TECHNICAL

# Stability of Low Linolenic Acid Canola Oil To Frying Temperatures

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**The effect of heating on the oxidation of low (1.6%) linolenic acid canola oil (C18:3) at frying temperature (185 ± 5°C) under nitrogen and air was examined and then compared to a laboratory deodorized (9.0%, C18:3) and a commercially deodorized (8.5%, C18:3) canola oil sample. A significantly lower development of oxidation was evident for the low C18:3 canola oil, based on the measurement of peroxide value (PV), thiobarbituric acid (TBA), free fatty acids (FFA), dienals and carbonyls. The greater stability of the low C18:3 canola oil was also reflected by a corresponding improvement in heated room odor intensity scores. Heating under nitrogen (rather than air) not only improved the odors but limited the oxidation in all oils. While the low C18:3 canola oil heated under nitrogen was acceptable in 94% of odor judgments, the same oil heated in air was acceptable in only 44%. This suggests that even low levels of C18:3 may contribute to the development of the heated room odor phenomenon.**

Good quality canola oil and soybean oil develop an unpleasant room odor when heated to frying temperatures. This phenomenon was noted in rapeseed oil by Niewiadomski (1) and documented in canola oil by Dobbs *et al.* (2) who characterized the heated odor as painty, with elements of buttery, sweet, sulfur-like and fishy notes. The room odor associated with heated soybean oil, however, has been shown to be less intense than that of canola oil, but stronger and/or less pleasant than that of heated corn, peanut, and sunflower oils (2,3). Mounts (4) maintained that the unacceptable room odor of soybean oil at frying temperatures was the main impediment to the expansion of the European market for the oil.

Oils heated at elevated temperatures in the presence of air undergo oxidation as well as thermal decomposition. Since it is readily oxidized, the high linolenic acid content (C18:3) of canola and rapeseed oils has been implicated in their susceptibility to room odor development on heating (5,6). The value of antioxidants in suppressing heated oil room odor is debatable. Evans *et al.* (7), using a combination of antioxidant and an antifoaming agent, and Mounts (4), using the antioxidant Tenox 6, reported improvements in the room odor scores of heated soybean oil. However, Vaisey-Genser and Ylimaki (8) found that anoxomer, a polymeric antioxidant, failed to improve the heated room odor of canola oil even though it markedly improved its shelf life.

Reducing the C18:3 content by hydrogenation was shown to modify the susceptibility of both soybean and canola oils to heated room odor development (2,9). Durance (10) reduced the C18:3 content of canola oil by blending it with cottonseed oil. This led to a distinct reduction in heated odor room intensity. An experimental low C18:3 canola cultivar, which was provided by the Plant Science Department of the University of Manitoba, offered a unique opportunity to examine its stability to room odor development at frying temperatures. This paper reports a comparison of the development of heated room odor in a low linolenic acid canola oil with two samples of high linolenic acid canola oils. To clarify the effects of oxidation, samples were heated both in air and under nitrogen.

## EXPERIMENTAL

*Materials.* Three canola oil samples were provided by POS Pilot Plant Corp., Saskatchewan, and included one sample of laboratory refined, deodorized low linolenic acid canola oil, one sample of laboratory refined, deodorized canola oil and one sample of commercially refined and deodorized canola oil.

*Methods.* Each of the three canola oil samples (150 ml) was heated in 250 ml pyrex beakers on a Corning Hot Plate (model PC-351) to 185 ± 5°C for 10 min either in air or under nitrogen (to exclude oxygen). After cooling, the samples were transferred to glass vials, flushed with nitrogen, capped and stored at −20°C for up to two weeks until all evaluations could be completed. The corresponding unheated oils were stored in a similar manner prior to testing. There were a total of nine treatments to be compared. The heating treatments were done twice to provide two replications. All analyses were duplicated for each replicate. Analytical work within a replicate was structured so that all the treatments were examined on only one day for any single index. For the sensory analysis duplicate tests were done on separate days.

Odor evaluation of each of the samples was conducted by eight members of a trained panel. They did the evaluations in a standard sensory testing room where the samples were presented under red light. Oil samples (50 ml) were placed in 80 ml red pyrex glasses covered with aluminum foil lids and coded with three digit random numbers. The oils were sniffed at 50°C, which is the recommended temperature for oil odor testing (11). To maintain a constant temperature, the glasses were placed on small Corning Hot Plates (PC-35) in waterbaths filled with distilled water. The nine treatments, plus an unheated sunflower seed oil, were tested by the panel in two sets (5 samples/set) with a five-minute break between sets. All panel sessions were held in the morning over a two-hour period. This was based on tests which showed that there were no changes in the peroxide values of the oils over this time period.

A 15 cm semi-structured line scale was used to evaluate the odor intensity of the oils. Panelists were required to place vertical strokes on the line scale to indicate their perceived odor intensity of the oil. A numerical value was obtained for odor intensity (OIV) by measuring the length

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(in cm) between the bland end point (zero) and the panelists stroke. Panelists were also requested to state whether or not each sample was acceptable using a forced-choice procedure. Acceptability was defined by the panel as a "willingness to use the oil."

In addition to the sensory analysis, oxidation of the oils was assessed by peroxide value (PV) (12), thiobarbituric acid (TBA) value (13), free fatty acids (14) and total carbonyls and dienals (15). The fatty acid compositions of the three oil samples were determined by gas chromatography on a Perkin-Elmer chromatograph with a fused silica capillary column (15 m × 0.25 mm i.d.) coated with bonded Supelcowax 10 (Supelco, Bellefonte). The oven temperature was run isothermally at 195°C with the injector and detector temperatures at 250°C. Samples were esterified with sodium methoxide. All of the chemical tests were done in duplicate.

For analysis of variance, each data set was treated as a factorial arrangement (3 Oil [O] Types × 3 Heat [H] Conditions).

## RESULTS AND DISCUSSION

The fatty acid compositions of the canola oil samples are summarized in Table 1. The low linolenic acid oil contained only 1.6% C18:3, as compared to 9.0 and 8.5% for the laboratory and commercially deodorized canola oil samples, respectively. Stellar, a cultivar that has since been commercially licensed, has C18:3 levels in the order of 3.0% (16).

Summary data from the analyses of the variance of assessments of odor intensity and of measurements of the five chemical indices of oxidation show that there were significant differences in all parameters among the three oil types. These data also show that there were large differences among the heating conditions imposed on them (Table 2). The significant interaction between these two effects (OxH) in the cases of the data for odor intensity, free fatty acids and dienals, points to different responses of the oil types to the various heating conditions. An examination of the individual treatment means (Table 3) showed that in each instance, the difference was one of degree, whereas the direction of differences was consistent.

In comparing the main effect of oil types, the low C18:3 oil was significantly different from the high C18:3 oils in all parameters (Table 4). There were no significant differences between the laboratory and commercially refined high C18:3 oils. This lends confidence in extrapolating the findings on the low C18:3 oil to commercial conditions, even though the material used in this study was refined in the laboratory. Less oxidative changes were observed when the oil was heated under nitrogen than when it was heated in air (Table 4).

It is evident from the individual treatment means in Table 3 that prior to heating, the three oils tested were similar in blandness and freedom from oxidation products. It is also evident that when heated to 185°C in either nitrogen or air, the low C18:3 oil suffered less change in every index than did either of the high C18:3 oils. This verifies the influence of C18:3 and its susceptibility to

TABLE 1

**Fatty Acid Composition of Refined, Deodorized Canola Oil Samples (% Methyl Esters)**

| Fatty acids | Low C18:3, laboratory refined | High C18:3, laboratory refined | High C18:3, commercially refined |
|---|---|---|---|
| C16:0 | 4.5 | 4.5 | 4.5 |
| C18:0 | 2.3 | 1.9 | 2.0 |
| C18:1 | 67.0 | 62.7 | 65.0 |
| C18:2 | 21.5 | 17.5 | 18.5 |
| C18:3 | 1.6 | 9.0 | 8.5 |
| C20:0 | 0.6 | 0.6 | 0.5 |
| C20:1 | 1.0 | 1.6 | 1.4 |
| C22:0 | 0.3 | 0.3 | 0.3 |
| C22:1 | 0.1 | 1.0 | 1.0 |

TABLE 2

**Summary of Analyses of Variance of Odor Intensity Values and Chemical Indices of Oxidation**

| Source of variability | Degrees of freedom | Mean square odor intensity | Degrees of freedom | Mean squares | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Peroxide value | TBA | Free fatty acids | Dienals | Carbonyls |
| Oil type (O) | 2 | 148[b] | 2 | 1.2[a] | 3.2[b] | 0.003[a] | 0.6[b] | 45.2[b] |
| Heat condition (H) | 2 | 1007[b] | 2 | 12.8[b] | 7.2[b] | 0.056[a] | 2.3[b] | 210.9[b] |
| Replications (R) | 1 | 1 | 1 | 0.0 | 0.0 | 0.000 | 0.0 | 2.8 |
| Judges (J) | 7 | 40[b] | — | — | — | — | — | — |
| OxH | 4 | 28[b] | 4 | 0.4 | 0.8 | 0.003[a] | 0.2[a] | 13.0 |
| OxR | 2 | 51 | 2 | 0.0 | 0.0 | 0.000 | 0.0 | 1.8 |
| OxJ | 14 | 10 | — | — | — | — | — | — |
| HxR | 2 | 1 | 2 | 0.2 | 0.0 | 0.000 | 0.0 | 4.0 |
| HxJ | 14 | 10 | — | — | — | — | — | — |
| RxJ | 7 | 14[a] | — | — | — | — | — | — |
| OxHxR | 4 | 36[b] | — | — | — | — | — | — |
| Error | 84 | 6 | 4 | 0.1 | 0.024 | 0.003 | 0.21 | 2.33 |

Note: For oil type, see Table 1. Heating condition—none, heating in air, and heating under nitrogen.

[a]Differences significant at $P < 0.5$.

[b]Differences significant at $P < 0.01$.

**TABLE 3**

**Effects of Heating on the Chemical and Sensory Indices of Oxidation of Low and High Linolenic Acid Canola Oils (Average of Duplicate Values in Two Replications)**

| Index[a] | Low C18:3, laboratory refined | | | High C18:3, laboratory refined | | | High C18:3, commercially refined | | | Least significant difference |
|---|---|---|---|---|---|---|---|---|---|---|
| | Unheated | Heated $N_2$ | Heated air | Unheated | Heated $N_2$ | Heated air | Unheated | Heated $N_2$ | Heated air | |
| PV | 0.30 | 1.00 | 2.30 | 0.50 | 1.80 | 4.00 | 0.00 | 2.10 | 3.50 | 1.67 |
| TBA | 0.01 | 0.31 | 0.84 | 0.03 | 1.90 | 2.57 | 0.03 | 2.09 | 3.14 | 0.83 |
| FFA | 0.03 | 0.05 | 0.15 | 0.05 | 0.08 | 2.16 | 0.15 | 0.06 | 0.27 | 0.09 |
| DIEN. | 0.01 | 0.16 | 0.58 | 0.03 | 0.44 | 1.54 | 0.02 | 0.91 | 1.64 | 0.51 |
| CARB. | 0.62 | 3.15 | 7.45 | 1.50 | 4.44 | 13.04 | 0.72 | 8.54 | 17.40 | 8.20 |
| OIV | 0.40 | 4.60 | 7.20 | 2.00 | 6.80 | 11.10 | 1.00 | 9.30 | 12.20 | 2.66 |
| ACCP. (%) | 100 | 94 | 44 | 100 | 62 | 19 | 100 | 31 | 0 | — |

[a]PV = Peroxide value (Meq/Kg); TBA = thiobarbituric acid value; FFA = free fatty acids (%); DIEN. = dienals (unsaturated carbonyls); CARB. = carbonyls; OIV = odor intensity value (max. 15); ACCP. = acceptability (%).

**TABLE 4**

**Comparison of the Main Effects of Oil Type and Heating Condition on Odor Intensity and Chemical Indices of Oxidation**

| Index[a] | Least significant difference | Effect of oil type | | | Effect of heating condition | | |
|---|---|---|---|---|---|---|---|
| | | Low C18:3, laboratory refined | High C18:3, laboratory refined | High C18:3, commercially refined | No heat | Heated in $N_2$ | Heated in air |
| PV | 0.650 | a[b] | b | b | a | b | c |
| TBA | 0.315 | a | b | b | a | b | c |
| FFA | 0.035 | a | a,b | b | a | b | c |
| DIEN. | 0.296 | a | b | b | a | b | c |
| CARB. | 3.114 | a | a,b | b | a | b | c |
| OI | 0.160 | a | b | b | a | b | c |

[a]As in Table 3.

[b]Within an effect, values in the same row bearing the same letter are not significantly different ($P < 0.05$); "a" represents the lowest mean value, and "c," the highest.

oxidation on heated room odor development in canola oil. These results are consistent with the findings of Mounts *et al.* (17), who reported improvement in heated room odor development for low linolenic acid soybean oils extracted from new genotypes.

The role of oxidation in the heated odor phenomenon was further confirmed by the observation that heating under nitrogen (rather than in air) gave more stability in all three oils. However, while oils heated under nitrogen were more stable in all respects than those heated in air, they still showed evidence of deterioration from the unheated state (Tables 2, 3, 4).

The dual benefit of blocking access to oxygen and reducing oxidation-susceptible C18:3 was illustrated by the response of the low C18:3 oil to heating under nitrogen. This was the most stable of the heat treatments examined (Table 3). None of the chemical indices of oxidation were significantly different from the unheated oil. While the odor intensity was significantly stronger than before heating, it was acceptable to 94% of the panelists. It has been noted earlier that the odor of stored unheated canola oils with TBA values of 0.49 or less remained acceptable (8). In the present case, however, the TBA value of low C18:3 canola oil heated under nitrogen was only 0.31.

The results of this study clearly show that a marked reduction in the linolenic acid content of canola oil from 8–9% to 1.6% reduced the development of heated room odor at frying temperatures. However, the room odor of the oil from a low linolenic acid cultivar of canola remained too strong to be considered acceptable when it was heated in air rather than under nitrogen. While it had a less intense odor than the high C18:3 oils, it was acceptable to only 44% of the panelists. The use of a nitrogen blanket in routine frying appears impractical. On the assumption that even 1.6% C18:3 triggers the development of heated room odor, the value of touch hydrogenation should be considered as a process to make low linolenic acid canola oil a premium frying medium.

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