TECHNICAL

A New Variety of Low-Linolenic Rapeseed Oil; Characteristics and Room-Odor Tests

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Two Canadian rapeseed oils, "Westar" and "low-linolenic", supplied by the Canola Council were studied and compared with a French rapeseed. The linolenic acid content of the low-linolenic variety is about 3%. This drop in the C18:3 is completely compensated for by an increase in the C18:2. Seventy-two percent of the triglycerides with at least one linolenic chain disappeared. A strong increase in the OOL and OLL was observed. The room-odor tests showed that the "low-linolenic" had a significantly higher odor score than the French rapeseed and the "Westar", both of these being very similar. A fruity odor dominated in the "low- linolenic", and the fishy painty odors were particularly reduced.

When used in deep fat frying, rapeseed oil and soybean oil give off an odor in the kitchen which is perceived to be unpleasant by the French homeowner, who is accustomed to peanut or sunflower oils. In 1981 and 1982, comparative room odor tests showed that fishy and painty odors were probably due to linolenic acid contents being between 6-10% (results presented at the 76th AOCS meeting, Philadelphia, May, 1985). It is well known that France, due to its legislation (1), is the only country in the world to exclude oils with more than 2% of linolenic acid for deep-fat frying, thus adaptation for these oils' use was not possible as in other countries. In 1983 and 1984 we showed that the addition of 2-5% of linolenic acid to sunflower fatty acids did not seem to have a noticeable influence on the room odor tests. In addition, the interesterified product of sunflower oil and trilinolenin was not considered to have a bad odor in room odor tests. In Canada, a genetic modification or rapeseed led to a "low-linolenic" spring variety. As the Canola Council had about 300 kg of "low-linolenic" rapeseed oil at their disposal at the end of 1986, we were interested in studying the properties of this oil. The Centre d'Etudes Techniques Interprofessionnel des Oléagineux Metropolitains (CETIOM) asked us to determine its composition and to carry out comparative room odor tests.

MATERIALS AND METHODS

Materials. Two samples (about 25 kg each) of neutralized, bleached rapeseed oils from "Westar" and "low-linolenic" varieties were provided by the Canola Council. The neutralized, bleached, French winter rapeseed oil from "Bienvenu" variety was provided by Lesieur Company (Boulogne Billancourt, France).

Pilot plant deodorization (2). The oils (2,500 ml each) were deodorized in a 3-liter stainless steel vessel equipped with a steam generator, a cryostat-condenser (-30°C) and a vacuum pump. The conditions were as follows: steam was injected at the rate of 4 g per 100 g of oil per hour under a reduced pressure of 1.5 mm Hg during 3.5 hr at 210°C + 1.5 hr at 180°C. Immediately after deodorization, the oils were cooled at room temperature with nitrogen. They were then stored at -18°C under nitrogen.

Percolation through silica gel. Bleached French rapeseed and "low-linolenic" rapeseed were percolated through silica gel in a column (ID = 7 cm) filled to a height of 52 cm with 1 kg of silica gel, 70-230 mesh. The non-diluted oil was percolated under a reduced pressure at a flow rate of 0.4-0.5 1/hr. The oils were deodorized, as above, after treatment.

Fatty acid analysis by gas liquid chromatography (GLC) (3). Methyl esters were prepared by interesterification with sodium methoxide according to NF T 60-233 procedure. One μl of the hexane extract was injected onto a laboratory-made glass capillary column (L = 30 m; ID = 0.4 mm; Carbowax 20M, film thickness 0.2 μm), through a splitter (1/100) in a DELSI Model DI 700 gas chromatograph (92600, Suresnes, France) equipped with a FID. The injection port and the detector were operated at 200°C while the column temperature was maintained at 180°C. The inlet pressure of the hydrogen carrier gas was 0.4 bar. The fatty acid identification was done by equivalent chain length (ECL).

Triglycerides analysis by high performance liquid chromatography (HPLC) (4,5). Triglycerides were analyzed on a Varian model 5500 (Varian Associates, Palo Alto, CA) ternary gradient HPLC equipped with a Rheodyne injection valve 7125 (10 μl loop), two columns (Superspher 10 CH 18 super, L = 250 mm, ID = 4 mm Merck, Darmstadt, Federal Republic of Germany) were linked in series with a zero dead volume union (Merck, ref. 15731); a Laser Light Scattering Detector (Varex, Rockville, MD) model L/LSD; and a Varian Vista 402 integrator. The following linear solvent gradient was used: acetonitrile:dichloromethane:acetone, from 80:15:5 to 20:60:20 in 60 minutes. Flow rate was 1 ml/min. The detector was used with a 1/5 split ratio (200 μl/min inlet flow rate), 2 l/min CO2 flow rate, and the evaporating tube was operated at 50°C. The identification of triglycerides species was done according to their partition number and a home-made, basic program (5).

Quality assessment. Ultra-violet spectra of oil samples were obtained on a Beckman (Fullerton, CA) spectrometer model DU 70 equipped with a Hewlett-Packard x/y chart recorder model Color pro 7440 A. Determinations of the Peroxide Value were done according to the IUPAC method 2.501 (6).

The room odor tests: Equipment, materials and sample preparation. The equipment was chosen in order to reproduce domestic frying conditions (7-9). The potatoes were of the "bintjes" variety and were cut into standardized pieces of one centimeter square and five to six centimeters long. In a 40-cubic meter room, 180 grams of potatoes were fried at 180°C for 5 min, plus dripping, plus 1 min of second frying. The surface (dm^2) to weight (kg) ratio of the frying bath was two. Eight fryings were con-

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ducted with each oil over a two-day period; the panel evaluated the room odor three times: for the first, the fourth and the eighth frying.

Evaluation. Each member of the panel was first asked to determine the overall strength of odor as a point on an intensity continuum; certain scores were given a definition of the odor in the room; it was, of course, possible to give intermediate scores (7-9). The scores were: 10—Unnoticeable frying odor; 8—slight frying odor, acceptable at home; 6—distinct odor, acceptable outside; 4—poor odor; 2—very poor and repulsive odor. The odor of the first frying with peanut oil (from Nigeria) was given a reference score of eight on the intensity continuum. Secondly, the panel members were asked to determine what characteristic odors they had perceived using a list of odor descriptions, and to rate the intensity as nil, slight, moderate or strong. The list of possible characteristics used was: nutty sweet fruity, grassy beany, buttery hydrogenated tallow, burnt acrid pungent rancid, painty plastic fishy. The panel was trained before the tests to detect these different odors.

Interpretation. The overall strength of odor was given by the mean score obtained from all the marks attributed by the panel members (7-9). The intensity of the odor characteristic was quantified by means of factors corresponding to the perceptions, i.e., 0 for none, 1 for weak, 2 for moderate and 3 for strong. The odor characteristics were then grouped in twos or threes in order to bring out the specific defects of heated oils. The characteristics nutty, sweet or fruity were left on their own and were considered as a quality for the tested oils. Considering that the number of the panel members differed between groups of 10 to 25, the sum of the characteristic intensities was balanced according to the real number of participants and adjusted to 10. The scores were given by the Pessac ITERG-CETIOM panel, which was made up of about 20 people; this is notable because the maximum possible number was 25. The panel was trained again before the experiments.

RESULTS AND DISCUSSION

Fatty acid composition. The fatty acid composition of the French and the two Canadian rapeseed oils are given in Table 1. In comparison, the fatty acid composition (mean values) of peanut oils from Africa and South America are also given. There are several notable points here. First, the "low-linolenic" rapeseed linolenic acid content is 3.1%. Compared to the "Westar" rapeseed (C18:3 = 11.3%), this represents a drop of about 72%. Compared with the French rapeseed (C18:3 = 7.3%), the drop is 58%. Second, this reduction has repercussions only on the linolenic acid content—the decrease in the C18:3 is 8.2% absolute value; the increase in the C18:2 is 8% absolute value. Third, the erucic acid content of the "low-linolenic" is very low (< 0.05%). And, finally, by comparison with the peanut oils, the "low-linolenic" has a linolenic acid content (28.6%) ranging from African oil (21.4%) to South American oil (37.9%); a linolenic acid content (3.1%) halfway between peanut (0.1%) and French rapeseed (7.3%); and less C16, C20, C22 or C24.

Triglycerides. Triglyceride compositions are given in Table 2. The total percentage of the triglycerides having one or two linolenic chains (LLnLn, LLLn, OLnLn, PLLn, OOLn, POLn) is as follows: French rapeseed, 17%; "Westar", 28.2%; and "low-linolenic", 8%. Thus, in relative values, 72% of the triglycerides having one or two linolenic acid chains disappeared, when we compare the "Westar" and the "low-linolenic". This value is about 50% for the French rapeseed in comparison with the "low-linolenic". The heavy increases in OLL and OOL in the "low-linolenic" rapeseed are noticeable.

Quality assessment. The peroxide value of the oils received from Canada as neutralized and bleached oils were: "Westar," 30- 31.8 meq/kg; and "low-linolenic", 58.6-59.4 meq/kg. These oils showed a high level of peroxidation due to their storage in Canada for 18 months at room temperature.

Percolation through silica. The characteristics in the visible and the UV areas are given in Table 3. The percolation through the silica gel column improved the color by a factor of three. The UV absorbencies were also improved, but the improvement is mainly marked for the "low-linolenic", due to its high level of peroxidation. After pilot plant deodorization, the peroxide values were obviously nil.

Room odor tests. The mean scores (true mean value at probability level 95%) appear in Figure 1. The dispersion

TABLE 1

Fatty Acid Composition of the Rapeseed Oil and Two Peanut Oils (Weight Percent)

Fatty acids	Rapeseed			Peanut	
	French	"Westar"	"Low Linolenic"	African	South American
16:0	5.3	3.7	3.9	10.3	11.2
16:1	0.3	0.2	0.2	0.07	tr[a]
18:0	2.0	1.6	1.7	3.7	3.3
18:1	60.9	58.6	59.4	56.6	38.7
18:2	20.9	20.7	28.6	21.4	37.9
18:3	7.3	11.3	3.1	< 0.1	0.1
20:0	0.6	0.6	0.7	1.7	1.7
20:1	1.4	1.4	1.5	1.2	1.3
22:0	0.4	0.3	0.5	3.1	3.9
22:1	0.4	0.5	< 0.05	tr[a]	tr[a]
24:0	—	—	—	1.5	1.6
N.I.	0.5	1.1	0.4	—	—

[a]tr = Trace.
[b]N.I. = Not identified.

TABLE 2

Triglycerides Species of the Rapeseed Oils (Weight Percent)

Triglycerides species	French w %	"Westar" w %	"Low-linolenic" w %
LLnL	—	0.7	—
LLLn	0.8	1.3	0.6
OLnLn	0.7	2.9	—
LLL	2.2	1.1	3.1
OLLn	4.7	9.2	3.0
PLLn	1.0	0.9	0.3
OLL	9.1	9.2	15.6
OOLn	8.2	11.5	3.6
PLL	2.0	1.4	1.8
POLn	1.6	1.7	0.5
OOL	22.9	19.8	27.6
POL	6.7	4.6	5.4
OLGa	1.7	1.2	1.8
OOO	26.1	23.9	24.3
StOL	2.1	1.8	2.2
POO	6.3	4.2	4.6
PPO	1.7	1.3	1.6
StOO	2.1	2.0	2.1
N.I.	—	1.3	1.9

Abbreviations: Ln = linolenic acid; L = linoleic acid; 0 = oleic acid; P = palmitic acid; St = stearic acid; Ga = gadoleic acid; N.I. = not identified.

TABLE 3

Spectral Characteristics of the Oils After Passing Through Silica Gel Column

		French rapeseed		"Low-linolenic"	
		bleached	silica treated	bleached	silica treated
E	420 nm[a]	0.27	0.10	0.30	0.10
E	232 nm	2.44	2.09	4.13	2.62
E	270 nm	0.74	0.56	1.42	0.81

[a]In the visible region on the pure oil.

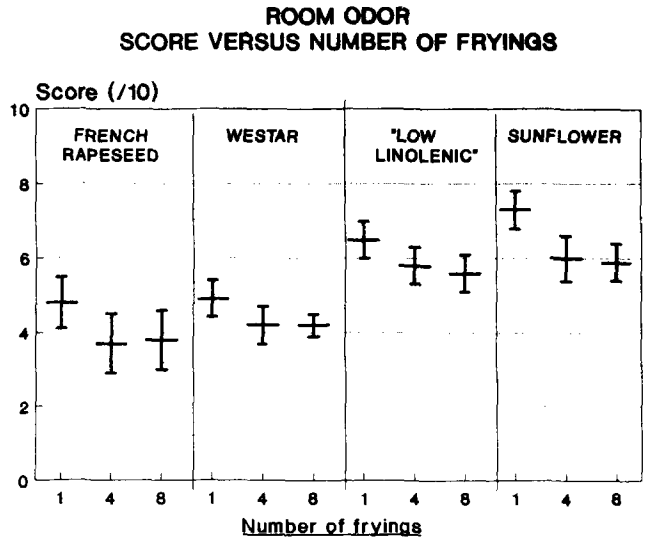

FIG. 1. Room odor: Scores of the three studied refined oils compared with sunflower. Tests after the first, fourth and eighth frying. Each bar represents Mean Value ± SEM (standard error mean value; $p < 0.05$; n ranging from 15-25).

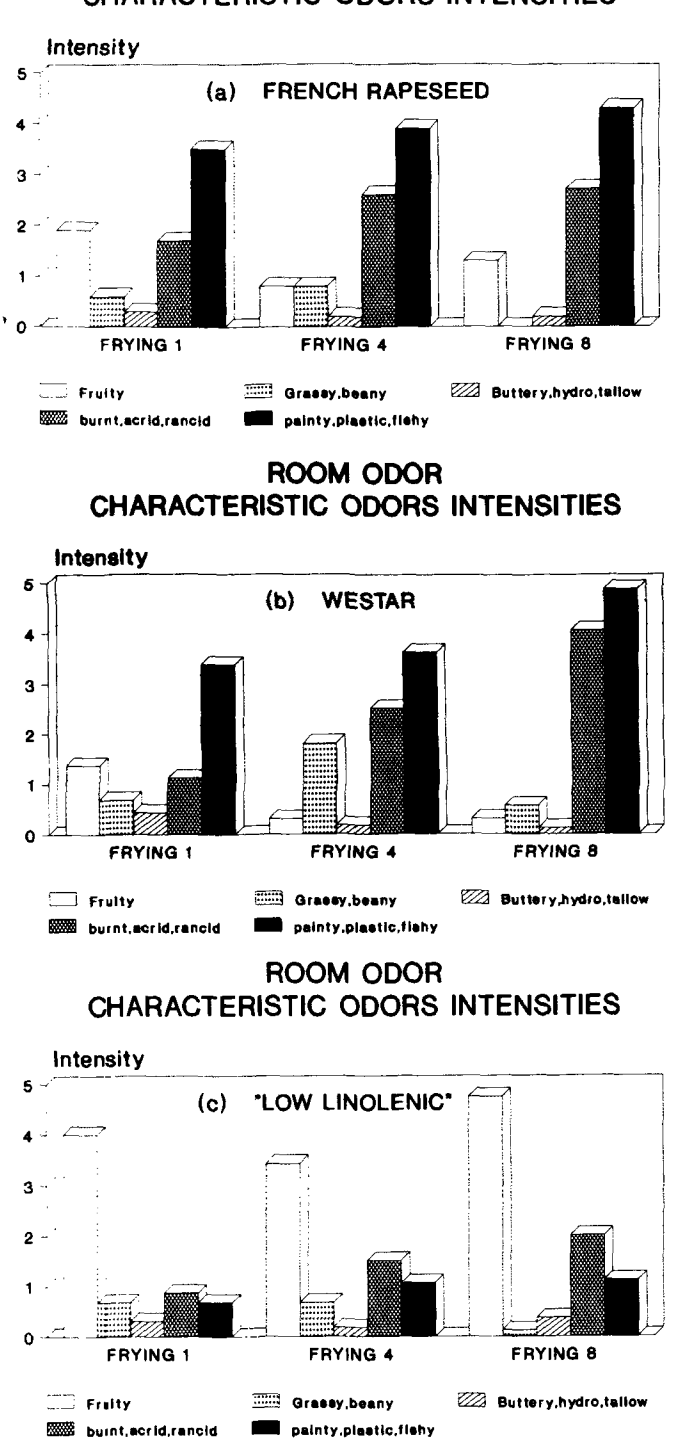

FIG. 2. Room order: Characteristic odors intensity: (a) French rapeseed oil, (b) "Westar" rapeseed oil; and (c) "Low-linolenic" oil.

of this mean value is indicated ($\pm \sigma_m t$, with σ_m = mean standard deviation and t = Fisher parameter value). The deviations of the mean scores were usually ± 0.5 to 0.6 point. Room odor tests (eight fryings over a two-day period with scores on the first, fourth and eighth frying) were conducted twice for the French rapeseed and for the

"low-linolenic", although this was not provided for in the procedure.

French rapeseed. The scores were always below a mean value of five from the first frying. At the fourth frying, the scores were between three and four. A slight increase in the scores was sometimes noticeable. This confirms the results that we have obtained for seven years.

"Westar". The scores at the first, fourth and eighth frying were quite similar to those of the French rapeseed.

"Low-linolenic". The scores obtained were significantly better than the two other rapeseed oils. At the first frying they were included between six and seven, as compared with four or five. This difference persisted at the fourth and the eighth frying. These scores were very close to those obtained with the sunflower oil.

Oils percolated through silica gel. Passing oil through silica gel did not improve the flavor scores significantly.

Characteristic odors intensity. The intensities for the first, fourth and eighth fryings can be seen in Figure 2.

French rapeseed and "Westar" (Figs. 2a and 2b). The fishy painty plastic odors, as well as the burnt acrid rancid ones, were very heavily predominant from the first frying. That is doubtless the reason why the scores were below the mean value. These unpleasant odors increased during the fryings, which both explains and confirms the decrease in the scores. The fruity odor judged as agreeable was unimportant, although a little more marked for the French rapeseed than for the "Westar", and with a slight increase at the eighth frying, exactly as we had observed repeatedly.

"Low-linolenic" (Fig. 2c). The fruity odor was predominant, which is comparable with what we had previously obtained for the sunflower oil. The acrid odor came in second place, while the fishy odor came in third place. A second series of fryings (second test) was less in favor of the "low-linolenic". This could be attributed to the panel becoming more critical, because a second series of frying for the French rapeseed showed a total absence of fruity odor at the fourth and eighth fryings.

Oils percolated through silica gel. Concerning the French rapeseed, no significant difference could be observed after percolation through silica gel. For the "low-linolenic", the passage of the oil through silica gel in the first frying clearly improved the intensity of the fruity odor judged as agreeable; and the defects became unimportant. This behavior was very likely due to the fact that the original oil was heavily oxidated and that the single refining could not completely eliminate the oxidized compounds; while elution through silica gel allowed their elimination. This is clearly visible on the UV spectra. On the other hand, at the fourth and eighth frying, the differences from the original oil were no longer significant. Therefore, the Canadian "low-linolenic" rapeseed oil with 3.1% of linolenic acid has a significantly better behavior in frying than the other rapeseed oils; this behavior is very close to that of a sunflower oil. It appears that the amount of linolenic acid is responsible for the good of bad room odor of the rapeseed oil since this parameter is the only variable.

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