

RELATIVE RETENTION TIMES OF 122 POLYCHLOROTERPENES.

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Introduction

Insecticide Toxaphene and similar products have been produced for many decades by chlorinating terpenic precursors, mainly camphene or pinene. The most effective insecticides contained 65-69 % of chlorine, which corresponds to hepta- to octachloroterpenes¹. However, hexachloro- and nonachlorocongeners are also present in technical products. Regarding terpene type, chlorinated bornanes are the main part, chlorinated bornenes, bornadienes, camphenes and dihydrocamphenes have been also detected or postulated in technical insecticide or environmental samples²⁻⁴. Recently a tricyclic compound has been reported⁵. For many years our laboratory has been involved in isolation and structure elucidation of chlorinated terpenes – potential components of insecticide Toxaphene²⁻¹². The present report is a brief summary of our effort and a reference on GC relative retention times for 122 chloroterpenes, synthesized in our lab.

Materials and Methods

Chlorinated terpenes were prepared by free-radical chlorination of 2,10-Dichlorobornane, 2,10,10-Trichlorobornane or 2,10-Dichlorocamphene to a desired extent, followed by fractionation on silica gel with hexane as eluent^{3,4,7,12}. As a rule, several successive crystallizations from different solvents were a way to final purification. A number of congeners have been then modified via chlorination, dechlorination or dehydrochlorination to yield further compounds. Relative retention times were determined against 2,2,5,5,8,9,9,10,10-Nonachlorobornane (Parlar no. 62)⁷⁻⁹.

The isolated compounds are listed in Table 1. The structures and numbering system of parent compounds are given below:

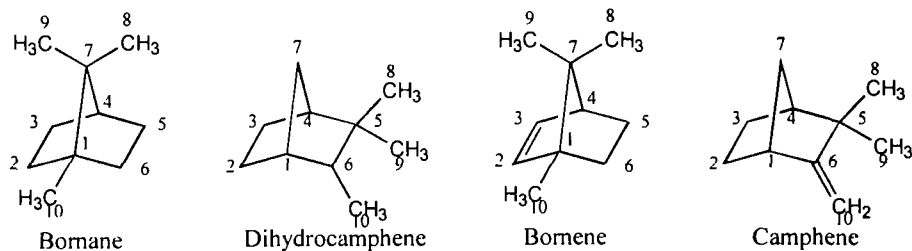


Table 1. Relative retention times of polychloroterpenes

Chemical name	RRT
POLYCHLOROBORNANES	
2-exo,5-endo,9,9,10-PeCB	0.6887
2-exo,5-endo,8,9,10-PeCB	0.7216
2,2,5,5,10,10-HxCB	0.7181
2-exo,5-endo,9,9,10,10-HxCB	0.7375
2-exo,3-endo,6-exo,8,9,10-HxCB	0.7667
2-endo,3-exo,6-exo,8,9,10-HxCB	0.7791
2-exo,5-exo,8,9,10,10-HxCB	0.8364
2-endo,3-exo,5-endo,6-exo,8,8,10-HpCB	0.7262
2-exo,3-endo,5-exo,9,9,10,10-HpCB	0.7639
2-exo,5,5,9,9,10,10-HpCB	0.7756
2-endo,3-exo,5-endo,6-exo,8,9,10-HpCB	0.7875
2,2,5,5,10,10,10-HpCB	0.7921
2-exo,3-endo,5-exo,8,9,10,10-HpCB	0.8319
2-exo,5,5,8,9,10,10-HpCB	0.8359
2,2,5,5,8,9,10-HpCB	0.8423
2,2,5-endo,6-exo,8,9,10-HpCB	0.8432
2-exo,3-endo,6-exo,8,9,10,10-HpCB	0.8468
2-exo,3-endo,5-exo,6-exo,8,9,10-HpCB	0.8472
2-exo,3-exo,5-endo,8,9,10,10-HpCB	0.8621
2-exo,3-endo,6-endo,8,9,10,10-HpCB	0.8592
2-exo,5-exo,6-endo,8,9,10,10-HpCB	0.8757
2,2,5-exo,8,9,10,10-HpCB	0.8765
2-endo,3-exo,5-endo,6-exo,8,8,10,10-OCB	0.8161
2-endo,3-exo,5-endo,6-exo,8,8,9,10-OCB	0.8282
2-exo,3,3,5-exo,6-endo,8,9,10-OCB	0.8610
2,2,5,5,9,9,10,10-OCB	0.8689
2,2,3-exo,5-endo,6-exo,8,9,10-OCB	0.8799

2-exo,3-exo,5,5,9,9,10,10-OCB *	0.8812
2-endo,3-exo,5-endo,6-exo,8,9,10,10-OCB	0.8825
2-exo,3-endo,5-exo,8,9,9,10,10-OCB	0.8857
2,2,5-endo,6-exo,8,8,9,10-OCB	0.8918
2,2,5-endo,6-exo,8,9,9,10-OCB	0.8918
2-exo,5,5,8,9,9,10,10-OCB	0.8986
2,2,5-endo,6-exo,8,9,10,10-OCB	0.9232
2,2,5,5,8,9,10,10-OCB	0.9347
2-endo,3-exo,6-exo,8,8,9,10,10-OCB	0.9388
2,2,5,5,6-exo,8,9,10-OCB	0.9438
2,2,3-exo,6-exo,8,9,10,10-OCB	0.9451
2-endo,3-exo,5-exo,6-exo,8,9,10,10-OCB *	0.9665
2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-NCB	0.9239
2-exo,3,3,5-exo,6-endo,9,9,10,10-NCB	0.9262
2,2,3-exo,5,5,9,9,10,10-NCB	0.9394
2,2,3-exo,5-endo,6-exo,8,9,10,10-NCB	0.9575
2-exo,3,3,5-exo,6-endo,8,9,10,10-NCB	0.9575
2,2,5-endo,6-exo,8,8,9,10,10-NCB	0.9618
2,2,3-exo,5,5,8,9,10,10-NCB	0.9719
2,2,5-endo,6-exo,8,9,9,10,10-NCB	0.9770
2,2,5,5,8,9,9,10,10-NCB	1.0000
2-endo,3-exo,5-exo,6-exo,8,8,9,10,10-NCB	1.0078
2,2,3-exo,5-endo,6-exo,8,9,9,10,10-DCB	1.0458
2-exo,3,3,5-exo,6-endo,8,9,9,10,10-DCB	1.0892
2-exo,3,3,6,6,8,8,9,10,10-DCB	1.1133
2,2,3-exo,5,5,8,9,9,10,10-DCB	1.1163
POLYCHLOROBORNENES	
3,6-exo,8,9,10-PeCBen	0.6463
5-endo,6-exo,8,9,10-PeCB-en	0.6550
2,6-exo,9,9,10,10-HxCB-en *	0.6567
3,5-exo,9,9,10,10-HxCB-en	0.6745
3,5-exo,6-endo,8,9,10-HxCB-en	0.6811
5,5,9,9,10,10-HxCB-en	0.6867
3,6,6,8,9,10-HxCB-en	0.6880

3,5-exo,8,9,10,10-HxCBen	0.6934
5,5,8,9,10,10-HxCB-en	0.7110
2,5-endo,6-exo,8,9,10-HxCBen	0.7127
3,6-exo,8,9,10,10-HxCBen	0.7138
3,6-endo,8,9,10,10-HxCBen *	0.7199
2,5-endo,8,9,10,10-HxCB-en	0.7439
3,5-exo,6-exo,8,9,10-HxCBen	0.7484
2,6-exo,8,9,10,10-HxCBen	0.7681
3,5-exo,6,6,8,9,10-HpCB	0.7428
2,5,5,9,9,10,10-HpCB-en	0.7433
2,5,5,9,9,10,10-HpCBen	0.7472
2,5-endo,6-exo,8,9,10,10-HpCB-en	0.7588
3,5-exo,6-endo,8,9,10,10-HpCB-en	0.7625
2,6-exo,8,8,9,10,10-HpCB-en *	0.7716
2,5,5,8,9,10,10-HpCB-en	0.7733
5,5,8,9,9,10,10-HpCB-en	0.7756
2,5-endo,6-exo,8,8,9,10-HpCBen	0.7858
3,5-exo,6-endo,8,9,10,10-HpCB-en	0.7881
3,5-exo,6-endo,9,9,10,10-HpCBen	0.8011
OCBen	0.7842
OCBen	0.7857
OCBen	0.7991
3,5-exo,6,6,8,9,10,10-OCBen	0.8240
2,5-endo,6-exo,8,8,9,10,10-OCBen	0.8259
OCBen	0.8362
3,5-exo,6-endo,8,9,9,10,10-OCBen	0.8458
2,5,5,6-exo,8,9,10,10-OCBen	0.8526
2,5-endo,6-exo,8,9,9,10,10-OCBen	0.8637
2,5,5,8,9,9,10,10-OCBen	0.8711
2,3,5-endo,6-exo,8,9,9,10,10-NCBen	0.9118
2,3,6,6,8,8,9,10,10-NCBen	0.9296
2,5-exo,6-exo,8,8,9,10-HpCBen	0.8718
OCBen	0.8482
POLYCHLORODIHYDROCAMPHENS	
2-exo,3-exo,6-exo,10,10-PeCDHC	0.7134
2-exo,3-exo,6-exo,9,10,10-	0.8053

HxCDHC	
2-exo,3-exo,6-exo,8,10,10-HxCDHC	0.8191
2,2,3-exo,6-exo,9,10,10-HpCDHC	0.8066
2,2,3-exo,6-exo,8,10,10-HpCDHC	0.8335
2,2,6-exo,8,9,10,10-HpCDHC	0.8717
2-exo,3-exo,6-endo,9,9,10,10-HpCDHC*	0.9060
2-exo,3-exo,6-exo,8,8,10,10-HpCDHC	0.9129
2,2,3-exo,6-exo,8,8,10,10- OCDHC	0.9313
2,2,3-exo,6-exo,8,9,10,10- OCDHC	0.9422
2-exo,3-exo,6-exo,8,9,9,10,10- OCDHC	0.9752
2,2,3-exo,6-exo,8,8,9,10,10- NCDHC	1.0248
2,2,3-exo,6-exo,8,9,9,10,10- NCDHC	1.0374
2-exo,3,3,6-exo,8,8,9,10,10- NCDHC	1.0416
POLYCHLOROCAMPHENES	
2-exo,3-exo,9,10,10-PeCC	0.6646
2-exo,3-exo,8,10,10-PeCC	0.6745
2,2,3-exo,9,10,10-HxCC	0.6840
2,2,3-exo,8,10,10-HxCC	0.6999
2-exo,3-exo,8,8,10,10-HxCC	0.7241
2,2,3-exo,8,9,10-HxCC	0.741
2-exo,3-exo,8,8,10,10-HxCC	0.7420
2,2,3-exo,8,8,10,10-HpCC	0.7549
2,2,3-exo,8,9,10,10-HpCC	0.7957
2,2,3-exo,8,8,9,10-HpCC	0.8073
2-exo,3-exo,8,9,9,10,10-HpCC	0.8384
2,2,3-exo,8,8,9,9,10-OCC	0.8435
2-exo,3,3,8,8,9,10,10-OCC	0.8582
2,2,3-exo,8,8,9,10,10-OCC	0.889
TRICYCLIC COMPOUND	
5,7-dichloro-3,3-bis(chloromethyl)-4-(1,1-dichloromethyl)tricyclo[2.2.1.0 ^{2,6}]heptane	0.7902

Summary

To date 122 congeners can be considered as isolated and characterized. Accumulated information on the structure - property correlations for polychloroterpenes, in combination with selective synthetic methods preparation of a congener of a given structure easily (relatively speaking) possible.

Acknowledgements

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