8. Camelina oil: Chemistry, properties and utilization

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1. Introduction

Camelina (Camelina sativa L.), an ancient crop native to Northern Europe and Asia, is relatively new to North America (Vollman et al., 1976). A member of the Brassicaceae family, it is also known as false flax, gold of pleasure and Leindotter (Zuhr, 1997). Camelina, once considered a weed, has now garnered considerable interest because of the healthy properties of the oil and its potential as a biofuel. For example, it has lower water, pesticide, and fertilizer requirements compared to rapeseed/canola, soybeans or sunflowers (Budin et al., 1995). Consequently the attractive production economics and minimal input requirements in its cultivation provides further added advantages (Zuhr, 1997; Pilgeram et al., 2007). In February 2009, the United States Food and Drug Administration (US-FDA) allowed an interim exception for the limited use of camelina meal as a feed ingredient in feedlot beef cattle and growing swine rations. The US-FDA also expressed no objection to feeding camelina meal to broiler chickens and laying hens up to...
10 per cent of their final diet. In 2010, Health Canada approved camelina oil as a novel food in Canada and allowed its sale for human consumption. Camelina meal, however, has not yet been approved as feed in Canada. This chapter will review both the historical development of this crop as well as the composition, stability, and nutritional properties of the oil for human use. In addition, the extensive research and interest in camelina oil as a source of biofuel will also be discussed.

2. History and agronomy

Archeological excavations in Europe and Scandinavia showed *Camelina sativa* (L) Crantz, *C. microcaroa* and *C. linicola* were all present in the Bronze Age (1500-400 BC) and in the Iron Age (400 BC-500 AD) (Zubr, 1997). A combination of *C. linola* and flax (*Linum usitatissimum*) seeds and cereals appeared to be an important part of the human diet during the Iron age where it was consumed as porridge and bread (Hatt, 1937; Hjelmquist, 1979). While the crop was grown in Europe, the Balkan region and in Russia up to the 1930s (Wacker, 1934), *C. sativa* became an economically important crop in the USSR in the 1950s (Gorjunova, 1954; Boev, 1956). The renewed interest in *C. sativa* was due to its high level of the ω-3 fatty acid, α-linolenic acid. Today in Western diets there is increasing concern regarding the imbalance between ω-6/ω-3 fatty acids that may be related to a number of chronic diseases (Dolecek, 1993; Skjernvold, 1993; de Lorgeril *et al.*, 1994).

*C. sativa* is extremely flexible as it is resistant to drought conditions and can be grown as an annual summer or biannual winter crop under different climatic conditions. The crop can be harvested using an ordinary combine harvester, although water content in the seed should not exceed 11% (Zubr, 1997). While it has a fairly short growing period, the seed yield can be affected by unfavourable weather conditions. Agronomic evaluation of camelina genotypes grown in different environments in the east of Austria by Vollman and co-workers (2007) found that the large-seeded genotypes with 1000-seed weight of up to 1.81 g were inferior in both yield and oil content to the small-seeded genotypes. This suggested that the large-seeded camelina genotypes were not agronomically viable. Significant variation among the small-seeded camelina genotypes, however, suggested the potential for improving both grain yield and oil content while increasing seed weight would be slow.

3. Composition and stability

3.1. Composition

*Camelina sativa* oil is characterized by its high content of linolenic acid and unique flavor. The oil is composed of more than 50 triacylglycerol
(TAG) constituents, of which over one third (>35%) contained gadoleic (20:1) and eicosadienoic (20:2) acids (Krist, 2006).

The fatty acid composition of *C. sativa* oil is affected by different cultivars, regions and growing conditions (Abramovic and Abram, 2005; Peiretti and Menweiri, 2007). In particular, these variations were ascribed to the combined effects of climatic and soil conditions under which the crop was grown (Zubr and Matthaus, 2002). Extraction and refining methods were also reported to affect the fatty acids of *C. sativa* oil (Eidhin, 2003a). Table 1, summarizes the fatty acid composition of camelina oil from seven summer cultivars and varieties grown in field trials at five remote localities in Central Europe, Northern Europe and Scandinavia (Zubr and Matthaus, 2002). Their results are consistent with many others studies in which the main mono- and

**Table 1.** Mean content of the fatty acids in camelina oil (% of total FA)\(^1\)\(^2\)

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>%</th>
</tr>
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<tbody>
<tr>
<td>C14:0</td>
<td>0.1</td>
</tr>
<tr>
<td>C16:0</td>
<td>5.4</td>
</tr>
<tr>
<td>C16:1</td>
<td>0.1</td>
</tr>
<tr>
<td>C18:0</td>
<td>2.5</td>
</tr>
<tr>
<td>C18:1</td>
<td>14.9</td>
</tr>
<tr>
<td>C18:2</td>
<td>15.2</td>
</tr>
<tr>
<td>C18:3</td>
<td>36.8</td>
</tr>
<tr>
<td>C20:0</td>
<td>1.3</td>
</tr>
<tr>
<td>C20:1</td>
<td>15.5</td>
</tr>
<tr>
<td>C20:2</td>
<td>1.9</td>
</tr>
<tr>
<td>C20:3</td>
<td>1.6</td>
</tr>
<tr>
<td>C22:0</td>
<td>0.3</td>
</tr>
<tr>
<td>C22:1</td>
<td>2.8</td>
</tr>
<tr>
<td>C22:2</td>
<td>0.2</td>
</tr>
<tr>
<td>C24:0</td>
<td>0.2</td>
</tr>
<tr>
<td>C24:1</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Unidentified</strong></td>
<td><strong>0.4</strong></td>
</tr>
</tbody>
</table>

\(^1\)Values represent the mean of seven summer cultivars and varieties grown in field trials in 1997 at five remote localities. \(^2\)Adapted from Zubr and Matthaus (2002).
polyunsaturated fatty acids (PUFA), oleic, linoleic, linolenic and eicosanoic acids ranged from 13.3-19.4%, 12.9-24%, 27.9%-40.3%, and 10.2-16.4%, respectively (Zubr, 1997; Shukla et al., 2002; Eidhin et al., 2003a; Hrastar et al., 2012; Frohlich et al., 2012). *C. sativa* is also a group member of the Brassicaceae with levels of erucic acid (22:1) ranging from 1.4-3.8%. As shown in Table 1 the level of C22:1 is well below the crucial 5% allowable for food use.

Thirty-one volatile compounds were identified in *C. sativa* oil obtained from Carinthia, Austria and pressed at room temperature. Of these, trans-2-butenal (9.8%) and acetic acid (9.3%), trans,trans-3,5-octadiene-2-one (3.8%) and trans,trans-2,4-heptadienal (3.6%), were predominant in the headspace of the examined camelina oil samples (Krist et al., 2006). The odour impressions of camelina oils seem to be based on flavour-active degradation products from long-chain fatty acids, giving a characteristic fatty and sweaty odour. Acetic acid, butyric acid (0.1%) and isovaleric acid (0.3%) are all responsible for a strong sour odour. These short-chain fatty acids are accompanied by odour-active degradation products such as aldehydes and ketones.

*C. sativa* oil also contains minor components, such as tocopherols, sterols, and polyphenols, some of which help make the oil more resistant to oxidative rancidity. The major sterols identified in *C. sativa* oil were sitosterol (1,884 ppm), campesterol (893 ppm) 5-avenasterol (393 ppm), brassicasterol (133 ppm), stigmasterol (103 ppm) and even a small amount of cholesterol (188 ppm) (Shukla et al., 2002). Szterk et al. (2010) investigated the chemical composition of crude *C. sativa* oil (CCSO) and showed the total amount of phytosterols in CCSO was 592.2 mg/100g. Of these, β-sitosterol accounted for over half at 361.3 mg/100g, followed by campesterol (109.6 mg/100g), brassicasterol (33.9mg/100g), cholesterol (33.7mg/100g), Δ5-avenasterol (25.7mg/100g), cycloartenil (18.5mg/100g) and stigmasterol (9.4mg/100g).

Tocopherols in refined camelina oil ranged from 580 mg/kg to 1564 mg/kg (Eidhin, 2010a; Zubr, 2009; Paterson, 1989). The refined oil usually contained a higher total tocopherol content compared to the unrefined camelina oil, ranging from 695 to 994 ppm (Zubr and Matthaus, 2002; Abramovic and co-workers, 2007; Eidhin et al., 2010). Abramovic and co-workers (2007) investigated the tocopherols and polyphenols present in *C. sativa* oil. Their results showed the content of polar phenolic compounds was 128 mg/kg (expressed as chlorogenic acid), while the content of α-tocopherol (α-T) was 41 ± 8 mg/kg, gamma-tocopherol (γ-T) (710 ± 19 mg/kg, and delta-tocopherol (δ-T) 12 ± 3 mg/kg. Neither beta tocopherol (β-T) or tocotrienols were detected in the fresh oil. The higher levels of tocopherols and phenolic compounds in camelina oil makes it more oxidatively stable.
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Compared to other highly unsaturated oils such as flax (Zubr, 1997; Pilgeram et al., 2007; Abramovic et al., 2007; Hrastar et al., 2009). Early work by Mortensen and Skibsted (1997) demonstrated δ-tocopherol had the highest reactivity against free radicals, and might also contribute to the high stability of oil.

3.2. Oxidative stability

Oxidation leading to rancidity is the major cause of quality loss of oils. The susceptibility of oils to lipid oxidation is mostly affected by fatty acid composition, especially polyunsaturated fatty acid, and the presence of minor antioxidant compounds (Kamal-Eldin, 2006). It is well known that unsaturated lipids are readily oxidized with the relative oxidation rate of stearic (C18:0), oleic (C18:1ω9), linoleic (C18:2ω6), and linolenic (C18:ω3) acids being 1:10:100:200 (Lin, 1991). The peroxide values (PV), p-anisidine values (AV), thiobarbituric acid reactive substances (TBARS), Total oxidation values (Totox), conjugated diene levels (CD), and conjugated triene levels (CT) all reflect increasing levels of primary and secondary products of lipid oxidation. These values have been extensively used to monitor the progress of lipid oxidation in oils and fatty food products.

Camelina oil being very high in polyunsaturated fatty acids (PUFA), especially α-linolenic acid (27.9%-40.3%), which makes it an important nutritional source. However, an oil so rich in α-linolenic acid makes it very susceptible to oxidation. Based in the formation of primary products (PV) of lipid oxidation, Eidhin et al (2003a) found camelina oil was more stable in terms of the peroxide value than sunflower, sesame and corn oils, and oils with a high content of polyunsaturated fatty acids, namely linseed oil and fish oil. However, it proved to be far less stable than commonly used rapeseed and olive oils when stored at 65°C in open containers.

Later research by Eidhin and O’Beirne (2010a) found that camelina oil (36.1% ALA) was more stable than tuna oil, omega-3 fish oil, salmon oil as indicated by significantly (p<0.05) lower levels of AV, TBARS and CT during storage for 20 days at 60°C (Figure 1). The levels of PV and TOTOX were similar for both camelina and fish oils up to day 10, although camelina exhibited the highest values up to day 20. With respect to CD values, camelina oil was significantly lower than tuna or omega-3 fish oils but was similar to salmon oil throughout the storage period. This difference was probably related to the antioxidants present in the oil. Compared with the tocopherol content and unsaturation index of tuna oil, omega-3 fish oil, salmon oil and camelina oil, they found that refined camelina oil had the highest tocopherol content (1564 mg/kg) and was less unsaturated than the
other three oils, however, its oxidative stability was fairly similar (Eidhin and O’Beirne, 2010a). The possible reason could be that the high tocopherol levels may have exceeded the optimum level for antioxidant protection of the oil as very high levels of tocopherols can increase the peroxidation rate during the induction period (Kamal-Eldin, 2006). Another study found that rosemary extract extended the Oxidation Stability Index (OSI) induction time.
by 60% of camelina oil compared to fresh untreated oil with 40% lower peroxide values after 11 months of storage (Abramovic and Abram, 2006).

There appeared to be an inverse relationship between initial ALA content and susceptibility to lipid oxidation as indicated by the AV, TOTOX, TBARS, CD, and CT values.

Eidhin and O’Beirne (2010b) later evaluated the oxidative stability of omega-3 rich camelina oil in food products during frying compared with sunflower. The results showed camelina oil was significantly (P < 0.05) higher in PV, AV, TBARS, CT and CD values compared to sunflower oil and significantly (P < 0.05) lower in iodine value after frying for 5 days at 175°C. This indicated that camelina oil was not stable enough for deep frying as sunflower oil. Frohlich et al (2012) also found that camelina oil had a much lower Oil Stability Index and higher p-AV in the oven storage test compared to either rapeseed or sunflower oils.

Abramovic (2007) investigated the relationship between the phenolic compounds and oxidation of camelina oil. They found that the content of polar phenolic compounds in the oil stored at 50°C was reduced to 72% of its initial value, and reduced to 21% of its initial value when stored at 65°C for 15 days. The content of polar phenolic compounds in the *C. sativa* oil decreased linearly with peroxide value and with p-anisidine value. Eidhin and O’Beirne (2010a) investigated the oxidation stability of different oils and found that with the exception of unsaturation indices, other factors such as tocopherol content, oil quality at time zero or the presence of minor compounds may have contributed to their oxidative stability.

The stability of camelina oil also appeared to be influenced by variety. Eidhin *et al.* (2003a) compared the oxidation stability between the Spring and Winter camelina oil. The results showed that Spring camelina had higher (P < 0.05) PV, AV, and TOTOX from day 5 to 16 and significantly higher TBARS (day 2 to 16) than Winter camelina and significantly lower CD (day 10 to 14) and CT (day 5 to 16). Winter camelina had higher CD and CT values than Spring camelina during storage, which can probably be attributed to difference in ALA levels, 40.2% for Winter camelina and 37.7% for Spring camelina. Differences in the amounts of tocopherols could also account for the greater stability of Winter camelina oil.

The processing method of camelina oil also affected its oxidative stability. Research showed that cold-pressed camelina oil had significantly (P < 0.05) lower PV, AV, Totox, TBARS, CD, and CT values than refined camelina oil throughout storage at 65°C (Eidhin *et al.*, 2003a). They also found that the effects of refining (alkali refining and deodorization) on the stability of camelina oil were much greater than cultivar effects. These differences could not be attributed to differences in ALA levels because
refined camelina oil and cold-pressed camelina oil had similar fatty acid profiles. They suggested that the effects of the refining process on tocopherol levels probably accounted for the large effects observed.

Generally speaking, fatty acid composition does not provide sufficient information to predict oil oxidative stability, other factors, such as minor components and processing methods also affect oxidative stability (Przybylski and Eskin, 2009).

4. Nutritional properties

*C. sativa* oil contains higher levels of α-linolenic acid (ALA, 27.9%-40.3%), an essential ω3 fatty acid (ω3FA), than most commonly used food oils. The consumption of ω3FAs has been associated with a reduced risk of coronary heart disease and a reduction in other inflammatory diseases. Consequently it is generally accepted that increasing the dietary intake of ω3FAs would have beneficial health effects. The biological benefits of ALA depend on its conversion to EPA and DHA *in vivo*. ALA is converted in the body to EPA and DHA via elongation and desaturation enzymes, as shown in many studies (Dyerberg et al 1980; Adam *et al*., 1986; Li *et al*., 1999), and a conversion rate of 15% has been reported (Emken *et al*., 1992). However, due to low consumption levels of ALA and the high consumption levels of linoleic acid (C18:2ω6) in modern diets, the conversion of ALA to EPA and DHA is very low (Dyerberg et al 1980; Sanders and Younger 1981).

Studies showed that camelina oil increased the proportion of ALA, EPA and DHA in the fatty acids of serum lipids and reduced serum low-density lipoprotein (LDL) cholesterol in mildly to moderately hypercholesterolemic human subjects (Karvonen *et al*., 2002). An increase in plasma ALA, EPA and DHA and reduced serum triglyceride levels was also reported in pigs following consumption of camelina oil (Eidhin *et al*., 2003b).

Furthermore, the extracted oil from *Camelina sativa* is considered to be a good remedy for various medicinal problems. In traditional medicine, it is used internally against stomach and intestine ulcers, gastritis, colicattacks and digestive problems. Topically applied, a healing effect on bruises, skin scratches, squeezing and sprains as well as skin diseases (e.g. acne) and inflammations is described in the literature (Rode, 2002).

5. Utilization for biofuels

Environmental concerns combined with the depletion of fossil fuel reserves has made renewable energy an attractive and alternative source of energy for the future (Demirbas, 2009; No, 2011). Of these, biodiesel fuels,
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mono-alkyl esters of long chain fatty acids from vegetable oils or animal fats, appears to be a very promising alternative for diesel engines (Atabani et al., 2013). Currently biodiesel fuels are produced from rapeseed by Lithuania and Member states of the European Union (Zaleckas et al., 2012). The second largest producer of biodiesel in the world is the United States, where 85% of the biodiesel is made from soybean oil (Canacki, and Sanli, 2008; Soriano and Narani, 2012). Alternative sources are being examined to minimise its impact on the food sector including Camelina sativa oil. However, the high content of polyunsaturated fatty acids in Camelina oil, as reflected by its high iodine value (IV), prevents it from complying with the IV requirements of Standard EN 14214 2003 for oils suitable for the production of biodiesel fuel. Zaleckas et al. (2012) combined 50% of the Winter variety of camelina oil with 50% pork fat so that the IV was sufficiently reduced for producing biodiesel fuel. They also added the antioxidant ionol (500 ppm) to this mixture which enhanced its oxidative stability. Soriano and Narani, (2012) also noted that compared to palm, mustard, coconut, sunflower, soybean and canola, the high level of ω-3 fatty acids in camelina oil was responsible for the poorest oxidative stability, the highest distillation temperature as well as greatest potential to form coke during combustion of the corresponding biodiesel made from camelina oil. In spite of these deficiencies, however, camelina biodiesel was still very comparable to soybean biodiesel at the B20 level.

Another way to reduce the polyunsaturated fatty acid content and lower the IV is by hydrotreatment. In 2009 both Japan Airlines and KLM Royal Dutch Airlines successfully flight tested an 80% blended hydrotreated renewable jet (HJR) fuel derived from camelina oil (http://uop.com/pr/8050.htm). Subsequent research by Shonnard et al., (2010) reported that an isoparaffin-rich jet fuel derived from camelina oil was also flight-tested by a commercial airline. Camelina oil was extracted and processed to remove any oil impurities and then converted to a hydrotreated renewable jet and/or a Green diesel (GD) by hydrogen. The blended hydrotreated fuel performed just as well as the petroleum and biodiesel fuel but produced substantially lower exhaust and greenhouse gas emissions of between 75-80% (Figure 2). The authors indicated that HJR will soon be certified for commercial jet engines with commercial volumes soon available. They projected that 800 million gallons of the environmentally-friendly camelina-based jet fuel could be produced.

Since biofuels are mono-alkyl esters of long chain fatty acids. Patil and co-workers (2011) examined ways of improving the transesterification of camelina oil. Increased fatty acid methyl ester conversion rates were found to be enhanced by both metal oxide catalysts as well as the mode of heating.
Figure 2. Contributions of greenhouse gases (GHG) to total emissions (Shonnard et al., 2010).

Higher yields of fatty acid methyl esters were achieved in the presence of BaO and SrO catalysts while the transesterification process was two orders of magnitude higher when heated in the microwave compared to conventional heating. Thus concluded that transesterification of camelina oil in the presence of heterogenous metal oxide catalysts, when microwave heated, resulted in higher yields of fatty acid methyl esters.

Camelina sativa biodiesel was recently evaluated by Ciubota-Rosie et al. (2013) as a viable fuel alternative using a detailed characterization based on both the European and American standards (EN 14214 and ASTM D6751). Using thirty parameters, they showed that the polyunsaturated fatty acid content, iodine value, cetane number and oxidative stability of camelina oil-derived biodiesel did not meet the quality specifications stipulated in the EN 14214 and ASTM D6751 standards. For camelina oil to be better suited for biodiesel, genetic engineering or conventional plant breeding would be required to reduce the high degree of unsaturation and molecular weight. Until that is achieved, however, blending or hydrotreating camelina oil appear to be alternative strategies for developing it for biodiesel.

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