REVIEW

Oat Lipids

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ABSTRACT: Oats are a significant world crop. While nutritional interest in food oats has concentrated on oats as a source of dietary fiber, the lipid component has both nutritional and technological potential. Thus, the lipid fraction of the oat grain determines in large measure its energy content and has a significant impact on nutritional quality. The oat lipids mediate the pasting properties of oat starch and hence influence functionality. Lipids are also implicated in the flavor/off-flavor attributes of oats. These aspects of oat lipids are reviewed together with analytical methods for assessing the lipid content of oats.

Paper no. J8818 in *JAOCS 76*, 159–169 (February 1999)

KEY WORDS: Analysis, extraction, fatty acid, lipids, oats, starch.

World oat production peaked (1) at an average 52 million tons in 1970/74 but fell progressively to 39 million tons in 1990/91. Traditionally, most of the oat crop has been consumed as animal feed, but nonfeed use (as food or industrial raw materials) has risen in recent years. Therefore, the focus has shifted to food usage, as consumers in some countries, notably the United States and Australia (2), have become aware of the potential benefits of oats. As stated by Hoffman (1): "Worldwide interest in oats continues. Research has focused on topics such as the changing role of oats in human diets . . . and the potential for increased oil content in oats."

While nutritional interest in food oats has concentrated on oats as a source of dietary fiber, oat oil has also been shown to have nutritional and technological potential. Breeders seek high oil contents for oats for animal feeding, in contrast, oats for human food use should have low oil. This reduces processing difficulties, calorie contents, and the potential for rancidity (3,4). Oats have not been used as a source of edible oil because the amount of oil in the caryopses of commercial oat cultivars is quite low compared to oil seed crops (5). Nevertheless, oats contain much higher levels of lipid than any other cereal grain (6,7), which makes them an excellent source of energy and unsaturated fatty acids (5,8–13). However, the development of new food applications of oats is often hampered by fat-related problems. The content of free fatty acids, for example, constitutes a measurable portion of the lipid fraction (11), and it has been shown that an excessive amount of free fatty acids adversely affects the flavor and storage quality of oats (14). As early as 1955, Hutchinson and Martin (14) noted significant differences among cultivars in free fatty acid content, but suggested that the differences were not large enough to be of concern in milling oats.

Interest in oat lipids has a number of aspects—metabolic energy for animal feed, lipid stability and storage in both feed and food, and the effects of lipids on functionality for processing. This paper critically reviews the latter aspect plus methods for analyzing lipids in oats. The lipid composition of oats and the significance of the lipid fraction are examined. Terms used in describing the oat grain are defined as follows. The oat grain of the normal covered crop consists of a husk or hull enclosing the groat (or kernel) which is known by its botanical name, the caryopsis. Naked oats comprise only groats. Bran describes the outer layers of the caryopses. However, the bran layer of oats is not as structurally distinct as, for example, the bran of wheat. Oat groats are softer than wheat grains and thus cannot be milled to yield such clearly defined flour and bran fractions as wheat. Indeed, it has been necessary to produce a definition of oat bran (15) for use in commerce and dietary work because of the poor anatomical definition of oat bran.

SIGNIFICANCE OF OAT LIPIDS

The lipid fraction of the oat grain determines in large measure its energy content and has a significant impact on nutritional quality *via* the fatty acid composition. The lipids probably mediate the pasting properties of the oat starch and hence influence functionality. Lipids are also implicated in the flavor/off-flavor attributes of oats.

Flavor and off-flavor. The contribution of lipids and their role as flavor generators in oats have been extensively investigated (16–19). Oat groats as collected from the field lack flavor. The distinctive flavor which is typical of oat products is the result of lipid oxidation products and *N*-heterocyclic compounds formed during heat processing (20) of the groats. Steam treatment alone, however, is not effective for flavor development, which requires direct heat from a kiln. Without this, oat products retain a flat, green taste, raw and slightly bitter (21). Fors and Schlich (22) found that the lipid content and preparation of the oats (heat or no heat treatment, milling before and after roasting) influenced the flavor com-

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position. The formation of flavor, particularly in heat-treated foods, is often associated with the Maillard reaction (23,24) and recent studies indicate that interaction between the Maillard reaction and lipid degradation products (25,26) may lead to the formation of desirable flavor compounds. Nevertheless, lipids are more commonly associated with the negative aspects of food flavor.

The lipids of sound, whole oats are stable and exhibit little change (27) under storage conditions of 20°C and 12–14% moisture. However, an increase in storage temperature and/or moisture content will increase hydrolytic degradation, which leads to stringent specifications for storage. Following kernel damage during harvesting or processing by grinding or flaking, oats are even more susceptible to the development of oxidative and hydrolytic rancidity (28) that causes rapid development of a bitter taste. Rancidity is the main limiting factor for the storage and handling of oat products. Liukkonen *et al*. (29) suggest that prevention of lipid hydrolysis, rather than oxidation, should be a primary goal in the manufacture of nondeteriorated oat products. The hydrolytic process is believed to be initiated by endogenous enzymes, lipases, which are liberated by cell damage. Significant variations have been reported (30–33) in the lipase activity of different oat cultivars. Nevertheless, the oat has remarkable lipase activity compared with other cereals (34), even before germination (35–37), and significant lipolysis can occur even at low moisture levels (30) in broken or crushed caryopses. In the production of oat products for human consumption, it is generally considered necessary to inactivate the lipases. This can be achieved by steam treatment but not by dry-heat treatment (30,38). Effective inactivation can be achieved by heating to 90–100°C at a moisture content above 12% (30). In contrast to the marked stability of ordinary oat flakes used for porridge, the shelf or storage life of ready-to-eat oat breakfast cereals such as puffed groats is still limited because of the development of oxidative rancidity (39).

Oxidative changes lead to the formation of volatile oxidation products, notably carbonyl compounds that are largely responsible for the odor of rancid oats. However, the time course of the development of rancid flavor is very distinct in different kinds of oat products (38) and is markedly affected by many factors because the reaction can take a number of paths. Temperature, moisture, and light, as well as the presence or absence of prooxidants and antioxidants (40–43), influence the reaction. Autoxidation compounds expected of a high linoleic acid content (44) have been observed in rancid oat groats, the most abundant volatiles (45,46) including hexanal, pentanal, 2,4-decadienal, octa-3,5-dien-2-one, and 1-pentanol. The same chemicals can contribute to flavors (16) or off-flavors (45) depending on their concentration. Fritsch and Gale (47) showed that rancid odors occurred in ready-to-eat oat cereals when the hexanal concentration reached 5–10 ppm. The formation of volatile lipid oxidation products was shown, by headspace analyses of hexanal, to be dependent on process design, but hexanal concentration was not related to the amount of free fatty acids (FFA).

Functional properties. Consumption of oats is closely dependent on their high starch content (approximately 60% of grain mass) and, hence, pasting properties of the oat starch are an important factor in determining consumer acceptance. Numerous studies have examined the relationships between starch lipids and the pasting properties of isolated starch. In studies on other starches, e.g., potato (48), the viscosity number (value) of the starch decreased with increasing concentration of FFA and reached a constant value, presumably because of saturation of the amylose helix with FFA. In wheat, Nierle and El-bayâ (49) studied the effects of fatty acids on starch pasting properties and showed a reduced gelatinization temperature following the addition of saturated fatty acids, while monounsaturated oleic acid increased pasting temperatures.

Oat lipids have also been shown to exert a significant influence on the pasting properties of the starch (50), as demonstrated in several studies using isolated oat starch. For example, Wang and White (51) examined the pasting properties of oat (and corn) starches isolated from groats containing a range of lipid contents from 6.2 to 11.2%. The onset of gelatinization and gel stickiness of the oat starches was positively correlated with the starch-lipid contents (52). In contrast, gel firmness, measured by the Voland-Stevens texture analyzer, and starch granule size and clarity were negatively correlated with starch-lipid content. Caution is necessary in interpretation of these results since the correlations might have been fortuitous due to clustering of data. However, data which are generally consistent have been reported (53–55) in a number of instances. Moreover, lipid removal from oat starch (56–58) decreased the swelling factor, peak viscosity, set-back, gelatinization temperature, freeze-thaw stability, and paste clarity ($pH > 4.0$), while increasing the thermal stability, amylose leaching, enthalpy of gelatinization, susceptibility toward α-amylase, and paste clarity ($pH < 4.0$).

Starch granules consist of chains of amylopectin packed together as double helices in clusters that create crystalline zones. Many of the physical characteristics of oat starch granule structure and behavior have been attributed to the crystalline regions of the granule, which are due to the amylopectin component (55,57). At the molecular level, gelatinization involves the uncoiling of the chains of amylopectin in the crystalline regions. Hydrogen bonds stabilizing the double helices of amylopectin are broken during this process and are replaced with hydrogen bonds with water. The effects of the lipid fraction are due to the influence of starch–lipid complexation (55,57,59,60), which will be discussed along with its impact on starch crystallinity, although other factors are probably also operative (61).

ANALYSIS

Various methods are used in the analysis of oat lipids. These may involve determination of the total lipid fraction or indi-

vidual classes of lipid. Such methods are complicated by measurements of operationally defined fractions such as total, free, and bound lipids. Furthermore, the measurement may be performed directly on the intact whole grain or following a preliminary extraction of either grain, groats, or oat flour. These differences reflect the diverse purposes of the analyses.

Total lipid. Total oat lipids, synonymous with oil or fat, have been determined by extraction, spectrometry, or analysis of fatty acids (Table 1). However, total lipid content is dependent on the method of determination and results of the three approaches are not directly comparable.

Extraction. Solvent extraction with gravimetric measurement has been most widely used in the determination of lipid content using a sample of ground groats (73). Extraction techniques exploit the solubility properties of the lipids using the full range of static and dynamic extractors including Soxhlet and Goldfisch systems. Solvent systems are equally diverse (Table 1), ranging from single-phase nonpolar solvents to multiphase polar mixtures (e.g., water-saturated *n*-butanol, WSB) which provide the ability to tailor the selectivity to meet specific needs. Nevertheless, few solvent systems extract cereal lipids efficiently. Although nonpolar solvents such as ether or hexane are effective in removing the so-called neutral lipids (an unfortunate but widely used term) from cereal grain, they are poor solvents for extracting polar lipids, particularly the phospholipids associated with membranes (63), which are more effectively extracted with polar solvents (74). Sahasrabudhe (66) compared seven extracting solvent systems (Fig. 1) and showed significant differences both in the total lipid recovered from *Hinoat* groats and in the proportion of the various classes of lipid. The total lipid as determined by extraction ranged from 5.6 to 8.8% compared with an estimated 7.02% by acid hydrolysis. All solvents extracted most of the triacylglycerols in a range of 3.1–3.6% with a mean value of 3.4%. The increase in the lipid extracted by polar solvents comprised mainly polar lipids.

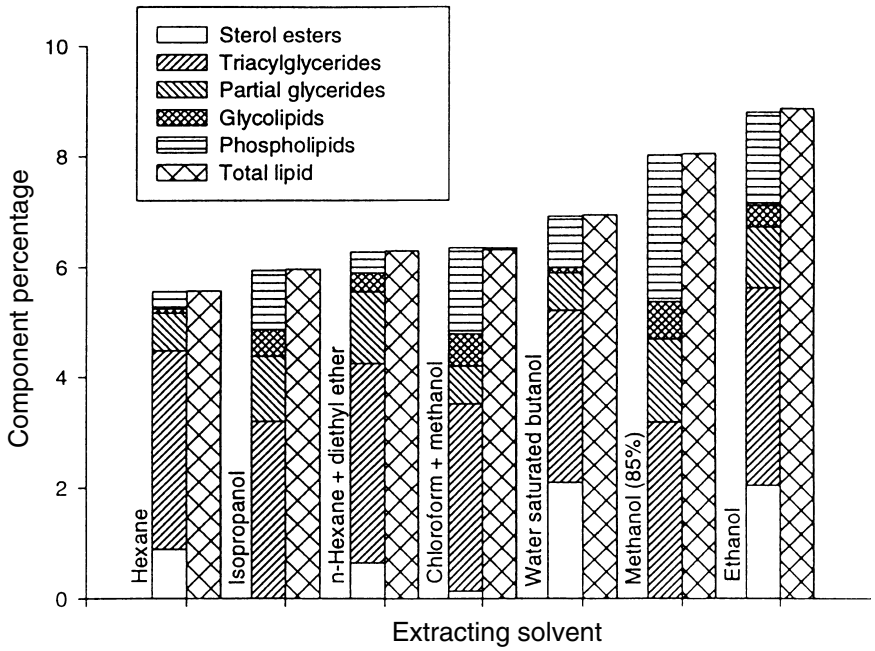
These results demonstrate both the need for caution in applying extraction procedures and the possible effects of using nonpolar solvents such as hexane, without adequate drying where slight variations in moisture content impact significantly on polarity. Sequential extraction of oats or groats with hexane, followed by solvents of increasing polarity, provides a crude fractionation of the lipids (14,63,65,75) into nonpolar (neutral or free) and polar (bound) lipids. The development of supercritical fluid extraction (SFE) has provided an alternative procedure for lipid recovery and fractionation. Fors and Eriksson (76) compared SFE with hexane extraction for recovery of lipids from two dehulled and milled oat varieties. Recovered lipids showed a similar fatty acid composition but differed greatly in phosphorus contents. The results suggest that SFE (particularly with supercritical carbon dioxide) provides a more homogeneous neutral lipid extract than conventional extraction with hexane. Further studies with SFE are warranted, as these may assist in defining more clearly the question of bound vs. free starch lipids.

Spectrometry. Spectrometric determination of lipid content offers the advantages of direct measurement on the intact grain, meal, or flour, with the potential for simultaneous analysis for several components. Lipid contents as determined by nuclear magnetic resonance [NMR (70)] were comparable with data from conventional nonpolar organic solvent extraction but, nevertheless, NMR measurement has had limited application. Most spectrometric determinations of oil content (77) are based on measurement in the near infrared region (NIR) at 1722, 2306, and 2346 nm and combinations thereof which correspond to the first overtones of the vibra-

TABLE 1
Total Lipid Content in Oat Grain or Groats (G)

Sample	Method	Oil (%)	Reference
54 British cultivars	Extraction with petroleum ether	5.0–10.1	14
6 U.S. cultivars (G)	Extraction with WSB[a]	5.0–9.6	62
U.S. cultivar	Saponification, acidification + petroleum ether extraction	6.6	4
445 U.S. cultivars	Extraction with hexane	2.0–11.0	30
9 Cultivars	Extraction with hexane	3.2–8.9	63
9 Cultivars	Modified Bligh and Dyer extraction	4.5–10.3	63
British cultivars (G)	Extraction with petroleum ether	6.0–7.9	27
42 Cultivars, 15 sites, 4 seasons	Extraction with diethyl ether	4.5–7.2	64
2 U.S. cultivars (G)	Extraction with diethyl ether then WSB	6.9–9.6	65
12 Canadian cultivars	Extraction with petroleum ether (b.p. 30–60°C)	4.2–11.8	66
British cultivars	Extraction	6.4–8.9	67
Swedish oats	Acid hydrolysis + diethyl ether	7.4	6
11 Australian cultivars	Extraction with diethyl ether then WSB	4.3–6.5	8
Finnish cultivar (G)	Extraction with chloroform/methanol	6.2	29
3 U.S. cultivars (G)	Nuclear magnetic resonance	3.0–8.0	68
56 U.S. F4 lines	Nuclear magnetic resonance	2.5–8.6	3
2 U.S. cultivars (G)	Nuclear magnetic resonance	3.5–7.5	69
4000 Entries (G)	Nuclear magnetic resonance	3.1–11.6	70
Finnish cultivars	Nuclear magnetic resonance	6.2–7.8	13
3 British lines	GC of fatty acid methyl esters–sulfuric acid in methanol	3.0–8.6	71
6 British lines	GC of fatty acid methyl esters-sulfuric acid in methanol	3.0–7.0	72

[a]G = groats; WSB, water-saturated *n*-butanol; GC, gas chromatography.



Solvent system	Total lipid (%)	Sterol esters	Triacylglycerols	Partial glycerides	Glycolipids	Phospholipids
n-Hexane	5.57	0.88	3.61	0.68	0.08	0.31
Isopropanol	5.96	—[a]	3.21	1.18	0.49	1.06
n-Hexane + diethyl ether (8:2)	6.29	0.64	3.61	1.3	0.34	0.38
Chloroform/methanol (2:1)	6.31	0.13	3.39	0.68	0.60	1.55
WSB	6.93	2.09	3.13	0.67	0.10	0.92
Methanol (85%)	8.03	+[b]	3.19	1.5	0.68	2.64
Ethanol	8.84	2.04	3.58	1.09	0.38	1.69

[a]—, Not detected.
[b]Trace.

FIG. 1. Composition of lipids extracted from *Hinoat* oat groats by different solvent systems. Results are expressed as percentage by mass (66).

tions of $(CH_2)_{n>4}$ and similar species. Calibration against a reference method is critical and the quality of the data relies heavily on the calibration set.

NIR as first applied in the early 1970s required careful grinding of the sample. Subsequent developments in instrumentation facilitated the testing of whole grains (78), and NIR results showed excellent correlation ($r^2 = 0.99$) with standard methods when validated using samples independent of those used in calibration development (79). More recently, NIR instruments capable of transmittance and reflectance measurement have become available. Williams and Sobering (80) compared the two systems for determination of oil in several grains and found that the two systems were comparable in accuracy and reproducibility.

Fatty acid summation. Despite the improvements in column technology in gas chromatography and development of the evaporative light scattering detector in high-performance liquid chromatography, such techniques have not been applied to oats or oat lipids, and fatty acid summation remains an important procedure. Ideally, quantification is achieved by reference to a suitable internal standard, typically heptadecanoic acid (71). A recent collaborative study (81) examined fatty acid summation for determination of total fat as well as saturated, unsaturated, and monounsaturated fat contents of cereals. Total fat was calculated as the sum of individual fatty acids expressed as triacylglycerol equivalents in accordance with nutrition labeling guidelines.

CONTENT AND COMPOSITION

The lipid content of oat grains depends on genetic and environmental factors as well as the method of determination (Table 1). Frey and Hammond (30) reported a 2.0–11.0% range in 445 U.S. cultivars, and the range of 3.1–11.6% was found among more than 4,000 entries in the world collection (70). A high lipid content of 15.5% in a U.S. experimental line of groats was reported by Hartunian-Sowa and White (54).

Classification of the lipid fraction. Lipid may be classified operationally based on solubility, chemically based on structural considerations, or according to location in the grain. The last-named is of most interest to the cereal chemist because cereal processing can dramatically alter the distribution. These classifications are not mutually exclusive.

Operational classification. Lipids have been classified as free or bound lipids based on their extraction properties. Youngs *et al*. (65) found that about 80% of the total groat lipids were free lipids extracted by nonpolar solvents such as *n*-hexane, whereas the remaining 20%, termed bound lipids, required polar solvents such as WSB for extraction. The diethyl ether-extractable and chloroform/methanol/WSB-extractable lipids have been compared (82) in oat flour and extruded materials. The lipid extracts differed significantly in fatty acid composition. Extrusion processing influenced the amount of extractable lipids, while fatty acid composition was not affected.

Classification by distribution in the grain. The hull, which constitutes between 20 and 36% of total grain mass (83), is composed primarily of cell wall material with reported lipid contents of 0.05 (29) to 2.9% (65). Youngs *et al*. (65) and Youngs (37) showed (Table 2) that the lipid concentration is much higher in the scutellum and embryonic axis than in starchy endosperm or bran. However, the content of the latter two fractions accounted for most of the total lipid because the embryonic axis and scutellum represent a relatively small proportion of the whole grain (65). This contrasts with the situation in other cereals (84). Caution is necessary in interpreting data on oat bran as it is not a distinct anatomical fraction and its composition may vary depending on the processing conditions. However, the above data were obtained on hand-dissected groats which enhances the confidence in the results. Moreover, Price and Parsons (85) reported a similar result of 92% of the total lipid in the endosperm and bran fractions. Liukkonen *et al*. (29,86,87) wet-fractionated oats into fiber, starch, and protein fractions under different pH conditions, and determined lipid contents and compositions in each fraction.

Starch. Oat starches, in contrast to those of wheat and maize, contain greater amounts of lipid ranging from 1 to 3% presumably as an amylose–lipid complex (52,54,55,58,61,88–93). From the perspective of starch functionality, the formation of a starch–lipid complex in which a saturated fatty acid chain occupies the core of the amylose helix is significant. A positive correlation has been found between the lipid content (in groats) and the amylose content in isolated oat starches (54,61,90). Morrison (94) has suggested that the explanation for this correlation, which holds for all nonwaxy cereal starches, may lie in the regulation of starch biosynthesis by lipids. The presence of more complexed lipids in oat starch relative to the starch of other cereals is supported by the relatively high value for the transition enthalpy for dissociation of the amylose–lipid complex compared to the values for other cereals (51,61,95,96).

TABLE 2
Lipid Concentration and the Distribution of Lipid in Oat Groat; Average of Two Cultivars (65)

Fraction	Lipid concentration (g kg^{-1}, dry wt basis)		Distribution in groat (%)
	Free	Bound	
Hull	22	6	
Groats	68	15	
Embryonic axis	116	37	2.1
Scutellum	205	35	6.4
Bran	80	13	38.2
Starchy endosperm	60	10	53.3

Morrison (94,97) identified three categories of lipid that are distinguishable experimentally. The internal lipids residing inside native starch granules, either in the cavity of the amylose helix or in the spaces between amylose and amylopectin, were considered the only true "starch lipids." Doublier *et al.* (56) found that the starch internal lipid content (1.3%) was considerably higher than the free extractable lipid value of 0.3%. The internally bound lipid renders as much as 60% of the amylose inaccessible to iodine in native oat starch. Acker and Becker (88) found that the lipids bound to starch remained stable during storage for a longer time. Apparently, the inclusion into the amylose helix acted as protection against autoxidation. Starch internal lipids are composed exclusively of monoacyl lipids (FFA and lysophospholipids). The proportion of lysophospholipids to FFA varies with species, but in oats 30% typically occurs as FFA (98).

Starch surface lipids are artifacts derived from the surrounding protein matrix of the endosperm. It was hypothesized that these compounds, which are also monoacyl lipids, formed inclusion complexes with amylose in the surface regions of the granule. The remaining lipids derived from endosperm, aleurone, and germ are termed nonstarch lipids. The majority are fully acylated (triacylglycerols, diacylglycolipids, and phospholipids) and can reside either in a free state or bound with proteins on the granule surface. FFA and monoacylglycerols may also be present from lipolysis on isolation and storage of starch (11).

Surface and nonstarch lipids are recovered by extraction with cold WSB or 1-propanol/water at ambient temperature. Negligible quantities of the starch internal lipids are extractable with traditional low-polarity fat solvents such as chloroform or ethoxyethane (94). Similarly, starch internal lipids are extracted very slowly and incompletely with polar solvents at ambient temperatures but are recovered efficiently by refluxing using Soxhlet apparatus (97). Cold extraction with chloroform/methanol/water (3:2:1) followed by hot extraction with 1-propanol has been used (58) to separate surface and nonstarch lipids from starch internal lipids. Hot extraction was significantly more effective in lipid removal, as only 6% of the original lipid remained in the starch following hot extraction whereas 52% remained after cold extraction. Hoover and Vasanthan (57), and later Hoover and Senanayake (59) distinguished between the free surface lipid obtained by cold extraction with chloroform/methanol (2:1) at 25°C and the free plus bound internal lipid extracted by hot 1-propanol/water (3:1). Lipids extracted from oat starch by chloroform/methanol amounted to 6.2% of total soluble starch lipids (TSL) as measured by acid digestion (57) while lipids obtained by extraction of the chloroform/methanol residue with hot propanol/water amounted to 92.9% of TSL. This meant that 0.9% of TSL were not extractable by solvents and were released only on hydroly-

sis by acid. Room temperature washing of oat starch with propanol/water did not alter the corresponding differential scanning calorimetry thermogram, whereas refluxing in the same solvent reduced the endotherm at 66°C and completely eliminated the one at 102–104°C suggesting the effectiveness of the latter approach in removal of internal lipids (95).

The effect of isolation procedure on two oat starches has been reported (99). The so-called internal lipids were practically identical in both starches. However, starch obtained by an alkaline treatment contained 21% less nonstarch lipid as total fatty acids, 63% less Kjeldahl-N, and the content of nonstarch FFA was lower than that in starch extracted under neutral conditions. In contrast, the water-treated starch contained almost threefold higher amounts of FFA which contributed up to 49% of nonstarch lipids. The authors concluded that isolation of starch under alkaline conditions both reduced the content of nonstarch lipids and maintained a better composition in the residual starch lipids.

Chemical classification. Chemical characterization ideally involves determination of the various lipid classes and individual compounds constituting those classes. Papers describing such work are rare and date largely from the 1970s and early 1980s. In most instances, characterization of the lipids is precluded by the diverse nature of the components and the limitations of analytical techniques. Nevertheless, the total lipid of oats can be conveniently fractionated (Table 3, Fig. 1) into triacylglycerols, phospholipids, glycolipids, FFA and sterols using lipid extracts or directly from groats or flour by column chromatography (4) or thin-layer chromatography (TLC) (4,29,63,66,100). For example, Sahasrabudhe (66) used TLC to separate the various lipid classes from extracts obtained with various solvents (Fig. 1). However, results from different authors vary considerably (Table 3) and comparison of data is complicated by differences in analytical procedure and in particular extracting solvent (4,29,63,66) and the method of expressing results (4,66).

All studies agree that triacylglycerol is the most abundant class (65,66). Phospholipids ranged from 5 to 26% of the total lipid (Table 3) with phosphatidylcholine (lecithin) accounting for 45–51% of the total phospholipid (65). Sterols (101) also showed a wide variation (Table 3), but differences in the method of reporting must be considered. For example, values are reported for sterol esters (63), the sum of free sterols plus sterol esters (66), or sterols plus sterol glucosides (65). FFA are particularly important because of their involvement in rancidity. However, there are also endogenous FFA in oat grains at natural levels which are generally too low to cause significant off-flavors. From Table 3 these levels ranged from 2.0 to 11.0% of the total lipid, which corresponds to 0.1–1.2% in the groat.

Fatty acid composition. The fatty acid composition of oat oil is important from both technological and nutritional standpoints. For example, linoleic and linolenic acids are essential fatty acids in mammalian nutrition (102), while palmitic acid increases oil stability against peroxidation and linolenic acid causes oil instability (103).

Total lipids. Long-chain fatty acids present either as triacylglycerols or as other acyl lipids constitute the bulk of the total lipid, as in other grains (104). The five fatty acids detected in every study (Table 4) on oat samples [palmitic (range 13–26%), stearic (1–3%), oleic (22–47%), linoleic (25–52%), and linolenic (1–3%) acids] together account for more than 95% of total fatty acids. Other acids detected in some studies and some varieties include lauric, palmitoleic, and arachidic acids (<0.1%) (30), the series of unsaturated C_{20} acids from 20:1 to 20:5 (0.5–3.0% in total) (66) and traces of lignoseric and nervonic (24:1) acids (105).

Lipid classes. Significant differences have been reported (8) between cultivars in both the free and bound lipid content and in the proportion of fatty acids in these lipids. Bound lipids have a higher concentration of palmitic acid and lower concentration of oleic acid (65,106). Oleic acid was commonly the major fatty acid in the triacylglycerol fraction, whereas linoleic acid usually predominated in the phospholipid and glycolipid fractions (63,66). This is not unexpected, as the polar lipids such as phospholipids are relatively enhanced in the bound lipid fraction (88).

Fatty acid correlations. Significant relationships have been reported between the total lipid content and individual fatty acids of oats (Table 5). Thus, with increasing lipid content, the proportions of palmitic and linoleic acids decreased (13) while oleic acid increased (9,12,30,62,63,72) over several varieties, sowing dates (72), and environments. The net effect is that unsaturation of the oil changes little. The relationships between

TABLE 3
Major Lipid Classes in Oats; Results are Quoted as Ranges Expressed as a Percentage of Total Fatty Acids or Total Lipid

Triacylglycerols	FFA	Phospholipids	Glycolipids	Sterol esters	Polar lipids (bound)	Comments	Reference
72.9[a]		10.1	17.0			United States	4
64.2–85.0	2.8–7.2	6.0–17.2	6.9–11.2[b]	0.1–0.6		9 Cultivars, Canada	63
32.4–50.6	2.0–11.0	7.1–12.1	10.9–11.9	1.4–2.8		6 cultivars, Canada	65[c]
43.1–56.4	4.0–10.5	11.6–26.0	5.8–9.6	2.1–4.0	20.2–34.2	2 cultivars, United States two seasons	66
78	2	10	9			Finland	10
78–79	3–4				17–19	Finland	29

[a]Termed as neutral lipids by the authors and includes free fatty acids (FFA), sterol esters, partial glycerides, and free sterols.
[b]Includes partial glycerides.
[c]Partial glycerides reported as 1.8–3.0%. Data are based on percentage total lipids except in Reference 63 (based on percentage total fatty acids) and Reference 100 (based on percentage crude oil).

TABLE 4
Relative Proportion of Different Fatty Acids of Total Oat Lipids (%)

14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	Others	Reference
	16.1		2.0	42.3	37.8	1.8			70
0.3–1.3	20.2–28.0		0.5–2.1	24.5–33.6	40.5–47.7	1.0–2.0			62
0.7	18.0	0.1	1.24	36.34	42.02	1.59			4
	14–23		1–4	29–53	24–48	1–5			30
	15.4–23.9		0.9–2.5	18.8–35.0	43.5–53.0	1.8–3.6			72
	15.6–17.7		1.4–1.7	33.5–39.4	40.1–46.5	2.3–2.9			27
0.4–0.8	16.2–21.8		1.2–2.0	28.4–40.3	36.6–45.8	1.5–2.5			9
0.4–0.5	17.0–20.6		2.6–1.9	36.9–41.7	36.9–38.8	1.3–1.4			65[a]
0.9	25.7		2.0	28.8	41.0	1.4			65[b]
<0.2	17.2–23.6		0.8–1.8	26.5–47.5	33.2–46.2	0.9–2.4	<0.2		63
0.5–4.9	14.9–25.8		1.6–3.9	25.8–41.3	31.3–41.0	1.7–3.7		0–3.1	66
	15.9–17.0		1.25–2.67	37.7–47.1	33.0–39.1	1.07–2.08			8[a]
	30.7–39.4		1.4–2.7	17.9–27.6	33.3–38.8	0.7–3.0			8[b]
0.4	16.4	0.3	1.6	37.8	38.6	1.7		3.0	29
	13.2–17.4		0.8–1.4	37.2–42.1	38.6–42.5	1.3–2.0		0.8–1.5	12
	15.6		1.4	42.3	38.1	1.3		1.3	11

[a]Free lipids.
[b]Bound lipids

total lipid and individual minor fatty acids are inconsistent and may reflect uncertainties in analytical methods as much as anything. Recently, total lipid and the absolute content of all major fatty acids were shown to be positively correlated (105).

Individual fatty acids are mostly negatively correlated (13,62,107). However, positive correlations have recently been demonstrated between the absolute content of different individual fatty acids (105).

FACTORS AFFECTING CONTENT AND COMPOSITION

Varietal effects. Cultivars exhibit wide ranges of lipid concentration (Table 1), and since the variation in lipid concentration among oat cultivars is greater than would be expected from the environmental effects, the heritability is sufficiently high to expect good progress from selection (3,30,69,108). From a study of 13 different crosses, Baker and McKenzie (3) reported that heritability of oil content was high in all crosses but one, a cross between sister cultivars. Based on the analysis of oil by ether extraction, there were no significant interactions between cultivar × year or cultivar × site, which suggests that relative oil contents will remain constant over a range of environmental conditions. Frey and Hammond (30) found that the oil percentage was only slightly affected by growing oats in five different locations in Iowa. Inheritance studies indicated that oil percentage was inherited polygenically, and there was a tendency for high oil percentage to be partially dominant. Karow and Forsberg (68) concluded that additive genes controlled oil percentage in the progeny of one cross (heritability was 82.5%) and that heterotic gene effects controlled oil in another cross (heritability was 62.1%). Brown and Aryeetey (69) suggested that the similarity between crossed and selfed groats on the same panicle was due to maternal and not cytoplasmic effects (means of reciprocal F2 populations were not significantly different), thus, selection for oil content among individual groats on the same plant would probably be ineffective in oats. Analysis of 17 oat cultivars grown in 1989 and 1990 at seven locations in South Dakota (n = 238) revealed cultivar to be an important factor (79) in influencing groat protein and oil content, while growing location was not a significant factor.

TABLE 5
Correlations Between Total Lipid and the Proportion of the Three Major Fatty Acids

Palmitic	Oleic	Linoleic	Reference
–0.89	+0.98	–0.98	63
–0.43	+0.66	–0.40	62
–0.08	+0.37	–0.38	30
	+0.36– +0.64	–0.32– –0.52	68
–0.83– –0.96	+0.70– +0.87	+0.20– +0.95	13
–0.46– –0.48	+0.59– +0.76	–0.44– –0.55	72
–0.76	+0.91	–0.85	9
–0.64	0.81	–0.39	105

Individual fatty acid composition in oat lipids also showed the greatest varietal variation (Table 4). Various studies involving different locations and growing seasons show heritabilities from 33 to 98% for the main fatty acids (9,68,107). Inheritance patterns for linolenic acid suggested additive genetic control while oleic and linoleic acids were each controlled, in part, by a partially dominant gene or genes (68). However, Thro *et al.* (107) indicated that additive gene action was the most important genetic component of variation among generation means of four additional matings for palmitic, oleic, and linoleic acids. Additive × additive effects were significant for oleic acid in one mating and for linoleic in the second, but dominance and epistatic effects involving dominance were of no importance in fatty acid inheritance (107).

Agronomy. Gullord (67) observed significant positive correlation between oil content and grain yield, while Brown and

Craddock (70) obtained a statistically significant positive correlation coefficient of 0.11 between oil content and groat weight, based on more than 4,000 determinations, but suggested it was too small to have practical importance in oat breeding. Opposite results for the correlations between lipid percentage and yield and between lipid and kernel weight have also been reported (62). In some situations, oil content is negatively correlated with protein level in the grain and may also be influenced by nitrogen fertility level (109). For instance, Brown *et al*. (5) reported a highly significant negative relationship between protein and lipids. However, there is no consistent relationship (62,110,111) between oil percentage and protein content, test weight, grain weight, kernel density, or percentage hull (3,67). Hence, none of these kernel characteristics can be used as an aid in selection for high oil content.

Lipid synthesis is affected by growing temperature. Low growth temperature has been associated (13,112,113) with increased oil content and increased oleic and linoleic acid concentrations, but with decreased concentrations of stearic and palmitic acids. The content and degree of unsaturation of the oat total fatty acid was higher in winter-sown than in spring-sown crops, indicating that low temperatures cause a higher synthesis of unsaturated fatty acids in oats (107). Humphreys *et al*. (114) suggested that oil content decreased after application of N fertilizer at the boot stage. The effects of delayed seeding on oil content are influenced by environmental conditions with the oil concentration decreasing with delayed seeding in most years. Although some cultivar × management treatments were significant, rankings of cultivar were generally consistent across treatments. It is concluded that if these characteristics are to be improved, genotype × management interactions should not adversely affect late-generation breeding material evaluation for these factors. Although most authors indicated that the environmental effect on oil concentration and composition was relatively small compared to the varietal effect, Jahn-Deesbach *et al*. (115) found that location and year effects were greater than the effects of cultivar or fertilizer. The lipid composition of Australian oats is determined by varietal characteristics and relatively unaffected by environments (105).

Storage. Lipids can undergo dramatic changes during storage, although data are limited to the effects on FFA levels. In whole oats or undamaged oat groats, lipids show little change during storage when stored at normal temperatures and low moisture levels (27), but FFA levels may rise in improperly stored or handled samples. For example, Welch (27) found that moist bruised grain yielded FFA levels of up to 16% of oil after 7 mon storage, in comparison with 4% in sound dry grain. Moreover, levels of FFA as high as 30–40% have been reported in experimentally processed oats (33) even when lipase has been inactivated. Molteberg *et al*. (11) found an increase of FFA in unground oats during storage when stored at 30 and 80% relative humidity.

Processing. Processing is reported to have various effects on lipid composition. Liukkonen *et al*. (29) reported that wet fractionation of oat flour from nonheated grains resulted in hydrolysis of triacylglycerols of the starch and protein fractions while the composition of fiber lipids remained very similar to that of whole grains. In dry flour prepared from industrially dehulled and subsequently wet-heat-treated grains, the proportion of triacylglycerols was lower and that of FFA higher than in flour from untreated grains, suggesting that some hydrolysis of triacylglycerols occurred during dehulling or wet heat treatment (29). Water soaking of the flours induced a significant decrease in the proportion of linoleic acid, suggesting the selective loss of esterified polyunsaturated fatty acids by soaking (29). Molteberg *et al*. (11) reported that the FFA content and fat acidity was reduced by an average of 50% during processing. They suggested that this reduction in FFA is probably due to complexing of fatty acids, while the relative reduction in linolenic acid during processing is related to an increasing content of volatile oxidation products. The total lipid content did not change significantly during processing. Liukkonen (87) reported that the FFA content of all fractions was reduced by soaking in alkaline water, suggesting a reduction in lipase activity. It was concluded that pH modifications during processing can be used to stabilize lipids in cereals. At values higher than pH 8, hydrolysis was reduced to 0–20% of that observed at an optimal pH of around 7 (87).

DISCUSSION

With the advent of greater use of nonfeed oat production, oat research has focused on lipid content and composition because of its importance to nutrition, flavor and off-flavor, and pasting properties. A number of methods for the analysis of oat lipids have been presented, but the results using different techniques are not directly comparable. This has led to operationally defined lipid fractions such as nonpolar (neutral or free) lipids and polar (bound) lipids. Lipids may also be classified according to their distribution within the grain based on solvent extraction, and this has given rise to classifications such as starch internal lipids, free extractable lipids, starch surface lipids, and nonstarch lipids. However, there is a need to establish an acceptable method for determination of true total lipid; and a precise method for fractionation, isolation, and localization of oat lipids is needed to explain starch lipid interaction during processing. In this connection, SFE techniques warrant closer examination.

There are no consistent relationships between oil percentage and other grain characteristics, which makes a priority the need for a rapid screening technique for identifying both high- and low-oil cultivars for the guidance of breeders.

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[Received March 13, 1998; accepted October 30, 1998]