Determination of Toxaphene

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Toxaphene was one of the most heavily used insecticides from the fourties to the seventies. Technical toxaphene is a complex mixture of polychlorinated compounds with an average composition of $C_{10}H_{10}Cl_8$, corresponding to an average molecular weight of 414[1].
The number of compounds that have been determined so far in technical toxaphene mixtures by GC/ECD and GC/MS varies between 175[2] and 670[3], and most of those compounds are polychlorinated 1.7.7-trimethyl-bicyclo[2.2.1]heptanes (bornanes).

formula	m.w.	possible isomers	optically inactive	enantiomeric pairs
$C_{10}H_{18}$*	138	1	1	-
$C_{10}H_{17}Cl_1$	172	12	2	5
$C_{10}H_{16}Cl_2$	206	69	7	31
$C_{10}H_{15}Cl_3$	240	256	12	122
$C_{10}H_{14}Cl_4$	274	696	22	337
$C_{10}H_{13}Cl_5$	308	1488	32	728
$C_{10}H_{12}Cl_6$	342	2608	42	1283
$C_{10}H_{11}Cl_7$	376	3840	52	1894
$C_{10}H_{10}Cl_8$	410	4818	56	2381
$C_{10}H_9Cl_9$	444	5192	60	2566
$C_{10}H_8Cl_{10}$	478	4818	56	2381
$C_{10}H_7Cl_{11}$	512	3840	52	1894
$C_{10}H_6Cl_{12}$	546	2608	42	1283
$C_{10}H_5Cl_{13}$	580	1488	32	728
$C_{10}H_4Cl_{14}$	614	696	22	337
$C_{10}H_3Cl_{15}$	648	256	12	122
$C_{10}H_2Cl_{16}$	682	69	7	31
$C_{10}H_1Cl_{17}$	716	12	2	5
$C_{10}Cl_{18}$	750	1	1	-
toxaphene congeners:		Σ = 32768*	512*	16128

* Includes the unchlorinated bornane

Table 1 formula, m.w., isomeric numbers, and chirality of polychlorinated bornanes in every degree of chlorination

Investigations using GC/FT-IR have led to the conclusion that higher contents of polychlorinated bornenes are not present in technical mixtures[4]. Recently, the theoretical number of polychlorinated bornanes has been determined to be 32767[5]. Table 1 shows the distribution of isomers for all degrees of chlorination. Table 1 also distinguishes between optically active and inactive polychloro bornanes.

Residues of toxaphene have been measured in the marine food chain of the Antarctic[6,7] as well as in the Arctic[8,9], confirming that toxaphene is a major organochlorine pollutant. Atmospheric transport has been shown to be responsible for the global distribution[10]. Toxaphene residues show a changed composition compared to the technical toxaphene[6]. In particular two compounds of the technical mixture, TOX8 and TOX9, are concentrated in higher organisms[7,11,12]. Recently, these two compounds were isolated from sea mammal samples[13,14].

We have used a wide range of techniques such as GC/ECD, GC/FID, multidimensional GC, GC/MS, MS/MS, ^{1}H-NMR combined with theoretical studies of the theoretical composition of technical toxaphene and its stereochemistry in order to address the following points:

The need for a uniform nomenclature for polychlorinated bornanes

How many compounds must we expect in technial toxaphene?

What is the stereochemistry of polychlorinated bornanes?

Structure elucidation of isolated polychlorinated bornanes

Confirming of the enantiomeric form by NMR

Confirming of the bornane skeleton for TOX8 and TOX9 by MS/MS

Which toxaphene compounds are stable?

Problems in quantitation of toxaphene residues by NCI/MS

Quantitative determination of toxaphene in sea mammals

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