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 nonconjugated 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.

REFERENCES

1. A.C.S. Committee Report, Analysis of Commercial Fats and Oils, Ind. Eng. Chem., Anal. Ed., *12*, 379 (1930).
2. A.O.C.S. Tentative Method Ka 2-47.
3. A.O.C.S. Tentative Method Ka 9-51 for 60-minute Wijs.
4. Blumer, L., German Patent 647,179, June 29, 1937; Saunders, S. L. M. (unassigned). British Patent 487,681, June 20, 1938; Ubben, R. T., (Armstrong Paint and Varnish Works), U. S. Patent 2,246,768, June 24, 1941.
5. Boeseken, J., and Hoevers, R., Rec. trav. chim., *49*, 1165 (1930).
6. Clocker, E. T., (unassigned), U. S. Patents 2,188,882-890, Jan. 30, 1940.
7. Coffey, C. A., Walton, W. T., and Britan, W., (Sherwin-Williams Co.), U. S. Patent 2,528,946, Nov. 7, 1950.
8. "Encyclopedia of Chemical Technology." Vol. V., p. 294, Interscience Encyclopedia Inc., New York, N. Y., 1950; Patton, T. C., Official Digest, Fed. of Paint and Varnish Production Clubs, 326, 149 (1952).
9. FIAT Final Report No. 729, "The German High Temperature Coal Industry," E. O. Rhodes, Feb. 5, 1946; private communication to the author from Adolph Kinsky, I. G. Uerdingen, Germany.
10. Freed, M., and Wynne, A. M., Ind. Eng. Chem., Anal. Ed., *8*, 278 (1936).
11. Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors," 11th edition, p. 426, distributed by the Henry A. Gardner Laboratory Inc., Bethesda, Md. (1950).
12. Grummitt, O. J., and Fleming, H., Ind. Eng. Chem., *37*, 485 (1945).
13. Kappelmeier, C. P. A., Paint Tech., *13*, No. 151, 261 (1948).
14. Klee, L., and Benham, G., J. Am. Oil Chem. Soc., *27*, 130 (1950).
15. Mikusch, von J. D., J. Am. Oil Chem. Soc., *29*, 114 (1952).
16. Priest, G. D., and Mikusch, von J. D., Ind. Eng. Chem, *32*, 1314 (1940).
17. Ross, J., Gebhart, A. I., and Gerecht, J. F., J. Am. Chem. Soc., *68*, 1373 (1946).
18. Scheiber, J., Farbe u. Lack., *55*, 147 (1949); Angew. Chem., *46*, 643 (1933); (unassigned), U. S. Patent 1,942,778, Jan. 9, 1934.
19. Siegel, E. F., and Moran, M. K., J. Am. Chem. Soc., *69*, 1457 (1947); Lavine, T. F., and Herkness, C., *ibid.*, *70*, 3951 (1948); Anderson, I. G., and Kenyon, J., *ibid.*, *70*, 3952 (1948).
20. Terrill, R. L., J. Am. Oil Chem. Soc., *27*, 477 (1950).
21. Van der Hulst, L. J. W., Rec. trav. chim., *54*, 639 (1935).

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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_{18} to C_{30}.

This paper describes the isolation by the amplified distillation method of Weitkamp (4) of the n-acids of even carbon number C_{18} to C_{30} 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_2SO_4, the reflux passing through a soxhlet extractor containing anhydrous $MgSO_4$ 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_2SO_4. 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[2] (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[3]), 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

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[1] Part V of this series: The Aliphatic Alcohols of Wool Wax, by K. E. Murray and R. Schoenfeld, J. Am. Oil Chem. Soc., *29*, 416-420 (1952).

[2] Prepared from chromatographic alumina from British Drug Houses Ltd., London, by warming with 2% HNO_3 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)].

[3] A trial chromatogram on the same sample gave a percentage of the n-esters of 39.4%.

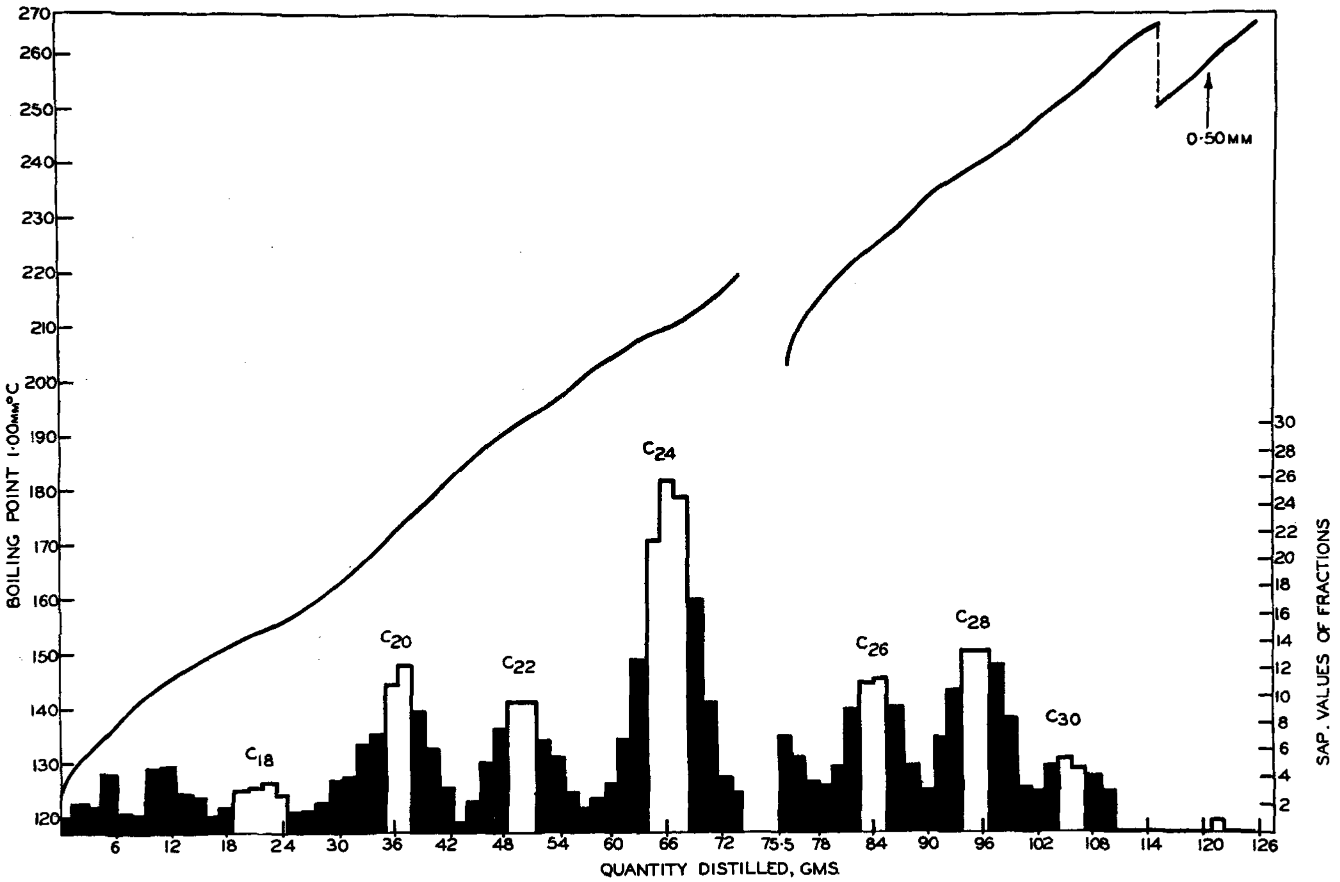

FIG. 1. Two-stage amplified distillation of the n-acid methyl esters.

isolation of the constituent acids will be described in a subsequent publication.

Amplified Distillation of the n-Esters

The separation of the methyl esters by amplified distillation follows the method of Weitkamp (4). The column (7) used in the present work was the same as used in a previous investigation (5).

To establish the boiling range of the mixed methyl esters, and thereby the boiling range of the amplifying oil needed, a trial amplified distillation was performed at 1.00-mm. pressure[4] with 5 g. of the esters and 100 g. of an oil of wide boiling range (130°-270°C.). This showed the presence of seven esters boiling from approximately 145° to 260°C. The main distillation (Figure 1) was carried out in two parts to allow the addition of further high-boiling amplifying oil required for the later stages of the distillation. The interruption was made at 220°, which had been shown in the trial distillation to lie midway between the boiling points of two adjacent esters. Details are as follows: The ester sample (5.09 g.) was mixed with amplifying oil (96 g.) of boiling range 130-250°C.[5] The distillation pressure was 1.00 mm., the boil-up rate approximately 150 g./hr. and the take-off rate 3 g./hr. Fractions of 1.5 g. were made and weighed to 0.01 g. After the distillation was stopped at 220°, a further charge of oil (48 g.) was added. This oil consisted of equal portions of ten-degree fractions over the ranges 210-220°C. and 250-300°C. The distillation was then resumed under the previous conditions, but when the head temperature reached 266°C., the pressure was reduced to 0.50 mm.

Saponification values for each of the 84 fractions were determined on the whole fractions, using the method of Hahn (8). These values, plotted against the amount distilled (Figure 1), show clearly the separation achieved by the distillation. Seven peaks are evident, each representing a methyl ester. The temperatures corresponding to these peaks (Table I) are close to the boiling points of the pure esters.[6]

Recovery and Identification of the Acids

The acids were isolated only from the peak fractions (unshaded in Fig. 1) to obtain samples as pure as possible for identification.

After the determination of the saponification values, the acids were present as potassium salts in a solution of cellosolve and xylene, which also still contained the amplifying oil. They were recovered as follows: The solvents were distilled off at reduced pressure and light petroleum (80-100°C.), and 40% aqueous ethanol was added to the residue. After warming, the aqueous alcoholic layer was separated and acidified, when the liberated acids were extracted

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[4] All distillation pressures are in millimeters of mercury.

[5] To ensure a more linear relationship between distillation temperature and amount distilled than is possible with commercial oils, the oils commercially available were roughly fractionated at 1.00 mm. into fractions having boiling ranges of 10°. From these the desired amplifying oil was prepared. In the present experiment it consisted of equal weights of twelve consecutive fractions.

[6] Cason and Sumrell (J. Org. Chem. *16*, 1193, 1951) have reported that in the presence of oil the temperature of the peak may deviate from the true boiling point by as much as 3-4°C. Such a variation has never been observed by us when esters and acetylated alcohols have been fractionated either alone or diluted with oil.

TABLE I

Acid	Peak temp. °C.[a]	Melting point °C.		Resolidification point		Crystal spacings, Å			
		This work[b] °C.	F. and P. (9) °C.	This work °C.	F. and P. (9) °C.	This work[d] ± 0.6 Å		F. and P. (9) ± 0.4 Å	
						d(001)B	d(001)C	d(001)B	d(001)C
n-Octadecanoic	155	68.2-68.3[c]	69.6	67.5	69.2	44.2	40.2	43.8	39.8
n-Eicosanoic	175	75.0	75.35	74.4	74.9	49.0	44.2	48.5	44.2
n-Docosanoic	193	79.9	79.95	79.3	79.6	53.0	48.4	53.0	48.3
n-Tetracosanoic	210	84.1	84.15	83.7	83.8	58.2	52.8	57.8	52.6
n-Hexacosanoic	225	87.5-87.6	87.7	87.0	87.2	62.3	56.5	62.2	56.2
n-Octacosanoic	240	90.5	90.9	89.9	90.4	......	61.3	67.2	61.1
n-Triacontanoic	253	93.1	93.6	92.5	93.2	72.3	66.1	71.4	65.2

[a] Boiling points at 1.00 mm. of the methyl esters above methyl stearate could not be found in the literature for comparison with these values. The peak at 155°C. agrees with a recent figure of 158.2°C. for methyl stearate [Scott *et al.* Ind. Eng. Chem., *44*, 174 (1952)], while the peaks at 175, 193, 210, and 225°C. agree to 1°C. with the b. pts. of the n-methyl esters at 1.95 mm. recorded by Weitkamp [J. Am. Chem. Soc., *67*, 447 (1945)] allowing 13°C. for the difference in pressure.

[b] Determined on resolidified samples in 1-mm. diameter tubes. The electric heating of the bath (Hershberg type) was so adjustable as to hold the temperature to 0.1°C.

[c] This was undepressed when repeated mixed with authentic stearic acid.

[d] Recorded on a flat plate camera 10 cm. from the specimen, which was mounted as a smear on a glass slide and oscillated over 15°. The radiation used was CuKα ($\lambda = 1.54$ Å).

with warm ethyl acetate. They were then crystallized twice from acetone.

The seven acids isolated from the peaks have been identified as those of even carbon number C_{18} to C_{30} by the agreement of their melting points and crystal spacings with the accepted data of Francis and Piper (9) (Table I). The recording of the spacings of both B and C forms for six of the acids is additional evidence of their identity. Finally microscopic examination of the acids was made after crystallization from a mineral oil ("Mineral Seal Oil") as described by Weitkamp (10). All samples showed the flat parallelopipeds with an acute profile angle of approximately 55° characteristic of the n-acids.

Discussion

Division between the distribution curves as shown in Figure 1 gives an approximate quantitative estimation of the composition of the methyl esters in the sample distilled. Percentages of esters are as follows: below C_{18} (calculated as C_{16} ester), 4%; C_{18}, 3%; C_{20}, 11.5%; C_{22}, 9%; C_{24}, 30%; C_{26}, 12%; C_{28}, 16.5%; C_{30}, 7%. There is a deficit of 7% which it does not appear possible to ascribe to the decomposition of higher esters as the C_{32} should have distilled over without decomposition in the highest fractions. No esters appeared to be present in the residues. Some of the ester fractions contained traces of esters of unidentified higher melting acids (separated by the insolubility of these acids in light petroleum), and no correction has been made for their presence in the above figures.

This investigation confirms the findings of Bowers and Uhl (2) and Koonce and Brown (3) that the acids range from C_{18} to C_{30} and that of Koonce and Brown that C_{24} is the principal acid. Earlier, Chibnall and others (11) had concluded from the high melting point of the carnauba acids that the acids were mainly C_{30}, C_{32}, and C_{34}. However these investigators were unaware of the presence of hydroxy acids, which invalidates their conclusion.

Summary

The proportion of normal acids among the acids of carnauba wax has been found, by a chromatographic separation method, to be 38%. The normal acid mixture has been separated into its components by amplified distillation of the methyl esters, which revealed the presence of the acids of even carbon number from C_{18} to C_{30}. The acids were identified by their melting points, long crystal spacings, and crystal habit. An estimate of their relative amounts is as follows: C_{18}, 3%; C_{20}, 11.5%; C_{22}, 9%; C_{24}, 30%; C_{26}, 12%; C_{28}, 16.5%; C_{30}, 7%.

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REFERENCES

1. Koonce, S. D., and Brown, J. B., Oil and Soap, *21*, 167 (1944).
2. Bowers, R. H., and Uhl, A. H., J. Am. Pharm. Asso., *30*, 10 (1941).
3. Koonce, S. D., and Brown, J. B., Oil and Soap, *22*, 217 (1945).
4. Weitkamp, A. W., J. Am. Oil Chem. Soc., *24*, 236 (1947).
5. Murray, K. E., and Schoenfeld, R., J. Am. Oil Chem. Soc., *28*, 461 (1951).
6. Clark, D. J., Hatt, H. H., Troyahn, W. J., Aust. J. Appl. Sci., *2*, 378 (1951).
7. Murray, K. E., J. Am. Oil Chem. Soc., *28*, 235 (1951).
8. Hahn, F. L., Anal. Chim. Acta, *4*, 577 (1950).
9. Francis, F., and Piper, S. H., J. Am. Chem. Soc., *61*, 577 (1939).
10. Weitkamp, A. W., J. Am. Chem. Soc., *67*, 447 (1945).
11. Chibnall, A. C., Piper, S. H., Pollard, A., Williams, E. F., and Sahai, P. N., Biochem. J., *28*, 2198 (1934).

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