Oxidative Stability of Seed Oils Extracted with Supercritical Carbon Dioxide[1]

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Dry-milled corn germ, soybean and cottonseed flakes were extracted (at 70–90 C and 12,000 psi) with supercritical carbon dioxide (SC-CO_2) to yield crude oils. Oxidative stability of the crude oils was determined and compared to similar products obtained by conventional expeller and/or prepress solvent extraction. Under Schall oven storage conditions (60 C), SC-CO_2-extracted oils undergo rapid deterioration and fail to show the normal induction period observed with conventional expeller and solvent-extracted crude oils. The levels of tocopherols found in SC-CO_2-extracted oils are comparable to those obtained by expeller or solvent extraction, while phospholipids present in significant amounts in conventional crude oils are essentially absent from SC-CO_2-processed crudes. The addition of phosphatides to SC-CO_2-extracted crude oils improves oxidative stability, which suggests that both tocopherols and phospholipids are required to stabilize crude oils against autoxidation. Heating of SC-CO_2-extracted crude oils to deodorization temperatures improves oxidative stability. The destruction of fat hydroperoxides under these conditions probably accounts for improved oxidative stability. A combination of heat and the addition of citric acid and phenolic antioxidants resulted in further improvement of oxidative stability.

Previous reports from this laboratory (1-8) and elsewhere (9—14) have described the extraction of oilseeds and wax esters with supercritical carbon dioxide (SC-CO_2). This technology has many potential advantages over hexane extraction or expeller pressing. These include ligher color, less color fixation, more neutral oil and a lower refining caustic requirement. The crude oils are, however, less stable toward autoxidation than conventionally processed oils (5-7). We report here some oxidative stability evaluations of SC-CO_2-extracted oils, along with some practical methods to stabilize them against autoxidation while in storage.

EXPERIMENTAL

The SC-CO_2 extraction methodology, oil processing and analytical methods have been described previously (5-7).Samples of crude dry-milled corn oil, cottonseed oil and crude degummed soybean oil were obtained from Illinois Cereal Mills (Paris, Illinois), Producer's Cottonseed Oil Co. (Fresno, California) and Riceland Foods (Stuttgart, Arkansas), respectively. The fluid lecithin was a commercially prepared product obtained from Central Soya (Ft. Wayne, Indiana). Tenox 20 was obtained from Tennessee Eastman (Kingsport, Tennessee). Deodorizations were carried out in a continuous system designed by Bitner et al. (15).

Oxidative stability was determined according to a modification of the Olcott method (16). Crude oil samples of 10.00 ± .01 g were stored at 60 C in 100-ml beakers under Schall oven (forced draft) conditions, followed by titration of the peroxides according to the official AOCS method (17). Soy flakes (9.0% moisture) were prepared from William's Variety seed, and extracted at a flake thickness of .015". Dehulled cottonseed (8.6% moisture) was cracked and flaked to a thickness of .007". The dry-milled corn germ was a commercially prepared sample and was extracted at 3% moisture. Crude oils from the CO_2-extraction were slurried with a small amount of filter aid and filtered under vacuum prior to further processing and analysis.

RESULTS AND DISCUSSION

The tocopherol, phosphorus and iron content of SC-CO_2, expeller and solvent-extracted oils are shown in Table 1. The tocopherol content of CO_2- and conventionally-extracted corn, soybean and cottonseed oils is about equal with respect to the extraction method used. Generally, CO_2-extracted oils show slightly less tocopherol content than commercially extracted crude oils. Because virtually all the phosphorus in crude oils is associated with phospholipids, a conversion factor can be used to estimate the phospholipid content of crude vegetable oil (18). The major difference between CO_2-extracted oils and expeller-or solvent-extracted crudes is shown by their phospholipid contents. For all practical purposes, phospholipids are insoluble in SC-CO_2. Expeller-processed cottonseed and corn oils con-

TABLE 1

Tocopherol, Phosphorus and Iron Content of CO_2-, Expeller- and Hexane-Extracted Crude Oil

Oil type	Extraction method[a]	Tocopherol (μg/g)	Phosphorus[b] (ppm)	Iron[c] (ppm)	Induction period[d] (days)
Soybean	CO_2	900-1000	1-3	0.3	2
Soybean	Hexane	1200-1500	500-600	0.7	8
Corn-dry	CO_2	1200-1800	1-3	0	2
Corn-dry	Expeller	1500-1700	120	0.3	10
Cottonseed	CO_2	700	1-5	0.2	3.5
Cottonseed	Expeller	920	380	1.9	10

[a]CO_2 extractions 80 C, 12,000 psi.
[b]AOCS method Ca 12-55.
[c]AOCS method Ca 15-75.
[d]Days to P.V. 20: 10 g oil, 100-ml beaker, 60 C forced draft oven.

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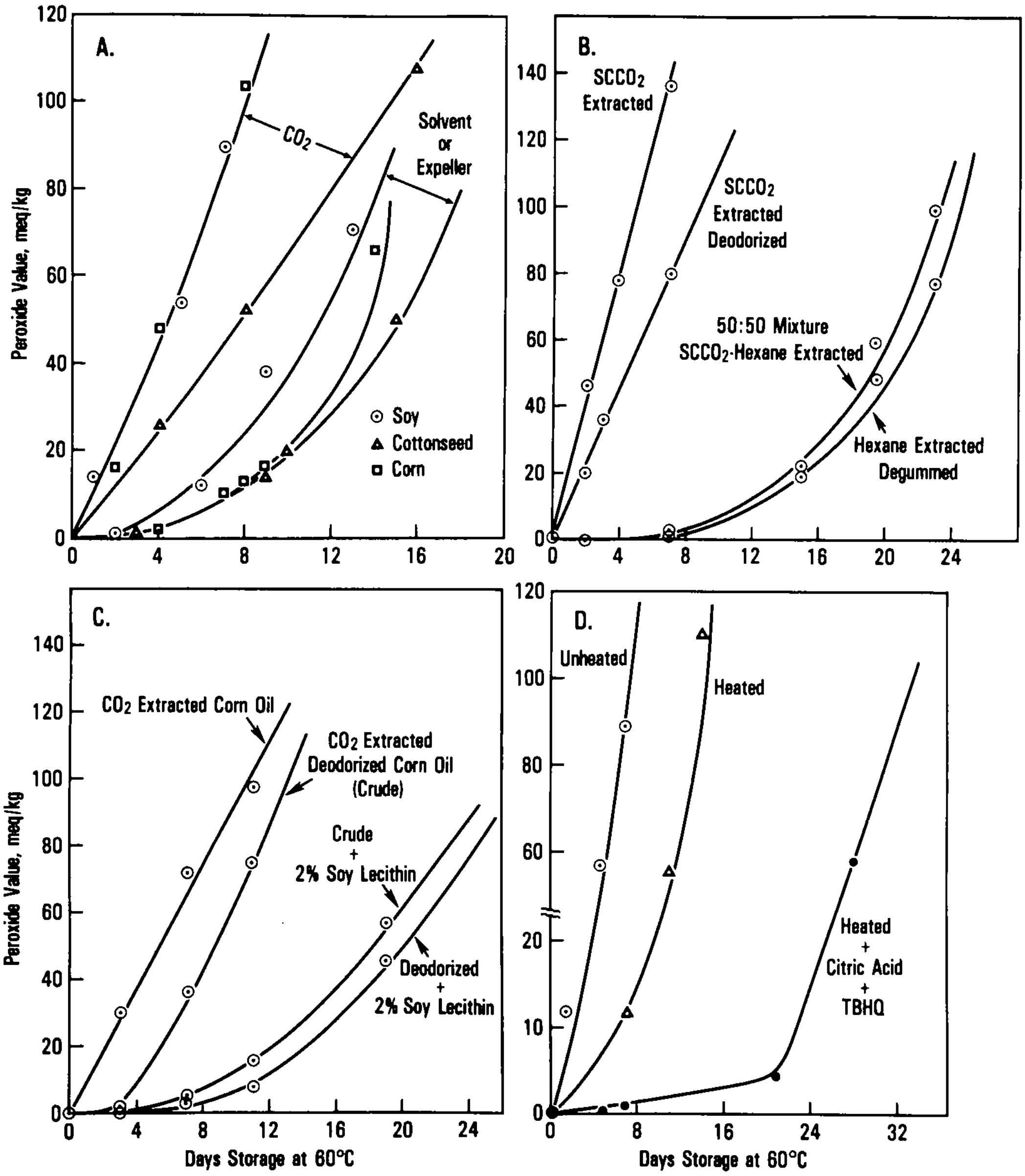

FIG. 1. Oxidative stability of SC-CO_2-extracted oils (80 C, 12,000 psi). A, SC-CO_2-, expeller- and solvent-extracted crude oils; B, SC-CO_2- and solvent-extracted crude degummed soybean oils; C, SC-CO_2- and expeller crude dry-milled corn oils; D, SC-CO_2-extracted crude soybean oil. Heated oils deodorized in thin film continuous deodorizer.

tain appreciable amounts of phospholipids. The phospholipid content of the commercial samples was 1.92%, 0.97% and 0.3% for soybean, cottonseed and corn oil, respectively (18). The iron content of CO_2-extracted oils is lower than that of commercial samples, probably because they are exposed to less metal. The oxidative stability of SC-CO_2 and commercially extracted crude oils was determined. In addition, crude oils tested with lecithin and commercial antioxidants were evaluated. The results are summarized in Figure 1. Figure 1A shows the relative oxidative stability of SC-CO_2 and commercially extracted oils. Commercially-extracted crude oils all show a significant induction period before peroxide development occurs during 60 C storage. On the other hand, CO_2-extracted oils show little or no induction period. CO_2-extracted soy and corn have about the same stability, while cottonseed oil is somewhat more stable. Gossypol pigments are known to function as antioxidants (19), and because gossypol is partially soluble in SC-CO_2, the SC-CO_2-extracted crude oil would be expected to exhibit some oxidative stability.

Oxidative stability data for a SC-SC_2-extracted soybean oil are shown in Figure 1B and compared to a hexane-extracted crude, degummed oil containing 100 ppm phosphorus. The SC-CO_2 crude oil fresh from the extractor shows rapid buildup in peroxides after storage. Deodorization of the oil resulted in improved oxidative stability. A crude hexane-extracted degummed soybean oil containing 100 ppm of phosphorus was also subjected to 60 C storage, as was a 50:50 mixture of the hexane- and CO_2-extracted crude oils. The blend of CO_2- and hexane-extracted oils was nearly as stable as the hexane-extracted oil alone. The marked improvement in stability is attributed to the phospholipids present in the hexane-extracted oil.

A similar experiment with crude CO_2-extracted corn oil is shown in Figure 1C. The stabilizing effect of added soybean phosphatides and the beneficial effects of heat are similar to that already discussed for soybean oil. More work is needed to establish the minimum amount of soybean phosphatides required to stabilize SC-CO_2-extracted oil. However, as little as 50 ppm phosphorus (0.16% phosphatide; percent phosphorus × 32) (18) affords improved oxidative stability. Commercial soy phosphatides (2%) used in stabilizing corn oil correspond to about 625 ppm phosphorus; this amount should be in excess of that required to stabilize the oil against oxidation.

The effect of heating, citric acid treatment and the phenolic antioxidant, tertiary-butyl hydroquinone (TBHQ) on the oxidative stability of SC-CO_2-extracted soybean oil are shown in Figure 1D. The results indicate that a combination of heat, citric acid and TBHQ is quite effective in stabilizing CO_2-extracted crude soybean oil.

The oxidative stability of unheated crude oils treated with the antioxidant TBHQ and with citric acid in combination with TBHQ is shown in Table 2. The peroxide values of the treated oils show marked improvement over that of the untreated controls. Citric acid and TBHQ are effective in stabilizing soybean, cottonseed and corn oil against oxidative deterioration. However, citric acid in combination with TBHQ shows no synergistic effect over TBHQ alone. This effect has been reported by other investigators (20).

Many factors contribute to the oxidative stability of fats and oils. These include the fatty acid composition, tocopherol, phospholipid and trace-metal contents. Lard, a saturated fat, does not contain tocopherol, but shows improved oxidative stability when tocopherols are added to the fat (21). Highly unsaturated fats, such as soybean and corn oil, contain high levels of tocopherol. On the other hand, studies made on soybean oil have shown that too much naturally occurring tocopherol can function as a prooxidant (22). Thus, depending on the fatty acid composition of a fat, tocopherol can act either as an antioxidant or a prooxidant.

Several investigators have shown that the oxidative stability of soybean oil decreases with processing (23,24). Crude oil is the most stable, and refined and bleached oil the least stable. Degumming and alkali refining reduce the phospholipid content of vegetable oil from 1–3% to essentially zero (25). Decreased stability shown by such oils has been attributed to loss of phosphatides. The function of phosphatides in protecting crude oils from oxidation is unclear. Whether phosphatides act as true antioxidants, metal inactivators or as oxygen barriers at the oil/air interface is uncertain. Studies carried out on lard showed that phosphatidylcholine and phosphatidylethanolamine exert a strong synergistic antioxidant effect in the presence of tocopherol, but by themselves act as prooxidants (19).

The improvement in oxidative stability afforded by heating (Fig. 1B–D) SC-CO_2-extracted oils probably results from destruction of minute amounts of hydroperoxides formed during extraction of the oils from the seed. Hydroperoxides are destroyed rapidly at deodorization temperatures. In addition, heat may destroy complexes between metals and secondary oxidation products (26). This would account for the marked improvement in oxidative stability observed for SC-CO_2-extracted soybean oil treated with citric acid and TBHQ (Fig. 1D).

The peroxide values of freshly extracted oils are usually zero and rarely exceed 0.5 meq/kg. Several SC-CO_2 extractions were made in which the extraction vessel, flakes and other equipment were flushed with nitrogen prior to heating and pressurization. Crude oils from these runs were no more stable than those extracted without flushing the system with inert gas.

Although more work is required to elucidate the mechanism by which SC-CO_2-extracted oils undergo oxidative deterioration, this study suggests that a number of factors are involved, including the highly unsaturated nature of the oils and the absence of phospholipids which act as oxygen inhibitors in unheated oils.

TABLE 2

Effect of Antioxidants on the Stability of Unheated Crude Oils Extracted with SC-CO_2

Oil	Days storage[a] (60 C)	Peroxide value (meq/kg) Control	Tenox-20[b]	TBHQ
Soybean	8	93.9	12.5	3.7
Cottonseed	6	34	2.5	2.0
Corn (dry milled)	6	20	2.5	2.1

[a]10 g oil, 100-ml beaker, 60 C, forced draft oven.
[b]Contains citric acid and tertiarybutylhydroquinone (TBHQ); antioxidants added at 0.02% by weight active ingredients.

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