Comparison of the Composition and Properties of Canola and Sunflower Oil Sediments with Canola Seed Hull Lipids

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ABSTRACT: The phase transition behavior and chemical composition of sediments from Canadian and Australian canola oils, as well as from sunflower oil, were studied by differential scanning calorimetry, X-ray diffraction, polarized-light microscopy, and chromatographic techniques. Australian canola sediment was similar to Canadian canola sediment in both melting and crystallization behaviors and chemical composition. Compared to canola sediment, sunflower sediment underwent phase transformation (melting and crystallization) at lower temperatures, and the enthalpies associated with the phase changes were greater. The X-ray diffraction patterns for these materials were similar, indicating identical crystalline structures. Sunflower sediment contained mainly wax esters (99%), while canola sediment contained about 72–74% of waxes. Moreover, sunflower sediment consisted of shorter-chainlength fatty acids and alcohols than canola sediment. A hexane-insoluble fraction from Canadian canola hull lipids had fatty acid and alcohol profiles and X-ray diffraction pattern similar to the corresponding oil sediment.

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KEY WORDS: Canola oil, canola seed hull lipids, composition, DSC, phase transitions, sediment, sunflower oil, waxes, X-ray diffraction.

Winterization is used in the vegetable oil industry to remove the high-melting lipid constituents from oils such as sunflower, soybean, and cottonseed. These lipid components must be removed from the oil, otherwise a hazy cloud or sediment may develop during storage, rendering the product unacceptable to consumers (1). Winterization, however, is energy-consuming. A typical operation involves cooling the oil to 6–7°C, holding at that temperature for several hours, and removing the precipitate by filtration (2). To overcome the high viscosity, the cold oil is normally heated up to 12–14°C before filtration (2).

A problem encountered in canola oil processing is that winterization may not always ensure a sediment-free product (3,4). Oil processors have reported that in some crop years, a sediment may still develop in batches of winterized canola oil. Studies on the additional sediment suggest that clouding in winterized canola oils may involve both wax esters and saturated triglycerides.

The exact cause of the apparent inefficiency in winterization of canola oil remains unclear. It is not known whether the geographical location is a factor in sediment formation in canola oil. Studies on sunflower oil sediment, which contains mainly waxes, suggested that neither location nor hybrid significantly influenced the wax content of the oil (5). However, the amount of hull and the wax content in the hull were related to both location and hybrid (5). An earlier study on open-pollinated and hybrid sunflower seed found an inverse relationship between the amount of hull in the seed and the wax content in the oil (6).

Our laboratory recently obtained a hazy canola oil sample from an Australian canola oil processor. This provided a unique opportunity to further examine the sedimentation phenomenon in canola oil. In this study, we report both the physical and chemical properties of Australian canola sediment in comparison to Canadian canola and sunflower oil sediments. A hexane-insoluble fraction (HIF), isolated from Canadian canola seed hull lipids, was also examined to further explore the relationship between hull components and sediment constituents in the oil.

MATERIALS AND METHODS

Canola oil samples that exhibited a tendency to form a sediment were obtained from Australian and Canadian oil processors. A sunflower oil sample was provided by a local sunflower oil refinery. Sediments were obtained from oils as described previously (1,3). Oil samples were stored at 0°C for about one week, and the sediment was separated from the oil by centrifugation (8000 × *g*). The residual oil in the sediment was removed by washing twice with cold petroleum ether (0°C) (3).

Canola hulls, provided by POS Pilot Plant Corp. (Saskatoon, Canada) were further purified by pneumatic separation

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to remove parts of groats. Hull lipids were extracted for 8 h in a Soxhlet apparatus with a solvent mixture of benzene and chloroform (2:1, vol/vol). The extract was stripped of solvent in a rotary evaporator. The oil obtained was mixed with hexane at a ratio of 1:5 (vol/vol) and stored at 0°C till a sediment appeared. The sediment was separated by filtration and washed with cold hexane (0°C) three times. The lipids in the hexane phase were analyzed and shown to consist of fatty acids typical of canola oil.

Differential scanning calorimetry (DSC) was performed on a Dupont thermal analyzer (Dupont 9900, Dupont, Wilmington, DE) with a DSC cell attachment (Dupont 910). The DSC instrument was calibrated with indium according to the manufacturer's instructions. Sediment samples were encapsulated in DSC pans and scanned in the temperature range of 5 to 100°C. The DSC scanning rate was 10°C/min or unless stated otherwise. An empty pan was used as an inert reference. Other experimental conditions were essentially the same as described before (1).

The X-ray diffraction (XRD) patterns of the sediments were obtained with an X-ray diffractometer (PW1710; Philips, Cincinnati, OH), operated with Cu Kα radiation at 40 kV and 40 mA (1).

The crystal morphology of sediments was studied by polarized-light microscopy. Microscopic specimens of the sediment were prepared by enclosing the material within glass slides, melting it by heating to about 85°C, and cooling it to room temperature with a temperature-controlled hot stage (Physitemp, Clifton, NJ). A transmitting light microscope (IIIRS; Zeiss, Oberkochen, Germany) was used for the experiments.

The composition of the sediments was analyzed by the thin-layer chromatography–flame ionization detector (Mark IV; Iatron, Tokyo, Japan) procedure (3). Compositions of fatty acids and fatty alcohols were determined by gas chromatography/mass spectrometry as described previously (3).

RESULTS AND DISCUSSION

The DSC melting curves of the sediments are shown in Figure 1. Australian canola sediment exhibited a melting peak at about 77°C (Fig. 1B), similar to that of Canadian canola sediment (Fig. 1A). These melting temperatures are within the range reported earlier for canola sediments isolated from canola oil or the filter cakes of winterized canola oil (75–77°C) (1,3,7). These results suggest that Australian and Canadian canola oil sediments contain similar lipid components, as melting transition is a physical property characteristic of the constituents in a solid substance.

The DSC melting peak of sunflower oil sediment was around 73°C (Fig. 1C), lower than that for canola sediments but consistent with previous reports on sunflower oil waxes (8). Using microscopy, Rivarola *et al.* (8) found that the melting temperature of sunflower waxes was about 73°C. Figure 1 shows that the melting endotherm for sunflower sediment

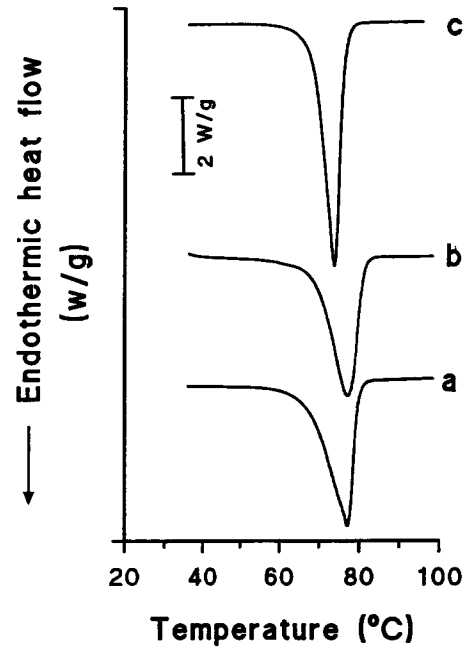

FIG. 1. Differential scanning calorimetry thermal curves of oil sediments obtained at a heating rate of 10°C/min: (A) Canadian canola sediment; (B) Australian canola sediment; and (C) sunflower sediment.

was sharper and the enthalpy of melting (190 J/g) higher compared to the two canola sediments (173 and 175 J/g for Australian and Canadian canola oil sediment, respectively) (1,3,7). Such differences in phase transitions suggest differences in the composition between the sunflower and canola sediments, and they imply different sedimentation behavior by these high-melting components in oil.

Figure 2 shows the DSC thermal curves of the HIF obtained from Canadian canola hull lipids. Compared to the DSC curves for oil sediments shown in Figure 1, the HIF had a lower-melting peak temperature (66°C), a wider endotherm, and a smaller enthalpy value of about 26 J/g. These results

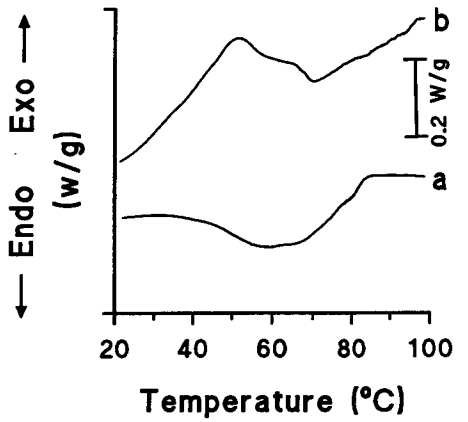

FIG. 2. Differential scanning calorimetry thermal curves of hexane-insoluble fraction from canola hull lipids obtained at a rate of temperature change of 10°C/min: (A) heating and (B) cooling; Endo, endothermal; Exo, exothermal.

suggest that HIF had a different lipid composition than the oil sediments.

The corresponding DSC crystallization curves for HIF and Canadian and Australian sediments are shown in Figures 2 and 3, respectively. Although a single peak was found during melting of the sediments, biphasic transitions were evident during crystallization with the exception of sunflower sediment, which showed a single sharp peak (Fig. 3C). This indicated that sediment formation in canola oil may be initiated by a fraction of high-melting constituents in the oil. The differences in crystallization behavior between sunflower and canola sediments suggested a heterogeneous character for the material derived from canola oil. The sunflower sediment appeared to be "purer" in terms of composition, containing fewer lipid classes.

The solid structures of the sediments were further examined by XRD. The results are shown in Figure 4 for sunflower (A), Australian canola (B), and HIF from canola hull lipids (C). Canadian canola sediment had essentially an identical XRD pattern (data not shown here) with that of Australian canola sediment (1). Although sunflower sediment exhibited different melting characteristics, the XRD data revealed similar crystalline structures to canola sediment. The short d-spacings obtained from the XRD are associated with the lateral packings of the long-chain molecules in the crystal. The particular XRD patterns shown in Figure 4 are typical of wax crystals from different origins (1). These results further suggest that sedimentation in these oils is mainly a crystallization process of waxy components with other components cocrystallizing in the sediment. The XRD pattern for the HIF from canola hull lipids showed a similar pattern to canola oil sediment, indicating that canola oil sediment may originate from seed hulls. Thus, correlation between waxy substances present in canola hull and oil might provide a way to predict the sedimentation phenomenon in canola oil.

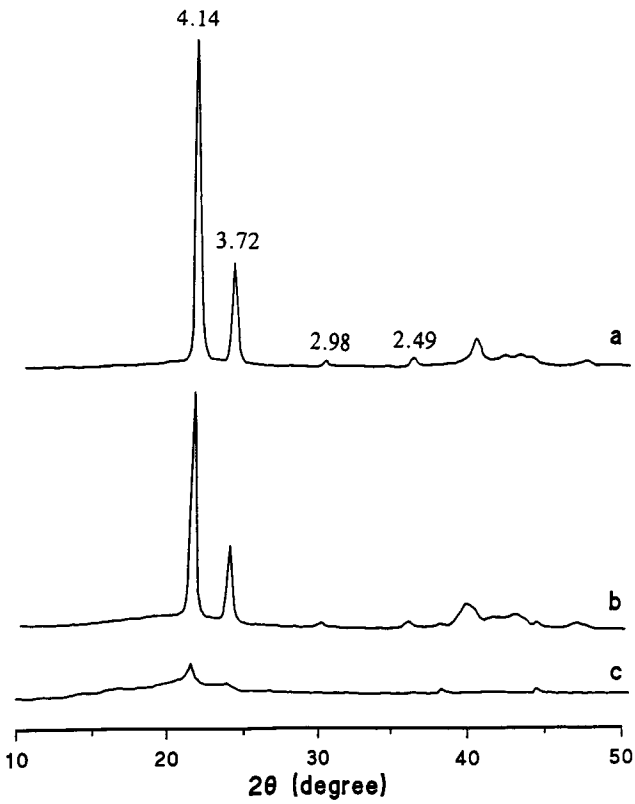

FIG. 4. X-ray diffraction patterns of oil sediments: (A) sunflower sediment; (B) Australian canola sediment; and (C) hexane-insoluble fraction from canola hull lipids. Numbers labelled in the figure are corresponding d-spacings.

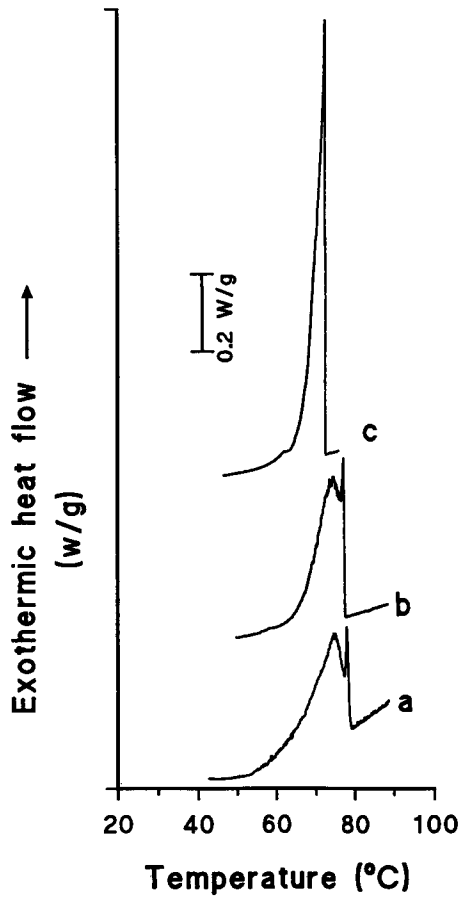

FIG. 3. Differential scanning calorimetry thermal curves of oil sediments obtained at a cooling rate of 1°C/min: (A) Canadian canola sediment; (B) Australian canola sediment; and (C) sunflower sediment.

Polarized-light microscopic studies of sediment crystals showed elongated rod-shaped morphology for both Australian canola and sunflower sediments, similar to Canadian canola sediment as reported previously (9). However, the phase transitions (melting and crystallization) and crystal morphology of the HIF were difficult to detect by microscopy. Nevertheless, DSC clearly showed phase transitions occurring during heating and cooling of the material (Fig. 2). Presumably, the content of the components in the HIF that would undergo a phase transition over the temperature range was low as evidenced by a much smaller DSC melting enthalpy.

Table 1 summarizes the composition of sediments from oils and the HIF from canola hull lipids. Both Canadian and Australian canola sediments contained a similar amount of waxes (73 and 74%, respectively). These data also compared well with the earlier studies on the canola oil sediment isolated from winterization filter cakes, which contained 78–80% wax esters (7,9). Other compounds present in the canola oil sediments included diglycerides (about 3%), free fatty alcohols (about 2%), and triglycerides, as well as free fatty acids in smaller amounts. As reported in earlier studies (7), polar compounds were also found in the canola oil sediments. These compounds could not be separated by the common solvents used for simple triglycerides and phospholipids, showed no color reactions with the phospholipid spray, and did not release any methyl esters by transesterification treatments. Polar complex carbohydrate derivatives (7) or very long-chain wax esters have been suggested for the nature of these substances (10).

The wax content in sunflower sediment (over 99%) was considerably higher than that in canola sediments. The only other detectable compound in sunflower sediment was free fatty alcohol (0.4%). Furthermore, there was only a small amount of polar components in the sediment derived from sunflower. These composition profiles are consistent with the DSC data shown above. With waxes as the major contributor in enthalpy, sunflower sediment gave a higher melting enthalpy than canola sediment.

The HIF from canola hull lipids contained around 49% waxes and similar proportions of other compounds with the exception of a larger amount of triglycerides compared to canola oil sediment. Extensive purification of this sediment did not remove the triglycerides. An earlier study on canola sediment indicated that the melting transition of waxy sediment was strongly influenced by the amount of triglycerides present in the material (1). With increase of the oil fraction in the sediment, the melting transition of sediment was broadened and shifted to lower temperatures. A small enthalpy at lower temperatures for melting of HIF as measured by DSC suggested that the triglycerides contributed little to the endothermic process and may act as a solvent depressing the melting of the solid waxy component (1).

Tables 2 and 3 show the fatty acid and fatty alcohol composition of the sediments. These data showed no significant differences between the fatty acid and alcohol constituents of

TABLE 1
Composition of Oil Sediments and Hexane-Insoluble Fraction (HIF) from Canola Hull Lipids

Component	Canadian canola	Australian canola	Sunflower	HIF
Waxes	72.3	74.2	99.4	48.4
Triglycerides	1.3	2.1	0.0	22.6
Diglycerides	2.7	2.4	0.0	0.5
Free fatty acids	0.2	0.4	0.0	0.5
Free fatty alcohols	1.9	2.4	0.4	1.8
Polar compounds	21.3	22.8	0.2	26.4

TABLE 2
Fatty Acid Composition of Oil Sediments and Hexane-Insoluble Fraction (HIF) from Canola Hull Lipids

Acid	Canadian canola	Australian canola	Sunflower	HIF
12:0	0.10	0.13	0.10	—
14:0	0.37	0.26	0.19	0.35
15:0	0.09	0.06	0.11	0.10
16:0	2.10	2.23	4.23	2.32
16:1	0.32	0.30	0.26	0.20
17:0	0.21	0.28	0.11	0.20
18:0	2.86	2.77	5.95	2.21
18:n	—	—	—	17.04
19:0	0.20	0.13	0.35	0.20
20:0	9.38	9.40	38.49	7.82
20:1	0.46	0.21	0.12	0.21
21:0	0.68	0.60	0.64	0.63
22:0	9.42	9.19	20.70	8.95
22:1	0.25	0.19	—	0.21
23:0	0.58	0.48	0.18	0.43
24:0	13.26	13.95	10.44	11.10
24:1	0.33	0.41	0.12	0.31
25:0	0.92	0.96	0.27	0.72
25:1	0.36	0.42	0.01	0.37
26:0	26.13	25.62	6.51	20.08
26:1	0.18	0.21	0.02	0.27
27:0	2.02	2.03	0.39	1.92
28:0	16.92	16.72	7.18	13.42
28:1	0.22	0.31	0.03	0.21
29:0	2.47	2.08	0.41	2.31
30:0	8.26	9.08	2.98	6.56
31:0	0.06	0.08	0.12	0.08
32:0	1.27	1.30	0.06	1.24
33:0	0.36	0.35	0.02	0.34
34:0	0.22	0.25	0.01	0.20

TABLE 3
Fatty Alcohol Composition of Oil Sediments and Hexane-Insoluble Fraction (HIF) from Canola Hull Lipids

Alcohol	Canadian canola	Australian canola	Sunflower	HIF
12:0				0.59
14:0				2.46
16:0				1.01
17:0				0.33
18:0	0.05	0.06	0.90	1.17
19:0			0.01	0.06
20:0	0.25	0.38	1.85	2.75
21:0	0.11	0.10	0.19	0.39
22:0	3.48	3.63	13.81	7.29
23:0	0.54	0.55	1.14	0.29
24:0	10.97	11.26	31.28	5.76
25:0	0.18	0.08	2.28	0.75
26:0	25.68	26.29	23.53	20.35
27:0	2.68	1.96	0.62	0.51
28:0	20.76	21.82	11.48	19.30
29:0	5.29	4.98	0.53	0.55
30:0	19.83	19.76	6.11	26.78
31:0	1.39	1.33	0.36	0.76
32:0	7.35	7.38	5.27	6.11
33:0	0.38	0.42	0.25	0.74

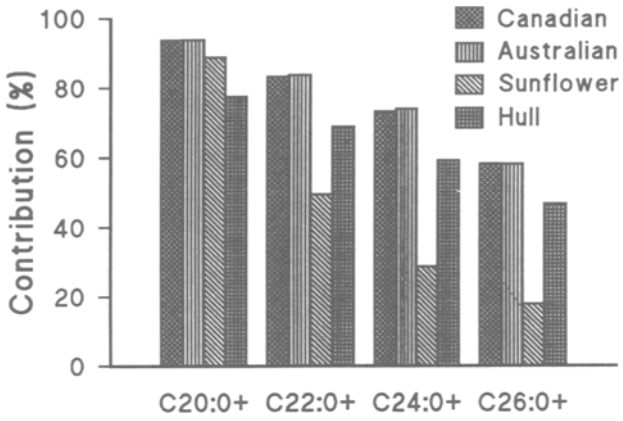

FIG. 5. Comparison of composition contribution of long-chain fatty acids in sediments. $C_{20:0}$+ denotes the percentage of the fatty acids with 20 or more carbon atoms in the chain, and so forth.

Canadian and Australian canola sediments. Figure 5 shows that, in both canola sediments, the saturated fatty acids with 20 or more carbon atoms accounted for about 93% of the total fatty acids, with $C_{24:0}$, $C_{26:0}$, and $C_{28:0}$ as the greatest amounts (Table 2). The fatty alcohol constituents in Canadian and Australian canola sediments were also similar: 94% of alcohols were those consisting of 24 or more carbon atoms (Fig. 6) with four saturated alcohols, i.e., $C_{24:0}$, $C_{26:0}$, $C_{28:0}$, and $C_{30:0}$, being the predominant species (Table 3).

The fatty acid and alcohol profiles of sunflower oil sediment obtained in this study compared well with the literature data on sunflower waxes (11). Although sunflower sediment was composed of similar lipid classes as canola sediment, significant differences were observed in the contents of long-chain fatty acids and alcohols between these sediments. Figure 5 shows that 83% of the acids in canola sediment were composed of 22 or more carbon atoms in the chain, compared to 50% for sunflower. The levels of fatty acids with 24 or more carbon atoms were 2.5 times higher in canola sediment than in sunflower. Furthermore, the fatty acids with 26 or more carbon atoms were 3.5 times higher in canola than in sunflower sediment. Table 3 shows that the sunflower sediment was also composed of relatively larger amounts of shorter-chainlength alcohols compared to canola sediment. Figure 6 shows that the fatty alcohols with 26 and more carbon atoms in canola sediment were twice that of sunflower. These results are in agreement with the DSC measurements, which showed that sunflower sediment had a lower DSC melting peak temperature than canola; melting temperatures of wax esters are proportional to their carbon chainlength (12). The high amounts of long-chain even-carbon fatty acids and alcohols in canola sediment may have a detrimental effect on the clarity of the oil by elevating the melting points of these compounds (12,13).

The fatty acid composition of HIF from canola hull lipids closely resembled that of canola oil sediment. This suggests that some long-chain fatty acids may be incorporated into the triglycerides in the HIF. However, there were significant amounts of shorter-chain alcohols from $C_{12:0}$–$C_{17:0}$ in HIF, which were not found in canola oil.

This study showed that sediment in canola oil is unique. Despite the lower proportion of wax esters compared to sunflower sediment, this material consists of longer-chain fatty acids and alcohols. The presence of long-chain fatty acids and alcohols in canola sediment should be an important factor in sediment formation in this oil. The results in this study suggest that the sedimentation phenomenon in both Canadian and Australian canola oils has similar molecular origin in terms of chemical composition and phase transition behavior. Furthermore, wax esters of long-chain fatty acids and alcohols, as major components of sediment in canola oil, could be traced to the seed hulls.

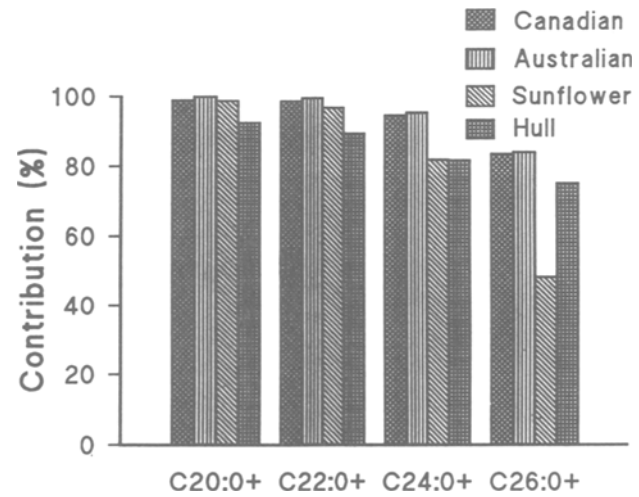

FIG. 6. Comparison of composition contribution of long-chain fatty alcohols in sediments. $C_{20:0}$+ denotes the percentage of the fatty alcohols with 20 or more carbon atoms in the chain, and so forth.

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