High-Oleic Safflower Oil. Stability and Chemical Modification

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Abstract

High-oleic acid safflower oil has been shown to have high-temperature oxidative stability comparable with that of hydrogenated vegetable oils. This stability, added to the ease of handling at low temperatures, should make the oil attractive as a commercial cooking oil. Epoxidation of the new safflower oil led to a product similar to epoxidized olive oil but lighter in color.

Introduction

SAFFLOWER OIL, like other vegetable oils, has instability problems which limit its use in cooking. Because of its high unsaturation (linoleic acid content greater than 75%, IV ca. 144), it is subject to oxidative and thermal deterioration. Precautions during packaging and addition of antioxidants and sequestering agents have successfully extended the shelf life of safflower oil (1) but have not given adequate protection to the oil at high temperatures. Partial hydrogenation of vegetable oils followed by winterization produces cooking oils of adequate stability, but further improvements in these techniques have been termed "both possible and desirable" (2). Such treatment may also add substantially to the cost of the oil.

Recent reference has been made (3) to the good qualities of a new variety of safflower in which the oleic acid content of the oil is 75% while the linoleic acid is <15%. The new variety (UC-1) developed by Knowles (4) is similar in appearance and oil content to the commercial US-10 variety. However, because of its lower unsaturation, it should be more stable toward oxidation (5) than an oil high in linoleate.

In addition to its use as a cooking oil, there are potential industrial applications for an oil of high oleic acid content. It can serve as a source of oleic acid or be used directly where an oil of intermediate unsaturation (ca. 88) is desirable. Epoxidation of the oil would be expected to give a reproducible stable product. In this paper we compare the stability of this safflower oil with that of other vegetable oils under severe conditions of temperature and exposure to oxidation. Some results from epoxidation reactions with this new oil are also reported.

Methods

High oleic safflower seeds (UC-1) (4) were obtained from P. F. Knowles. The seeds were crushed and extracted three times with hot Skellysolve "B." Extracts were combined and separated from a small aqueous phase and dried over anhydrous magnesium sulfate. The extract was filtered and the solvent removed at 60–70C under reduced pressure. The clear, yellow product, containing no solids at 0C, amounted to 32.5% of the total weight of the seeds. A portion of the oil was refined and deodorized. It was treated with a 2% vol of a caustic solution prepared by dissolving 17 g of sodium hydroxide pellets in enough water to make 100 ml of solution. After being shaken vigorously with the caustic solution at room temperature for 2 min, the oil was centrifuged in a laboratory centrifuge for 10 min and decanted from the insoluble material. Gums removed by this treatment were approximately 2% of the total weight of the oil. After a water wash (5% vol) the sample was again centrifuged and decanted, then bleached with 1% wt special Filtrol bleaching clay at 110–115C for 15 min. After filtration the oil was deodorized by steam stripping for 2 hr at 203C and 20 mm of mercury, with 35% wt of steam. The product was a light oil with bland taste and essentially no odor.

TABLE I

Oxidative Polymer Formation and Viscosity Changes in Cooking Oils[a]

Oil	Viscosity at 25C (stokes)		% Polymer formed	% Solid polymer
	Before oxidation	After oxidation		
UC-1 (crude)	0.65	2.00	29.1	0.20
UC-1 (refined, deodorized)	0.65	2.50	26.8	0.20
Commercial safflower	0.65	4.70	48.1	0.25
Commercial safflower (deodorized, not stabilized)	0.50	4.00	51.0	0.25
Commercial soybean	0.65	4.00	37.0	1.1
Commercial cottonseed	0.65	3.20	37.8	0.8
Commercial hydrogenated frying oil	0.85[b]	2.75	34.1	0.4

[a] Conditions: 185C, air at 200 ml/min for 18 hr.
[b] Oil was supercooled at 25C.

All the other oils were obtained locally at retail, with the exception of the unstabilized high-linoleic safflower oil. All the samples had initial peroxide values of 1–2 meq/kg (6) and were used without further treatment.

Eighty-gram samples of the oils were oxidized in a 250-ml flask equipped with thermometer, capillary bubble tube, and condenser connected to a cold trap cooled with dry ice-acetone (3). The flask was heated in a controlled-temperature oil bath to 185C ± 1C while air was bubbled in a 200 ml/min ± 10 ml/min. After 18 hr under these conditions the samples were cooled and stored under nitrogen at −25C until they were analyzed. At this time all the oils had a strong rancid odor. During early experiments aliquot portions for determination of peroxide values were removed. However these values were consistently low (ca. 1) throughout the oxidation because of rapid thermal decomposition of the peroxides as they formed. Peroxide values were not determined in later runs.

Viscosities of the oils, both before and after oxidation, were measured at 25C by using a Gardner Bubble Viscometer. Any solid polymer formed during the reaction was weighed in the reaction flask after it was washed repeatedly with Skellysolve "F." Soluble polymer was determined by converting the

TABLE II

Unoxidized Oils—Major Fatty Acid Content, %[a]

Oils	Fatty acids				
	16:0	18:0	18:1	18:2	18:3
UC-1 (crude)	5.4	1.7	80.7	12.2	....
UC-1 (refined, deodorized)	5.4	1.7	80.7	12.2	....
Commercial safflower	7.1	2.2	12.8	77.9	....
Commercial safflower (deodorized, not stabilized)	6.9	2.7	13.6	76.8	....
Commercial soybean	11.3	3.6	25.0	53.4	6.7
Commercial cottonseed	23.7	3.0	19.4	53.9	....
Commercial hydrogenated frying oil	24.8	3.8	50.8	20.6	....

[a] Determined by GLC analysis of methyl esters.

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TABLE III

Oxidized Oils—Major Fatty Acid Content, %[a,b]

Oils	Fatty acids					Reactivity ratio (linoleic/oleic)[c]
	16:0	18:0	18:1	18:2	18:3	
UC-1 (crude)	6.8	2.1	86.7	4.4	....	5.0
UC-1 (refined, deodorized)	7.0	3.5	83.3	6.2	....	2.2
Commercial safflower	10.6	3.9	16.6	68.9	....	2.6
Commercial safflower (deodorized, not stabilized)	15.4	4.5	22.1	58.0	....	3.0
Commercial soybean	16.1	5.5	28.8	45.7	3.9	2.0[d]
Commercial cottonseed	31.1	3.2	22.3	43.4	....	3.6
Commercial hydrogenated frying oil	38.6	5.1	52.8	3.5	....	2.8

[a] Trace fatty acids and dimer acids were neglected.
[b] Determined by GLC analysis of methyl esters.
[c] Reactivity ratios calculated on the assumption that no saturated fatty acids were converted to polymer.
[d] Reactivity ratio, linolenic:oleic, 2.9.

oxidized oils to their methyl esters by sodium methoxide catalyzed transesterification. A weighed amount of the methyl esters was distilled up to 185C at 0.5 mm of mercury. Residue in the distillation flask was reported as polymer. Values indicated in Table I are for soluble plus insoluble polymer.

Fatty acid composition of the fresh and oxidized oils was determined by converting the triglycerides to methyl esters as described above, followed by quantitative gas-liquid chromatography (GLC) at 195C on a 10-ft, ¼-in. column packed with diethylene glycol succinate on Chromosorb W. Response factors for the various esters were obtained at this laboratory. Results are shown in Tables II and III. Only palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), and linolenic (18:3) acids are reported although trace amounts of other acids are present in the fresh oils and polymerized acids are found in the oxidized samples. Some crude reactivity ratios (Table III) were calculated by assuming that saturated acids were not oxidized. These acids were then used as internal standards to determine the amount of unsaturated acids reacted. The amount of a given acid converted was related to its original concentration to obtain its relative reactivity.

Epoxidations of high-oleic safflower oil and of olive oil were done by treating the oils with 1.7 times the theoretical amount of hydrogen peroxide in acetic acid, in the presence of Dowex-50, a cation exchange resin (7). Oxirane values were determined by titration with hydrochloric acid (8), and iodine values were obtained by a modified Wijs method (9).

Results and Discussion

Polymerization is the most easily observed of the high-temperature reactions of cooking oils. It may occur as thermal polymerization at temperatures above 300C (10) or as oxidative polymerization at frying temperatures (185–200C) (11). Oxidative polymerization at the oil-air interface may actually cause lacquers and varnishes to form, but these are a minor part of the total polymer. The quantity of varnish appeared to be greatly influenced by the degree of agitation and the location of the capillary bubble tube. Increase in the viscosity of the oil and measurement of the total polymerized fatty acids proved to be more reproducible under the conditions employed.

The high-oleic safflower oil formed less polymer and showed less viscosity increase under conditions of the very severe test than any of the other nonhydrogenated vegetable oils. It was comparable in stability with the hydrogenated oil and had a viscosity of 2.25 stokes at 0C. The hydrogenated oil was semisolid at room temperature. Refined, deodorized UC-1 oil was about as stable as the crude sample although the latter still contained natural phosphatide material. Bolland (12) has indicated a reactivity ratio of ca. 12:1 for pure linoleate to pure oleate. However Gunstone and Hilditch (5) show that a small amount of linoleate mixed with oleate esters catalyzes oxidation of the oleates. Hence the varying reactivity ratios less than 12:1 are not surprising. The overall stability of both refined and unrefined UC-1 oil was greatest because of its high oleic acid content. It has also been shown by Bratcher and Kemmerer (13) that the induction period at 50C for UC-1 is approximately four times that of similarly treated commercial safflower oils. This finding indicates that the shelf life of UC-1 should be correspondingly long.

Some comment should be made regarding the test methods. Our oxidation procedure is a very severe one and is carried out without addition of food, moisture, or make-up oil. At an early stage of the experiments moist cotton balls were added to the oil, following the method of Krishnamurthy et al. (14), but this procedure had essentially no influence on polymer formation in the system. Ramel et al. (15) and Perkins and Van Akkeren (16) have also noted that foods actually may have a protective effect on oils used in frying. Thus, while our method does not reproduce actual frying conditions, it does demonstrate effectively the relative oxidative stabilities of the various oils at a temperature in the frying range.

TABLE IV

Epoxidation of Olive Oil and High-Oleic Safflower Oil

Starting material	Hydrogen[a] peroxide conc (%)	Catalyst[b] (%)	Time (hrs)	Temp. (C)	Conversion[c] to oxirane (%)	I.V.	Gardner color
Olive oil	30	2	7	77	76	4.6	3
Olive oil	50	2	7	76	79	2.4	1
High-oleic safflower oil	30	20	2.5	100	45	36.6	3
High-oleic safflower oil	30	20	6	67	54	30.3	2
High-oleic safflower oil	30	2	7	79	87	2.9	0
High-oleic safflower oil	30	20	7	82	81	1.6	2
High-oleic safflower oil	50	2	7	77	81	0.4	0

[a] Molar ratio of peroxide:double bonds = 1.7.
[b] In all cases the catalyst was Dowex-50 ion exchange resin.
[c] Percentage of original double bonds converted to epoxide.

Epoxidation of olive oil and high-oleic safflower oil led in each case to light-colored semisolid products. Conversions were generally higher with unrefined UC-1, and there was less color in the epoxidized safflower oil, especially at low catalyst concentrations. Greenspan and Gall (17) also noted that high-linoleic safflower oil yielded an epoxide of good stability and color. The epoxidized UC-1 oil should find market potential as a plasticizer and stabilizer.

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REFERENCES

1. Blum, J. E., JAOCS *43*, 416–417 (1966).
2. Cowan, J. C., Food Technol. *19*, 1413–1416 (1965).
3. Fuller, G., G. O. Kohler and T. H. Applewhite, JAOCS *43*, 477–478 (1966).
4. Knowles, P. F., A. B. Hill and J. E. Ruckman, Calif. Agr. *19*(12): 15 (1965).
5. Gunstone, F. D., and T. P. Hilditch, J. Chem. Soc. 1022–1025 (1946).
6. American Oil Chemists' Society Official and Tentative Methods, Revised 1964, No. Cd 8–53.
7. E. I. Du Pont de Nemours, Bulletin P. 61–454, "Hydrogen Peroxide-Resin Techniques for Epoxidation of Unsaturated Fats, Oils, and Derivatives."
8. J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss, "Organic Analyses," Vol. 1, Interscience, New York, 1953, p. 127–154.
9. Guenther, E., "The Essential Oils," Vol. 1, Van Nostrand, 1948, p. 305–306.
10. Sonntag, N. O. V., in Markley K. S., "Fatty Acids," Ed. 2, Part 2, Interscience, New York, 1961, p. 985–1060.
11. Rock, S. F., and H. Roth, JAOCS *41*, 228–230 (1964).
12. Bolland, J. L., Trans. Faraday Soc. *44*, 669–677 (1948).
13. Bratcher, S., and A. R. Kemmerer, private communication.
14. Krishnamurthy, R. G., T. Kawada and S. S. Chang, JAOCS *42*, 878–882 (1965).
15. Ramel, P., A. M. LeClerc, J. Dumain and D. Faucquembergue, Rev. Franc. Corps Gras *12*, 153–165 (1965).
16. Perkins, E. G., and L. A. Van Akkeren, JAOCS *42*, 782–786 (1965).
17. Greenspan, F. P., and R. J. Gall, Ibid. *33*, 391–394 (1956).

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