Flavor and Oxidative Stability of Some Linolenate-Containing Oils[1]

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Abstract

Because crambe, mustard seed, and rapeseed oils, like soybean oil, contain linolenate ester, they have been examined and compared with soybean oil for flavor stability after accelerated storage and after exposure to fluorescent light. Tests showed that the Cruciferae oils did have similar flavor characteristics and that the addition of citric acid did improve their stability. When exposed to light, the citric acid-treated Cruciferae oils differed from soybean oil; they developed a rubbery flavor, whereas soybean oil developed a grassy flavor. Oxidative stability determined by the active oxygen method confirmed results of oven storage tests. This work supports the belief that if linolenic acid is present in an edible oil, it is a precursor to typical off-flavor development.

Introduction

MANY RESEARCH WORKERS believe that off-flavors in soybean oil are caused by the linolenate ester present in the oil (2,4,12,15). Because linolenate content of Cruciferae oils is similar to that of soybean oil, a study was designed to determine whether flavor and oxidative stabilities of the oils were also similar. If so, any similarities observed would support the theory that the off-flavor development in soybean oil is caused by linolenate.

Armstrong and McFarlane (1) and Dutton, Lancaster, Evans, and Cowan (11) have pointed out that sunflower, cottonseed, corn, peanut, and olive oils, which are relatively free of linolenate, develop rancid flavors on storage rather than the off-flavors of linolenate-containing oils. Holm (19) stated that small amounts of oxygen produced volatile aldehydes in linolenate-containing oils and that these could not be wholly prevented as long as linolenate was present. Attempts have been made to eliminate or reduce the amount of linolenate in oils by various methods such as polymerization, hydrogenation, selective extraction, and selective hydrogenation. Durkee (10) in 1936 suggested that selective hydrogenation might be the answer by reducing linolenate to linoleate. Lemon (26) found that in hydrogenating linseed oil, linolenate was converted to isomers of linoleate, which he felt were responsible for the off-flavor developed in heated oils.

In 1951, Dutton et al. (11) of the Northern Laboratory increased the evidence for the linolenate theory, first, by a qualitative study of the storage flavors of soybean oil in which the linolenate content had been significantly lowered by furfural extraction and, secondly, by flavor identification studies of aged soybean oil, aged cottonseed oil, and aged cottonseed oil interesterified with linolenate. The first study showed that in the raffinate fraction, rancid flavor responses predominated, whereas in the extract fraction, the flavors asssociated with off-flavor development in soybean oil predominated. In the second study of aged oils, cottonseed oil interesterified with linolenate developed off-flavors similar to those of soybean oil rather than those of cottonseed oil.

In another study at our laboratory when stabilities of two soybean oils containing 5 and 10% linolenate, respectively, were compared, the oil containing 5% linolenate was significantly more stable than the oil containing 10% (14). Also, studies on hydrogenated-winterized soybean oils showed that when the linolenate in soybean oil was decreased from 7 to about 2%, a significant increase in flavor and oxidative stabilities was achieved (13).

The Cruciferae oils compared with soybean oil were crambe, mustard seed, and rapeseed. Use of these oils in many countries other than the United States is neither new nor unusual. Crambe is being studied in this country as a potential new crop for industrial markets (45). However in some countries, the oil has been used as a food oil. Krzymenski, Moldenhawer, and Niewiadomski of Poland, reported that oil from *Crambe abyssinica* was suitable as a cooking oil and for use in margarine (24,33,37). Vasil'ev's investigations of crambe in Russia indicated the oil to be suitable for edible purposes (46).

Mustard seed oil has been utilized as a seasoning in Spain (47); as salad and cooking oil in India (16,22, 39), Russia (33), and China (16); and in Canada for shortenings, salad oils, mayonnaise, and pastries (29, 30). Mustard seed is grown in the United States only for use as a condiment with excess amounts being exported (45).

Rapeseed oil is more widely used and is produced in appreciable amounts in many countries (32,44). During World War II, when fat supplies were curtailed, Germany and France used rapeseed oil in margarine, and it became an important source of edible fat in the diet (3,7,8,17,25,38,41). Japan produces some rapeseed oil for frying and cooking as well as for shortenings and margarine (5,18,23,36). However, the domestic supply is usually supplemented by imported rapeseed and soybeans (32). Rapeseed is also imported by Italy when the amount of native olive oil is short (32). Properly and carefully processed rapeseed oil has good keeping qualities and is suitable for edible use according to Polish and Russian scientists (6,21,40,42). Swedish research workers, Holm, Ekbom, and Wode (20) found that rapeseed oil with an initial aldehyde content of 0.5, stored in completely filled drums for 4 years at room temperature, was equal to freshly refined rapeseed oil with an aldehyde content of 2, the value to which the stored oil had increased. Such stability would be favorable to its use. Since the introduction of rapeseed to Canada in 1941, research there has been concerned not only with the development of new varieties, but with the use of the oil for edible purposes. Canadian scientists found rapeseed oil to be reasonably satisfactory for such food products as salad oils, margarine, and shortenings (12,28, 31). Both Sallans (43) and Downey and Craig (9)

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TABLE I

Flavor Evaluation: Initial

Oil	Without citric acid		With citric acid (0.01%)	
	Score	Description	Score	Description
Crambe seed	8.3	Buttery, beany, grassy	8.8	Bland, buttery, beany
Mustard seed	8.3	Buttery, beany	8.0	Buttery, beany, grassy
Rapeseed	7.8	Buttery, nutty	8.4	Buttery, nutty
Soybean	8.3	Buttery, beany, grassy	8.5	Buttery, beany

indicated that while approximately 90% of Canadian rapeseed oil was exported, there was an increasing demand for it as an edible product.

Although these Cruciferae oils have not been used in this country, Linteris and Thompson (27) did find that mustard seed and rapeseed stearins dispersed in cottonseed oils produced a liquid shortening with the aerating action necessary to produce a satisfactory cake. This area may be where the Cruciferae oils will find their greatest edible use in the United States.

Materials and Methods

Some of the oils in this test were prepared at the Northern Laboratory; some were received from Canada and Sweden as refined and bleached oils.

Flavor stability was evaluated following the procedure established earlier at the Northern Laboratory (34,35). After accelerated storage at 60C or after exposure to light for 2 hr, samples were evaluated along with control samples by a panel of 20 trained judges. Oils were warmed to 55C immediately before tasting and if color differences were apparent, they were minimized by the use of red lights in the taste panel room. A 10-point scoring system was used for judging quality and intensity of flavor. Analysis of variance and the F-test were used to test the sample means for differences.

Immediately after aging or exposure to light, peroxide values were determined by the Wheeler method (48). Stability was also measured by determination of peroxide values after holding the oils for 8 hr under AOM (active oxygen method) conditions.

Discussion and Results

Although soybean oil at present accounts for about 40% of the total food fats and oils used in the United States, the problem of stability and off-flavor development remains. If linolenate is the precursor to such off-flavor development, then it would seem logical that other oils containing comparable amounts of linolenate should behave in a like manner. The crambe, mustard seed, rapeseed, and soybean oils used in this study contained nearly equal amounts of linolenate: 7, 8, 9 and 8%, respectively. The Cruciferae oils were refined, bleached, and deodorized in the same manner as the soybean oil. Initially, all oils were of good quality. Flavor descriptions shown in the tables are listed in order of their predominance based on the number of responses as reported by the taste panel members. Flavors were similar, buttery flavors predominating, with the typical nutty or beany flavors present in smaller amounts. Citric acid improved quality of the oils except for mustard seed oil. The grassy responses in crambe and soybean oil were reduced or eliminated. Mustard seed oil showed no improvement in quality, and the grassy response became more dominant in the citric acid-treated oil (Table I).

After storage for 4 days at 60C, all oils had the off-flavors usually found in aged soybean oil. Crambe oil was definitely more painty than the soybean, mustard seed, or rapeseed oils. Soybean oil generally develops the painty flavor in the later stages of deterioration. In this test, the real value of citric acid was again demonstrated. The quality of all oils was significantly improved and off-flavor development was definitely retarded. All oils showed a shift in flavor descriptions. Crambe oil was rancid rather than painty; buttery, beany, and grassy replaced the rancid responses for soybean, mustard seed, and rapeseed oils (Table II).

TABLE II

Flavor Evaluation: 4 Days, 60C

Oil	Without citric acid		With citric acid (0.01%)	
	Score	Description	Score	Description
Crambe seed	4.1	Painty, rancid, grassy	7.3	Rancid, buttery, beany
Mustard seed	4.9	Beany, grassy, rancid	6.5	Beany, rancid
Rapeseed	4.9	Rancid, painty, grassy, beany	6.8	Buttery, grassy, beany, rancid
Soybean	5.6	Rancid, grassy, beany	7.0	Buttery, beany, grassy, rancid

TABLE III

Flavor Evaluation: 2-Hr Light Exposure

Oil	Without citric acid		With citric acid (0.01%)	
	Score	Description	Score	Description
Crambe seed	7.2	Buttery, beany	5.7	Rubbery, grassy, buttery
Mustard seed	4.6	Rancid, buttery, grassy	2.1	Rubbery, rancid, grassy
Rapeseed	6.9	Buttery, grassy	4.8	Rubbery, buttery
Soybean	6.1	Grassy, buttery, rancid	6.5	Grassy, buttery, rancid

TABLE IV

Flavor Evaluation of Swedish and Canadian Rapeseed Oils

Treatment	Swedish				Canadian	
	Continuous screw-pressed		Extracted		Extracted	
	W/O C.A.[a]	With C.A.	W/O C.A.	With C.A.	W/O C.A.	With C.A.
Initial flavor	7.8	8.4	8.0	8.1	7.7	7.4
4 Days, 60C	4.2	7.0	4.9	6.9	4.5	6.1
2-Hr. light exposure	6.8	4.8	5.8	2.9	4.0	5.4
AOM value[b]	20.0	9.0	15.1	4.6	22.4	21.4

[a] W/O = without; C.A. = citric acid (0.01%).
[b] Peroxide values after 8 hr under AOM conditions.

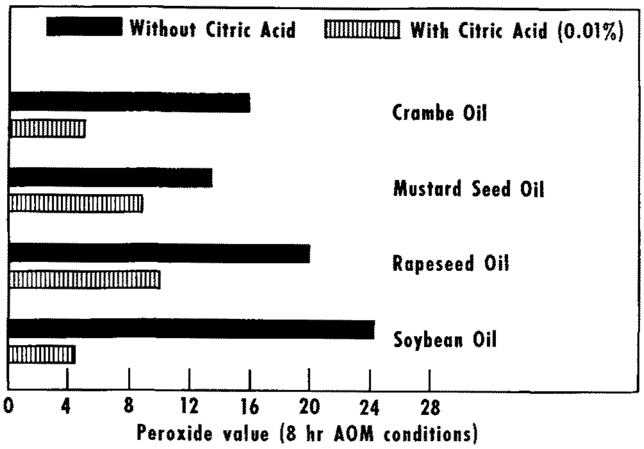

FIG. 1. Oxidative stability of oils as determined by the active oxygen method.

The deleterious effect of light on the flavor stability of edible oils is well known. After exposure for 1 hr to fluorescent light, the flavor score for soybean oil drops significantly, and a distinct type of grassy flavor develops that is easily recognized by taste panel members (35). The addition of citric acid to soybean oil did not protect the oil against light for there was no apparent change of flavors in the soybean oil tested. The Cruciferae oils on exposure to light responded differently. There was a significant drop in flavor score, and the development of a definite rubbery flavor was often accompanied by a garlic or onion-like flavor. This taste may be due to isothiocyanate compounds introduced into the oils from the meal during extraction and not completely removed by deodorization. Since these responses did not appear in the oven-storage tests, possibly off-flavor precursors are affected more by light than by heat (Table III).

Stability after 8 hr under AOM conditions confirmed the oven-storage tests. From the lower AOM values for citric acid-treated samples more stable oils could be predicted (Fig. 1). However, stability to light could not be estimated.

Refined and bleached samples of continuous screw-pressed and extracted rapeseed oils were received from Sweden and deodorized in the laboratory. Initially, there was no difference in the flavor quality of the oils. AOM values indicated increased stability for the citric acid-treated samples. This stability was confirmed by oven-storage tests. After 4 days at 60C, the citric acid-treated continuous screw-pressed and extracted oils were significantly better than the untreated samples. As before, when exposed to light, the citric acid-treated oils were significantly poorer in quality and were described as having a rubbery flavor. When the continuous screw-pressed oil was evaluated with the extracted oil, the former was more stable, except in the oven-storage test where no difference was shown between the stability of untreated oils (Table IV).

The same pattern of flavor results, exclusive of the light test, was obtained when a refined and bleached sample of rapeseed oil from Canada was deodorized in the laboratory and subjected to stability tests. Again, there was no difference in initial quality between citric acid-treated and untreated samples; the citric acid-treated sample was more stable after oven storage for 4 days at 60C than the untreated sample. The charactertistic rubbery flavor was present in both light-exposed samples and for the first time, a citric acid-treated sample, after 2 hr exposure to light, was given a higher flavor score than the untreated sample. These results are shown in Table IV.

The results of this study confirm the belief that when linolenic acid is present in oils, off-flavors will develop after storage or upon exposure to light. Crambe, mustard, and rapeseed oils contained linolenic acid in amounts similar to soybean oil and developed off-flavors like those of soybean oil with the exception of the citric acid-treated samples which, when exposed to light, developed an entirely different flavor. This difference in flavor projects a new problem for study.

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