Particle Size Effects on Supercritical CO_2 Extraction of Oil-Containing Seeds

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ABSTRACT: Rosehip seeds were milled, sieved, and extracted with 26.3 g/g substrate/h of supercritical carbon dioxide (CO_2) at 40°C and 300 bar. The extraction kinetics were characterized by an initial solubility-controlled period (8.78 g oil/kg CO_2 at 40°C and 300 bar), followed by a transition period to a final mass transfer-controlled process. The integral yield of oil approached an asymptotic value that was dependent on the particle size of the substrate: 57.1 g oil/kg dry oil-free substrate (large particles), 171.0 g/kg (medium-size particles), or 391.5 g/kg (small particles). Based on gravimetric determinations and microscopic analysis, our size-classification process segregated seed parts having different oil contents. Particles ≥0.85 mm were mainly composed of tough, lignified testa fragments devoid of oil, whereas particles ≤0.425 mm contained mostly brittle, oil-rich germ fragments. The segregation of seed in fractions with different oil contents may be a common occurrence in supercritical extraction experiments, especially for seeds with thick and/or hard testa and small germ, whose fractions can be separated by sieving.

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Supercritical carbon dioxide (SC-CO_2) is a nontoxic alternative to organic solvents for oil extraction from plant material (1). Conventional solvent extraction produces low-quality oil requiring extensive refining operations (2), whereas deoiling by pressing is customary only for seeds containing ≥20% oil (3).

Rosehip *(Rosa aff. rubiginosa)* seed, an inexpensive natural source of unsaturated FA, is a potential candidate for SC-CO_2 extraction of oil. Rosehip oil finds use in cosmetics and other high-value applications. del Valle *et al.* (4) assessed the effects of process temperature, pressure, and time on the yield and quality of rosehip oil by using response surface methodology. Optimal conditions to extract high-quality oil were 40°C and 300 bar. Eggers *et al.* (5) reported that extraction rate and yield were the same for rosehip seeds milled with a blade grinder (Sautier mean or volume-surface mean diameter of 1.15 mm), or flaked in a roller mill (1 mm gap). The apparent solubility (g extracted oil/kg utilized CO_2, in the initial stages of extraction) was virtually unaffected by process conditions for extraction pressure ≥500 bar, at 40–80°C, and using 8.6–28.6 g CO_2/g substrate/h. However, the apparent solubility of rosehip oil decreased when the extraction pressure was decreased from 500 to 300 bar (5). Reverchon *et al.* (6) assessed and modeled the effects of process temperature and pressure, superficial solvent velocity, and substrate particle size on extraction kinetics of ground rosehip seeds. The apparent solubility at 40°C increased from 0.5 g/kg at 101 bar to 40.0 g/kg at 671 bar and was not affected by process temperature or solvent flow rate. Reverchon *et al.* (6) observed that the amount of oil that was available for immediate extraction increased as particle size was reduced, and attributed this to the associated increase in specific surface.

Besides the effect of the process temperature and pressure on the apparent solubility of oil in the extracting solvent, SC-CO_2 extraction of oilseeds depends strongly on substrate pretreatment (7). Prior to extraction, the oil-containing plant cells should be broken by flaking or some similar process. Compression and shear forces developed between smooth rollers that rotate at differential speeds during flaking flatten the seed cotyledon pieces, the end result being the extensive deformation and fracture of the cell contents and separation of cell wall from the cytoplasm (3). Fattori *et al.* (8) compared the effects of flaking, chopping, crushing, and other less effective pretreatments on the extraction rate and oil yield of canola seeds treated with SC-CO_2 at 55°C and 360 bar. The crushed seeds produced slightly lower oil yield than chopped or flaked seeds. In addition, there was no additional positive effect of 30 min cooking at 90°C on extraction of flaked seeds (8). Oil yield from flaked soybeans treated with SC-CO_2 at 50°C and 537 bar increased as flake thickness decreased, from 66.0% for 0.81-mm-thick flakes to 97.4% for 0.10-mm-thick flakes, which was attributed to the associated increase in cell distortion (9).

Particle size reduction by milling not only increases the specific area (surface area-to-volume ratio) of oilseed materials but also ruptures cell walls. In small particles with large specific areas, there is more oil on the surface than in inner, unbroken cells. Thus, since there is apparently no diffusion through undamaged cell walls (10), oil yield may be higher when extracting smaller rather than larger particles.

In this work we assessed an alternative hypothesis for the effect of sample particle size on extraction rate and yield of SC-CO_2 extraction processes, namely, that seed parts with different oil contents may be segregated during sample preparation. Rosehip seeds were used as a model system, and microscopic evidence was gathered. Microscopy may help in

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assessing the effect of sample pretreatment on the kinetics and yield of SC-CO_2-based extraction processes. Examples that include the use of microscopy for assessing extraction effectiveness for oil-containing seeds exist (6,9,11,12).

MATERIALS AND METHODS

Extraction substrates. Rosehip *(Rosa aff. rubiginosa)* seed samples were processed by Novbeltec S.A. (Santiago, Chile) in a roller mill with a 0.5 mm gap. Milled samples were size classified in a Ro-Tap test sieve shaker (W.S. Tyler, Mentor, OH). Three fractions were separated: −8/+20 mesh Tyler (0.85 mm < particle diameter [D_p] < 2.36 mm); −20/+35 mesh Tyler (0.425 mm < D_p < 0.85 mm); and −35/+100 mesh Tyler (0.150 mm < D_p < 0.425 mm). Samples were kept in sealed plastic bags in a refrigerator up to the time of analysis.

Supercritical extraction. Experiments were carried out using a Thar Designs (Pittsburgh, PA) SFE-1L process development unit, equipped with an automatic control system for controlling the extraction temperature and pressure. Liquid CO_2 (≥99.8% pure) from AGA S.A. (Santiago, Chile) was used as the solvent. Extraction vessels (20 mm diameter; 50 cm^3 volume) were loaded with *ca.* 26 g milled substrate and placed in a convection oven set at 40°C. After a 2-min static extraction period, when extraction pressure (300 bar) had been reached, a P-200A-220V pump (Thar Designs) was set to the desired flow rate (11.4 g CO_2/min). The extraction pressure was subsequently maintained by a BPR-A-200B1 backpressure regulator (Thar Designs). The outlet line of the BPR was connected to the inlet port of a Swagelock (Solon, OH) SS-43YF2 six-port, two-way valve that allowed periodic switching of oil collection between 15-cm^3 capacity glass vials with polytetrafluoroethylene silicone septa (Supelco, Bellefonte, PA). Twelve unequally spaced samples were taken in all cases, and the total extraction time was 90 min. These glass vials were kept in a thermostated bath set at 50°C. The outlet port of the six-port, two-way valve was connected to an Omega (Stamford, CT) FMA5700 flowmeter equipped with an Omega DPF65 totalizer. Extraction experiments were performed in duplicate.

The oil yield was expressed in units of dry oil per unit mass (dried and oil-free) of substrate. In order to remove water from extract samples, vials were dried in an oven (Binder WTC, Tutlingen, Germany) set at 70°C prior to weighing. Recovered oil was assessed gravimetrically by difference with cleaned and dried vials. Percentage recovery of extract was estimated by determining the mass and moisture and oil contents of the spent substrate (13).

Chemical analysis. Untreated and spent samples were finely ground with a mortar and pestle prior to analysis. Moisture content was determined gravimetrically by drying in the oven (105°C) to a constant final weight (*ca.* 24 h). Oil content was determined gravimetrically by extracting to exhaustion with technical-grade hexane (TCL, Santiago, Chile) in a Soxhlet apparatus. Hexane was mostly recovered in a Fisatom (São Paulo, Brazil) rotary evaporator that was operated with a Vacuubrand (Wertheim, Germany) vacuum pump, and residual solvent traces were removed in the oven (*ca.* 2 h at 100°C).

Microscopy. Sample preparation for light microscopy was done according to standard procedures (14). Untreated seeds were moistened to assist in sample preparation. Moistened seeds and milled seed samples were fixed for 48 h using a 1:1:18 mixture of formalin, acetic acid, and 70% aqueous ethanol and then dehydrated by a 30-min immersion in a series of aqueous solutions with increasing ethanol concentration (50, 70, 95, and 100%), followed by 15 min immersion in pure *tert*-butanol. Dehydrated samples were then embedded with a liquefied mixture of *tert*-butanol and paraffin prior to cutting thin slices (18 µm thick) using a manual microtome (Jung, Heidelberg, Germany). Thin slices were fixed to slides with the aid of an albumin preparation, and paraffin was removed by treating samples with xylol, a series of aqueous solutions with a decreasing ethanol concentration, and distilled water. Staining was done with safranine (to redden cell chromosomes, nuclei, and lignified walls) and fast green (to mark other cellular structures with green color), followed by washing out excess stain with eugenol. A Nikkon (Kawasaki, Japan) Optiphot 142915 light microscope equipped with a Nikkon FX-35A photographic camera was utilized to view and record representative images.

RESULTS AND DISCUSSION

Figure 1 shows integral oil extraction yields of rosehip seed as a function of solvent usage and sample particle size. Trend

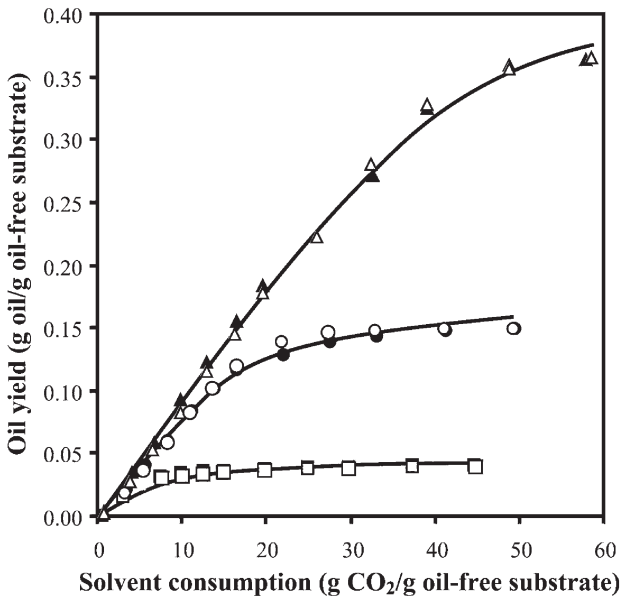

FIG. 1. Integral oil yields of ground rosehip seed treated with supercritical CO_2 at 40°C and 300 bar as a function of solvent usage and sample particle diameter (D_p): (□) 0.85 mm < D_p < 2.36 mm; (○) 0.425 mm < D_p < 0.85 mm; and (△) 0.150 mm < D_p < 0.425 mm. Filled symbols represent experimental results corresponding to first replicate; empty symbols, experimental results corresponding to second replicate; and lines, predictions based on Sovová's model (15).

lines were fitted using the kinetic model of Sovová (15) for supercritical extraction of solid substrates in packed beds, using the detailed analytical solution of Esquivel *et al.* (16). This fundamental model is based on differential mass balance equations for thin cylindrical sections of the packed bed; thus, it is of interest for the scaling up of laboratory or pilot-plant data for the design of full-scale processes (17). It considers that ground plant tissue consists of broken and intact cells and that the extraction rate depends on internal and external mass transfer parameters. To implement the model, we assumed that the partition of oil between SC-CO_2 and the solid matrix was constant. The best-fit value for the apparent solubility of rosehip seed oil at 40°C and 300 bar yielded y_r = 8.78 g oil/kg CO_2, which compares well with the actual solubility of 8.99 g oil/kg CO_2 that is predicted by the correlation of del Valle and Aguilera (18). It has been claimed that apparent solubilities for SC-CO_2 extraction of TG from seeds that contain C_{54}-type oils (where the majority of the FA have 18 carbon atoms), such as rosehip oil (5), can be accurately estimated using the aforementioned correlation (19).

We assumed that the external mass transfer coefficient for the supercritical fluid phase (k_f) depends on D_p according to

$$k_f = \frac{m}{D_p^{1-n}} \quad [1]$$

where n = 0.54 (20,21). Equation 1 is derived from a dimensionless analysis for mass transfer phenomena in packed beds (13), and parameter m is constant since the superficial solvent velocity was unchanged and the physical transport properties of the loaded supercritical phase depend only on extraction temperature and pressure, which also were kept constant. Based on the best-fit value for $m\rho_s/\rho$ (1.94×10^{-8}), it was possible to estimate that the values of ($k_f \rho/\rho_s$) increased from 3.75×10^{-7} to 8.27×10^{-7} m/s as a result of an increase in D_p, where ρ_s and ρ are the densities of the solid substrate and SC-CO_2, respectively. These values are slightly smaller, but of the same order of magnitude, than literature values for supercritical extraction of oil-containing plant material (13).

In Sovová's model (15), the internal mass transfer coefficient ($k_s\ x/y_r$) diminishes proportionally to the residual oil content in the solid matrix (x). We assumed that k_s was constant and obtained a best-fit value (1.76×10^{-7} m/s) that was of the same order of magnitude as those reported by other authors for various oilseeds (12).

Finally, we assumed that the free oil fraction (α) depended on the pretreatment of the solid. Best-fit values of α were: 0.000 (for particles with D_p = 0.85–2.36 mm), 0.031 (D_p = 0.425–0.85 mm), and 0.021 (D_p = 0.150–0.425 mm). The Sovová model (15) fitted our experimental data fairly well (Fig. 1). It is also evident (Fig. 1) that the asymptotic oil yield depended on sample particle size.

Similarly to us, many researchers have found that the extraction yield of oil from oil-containing seeds with SC-CO_2 decreases as particle size increases. As an example, Sovová *et al.* (21) reported that nearly asymptotic yields of milled grape seeds treated with 12–20 g SC-CO_2/g substrate/h were as follows: 53.5 g oil/kg oil-free substrate for 1.13 mm diameter (Sautier mean) particles, 66.1 g/kg for 1.06 mm particles, 111.7 g/kg for 0.63 mm particles, and 125.8 g/kg for 0.60 mm particles following 11–25 h extraction time at 40°C and 280 bar. Also, Catchpole *et al.* (22) reported that coriander seeds yielded 35.3 g oil/kg substrate for the milled seeds passing through 0.95-mm-diameter openings, and 75.0 g/kg for 0.56-mm openings following ≥6 h extraction with 3–10 g/g substrate/h of SC-CO_2 at 40°C and 250 bar. Apparently, in both of these cases all seeds passed through a single size-reduction device whose working conditions were so varied as to achieve different milling grades. For example, coriander seeds were ground with a knife mill to different particle sizes by changing the size of the openings in a sieve plate that was fixed under the rotating blades (22).

Since seeds were fully processed in the size-reduction device, no grounds existed in the previous two studies for claiming that segregation of seed parts with different oil contents would give rise to variations in oil yield between samples with different milling treatments. This may not be the case where particle sizes are adjusted by milling and subsequent sieving (6,10,23), as in our work. Roy *et al.* (23) extracted milled tomato seeds with 17.9 g SC-CO_2/g substrate/h [estimate made assuming a load density of 0.4 g/cm^3 in the extraction vessel] and provided no experimental evidence to support their claim that oil yield may be independent of particle size. Indeed, nearly asymptotic yields following *ca.* 12 h extraction at 40°C and 245 bar were as follows: 131.9 g oil/kg oil-free substrate for 1.02-mm-diameter (mean) particles, 222.2 g/kg for 0.65-mm particles, 305.5 g/kg for 0.46-mm particles, and 409.7 g/kg for 0.25-mm particles. On the other hand, oil recovery from ground and sieved peanuts following a 3-h extraction with 9.4 g/g substrate/h of CO_2 at 25°C and 550 bar was 36% (asymptotic value) for D_p = 3.35–4.75 mm, 51% (asymptotic value) for D_p = 2.36–3.35 mm, 60% (asymptotic value) for D_p = 1.76–2.36 mm, 77% for D_p = 1.18–1.76 mm, and 82% for D_p = 0.864–1.18 mm (10).

It has been claimed that milling operations not only increase the interfacial area but also release oil from cells, which is especially important when cell walls are virtually impervious to the extraction solvent (20). This claim is supported by the common experimental observation that it is nearly impossible to extract oil from uncracked seeds. As an example, virtually no oil is extracted from intact colza seeds using high-pressure CO_2 (24), only 3% of the oil (asymptotic value) is extracted from peanut halves (mean diameter of 10 mm) (10), and only 1.3 g oil/kg is extracted from coriander seeds cracked in halves using a roller mill with a wide gap (22). This trend is not limited to just supercritical extraction, since Othmer and Agarwal (25) were able to extract just 0.08–0.19% of the original oil from half or whole soybeans following 1 wk of extraction with hexane.

Are intact cell walls truly impervious to SC-CO_2? This question was critically assessed by Femenia *et al.* (26), who measured compositional changes in cell walls of raw and toasted almond seeds as a function of oil extraction extent. For

a low degree of extraction (*ca.* 33% oil removed with SC-CO_2 at 50°C and 330 bar), pectic and hemicellulosic components were modified, whereas at a higher degree of extraction (*ca.* 67% oil removed) all cell wall components, including cellulose, suffered chemical changes. As evidenced by light microphotographs, these changes increased the porosity of cell walls, thus allowing the removal of FA chains that were initially contained in unbroken cells. In agreement with this assessment, Marrone *et al.* (11) demonstrated that yield of oil from fresh almond seeds that were milled to different particle sizes and treated with SC-CO_2 at 40°C and 350 bar was unaffected (540 g oil/kg seed) by sample pretreatment and extraction conditions. However, this may be a species-specific result.

Reverchon *et al.* (6) assessed the effect of particle size of presumably ground and sieved rosehip seeds on extraction rate and oil yield by using 27.7 g/g substrate/h of SC-CO_2 at 40°C and 671 bar. Reported oil yields were 49, 52, and 74 g oil/kg substrate for particles with Sautier mean diameters of 1.03, 0.79, or 0.42 mm, respectively. Although large particles could lead to long, diffusion-controlled extraction processes, slow diffusion may affect the extraction kinetics of sufficiently large peanut pieces, unlike results found for milled tomato or rosehip seed particles ≤1 mm in diameter. According to Reverchon *et al.* (6), there were microstructural effects that explained the slow extraction kinetics of these relatively small rosehip particles, since no specific oil-bearing structures could be found in the seeds when using scanning electron microscopy (SEM). The investigators claimed that rosehip oil might be contained in lignified channels of 20–30 µm diameter, and a length proportional to particle size (6).

As noted previously, we suggest that our size–classification process, the same as that of Reverchon *et al.* (6), segregated seed parts having different oil contents. To support this hypothesis, we determined the oil content in our three fractions by exhaustive hexane extraction of finely reground samples. These were as follows: 57.1 g oil/kg dry, oil-free substrate [for particles with D_p = 0.85–2.36 mm, 74.1% (mass) of ground rosehip seeds], 171.0 g/kg (D_p = 0.425–0.85 mm, 12.6% of ground seeds), and 391.5 g/kg (D_p = 0.150–0.425 mm, 4.8% of ground seeds). These values were set as the asymptotic yields in the Sovová model (15). Furthermore, we observed samples of untreated seeds (Fig. 2) and size-classified particles (Fig. 3) under the light microscope.

Figure 2 shows that rosehip seeds do contain oil-bearing structures, although they are enclosed in a thick (*ca.* 220 µm thickness) and highly lignified testa. Figure 2A shows rapidly dividing meristematic cells that originate from the seed germ; for this figure, germination was initiated by the premoistening step. We determined that *ca.* 82% (w/w) of the milled rosehip seed was ≥0.85 mm in diameter, so that most of the seed corresponds to testa. Figure 2A gives a false impression about the actual size of the germ in a dormant seed, as a consequence of the rapid cell division of meristematic cells during germination. The amplified views of cells in seed testa (Fig. 2B) and germ (Fig. 2C) led us to hypothesize that the SEM picture of Reverchon *et al.* (6) corresponded to lignified testa devoid of oil.

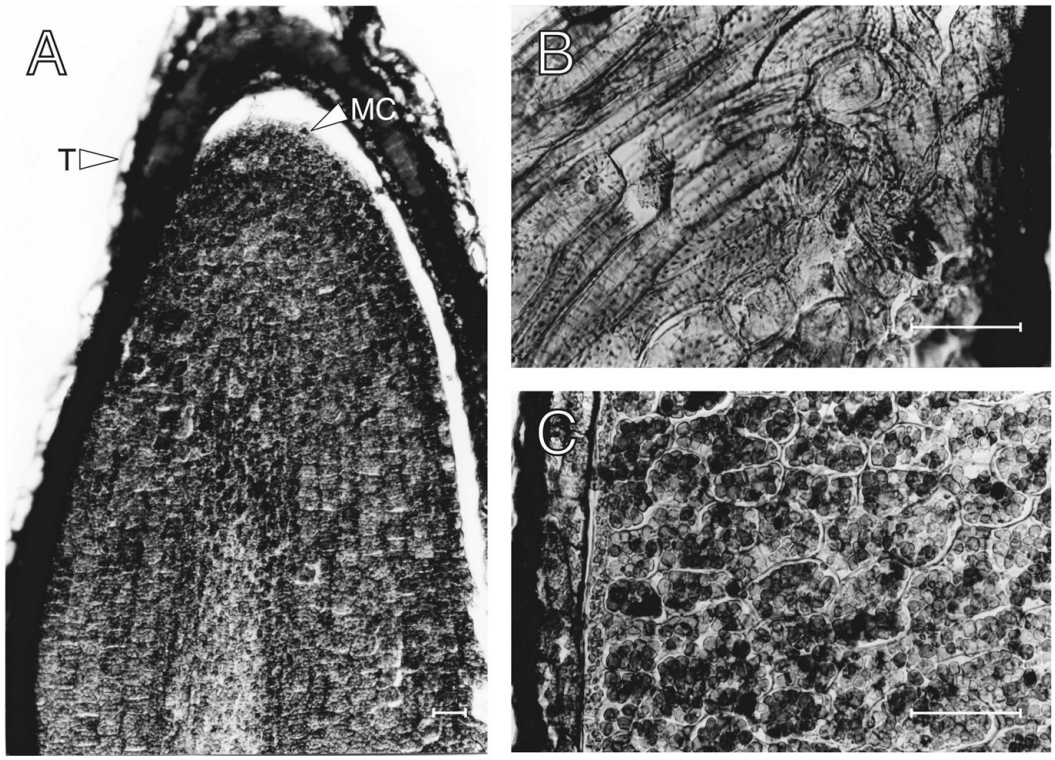

FIG. 2. Light photomicrographs of premoistened rosehip seed: (A) whole seed; (B) enlarged view of cells from seed testa ("T" in microphotograph A); (C) enlarged view of meristematic cells from seed germ ("MC" in microphotograph A). Bars = 100 µm.

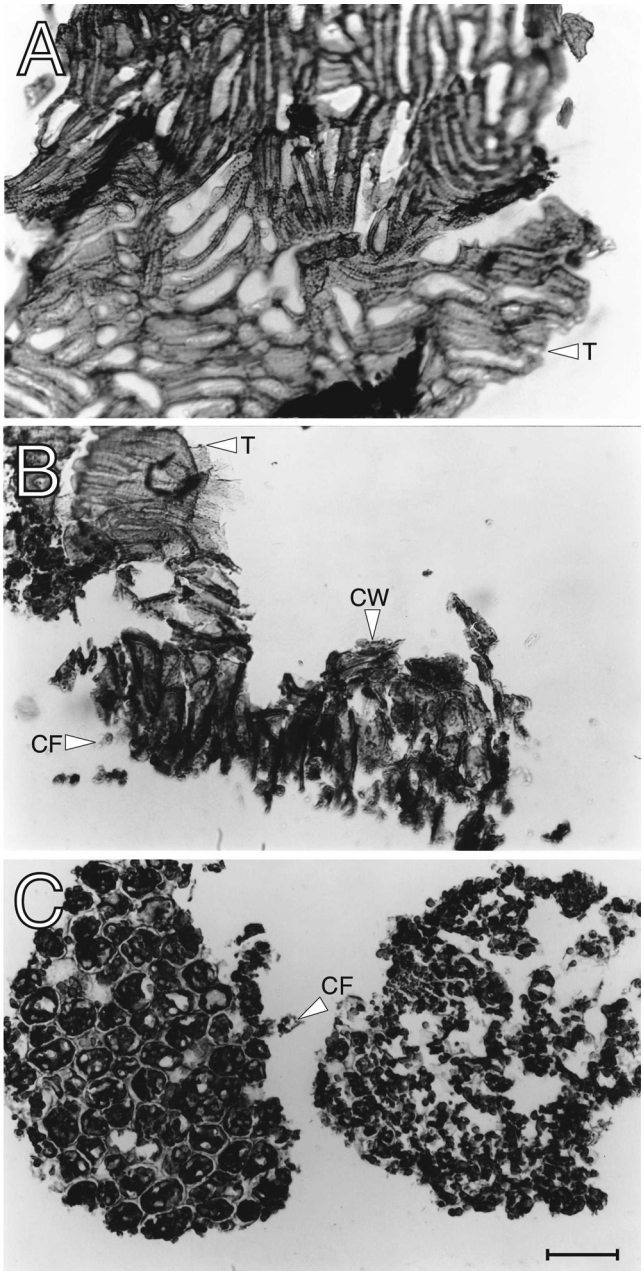

FIG. 3. Light photomicrographs of ground rosehip fractions analyzed in this study: (A) 0.85 mm < particle diameter (D_p) < 2.36 mm; (B) 0.425 mm < D_p < 0.85 mm; and (C) 0.150 mm < D_p < 0.425 mm. "T" indicates cells from seed testa; "CF," cell fragments from seed germ; and "CW," cell wall fragments from seed germ. Bar = 100 μm.

Figure 3 shows that the rosehip seed fraction of large (0.85–2.36 mm) particles (Fig. 3A) contained mainly testa fragments, whereas that of small (0.150–0.425 mm) particles (Fig. 3C) contained mostly seed germ fragments. This, in turn, was probably related to the mechanical properties of the two components (a tough, protective testa; a brittle germ). The separation was not perfect, though, and some germ fragments were carried by seed testa fragments and vice versa (*cf.* Fig. 3B). Cells from testa and seed germ were not modified by the hydration process applied to intact seeds (compare cells noted in Fig. 3 with those in Figs. 2B and 2C, respectively). The size of fragments in the microphotographs was not representative of the actual particle size, since the former corresponded to cross-sectional views of the particles. This nonrepresentativeness was compounded by the inherent difficulty of embedding in paraffin and slicing with the micrometer unmoistened particles (microphotographs correspond to the outer, less dense portions of the paraffin block).

Based on evidence here provided, we strongly believe that segregation of oil-containing seeds in fractions with different oil contents may be a common ocurrence in supercritical extraction studies, especially when using as a substrate seeds with a thick and/or hard testa and a small germ (e.g., tomato, grape, rosehip), and when samples of different particle size are separated by sieving. Therefore, oil content determinations and microstructural observations of seed fractions always should be performed in supercritical extraction studies to clarify substrate pretreatment- and/or size-related effects.

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