Table I.Effect of Autoclaved Wheat Ergot Sclerotia onthe Performance of Male Leghorn Chicks after SevenDays of Feeding

dietary wheat	feed consumed, g	weight	f <b>e</b> ed/gain	
ergot, %		gained, g	ratio	
0	$\begin{array}{r} 114.1^a \pm 1.1a^b \\ 78.9 \pm 2.8b \\ 61.6 \pm 1.5c \end{array}$	61.1 ± 0.9a	1.87 ± 0.02a	
4 (autoclaved)		29.4 ± 1.8b	2.68 ± 0.09b	
4		13.9 ± 1.0c	4.52 ± 0.36c	

<sup>a</sup> Mean  $\pm$  standard error per bird for five birds per pen and four pens per treatment. <sup>b</sup> Means in the same column with different letters differ significantly at P < 0.05according to the Student-Newman-Keuls multiple range test.

percentage of the  $\alpha$  isomers in all the peptide alkaloids (ergocornine, ergocristine, ergocryptine, ergosine, and ergotamine) taken together increased from 9% to 19% while the total amount of these alkaloids remained about the same; after 40 min the percentage had increased to 41% while the total amount decreased. The simpler nonpeptide alkaloid ergometrine did not undergo this isomerization to any great extent prior to decomposition.

Ergot alkaloids are photosensitive (Stoll and Schlientz, 1955); however, irradiation of ground sclerotia with UV light for 54 h did not alter total alkaloid levels or individual alkaloid composition. The light would not be expected to penetrate very far into the sclerotial tissue, although Silber and Bischoff (1954) reported that alkaloids are concentrated in the outer layers and levels decrease toward the center.

Autoclaving ergot sclerotia at 121 °C for 30 min resulted in a 24.6% reduction in total alkaloid content. The treated ergot had a reduced toxic effect on growing chicks (Table I). Toxic effects, such as reduced feed consumption and weight gain, are directly proportional to the alkaloid levels in the diet (Young and Marquardt, 1982); the observed feed consumption and weight gain values are in reasonable agreement with those calculated (74.5 and 25.5 g, respectively) for ergot with a 24.6% reduced alkaloid content. Another benefit of autoclaving was a significant improvement in the feed/gain ratio (Table I).

Heat generated in the feed pelleting process probably reduces the alkaloid content in ergot-contaminated feed and accounts for the reduced toxicity of such treated feeds (Friend and Macintyre, 1969; Bragg et al., 1970; O'Neil, 1980).

The results of these experiments show that detoxification of ergot sclerotia is possible. Further studies are under way to establish the practicality of these findings.

## ACKNOWLEDGMENT

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**Registry No.** Ergometrine, 60-79-7; ergosine, 561-94-4; ergotamine, 113-15-5; ergocornine, 564-36-3; ergocryptine, 511-09-1; ergocorninine, 564-37-4; ergocristine, 511-08-0; ergocristinine, 511-07-9; ergocryptinine, 511-10-4; ergometrinine, 479-00-5; ergotaminine, 639-81-6; chlorine, 7782-50-5; sulfur dioxide, 7446-09-5; hydrogen chloride, 7647-01-0.

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# Effects of Processing on the Sodium:Potassium and Calcium:Phosphorus Content in Foods

C. Jane Wyatt\* and K. Ronan

The effects of processing on sodium:potassium (Na:K) and calcium:phosphorus (Ca:P) ratios in peanuts, wheat, tuna, canned green beans, whole kernel and cream-style corn, carrots, peaches, frozen green beans, corn, broccoli, cauliflower, and french fried potatoes were studied. Minerals were determined in samples taken at various stages during processing. Processing of canned vegetables caused a loss in phosphorus and an increase in the Na:K ratios, when salt was added. Freezing vegetables had very little effect on the minerals studied. Processing of peanuts resulted in an increase in Na:K ratios in peanut butter. Mineral content of whole wheat flour was unaffected by milling, whereas the potassium and phosphorus content of white flour was reduced. In tuna, canning in either oil or water affected mineral values.

Many studies have been conducted over the years on the nutrient composition of processed foods. The majority of these studied have been concerned with the losses of water-soluble vitamins during processing. Few studies have been conducted on the effect of processing on the mineral content.

General commercial processes which may result in mineral losses include peeling, blanching, and cooking (Fennema, 1976). Losses of minerals due to peeling or trimming of fruits and vegetables may result due to une-

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Table I	Effects of	Processing on	Peanuts (	(n = 12)	ì
Table I.	Effects of	FIOCESSING ON	i canuts	(n - 14)	,

	mg/100 g dry wt								
treatment	% moisture	% fat	Na ± SD	K ± SD	Ca ± SD	P ± SD	Na:K	Ca:P	
raw roasted blanched peanut butter	$\begin{array}{c} 6 \pm 0 \\ 1 \pm 0.12 \\ 1 \pm 0.15 \\ 2 \pm 0.61 \end{array}$	$\begin{array}{c} 48 \pm 1 \\ 50 \pm 0.86 \\ 50 \pm 0.71 \\ 48 \pm 6 \end{array}$	$20 \pm 5 \\ 18 \pm 4 \\ 24 \pm 9 \\ 422 \pm 215$	$\begin{array}{r} 601 \pm 35 \\ 599 \pm 36 \\ 552 \pm 48 \\ 530 \pm 41 \end{array}$	$54 \pm 0 \\ 54 \pm 10 \\ 44 \pm 10 \\ 43 \pm 7$	$\begin{array}{r} 365 \pm 25 \\ 380 \pm 11 \\ 378 \pm 14 \\ 342 \pm 15 \end{array}$	$\begin{array}{c} 0.04 \pm 0.01 \\ 0.03 \pm 0.01 \\ 0.04 \pm 0.01 \\ 0.58 \pm 0.51 \end{array}$	$\begin{array}{c} 0.15 \pm 0.03 \\ 0.14 \pm 0.03 \\ 0.12 \pm 0.02 \\ 0.13 \pm 0.02 \end{array}$	

<sup>a</sup> Data presented in the tables are mean values of three lots of each product. Each analysis was run in triplicate. Resultant values were large in some instances when large variations occurred between lots.

qual distribution of minerals in the food (Harris and Von Loesecke, 1960). Increases in the sodium content of peeled products may occur if sodium hydroxide is used in the removal of the skins (Bender, 1973).

In 1979 Elkin (1979) studied the mineral levels in canned and raw green beans, peaches, and sweet potatoes. In canned green beans, decreases in calcium, phosphorus, magnesium, and potassium and an increase in sodium was observed compared to the raw product. It was concluded that these results were due to an interchange of minerals in the beans with those in the blanching water and in the sodium-containing canning brine. The canned peaches did not retain 100% of the mineral concentrations found in the raw product. The losses were so small, however, that they were attributed to experimental error. Canned sweet potatoes showed complete retention of calcium, phosphorus, and magnesium. Rather large deviations from 100% retention were seen for potassium, manganese, copper, and zinc, but it was unclear if these differences were due to experimental error or if actual losses occurred due to processing.

Some minerals in foods seem to be more important than others in terms of their health implications. Individually both calcium and phosphorus play important roles in the body, yet research indicates it is the relationship of calcium to phosphorus in the diet that is of critical importance for optimum nutrition and health (Linkswiler and Zemel, 1979). The ideal ratio of calcium to phosphorus in the diet is 1:1 (National Academy of Sciences, 1974) although most American diets are much richer in phosphorus than calcium (Linkswiler and Zemel, 1979).

High levels of dietary sodium have been associated with hypertension. However, an interesting reciprocal relationship between sodium and potassium and their interaction in the development of hypertension is indicated (Meneely and Battarbee, 1976). Evidence suggests a diet high in sodium chloride coupled with a diminishing intake of potassium can bring on the onset of hypertension (Haddy, 1980). It appears that potassium may have a protective effect against excess sodium and that the ratio of sodium to potassium in the diet is most important when controlling hypertension (Frank and Mickelsen, 1969; Weinsier, 1976; Meneely, 1973).

How processing affects sodium:potassium and calcium:phosphorus ratios in certain foods was the subject of this study.

#### MATERIALS AND METHODS

Samples of commercially processed peanut butter, white and whole-wheat flours, tuna canned in oil and water, canned green beans, whole kernel and cream-style corn, carrots, peaches, frozen green beans, corn, broccoli, cauliflower, and french fried potatoes were obtained. Several lots of each food were taken at various stages during the processing of the product.

Four different lots of peanut samples were procured from a commercial peanut butter manufacturer in Oregon. Samples included raw, roasted, blanched peanuts, and the finished product. The lots sampled were as follows: 100% runner peanuts; 100% Spanish style peanuts; a mixture of 50% Spanish style and 50% runner peanuts; 100% runner peanuts (old-fashioned style). The finished products from the different lots were creamy-style peanut butter, chunky-style peanut butter, and old-fashioned-style peanut butter.

**Tuna Fish.** Four lots of tuna were obtained from a commercial processor in Oregon. The lots were skipjack, extra small yellow fin, large yellow fin, and albacore. Samples from each lot were raw, precooked, canned in oil, and canned in water tuna.

Flour. Three lots of white flour were obtained from a commercial flour mill in Oregon. The samples from each lot were whole-wheat kernels, wheat germ, mill run (bran), low-grade flour (prior to finishing for white flour), unbleached-unenriched flour, bleached-unenriched flour, and bleached-enriched flour. Three lots of whole-wheat kernels and whole-wheat flour were also obtained from a commercial flour mill in Washington.

**Fruits and Vegetables.** Three lots of each food item were collected over a 2-year processing season from three different processors in Oregon, Washington, Idaho, and California. The samples were taken from the processing line, packed in ice for transport to the laboratory, frozen at -10 °C, and held until analyzed. The canned samples were stored at room temperature.

Samples were homogenized in a Waring blender, ashed in a muffle furnace at 550 °C for 24 h, and made to volume with deionized water for subsequent mineral analysis. Sodium, potassium, and calcium contents of fruit and vegetable products were measured on the ashed samples by flame photometry ("Perkin-Elmer Model 21 Coleman Flame Photometer Operating Directions", 1979). The procedure of Noller and Bloom (1978) using a Perkin-Elmer Model 303 atomic absorption spectrophotometer was used for Na, K, and Ca content on all other foods.

Moisture and fat were determined by AOAC procedures (1975). Phosphorus was determined according to the method of Eng and Noble (1968). All analyses were run in triplicate.

Data were statistically analyzed by analysis of variance to determine the effect of processing on mineral values. Treatment mean values were compared by the least significant differences method to determine which processing treatments caused a significant effect on mineral level compared to raw values (Snedecor and Cochran, 1967).

# RESULTS AND DISCUSSION

The effect of processing on peanuts are presented in Table I. The moisture content decreased from an average of 6% in the raw peanuts to 1% in the roasted product. This loss of moisture was probably due to the high heat used to roast the peanuts. The fat content of the peanuts was relatively unaffected by processing, averaging 49%. There were no significant differences in sodium levels of the raw peanuts from the four lots examined. However, there were significant differences in potassium, calcium, and phosphorus among the different lots. No significant differences were observed between the raw and roasted

Table II.	Effects of	Processing	on Wheat (	(n = 9	)
<b>TUDIO T</b>					

			mg/100 g dry wt					
treatment	% moisture	% fat	Na ± SD	K ± SD	Ca ± SD	P ± SD	Na : K	Ca:P
kernel	11 ± 1	$1 \pm 0.47$	28 ± 0.88	314 ± 9	$25 \pm 0.78$	$404 \pm 96$	$0.09 \pm 0.01$	$0.07 \pm 0.02$
bran	$13 \pm 0.31$	$4 \pm 0.05$	$25 \pm 4$	$1172 \pm 12$	$76 \pm 0.42$	$1267 \pm 43$	$0.68 \pm 1.14$	$0.06 \pm 0.00$
germ	$12 \pm 0.78$	$11 \pm 1$	$33 \pm 3$	$955 \pm 28$	51 ± 7	$1146 \pm 14$	$0.04 \pm 0.01$	$0.05 \pm 0.01$
low grade	$13 \pm 0.23$	$2 \pm 0.76$	$24 \pm 6$	$193 \pm 25$	$25 \pm 1$	$316 \pm 78$	$0.13 \pm 0.06$	$0.08 \pm 0.02$
untreated	$12 \pm 0.12$	$1 \pm 0.06$	$12 \pm 3$	$73 \pm 3$	$17 \pm 0.71$	$122 \pm 4$	$0.16 \pm 0.04$	$0.14 \pm 0.00$
bleached, not enriched	$13 \pm 0.15$	$1 \pm 0.08$	$12 \pm 3$	76 ± 7	$20 \pm 3$	$128 \pm 3$	$0.16 \pm 0.04$	$0.16 \pm 0.03$
bleached, enriched	$13 \pm 0.29$	$1 \pm 0.03$	$12 \pm 3$	$86 \pm 0.12$	$18 \pm 1$	$127 \pm 5$	$0.15 \pm 0.06$	$0.15 \pm 0.00$
whole-wheat kernel	$11 \pm 0.20$	$1 \pm 0.08$	29 ± 3	306 ± 28	$27 \pm 3$	377 ± 29	$0.10 \pm 0.01$	$0.07 \pm 0.02$
whole-wheat flour	$12 \pm 0.22$	$2 \pm 0.24$	26 ± 2	315 ± 15	$25 \pm 2$	$343 \pm 62$	$0.08 \pm 0.01$	$0.07 \pm 0.01$

Table III.	Effects of	Processing or	I Tuna	(n = 12)	)
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treatment	mg/100 g dry wt								
	% moisture	% fat	Na ± SD	K ± SD	Ca ± SD	P ± SD	Na:K	Ca:P	
raw precooked canned in oil canned in water liquid	$70 \pm 465 \pm 360 \pm 272 \pm 3$	$3 \pm 6$ $5 \pm 10$ $37 \pm 5$ $6 \pm 11$	$\begin{array}{r} 1349 \pm 538 \\ 887 \pm 375 \\ 700 \pm 209 \\ 950 \pm 309 \\ 275 \pm 101 \end{array}$	$1022 \pm 298 \\ 752 \pm 201 \\ 432 \pm 138 \\ 640 \pm 136 \\ 143 \pm 37$	$26 \pm 12 \\ 18 \pm 7 \\ 19 \pm 8 \\ 37 \pm 8 \\ 5 \pm 2$	$836 \pm 115 \\775 \\560 \pm 127 \\616 \pm 85 \\190 \pm 118$	$\begin{array}{c} 1.37 \pm 0.48 \\ 1.24 \pm 0.42 \\ 1.87 \pm 1.06 \\ 1.61 \pm 0.80 \\ 2.15 \pm 1.17 \end{array}$	$\begin{array}{c} 0.04 \pm 0.02 \\ 0.03 \pm 0.01 \\ 0.04 \pm 0.01 \\ 0.06 \pm 0.02 \\ 0.03 \pm 0.01 \end{array}$	

peanuts for any of the minerals. Blanching caused significant losses of potassium and calcium but not of sodium and phosphorus. On the average, 92% of the potassium and 84% of the calcium found in the raw peanuts was retained after blanching. The blanching treatment promoted leaching of calcium and potassium from the peanuts. Blanching also removed the peanut skins which contain a greater concentration of calcium and the same concentration of potassium as the peanut (Watt and Merrill, 1963). On the average, 88% of the potassium, 83% of the calcium, and 95% of the phosphorus found in the raw peanuts was retained in the peanut butter. Peanut butter contained lower concentrations of potassium, calcium, and phosphorus than the raw peanut. Lower levels of potassium and calcium were expected as significant losses of these minerals occurred during blanching. The sodium content of the peanut butter increased due to the addition of salt for flavor.

All finished products contained significantly higher sodium:potassium ratios than the raw peanuts. These increases were due to the addition of salt to the peanut butter and the loss of potassium during blanching. Despite the salt added to peanut butter, the finished product has a low sodium:potassium ratio due to the high concentration of potassium in peanuts. The calcium:phosphorus ratios of the different treatments were not significantly different. They were all very low because peanuts naturally contain a much higher concentration of phosphorus than calcium.

The effects of milling wheat are presented in Table II. The moisture content was about 12% in all wheat products. The whole-wheat kernel and whole-wheat flour contained about 2% fat. The germ portion of the kernel contained the greatest concentration of fat, averaging 11%. The bran contained about 4% and the different white flours about 1% fat. The low-grade flour contained a slightly higher concentration of fat than the other white flour (2%) because it characteristically contains fragments of the bran and germ portion of the kernel which contained relatively high concentrations of the fat.

Bran contained the greatest concentration of potassium, calcium, and phosphorus of the products studied. The germ portion of the whole wheat kernel also contained high levels of potassium, calcium, and phosphorus but they were

significantly less than those in the bran. The sodium concentration of the germ was significantly greater than that in bran. Untreated, bleached-not enriched, and bleached-enriched white flour contained lower levels of all minerals than the kernel, germ, and bran samples. On the average 45% of the sodium and 27% potassium, 75% calcium, and 33% phosphorus found in the kernel were retained in the white flour. Bleaching and enriching did not affect the mineral content of the experimental white flours. No significant differences were seen in the sodium, potassium, calcium, and phosphorus levels of the untreated, bleached-not enriched, and bleached-enriched flours. The potassium and phosphorus levels in the lowgrade flour were significantly greater than those in the other white flours but lower than those in the kernel, germ, and bran. Low-grade flour characteristically contains fragments of bran and germ and a high percentage of ash. Therefore, higher levels of the individual minerals were expected (Jones, 1958).

Whole-wheat flour is characterized as containing the endosperm as well as the bran and germ of the kernel. Therefore, whole-wheat flour was expected to contain the same concentration of minerals as the kernel. There was no significant differences between the minerals in the kernel and whole-wheat flour.

Processing had no effect on the sodium:potassium ratio for whole-wheat flour, but there was a significant effect in white flour. The calcium:phosphorus ratios of the kernel and the whole-wheat flour were not significantly different although the ratio of the white flour was significantly greater. Milling wheat into white flour increased the calcium:phosphorus ratio due to the removal of bran and germ which contained high concentrations of phosphorus.

The effects of processing tuna fish are presented in Table III. Moisture decreased due to precooking and increased in the canned in water samples for all species. As expected, a large increase in the fat content of the canned in oil samples was observed. Precooking did not have a significant effect on the fat content of the samples. Albacore has a higher fat content than the other species of fish.

Precooking resulted in significant losses of sodium and potassium in all species of fish, calcium losses in skipjack

Table IV. Effects of Processing on Mineral Content of Canned Fruits and Vegetables (Mean Values, n = 9)

			mg/100 g dry wt					
product	treatment	% moisture ± SD	Na ± SD	K ± SD	Ca	P ± SD	Na:K	Ca:P
green beans	raw	91 ± 6.1	69 ± 24.0	929 ± 677.1	<1	$1073 \pm 73$	0.07	
-	blanched	$92 \pm 2.2$	$42 \pm 19.3$	967 ± 390	< 1	$82 \pm 20$	0.04	
	solids and liquid	$94 \pm 2.5$	$2115^a \pm 1372.9$	$1570^{a} \pm 198$	61	$49 \pm 9$	1.34	1.24
	drained solids	$93 \pm 8.7$	$1622^a \pm 1091.3$	$1310^{a} \pm 259$	77	$55 \pm 24$	1.23	1.41
	liquid	$96 \pm 0.2$	$3927^a \pm 2812.1$	$2546^{a} \pm 420$	55	$76 \pm 12$	1.54	0.72
corn,	raw	$75 \pm 5.5$	$37 \pm 10$	$689 \pm 332$	< 1	$308 \pm 205$	0.05	
whole kernel	solids and liquid	$81 \pm 3.2$	$785^{a} \pm 101$	$890 \pm 41$	<1	$511 \pm 576$	0.88	
	drained solids	$76 \pm 3.3$	666 ± 113	$695 \pm 437$	< 1	$370 \pm 331$	0.95	
	liquid	<b>89</b> ± <b>3</b> .5	1537ª ± 531	$1633^{a} \pm 43$	<1	$919 \pm 1094$	0.94	
corn,	raw	71	$27^{a}$	913	$<\!1$	913	0.03	
cream style	blanched	74	798	1001	5	1001	0.79	
-	canned	73	773	1063	< 1	1063	0.72	
carrots	raw	$85 \pm 1.6$	$206 \pm 83$	$2492 \pm 654$		$186 \pm 88$	0.08	
	blanched	$87 \pm 6.9$	$318 \pm 39$	$1471^{a} \pm 109$		$60^{a} \pm 26$	0.22	
	solids and liquid	$92 \pm 5.9$	$1278^{a} \pm 339$	$1818^{a} \pm 792$		$114^{a} \pm 26$	0.70	
	drained solids	$91 \pm 2.6$	$1268^a \pm 290$	$1628^{a} \pm 462$		$124^{a} \pm 31$	0.78	
	liquid	$94 \pm 2.5$	$1712^{a} \pm 439$	$2122^{b} \pm 1045$		$117^{a} \pm 69$	0.81	
peaches	raw	$88 \pm 8.1$	$51 \pm 93$	$1293 \pm 259$		$305 \pm 308$	0.04	
•	blanched	$90 \pm 1.6$	$97^{a} \pm 41$	$1464^{a} \pm 818$		$320 \pm 321$	0.06	
	solids and liquid	$79 \pm 5.4$	$59 \pm 8$	$308^{a} \pm 132$		$39^{a} \pm 18$	0.19	
	drained solids	$79 \pm 4.3$	$48 \pm 12$	$341^{a} \pm 44$		$42^{a} \pm 9$	0.14	
	liquid	$79 \pm 4.3$	$63 \pm 15$	$329^{a} \pm 17$		$35^{a} \pm 15$	0.19	

<sup>a</sup> Values were significantly different at the 1% level. <sup>b</sup> Values were not significantly different at the 1% level but were significantly different at the 5% level.

and albacore, and a loss of phosphorus in skipjack only. The steam treatment used to precook the fish may have caused these losses by promoting leaching of the minerals from the fish. On the average, 65% of the sodium, 75% potassium, 78% calcium, and 97% phosphorus found in the raw tuna samples was retained after precooking. Sodium is mainly extracellular in fish which would facilitate the leaching of sodium from the fish during precooking. Potassium, on the other hand, is found primarily intracellularly, thereby preventing leaching of this mineral. However, some potassium was lost during precooking in this study. Love reported in 1961 that freezing fish in a sodium chloride brine often causes cells to rupture. If the cells were damaged in this manner during freezing, potassium would have been more readily lost during precooking.

The effects of processing on the mineral content of canned fruit and vegetables are shown in Table IV. Processing had a significant effect on the sodium and potassium content in canned green beans. The average mean values showed there was no significant effect of blanching the raw green beans on sodium and potassium content; however, there was a significant effect due to retorting. The addition of salt brine as the cooking liquid resulted in a noticeable increase in the sodium content of the canned item. Two lots of whole kernel corn and one lot of cream-style corn were analyzed. There was a significant difference in the sodium content of the canned solids and liquid compared to raw corn. However, there was no significant difference between drained solids and the raw corn. There was no significant difference in potassium content between the raw corn and the solids and liquid and drained solids although there was a significant increase in the potassium content of the liquid. The addition of salt in cream-style corn significantly increased the sodium content while potassium content was not affected.

Processing significantly affected the sodium and potassium content of cannot carrots even in the lot where no salt was added. The treatment means showed that blanching did not affect the sodium content although there was a significant increase in sodium due to other processing treatments. Processing caused significant losses of potassium with a large amount of the potassium contained in the drained liquid.

Processing had a significant effect on the sodium and potassium content of canned peaches. The mean sodium and potassium values showed blanching caused a significant increase in sodium and potassium content; however, there were no significant differences between the sodium contents in the canned solids and liquid, drained solids, or liquid as compared to those of the fresh peach. The increase in sodium in the blanched item is probably due to residual lye remaining on the fruit from caustic lye used to peel the fruit. There was a significant difference in potassium content for all treatments of canned peaches.

In many of the foods sampled the calcium content was too low to be accurately measured (<1 ppm). The canned vegetables did have measurable levels of calcium and these levels were significantly affected by processing. Processing also had a significant affect on the phosphorus content of green beans. Processing had a significant affect on the phosphorus content in whole kernel corn. The mean values showed a significantly lower phosphorus content in the canned solids and liquid than in the raw corn although there was no significant difference in the phosphorus content between the drained solids and the raw product. There was a significant increase in the phosphorus content in the canning liquid. The calcium content in canned carrots was below the limits of detection in some samples. Processing significantly affected the phosphorus content of canned carrots. The treatment means show a significant loss in phosphorus due to all treatments.

Processing had a significant effect on the phosphorus content of peaches. The mean values showed no significant difference in the phosphorus content due to the blanching treatment. However, there was significantly less phosphorus in the canned products compared to the fresh peach.

In Table V the effects of processing on the mineral content of frozen vegetables are shown. In green beans, processing did not affect the sodium and potassium content. Freezing of cauliflower had no significant effect on the sodium content; however, in two of the lots studied

Table V. Effects of Processing on the Mineral Content of Frozen Vegetables (Mean Values, n = 9)

			mg/100 g dry wt			
product	treatment	% moisture	Na ± SD	K ± SD	P ± SD	Na:K
green beans	raw	91 ± 0.6	66 ± 15	1048 ± 891	85 ± 74	0.12
	blanched	$91 \pm 0.6$	$59 \pm 30$	$900 \pm 394$	$85 \pm 41$	0.06
	frozen	$92 \pm 6$	$52^{a} \pm 17$	877 ± 487	$97 \pm 65$	0.04
cauliflower	raw	$93 \pm 4$	$133 \pm 46$	$3362 \pm 860$	$273 \pm 49$	0.03
	blanched	$93 \pm 4$	$115 \pm 36$	$2585^{b} \pm 669$	$246 \pm 23$	0.04
	frozen	$93 \pm 3$	$127 \pm 64$	$2141^{a} \pm 703$	$240 \pm 62$	0.05
broccoli	raw	$89 \pm 2$	$164 \pm 98$	$2155 \pm 461$	$368 \pm 178$	0.07
	blanched	$91 \pm 2$	$169 \pm 142$	$1486^{a} \pm 461$	$110^{a} \pm 37$	0.11
	frozen	$91 \pm 2$	$148^{a} \pm 161$	$2219 \pm 1132$	$391 \pm 288$	0.06
corn	raw	$75 \pm 3$	$36 \pm 7$	$810 \pm 301$	$136 \pm 23$	0.04
	blanched	$74 \pm 2$	$39 \pm 14$	$599^{a} \pm 288$	$112 \pm 18$	0.06
	frozen	$75 \pm 3$	$28 \pm 12$	$769 \pm 327$	$136 \pm 16$	0.03
french fried potatoes	raw	$74 \pm 6$	$61 \pm 34$	$1171 \pm 493$	$185 \pm 59$	0.15
-	peeled	74 ± 7	$105^{a} \pm 47$	$1066 \pm 278$	$229^{a} \pm 115$	0.09
	blanched	$76 \pm 8$	$62 \pm 20$	$593^{a} \pm 127$	$170 \pm 37$	0.10
	fried	$68 \pm 2$	$59 \pm 10$	$673^a \pm 173$	$200 \pm 61$	0.08
	frozen	66 ± 4	$63 \pm 15$	$653^a \pm 250$	$187 \pm 92$	0.09

<sup>a</sup> Values were significantly different at the 1% level. <sup>b</sup> Values were not significantly different at the 1% level but were significantly different at the 5% level.

there was a significant effect on the potassium content. The mean of three lots of cauliflower showed no significant effect due to freezing on sodium content and a significant loss of potassium compared to the raw by blanching and freezing. Only two lots of broccoli were available for study because of the limited number of firms processing broccoli in the Northwest. Their mean showed a significant loss of sodium by freezing but no significant difference in the potassium content of the frozen product compared to that of raw broccoli. Processing had no significant effect on the sodium and potassium content in frozen corn. The mean of three lots of french fried potatoes obtained from three different processors showed a significant increase in sodium from the peeling operation only. No significant effect on sodium content was observed for the other operations. The increase in sodium content for the peeled sample was probably due to residual lye from the lye peeling process which is removed during further processing. There was no significant loss of potassium due to the peeling operation but blanching, frying, and freezing caused a significant loss of potassium from the raw, fresh potato.

Calcium values were too low to be measured in most frozen vegetables. Freezing of green beans, cauliflower, and corn did not affect the phosphorus content. There was a significant loss of phosphorus during blanching in broccoli; however, no significant loss was observed in the frozen product. The means of three lots of frozen french fried potatoes showed a significant increase in phosphorus content after peeling. SAPP (sodium pyrophosphate) is commonly added to cut potatoes to prevent discoloration during processing. Any increase in sodium or phosphorus content from this additive was not seen in the mean values. There was no effect on the phosphorus levels by blanching, frying, or freezing.

#### CONCLUSIONS

Processing peanuts into peanut butter resulted in an increase in the sodium:potassium ratio due to the addition of salt to the finished product and the loss of potassium during precooking. The calcium:phosphorus ratio was unaffected by processing.

The sodium:potassium and calcium:phosphorus ratios of whole-wheat flour were unaffected by processing. White flour had a higher sodium:potassium and calcium:phosphorus ratio than the whole kernel. These increased ratios were due to the separation of bran and germ, which contained high levels of potassium and phosphorus, from the endosperm in the milling of white flour.

Processing resulted in a general increase in the sodium:potassium ratio of tuna canned in oil and in water and an increase in the calcium:phosphorus ratio of tuna canned in water. The increases in the sodium:potassium ratios were due to freezing tuna in a salt brine, adding salt to the finished product, and the losing potassium during precooking. The increased calcium:phosphorus was due to the absorption of calcium from the water broth in which it was packed.

Canning of green beans, whole kernel corn, and carrots affected the sodium:potassium ratio. There was a high concentration of both sodium and potassium in the canning liquid for vegetables.

Canning of peaches did not have an effect on sodium:potassium ratios. There was a slight increase in the sodium and potassium content of the blanched product reflecting residual lye from the peeling operation which is subsequently lost with further processing.

Calcium content of fruits and vegetables was very low. A significant loss of phosphorus was observed during the canning of most products. A high concentration of phosphorus was measured in the liquid showing a leaching of phosphorus into the canning liquid.

Freezing had little effect on the sodium:potassium ratios for any of the frozen vegetables studied. In the processing of frozen french fried potatoes, there was a significant increase in phosphorus in the peeled sample; however, there were no significant differences in the phosphorus content in further stages of processing. For the other vegetables studied, frozen green beans, cauliflower, broccoli, and corn, freezing did not significantly affect the phosphorus content.

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**Registry No.** Na, 7440-23-5; K, 7440-09-7; Ca, 7440-70-2; P, 7723-14-0; NaCl, 7647-14-5.

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# Properties of Two Toxins Newly Isolated from Oysters

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Two toxins were newly isolated from the hepatopancreas of toxic oysters. The structures of two of these were deduced to be carbamoyl-*N*-sulfo-11 $\alpha$ -hydroxysaxitoxin sulfate (1) and the 11 $\beta$  epimer (2), based on elemental analysis, electrophoresis, TLC, <sup>1</sup>H and <sup>13</sup>C NMR, and conversion experiments. 1 revealed little toxicity on intraperitoneal injection into mice. 2 gave a specific toxicity of 300 ± 15 mouse units/mg. Upon mild acid hydrolysis, 1 and 2 were converted to highly toxic compounds: 11 $\alpha$ -hydroxysaxitoxin sulfate and its epimer.

We have already reported on some properties of the two toxins newly isolated from the oyster *Crassostrea gigas* cultured in Senzaki Bay, Yamaguchi, Japan (Onoue et al., 1981). Both toxins revealed an extremely low toxicity in mice as well as quite different chromatographic and electrophoretic behaviors from the previously known toxins.

Meanwhile, two analogous toxins have been isolated from cultures of *Protogonyaulax* sp. (Hall et al., 1980) and *Gonyaulax tamarensis* (Kobayashi and Shimizu, 1981). The structures of two of these were then determined by X-ray crystallography as carbamoyl-N-sulfo-11 $\alpha$ hydroxysaxitoxin sulfate and the 11 $\beta$  epimer (Wichmann et al., 1981).

Our continuous efforts were made to characterizing the two isolated oyster toxins, since characterization or identification of them may provide evidence for the involvement of the above two species of dinoflagellates in the infestation to shellfish.

## MATERIALS AND METHODS

Toxic Oysters. Toxic specimens of the oyster C. gigas cultured in Senzaki Bay, Yamaguchi, Japan, were collected in Jan 1979 and 1980. The oysters, after being shucked, were kept frozen below -20 °C for 3-10 months. The hepatopancreas was removed from the partially thawed oysters and used for the extraction and purification of toxins. The toxicity of organ was determined by using the

standard mouse bioassay for paralytic shellfish poison (AOAC, 1975).

**Extraction Procedure.** One kilogram of hepatopancreas  $(240 \pm 12 \text{ mouse units } (MU)/g)$  was homogenized for 3-5 min with 2000 mL of 80% ethanol adjusted to pH 2 with 1 N HCl. The homogenate was centrifuged at 5000g for 20 min. These steps were repeated twice for the residue. The combined supernatant was concentrated in vacuo to 500 mL and washed 5 times with 300 mL of chloroform. The aqueous layer (220 000 MU) from which the residual chloroform was removed by evaporation was adjusted to pH 5.5 with 1 N NaOH.

Activated Charcoal Treatment. Water-washed activated charcoal (Wako Pure Chemical Industries), 750–800 mL, was added under agitation to the toxin extract and filtered through a Büchner funnel. The charcoal on the funnel was thoroughly washed with water and eluted with 3000 mL of 20% ethanol containing 1% acetic acid. The toxic eluate (152 000 MU) was concentrated in vacuo to 300 mL and lyophilized.

Chromatography on Bio-Gel P-2. The lyophilized toxins were dissolved in 350 mL of water and applied to a Bio-Gel P-2 (Bio-Rad Laboratories) column ( $6.5 \times 50$  cm). After half of the bed volume (800 mL) of water was passed through the column at a flow rate of 3 mL/min, the toxins were eluted with 2000 mL of 0.15 M acetic acid. The toxic eluate ( $150\,000$  MU) was concentrated and lyophilized.

Chromatography on Amberlite CG-50 II. The geltreated toxins were dissolved in 5 mL of water, placed on an Amberlite CG-50 II (Rohm and Haas Co.) column (H<sup>+</sup> form,  $1.5 \times 95$  cm) and fractionated with 100 mL of water and then 350 mL each of 0.1 and 0.5 M acetic acid. The water eluate (50 000 MU) was lyophilized and purified by

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