

Conversion of Methyl Ricinoleate to Methyl 12-Ketostearate with Raney Nickel

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Abstract

A convenient laboratory preparation of methyl 12-ketostearate is described. Methyl ricinoleate is converted to methyl 12-ketostearate in 70-75% yield by Raney nickel. The type and quantity of Raney nickel have a marked influence on the yield as well as on the time and temp required for the conversion. The reaction is not a direct isomerization as previously assumed but appears to be a two-step process. Methyl ricinoleate is hydrogenated rapidly to methyl 12-hydroxystearate which is then dehydrogenated slowly to the product. Hydrogenolysis of the alcohol function is a competing reaction which is minimized by the proper choice of reaction conditions.

Introduction

METHYL 12-ketostearate is usually prepared from methyl ricinoleate by two general methods. In one method, methyl ricinoleate is hydrogenated to methyl 12-hydroxystearate which is then oxidized by chromic acid to methyl 12-ketostearate (1,2,3). This procedure has the disadvantage of requiring two separate steps. In the other method, methyl ricinoleate is converted by catalysts to methyl 12-ketostearate. Some of the catalytic techniques require the use of a combination of high temp, pressure and expensive catalyst (4,5). Where Raney nickel was used, an isomerization reaction was assumed although no study of the mechanism was made (6,7). Furthermore, the reaction was not reproducible (6). The present investigation, using Raney nickel catalyst, was made to determine important variables affecting yield and purity and to elucidate the mechanism of the reaction.

Experimental

Starting Materials

Methyl Ricinoleate. This ester was prepared by base-catalyzed alcoholysis of castor oil and purified by fractional distillation of the mixed methyl esters under reduced pressure (8). The methyl ricinoleate content was >95% as shown by gas liquid chromatography (GLC).

Raney Nickel. Four types of Raney nickel were evaluated. One was a commercial catalyst designated "No. 28 Raney active Nickel Catalyst in Water," provided by W. R. Grace & Co., Raney Catalyst Division, Chattanooga, Tenn. We prepared W-4, W-6, and W-7 catalysts using the methods of Adkins and co-workers (9,10). These 3 catalysts are washed differently. W-7 is washed only slightly. Consequently, alkali remains on the catalyst (9). W-4 and W-6 are washed thoroughly to remove all water-soluble impurities (10), but W-6 is washed under a half atmosphere of hydrogen pressure (9).

Chromatographic Techniques

Gas Liquid Chromatography. The reaction was followed primarily by the use of GLC. We used a 1-mv

recorder in conjunction with a 4-filament, laboratory-constructed, programable instrument. Stainless-steel columns (8-ft, 1/8 in.) were packed with 15% diethylene glycol succinate (DEGS) on 70-80 mesh Gas-Chrom P. Analysis were made using on-column injection at 228-233C with a helium flow rate of about 80 ml/min and a filament current of 225 ma. Under these conditions a sample could be analyzed in ca. 5 min. This speed was used because some of the reactions were complete in 3-5 min. Samples (10-20 mg) of the reaction mixture were taken during the course of the conversion, diluted to a 20% solution with benzene, and injected onto the column.

Thin Layer Chromatography. To supplement GLC findings and to detect certain compounds formed during the reaction which were not eluted during GLC, thin-layer chromatography (TLC) on chromatostrips (11) was employed. A 10% chloroform solution of crude reaction mixture was spotted on a chromatostrip coated with 5% starch-bonded Merck 7729 silica gel. The developing solvent was 70% Skel-lysolve F-30% diethyl ether (v/v). Spots were detected under UV illumination after the strip had been sprayed with 0.02% 2', 7'-dichlorofluorescein in ethanol.

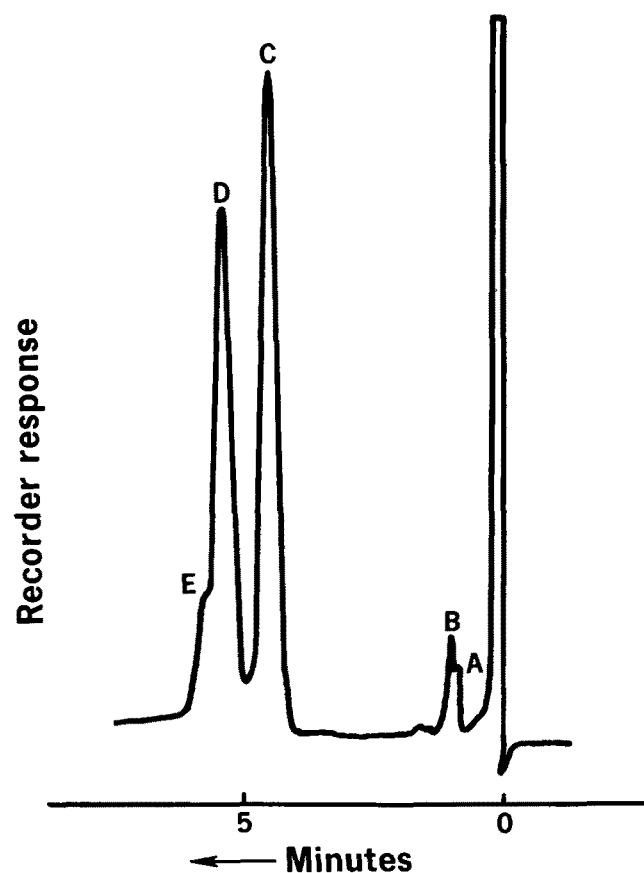


Fig. 1. GLC of compounds present during the conversion of methyl ricinoleate to methyl 12-ketostearate.

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Reaction Procedure

In addition to the four types of Raney nickel evaluated, catalyst quantity, time and temp were varied over a wide range. A typical example of the way in which the reaction was run follows: A tared 50-ml Ace "Mini-Lab" reaction flask was charged with 11.9 g of methyl ricinoleate and 11.9 g of moist W-4 Raney nickel. Caution: Because dry Raney nickel is pyrophoric, the catalyst must always be covered with solvent. The flask head was fitted with a mechanical stirrer, thermometer and nitrogen inlet tube. The mixture, under nitrogen, (the reaction may be conducted either under a blanket of nitrogen or with nitrogen bubbling slowly through the mixture) was stirred and heated to 152–175°C during one-half hour and kept in this temp range for about an hour. After the mixture was cooled to room temp it was treated with an excess of hot methanol and filtered. The filtrate was concentrated on the steam bath under a stream of nitrogen; the resulting oil crystallized on cooling. After one recrystallization from methanol, 8.6 g (72%) of methyl 12-ketostearate was obtained, mp 45.0–45.5°C. Reported mp is 45.3–46°C (3).

In some experiments a modified reaction flask was used. It contained a medium fritted-glass disc and a stopcock which allowed the product to be drained away from the catalyst. This arrangement permitted evaluation of catalyst re-use.

Results and Discussion

Mechanism

GLC analyses showed that five peaks were always present during the reaction; their relative sizes varied with conditions and extent of reaction. An example of one of these chromatograms is shown in Figure 1. C was established as methyl 12-ketostearate and E as methyl ricinoleate by comparing relative retention times of these two peaks with those of the known compounds. The methyl 12-ketostearate used for comparative purposes was prepared by hydrogenation of methyl ricinoleate followed by oxidation of the methyl 12-hydroxystearate with chromic acid (3). It was suspected that D might be methyl 12-hydroxystearate, since the retention times of D and authentic 12-hydroxystearate were identical.

To establish the identity of D, a standard mixture of methyl ricinoleate, methyl 12-hydroxystearate, and methyl 12-ketostearate was spotted on silica gel chromatostrips impregnated with silver nitrate (12). Instead of dichlorofluorescein, 20% H₂SO₄ (w/w) and charring were used for detection. The three compounds had R_f values of 0.21, 0.38 and 0.68, respectively. A sample from a reaction mixture chosen for comparison was shown by GLC to contain C (the ketostearate) and D but not E (methyl ricinoleate). The R_f values for the two spots observed in this mixture corresponded exactly to those of the hydroxy and ketostearates. Thus both GLC and TLC indicated that the hydroxystearate was present during the reaction.

From another reaction mixture the hydroxystearate was isolated by recrystallization from Skellysolve B. The solid so obtained melted at 56.5–57.5°C. A mixed melting point with authentic methyl 12-hydroxystearate (mp 56.5–57.5°C) showed no depression. The IR spectra also were identical.

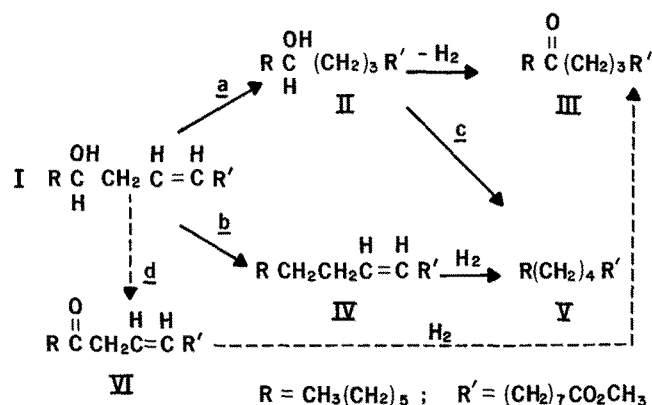
To demonstrate that methyl 12-hydroxystearate could function as an intermediate, it was subjected to the same conditions used to convert methyl ricinoleate to methyl 12-ketostearate. From this reaction, methyl 12-ketostearate was obtained in 69% yield. It

was identical to authentic methyl 12-ketostearate as assessed by melting points, mixed melting point, and IR spectra.

Nuclear magnetic resonance (NMR) spectroscopy indicated that no more than 1% of ethyl esters was present in the crude and recrystallized product. These esters might have been formed through transesterification of methyl esters by ethanol present with the laboratory-made catalysts.

Peaks A and B of Figure 1 were next identified. Comparison of the GLC retention times of A and B with those of methyl stearate and methyl oleate, respectively, showed them to be identical. A mixture containing A and B produced a spot (TLC) which had the same R_f as the spot from a mixture of known methyl stearate and oleate. Furthermore, this spot from the mixture including A and B was shown, by use of fluorescein-bromine (11) in the TLC detection, to contain an unsaturated compound. Since this particular sample contained no methyl ricinoleate (by GLC) the unsaturation was presumably due to methyl oleate. Thus it appears that peaks A and B correspond to methyl stearate and oleate, respectively, although no further efforts were made to confirm their identity.

Several possible mechanisms which could account for the observed products are presented below. The



main route taken by the reaction is shown by a: Methyl ricinoleate (I) is hydrogenated to methyl 12-hydroxystearate (II) which is then dehydrogenated to give methyl 12-ketostearate (III). The rate of appearance and disappearance of the intermediate (II) as determined by GLC, show that the hydrogenation proceeds much more rapidly than the dehydrogenation. Also, dehydrogenation begins before hydrogenation is completed. These results exclude a concerted mechanism in which hydrogenation and dehydrogenation

TABLE I
Effect of Gas Used on Course of the Reaction^a

Gas	Time, hr	Temp, °C	% of compounds by GLC		
			Me-ket ^b %	Me-OH ^c %	Hyd prod ^d %
H ₂	0	26	0	0	0
	0.07	42	—	—	—
	0.15	38	58	38	4
	0.73	26	18	78	4
	1.00	26	10	85	5
	1.50	25	5	90	5
N ₂	1.80	25	—	—	—
	2.80	31 ^e	18	77	5
	2.97	86	77	18	5
	3.14	140	77	18	5
	3.41	176	77	18	5

^a 23.8 g of W-7 Raney Ni was used with 11.9 g of methyl ricinoleate.

^b Methyl 12-ketostearate.

^c Methyl 12-hydroxystearate.

^d Hydrogenolysis products: methyl oleate and methyl stearate.

^e Began heating at this point.

TABLE II
 Effect of Catalyst Type on Yield^a

Catalyst type	Time, hr	Temp. °C	% of compounds by GLC			Product yield, %	Melting point, °C
			Me-ket ^b	Me-OH ^b	Hyd prod ^b		
Commercial.....	0.60	172-193	93	1	6	60	45.8-46.0
W-4.....	0.83	152-175	85	5	10	72	45.0-45.5
W-6.....	2.25	180-200	86	4	10	53	45.5-46.0
W-7.....	0.75	225	93	0	7	22	Not determined ^c

^aIn each case, 11.9 g moist catalyst was used with 11.9 g methyl ricinoleate. The commercial catalyst, as used, contained ca. 36% water by wt, the laboratory catalysts ca. 30% ethanol by weight.

^bSee footnotes to Table I.

^cProduct was an impure pasty solid.

ation occur at the same rate as well as conversion only through a simple isomerization involving no intermediates. It can also be concluded that the hydrogen which saturates the double bond must be provided predominately by the catalyst rather than the hydrogen later lost at the 12-position. Catalyst concn has been found to play a much more important role than might have been anticipated; it appears that the Raney nickel acts as a reactant rather than as a true catalyst.

When insufficient Raney nickel is used or when it is not sufficiently activated, hydrogenolysis by routes *b* and *c* become strongly competitive with route *a*. Even under the best conditions these side reactions could not be eliminated entirely. Since the amount of methyl oleate (IV) formed is generally greater than the amount of methyl stearate (V), route *b* appears to be more important than route *c*. Methyl ricinoleate could also conceivably undergo dehydration to give a mixture of methyl 9,12- and 9,11-linoleates. The absence of any substantial amounts of linoleates in the GLC shows dehydration does not take place to any significant extent.

Another reaction which could occur simultaneously with *a* is shown in *d*. In this case dehydrogenation of I would give methyl 12-ketooleate (VI) (13) which on hydrogenation would yield III. This did not seem likely since dehydrogenation was found to be much slower than hydrogenation in this system. As a check, however, methyl 12-ketooleate was synthesized by chromic acid oxidation of methyl ricinoleate (13). The product had essentially the same refractive index as that reported. The IR and NMR spectra were consistent with the structure of methyl 12-ketooleate. Under suitable GLC conditions this methyl 12-ketooleate was found to elute between the methyl 12-ketostearate and the methyl 12-hydroxystearate. For these GLC determinations the instrument used was an F & M 720 containing 4-ft, 0.25-in., stainless-steel columns packed with 15% DEGS on 70-80 mesh Gas-Chrom P. The oven temp was 215°C with a helium flow of 50 ml/min. A run was then made to determine how rapidly methyl 12-ketooleate would be converted to methyl 12-ketostearate with the catalyst. The reaction rate for this conversion was approximately the same as that observed in the conversion of methyl ricinoleate to methyl 12-ketostearate, under similar conditions. The methyl 12-ketostearate from

the methyl 12-ketooleate was identified by melting point, mixed melting point, and IR spectrum. This information indicates that if the ketooleate were formed during the reaction its presence could be detected.

A typical conversion of methyl ricinoleate to the ketostearate was then made and samples were removed when GLC indicated 25% and 82% product had been formed. The chromatograms of these samples did not indicate the presence of any methyl 12-ketooleate. Therefore, this compound is not formed to any detectable extent in the reaction.

Since Raney nickel promotes both hydrogenation and dehydrogenation, the possibility was considered that some ketostearate might be hydrogenated back to hydroxystearate. When the reaction was run under nitrogen there was no evidence of this. In one run, however, a hydrogen atm was used during part of the reaction, a nitrogen atm during the remainder. The results of this experiment are shown in Table I.

The methyl 12-ketostearate initially formed was slowly hydrogenated to methyl 12-hydroxystearate. When hydrogen was replaced by nitrogen and heat applied, the hydroxystearate was dehydrogenated to the ketostearate, showing that hydrogenation of the ketostearate occurs only in a hydrogen atmosphere.

Factors Affecting the Yield of Product

To determine the optimum conditions for the conversion of methyl ricinoleate to methyl 12-ketostearate, the following factors were investigated: 1) type of catalyst; 2) wt ratio of catalyst to starting material; 3) dependence of time and temp on the first two factors; 4) feasibility of catalyst re-use; 5) modification of the catalyst to improve its activity; and 6) relationship of catalyst age to its activity.

1. The effect of catalyst type on the yield of product is shown in Table II. A somewhat lower yield was obtained with the commercial catalyst than with the W-4, perhaps due in part to saponification and/or estolide formation by the commercial catalyst. Since W-4 is washed more thoroughly than the commercial catalyst, the alkali which presumably causes these side reactions is removed. In this connection, Hanford et al. (7) claim that "traces of alkali in the catalyst are beneficial since the activity of the catalyst is thereby enhanced." Our experiments show, however, that not only is alkali unnecessary but better yields

 TABLE III
 Effect of Weight Ratio of Commercial Catalyst to Starting Material on Yield^a

Ratio of cat/MeRi	Time, hr	Temp. °C	% of compounds by GLC			Product yield, %	Melting point, °C
			Me-ket ^b	Me-OH ^b	Hyd prod ^b		
2:1.....	1.00	128-160	90	0	10	64	45.7-46.0
1:1.....	0.60	172-193	93	1	6	60	45.8-46.0
0.5:1.....	0.85	196-233	83	7	10	60	46.0-46.5
0.25:1.....	1.50	197-234	80	0	20	47	Not determined ^c

^aIn each case, the moist catalyst was used with 11.9 g of methyl ricinoleate.

^bSee footnotes to Table I.

^cProduct was an impure pasty solid.

TABLE IV
 Effect of Reusing the Catalyst on Yield^a

Catalyst type	Run	Time, hr	Temp, °C	% of compounds by GLC		
				Me-ket ^b	Me-OH ^b	Hyd prod ^b
comm.....	1st	0.50	130-160	81	11	8
	2nd	1.00	160-218	60	15	25
W-6	1st	0.25	216-228	82	13	5
	2nd	0.62	200-238	72	17	11

^aIn both cases 37.2 g of moist catalyst was used initially with 37.2 g methyl ricinoleate.

^bSee footnotes to Table I.

are obtained without it. This effect was very noticeable with W-7, where the alkali present caused a drastic reduction in yield and purity. It was the least satisfactory of all four catalysts for this reaction. Although W-6 differed from W-4 only slightly in its preparation, its activity was inferior as judged by lower product yields and more stringent time and temp requirements.

2. The effect of the weight ratio of catalyst to starting material on product yield is shown in Table III. Raising the ratio above 0.5:1 had no effect on yield. With a ratio of 0.25:1, the product was not of satisfactory purity, and hydrogenolysis was more pronounced, showing that whereas a ratio of 0.5:1 or higher gives satisfactory results, a ratio of 0.25:1 does not. Although a strict comparison of this type was not made with the other catalysts, the same trend was observed.

3. One other trend that can be seen in Table III is the increase in the temp and/or time required as the ratio of catalyst to starting material decreases. Previous investigators (6,7) have carried out this reaction with 10-20% by wt of catalyst (presumably moist) for several hours at 200-275°C. As shown in the experiments where higher catalyst concentrations were employed, considerably milder conditions could be used.

4. Several runs were made to determine whether a given batch of catalyst could be re-used. After a first run was made, the product was drained off and the reactor was charged with the same wt of methyl ricinoleate employed initially. The results of two experiments of this type are shown in Table IV. Longer times and higher temp were required in the second runs, so the activity of the catalyst had apparently decreased. Also evident is a significant decrease in the percentage of methyl 12-ketostearate and a corresponding increase in the percentage of hydrogenolysis products. Thus, it was not feasible to re-use the catalyst.

The decrease in catalytic activity may be due to a collapse of the active sites after consumption of the catalyst's chemisorbed hydrogen. Many workers have shown that when the hydrogen of Raney nickel

is removed by either chemical (14,15) or physical means (16), activity is drastically reduced. Adsorption of organic materials on the catalyst may also cause its deactivation. The ability of Raney nickel to strongly adsorb organic compounds is well known. In one study of the dehydrogenation of secondary alcohols with nickel catalysts, the ketone produced was shown to have a markedly higher adsorption coefficient than the alcohol (17) and strongly inhibited further reaction.

5. To obtain a more active catalyst, various preparative modifications were made. Since W-4 performed better than the less thoroughly washed W-7, the commercial catalyst was also water-washed in the same manner as W-4 had been. The washed commercial catalyst was then run at the 1:1 and 0.5:1 ratios (Table V). At the 1:1 level the yield of product with the washed catalyst was superior to that with the unwashed material although the reaction time was about doubled. At the 0.5:1 level, the percentage of hydrogenolysis products with the washed catalyst was decidedly higher than with the unwashed. Thus, the washed catalyst is superior at the 1:1 level but inferior at the 0.5:1 level.

To insure that the commercial catalyst was saturated with hydrogen, it was heated under 20-50 psi hydrogen pressure at 85°C for 1 hr. The isolated yield, with a 0.5:1 ratio, was nearly as large as the yield with untreated catalyst (Table V). At the 0.25:1 level, the hydrogen pretreated catalyst was inferior, as shown by the excessive amount of hydrogenolysis products.

Since hydrogen addition did not enhance catalyst activity, chemical means were then used for hydrogen removal. This is known to lower the hydrogenating ability of the catalyst but it could not be safely assumed that it would deactivate the hydrogenation-dehydrogenation function of the Raney nickel. The two chemicals used to modify the catalyst were benzoquinone and cyclohexene. The reaction between the hydrogen of the W-4 catalyst and benzoquinone converted most of the latter to hydroquinone and/or quinhydrone, showing that at least part of the hydrogen reacted. The resulting catalyst, however, gave a much poorer performance (Table V). Cyclohexene apparently was dehydrogenated by the catalyst rather than hydrogenated as expected, based upon UV examination of the reaction mixture. In any case, use of this catalyst resulted in excessive amounts of hydrogenolysis products (Table V).

Additional investigation showed that hydrogen treatment of the catalyst after it was used did not reactivate it. In two experiments, a batch of catalyst was used and then washed with hot alcohol to remove organic material. In one case, fresh methyl

 TABLE V
 Effect of Modifying the Catalyst on Yield

Catalyst	Modification of catalyst	Ratio of Cat/MeRi	Time, hr	Temp, °C	% of compounds by GLC			Product yield, %
					Me-ket ^a	Me-OH ^a	Hyd prod ^a	
Comm.....	None	1:1	0.60	172-193	93	1	6	60
	Washed	1:1	1.00	175-185	80	10	10	73 ^b
	None	0.5:1	0.85	196-233	83	7	10	60
	Washed	0.5:1	1.25	172-193	75	0	25
	Hydrogen pretreated	0.5:1	1.00	198-201	82	0	18	58
	Hydrogen pretreated	0.25:1	0.50	195-233	44	0	56
W-4	None	0.25:1	1.50	197-234	80	0	20	47
	Benzoquinone treated	1:1	0.25	215-230	31	35	34
	Cyclohexene treated	1:1	0.13	203-211	43	5	52

^aSee footnotes in Table I.

^bFrom the mother liquor an additional 13% of less pure product was recovered.

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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NMR spectra and interpretation by R. E. Lundin.

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Trace Elements in Edible Fats. IX. Influence of Demetalization on the Oxidative and Flavor Stabilities of Soybean Oil¹

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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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