

Starch Lipids of Barley and Malt

A. KAUKOVIRTA-NORJA,^{1,2} P. REINIKAINEN,³ J. OLKKU,³ and S. LAAKSO¹

ABSTRACT

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Barley and malt starches were compared with respect to their lipid content and composition. The starch lipids were first fractionated into internal and surface lipid fractions followed by lipid class and fatty acid analyses of each fraction. Barley starch contained 13 mg/g lipids, of which 9.3 mg were internal lipids and 3.7 mg were surface lipids. The total lipid content of malt starches varied between 11 and 13 mg/g of starch. However, malt starch contained only 1 mg of surface lipids; therefore, the internal lipid contents were as high as or even higher than those in the corresponding fraction of barley starch. Lipid class analyses suggested that the ability for hydrolysis of starch surface lipids was in-

creased in malt. The hydrolysis occurred during the malting or the isolation process, resulting in reduced surface lipid content in malt starch. However, no reduction in the portion of polyunsaturated fatty acids was seen; therefore, lipid oxidation could not have been responsible for the lower content of malt starch surface lipids. Also, not only was the content of starch internal lipids higher in malt, but the composition of these lipids was different when compared to barley starch. The increase in starch internal lipids during malting may be due to transportation and reacylation of free fatty acids that had been liberated by hydrolysis from surface lipids.

Cereals such as barley, rice, maize, oat, and wheat contain starch-associated lipids. Lipids of cereal starches can be divided into surface and internal lipids (Morrison 1981). Surface lipids include lipids that are attached to the surface of starch granules *in situ* or become attached during the isolation of starch. In addition, such lipids are extractable with cold solvents. Surface lipids are occasionally referred to as non-starch lipids (Morrison 1981, Galliard and Bowler 1987). Surface lipids are similar to lipids that are found in other parts of the kernel and consist of triglycerides, polar lipids, and small amounts of diglycerides and free fatty acids (Morrison 1981). Internal lipids are mainly monoacyl lipids (lysophospholipids) and free fatty acids present as inclusion complexes with amylose (Acker 1977, Morrison 1981). Internal lipids are poorly extractable and usually require hot alcoholic extraction that influences the granule structure (Morrison 1985a).

It has been suggested that starch lipids influence the gelatinization temperature, leaching of soluble polysaccharide, and swelling of starch (Tester and Morrison 1990). Starch can also complex added lipids under some conditions. Starch lipids and especially amylose-lipid complexes have been studied primarily with reference to the behavior of starch in the baking industry and dough making (e.g., Morrison 1978a, Riisom et al 1984, Nierle and El Bayâ 1990). The most studied cereal lipids have been wheat and maize lipids (Hanna and Lelievre 1975, Melvin 1979, Eliasson et al 1981, Morrison et al 1984, Eliasson et al 1988, Takahashi and Seid 1988). Lipid-starch interactions have received considerable attention with reference to germination (Baisted 1981, Baisted and Stroud 1982, Baisted 1983, Fujikura and Baisted 1983, Fujikura and Baisted 1985, Lundgard and Baisted 1986). It is evident that some aspects of germination bear a resemblance to industrial malting processes. However, although many of these studies give valuable physiological data about hydrolysis of starch and starch-lipid complexes during germination in nature, they can not directly be coupled to malting where hydrolysis of starch is controlled and usually very low.

Even though malting of barley and the further use of malt in brewing has been studied from many aspects, the behavior of starch-lipid complexes during malting and brewing is poorly un-

derstood. Earlier studies on mashing suggested that fine particles in spent grains can contain starch with high amylose and lipid content (Kano 1975). It was further suggested that these fine particles might retard mash filtration (Bathgate et al 1973, Barrett et al 1975, Krüger and Strobl 1984). However, only limited information is available on the actual starch-lipid complexes, and the basic data concern barley varieties that contain differing amounts of starch amylose and lipids (Morrison et al 1984, Morrison 1985b, Gudmunsson and Eliasson 1992). Therefore, the aim of the present work was to 1) study the quality of barley and malt starch lipids and the influence of the malting process on starch lipids and 2) discuss the role of starch lipids when barley and malt are used as raw materials in food processing.

MATERIALS AND METHODS

Barley

The Finnish malting barley cv. Kymppi (harvested in 1991) was used in all experiments.

Other Materials

The standards for thin-layer chromatography (TLC) and gas-liquid chromatography (GLC) analyses were purchased from Sigma Chemical Co. (St. Louis, MO) and were as follows: dipentadecanoyl phosphatidylcholine (P-7285), heptadecanoic acid (H-3500), triheptadecanoin (T-2151), dipentadecanoin (D-8508), heptadecanoyl lysophosphatidylcholine (L-5257), phosphatidyl ethanolamine (P-3511), phosphatidyl-DL-glycerol (P-0514), phosphatidyl inositol (P-5766), phosphatidyl-L-serine (P-7769), and heptadecanoic acid methyl ester (H-4515). Silica gel plates (5721) were purchased from Merck (Darmstadt, Germany). HPLC grade solvents were used for all fatty acid analyses. All other chemicals were of reagent or higher grade.

Malting

Maltings were carried out using 44-hr steeping with varying wet and dry periods, six-day germination, and 21-hr kilning. Different aeration conditions during the steeping period were achieved by using steeping without dry periods (anaerobic conditions), steeping in water with 0.75 % H₂O₂ (highly oxidative conditions), and steeping with varying wet and dry periods (control, intermediate aeration conditions).

Starch Isolation

The barley and malt samples were ground to a fine powder with a Schnitzer (model KE) natural stone flour mill (Schnitzer KG

¹Helsinki Univ. of Technology, Kemistintie 1, P.O.Box 6100, FIN-02015 TKK, Finland.
²Corresponding author. Phone: 358-9-451 2555; Fax 358-9-462 373. E-mail: Anu.Kaukovirta-Norja@hut.fi.
³Oy Lahden Polttimo AB, P.O. Box 22, FIN-15141 Lahti, Finland.

Getreidemühlen, St. Georgen, Germany). The flour was suspended in distilled water and mixed for 15 min in a water bath at 14°C. The slurry was homogenized and the bran was separated by using a 0.5-mm sieve. The remaining slurry was centrifuged (5,860 × g) and the resulting protein and starch layers were separated. The malt starch was washed twice with cold water to remove the α-amylase present in malt. The isolated starch samples were freeze-dried and used for the determinations. The protein content of starches was determined as Kjeldahl-N using a nitrogen-protein conversion factor of 6.25.

Measurement of Lipolytic and Oxidative Activity of Starches

The lipolytic and oxidative activity of the samples were measured as previously described by Kaukovirta-Norja et al (1993).

Water Soaking Experiment

A 0.5-g sample of barley or malt flour or starch was soaked for 15 hr (mixing speed 200 rpm, 23°C) in 2.5 ml of distilled water. Prior to lipid extraction of the untreated samples, 2.5 ml of distilled water was added after the chloroform-methanol (2:1, v/v) addition.

Lipid Extraction

Chloroform-methanol extraction. Barley, malt, and the starch samples from the water soaking experiment were extracted by shaking (240 rpm, 26°C) in 19 volumes chloroform-methanol (2:1, v/v) according to Folch et al (1957). Extraction was repeated twice (1 × 6 hr, 1 × 2 hr). The extracts were combined and evaporated to dryness under N₂ in a rotary evaporator. Lipids were dissolved in 10 ml of chloroform-methanol (1:1 v/v), divided into aliquots of 500–1,000 μl in test tubes, evaporated to dryness under N₂, and stored at –20°C under N₂ before analysis. The samples were used to determine total fatty acids and major lipid classes.

Propanol-water extractions. With the traditional lipid extraction method (Folch et al 1957), most of the lipids on the outside of starch granules can be extracted. Hot solvents are required to extract the lipids inside the starch granules (Morrison 1981). The term surface lipids is used in this article to describe the lipid fraction of starch granules that can be extracted by cold solvents. This definition is also used by Morrison (1981) and Galliard and Bowler (1987). Surface lipids were extracted by *n*-propanol-water mixtures (3:1, v/v) at 20°C for 30 min using a ratio of 20 ml of solvent/2 g of starch. Surface lipid extracts were then evaporated and treated as described above. The total fatty acids and the major lipid classes were determined from these samples. In addition, the susceptibility to hydrolysis and gelatinization properties of the starches were assayed.

Total lipids of barley and malt starches were extracted according to Morrison (1985b) by *n*-propanol-water mixture (3:1, v/v) at 90–100°C using a ratio of 20 ml of solvent/1 g of starch without the preceding extraction of surface lipids. The extraction was repeated three times (2 × 2 hr, 1 × 1 hr). The extracts were combined and treated as described above. Internal starch lipids were determined as the difference between total and surface lipids of starch.

Separation of Lipid Classes

The dried extracts were redissolved in 200 μl of chloroform-methanol (1:1, v/v), followed by the addition of 50 μg each of the polar lipid (PL), diglyceride (DG), free fatty acid (FFA), and triglyceride (TG) standards. The samples were then applied to silica plates. PL, TG, DG, and FFA were separated by developing the plates with petroleum ether-diethyl ether-acetic acid (80:30:1, v/v). For analyses of individual phospholipid classes, the samples were supplemented with 50 μg of PL and lysophosphatidylcholine (LPC) standards. Phospholipids were separated by developing the plates with chloroform-methanol-acetic acid-water (60:35:10:5). Lipid classes were visualized by spraying with 0.01% Rhodamine

6G and detected under UV light, scraped off, and used for fatty acid determination. Lysophosphatidylethanolamine (LPE) or lysophosphatidylglycerol (LPG) heptadecanoic acid methyl ester (30 μg) was added to test tubes prior to fatty acid determination (Liukkonen et al 1992).

Preparation and Analysis of Fatty Acid Methyl Esters

Fatty acids were saponified and converted to methyl esters as described by Suutari et al (1990). The methyl esters were analyzed using GLC and major fatty acids were identified by comparing their retention times with those of known standards. The total extractable fatty acids were determined by adding 30 μg of an internal standard, heptadecanoic acid methyl ester, to each sample prior to saponification and methylation.

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 used (Hewlett-Packard, PA). The column temperature was programmed from 70 to 200°C at a rate of 25°C/min. The column inlet pressure was 150 kPa. The flow rate for the makeup gas, He, was 30 ml/min, and the flow rates for the detector gases were 40 ml/min H₂ and 400 ml/min air. The column flow rate was 1.0 ml/min and the septum purge flow rate 1–2 ml/min. The split ratio was set at 1:20. Peak areas were measured by using a 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 the total peak area. Absolute amounts of the individual fatty acids in total lipids were calculated per gram dry weight of the sample by comparison of the peak area to that of the internal methyl ester standard without any conversion factors. The total amount of fatty acids was determined as the sum of all individual fatty acids. Amounts of major lipid classes per gram dry weight of the sample were determined by comparing the total peak area of all the fatty acids from a lipid class to that of the corresponding standard. The distribution of different lipid classes was determined as a percentage of the sum of the weights of lipid classes. The amounts of LPE and LPG were determined by multiplying the amount of fatty acids in a lipid class by appropriate factors, which were 467/284 for LPE and 499/284 for LPG. The amounts of internal lipids were obtained by subtracting the amounts of surface lipids from the amounts of lipids obtained in propanol-water extraction at 90–100°C.

The degree of fatty acid unsaturation (DUS) (Δmol^{-1}) in the lipid fraction was calculated as $\Delta\text{mol}^{-1} = [\Sigma (\% \text{ monoene}) + 2 \times (\% \text{ diene}) + 3 \times (\% \text{ triene})] / 100$.

Accuracy of the Results

The data on starch lipids are mean values of duplicate determinations. The data on barley and malt lipids are mean values of five to eight extractions. The standard deviations (SD) for different lipid classes were at the maximum 10% for PL, 7% for TG, 4% for DG, and 5% for FFA fraction.

RESULTS AND DISCUSSION

Total Lipid Contents of Starches

Starches were isolated from barley and malt grains containing 3.1 and 2.7% (w/w) lipids, respectively, when analyzed by the common lipid extraction method of Folch et al (1957). The total lipid contents of barley and malt grains were in accordance with values reported in the literature (e.g., Morrison 1978b). It was therefore assumed that this grain variety would also be represen-

tative with respect to the amount of starch lipids in the total extracted lipids. Isolated starches from barley and malt had the same color and fresh odor. The protein content was 1.3% for barley starch and 0.4–0.8 % for malt starches. Furthermore, there was no detectable lipoxigenase or hydrolytic activity in either of the starch samples.

The hot solvent extraction with *n*-propanol-water mixture (Morrison 1981) yielded 13 (± 0.5) mg of lipid per gram of barley starch, whereas the respective value for malt starch was 11 (± 0.4) mg/g. It is thus evident that the malting process had caused a decrease in the lipid-starch ratio.

Distribution of Starch Lipids into Surface and Internal Lipids

Starch lipids were separated into surface and internal lipids according to their extractability into cold or hot *n*-propanol-water mixtures (Morrison 1981). Analysis of the cold-solvent extract indicated that barley starch contained 3.7 mg/g surface lipids, whereas malt starch contained 1.0 mg/g. Thus, malt starch contained approximately one-fourth of the amount of surface lipids of barley starch. The internal lipid contents of barley and malt starches were 9.3 and 9.9 mg/g, respectively. Therefore, the difference in the total lipid content between barley and malt starches was attributable to differences in the surface lipid content of the starches. The internal starch lipids contributed the major portion to the total starch lipids. Such findings are in accordance with previous reports in the literature, which state that cereal starches contain approximately 1% lipids that mainly consists of lipid classes inside of the starch granules (Morrison 1978a, Baisted 1983). In light of the results presented above, it is evident that the malting process caused changes in the barley, resulting in altered interaction of the surface of the starch granule with lipids, whereas the inside of the granules appears to stay more intact.

Lipid Class and Fatty Acid Composition of Starch Lipids

The lipid class composition of surface lipids is presented in Table I. It is evident that, although the surface lipid content of malt starch was lower than that of barley, the absolute amount (mg lipid/g starch) of the FFA pool was four-fold greater than that of barley surface lipids. Furthermore, because the amounts of PL and TG for surface lipids of malt starch were one-fourth and one-sixth of the amount detected in barley starch, it could be suggested that extensive lipid hydrolysis had occurred in malt starch surface lipids converting PL and TG to FFA. However, the FFA pool of the surface lipids of malt starch was not increased to a level that would completely account for the diminished amounts of acyl lipid classes (PL and TG). The possibility that the liberated fatty acids migrated to the cytosol of the kernel was unlikely because the amount of FFA in the whole malt kernel was not increased when analyzed by the Folch method (Kaukovirta-Norja et al 1993). Instead, the role of β -oxidation can not be excluded. However, the fact that the FFA pool remains stable in the kernel during the whole malting process does not support this possibility. Hydroperoxide analyses by the HPLC-chemiluminescence method applied to whole barley and malt flours did not show any accumulation of lipid hydroperoxides in malt. However, the possibility that hydroperoxide accumulation did not occur due to the presence of hydroperoxidase activity (Schwarz and Pyle 1984) still remained. Therefore, the fatty acid composition of each of the individual lipid classes of the surface lipids of barley and malt starches were determined separately and the respective DUS of lipid classes was calculated.

In the surface lipids of malt starch, the DUS value of acyl lipids, e.g., TG and PL, was equal to or slightly lower than that of surface lipids of barley starch (Table II). On the other hand, DUS of deacylated lipids such as DG, and in particular FFA were slightly to considerably higher for surface lipids of malt starch. Thus, the high DUS value in the FFA pool of malt starch surface lipids indicates that extensive hydrolysis of lipids without oxida-

tion of the liberated 1,4-pentadiene fatty acids may have occurred on the surface of starch granules.

The distribution of the internal lipids into lipid classes is shown in Table III. The composition of internal lipids of barley starch was generally similar to that reported previously (Morrison et al 1984), with PL dominating in excess of 80%. Lysophospholipids were the largest group in the PL fraction. Comparison to malt starch showed that the amount of PL was equal to that of barley starch but with reduced DUS (Table II). Instead, the FFA fraction with a marked increase in DUS was larger. Low quantities of TG were present in the internal lipids of malt starch only. Earlier studies on barley starch or on starches of other common cereals have not shown that TG would be associated with internal lipids of starch granules. The present results therefore suggest that starch granules of malt that are partly disrupted or porous after malting may allow for an exchange of starch internal lipids with their surroundings. Accordingly, the free fatty acids liberated from surface lipids would be the most likely candidates to first integrate with the granules.

Three Different Maltings—Three Starch Lipid Spectra?

The malting process was varied in order to verify that the reduction in the surface lipids and the appearance of TG in internal lipids of malt starch were not a coincidence. The aeration conditions during steeping were varied from totally anaerobic to highly oxidative.

In these experiments, surface lipid contents of malt starches varied from 0.64 to 1.13 mg/g and that of internal lipids from 10.57 to 11.53 mg/g starch (Table IV). The composition of the surface lipids of the starches was very similar to the surface lipids of malt starch in the first trial (Table I), and again their amount was only one-fourth of the amount of surface lipids of barley starch. All of these three malt starches contained more than 10 mg of internal lipids per gram of starch with small amounts of TG (Table IV). The increased level of internal lipids as compared to barley (Table III) and the appearance of the TG fraction further

TABLE I
Lipid Class Composition (mg/g of starch) of Surface Lipids of Barley and Malt Starches^a

Starch	Polar Lipids ^b	Triglycerides	Diglycerides	Free Fatty Acids	Total
Barley	1.20	2.29	0.18	0.05	3.72
Malt	0.32	0.37	0.06	0.21	0.96

^a Analysis performed two times with <10% variability in results.

^b Maximum standard deviation for each lipid class is presented in text.

TABLE II
Degree of Unsaturation (DUS) of Starch Lipids of Barley and Malt^a

	Barley		Malt	
	Surface	Internal	Surface	Internal
Polar lipids	1.43	0.87	1.35	0.82
Triglycerides	1.46	0.00	1.44	1.24
Diglycerides	1.27	0.18	1.44	0.18
Free fatty acids	0.36	0.15	0.87	0.37

^a Analysis performed two times. Standard deviation for DUS values was <0.05.

TABLE III
Lipid Class Composition (mg/g of starch) of Internal Lipids of Barley and Malt Starches^a

Starch	Polar Lipids ^b	Triglycerides	Diglycerides	Free Fatty Acids	Total
Barley	7.40	0.00	0.67	1.19	9.26
Malt	7.46	0.28	0.67	1.46	9.87

^a Analysis performed two times with <10% variability in results.

^b Maximum standard deviation for each lipid class is presented in text.

supports the fact that an exchange of lipids and even an accumulation of lipids in malt starch granules.

Comparison of Starch Surface Lipids to Whole Kernel Lipids

According to previous data, the composition of lipid classes and their DUS in whole barley and malt are very similar (Kaukovirta-Norja et al 1993). Earlier data also showed that a much stronger hydrolysis of acylated lipids, especially polar lipids, with a simultaneous increase of FFA, can be observed in malt flour than in barley flour after water treatment. As the isolation of starch and most starch-based industrial processes occur in water solutions, it is important to compare starch surface lipids to the lipids of water-treated whole barley and malt (Fig. 1).

The lipid class composition of barley starch surface lipids was very similar to the lipid class composition of both native barley flour and water-treated barley flour (Fig. 1). However, the lipid class composition of surface lipids of malt starch differed both from that of native malt flour and from water-soaked malt flour (Fig 1). In whole malt flour, the PL fraction in particular was degraded during the water treatment and its proportion therefore decreased remarkably (from 26 to 8%), while the proportion of TG remained unchanged (67%) compared to untreated, native, malt flour. In the surface lipids of malt starch the proportions of TG and PL were approximately equal (30–40%), which suggests that the hydrolysis of TG was stronger than that of PL on the sur-

face of starch granules during the malting process itself or during the isolation of starch. This indicates that the reaction milieu near the starch granules is different from the rest of the malt kernel and provides a favorable site for TG hydrolysis. Oxidation of liberated fatty acids occurs if other prevailing conditions allow such reactions to proceed.

In untreated barley and malt flour, the DUS of the total FFA fraction was 0.9–1.1 (Table V). After water treatment of these flours, DUS of FFA was lower in barley and higher in malt, suggesting further oxidation of liberated unsaturated fatty acids in barley but not in malt (Kaukovirta-Norja et al 1993). Surface lipids of both barley and malt starch had lower DUS in their FFA pool than that of the lipids of water-treated whole flours (Table V). Special attention should be paid to the very low content and proportion of linoleic acid in the FFA fraction of surface lipids of barley starch (Table VI), which might indicate the same phenomenon as was seen in water-treated barley flour (Kaukovirta-Norja et al 1993), i.e., the possibility of further oxidation of liberated fatty acids on the surface of barley starch granules. The present results also support the earlier observation of high oxidizing activity in untreated, quiescent barley (Kaukovirta-Norja et al 1993).

Contribution of Starch Lipids to Total Lipids

Internal lipids of starches are not extractable from the granular structure by organic solvents at ambient temperatures (Morrison et al 1975). However, the lipid contents of cereals are usually assayed by using extraction methods that do not remove internal starch lipids (e.g., Folch et al 1957). The results of the present study show that by using the method of Folch et al (1957), an underes-

TABLE IV
Starch Lipids of Three Malts (mg/g of starch) from Different Maltings^a

	Surface			Internal		
	Malt 1	Malt 2	Malt 3	Malt 1	Malt 2	Malt 3
Polar lipids ^b	0.28	0.44	0.50	8.97	9.26	9.54
Triglycerides	0.16	0.30	0.40	< 0.0	0.14	0.16
Diglycerides	0.04	0.04	0.05	0.43	0.30	0.48
Free fatty acids	0.16	0.22	0.18	1.17	1.09	1.34
Total	0.64	1.00	1.13	10.57	10.80	11.53

^a Analysis performed two times with <10% variability in results.

^b Maximum standard deviation for each lipid class is presented in text.

TABLE V
Degree of Unsaturation (DUS) of Free Fatty Acid Pool of Untreated and Water-Treated Barley and Malt and Corresponding Starches^a

	Untreated	Water-Treated	Starch, Surface	Starch, Internal
Barley	0.90	0.60	0.36	0.15
Malt	1.10	1.20	0.87	0.37

^a Analysis performed two times. Standard deviation for DUS values was <0.05.

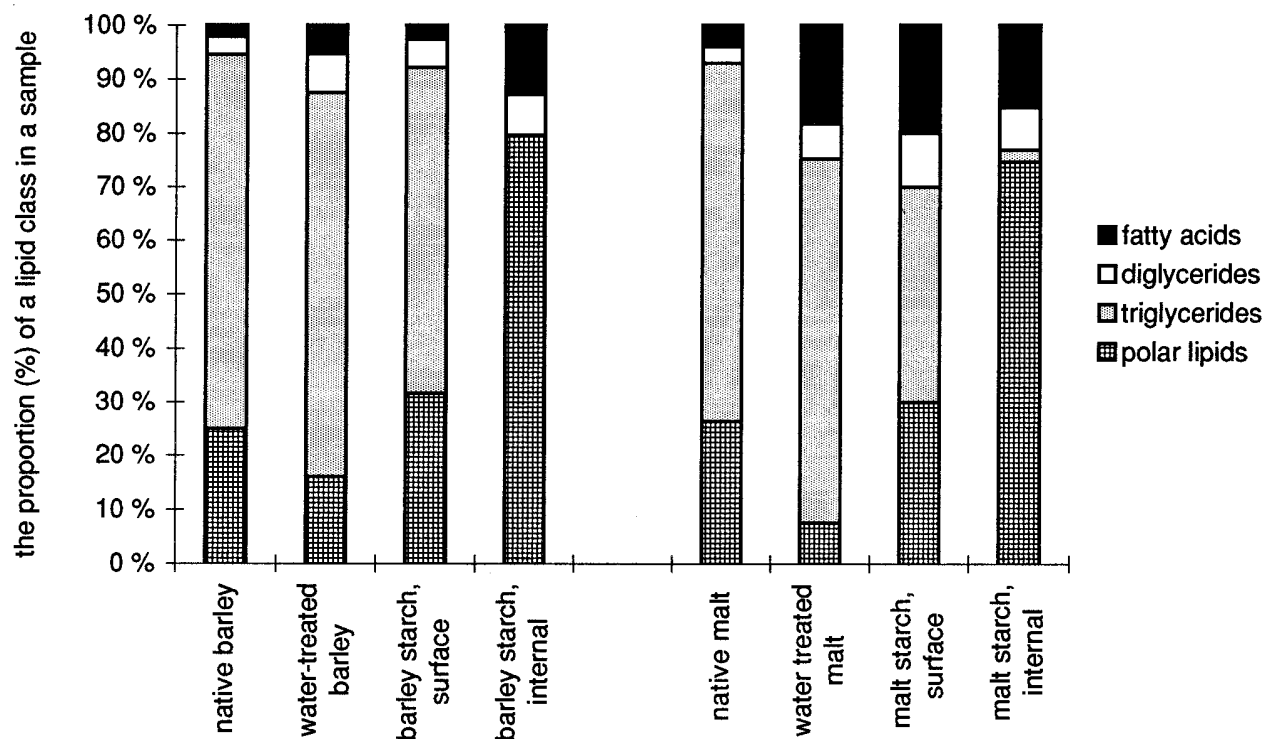


Fig. 1. Lipid class composition of native barley and malt, water-treated barley and malt, and surface and internal lipids of barley and malt starches.

timination of total lipid content of the kernel will result. When the amount of starch internal lipids was added to the amount of other lipids, the total lipid content of barley and malt increased from 3.1 to 3.7% and 2.7 to 3.3%, respectively (Table VII). These lipid contents still fall into the wide range referred to by Morrison (1993) but do indicate that the lipid contribution of both barley and malt to food processes can be underestimated in some circumstances.

As the starchy endosperm represents most of the total kernel weight, relatively small changes in starch lipid content are reflected in the total kernel lipids. By assuming that both barley and malt kernels contain 60–65% starch (Harris 1962) it can be estimated that starch granules would contain almost 20% of all the lipids of barley and malt kernels representing 0.8% of the weight of barley kernel and 0.65% of malt kernel (Table VII). What should not be ignored is that both in the barley and malt kernel starch lipids can contain over 50% of all the FFAs (Table VII).

Significance of Starch Lipids of Barley and Malt in Food Processes

In light of the present study, it is evident that barley and malt starches contribute two groups of lipid to food processes. These lipids probably differ in reactivity due to their different association with starch particles. The starch surface lipids are exposed continuously throughout the process, beginning with the initial moments of the water process while the reactivity of internal lipids is likely to be dependent on changes in the starch. Furthermore, very different situations may arise during such processes. For example, during mashing the temperature is usually increased slowly and is quite moderate throughout the whole process. On the other hand, in processes in which the initial temperatures are very high, the leakage of starch lipids from the interior of the granule can be remarkably fast, due to faster degradation of the starch particles at high temperatures.

The results also suggest that as malt starch is partly degraded and is known to form pores (Palmer 1989), lipid change, transport and even reacylation between outer and inner parts of the granules may be possible. As a result of such a change in lipids, the internal lipids could become reactive during processing of malt. During mashing and beer production—the main application of malt—these starch-originated, reactive lipids are not only susceptible to

further oxidation and formation of off-flavors, but they might also react and form complexes with proteins and other compounds (Matheis and Whitaker 1987, Meshehdani et al 1990). This can result in gel formation, which may impair filtration operations in breweries. On the other hand, if starch surface lipids migrate inside the granules they might form new linkages between amylose and amylopectin and consequently change the physico-chemical properties of starch during processing. Furthermore, the migration of lipids into starch granules might protect lipids from oxidation during processing until all the starch has been degraded. In many processes, e.g., mashing, a part of the starch stays undegraded (Barrett et al 1975) and therefore lipids might be protected during the entire process and at the end be carried out of the process with spent grains.

The role of starch lipids in brewing has received little research attention in the past. Furthermore, the influence of starch lipids on flavor stability and process technology (e.g., filtration of wort) has not been considered in any depth. However, the quantitative and qualitative results of this study show that the effect of starch lipids on flavor instability and formation of off-flavor compounds during brewing needs to be studied further. Off-flavors and off-odors from starch lipids could result from a similar mechanism that lipids from the other parts of the kernel undergo (Drost et al 1990). Such a series of reactions is very dependent on the level of hydrolytic and oxidative enzymes, antioxidants, and pro-oxidants in the process.

CONCLUSIONS

The observed lower amount of starch lipids in malt when compared to barley was seen to be solely due to a lower amount of starch surface lipids in malt. Lipid class analyses showed that the decrease of surface lipids of malt starch was a result of an increased lipolytic potential in malt and the further loss of liberated fatty acids. However, fatty acid analysis showed that no specific oxidation of polyunsaturated fatty acids was seen, indicating that oxidation of lipids was not responsible for the loss of lipids. Instead, the amount of internal lipids of malt starch was moderately higher than that of barley starch. The detailed analysis of internal lipids of barley and malt starch showed that not only the amount but also the composition of internal lipids of malt starch differed from that

TABLE VI
Fatty Acid Composition (%) of FFA-Fraction in Untreated Barley and Malt, in Water-Treated Barley and Malt, and in Surface Lipids of Barley and Malt Starches^a

Fatty Acid	Untreated Barley	Untreated Malt	Water-Treated Barley	Water-Treated Malt	Barley Starch, Surface	Malt Starch, Surface
Palmitic acid (16:0w)	40	38	54	37	53	46
Stearic acid (18:0w)	8	4	5	2	21	6
Oleic acid (18:1 n-9)	9	7	14	8	8	8
Linoleic acid (18:2 n-6,9)	37	45	24	47	14	35
Linolenic acid (C 18:3 n-6,9,12)	1	5	1	5	0	3
Others ^b	6	2	3	1	4	3

^a Mean values from minimum of two replicate determinations. Standard deviation was <5%.

^b Includes 14:0, 16:1 (n-7), and 18:1 (n-7).

TABLE VII
Contribution of Different Starch Lipids to Total Lipids of Barley and Malt^a

Lipid Class	Lipids in Whole Grain (mg)	Starch Lipids (mg)			Lipids in Whole Grain (mg)	Starch Lipids (mg)		
		Internal	Surface	% ^b		Internal	Surface	% ^b
Polar lipids	1,260	480	80	44	1,150	450	20	41
Triglycerides	2170	0	150	7	1790	20	20	2
Diglycerides	140	40	10	40	120	40	<10	36
Free fatty acids	150	80	< 10	54	200	90	10	50
Total lipids	3,720	600	240	16	3,260	600	50	18

^a 100 g of barley and malt were used. Analysis performed two times with <10% variability in results.

^b Proportion (%) of starch lipids of all kernel lipids.

of barley starch. The changes in internal lipids of starch, and the reduction of the amount of surface lipids of starch granules during malting was thought to be an indication of an exchange of lipids between internal and surface parts of a starch granule.

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