

## Comparison of Volatile Aldehydes Present in the Cooking Fumes of Extra Virgin Olive, Olive, and Canola Oils

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Emissions of low molecular weight aldehydes (LMWAs) from deep-frying of extra virgin olive oil, olive oil, and canola oil (control) were investigated at two temperatures, 180 and 240 °C, for 15 and 7 h, respectively. The oil fumes were collected in Tedlar bags and then analyzed by gas chromatography–mass spectrometry. Seven alkanals (C<sub>2</sub>–C<sub>7</sub> and C<sub>9</sub>), eight 2-alkenals (C<sub>3</sub>–C<sub>10</sub>), and 2,4-heptadienal were found in the fumes of all three cooking oils. The generation rates of these aldehydes were found to be dependent on heating temperature, showing significant increases with increases in temperature. The LMWA emissions from both kinds of olive oils were very similar and were lower than those observed from canola oil under similar conditions. These results suggest that frying in any type of olive oil, independent of its commercial category, will effectively decrease the generation of volatile aldehydes in the exhaust. This fact is important because less expensive refined olive oil is usually used for deep-frying operations, whereas extra virgin olive oil is usually used as salad dressing.

**KEYWORDS:** Acetaldehyde; acrolein; canola oil; deep-frying; indoor emissions; GC-MS; olive oil

### INTRODUCTION

Different oils (of both animal and vegetable origin) are used for deep-frying in different cultures. Deep-fat frying, which may be considered as a rapid combination of drying and cooking, is widely used both domestically and commercially (1). During deep-frying, fats and oils are repeatedly used at elevated temperatures in the presence of atmospheric oxygen and receive maximum oxidative and thermal abuse (2, 3). These extended thermal oxidative conditions associated with deep-frying can lead to degradation of cooking oils. Some of these cooking oil degradation products can have adverse effects on human health. Several studies have shown that oil fumes resulting from heating edible oils, such as rapeseed oil, soybean oil, peanut oil, and lard, to high temperature exhibit mutagenicity and genetic toxicity (5–7). However, recent studies have shown that unsaturated oils such as olive oil have high thermal oxidative stability (8). These properties of olive oil have been attributed to its fatty acid composition, which is characterized by a high monounsaturated-to-polyunsaturated fatty acid ratio and the presence of minor compounds with powerful antioxidant activity, among which polyphenols particularly stand out (8). However, no extended deep-frying studies have been conducted on olive oil to test this hypothesis.

Olive oil is an important cooking oil used extensively in the Americas and Europe. It is an integral part of the cultural and

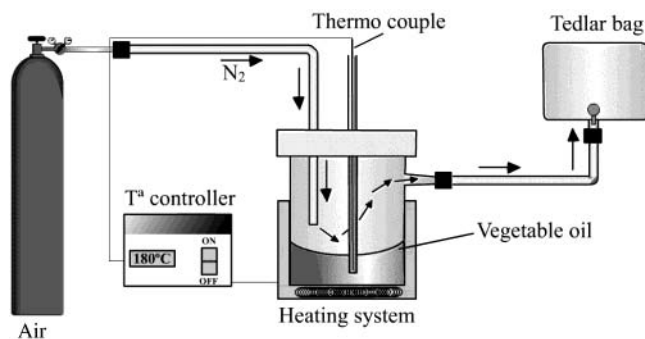
culinary heritage of the Mediterranean countries and a product that is set apart by its organoleptic and nutritional qualities. Spain is the main world producer of olive oil; in the 2001/2002 crop year (November 1–October 31), Spain produced a total of 1,411,400 t of 2,463,700 t produced by the European Union and 2,825,500 t produced worldwide (9). In addition, Spain is the second highest consumer of olive oil (631,200 t, 33.3% of the total EU consumption) behind only Italy (735,000 t, 38.8%); the world and EU consumptions for the season 2001/2002 were 2,601,500 and 1,893,800 t, respectively (9).

There are several types of olive oils (extra virgin, virgin, or just “olive oil”) available in world supermarkets. Extra virgin olive oil is made directly from olives without any chemical treatments. Sometimes, due to unfavorable climate conditions or deficiencies in the production process, virgin olive oils have a high degree of acidity and/or defective flavor, color, or aroma. These oils, called “lampante virgin oils”, must undergo a refining process to correct these defects. This is how “refined olive oil” is obtained, a product that maintains the chemical structure of olive oil but does not have any aroma or flavor. This product is not marketable, but a certain quantity of extra virgin, virgin, or ordinary virgin olive oil is added to the oil to give it some aroma and flavor to obtain the commercial category called “olive oil” (10). Refining techniques, including caustic-refining (11), bleaching (12), and deodorizing, adsorption, and membrane filtration (13), could reduce the color, unpleasant flavor, and content of free fatty acids in various edible oils. Unfortunately, some of the refining processes have been reported to decrease the contents of natural antioxidants such as tocopherols and

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**Figure 1.** Schematic representation of experimental system used in frying simulation.

oryzanols (14, 15). Most of these studies on “olive oil” are focused on improving the organoleptic quality and shelf life of oil but not the safety of the oil fumes.

In the present study on cooking fumes from olive oils, we decided to investigate cooking fumes from both extra virgin olive oil and refined “olive oil.” Our objective was to understand the effects of the refining processes of olive oil on the nature of compounds present in the oil fumes. The inclusion of refined “olive oil” also helped us investigate the hypothesis that antioxidants are responsible for higher thermal oxidative stability of olive oil, and because refined “olive oil” has a lower antioxidant content, it will be more susceptible to thermal and oxidative degradation during deep-frying operations than extra virgin olive oil (14, 16–18). We decided to use canola oil as a high oleic acid oil control because of its higher smoke point (238 °C) compared to olive oil (210 °C) (2). Canola is made from a kind of rapeseed that meets high standards of oil and meal quality. It is a member of the mustard family, a very large family that produces seed with a high content of both oil and protein (19).

To our knowledge, no studies have been conducted that compare the impact of heating two different types of olive oils, extra virgin olive oil (no chemical treatment) and olive oil (refined) with control oil (canola oil), for long periods of time (simulating real cooking conditions use in homes, restaurants, and food industries) on aldehyde emissions. In this paper, gas chromatography–mass spectrometry (GC-MS) was used to isolate, identify, and quantify the volatile compounds from three types of cooking oils, extra virgin olive, olive oil, and canola oils, at 180 and 240 °C, for 15 and 7 h, respectively. Aldehydes, especially acrolein, were the focus of product analysis because they are the major products of cooking oil degradation and also due to their capacity to induce toxicological effects (e.g., their reactivity with amino groups of proteins) (2, 20, 21).

## MATERIALS AND METHODS

**Materials.** Canola oil, extra virgin olive oil, and olive oil were purchased from a local supermarket.

**Experimental System and Sampling.** The experimental system used to conduct this study is shown in **Figure 1**. This system consists of a hermetic Pyrex reactor heated by a hemispherical heating mantle, and the heating is controlled by a thermocouple that was placed inside the oil. For this study, cooking oils were heated to 180 °C (regular deep-frying temperature) or 240 °C (temperature just above the maximum smoke point of the cooking oils studied). Air at flow rate of 1 L/min was supplied to the reactor. This air flow ensured total removal of fumes generated from heating the oil. The inlet air line was designed such that it was far enough from the oil surface to minimize changes in the diffusion layer but at the same time the air flow was sufficient enough to prevent stagnant flow zones and to transport all of the compounds evolved/formed as the cooking oils were heated. The reactor exhaust

gases were collected in 500 mL Tedlar bags (Supelco, Bellefonte, PA). The collected gas samples were then analyzed by GC-MS and GC-FID. The product stability was analyzed according to the specifications in U.S. EPA sampling method 40 during the time between sampling and analysis. Experiments were run in duplicate.

**Analytical Procedure.** A Hewlett-Packard (HP) model 5890 gas chromatograph combined with an HP-5970 series mass selective detector and an FID detector equipped with a 30.0 m × 0.53 mm i.d. Supel-Q Plot column (Supelco) was used to perform the analyses of collected gas samples. For the analysis, 0.5 mL of gas was directly injected in the gas chromatograph. The limit of detection observed (1 mg/m<sup>3</sup>) was enough for the purposes of this study, and therefore no concentration or derivitization methods were used. The oven temperature was held at 35 °C for 5 min and then programmed to 230 °C at 4 °C/min and held for another 5 min. Products were identified by comparing product mass spectra with a mass spectral database (NIST). Acrolein and acetaldehyde identifications were then confirmed using laboratory standards. Quantification of acrolein and acetaldehyde was performed using MS response factors from standard calibration curves. An average of acrolein and acetaldehyde response factors was then used to quantify other compounds identified in this study.

## RESULTS AND DISCUSSION

This study was focused on identifying and quantifying aldehyde (including acrolein) emissions from extended heating of cooking oils. The aldehydes were chosen because of their possible contributions to carcinogenicity (14, 22). **Tables 1–6** show the aldehyde yields as generation rate from canola, extra virgin olive, and olive oils during heating at 180 and 240 °C. The generation rate is the amount of a particular compound being generated (milligrams) per unit time (hours) of deep-frying at the specific temperature and per unit volume (liters) of the oil being used. Sixteen aldehydes, namely, acetaldehyde, acrolein, propanal, butanal, 2-butenal, pentanal, 2-pentenal, hexanal, 2-hexenal, heptanal, 2-heptenal, 2,4-hetadienal, 2-octenal, nonanal, 2-nonenal, and 2-decenal, were detected in the cooking oil fumes.

**Alkanals.** Seven alkanals from C<sub>2</sub> to C<sub>9</sub> were observed in the outlet gas stream (acetaldehyde, propanal, butanal, pentanal, hexanal, heptanal, and nonanal). The rate of alkanal generation increased significantly with increases in temperature. In general, hexanal and nonanal were the dominant compounds in the cooking oil fumes at 180 °C; however, in both olive oils and at 240 °C, heptanal became more abundant, especially in the olive oil. Fujisaki et al. (23) found that hexanal and nonanal were the dominant alkanals produced from high-oleic safflower oil during heating at 180 °C with water spray in atmospheres of 10 and 20% oxygen, whereas acetaldehyde predominated in atmospheres of 2 and 4% oxygen. Because in the present experiment regular air was being passed through the cooking system, the experimental conditions resembled an atmosphere of ~20% oxygen; thus, our results agree with those of Fujisaki et al. (23).

The formation of acetaldehyde from cooking oils statistically increased when the temperature was increased from 180 to 240 °C (**Table 7**). The emission rates of acetaldehyde at 180 and 240 °C were 10.8 ± 0.5 and 36.3 ± 1.7 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup> for canola oil, 5.1 ± 0.4 and 14.7 ± 0.4 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup> for extra virgin olive oil, and 4.2 ± 0.6 and 9.1 ± 0.9 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup> for olive oil (these values represent the means for the whole period of time monitored, 15 h at 180 °C and 7 h at 240 °C) (**Table 7**). Although acetaldehyde is “generally recognized as safe” by the FDA for its intended use as a synthetic flavoring substance and coadjuvant, it is safer to reduce its emission because it has been demonstrated that acetaldehyde inhalation by hamsters is capable of inducing laryngeal and nasal carcinomas (24, 25).

**Table 1.** Generation Rate (Milligrams per Hour per Liter of Oil) of Volatile Aldehydes from Canola Oil Heated at 180 °C

	heating time			
	1 h	5 h	9 h	15 h
<b>alkanals</b>				
acetaldehyde	15.5 ± 2.2 <sup>a</sup>	10.2 ± 0.7	13.2 ± 1.2	10.7 ± 0.3
propanal	17.4 ± 2.8	15.6 ± 0.5	23.0 ± 2.0	19.6 ± 1.0
butanal	4.5 ± 0.6	4.0 ± 0.2	5.7 ± 0.3	5.1 ± 0.2
pentanal	32.7 ± 7.4	28.8 ± 1.0	33.2 ± 2.2	34.4 ± 1.8
hexanal	56.8 ± 13.5	56.1 ± 1.7	61.3 ± 5.2	66.1 ± 2.9
heptanal	17.1 ± 4.2	13.7 ± 0.5	14.8 ± 1.7	15.7 ± 0.6
octanal	nd <sup>b</sup>	nd	nd	nd
nonanal	42.7 ± 11.1	30.9 ± 2.5	134.0 ± 27.4	49.0 ± 5.4
decanal	nd	nd	nd	nd
<b>alkenals</b>				
acrolein	69.7 ± 11.9	52.4 ± 3.3	66.9 ± 5.3	52.8 ± 1.8
2-butenal	1.4 ± 0.2	1.2 ± 0.1	1.0 ± 0.1	1.7 ± 0.1
2-pentenal	9.4 ± 2.6	8.4 ± 0.4	10.9 ± 0.8	11.8 ± 0.2
2-hexenal	5.9 ± 1.5	5.0 ± 0.3	4.7 ± 0.7	5.3 ± 0.1
2-heptenal	26.2 ± 7.4	30.0 ± 2.2	29.7 ± 5.0	38.1 ± 2.3
2-octenal	4.6 ± 1.2	4.9 ± 0.4	5.4 ± 0.7	12.2 ± 1.1
2-nonenal	2.5 ± 0.3	2.4 ± 0.2	1.6 ± 0.4	5.5 ± 0.7
2-decenal	5.5 ± 1.4	1.8 ± 0.2	1.8 ± 0.3	8.3 ± 1.0
2-undecenal	nd	nd	nd	nd
<b>alkadienals</b>				
2,4-heptadienal	27.3 ± 7.8	31.3 ± 2.7	29.1 ± 6.2	50.8 ± 5.2
2,4-nonadienal	nd	nd	nd	nd
2,4-decadienal	nd	nd	nd	nd
<b>total aldehydes</b>	<b>339.0 ± 75.2</b>	<b>296.6 ± 11.6</b>	<b>436.1 ± 49.8</b>	<b>387.2 ± 20.0</b>
total oleic acid derivatives	48.2 ± 12.3	32.7 ± 2.4	135.8 ± 27.3	57.3 ± 6.9
total linoleic acid derivatives	138.3 ± 31.9	132.2 ± 4.7	144.2 ± 13.6	167.1 ± 7.4
total glycerol derivatives	69.7 ± 11.9	52.4 ± 3.3	66.9 ± 5.3	52.8 ± 1.8

<sup>a</sup> ± values stand out for standard error of the mean. <sup>b</sup> Not detected.

**Table 2.** Generation Rate (Milligrams per Hour per Liter of Oil) of Volatile Aldehydes from Canola Oil Heated at 240 °C

	heating time			
	0 h	2 h	4 h	7 h
<b>alkanals</b>				
acetaldehyde	35.2 ± 1.2 <sup>a</sup>	38.1 ± 1.4	42.5 ± 4.2	26.6 ± 4.5
propanal	63.6 ± 2.3	67.8 ± 0.3	70.3 ± 8.5	38.3 ± 5.8
butanal	25.9 ± 0.7	29.1 ± 1.6	33.4 ± 3.1	22.3 ± 2.9
pentanal	124.7 ± 9.1	122.2 ± 1.4	116.6 ± 13.3	65.9 ± 11.9
hexanal	174.8 ± 1.3	198.6 ± 5.4	217.1 ± 24.1	132.6 ± 15.9
heptanal	91.0 ± 9.1	89.9 ± 6.9	96.6 ± 11.1	61.2 ± 8.5
octanal	nd <sup>b</sup>	nd	nd	nd
nonanal	168.2 ± 4.7	155.4 ± 5.6	171.1 ± 40.2	92.7 ± 2.6
decanal	nd	nd	nd	nd
<b>alkenals</b>				
acrolein	321.8 ± 19.4	298.6 ± 14.3	263.8 ± 36.1	122.4 ± 22.1
2-butenal	1.8 ± 0.1	2.5 ± 0.6	1.8 ± 0.2	1.2 ± 0.2
2-pentenal	76.7 ± 3.6	51.9 ± 6.6	50.0 ± 8.3	19.3 ± 6.8
2-hexenal	17.2 ± 1.0	17.3 ± 0.5	18.0 ± 2.4	9.5 ± 1.5
2-heptenal	150.3 ± 13.8	141.6 ± 10.4	139.6 ± 23.4	67.3 ± 9.7
2-octenal	27.0 ± 2.1	25.6 ± 8.4	29.3 ± 6.3	15.7 ± 0.9
2-nonenal	10.7 ± 3.9	14.7 ± 3.5	15.7 ± 4.6	10.3 ± 1.0
2-decenal	44.5 ± 2.9	32.1 ± 3.6	25.6 ± 6.9	24.5 ± 3.3
2-undecenal	nd	nd	nd	nd
<b>alkadienals</b>				
2,4-heptadienal	202.9 ± 16.6	186.6 ± 23.4	160.3 ± 28.9	75.6 ± 6.7
2,4-nonadienal	nd	nd	nd	nd
2,4-decadienal	nd	nd	nd	nd
<b>total aldehydes</b>	<b>1536 ± 74</b>	<b>1472 ± 144</b>	<b>1451 ± 221</b>	<b>785.2 ± 95.6</b>
total oleic acid derivatives	212.7 ± 1.8	187.5 ± 92.5	196.7 ± 47.1	117.2 ± 0.7
total linoleic acid derivatives	522.5 ± 21.3	540.8 ± 27.8	560.8 ± 75.9	318.3 ± 41.2
total glycerol derivatives	321.8 ± 19.4	298.6 ± 14.3	263.8 ± 36.1	122.4 ± 22.7

<sup>a</sup> ± values stand out for standard error of the mean. <sup>b</sup> Not detected.

**Alkenals.** The main product of interest in this class is acrolein. A direct analysis of acrolein is extremely difficult. It is usually converted to a more stable compound for analysis due to its high instability. The sampling and analytical methods used in this study proved to be capable of analyzing acrolein under the experimental conditions of this study. Brewer et al. (26)

successfully used a similar experimental setup to study volatile compounds and sensory characteristics of frying fats.

Including acrolein, eight C<sub>3</sub>–C<sub>10</sub> 2-alkenals were found (acrolein, 2-butenal, 2-pentenal, 2-hexenal, 2-heptenal, 2-octenal, 2-nonenal, and 2-decenal) in the cooking oil fumes. Acrolein, pentenal, heptenal, and decenal were the main components in

**Table 3.** Generation Rate (Milligrams per Hour per Liter of Oil) of Volatile Aldehydes from Extra Virgin Olive Oil Heated at 180 °C

	heating time			
	1 h	5 h	9 h	15 h
<b>alkanals</b>				
acetaldehyde	7.1 ± 1.3 <sup>a</sup>	4.4 ± 0.1	7.7 ± 0.9	3.9 ± 0.1
propanal	5.2 ± 0.4	3.7 ± 0.1	8.6 ± 1.2	3.5 ± 0.1
butanal	3.9 ± 0.4	3.5 ± 0.1	8.2 ± 1.3	3.4 ± 0.2
pentanal	10.8 ± 1.4	8.2 ± 0.3	19.8 ± 3.0	7.5 ± 0.4
hexanal	42.9 ± 4.0	30.0 ± 1.0	53.5 ± 6.8	24.5 ± 1.3
heptanal	13.3 ± 0.7	10.4 ± 0.6	19.3 ± 2.5	12.2 ± 1.0
octanal	nd <sup>b</sup>	nd	nd	nd
nonanal	32.4 ± 1.6	23.4 ± 2.5	23.3 ± 3.8	22.2 ± 3.1
decanal	nd	nd	nd	nd
<b>alkenals</b>				
acrolein	14.5 ± 2.2	8.3 ± 0.5	15.4 ± 1.6	4.4 ± 0.2
2-butenal	2.4 ± 0.2	1.4 ± 0.1	2.8 ± 0.4	0.9 ± 0.1
2-pentenal	2.6 ± 0.5	2.0 ± 0.4	4.3 ± 0.7	1.1 ± 0.2
2-hexenal	2.3 ± 0.1	1.6 ± 0.1	1.9 ± 0.1	1.0 ± 0.1
2-heptenal	12.0 ± 0.8	8.7 ± 1.0	9.9 ± 1.6	4.7 ± 0.6
2-octenal	4.8 ± 0.5	3.2 ± 0.4	2.5 ± 0.5	1.9 ± 0.3
2-nonenal	6.4 ± 1.2	4.5 ± 0.3	1.3 ± 0.7	1.6 ± 0.5
2-decenal	19.7 ± 3.4	8.8 ± 0.2	5.2 ± 1.3	6.2 ± 1.3
2-undecenal	nd	nd	nd	nd
<b>alkadienals</b>				
2,4-heptadienal	18.5 ± 0.7	13.8 ± 1.5	18.6 ± 2.9	12.8 ± 1.9
2,4-nonadienal	nd	nd	nd	nd
2,4-decadienal	nd	nd	nd	nd
<b>total aldehydes</b>	<b>198.7 ± 13.5</b>	<b>136.0 ± 12.9</b>	<b>202.7 ± 29.2</b>	<b>111.9 ± 10.3</b>
total oleic acid derivatives	52.0 ± 4.4	32.2 ± 7.7	28.5 ± 5.1	28.4 ± 4.3
total linoleic acid derivatives	84.0 ± 5.2	59.1 ± 2.5	94.8 ± 11.3	44.2 ± 2.7
total glycerol derivatives	14.5 ± 2.2	8.3 ± 0.5	15.4 ± 1.6	4.4 ± 0.2

<sup>a</sup> ± values stand out for standard error of the mean. <sup>b</sup> Not detected.

**Table 4.** Generation Rate (Milligrams per Hour per Liter of Oil) of Volatile Aldehydes from Extra Virgin Olive Oil Heated at 240 °C

	heating time			
	0 h	2 h	4 h	7 h
<b>alkanals</b>				
acetaldehyde	13.6 ± 0.5 <sup>a</sup>	14.5 ± 0.3	15.8 ± 0.4	14.2 ± 0.6
propanal	13.1 ± 0.3	14.1 ± 0.7	16.1 ± 0.1	14.2 ± 0.1
butanal	15.9 ± 0.4	17.1 ± 0.6	18.9 ± 0.2	17.1 ± 0.1
pentanal	30.0 ± 0.3	31.2 ± 0.2	32.0 ± 0.4	27.3 ± 0.3
hexanal	45.5 ± 1.0	51.9 ± 1.6	52.9 ± 0.4	53.1 ± 1.9
heptanal	33.3 ± 0.9	46.1 ± 3.6	47.7 ± 0.9	56.5 ± 12.1
octanal	nd <sup>b</sup>	nd	nd	nd
nonanal	36.5 ± 1.1	51.1 ± 12.1	56.2 ± 1.6	90.9 ± 32.0
decanal	nd	nd	nd	nd
<b>alkenals</b>				
acrolein	30.4 ± 1.3	26.1 ± 0.1	24.0 ± 0.5	17.9 ± 0.2
2-butenal	5.1 ± 0.1	4.4 ± 0.1	3.9 ± 0.3	2.9 ± 0.1
2-pentenal	5.4 ± 0.6	5.2 ± 0.1	4.6 ± 0.4	4.3 ± 0.3
2-hexenal	2.0 ± 0.1	2.5 ± 0.1	2.4 ± 0.1	2.3 ± 0.5
2-heptenal	12.5 ± 0.1	16.8 ± 1.1	13.5 ± 0.2	14.9 ± 4.0
2-octenal	5.3 ± 1.1	5.1 ± 0.3	5.1 ± 0.4	5.7 ± 1.9
2-nonenal	4.5 ± 1.0	2.5 ± 0.7	4.2 ± 0.3	6.0 ± 2.3
2-decenal	6.4 ± 0.3	6.2 ± 0.5	13.0 ± 0.1	34.0 ± 14.7
2-undecenal	nd	nd	nd	nd
<b>alkadienals</b>				
2,4-heptadienal	19.5 ± 0.9	30.2 ± 4.0	29.4 ± 0.8	42.2 ± 13.0
2,4-nonadienal	nd	nd	nd	nd
2,4-decadienal	nd	nd	nd	nd
<b>total aldehydes</b>	<b>278.9 ± 0.6</b>	<b>325.1 ± 30.5</b>	<b>339.7 ± 1.7</b>	<b>403.5 ± 83.0</b>
total oleic acid derivatives	42.9 ± 0.8	57.3 ± 17.4	69.2 ± 1.4	124.9 ± 46.6
total linoleic acid derivatives	111.4 ± 0.8	122.0 ± 4.2	123.6 ± 0.3	121.2 ± 10.4
total glycerol derivatives	30.4 ± 1.3	26.1 ± 0.1	24.0 ± 0.5	17.9 ± 0.2

<sup>a</sup> ± values stand out for standard error of the mean. <sup>b</sup> Not detected.

this class of aldehydes and constituted ~80% of total alkenals in the canola oil fumes at 240 °C. However, at 180 °C acrolein and heptenal were the main components, accounting for >65% of total alkenals in this same oil. Acrolein was the major degradation product from canola oil at both temperatures. The concentration of 2-decenal was higher in both olive oils than

in canola oil at 180 °C; its concentration was even higher than that of acrolein in extra virgin olive oil at 180 °C as acrolein formation is reduced at this temperature (*vide infra*).

In an earlier study, Umamo and Shibamoto (27) found no acrolein formation when corn oil was heated to 180 °C. However, in a later study using a *N*-methylhydrazine conversion,

**Table 5.** Generation Rate (Milligrams per Hour per Liter of Oil) of Volatile Aldehydes from Olive Oil Heated at 180 °C

	heating time			
	1 h	5 h	9 h	15 h
<b>alkanals</b>				
acetaldehyde	3.5 ± 0.8 <sup>a</sup>	4.5 ± 0.3	4.4 ± 0.1	4.0 ± 0.1
propanal	4.0 ± 0.7	5.1 ± 0.3	4.3 ± 0.1	3.9 ± 0.2
butanal	3.2 ± 0.6	4.2 ± 0.3	4.6 ± 0.1	2.9 ± 0.4
pentanal	7.6 ± 1.0	9.5 ± 0.6	9.9 ± 0.2	6.0 ± 1.0
hexanal	24.2 ± 4.0	29.9 ± 1.4	31.7 ± 1.6	19.2 ± 3.3
heptanal	8.2 ± 2.8	12.0 ± 0.7	15.0 ± 1.1	9.1 ± 2.0
octanal	nd <sup>b</sup>	nd	nd	nd
nonanal	14.3 ± 5.8	18.0 ± 0.5	20.5 ± 2.1	11.6 ± 5.3
decanal	nd	nd	nd	nd
<b>alkenals</b>				
acrolein	10.5 ± 0.4	10.1 ± 0.6	6.5 ± 0.6	4.6 ± 0.5
2-butenal	1.5 ± 0.2	1.9 ± 0.2	1.3 ± 0.1	0.9 ± 0.1
2-pentenal	1.5 ± 0.2	1.6 ± 0.1	1.6 ± 0.2	0.7 ± 0.4
2-hexenal	1.2 ± 0.2	1.4 ± 0.1	1.2 ± 0.1	0.6 ± 0.2
2-heptenal	5.7 ± 1.6	6.2 ± 0.1	6.0 ± 0.7	2.7 ± 1.1
2-octenal	1.5 ± 0.7	1.9 ± 0.1	2.1 ± 0.2	1.4 ± 0.5
2-nonenal	2.2 ± 1.1	2.9 ± 0.1	2.6 ± 0.5	1.0 ± 0.8
2-decenal	8.1 ± 3.8	6.7 ± 0.5	8.4 ± 1.3	2.6 ± 0.8
2-undecenal	nd	nd	nd	nd
<b>alkadienals</b>				
2,4-heptadienal	6.7 ± 2.8	10.0 ± 0.5	13.2 ± 1.3	7.3 ± 2.7
2,4-nonadienal	nd	nd	nd	nd
2,4-decadienal	nd	nd	nd	nd
<b>total aldehydes</b>	<b>103.9 ± 22.9</b>	<b>126.0 ± 5.5</b>	<b>133.0 ± 8.1</b>	<b>78.5 ± 23.7</b>
total oleic acid derivatives	22.4 ± 9.6	24.8 ± 0.8	29.0 ± 3.4	14.2 ± 1.1
total linoleic acid derivatives	44.7 ± 7.5	55.0 ± 2.5	56.6 ± 2.7	34.2 ± 0.6
total glycerol derivatives	10.5 ± 0.4	10.1 ± 0.6	6.5 ± 0.6	4.6 ± 0.5

<sup>a</sup> ± values stand out for standard error of the mean. <sup>b</sup> Not detected.

**Table 6.** Generation Rate (Milligrams per Hour per Liter of Oil) of Volatile Aldehydes from Olive Oil Heated at 240 °C

	heating time			
	0 h	2 h	4 h	7 h
<b>alkanals</b>				
acetaldehyde	7.1 ± 0.3 <sup>a</sup>	7.3 ± 0.7	9.0 ± 1.3	8.1 ± 2.8
propanal	4.0 ± 0.4	3.8 ± 0.8	1.9 ± 0.1	1.4 ± 0.5
butanal	1.4 ± 0.4	2.9 ± 0.3	1.7 ± 0.3	1.6 ± 0.1
pentanal	15.7 ± 0.3	16.2 ± 0.7	14.9 ± 3.0	9.6 ± 0.6
hexanal	7.5 ± 0.2	10.6 ± 0.3	7.7 ± 3.0	8.2 ± 0.4
heptanal	55.1 ± 4.1	105.8 ± 7.3	33.4 ± 14.7	65.4 ± 5.6
octanal	nd <sup>b</sup>	nd	nd	nd
nonanal	27.2 ± 2.6	28.2 ± 0.9	24.6 ± 1.8	5.6 ± 0.6
decanal	nd	nd	nd	nd
<b>alkenals</b>				
acrolein	33.8 ± 0.6	37.9 ± 0.6	32.3 ± 1.2	20.9 ± 0.8
2-butenal	0.8 ± 0.1	0.8 ± 0.1	0.8 ± 0.1	0.8 ± 0.1
2-pentenal	3.5 ± 0.1	4.1 ± 0.2	3.8 ± 0.1	3.7 ± 0.4
2-hexenal	37.7 ± 10.9	17.8 ± 2.3	4.0 ± 0.8	11.5 ± 0.9
2-heptenal	5.5 ± 0.8	7.4 ± 0.1	7.1 ± 0.2	4.4 ± 0.6
2-octenal	8.5 ± 0.1	9.7 ± 0.8	6.7 ± 1.1	6.8 ± 4.3
2-nonenal	2.9 ± 0.1	5.3 ± 0.1	5.4 ± 0.6	4.1 ± 0.3
2-decenal	20.9 ± 0.3	16.8 ± 2.0	27.4 ± 1.4	28.1 ± 5.9
2-undecenal	nd	nd	nd	nd
<b>alkadienals</b>				
2,4-heptadienal	27.7 ± 6.2	42.5 ± 0.1	37.8 ± 0.4	25.8 ± 6.3
2,4-nonadienal	nd	nd	nd	nd
2,4-decadienal	nd	nd	nd	nd
<b>total aldehydes</b>	<b>259.2 ± 5.1</b>	<b>317.1 ± 3.1</b>	<b>218.4 ± 32.3</b>	<b>205.8 ± 11.5</b>
total oleic acid derivatives	48.1 ± 2.9	45.1 ± 2.9	52.0 ± 0.3	33.7 ± 6.4
total linoleic acid derivatives	47.1 ± 2.1	56.5 ± 1.0	50.8 ± 8.8	41.1 ± 21.9
total glycerol derivatives	33.8 ± 0.6	37.9 ± 0.6	32.3 ± 1.2	20.9 ± 0.8

<sup>a</sup> ± values stand out for standard error of the mean. <sup>b</sup> Not detected.

Yasuhara and Shibamoto (20) found significant amounts of acrolein in an outlet of a kitchen ventilator and concluded that one of the likely sources was the corn oil used in the kitchen for frying meat and fish. In common home-cooking practices such as deep-fat frying, temperatures >200 °C are rarely used;

therefore, to estimate real emissions of acrolein from homes, only data obtained at 180 °C be considered.

The results of this study show that the generation rate of low molecular weight aldehydes is constant with heating time and the aldehyde profile is almost constant up to 15 h of heating at

**Table 7.** Generation Rate (Milligrams per Hour per Liter of Oil) of Acetaldehyde and Acrolein during Heating of Cooking Oils at 180 and 240 °C<sup>a</sup>

cooking oil	temp (°C)	acetaldehyde	acrolein
canola	180	10.8 ± 0.5	52.6 ± 2.4
	240	36.3 ± 1.7	239.9 ± 26.5
extra virgin olive	180	5.1 ± 0.4	9.3 ± 1.2
	240	14.7 ± 0.4	24.2 ± 1.7
olive	180	4.2 ± 0.6	9.6 ± 0.9
	240	9.1 ± 0.9	33.6 ± 2.0

<sup>a</sup> Values represent the means for the whole period of time monitored, 15 h at 180 °C and 7 h at 240 °C.

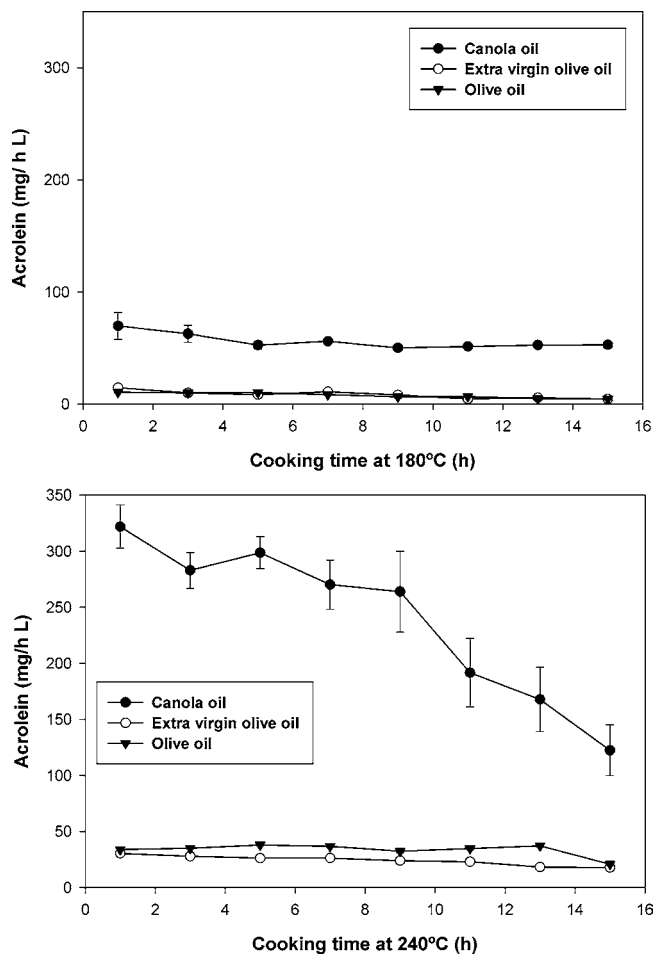
180 °C. This is consistent with the findings of Umano and Shibamoto (27), who concluded that the amount of acrolein formed from heated corn oil at 300 °C showed an almost linear relationship with heating time. Also, Yasuhara and Shibamoto (20), studying the amount of acrolein evolved from heated vegetable oil (corn oil), found that the concentration of acrolein became almost constant (~140 µg/L) after 1 h.

The formation of acrolein from cooking oils increased significantly when cooking temperature was increased from 180 to 240 °C (Table 7). The emission rates of acrolein at 180 and 240 °C were, respectively, 52.6 ± 2.4 and 239.9 ± 26.5 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup> for canola oil, 9.3 ± 1.2 and 24.2 ± 1.7 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup> for extra virgin olive oil, and 9.6 ± 0.9 and 33.6 ± 2.0 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup> for olive oil. (These values represent the means for the whole period of time monitored, 15 h at 180 °C and 7 h at 240 °C.)

One of the most important findings of the present study is that the rate of acrolein generation from canola oil decreased significantly with the cooking time at 240 °C (Figure 2). This decrease in acrolein was not observed from both olive oils at either temperature. This decrease in acrolein emission with time was also not observed in the corn oil cooking experiments of Shibamoto and co-workers (20, 27).

Acrolein can form via thermolysis of glycerol at temperatures >230 °C (1, 6). However, in the present study acrolein was formed even at the lowest studied temperature of 180 °C. This means that a lower temperature (180 °C) pathway for formation of acrolein also exists. Umano and Shibamoto (27), on the basis of their observation of acrolein formation under a nitrogen stream, proposed that under thermal oxidative conditions acrolein formation was likely due to a free radical mechanism involving homolytic fission of R-O (11), and results from the present experiment support this proposed mechanism as well. The observed decrease in acrolein emissions from canola oil at higher temperature (240 °C) could probably be due to the fact that at high temperatures either the reactant from which acrolein was formed has depleted or some other product formation channel from the same reactant has become more dominant than acrolein formation. It is known that at higher temperatures triacylglycerols (TAG) mainly form TAG polymers, with the rate of formation dependent on the content of unsaturated fatty acids. It is plausible that at higher temperatures and with an increase in time, TAG present in canola oils start to polymerize to make TAG polymers instead of oxidizing and making acrolein. Because the formation of TAG polymers is dependent on the content of unsaturated fatty acids, this may be why decreases in the acrolein generation rate were observed in only canola oil and not in extra virgin and regular olive oils.

**Alkadienals.** 2,4-Heptadienal was the only compound found in this class. In general, the rate of heptadienal formation increased with temperature and was constant with time. This



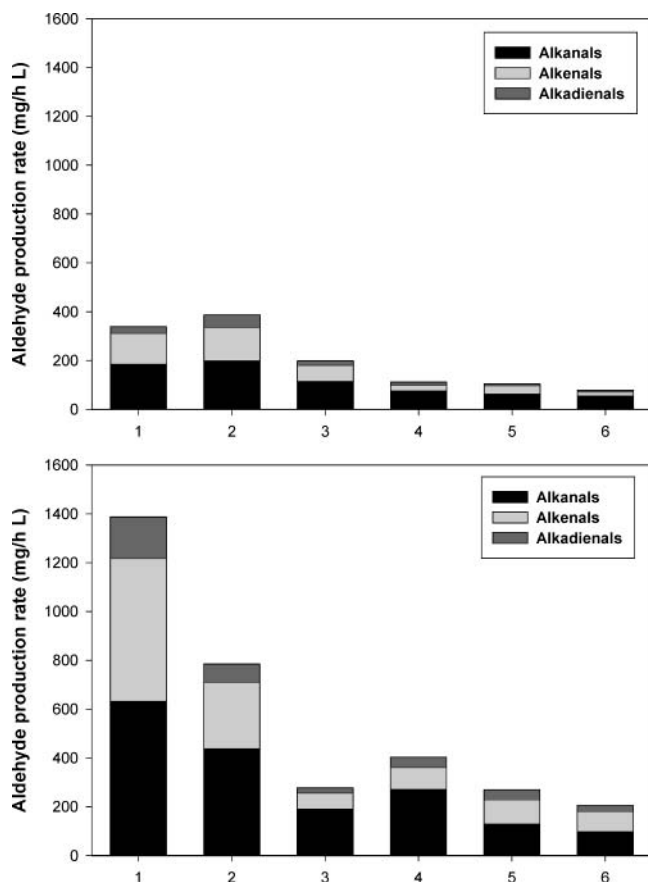
**Figure 2.** Acrolein (mg/h L<sub>oil</sub>) emissions from canola, extra virgin olive, and olive oils heated at two different temperatures, 180 °C (top) and 240 °C (bottom).

was true for all of the oils and conditions investigated with the exception of canola oil at 240 °C, for which it decreased with time.

**Total Aldehydes.** Figure 3 shows the sum of the three types of aldehydes in canola, extra virgin olive, and olive oils during heating at 180 and 240 °C for 15 and 7 h, respectively. The total amount of aldehydes increased with temperature. This perhaps could be attributed to an increase in the oxidation rate of fatty acids with increases in temperature. In general, the aldehyde class distribution was found to be independent of temperature. The only significant change was a decrease in total aldehydes from canola oil at 7 h because at 240 °C and longer heating times canola TAG polymerization reactions become more dominant than TAD oxidation reactions.

Furthermore, the total amount of volatile aldehydes was between 60 and 70% of all volatile compounds in the frying oil, with octane, heptane, hexane, pentane, butane, 2-propanone, and 1-pentanol being the most abundant nonaldehydic compounds.

**Total Volatile Compounds.** At both 180 and 240 °C, higher amounts of total volatile compounds (521 and 2165 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup>) were generated from canola oil than from extra virgin olive oil (380 and 791 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup>) and olive oil (259 and 1154 mg h<sup>-1</sup> L<sub>oil</sub><sup>-1</sup>) (data corresponds to 1 h of heating). A possible reason is that lower amounts of antioxidant agents are present in the canola oil as compared to olive oils, which leads to higher thermal oxidation, even though the refining process of olive oil could have reduced its antioxidant content. Also as



**Figure 3.** Total aldehydes generated in the exhaust of canola, extra virgin, and olive oils heated at 180 °C (top) and 240 °C (bottom) (1 = canola oil, 1 h; 2 = canola oil, 15 or 7 h; 3 = extra virgin olive oil, 1 h; 4 = extra virgin olive oil, 15 or 7 h; 5 = olive oil, 1 h; 6 = olive oil, 15 or 7 h).

**Table 8.** Typical Fatty Acid Composition of Canola and Olive Oils (37)

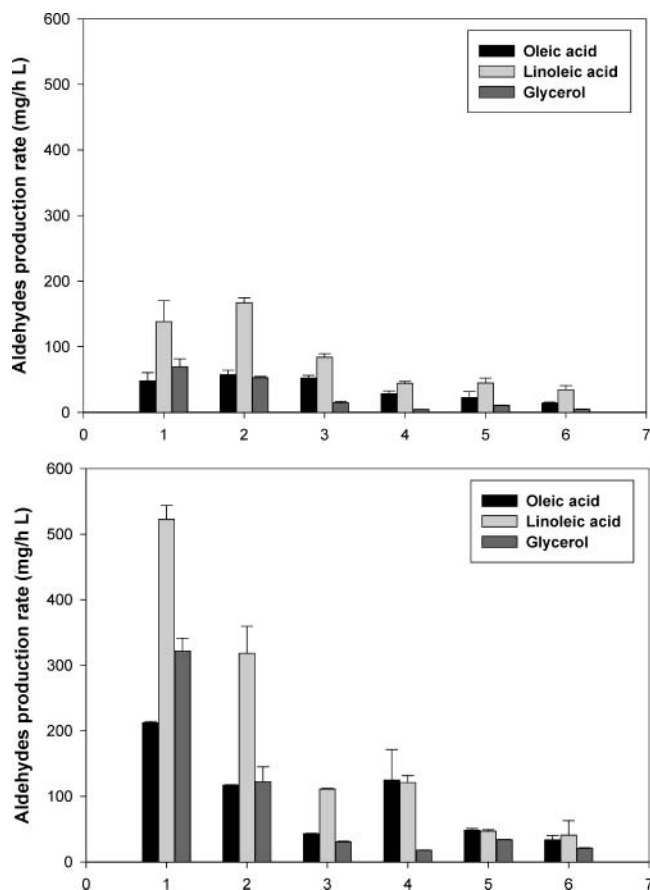
oil type	fatty acid composition (%)					
	palmitic (16:0)	stearic (18:0)	oleic (18:1)	linoleic (18:2)	linolenic (18:3)	eicosenoic (20:1)
canola	4.1	1.8	63.0	20.0	8.6	1.9
olive	15	0	75.0	9.0	1.0	0

shown in **Table 8**, canola oil has a higher linolenic acid content (20%) than olive oils (9%) and because the autoxidation rate of linolenic acid is 77 times higher than that of oleic acid, we conclude that canola oil is more susceptible to thermal oxidation and, therefore, emission of volatile compounds, including aldehydes (22, 28).

**Suggested Origin of Volatile Aldehydes.** **Figure 4** shows the major aldehydes observed in the exhaust of canola and olive oils grouped according to their origin (oleic acid, linoleic acid, or glycerol) (23, 29, 30).

At both 180 and 240 °C, the sum of aldehydes derived from linoleic acid (acetaldehyde, pentanal, hexanal, 2-heptenal, 2-octenal, and 2-nonenal) was higher than that from oleic acid (nonanal and 2-decenal) in all three cooking oils. The ratio of linoleic acid related compounds to oleic acid related compounds was significantly lower in both olive oils, with the ratio being almost one in olive oil at 240 °C.

In general, the amount of oleic acid is higher in olive oils than in canola oil; however, linoleic acid is higher in canola than in olive oils (**Table 8**). This is consistent with experimental



**Figure 4.** Grouping of volatile aldehydes by origin from canola, extra virgin, and olive oils at heating temperature of 180 °C (top) and 240 °C (bottom) (1 = canola oil, 1 h; 2 = canola oil, 15 or 7 h; 3 = extra virgin olive oil, 1 h; 4 = extra virgin olive oil, 15 or 7 h; 5 = olive oil, 1 h; 6 = olive oil, 15 or 7 h).

results of this study, which show that higher amounts of volatile aldehydes were produced from canola oil than from both types of olive oil. The patterns of aldehydes generated from all three types of cooking oils studied illustrate the importance of linoleic acid as a precursor of volatile aldehydes.

This experimental observation seems to imply that the fatty acid composition of cooking oils is more important in determining the nature and concentration of the aldehydes being formed during deep-frying operations than the presence of natural antioxidant compounds.

**Conclusions.** From a food industry point of view, one of the most important conclusions to be drawn from this study is that proper control of oil temperature will increase the life of the oil being used for deep-frying purposes and at the same time will reduce the indoor emission of aldehydes. Formation of aldehydes during deep-frying operations depends mainly on its temperature, and the formation rate is almost constant with time except for canola oil at 240 °C. Even under extreme conditions, maintaining a temperature of 240 °C for 7 h, the aldehyde generation rate from both olive oils was constant and statistically equal to that found after 1 h at experimental conditions. At temperatures as low as 180 °C, acrolein formation was present in the fumes of all three cooking oils investigated in this study. This temperature is the optimum for deep-frying operations; therefore, formation of acrolein in home cooking has to be considered an indoor pollution problem. On the other hand, during cooking the acrolein would be distributed in an open ambient area, so the actual concentration to which persons in kitchens and food industry workers would be exposed will be

lower. The use of olive oils in deep-frying operations will decrease the generation of volatile aldehydes in the exhaust, independent of its commercial category (extra virgin or regular), and therefore, independent of the refining process to which the olive oil has been submitted. This is especially important due to the lower selling prices of regular olive oil compared to extra virgin olive oil. Because some of the aldehydes (especially acrolein) are toxic, using olive oils for deep-frying operations will reduce potential health risks by reducing aldehyde formation.

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