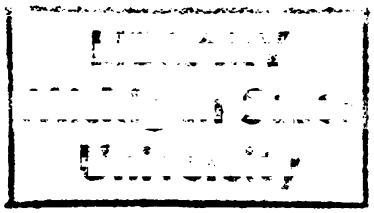

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Elizabeth Angeline Kumor

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James Dawgray
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THE CHARACTERIZATION AND STABILITY OF THE LIPIDS IN OAT CEREAL

By

Elizabeth Angeline Kumor

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ABSTRACT

THE CHARACTERIZATION AND STABILITY OF THE LIPIDS IN OAT CEREAL

By

Elizabeth Angeline Kumor

The lipid composition of oat cereal and the effect of the addition of mixed tocopherols on the stability of oat cereal during storage was determined. Oat lipid extract contained 80.1% neutral lipid, 11.5% glycolipid and 8.4% phospholipid. Eight compounds were observed in the nonpolar lipid class, while 18 compounds were present in the polar lipid class. The major fatty acids in oat were linoleic, oleic and palmitic acids. In the non-saponifiable fraction, β-sitosterol was the major phytosterol identified: α-tocopherol was the major tocol. Co-elution of both α-tocopherol and cholesterol hindered the determination of actual values of both of these compounds.

Hexanal concentration, TBARS and fatty acid profile were determined as measures of lipid stability in control and tocopherol-treated oat cereals held at 21 and 40°C for 9 and 24 weeks, respectively. No significant differences ($p<0.05$) were noted between treatments at the respective temperatures for each of the parameters measured.

ACKNOWLEDGEMENTS

The Author wishes to extend a warm, full embrace of gratitude to all of those she has met on her course toward this achievement. Each one of them , however long or brief the encounter, has contributed to her personal, as well as professional, development. Thank you all.

TABLE OF CONTENTS

LIST OF TABLES

Table | Page

LIST OF FIGURES

INTRODUCTION

Oat grain, although a good source of quality protein, is not incorporated into products as extensively as either wheat or maize. This is due to the higher concentration of lipid in oat in comparison to other cereal grains. The fatty acid composition of cereal lipids, including oat, is highly unsaturated, and this contributes to the susceptibility of oat products to rancidity development.

Oat contains compounds possessing antioxidative properties including sterols (White and Armstrong, 1986), tocopherols (Hammond, 1983) and hydroxycinnamic acid derivatives (Daniels and Martin, 1941). Although oat has this inherent antioxidative nature, it is still highly susceptible to lipid oxidation. A better understanding of the total composition of the lipid in oat could enable introduction of useful measures to increase the shelf-life of oat products.

The current study was conducted in two phases. The first phase was dedicated to the complete analysis of the oat lipid extract to better understand the mechanism of lipid oxidation in oat and oat products. The second objective of the study was to determine the effect of the addition of mixed tocopherols to oat cereal on the oxidative stability of the cereal during storage.

REVIEW OF LITERATURE

The lipid content of oats is among the highest of the cereal grains. Frey and Hammond (1975) analyzed 445 oat cultivars and collections, determined an oil range of 2.0 - 11.0%, and postulated a lipid content of 16% would need to be achieved for oat grains to be a profitable source of oil. Analysis of approximately 1200 oat kernel samples by Hutchinson and Martin (1955) revealed oil contents ranging from 4.4 - 11.2%. The variation among these samples was attributed to cultivar differences. Compared to barley and wheat, (average lipid content, 2.7%), oat exhibits a much greater genetic diversity (2.3 - 7.0% lipid). The total fatty acid content in oat can vary from that of barley and wheat to values as three times as high (Welch, 1975). Rye, maize, sorghum and triticale contain 3.6, 5.8, 3.3 and 2.4% lipid, respectively (Price and Parsons, 1975). The lipid constituents of oat grain play an important role in the development of rancidity in oat cereal.

Lipid Composition of Oat

Fatty Acid Content of Total Lipid

The fatty acid profiles of cereal grains are similar and consist mainly of palmitic ($C_{16:0}$), oleic ($C_{18:1}$), and linoleic ($C_{18:2}$) acids in varying proportions (Morrison, 1983). Oat contains approximately equal amounts of $C_{18:1}$

and $C_{18:2}$ fatty acids, while most other cereals display a greater portion of $C_{18:2}$ (Price and Parsons, 1975). Youngs and Puskulcu (1976) analyzed 15 cultivars of oat groats and observed a trend toward a higher percent unsaturation in samples which contained a greater concentration of lipid than in those containing less lipid. They also observed an increase in $C_{18:1}$, a decrease in $C_{18:2}$ and $C_{16:0}$, and an overall decrease in total saturated fatty acids with subsequent increase in total lipid content. de la Roche et al. (1977) observed similar trends and cited a negative correlation between total lipid and $C_{16:0}$ and $C_{18:2}$ contents, and a positive correlation with $C_{18:1}$. No relationship was cited between increased lipid content and free fatty acid (FFA) content, though as lipid content increased a subsequent proportional increase in FFA would be expected.

The fatty acid composition of several cereal grains is shown in Table 1. Stearic ($C_{18:0}$) and linolenic ($C_{18:3}$) acids are minor components in these grains, while myristic ($C_{14:0}$) and palmitoleic ($C_{16:1}$) acids are present in trace amounts. Sahasrabudhe (1979) identified the various long chain fatty acids in oats, including $C_{20:1}$, $C_{20:4}$, $C_{20:5}$, $C_{22:0}$ and $C_{22:1}$ which comprise 0.1 - 3.2% of the total lipid fraction. Data in Table 1 also better illustrate the discrepancy in the relative proportions of $C_{18:1}$ and $C_{18:2}$ found in oat and other cereal grains.

Table 1. Fatty acid composition[1] of seven cereal grains.

	Fatty acid[2]						
Grain	$C_{14:0}$	$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
Barley	0.5	20.8	0.2	1.0	17.8	55.3	4.4
Corn	0.4	13.4	0.2	1.9	24.0	59.3	0.8
Oats	0.7	18.0	0.1	1.2	36.3	42.0	1.6
Rye	0.3	15.0	0.4	0.8	19.2	57.6	6.8
Sorghum	0.2	19.5	0.8	1.7	28.1	44.7	5.0
Triticale	0.1	16.6	0.2	0.6	13.7	63.8	5.0
Wheat	0.2	17.2	0.3	1.4	20.4	57.7	2.8

[1]From Price and Parsons (1975).
[2]Percent by weight of total lipid.

Price and Parsons (1979) reviewed the distribution of the fatty acids in oat grain fractions. The hull, which comprises approximately 10% by weight of the whole grain, contains greater amounts of $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{18:0}$ and $C_{18:3}$, and less $C_{18:1}$ and $C_{18:2}$ fatty acids compared to the embryonic axis and the bran-endosperm. Oat flakes and flour are processed from oat groat (dehulled grain) which includes the bran-endosperm portion that contains an appreciably higher concentration of lipid in comparison to similar portions from other cereal grains. Hence, the oil content in oat is primarily determined by the amount of kernel present in the grain because approximately 90% of the oil is located in this fraction (Hutchinson and Martin, 1955).

Composition and Distribution of Lipid Classes in Oat Grain

Aylward and Showler (1962) isolated an acetone-insoluble phospholipid (PL) fraction from oat which comprised 10.2% of the total lipid material. Phospholipids that were present included phosphatidylcholine (PC), phosphatidylethanolamine (PE), and a serine-containing phosphatide which, most likely, was phosphatidylserine (PS). Similar results were obtained by Price and Parsons (1975) who determined that the PL fraction of oats comprised 10.1% of the total lipid extract. The separation by Price and Parsons (1975) of the three classes - neutral lipid (NL), glycolipid (GL), and PL - was accomplished by silicic acid column chromatography employing appropriate solvents to elute specific classes of lipid. de la Roche et al. (1977) analyzed nine oat strains of Avena sativa L. by thin layer chromatography and determined that the phospholipid content was strain-dependent and ranged from 6.8 - 22.2%. The phospholipid content was determined by a phosphorus assay.

Sahasrabudhe (1979) separated oat lipid extracts from six strains into various classes and obtained average values of 71.9% NL, 8.3% GL and 19.7% PL. Price and Parsons (1975) had previously reported similar findings, although slight differences in quantities of the polar lipids were observed (17.0% GL and 10.1% PL). These values were determined for the oat cultivar, 'Chief'. In a study analyzing the acyl lipid composition of nine oat strains, de la Roche et al. (1977) observed a significant relationship between the

proportions of two acyl lipid classes and the total lipid content; an increase in proportion of triacylglycerol content and concomitant decrease in PL was associated with an increase in total lipid content.

The distribution of the lipid classes varies within the fractions of the grain. The hull and bran-endosperm contain less NL than the embryonic axis, while the PL concentration is greatest in the bran-endosperm fraction (Price and Parsons, 1979). Thus, the lipid contained in the hull would be expected to exhibit greater saturation than other fractions.

Analysis of the fatty acid composition of the NL, GL and PL classes indicates a greater degree of unsaturation in the GL and PL classes than that found in the NL class (Aylward and Showler, 1962; de la Roche et al.,1977; Price and Parsons, 1979; Sahasrabudhe, 1979). This greater degree of unsaturation is due to a greater proportion of $C_{18:2}$ in the polar lipids than in the nonpolar lipids. The polar lipid class also contains a greater concentration of $C_{16:0}$ than the nonpolar class.

Table 2 contains the fatty acid composition of the 3 lipid classes. Of particular interest are the differences associated with the PL and NL fractions. There is a substantial proportion of $C_{16:0}$ and $C_{18:2}$ fatty acids present in the PL class in some strains of oat. These strains can contain as much as 99% more $C_{16:0}$ and 30% more

$C_{18:2}$ fatty acids in the PL class than in the NL class (de la Roche et al., 1977; Price and Parsons, 1979).

Table 2. Fatty acid distribution[1] in major lipid classes in oat.

Class[2]	Fatty acids(mole percent)							
	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:x}$[3]	$C_{22:x}$[4]
TG	1.5	14.8	2.2	43.3	35.0	2.0	0.5	0.1
GL	4.3	22.1	4.4	25.1	36.2	4.0	3.0	1.2
PL	2.2	28.1	4.2	21.3	38.1	2.8	2.0	0.3

[1] Adapted from Sahasrabudhe (1979)
[2] TG, triacylglycerol; GL, glyclolipid; PL, phospholipid.
[3] Includes $C_{20:1}$ to $C_{20:5}$.
[4] Includes $C_{22:0}$, $C_{22:1}$ and $C_{24:0}$.

de la Roche et al. (1977) cited a diversity in fatty acid values of oat lipid classes of nine oat samples which was attributed to cultivar differences. An equally important contributor to such diversity is the method of solvent extraction of the lipid. In a comparison of seven different solvent systems, Sahasrabudhe (1979) cited lipid contents ranging from 5.6 - 8.8% for the 'Hinoat'cultivar of oat. Increasing the polarity of the solvent systems resulted in an increase in the polar lipid fractions with subsequent decrease in NL fractions.

Grain contains bound and unbound lipid (Morrison, 1978). Bound lipid is characterized by association with starch in which it is incorporated into a lipid-amylose inclusion complex that inhibits extractability of the lipids

affiliated with these moieties. These lipids are usually polar in nature. The hydrophobic interior of the helical amylose structure can accommodate lipophilic substances of suitable dimension, such as lysoPC (Krog, 1971).

Due to the tight binding of the acyl chain in the amylose core, Morrison (1978) concluded that dry organic solvents do not sufficiently remove the lipids, and repeated extractions with hot water-saturated butanol is necessary to effect a successful removal of lipids. Sahasrabudhe (1979) included chloroform:methanol (2:1) and water-saturated butanol in a comparison of solvent systems for the extraction of oat lipid. He observed a slight difference in total lipid recovery, 6.3 versus 6.9%, and a greater phospholipid content in the chloroform:methanol extracts than in the water-saturated butanol extracts. All other components were also in greater concentration in the chloroform:methanol extract, which appeared to be a sufficient system for extraction of bound lipid.

Constituents of the Lipid Classes

Triacylglycerols constitute from 37.5 - 85.8% of the total lipid extract and are the primary components in the NL class (de la Roche, 1977; Youngs, 1977; Sahasrabudhe, 1979). Other nonpolar compounds associated with the NL class are FFAs, partial glycerols, free sterols and sterol esters, which comprise from 5.6 - 18.0% of the total lipid extract. The abundance of FFA in an oat sample is dependent upon the extent of lipase activity in the grain and is influenced by

moisture content, physical damage, and temperature (Hutchinson and Martin, 1955; Welch, 1977). To minimize this enzymic activity, the grain is dried to less than 10% moisture and held at moderate storage temperatures. Storage and good handling practices designed to maintain grain integrity also deter lipolytic activity in the grain (Galliard, 1983b).

Pan and Hammond (1983) examined the stereospecificity of fatty acids in the triacylglycerols of Avena sativa and Avena sterilis strains. They observed that the saturated fatty acids $C_{16:0}$ and $C_{18:0}$ were concentrated in the Sn-1- and Sn-3-positions, while the unsaturated fatty acids $C_{18:1}$ and $C_{18:2}$ occurred in greater proportion at the Sn-2-position. The occurrence of $C_{18:3}$ in all three positions was quite homogeneous, contrary to what would be expected from current distribution theories (Dugan, 1976; Nawar, 1985).

The major components of the GL class are digalactosyldiacylglycerol (DGDG) and monogalactosyl-diacylglycerol (MGDG) which constitute approximately 41 and 19% of this class, respectively (Sahasrabudhe, 1979). Monogalactosylacylglycerol, digalactosylacylglycerol and sterylglucosides (SG) comprise the remaining GLs that have been identified in oats.

Phosphatidylcholine (PC) is the major phospholipid in oat and has been identified in several other grains including barley (Shin and Gray, 1983) and wheat (MacMurray

and Morrison, 1970). Phosphatidylethanolamine (PE), lysoPE and lysoPC, as well as PC, comprise the majority of components present in the PL class. Other compounds identified include phosphatidic acid (PA), phosphatidylinositol (PI), phosphatidylglycerol (PG), PS, and lysoPS. Bomstein (1965) confirmed the presence of N-acyl derivatives of PE and lysoPE in wheat. Dawson et al. (1969) identified similar compounds in oat, as well as in soy, pea seed, beans and stick beans. These derivatives have a hydrogen replaced at the nitrogen of the ethanolamine moiety with a hydrocarbon chain, thereby decreasing the polarity. Sahasrabudhe (1979), using thin layer chromatography to separate polar compounds in oat lipid extract, observed two spots near the solvent front when plates were developed in a nonpolar solvent. These spots were identified as acylPE and acyllysoPE in the PL class of the 'Hinoat' strain of oat. This same sample also contained acyl derivatives of SG and MGDG.

Rancidity in Cereals

Lipid-containing foods have the potential to develop undesirable flavor and odor characteristics through decomposition of the lipid components (Frankel, 1982). Other chemical changes associated with the aging process, such as proteolysis may also occur. Susceptibility to deterioration is not solely dependent on the concentration of lipid present, but rather this susceptibility is affected to a greater extent by the fatty acid composition. More

importantly, the degree of unsaturation will determine the rate of deterioration. The composition of the unsaturated fatty acids in cereal grains, including oat, has been well established (Price and Parsons, 1975; Morrison, 1978). The high concentration of unsaturated fatty acids in cereal grains predisposes these crops to rancidity development. Flavor deterioration is associated with changes that result from the reaction of lipid components with atmospheric oxygen, i.e., oxidative rancidity. Deterioration can also occur through hydrolytic processes which enzymatically or microbiologically induce rancidity.

Hydrolytic Rancidity

The development of hydrolytic rancidity in foods generally involves degradation of lipids through the action of a lipase which results in the production of FFAs (Dugan, 1976). The FFAs are then capable of involvement in the oxidative chain reaction to be discussed later in the text. The lipase that is present in oat is potentially more active than the lipases found in other cereal grains (Widhe and Onselius, 1949). Thus, Galliard (1983a) emphasized that caution must be taken to reduce the possibility of residual enzymic activity in an oat product. Damage resulting from the dehulling of oat prior to utilization for consumption can induce lipase activity (Galliard, 1983a). Also, the potential for enzyme activity in the damaged oat is enhanced by sufficient moisture content and temperature (Hutchinson and Martin, 1952). Appropriate kilning processes should

inactivate the enzyme, rendering it incapable of producing substantial levels of FFA which contribute to the development of soapy or bitter off-flavors in the cereal products (Matlashewski, 1982). Oat flakes are less susceptible to residual lipase activity due to an additional heat treatment during processing (Hutchinson and Martin, 1952). Nevertheless, the possibility remains that lipase may contribute to off-odor development should there be inadequate control of processing temperatures to inactivate this enzyme.

Lipase attacks the ester linkages of tri-, di-, and in some cases, monoacylglycerol molecules, producing FFAs which are then highly reactive substrates for autoxidation (Brockerhoff and Jensen, 1974; Galliard, 1983a). Free fatty acids produced in the seeds of plants are metabolized for energy. Matlashewski et al. (1982) compared the lipase activity of four cereal grains that were both germinated and ungerminated. They determined oat lipase to be substantially more active than the lipases in wheat, barley or rye in both stages of germination. Sahasrabudhe (1982) determined that complete oat grain fracture was essential for lipase to act due to localization of the enzyme in the aleurone layer. Lipid is concentrated in the sub-aleurone layer of the oat grain and less than 10% of the lipase activity was detected in the endosperm. A majority of the lipase activity was detected outside the endosperm as would be expected due to this greater concentration of lipase in

the aleurone layer. Martin and Peers (1953) observed that purified oat lipase cleaved only one butyric radical from tributyrin, indicating specificity, while no hydrolysis of mono- and dibutyrin was achieved.

It should be noted that the contribution of lipase activity toward the development of rancidity in oat cereal is not a major concern as appropriate processing techniques will inactivate the enzyme. However, should there be some residual activity, the FFAs produced increase the susceptibility of the lipids to autoxidative reactions.

Oxidative Rancidity

The majority of the deteriorative products of lipids in oat cereal arise from the oxidation of the unsaturated fatty acids. Post-processing conditions contribute to the rate by which oxidation will occur. Autoxidation has been discussed extensively (Dugan, 1976; Nawar, 1985; Paquette et al., 1985a,b). Essentially, the scheme involves a free radical chain mechanism influenced by the concentration of oxygen, temperature, light and catalysts, particularly metals capable of existing in two valence states (Dugan, 1976). The reaction is defined in three steps: (1) initiation, when there is the formation of free radicals; (2) propagation, when there is the accumulation of hydroperoxides plus additional free radical formation; and (3) termination, which involves the formation of non-radical products. The reaction sequence of the three stages is as follows:

Initiation	$RH \longrightarrow R^{\cdot} + H^{\cdot}$
Propagation	$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$
	$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$
Termination	$R^{\cdot} + R^{\cdot} \longrightarrow RR$
	$ROO^{\cdot} + ROO^{\cdot} \longrightarrow ROOR + O_2$
	$R^{\cdot} + ROO^{\cdot} \longrightarrow ROOR$
	$2RO^{\cdot} + 2ROO^{\cdot} \longrightarrow 2ROOR + O_2$

Termination products undergo further decomposition to produce a variety of short chain aldehydes, alcohols and ketones, or they may complex to form higher molecular weight polymers and other compounds (Dugan, 1976; Frankel, 1984; Nawar, 1985).

The initiation stage, where a hydrogen is abstracted from an unsaturated hydrocarbon, is not fully understood. The hydrogen atom is quite labile and easily removed from the carbon adjacent to the double bond forming a relatively stable allylic free radical. This free radical is then available for reaction with oxygen, and subsequently hydrogen, to form a conjugated hydroperoxide which may shift from a cis to trans configuration. Dependent upon the subject of oxidation, i.e. $C_{18:1}$, $C_{18:2}$, $C_{18:3}$, specific postional hydroperoxy isomers result (Wu et al.,1977). The rate of oxidation is also dictated by the substrate (Nawar, 1985). Methyl linolenate is oxidized more quickly than methyl linoleate which in turn is oxidized more quickly than methyl oleate. This same trend is reflected in the length of the induction period: the greater the degree of unsaturation, the shorter the induction period. By the

initial stage of propagation, flavor deterioration is recognized.

An alternative mechanism of lipid oxidation occurs through the direct addition of singlet oxygen to the double bond producing a hydroperoxy radical which is then involved in propagation. Singlet oxygen is generated from the transfer of energy from an excited (triplet state) sensitizer such as chlorophyll, to triplet oxygen (Rawls and Van Santen, 1970; Carlsson, 1976). This mechanism requires ultraviolet light to proceed. Both conjugated and non-conjugated positional isomers are observed as products of singlet oxygen-induced oxidation (Terao and Matsushita, 1977).

Hydroperoxides may also be formed by the action of lipoxygenase, if it is present in the food system. Enzyme activity requires the availability of a cis, cis 1,4-pentadiene system and involves the complexation of a substrate such as linolenate, and the enzyme which has oxygen adsorbed to it (Dolev et al., 1967). Lipoxygenase holds the reactant and substrate in proximity, thereby contributing to the formation of hydroperoxides. The enzyme has a greater affinity for FFAs than for triacylglycerols (Galliard, 1983b). There is much substrate specificity in this reaction and oat lipoxygenase yields almost exclusively 9-hydroperoxido-cis,10 trans,12-octadecadienoic acid on oxidation of linoleic acid (Galliard, 1983a). These hydroperoxides are susceptible to decomposition in a manner

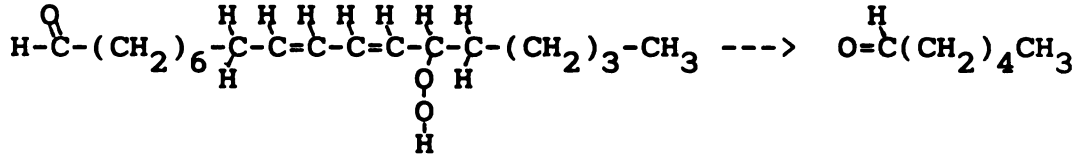
similar to hydroperoxides which have been formed by the autoxidative process (Gardner, 1983).

Secondary Oxidation Products and their Analysis

Hexanal

Hydroperoxides formed from lipid oxidation are labile intermediates and undergo various degradative processes to form a range of products, some of which are represented in Figure 1.

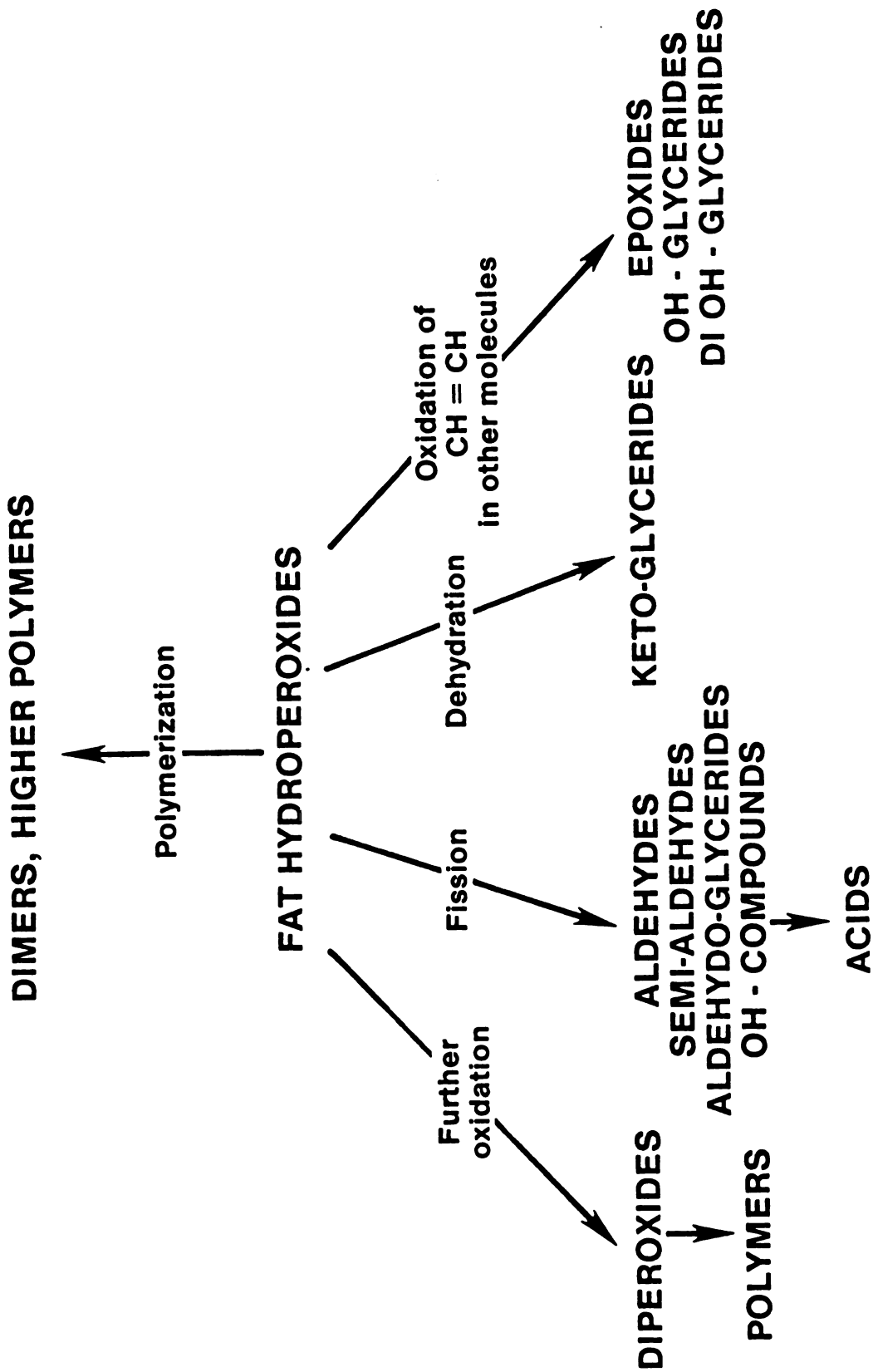
Hexanal is one of the major secondary oxidation products of linoleic acid (Frankel et al., 1981). Since linoleic and oleic acids comprise over 80% of the fatty acids in oat, the accumulation of hexanal has been used as an indicator of the degree of rancidity in oat cereal (Fritsch and Gale, 1977). It is derived from the 13-hydroperoxide of linoleate as follows (Dugan, 1976):



13-hydroperoxide hexanal

Extremely low concentration of hexanal is sufficient to render a product undesirable. Fritsch and Gale (1977) employed direct analysis of headspace volatiles to determine the accumulation of hexanal in oat, corn, wheat and mixed cereals stored at 37^{o}C over a period of 12 weeks. Their results indicated that a product which contained greater than 5 mg/kg of hexanal was considered rancid. Heydanek and McGorrin (1981b) reported the presence of hexanal, as well

Figure 1. Pathways for the decomposition of hydroperoxides.


DIMERS, HIGHER POLYMERS
Polymerization
FAT HYDROPEROXIDES
Oxidation of
CH = CH
in other molecules
EPOXIDES
OH - GLYCERIDES
DI OH - GLYCERIDES
Dehydration
KETO-GLYCERIDES
Fission
ALDEHYDES
SEMI-ALDEHYDES
ALDEHYDO-GLYCERIDES
OH - COMPOUNDS
ACIDS
Further
oxidation
DIPEROXIDES
POLYMERS

as pentanal and 2,4-decadienal in rancid oat groats, and concluded that these components would be pertinent indicators of rancidity. These researchers (1980) had previously determined the presence of these compounds in cooked oatmeal of acceptable quality, thereby suggesting that a change in concentrataion of these volatiles in oat may be of greater significance than their mere presence.

Analysis of headspace volatiles as a measure of lipid degradation is now widely accepted (Min and Kim, 1985; Reineccius, 1985). Scholz and Ptak (1966) employed a direct injection technique in the analysis of cottonseed oil volatiles. This method involved application of the sample directly onto the gas chromatograph without prior isolation of volatiles. However, continuing use of direct sampling injection contributed to column decay, and thus, alternate methods which concentrate volatiles prior to analysis were developed.

Dupuy et al. (1971) modified the direct injection method by packing the GC glass injection port liner with oil-coated glass wool. The volatiles were eluted by the carrier gas of the chromatograph and swept onto the column for analysis. This method maintained segregation of the sample and column, thereby extending the life of the column. This basic method has been modified for the analysis of products such as vegetable oils (Jackson and Giacherio, 1977; Min, 1981), mayonnaise (Min and Tickner, 1982) and cereal products (Legendre et al., 1978).

Sampling the headspace vapors can also be used in the analysis of volatiles. Although this method would appear quite adequate, the components in the headspace vapor do not exist in sufficient concentration. Hence, only major peaks are identified (Reineccius, 1985).

Headspace concentration techniques include the use of porous polymer traps such as Tenax GC, and have been successfully used in the analysis of headspace volatiles of carrot (Simon et al., 1980), cooked beef (Galt and MacLeod, 1984), oat (Heydanek and McGorinn, 1981a,b), and vegetable oils (Min and Kim, 1985). In comparison to the continuous solvent extraction method described by Likens and Nickerson (1966), entrapment of volatiles onto polymer supports is less time consuming and less costly.

Appropriate precautions concerning the type of polymer to employ, mode of elution of the adsorbed volatiles, and artifactual formation of flavor compounds must be considered. Jennings and Filsoof (1977) compared headspace sampling techniques, distillation extractions and porous polymer isolates for volatile analyses of pork, Zinfandel wine, cantaloupe, peaches, gasoline and tobacco. Results varied depending upon the product, but both Porapak Q and Tenax GC provided adequate profiles of the volatile components. The temperatures employed for regeneration of, concentration on, and desorption from these two polymers should not induce the development of artifacts which may be incorrectly identified as constituents of the product.

Lewis and Williams (1980) observed compounds such as benzaldehyde, acetophenone, isopropylbenzyl alcohol, phenol and furans when these polymers were held above their normal operating temperatures. These compounds were eluted from the polymer traps after regeneration of the traps, and prior to their use for the collection of volatiles.

Malonaldehyde

Another compound which has been used as an indicator of the degree of lipid oxidation in foods is malonaldehyde. This compound is generated by the degradation of polyenes, particularly trienoic and tetraenoic fatty acids (Dahle et al., 1962). It may also be derived from further oxidation of 2,4-decadienal, a secondary oxidation product of linoleate (Dugan, 1976). Malonaldehyde is a very reactive dicarbonyl compound and this reactivity is used in its determination. Malonaldehyde (1 mole) can react with two moles of 2-thiobarbituric acid (TBA), resulting in the formation of a pink chromagen. This reaction has long been employed as a measure of the degree of lipid oxidation, particluarly in meat systems (Traladgis et al., 1960). Absorbance of the pink complex is monitored at 532nm and is mormally converted to ug malonaldehdye/g sample by an appropriate conversion factor. Since the initial development of the procedure, a host of researchers have supported, rejected or altered the theory behind the mechanism (Kwon et al., 1965; Ho and Brown, 1966; Marcuse and Johansson, 1973; Pryor et al., 1976; Melton, 1983).

The most prominent observation is the evidence that TBA can react with other food components besides malonaldehyde to produce complexes which also have characteristic absorption at 532nm. These constituents have been identified as 2,4-alkadienals and, to a lesser degree, 2-alkenals (Marcuse and Johansson,1973). It may be more accurate to define compounds which produce this pink chromagen as thiobarbituric acid-reactive substances (TBARS) rather than malonaldehyde exclusively. However, the method is still applicable to monitor rancidity development as these substances are also products of lipid oxidation (Melton, 1983). Reactivity of malonaldehyde with various food constituents also contributes to the empirical nature of this methodology (Kwon et al., 1965; Labuza, 1971; Melton, 1983).

The TBA test is widely applied, and in tandem with measurement of hexanal development, can be considered an adequate measure of oxidative rancidity.

Antioxidants in Oat

Oat flour has displayed antioxidative capabilities when sprinkled over bacon and potato chips, and when added to fat, margarine and mayonnaise (Supova et al., 1959). Oat contains components which may be responsible for this characteristic. Three potential sources are phytosterols, tocopherols and hydroxycinnamic acid derivatives .

Phytosterols

Cereal grains and cereal products contain a wide variety of sterols, the most abundant of which is β-sitosterol (Idler et al., 1952). These workers reported that β-sitosterol constitutes 56.0% of the sterol fraction, and also identified two other sterols in oat through the application of column chromatographic and infrared spectrophotometric techniques. These were Δ^5- and Δ^7-stigmastadiene-3β-ol. The second major sterol in oat is Δ^5-avenasterol, rather than campesterol which is characteristic of most cereal grains (Barnes, 1983). The three phytosterols β- sitosterol, Δ^5-avenasterol, and Δ^7-avenasterol comprise 73.7% of the sterols (Knights, 1968).

Table 3. Sterol composition[1] of oat grain A. sativa.

Sterol	Percent composition
Sitosterol	39.0
Campesterol	6.4
Stigmasterol	5.0
Δ^5-Avenasterol	21.2
Δ^7-Avenasterol	13.5
Cholesterol	5.8
Δ^7-stigmasten-3β-ol	6.4
Δ^7-cholesten-3β-ol	2.8

[1]Adapted from Knights (1968).

Knights and Laurie (1967) identified a total of fourteen sterols in oat seed. Table 3 summarizes the sterol composition of oat grain.

Cycloartenol is the first cyclic product formed from squalene oxide in phytosterol biosynthesis, and serves as a precursor to many other sterols (Barnes, 1983). The biosynthesis of the major phytosterols involves the modification of the side chain to produce 24-methylene sterols, such as campesterol (Goodwin, 1980). A second methylation of the side chain can alternately occur to form the 24-ethylidene group of sterols which includes Δ^7-avenasterol, Δ^5-avenasterol and β-sitosterol. This explains the presence of these sterols in oat.

There has been increased interest in Δ^5-avenasterol as it has been shown to display antioxidative properties at frying temperatures (Sims et al., 1972; Boskou and Morton, 1975; Boskou and Morton, 1976; Gordon and Magos, 1983). This characteristic has been attributed to the ethylidene side chain at C_{28} which contains unhindered allylic carbon atoms that are available to react with lipid free radicals (Gordon and Magos, 1983). Isomerization to the more stable allylic tertiary free radical follows. This process is responsible for interruption of the autoxidative processes. The relatively high concentration of Δ^5-avenasterol in oat indicates that this grain may be a potential source of antioxidative activity.

Tocopherols

Green et al. (1955) reported the presence of five tocopherols in oat oil - α-28%, γ-36%, δ-10%, ε-4% and λ-22%. The total tocol content was determined to be 0.61 mg/g of oat oil extract. These compounds were identified through application of paper chromatographic techniques which have subsequently been replaced by more sensitive measures such as high performance liquid chromatography and gas chromatography.

Herting and Drury (1969) observed up to a three fold variation in α-tocopherol levels in oat samples from the same lot of grain and determined that the α-tocopherol content was at least two times greater than α-tocotrienol in oat grain and oat products. These researchers postulated that the destruction of α-tocopherol in oat products is dependent upon the degree of processing of that product. Oat meal displayed no loss of α-tocopherol, whereas processing to oat flour resulted in up to 95% loss of this tocol.

Slover et al. (1969) analyzed oat seed and cited the presence of α-tocotrienol which was determined to be the most abundant tocol, as well as β-tocotrienol, α-tocopherol, and β-tocopherol. Chow et al. (1969) also determined α-tocotrienol to be the major tocol in oat lipid. Phronen et al. (1986) analyzed rolled oats and found the α-tocotrienol concentration to be over two times greater than the α-tocopherol concentration. These data do not agree with the

results of Herting and Drury (1969) who reported that α-tocopherol was the major tocol in oat. The discrepancy may be explained by the variation in procedures used for tocol determination. Variation may also be influenced by the cultivar of oat, the location of field, and the time of harvest (Herting and Drury, 1969).

Minor amounts of the γ and δ tocols in oat have been identified by Chow et al. (1969). Rao and Perkins (1972) observed the presence of the β- and γ-isomers, though they cited difficulty with the separation of these two compounds. Slover et al. (1983) were able to differentiate between the isomers through the application of gas chromatographic techniques and determined the tocol and sterol content of several vegetable oils.

Tocopherols exhibit antioxidative properties and have been shown to be effective in delaying oxidation in a variety of foods (Dugan, 1980). Cort (1974) showed the tocopherols to be more effective as antioxidants in animal fats than in vegetable oils. The antioxidative nature of the tocopherols is attributed to their phenolic structure. Lipid free radical formation is interrupted by the donation of a proton from the phenolic hydroxyl group of the tocopherol to the lipid radical. This reaction removes the lipid from the autoxidative pathway. Due to resonance delocalization, a relatively stable antioxidant radical is formed (Nawar, 1985).

The activity of tocopherol is concentration dependent, which concurrently is affected by the substrate, and to a certain extent, by the temperature (Dugan, 1980). Tocopherols have an extended alkyl chain which makes them highly miscible in lipid and contributes to their antioxidative effectiveness (Dziezak, 1986).

Established data concerning the order of effectiveness of α-, β-, γ- and δ-tocopherols as antioxidants have recently been challenged. Burton et al. (1983) determined the rate constants for the reactions of these tocopherol isomers with peroxyl radicals of either styrene or di-t-butyl ketone. The order of antioxidant activity proved to be the same as biological activity ($\alpha > \beta \geq \gamma > \delta$) which is contrary to the theory accepted previously (Lea and Ward, 1959). Positioning of the methyl group(s) on the aromatic ring determines the efficacy of the isomer to function as a primary antioxidant (Lea and Ward, 1959). It has been theorized that the greater the degree of methyl substitution present, the greater steric hindrance to lipid free radicals (Howard and Ingold, 1963). However, the recent data of Burton et al. (1983) suggest that the antioxidative property can be attributed to the stabilization of the unpaired electrons of the phenoxyl radical by the p-type lone pair of electrons on the ethereal oxygen. The resultant weaker O-H bond of the phenol leaves it more vulnerable to interactions with lipid free radicals. The ortho and para positioning of the methyl group on the phenol affects the stability of the

resulting phenoxyl radical and, therefore, influences the antioxidative capacity of the tocol (Burton et al., 1983).

Yamaoka et al. (1985) studied the antioxidative capacity of γ- and δ-tocotrienol in methyl linoleate. They concluded that the tocotrienols exhibited slightly greater antioxidative activity than their respective tocopherol isomers.

Hydroxycinnamic Acid Derivatives

Dahle and Nelson (1941) conducted studies to determine the fractions responsible for the antioxidative properties of oat and soy flour. Oat flour appeared to be more effective than soy flour when incorporated into a dehydrated milk fat system. A phospholipid fraction, as well as an alcohol extract were purported to be the most efficient antioxidative components. Later work by Daniels et al. (1963) elucidated the components responsible for this characteristic in oat. Compounds with phenolic properties were isolated and responded comparatively to propyl gallate and butylated hydroxyanisole (BHA) when antioxidative capacity was measured by an oxygen absorption apparatus. Subsequent studies by Daniels and co-workers (1967,1968) revealed the presence of 24 phenolic antioxidants in oats, of which caffeic acid-containing molecules displayed the greatest antioxidative activity. Those fractions which contained ferulic acid constituents also exhibited these same characteristics, although the potency was less intense. The capacity of these derivatives to function as

antioxidative substances is due to their phenolic nature, and, therefore, react as would the tocopherols, BHA or BHT (Daniels and Martin, 1967).

Materials and Methods

Materials

Oat Cereal

The oat cereal was processed by the Gerber Products Co., Fremont, MI as per their standard processing procedures. The oat flour used in cereal production was comprised of a blend of cultivars grown in the Mid-West.

Lipid Standards

All phospholipid, glycolipid, neutral lipid, fatty acid methyl ester and hexanal standards were obtained from Sigma Chemical Co., St. Louis, MO. N-Acyllysophosphatidyl-ethanolamine was synthesized according to Dawson et al. (1969) and involved acylation of lysophosphatidyl-ethanolamine at the amine group using triethylamine and stearoyl chloride (both purchased from Sigma Chemical Co.).

β-Sitosterol, stigmasterol, campesterol, cholestanol and cholesterol were purchased from Steraloids, Inc., Wilton, NH.

Tocopherol standards were donated by Gerber Products Co., while α-tocotrienol was kindly supplied by Hoffman LaRoche, Hutley, NJ. The 5,7-dimethyltocol used as an internal standard for non-saponifiable analysis was purchased from Supelco Inc., Bellefonte, PA.

Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMS) and silylation grade pyridine were purchased from Pierce Chemical Co., Rockford, IL.

All other reagents and chemicals used were analytical grade.

Chromatographic Materials and Chemicals

Silica G and H were purchased from Merck, Darmstadt, Germany. Silicic acid, 325 mesh, was obtained from Sigma Chemical Co.

Methods

Classification and Identification of Lipid Components

The initial phase of this study involved the separation of total lipid into neutral lipid, glycolipid and phospholipid classes. Each of these fractions was further analyzed to determine compositional profile as well as fatty acid content. Constituents of the phytosterol fraction in oat were also identified.

Extraction of Lipid

Lipid was extracted from oat cereal according to a modified version of the Bligh and Dyer (1959) procedure as described by Ostrander and Dugan(1961). A 100g portion of oat cereal was hydrated with 74ml of distilled water and blended for 2 minutes in a Waring blender. A 200ml volume of methanol was then added and the mixture blended for 5 minutes. Chloroform (100ml) was added and blended for 2 minutes. This was followed by the addition of another 100ml aliquot of chloroform and blended for 30 seconds. A 100ml

portion of distilled water was added to the mixture which was then blended for 10 seconds. The sample was filtered, re-extracted with 75ml of chloroform and re-filtered. The chloroform layer was collected and concentrated to 50 ml on a Buchi Rotovapor R rotary evaporator (Buchi Inc., Switzerland). Percent fat was determined from 1ml portions of the concentrate.

Separation of Extracted Lipid into Classes

Column chromatographic techniques were employed to separate the extracted lipids into NL, GL and PL classes. Preparation of silicic acid was carried out according to Hirsch and Ahrens (1958). Four 50ml portions of anhydrous methanol were used to wash 50g of 325 mesh silicic acid. The silicic acid was then held at 100^{o}C for 24 hours to dry and to activate. A 10g sample of the prepared silicic acid was dispersed in chloroform and poured into a 30 cm x 2 cm glass column with one inch of glass wool packed into the bottom. The silicic acid was allowed to settle overnight and rinsed several times with chloroform. Anhydrous sodium sulfate (5g) was placed onto the column prior to use.

Approximately 200mg of the lipid extract in chloroform were applied to the column. The NL class was eluted from the column with chloroform, the GL class with acetone and the PL class with methanol. Fifty ml portions of each solvent were used. This procedure was similar to that described by Hirsch and Ahrens (1958). The solvent extracts were concentrated in a Buchi Rotovapor R rotary evaporator

(Buchi Inc., Switzerland) under conditions designed to induce minimum oxidative stress from temperature. Trace amounts of solvent were removed under a stream of nitrogen. Samples were redissolved in 1ml of chloroform after weight determination, flushed with nitrogen and stored at -20^{0}C.

Table 4. Thin layer chromatographic conditions for the separation of lipid classes.

Class[1]	Solvent	Detection Reagent[2]
NL	hexane:methanol:acetic acid 85:15:2	Chromic-sulfuric acid
GL	chloroform:methanol:water 75:25:4	-napthol
PL	chloroform:methanol:ammonium hydroxide[3] 65:35:4	ninhydrin (PE,LPE,PS,LPS)
	chloroform:acetone:methanol: acetic acid:water[4] 50:20:10:10:5	Dragendorff (PC,LPC)
		Zinzadze (P-containing)

[1]NL, neutral lipid; GL, glycolipid; PL, phospholipid.
[2]Stahl (1969).
[3]First dimension.
[4]Second dimension.

Thin-Layer Chromatography of Lipid Classes

Analytical glass thin-layer chromatography plates (20 x 20cm) spread at a thickness of 0.5mm were prepared using either silica gel G for NL, or silica gel H for polar lipids. Plates were allowed to dry undisturbed at room temperature overnight. Prior to use, the plates were activated at 100^{0}C for 1 hour. One-dimensional thin layer

chromatography was used for the separation of NL and GL fractions. Two-dimensional thin layer chromatography was used to obtain adequate separation of components of the PL class. Conditions employed for the study are listed in Table 4. Standards were developed concomitantly with each class. Visualization of the spots was achieved by spraying the plates with specific reagents (Table 4). Spot colors and R_f values were recorded.

Fatty Acid Analysis of Total Lipid and Lipid Classes

Fatty acid methyl esters were prepared according to the method described by Morrison and Smith (1964). Total lipid extracts, as well as the lipid class extacts, were prepared under conditions suggested for triacylglycerols. Analysis of the methyl esters was achieved with a Hewlett Packard 5830A gas chromatograph equipped with a glass column (3m x 2mm id) packed with 10% SP 2330 on 100/120 Supelcoport (Supelco, Inc., Bellefonte, PA). The gas chromatograph was temperature programmed from 150^{0}C (held initially for 1 minute) to 225^{0}C and then held for 10 minutes. The temperature was increased at a rate of 1.5^{0}C/minute. Injection and detector temperatures were 200^{0}C and 300^{0}C, respectively. The carrier gas (nitrogen) flow rate was 31 ml/minute. Component fatty acids were identified by comparing the relative retention times of known fatty acid methyl ester standards.

Sterol Analysis

Saponification, derivatization and identification of the phytosterols in oat cereal were achieved through a combination of the methods of Itoh et al. (1973) and Slover et al. (1983). Approximately 100g sample of oat oil extract in chloroform were placed in a 15 x 150mm screw cap test tube. Fifty ug of 5,7-dimethyltocol was used as an internal standard. After removal of the solvent under nitrogen, 1ml of 1N ethanolic potassium hydroxide was added. The tubes were sealed with teflon lined caps and placed in a dark place for at least 16 hours. A cold saponification method was chosen to ensure no deleterious alteration of the sample as a result of the application of heat as in refluxing procedures (Chicoye et al., 1968).

The above reaction mixture was diluted with 2ml of distilled water, followed by extraction with four 1ml portions of isopropyl ether. Between extractions, the samples were centrifuged (Model CL centrifuge, Damon/IEC Division, Needham, MA) at 2000rpm for 5 minutes and the upper ether phase containing the non-saponifiable fractions were transferred to screw-capped vials.

Upon completion of the extraction process, the ether was evaporated under a stream of nitrogen and the non-saponifiables derivatized by the addition of 50ul of silylation-grade pyridine and 50ul of BSTFA containing 1% TMS. This mixture was allowed to sit for at least 15 minutes at room temperature. The analyses were carried out

using a Hewlett Packard model 5890 gas chromatograph equipped with a flame ionization detector. A 30m x 0.2mm OD methyl silicone fluid capillary column (Hewlett Packard, Avondale, PA) held isothermally at 260^{0}C was employed. Injection and detector temperatures were 275^{0} C and 300^{0} C, respectively. The split ratio was 20:1 and helium was used as carrier gas at a flow rate of 0.33 ml/min. Mass spectral analysis was carried out using a JEOL Mass Sectrometer model number HX110 equipped with an electrical ion source under the same conditions described for GC analysis alone. Accelerating voltage was 10eV and ionizing energy was 70eV. Identification of components was achieved by comparison of retention times and mass spectra data to those of known standards.

Stability of Oat Cereal During Storage

The second phase of this study involved the measurement of the effect of mixed tocopherols on the stability of oat cereal. The samples designated as 'control' do not contain added tocopherols.

Preparation of the Oat Cereal Storage System

Approximately 200 g portions of oat cereal were packaged in polyethylene pouches (2.135 um in thickness) which were then heat sealed and placed in NRC90MIL 5 gallon high density polyethylene buckets (Letica Corp., Rochester, MI). The relative humidity in the buckets was maintained at 51 $\pm$ 1.5% with a saturated magnesium nitrate solution. The humidity in the buckets was monitored using a Hygrosensor

humidity sensor, model no.15-3001 (Hygrodynamics, Silver springs, MA). Buckets were stored at either 21 $\pm$ 1.5^{0}C and the samples analyzed at 2, 4 and 6 months, or at 40 $\pm$ 2^{0}C and the samples analyzed at 3, 6 or 9 weeks. Both control samples and those containing the mixed tocopherols were held at each temperature.

Measurement of Stability of Oat Cereal During Storage

Hexanal

Analysis of the headspace volatiles was achieved using a method similar to that devised by Gloria (Personal Communication, 1986). A 30g sample was weighed into a 250 ml round bottom flask fitted to a 24/40 pyrex condenser connected to a glass elbow joint. A Tenax GC collection trap (0.2g Tenax GC, 80/100 mesh, Ohio Valley Specialty Chemicals, Marietta, OH. in a 9.0mm x 0.6mm glass tube) was placed between the elbow and vacuum pump. Traps were held in contact with the elbow with tygon tubing so as to maintain glass contact and prevent interaction between volatiles and the plastic. Samples were held at 55 C for 1 hour at 20 inches Hg.

The volatiles were eluted from the Tenax GC trap with 2ml diethyl ether, centrifuged at 700rpm for 5 minutes. The traps were then re-extracted with 1ml diethyl ether followed by centrifugation for 3 minutes. The combined extracts were evaporated under nitrogen to 0.2ml. A 1.5ul sample was injected onto the column. Hexanal was analyzed using a Hewlett Packard 5890 gas chromatograph equipped with a 30m x

0.25mm OD heliflex bonded fsot Superox column (Alltech Associates,Inc., Deerfield, IL). Injection and detector temperatures were 200°C and 275°C, respectively. The gas chromatograph was programmed from 30°C (held initially for 12 min) to 170°C at a rate of 10°C/minutes for sample determination. Helium was used as the carrier gas at a flow rate of 0.75ml/min. The split ratio was 20:1. Hexanal was identified by comparing the relative retention time of a known standard. A standard curve was used to quantitate hexanal, reported as mg/kg.

Thiobarbituric Acid Reactive Substances (TBARS)

The measurement of TBARS was conducted using a modification of the method described by Sakamaki (1986). A sample of the original oil extract was measured rather than carrying out an additional extraction of a 20g sample of oat cereal. The oil extract contained at least 0.5g of oat oil and corresponded to concentrations found by the suggested method. After evaporation of solvent using nitrogen, samples were weighed and then redissolved in 10ml of benzene. A 10ml portion of 0.02M 2-thiobarbituric acid dissolved in equal portions of distilled water and glacial acetic acid was added to the sample which was then mixed for 1 minute. This mixture was then centrifuged for 15 minutes at 1700rpm (model CL centrifuge, Damon/IEC Division, Needham, MA). The upper phase containing TBARS was collected, transferred to a glass test tube, and placed in a 100°C water bath for 30 minutes for color development.

After the samples were cooled, they were passed through cellulose columns to remove any yellow pigment that may have developed as described by Sakamaki (1986). Values reported are absorbance values at 532nm and standardized to 0.5g of sample.

Changes in Fatty Acid Content

Changes in the fatty acid profiles of the total lipid extracts and the PL class were evaluated using the GLC procedure described earlier for fatty acid methyl esters. Values are reported as a ratio of $C_{16:0}$ to each unsaturated fatty acid.

Identification of Tocols in Oat Cereal

Sample extracts were prepared as described under "sterol identification". Both tocols and sterols were detected simultaneously employing these methods. Standard mixtures of α-, β-, γ- and δ-tocopherols were subject to the same preparative conditions as the sample extracts at each saponification. The recovery for tocol standards was determined to range from 85-92%. The α-tocopherol concentration in oat cereal was reported as percent of total tocol. Identification was verified by comparison of retention times to those of the standard compounds. Chromatographic and mass spectrometric conditions were similar to those described for sterol analysis.

Analysis of Experimental Data

The experimental design for the oat stability study was a completely randomized arrangement with a two by four

factorial of treatment and time, respectively. All data collected from the oat stability test were subject to the ANOVA procedure of the Microstat stastical package (1984). Comparison of means were made according to Scheffe's method. Intepretation of all data was in accordance with the suggestions of Gill (1978).

RESULTS AND DISCUSSION

Classification and Identification of Lipid Components

The separation of the oat lipid extract into lipid classes gave values similar to those observed in earlier studies by Price and Parsons (1975), de la Roche et al. (1977), and Sahasrabudhe (1979). The percent composition of each class is presented in Table 5. The purity of the lipid classes was determined by thin layer chromatography. The polar classes were developed in the nonpolar solvent system which consisted of hexane:methanol:water in a ratio of 85:15:2. The nonpolar class was developed in the polar solvent system which consisted of chloroform:methanol:water in a ratio of 75:25:4. If more than one band was present, the sample was labelled impure.

Table 5. Class composition[1] of total lipid extract of oat cereal[2].

Lipid Class	Percent Composition
Neutral lipid	80.1
Glycolipid	11.5
Phospholipid	8.4

[1] n=6
[2] 5.1% oil on dry weight basis.

There was a greater concentration of GL relative to that of PL, though a slight impurity was detected in the GL fraction, indicating actual values would vary slightly. This was recognized as a NL contaminant which may be eliminated through a more sophisticated gradient elution system than the one employed. No impurities were detected in either the NL or the PL classes. Percent total lipid is also presented in Table 5.

Oleic, linoleic and palmitic acids comprised over 95% of the fatty acid composition of the total lipid extract (Table 6). The percentage of $C_{18:2}$ was only slightly greater than $C_{18:1}$. Fatty acids which constituted the remaining 5%, in decreasing concentration, were linolenic, palmitoleic, and arachidic, with trace amounts of myristic, behenic, erucic and lignoceric. These values are similar to those previously reported (Price and Parsons, 1975; Welch, 1975; Youngs and Puskulcu, 1976; de la Roche et al., 1977; Sahasrabudhe, 1979).

The fatty acid compositions of the individual lipid classes are also shown in Table 6. Difference in the percentages of fatty acids, particularly $C_{18:1}$ and $C_{18:2}$, are noted between the polar and nonpolar classes. de la Roche et al. (1977) observed an 83% higher content of $C_{16:0}$, and 26% higher content of $C_{18:2}$ in the PL class of oat compared to the TG fraction. The NL fraction is composed mainly of TG. These researchers observed less $C_{18:1}$ and $C_{18:3}$ (52% and 26%, respectively) in the PL class of oat

Table 6. Fatty acid composition[1] of total lipid extract and lipid classes of oat cereal.

Fatty acid	Total lipid	Lipid classes[2]		
		NL	GL	PL
14:0	tr[3]	tr	tr	tr
16:0	15.8	14.6	17.0	25.6
16:1	0.3	0.2	tr	tr
18:0	1.9	1.9	2.2	1.3
18:1	38.9	41.2	29.4	19.2
18:2	40.2	38.3	43.1	51.1
18:3	2.3	2.3	2.5	2.0
20:0	0.2	0.2	tr	tr
22:0	tr	tr	tr	tr
22:1	0.3	0.2	tr	tr
24:0	0.2	0.3	tr	tr

[1]n = 6, expressed as area percent of total fatty acid of each class.
[2]NL, neutral lipid; GL,glycolipid; PL, phospholipid.
[3]tr = trace.

compared to the TG fraction. Similar trends were noted in values obtained in the present research.

Thin layer chromatography of the three lipid classes provided identification of components in support of findings by Price and Parsons (1975), Sahasrabudhe (1979) and Youngs et al. (1977). Components of the three lipid classes are shown in Table 7. The NL class contained eight components, seven of which were identified. These were monoacylglycerol, 1,2,-diacylglycerol, 1,3-diacylglycerol, sterol, free fatty acid, triacylglycerol and steryl ester. Of the six compounds detected in the GL class, five were identified as digalactosyldiacylglycerol, cerebroside, sterylglucoside, monogalactosyldiacylglycerol and esterified sterylglucoside. The unknown spot could be acyl-MGDG as it was found between esterified steryl glucoside and the solvent front, similar in location to a component detected by Sahasrabudhe (1979).

One-dimensional TLC was applied to the detection of the PL components, but insufficient separation was obtained. Only eight spots were detected using this method. Subsequently, two-dimensional TLC was employed, and 11 compounds were observed. These compounds were phosphatidylserine, lysophosphatidylcholine, phosphatidylcholine, phosphatidylinositol, lysophosphatidylethanolamine, phosphatidylethanolamine, phosphatidylglycerol, diphosphatidylglycerol, phosphatidic

Table 7. Composition[1] of the nonpolar and polar lipid classes of oat cereal.

Class[2]	Component	R_f[3]	
NL	Monoacylglycerol	0.01	
	1,2-Diacylglycerol	0.07	
	1,3-Diacylglycerol	0.08	
	Sterol	0.10	
	Unknown	0.21	
	Free fatty acid	0.28	
	Triacylglycerol	0.36	
	Steryl ester	0.79	
GL	Digalactosyldiacylglycerol	0.52	
	Cerebroside	0.59	
	Sterylglucoside	0.69	
	Monogalactosyldiacylglycerol	0.77	
	Esterified sterylglucoside	0.84	
	Unknown	0.91	
PL		x	y
	Lysophosphatidylcholine	0.14	0.10
	Lysophosphatidylethanolamine	0.19	0.14
	Phosphatidylinositol	0.25	0.08
	Phosphatidylcholine	0.31	0.22
	Phosphatidylserine	0.32	0.07
	Phosphatidylethanolamine	0.42	0.34
	Phosphatidylglycerol	0.48	0.42
	Diphosphorylglycerol	0.52	0.46
	N-acyllysophosphatidylethanolamine	0.59	0.65
	Phosphatidic Acid	0.64	0.02
	N-lysophosphatidylethanolamine	0.81	0.81

[1] n = 6.
[2] NL, neutral lipid; GL, glycolipid; PL, phospholipid.
[3] Solvent systems: NL = hexane:methanol:acetic acid; GL = chloroform:methanol:water; PL(x) = chloroform:acetone: methanol:acetic acid:water; PL(y) = chloroform:methanol: ammonium hydroxide.

acid, N-acylphosphatidylethanolamine and N-acyllysophosphatidylethanolamine. Sahasrabudhe (1979) detected 22 components in the polar lipid class of lipids extracted from 'Hinoat' oat, two of which were not identified. The present data support these previous findings.

The major sterol components identified in oat cereal are listed in Table 8. Most of the phytosterols, β-sitosterol, stigmasterol, campesterol, 7,(5α)-cholestene-3β-ol and cholesterol, were identified through GC-MS analysis and by comparison to known standards. Δ^5-Avenasterol could only be tentativley identified by comparison to established mass spectral data (Knights and Laurie, 1967; Boskou and Morton, 1975; White and Armstrong, 1986).

Table 8. Phytosterol content of oat cereal[1].

Sterol	Percent Composition
Cholesterol	3.5[2]
7,(5α)-cholesten-3β-ol	0.8
Campesterol	7.4
Stigmasterol	5.2
β-Sitosterol	51.2
Δ^5-Avenasterol	32.1

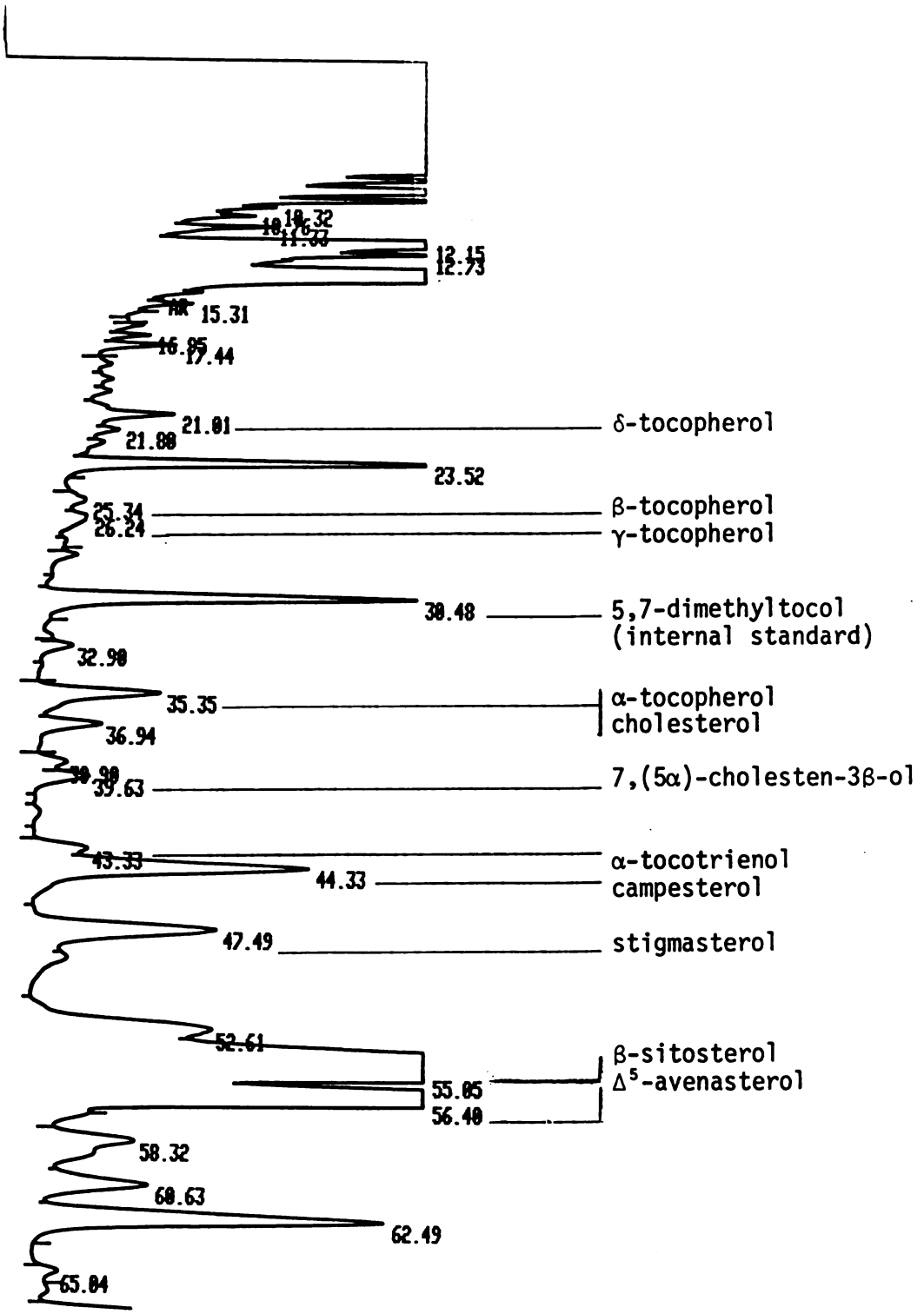
[1]n = 2; identified by GC-MS, except Δ^5-avenasterol.
[2]Includes α-tocopherol.

Knights and Laurie (1967) confirmed the presence of 14 sterols in oat seed through the application of GC-MS techniques. Knights (1968) later reported that β-sitosterol and campesterol comprised up to 90% of the total phytosterol composition in oat seed. Through the application of a more sensitive GC technique, Knights and Laurie (1968) were able to more efficiently separate the phytosterols. What they had previously identified as β-sitosterol was determined to be this phytosterol as well as Δ^5-avenasterol.

In the present study these two compounds were also identified as the major sterols in oat cereal. Figure 2 shows a chromatogram of the TMS derivatives of the phytosterols and the tocols. β-Sitosterol and Δ^5-avenasterol comprise over 83% of the sterol fraction and, in addition to campesterol, make up 90% of the total phytosterol composition.

The tocol content of dry oat cereal is shown in Table 9. The β- and γ-isomers of tocopherol were sufficiently separated by the method employed, though the β-tocol was not observed consistently in all samples (Figure 2). Levels of these two tocols were quite low, as some may have been lost in the steps required for identification. It is interesting to note the levels of α-tocopherol and α-tocotrienol. The higher concentration of α-tocopherol relative to that of α-tocotrienol is both in agreement with, and in opposition to, values determined from previous research. Herting and Drury (1969) reported the

Figure 2. Gas chromatogram of the non-saponifiable fraction of oat cereal lipid.


15.31
21.01
δ-tocopherol
21.88
23.52
β-tocopherol
γ-tocopherol
30.48
5,7-dimethyltocol
(internal standard)
32.98
35.35
α-tocopherol
cholesterol
36.94
39.63
7,(5α)-cholesten-3β-ol
α-tocotrienol
44.33
campesterol
47.49
stigmasterol
β-sitosterol
55.05
Δ5-avenasterol
56.40
58.32
60.63
62.49
65.04

concentration of α-tocotrienol to be less than α-tocopherol in a variety of oat products, as well as in the oat grain.

Table 9. Tocol content[1] of oat cereal.

Tocol	Percent Composition
α-Tocopherol	38.0[2]
β-Tocopherol	8.2
γ-Tocopherol	18.0
δ-Tocopherol	9.7
α-Tocotrienol	26.1

[1]n = 2; identified by GC-MS.
[2]Includes cholesterol.

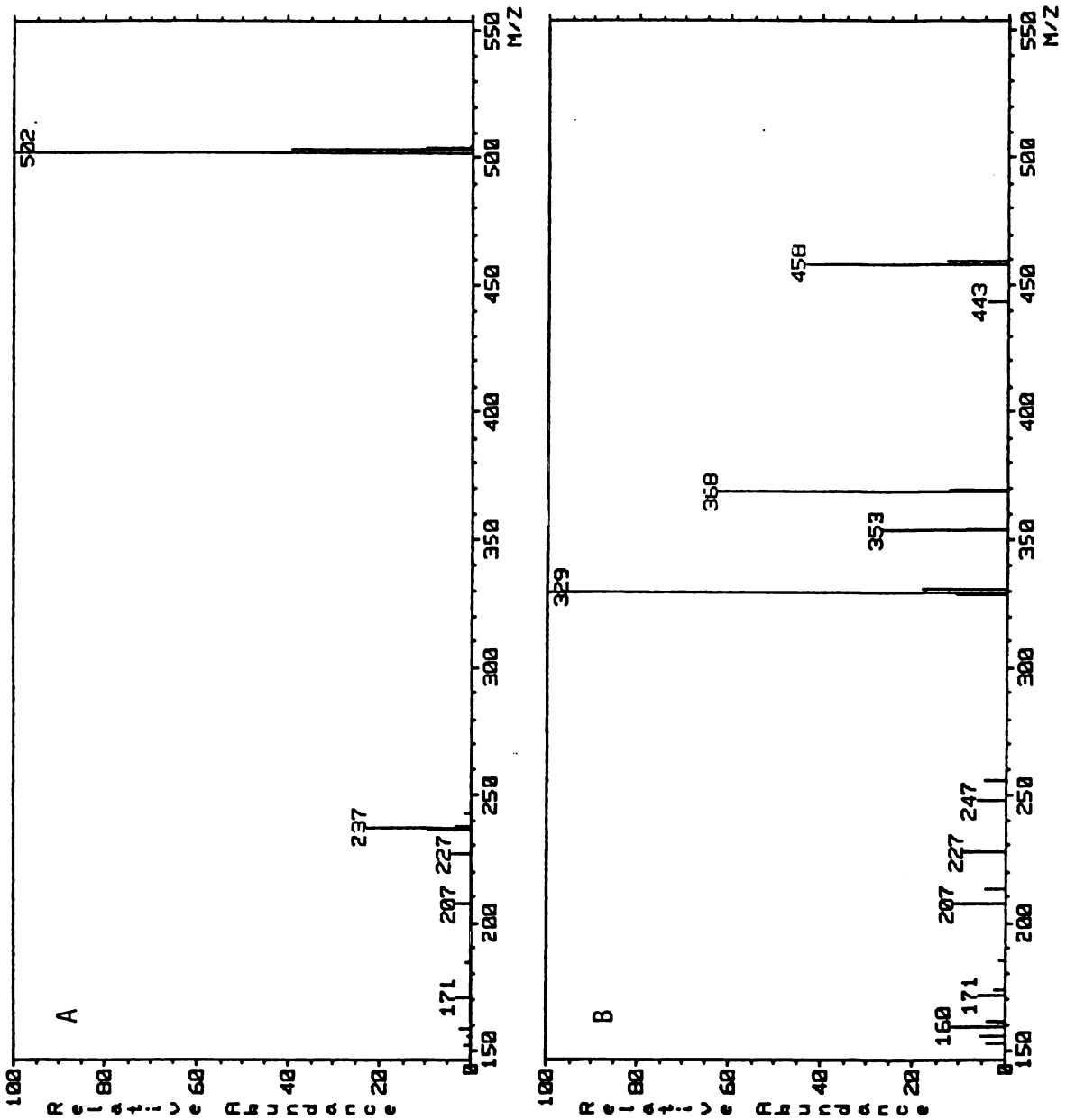
This was also observed in the present study. The levels for these two tocols determined by Rao and Perkins (1972), Slover (1968) and Slover et al. (1971) indicate the α-tocotrienol content to be much higher than α-tocopherol. These values were determined from the oat seed or groat. The conditions used in processing the samples may have contributed to the discrepency in the results, although Phronen et al. (1986) found the α-tocotrienol content of rolled oats to be 100% greater than the α-tocopherol content. However, the oat cereal analyzed in the present study was composed of oat flour which had been exposed to extensive processing prior to incorporation into a cereal.

The identification of α-tocopherol and cholesterol was hindered by their co-elution as determined under the present

GC conditions (Figure 2). The application of MS to the identification of the compounds indicated both cholesterol and α-tocopherol were present under the same peak (Figure 3). From this findings, α-tocopherol may have been misidentified as cholesterol in previous studies concerning sterol content of oat. If the quantitation of cholesterol included α-tocopherol, the data would be spurious. The technique of temperature programming, rather than analyzing samples under isothermal conditions, may alleviate the co-elution problem and increase the accuracy of component identification.

Co-elution may also contribute to the discrepancy in the α-tocopherol and α-tocotrienol contents as the exact amount of α-tocopherol in the oat sample was unknown. The value presented in Table 9 for α-tocopherol includes cholesterol, and hence, is not a true representation of α-tocopherol content.

Figure 3. Mass spectra of A: α-tocopherol and B: cholesterol in the non-saponifiable fraction of oat cereal lipid.


A
B
Relative Abundance
M/Z
100
80
60
40
20
0
150
200
250
300
350
400
450
500
550
502
237
227
207
171
329
368
353
458
443
247
227
207
171
160

Stability of Oat Cereal During Storage

The application of antioxidants to a variety of foods has long been accepted as a feasible means of delaying the onset of lipid oxidation and extending their acceptability. The effectiveness of natural, as well as synthetic antioxidants has been extensively documented (Dugan, 1976; Pokorny, 1971; Cort, 1974; Porter et al., 1977; Ragnarsson et al., 1977; Reinton and Rogstad, 1981; Widicus and Kirk, 1981). Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are two of the more effective synthetic antioxidants. Of the natural antioxidants, the tocopherols have proven to be effective. Though usually less active than BHA or BHT, the tocopherols are important when there is concern of adding synthetic compounds to food.

In the present study, mixed tocopherols did not provide a significant ($p<0.05$) protective effect against rancidity development as monitored by hexanal concentration, TBARS and changes in fatty acid profiles. Data are presented as the mean value of two replications. Since it was not known whether sampling periods for the storage temperatures correlated to one another, no attempt at comparisons across temperatures was made.

Table 10 contains hexanal data for oat cereal samples held at $21^{0}C$ and $40^{0}C$. Hexanal concentration significantly increased ($\alpha=0.05$) over time for samples held at $40^{0}C$, while no differences were observed for samples held at $21^{0}C$. In food systems containing substantial amounts of linoleic

acid such as oat cereal, hexanal is a good indicator of lipid oxidation (Labuza, 1971; Frankel, 1982; Min and Kim, 1985). Heydanek and McGorrin (1981b) determined hexanal to be the most abundant volatile found in rancid oat groats, and Fritsch and Gale (1977) noted the same finding in oat cereal.

Table 10. Hexanal concentrations[1] (mg/kg) in oat cereal held at 21°C and 40°C.

Sampling time[2]	21°C		40°C	
	Control	Toc	Control	Toc
1	0.3 (0.0-0.5)[3]	0.3 (0.0-0.5)	0.3[a] (0.0-0.5)	0.3[a] (0.0-0.5)
2	3.4 (1.6-5.1)	2.2 (1.0-3.5)	1.3[a] (1.2-1.3)	0.9[a] (0.5-1.2)
3	2.7 (1.7-4.0)	1.5 (1.3-1.7)	1.6[a,b] (1.2-2.0)	1.1[a,b] (1.0-1.2)
4	3.4 (1.8-5.0)	3.9 (1.3-6.5)	2.7[b] (3.1-2.3)	3.2[b] (1.7-4.6)
	SE = 1.4		SE = 0.6	

[1]Analysis carried out in duplicate for each of the two replications.
[2]Samples held at 21°C analyzed at 0, 8, 16 and 24 weeks. Samples held at 40°C analyzed at 0, 3, 6 and 9 weeks.
[3]Ranges given in parentheses.
[a,b]Means with the same letter are not significantly different at $\alpha = 0.05$.

Fritsch and Gale (1977) monitored the concentration of hexanal in samples of oat, corn and wheat cereals held at 37°C for up to 12 weeks. They determined a level of 5 mg/kg to indicate a significant deterioration in quality. Wallace

(Personal Comm, 1986) also proposed 5 mg/kg of hexanal as indicative of an unacceptable oat cereal. After 9 weeks, oat samples had not yet reached this level when held under the conditions of this study. Mean values in Table 10 do not reflect rancidity development as indicated by a level of 5 mg/kg of hexanal, though the ranges at 24 weeks for both treatments included this concentration.

Hexanal concentrations generally increased over time for samples held at both temperatures (Table 10). A slight deviation was noted in the samples held at 21^0 C at sampling period three (16 weeks). This suggests the participation of hexanal in alternate reaction pathways rendering it unavailable for detection at that time. Carbonyls such as hexanal, formed by degradation of lipid hydroperoxides, can participate in condensation reactions with amines (Sathe et al., 1984). This leads to the formation of a Schiff base, an intermediate in the Maillard reaction sequence. Saturated aldehydes are also capable of undergoing oxidation to form the corresponding acids (Nawar, 1985). Dimerization and condensation of these acids can then occur. Beyond 16 weeks of storage, concentrations of hexanal may have increased to levels in excess of those required for these side reactions, noted as an increase in concentration at 24 weeks. Reaction rates may have been accelerated at 40^0C storage, thereby masking this trend.

Although the temperature variable was controlled, it would be quite difficult to determine the contribution of

the constituents of oat cereal toward the production of hexanal. In studying reactions in food systems, McWeeny (1968) stated that the concentration of a product is dependent upon the rate of all possible reactions (accumulation, degradation and complexation) of which it is involved. He also suggested that a negative rate of change of the reaction can arise when the substrate is involved in an alternate pathway, the product reacts further, or the reversal of the reaction occurs. When each of these reactions are positive, there will be a net negative effect on the rate of change with temperature of the reaction. This may be recognized as an apparent loss of the product at some point in time.

There were no significant differences ($p<0.05$) in TBARS between treatments at both temperatures, and no significant differnces in TBARS over time were observed (Table 11). Caldwell and Grogg (1955) monitored the stability of oat cereal held at 38 ^{0}C by the production of TBARS. They observed variability in absorbance values for different lots of the same cereal. One lot was determined to be rancid after 3 weeks of storage, while a second lot was rancid after 20 weeks. All lots of a second type of dry oat cereal remained acceptable after 20 weeks of storage at this same temperature.

Labuza (1971) has stated that the use of the TBA test for determination of rancidity in dehydrated low-fat food systems results in data which are variable and empirical.

Table 11. TBARS[1] of oat cereal held at 21°C and 40°C.

Sampling time[2]	21°C		40°C	
	Control	Toc	Control	Toc
1	3.4 (0.9-5.9)[3]	3.4 (0.9-5.9)	3.4 (0.9-5.9)	3.4 (0.9-5.9)
2	3.7 (2.7-4.7)	4.5 (2.2-6.8)	7.3 (3.2-11.4)	5.2 (2.6-7.7)
3	8.6 (4.1-13.6)	9.2 (3.2-15.2)	9.6 (5.0-14.1)	6.2 (3.3-9.1)
4	20.1 (11.9-28.3)	17.8 (8.1-27.4)	8.7 (4.3-13.1)	8.5 (4.0-13.1)
	SE = 5.6		SE = 3.6	

[1]Reported as absorbance x 100 at 532nm; analysis carried out in triplicate for each of the two replications.
[2]Samples held at 21°C analyzed at 0, 8, 16 and 24 weeks.
[3]Samples held at 40°C analyzed at 0, 3, 6 and 9 weeks.
Ranges given in parentheses.

Malonaldehyde is a highly reactive compound and is more than likely involved in alternate, competitive reactions besides complexation with TBA. Such reactions could involve the condensation of malonaldehyde, an α-dicarbonyl compound, with a protein (Whistler and Daniel, 1985). This is known as the Strecker degradation pathway. This could account for the absence of a significant increase in TBARS. Also, due to the low amount of lipid in cereals as compared to meat systems, the accumulation of TBARS may not be as rapid. Therefore, measurement of TBARS may not be an accurate indicator of lipid oxidation in accelerated storage studies of oat cereal.

Changes in the profiles of $C_{18:1}$, $C_{18:2}$ and $C_{18:3}$ were monitored by gas chromatography over the entire storage period. Since the PL class is associated with the membrane system where greater oxidation occurs, PLs were analyzed, as well as the total lipid extracts. Tables 12 and 13 contain values which represent changes in the linolenic acid content over time.

Table 12. Profile of linolenic acid content[1] in total lipid extract of oat cereal held at 21°C and 40°C.

Sampling time[2]	21°C		40°C	
	Control	Toc	Control	Toc
1	7.0[a] (6.8-7.4)[3]	6.8[a] (6.5-7.1)	7.0 (6.8-7.4)	6.8 (6.5-7.1)
2	7.4[a,b] (7.1-13.2)	7.3[a,b] (6.9-10.5)	6.7 (6.0-7.2)	6.6 (4.8-7.5)
3	7.5[b] (7.3-8.0)	8.3[b] (7.3-8.7)	7.4 (7.2-7.7)	7.3 (6.9-7.5)
4	7.6[b] (7.4-7.8)	7.5[b] (6.9-7.8)	7.5 (7.2-8.0)	7.3 (6.4-8.2)
	SE = 0.2		SE = 0.4	

[1]Reported as ratio of $C_{16:0}$:$C_{18:3}$; analysis carried out in triplicate for each of the two replications.
[2]Samples held at 21°C analyzed at 0, 8, 16 and 24 weeks.
[3]Samples held at 40°C analyzed at 0, 3, 6 and 9 weeks.
[3]Ranges given in parentheses.
[a,b]Means with the same letter are not significantly different at $\alpha = 0.05$.

Data pertaining to oleic and linoleic acid contents are found in the Appendix. An increase over time would indicate a decrease in the FA. The only change observed was the

significant ($p<0.05$) decrease in $C_{18:3}$ in both the PL class (Table 13) and the total lipid fraction (Table 12) in samples held at 21°C. This was noted for both treatments.

Table 13. Profile of linolenic acid content[1] in phospholipid class of oat cereal held at 21°C and 40°C.

Sampling time[2]	21°C		40°C	
	Control	Toc	Control	Toc
1	10.2[a] (8.6-12.5)[3]	9.8[a] (9.0-10.8)	10.2 (8.6-12.5)	9.8 (9.0-10.8)
2	12.3[a,b] (10.5-13.2)	10.8[a,b] (9.6-13.1)	11.6 (9.3-13.8)	10.8 (7.8-12.8)
3	14.4[b] (10.8-16.3)	13.0[b] (10.2-16.0)	12.0 (10.5-14.0)	10.9 (10.3-11.7)
4	13.0[a,b] (11.5-16.7)	11.6[a,b] (10.4-12.9)	13.4 (10.3-17.2)	11.8 (10.2-13.8)
	SE = 0.09		SE = 1.5	

[1]Reported as ratio of $C_{16:0}$:$C_{18:3}$; analysis carried out in triplicate for each of the two replicates.
[2]Samples held at 21°C analyzed at 0, 8, 16 and 24 weeks.
[3]Samples hald at 41°C analyzed at 0, 3, 6 and 9 weeks.
[3]Ranges given in parentheses.
[a,b]Means with the same letter are not significantly different at $\alpha = 0.05$.

The loss of $C_{18:3}$ would also be expected at 40°C storage, but this was not the case (Tables 12 and 13). It is possible the gas chromatographic technique employed was not as sensitive as required to detect such subtle changes. Also, the kinetics of oxidation differ at various temperatures, especially when considering a complex system such as a food (McWeeny, 1968). Elevated temperature

conditions more often reflect actual activity in oils or lard, whereas with systems such as the one under study, they do not (Labuza, 1971).

The increase in TBARS is parallel to the decrease in $C_{18:3}$, as would be expected. Malonaldehyde arises from the degradation of this fatty acid, as well as from the secondary oxidation products of linoleic acid (Dugan, 1976).

Table 14. α-Tocopherol content[1] of oat cereal held at 21°C and 40°C.

Sampling[2] time	21°C		40°C	
	Control	Toc	Control	Toc
1	100 (67-137)[3]	495 (227-707)	100 (67-137)	495 (227-707)
2	72 (55-94)	314 (50-570)	88 (77-113)	384 (70-692)
3	84 (76-90)	339 (73-587)	84 (56-105)	402 (117-721)
4	63 (43-78)	45 (19-67)	69 (51-83)	267 (88-442)
	SE = 155		SE = 187	

[1]Reported as percentage of control at time 1 (day 0); analysis carried out in duplicate of each of the two replications.
[2]Samples held at 21°C analyzed at 0, 8, 16 and 24 weeks.
[3]Samples held at 40°C analyzed at 0, 3, 6 and 9 weeks.
[3]Ranges given in parentheses.

Variability in the data collected was large in each of the two sets of treatments. This can be seen in the large standard errors of a treatment/time combination for all

data in Tables 10, 11 and 14. This was most evident in changes observed in the α-tocopherol content (Table 14). There were no significant difference ($p<0.05$) between the two treatments at either low or high temperature, and there were no significant decreases in the levels noted over time. Differences would be expected to be significant for samples held at both temperatures for both treatment and time due to the difference in initial concentrations, and obvious losses over time.

Widicus and Kirk (1981) determined that the rate of α-tocopherol degradation in a dehydrated model food system was dependent upon temperature, oxygen concentration and water activity. An increase in any of these parameters elicited an increase in destruction of α-tocopherol. Also important was the concentration of the tocol. They observed that the rate of loss was much greater when α-tocopherol was present at 250 ug/g versus 125 ug/g in the model system. Therefore, it must be determined whether the initial concentration of tocopherol is adequate to elicit a protective effect while minimizing the degradation rate of the antioxidant.

When each set of treatments was considered individually, the first set, i.e., those two batches, one control and one containing tocopherol, processed and stored to initiate the study, exhibited trends as expected: a protective effect was afforded the oat cereal by the tocopherol treatment. Observations from the second set of treatments, i.e., those two batches processed and stored to

duplicate the study, depicted no differences between the two treatments as seen by similar hexanal concentrations and TBARS values. This was noted for samples held at both temperatures. The initial α-tocopherol level for set I samples and set II samples was greatly different as can be seen by the ranges given in Table 14.

The use of α-tocopherol as an antioxidant in oat, as well as wheat and rice, cereal has been studied by Anderson et al. (1963). Rather than observing a protective effect, these researchers noted little changes in the stability of the cereals at low levels of the antioxidant. However, at higher concentrations of α-tocopherol, a prooxidative effect was seen. Incorporation of either BHT or BHA was effective, and the application by the use of an atomizer post-process displayed the most protection. The use of α-tocopherol was not much more effective than the δ-isomer. The present study reflects these same trends in respect to α-tocopherol. The use of an alternative application may increase the effectiveness of the antioxidant. This is especially true in light of the high heat lability of the tocopherols and, subsequently, the poor carry through capabilities (Dziezak, 1986).

From the discrepancy noted between initial levels of α-tocopherol in each batch, it is reasonable to conclude there was variability in processing conditions. It appears more of the tocopherols were destroyed during the processing steps for the second set of samples, implying the

probability of greater antioxidant activity at the process time. The incorporation of the tocopherols may not have been complete, and dispersion in some sort of carrier, such as glycerol or corn oil may increase the ease of blending of the antioxidant into the system.

The stability of the second set of samples appeared to be greater than the first set of treatments. Differences were also apparent between the two control treatments. If the processing conditions were, in fact, more severe, a greater degree of browning due to the Maillard reaction may have occurred. This reaction would supply a low concentration of intermediate compounds or end products which have been shown to elicit antioxidative capacity (Lingnert and Eriksson, 1980; Beckel and Walker, 1983).

In studying the effectiveness of tocopherols as antioxidants, Cort (1974) determined δ- and α-tocopherol to be equally or more active than BHA or BHT in oleic acid. However, both tocols were less effective than either synthetic antioxidant in linoleic acid. These same trends were observed when the antioxidants were applied to actual animal fats and vegetable oils. It appears that in the oat cereal used in this study, tocopherols do not provide a sufficient protective effect to extend the shelf-life of the product. However, failure to observe a marked antioxidant effect of the tocopherols could be due to the lack of rancidity development in control samples.

SUMMARY AND CONCLUSIONS

The analysis of oat lipid resulted in a detailed profile of the lipid classes, as well as the fatty acid composition of each class. The major fatty acids of the total lipid extract were linoleic, oleic and palmitic acids which comprised over 95% of the total fatty acids. The polar lipid class contained a greater amount of palmitic and linoleic acids than the nonpolar lipid class. Seven compounds were identified in the neutral lipid class, five in the glycolipid class and 11 in the phospholipid class. All data were in agreement with those of Price and Parsons (1975) and Sahasrabudhe (1979).

The major sterols identified in the oat lipid extract were β-sitosterol and Δ^5-avenasterol, and comprised over 83% of the total phytosterol composition. Gas chromatographic analysis of the total nonsaponifiable fraction resulted in the co-elution of α-tocopherol and cholesterol, hindering accurate quantitation of each of the two compounds. The α-tocopherol content was greater than that for α-tocotrienol. The opposite trend would be expected.

The application of tocopherols for use as antioxidants was not effective in increasing the stability of oat cereal. Wide variation in response to the antioxidant treatment was observed between batches when lipid oxidation was measured

by hexanal concentration, TBARS, α-tocopherol loss and changes in fatty acid profiles. These differences reflect the possibility of fluctuation in the processing conditions. Accelerated shelf-life storage did not appear to result in acceleration of lipid oxidation.

FUTURE RESEARCH

The results presented in this study necessitate the development of alternate measures to delay the onset of rancidity development in oat cereal. A complete analysis of the effects of the processing conditions on oat constituents, especially the lipid fraction, precludes the application of methods of stabilization. The determination of the extent to which lipid is destabilized during processing would provide a basis for further decisions concerning the use of antioxidants.

The method of application of the tocopherols should be explored. Understanding the dynamics of the oat cereal system during processing would indicate the appropriate time at which antioxidant addition would be most effective in delaying rancidity development. Due to the apparently poor carry-through properties of the tocopherols and their own susceptibility to oxidation, their addition to the cereal post-processing may prove to be more effective than the present mode of incorporation.

Investigations into genetic breeding could result in the development of oat seed which contain a lower amount of unsaturated lipid. This would extend the shelf-life of the oat cereal by diminishing the probability of rancidity development.

APPENDIX

Appendix

Oleic and Linoleic acid Profiles of the Total Lipid Extract and the Phospholipid Class of Oat Cereal

Table 15. Profile of oleic acid content[1] in phospholipid class of oat cereal held at 21°C and 40°C.

Sampling time[2]	21°C		40°C	
	Control	Toc	Control	Toc
1	1.2	1.2	1.2	1.2
2	1.3	1.3	1.3	1.4
3	1.3	1.4	1.2	1.3
4	1.2	1.3	1.2	1.3

[1] Reported as ratio of $C_{16:0}:C_{18:1}$.
Analysis carried out in triplicate for each two replicates.
[2] Samples held at 21°C analyzed at 0, 8, 16 and 24 weeks.
Samples held at 40°C analyzed at 0, 3, 6 and 9 weeks.

Appendix

Table 16. Profile of oleic acid content[1] in total lipid extract of oat cereal held at 21°C and 40°C.

Sampling time[2]	21°C		40°C	
	Control	Toc	Control	Toc
1	0.4	0.4	0.4	0.4
2	0.4	0.4	0.4	0.4
3	0.4	0.4	0.4	0.4
4	0.4	0.4	0.4	0.4

[1]Reported as ratio of $C_{16:0}$:$C_{18:1}$.
Analysis carried out in triplicate for each of the two replicates.
[2]Samples held at 21°C sampled at 0, 8, 16 and 2 weeks.
Samples held at 40°C samples at 0, 3, 6 and 9 weeks.

Table 17. Profile of linoleic acid content[1] in phospholipid class of oat cereal held at 21°C and 40°C.

Sampling time[2]	21°C		40°C	
	Control	Toc	Control	Toc
1	0.5	0.5	0.5	0.5
2	0.5	0.5	0.5	0.5
3	0.5	0.6	0.5	0.5
4	0.5	0.5	0.5	0.5

[1]Reported as ratio of $C_{16:0}$:$C_{18:2}$.
Analysis carried out in triplicate for each of the two replicates.
[2]Samples held at 21°C analyzed at 0, 8, 16 and 24 weeks.
Samples held at 40°C analyzed at 0, 3, 6 and 9 weeks.

Appendix

Table 18. Profile of linoleic acid content[1] in total lipid extract of oat cereal held at 21°C and 40°C.

Sampling time[2]	21°C		40°C	
	Control	Toc	Control	Toc
1	0.4	0.4	0.4	0.4
2	0.4	0.4	0.4	0.4
3	0.4	0.4	0.4	0.4
4	0.4	0.4	0.4	0.4

[1]Reported as ratio of $C_{16:0}:C_{18:2}$.
Analysis carried out in triplicate for each of the two replicates.
[2]Samples held at 21°C analyzed at 0, 8, 16 and 24 weeks.
Samples held at 40°C anlyzed at 0, 3, 6 weeks.

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