

# A Study of the Alcohols of Carnauba Wax

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Previous researches on the alcohols of carnauba wax have been reviewed in the preceding paper (3). Summarizing briefly, several investigators have claimed the isolation of ceryl alcohol ( $C_{26}$ ) and melissyl alcohol ( $C_{30}$ ), and one worker has claimed to have isolated a di-hydroxy alcohol ( $C_{25}$ ). None of these compounds was pure, but, rather, each was a mixture of close homologs. More recently, evidence has been brought forward which indicates the presence of the  $C_{32}$ ,  $C_{34}$ , and  $C_{36}$  alcohols in the wax.

For the most part, the investigators who claimed isolation of pure alcohols used fractional crystallization to separate one alcohol from another. It has been found, as we have shown below, that this method is inadequate for this purpose. Other investigators have attempted separation of the alcohols by fractional distillation of their acetates in vacuo, but this method also did not yield pure compounds. As described below, the purest alcohols yet prepared from carnauba wax have been isolated by fractional distillation of the free alcohols themselves. So far as the authors know, this is the first such successful fractional distillation.

## Preparation of Crude Wax Alcohols

Four hundred grams of No. 3 Chalky carnauba wax<sup>3</sup> were dissolved in 500 cc. of toluene by heating on a steam bath. One hundred forty grams of KOH were dissolved in 2000 cc. of 95 per cent ethyl alcohol, and this solution was added to the solution of wax. The combined solutions were refluxed on the steam bath for 19 hours. At the end of this period the alcohol and toluene were distilled off, and the residue was heated on the steam bath for 48 hours. The resulting hard cake was powdered in a ball mill, and extracted with ethyl ether in a modified Soxhlet extractor (1) for 475 hours. Two hundred sixteen grams of crude alcohols—54 per cent of the original weight of wax—were thus obtained. These alcohols had a melting point of 84-89°, a saponification number of 0, and a neutral equivalent of 0.

## Fractional Crystallization of Alcohols

Two hundred eighty grams of alcohols were prepared in the above manner, and subjected to fractional crystallization as shown in Chart I.

The precipitates in Chart I are designated by the letter P followed by the numbers which identify them in the fractionation, thus, P-1, P-1<sub>2</sub>, P-2<sub>1</sub>, P-2<sub>2</sub>, etc. The filtrates were similarly designated as F followed by the appropriate numbers. All melting points (m.p.), resolidification points (r.p.), and re-melting points (r.m.p.) are corrected values. Each precipitate was heated at 60° to constant weight before its melting point was determined.

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Since the melting point of P-6<sub>1</sub> was almost the same as that of the preceding corresponding fractions, no further change seemed possible by this method. Samples of P-6<sub>1</sub> were then re-crystallized from ten per cent solutions of the solvents listed in Table I below:

TABLE I.  
Recrystallization of Fraction P-6<sub>1</sub> From Various Solvents

Solvent	M.P.°C.	R.P.°C.	R.M.P.°C.
Toluene.....	86.4-86.8	85.8-85.2	86.5-86.8
Skellysolve B.....	86.5-86.8	85.8-85.6	86.4-86.7
Chloroform.....		86.0	86.6-87.0
Trichloroethylene.....	86.6-86.8	85.9-85.5	86.6-86.8

On the basis of melting point, P-6<sub>1</sub> was homogeneous, and corresponded to that of the product which previous investigators have termed melissyl alcohol. On the same basis, P-5<sub>3</sub> probably would have been termed ceryl alcohol. In order to verify these conclusions, these two compounds were subjected to the analytical method of Piper and co-workers (5) except that no crystal spacings were measured. The necessary derivatives were prepared by the methods described later under the isolation of wax alcohols by fractional distillation. The melting points of the fractions and their derivatives are shown in Table II below:

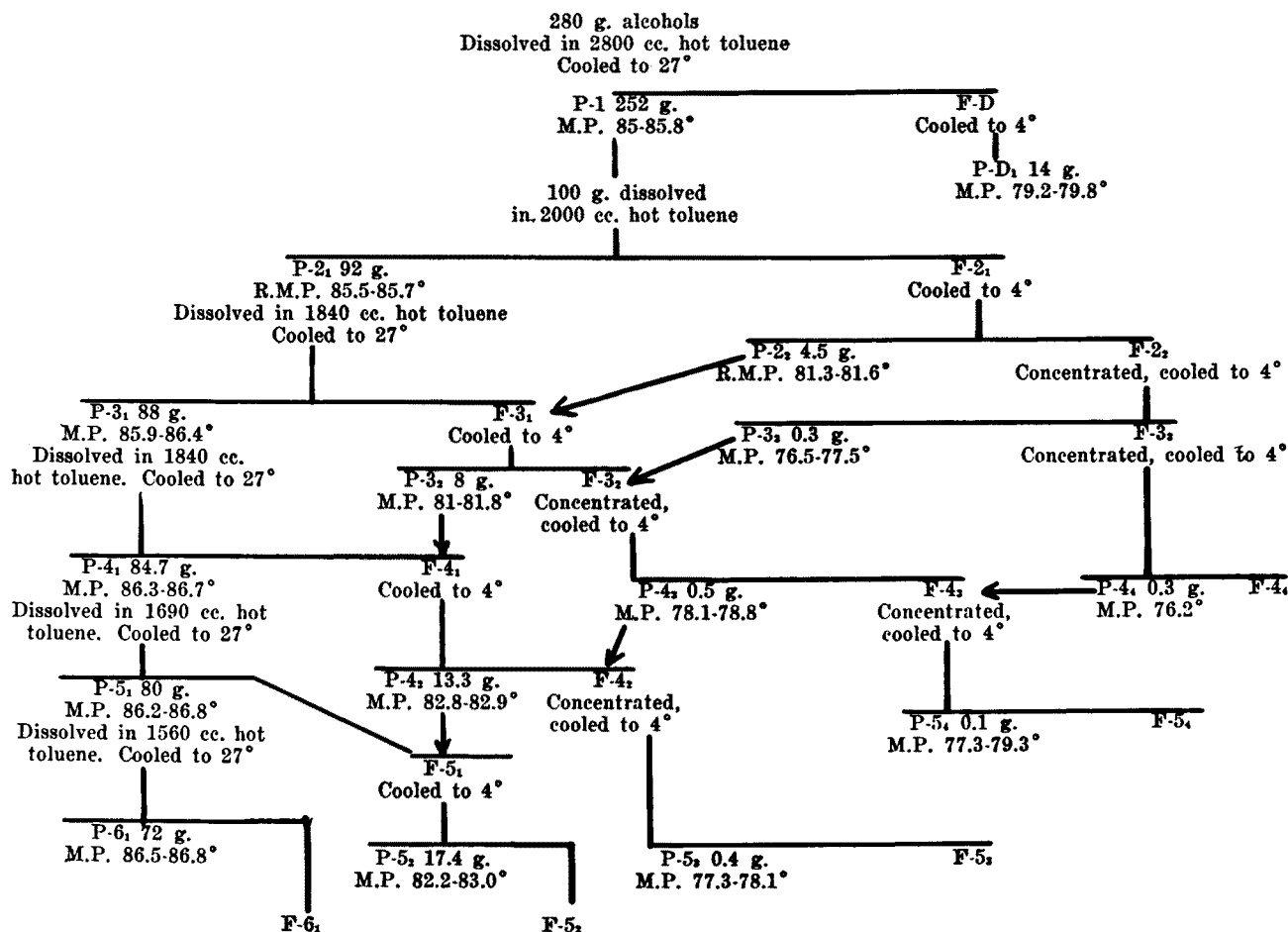
TABLE II.  
Summary of Fractions P-6<sub>1</sub> and P-5<sub>3</sub>

Fraction	Alcohol		Acid		Ester
	M.P.°C.	R.P.°C.	M.P.°C.	R.P.°C.	M.P.°C.
P-6 <sub>1</sub>	86.4-86.8	85.8	90.8-91.0	90.0	71.6-72.3
P-5 <sub>3</sub>	77.3-78.1	77.2	84.5-84.8	84.2	68.3-68.6

Comparing these constants with those of Piper and co-workers which appear in Table V, it is seen that although the melting point of P-6<sub>1</sub> is almost identical with that of the  $C_{30}$  alcohol, the melting point of its derived acid is only 4° higher. According to Pollard (6) this indicates that the original alcohol was not pure. Fitting the melting points of the alcohol and the derived acid to the curves described by Piper (5), it is found that P-6<sub>1</sub> is an approximately 50:50 mixture of the  $C_{30}$  and  $C_{32}$  alcohols plus a trace of higher homologs as shown by the high melting point of the ethyl ester of the acid. This mixture is not surprising in view of the finding, described below, that the  $C_{32}$  alcohol is even more abundant in the wax than is the  $C_{30}$  alcohol.

It is further seen that the melting point of P-5<sub>3</sub> is 2° lower than that of the  $C_{26}$  alcohol. Moreover, the melting point of the acid derived from P-5<sub>3</sub> is approximately 7° higher than the melting point of P-5<sub>3</sub> itself which would indicate that this fraction should be quite pure. However, the melting point of the ethyl ester of the derived acid is approximately 8° above that of the ethyl ester of the  $C_{26}$  acid, which indicates that the original alcohol was not pure. Therefore, P-5<sub>3</sub> fits no simple pattern, and while it may contain some of the  $C_{26}$  alcohol, it is not pure but is a complex mixture.

CHART I  
Fractional Crystallization of Wax Alcohols



Since a 50:50 mixture of alcohols was the purest compound obtainable by fractional crystallization, this is not an adequate method for the isolation of high molecular weight alcohols from the wax. Therefore, the lack of agreement among the workers who depended solely upon this method is not surprising.

#### Separation of Wax Alcohols by Fractional Distillation

*Description of Apparatus.* The distillation apparatus was an electrically heated and glass helices packed column similar to that described by Longenecker (4). It consisted of a distillation column, 51 cm. in length and 2.5 cm. in diameter. The column was heated externally by means of two nichrome wire coils each of which covered one-half the length of the column. It was thus possible to control independently the temperature of each half of the column. The 500 cc. still pot, fitted with a thermometer well, was heated by means of an electric heating mantle. The still head was equipped with an air condenser, a stopcock for variable take-off, and a modified Perkin triangle for changing receivers. The slight rise of pressure in the system resulting from the change in receivers was overcome within 30 seconds after replacement of the receiver. A small nichrome wire unit heated the lower portion of the still head in order to prevent solidification of the distillate. A Cenco Hy-Vac pump, a McLeod gauge, and an acetone-dry ice trap between the pump and the still comprised the rest of the

system. All connections were standard taper ground glass joints except that one between the receiver and the still head where a rubber stopper sealed to the glass with shellac was found to be adequate.

*Procedure.* The distilland consisted of 213 g. of crude wax alcohols, prepared as above, which had been crystallized once from a 10 per cent solution in toluene at 27°. The distillation required 14 hours using complete take-off. This was necessary because it was impossible to heat the still head sufficiently to maintain suitable conditions for a reflux ratio. The data of the distillation are shown in Table III below:

TABLE III.  
Fractional Distillation of Wax Alcohols

Fraction No.	Pressure mm.	Boiling Range °C.	Weight g.	M.P. °C.
1.....	0.28	up to 215	2.7	.....
2.....	0.8	215-233	3.8	85.8-95.5
3*.....	1	233-250	10.4	82.8-83.8
4*.....	0.77	236-244	38.2	84.8-85.8
5*.....	0.54	244-246	28.0	87.8-88.8
6*.....	0.58-0.83	243-245	34.0	87.8-88.8
7*.....	1	246-265	17.2	85.8-85.8
8*.....	0.96-0.6	260-225	32.8	80.8-82.8
Hold-up.....	.....	.....	1.6	.....
Residue.....	.....	.....	35.9	.....
Total.....	.....	.....	204.6	.....

Total recovered, 96 per cent.  
Total distilled, 82.4 per cent.

\* Pure alcohols isolated from these fractions.

All the fractions were a pale brown color from the slight decomposition which occurred during the distillation. Since the melting points of most of the fractions did not agree with the published values of Piper (see Table V) for the alcohols expected, each fraction was re-crystallized at room temperature from a 10 per cent solution in toluene until the melting point became constant. All the fractions lost their brown color during the first recrystallization. Fractions 1, 2, and 3 were white amorphous powders; Fractions 4, 5, 6, and 7 were crystalline, glistening plates; and Fraction 8 was a finely crystalline powder. After the first recrystallization, the recovery for Fraction 8 was less than 25 per cent as compared with an average recovery of 80 to 85 per cent for the fractions excluding numbers 1 and 2. These latter two appear to be of a different chemical nature from the other fractions since their melting points were higher than those of subsequent fractions. They have not yet been further investigated. The data for the recrystallizations is given in Table IV below:

TABLE IV.  
Melting Points of Fractions After Recrystallizations.

No.	Original M.P.°C.	First M.P.°C.	Second M.P.°C.	Third M.P.°C.	Third R.P.°C.
1.....		90-96	94.9-96.9	94.9-96.9	.....
2.....	85-95	92-98	94.9-97.9	96.9-97.9	.....
3.....	82-83	83.1-84.0	83.4-83.6	82.9-83.3	81.8
4.....	84-85	85.4-86.5	86.1-86.5	86.0-86.5	86.0
5.....	87-88	87.4-88.7	88.2-89.7	88.4-89.8*	87.2*
6.....	87-88	88.5-89.5	89.0-89.8	89.5-89.9	87.3
7.....	84-85	87.0-88.0	88.2-88.6	88.3-88.7	87.7
8.....	80-82	85.7-86.8	88.5-89.2	89.3-89.6	88.9

Weight of Fractions g.

No.	Original	First	Third
1.....	2.7	2.3	1.7
2.....	3.3	2.6	3.0
3.....	10.4	8.7	7.3
4.....	38.2	30.5	29.1
5.....	28.0	23.5	22.3*
6.....	34.0	27.8	26.3
7.....	17.2	10.7	10.1
8.....	32.8	6.0	5.8

\* Fourth recrystallization.

Like P-6, and P-5, above, fractions 3, 4, 5, 6, 7, and 8 were subjected to Piper's method of analysis except that their long crystal spacings were not measured. The derivatives for this analysis were prepared as follows:

**Acetates.** A modification of the method of Shriner and Fuson (7) was used. Five-tenths gram of the alcohol<sup>4</sup> was refluxed with 0.25 g. of anhydrous sodium acetate, 2.5 cc. of acetic anhydride, and 5 cc. of pyridine for 8 hours. Water was then added, and the mixture was heated for an additional one hour. It was allowed to cool, and the solid layer was taken off the top. This layer was washed with cold water and dissolved in 28 cc. of boiling absolute ethyl alcohol. Upon cooling, a gelatinous precipitate was formed. This precipitate was filtered off, taken up in Skellysolve F, and recrystallized to a constant melting point. The acetates were obtained in a crystalline state only with difficulty.

**Acids.** A modification of the method of Pollard *et al.* (6) was used. Nine-tenths gram of the alcohol was dissolved in 40 cc. of warm glacial acetic acid. One gram of chromic oxide (Merck) was partially dissolved, partially suspended in 10 cc. of warm

glacial acetic acid. This mixture was added to the acid solution of the alcohol in portions over a period of 15 minutes while the latter was kept warm on the steam bath. After the final addition of chromic oxide, resulting mixture was kept on steam bath for an additional one hour, then poured into warm water. The crude acid layer was extracted with several portions of warm benzene. The combined extracts were filtered and treated with warm sodium ethylate in ethyl alcohol. The precipitated soaps were centrifuged off, and washed several times with ethyl ether followed each time by centrifuging. After removal of the ether, the soaps were decomposed by heating over dilute aqueous hydrochloric acid. The crude acid was separated from the aqueous layer after cooling, and was recrystallized from a mixture of benzene and acetone until the melting point was constant. Progressively smaller amounts of benzene were used during the recrystallizations until finally the solvent was pure acetone.

**Ethyl Esters.** Ten milligrams of the acid were heated on the steam bath with one drop of concentrated sulfuric acid and 10 cc. of absolute ethyl alcohol for 12 hours. The solution was then poured slowly into cold distilled water whereupon the esters formed a solid layer on top. This was removed, washed with water, and recrystallized from acetone until the melting point was constant.

The summarized data for the various fractions and their derivatives appear in Table V below, together with values found by Piper and co-workers.

Considering Fractions 3, 4, 5, 6, and 8 of Table V, the melting point of each derived acid is at least 6° above that of the parent alcohol, while the melting point of the acid from Fraction 7 is only 5° above that of its alcohol. Therefore, all of these fractions, with the possible exception of No. 7, are of a good degree of purity.

Using the curves described by Piper (5), and on the basis of the melting points of the alcohols, acids, and ethyl esters, it is estimated that Fractions 3 and 4 are 95 per cent C<sub>28</sub> and C<sub>30</sub> alcohols respectively. In each case, the remaining 5 per cent consists of the next higher even carbon homolog plus a trace of even higher homologs as shown by the high melting points of the ethyl esters, and of the acetates. Fraction 5 is 95 per cent C<sub>32</sub> and 5 per cent C<sub>30</sub> with traces of lower homologs since the melting point of the ethyl ester is slightly low. On the basis of the melting point of the alcohol, Fraction 6 is 100 per cent C<sub>32</sub> alcohol. However, the melting point of the acid and ethyl ester are slightly low, and point to a composition of 92 per cent C<sub>32</sub> and 8 per cent C<sub>30</sub>.

TABLE V.  
Summary of Fractions 3, 4, 5, 6, 7, and 8.

Fraction	Alcohol M.P.°C.	R.P.°C.	Acetate M.P.°C.	Acid M.P.°C.	R.P.°C.	Ethyl Ester M.P.°C.
3.....	82.9-83.2	81.8	67.6-67.8	89.1-89.4	88.8	70.8-70.9
4.....	86.0-86.5	86.0	71.5-71.8	92.9-93.1	92.7	71.8-72.0
5.....	88.4-89.8	87.3	.....	95.1-95.3	94.8	72.0-72.1
6.....	89.5-89.9	87.3	.....	95.5-95.8	95.3	72.0-72.2
7.....	88.3-88.7	87.7	.....	93.5-93.7	92.8	73.9-74.2
8.....	89.5-89.6	88.9	74.8-75.0	96.5-96.8	96.5	75.2-75.4

Published Values of Piper (5)

C <sub>28</sub>	79.5-79.8	79.1	60.0-60.1	87.8-88.0	87.5	60.1-60.2
C <sub>28</sub>	83.2-83.4	82.8	64.6-64.8	90.8-91.1	90.5	64.7-64.8
C <sub>30</sub>	86.3-86.5	85.9	69.1-69.2	93.6-93.9	93.4	68.8-68.9
C <sub>32</sub>	89.3-89.5	88.9	72.6-72.8	96.1-96.3	95.5	72.6-72.8
C <sub>34</sub>	91.9-92.2	91.6	75.5-75.8	98.3-98.5	97.8	75.6-75.8

<sup>4</sup> Lesser amount was used in the case of P-5<sub>a</sub>.

Fraction 7 does not fit into any pattern for a binary mixture, but does fit fairly well into the pattern for a ternary mixture which is mostly  $C_{32}$  and  $C_{34}$  with small amounts of  $C_{36}$ . Fraction 8 is virtually 100 per cent  $C_{32}$  alcohol but with small amounts of higher homologs as shown by the high melting points of the ethyl ester and acetate.

Carbon and hydrogen analyses were run on Fractions 3, 4, and 8 as shown in Table VI below:

TABLE VI.  
Carbon, Hydrogen Analyses of Alcohols\*

	Calcd. for $C_{28}H_{57}OH$	Found Fr. 3	Calcd. for $C_{30}H_{61}OH$	Found Fr. 4	Calcd. for $C_{32}H_{65}OH$	Found Fr. 8
% C	81.87	81.70	82.11	82.32	82.32	82.79
% H	14.23	14.38	14.24	14.17	14.25	14.27

\*We are indebted to J. E. Varner of the Chemistry Department for these analyses.

### Discussion

Fractional distillation of the free alcohols can, therefore, be used to separate the higher homologs of the n-aliphatic alcohols. It does have limitations in that slight decomposition does occur and the recrystallization of the fractions is necessary. However, with refinement in apparatus and technique these difficulties could be minimized.

Despite its limitations, this method has made possible for the first time the isolation from carnauba wax of the  $C_{28}$  alcohol, the  $C_{30}$  alcohol, and the  $C_{32}$  alcohol, in states of purity of 95 per cent or better. Moreover, by this method further evidence has been found to support the inference of Chibnall (2) that the alcohols of the wax include the  $C_{34}$  alcohol, and perhaps even higher homologs.

Finally, although previous workers had believed that the  $C_{30}$  alcohol was the principal alcohol of

carnauba wax, it has been possible to show by means of this method that the  $C_{32}$  alcohol is even more abundant in the wax than is the  $C_{30}$  alcohol.

### Summary and Conclusions

1. Fractional crystallization alone is not an adequate method for isolating pure alcohols from carnauba wax.

2. More than 50 per cent of the alcohols of carnauba wax can be distilled at 0.5 mm. pressure without serious decomposition.

3. Fractional distillation of the free wax alcohols at 0.5 mm. is a useful method of separating these compounds, but recrystallization of the resulting fractions is necessary.

4. There are substances in the unsaponifiable portion of carnauba wax which are of an unknown nature but which are probably not n-aliphatic alcohols.

5. For the first time, three alcohols, octacosanol ( $C_{28}$ ), triacontanol ( $C_{30}$ ), and dotriacontanol ( $C_{32}$ ) have been isolated from carnauba wax in states of purity of 95 per cent or better.

6. Dotriacontanol is even more abundant in the wax than is triacontanol.

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## Oil From Tumbling Mustard Seed

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ALTHOUGH not a major item in our fat and oil commerce, rapeseed oil has performed a variable but significant role during the past decade in our domestic oil industries. In 1935 and 1936, it was used in considerable amounts in shortening, and to a lesser extent in soaps. In addition, there has been a fairly constant consumption of this oil in the manufacture of lubricants and rubber substitutes. Tariff restrictions were imposed in 1936 and 1938 which resulted in a discontinuance of large-scale use of the oil for food purposes, but denatured rapeseed oil for use in lubricants and rubber substitutes was exempted. Importations for these latter purposes continued, therefore, until war developments cut off supplies, which had been obtained almost entirely from Japan.

Rapeseed oil is of particular value in certain lubricants and in factice because of its content of erucic acid, a mono-unsaturated fatty acid containing 22

carbon atoms, which is present to the extent of about 50 percent of the component fatty acids in the oil. Few oils contain appreciable proportions of erucic acid, and that obtained from rapeseed is the only one that has been consistently available in any quantity. For use in marine lubricants, for which purpose it is blown to achieve a high viscosity, and in rubber substitutes, rapeseed oil is a difficultly replaceable item.

With the loss of its normal supplies of rapeseed oil, it was necessary for the United States to resort to whatever substitutes or new sources could be found. Initially, mustardseed oils from domestically grown seed were used to augment stocks, for these are quite similar to rapeseed oil both in composition and in their physical properties. More recently, however, it has been possible to procure substantial quantities of rapeseed oil from Argentina.

During the months when the rapeseed oil shortage threatened to assume serious proportions, considerable thought was given to the production of substitutes from still other oilseeds which had heretofore

<sup>1</sup>This is one of four regional research laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.