Summary

Sulfur compounds of the tridentate class having at least 2 carboxy groups in α or β position to the coordinating atom have been found to be effective in the stabilization of soybean oil. Comparing model compounds with different coordinating atoms, the order of effectiveness appears to be $S > N > O$. This order of effectiveness follows an order of increasing electronegativity.

Carboxymethylmercapto butyric acid, carboxymethylmercapto phenyl propionic acid, the monoethyl ester of carboxymethylmercapto succinic acid, p-toluene sulfonic acid, α,α'-thio-di-n-caproic acid, and sulfur dioxide all improved the oxidative stability but gave undesirable flavors.

Thiodiacetic acid, β,β'-thiodipropionic acid, carboxymethylmercapto succinic acid, and the monooctadecyl ester of carboxymethylmercapto succinic acid were found to be excellent stabilizers. The first two may be added either on the upgrade or the downgrade of deodorization, but the heat instability of the latter two limits their addition to the downgrade. All these compounds improved the flavor stability as well as the oxidative stability. The monooctadecyl ester has the added advantage in that it is oil soluble.

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A Halogenation Method for the Determination of the Total Unsaturation of Tung Oils and of Eleostearic Acids[1]

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THE value of various halogen absorption methods for the determination of unsaturation in tung oil and other oils containing conjugated double bond systems has recently been reviewed by Benham and Klee (1, 3). These authors proposed use of the Rosenmund-Kuhnhenn reagent (pyridine-sulfuric acid-bromine-acetic acid) and mercuric acetate as a catalyst for the determination of the iodine value of such oils. The original Rosenmund-Kuhnhenn method with no mercuric acetate catalyst results in iodine values of about 160 for tung oil. Klee and Benham (3) obtained an iodine value of 156.7 for a sample of fresh tung oil, using the Rosenmund-Kuhnhenn method without mercuric acetate and 250.6 for the same oil when mercuric acetate was added. An iodine value of 250 for tung oil is higher than would be expected on the basis of the generally accepted composition of tung oil (2). This fact was evidently recognized by Klee and Benham, but their efforts to determine whether substitution reactions might be the cause for the high iodine value resulted only in some evidence for the absence of any secondary substitution reaction.

Recently a method for the determination of total unsaturation of tung oil by quantitative catalytic hydrogenation was published (4). Using this method, iodine values of 225-241 for various tung oils were obtained. These values are in good agreement with those to be expected for such oils. Application of the method proposed by Klee and Benham to a tung oil with a hydrogen-iodine value of about 230 in this laboratory at first gave very erratic and generally high values. Klee and Benham reported that "during preliminary tests it was noted that the presence of light during absorption affected the results to a slight degree." On investigation it was found that exposure to light had a very marked effect both upon the blanks and on the solutions containing the oil samples. A series of determinations on samples of a tung oil run in the same way, except that the samples and their accompanying blanks were stored for the 2-hour reaction period under different conditions of illumination, gave iodine values ranging from 250 when the solutions were stored in a dark cabinet to 56 when they were exposed to bright sunlight. Even a few minutes' difference in exposure to light in a partially darkened laboratory (illumination less than 0.5 foot-candle as measured by a lightmeter) resulted in distinctly different iodine values.

Consistent and reproducible results could however be obtained by taking suitable precautions against exposure to light. The iodine values for tung oil

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TABLE I

Effect of Order of Addition and Excess of Bromine Reagent

Sample	Mercuric acetate added	Excess of reagent[a]	Reaction time	Iodine values found by	
				Halogenation	Hydrogenation
		%	*hours*		
α-Eleostearic acid, 97%	Last	122	1	289.5	271.9
	Last	203	1	297.5	
	First	202	1	265.8	
	First	211	1	267.4	
	First	220	1	267.7	
	First	243	1	271.5	
β-Eleostearic acid, 97%	Last	225	1	297.5	270.6
	Last	305	1	300.4	
	First	317	1	279.8[b]	
	First	331	1	280.9[b]	
Tung oil, domestic	Last	136	1	248.9	232.3
	Last	158	1	249.2	
	First	115	1	227.6	
	First	162	1	229.2	
	First	222	1	231.9	
	First	222	1	232.2	
	First	326	1	235.6	
	First	160	2	231.1	
	First	246	2	232.4	
	First	414	2	234.0	

[a] 100(B—S)/S, where B and S represent the volumes of thiosulfate solution used for blank and sample titrations, respectively.

[b] These values are too high due in part to the use of excesses of reagent higher than those recommended.

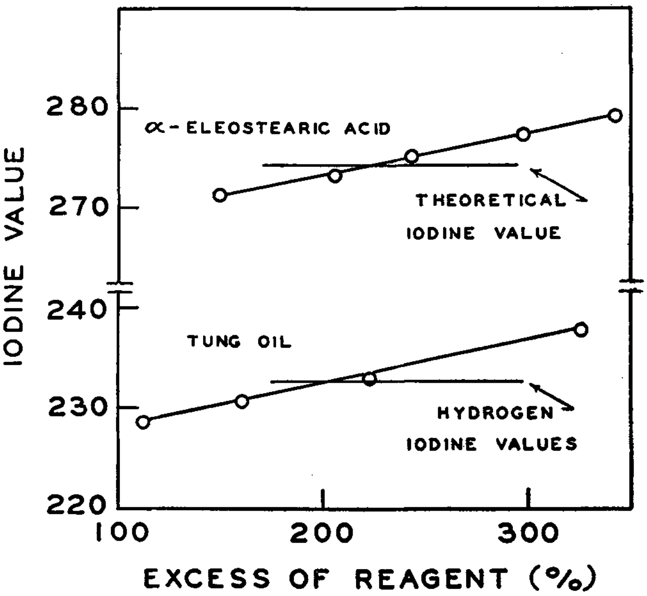

FIG. 1. Effect of excess of reagent on iodine values.

obtained in this way, about 250, were in good agreement with those reported by Klee and Benham for fresh tung oil but were about 8% higher than the values to be expected from the unsaturation present as measured by quantitative catalytic hydrogenation. Similar results were obtained if low actinic (red) reaction flasks were used with moderate precautions to avoid unnecessary exposure to light. Also iodine values of about 290 were obtained for α-eleostearic acid (97% pure as determined spectrophotometrically) whereas the calculated iodine value for the pure acid is 273.5.

Scotti (5), who first introduced the use of mercuric acetate in acetic acid to shorten the reaction time in iodine value determinations, studied the effect of varying the order of addition of the reagents, noted that the order of addition of mercuric acetate and the halogen made a difference in the results obtained, and recommended that the mercuric acetate be added after the halogen reagent. In the present work it was found that, in the case of tung oil, if the order of addition is reversed, *i.e.*, if the mercuric acetate is added before the Rosenmund-Kuhnhenn reagent, and provided care is taken to exclude light, consistent and reproducible iodine values are obtained. These are in good agreement with those to be expected from the unsaturation present as measured by quantitative catalytic hydrogenation. Further, in the case of the eleostearic acids, the iodine values thus obtained are in good agreement with the theoretical values. Typical data obtained showing the effect of order of addition of reagents, excess of Rosenmund-Kuhnhenn reagent, and reaction time are given in Table I. The effect on the observed iodine value of excess of halogenation reagent in the range 100 to 400% excess, using the new order of addition of reagents for a tung oil and for pure α-eleostearic acid, is shown in Figure 1.

Iodine values obtained for various tung oils and for α- and β-eleostearic acids, using the procedure described below, are given in Table II. For comparison the hydrogen-iodine values obtained by quantitative catalytic hydrogenation of these materials are included. Equally acceptable results were obtained by another analyst, previously unfamiliar with the determination of iodine values by this method, using this procedure. Furthermore good agreement was found between hydrogen-iodine values obtained by catalytic quantitative hydrogenation and iodine values obtained by this procedure with various samples of partially hydrogenated tung oil, one of which contained as much as 14% of conjugated dienoic acid.

On the basis of these results the following method for the determination of the iodine value of tung oil and of eleostearic acid is suggested.

Reagents

a) Rosenmund-Kuhnhenn reagent: This may be prepared as described by Benham and Klee (1). "Place 40 ml. of C. P. glacial acetic acid in each of three Pyrex Erlenmeyer flasks. To the first add slowly 28.4 ± 0.2 g. of C. P. pyridine, with cooling. To the second

TABLE II

Comparison of Iodine Values Obtained by Different Methods

Sample	Excess of reagent[a] %	Value	Catalytic hydrogenation value
Tung oil, domestic	222	231.9	232.3
	222	232.2	
Tung oil, Chinese	240	228.7	227.9
	259	228.6	
	266	228.1	
Tung oil, Chinese (3-5 yrs. old)	188	224.3	228.6
	298	225.9	
Tung oil, Nyasaland *(A. montana)*	260	215.9	216.0
	260	219.4	
	291	215.4	
Tung oil, isomerized (β)	235	230.7	229.2
	269	230.9	
	319	230.8	
α-Eleostearic acid, 100%	208	272.8	272.8
	243	274.4	
	247	272.3	
β-Eleostearic acid, 98%	216	273.2	270.2
	230	270.5	
	230	274.7	

[a] 100 (B-S) S, where B and S represent the volumes of thiosulfate solution used for blank and sample titrations, respectively.

flask add slowly 35.5 ± 0.2 g. of C. P. concentrated sulfuric acid, with cooling. When cool, add the contents of the second flask to the contents of the first flask, with further cooling. To the third flask add the contents of a 1-oz. bottle of C. P. bromine (28.35 g.). Add this latter solution to the mixture of the first two solutions and make up to one liter with C. P. glacial acetic acid. Mix thoroughly and transfer to a 4-liter amber bottle with a screw stopper. Add a further 2,500 ml. of C. P. glacial acetic acid, making a total of 3,500 ml. of reagent. In this way the weighing or measuring of bromine is eliminated. The reagent is approximately 0.1N with respect to bromine."

b) Mercuric acetate solution: Dissolve 25 g. of C. P. mercuric acetate in C. P. glacial acetic acid and dilute to 1 liter with C. P. glacial acetic acid.

c) Potassium iodide solution: Dissolve 150 g. of KI, free of KIO_3 in distilled water and dilute to 1 liter with water.

d) Starch indicator solution: This may be prepared in the same way as that used for A.O.C.S. Tentative Method Ka 9-51. "Make a homogeneous paste of 10 g. of soluble starch in cold distilled water. Add to this 1 liter of boiling distilled water, stir rapidly and cool. Salicylic acid (1.25 g. per liter) may be added to preserve the indicator."

e) Standard sodium thiosulfate solution (0.1N): Dissolve 24.89 g. of A.C.S. grade $Na_2S_2O_3 \cdot 5H_2O$ in distilled water that has been well boiled to free it from CO_2 and dilute to 1 liter with boiled distilled water. This solution will be approximately 0.1N, but it should be standardized by an approved method.

f) Carbon tetrachloride: A.C.S. grade.

Analytical Procedure

To a 250-ml. glass-stoppered low-actinic (red) flask add 5 ml. carbon tetrachloride. In this dissolve 75 to 85 mg. of tung oil weighed to 0.1 mg.[3] If several samples are to be run they should not all be weighed out at once in a series, but each sample weighed out should be treated with the Rosenmand-Kuhnhenn reagent before the next sample is weighed. Make sure that the sample is completely dissolved, and then in a darkened room (light intensity preferably less than 0.5 foot-candle) pipette into the flask 10 ml. of the solution of mercuric acetate in acetic acid. Swirl the flask 2 or 3 times and then add exactly 50 ml. of Rosenmund-Kuhnhenn reagent. The flask should be kept partly covered while the pipette is draining, and the stock bottle containing the Rosenmund-Kuhnhenn reagent should be kept stoppered when it is not in use to minimize loss of bromine. Fresh reagent should be prepared if the concentration drops below 0.09N with respect to bromine. Moisten the stopper with the potassium iodide solution, stopper the flask, swirl it until the solutions are well mixed (2 or 3 seconds), and put the flask away immediately in a very dark place, *e.g.*, in a closed cupboard, at a temperature of 23 to 27°C. After one hour bring the flask out into the darkened laboratory, add 20 ml. of the potassium iodide solution by pipette, swirl 2 or 3 times, add 20 ml. of distilled water, swirl again, stopper the flask, and allow it to stand for one minute. Then, using normal illumination, rinse the stopper and the neck of the flask with about 10 ml. of distilled water and titrate the released iodine with 0.1N sodium thiosulfate as follows: From a 50-ml. burette add rapidly with continuous agitation all but 5 to 10 ml. (about 25 to 30 ml.) of the required thiosulfate solution to the low-actinic flask. Then transfer the contents of the low-actinic flask to a colorless flask, rinsing 3 times with a total of about 30 ml. of distilled water. Complete the titration in the colorless flask in the usual manner using starch indicator when near the end point.

With each group of samples conduct at least two blank determinations exactly as described above except that no oil is added and in the titration about 40 to 45 ml. of thiosulfate is run into the low-actinic flask before the solution is transferred to a colorless flask.

Calculations

The iodine value is calculated as follows:

$$\text{Iodine value} = \frac{(B-S)\,(N \times 12.69)}{W}$$

B = ml. of thiosulfate used for the blank.

S = ml. of thiosulfate used for the sample.

N = Normality of the thiosulfate.

W = Sample weight in grams.

Summary

A new modification of the Rosenmund-Kuhnhenn method has been developed for determining the total ethylenic unsaturation of tung oil and of eleostearic acids. With tung oils this method results in iodine values which are in agreement with those obtained by quantitative catalytic hydrogenation and, in the case of α- and β-eleostearic acids, with the theoretical value. Good agreement was found with hydrogen-iodine values of various partially hydrogenated tung oils. An essential feature of the method is the addition of mercuric acetate to the oil prior to the addition of the Rosenmund-Kuhnhenn reagent in contrast to the Benham-Klee modification in which the Rosenmund-Kuhnhenn reagent is added first. The latter method gives iodine values for tung oil and for eleostearic acid approximately 8% higher than those obtained by quantitative catalytic hydrogenation. Light was found to affect the results obtained by both methods so greatly that use of low-actinic flasks, addition of the Rosenmund-Kuhnhenn reagent in a partially darkened room, and storage of the reactants in complete darkness during the reaction period (1 hour) is recommended.

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[3] With a normal tung oil this will result in a 200 to 250% excess of the Rosenmund-Kuhnhenn reagent. If pure eleostearic acid is used the sample size should be reduced to 65 to 75 milligrams. In the case of partially hydrogenated tung oils the sample size should be increased so as to provide a 200 to 250% excess of Rosenmund-Kuhnhenn reagent.