

The procedure as described appears to separate all of the oxygenated derivatives of autoxidation from the unoxidized esters. Whether the oxidized fraction consisted almost entirely of monohydroperoxides as in the autoxidized methyl linoleate or contained a large proportion of secondary reaction products as in the autoxidized methyl oleate and linolenate, it was all separated in the alcoholic phases.

Semi-automatic extraction equipment of the Craig type can also be employed for the separation of the oxidized and unoxidized fractions of autoxidized fatty esters, but their value is limited by their small capacities and the relatively low concentration of materials that must be used.

### Summary

Details of a countercurrent extraction procedure for the quantitative separation of the oxidized and unoxidized fractions of autoxidized fatty acid esters is described.

The utility of the process is demonstrated by the quantitative separation of the oxidized from the unoxidized fractions of autoxidized methyl linoleate, linolenate, and oleate.

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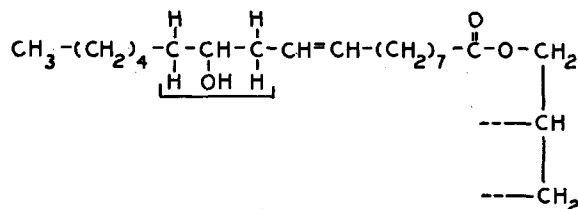
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## Alternative Methods for Dehydrating Castor Oil<sup>1</sup>

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THE importance of dehydrated castor oil in coatings is shown by an annual consumption of some 30,000,000 lbs., which is about 5-6% of all drying oils used in coatings (8). Actually this oil is somewhat more important than the 5% figure indicates because its properties, which are intermediate to those of highly conjugated tung oil and non-conjugated linseed oil, make it especially valuable. Its use would undoubtedly increase if greater quantities were available at lower cost.

Castor oil is a unique non-drying oil in that it can be readily converted to a drying oil by the chemical reaction of dehydration:



This transformation of the ricinoleic acid groups to isomeric octadecadienoic acid groups is analogous, in its simplest terms, to the formation of propylene from isopropyl alcohol.

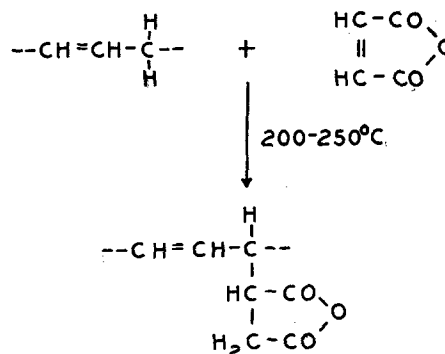
From the extensive literature on dehydrating methods which consist of several hundred patents and journal articles (20), there appear to be four important considerations, in addition to the factor of processing cost: a) the dehydration reaction must be substantially complete to obtain an oil of good drying and film properties; b) the competitive reaction of polymerization or heat bodying must be controlled to avoid a viscous or even gelled product; c) catalysts for the dehydration must either be innocuous if left

in the oil or readily removable; and d) an increase in the amount of two double bond conjugation over the 20-30% usually obtained would be desirable. With these factors in mind several new dehydration methods have been studied.

### Dehydration by Oil-Maleic Adducts

The first of these dehydration methods is a variation of a method described earlier in which castor oil is heated with a quantity of phthalic anhydride insufficient to esterify all of the alcoholic hydroxyl groups (4). At the end of the reaction period there is free phthalic anhydride (or acid) which can be removed by filtration or esterified by a polyalcohol. Our development consists in the use of the addition compound from maleic anhydride and a non-conjugated oil, such as linseed or soya as the acid anhydride. The product then consists of dehydrated castor oil and a maleinized drying oil which need not be separated because it contributes valuably to film formation.

The reaction of maleic anhydride with non-conjugated oils at temperatures of about 200°C. is well known in the coatings industry (6). The most probable course of this reaction is as follows:



<sup>1</sup> Presented before the American Oil Chemists' Society, Houston, Tex., April 29, 1952.

The process is one of addition in which a methylene group adjacent to a double bond in the unsaturated fatty acids of linseed oil, for example, adds to the double bond of maleic anhydride so that a hydrogen atom goes to one carbon atom and the fatty acid radical to the other carbon. The product shown schematically is thus an alkyl succinic anhydride. The earlier literature suggests other structures, but this seems to be well established (17).

This maleic adduct provides a high molecular weight, non-volatile acid anhydride. When such a product is added to castor oil and the mixture heated at 275-300°C., the castor oil is effectively dehydrated.

**Typical Procedure.** The reaction between castor oil and an equal weight of a linseed oil-maleic anhydride adduct, which contains 5% of anhydride with respect to a linseed oil, is typical of the process. In a 3-l. three-necked flask fitted with a Glascol heater, stirrer, thermometer, and nitrogen inlet tube reaching to the surface of the reaction mixture was placed 612.5 g. of alkali refined linseed oil. This was heated to 225°C., and a well mixed slurry of 37.5 g. of maleic anhydride and 100 g. of linseed oil was slowly added. The temperature was raised to 250° and held until all the maleic anhydride had reacted. This was determined by removing 1-2 g. of the oil, washing well with water in a separatory funnel and titrating the aqueous layer with standard base for maleic acid. The reaction time at 250° is 15-30 minutes.

The temperature was then brought to 275°, and 750 g. of No. 3 grade castor oil was added. At the end of 2 hours the temperature was increased to 300°. Samples were removed at various time intervals and examined for viscosity, color, etc., as shown in Table I and Figure 1.

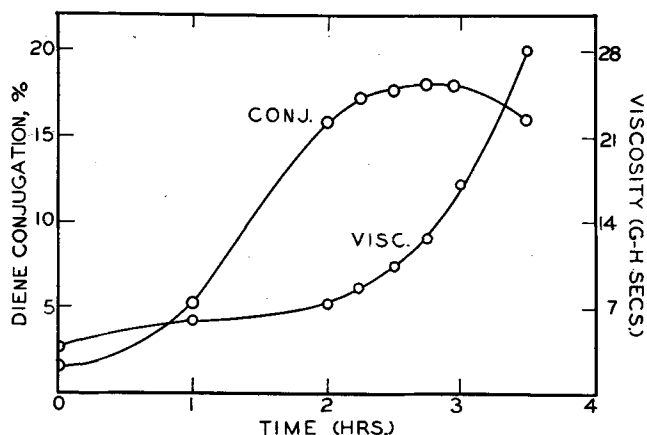


FIG. 1. Dehydration of castor oil at 275-300°C. with an equal weight of linseed-maleic adduct (5% maleic).

**Discussion.** It will be noted from Figure 1 that the two double bond conjugation reaches a maximum of about 18% in 3 hours and then decreases as polymerization proceeds. At 3 hours the dehydration is substantially complete as shown by the hydroxyl content of 0.2% (Table I). The maximum in iodine value of 128 is reached before this 3-hour point. This is probably due to the bodying reaction, which is usually accompanied by an early decrease in iodine value with respect to the viscosity increase. The 18% conjugation is somewhat higher than one would expect on the basis of about 50% of dehydrated castor oil in the mixture. The maleic adduct contributes only 1.6% to this value.

The property of rapid bodying is shown further by the Browne gel test (11) run at 305°, which requires 50-60 minutes for this product, 40 minutes for a commercial dehydrated castor oil of 98 seconds viscosity, and more than 300 minutes for an alkali refined linseed oil.

The dehydrating action of the maleic anhydride compound is shown by a model experiment in which a mixture of equal weights of castor and linseed oils was heated at 300° for 6.25 hours. The maximum conjugation during that period was only about 10%.

The variables considered in this dehydration method were a) temperature, b) time, c) concentration of maleic anhydride in the non-conjugated oil and in the whole mixture, d) the non-conjugated oil, and e) replacement of maleic anhydride by fumaric acid.

Temperature and time are complementary variables. At higher reaction temperatures the time required decreases. In general, temperatures below 275° give incompletely dehydrated mixtures of high viscosity. The optimal temperature is 275-300°. The reaction time depends not only on temperature but also on the amount of combined maleic anhydride present. The rate of dehydration increases with the concentration of maleic anhydride up to the point where there is sufficient anhydride (calculated as dibasic) to esterify all of the hydroxyl groups. Very likely the rate continues to increase at still higher concentrations, possibly to the point where there is one mole of anhydride for the hydroxyl, but this was not established. In the experiment described the 2.5% of combined maleic is less than one-half the theoretical amount for complete esterification.

The desired amount of maleic anhydride can be obtained either by varying the quantity combined with the non-conjugated oil or by varying the amount of adduct added to the castor oil. In the case of linseed oil the maximum amount of anhydride that can be reacted with it is not less than 33% by weight. One part of a 30% adduct, for example, with 11 parts

TABLE I  
Dehydration of Castor Oil (750 g.) with Linseed-Maleic Anhydride (750 g., 5% Maleic)

Sample	Hrs.	Temp. <sup>a</sup> °C.	Visc., Secs. <sup>b</sup>	Color <sup>c</sup>	Acid No. (2)	I. No. (3)	% OH (10)	% Diene Conj. <sup>d</sup>	n <sub>D</sub> <sup>20</sup>
1.....	0	275	3.9	6	15.2	124	2.25	1.6	1.4829
2.....	1	275	6.3	6	17.4	124	2.10	5.3	1.4833
3.....	2	300	7.2	7	26.6	128	1.13	15.9	1.4855
4.....	2.25	300	8.6	7	27.4	126.5	0.82	17.4	1.4867
5.....	2.5	300	10.4	7	28.3	123.5	0.55	17.8	1.4873
6.....	2.75	300	12.6	7	28.8	120	0.46	18.1	1.4882
7.....	3	300	17.0	7	29.2	117.5	0.20	18.0	1.4889
8.....	3.5	300	28.0	8	28.8	114	0.10	16.2	1.4894

<sup>a</sup> The temperature was held within  $\pm 2^\circ$  by a variable transformer.

<sup>b</sup> Gardner-Holdt, 25°C.

<sup>c</sup> Gardner-Holdt scale.

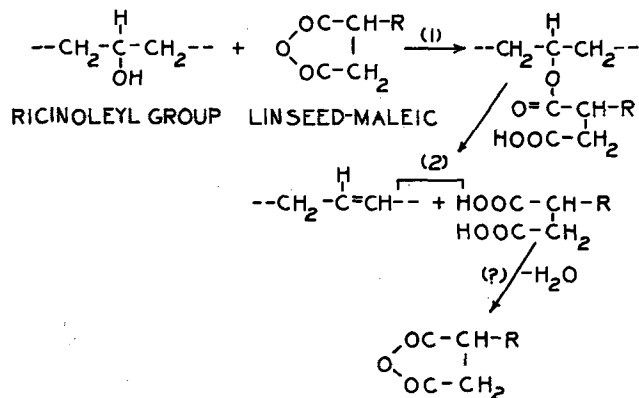
<sup>d</sup> Determined in Phillips Petroleum spectrographic grade of iso-octane in a Beckman Model DU ultraviolet spectrophotometer; (ref. 21).

of castor oil would give a mixture containing 2.5% of anhydride, but the high castor oil/anhydride ratio, as compared with the experiment described, would result in a slower rate of dehydration. To maintain the same rate of dehydration three parts of castor oil and one part of 30% adduct, which makes the anhydride concentration 7.5%, would have to be taken.

Besides castor oil the second oil may be varied widely within the requirements that it be capable of reacting with maleic anhydride and that its presence in the final product be desirable. Soybean and various fish oils have been used.

In place of maleic anhydride, fumaric acid can be combined with the second oil and this adduct used to dehydrate the castor oil. From a limited comparison of a linseed-maleic adduct with a linseed-fumaric adduct, it appears that the maleic compound gives more rapid dehydration.

**Reactions.** The reactions which probably occur when a linseed-maleic compound dehydrates castor oil are as follows:



The initial reaction (1) must be a fairly rapid esterification of the combined maleic anhydride with the ricinoleyl groups to form the acid-ester. This acid-ester might esterify another ricinoleyl group or, more likely, it thermally decomposes according to equation (2) with the removal of a hydrogen from the ricinoleic acid portion, and the formation of a new double bond. This decomposition of castor oil esters occurs with the acetate and other esters (12). The other product is the maleic adduct, not in the form of the anhydride, but in the form of a dibasic acid. This dibasic acid is then available for further esterification of hydroxyl groups, followed by decomposition, or it might be dehydrated to the anhydride adduct which then could be esterified. Either as the acid or the anhydride, the adduct is thus regenerated for subsequent reaction. At the end of the process the castor oil is substantially completely dehydrated and the linseed-maleic adduct is present either in the form of the anhydride or the acid. Data on the change in acid number with time (Table I) indicates that the final product contains more of the dibasic acid than it does of the anhydride. The acid value of the starting mixture measured in benzene-alcohol by the usual procedure (2) is 15.2 or about one-half of the calculated value of 28.6 (19). At the end of 3.5 hours in the dehydration reaction the acid value is 28.8. The close check may be fortuitous since cracking of the glycerides has undoubtedly formed some free acids.

The possibility that the dehydration may be catalyzed by the maleic acid adduct has been considered,

but it is probably too weak an acid to have any appreciable catalytic action. The acidity here might be roughly indicated by the dissociation constants for succinic acid:  $\text{pK}_{a_1}$  4.17,  $\text{pK}_{a_2}$  5.64.

There appear to be some advantages of this method of dehydration over the conventional use of catalysts. By dehydration of castor oil in the course of making a product, instead of starting with dehydrated castor oil itself, the operation should be more economical. Furthermore the process is highly flexible in producing a wide range of mixtures containing dehydrated castor oil and a maleic-treated oil for use in coatings or other products. Subsequent steps of esterification or alcoholysis could be most advantageously taken directly in the reaction kettle where the maleic compound and dehydration were done.<sup>2</sup>

Related to this dehydration process is the making of dehydrated castor oil alkyds directly from castor oil *via* the dehydrating action of phthalic anhydride or its derivatives. According to reports on the German chemical industries (9), this process was widely used there, and improvements have been made in this country (7). In a typical preparation castor oil and glycerol were heated to 150°C., phthalic anhydride added, and the mixture brought to 250° for 6-8 hours until the proper viscosity and acid value were obtained. Gelation was avoided by rapid heating from 150 to 250°. Reactions of alcoholysis, esterification, and ester interchange must occur here along with dehydration by decomposition of intermediate phthalate esters of the ricinoleic acid groups.

#### Dehydration of Castor Acids

This work is based on the publications and patents of Scheiber and others (5, 18), who claim that dehydrated acids with 70-90% of conjugation can be made, in contrast with 20-30% found in dehydrated oils (13, 16). As far as we know, these claims have not been substantiated in this country (20). After preliminary experiments based on Scheiber's United States patent (18), dehydrated acids in about 80% of the theoretical yield containing 60% of two double bond conjugated isomers were obtained. The steps in this process are as follows:

**Procedure.** First, castor oil (No. 1 grade) was saponified in the usual way to give castor acids. Next these acids [Neut. Eq. 299.5; calculated for ricinoleic acid, 298.5; percentage of hydroxyl 5.02 (10); calculated, 5.7] were heated with 10% by weight of 4-8 mesh activated alumina (Harshaw Chemical) for 3.5 hours at a temperature of 225°C. while nitrogen was bubbled through to agitate the mixture and remove water. In the third step the acids were vacuum-distilled at 200-220°C. at about 1 mm. pressure. The pot temperature during distillation was 290-310°. This vacuum distillation was very slow, in fact, much slower than the usual distillation of 18 carbon atom fatty acids. This indicated that the acids as such were not present in the product obtained on heating with alumina but were being formed by thermal decomposition.

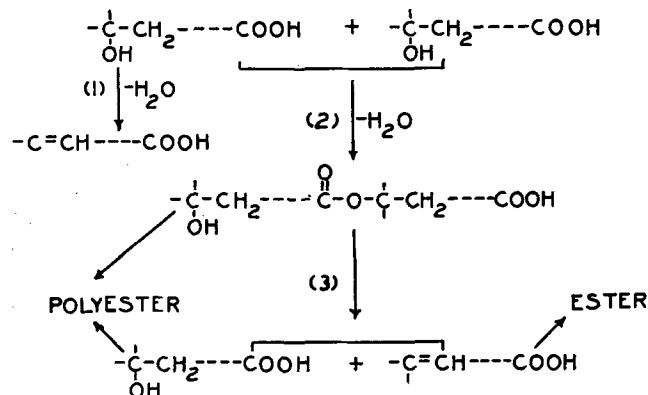
Starting with 1,300 g. of castor acids and 130 g. of alumina in a 2-l. Claisen flask, the yield of distilled product after 4.5 hours of distillation was 958 g., 80% of the theoretical, neutral equivalent 302, cal-

<sup>2</sup>Patent protection is being sought on the general process described here.

culated for octadecadienoic acids, 280.5; % conjugation, 60; Gardner-Holdt color, 5-6.

**Discussion.** The key step in preparing these highly conjugated acids is the catalytic action of alumina at 225° prior to distillation. Possibly this step had been overlooked in previous attempts to duplicate the work of Scheiber. At lower temperatures or shorter times the yield of acids is small, and the concentration of conjugated isomers is low. Without alumina the vacuum distillation step gives practically no distillate and the acids gel. Of the various other catalysts mentioned (18) only silica gel was tried, and it appeared to be less effective than alumina.

The following reactions are believed to occur:<sup>3</sup>



When the acids are heated with alumina, two main reactions are possible. By reaction 1 there is direct dehydration to octadecadienoic acids, and by reaction 2 there is esterification or estolide formation to form linear polyesters from ricinoleic acid. Reaction 3 shows the formation of the new double bond by decomposition of the ester which eliminates the acyloxy group and a hydrogen atom, thus regenerating the acid. Very probably most of the dehydration goes by this route since the vacuum distillation is so slow.

There is no obvious explanation for the formation of highly conjugated dehydrated acids under these conditions. No specific literature reference to the action of an alumina catalyst on castor oil itself was found, but all methods of dehydrating the oil appear to give the usual 20-30% yield of conjugated product (20). Dehydration *via* an intermediate castor oil ester such as the acetate again gives only 20-30% of conjugation (12). Furthermore the action of the alumina is not one of isomerizing non-conjugated acids to conjugated. This was demonstrated by a model experiment in which ordinary dehydrated acids (Baker Castor Oil's 9-11 Acids, 31.4% conjugated) were put through this process starting with the step in which the acids are heated with alumina. There was no significant increase in two double bond conjugation.

Possibly the alumina catalyzes the isomerization of the intermediate ester prior to decomposition, either by shifting the 9,10 double bond or the ester group or both. To test this explanation it would be necessary to determine the diene structure of the dehydrated acids. Recent work shows the presence of a small amount of the 8,10 isomer in addition to the 9,11 acid (15).

With respect to the configuration of these acids, an infrared examination by D. H. Wheeler and Mr. Tol-

<sup>3</sup>For simplicity the new double bond formed here is shown in one position only. It actually could be at either the 11,12 or 12,13 carbons in the chain.

berg of the Research Department of General Mills Inc. indicated that the conjugated acids present were largely *cis*, *trans*. Thus the new double bond formed by the dehydration is mostly *trans*.

**Glyceride Properties.** The acids of 60% conjugation were redistilled and the fraction boiling 208-211°/1 mm. was collected; the neutral equivalent was 281; % hydroxyl, 0; % conjugation, 56.7; iodine number (14), 185; Gardner-Holdt color, 1-2; calculated neutral equivalent for octadecadienoic acids, 280.5; calculated iodine number, 181. These acids were converted to the glyceride by esterification with glycerol in the presence of *p*-toluenesulfonic acid as a catalyst and xylene as the co-distilling solvent. The product was washed with water, dried, and the properties listed in Table II noted. For comparison a typical commercial oil, Spencer Kellogg's Synthenol, was also analyzed.

TABLE II  
Properties of Synthetic Glyceride and Synthenol

	Syn. Gly.	Spencer Kellogg's Synthenol
% Diene conjugation <sup>a</sup> .....	52	26
Iodine No. (total) (14).....	183 <sup>b</sup>	156
Acetyl No. (1).....	5	28
Acid No. (2).....	10.6	4.8
Viscosity (G-H secs., 25°C.).....	1.8	2.6
$n_D^{20}$ .....	1.4868	1.4820
Color (Gardner-Holdt).....	10	5
Dry-to-touch.....	30 min.	120 min.
Relative tack: <sup>c</sup>		
24 hrs.....	Some	More
48 hrs.....	Free	Some
72 hrs.....	Free	Free
Water resistance (100°C., 1.5 hrs.) <sup>d</sup> .....	Cloudy	Cloudy
Alkali resistance (1% NaOH) <sup>e</sup> .....	1-2 min.	1-2 min.
Soap resistance (1% Na oleate) <sup>e</sup> .....	1 hr.	1 hr.

<sup>a</sup>Determined in Phillips Petroleum spectrographic grade of iso-octane in a Beckman Model DU ultraviolet spectrophotometer; (ref. 21).

<sup>b</sup>The calculated iodine number for glyceryl trioctadecadienoate is 174. There is no apparent explanation for the high value found here or for the acids used in the preparation of the glyceride.

<sup>c</sup>Determined on 0.003 in. thick films on tin test panels with 0.2% lead and 0.02% cobalt naphthenates as driers by a finger test.

<sup>d</sup>The films were intact but remained cloudy after 24 hours.

<sup>e</sup>Times required for the films to fail.

Noteworthy properties of the synthetic glyceride are the relatively high values for conjugation and iodine number and the low value for the acetyl number.

The results of a rough comparison of film properties of the two oils are given in Table II. The highly conjugated glyceride dried noticeably faster and became tack-free in considerably less time. Like other highly conjugated oils it formed a wrinkle film. There was no significant difference between the two films in water, alkali, and soap resistance.

While the acids and glyceride obtained here had 60 and 52% conjugation, respectively, it was quite possible that further study of the conditions of preparation would yield the 70-90% conjugation described by Scheiber (18).

#### Dehydration by Cation Exchange Resins

A few exploratory experiments in the use of cation exchange resins, in the acid form, as dehydration catalysts have been carried out. The resins used were Dow Chemical's Dowex 50, a sulfonated styrene copolymer, and Rohm and Haas' Amberlite IR-120, which is also a sulfonated resin. In a typical experiment a mixture of castor oil and 5% by weight of Dowex 50 was heated at 225°C. in a three-necked flask with agitation and a current of nitrogen. The

rate of dehydration under these conditions was slow: at the end of 13 hours the acetyl number of 75 indicated that the oil was about 50% dehydrated. The two double bond conjugation in this partly dehydrated oil was 9.6% or, on the basis of complete dehydration, 19.2%.

Higher reaction temperatures were tried although the resins were not entirely stable. At 275° with 5% of Dowex 50 castor oil was 93% dehydrated (by acetyl number) in 10 hours. The conjugation was disappointingly low: 17.4% , and the color of the oil was more than 18 (G-H). The film properties, compared to Synthenol, were generally inferior with respect to drying time, tack, and resistance to water, alkali, and soap.

### Summary

Castor oil can be effectively dehydrated by non-conjugated oil-maleic anhydride adducts to give useful paint or varnish oils. Castor acids dehydrated in the presence of alumina form diene acids of 60% two double bond conjugation. The glyceride from these acids dries more rapidly to a tack-free film than conventional dehydrated castor oil. In both of these processes the course of dehydration is believed to be the decomposition of esters of the alcohol groups in ricinoleic acid. Acidic ion exchange resins exert some catalytic effect in the dehydration of castor oil, but the oil so made is inferior in color and film properties.

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## Studies of Waxes. VI. The n-Acids of Carnauba Wax

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THE extensive early investigations of the constituent acids of carnauba wax have been reviewed by Koonce and Brown (1). They concluded that in the light of present knowledge none of the acids previously isolated could be considered pure although Bowers and Uhl (2) had more recently isolated arachidic acid, estimated to be 97 mole-% pure. Koonce and Brown (3) have since reported that the most abundant normal acid is tetracosanoic acid, which they isolated in a purity of more than 95%. They agreed with the evidence of Bowers and Uhl that the n-acids ranged from C<sub>18</sub> to C<sub>30</sub>.

This paper describes the isolation by the amplified distillation method of Weitkamp (4) of the n-acids of even carbon number C<sub>18</sub> to C<sub>30</sub> in a state of sufficiently high purity for their sure identification.

### Preparation of the Mixed n-Methyl Esters

The crude carnauba wax acids were obtained during an earlier investigation of the wax alcohols (5). They had an acid equivalent of 521 and melted from 75.5-78.0°C. The acids (80.0 g.) were methylated by refluxing for 20 hours with 1:1 methanol-benzene (1 l.) containing 1% H<sub>2</sub>SO<sub>4</sub>, the reflux passing through a Soxhlet extractor containing anhydrous MgSO<sub>4</sub> to remove azeotropically entrained water (6). On dilution with water (1.5 l.) and warming to 55°C., the

separated benzene layer containing the esters was washed repeatedly with warm water until free of H<sub>2</sub>SO<sub>4</sub>. The methyl esters recovered from solution weighed 78.7 g. and melted from 73.0-76.5°C. The acid number was 1.2, indicating approximately 1% unesterified acids.

A large difference between the saponification number of these esters (127) and their saponification number after acetylation (164) indicated the presence of a considerable amount of hydroxylated esters. These were separated from the n-esters by adsorption on alumina: 30.0 g. of the crude esters dissolved in 180 ml. of warm light petroleum (60-80°C., aromatic-free), were adsorbed on a column of neutral alumina<sup>2</sup> (600 g.) kept at 50°C. by an electrically wound jacket. The n-esters were completely eluted from the column with more light petroleum (1 l.). They weighed 11.2 g. (37.9% of the total<sup>3</sup>), melted from 57-65°C., and had a saponification number of 151. Further elution with benzene-ethanol, toluene-ethanol, and chloroform-acetic acid mixtures yielded the higher melting hydroxy esters with a total recovery of 99.3%. The investigation of these mixed hydroxy esters and the

<sup>2</sup>Prepared from chromatographic alumina from British Drug Houses Ltd., London by warming with 2% HNO<sub>3</sub> and washing by decantation with distilled water until the washings were free from acid. It was then dried at 105°C., heated to 500°C. for 5 hrs., and partially deactivated by keeping over water in a closed vessel for 30 hrs., when it had the desired activity of III/IV determined by the method of Brockmann and Schodder [*Ber.* 74, 73 (1941)].

<sup>3</sup>A trial chromatogram on the same sample gave a percentage of the n-esters of 39.4%.

<sup>1</sup>Part V of this series: The Aliphatic Alcohols of Wood Wax, by K. E. Murray and R. Schoenfeld, *J. Am. Oil Chem. Soc.*, 29, 416-420 (1952);