Water-Induced Lipid Changes in Oat Processing

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Oat flours prepared from hulled, dehulled, or heat-treated grains were studied for lipid changes in aqueous suspensions. These data were compared to lipid profiles of fiber, protein, and starch fractions obtained in a wet fractionation process. The appearance of free fatty acids (FFA) at the expense of triglycerides (TG) but not their rapid oxidation was a response to water soaking of the flours; the lipids of hulled and dehulled grains were neither hydrolyzed nor oxidized under similar conditions. Wet fractionation of oat flour from nonheated grains resulted in TG hydrolysis in starch and protein fractions so that FFA content rose to 21% and 30%, respectively, while the lipids of fiber remained very similar to that of whole grains. Since TG, polar lipid, and FFA fractions in whole grains comprised about 78%, 19%, and 3% of total lipids, very little of the oat's original lipid composition prevailed in the starch and protein fractions. Therefore, prevention of lipid hydrolysis rather than oxidation should be a primary goal in the manufacture of nondeteriorated oat products.

INTRODUCTION

Oats are receiving nutritional interest because of their high-quality protein, good fatty acid composition, and high fiber content. However, the development of new food applications of oats is often hampered by fat-related problems. Oat groats have the highest lipid content among the common cereal grains, and the lipid is distributed throughout the kernel. The oat is also distinctive because it has remarkable lipase activity in ungerminated seed (Youngs, 1986). Also, phospholipase (Acker and Ernst, 1954) and lipoxygenase (Pomeranz, 1971; Popov and Chelev, 1959) activities have been found. In industrial oat fractionation processes, where the grains are ground and soaked in water, the cellular intrastructure is destroyed with uncontrollable mixing of the lipids and the hydrolytic and oxidative activities. Such a slurrying step contributes to rapid development of unpleasant flavor which is carried onto the final oat products such as bran/fiber, protein, and starch. Generally, the deterioration is believed to be initiated by hydrolysis of esterified fatty acids. In oats the released fatty acids are mostly unsaturated (Youngs, 1986) and therefore susceptible to oxidation by lipoxygenase and nonenzymic catalysts. However, little information exists about the possible mutual effects of oat lipids and its hydrolytic and oxidative activities in the water slurries of ground oats. Therefore, efficient strategies for preventing deteriorative lipid changes in industrial processes are also lacking. Short processing times and steam treatments are typical pretreatments in industry to eliminate undesired enzyme activities (Youngs, 1978). Laboratory methods include wet or dry scrubbing of the outer layers of kernels (Hutchinson et al., 1951; Martin and Peers, 1953; Urquhart et al., 1983) and soaking of dehulled grains in acids or ethanol (Frey and Hammond, 1975; Kent, 1983) before they are ground. The efficiency of such and any other new pretreatments can be evaluated only if the initial lipid conversions in the processes are sufficiently known. Once initiated, the deteriorative processes are difficult to eliminate, and the accumulation of unwanted lipid products in the final products cannot be avoided. Therefore, we examined first the instant effects of water soaking on oat lipids and second the effect of the subsequent wet fractionation process on lipid composition of oat fiber, protein, and starch fractions.

MATERIALS AND METHODS

Materials. Oat grains were the Finnish cultivar Veli harvested in 1989. Dipentadecanoylphosphatidylcholine, heptadecanoic acid, triheptadecanoin, and heptadecanoic acid methyl ester were used as the standards in TLC and GLC analyses and were purchased from Sigma. Silica gel plates were purchased from Merck. HPLC grade solvents were used for all fatty acid analyses. All other chemicals were of reagent grade or better.

Water Soaking. The oat samples were as follows: hulled grains, dehulled grains, flour made from both of those grains, and flour from wet heat-treated grains and hulls. Dehulling was performed either manually or industrially when grains were subsequently wet heat-treated for 20–30 min at 70–80 °C. Grains were ground to a fine powder just prior to soaking in a Schnitzer (Model KE) natural stone flour mill. A 1-g sample representing grains, flour, or hulls was soaked for 0–120 h in a 50-mL shaking flask (200 rpm, 20 °C) in 5 mL of distilled water. Soaked grains were ground in a mixture of chloroform–methanol (2:1 v/v) with a mortar, and this mixture was used as such for lipid extraction. Soaked flour or hulls were extracted without any pretreatments.

Oat Fractionation. Sixty-five grams of ground, dehulled oats was slurried in 15 °C water to form an approximately 24% slurry (dry substance content). The slurry was mixed with a pestle for 15 min at 15 °C and homogenized with an Ultra Turrax for 1 min. The fiber fraction was separated from the protein–starch mixture in a continuous saftcentrifuge (AEG Model ESF 102) and washed with water. The protein–starch mixture was screened (mesh size 88 μm) to remove residual fiber and separated by centrifuging (16266*g*) for 20 min. The fiber, protein, and starch fractions so obtained were freeze-dried, stored in vacuum at room temperature, and used for lipid extractions.

Lipid Extraction. Oat samples were extracted by shaking (250 rpm, 28 °C) for 8 h in 19 volumes of chloroform–methanol (2:1 v/v) according to the method of Folch et al. (1957). The mixtures were centrifuged (1464*g*) for 10 min to remove insoluble material. The extraction was repeated for 2 h with the same amount of chloroform–methanol. The extracts were combined and evaporated to dryness in a rotary evaporator. Lipids were dissolved in 20 mL of chloroform–methanol mixture (100:1 v/v), divided as 1-mL portions in test tubes, evaporated dryness under N_2, and stored at −20 °C under N_2 before analysis. The samples were used to determine the absolute and relative amounts of

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Table I. Fatty Acid Composition and Content of Oat Samples

sample	soaking time, h	fatty acid composition,[a] % 14:0 ω	16:0 ω	16:1 n-7	18:0 ω	18:1 n-9	18:2 n-6,9	18:3 n-6,9,12	others[c]	fatty acid content,[a,b] mg/g
flour from hulled grains	0	0.31 ± 0.01[d]	16.6 ± 0.4	0.32 ± 0.12	1.9 ± 0.2	37.8 ± 0.1	38.2 ± 0.4	1.5 ± 0.1	3.4 ± 0.4	47.2 ± 2.5
	15	0.30 ± 0.07	17.6 ± 0.3	0.35 ± 0.13	2.0 ± 0.5	39.4 ± 0.2	35.5 ± 0.5	1.3 ± 0.1	3.5 ± 0.3	45.5 ± 2.3
flour from dehulled grains	0	0.44 ± 0.29	16.4 ± 0.4	0.25 ± 0.02	1.6 ± 0.2	37.8 ± 0.3	38.6 ± 0.1	1.7 ± 0.1	3.0 ± 0.3	61.9 ± 1.3
	15	0.24 ± 0.09	17.7 ± 0.9	0.26 ± 0.03	2.0 ± 0.1	38.9 ± 0.5	36.2 ± 0.5	1.4 ± 0.1	3.3 ± 0.0	56.9 ± 2.0
flour from dehulled and steamed grains	0	0.26 ± 0.03	16.3 ± 0.7	0.20 ± 0.03	1.7 ± 0.1	38.3 ± 0.1	38.5 ± 0.2	1.4 ± 0.0	3.3 ± 0.2	42.5 ± 2.1
	15	0.26 ± 0.01	18.0 ± 0.7	0.24 ± 0.04	1.7 ± 0.1	39.0 ± 0.0	36.4 ± 0.8	1.2 ± 0.1	3.2 ± 0.0	43.8 ± 2.7
hulled grains	0	0.26 ± 0.01	16.8 ± 0.2	0.27 ± 0.08	1.6 ± 0.0	38.4 ± 0.7	37.6 ± 1.1	1.5 ± 0.1	3.5 ± 0.1	38.3 ± 4.4
	15	0.24 ± 0.02	16.8 ± 0.2	0.25 ± 0.01	1.9 ± 0.1	38.6 ± 0.7	37.9 ± 1.8	1.5 ± 0.2	2.8 ± 1.0	43.9 ± 4.7
dehulled grains	0	0.25 ± 0.02	16.6 ± 0.3	0.30 ± 0.10	1.9 ± 0.4	37.4 ± 0.1	38.8 ± 0.2	1.5 ± 0.1	3.3 ± 0.0	50.7 ± 3.6
	15	e	16.3 ± 0.2	0.22 ± 0.01	1.6 ± 0.0	38.0 ± 0.7	38.1 ± 1.1	1.4 ± 0.1	4.0 ± 1.4	56.3 ± 5.6
hulls	0	6.0 ± 0.2	37.0 ± 1.3	1.0 ± 0.2	6.5 ± 1.5	7.7 ± 0.2	10.3 ± 0.5	5.1 ± 0.1	26.4 ± 0.4	0.514 ± 0.326
	15	5.2 ± 0.4	34.7 ± 0.9	2.0 ± 0.9	6.4 ± 1.8	8.4 ± 2.3	11.1 ± 1.5	5.4 ± 0.6	26.8 ± 0.7	0.582 ± 0.325

[a] Mean values are from two replicated determinations. [b] mg/g = mg of fatty acid/sample wt at 8–10% moisture content. [c] Includes 12:0, 18:1(n-7), and unidentified fatty acids. [d] Mean ± SD. [e] Not detected.

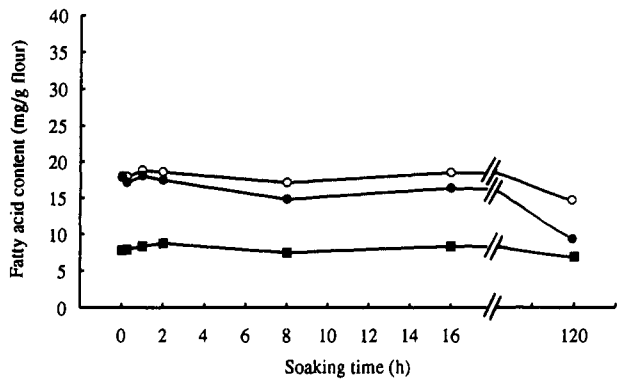

Figure 1. Effect of water soaking at 20 °C on absolute fatty acid content of hulled oat flour. (■) Palmitic acid; (○) oleic acid; (●) linoleic acid.

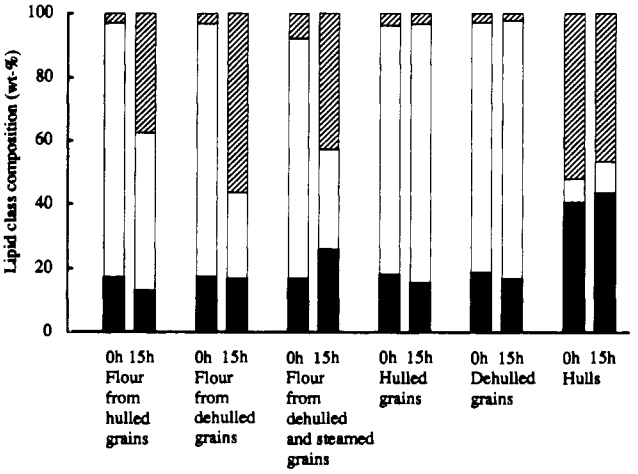

Figure 2. Lipid composition of different oat samples during 15-h soaking in water at 20 °C. (Slashed bar) Free fatty acids; (open bar) triglycerides; (black bar) polar lipids.

fatty acids in total lipids, major lipid classes, and the percentage fatty acid distributions in the major lipid classes.

Separation of Major Lipid Classes by TLC. The samples were redissolved in a small amount of chloroform–methanol (100:1 v/v) and supplemented with the PL, FFA, and TG standards, 50 μg each. Portions of the mixtures were applied on silica plates, and the plates were developed with petroleum ether–diethyl ether–acetic acid (80:30:1). Lipid classes were visualized after spraying 0.01% Rhodamine 6G under UV light, scraped off, and used for fatty acid determinations.

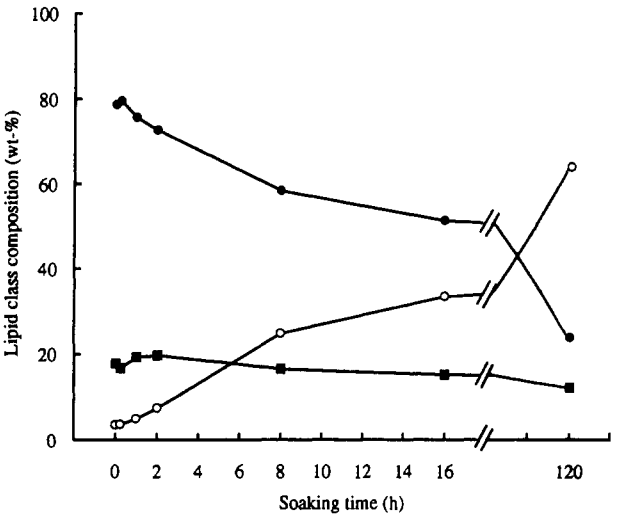

Figure 3. Lipid composition of hulled oat flour in water soaking at 20 °C. (○) Free fatty acids; (●) triglycerides; (■) polar lipids.

Preparation and Analysis of Fatty Acid Methyl Esters. Fatty acid methyl esters were prepared by saponification and methylation essentially as described by Suutari et al. (1990). The methyl esters were analyzed by GLC. The major fatty acids were identified by comparing their retention times with standard (Sigma). To determine the total amounts of different lipid classes, a mixture of PL, FFA, and TG standards was added prior to lipid class separation as described above. The extractable total fatty acids were determined by adding 30 μg of heptadecanoic acid methyl ester prior to saponification.

Gas Chromatography. A Hewlett-Packard Model 5890A gas chromatograph equipped with a flame ionization detector, a capillary inlet system, a HP-FFAP (25 m × 0.2 mm × 0.3 μm) column, and a Model 7673A high-speed automatic liquid sampler with a 10-μL syringe was employed. The column temperature was programmed from 70 to 200 °C at the rate of 25 °C/min. The injector and detector were maintained at 250 °C. The column inlet pressure was 150 kPa. The flow rate for the makeup gas was 30 mL/min He; the flow rates for the detector gases were 40 mL/min H_2 and 400 mL/min air. The column flow rate was 1.0 mL/min and the septum purge flow rate 1–2 mL/min. Split injection at a split ratio of 1:20 was employed. Peak areas were measured by using Hewlett-Packard Model 3365A integrator.

Calculations. The relative amounts of fatty acids in total lipids and in different lipid classes were determined as a percentage of total peak area. The absolute amounts of the individual fatty acids in total lipids were calculated per 1 g of sample by comparison of the peak areas to that of the methyl ester standard without using any conversion factors. The total

Table II. Lipid Compositions and Weight Distributions of Oat Fiber, Protein, and Starch Fractions

fraction[a]	lipid composition, wt % (lipid content, mg/g)[b] TG	PL	FFA	wt distribution,[c] %
fiber	78.5 ± 1.9[d] (66.2)	14.9 ± 1.1 (12.6)	6.6 ± 2.8 (5.7)	18.9 ± 0.7
protein	54.6 ± 9.0 (162.1)	15.0 ± 2.6 (44.6)	30.3 ± 11.6 (102.6)	28.9 ± 3.4
starch	56.7 ± 7.8 (15.8)	22.7 ± 3.2 (6.7)	20.6 ± 4.6 (6.1)	52.2 ± 4.1

[a] Wet fractionation was replicated two times. [b] mg/g = mg of lipid/sample dry wt. [c] Total recovery 88.4 ± 1.2% (dry wt basis). [d] Mean ± SD.

Table III. Fatty Acid Compositions and Contents of Oat Triglycerides

sample	soaking time, h	fatty acid composition,[a] % 16:0 ω	18:0 ω	18:1 n–9	18:2 n–6,9	18:3 n–6,9,12	others[c]	TG content,[a,b] mg/g
flour from hulled grains	0	15.7 ± 0.3[d]	1.0 ± 0.1	38.1 ± 1.8	40.7 ± 2.0	2.2 ± 0.3	2.4 ± 0.6	50.5 ± 1.3
	15	16.5 ± 0.6	1.2 ± 0.1	38.2 ± 0.9	39.7 ± 0.5	2.1 ± 0.3	2.3 ± 0.8	32.3 ± 6.3
flour from dehulled grains	0	15.7 ± 0.3	1.2 ± 0.0	38.1 ± 0.1	40.5 ± 0.7	2.1 ± 0.0	2.4 ± 0.9	62.7 ± 2.1
	15	17.4 ± 0.3	1.2 ± 0.0	37.0 ± 1.1	38.8 ± 2.0	2.8 ± 0.3	2.9 ± 0.9	19.1 ± 1.5
flour from dehulled and steamed grains	0	15.6 ± 0.5	1.1 ± 0.0	37.0 ± 1.1	42.0 ± 2.1	1.9 ± 0.1	2.4 ± 0.6	51.9 ± 2.3
	15	16.7 ± 1.3	1.2 ± 0.1	37.2 ± 0.2	38.7 ± 1.3	2.0 ± 0.4	4.2 ± 0.7	17.2 ± 2.0
hulled grains	0	15.6 ± 0.7	1.0 ± 0.0	38.8 ± 0.1	40.1 ± 1.0	2.0 ± 0.1	2.6 ± 0.2	43.3 ± 10.2
	15	15.6 ± 0.5	1.2 ± 0.1	37.6 ± 0.5	40.8 ± 0.1	2.0 ± 0.0	2.7 ± 0.0	50.3 ± 3.5
dehulled grains	0	15.9 ± 0.3	1.1 ± 0.0	37.9 ± 0.0	41.6 ± 0.3	2.1 ± 0.0	1.5 ± 0.0	56.2 ± 2.9
	15	15.7 ± 0.1	1.4 ± 0.4	39.2 ± 1.6	40.2 ± 1.6	1.8 ± 0.2	1.6 ± 0.3	60.2 ± 6.5
hulls	0	37.6 ± 0.1	10.8 ± 1.2	26.7 ± 0.3	11.7 ± 3.0	[e]	13.3 ± 2.0	0.038 ± 0.025
	15	30.4 ± 0.7	10.0 ± 3.5	24.8 ± 3.7	15.3 ± 6.1	3.8 ± 0.4	15.7 ± 5.9	0.058 ± 0.002

[a] Mean values are from two replicated determinations. [b] mg/g = mg of TG/sample wt at 8–10% moisture content. [c] Includes 12:0, 14:0, 16:1(n–7), 18:1(n–7), and unidentified fatty acids. [d] Mean ± SD. [e] Not detected.

Table IV. Fatty Acid Compositions and Contents of Oat Polar Lipids

sample	soaking time, h	fatty acid composition,[a] % 16:0 ω	18:0 ω	18:1 n–9	18:2 n–6,9	18:3 n–6,9,12	others[c]	PL content,[a,b] mg/g
flour from hulled grains	0	22.9 ± 0.7[d]	3.4 ± 1.0	21.9 ± 1.3	47.4 ± 0.3	2.6 ± 0.1	1.8 ± 0.7	11.0 ± 1.5
	15	25.6 ± 0.2	4.4 ± 1.8	24.6 ± 1.6	41.2 ± 0.7	2.2 ± 0.1	2.0 ± 0.4	8.5 ± 0.1
flour from dehulled grains	0	23.3 ± 0.0	3.0 ± 1.4	21.3 ± 0.9	48.0 ± 1.5	2.3 ± 0.1	2.1 ± 1.1	13.9 ± 0.6
	15	29.8 ± 1.4	3.4 ± 1.0	23.1 ± 0.4	39.7 ± 0.2	1.9 ± 0.3	2.2 ± 0.8	12.2 ± 0.9
flour from dehulled and steamed grains	0	23.0 ± 1.8	1.8 ± 0.2	20.8 ± 0.2	50.1 ± 1.8	2.2 ± 0.1	2.0 - 0.2	11.8 ± 0.0
	15	28.4 ± 0.7	2.3 ± 0.3	25.2 ± 1.3	40.3 ± 0.2	2.1 ± 0.2	1.7 ± 0.8	14.4 ± 0.9
hulled grains	0	24.9 ± 1.0	2.3 ± 0.9	21.2 ± 1.5	47.5 ± 0.4	2.1 ± 0.1	2.0 ± 0.9	10.0 ± 0.2
	15	25.1 ± 0.3	2.5 ± 0.3	21.6 ± 0.4	46.1 ± 0.2	2.4 ± 0.6	2.4 ± 0.6	9.7 ± 0.6
dehulled grains	0	24.2 ± 0.8	3.5 ± 2.4	20.7 ± 1.2	47.4 ± 1.5	2.2 ± 0.4	1.9 ± 0.6	13.5 ± 1.4
	15	24.9 ± 0.7	2.1 ± 0.8	19.9 ± 0.1	48.3 ± 0.8	2.4 ± 0.0	2.3 ± 0.8	12.7 ± 0.1
hulls	0	45.2 ± 2.9	4.8 ± 2.3	5.9 ± 0.4	15.1 ± 1.9	8.7 ± 2.5	20.2 ± 0.4	0.205 ± 0.002
	15	38.3 ± 2.8	4.6 ± 0.3	5.4 ± 0.7	15.4 ± 0.7	10.6 ± 0.3	25.8 ± 3.6	0.268 ± 0.085

[a] Mean values are from two replicated determinations. [b] mg/g = mg of PL/sample wt at 8–10% moisture content. [c] Includes 12:0, 14:0, 16:1(n–7), 18:1(n–7), and unidentified fatty acids. [d] Mean ± SD.

amount of fatty acids was a sum of all fatty acids. The amounts of major lipid classes per 1 g of sample were determined by comparing the area of the fatty acids from a lipid class to that of the corresponding standard. As an approximation, it was assumed that the polar lipids consist of phosphatidylcholine only. The percentage distribution of different lipid classes was determined as a percentage of total weights of lipid classes.

RESULTS AND DISCUSSION

Oat flour–water slurries were studied for time-dependent changes in the total fatty acids, lipid classes, and fatty acid compositions within the major lipid classes to identify initial lipid conversions. The data were compared with lipid changes occurring during fractionation of oat flour onto fiber, starch, and protein fractions in a wet fractionation process.

Effect on Total Fatty Acids. The major fatty acids of nonsoaked oat grains or the respective flour were palmitic, oleic, and linoleic acids (Table I). Myristic, palmitoleic, stearic, and linolenic acids occurred in lesser amounts. The percentage and absolute amounts of fatty acids were very similar to those reported by Youngs et al. (1982). The total fatty acids comprised 5–6% of the weight of dehulled oat or the respective flour at 8–10% moisture level. Hulls comprised about 22% of the weight of whole grains, and their fatty acid content was very low (0.05–0.06% by weight). So hulled grains or the respective flour contained slightly lower absolute amounts of fatty acids than dehulled grains or its respective flour. The percentage fatty acid composition of hulls also differed remarkably from those of whole grains or flour.

Figure 1 shows the effect of soaking time on the amount of fatty acids of oat flour prepared from hulled oat. The corresponding data on all of the samples after 15 h of soaking can be seen in Table I. In flour the relative proportion of linoleic acid decreased by less than 3 percentage points during the 15-h soaking, suggesting that only slight linoleic acid oxidation might have occurred in the beginning of the soaking. This is consistent with the

Table V. Fatty Acid Compositions and Contents of Oat-Free Fatty Acids

sample	soaking time, h	fatty acid composition,[a] % 16:0 ω	18:0 ω	18:1 n-9	18:2 n-6,9	18:3 n-6,9,12	others[c]	FFA content,[a,b] mg/g
flour from hulled grains	0	25.9 ± 0.2[d]	4.5 ± 0.6	26.3 ± 2.1	39.7 ± 2.9	e	3.7 ± 1.2	1.9 ± 0.1
	15	18.1 ± 1.2	1.2 ± 0.2	39.5 ± 0.1	37.0 ± 0.2	1.4 ± 0.3	2.8 ± 1.3	24.4 ± 2.1
flour from dehulled grains	0	25.3 ± 0.2	2.7 ± 0.0	28.5 ± 0.2	40.7 ± 1.9	e	2.9 ± 1.6	2.5 ± 0.4
	15	17.4 ± 0.6	1.1 ± 0.1	41.1 ± 1.1	36.3 ± 2.0	1.2 ± 0.1	2.9 ± 1.5	40.5 ± 5.9
flour from dehulled and steamed grains	0	18.3 ± 0.5	2.1 ± 0.6	31.8 ± 2.4	42.1 ± 1.8	2.3 ± 0.5	3.4 ± 0.1	5.4 ± 0.6
	15	14.6 ± 1.6	0.98 ± 0.01	39.9 ± 0.9	39.8 ± 1.5	1.4 ± 0.2	3.3 ± 0.7	23.6 ± 1.9
hulled grains	0	29.0 ± 1.2	3.3 ± 0.2	29.6 ± 2.0	36.6 ± 2.6	e	1.5 ± 0.8	2.0 ± 0.2
	15	28.0 ± 1.3	4.7 ± 1.6	28.6 ± 0.5	36.2 ± 4.6	e	2.5 ± 1.2	2.0 ± 0.1
dehulled grains	0	27.8 ± 1.9	3.4 ± 0.3	25.9 ± 1.8	39.2 ± 1.6	e	3.7 ± 1.8	2.0 ± 0.4
	15	29.7 ± 3.9	3.5 ± 0.0	25.4 ± 0.8	38.9 ± 1.6	e	2.6 ± 1.5	1.6 ± 0.2
hulls	0	58.6 ± 2.3	7.9 ± 0.2	8.2 ± 1.0	5.2 ± 0.2	1.6 ± 0.8	18.5 ± 2.9	0.268 ± 0.016
	15	60.2 ± 3.3	8.7 ± 1.1	9.1 ± 1.0	6.2 ± 2.1	1.6 ± 1.0	14.2 ± 0.4	0.280 ± 0.024

[a] Mean values are from two replicated determinations. [b] mg/g = mg of FFA/sample wt at 8–10% moisture content. [c] Includes 12:0, 14:0, 16:1(n-7), 18:1(n-7), and unidentified fatty acids. [d] Mean ± SD. [e] Not detected.

studies showing very low lipoxygenase activity in oats, about 10% of the activity of rye, wheat, or barley, and this low activity seems to result from inhibition by natural antioxidants (Pomeranz, 1974). However, during a prolonged soaking period (120 h) the amount of linoleic acid reduced remarkably concomitantly with a reduction of other fatty acids (Figure 1). During such a long soaking period deterioration of the water–flour slurry may also be associated with the development and growth of microflora.

When oats were wet-fractionated into fiber, protein, and starch, the lipids were carried into each fraction. Extractable total fatty acids comprised about 5%, 14%, and 1.4% of the dry weight of fiber, protein, and starch, respectively. Percentage fatty acid compositions in these fractions were very similar to that of oat flour or whole grains. Even though lipid changes did not appear during the soaking or fractionation in the analyses of total fatty acids, changes within the lipid classes may have occurred. Therefore, the corresponding samples were also analyzed with respect to soaking- and fractionation-induced changes in lipid class compositions.

Effect on Percentage Distribution of Major Lipid Classes. The TG fraction is the major lipid class in oats (Sahasrabudhe, 1979; de la Roche et al., 1977; Price and Parsons, 1975). According to present data on dry grains or flour TG represent 78–79% of total lipids (Figure 2). The proportions of PL and FFA varied between 17–19% and 2.9–3.7%, respectively. Other components, such as partial glycerides and sterols and steryl esters, were present only in small amounts. In dry flour prepared from industrially dehulled and subsequently wet heat-treated grains, the proportion of TG was already lower and that of FFA higher than in flour from untreated grains. So it seems that some TG hydrolysis occurred prior to soaking. The dehulling process resulted in visible mechanical damages to about 50% of the grains. So it cannot be ascertained how much of the hydrolysis occurred before, during, or after the wet heat treatment process. However, the destructive effect of dehulling or heating was selective; the percentage amount of PL in flour made from those heated grains was similar to those made from nonheated grains. The lipid class composition of hulls was markedly different from that of whole grains or the respective flours (Figure 2). FFA was a major fraction and PL and TG were minor fractions making up to 52%, 41%, and 7.3%, respectively.

Figure 3 shows the effect of soaking time on lipid hydrolysis of oat flour prepared from hulled grains. The first changes in lipid class distribution of water–flour slurry could be seen after 1 h when the amount of FFA increased as a result of TG hydrolysis. After 120 h, FFA comprised 64% of lipids and TG was decreased to 23%. The minor PL hydrolysis began later than TG hydrolysis, and during the 120-h soaking period the percentage of PL decreased from 18% to 12%. The corresponding data on all of the oat samples after 15 h of soaking can be seen in Figure 2. Flours from dehulled grains were more susceptible to TG hydrolysis than flours ground from hulled grains. After 15 h, TG comprised 27% and 49% of lipids in dehulled and hulled flour, respectively. In water–flour slurry of hulled grains the percentage of PL decreased from 17% to 13%, but in the respective slurry of dehulled grains it remained unchanged. The amounts of partial glycerides did not increase during the soaking, suggesting that all bonds of triglycerides were hydrolyzed. The amounts of sterols and steryl esters also remained unchanged. The results also indicate that at least mild heat treatments may not sufficiently inactivate TG-hydrolyzing enzymes. During the 15-h soaking the relative amount of TG in flour from wet heat-treated grains decreased from the initially low 75% to 31% while the relative amount of FFA increased from 7.9% to 43%. Therefore, more intensive heating to overcome the phenomenon may be required with possible consequences on natural antioxidants, oxidative rancidity (Pomeranz, 1971), and protein and starch quality (Yiu, 1986). It can be concluded that mechanical damage during dehulling in combination with wet heat treatment increases FFA levels in dry grains and makes them especially susceptible to further TG hydrolysis upon soaking in water.

According to Welch (1977) whole oats stored at low moisture levels and at normal temperatures show little lipid changes and there is no difference between hulled or dehulled undamaged grains. Our study indicated that even during a 15-h soaking period neither hulled nor dehulled whole grains changed significantly with respect to lipid class composition, although the grains swelled during soaking (Figure 2). The lipids of hulls also remained stable during soaking (Figure 2).

The percentage lipid distribution in dry fiber, starch, and protein fractions is presented in Table II. The fiber fraction was most resistant to hydrolysis, and its lipid class composition resembled that of nonsoaked oat flour. In protein and starch fractions the amounts of FFA were 30% and 21%, respectively, at the expense of TG. Starch and protein products comprised over 80% of the total lipids in dehulled oats. Therefore, the extent of hydrol-

ysis in these products indicates that the original lipid composition of oats was practically lost. The hydrolysis will probably be emphasized further in processes longer than the present laboratory-scale procedure.

Effect on Fatty Acid Composition of Major Lipid Classes. The fatty acid compositions of TG fractions in oat grains and in the corresponding flour (Table III) were rather similar to those of oat total lipids (Table I) because the TG fraction was the major lipid class. Table III shows that fatty acid composition of TG did not change very much during soaking of the flour even though substantial triglyceride hydrolysis occurred (Figure 2). This reflects either random distribution of fatty acids in TG or lack of positional specifity of hydrolysis. However, a closer evaluation of the data in Table III reveals a slight reduction in the proportion of linoleic acid in TG of soaked flour, especially soaked flour made from wet heat-treated grains. Whole grains were resistant to TG hydrolysis (Figure 2), and this was also shown by unchanged fatty acid composition during soaking (Table III).

The PL fractions of oat grains or the corresponding flour were rich in linoleic acid (about 47%). The relative amounts of palmitic and oleic acids were slightly over 20% each (Table IV). Even though the effect of soaking could not be seen in the total fatty acid compositions (Table I), the fatty acids of polar lipids of flour were changed. The relative amount of linoleic acid remarkably decreased, and palmitic and oleic acids correspondingly increased (Table IV), suggesting that the soaking induced a selective loss of esterified polyunsaturated fatty acids. Flours from hulled and dehulled grains behaved identically in this respect. In the flour made from wet heat-treated grains the proportion of acylated linoleic acid also decreased and those of palmitic and oleic acids correspondingly increased during soaking (Table IV) even though PL hydrolysis was not seen on the basis of lipid class distribution (Figure 2). These observations indicate that mild heat treatments are of minor contribution in the prevention of lipid changes as a whole. In whole grains percentage distribution of fatty acids in PL did not change during soaking (Table IV).

In the FFA fractions of nonsoaked grains and the corresponding flour linoleic acid constituted about 40% (37–41%) of total and palmitic and oleic acids about 27% (25–30%) each (Table V). Figure 2 showed that soaking of the flour increased strongly the amount of FFA. As a consequence, the percentage amounts of linoleic and palmitic acids in FFA decreased and that of oleic acid increased (Table V). After soaking of the flour for 15 h, the fatty acid distribution among the FFA was very similar to that of total lipids and TG, suggesting that hydrolysis but not oxidation of fatty acids is a primary response to soaking. Again, the whole grains proved stable during the soaking period when evaluated on the basis of fatty acids. The composition of the FFA in hulls differed remarkably from those of flour or whole grains and was unaffected by the soaking procedure (Table V).

When fatty acid compositions of TG, PL, and FFA were determined separately in fiber, protein, and starch fractions, it appeared that they resembled those obtained in nonsoaked or soaked oat flour depending on the extent of lipid hydrolysis.

The present study establishes that water soaking of oat flour induces hydrolysis of lipids and that the phenomenon is emphasized in oat wet fractionation probably because of the strong homogenizations included. So the prevention of FFA formation should be a primary goal in the preparation of good quality oat products in wet processes. This work is in progress in our laboratory.

ABBREVIATIONS USED

GLC, gas–liquid chromatography; TLC, thin-layer chromatography; TG, triglycerides; PL, polar lipids; FFA, free fatty acids. Fatty acids are denoted by the number of carbon atoms followed after colon by the number of double bonds.

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