

erature values. However, a wide range existing in the literature cannot be compared with the present data because the present study was in human beings compared to earlier studies with animals. Moreover, the nature of the diets is different; in earlier studies, individual food items were used while in the present study mixed foods were used. Moreover, the present study indicated that the source of protein and a change in energy levels has a significant effect on lysine absorption.

Lysine absorption from various diets was found to be positively related to nitrogen balance of the subjects, and the correlation coefficient ( $r = 0.69$ ) was found to be highly significant ( $P < 0.01$ ) at a lower level of energy. Though an increase in lysine absorption showed an improvement in nitrogen balance at a higher level of energy, it could not attain significance. Similarly, lysine absorption at a lower level of energy was significantly ( $P < 0.01$ ) related to biological value ( $r = 0.55$ ) and net protein utilization ( $r = 0.54$ ), but only a trend was found at higher level of energy intake. Thus, the effect of lysine absorption on nitrogen balance, biological value, and net protein utilization was more pronounced only for lower levels of energy intake, thus stressing the need for supplementation of wheat diets at low energy intake common in Indian diets.

Registry No. Lys, 56-87-1.

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## Cereal Products as a Source of Polycyclic Aromatic Hydrocarbons

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Gas chromatography-mass spectrometry was used for the determination of 25 polycyclic aromatic hydrocarbons (PAH) in cereal products available in Finland. Even though the levels of PAH in ordinary cereal products were low, the high level of consumption of these products (67.7 kg/person annually) makes them a significant source of PAH. The level of PAH in bolted flours and milled oats and wheat ranged from 25 to 38  $\mu\text{g}/\text{kg}$  and in rolled oats was 64  $\mu\text{g}/\text{kg}$ . The average concentration of PAH in bran was 220  $\mu\text{g}/\text{kg}$ . One specialty smoked cereal product contained PAH in concentrations as high as 4500  $\mu\text{g}/\text{kg}$  and benzo[a]pyrene in concentrations 100 times higher than in other cereal products. The average annual intake of the 25 PAH compounds from ordinary cereal products was estimated to be 2000  $\mu\text{g}$  per capita.

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous pollutants formed by the incomplete combustion of organic materials. By 1976 more than 30 PAH and several hundred derivatives of PAH were reported to have carcinogenic effects (Dipple, 1976). In the atmosphere PAH are present both as particles and in the vapor phase, and they can be transported long distances. Numerous studies have shown that the atmospheric deposit of PAH onto grains, leafy vegetables, fruits, and oil plants forms an important source of PAH in the diet (Grimmer and Duvel, 1970). Another important source is the smoking and grilling of foods (Santodonato et al., 1983). However, the low rate of consumption of smoked and grilled foods reduces their importance as a PAH source. Tobacco smoking is a third contributor to PAH exposure (Wynder and Hoffman, 1967), and the direct heating of food with air-containing

combustion gases, a fourth. Indeed some foods such as copra are traditionally dried without a heat transformer, and the smoke is directly in contact with large surface areas of the food. The use of natural gas and heating oil as a heat source without a heat transformer is a source of risk in many countries (Hutt et al., 1978).

We studied cereal products representative of consumption and of the most important farming areas in Finland. Among the samples were flours dried without a heat transformer and a local delicacy "talkkuna", a mixture of flours made from smoked oats, barley, and peas, which is eaten with dairy products.

#### EXPERIMENTAL SECTION

**Samples.** Commercial product samples were obtained from local retail outlets and pooled from five central government storages in the spring and autumn of 1985 (Figure 1). The sampling was representative of the major cereal products available in Finland and of the main farming areas (>75%).

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Table I. PAH in Cereal Products ( $\mu\text{g}/\text{kg}$ )<sup>a</sup>

no.	compound	bolted wheat flour (n = 7)	bolted rye flour (n = 1)	rolled oats (n = 2)	milled oats (n = 3)	milled wheat (n = 19)	bran (n = 1)	smoked oats, barley, and beans	
								A	B
1	biphenyl	0.2	b	0.1	1.0	0.3	0.6	6.3	
2	acenaphthylene								
3	acenaphthene	0.6	0.6	0.7		0.7	1.6	2.3	
4	methylbiphenyl, sum	0.6	0.2	0.2	2.5	0.6	0.4	2.6	
5	dibenzofuran	2.1	1.4	4.1	2.6	1.0	4.7	160	3.1
6	fluorene	1.3	2.0	2.3	2.7	1.7	5.9	87	6.4
7	dibenzothiophene	0.6	0.5	1.8	2.0	1.0	0.9	4.3	0.8
8	phenanthrene	9.9	14	29	14	10	94	1200	83
9	anthracene	0.5		1.3			9.4	150	19
10	carbazole								
11	methylanthracene + methylphenanthrene, sum	2.4	0.8	3.9	5.8	3.7	5.2	51	15
12	phenylanthracene	b			0.2	0.2		14	1.2
13	fluoranthene	3.0	3.8	13	1.5	1.8	130	790	70
14	pyrene	5.5	2.6	5.4	1.6	1.6	47	630	60
15	benzofluorene, sum	2.4	0.9	0.6	0.5	0.6	29	100	25
16	benz[a]anthracene	b	0.1	0.2	b	b	11	110	6.3
17	chrysene + triphenylene	0.4	0.3	0.5	1.3	0.3	9.7	320	7.2
18	benzofluoranthene, sum	1.4	0.6	0.5	1.4	0.6	16	500	2.5
19	benzo[e]pyrene	0.4		0.1	0.7	0.2	5.2	170	0.4
20	benzo[a]pyrene	0.4		0.3	0.4	0.2	5.4	160	0.6
21	perylene	0.1				b	0.7	24	
22	methylcholanthrene, sum								
23	indeno[1,2,3-cd]pyrene								
24	dibenzanthracene, sum								
25	benzoperylene, sum								
	total PAH	32	28	64	38	25	380	4500	300

<sup>a</sup> Averages of n. <sup>b</sup> <0.1  $\mu\text{g}/\text{kg}$ .

**Sample Analyses.** The extraction and cleanup procedure was carried out as described by Grimmer and Böhnke (1975) but with some modification such as caffeine complexation (Sargedos et al., 1981). Gas chromatography-mass spectrometry (GC-MS) analyses were carried out as described by Tuominen et al. (1986). A Hewlett-Packard 5970 mass-selective detector was used coupled to a Hewlett-Packard 5790 gas chromatograph equipped with a 12 m  $\times$  0.20 mm (i.d.) cross-linked methyl silicone capillary column (film thickness 0.33  $\mu\text{m}$ ). The column oven temperature was programmed from 70  $^{\circ}\text{C}$  at 15  $^{\circ}\text{C}/\text{min}$  to 275  $^{\circ}\text{C}$ . Splitless injection technique was applied. The injector temperature and the temperature of the interface tube were both 300  $^{\circ}\text{C}$ . The electron-impact energy was 70 eV. The ions monitored in selective ion monitoring (SIM) were  $m/e$  152, 166, 168, 178, 184, 192, 202, 204, 206, 216, 228, 252, 276, and 278. Figure 2 gives an example of the selected-ion monitoring of PAH. Qualification has been made by means of the standard mixture. Compounds were distinguished on the basis of an indices and ions described elsewhere (Tuominen et al., 1986). The detection limit for each compound was calculated to be approximately 20 pg/injection (1  $\mu\text{L}$ ).

**Quantifications.** 3,6-Dimethylphenanthrene, 1,1'-biphenyl, and 3-methylcholanthrene were used as internal standards. Because of the many liquid-liquid partitions there were losses of PAH. Previous recovery experiments showed that some losses of PAH also occur during the  $\text{SiO}_2$  column cleanup. In general, concerning PAH analyses, recoveries of the compounds were found to vary between 40 and 100% for the quantitation of PAH at a level of 0.1  $\mu\text{g}/\text{kg}$  and were strongly dependent on the molecular weights (Hopia et al., 1986). In this study the recoveries of internal standards were 30–50%. The recoveries of the internal standards were taken into account in calculating the concentrations in Table I.

**Reagents.** All organic solvents were distilled in glass. KOH, NaCl,  $\text{Na}_2\text{SO}_4$ , and caffeine ( $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ ) were

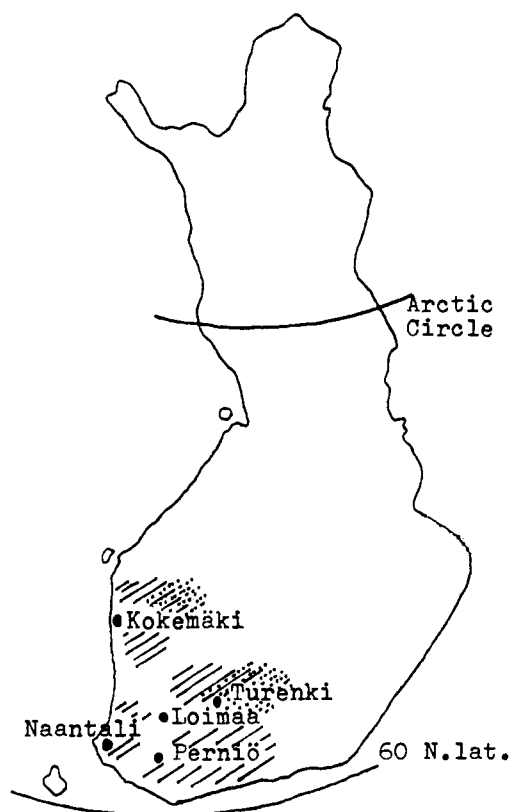


Figure 1. Main farming areas (□) and the local talkkuna consumption areas (○) in Finland.

reagent grade (Merck). The polycyclic aromatic hydrocarbons (PAH) investigated in this work are listed in Table I. A standard mixture was prepared in cyclohexane.

#### RESULTS AND DISCUSSION

The results of the PAH analyses are presented in Table I. As can be seen in Figure 2, no interfering peaks were

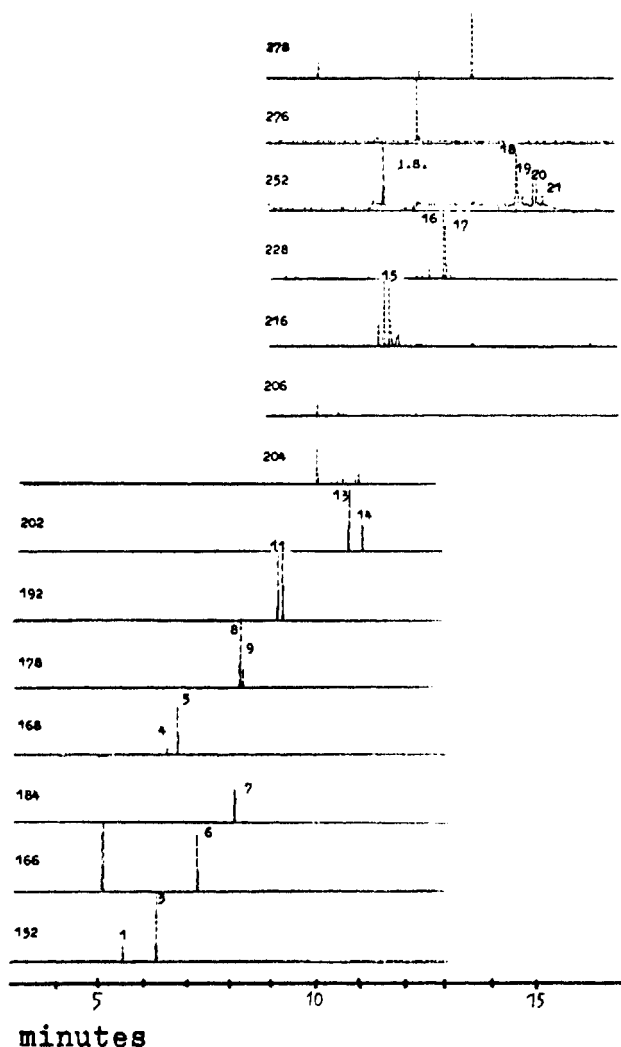


Figure 2. GC-MS selective-ion monitoring separation of 18 PAH found in a bran sample. Compounds listed in Table I.

observed. The concentration of PAH appears to be similar in all samples of the same type, and a little lower than the level found in lettuce. As expected, the bran contained higher levels of PAH than the milled grains and bolted flours. The PAH concentrations were comparable to those found in Sweden (Larsson, 1986) and in other countries (Fritz and Engst, 1983; Lawrence and Weber, 1984a,b). The specialty talkkuna made from smoked barley, oats, and peas contained high levels of PAH. The highest PAH concentration was found in the product where wet grains were exposed with smoke and the whole mixture was milled (procedure A, Table I). The other talkkuna product was smoked similarly, but bran was separated before milling (procedure B, Table I).

Three samples of wheat dried with light heating oil as an energy source and without a heat transformer were studied, but no increase in PAH concentrations was observed (data not shown separately). Likewise, concentrations of PAH were similar in grains dried in warm and cold air.

The Federal Republic of Germany, Austria, and Poland are using a limit of 1  $\mu\text{g}/\text{kg}$  for benzo[a]pyrene in smoked meat products. In Finland there is no maximum limited for compounds related to PAH. However, in order to avoid excessive intake of PAH, it would be reasonable to avoid high levels of PAH-containing products. At present there is no conclusive data concerning the relationship between PAH and cancer. In many toxicological studies it has been indicated that some PAH, e.g. benzo[a]pyrene, dibenz-

[a,h]anthracene, and benz[a]anthracene are very carcinogenic compounds (Jones and Freudenthal, 1978; Blackburn and Kellard, 1986).

## CONCLUSIONS

The total consumption of cereal and flours in Finland is about 68 kg/person per year. With bolted wheat and rye making up 60% and 30%, respectively, of this figure, the corresponding PAH intake must approach 2000  $\mu\text{g}/\text{person}$  per year. About 700 000 kg of smoked talkkuna a year is consumed in Finland, of which 500 000 kg, equivalent to a yearly consumption of 0.14 kg/person, is prepared in accordance with procedure A. Thus, the average yearly intake of PAH from this source is 430  $\mu\text{g}/\text{person}$ . However, the consumption is not evenly distributed within the population, and there are many individuals who consume talkkuna almost every day. The PAH risk for these people can be compared with the intake for people who regularly eat smoked or hard grilled sausages and beef (Larsson et al., 1983).

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**Registry No.** Biphenyl, 92-52-4; acenaphthylene, 208-96-8; acenaphthene, 83-32-9; methylbiphenyl, 28652-72-4; dibenzofuran, 132-64-9; fluorene, 86-73-7; dibenzothiophene, 132-65-0; phenanthrene, 85-01-8; anthracene, 120-12-7; carbazole, 86-74-8; methylanthracene, 613-12-7; methylphenanthrene, 31711-53-2; phenylanthracene, 35465-71-5; fluoranthene, 206-44-0; pyrene, 129-00-0; benzofluorene, 61089-87-0; benzanthracene, 56-55-3; chrysene, 218-01-9; triphenylene, 217-59-4; benzofluoranthene, 56832-73-6; benzo[e]pyrene, 192-97-2; benzo[a]pyrene, 50-32-8; perylene, 198-55-0; methylcholanthrene, 56-49-5; indeno[1,2,3-cd]pyrene, 193-39-5; dibenzanthracene, 67775-07-9; benzoperylene, 11057-45-7.

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