28, 385-388
5. Nikiforov V, Tribulovich V, Karavan V; *Organohalogen Compounds* **1995**, 26, 393-396
6. Stern G, Loewen M, Kidd K, Miskimmin B, Muir D.C.G, Schindler D, Westmore J; *Organohalogen Compounds* **1995**, 26, 363-367
7. Vetter W, Klobes U, Krock B, Luckas B, Glotz D, Scherer G; *Environ. Sci. Technol.* **1997**, 31, 3023