Improving the Oxidative Stability of Polyunsaturated Vegetable Oils by Blending with High-Oleic Sunflower Oil[1]

E.N. Frankel* and **S-W. Huang**
Department of Food Science and Technology, University of California, Davis, California 95616

Mixing different proportions of high-oleic sunflower oil (HOSO) with polyunsaturated vegetable oils provides a simple method to prepare more stable edible oils with a wide range of desired fatty acid composition. Oxidative stability of soybean, canola and corn oils, blended with different proportions of HOSO to lower the respective levels of linolenate and linoleate, was evaluated at 60°C. Oxidation was determined by two methods: peroxide value and volatiles (hexanal and propanal) by static headspace capillary gas chromatography. Determination of hexanal and propanal in mixtures of vegetable oils provided a sensitive index of linoleate and linolenate oxidation, respectively. Our evaluations demonstrated that all-*cis* oil compositions of improved oxidative stability can be formulated by blending soybean, canola and corn oils with different proportions of HOSO. On the basis of peroxide values, a partially hydrogenated soybean oil containing 4.5% linolenate was more stable than the mixture of soybean oil and HOSO containing 4.5% linolenate. However, on the basis of volatile analysis, mixtures of soybean and HOSO containing 2.0 and 4.5% linolenate were equivalent or better in oxidative stability than the hydrogenated soybean oil. Mixtures of canola oil and HOSO containing 1 and 2% linolenate had the same or better oxidative stability than did the hydrogenated canola oil containing 1% linolenate. These studies suggest that we can obviate catalytic hydrogenation of linolenate-containing vegetable oils by blending with HOSO.

KEY WORDS: Flavor stability, headspace volatiles, high-oleic sunflower oil, hydrogenation, linoleate, linolenate, oxidative stability, peroxide values, polyunsaturated oils, vegetable oil blends.

Because the health and nutritional aspects of edible oils in foods and food products are receiving increasing attention, it is becoming important to formulate new vegetable oil compositions of improved stability and nutritional value. Hydrogenation of polyunsaturated vegetable oils is becoming less appealing because of recent evidence that *trans* isomers may have adverse nutritional effects (1–3).

From many early studies of oxidative stability of edible oils varying in fatty acid composition, it is now well recognized that the oxidative rancidity of mixtures of fats is largely related to their contents of linoleic and linolenic acids. The classical work of Gunstone and Hilditch (4) showed that the addition of 1 to 5% methyl linoleate to methyl oleate significantly decreased the oxidative stability measured by the length of the induction period at 20°C. Cowan *et al.* (5) later reported significant improvements in flavor and oxidative stability of soybean oil by lowering the linolenate content by blending with different levels of peanut oil. Purdy (6) reported that the stability of high-oleic sunflower (HOSO) and safflower oils by the active oxygen method (AOM) increased in direct relation to their content of 18:1. An AOM value of up to 100 h [to reach a peroxide value (PV) of 100] was obtained for 89% 18:1 and 1% 18:2, and decreased to 10 h with 12% 18:1 and 70% 18:2. HOSO is now commercially available in the United States and has a fatty acid composition similar to that of olive oil (7).

The oxidative stability of edible oils and food emulsions has been difficult to evaluate in view of questionable conditions and methodology used to follow oxidation. The current methods to determine oxidative and flavor stability of food lipids were reviewed recently to reevaluate the effects of conditions of oxidation, and the analytical methods used to determine extent and endpoint of oxidation were described (8). The AOM stability method, like other high-temperature stability methods, may be of questionable validity because, at 100°C, the rate of oxidation is highly dependent on oxygen, the mechanism of oxidation changes, the determination of PV becomes unreliable, and the end point is beyond the level where flavor deterioration occurs in polyunsaturated vegetable oils (8,9).

This paper reports a study aimed at preparing more-stable vegetable oils with a wide range of desired fatty acid compositions by mixing different proportions of HOSO with soybean, canola and corn oils. Another goal was to determine if an alternate approach to hydrogenation can be developed to preparing stable all-*cis* vegetable oils by blending with HOSO. Stability tests, based on PV and volatile analyses, were done at 60°C to avoid the difficulties of high-temperature stability tests (8,9).

EXPERIMENTAL PROCEDURES

Materials. Refined, bleached and deodorized soybean, HOSO, canola (low-erucic rapeseed oil) and corn oils, and refined, bleached, hydrogenated, deodorized soybean and canola oils were obtained commercially with citric acid added. Initial quality was checked by determining PV colorimetrically (10). Fatty acid composition was determined by gas chromatography (GC) of the methyl esters prepared by alkali-catalyzed transesterification (11) (Table 1).

Oxidation. Oil samples (5 g) weighed into screw-capped 25-mL Erlenmeyer flasks were oxidized in duplicate at 60°C, in the dark, in a shaker oven (Lab-Line Instrument, Inc., Melrose Park, IL). Oxidative stability was evaluated by analyzing oil samples periodically for PV and for volatiles by static headspace GC. All analyses were done in duplicate.

Static headspace GC. Oil samples of 0.10 g were weighed into special 6-mL headspace vials, sealed with silicone rubber Teflon caps with a crimper and heated to 100°C for 15 min. A procedure was developed to determine hexanal and propanal within 6 min by using a Perkin-Elmer Sigma 3B gas chromatograph with an H-6 headspace sampler (Norwalk, CT) and a capillary DB-1701 column (30 m × 0.32 mm, 1 μm thickness; J&W, Folsom, CA) heated isothermally at 65°C. The GC conditions were: helium linear gas velocity, 20 cm/s (helium head column pressure 30 p.s.i); splitless injector temperature, 180°C; and detector temperature, 200°C.

After heating, the bottles were pressurized for 30 s before injection. Volatile compounds were identified by comparison of retention times with those of authentic

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*To whom correspondence should be addressed.

TABLE 1

Fatty Acid Composition of Vegetable Oils Used for the Oxidation Experiments[a]

Fatty acids (%)	Soybean A	Soybean B	HOSO A	HOSO B	Canola A	Canola B	Corn	Hydrogenated Soy	Hydrogenated Canola
16:0	10.4	10.8	4.4	4.0	3.9	4.1	10.8	9.1	6.0
18:0	4.2	4.2	4.5	4.3	1.8	1.9	2.1	4.1	7.0
18:1*c*	24.7	23.2	77.4	79.2	61.3	60.5	26.3	29.6	60.0
18:1*t*	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.2	17.1
18:2*c*	53.8	54.7	12.5	11.1	21.9	22.8	59.8	43.5	8.9
18:3*c*	6.9	7.1	0.1	0.4	9.5	9.9	1.0	4.5	1.0
22:0	0.0	0.0	1.1	1.0	0.3	0.4	0.0	0.0	0.0
22:1*c*	0.0	0.0	0.0	0.0	1.3	0.3	0.0	0.0	0.0

[a] Abbreviations: HOSO = high-oleic sunflower oil; Soy = soybean oil; *c* = *cis*; *t* = *trans*.

reference compounds. Peak areas for individual volatiles and for total volatiles were integrated electronically (C-R3A Chromatopac; Shimatzu Corp., Kyoto, Japan) to determine oxidative stabilities. The main volatile products detected in soybean oil oxidized at 60°C included pentane, propanal, hexane, pentanal and hexanal (Fig. 1a). The main volatile products in HOSO oxidized at 60°C included pentane, hexane, heptane, pentanal and hexanal (Fig. 1b). Soybean oil produced propanal and more hexanal than HOSO, whereas HOSO produced no propanal and more heptane. Propanal, hexanal and heptane are important volatile products expected from the oxidation of 18:3, 18:2 and 18:1, respectively (12).

Statistical analyses. Analysis of variance (ANOVA) was used to determine the least significant means between mean values (13) of duplicate oxidations and duplicate analyses of PV and of headspace volatiles. One-way ANOVA was calculated on measurements taken after each day of oxidation. A significance level is $P < 0.05$ unless otherwise indicated.

RESULTS AND DISCUSSION

Stability of mixtures of polyunsaturated oils and HOSO. The objective of this work was to reduce the level of 18:3 and 18:2 in soybean and canola oils by adding different amounts of HOSO. By blending with HOSO, the 18:3 content of soybean and canola oils can easily be lowered to the same levels as partial hydrogenation (Table 2). Blends of HOSO with corn oil were prepared also to lower the 18:2 content to 20 and 40%.

Results in Figure 2a show that the oxidative stability of soybean oil at 60°C, based on PV, was significantly increased by blending with HOSO to lower the 18:3 content to 2 or 3%. ANOVA indicated that the oxidative stability, based on PV, was significantly different among all oils after 6 d of oxidation. Determinations of hexanal formation showed also that soybean oil stability can be increased by blending with HOSO (Fig. 2b). ANOVA showed that the mixtures were all significantly more stable than soybean oil, but the blend containing 2% 18:3 was not significantly different from HOSO after 8 d of oxidation. If we assume that analysis of hexanal is closely related to flavor, we can reasonably conclude that the flavor stability will also be improved in mixtures of soybean oil and HOSO.

The oxidative stability of canola oil was significantly increased by blending with HOSO to lower the 18:3 content to 2 or 3% (Fig. 3a). ANOVA showed that both mixtures were more stable than canola oil after 6 d of oxidation. These mixtures were neither significantly different

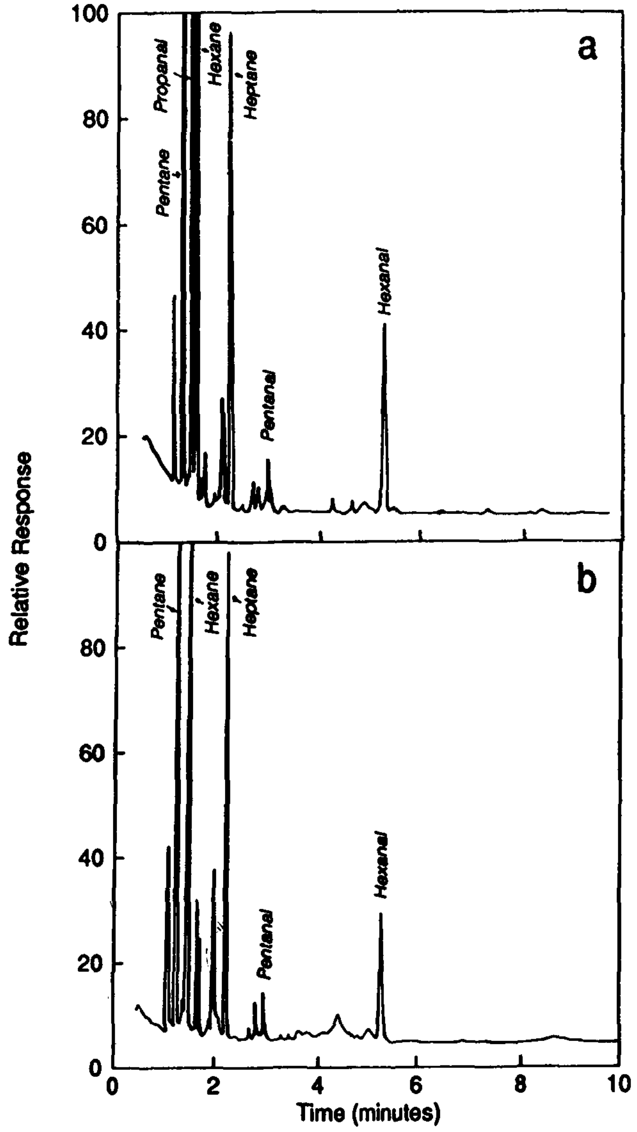

FIG. 1. Gas-chromatographic headspace analyses: a: soybean oil oxidized at 60°C (peroxide value 9.1); b: high-oleic sunflower oil oxidized at 60°C (peroxide value 2.1).

TABLE 2

Fatty Acid Composition of Vegetable Oil Mixtures Used for the Oxidation Experiments[a]

Fatty acids (%)	Soybean/HOSO			Canola/HOSO			Corn/HOSO	
	27:73	41:59	63:37	7:93	17:83	27:73	18:82	59:41
Sats	10.5	11.4	12.7	8.3	8.0	7.8	9.2	11.1
18:1	63.5	55.6	43.7	78.7	76.8	75.0	70.4	48.2
18:2	24.0	30.0	39.1	12.0	13.2	14.2	20.0	40.0
18:3	2.0	3.0	4.5	1.0	2.0	3.0	0.4	0.7

[a] Abbreviations: HOSO = high-oleic sunflower oil, Sats = saturates (palmitate + stearate).

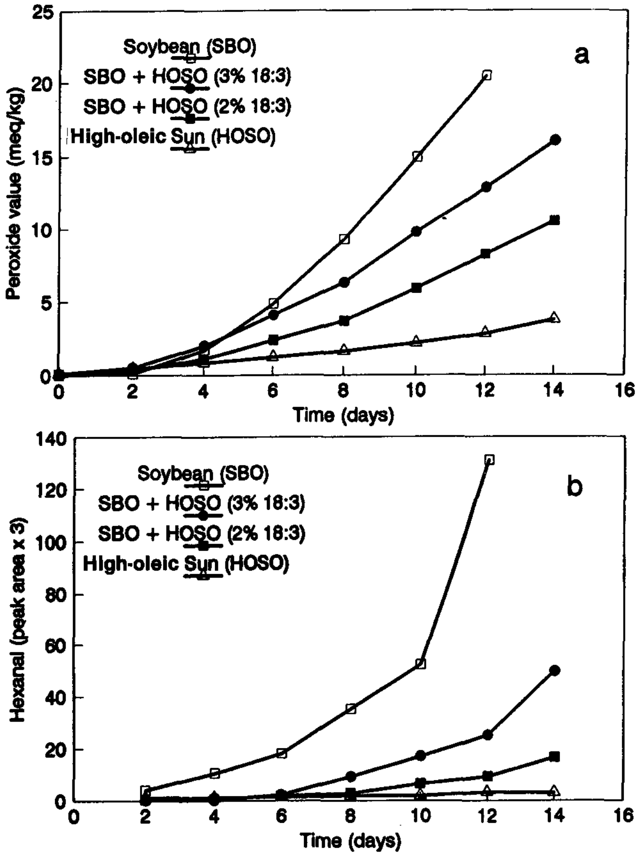

FIG. 2. Oxidative stability of SBO and mixtures of SBO with high-oleic sunflower oil (HOSO) oxidized at 60°C: a: based on peroxide values; b: based on headspace gas-chromatographic analysis of hexanal.

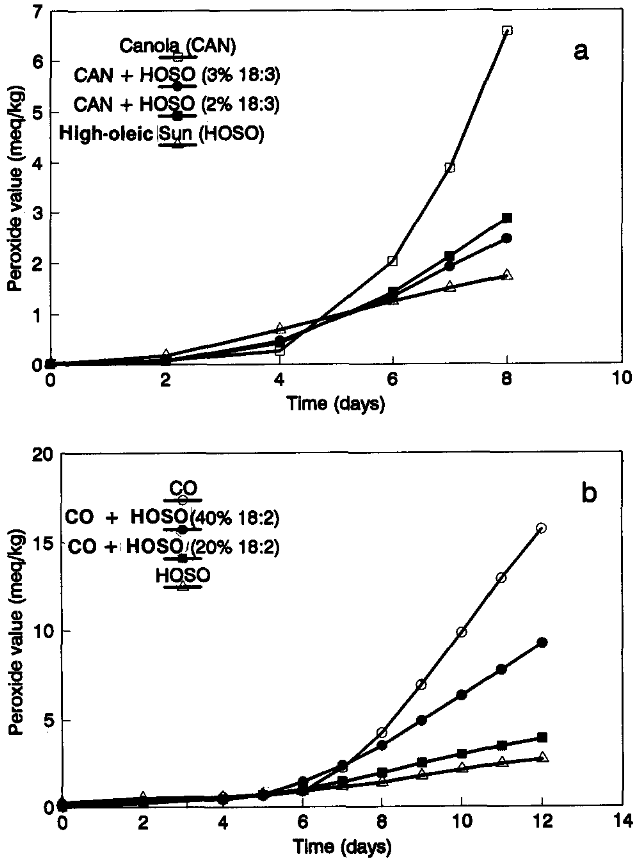

FIG. 3. Oxidative stability of vegetable oils based on peroxide values: a: CAN and mixtures with HOSO oxidized at 60°C; b: corn oil (CO) and mixtures with HOSO oxidized at 60°C. See Figure 2 for other abbreviation.

from HOSO nor were there differences between them after 6 and 7 d of oxidation, but they were significantly less stable than HOSO after 8 d of oxidation. The oxidative stability of corn oil was significantly improved by adding HOSO to lower the 18:2 level from 60 to 40 and 20% (Fig. 3b). After 7 d of oxidation, both mixtures were significantly more stable than corn oil, and less stable than HOSO.

Stability of vegetable oil mixtures vs. hydrogenated oils. To simulate the composition of a commercially hydrogenated soybean oil containing 4.5% 18:3, soybean oil was blended with HOSO to lower the 18:3 content to 4.5 and 2% (Table 2). The composition of a commercially hydrogenated canola oil containing 1.0% 18:3 was simulated by blending canola oil with HOSO to lower the 18:3 content to 1 and 2% (Table 2).

The hydrogenated soybean oil containing 4.5% 18:3 produced lower PVs than did the mixture of soybean oil and HOSO containing the same 4.5% 18:3 (Fig. 4a). After 9 d of oxidation, the mixture of soybean oil and HOSO containing 2% 18:3 produced lower PVs than did the hydrogenated soybean oil, and ANOVA showed significant differences among all samples tested. Although the hydrogenated soybean oil had greater stability than the

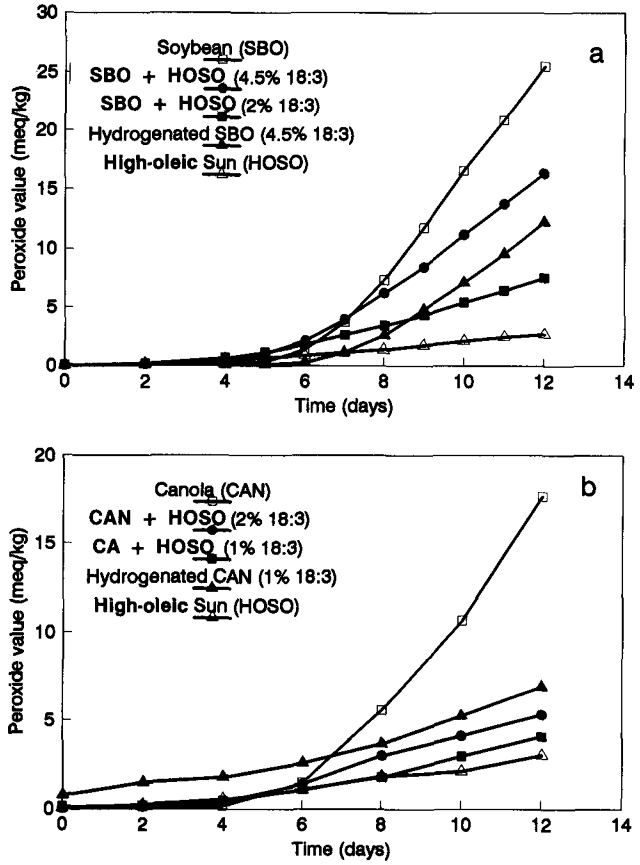

FIG. 4. Oxidative stability of vegetable oils and hydrogenated vegetable oils based on peroxide values: a: SBO, mixtures of SBO with HOSO and hydrogenated SBO oxidized at 60°C; b: CAN oil, mixtures of CAN oil with HOSO and hydrogenated CAN oil oxidized at 60°C. See Figure 2 for other abbreviations.

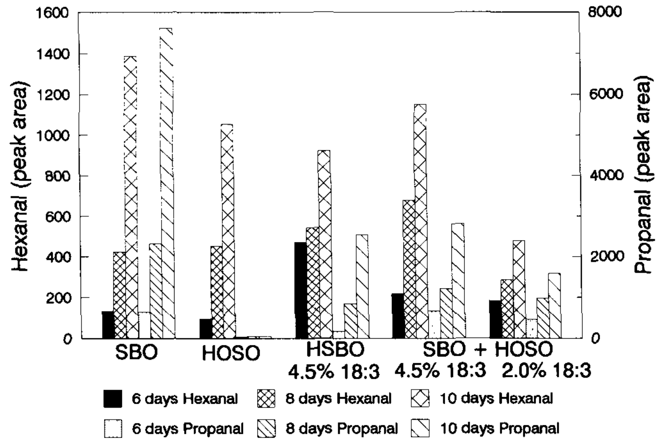

FIG. 5. Oxidative stability of SBO, HOSO, hydrogenated soybean oil (HSBO) and mixtures of SBO and HOSO, based on headspace gas-chromatographic analysis of hexanal and propanal. See Figure 2 for other abbreviations.

corresponding mixture of soybean oil and HOSO containing 4.5% 18:3, based on PV analyses, this difference in stability was not supported by the headspace volatile analyses presented below.

The mixture of canola oil and HOSO containing 2% 18:3 produced lower PVs than did the hydrogenated canola oil containing 1% 18:3, but the differences were not significant after 8 and 10 d of oxidation (Fig. 4b). The initial PV of the hydrogenated canola oil was slightly higher than that of the other oils tested. The mixture of canola oil and HOSO containing 1% 18:3 produced significantly lower PVs than did the hydrogenated canola oil at all times of oxidation. There also was no significant difference in stability between HOSO and the mixture containing 1% 18:3. Therefore, canola oil and HOSO mixtures containing 1 or 2% 18:3 had the same oxidative stability as that of hydrogenated canola oil containing 1% 18:3.

Based on headspace volatile analyses, the hydrogenated soybean oil had higher hexanal values than did unhydrogenated soybean oil at 6 and 8 d of oxidation and a lower hexanal value at 10 d; the propanal values were significantly lower at 8 and 10 d of oxidation (Fig. 5). The mixture of soybean oil and HOSO containing 4.5% 18:3 had significantly lower hexanal values than did the hydrogenated soybean oil at 8 and 10 d, and lower propanal values at 6, 8 and 10 d of oxidation. The mixture of soybean oil and HOSO containing 2% 18:3 had significantly lower hexanal and propanal values than did hydrogenated soybean oil at 6, 8 and 10 d of oxidation. Therefore, based on volatile analyses, both mixtures of soybean oil and HOSO containing 2.0 and 4.5% 18:3 were equivalent or better in oxidative stability than the hydrogenated soybean oil.

The present work showed that different trends in oxidative stability were evident between the hydrogenated soybean oil and a mixture of soybean oil and HOSO of the same 18:3 content, depending on whether oxidation is based on PV (Fig. 4a) or on headspace volatiles (Fig. 5). This illustrates how varied results can be obtained by different methods measuring different products of oxidation. For this reason, the use of more than one testing method is recommended in the evaluation of oxidative stability of food lipids (8). Thus, it is important to distinguish between hydroperoxide formation and its decomposition. Assuming that hexanal and propanal determinations, which measure the decomposition of hydroperoxides, are more closely related to flavor deterioration than PV measurements of hydroperoxide formation, the results based on volatile analyses (Fig. 5) may be more relevant to flavor stability than the results based on PV (Fig. 4a). The relationship of volatile vs. PV determinations to flavor, of course, needs to be substantiated by sensory testing.

The hydrogenated canola oil gave a significantly lower hexanal value than did unhydrogenated canola oil at 10 d, and lower propanal values at 8 and 10 d (Fig. 6). Both mixtures of canola oil and HOSO, containing 1 or 2% 18:3, had significantly lower hexanal and propanal values than did the hydrogenated canola oil at 8 and 10 d of oxidation. Therefore, we can conclude that the mixtures of canola oil and HOSO containing 1 or 2% 18:3 were equivalent or better in oxidative stability than was the hydrogenated canola oil.

This study showed that mixing different proportions of HOSO with soybean, canola and corn oils provides a simple method to prepare more stable edible oils, with a

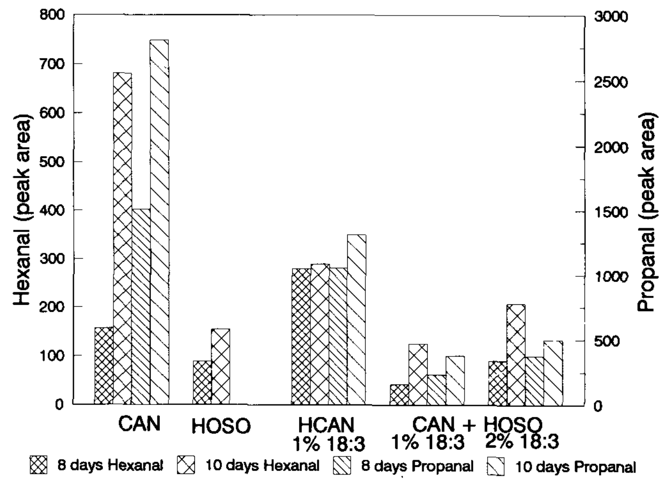

FIG. 6. Oxidative stability of CAN, HOSO, hydrogenated canola oil (HCAN) and mixtures of CAN and HOSO, based on headspace gas-chromatographic analysis of hexanal and propanal. See Figures 2 and 3 for other abbreviations.

wide range of desired fatty acid composition. A number of vegetable oil blends are now available on the market. Hydrogenation is becoming less attractive because *trans* isomers are nutritionally questionable (1–3). Also, hydrogenated oils are known to produce "hydrogenation" odors and flavors during frying that are considered objectionable (14,15). Oxidatively stable all-*cis* oils can be prepared by blending HOSO with polyunsaturaed oils as an alternative technology to hydrogenation. These blends need to be further evaluated by sensory techniques for flavor stability and for frying performance. Genetically modified vegetable oils may also provide improved fatty acid compositions and oxidative stability (16), but they are not yet commercially available. Therefore, the technology of blending HOSO with polyunsaturated oils may have growth potential if availability of HOSO improves with demand.

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