POLYCHLOROPINENE - TOXAPHENE ANALOG PRODUCED IN THE USSR WAS NON-RACEMIC

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Abstract
A specimen of the historical insecticide Polychloropinene, produced in the USSR until 1991 was analyzed on GC-MS with chiral stationary phase. Comparison with racemic standards of two major Toxaphene congeners, Parlar no. 26 and Parlar no. 50 and with pure enantiomers of these congeners revealed that Polychloropinene is enriched with (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26) and (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane (Parlar no. 50). Therefore, Soviet Polychloropinene was a source of non-racemic Toxaphene congeners into the environment.

Introduction
Toxaphene is one of the 12 priority POPs (Stockholm Convention). Toxaphene was produced by chlorination of camphene. A similar insecticide, Polychloropinene was produced in the USSR by similar method – hydrochlorination of pinene followed by free-radical chlorination. Toxaphene consists mainly of polychlorinated bornanes. These compounds are chiral (Fig.1).

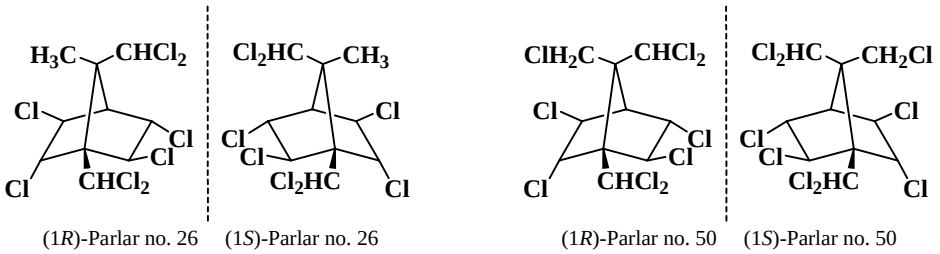


Fig. 1. Chirality of Toxaphene congeners Parlar no. 26 and Parlar no. 50.

A method for preparation of pure enantiomers of Toxpahene congeners has been developed recently[1]. An optically active α-pinene was hydrochlorinated. The product, containing mainly 2-*endo*-chlorobornane and 2-*endo*-chlorofenchane also was found optically active. The crude product was further chlorinated under irradiation to the desired extent of chlorination (Fig. 2).

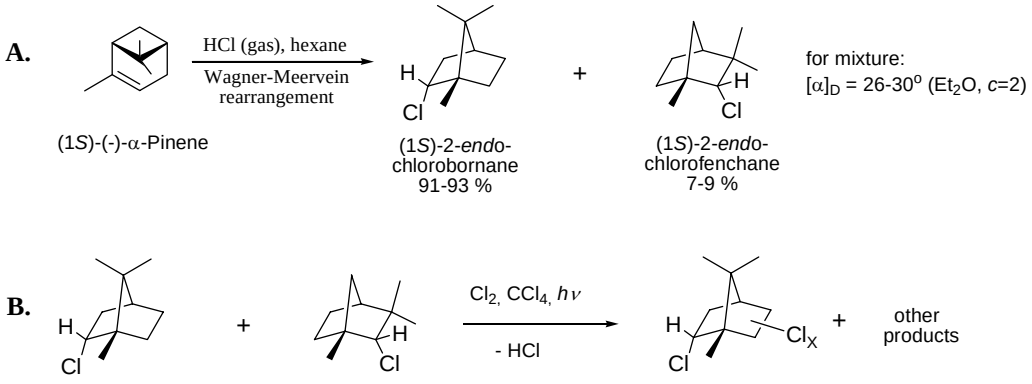


Fig. 2. Stereoselective hydrochlorination(A) of α-pinene and chlorination(B) of a mixture of 2-*endo*-chlorobornane and 2-*endo*-chlorofenchane.

The mixture of polychlorobornanes was separated on silicagel column with hexane as eluent; a series of enantiomerically pure Toxaphene congeners was isolated (Fig. 3).

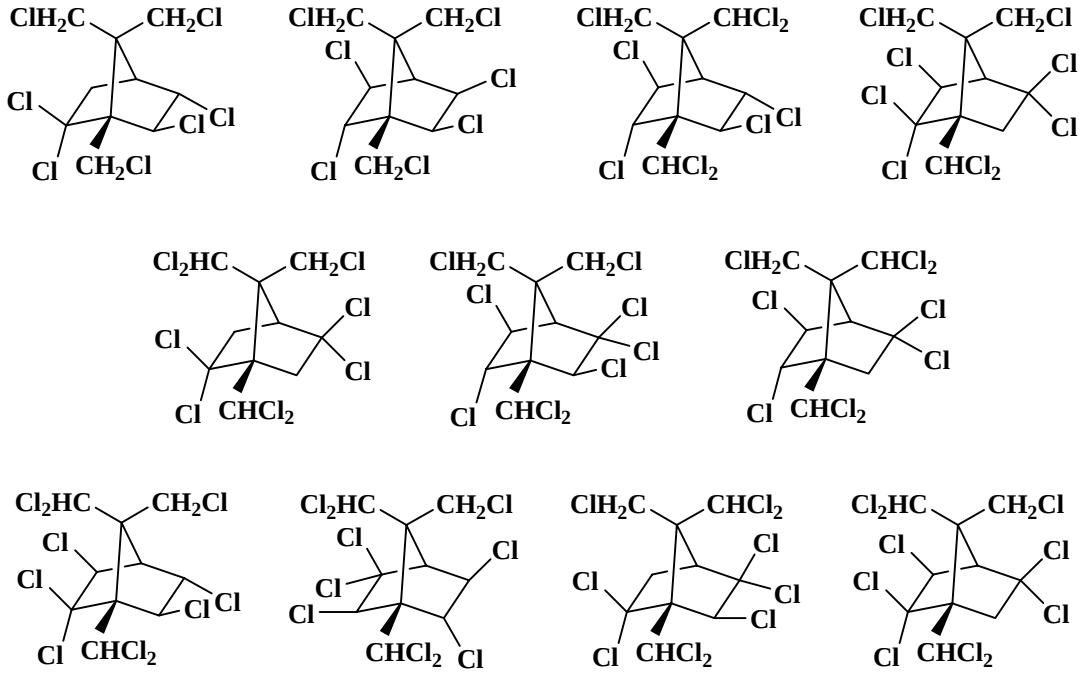


Fig. 3. Structures of enantiomerically pure Polychlorobornanes obtained from (*1S*)-α-pinene.

Absolute configuration of several isolated congeners was established by direct X-Ray structural analysis[1-4]. Absolute configuration of (1*S*)-2,2,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Decachlorobornane was established with help of Vibrational Circular Dichroism (VCD method)[5]. GC on chiral stationary phases confirmed enantiomeric purity – all isolated congeners eluted as single peaks.

All enantiomers retained configuration of the starting material; thus chemical transformations preserved enantiomeric purity. According to *R/S* nomenclature some of the congeners are (1*R*), others – (1*S*); therefore general and practically useful description of their enantiomeric structure is as follows. All isolated polychlorobornanes have configuration as shown of Fig.4: when bridgehead CH_2Cl or $CHCl_2$ group is directed to the reader (while bridge is directed upwards), 2-*endo*-Cl is on the left side.

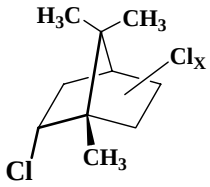


Fig. 4. Common chiral feature of isolated polychlorobornanes.

Earlier we recognized that our laboratory method is a replica of industrial production protocol for Polychloropinene[1] and suggested that Soviet Polychloropinene was non-racemic. Presumably, natural pinene was used for production. It is well-known that terpenes from natural sources are often non-racemic.

Recently we have aquired an old standard sample of Polychloropinene.

Our goal was to isolate two major Toxaphene congeners Parlar no. 26 and Parlar no. 50 from Polychloropinene, to determine enantiomeric purity of these two congeners and to establish absolute configuration of major and minor enantiomers.

Materials and Methods

Enantioselective GC analyses were performed at conditions as follows:

GC – Hewlett-Packard 5890 Series, Detector type – NICI. Injector: split/splitless. Column: chiral GC phase (BGB 172 (BGB Analytics, Waedenswil, Switzerland) 30 m, 0.25 mm, 0.25 um; chiral separator: 20% *tert*-butyldimethylsilyl-beta-cyclodextrin dissolved in BGB-15 (15% phenyl-, 85% methylpolysiloxane). Temperature program: initial temperature 110°C 2 min, 15C°/min up to 200°, 2C°/min up to 240°C, final temperature 240°C for 20 min.

The specimen of Polychloropinene (0.5g) was marked as "Polychloropinene, Riga factory "Reaktiv"". The specimen appearance was dark yellow wax. A 20mg sample was taken, dissolved in 1ml of hexane and separated into 20 fractions on a 60 cm high, 1cm i.d. glass column filled with silica gel 0.035-0.070mm(Acros). Fractions, containing Parlar no. 26 and Parlar no. 50 were subjected to chiral GC analyses.

Racemic standards of Parlar no. 26 and Parlar no. 50 were from LGCPromochem, Wesel, Germany.

Results and Discussion

Satisfactory enantioselective separation was achieved. Previously isolated (1*R*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26) and (1*R*)-2- *endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane (Parlar no. 50) both are found to be first eluting enantiomers. Polychloropinene, however, was found enriched in the second eluting enantiomer of Parlar no. 26 and in the second eluting enantiomer of Parlar no. 50 (Fig. 5).

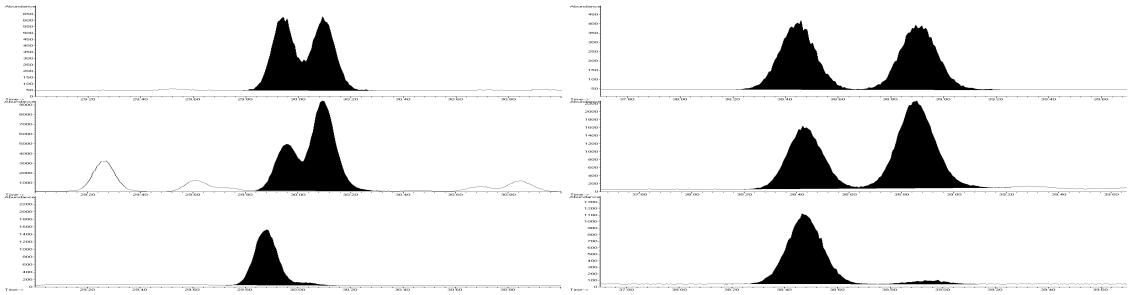
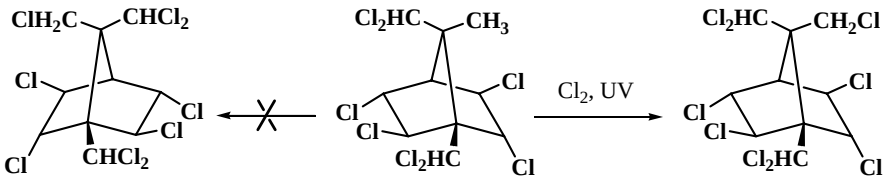


Fig. 5. Enantioselective separation of Parlar no. 26 (left) and Parlar no. 50 (right). Upper line – racemic standard, middle line – corresponding fractions of Polychloropinene, lower line – (1*R*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26) and (1*R*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane (Parlar no. 50).

Therefore Soviet Polychloropinene is enriched in (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26) and (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane (Parlar no. 50). Enantiomeric ratio is close to 2:1 for Parlar no. 26 and to 1.5:1 for Parlar no. 50. Reason for the difference in enantiomeric ratio is not clear to us at the moment; this difference requires further investigation. It is unlikely that partial racemization takes place upon chlorination of Parlar no. 26 to Parlar no. 50 (Fig. 6).



(1*R*)-Parlar no. 50 (1*S*)-Parlar no. 26 (1*S*)-Parlar no. 50

Fig. 6. Racemization is unlikely during chlorination of Parlar no. 26 to Parlar no. 50.

Our findings confirm the hypothesis of non-racemic composition of Polychloropinene[1]. Obviuosly, the specimen of Polychloropinene, enriched in (1*S*) enantiomers of Parlar no. 26 to Parlar no. 50 was produced from non-racemic pinene, enriched in (1*R*)-(+)-α-pinene.

Russian turpentine from *Pinus Silvestris* is dextrorotatory, $[\alpha]_D$ = +15°25' - +24°. This corresponds to enantiomeric ratio 1.5-2 and nicely correlates with our finding on enantiomeric purity of Parlar no. 26 and Parlar no. 50 isolated from the specimen of Polychloropinene.

However, it is not possible to say that all Polychloropinene was enriched in (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26) and (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane (Parlar no. 50) to the extent found in present work. Enantiomeric composition may vary from one geographical region to another, from year to year, from season to season and also from the source part of the tree (optical rotation of Russian turpentine from needles of *Pinus Silvestris*, for instance, can be as low as $[\alpha]_D$ = +7°3'; it is unclear, however, is the difference due to lower enantiomeric ratio or due to lower content of α-pinene in needles). Moreover, another (presumably minor) source of Russian turpentine is *Larix Sibirica Ledebour*, ethereal oil from its needles contains ca 70% of (1*S*)-(-)-α-pinene and ca 30% of bornylacetate; $[\alpha]_D$ = -40° - -42°. It is unlikely this oil was used for insecticide production, but this matter also needs further research.

At present time the following conclusions can be made:

1. Soviet Polychloropinene was non-racemic and thus it was the source of non-racemic input of Toxaphene congeners into the environment.
2. Therefore Toxaphene is the only non-racemic pollutant of the12 priority POPs.
3. Elution order of the two most important Toxaphene congeners is as follows. Parlar no. 26: (1*R*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane – first, (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane – second. Parlar no. 50: (1*R*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane – first, (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane – second.
4. The specimen of Soviet Polychloropinene is enriched in (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,10,10-Octachlorobornane (Parlar no. 26, ER = 2) and in (1*S*)-2-*endo*,3-*exo*,5-*endo*,6-*exo*,8,8,9,10,10-Nonachlorobornane (Parlar no. 50, ER = 1.5).

Acknowledgements

This work was done with financial support of Norwegian Research Council, Project no. 185104/S50.

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