Excretion of Some Pure PCB Isomers in Milk of Cows

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Polychlorinated biphenyls (PCB's) are mixtures of different isomers of chlorinated biphenyl regarding the chlorine number and the chlorine position in the molecule. They are generally considered to be quite resistant to chemical and enzymatic degradation. Recent experiments with technical PCB's indicate that certain components are metabolised in the animal organisms. Thus, mammalian and avian metabolism (hydroxylation) of chlorobiphenyls seems to become increasingly more difficult when the number of chlorine atoms increases in the molecule (BLOCK and CORNISH 1959, BAILEY and BUNYAN 1972, HUTZINGER et al.1972, BENTHE and SCHMOLDT 1973, BAGLEY and CROMATRIE 1973). Some data also indicate that the chlorine positions are very important for the hydroxylation (FRIES et al. 1973, BENTHE and SCHMOLDT 1973).

In the present report we have studied the residue excretion in milk by cows fed on some pure PCB isomers (of different chlorine position) with the intention to observe the differences in metabolism.

The synthesis of the four compounds: 2,2', 6,6' - tetrachlorobiphenyl, 3,3', 5,5' - tetrachlorobiphenyl, 2,2',4,4', 6,6' - hexachlorobiphenyl and 3,3',4,4',5,5' - hexachlorobiphenyl was made according to the procedures of HUTZINGER et al. (1971) and VAN ROOSMALEN (1934). Two actively lactating cows were orally given 0,3 g of each isomer of tetrachlorobiphenyls and to other two cows was given 0,3 g of each isomer of hexachlorobiphenyls - as a single dose; the cows were weighing from 340 to 385 kg. From each cow milk was collected for 25 days. PCB isomers were extracted from samples and consequently analysed according to the method of YOUNG and BURKE (1972) and to the method described in PESTICIDE ANALYTICAL MANUAL (1972).

Milk samples obtained before the start of PCB isomers feeding did not contain detectable PCB residues or significant interferences in the gas-liquid chromatographic analyses. Varian G.L.C. Mod.17oo instrument equipped with an electron capture (tritium) detector was used. A glass column was packed with 2,5% QF-1 and 2,5% DC-2oo on 1oo-12o mesh Varaport 3o. Column temp. was 190°C. The carrier gas was purified nitrogen, 6o ml/min. flow rate. Under these conditions the retention times relative to p,p'DDE (1,oo) were: 2,2',6,6' - 0,31; 3,3; 5,5' - o,73; 2,2',4,4', 6,6' - 0,72; and 3,3',4,4',5,5' - 3,56

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for tetra- and hexa-chlorobiphenyls respectively. The levels of PCB isomers in milk fat after the feeding are presented in Fig.1.

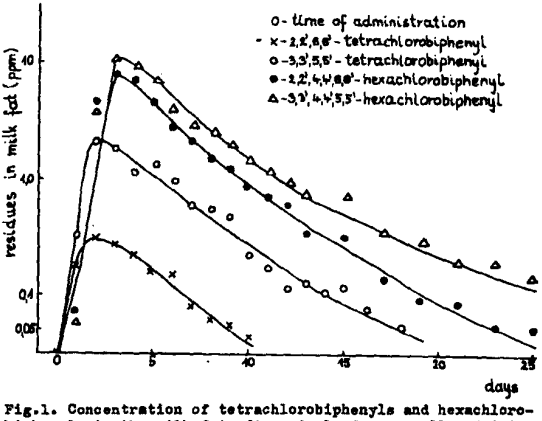

Fig.1. Concentration of tetrachlorobiphenyls and hexachlorobiphenyls in the milk fat after single doses orally administered. Each point is an average of the milk analysis of the two cows.

Concentration of mentioned PCB isomers in milk fat quickly rose in the first days; tetrachlorobiphenyls reached maximum of the excreted amount (0,3 resp. 2,1 ppm) the 2nd day an hexachlorobiphenyls the 3rd day (8,2 resp.10,5 ppm). Then there was a decline in the levels of PCB isomers in the milk fat. A very rapid decline in the level of 2,2',6,6' - tetrachlorobiphenyl and 3,3',5,5' - tetrachlorobiphenyl confirms the metabolic hydroxylation of lower PCB homologs.

In this report we intend also to explain the possible reasons of the rapid metabolism of tetrachlorobiphenyl and hexachlorobiphenyl in mammalians.

One reason could be the influence of metabolism on different steric configuration of the biphenyl molecule. As to the molecular model, ortho substitution produces strong sterical repulsion; a spectroscopyc analysis showed that it exists in twisted conformation (DREESKAMP et al. 1972). This reflects the decrease of the double bond character between the rings and the electronic effect of one ring to the other one. This makes chlorinated biphenyl molecule electronic mo-

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re similar to chlorinated benzene (PARKE and WILLIAMS 1960) which seems not to be so stable as PCB's to metabolism. Sterically hindered para position, which is usually preferable for metabolic attack (BLACK and CORNISH 1959), may play some role (for higher stability) in 3,3',5,5' - tetrachlorobiphenyl. The electronic effect of p-chlor substitution stabilises the planar form and so the metabolic stability of 3,3',4,4'; 5,5' - hexachlorobiphenyl is increased.

It would be possible to explain the quickly disappearance of 2,2',6,6' - tetrachlorobiphenyl also by the view of the polar character of the compounds. From the low Beroza p-values (BEROZA et al. 1969) in the hexane-acetonitrile system we expect a high polar character. The partition values for 2,2',6,6' -, 3,3',5,5' - tetra and 2,2',4,4',6,6' -, 3,3',4,4',5,5' - hexa-chlorobiphenyls in hexane-acetonitrile were 0,45; 0,69; 0,71; and 0,62 respectively. This may be reflected in a way of excretion; thus, this excretion of the polar compounds is more intensive in the polar medium (urin, milk) than in a nonpolar /cow's fat tissue/ (PLATONOW et al. 1971). This reasoning is rather speculative and is supported only by one isomer.

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