Flavor Evaluation of Copper-Hydrogenated Soybean Oils[1]

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Abstract

The use of copper catalyst to reduce selectively the linolenate in soybean oil improves its flavor stability. As previously shown, the copper must be removed or properly inactivated to obtain an oil of high initial quality. In oven and heat tests, odor and flavor development in the hydrogenated soybean oil samples correlate surprisingly well with actual levels of linolenate, but there were some differences in overall responses among cottonseed oil, copper-reduced (0.0% linolenate) and nickel-reduced (3.0% linolenate) soybean oils. The taste panel generally scored the last three oils in the following order: cottonseed oil, copper-reduced and nickel-reduced soybean oil.

Introduction

The use of copper-chromite and copper-oxide-supported catalysts for hydrogenating soybean oil has been extensively investigated at the Northern Regional Research Laboratory and elsewhere (1–10). These studies have established that copper catalysts have a selectivity as high as 15 or more for linolenate, where selectivity is the ratio of the rate of hydrogenation of linolenate divided by the rate of hydrogenation of linoleate. Some of these reports indicate that flavor or oxidative stability was improved.

Okkerse et al. (5) showed that oils degummed, refined, bleached and dried, reduced with copper, and refined with phosphoric acid had good stability. These Dutch workers found that 14 of 20 tasters preferred soybean oil hydrogenated with copper catalyst to unhydrogenated oil initially and 19 of 19 after the oil was stored two weeks at 15 C in the dark. They also scored two samples of copper-reduced oil equal to a refined sunflower seed oil after one day in diffuse daylight, and one sample slightly higher and the other not quite so high as the refined sunflower oil after three days. Under similar aging conditions, other Dutch workers (4) scored a copper-reduced oil containing 0.7% linolenate slightly higher than one having 2.0%; both reduced soybean oils scored higher than a sunflower seed oil of 0.1% linolenate. Beal et al. (11) reported that copper-reduced oils, bleached or resin-treated to remove copper and deodorized with citric acid, had good initial quality. Scores of 7.7 and 7.8 initially dropped only to 6.0 to 6.5 on aging these oils for four and eight days at 60 C. Kuwata and coworkers (10) hydrogenated soybean oil with a copper-chromite catalyst to give different levels of linolenate and reported that such oils had good stability during long storage. Since Koritala (12) found a copper catalyst based on a copper-ammonium complex had high activity and selectivity for linolenate over linoleate, we studied the flavor stability of oils hydrogenated with this catalyst. Work with copper-chromite-reduced oils is also reported. Different levels of linolenate were evaluated for flavor score initially, after four and eight days at 60 C, after heating to 150, 170 and 200 C and with room odor tests. Similar comparisons of 0.0% linolenate oils were made with nickel hydrogenated-winterized soybean oil and cottonseed oil.

Methods and Materials

Degummed and alkali-refined soybean oils, cottonseed salad oil, and a nickel-reduced-winterized soybean oil were obtained from commercial suppliers. Degummed oils were alkali-refined and bleached; alkali-refined oils were bleached; bleached oils were deodorized in all-glass laboratory apparatus as previously described (13,14). When desired, the oils were redeodorized with antioxidants and antifoam agents added during the last stages of deodorization. Hydrogenations were carried out according to the procedures of Koritala and Dutton (6,7,12).

A typical hydrogenation with copper-oxide or copper-chromite catalyst was effected as follows: A laboratory refined and bleached soybean oil (3 liters) was heated for 2 hr at 175 C in the presence of a catalyst and an initial hydrogen pressure of 30 psi. The catalyst from copper-ammonium complex (12) contained 3.3 g as cupric oxide deposited on 50 g of silica gel. The oil was filtered, bleached with 1% activated clay (Superfiltrol) and deodorized as described previously (14).

Peroxide values were determined by a modification of the Wheeler method (15) and the active oxygen method (AOM) values were obtained by determining peroxides after 8 hr under AOM conditions (16).

Fatty ester analyses were performed by gas liquid chromatography (GLC), and linolenate was determined by alkali-isomerization (6). Compositions of the original and hydrogenated oils are given in Table I. The analyses of the cottonseed salad oil by GLC and alkali-isomerization were 0.6 myristate, 16.8 palmitate, 0.6 palmitoleate, 2.5 stearate, 22.0 oleate, 56.7 linoleate and 0.9% linolenate. Calculated IV was 119.8. Although the linolenate content suggests that this cottonseed oil might have been contaminated with a small amount of soybean oil, the palmitoleate, stearate and oleate contents suggest it was not. All flavor evaluations were made by our research taste panel. Various sample preparations and evaluating techniques were used. Some evaluations were conducted with samples aged at 60 C for four and eight days in bottles two thirds full (17). Others were carried out with samples heated rapidly to 150, 170 and 200 C, cooled to 55 C and evaluated in the same manner as the four- and eight-day samples. Finally, room odor tests were carried out by a procedure that will be more fully described later (Evans et al., unpublished). From 150 to 300 cc of oil samples were heated to 380 F (193 C) in an open deep-fat fryer in two new relatively odor-free laboratory rooms. Members of the taste panel were asked to enter the rooms and to score and describe the oil odors.

In these room odor tests, a flavor intensity value (FIV) was used to quantitize the flavor and odor of the oils. FIV equals the intensity-weighted summations of the flavor responses divided by the number of tasters: FIV = [(number of weak responses) + 2 (number of medium responses) + 3 (number of strong

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[1] One of 10 papers to be published from the Symposium "Hydrogenation," presented at the AOCS Meeting, New Orleans, April 1970.
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TABLE I

Composition of Soybean Oils (wt. %)

Component	Original oils		Copper reduced from A			Copper chromite reduced from B		Nickel-reduced-winterized	
	A	B						From B	Commercially
Palmitic	10.2	10.6	9.6	10.3	9.7	10.6	10.5	10.5	8.6
Stearic	4.6	4.6	4.2	4.7	4.1	4.9	5.0	5.2	3.9
Monoene	25.5	23.8	30.9	32.2	51.1	38.4	29.5	43.0	46.3
Diene	51.8	52.8	53.2	51.4	35.1	45.6	51.7	38.5	38.1
Triene	7.8	8.4	2.0	1.3	0.0	0.1	2.7	3.3	3.0
IV	131.4	133.4	123.4	119.6	104.7	113.3	122.5	111.0	113.7

responses]/n, where n is the number of tasters. Limits of the flavor intensity values will, of course, be from 0.0 to 3.0.

Results and Discussion

Early tests demonstrated that soybean oil hydrogenated to low linolenate content with copper-chromite as a catalyst was more stable than the original oil. In Table II note that the flavor scores for the copper-reduced oil were highly significantly above the control oil at four and eight days. Copper-chromite catalyst was used in preparation of the copper-reduced oils reported in Tables II-IV. Flavor responses shown are typical of soybean oils subjected to these conditions.

If the hydrogenations were stopped at about 3.0% linolenate—a value comparable to that obtained commercially for nickel hydrogenated-winterized soybean oil—winterization of the copper-reduced oil was unnecessary, but no superiority in flavor stability was achieved. Note in Table III that the copper-reduced oil with 2.7% linolenate has flavor scores, AOM values and flavor responses comparable to the nickel-reduced and winterized oil prepared by engineers at the Northern Laboratory. When copper-reduced oil with 0.1% linolenate was compared organoleptically with the nickel-reduced oil with 3.3% linolenate, flavor scores indicated that we did achieve superior stability in the copper oil but failed to achieve equal initial quality. Table IV shows that the copper-reduced oil of 0.1% linolenate content was just as stable in the 8 hr AOM test as the nickel oil and that copper-reduced oil scored higher after aging for four days at 60 C.

Comparison of Soybean Oils Low in Linolenate

Evaluations were made of hydrogenated oils prepared with Koritala's recently announced copper catalyst (12). It combines high selectivity with high reactivity and stability. Practical tests were designed with the knowledge that removal of trace amounts of catalysts before deodorization was desirable (5,11) and that reuse of catalyst was required. Oil samples were prepared with catalysts previously used once (second use) and twice (third use) and the resulting oils had 1.3 and 2.0 linolenate, respectively. The catalysts were still active and useful after four hydrogenations.

TABLE II

Comparison of Copper-Chromite-Reduced Soybean Oil With Unhydrogenated Control

Storage 60 C, days	Flavor scores and significance[a]		
	Control, Ln 8.4%	Sig.	Copper reduced, Ln 0.1%
0	7.5(0.0)	+	7.5(0.0)
4	4.7(3.0)	**	6.7(0.5)
8	4.2(11.0)	**	6.1(3.2)
AOM, 8 hr, PV	19.0		3.4
	Flavor responses		
0	Buttery		Buttery
4	Rancid, buttery, grassy		Buttery, beany
8	Painty, rancid, grassy		Buttery, rancid

[a] The (+) indicates no statistical significance at the 5% level; (*) denotes significance at the 5% level; (**) shows significance at the 1% level; Ln represents linolenate; values in parentheses are peroxide values, milliequivalents per kilo.

Bleaching the oil before hydrogenation prolongs the activity of the copper catalysts (8). We confirmed that bleaching the oil after hydrogenation improves initial flavor and flavor stability and also lowers copper content (11). If copper is not removed by bleaching or is not inactivated before or during early stages of deodorization, the initial flavor quality of the oil is lowered; results are given in Table V. Data show that this oil has excellent oxidative stability because treatment with citric acid apparently inactivates the copper without removing it, but initial flavor suffers.

Examination of data in Table VI indicates that all these oils had excellent initial flavor, as well as oxidative and flavor stability. It was necessary to subject them to prolonged exposure in accelerated storage at 60 C or to test them as cooking oils to create significant differences among them. No significant difference in flavor scores was found after four days at 60 C, but after eight days at 60 C the copper-reduced oils were significantly higher in flavor score even though the original oil had performed excellently. The copper-reduced oils were rated at flavor scores of about 6, which we generally believe to be acceptable.

One test that is frequently used to evaluate cooking oils is the heat test. The oil is heated to a given temperature, cooled to 55 C and evaluated by the taster or taste panel. In tests with oil heated to 170 C, all the copper-reduced oils were significantly higher in flavor score than the original oil sample. Tests with oils heated to 200 C showed that the copper sample with the 1.3% linolenate scored significantly higher than the copper samples with 2.0% linolenate and highly significantly above the original oil. Lowering linolenate value from 7.8% to 2.0% made a significant improvement and further reduction to 1.3% gave additional improvement.

In related tests, when soybean oils were hydrogenated with a commercial copper-chromite catalyst to linolenate contents of 0.4%, 1.4% and 5.5%, flavor scores and oxidative stabilities were inversely related to linolenate content. Initially, all oils scored 7.4 to 7.9, but after eight days at 60 C, the respective flavor

TABLE III

Comparison of Copper-Chromite-Reduced With Nickel-Reduced-Winterized Soybean Oil at Comparable Linolenate Contents

Storage 60 C, days	Flavor scores and significance[a]		
	Copper reduced,[b] Ln 2.7%	Sig.	Nickel reduced,[b] Ln 3.3%
0	8.0(0.0)	+	8.4(0.0)
4	5.7(0.9)	+	6.2(2.1)
AOM, 8 hr, PV	5.5		4.6
	Flavor responses		
0	Buttery		Buttery
4	Rancid		Rancid

[a] See footnote a, Table II.

[b] Copper-chromite and nickel-reduced oils. The nickel-reduced oil was winterized.

TABLE IV

Comparison of Copper-Chromite-Reduced Oil of Low Linolenate Content With Nickel-Reduced-Winterized Soybean Oil

Storage 60 C, days	Flavor scores and significance[a]		
	Copper reduced,[b] Ln 0.1%	Sig.	Nickel reduced,[b] Ln 3.3%
0	7.5(0.0)	*	8.4(0.0)
4	7.1(0.5)	*	5.6(2.2)
AOM, 8 hr, PV	3.4		4.6
	Flavor responses		
0	Buttery, beany		Buttery, beany
4	Buttery, rancid		Grassy

[a] See footnote a, Table II.
[b] See footnote b, Table III.

Table VI

Comparison of Copper-Reduced Oils With Low Linolenate Contents

Condition	Original plus citric acid		Copper-reduced oils		
			Third use of catalyst		Second use of catalyst
	Flavor scores and significance[a]				
Initial	8.1(0.0)	+	8.3(0.0)	+	8.4(0.0)
Aged 60 C, eight days	5.0(1.0)	*	6.6(0.6)	+	6.6
			(*)		
Heat test, 170 C	3.6(2.7)	*	4.7(2.7)	+	4.4(3.0)
			(*)		
Heat test, 200 C	2.3(2.9)	+	2.6(3.8)	*	3.4(2.4)
			(**)		
Linolenate content	7.8		2.0		1.3
AOM, 8 hr, PV	10.2		4.0		4.2

[a] See footnote a, Table II; copper catalyst from copper ammonium complex (12).

scores were 6.1, 5.7 and 4.2. Peroxide values after 8 hr under AOM conditions were 7.0, 8.0 and 15 and were positively related to their linolenate contents of 0.4%, 1.4% and 5.5%, respectively. Data compiled from some 38 different samples, however, showed little correlation between the peroxide values in the AOM tests and iodine values or linolenate content. Apparently other factors had more effect on the level of peroxide achieved in the AOM test than did linolenate content or iodine value. This work with oils reduced by copper-chromite, as well as the work with the copper catalyst from the ammonium complex, suggested that additional tests with oil containing a minimum of linolenate were desirable.

The same general flavor evaluations were obtained for oil in which the linolenate was substantially eliminated (Table VII). The initial qualities of this oil and the original unhydrogenated oil were excellent; flavor scores of both approached 8. Treatments more severe than four days at 60 C were again necessary to achieve differences. If peroxide value is a criterion, the oxidative stability of these oils was approximately the same. Thus the peroxide values of the copper-reduced and unhydrogenated oil were equal, but the flavor score of the copper-reduced oil was highly significantly above the unhydrogenated oil after eight days at 60 C. Consequently, the flavors of the copper-reduced oil must be different. A similar observation holds for oils from the heat test at 200 C. Accordingly, consideration of flavor responses was definitely indicated.

The flavor responses for unaged oils were generally reported as buttery with FIVs ranging from 0.8 to 1, nutty, from 0.2 to 0.4 and beany 0.0 to 0.2, respectively. The results of several tests on unhydrogenated soybean oil and copper-reduced oils containing 0.0%, 1.3% and 2.0% linolenate are included in the following compilation. In both the copper-reduced and the unhydrogenated oils after four days at 60 C, buttery responses had not dropped much with FIVs ranging from 0.3 to 0.9, but rancid values had increased up to 0.7 and beany values up to 0.5. Grassy FIVs increased up to 0.4 and appeared at the higher levels in unhydrogenated oils. After eight days at 60 C, the buttery responses were about equal in all samples at 0.5 FIV. Rancid values were high for the unhydrogenated oil at 1 to 1.9 but were substantially lower for the all-copper-reduced oils at 0.5 to 0.6. Painty and grassy responses were also higher at 0.4 to 0.6 for unhydrogenated oil in comparison to 0.1 to 0.4 values for most of the copper-reduced oils with none in the 0.0% linolenate sample.

The flavor responses of oils heated to 150, 170 and 200 C and cooled to 55 C before tasting showed definite patterns. The copper-reduced oils at 150 C had buttery FIVs of 0.8 and 0.9 and rancid 0.1 to 0.5; unhydrogenated oils had lower buttery responses ranging from 0.3 to 0.5 with high rancid responses from 0.5 to 0.8. As the temperature increased to 170, grassy responses increased in unhydrogenated oils ranging from 0.6 to 1.0, whereas in the copper-reduced oils (0.0% linolenate) they were 0.0 to 0.5. Rancid responses were relatively high for all samples with FIVs ranging from 0.7 to 1.0. The big difference in responses was found in painty where FIVs for unhydrogenated oil ranged from 0.8 to 1.1 and for the copper-reduced oils from 0.2 to 0.3. The unhydrogenated oils also had higher values for fishy and grassy responses.

Heat tests at 200 C gave rather convincing evidence that differences appear to be associated with linolenate content. Figure 1 shows unhydrogenated oils with high painty responses of 1.5 to 1.6 with a reduction in FIVs that follows linolenate content. Fishy responses were also high for the unhydrogenated oils at FIVs 0.5 to 0.8; this flavor was negligible with copper-reduced oils. Rancid responses were remarkably close together at 1.2 to 1.4 for all oils.

Another dramatic difference in flavor responses came in our room odor tests on soybean oils containing

TABLE V

Effect of Bleaching on Copper-Reduced Oils

Condition	No bleach plus citric acid		Bleach plus citric acid
	Flavor scores and significance[a]		
Initial	6.9(0.0)	**	8.4(0.0)
Aged eight days at 60 C	6.1(6.3)	+	5.9(8.6)
Heat to 200 C	2.7(2.1)	*	3.4(2.4)
Copper (ppm) after hydrogenation[b]			
Before bleaching	0.22		0.22
After bleaching			0.01
After deodorization	0.15		0.01

[a] See footnote a, Table II.
[b] Copper catalyst from copper ammonium complex (12).

TABLE VII

Comparison of Copper-Reduced Oil Having 0.0% Linolenate With Unhydrogenated Oil-Flavor Scores and Significance

Condition	Copper-reduced oil	Sig.[a]	Original oil
Initial	7.7(0.0)	+	7.8(0.0)
60 C, four days	6.5(0.8)	+	6.2(0.7)
60 C, eight days	5.7(6.2)	**	4.2(6.2)
Heat test, 150 C	5.3(0.7)	*	4.2(0.9)
Heat test, 170 C	4.2(2.1)	+	3.7(2.3)
Heat test, 200 C	3.8(3.6)	**	2.2(2.8)
AOM, 8 hr, PV	5.0		5.8
Triene, %	0.0		7.8

[a] See footnote a, Table II.

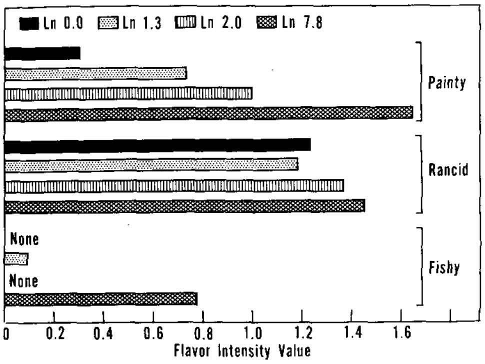

FIG. 1. Flavor responses as measured by flavor intensity values of soybean oils containing from 0.0% to 7.8% linolenate (Ln). Oils were heated to 200 C and then cooled to 55 C before tasting.

0.0% linolenate. Figure 2 presents the results of these tests in FIVs for hot-oil, rancid and fishy responses. Hot oil is a response apparently associated with heated oil and popcorn fryers. The copper-reduced oil with 0.0% linolenate content was high in hot-oil responses and low in rancid and fishy. The unhydrogenated soybean oil was the reciprocal-high rancid and fishy responses and low hot-oil responses.

In another room odor test, a commercial nickel-reduced-winterized soybean oil containing antioxidants gave FIVs of 0.8 for hot oil, 0.4 for fishy and 0.3 for rancid. Copper-reduced soybean oil and unhydrogenated soybean oil without added antioxidants or silicone gave respective responses of hot oil, 0.8 and 0.3; rancid, 0.4 and >0.2; and fishy, 0.2 and 1.2.

Cottonseed Oil vs. Copper-reduced and Nickel-reduced Soybean Oils

After establishing that copper-reduced oils gave higher flavor scores and responses different from those of unhydrogenated soybean oil, a direct comparison with cottonseed salad oil and nickel-reduced-winterized soybean oil was undertaken. Cottonseed oil containing 0.1% of Tenox 6 and 5 ppm of methyl silicone, copper-reduced soybean oil (0.0% linolenate) with the same additives, and a sample of a commercial nickel-reduced-winterized soybean oil containing similar additives were chosen. We believe the samples were representative of better quality if not the best quality of each type of oil. Room odor and heat tests were run (Table VIII, Fig. 3 and 4).

These three oils showed comparatively good initial flavor and flavor stability. Buttery and bland responses were characteristic with FIVs of 0.9 to 1.0 and of 0.3 to 0.4, respectively. Heating to 150 C and then smelling and tasting the cooled oil resulted in no significant difference in scores and no major differences in odor and flavor responses. Buttery was still a major response and rancid contends for the highest FIVs. At 170 C, cottonseed oil was given a higher flavor score than either of the others and highly significantly above copper-reduced oil. Rancid responses were high for the cottonseed and copper-reduced oils at FIVs of 0.9 and 1.2, but painty responses appeared in the copper-reduced and nickel-reduced oils having FIVs of 0.4 and 0.3, respectively. Although heating to 170 C appeared to have a greater oxidative as well as flavor effect on the copper-reduced oil than on the nickel-reduced oil (see peroxide values), further heating to 200 C had a much greater effect on the nickel-reduced than on the copper-reduced or cottonseed oils.

In the heat test at 200 C, scores for cottonseed oil were significantly above the other two oils when tasted

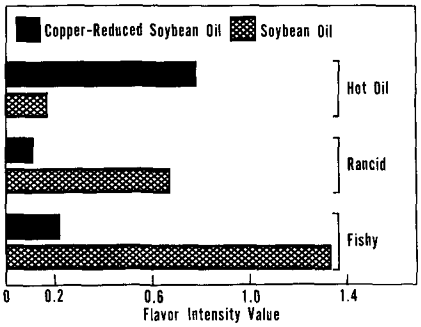

FIG. 2. Odor responses as measured by flavor intensity values of soybean oils containing 0.0% and 7.8% linolenate. Oils heated to 193 C in a fry pan and room odors described.

TABLE VIII

Comparison of Cottonseed Oil With Copper-Reduced and Nickel-Hydrogenated-Winterized Soybean Oils: Heat and Room Odor Tests—Scores and Significance[a]

Condition	Cottonseed		Copper reduced		Nickel reduced
Initial					
Odor	8.0	+	7.5	+	7.8
			(+)		
Flavor	8.1	+	7.4	+	7.4
			(+)		
Heat test, 170 C					
Odor	6.1(1.7)	+	5.1(1.6)	+	5.5(0.6)
			(+)		
Flavor	5.3	**	4.0	+	4.6
			(+)		
Heat test, 200 C					
Odor	4.7(0.3)	+	3.9(0.4)		
	5.6(0.8)			*	4.4(1.0)
			5.1(0.8)	**	3.9(0.8)
Flavor	3.9	**	3.1		
	4.6			*	3.2
			3.9	**	2.8
Room odor	6.4	+	5.9		
	7.1			*	6.0
			6.1	+	5.7
AOM, 8 hr, PV	2.9		2.0		1.1

[a] See footnote a, Table II.

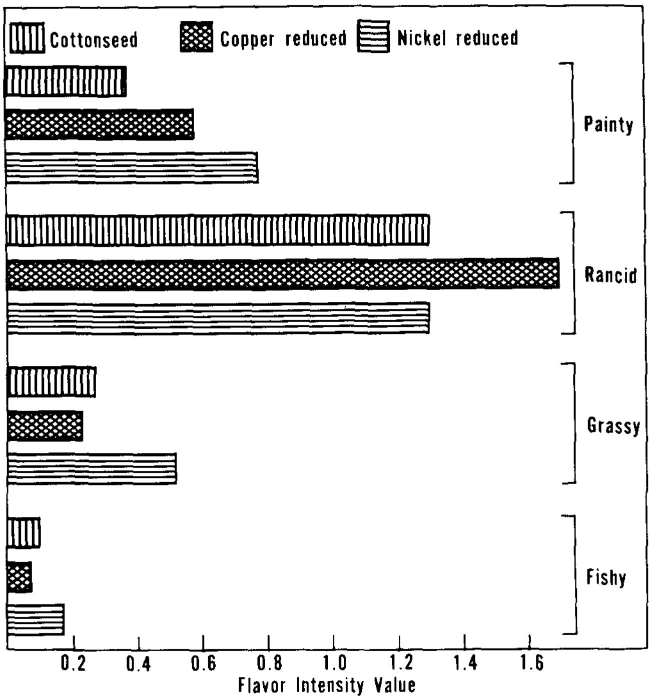

FIG. 3. Flavor responses as measured by flavor intensity values of cottonseed, copper-reduced soybean and nickel-reduced-winterized soybean salad oils. Oils heated to 200 C and cooled to 55 C for tasting.

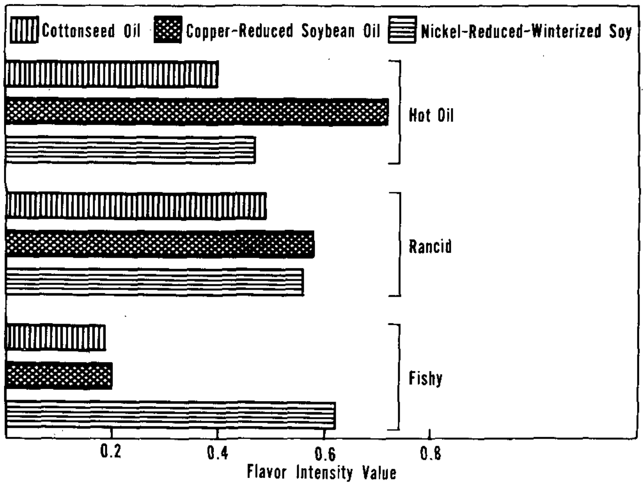

FIG. 4. Odor responses as measured by flavor intensity values of cottonseed, copper-reduced soybean and nickel-reduced-winterized soybean salad oils. Oils heated to 193 C in a fry pan and room odors noted.

but were not significantly higher than the copper-reduced oil when smelled. The copper-reduced oil and cottonseed oil were scored significantly or highly significantly above the nickel-reduced oil when either tasted or smelled.

In room odor tests, scores for cottonseed oil were significantly higher than the nickel-reduced oil but not significantly above the copper-reduced oil. The latter scored higher than the nickel-reduced oil but not significantly.

Figure 3 shows the important flavor responses given by panel members for the three oils subjected to the heat test at 200 C. The cottonseed oil was low in painty, fishy and grassy responses as measured by FIVs. Compared to cottonseed, copper-reduced oil was slightly higher in painty responses but slightly lower in both grassy and fishy. The nickel-reduced oil was the highest of the three in painty, grassy and fishy responses as measured by FIVs.

Figure 4 gives FIV results on room odor tests. These flavor values are the average of three different odor tests in which the three oils were tested one against the other, i.e., cottonseed vs. copper-reduced, cottonseed vs. nickel-reduced, and copper-reduced vs. nickel-reduced. In the copper-reduced oil, hot-oil and rancid responses overshadow the low fishy responses. Results were the same with cottonseed oil, but none of these responses were as high as with the copper-reduced oil. Although hot oil and rancid responses were high, fishy responses were slightly higher at FIVs of 0.6 for nickel-reduced oil.

In studies with flavor intensity values, we have generally considered that a value should be above 0.25 to have much significance or have at least one fourth of the panel report the response. The hot oil and rancid responses are above this level in all three oils. Only the nickel-reduced oil and unhydrogenated oil were above this value for fishy responses in the room odor tests.

Private reports from Europe indicate that some refiners believe that nickel-reduced-winterized soybean oil does give fishy odors in a room when the oil is heated to frying temperatures, Our results confirm their reports.

One can ask why copper-reduced oil of 0.0% linolenate is not scored equal to cottonseed. The answer is probably the presence of certain isolinoleates that remain in the oil. Analysis (18) shows that these copper-reduced oils contain as much as 5.2% to 6% of isolinoleate when the original oil contained 7.3 to 8.0 linolenate. Although lowering linolenate content from about 8% to 0.0% substantially improves soybean oil for use as a salad and cooking oil, the effect of isolinoleate remains.

ACKNOWLEDGMENT

R. E. Beal and L. T. Black prepared and analyzed some of these samples; Archer Daniels Midland, Inc., A. E. Staley Manufacturing Company, Humko Products—Division of National Dairy Products Company, and Procter & Gamble Company supplied samples; the members of the taste panel have served faithfully through these studies.

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[Received July 14, 1970]