TABLE I

Percentage Composition and Iodine Numbers of Alkali Isomerized Lespedeza Oils

	Iodine No. (Wijs)	Triene (%)	Diene (%)	Monoene (%)	Saturated (%)
Korean	150.9	28.1	30.3	21.5	20.2
Kobe	149.7	23.1	26.5	42.9	7.5
Sericea	153.8	22.2	41.8	19.4	16.6
Linseed	181.8	44.0	13.8	35.4	6.8

numbers, there is less triene and more diene structure present in each. For the three oils the amounts of mono- and di-unsaturation vary over a wider range than the amounts of triene structure. Of the three the sample of oil from the Kobe species most nearly resembles linseed oil. The wide differences in percentage of saturated acids in view of small differences in iodine value of the oils do not fit the pattern for other oil seeds and should be confirmed by additional determinations before final acceptance.

Summary

The ultraviolet absorption spectra of the oils obtained from lespedeza seeds of three species show an absorption similar to that of linseed oil. The spectra for the alkali isomerized lespedeza seed oils show triene conjugation equivalent to that which would be produced by the presence of 22-28% of a triunsaturated nonconjugated acid (such as linolenic acid) and 26-42% of a diunsaturated nonconjugated acid (such as linoleic acid). The presence of conjugated triene structure in the oil as extracted from a seed-hull mixture ground with stainless steel balls was indicated by an absorption maximum at 270 mμ. Elimination of other possibilities suggest that this absorption is caused by a metal-catalyzed isomerization or other reaction taking place only in the mixture.

Acknowledgment

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REFERENCES

1. Wiley and Cagle, J. Am. Oil Chem. Soc., *27*, 34 (1950).
2. Wiley and Cagle, J. Am. Oil Chem. Soc., *28*, 89 (1951).
3. Mitchell, Kraybill, and Zscheille, Anal. Chem., *15*, 1 (1943).
4. Cowan, Ind. Eng. Chem., *41*, 294 (1949).
5. Radlove, Teeter, Bond, Cowan, and Kass, Ind. Eng. Chem., *38*, 997 (1946).
6. Swain and Brice, J. Am. Oil Chem. Soc., *26*, 272 (1949).

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Studies of Waxes. III. The Alcohols of Carnauba Wax[1]

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IN a review of previous work on composition of carnauba wax Koonce and Brown (1) concluded that it was probable the wax contained straight chain alcohols of even carbon number from C_{26} to C_{34}—the higher alcohols dominating—and a dihydric alcohol, possibly $C_{23}H_{46}(CH_2OH)_2$. The monohydric alcohols however had never been isolated in a pure condition. Later, in their work, Koonce and Brown (2) fractionally distilled the alcohols and from the melting points of the alcohols and their derivatives concluded that the alcohols C_{28}, C_{30}, and C_{32} had been isolated in a purity of approximately 95%, C_{32} being the major constituent. They used the customary helix-packed column at a pressure of 0.28-1 mm. and reported serious decomposition of the charge, due no doubt to the high pressure drop through this type of column.

This paper describes an investigation of the composition of the non-saponifiable portion[2] of carnauba wax using a modified spinning band column developed in this laboratory (3). This column has a very low pressure drop and a high efficiency at low operating pressures and has proved very suitable for the fractionation of such high boiling material.

Saponification of the Wax and Acetylation of the Wax Alcohols

A sample of high grade carnauba wax (Flores Yellow No. 1) was filtered while molten through a heated sintered glass funnel and was found to be almost free from dirt. The cleaned wax (200.0 g.) was saponified by boiling with alcoholic KOH (50 g. in 1 litre 97% alcohol) and petroleum ether (b.p. 80-100°C., 500 ml.) for 24 hr. Water (600 ml.) was then added and the petroleum ether layer separated while hot. The aqueous alcoholic layer was further extracted twice with petroleum ether, the extracts being combined with the first petroleum ether extract and then washed twice with hot 40% aqueous alcohol. These alcoholic washings were extracted three times with petroleum ether. All the petroleum ether extracts were then combined and washed twice with hot 30% aqueous alcohol. The solvent was removed by heating on a steam bath, first under slightly reduced pressure, and finally at 1 mm. The recovered alcohols were pale yellow, melted from 84.8 to 85.5°C. and weighed 107.0 g. or 53.5% of the wax. They were free from acids and unsaponified esters (acid value, 0; saponification value, 0).

The acids were recovered from the combined aqueous alcoholic layer and washings by acidification with HCl and hot extraction with petroleum ether. They weighed 86.8 g. or 43.4% of the wax. Alcohols and acids recovered represent 96.9% out of an expected yield, calculated from the saponification number, of 102.5%. A further 4.6% of a brown resinous material, probably resin acids, was recovered from the acidified aqueous alcoholic liquors, after removal of the acids, by concentrating them to half volume and extracting with ethyl acetate.

The alcohols (91.5 g.) were acetylated by boiling with acetic anhydride (180 g.) for 6 hr., and removing excess anhydride under vacuum at 100°C., finally

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[1] Part II of this series: H. H. Hatt, P. H. A. Strasser, W. J. Troyahn, Proc. Queensland Soc. Sugar Cane Tech. 17th Conference, p. 61.

[2] For convenience hereafter referred to as the wax alcohols.

at 1 mm. pressure. Subsequent washing of a small sample of these acetates with hot water did not lower the saponification value appreciably. Yield, 100.3 g.; sap. value, 120.2, 119.8, 119.6, mean 119.9; micro-acetyl, 9.5%, 9.5%. (Calc. S.V. from micro-acetyl 124, micro-acetyl from S.V. 9.2%).

Fractionation of the Acetylated Alcohols

The acetylated alcohols (69.3 g.) were fractionated in a spinning band column with a rotor length of 366 cm., at a pressure of 0.50 mm., a boil-up rate of approximately 100 g./hr., and a take-off rate of 5-6 g./hr. Twenty-two fractions (total 61.2 g., 87.6% of the charge) were collected. The undistilled part of the charge comprised the residue in the column (9.8%), the residue in the pot (0.6%), and material lost or recovered by the liquid air trap (2.0%). The weight of distillate is shown plotted in Figure 1 against the head temperature. Two plateaux at 257°C. and 268-269°C. are prominent, the upper being shown by a broken line, as a fault developing in the temperature recorder prevented an accurate record being made. Saponification values of fractions from each plateau were as follows: fraction 15 (257°C.), 110.2, 110.2, 110.3, mean 110.2 (theory for $C_{32}H_{65}OCOCH_3$, 110.2); fraction 21, 104.9, 104.5, 105.2, 105.1, mean 104.9 (theory for $C_{34}H_{69}OCOCH_3$, 104.7).

The combined fractions 13 and 14 were saponified and the recovered alcohol chromatographed on alumina at 50°C. by a procedure described later, and then crystallized from petroleum ether. It was obtained as large laminae M.P.[3] 89.2-89.4° C., R.P.[4] 88.8° C. The agreement between these values and those of synthetic dotriacontanol published by Piper *et al.* (4) (M.P. 89.3-89.5°C., S.P. 88.9°C.) confirms the above evidence from the saponification values that the main plateau at 257°C. corresponds to the acetate of dotriacontanol, the upper plateau then representing the C_{34} acetate. Although Figure 1 showed an indefinite plateau which would correspond to the C_{30} acetate, it seemed probable that all the low boiling fractions (1-9) were mixtures, and rather than determine their compositions by the methods of Piper and co-workers it was considered that a better separation of the alcoholic constituents would be obtained by the technique of amplified distillation.

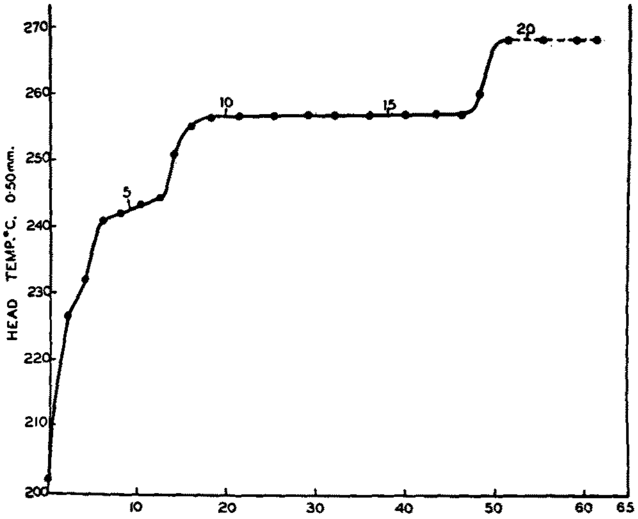

FIG. 1. Simple fractional distillation of the acetylated wax alcohols. 0.50 mm.

Separation of the Alcohols by Amplified Distillation

Weitkamp (5) has applied the technique of amplified distillation to the separation of the fatty acids by fractional distillation of their methyl esters with a hydrocarbon oil boiling over the same range. The fatty acids themselves gave poor separations owing to azeotrope formation with the hydrocarbons in the oil. For the same reason the free alcohols would be unsatisfactory, but it has been found that the acetylated alcohols distill with hydrocarbon oils without formation of azeotropes. This is evident from Figure 2 which shows the elimination curves of the acetates of n-hexadecanol and n-octadecanol, obtained by fractionally distilling 3.0 g. of a 1:1 mixture of them with 60 g. of a commercial oil in a spinning band column (rotor length, 145 cm.) at 1.00 mm. pressure. It is seen that the curves are practically symmetrical, but their shape can be modified slightly by changes in distillation conditions particularly in the take-off rate (e.g., the C_{32} curve in Figure 3). The peaks of the curves correspond to the true boiling points of the acetates.

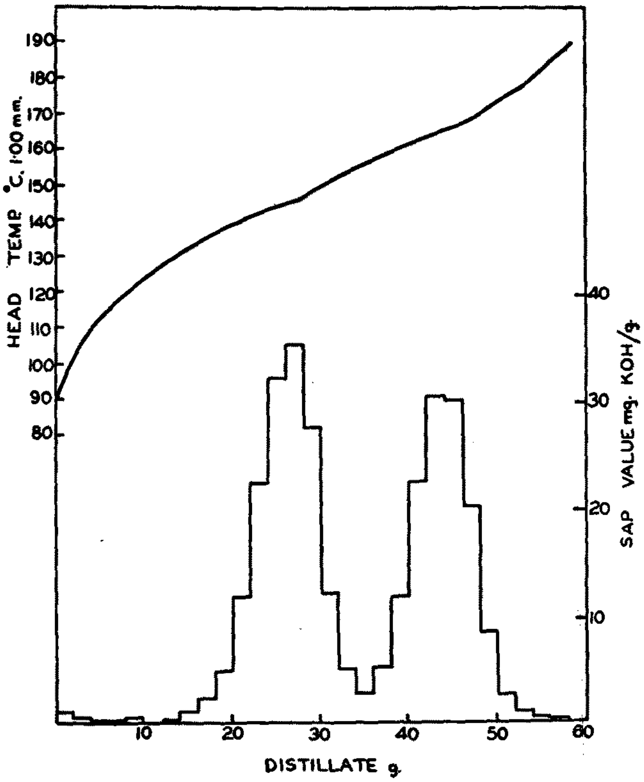

FIG. 2. Amplified distillation of acetates of hexadecanol and octadecanol. 1.00 mm.

This technique has been applied to the separation of the carnauba wax alcohols as follows: The acetylated alcohols (5.00 g.) were fractionally distilled with an amplifying agent (101.5 g.), which consisted

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[3] Melting points were made on previously melted and resolidified samples in 1 mm. capillary tubes, using an Anschutz thermometer, and a bath similar to that of Hershberg [Ing. Eng. Chem., Anal. Ed., *8*, 312 (1936)]. Comparison of the melting points of the isolated n-alcohols is made where possible with the data of Piper *et al.* (4) rather than the more recent data of Francis *et al.* (11), who used a more precise melting point method giving slightly lower values.

[4] Resolidification point (with nucleus).

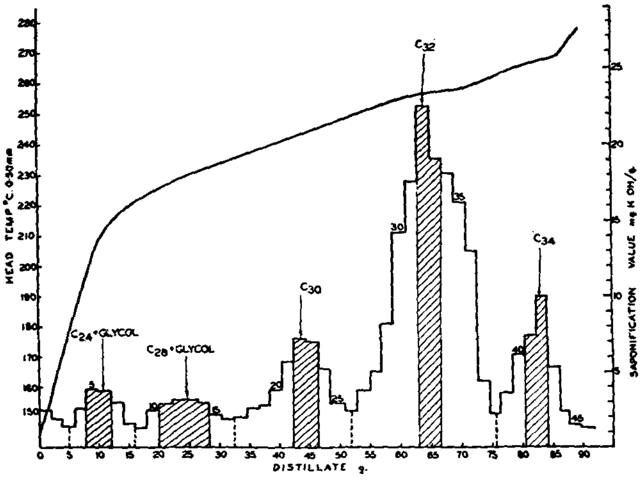

FIG. 3. Amplified distillation of the acetylated wax alcohols. 0.50 mm.

of a mixture of a commercial oil (86.5 g., boiling range, 190-280°C. at 0.5 mm.) and ceresin wax (15 g., previously refluxed with alc. KOH). The latter was added to widen the boiling range of the oil and so provide a fore-run and a small residue in the pot. A spinning band column (3) (rotor, 366 cm.) was used at 0.50 mm. pressure, a boil-up rate of approximately 100 g./hr., and a take-off rate of 4.5 g./hr. Forty-six fractions (92 g.) were collected in tared test tubes, and their saponification values determined by refluxing for 30 min. with 0.1 N KOH, the excess alkali being titrated while hot with 0.1 N HCl, with the addition of petroleum ether (10 ml.) to dissolve the alcohols and the oil thrown out of solution.

From Figure 3 it is seen that in the amplified distillation of the acetates there are five distribution curves with maxima at 196-215°C., 227-232°C., 244° C., 257°C., and 267°C. Separation of the various acetates is evidently not quite complete since some overlapping of the curves is apparent. For this reason the alcohols were isolated only from the peak fractions (shown shaded). Their separation from the accompanying amplifying oil was effected as follows: A solution of the alcohol and oil in aromatic-free petroleum ether (60-80°C.) was passed through a column of activated alumina[5] (British Drug Houses Ltd., London) kept at 50°C. by an electrically heated glass jacket. The adsorbed alcohols were washed free of hydrocarbons with more petroleum ether and were eluted with benzene. Crystallized twice from petroleum ether, all but Sample 1 were obtained as large thin laminae. Melting point data are given in Table I.

It is clear from the melting point of Sample 4 and its acetate that the elimination curve with its peak at 257°C. is that of the acetate of dotriacontanol, confirming the finding of the simple fractionation that C_{32} is the major alcohol of the wax. Samples 3 and 5 have slightly low melting points for pure specimens of C_{30} and C_{34}, respectively, and it is probable that both are contaminated by small amounts of C_{32} as suggested in Figure 3 by the wide range covered by the C_{32} elimination curve. The alcohols below C_{30} do not give sharp elimination curves due to the presence of glycols in the same boiling range. In order to interpret the results in this range accurately it was considered necessary first to find the boiling points of the C_{24}, C_{26}, and C_{28} n-acetates. These were obtained from an amplified distillation of acetylated "ceryl" alcohol (Eastman-Kodak), which was at the same time shown to be a mixture of the corresponding alcohols. It is then found that the boiling point of the C_{28} acetate (232°C., 0.50 mm.) corresponds with the boiling range of Sample 2, and this, with the close agreement of its melting point with pure C_{28}, characterizes it as octacosanol. The wide boiling range of Sample 1 (196-214°C.) straddles the boiling point of the C_{24} acetate (205°C.), and the suggestion that

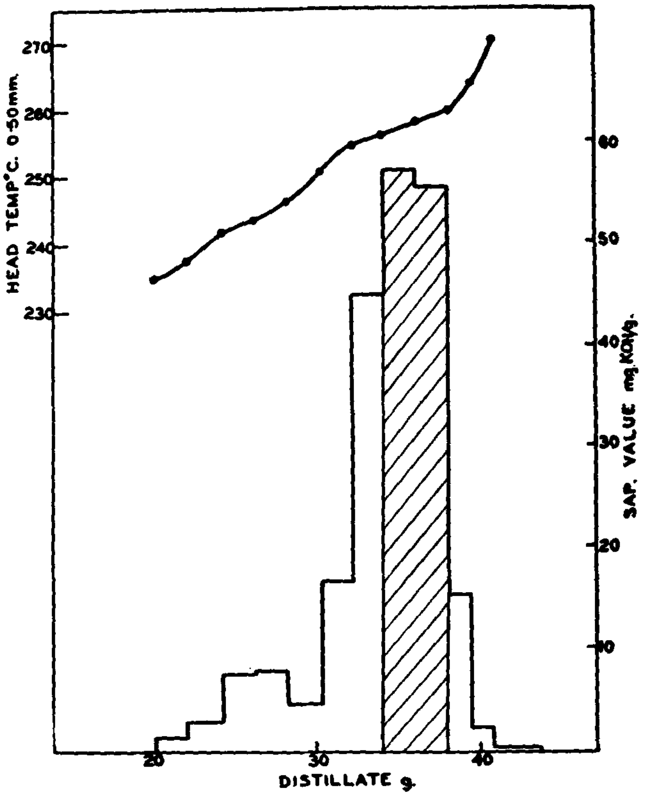

FIG. 4. Amplified distillation of mixture of C_{30}-C_{32} acetates (Fraction 11). 0.50 mm.

TABLE I

Sample	Fractions	Peak Temp. °C.	Alcohol		Acetate M.P.°C.	Published Values			
			M.P. °C.	R.P. °C.(with nucleus)			Alcohol		Acetate M.P.°C.
							M.P.°C.	S.P.°C.	
1	5, 6	196-214	74.3-74.6	73.6	......	C_{24}(11)	75.3	74.8 (R.P.)	......
2	11-14	227-232	82.8-83.0	82.6	......	C_{28}(4)	83.2-83.4	82.8	......
3	22, 23	244	85.4-85.6	85.1	......	C_{30}(4)	86.3-86.5	85.9	......
4	32-33	257	89.3-89.5	88.9	72.4-72.5	C_{32}(4)	89.3-89.5	88.9	72.6-72.8
5	41-42	267	91.4-91.9	90.9	75.3-75.4	C_{34}(4)	91.9-92.2	91.6	75.5-75.8

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[5] British Drug Houses Ltd., London. Activity, Grade II/III determined by the method of Brockmann and Schodder [Ber. *74*, 73 (1941)].

Sample 1 is mainly tetracosanol is in agreement with its melting point. Appreciable amounts of hexacosanol appear to be absent as the boiling point of the C_{26} acetate (219°C.) corresponds to the minimum between the peaks of Samples 1 and 2.

To isolate a larger sample of dotriacontanol for further characterization, Fraction 11 (3.58 g.), taken from the simple fractional distillation of the acetates, was subjected to an amplified distillation with 45 g. of a carrier oil (range 200-280°C.) but with an otherwise unchanged procedure. The results of this distillation have been included (Figure 4) because they demonstrate the clarity with which the amplified distillation technique reveals the presence of small amounts of impurity of an adjacent member of the series. Fraction 11, being at the beginning of the C_{32} plateau, contained a small amount of C_{30}, which was almost completely separated by this distillation. Recovery of saponifiable material was practically quantitative (102%). The C_{32} alcohol was recovered from the shaded fractions by the chromatographic procedure already described. Crystallized twice from petroleum ether, it was obtained as large laminae. M. P. 89.3-89.5°C., R.P. 88.9°C., M.P. of acetate 72.4-72.5°C.

Isolation of Glycols

Sturcke (6) has reported the isolation of a glycol, M.P. 103.5°C., to which he attributed the formula $C_{23}H_{46}(CH_2OH)_2$, but the lower melting point recorded for the corresponding dibasic acid (102.5°C.) suggests that his preparation was impure. A glycol of such chain length would be expected to be found in the lower boiling fractions of the acetates. Fractions 3 and 4 of the simple fractionation of the acetates were found to have a different crystalline appearance and high saponification values so that it seemed likely that the glycol was contained in these two fractions. They were saponified and the recovered alcohol (3.61 g.) was adsorbed on activated alumina at 50°C. and eluted in turn with benzene and acetone. The material eluted by acetone (0.59 g.) was crystallized from benzene and obtained as small dendritic crystals. M.P. 106.1-106.6°C. Found, C., 77.7% H, 13.2% O, 8.7%. The high melting point and analyses confirmed that the material was a glycol but the dendritic crystal habit and wide melting range suggested that it was a mixture. This was confirmed by the isolation from Fractions 5-6 and 11-14 of the amplified distillation of small amounts of two high melting alcohols, M.P. 102.7-103.0°C. and 108.0-108.4°C., respectively. The original material (M.P. 106.1°C.) was therefore acetylated and fractionated with an amplifying oil. Saponification values of fractions in the range 200-245°C. showed a large elimination curve with its peak at 229°C. with small ones at approximately 213°C. and 245°C. Alcohols recovered by the chromatographic separation above had the properties summarized in Table II.

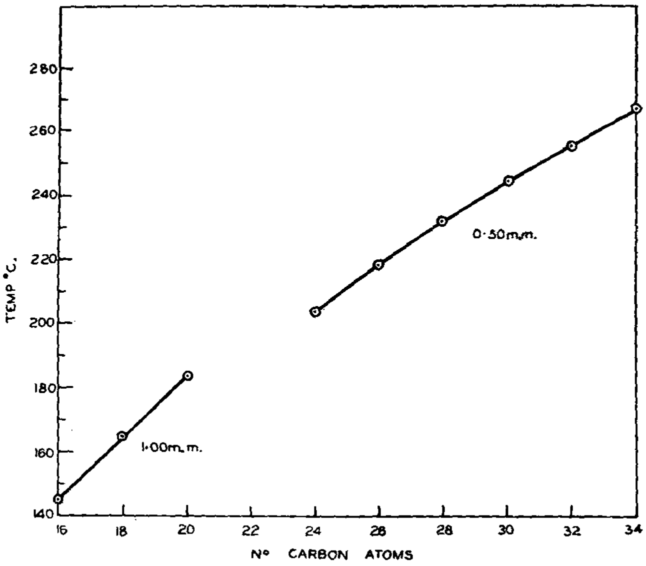

FIG. 5. Boiling points of the n-alkyl acetates. C_{16}-C_{20} at 1.00 mm. C_{24}-C_{34} at 0.50 mm.

From the characteristics of Sample 2 and its acetate it is difficult to differentiate between the composition $C_{23}H_{46}(OH)_2$ and $C_{24}H_{48}(OH)_2$, but the melting and boiling points and the oxygen content of the three samples suggest that they form a homologous series differing by two carbon atoms. Larger amounts of these glycols are being isolated for further study of their constitution.

An estimate of the percentage of glycols in the wax alcohol fraction was made by adsorbing 4.1 g. of the alcohols on alumina at 50°C., eluting first the monoalcohols with benzene and then the glycols with acetone. The material eluted by acetone (0.128 g.,

TABLE II

Sample	1	2	3
Amount isolated	12 mg.	160 mg.	8 mg.
Temp. of peak	Approx. 213°C.	229°C.	Approx. 245°C.
Cryst. form	Long flat prisms from acetone-benzene	Clusters of long flat prisms from acetone-benzene	Small needles from acetone
	From mineral oil, similar to 2	From mineral oil under microscope, flat parallelopipeds	From mineral oil similar to 2
M.P.°C. R.P.°C.	105.5-105.8 105.4	108.4-108.6 108.0	109.6-110.2 109.6
Diacetate	......	Large laminae from acetone M.P. 73.4-73.6°C. Microacetyl found, 19.5% Eq. Wt. by saponification of 20-mg. sample, 218 Calc. for $C_{23}H_{46}(OAc)_2$: Microacetyl, 19.5% Eq. Wt., 220	......
Analyses found[a] Analyses calc.	O, 9.3% For $C_{21}H_{42}(OH)_2$; O, 9.8%	C, 77.3%; H, 13.2%; O, 8.6% For $C_{23}H_{46}(OH)_2$; C, 77.5%, 13.5%; O,9.0%	O, 8.3% For $C_{25}H_{50}(OH)_2$;O, 8.3%

[a] Oxygen was determined by the direct micro-analytical method of Unterzaucher.

3%) was crystallized from acetone (0.120 g., M.P. 101.5-103.0°C.), but its low oxygen content (found 7.5%) indicated an impurity of approximately 30% of monoalcohols, thus making 2% a conservative estimate of glycols in the wax alcohol fraction.

Isolation of the Hydrocarbon Fraction

It was assumed that the small amount of hydrocarbon, M.P. 59.5°C., reported present by earlier workers (6, 7) would be in the lowest boiling fractions of the simple fractional distillation. Fractions 1 and 2 dissolved in petroleum ether were therefore chromatographed together on alumina, and the adsorbed material was completely eluted by petroleum ether. Saponification values on recovered material from the fractions collected showed that separation from the acetylated alcohols was incomplete, but the hydrocarbons were contained in the first fraction (1.5 g. S.V. 79). Rechromatographing of this fraction (in a like manner) after saponification gave 0.38 g. of material, which was crystallized from alcohol-benzene. M.P. 64.6-65.0°C. Found O, 0.2%. After heating with conc. H_2SO_4 at 125°C. for 1 hr., and crystallizing from alcohol-benzene, the hydrocarbon melted at 63.0-63.5°C. (R.P. 62.6°C.) but showed none of the distinct transition points characteristic of pure hydrocarbons and simple mixtures thereof (8). For this reason it must be considered a complex mixture probably consisting as in other waxes (9) of an odd numbered series of straight chain hydrocarbons.

Discussion of Results

The results of this investigation agree with the conclusions of Chibnall and co-workers (9) that the normal primary alcohols of carnauba wax consist mainly of the alcohols C_{30}, C_{32}, and C_{34}, and with the finding of Koonce and Brown (2) that dotriacontanol is present in greatest amount. The excellent separation achieved by the amplified distillation technique has made more positive than hitherto the identification of the alcohols present, and from the areas under the distribution curves the percentage composition of the primary alcohols can be estimated. Division is made at the dotted lines in Figure 3. The composition is as follows: Below C_{24} (calc. as C_{20}) : 1%, $C_{24}(+C_{26})$: 4%, C_{28} : 5%, C_{30} : 14%, C_{32} : 51%, C_{34} : 14%. Allowing for glycols (2%) and hydrocarbons (0.7%), the deficiency of approximately 8% is probably due to partial decomposition of the C_{34} acetate for which there is some evidence. a) A small amount of acidic material from the liquid air trap, equivalent to 5.3 ml. 0.1 N HCl, indicated that some decomposition occurred during the amplified distillation. b) The amplified distillation of the C_{30}-C_{32} sample (Figure 4) was practically quantitative. c) The C_{34} elimination curve in Figure 3 shows a sudden drop on its higher boiling side, and the peak occurs lower than would be expected for the boiling point of the C_{34} acetate. d) No evidence has been obtained for the presence of higher alcohols in the residues. e) The simple distillation of the acetates showed more than 25% boiling above the C_{32} acetate.

It was noticed that decomposition was more extensive in earlier trial distillations and this was considered to be catalyzed by decomposed carbonaceous material on the band, or by small amounts of copper oxide from spot welding electrodes, as it was decreased considerably by their removal with fuming nitric acid.

Recent investigations of wax alcohols by fractional distillation (2, 10) have been made with helix-filled columns approximately 50 cm. in length, which besides their high pressure drop could not have been very efficient at the low pressures used. Thus Schuette and Baldinus (10) found their fractions of the candelilla wax alcohols to be all ternary mixtures. Koonce and Brown (2) deduced the composition of their carnauba wax alcohol fractions from the melting points of the fractions themselves, the derived acids, their ethyl esters, and in some cases of the acetates. This method can give only an approximate evaluation of the alcohols present and may be most unreliable if compounds other than normal alcohols are also present. It would seem that glycols must have been present in the first three or four fractions obtained by Koonce and Brown, and the high melting point of the acid derived from their Fraction 3 should be ascribed to their presence rather than to the isolation of almost pure octacosanol.

By its efficient separation of the n-acetates up to C_{32} without decomposition, the use of the spinning band column in this investigation considerably simplifies the identification of the wax alcohols. Employing the amplified distillation technique good separation of the minor constituents is possible, but to isolate reasonable amounts of these minor alcohols it is suggested that the main bulk of the acetylated wax alcohols be first simply distilled and the fractions containing the minor alcohols be submitted to a separate amplified distillation. If the distillations are performed at a fixed pressure (e.g. 0.50 mm.), the boiling points of the constituent n-acetates, observed as the peaks of their elimination curves, may be used along with the melting points of the alcohols isolated chromatographically from the peak fractions for the characterization of the constituent alcohols.

This work confirms Weitkamp's findings that the amplified distillation technique possesses considerable advantages when only small amounts of material are available. Thus in the distillation represented by Figure 3, 5 g. of material was divided into 46 fractions in which the presence of 8 different compounds was demonstrated. It is doubtful whether this would have been possible with a conventional micro- or semimicro-distillation apparatus.

Summary

A study has been made of the composition of the non-saponifiable portion of carnauba wax by acetylation followed by fractionation in a spinning band column, using both simple fractional and amplified distillation. The straight chain alcohols of even carbon number, C_{24} to C_{34}, were estimated to be present in the following percentages, below C_{24} : 1%, C_{24} $(+C_{26}?)$: 4%, C_{28} : 5%, C_{30} : 14%, C_{32} : 51%, C_{34} : 22%. In addition, three high melting alcohols, totalling 2% of the wax alcohols, have been isolated and appear to be closely related glycols. The hydrocarbon fraction (M.P. 63.0-63.5°C.) forms less than 1% of the non-saponifiable fraction and is considered to be a mixture.

Acknowledgments

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REFERENCES

1. Koonce, S. D., and Brown, J. B., Oil and Soap, *21*, 167-170 (1944).
2. Koonce, S. D., and Brown, J. B., *ibid.*, *21*, 231-234 (1944).
3. Murray, K. E., J. Am. Oil Chem. Soc., *28*, 235 (1951).
4. Piper, S. H., Chibnall, A. C., and Williams, E. F., Biochem J., *28*, 2179 (1934).
5. Weitkamp, A. W., J. Amer. Oil Chem. Soc., *24*, 236-38 (1947).
6. Sturcke, H., Ann., *223*, 283 (1884).
7. Gottfried, S., and Ulzer, F., Chem. Umschau, *33*, 141 (1926).
8. Piper, S. H., Chibnall, A. C., Hopkins, S. J., Pollard, A., Smith, J. A. B., and Williams, E. F., Biochem, J., *25*, 2072 (1931).
9. Chibnall, A. C., Piper, S. H., Pollard, A., Williams, E. F., and Sahai, P. N., Biochem. J., *28*, 2189 (1934).
10. Schuette, H. A., Baldinus, J. G., J. Am. Oil Chem. Soc., *26*, 530 (1949).
11. Francis, F., Collins, F. J. E., Piper, S. H., Proc. Roy. Soc. London, *158A*, 691 (1937).

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Heat Polymerization of Safflower Oil[1]

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FOR some time the oil chemist has been intrigued by the potentialities of safflower seed oil in the field of drying oils and organic coatings (1, 2). However only during the last 12 months has safflower oil appeared on the competitive American vegetable oil market in sufficient quantity to stimulate interest in its commercial usage on a national scale. In view of the interest in this relatively new oil, a study was undertaken in an attempt to obtain some basic information regarding its heat bodying characteristics under practical conditions. With the wealth of information on the bodying of linseed oil under various conditions, it was felt that similar practical work on safflower oil, even though limited in scope, would be of general interest and value to the industry.

A study was made of the polymerizing rate of safflower oil at temperatures of 575°, 585°, and 595°F. A commercial grade of safflower oil was processed in 1,000-gallon batches, and similar runs were made with linseed and soybean oils for the purpose of comparison. All cooks were made in the same kettle under identical conditions. In each case the oils were heated to 200°F.; at this point a vacuum of about 29½ inches and a mild inert gas sparge were applied to the kettle while heating was continued to gain polymerizing temperature. This temperature was maintained until the desired viscosity was reached, at which time the oil was cooled to 300°F. and vacuum released. In each cook samples were taken at intervals, and a sufficient amount of each sample was retained in order that accurate determinations of acid number, viscosity, iodine number, and refractive index could be made.

The safflower oil used in this study was a shipment from the 1950 California crop. The constants of this oil, together with the constants of the linseed and soybean oils used, are shown in Table I. It should be noted that the iodine value of the linseed oil, though acceptable, is on the low side of commonly used specifications. However the rate of polymerization was normal and did not reflect the low iodine number.

The equipment used to obtain the data for this study was a commercial installation, comprising a 1,200-gallon stainless steel process kettle of recent design (Fig. 1). It is equipped for use of high vacuum as provided by steam jet ejectors. An inert gas sparge of nitrogen and carbon dioxide is used in conjunction with the vacuum, and vigorous agitation is supplied by a direct drive turbine type agitator. Instrumentation of this equipment was very helpful in the study inasmuch as an automatic temperature control of ± 2°F. was obtained during each of these cooks. Indirect natural gas fires are used as the heat source. Rapid cooling of the processed oil is obtained by use of internal stainless steel coils employing water as the cooling medium.

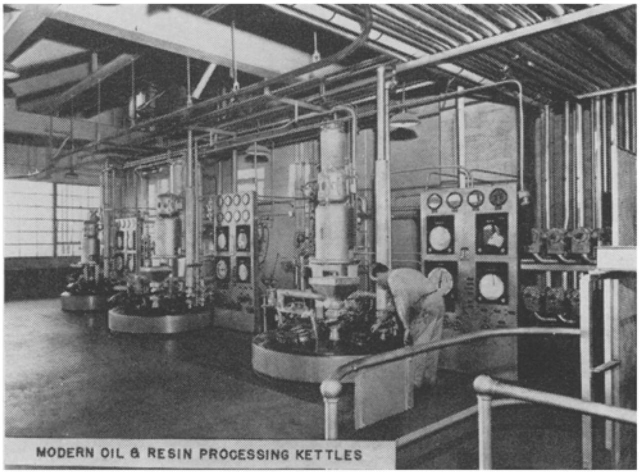

FIG. 1.

The data obtained from the various runs is presented in graphical form. Viscosity is chosen as the common denominator, and in all cases zero time is taken as the time at which polymerization temperature is reached. It should be mentioned that the acid number was easily maintained at a rather low level, between 5 and 7, during all the cooks, hence a comparison of the acid numbers of the various oils was considered to be of no significance.

In considering the effect of temperature on the rate of polymerization (Fig. 2), it is found that safflower oil behaves in much the same manner as other fatty oils, possessing an appreciable degree of unsaturation.

TABLE I

	Safflower		Linseed		Soybean	
	Initial	Final	Initial	Final	Initial	Final
Viscosity						
(Poises)	0.4	55	0.4	56	0.4	40
(Gardner)	A-	Z_3-Z_4	A-	Z_3-Z_4	A-	Z_2-Z_3
Color[a]	10	4	7-8	6-7	6	7-8
Acid value	0.41	6.5	0.50	6.25	0.52	3.5
Iodine number	142	99.5	175	113	135.5	85
Refractive index	1.474	1.484	1.478	1.489	1.4742-1.4763[b]	....

[a] Gardner, 1933.
[b] Jamieson, F. G., "Vegetable Fats and Oils," p. 305, New York, Reinhold, 1943.

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[1] Presented at the 24th Annual Fall Meeting, American Oil Chemists' Society, San Francisco, Calif., Sept. 26-29, 1950.