

Copper-Hydrogenated Soybean and Linseed Oils: Composition, Organoleptic Quality and Oxidative Stability¹

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ABSTRACT

Copper and nickel hydrogenations give a wide distribution of double bonds in the monoene fraction from both reduced soybean and linseed oils. With copper catalysts, high pressure hydrogenation reduces the extent of this double bond distribution when compared with low pressure hydrogenation. With nickel catalysts, some $\Delta 17$ -octadecenoate is formed but less than with a copper catalyst. In room odor evaluations, copper-hydrogenated soybean (CuHSB) oil gave higher scores and lower fishy responses than nickel-hydrogenated soybean oil after both had been exposed to fluorescent light. A mixture of CuHSB oil (33%) and peanut oil received room odor scores equal to or better than peanut oil alone, whether light exposed or not. Although hydrogenated products with remarkable stability to oxidation were obtained by copper hydrogenation of linseed oil, these oils have lower organoleptic stability when compared to nickel-hydrogenated, winterized soybean oil.

INTRODUCTION

In previous papers, the Northern Laboratory has reported on the composition (1-4) as well as organoleptic and oxidative stability of copper-hydrogenated soybean (CuHSB) (5) and copper-hydrogenated linseed (CuHLS) oils (6). Briefly, this paper reviews our latest work on hydrogenation with copper catalysts, and the effects of such hydrogenations on the fatty acid composition of both soybean and linseed oils and on their oxidative and organoleptic stability. New information is reported on composition; effect of fluorescent light on stability, particularly on room odor scores of CuHSB oil; stabilities of mixtures of CuHSB and CuHLS oils with other oils; and organoleptic and oxidative stability of CuHLS oil.

METHODS AND MATERIALS

Refined and bleached soybean and linseed oils; refined, bleached and deodorized peanut, safflower and nickel-hydrogenated, winterized soybean (NiHWSB) oils; and a vegetable shortening, primarily from soybean oil (NiHSB-

S), were obtained from commercial sources. Refined and bleached oils were deodorized in an all-glass laboratory apparatus previously described. Usually oils were deodorized with citric acid, antioxidant and antifoam agents being added during the cooling stages of deodorization. Low pressure hydrogenations were carried out as reported earlier by Koritala and Dutton (1) and by Moulton et al. (3).

A typical high pressure hydrogenation with a copper-chromite catalyst was as follows: A laboratory refined and bleached linseed oil was heated at 170 C with 3% copper-chromite catalyst for 5.25 hr in a 3 gal stainless steel converter provided with electric thermostated heating and cooling coils, a turbine-type gas-dispersing agitator and baffles. The initial pressure of 600 psig was maintained throughout the hydrogenation. Oil was filtered, vacuum-bleached with 1% activated clay and deodorized as previously described (6,7).

Oils were treated during the final stage of deodorization with 0.01% citric acid, 0.076% Tenox 6 (Eastman Chemical Products, Inc.) containing butylated hydroxyanisole, 10%; butylated hydroxytoluene, 10%; propyl gallate, 6%; propylene glycol, 12%; glyceryl monooleate and corn oil, 28% each; and 5 ppm methyl silicone-antifoam A compound (Dow Corning Corp.). Deviations from this procedure are noted in the appropriate table.

Peroxide values (PV) were measured by a modified Wheeler method (8), and values for the active oxygen method (AOM) were obtained by determining peroxides after 8 hr under AOM conditions (9) or at intervals until the PV went over 100.

Fatty ester analyses were performed by gas liquid chromatography (GLC), alkali isomerizations and IR and UV absorption as detailed previously (4). Initial and aged oil samples were scored for flavor by methods already reported (10). Room odor evaluations were conducted by the method of Evans et al. (11). Oils were exposed to fluorescent light in a modification of equipment described by Moser et al. (12), in which the bottles slowly rotate to be evenly exposed on all sides. Hydrogenated esters were separated into *trans*- and *cis*-monoene fractions on a rubber column (13) with acetone and water as the eluent, followed by chromatography on a silver-saturated cation exchange resin (14). Position of the double bonds in the monoene fraction was determined by reductive ozonolysis and by gas chromatography according to the method of Johnston and Dutton (15).

RESULTS AND DISCUSSION

Composition

Fatty acid compositions representative of the unhydrogenated oils used in these studies are given in Table I. Similar analyses for the hydrogenated oils appear in Table II. With the nickel and copper-chromite catalysts, it is possible to lower linolenate content of hydrogenated products from both soybean and linseed oils to less than 1%. It is somewhat more difficult to reach this low linolenate content with linseed than with soybean oil. Consequently, to reduce the linolenate to a minimum, higher pressure and additional catalyst were used. With soybean oil, copper chromite can catalyze complete reduc-

¹Presented at the ISF 11th Congress, Göteborg, Sweden, June 1972.

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TABLE I

Fatty Acid Composition of Unhydrogenated Oils as Determined by Gas Liquid Chromatography

Acid	Soybean	Linseed	Rapeseed ^a	Peanut ^a	Safflower
C16:0	11	6	3	13	6
C18:0	4	4	1	3	2
C18:1	23	19	11	41	77
C18:2	54	15	13	39	15
C18:3	8	56	8	—	—
C22:1			53		

^aContained small amounts of other acids.

TABLE II
Fatty Acid Composition of Hydrogenated Products^a by
Gas Liquid Chromatography and Other Methods

Acid	NiHWSB ^a	CuHSB	CuHLS	CuHLS	NiHSB-O	NiHLS	NiHSB-S
C16:0	10	12	6	6	11	6	13
C18:0	5	4	5	4	5	8	11
C18:1	48	42	50	60	43	62	51
C18:2	35	43	39	31	39	24	25
C18:3	3	0.3	0.7	0.2	3	0.3	---
Calcd IV	111	111	112	105	111	96	87
<i>trans</i> , %	---	15	39	53	12	59	21
Conjugatable diene	--- ^b	41	11	1.3	33	0	20
Conjugatable triene	---	0	0.9	0	---	0	---
Conditions (170 C for experimental oils)							
Pressure, psig	--- ^c	30	100	600	10	5-10	--- ^c
Catalyst, %	---	1	1	3	0.03	0.07	---

^aAbbreviations refer to nickel-hydrogenated winterized soybean (NiHWSB); copper-hydrogenated soybean (CuHSB); copper-hydrogenated linseed (CuHLS); nickel-hydrogenated soybean (NiHSB-O); nickel-hydrogenated linseed (NiHLS) oils; and a commercial all-vegetable (NiHSB-S) shortening.

^bConjugatable diene usually slightly lower 3 to 5% than the gas liquid chromatography analyses for C18:2 in NiHWSB oil (16).

^cCommercial.

tion of linolenate and retain more of conjugatable diene and *cis,cis*-linoleate than is possible with nickel hydrogenation and winterization procedures (2,16). With linseed oil almost all the linoleate, as measured by alkali isomerization, is lost at 600 psig, the pressure employed to reduce linolenate to below 1%. Even at 100 psig, the "essential" fatty acid or linoleate measured by alkali isomerization is ca. 11%, contrasted to 41% for CuHSB oil. Also the "isolinoic" acid content (diene by GLC-minus-diene by alkali isomerization) was high in the CuHLS oil. The high amount of catalyst used is indicative of the loss of catalyst activity when double bleaching to remove catalyst poisons is not carried out. Removal of poisons might make the lower linolenate oil possible to achieve at pressures of 30-75 psig.

The high pressure of 600 psig was used in an attempt, not only to reduce the movement of unsaturation during hydrogenation, but also to improve flavor stability of the CuHLS oil by hydrogenating all the linolenate. Examination of Table III suggests that the high pressure did reduce the movement of double bonds. Under 8 and 75 psig, 1.7 and 0.3%, respectively, of Δ 17-octadecenoate were formed (4), but it was not found in oil hydrogenated at 600 psig. Both copper and nickel apparently move the double bond extensively, as measured by the analyses for position of unsaturation in the monoene fraction. Although the Δ 17-

octadecenoate acid was not detected in NiHWSB oil, it was in commercial shortening (NiHSB-S) made primarily from soybean oil and in nickel-hydrogenated linseed oil. The positions of unsaturation in the monoene fraction of copper- and nickel-hydrogenated oils are about the same. Differences in the quantity of isomers present will depend on the conditions and extent of hydrogenation and the starting material.

ORGANOLEPTIC EVALUATION

In extensive organoleptic tests reported earlier (5), CuHSB oil was found to be intermediate between NiHWSB oil and cottonseed salad and cooking oils and to give a low number of fishy responses in room odor tests.

Since the flavor and odor scores of CuHSB oil generally increased as linolenate content decreased, it was concluded that this ester was the main precursor of undesirable flavors and odors. The lowering of certain room odor responses agreed with this conclusion; however new room odor responses were encountered that might well have come from the many isomeric monoenes and dienes formed during hydrogenation and not present in the original oil. Because the effect of light on CuHSB oil was not previously explored, investigations comparing the effect of light on CuHSB and NiHWSB oils were undertaken.

TABLE III
Monoene Isomers in Hydrogenated Oils^a

Conditions	CuHLS ^b	CuHLS ^b	CuHLS	CuHSB	NiHSB-O	NiHLS	NiHSB-S
Pressure, psig	8	75	600	30	10	5-10	--- ^c
Catalyst, %	1	1	3	3	0.03	0.07	---
Calculated IV	112	107	105	113	111	96	87
Δ 6	0.2	0.2	---	---	---	0.5	---
Δ 7	0.3	0.6	0.4	0.3	0.3	1.2	0.6
Δ 8	1.6	1.6	2.3	2.1	2.1	4.2	2.7
Δ 9	23.3	25.0	19.3	22.1	26.0	16.8	27.1
Δ 10	3.9	4.3	9.0	3.1	3.2	9.2	6.6
Δ 11	6.1	6.9	9.0	4.9	3.7	8.8	6.2
Δ 12	6.4	6.1	8.4	2.6	5.3	7.5	4.8
Δ 13	6.3	5.5	5.2	1.6	0.8	5.5	2.0
Δ 14	4.5	4.0	3.5	0.9	0.3	3.8	0.5
Δ 15	3.4	2.1	2.0	0.6	0.4	2.9	---
Δ 16	1.2	0.9	0.5	0.2	0.1	1.7	---
Δ 17	1.7	0.3	---	0.2	---	0.1	0.1

^aSee Table II for key to abbreviations.

^bSee Vigneron et al. (4) for additional information.

^cCommercial all-vegetable shortening.

TABLE IV

Effect of Light on Flavor Scores^a and Peroxide Values of Soybean Oils

Oil	Flavor scores and significance		
	Exposure		
	Initial	3 hr	Sig ^b
Unhydrogenated ^c	7.6(0.4)	5.4(1.4)	**
NiHWSB ^d	7.5(0.2)	5.6(1.3)	**
CuHSB ^d	8.0(0.4)	5.9(1.7)	**

^aFlavor scores are given on a basis of 1-10 (Reference 10). Values in parentheses are peroxide values.

^b**Denotes significance at the 1% level; *significance, at the 5% level; and none, no significance at the 5% level.

^cOnly citric acid added.

^dSee Table II for key to abbreviations.

TABLE V

Effect of Light on Room Odor Scores^a and Responses^b of CuHSB and NiHWSB^c Oils

Oil	Room odor scores		
	No exposure	Exposure, 8 hr	Sig
NiHWSB	6.1	4.2	**
CuHSB	6.2	5.9	None

Odor responses	Odor intensity values ^b		
	Hot oil	Rancid	Fishy
No exposure			
NiHWSB	0.3	0.3	0.1
CuHSB	0.3	0.3	0.0
8 hr Exposure			
NiHWSB	0.2	1.1	0.6
CuHSB	0.5	0.5	0.1

^aScore based on scale of 1-10 (11).

^bScore based on a scale of 1-3 (11) where 1 is weak, 2 medium and 3 strong odor.

^cSee Table II for key to abbreviations.

Copper-Hydrogenated Soybean Oil

Exposure of unhydrogenated soybean oil in glass bottles to fluorescent light lowers its flavor score and increases its PV (12). In similar exposure tests with CuHSB and NiHWSB oil, flavor scores were lowered and PV increased. Generally the CuHSB oil scored higher than the NiHWSB oil or the unhydrogenated soybean salad oil when unexposed oils were tested against exposed oils. In direct comparisons between light-exposed CuHSB and NiHWSB oils, no significant differences appeared. CuHSB oil scored

TABLE VI

Effect of Fluorescent Light on Room Odor Scores and Responses:^a Direct Comparison of NiHWSB to CuHSB^a Oil

Condition	Odor scores		
	CuHSB	NiHWSB	Sig ^a
Room odor evaluations			
8 hr Exposure	5.8	5.3	None
Room odor responses (Odor intensity values)			
Rancid	0.5	0.7	
Fishy	0.0	0.4	
Hot oil	0.4	0.5	

^aFor information on abbreviations, odor scores, odor intensity values and sig, see Tables II, IV and V.

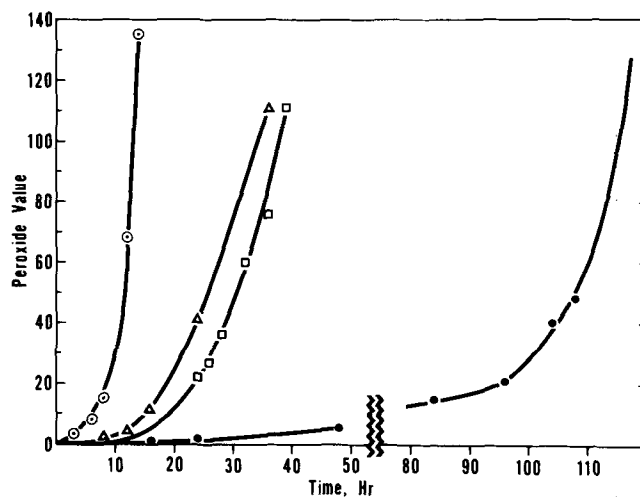


FIG. 1. Active oxygen method (9) stability curves for linseed oil \circ , hydrogenated-winterized soybean oil Δ , copper-hydrogenated soybean oil \square and copper-hydrogenated linseed oil \bullet .

higher. Table IV gives data on the testing of light-exposed oils against unexposed oils.

When NiHWSB and CuHSB oils were exposed to light and evaluated by room odor tests, the CuHSB oil received higher scores while light exposure did not lower its score very much. Data in Table V also indicate that very little increase in fishy responses occur when CuHSB oil is exposed to light and subjected to room odor tests. When NiHWSB oil was exposed to light, there was generally an increase in fishy responses in the room odor test. In direct comparisons between light-exposed CuHSB and NiHWSB oils reported in Table VI, the CuHSB oil scored higher and

TABLE VII

Effect of Fluorescent Light on Room Odor Test of Peanut Oil and Peanut (67%)-CuHSB^a Oil Mixture

Oil	Room odor scores ^a		
	No exposure	Exposure, 8 hr	Sig ^a
Peanut ^b	6.3	6.3	None
CuHSB (33%)	7.4	6.3	*

Responses	Odor intensity values ^a			
	Peanut	CuHSB (33%)	Peanut	CuHSB (33%)
Hot oil	0.6	0.3	0.4	0.3
Rancid	0.2	—	0.6	0.4
Burnt	0.2	—	0.2	0.3

^aFor information on abbreviations, scores, sig and odor intensity values, see Tables II, IV and V.

^bNo additives.

TABLE VIII
Flavor and Oxidative Stability of Copper-Hydrogenated Linseed Oil Compared to Nickel-Hydrogenated, Winterized Soybean Oil

Condition	Flavor or odor scores		
	CuHLS (0.2% Ln) ^a	NiHWSB (3.0% Ln) ^b	Sig ^b
Initial	7.6(0.0)	6.9(0.1)	*
4 Days at 60 C	4.3(0.8)	5.4(0.8)	*
8 Days at 60 C	3.3(0.9)	5.1(2.8)	**
Room odor test with initial oil	4.9	5.6	None
Responses after 8 days at 60 C – flavor intensity values			
Rancid	1.5	1.2	
Buttery	—	0.6	
Painty	0.9	0.4	
Fishy	0.3	—	
Grassy	0.3	0.5	
Responses after heating to 192 C – room odor values			
Rancid	0.8	0.7	
Hot oil	0.3	0.4	
Fishy	—	0.4	
Miscellaneous	2.0	0.7	
Peroxide value 8-hr AOM ^a	0.4	1.2	

^aGas liquid chromatography indicated 0.2% linolenate (Ln) and alkali isomerization indicated 0%; AOM, active oxygen method; 1 ppm of methyl silicone added to CuHLS oil.

^bSee Tables II, IV and V for explanation of abbreviations, flavor score, flavor intensity values (11) or odor intensity values and sig; commercial oil.

TABLE IX

Direct Comparison of Copper-Hydrogenated Linseed Oil with Nickel-Hydrogenated, Winterized Soybean Oil: Room Odor Tests

CuHLS ^a		NiHWSB (3% Ln)	
Ln, %	Odor score	Odor score	Sig
1.9	4.5	5.9	**
1.7	4.2	6.2	**
0.8	4.9	5.6	None

^a0.1% Tenox 6 and 1 ppm methyl silicone added to first two oils; 0.076% Tenox 6 and 1 ppm methyl silicone added to third CuHLS oil.

had fewer fishy responses. Indeed a fishy response for CuHLS oil is usually not reported by most of the panel members testing the oils.

Room odor evaluations of light-exposed peanut oil and a mixture of peanut oil with CuHLS oil both gave relatively high scores. The unexposed mixture also received a relatively high score in the room odor test. No fishy responses were noted with either the peanut oil or its mixture with CuHLS oil. Table VII contains data from these room odor evaluations.

Substantially lowering linolenate in soybean oils generally raises their flavor and odor scores, whether or not the oils have been exposed to light. The increase in quality is not so much as would be expected if only linolenate were involved.

Copper-Hydrogenated Linseed Oil

The improvements achieved with CuHLS oil (5) led us to try a copper catalyst with linseed oil. Hydrogenations with copper chromite at 30-600 psig readily gave products with less than 2% linolenate. These CuHLS oils had unusual oxidative stability. In Figure 1, the curves obtained in tests run by AOM are given for linseed, NiHWSB, CuHLS and CuHLS oils. The latter proved to have an AOM stability of more than 100 hr. Its flavor stability, however, proved to be inferior to NiHWSB oil when direct comparisons were made with samples aged at 60 C (Table VIII). After 4 and 8 days of aging, the CuHLS oil was scored significantly lower than NiHWSB oil. PV determined on the oil aged at 60 C and in the 8 hr AOM test confirm the excellent oxidative

TABLE X

Room Odor Score of Mixtures of Copper-Hydrogenated Linseed (CuHLS)^a Oil with High Oleic Safflower (HOS) Oil and Nickel-Hydrogenated, Winterized Soybean (NiHWSB) Oil

Room odor scores			Sig
HOS (100%) ^b			
6.0	6.1		None
6.4		5.3	**
NiHWS (100%) ^c			
6.8	7.0		None
7.3		5.7	**

^a0.1% Tenox 6 and 5 ppm of methyl silicone.

^bNo additives.

^cCommercial.

stability found in the prolonged AOM test. Despite this oxidative stability, the CuHLS oil received a flavor score of less than 4 at PV of 1. In the room odor test reported in the table, no significant difference was found. In most tests on room odor when linolenate of the CuHLS oil was above 1%, significant differences occurred between CuHLS and NiHWSB (3%) (Table IX). CuHLS oil was always scored lower than NiHWSB oil when the aged or heated samples were compared.

In further tests with mixtures of CuHLS oil with NiHWSB or a high oleic safflower oil, ca. 20% CuHLS oil

TABLE XI

Flavor Scores for Linseed Oils^a
Aged at 60 C

Sample	Initial score	Aged score
Linseed oil-I	7.1(0.0)	3.3(9.3) ^b
Linseed oil-II	8.2(0.0)	4.5(2.3) ^b
CuHLS oil	8.3(0.0)	5.9(0.3) ^c
NiHWSB oil ^d	7.8(0.6)	6.5(0.4) ^c

^aSample I refined, bleached and deodorized; II similar to I but contained added stabilizers, 0.1% Tenox 6; CuHLS oil had 0.1% Tenox 6 and 1 ppm methyl silicone.

^bOils aged 2.67 days.

^cOils aged 4 days.

^dCommercial.

could be added to the other two oils without substantially lowering room odor scores. Greater amounts of CuHLS oil in the mixtures led to significant reduction in this odor score (Table X).

Linseed oil is generally not used as an edible oil in the U.S. In recent years, its price has been sufficiently below soybean oil for long enough periods to merit considerations. Although oxidative and flavor stability are substantially improved, flavor scores at low levels of oxidation are sufficiently low to suggest that more improvement is needed before the CuHLS oil can be seriously considered as an edible product by the trade, while soybean oil remains readily available.

An examination of Table II will show that the one main difference between NiHWSB and CuHLS oil is the apparent amount of "isolinoleic" acid. The CuHLS oil contained ca. 30% isolinoleic, whereas NiHWSB oil usually contains no more than 3-5% of this acid (16). This amount of isolinoleic could easily account for lower flavor and room odor scores obtained with CuHLS oil and the larger number of "miscellaneous" responses, compared to NiHWSB oil (Table VIII). "Miscellaneous" includes responses such as leather, musty, goat, pump oil, fruit, orange peel, etc.

CuHLS oil is a decided improvement over unhydrogenated linseed oil given similar refining treatments. Data in Table XI show that high initial flavor score could be achieved in laboratory refining, but CuHLS oil was much more flavor stable. Indeed, in this particular test, there was no significant difference in flavor scores between CuHLS and NiHWSB oil. In tests carried out to 8 days, the NiHWSB oil received a significantly higher score.

ACKNOWLEDGMENTS

R.E. Beal and L.T. Black furnished some of the samples and

analyses reported. J. Deal and members of the taste panel served throughout the studies. Anderson-Clayton Foods, Pacific Vegetable Corp. and A.E. Staley Manufacturing Co. furnished various commercial samples. E.W. Bell conducted the first hydrogenations at 600 psig with copper chromite and linseed oil, and was able to obtain zero linolenate content. His work will be reported elsewhere.

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[Received October 18, 1972]