AGRICULTURAL AND FOOD SCIENCE

Vol. 13 (2004): 88–99.

Review article

Role of lipid reactions in quality of oat products

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In traditional oat processing practice the control of lipid reactions relies largely on empirical experiences and dogmatic principles rather than on profound understanding of the underlying mechanisms. However, in today's global food markets, the industry faces strict challenges in the development of new processes and applications where the prior experience is unsatisfactory or insufficient. The storage stability of novel oat products can be greatly enhanced by taking the mechanisms of lipid deterioration into account, and by adjusting the processing conditions accordingly so that these reactions can be minimized. The lipid reactions in oat products result in two different unwanted properties: bitter, astringent, taste or a rancid flavor. Chemically, these properties are associated to enzymatic hydrolysis of ester bonds and non-enzymatic oxidation of unsaturated fatty acyl chains respectively. The processing history oat product has a huge impact on which of these reactions predominates in oat products. The review focuses on the reactions of lipids in processed oat products, and identifies factors that are critical for enhanced shelf-life.

Key words: oat, lipids, storage stability

Introduction

Even though many cereals are palatable as harvested, they are usually processed to consumer products with increased nutritional, technological or commercial value. However, such processing will inevitably induce changes in the natural organization of seed lipids. Many of these changes render lipids more susceptible towards deteriorative reactions. On the other hand, processing techniques based on novel information on lipid reactions can also be used to enhance the stability of cereal lipids. This can be achieved not only by inactivating the deteriorative enzymes, but also by introducing processing steps by which the favorable molecular organization and phase distribution of lipids are enhanced.

Processing induced changes in the molecular organization between lipids and other flour components are enforced by mechanical and thermal energy. Cereal lipids themselves are liquid over the ambient temperature range, and thus no phase changes are expected to occur in the continuous lipid phase during processing. The viscosity of lipids does, however, change dra-

Manuscript received June 2003

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matically in the temperature range encountered during cereal processing (Abramovic and Klofutar 1998). The low viscosity in the elevated temperatures increases the mobility of lipids and thus increases the chances of disintegration of native molecular organization. Concurrently, the disruption of grain structure upon milling brings the lipolytic enzymes and lipids into close contact. Especially non-inactivated oat is known to form a bitter taste due to enzymatic deterioration induced by milling. In the typical milling processes, subcellular components such as starch granules and oil-bodies are likely to remain intact. However, heating, introduction of extensive mechanical energy, enzymatic treatments and various aqueous treatments can cause the individual components to lose their integrity and as such lead to changes in molecular mobility.

Reactions of cereal lipids during processing can be divided into reactions which are catalyzed by the enzymes present in cereals, and reactions which occur without the involvement of enzymes. Most of the enzymatic reactions documented in the scientific literature are related to hydrolytic or oxidative pathways or to non-oxidative isomerization of carbon-carbon double bonds structures. Non-enzymatic reactions are limited to the reactions related to oxidative pathways and isomerizations, as the non-enzymatic lipid hydrolysis is exceedingly slow at ambient pH and temperature values typically encountered during cereal processing. For certain lipid compounds intramolecular acyl migration within glycerol structures has been reported to occur without enzyme activity also at ambient conditions (Plueckthun and Dennis 1982). However, the relevance of such acyl migration for the quality of lipid containing food products is likely a small or non-existent.

Enzymatic hydrolysis

Most of the fatty acids found in plant seeds are esterified to a specific alcohol molecule, glycerol. The trans-esterification reaction in which the acyl group is transferred from the glycerol to water is generally referred to as lipid hydrolysis (Fig. 1). This, as well as the reverse reaction, the synthesis of acylglycerols from glycerol and free fatty acids, is catalyzed by lipase enzyme (EC 3.1.1.3).

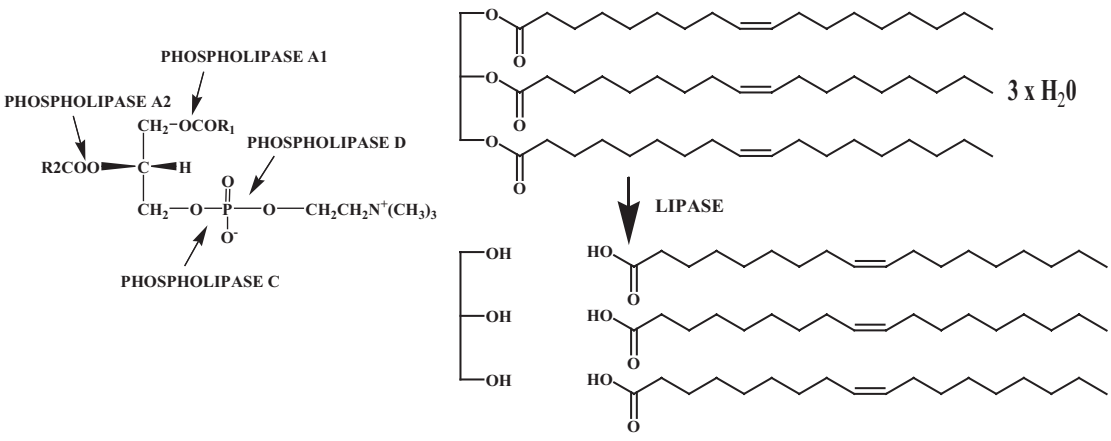

Fig. 1. Hydrolysis of polar membrane lipids and neutral storage lipids.

The water activity has an utmost important role in determining lipase activity. Water affects both the enzyme activation and the thermodynamical equilibrium of the reaction. Different lipases have different water activity values at which activation is established and the literature on microbial lipases suggests that these values are well below a water activity of 0.3 (Wehtje and Adlercreutz 1997). The water amount required is much smaller than for most other enzymes, corresponding roughly to a mono or multiple adsorption layer of water surrounding the enzyme (Caro et al. 2002). As water is also a reactant in the lipase reaction, it also affects on the equilibrium of the reaction. The reaction equilibrium has been reported to change from the synthesis to the hydrolysis of esters in the water activity range of ca. 0.2 to 0.3 (Svensson et al. 1994). However, the equilibrium is also a function of other substrates involved, namely free fatty acids, glycerol and different acylglycerols. Thus the reaction equilibrium in a cereal matrix can not be deduced solely based on the water content. It is, however, evident that in most situations encountered upon cereal processing, where water activities lie well above 0.4, the lipid hydrolysis is a thermodynamical downhill. Consequently, the hydrolysis of esterified lipids in enzyme active cereal products can easily proceed to an extent that is perceived as sensory flaw. In water activities above 0.8 the amount of free water becomes remarkable, and the lipase catalyzed hydrolysis can either increase or decrease as a function of water activity, depending on the substrate concentration, distribution of substrates between aqueous and oil phases and probably also on the source of the lipase (Adlercreutz et al. 2002, Ma et al. 2002).

Different enzymes are responsible for the hydrolysis of neutral triacylglycerols and polar phospho- and glycophospholipids. Cereal seeds contain apparently only 1 or up to 3 different isoenzymes of lipases acting on storage lipids (Baxter 1984, O'Connor et al. 1989, Peterson 1999, Edlin et al. 2002). On the other hand, the hydrolysis of phospholipids in plant membranes is a far more controlled process involving the induction of plant defense system, and multiple isoenzymes of each phospholipase classified in Figure 1 (Wang 2001). During various processes, cereal lipids may also be exposed to microbial lipase and the role of microbial enzymes in cereal lipid reactions is a controversial subject (O'Connor et al. 1992).

The synthesis of cereal hydrolytic enzymes is induced by hormone signals from embryo tissue, leading eventually into protein synthesis or proenzyme activation in the aleuronic and apparently partly also in the endosperm tissues (Tavern and Laidman 1969, Laidman and Tavern 1971, Gallie and Young 1994). Mature oat grains have a remarkable lipase activity even if the germination is not started (O'Connor et al. 1992). During fractionating of oat, the lipase activity has been found to be present both in the aleuronic rich bran fraction as well as in the endosperm fractions obtained from the inner parts of grains (Hutchinson et al. 1951, Ekstrand et al. 1992, Lehtinen et al. 2003). The presence of high lipase activity in the endosperm fraction of non-germinated oat is puzzling. Assuming that the presence of the activity is related to incipient germination, the presence of induction, synthesis and transport mechanisms would be expected also for other hydrolytic activities. In non-germinated oat these activities are, however, not detected consistently with lipase activity. Also the fact that neither lipid hydrolysis nor an increase in lipase activity is observed during early germination, suggests that the lipase activity present in mature oat grain is not related to the germination process (Peterson 1999, Outinen 1999). More likely, the activity represents either a residual activity originating from the lipid synthesis upon the seed development or is related to some other biological function such as defense systems (Urquhart et al. 1983).

Many microbial lipases discriminate between the different acyl groups and have different affinities for fatty acids acylated to different OH-groups of glycerol. For wheat and oat lipases the provided data is somewhat conflicting. When endogenous lipolysis in oat products is followed, no such specificity has been reported (O'Connor

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et al. 1992, Heiniö et al. 2002). In these cases the slight difference in the proportion of fatty acids moieties in triacylglycerol and free fatty acid pools is likely a sign of further oxidative reactions of unsaturated free fatty acids rather than of lipase specificity towards unsaturated fatty acids (Warwick et al. 1979). Furthermore, the lipid hydrolysis in oat proceeds apparently without any accumulation of di- or monoacylglycerols. Rather, once the triacylglycerols are accessible to lipase, all three acyl groups are subsequently rapidly converted to free fatty acids (Liukkonen et al. 1993). However, when the hydrolysis of supplied 1,2,3-trihexanoylglycerol by oat lipase was studied, a strong positional specificity of hydrolysis was observed (Yasuhide et al. 1997).

Even though the hydrolysis of neutral storage lipids in oat is faster than in other cereals, the hydrolysis of polar lipids during oat processing and storage is minimal and detailed information on the hydrolysis of oat polar lipids is sparse (Liukkonen et al. 1992). However, in barley and especially in barley malt, the hydrolysis of polar lipids occurs swiftly once the seed is milled and the water content is increased. In such a case phospolispases show notable specificity for different acyl groups in such a manner that unsaturated fatty acids are most easily hydrolyzed (Kaukovirta-Norja et al. 1998).

Enzymatic oxidation of acylglycerols

Fatty acids in cereal lipids contain 0–3 double bonds. The presence of these double bonds adds extra reactivity to the lipid compounds, and enoic groups can undergo different isomerization or oxidization reactions (Fig. 2). Lipoxygenase (EC 1.13.11.12) is an abundant enzyme in plants and catalyzes the non-reversible oxidation of *cis,cis*-1,4-pentadiene moieties in acyl groups to a respective acyl hydroperoxide. The lipoxygenase reaction rate in different cereals varies greatly and barley and wheat have high lipoxygenase activity, whereas in rye and oat the reaction is slow (Fretzdorff and Jördens 1986, Lehtinen et al. 2000). Cereals contain multiple isoenzymes with lipoxygenase activity and cDNA sequences of two lipoxygenases from germinating barley have been determined (Shiiba et al. 1991, Hugues et al. 1994, Van Mechelen et al. 1999). These isoenzymes have apparently different substrate specifity, different distribution in various tissues and produce different hydroperoxide isomers in different proportions, but otherwise the biological role of these isoenzymes is unknown (Schmitt and Van Mechelen 1997, Feussner and Wasternack 1998).

Enzymatic oxidation of double bonds in acyl chains consists of series of reactions. In many plant tissues the hydroperoxides formed by the lipoxygenase reaction are further cleaved by hydroperoxide lyase (EC 4.1.2.-), an enzyme which has been extensively studied in cucumber, tomato and beans (Matsui et al. 2000, Suurmeijer et al. 2000, Noordermeer et al. 2001). The presence of hydroperoxide lyase in cereal grains has not been published in the scientific literature, but the presence of typical reaction products of this enzyme suggests that it is abundant also in cereals (Sjövall et al. 2000, Parker et al. 2000, Sides et al. 2001). In oat, a lipoperoxidase (EC 1.11.1.-) activity is responsible for the conversion of hydroperoxides to relevant hydroxyacids (Biermann and Grosch 1979). These hydroxyacids are suggested to be partially responsible for the bitter taste associated with the enzymatically active oat (Biermann et al. 1980).

As a consequence of these reactions, wide spectrums of products are formed. In many cereals linoleic acid is the most abundant substrate for the lipoxygenase reaction. The lipoxygenase reaction produces mainly two different isomers of hydroperoxide linoleic acid, namely 9- and 13- hydroperoxide linoleic acids. The cleavage of 9-hydropreoxide linoleic acid further, yields mainly 8–10 carbon monoenoic compounds, whereas the cleavage of 13 hydroperoxide linoleic acid yields 5–7 carbon compounds with no

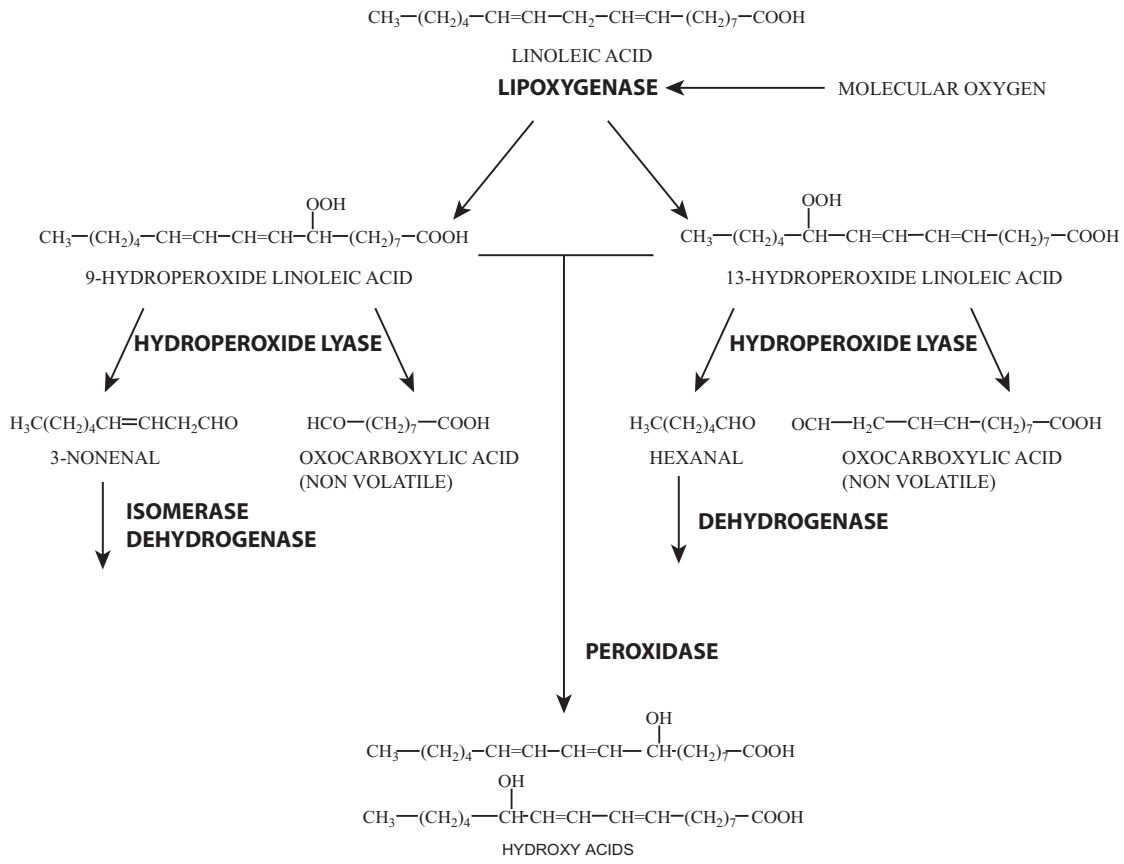

Fig. 2. Simplified scheme of the reactions in the enzymatic oxidation of linoleic acid in cereals (modified after Noordermeer et al. 2001 and Biermann et al. 1980).

double bonds. Upon cleavage both isomers yield also the non-volatile oxo-carboxylic acid compound with 8 to 12 carbons (Galliard and Matthew 1977, Olias et al. 1990).

Non-enzymatic reactions

Whereas the enzymatic oxidation of enoic structures uses molecular, triplet state oxygen as a primary substrate, the non-enzymatic oxidation occurs only after pre-formation of reactive acyl or oxygen species. Thus non-enzymatic oxidation is initiated by factors such as radicals, metal-ions and photons with an energy level capable of triggering endogenous photosensitive molecules. However, once the reaction is initiated, the reaction itself can provide the radicals that will cause the reaction to continue. The presence of endogenous antioxidants in cereals has a marked effect on the onset of non-enzymatic oxidation due to their capability to quench these reactive molecule species into non-reactive form.

Many products of the non-enzymatic oxidation are the same as in the enzymatic oxidation (Fig. 3). However, the fatty acid hydroperoxides may accumulate if neither hydroperoxide lyase nor lipoperoxidase are present. In this case, the

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rate of hydroperoxide decomposition is set by the molecular environment of fatty acid hydroperoxides, i.e. the presence of antioxidants and metal-ions or other radical forming compounds, phase distribution and presence of amino acids and sugars (Nishiike et al. 1999, McClements and Decker 2000, Mäkinen and Hopia 2000). Certain antioxidants slow the decomposition of hydroperoxides, which can reduce the overall rate of lipid oxidation, as the decomposition of hydroperoxides will provide less radicals for the initial H^* abstraction from the fatty acid. However, the role of antioxidants is not straightforward, as in some cases antioxidants can actually increase the decomposition of hydroperoxides, possibly by reducing metal ions into more active form (Mäkinen et al. 2001). Lipid may also form polymeric compounds upon

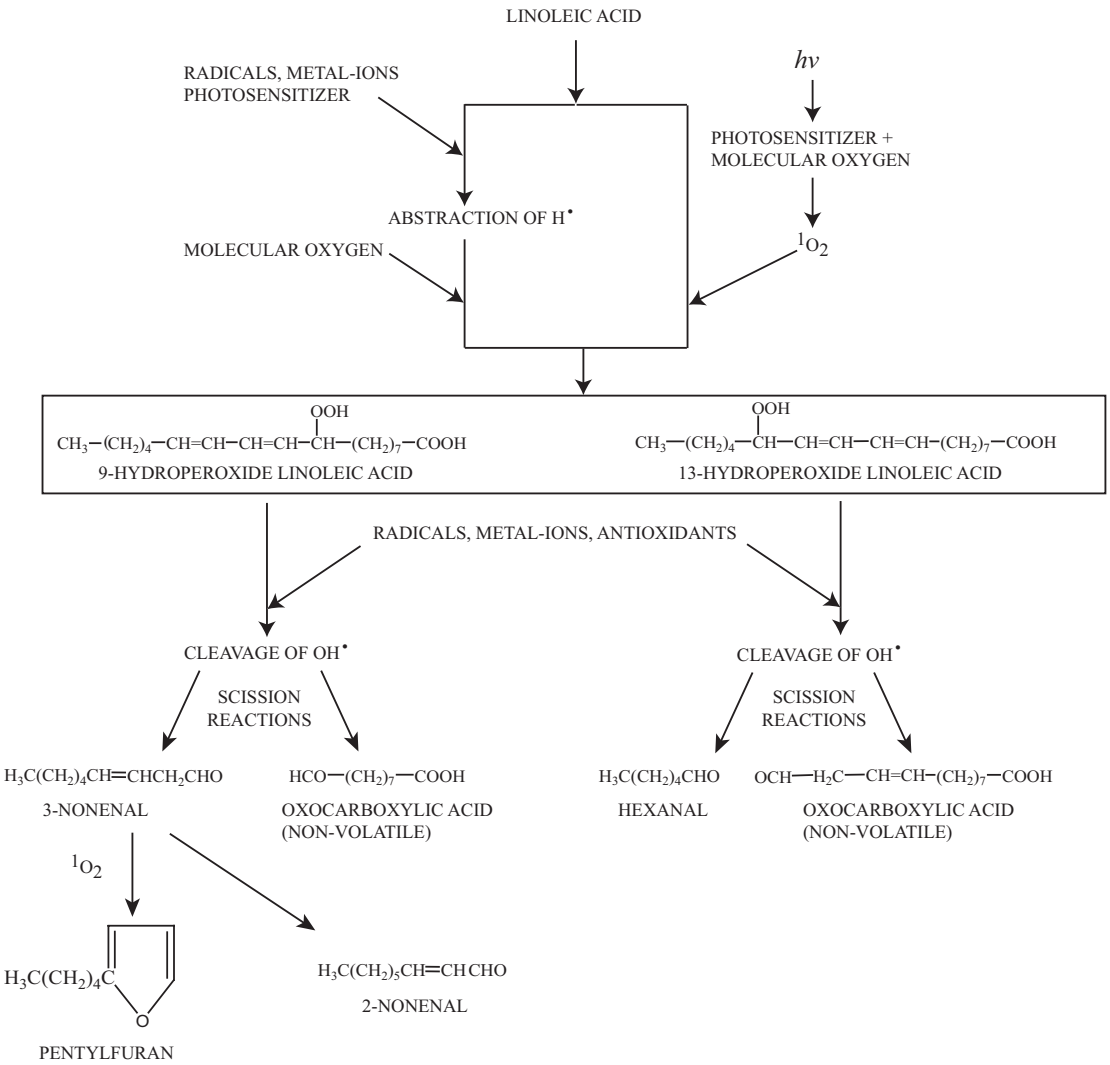

Fig. 3. Simplified scheme of the reactions in the non-enzymatic oxidation of linoleic acid in cereals (modified after Min and Boff 2002). In addition to 9-and 13-hydroperoxides also 10- and 12-hydroperoxides are formed upon photo-oxidation of linoleic acid.

oxidation. These are formed mainly in the highly unsaturated oils such as fish or linseed oils, or in oils that have been excessively heated such as frying oils (Neff et al. 1988, Shukla et al. 1991).

The lipid oxidation products may also undergo different isomerization reactions. The occurrence of trans-2-nonenal (T2N) is associated with the cardboard flavor in beer (Jamieson and Van Gheluwe 1970, Noeel et al. 1999). The formation of the T2N has been suggested to involve an isomerase reaction in which the 3-nonenal is isomerized to T2N (Galliard et al. 1976). However, neither 2- or 3-nonenal products have been reported in rancid oat or wheat germ or, if present, are detected at very low abundance (Sjövall et al. 2000, Heiniö et al. 2001). Instead, 2-pentyl furan is detected in stored cereals and may represent the major product from the cleavage of 9-hydroperoxide linoleic acid. The conversion of straight chain structure of nonenal into cyclic furan structure can be initiated by the singlet oxygen as shown by Min and Boff (2002), and it seems plausible, that the oxidative stress in cereal matrix is responsible for the instability of 3-nonenal. Interestingly, studies in which purified 9-hydroperoxide linoleic acid has been used as a substrate, the 3-nonenal formed via the hydroperoxide lyase reaction, appears to be stable at least for analytical purposes (Gargouri and Legoy 1998).

The enoic structures found in unsaturated fatty acids do not undergo spontaneous isomerization at the ambient processing conditions met during cereal processing. However, in the presence of catalyst such as transition metal ions or at temperatures above 200˚C, both cis/trans and positional isomerization can occur in unsaturated fatty acids (Wolff 1993, Kemeny et al. 2001). During thermal processing of cereals temperatures are usually well below 200˚C and for example upon extrusion, the formation of trans fatty acids is relatively low, 1–1.5% of total unsaturated fatty acids (Maga 1978).

Relevance of lipid reactions to quality of cereal products

The most significant result of lipid reactions is their effect on sensory and rheological properties of cereal products (Cumbee et al. 1997, Jacobsen 1999). A loss of nutritive value (Andersen et al. 1986) and even cytotoxicity (Esterbauer 1993) has also been associated with extensive oxidation of unsaturated fatty acids (Fig. 4). Formation of rancid flavor due to lipid oxidation is a relatively well known phenomenon, whereas relevance of lipid hydrolysis, disruption of cellular structures and lipid interaction with other flour components is less evident.

Analytically the extent of lipid oxidation in food materials is characterised by using parameters such as the amount of remaining intact unsaturated fatty acids, presence of fatty acids hydroperoxides and presence of secondary oxidation products. These parameters are valuable tools for studying the lipid oxidation and for developing products with increased storage stability. However, the relevance of these parameters in explaining the sensory properties is limited, as the sensory impact of different food products differs widely (Jacobsen 1999). Hexanal is the most abundant and easily detectable secondary oxidation product and thus often used as a marker of lipid oxidation (Fritsch and Gale 1977, Frankel et al. 1989). Still, it is clear, that neither hexanal nor any other volatile lipid oxidation product is solely responsible for the perceived rancidity. Rather, flavors such as paint- or cardboard-like odor associated with the rancidity are apparently caused by a combination of different volatile carbonyl compounds (Heydanek and McGorrin 1981, Zhou et al. 1999, Heiniö et al. 2002). These compounds are reported also in rancid oat products in which their concentration in headspace of cereal sample increases approximately 2 to 100 fold during storage (Sjövall et al. 2000, Heiniö et al. 2002).

The consequences of the hydrolysis of triacylglycerols to free fatty acids and partially es-

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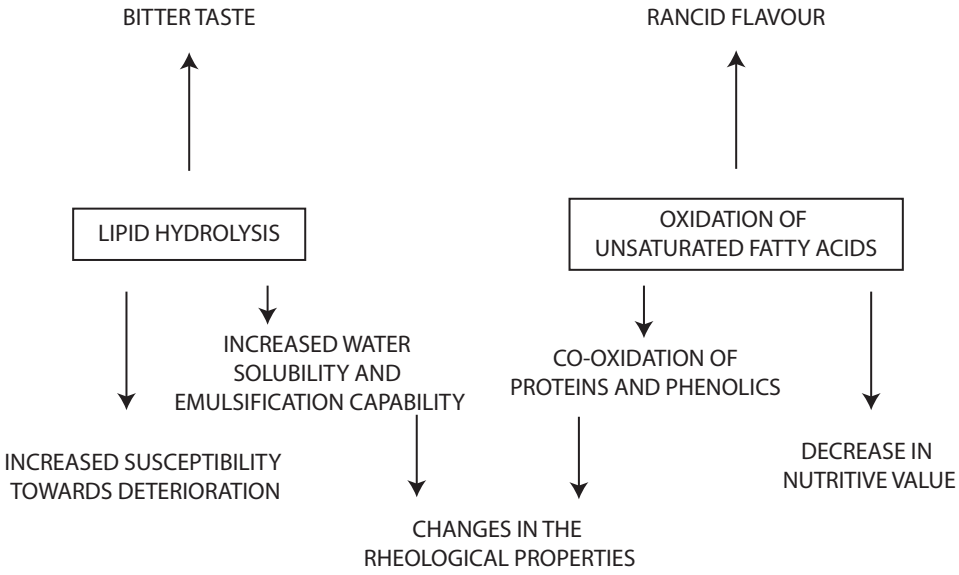

Fig. 4. Lipid reactions causing sensory and rheological changes in cereals.

terified glycerols are reflected both on changes in technical properties and on changes in perceived sensory properties. The prior dogma has been that the hydrolysis of acylglycerols renders the unesterified fatty acids moieties susceptible towards oxidation and thus increases the risk for rancidity.

The free fatty acids in cereals formed via hydrolysis have such long carbon chains that they are virtually non-volatile. The bitter taste of free unsaturated fatty acids, mainly linoleic and linolenic acids, has been observed in the aqueous emulsions at concentrations above 0.7 and 0.1 mg g^{-1} respectively (Stephan and Steinhart 2000). In dry oat material, in which extensive lipid hydrolysis has occurred, the concentrations of these acids is ca. 10 and 0.5 mg g^{-1} respectively (Sippola 2002). However, the bitter taste in such oat is suggested to be due to the presence of long chain hydroxyacids rather than to free fatty acids (Biermann et al. 1980). Biermann et al. (1980) also postulated that the bitter taste associated with non-heat treated oat products results from the formation of a hydroxygroup in the carbon chain of monoglyceridelinoleate. However, the hydrolysis of neutral storage lipids is well characterised in the scientific literature, and it appears that the hydrolysis proceeds rapidly to glycerol and free fatty acids. The accumulation of partially hydrolyzed triglycerols, such as monoglyceridelinoleate has not been observed (Liukkonen et al. 1992). One possibility is that the hydroxy fatty acid is formed while the fatty acid is still acylated to glycerol and that the formed hydroxyacylglycerol is discriminated by oat lipase and thus accumulates into the monoglyceride pool.

Prevention of unwanted lipid reactions during processing and storage of oat products

The hydrolysis reaction of acylglycerols can be very rapid once the oat is milled, and enzyme active oat products develop a characteristic bitter taste within weeks or months after milling.

Conventionally this reaction is prevented by inactivating the enzyme activities either from whole kernels or from the product obtained shortly after milling. The enzyme inactivation is most easily achieved by moist heat. If this enzyme inactivation is adequate, then oat can be processed even by aqueous processes without the development of bitterness.

However, the enzyme inactivation posses a risk, that it will promote the non-enzymatic oxidation of unsaturated fatty acids during subsequent storage of oat product. Compared to the bitter taste associated with enzyme activated oat products, the consequences of non-enzymatic oxidation are perceived as rancid flavor. It appears that the development of rancidity is dependent on the severity of heat treatment (Lehtinen et al. 2003). Thus an optimum enzyme inactivation scheme should enable the inactivation of lipolytic enzyme and yet simultaneously prevail the endogenous resistance towards oxidation. This requires an effective control over severity of heat treatment. Extrusion seems to be promising in this respect, due to the rapid heat transfer, that enables the strict control over the intensity of heat treatment.

One strategy to reduce the risk for lipid related storage problems is to produce products with lower lipid content than normal oat products. This can be achieved by choosing oat varieties with lower lipid content or by removing part of the lipids by extraction process. However, the effect of extraction process on the other functional properties of oat is not clear (Hoover et al. 1994).

Conclusions

The highly valuable nutritional properties of oat flour makes it an interesting alternative component for various food products. However, the limited storage stability can reduce the usability of oat products. To ensure the sufficient shelf life, the lipid reactions during and after oat processing must be minimized. This can be achieved by inactivating endogenous lipid degrading enzymes and by avoiding oxidative processing steps such as excessive heating. Also the packing material of product, especially the permeability for UV-radiation, moisture and oxygen, can have a huge impact on the storage stability.

Two different kind of deterioration that can be linked to lipid reactions are typical for oat products: 1) bitter, astringent, taste that occurs after enzymatic hydrolysis reactions and 2) rancid, paint-a-like, flavor that results from non-enzymatic oxidation. Separately these reactions are relatively easy to control, but often the actions taken to prevent the other, may actually promote the other. For example if oat kernels are heated excessively in order to ensure comprehensive inactivation of lipase, the heating can instead promote unwanted oxidation reactions. However, by implementing processing steps that are easily monitored and that can be effectively controlled, it is possible to produce oat products with similar stability compared to corresponding products from other cereals. Extrusion is an attractive solution for enzyme inactivation, as the heat exchange is fast and easily controlled.

Acknowledgment. This review is partly based on the author's academic thesis "Reactivity of lipids during cereal processing" available online at http://lib.hut.fi/Diss/2003/isbn9512265575/.

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SELOSTUS

Rasvojen reaktiot prosessoiduissa kauratuotteissa

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Perinteisten kauratuotteiden valmistuksessa säilyvyyttä rajoittavia rasvojen reaktioita on pyritty hallitsemaan kokemuksiin perustuen. Prosessointitapojen monipuolistuessa ja uusien tuotteiden ilmestyessä markkinoille perinteisen prosessiosaamisen rinnalle tarvitaan uutta tietoa ei-toivottujen reaktioiden mekanismeista ja niihin vaikuttavista tekijöistä sekä keinoista, joilla näitä reaktioita voidaan hallita. Tiedon tarve korostuu markkinoiden kehityttyä maailmanlaajuiseksi samalla kun tiukentuva lainsäädäntö ja muuttuvat kulutustottumukset asettavat kauratuotteiden säilyvyydelle aikaisempaa huomattavasti suurempia vaatimuksia.

Kauran rasvojen aiheuttamat aistittavat ongelmat ilmenevät hyvin monimuotoisesti. Niiden primäärisenä aiheuttajana voidaan kuitenkin pitää kahta rasvojen perusreaktiota, esterisidoksen hydrolyysiä ja tyydyttymättömien rasvahappoketjujen hapettumista. Edellisen tunnusmerkkinä pidetään kitkerää, polttavaa makua, kun taas jälkimmäinen on tunnistettavissa eltaantuneena, maalimaisena hajuna. Näiden reaktioiden yhteisvaikutuksena kauran aistittavat ongelmat voivat kuitenkin esiintyä hyvin monimuotoisena. Laadukkaaseen kauran prosessointiin tulee siten kuulua rasvojen hydrolyysin ja hapettumisen esto sekä tuotteiden formulointi siten, että edellytykset näille reaktioille ovat mahdollisimman vähäiset. Tässä katsauksessa keskitytään rasvojen reaktioihin prosessoiduissa kauratuotteissa, ja käydään läpi prosessointiin liittyviä tekijöitä, jotka ovat kriittisiä kauratuotteiden säilyvyyden kannalta.