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Oat Oil

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Introduction

Farmers have historically cultivated oats for numerous uses (e.g., hay, pasture, silage) other than for cash grain (Welch, 1995). About 15 species of oats are grown in cooler regions of the world—primarily Russia, Canada, the United States, Finland, Sweden, Germany, and Poland. The vast majority of the oats grown throughout the world are the cultivated oat, *Avena sativa*. Historically, oats were generally less favored for food use than other grains because of a bland taste and a tendency to undergo spoilage. Nevertheless, oats became a staple in Germany, Ireland, Scotland, and the Scandinavian countries. Scottish settlers introduced oats to the New World in the early seventeenth century (Anon, 2005). The more traditional use of oats as feed for working horses has diminished. Moreover, other cereals have provided better returns to farmers, and worldwide production of oats was in a long-term decline until relatively recently. For example, Russia produced 9.4 million tons in 1998 but only 4.5 million in 2000 (Anon, 2006). Total world production in 2005 was 24.6 million tons (Manunsell, 2007) although only a very small proportion was for human food use and approximately 3 million tons of the oat crop entered world commerce.

The oat crop provides a range of products that are used as animal feeds, in human foods, and as industrial raw materials. These products include crop silage, straw, grain, and grain derivatives. The oat grain is comprised of three main structures, namely, the bran, endosperm, and the germ (embryo). The proximate composition of the grain is given in Table 16.1. Wide variations appear in these data dependent on cultivar, growing conditions, agronomic practices, and even the analytical methodology. As with other grains, starch remains the most abundant component where it constitutes about 35–55% of the dry matter of the entire oat grain. Compared to other cereals, oats are characterized by a lower carbohydrate content (Ozcan et al., 2006), with higher protein and lipid contents. Indeed, oat contains the highest lipid concentration among cereal grains (Gudmundsson & Eliasson, 1989; Peterson & Wood, 1997;

Table 16.1. Proximate Composition of Oat Grain—Average Values and Ranges (% dry basis)

Crude protein	Oil	Carbohydrate (starch+sugars)	Neutral detergent fiber	Ash
10.7 (7.2–16.1)	5.0 (1.9–8.0)	47.8 (39.1–57.2)	31.5 (25.5–36.4)	2.9 (2.1–4.1)

Data compiled from reference (Welch, 1995)

Price & Parsons, 1975; Zhou et al., 1999a). The oat grain is also rich in unsaturated lipids and lipolytic enzymes such as lipases and lipoxygenases, thus accounting for the greater tendency of oats to undergo oxidative spoilage.

The oil content of oat cultivars varies widely (e.g., 3.1–11.6% in over 4,000 entries of world oat collection) (Brown & Craddock, 1972). Oat lines with oil contents outside this range also exist including developed lines with 14.5% and 16.2% oil (Baker & McKenzie, 1972; Branson & Frey, 1989; Frey & Hammond, 1975; Sahasrabudhe, 1979; Schipper & Frey, 1991). However, the most common range is 5–9%. The majority of oat lipids are found in the endosperm, especially in the aleurone and subaleurone cells (White et al., 2006; Youngs, 1986; Youngs et al., 1977). The germ contains the highest concentration of lipids in oats, but as it represents only about 7% of the total kernel weight, its contribution to total kernel oil is minor. Moreover, it is more economical to extract the oil from the whole kernel due to the structural location of the germ within the kernel. The oil is present in oil bodies (Banas et al., 2000; Peterson & Wood, 1997; White et al., 2006). In oilseeds, the oil bodies (0.5–2.5 μm in diameter) are composed of ca. 94–98% triacylglycerols, 0.5–2% phospholipids, and 0.5–3.5% of small basic proteins called oleosins of 15–26 kDa (Tzen et al., 1993). Since oat lipids contain much higher levels of phospholipids and glycolipids than oilseeds, the composition of the oil bodies in oats needs to be studied.

Apart from use as animal feed, oats are used in a range of human foods that include raw oats, rolled oats, oat flakes, oat bran, and oat flour. Oat flour and extracts were among the first antioxidants proposed for the stabilization of lipids and lipid-containing foods (Duve & White, 1991; Emmons & Peterson, 1999; Peters & Musher, 1937). A special fine ground oat flour marketed under such names as Avenex and Aveeno was commercially available and used as a stabilizer in products as diverse as ice cream, fish oil, and cereals (Welch, 1995). Oats may provide a useful substitute for wheat products in patients suffering coeliac disease (Hogberg et al., 2004). Oat oil also finds a market but primarily for nonedible applications. Crude oat oil contains a very high level of antioxidants, more than every major oilseed, grain, or grain by-product except wheat germ. Oat oil has excellent shelf-life stability due to the high content of antioxidants unique to oats. Lipids, especially polar lipids, improve loaf volume, grain and texture and delay staling in bread (Erazo-Castrejon et al., 2001). Oat oil with its relatively high content of polar lipids is ideally suited to

this application and may ultimately replace existing additives used for this purpose. If this happens, this will open a new market for oat oil which, although commercially available, is currently a speciality oil, with limited food applications.

Processing

One can extract oat oil from the grain or its pearling fractions by using numerous organic solvents, mainly hexane and petroleum fractions of comparable volatility. Other possible solvents include acetone, methanol, ethanol, 1- and 2-propanols, *tertiary*-butanol, diethyl ether, which one can use separately, in mixtures, or sequentially (Boczewski, 1980; Martin, 1964; Moreau et al., 2003; Potter et al., 1997; Washburn, 1953). These solvents is naturally eliminated by distillation. Another possible route is to use supercritical fluids (e.g. supercritical carbon dioxide) where the solvent naturally separates out the oil upon vessel depressurization at the end of the extraction (Aro et al., 2007; Fors & Eriksson, 1990). The, the obtained oat oils vary significantly

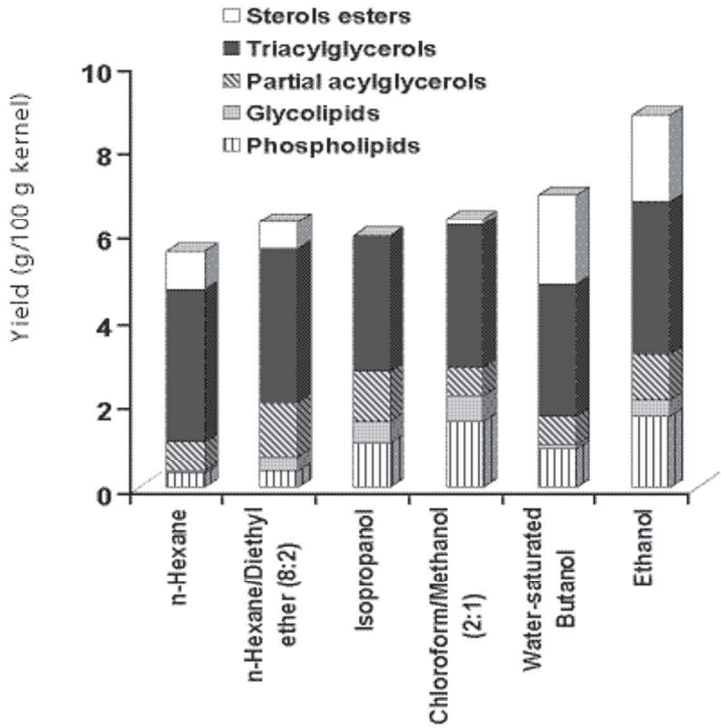

Fig. 16.1. Effect of extraction solvent on yield and relative proportions of lipid classes in oats. Data from Sahasrabudhe, 1979.

in their chemical and physical properties, depending on the extraction solvent(s) and temperatures (Fig. 16.1). Oat oils extracted with diethyl ether in a Soxhlet apparatus at 25 degree C (Ozcan et al., 2006), ethanol or carbon dioxide (Ceapro Inc., private communication, 2008) had refractive indices of 1.47plus/minus 0.01 and specific gravity of 0.92 plus/minus 0.01 g/cm3.

The oat grain is rich in enzyme activities that cause lipid peroxidation, including lipases, lipoxygenases, and superoxide dismutases (Giannopolitis & Ries, 1977; Youngs, 1986). These enzymes affect the free fatty acid content and the level of peroxides in the oil, depending on the water activity of the extracted oat, the extraction method, and the temperature of extraction. The level of antioxidants also determines the oxidative status of the extracted oil, including the free and esterified forms of benzoic and cinnamic acids, quinones, flavones, flavonols, chalcones, flavanones, anthocyanidins, and aminophenols as well as tocopherols and tocotrienols (Collins, 1986). Generally oat oil has very high oxidative stability and can stabilize other oils and oil-containing products. The phospholipid fraction seems to be responsible for the greatest part of the stabilization effect (Forssell et al., 1990, 1992).

The color of crude oat oils extracted with different solvents covers the range from light brown, amber brown, tan brown to dark brown and brownish black. The extracted crude oil contains fine protein particles that filtration can remove. One can refine the crude oil in a series of steps, including washing with water to remove some glycolipids and gums, neutralization with alkali to remove free fatty acids, degumming with phosphoric or citric acid to remove phosphatides, alkali neutralization to remove free fatty acids, winterization to remove high-melting triacylglycerols, treatment with activated bleaching earth or activated carbon to remove color, and heating under high vacuum to achieve deodorization (Potter et al., 1997). However, numerous difficulties are associated with the refining of oat oil. For example, the oil contains high levels of free fatty acids and phosphatides, the removal of which is expensive and leads to considerable product losses. U.S. Patent 6,113,908 (Paton et al., 2000) discloses that drying oat pearlings to below 4% moisture allows the endogenous oat lipase to catalyze the esterification of free fatty acids to glycerides and to reduce their level in the oil. Furthermore, pre-extraction of the pearlings with aqueous ethanol was found to selectively remove color and phospholipids and decrease losses on subsequent extraction with hexane or other nonpolar solvents.

Supercritical fluid technologies can also extract and fractionate oat oil. (Aro et al., 2007; Fors & Eriksson, 1990). Extraction with pure carbon dioxide under supercritical conditions (e.g., 70°C, 450 bar and 0.4 L/min) yielded an oil mainly composed of triacylglycerols while the addition of organic modifiers (e.g., ethanol) enables extraction of polar lipids. The two supercritical solvents were used sequentially to remove neutral and polar lipids in separate fractions (Aro et al., 2007). The polar lipid fraction mainly contained digalactosyl diacylglycerol (DGDG) (43%) and phosphatidylcholine (13%).

Oat Enzymes and Oil Stability

The oat kernel has a high activity of lipase(s) (EC 3.1.1.3) with an optimal pH of 7.5 and temperature of 37.5°C (O'Connor et al., 1992; Sahasrabudhe, 1982). Oat lipase(s) are localized in the aleurone layer as well as the endosperm (Ekstrand et al. 1992; Ekstrand et al. 1993; Hutchinson et al. 1951; Hutchinson et al. 1955; Lehtinen et al. 2003; Urquhart et al. 1983). The indication is that hydrolysis of triacylglycerols by oat lipase(s) does not yield partial glycerides, but is rather a complete hydrolysis to three free fatty acid moieties leading to bitter taste (Liukkonen et al., 1993). Hydrolysis of oat triglycerides during storage or processing increases the susceptibility of the freed fatty acids toward oxidative deterioration by molecular oxygen (Warwick et al., 1979). Enzyme inactivation is generally achieved by subjecting the milled oat products to moist heat (e.g., during extrusion) (Lehtinen & Laakso, 2004). On the other hand, this active lipase in ground oats and moist oat caryopses was reported to contain enough lipase activity to be useful for several applications in fatty acid hydrolysis (Parmar & Hammond, 1994; Piazza et al., 1989; Piazza, 1991; Piazza & Farrell, 1991).

Unlike the lipase activity, the activity of lipoxygenase (EC 1.13.11.12) in oats is weak, and a lipoperoxidase activity (EC 1.11.1) is responsible for the conversion of hydroperoxides to corresponding hydroxy acids (Biermann et al., 1980). The different enzymes involved in the oxidation of oat lipids and the main products of these oxidations are shown in Fig. 16.2. Isomerization and/or further oxidation of these products may form other oxidation products. For example, 3-nonenal is unstable and can isomerize to 2-nonenal or under catalysis by singlet oxygen to pentylfuran. When the kernel is dry and intact, lipid hydrolysis and oxidation reactions are minimal and insignificant. However, when the kernels are disrupted during milling, these reactions are significant and lead to pronounced off-flavor and loss of nutritive value including lowering of tocopherols and tocotrienols. Oils obtained from carefully processed oats may have a free fatty acid content of ca. 5% and a peroxide value of about 5–10 mequiv oxygen/kg oil. At a peroxide value of ca. 20 mequiv oxygen/kg, rancidity is evident.

Edible and Nonedible Applications

Oat bran and oat oil are normally not consumed as a food supplements but are used in food preparations. For example, the addition of oat oil, especially its polar lipid fraction, to bread formulations increased loaf volume and improved bread appearance and resistance to staling (Erazo-Castrejon et al., 2001). Crude oat oil (and shortening) (at 3%) increased loaf volume by approximately 11% over the zero lipid formulation, while the polar lipid fraction increased loaf volume by nearly the same amount when added at only a 0.5% level. The effect of oat lipids was stronger in breads made of a weak flour (10% protein) than in breads made of a strong flour (14% protein).

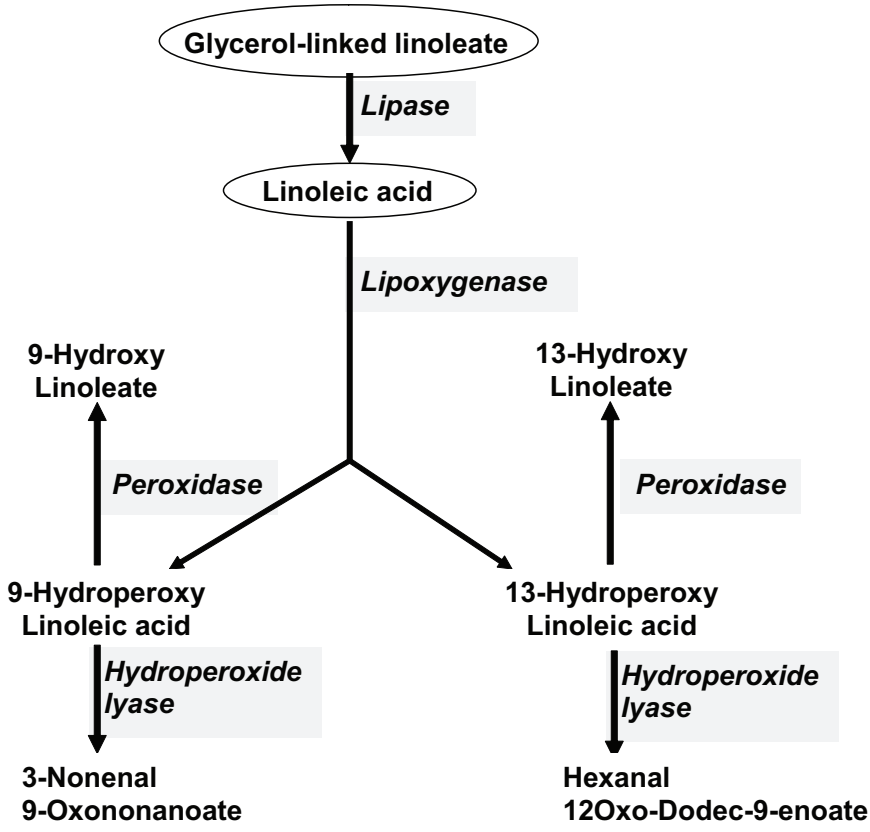

Fig. 16.2. Some oat grain oxidation-relevant enzymes and their involvement in the generation of rancid molecular species from triacylglycerol-bound linoleate residues.

These effects of oat oil were attributed to the amphipathic properties of polar lipids that make them able to interact with starch, proteins, and other bread components. Since oat polar lipids may form inclusion complexes with starch, they can modulate the pasting properties of starches leading to increased swelling, peak viscosity, setback and gelatinization temperatures, and freeze-thaw stability (Zhou et al., 1999b). The use of oat oil in bread baking is also promoted as "heart-healthy," since vegetable shortenings traditionally used to increase loaf size contain *trans* fatty acids, the consumption of which are associated with heart disease. Replacing these shortenings with oat oil, known to be free of *trans* fatty acids, therefore offers a healthier alternative for improved bread quality and shelf life (Hardin, 2000).

So far, no standard definition exists for *oat oil*, which poses a difficulty for its potential uses and applications and necessitates proper physicochemical description of the products.

Cosmetics

The use of oat oil in personal-care products represents a natural extension of the historical use of oatmeal and oatmeal fractions for improving the skin (Aburjai & Natsheh, 2003) in that oatmeal is historically known for its skin soothing and itch- and irritation-relieving properties (Kurtz & Wallo, 2007). Oat oil and its fractions have numerous pharmacological and dermatological properties that make them attractive for pharmaceutical and cosmetic applications (Blom et al., 1996; Dull, 1997). For example, oat oil has the ability to emulsify large quantities of water, thus making it very effective in hydrating and moisturizing epidermal layers (Aburjai & Natsheh, 2003). Phenolic compounds present in the oil provide protection against ultraviolet light as well as providing antioxidant and anti-inflammatory activities; saponins impart a cleansing activity while the phospholipids provide moistening and buffer activities.

Cosmetic formulations can include oat oil and colloidal components of the oat meal (Kurtz & Wallo, 2007). Oat oil is a clear, lightly colored oil with a mild natural odor that is rich in phospholipids and glycolipids (polar lipids), and free of *trans* fatty acids is generally preferred in cosmetic formulations. It has a stabilizing property in emulsions and oils and an excellent shelf-life stability due to the high content of antioxidants found in oats (Anon, undated_b). The oil is claimed to improve the elasticity of the skin and hair and has strong skin-hydrating and moisturizing properties. In skin- and hair-care formulations, a 1–5% concentration is recommended (Anon, 1997–2008). Oat oil is available as a viscous liquid, or alternatively one may spray dry (co-dry) it on various solid supports up to a maximal level of 70% by weight (Dull, 1997). The spray-dried product is advantageous because one can easily mix it with other active ingredients in the preparation of packed powder cosmetic formulations (Dull, 1997). Furthermore, one can dose it into colloidal oatmeal formulations to increase oil content and to enhance the moisturization properties of skin-care lotions and creams (Dull, 1997). Various patents relating to the use of oats in cosmetic preparations exist; however, patents relating specifically to oat oil are less common. One particular patent claims that formulations incorporating oat oil compositions have antioxidant and other "dermatologically beneficial properties." The compositions inhibit ultraviolet (UV) irradiation-induced lipid peroxidation, and are thus useful for inhibiting UV irradiation-induced skin damage (Potter et al., 1997).

Acyl Lipids

Solvent extraction or supercritical fluid extraction can recover oat oil from the grain. The oil yield of the grain is very dependent on the nature of the extracting solvent (Matz, 1991). The efficiency of extractions with pressurized solvents (hexane, methylene chloride, isopropanol, ethanol) of polar and nonpolar oat lipids was examined (Moreau et al., 2003). The effects of solvent polarity and temperature were

tested on the recovery of total lipids, triglycerides, glycolipids, and phytosterols. Lipid values obtained by extraction with ethoxyethane (diethyl ether) are often termed "free lipids" to distinguish them from those lipids more or less strongly bound to saccharide or protein components. Normalizing the material extracted with ethoxyethane to 100%, the equivalent yield for material extracted by ethanol was 128% which equaled to values obtained by acid hydrolysis methods (Zhou et al., 1999a). Three categories of lipids were identified (Morrison, 1981, 1988) 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." Such lipids are composed exclusively of monoacyl lipids (free fatty acids and lysophospholipids). Starch surface lipids are artifacts derived from the surrounding proteinaceous matrix of the endosperm, and 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.

Negligible quantities of the starch lipids are extractable with traditional low-polarity solvents such as chloroform or diethyl ether (Morrison, 1988). Surface and nonstarch lipids, and internal granular lipids, are readily separated by extraction with propan-1-ol/water at ambient temperature or cold water-saturated butan-1-ol (to recover nonstarch and surface lipids) or by refluxing using Soxhlet apparatus to recover internal lipids (Morrison, 1981). Alternatively, cold extraction with chloroform:methanol:water (3:2:1) followed by hot extraction with propan-1-ol was used (Gibinski et al., 1993) to separate the two groups. 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.

The major fatty acids in oats are palmitic acid (16:0, 14–23%), stearic acid (18:0, 0.5–3.9%), oleic acid (18:1, 29–52%), linoleic acid (18:2, 26–48%), and linolenic acid (18:3, 1–3.5%) (De la Roche et al., 1977; Frey & Hammond, 1975; Karow, 1980; Sahasrabudhe, 1979; Youngs & Puskulcu, 1976; Zhou et al., 1999a). Minor amounts of other fatty acids are also present [e.g., lauric (12:0), dodec-9-enoic (12:1), myristic (14:0), palmitoleic (16:1), arachidic (20:0), eicosenoic (20:1), behenic acid (22:0), erucic (22:1), lignoceric (24:0), and nervonic (24:1)]. Another fatty acid, the oxylipin 15(*R*)-hydroxy-(9*Z*, 12*Z*)-octadecadienoic acid (or avenoleic acid), was also found at very small levels in oat grains as part of a specific glycolipid (Hamberg & Hamberg, 1996). The oil content of oats is highly heritable (Baker & McKenzie, 1972) and is inherited polygenically with additive and nonadditive gene actions (Brown et al., 1974; Frey et al., 1975). Selection for high oil oat cultivars tends to increase the percentage of oleic acid at the expense of that of linoleic acid (Frey & Hammond, 1975; Schipper & Frey, 1991, 1992; Thro & Frey, 1985; Thro et al., 1985).

Oat lipids represent a heterogeneous mixture of acyl lipids, which are classified into neutral and polar lipids. The neutral lipids, mainly triacylglycerols, account for 50–60% of total oat lipids (Sahasrabudhe, 1979). The composition of the triacylglycerols in one sample of oats was as follows: POP (2.3%), PLP (1.8%), POO (8.5%), SOO (0.7%), PLO (11.7%), SLO (1.2%), OOO (13.4%), OOL (26.8%), PLL (6.2%), PLLn (0.6%), OLL (16.3%), OLLn (1.5%), LLL (6.0%), and LLLn (1.2%). Indeed, this composition will vary in cultivars mainly depending on the relative variation in oleate (O) and linoleate (L) residues with minor effects of palmitate (P), stearate (S), and linolenate (Ln) residues.

Oat oil is rich in phospholipids (6–26%) and glycolipids (6–17%) (Alkio et al., 1991; Bedford & Joslyn, 1937; Forssell et al., 1992; Sahasrabudhe, 1979; Youngs et al., 1977; Zhou et al., 1999a). The phospholipids of oats are dominated by lecithin or phospatidylcholine (PC; 1,2-diacyl-*sn*-glycero-3-phospho-1′-choline), which accounts for about 50% of the total (Youngs et al, 1977) followed by phophatidylethanolamine (PE; 1,2-diacyl-*sn*-glycero-3-phospho-1′-ethanolamine) and phosphatidylglycerol (PG; 1,2-diacyl-*sn*-glycero-3-phospho-1′-*sn*-glycerol) (Sahasrabudhe, 1979). Numerous other minor phospholipids were isolated from oats including *N*-acylated glycerophospholipids such as *N*-acylphosphatidylethanolamine (*N*-acyl-PE; 1,2-diacyl-*sn*-glycero-3-phospho-(*N*-acyl)-1′-ethanolamine) and *N*-acyl-phosphatidylglycerol (*N*-acyl-PG; 1,2-diacyl-*sn*-glycero-3-phospho-(3′-acyl)-1′-*sn*-glycerol) (Holmback et al., 2001). Recent reports indicate the importance of *N*-acyl PE as precursors for *N*-acylethanolamines, which in turn play a physiological role during germination of seeds (Chapman et al., 1999) and in defense systems in plants (Tripathy et al., 1999). The major *N*-acylated fatty acids in these phospholipids are 16:0, 18:2, and 18:1 (Holmback et al., 2001).

As mentioned above, the major glycolipid in oat lipids is DGDG (Andersson et al., 1997; Aro et al., 2007; Hauksson et al., 1995). About 65% of avenoleic acid is bound to a galactolipid having the structure 1-[(9′*Z*,12′*Z*)-octadecadienoyl]-2-[15′′*R*-{(9′′′*Z*,12′′′Z)-octadecadienoyloxy}-(9′′*Z*,12′′*Z*)-octadecadienoyl]-3-(α-D-galactopyranosyl-1-6-β-D-galactopyranosyl)-glycerol, which is present in oat kernels at ca. 500 ppm (Hamberg et al., 1998). Whereas Hamberg et al. (1998) reported the occurrence of a DGDG with a third fatty acid (a mono-estolide), Moreau et al. (2008) presented evidence that oat kernels also contain DGDG di-estolides, DGDG tri-estolides, TriGDG, TetraGDG, and several TriGDG and TetraGDG estolides.

Minor Lipid Components

The nonacyl lipid components of oat oil, also known as the unsaponifiable fraction, contain sterols, hydrocarbons, tocopherols/tocotrienols, phenolic compounds, saponins, carotenoids/chlorophylls, and other pigments, etcetera. The total level of these in the oil is indeed dependent on the oil extraction method. Oils from four

Turkish oat varieties, extracted with diethyl ether, were found to contain about 4% unsaponifiable materials (Ozcan et al. 2006).

Like other cereals, the oat grain is rich in sterols that are present in free, esterified, glycosylated, and acylglycosylated forms. The free and esterified sterols, but not the glycosylated sterols, are usually co-extracted with oil. The range of levels of sterols in the oils from five Swedish cultivars was 0.15–0.35%, the major sterols being β-sitosterol (54%), Δ^5-avenasterol (26%), campesterol (8%), Δ^7-avenasterol (8%), and stigmasterol (4%) (Määttä et al., 1999). The Δ^5- and Δ^7-avenasterols are subject to acid-catalyzed isomerization (e.g., in acid-clay bleaching during the refining of oat oil) (Kamal-Eldin et al., 1998). This concentration of sterols is intermediate between that of low-sterol oils (<0.1%), such as coconut and avocado oils, and oils with a relatively high content up to 0.4%, such as canola and corn oils (Phillips et al., 2002). Plant sterols produce a wide spectrum of biological activities in animals and humans. Comprehensive reviews are available on their diversity, analysis, health-promoting uses (Moreau et al., 2002), metabolism, and potential therapeutic action (Ling & Jones, 1995).

The total vitamin E (tocopherol/tocotrienol) content range is approximately 20–40 ppm (Emmons & Peterson, 1999; Handelman et al., 1999; Peterson, 1995; Peterson & Qureshi, 1993). α-Tocotrienol is generally the major E-vitamer (ca. 65%) followed by α-tocopherol (20–25%) and small amounts of β-tocopherol and β-tocotrienol (10–15%) (Bryngelsson et al., 2002). Analysis of hand-dissected oat kernels showed that α- and γ-tocopherols are concentrated in the germ while the tocotrienols are concentrated in the endosperm and absent from the hull (Peterson, 1995).

No comprehensive or specific study has investigated the rest of the components in the unsaponifiable fraction in oat lipids. However, a large variety of phenolic compounds were isolated and characterized in oat grains. These occur as free compounds, or as soluble conjugated and insoluble bound forms (Ryan et al., In press). Although the distribution between free, soluble, and bound forms varies widely between different cereals, phenolic compounds are rarely found in the free form in cereals; the majority are bound *via* covalent link with cell-wall polysaccharides. In whole oat grains, free phenols accounted for 25% of the total, while the remaining 75% were in bound form (Adom & Liu, 2002). The distribution of ferulic acid between free, soluble, conjugated, and bound forms in oat grains was 0.4%, 1.8%, and 97.8%, respectively (Adom & Liu, 2002; May et al., 2005). During the 1960s, a number of phenolic acid esters were identified as monoesters and α,ω-diols of C26 and C28 alkanols and glycerol and as monoesters of 26- and 28- hydroxyhexacosanoic acid (Daniels et al., 1963; Daniels & Martin, 1961, 1964a, 1964b, 1965a, 1965b, 1968). After alkaline hydrolysis, these are expected to be present in the unsaponifiable fraction as hydroxycinnamic acids, mainly caffeic and ferulic acids. Another group of special antioxidants in oat comprises the avenanthramides (Collins, 1989; Dimberg

et al., 1993), avenalumic acid (Collins et al., 1991), and β-truxinic acid (Dimberg et al., 2001). Avenanthramides are found exclusively in oats (*Avena sativa* L.). Avenanthramides-2p (*N*-(4′-hydroxycinnamoyl)-5-hydroxyanthranilic acid), -2c (*N*-(3′,4′-dihydroxycinnamoyl)-5-hydroxyanthranilic acid), and -2f (*N*-(4′-hydroxy-3′-methoxycinnamoyl)-5-hydroxyanthranilic acid) are most commonly investigated since they consistently appear in higher concentrations in extracts (Jastrebova et al., 2006; Peterson et al., 2002; Thomas et al., 2006). In fact, avenanthramide-2c constitutes about one-third of the total avenanthramide content in oat grain (Nie et al., 2004). Avenanthramides constitute by far the major unbound phenols present in oat grains. Nevertheless, total concentrations of avenanthramides in oats are small, 2–289 mg/kg (Ryan et al., 2007). Concentrations of different phenolic antioxidants (Fig. 16.3) in oat oils were not investigated but will depend on the extraction method. No comprehensive study has investigated these other types of components.

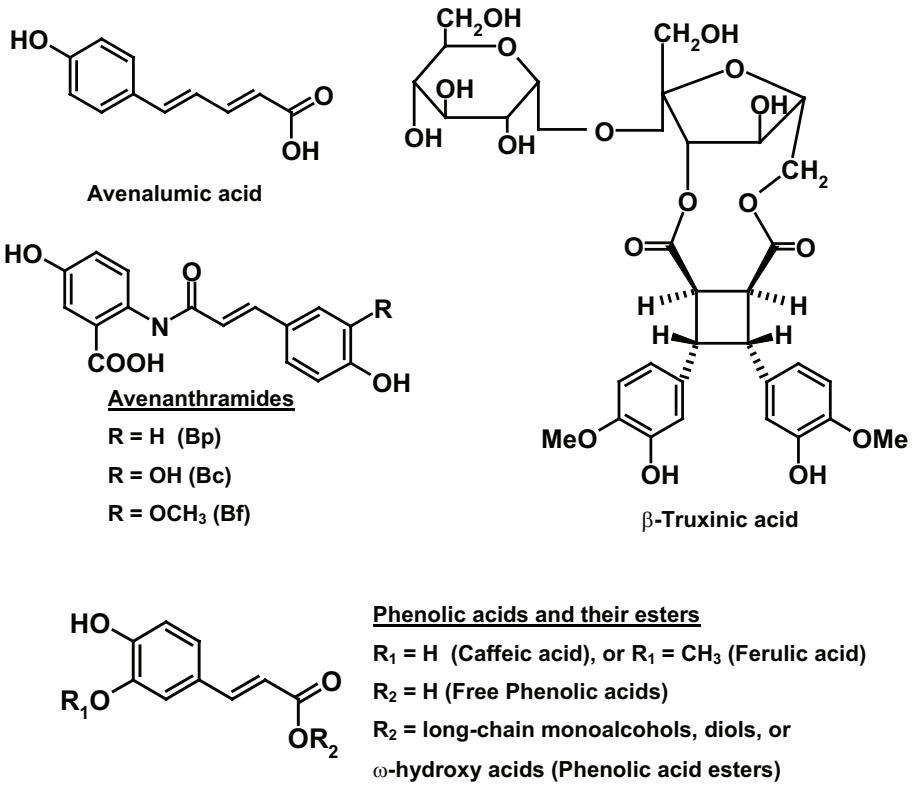

Fig. 16.3. Chemical structures of some unique antioxidant compounds in oat grains (see text for details).

Flavor and Aroma Compounds

As recently as 2004, the production of oat oil was a minor part of the commercial activity of oats: "Currently, oat oil is not processed as a food oil, primarily for economic reasons, although it might become feasible if high-oil cultivars with good agronomic characteristics are developed" (Peterson, 2004). Consequently, little is published regarding the flavor and aroma of oat oil.

Fors and Schlich have made the most comprehensive analysis of oat oil aroma compounds. (Fors & Schlich, 1989). Although the overall goal of this work was related to oat cereal flavor, it is one of very few studies where sensory analysis has been performed on the oil itself. Moreover, the oil of "crude," that is, nonroasted, oats was examined in the study, which has more relevance to commercial oat oil, which is derived from uncooked oats. Fors' and Schlich's report is not cited for studies of oat oil (ISI Database)—an indication that little in the way of sensory analysis was performed on the aroma and flavor of oat oil.

In the Fors and Schlich (1989) study, eight oils were prepared from four treatments consisting of various combinations of heating/roasting and milling, across two varieties—Magne and Chihuahua—and subjected to gas chromatography–mass spectrometry (GC–MS). GC–olfactometry (GC–O) and analysis by a sensory panel was performed on Magne oils from the four treatments. More than 100 compounds were identified by GC–MS and of those, 75 were quantified (Table 16.2). PCA on the GC–MS data related various chemical classes to the different treatments. For example, heated oil from crude oats was characterized by aldehydes, whereas the unheated oil was characterized by alcohols, ketones, and hydrocarbons. On the other hand, oils that were prepared from roasted oats were characterized by nitrogen or oxygen containing heterocycles.

Interestingly, the sensory panel preferred the oils prepared from roasted oats, and similarities were noted with sesame oil and Swedish crispbread. GC-O analysis revealed notes such as roasted, peanut, butterscotch, sesame seeds, and creamy, caramel-like. Compounds identified and given these descriptors included 2-furfurylalcohol, 2-methylfurfural, 2,6-dimethylpyrazine, and acetylpyrazine. Compounds in the oil from crude oats were given descriptors such as herbaceous, green, pungent, plant-like, spicy, green-house, and moldy from GC–O. Saturated and unsaturated aldehydes were identified as giving these attributes. For example, the presence of hexanal was revealed in the odor of "newly cut grass."

Allergic and Toxic Compounds

No reports exist in the scientific literature on allergic or toxic reactions to oat oil (ISI database). Searching the Web reveals a large number of sites claiming the low allergy potential of oat products.

Table 16.2. Oat Oil Volatile Compounds and Associations with Processing (adapted from Fors & Schlich, 1989)

Class	Compounds identified	Association of compounds with oil[a]
Alcohols	butanol, pentanol, heptanol, octanol, l-octen-3-ol	CORC[b] ++
	3-penten-2-ol	MARC +
	hexanol	COUM +
Aldehydes	hexanal, (E,Z)-2,4-decadienal, heptanal, (E,E)-2,4-decadienal, 2-nonenal, 2-ethylhexenal, 2-hexenal, 2,4-heptadienal, 2-undecenal, 2,4-nonadienal, 2-Heptenal, nonanal, decenal, decanal, 2-octenal, octanal	CORC ++
Ketones	2-pentadecanone, dodecadione, cyclic ketone	CORC ++
	2-heptadecanone	COUM, CORM, MBRM +
	Trimethylpentadecanone	
N-Heterocycles	Pyridine Pyrazines unsubstituted, 2,3-dimethyl, 2,5-dimethyl-3-ethyl, methyl, 2-ethyl-6-methyl, 2,5-dimethyl, 2-ethyl-5-methyl, 2,6-dimethyl, acetylmethyl, 2-(2-furyl), ethyl, 2-methyl-5-(methylethyl), trimethyl Pyrroles 2-acetyl, N-methyl-2-furyl, 1-formyl, l-furfuryl-2-formyl, 5-methyl-2-formyl	MARM ++
	dimethylethylpyrazine 2-methyl, dihydrocyclopentapyrazine	MBRM ++
	pentylpyridine	CORC ++
O-Heterocycles	furfural 2-furanylethanone, furanmethanolacetate, hydroxymethylfurfural, 2-methyltetra (or dihydro) furanone, 5-methyl-2-furfural, 2-furanmethanol	MARM ++
	pentylfuran, octylfuran	CORC ++
Hydrocarbons	dodecane, 2-ethyldodecane, 8-methyldecene heneicosane, hexadecene	COUM ++ CORM ++
	dodecene, pentadecane, hexadecane, tetradecane	CORC +
	nonadecane	COUC +
	octadecene	CORM +

[a] ++ = very good association; + = good association

[b] Processing and variety code: COU = crude oats, unheated; COR = crude oats, roasted; MBR = ground roasted oats, milled before roasting; MAR = whole roasted oats, milled after roasting; M = Magne variety 7.4% lipid; C = Chihuauhua variety 8.3% lipid.

Health Benefits of The Oil and Oil Constituents

For centuries, oats were valued for their medicinal qualities. Ground oat preparations were used on the skin for drying and healing as early as 400 B.C., while seventeenth-century New World immigrants used the grain to relieve stomach aches and other ailments (Anon, 2006). More recently, the health benefits of oats were ascribed mainly to the water-soluble mixed linkage (1,3)(1,4)-β-D-glucans (Colleoni-Sirghie et al., 2003), which are the predominant polysaccharide constituents of endosperm cell-walls constituting approximately 85% of the wall in oats (Miller et al., 1995). The health benefits of oats are also often attributed to the presence of various phytochemicals (Zadernowski et al., 1999), including tocols, plant sterols and stanols, and saponins rather than the bulk components. These lipophilic compounds function as antioxidants, and prospective population studies consistently suggest that when consumed in whole foods, antioxidants are associated with significant protection against cancer and cardiovascular disease. The broad range of antioxidant activities from these phytochemicals is probably a significant factor in providing many health benefits. The most abundant antioxidants in oats are Vitamin E (tocols), phytic acid, and phenolic compounds including avenanthramides but flavonoids and sterols are also present (Emmons et al., 1999; Emmons & Peterson, 1999; Peterson, 2001). Depending on the extraction solvent and protocol, these same compounds can be transferred to the oat oil following extraction and thus provide potential health benefits to the oil.

Like palm oil, which has been reported to contain high levels of tocotrienols, the oils of oats, barley, and certain other grains also contain levels of tocotrienols that may be sufficiently high to impart them with health-promoting benefits. Tocols are lipophilic and thus intimately associated with lipid components of the sample matrix. An intrinsic association between the tocols and oil bodies was suggested (White et al., 2006) in which the tocols provide oxidative stability to the membrane and/or oil of oat oil bodies. However, in a more recent trial, tocol and lipid concentrations were not correlated (Peterson et al., 2007). Sterols and tocols are present in oat oil extracted with hexane, but most of the other phenolic antioxidants are not extracted with hexane they are probably partially extracted when oat oil is obtained by extraction with ethanol or other more polar solvents. Tocotrienols were shown to have these abilities: to inhibit hydroxymethylglutaric acid-CoA enzyme activity leading to cholesterol-lowering effects (Parker et al., 1993; Qureshi et al., 1986, 1991, 1989; Raederstorff et al., 2002; Wang et al., 1993), to reduce endothelial expression of adhesion molecules and adhesion to monocytes (Theriault et al., 2002), to minimize atherosclerotic lesions in ApoE-deficient mice (Qureshi et al., 2001), and to inhibit the growth and proliferation of human breast cancer cells (Nesaretnam et al., 1998). Plant sterols are also known for cholesterol-lowering effects even though at much higher doses than may be provided by oat oil. The phenolic compounds in oat oil may contribute to the antioxidant and anti-inflammatory effects of the diet.

The group of Li and co-workers found that the addition of oat lipids to experimental diets induced the formation of three oat-specific I-compounds in liver DNA of female rats (Li et al., 1992; Li & Randerath, 1990; Randerath et al., 1999). I-(endogenous)-compounds represent bulky covalent DNA modifications that increase with age and are detected by ^{32}P-postlabelling (Randerath et al., 1999). Type-1 I-compounds are modified by age, sex, and diet, where oat oil is a significant inducer, while carcinogens and tumor promoters are significant suppressors (Randerath et al., 1999). Since the connection of I-compounds to cancer is unknown, the pronounced effects of oat lipids may be protective or stimulative to cancer, which deserves elaborated investigations.

Other Issues

An ISI Web of Science search for oat oil and adultera or authentic yields zero references. The same situation arises when using Biological Abstracts and Biosis previews databases. Such results show that adulteration of oat oil is essentially nonexistent. This is understandable in light of the very low global production of oat oil and the fact that oat oil is not generally consumed as a food product, but rather is used only in food preparations.

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