Investigation on Polychlorinated Quaterphenyl in Kanemi Rice Oils Caused the "Yusho"

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Previously, we reported that the organochlorinated compounds, which were not PCB and PCDF, were detected largely in Kanemi rice oils caused the "Yusho."^{1,2)} It was clear that the chlorine concentrations of the chemicals were 287 to 537 ppm by neutron activation analysis and that polychlorinated quaterphenyls (PCQs) were detected largely in them by GC-MS.

In this paper, the simple analytical method for PCQ was established and PCQ in Kanemi rice oils were determined. In addition, the ratios of PCQ/PCB and PCDF/PCB in the oils were investigated.

Method

1) PCQ standard

PCQ standard was obtained from Kanechlor 400 (KC-400) used as the thermotransfer medium, containing 28,000 ppm of PCQ, by repeating of Florisil column and silica gel thin

layer chromatography-clean up. The standard, which contained 2% PCB as the impurity, was composed of penta- to deca-chlorinated quaterphenyl and contained 45.5% chlorine (by MCD-GC analysis).

2) The concentration of PCQ in Kanemi rice oils caused the "Yusho"

Sample was saponified, extracted and concentrated by the method described previously.²⁾ The concentrated extract was chromatographed over Florisil column (20 g, overnight activation at 130°) prepared in a 1.8 cm i.d. glass column. PCB was eluted with 130 ml of *n*-hexane and 50 ml of 2% diethylether in *n*-hexane solution. PCQ was eluted thereafter with 100 ml of 5% diethylether in *n*-hexane solution. The last fraction was analysed by ECD-GC (for the determination of PCQ) and MCD-GC (for the determination of chlorine concentration of PCQ). The determination of PCQ was carried out by measuring of the total peak areas.

Table 1. Chlorine Concentration of PCQ, PCB and PCDF Fractions Isolated from Kanemi Rice Oils Caused the "Yusho"

Production date	Concentration of chlorine (ppm)				PCQ/PCB (g/g)	PCDF/PCB (μg/g)
	OC ^{a)} , 1, 2)	PCQ	PCB ^{b)} , 3, 4)	PCDF ^{3, 4)}		
Feb. 5th, 1968	537	450 (866)	500 (983)	3.98 (7.40)	0.88	7,500
Feb. 9th, 1968	287	207 (490)	80 (151)	0.95 (1.90)	3.25	12,600
Feb. 10th, 1968	343	248 (536)	83 (155)	1.15 (2.25)	3.46	14,500

^{a)} Organochlorinated compounds, which were free from PCB and PCDF, in the hexane extract from the saponified oil

^{b)} The values were calculated from the precise data showing the concentration of PCB by the determination with the method of the author *et al.*⁵⁾ The values of other columns were obtained by MCD-GC pattern

The value in the parenthesis shows the concentration of each compound

3) Heat treatment of the nondeodorized rice oil spiked with KC-400 used as the thermotransfer medium

The nondeodorized rice oil was spiked with 3,000 ppm of KC-400 used as the thermotransfer medium, which contained 28,000 ppm of PCQ and 20.2 ppm of PCDF. The oil was poured

into the beaker and heated for 1 hr at various temperatures as shown in Table 2, with stirring.

Result and Discussion

1) PCQ in Kanemi rice oils

As shown in Table 1, it was clear that the chlorine concentrations of PCQ in Kanemi rice

Fig. 1. Gas chromatograms of PCB in Kanemi rice oil, the heated rice oil spiked with KC-400 used as the thermotransfer medium and KC-400 used as the thermotransfer medium GC, Varian Aerograph 2100 equipped with ^{63}Ni -ECD; column, 2 mm $\times$ 1.8 m glass column packed with 2% OV-1 on Gaschrom Q (100~120 mesh); injector, column and detector temp., 220, 190 and 310°C, respectively; carrier gas, N_2 (10 ml/min)

Table 2. Retention of PCB, PCQ and PCDF in Heated Rice Oils Spiked with 3,000 ppm of KC-400 used as the Thermotransfer Medium

Heating temp. (°C)	Retention (ppm)			PCQ/PCB (g/g)	PCDF/PCB ($\mu\text{g/g}$)
	PCB	PCQ	PCDF		
Room temp.	3000	83.3	0.0606	0.028	20.2
200~210	1951	73.4	0.0456	0.042	25.9
220~230	1284	67.4	0.0376	0.059	32.4
240~250	638	74.8	0.0248	0.131	43.0
260~270	224	68.0	0.0154	0.341	76.6

oils were 207 to 450 ppm and that the most of organochlorinated compounds, which were free from PCB and PCDF, was PCQ. The concentration of PCQ were 490 to 866 ppm, and the ratios of PCQ/PCB were extraordinary high (0.88~3.46).

2) Heat treatment of the rice oil spiked with KC-400 used as the thermotransfer medium

As shown in Table 2, the amount of PCB retained in the oil decreased rapidly with rising of heating temperature. The component ratio of PCB which residued in the oil, changed also with rising of heating temperature, and consequently, the pattern of PCB which residued in the oil by heating at 260~270°C was similar to that of PCB in Kanemi rice oil produced on February, 5th in 1968.

The pattern of PCQ which residued in the oil did not change, and the residued rates of PCQ were almost constant at various heating temperatures. PCDF in the oil was on the decrease with increasing of heating temperature, but the residue rate of PCDF was higher than that of PCB.

As described above, the residued rates of three chemicals were very different, and consequently, it was that the ratios of PCQ/PCB and PCDF/PCB in the oil increased rapidly with increasing of heating temperature.

The ratios of PCQ/PCB and PCDF/PCB in the oil heated at 260~270° were fairly lower

than those in Kanemi rice oil produced on February, 5th in 1968. The difference might attribute to original PCQ and PCDF level in the thermotransfer medium. The PCDF concentration in other thermotransfer media and KC-400s heated in glass ampoules were 11 to 25 times higher⁶⁾ than that of the thermotransfer medium used in this experiment. Therefore, after KC-400 used as the thermotransfer medium leaked out into the Kanemi rice oil in the deodorization tank, the ratios of PCQ/PCB and PCDF/PCB in the oil might be extraordinary high.

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