Effects of Storage and Heat Processing on the Content and Composition of Free Fatty Acids in Oats

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ABSTRACT

The effects of storage and heat processing on the content and composition of free fatty acids (FFA) in oats (*Avena sativa* L.) have been studied. Samples of three cultivars (Kapp, Mustang, and Svea) were stored at 30, 55, and 80% rh for 3.5 and 15.5 months before heat processing of hulled and dehulled grains. Results from gas chromatographic analysis of individual FFA were closely correlated ($r = 0.962$) with measurements of acidity by titration of ethanol extracts. No significant differences in acidity were detected among the cultivars studied. After 3.5 months, the FFA content in the cultivar Kapp was 3.5 and 6.6 mg/g of dry matter when stored at 30 and 80% rh, respectively. After 15.5 months, FFA content increased to 5.4 and 11.3 mg/g of dry matter when stored at 30 and 80% rh, respectively. Measurement of acidity by titration was less specific and resulted in smaller relative differences. During processing, the FFA content and fat acidity was reduced by an average of 50%. This reduction in FFA is probably due to complexing of fatty acids, while the relative reduction in linolenic acid during storage and processing is related to an increasing content of volatile oxidation products, of which hexanal is an indicator. The total lipid content of oats did not change significantly during processing. After 15.5 months of storage, the lipid content was lower at 80% rh than at 30% rh; the content of ether-extractable lipids was 0.77 percentage points lower, while the content of total fatty acids was 0.43 percentage points lower. No such differences were detected by ether extraction after acid hydrolysis.

Lipids and lipid-associated components are key factors in the quality of oats and oat products. This is due to a relatively high lipid content, a large proportion of unsaturated fatty acids, and a significantly more active lipase than that of either barley or wheat (O'Connor et al 1992). Oats contain antioxidants, and oat lipids are stable in mature, undamaged grains (Welch 1977) and in sufficiently heat-treated oat products (Galliard 1989). Under unfavorable storage conditions, or in untreated oat products, however, lipolytic activity will cause rapid release of free fatty acids (FFA), which may then be oxidized and cause rancidity. Oxidative rancidity may also be caused by overprocessing (Martin 1958). Thus, adequate storage conditions (Frey and Hammond 1975) and appropriate heat treatment for inactivation of lipolytic enzymes before milling of oats (Galliard 1989) are essential in achieving stable oat products.

Because unsaturated FFA in oats are susceptible to oxidation and may form components with undesirable aroma and taste (Galliard 1989), analysis of the amount of FFA may be useful in the prediction of lipid stability in oats. For oats to be processed into food products, a maximum FFA level of 5% of hexane-extractable lipids has been suggested (Galliard 1983). FFA in oats enhance formation of bitter compounds (Pomeranz 1974), while FFA in suspensions of wheat bran have been closely related to O_2 uptake (Galliard 1986) and intensity of off-flavor (Galliard and Gallagher 1988). Ekstrand et al (1993), however, did not find the level of FFA in oats to be directly related to lipase activity or content of volatile oxidation products.

Generally, the concentration of FFA in cereal grains increases with increasing moisture content and storage time (Clayton and Morrison 1972, Schweizer et al 1974, Frey and Hammond 1975, Welch 1977, Sahasrabudhe 1979, Galliard 1989). The critical moisture content for storage is 14.5–15% (w/w) for most cereals, whereas for oats it is 13.5–14% (Kazakov et al 1972). Above this level, lipases and other degradative enzymes exhibit a sharp increase in activity. As oats are commonly stored for more than a year at ambient temperatures and at moisture contents close to or above the critical level, more knowledge about the effects of storage conditions used in commercial mills on the stability of lipids and FFA content is needed.

A typical commercial heat-processing method for oats in Europe includes steam stabilization, which inactivates most of the enzymes, followed by kiln-drying, which contributes mainly to flavor development. The oats may be dehulled before or after heat processing (Kent and Evers 1994). The choice of procedure, including the time of dehulling, affects the intensity of the heat process and thereby the quality of the oat products. Processing is reported to have various effects on the content of FFA in cereals. Schweizer et al (1974) found reduction of FFA during roller-drying of wheat, while Liukkonen et al (1992) reported increase in FFA during wet heat-treatment of oats. Commercial processing of oats is not found to significantly change the FFA levels (Oomah 1987, Ekstrand et al 1993).

The aim of this study was to investigate the effects of storage time, moisture content during storage, and heat treatment procedure on the content and composition of FFA in three cultivars of oats. Comparison with analyses of acidity, total fatty acid composition, and lipid content was performed as part of our study, as well as analysis of lipid oxidation products.

MATERIALS AND METHODS

Oat Samples

Three different cultivars of oats: Kapp, Mustang, and Svea, grown in 1990 at the research station of Apelsvoll, Norway, were used. After harvesting, the oat samples were stored at ambient conditions for about one month before the experiment started. When the storage study was initiated, the moisture contents were 11.4, 11.3, and 11.0% for Kapp, Mustang, and Svea, respectively. During the experiment, 5-kg batches of oat grains were stored in nylon nets in rooms at 30, 55, and 80% rh. Processing and analyses were performed after 3.5 and 15.5 months of storage. The temperature during storage was 20°C for the first 8 months and 15°C for the last 7.5 months.

Processing

A pilot process was developed to simulate typical commercial processes in Norway. The oats were subjected to processing either directly (with hulls) or after dehulling (as groats), as indicated in Figure 1.

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Heat processing. The oats were soaked in water for 2 min before heating. The drained samples were spread out on perforated plates and stabilized by steaming in a baking oven (100°C, 10 min; Sveba US 2 H, Sweden). Drying was performed on smaller plates with the oats wrapped in lined paper bags. The hulled and dehulled samples were dried at 100°C for 4 and 3.5 hr, respectively.

Dehulling. Batches of 100-g samples were dehulled in about 1 min by a laboratory oat dehulling machine (Streckel & Schrader K.G., Hamburg, Germany), operating at 8 atm. Remaining hulls were removed by hand. Dehulled samples were stored under nitrogen at −20°C until analysis. Milling was performed on a Retsch Ultra centrifugal mill, 0.5-mm screen (Kurt Retsch GmbH & Co, Haan, Germany).

Lipid Analyses

Ether-extractable lipids. The content of diethylether extractable lipids was determined by Soxtec extraction (Soxtec System HT 1043/1046, Tecator AB, Höganäs, Sweden), with 15 min of boiling and 30 min of rinsing (Tecator AN 301, ASN 3414).

Ether-extractable lipids after acid hydrolysis. Acid hydrolysis was performed by heating 3 g of flour in 50 ml of 3*M* HCl in a boiling water bath for 1 hr before filtration (Schleiche & Shüll White Ribbon filters, no. 589[2]). The residue was rinsed with distilled water (pH 4–6), dried, and extracted with diethylether as described above.

Gas chromatographic analysis of fatty acids. Lipids from 0.3 g of flour were extracted with 6 ml of chloroform, methanol, and water-saturated *n*-butanol (C-M-WSB; 3:2:1, v/v) for 3 hr. Trinonadecanoin (0.5 mg/ml of extract) was used as an internal standard. The lipids were transesterified overnight at room temperature by a mixture of benzene, methanolic HCl, and 2,2-dimethoxypropane (1:1:0.2, v/v). The methylated fatty acids were extracted with hexane and analyzed on a Hewlett-Packard gas chromatograph (5890 series II; Cheadle Heath, UK) equipped with flame-ionization detector and capillary column (J&W DB-23; 30 m × 0.25 mm i.d., 0.25 μm film). The column temperature was programmed from 50 to 160°C (20°C/min) and up to 220°C (3°C/min), keeping the initial and final temperatures for 5 min.

Fat Acidity

The acidity of ethanol extracts from oats, containing mostly FFA, was determined by a modified titration method (ISO 1986), expressing the results as milligrams of KOH/100 g of dry matter. The modification included use of automatic endpoint titration to pH 9.0, using a reference electrode instead of phenolphthalein as an indicator.

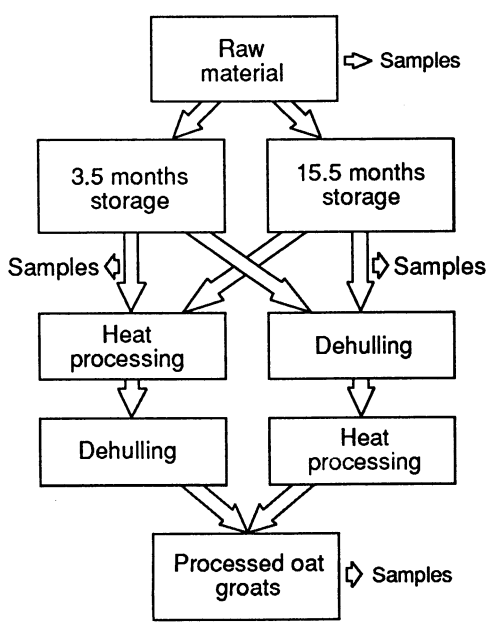

Fig. 1. Storage and processing of oat samples.

FFA

The FFA in 5 g of flour were extracted with 20 ml of 96% ethanol for 1 hr before centrifugation, concentration, and separation from other lipids by thin-layer chromatography (TLC). Trinonadecanoin (0.25 mg/ml of extract) was used as an internal standard. TLC was performed on DC-Fertigfolien F 1500 (Schleiche & Schüll), with a solvent system consisting of petroleum ether (bp 40–60°C), diethylether, and acetic acid (113:20:1, v/v). Staining was performed by spraying with 0.1% dichlorofluorescein. The area of the plate containing FFA was scraped off and the FFA was extracted into methanol. After evaporation of the solvent with N_2, the FFA were dissolved in toluene, methylated with HCl-methanol, and analyzed by gas chromatography (GC) as described for analysis of fatty acids in total lipids.

Volatile Lipid Oxidation Compounds

Volatile lipid oxidation compounds were detected by static head-space analysis using a gas chromatography-mass spectroscopy system with cryocooling (Hewlett-Packard 5890/5970; Cheadle Heath, UK). Sample preparation included heating 3 g of freshly milled groats in Teflon-sealed ampules to 100°C. Toluene was used as an internal standard. After incubation for 1 hr, a gas-tight syringe was used to inject 2 ml of head-space gas splitless in the CO_2 cold trap. The cold trap was turned off after 1 min, as the temperature program started. The temperature program was 2–220°C, increasing by 10°C/min and keeping the initial and final temperatures for 5 min. The injector temperature was 120°C. A nonpolar capillary column (J&W DB-5MS; 30 m × 0.25 mm i.d., 1 μm film) was used, with He as carrier gas. The results are expressed relative to the amount of toluene in the head-space gas, adjusted for the moisture content as: (area of hexanal × 100)/area of toluene.

Moisture Content

The moisture content was determined using a Sartorius Thermo Control infrared dryer, where the temperature was maintained at 130°C until a stable weight was achieved.

Statistical Analysis

Statistical analyses were performed using the Statistical Analysis System (version 6.04) (SAS Institute, Cary, NC). For ANOVA and Tukey's test, differences between samples are reported to be significant when $P < 0.05$.

RESULTS

Moisture Content

The moisture content in the oat samples was influenced by both storage and processing conditions (Table I). During storage

TABLE I
Moisture Content (%) in Unprocessed and Processed Oat Samples After Storage at Relative Humidities of 30, 50, and 80% for 3.5 and 15.5 Months[a,b]

	Months of Storage	
Processing Conditions	**3.5**	**15.5**
Unprocessed		
30% rh	9.3 d	9.3 e
55% rh	12.5 b	12.3 b
80% rh	14.8 a	14.6 a
Processed with hulls		
30% rh	10.6 c	11.0 cd
55% rh	9.2 d	10.2 de
80% rh	9.4 d	11.7 bc
Processed without hulls		
30% rh	8.4 de	6.8 fg
55% rh	8.1 e	6.2 g
80% rh	9.2 d	7.4 f

[a]Moisture content was 11.2% before storage.
[b]Results are based on two replicates and three cultivars. Values within one storage period sharing the same letter are not significantly different ($P < 0.05$).

at 30, 55, and 80% rh, the moisture content of unprocessed oats equilibrated from an average of 11.2% to 9.3, 12.4, and 14.7%, respectively. Heat treatment of samples without hulls resulted in lower moisture content than that of heat treatment of samples with hulls, especially after 15.5 months. The moisture content in the raw material had no influence on the moisture content in the processed oats.

Lipid Content

The lipid content from ether extraction, with and without acid hydrolysis, was determined in samples stored at 30 and 80% rh for 15.5 months. No significant changes in lipid content were found during heat processing by either of the methods. Results are presented as means of processing conditions (Fig. 2). The lipid content in Kapp was significantly higher than those of Svea and Mustang. The total lipid content, analyzed by ether-extraction after acid hydrolysis, was 10.1, 8.8, and 9.0% (mean values) for the three cultivars (Kapp, Mustang, and Svea, respectively); lipid content from ether extraction alone was 8.6, 7.6, and 7.9%, respectively. No differences in total lipid content (using ether-extraction after acid hydrolysis) were found among storage conditions. The lipid content after ether extraction alone was 0.7–0.9% (mean value 0.77%) lower for samples stored at the highest moisture level.

Fat Acidity

Only minor differences in fat acidity were found among the three oat cultivars. Table II presents the fat acidity, measured by titration, as means for the three oat cultivars. Fat acidity increased significantly with increasing relative humidity and increasing storage time for all processes. In unprocessed samples, the difference between the highest and lowest relative humidity increased from 20.2 mg of KOH/100 g of dry matter (45.7–65.9) after 3.5 months of storage to 34.4 (52.9–87.3) after 15.5 months of storage. One year of storage increased the acidity by 7.2, 15.2, and 21.4 mg of KOH/100 g of dry matter for the storage conditions 30, 55, and 80% rh, respectively. Heat processing decreased the fat acidity significantly. The reduction was an average of 40% for oats processed with hulls and 45% for oats processed without hulls. The average fat acidity after 3.5 months was lower for oats processed without hulls, while no significant differences were found among heat processes after storage for 15.5 months.

Total Fatty Acids and FFA

The influence of storage and heat treatment on individual and total FFA in the cultivar Kapp was measured by TLC-GC (Table III). The amount of total FFA increased with increasing relative humidity and time of storage and decreased during heat processing. The mean reduction in total FFA during processing was greater in samples processed with hulls (61%) than samples processed without hulls (52%). The FFA contained 42–52% linoleic acid, 27–32% oleic acid, 17–21% palmitic acid, and small amounts (1–3%) of stearic and linolenic acids. Linear relationships were found between the individual FFAs and the total FFA content ($r > 0.946$) (Table III). Linolenic acid (C18:3) showed the lowest correlation with total FFA, due to a lower level in processed samples than in unprocessed samples (Fig. 3).

Table III also compares the composition of the FFA with the fatty acid composition of total lipids in unprocessed Kapp after 15.5 months of storage. Fatty acid composition in total lipids was little influenced by storage conditions, and the results are presented as means of storage conditions. FFA contained greater amounts of linoleic, palmitic, and linolenic acids (means of 9.4, 4.0, and 1.0%, respectively) than did the total lipids, whereas the percentage of oleic acid was about 12% lower.

A linear relationship was found between FFA content, determined by TLC-GC, and fat acidity, determined by titration of ethanol extracts ($r = 0.962$; $P < 0.001$) (Fig. 4).

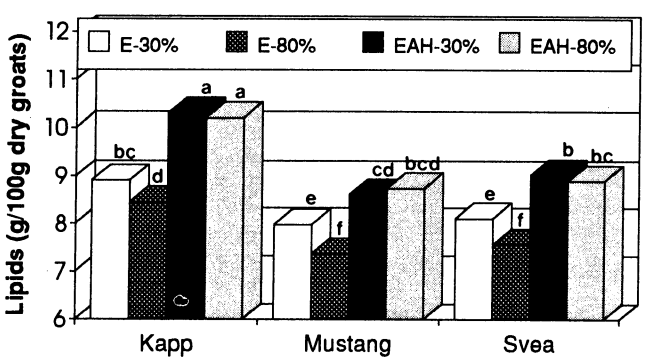

Fig. 2. Lipid content in oats stored for 15.5 months. Effects of cultivar, storage condition (30 and 80% rh) and extraction procedure (E = ether-extractable lipids, EAH = E after acid hydrolysis). Results are means of duplicate samples and three processes. Values sharing the same letter are not significantly different ($P < 0.05$).

Volatile Lipid Oxidation Products

Hexanal, the major volatile lipid oxidation product with the greatest changes during storage and processing, was used as an indicator of the total content of oxidation products. The concentration of hexanal in samples of the cultivar Kapp (Fig. 5) increased during storage, parallel with the increasing levels of FFA (Table III). In contrast to the changes in FFA, processing increased the hexanal levels by ~3× for samples with hulls and ~4× for samples without hulls. Both unprocessed and processed oats, stored at 80% rh for 15.5 months had ~2× the concentration of hexanal as compared to the oats stored at 30% rh.

DISCUSSION

Oat cultivars with large grains and a low hull content are usually most desirable for human consumption. In Norway, the cultivar Mustang is often preferred for industrial processing because of its large grains. Kapp had the highest lipids content (Fig. 2), which is especially important for use in animal feed. For human consumption, however, the lipid composition, and thereby its susceptibility to degradation, is more important than the lipid content.

Oat lipids contain about 80% unsaturated fatty acids, which may be liberated through lipolytic activity. Due to the susceptibility of unsaturated FFA to subsequent oxidative reactions, the amount of FFA, or fat acidity, which is mostly caused by FFA, are commonly used as quality parameters in oats (Pomeranz 1971).

For the Kapp cultivar, fat acidity, determined by titration of ethanol extracts (Table II), and FFA content, determined by TLC-GC, (Table III) were highly correlated ($r = 0.962$; $P < 0.001$) (Fig. 4). Thus, in this study, fat acidity could be used to estimate the FFA content. However, the percentage change in FFA was

TABLE II
Fat Acidity in Processed and Unprocessed Oat Groats After Storage at Relative Humidities of 30, 50, and 80% for 3.5 and 15.5 Months[a,b]

	Months of Storage	
Processing Conditions	**3.5**	**15.5**
Unprocessed		
30% rh	45.7 c	52.9 c
55% rh	54.0 b	69.2 b
80% rh	65.9 a	87.3 a
Processed with hulls		
30% rh	27.6 fg	32.7 e
55% rh	30.7 ef	43.0 d
80% rh	38.8 d	53.2 c
Processed without hulls		
30% rh	22.0 h	29.4 e
55% rh	25.8 gh	40.6 d
80% rh	32.7 e	57.0 c

[a] Results expressed as mg of KOH/100 g of dry groats.
[b] Results are based on two replicates and three cultivars. Values within one storage period sharing the same letter are not significantly different ($P < 0.05$).

larger when measured by TLC-GC than when measured by titration. This is due to the contribution of ethanol-soluble acids other than FFA. A fat acidity of about 20 mg of KOH/100 g of dry matter, as found by extrapolation, would be detected in samples without FFA. This is important to consider when interpreting the results from fat acidity titrations.

Only minor differences in fat acidity were found between the different cultivars in our study. This is consistent with results from previous studies, where the effect of cultivar was reported to be less important for FFA content than the environmental effects and the postharvest treatment (Hutchinson and Martin 1955, Youngs et al 1977). The constant level of FFA, expressed

TABLE III
Content of Individual and Total Fatty Acids in Lipids[a] and Free Fatty Acids[b] (FFA) in Groats of the Cultivar Kapp

Processing Conditions	Individual Fatty Acids (% of total fatty acids)						Total Fatty Acids (mg/g of dry matter)
	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Others	
Total lipids (15.5 months of storage)							
Unprocessed	15.6 (0.1)	1.4 (<0.1)	42.3 (0.4)	38.1 (0.3)	1.3 (<0.1)	1.3 (0.0)	73.9 (0.4)
FFA (3.5 months of storage)							
Unprocessed							
30% rh	19.4	1.5	30.4	45.0	2.8	0.9	3.5
50% rh	17.8	1.3	30.9	45.8	3.1	1.1	5.0
80% rh	17.6	1.2	28.5	49.0	2.7	1.0	6.6
Processed with hulls							
30% rh	19.1	2.1	29.7	47.2	2.0	0	1.3
50% rh	19.0	2.0	29.4	48.0	1.7	0	1.6
80% rh	16.8	1.5	27.1	52.3	1.9	0.4	2.6
Processed without hulls							
30% rh	20.1	2.0	30.9	45.5	1.6	0	1.5
50% rh	19.8	1.9	32.0	44.8	1.6	0	2.0
80% rh	17.6	1.5	29.8	48.5	1.8	0.9	3.2
FFA (15.5 months of storage)							
Unprocessed							
30% rh	20.4	1.4	31.8	43.0	2.4	1.1	5.4
50% rh	20.4	1.4	30.6	44.1	2.5	1.0	6.9
80% rh	18.0	1.1	28.3	49.3	2.2	0.9	11.3
Processed with hulls							
30% rh	20.3	1.9	32.2	44.4	1.4	0	2.0
50% rh	19.0	1.7	31.6	45.5	1.4	0.8	3.3
80% rh	15.9	1.3	28.0	51.9	1.7	1.2	5.0
Processed without hulls							
30% rh	20.9	1.8	32.5	42.6	1.3	0.9	2.7
50% rh	20.6	1.8	30.5	45.0	1.4	0.8	3.3
80% rh	17.3	1.4	29.7	49.5	1.5	0.7	6.7
Correlation coefficient between FFA and total FFA[c]	0.990	0.983	0.996	0.995	0.946	0.963	

[a]Extraction solvent chloroform, methanol, and water-saturated *n*-butanol (3:2:1, v/v). Results are means of 30% rh and 80% rh with two replicates. Standard deviation in parenthesis.
[b]Extraction solvent 96% ethanol. Results are means of two replicates.
[c]Correlations are based on mg/g of dry matter of individual and total FFA.

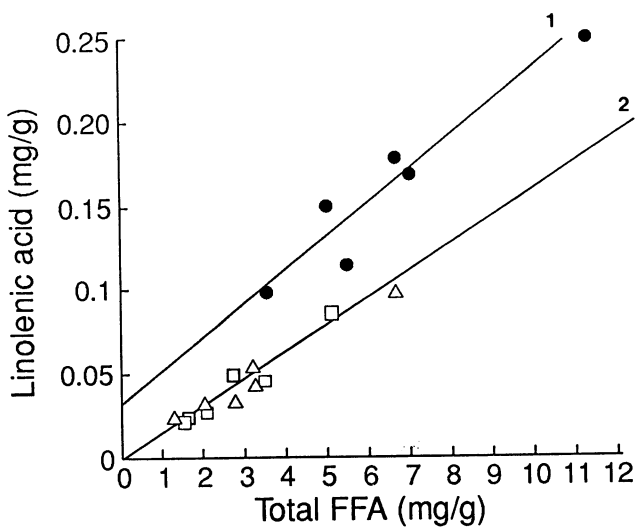

Fig. 3. Relationship between changes in total free fatty acids (FFA) and free linolenic acid (C18:3). Linear regression lines: 1, unprocessed samples (●) ($r = 0.971$, $y = 0.032 + 0.020x$); 2, samples processed with (□) and without hulls (△) ($r = 0.974$, $y = -0.001 + 0.016x$).

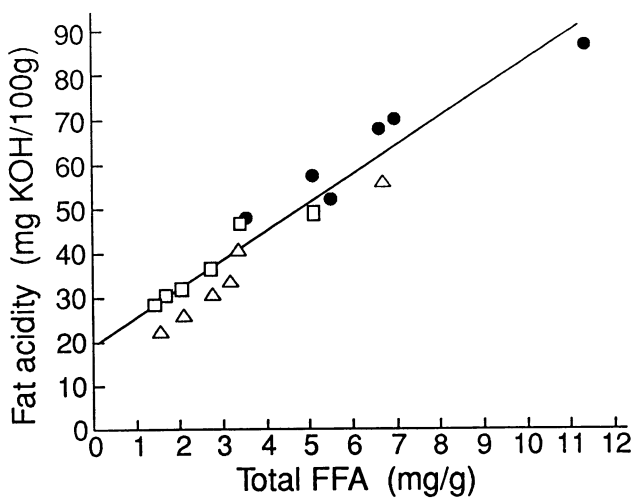

Fig. 4. Linear regression between results from analysis of fat acidity and total free fatty acids (FFA) by gas chromatographic analysis ($r = 0.962$, $y = 19.05 + 6.52x$). Unprocessed samples (●), samples processed with hulls (□), and samples processed without hulls (△).

as fat acidity, in oat cultivars with different lipid contents, is in agreement with results reported by Hutchinson and Martin (1955). The results are in contrast to results of Sahasrabudhe (1979) and de la Roche (1977), who found greater proportions of FFA (wt% of dry groat) in high lipid oats. In the present study, fat acidity (Table II) and FFA (Table III) increased significantly with increasing moisture content during storage and increasing time of storage. This is in agreement with previously reported results for FFA in oats (Frey and Hammond 1975, Welch 1977, Sahasrabudhe 1979) and wheat (Clayton and Morrison 1972, Schweizer et al 1974, Galliard 1989). Only minor increases in fat acidity with storage were found in this study for the lowest relative humidity level (9.3% moisture content). This is in accordance with earlier results reported for FFA content in undamaged kernels (Frey and Hammond 1975, Welch 1977). For broken kernels, however, lipase activity has been detected even at moisture contents below 7.5% (Frey and Hammond 1975).

Increase in the total amount of FFA during storage might be attributed to activities of lipases as well as lipolytic acyl-hydrolases, present in flour and mold (Morrison 1978). The critical level of relative humidity for growth of storage fungi is about 75% rh (Pomeranz 1971). Storage stability is also affected by temperature, and safe storage life of grains at 15°C is ~2× the safe storage life at 20°C (Bailey 1971). Thus, the possibility of mold growth cannot be excluded in the samples of the present study, which were stored at 80% rh and 20°C. The decrease in temperature from 20 to 15°C after 8 months of this experiment, decreased the risk of mold infestation and may also have resulted in somewhat lower rates of lipid degradation, particularly after 15.5 months at 80% rh. As the change in temperature was performed on all samples, and the content of FFA was within the expected level caused by the actual moisture contents, the temperature effect in this experiment is considered to be minor.

Heat processing, with sufficient inactivation of lipolytic enzymes, is necessary to prevent development of rancidity in milled oats. Activity of peroxidase, the most thermostable degradative enzyme, has been suggested as the best index for an effective heat treatment (Pomeranz 1974). For all heat-processed samples in the present study, low levels of peroxidase activity were determined (results not shown), indicating a sufficient inactivation of the enzymes during processing.

During heat processing, the mean reductions in the levels of fat acidity (Table II) and FFA (Table III) in Kapp were 43 and 56%, respectively, after averaging processes and storage periods. Although the two methods were highly correlated ($r = 0.962$), some systematic differences were found among heat processes; samples processed without hulls generally had lower acidity levels than those of the samples processed with hulls (Fig. 4). FFA levels were lower in the oats processed with hulls. This difference was probably caused by the nonspecificity of the fat acidity method, as ethanol may extract acids other than fatty acids. During the two processes, the level of these acids and the FFA may be affected differently. The more direct heat transfer and a lower moisture content in samples processed without hulls probably contributed to a greater reduction in the acidity caused by acids other than FFA. We are unable to explain the exception for samples stored at 80% rh for 15.5 months.

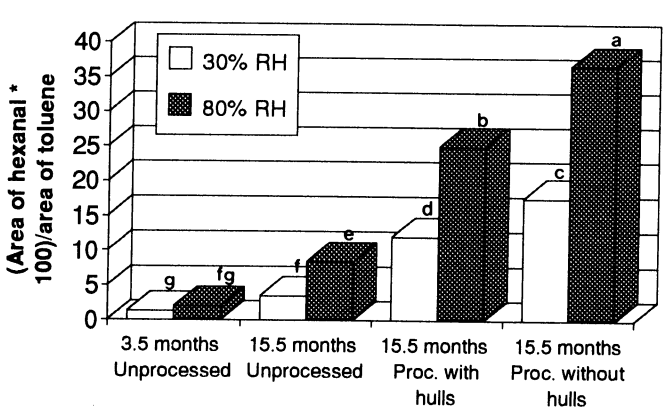

Fig. 5. Development of hexanal during storage and processing of the cultivar Kapp.

The general reduction of FFA during heat processing is in accordance with results from roller-drying of wheat in excess water (Schweizer et al 1974). In processing oats using both dry heat and steam, however, an increase in FFA was observed during dry heat treatment, followed by a fairly small decrease during steam preparation and drying (Ekstrand et al 1993). In the present process, an increased level of FFA may have been prevented by quick inactivation of the lipolytic activity in the grains.

It has been suggested that oxidation of linoleic and linolenic acid can explain decreases in FFA during processing (Schweizer et al 1974, Lilja and Lingnert 1989). In the present study, however, all individual FFA changed at approximately the same rate as the total FFA during storage and processing for the cultivar Kapp ($r > 0.946$) (Table III). This is consistent with the results of Clayton and Morrison (1972) and indicates that the composition of FFA is affected by storage and processing only to a minor degree. Some oxidation of free linolenic acid is likely to have occurred, however, as the content of this fatty acid decreased during storage and processing and had the lowest correlation to total FFA. The low levels of free linolenic acid and small changes of free linoleic acid, makes oxidation an unlikely explanation to the major losses of FFA (Table III and Fig. 3). In our study, the main loss of FFA during heat processing is most likely caused by complexing with starch or proteins. Complexes between FFA and amylose were reported by Goering et al (1975) in studies with barley starches in an amylograph. Binding of other lipids may also occur during processing, as indicated by reduced extractability of lipids by nonpolar solvents in wheat, pasta, and bread (Barnes et al 1981, Addo and Pomeranz 1991, Clawson and Taylor 1993). In our study, however, the lipid content after ether extraction, with and without acid hydrolysis, remained fairly constant during heat processing. Thus, evidence for heat-induced lipid binding was found for FFA but not for other lipids.

Even though lipid oxidation may not explain the major reductions in FFA during processing, some oxidative degradation of the unsaturated fatty acids did take place during both storage and processing. This was expressed by increasing levels of hexanal, which is a major volatile compound in oats (Heydanek and McGorrin 1981) that is commonly used as an indicator for lipid oxidation (Heydanek and McGorrin 1981, Lilja and Lingnert 1989, Ekstrand et al 1993). The effect of moisture content on the content of hexanal was clearly demonstrated in this experiment. The moderate variations in storage and processing conditions affected not only FFA levels, but also, to a great extent, the oxidative degradation of the processed oats (Fig. 5). During storage of unprocessed oats, the content of both FFA and hexanal increased with time and increasing moisture content. However, no relationship between the development of volatile oxidation products and FFA content was found across the heat processes.

The methods used for extraction of lipids in our study were ether extraction and ether-extraction after acid hydrolysis. Acid hydrolysis increased the yield of ether-extractable lipids from an average of 8.1 to 9.3%, for the three cultivars (Fig. 2). This is in agreement with results reported by Hutchinson and Martin (1955). Hydrolysis liberates lipids associated with cereal starches (Morrison 1988).

The qualitative liberation of FFA during storage was studied by GC analysis of FFA and fatty acids in total lipids (Table III). The FFA fraction contained relatively more palmitic, linoleic, and linolenic acid than the total fatty acid fraction, while the level of oleic acid was lower. Fatty acid in total lipids was extracted by C/M/WSB, while FFA was extracted by ethanol. This difference in extraction procedures may have caused some differences, but it was not expected to cause the major differences found in this experiment. Oleic acid is less susceptible to oxidation than are linoleic and linolenic acid, and the low level of oleic acid is most probably not due to greater degradation of oleic acid after hydrolysis. Specific hydrolysis of linoleic acid, palmitic, and

linolenic acid, is therefore a more likely explanation. In vitro studies by O'Connor (1992) indicated no such obvious substrate specificity for oat lipase. The results could, however, be explained by specific hydrolysis of polar lipids, which are found to be particularly rich in linoleic acid (Liukkonen et al 1992), or by activity of mold lipases with substrate specificity. Greater losses of esterified polar lipids, compared with triglycerides, have been demonstrated during storage of wheat in a number of studies (Daftary and Pomeranz 1965, Clayton and Morrison 1972, Schweizer et al 1974). A loss in the relative amount of esterified linoleic acid is also found during water soaking of oat flour (Liukkonen et al 1992).

Storage of wheat has been found to cause losses both in WSB-extractable lipids (Clayton and Morrison 1972, Schweizer et al 1974) and ether extractable lipids (Daftary and Pomeranz 1965). In our study, the reduction in ether and C/M/WSB-extractable lipids was affected by the relative humidity during storage, as the content of extractable lipids was lower at 80% rh than 30% rh. Due to low extractability of polar lipids in ether, the changes must be partly caused by the nonpolar fraction, in addition to the polar fraction as indicated above. No reduction in extractable lipids was found by the acid hydrolysis method. This is in accordance with results obtained by acid hydrolysis of stored wheat (Clayton and Morrison 1972) and indicates that respiration or oxidation is probably not the main reason for the loss in ethanol and C/M/WSB-extractable lipids during storage. The reduction in extractable fatty acids may be due to lipid binding, while the greater reduction in ether-extractable material during storage may also be due to loss of water-soluble parts of lipid molecules during hydrolysis, as suggested by Clayton and Morrison (1972).

CONCLUSIONS

Low FFA content in unprocessed oats is useful in minimizing development of rancidity in oat products. The results from the present study showed that the FFA content increased with increasing moisture content and time of storage, but decreased during processing. The close relationship between the levels of individual FFA during both storage and processing indicated complexing of fatty acids rather than oxidation. Some oxidative degradation of unsaturated fatty acids did, however, take place during storage and processing, as indicated by increasing levels of hexanal. The content of fatty acids, as analyzed by TLC-GC, was closely related to the acidity of an ethanol extract, as analyzed by titration. Titration is less specific and includes acids other than FFA.

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