PCB/fish

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NEW CONJUGATES OF PCB IN THE METABOLIC PROCESS

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PCB was administered to mice mixed in their feed. After it had been accumulated in their adipose tissue, exercise loads were applied by means of a rotating cage in order to mobilize the fat. As a result, the PCB metastasized to the liver together with immigration of the fat. However, a comparison of the gas chromatography (GC) patterns of the PCB in the adipose tissues and that in the liver shows that the several peaks of low chlorinated substances have disappeared in the PCB in the liver, and it is directly visible that it has been metabolized. It was learned from gas chromatography and gas-mass (GC/MS) identification of pure PCB that these are peaks of 3, 4, and 5-chlorinated substances. Next we made studies of these metabolites.

These metabolites are saponified by alkali, and their decomposition products are detected by GC after conversion to TMS (HMDS). They cannot be detected by the PCB analysis method since they are adsorbed by activated silica gel and are dissolved in hot methanol. The livers were pulverized in a low-temperature chamber at 0°C by means of a blender in acetone and by means of ultrasonic crushing. The centrifugal supernatant liquid was extracted by 0°C methanol concentrated under reduced pressure at 40°C, and it was extracted again together with the PCB by means of 0°C n-hexane dried under reduced pressure at 40°C. Detection by gas chromatography was performed at a high flow rate and constant pressure, raising the column temperature from 180°C at a rate of 2°C per minute. The results are shown in the figure on the left.

As a result of GC/MS analysis of the metabolites (the figure on the right), the metabolite of the 3-chlorinated substance had an m/e of 334, and three isomer peaks were detected. The metabolite of the 4-chlorinated substance had an m/e of 368, and eight isomer peaks were detected. The metabolite of the 5-chlorinated substance had an m/e of 402, and five isomer peaks were detected. The same cleavage mode was common to all peaks. After first

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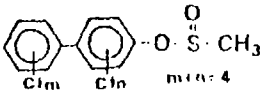
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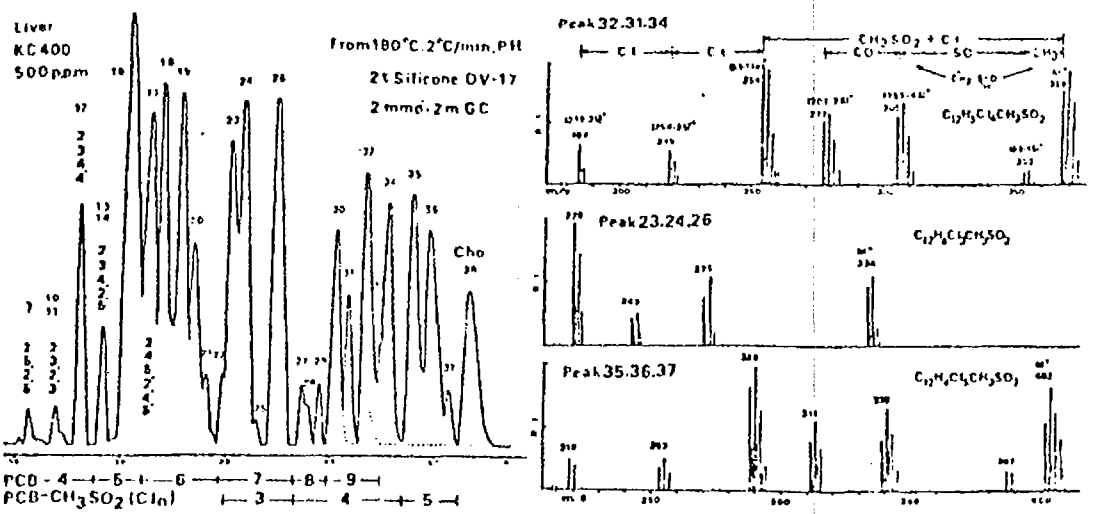
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displaying $(M-15)^+$, $(M-63)^+$, $(M-91)^+$ and $(M-114)^+$, the detachment of Cl was shown by the number of substitutions. All of the M^+ also displayed the same isotope peaks as C, Cl, and S. The fragment ions above M-91 after the detachment of S displays the isotope peaks of C and Cl. As a result of high resolution mass spectrometry and tracing analysis by means of spectrum computer composition analysis, the MW368 and its fragment ions were found to have a composition of $C_{12}H_5Cl_4$-CH_3SO_2, and the supposed structural formula shown on the right was obtained. MW334 was $C_{12}H_6Cl_3$-CH_3SO_2, and MW402 was $C_{12}H_4Cl_5$-CH_3SO_2. They were all compounds of CH_3SO_2.



The ratio with which these metabolites were produced was: liver > kidney > heart > brain, and their ease or difficulty was: KC400 > 300 > 500 > 600. The amounts produced inside the liver when KC400 was administered at 500 ppm were: mouse > rat > guinea pig.

Thus, the conclusion was reached that the $C_{12}H_{6,5,4}Cl_{3,4,5}$-$CH_3SO_2$ were new metabolites differing from PCB-OH, a metabolite of some of the 1, 2, and 4-chlorinated substances. Sixteen metabolites of the same type were obtained from the 3, 4, and 5-chlorinated substances of PCB. It was concluded that they are universal water-soluble new conjugates in that there are no sex differences or species differences with rats and guinea pigs.



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