ricinoleate and the catalyst were heated at 90C while hydrogen was bubbled through the mixture for 0.5 hr. The alcohol-washed catalyst in the second case was heated to 300C for 2 hr while hydrogen was passed through it. These hydrogen-treated catalysts gave unsatisfactory results as evidenced by slow conversions and high percentages of hydrogenolysis products.

6. The last factor investigated was the decrease in activity of the W-4 and commercial catalysts with age. A comparison between a batch of W-4 catalyst 7 days old and another 48 days old showed that at the 1:1 level the reaction time with the newer catalyst was about one-third that of the older one. The yield with the newer catalyst was 72% (Table II). GLC results suggest a similar yield with the older catalyst. A batch of commercial Raney nickel about 2 months old was then compared with a fresh batch prepared the same way. No significant difference was observed in either the rate of the reaction or the yield (60%) when these two catalysts were run at the 0.5:1 level.

Since our results show that dehydrogenation of methyl 12-hydroxystearate is a key step in this reaction, use of a more efficient dehydrogenating catalyst might accelerate this step, greatly reduce the amount of catalyst required, and reduce or even eliminate hydrogenolysis. This approach is currently being investigated.

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Trace Elements in Edible Fats. IX. Influence of Demetalization on the Oxidative and Flavor Stabilities of Soybean Oil[1]

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Abstract

Crude and degummed soybean oils were demetalized by passing through columns packed with cation exchange resins. These oils were refined, bleached, deodorized and compared with untreated oils for oxidative and flavor stabilities. Treatment of oils with resin lowered metal content and increased stability as measured by oxidative and sensory tests.

Introduction

The important role generally assumed to the presence of heavy metal traces in the edible oils due to their prooxidant action has received in the last years strong support through the work of Tappel (10–12), Uri (5,13–16) and the research group of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture (1). Tappel concluded that complexes of iron and copper with linoleate peroxide were factors in the initiation of the chain reactions. Uri does not believe in a direct reaction between the oxygen and the unsaturated fatty acid but rather in a reaction catalyzed by metal ions with formation of free radicals. Cooney and co-workers (1) attributed catalytic action to coordination complex between iron and a secondary oxidation product. On the other hand it has been possible to show that metal inactivating agents are effective in stabilizing oils (2).

Great efforts have been made in order to find more efficient metal inactivating agents. These is, evidently, another way of solving this problem and this is to eliminate the metals from the oils. So, we were able to show how the demetalized olive oils, using cation exchange resins, had a fairly superior stability (17–19). Lately (20) we have studied the demetalization of crude degummed soybean oils and the present paper reports on the effects that the demetalization has on their stabilities after refining, bleaching and deodorizing.

TABLE I
Demetalization of Soybean Oil

Sample	Iron	Metal content (ppm)		
		Manganese	Copper	Zinc
B-2, Original	2.82	0.225	0.028	1.72
B-2, Demetalized	1.34	0.037	0.013	0,23
% Demetalization	53	84	54	87
837, Original	0.88	0.281	0.019	1.16
837, Demetalized	0.40	0.000	0.002	0.08
% Demetalization	55	100	90	93
847, Original	3.42	0.597	0.023	2.85
847, Demetalized	1.69	0.000	0.006	0.00
% Demetalization	51	100	74	100

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TABLE II

Effect of Demetalization on Constants of Soybean Oil

Soybean oil sample	Acid value mgKOH/g	Peroxide value meq/kg	Tocopherol µg/g	Absorbance $E^{1\%}_{1\,cm}$		
				230 mµ	274 mµ	322 mµ
837, Original	0.8	14.7	1,300 (853)[a]	4.99	0.272	0.064
837, Demetalized	0.9	12.5	1,240 (1,075)	4.31	0.335	0.083
847, Original	0.9	9.6	1,295 (929)	3.12	0.340	0.073
847, Demetalized	1.7	9.6	1,229 (992)	2.77	0.329	0.082

[a] Values in ( ) obtained on oils after refining, bleaching and deodorizing.

Experimental

Crude degummed soybean oils from the United States were demetalized following the method previously described (20). Oil sample B-2, in acetone, was passed through a 1.5 x 15 cm column packed with Amberlite CG-120-I resin; soybean oils 837 and 847, in hexane, were passed twice through a 4.3 x 30 cm column packed with the same resin. The oils were then refined, bleached and deodorized for 3 hr at 210C, 3 mm Hg. All laboratory operations were carried out in glass, free from metal contamination.

Oxidative stability of the oils was tested by determination of peroxide values after 8 hr under AOM conditions (8). A micro-spectrophotometric method using N,N-dimethyl-p-phenylendiamine as the colorimetric reagent was used to follow peroxide development in samples (21). This method was also used when the sample was too small for the usual peroxide test.

Tocopherols were determined by a modified method of Stern and Baxter (9). Silicic acid columns were used to eliminate peroxides in oxidized samples (3,4). An aliquot of the benzene solution of the peroxide free oil, containing 4 to 25 µg of tocopherol was used, as this was the range of the calibration curve. The vol of solvent and solutions was proportionally reduced so that the final volume was 5 ml.

Flavor stability was determined by an analytical-type taste panel. The oil was evaluated for initial quality and after 3 days' storage at 60C. Samples were presented to the tasters in code-marked cognac glasses specially designed with a flat base which allows a good concn of the flavor and a good distribution of the oil over the walls of the glasses by twirling the glass. Soybean oil B-2 was evaluated following the procedure of Mahoney and co-workers (6) and samples 837 and 847 were evaluated by the method of Moser et al. (7).

Results and Discussion

The metal content of crude and degummed soybean oil, passed through the cation exchange resins, was reduced without greatly altering the composition of the oil. The effectiveness of this treatment is shown in Table I, and the change in some constants of the oils by the demetalization is shown in Table II. A slight decrease in tocopherol and, as should be expected, a slight increase in acidity, was observed. The demetalization of the crude oil resulted in smaller loss of tocopherols during refining, bleaching and deodorizing than the control samples.

TABLE III

Flavor and Oxidative Stability of Demetalized Soybean Oil

Sample	Oxidative stability 8 hr A.O.M. P. V.	Flavor stability 3 days at 60C	
		P. V.	Score
B-2, Original	315	21.7	7.3[a]
B-2, Demetalized	70	2.2	2.7
837, Original	214	2.8	7.8[b]
837, Demetalized	103	1.0	8.5
847, Original	89	4.8	6.5[b]
847, Demetalized	81	2.6	7.4

[a] Flavor evaluation by method of Mahoney and co-workers (6) where 1 is a high quality oil and 10 is poor quality oil.

[b] Flavor evaluation by method of Moser et al. (7) where 10 is the score for an excellent oil and 1 the score for a very poor quality oil.

TABLE IV

Change of Tocopherol and Peroxides in AOM Test of Original and Demetalized Oils

Treatment	Original oil 837		Demetalized oil 837	
	Tocopherol µg/g 1300	Peroxides meq/kg 14.7	Tocopherol µg/g 1240	Peroxides meq/kg 12.5
Crude refining and deodorization	860	0	1080	0
A.O.M.— 5 hr	420	50	720	145
6 hr	280	60	520	55
7 hr	180	75	475	65
8 hr	50	95	280	80
9 hr	5	180	1235	88
10 hr	13	460	15	150

The favorable effects of demetalization on the oxidative and flavor stabilities are shown in Tables III and IV. In all experiments the flavor of the demetalized oil was of higher quality than the control sample although only the oils B-2 and 847 were significantly better when results were analyzed statistically.

The effect of the demetalization on the oxidative stability of oil B-2 was superior to that of soybean oils 837 and 847. This fact was confirmed by the results of the flavor tests.

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