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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · SEPTEMBER 1992

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ISOLATION AND IDENTIFICATION OF TWO MAJOR RECALCITRANT TOXAPHENE CONGENERS IN AQUATIC BIOTA.

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Toxaphene (Polychlorinated camphene; PCC) is a major organochlorine contaminant in fish and marine mammals in North America and European waters due to substantial use for insect control on cotton and other crops in the 1960's and 70's. Toxaphene residues in aquatic biota do not resemble the technical material, as analysed by high resolution gas chromatography, and the identities of the individual components in environmental samples has not heretofore been determined because of their structural complexity. We report here the first isolation of two major PCC congeners, T2 and T12, present in fish and marine mammal fat from the Canadian arctic, from two kg of beluga whale (*Delphinapterus*) fat using polymeric film dialysis¹ and high pressure liquid chromatography and identification by ¹H nuclear magnetic resonance (with difference decoupling and difference Nuclear Overhauser Effect experiments) and high resolution mass spectrometry (Electron impact, electron capture negative ion mass spectrometry and daughter (B/E) linked scanning).

Results and discussion

The 500 MHz ¹H NMR spectra of T2 and T12 were essentially first-order with chemical shifts (Table 1) and coupling constants (Table 2) characteristic of the norbornane ring system. Except for impurities introduced during isolation (resonances < 2.0 ppm) T2 and T12 constitute virtually 100% of their respective samples. Integration revealed the presence of ten protons in T2 and nine in T12 (therefore eight and nine chlorines, respectively). This result is corroborated by the observation of an intense (M-Cl)⁻ ion cluster centered on m/z 377 in the electron capture negative ion mass spectrum of T2 and on m/z 413 in that of T12. T2 was identified as 2-*exo*,3-*endo*,5-*exo*,6-*endo*,8,8,10,10-octachlorobornane and T12 as its nonachloro- analog (2-*exo*,3-*endo*,5-*exo*,6-*endo*,8,8,9,10,10-nonachlorobornane). The observed chemical shifts and coupling constants for T12 are virtually identical to those reported for toxicant A_c². There is little likelihood of so close a correspondence in spectra for dissimilar structures and therefore,

T12 and A_c must correspond to the same toxaphene congener.

Total T2 and T12 concentrations in samples from Northern Quebec, (all based on lipid weight) ranged from 127 ng/g in Arctic char (*Salvelinus alpinus*), to 3653 ng/g in male beluga whale blubber, and 220 ng/g in breast milk of Inuit women (Table 3). T2 and T12 were present in all samples at concentrations similar to, or greater than, well known recalcitrant organochlorines, 4,4'-DDE and 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153).

References

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Table 1. ¹H NMR Chemical Shift Data for T2 and T12 (ppm).*

	H ₂	H ₃	H ₄	H ₅	H ₆	H ₈	H _{9a}	H _{9b}	H _{9c}	H ₁₀
T2	4.62 (d)	4.15 (t)	2.27 (dd)	4.64 (d)	5.12 (dd)	6.45 (d)	1.57 (d)	1.57 (d)	1.57 (d)	6.20 (s)
T12	4.68 (d)	4.38 (t)	2.98 (dd)	4.61 (d)	4.91 (dd)	6.75 (d)	3.87 (dd)	4.47 (d)	-	5.78 (s)

* In C₆D₆ with C₆D₅H as the reference; doublet centers are reported; s = singlet, d = doublet, dd = doublet of doublets, t = triplet.

Table 2. ¹H NMR Coupling Constant data for T2 and T12 (Hz)*

	J ₂₃	J ₃₄	J ₄₆	J ₅₆	J _{89a}	J _{8(9a,b,c)}	J _{9ab}
T2	4.6	4.6	1.2	4.8	-	0.8	-
T12	5.0	4.5	1.1	4.8	2.0	-	13.1

* In C₆D₆; Derived from first-order analysis.

Table 3. Concentrations (ng/g lipid weight) of T2 and T12 and other recalcitrant organochlorines in samples of aquatic biota and human milk from the Canadian Arctic.

Sample	Location	N	Sex	T2 ^a	T12 ^a	ΣPCC ^b	4,4'DDE	PCB 153
Milk	N. Que (Ungava)	3	-	69.5±23.3	151±44.6	294±116	185±150	115±69.3
A. char ^c	N. Que (Ungava)	7	F	43.6±29.0	83.2±53.0	456±283	40.7±28.2	18.4±8.0
A. char ^c	N. Que (Ungava)	13	M	73.9±31.4	137.9±64.3	625±249	65.5±28.1	29.2±12.9
Beluga	E. Hudson Bay	8	F	602±309	1050±693	2030±994	556±394	129±85.0
Beluga	E. Hudson Bay	8	M	1300±325	2350±380	4130±765	1280±396	322±750

^a T2 and T12 were quantified by GC-ECD.

^bΣPCC is the sum of the concentrations of all toxaphene components determined with individual GC-ECD response factors and confirmed by GC-ECNIMS³.

^cArctic char-whole fish.

