A STUDY OF CARNAUBA

I PRELIMINARY INVESTIGATION OF *COPERNICIA CERIFERA*

II CHEMICAL INVESTIGATION OF CARNAUBA WAX

III WATER-IN-OIL EMULSIFYING POWER OF CARNAUBA WAX ALCOHOLS AND ACETATES

A thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

by

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Forward

The leaves of Copernicia cerifera yield carnauba wax, a valuable product which plays an important part in industry[1] and is beginning to find its way into the art of pharmacy.[2] While the author's interest lay in a chemical examination of this wax, he was intrigued by the plant's ability to manufacture this peculiar hard substance. This phenomenon stimulated a preliminary investigation of the leaves of this plant in order to gain a better understanding of the chemistry of the plant's processes.

Miriam L. Bombard states[3] "if the plant kingdom were a monarchy in which but a single family of plants had the hereditary right to rule, the palms would unquestionably hold this honored position. The greatest naturalist, Linnaeus, in a rather whimsical "social" ranking of the plants of the world, placed the palms first, further distinguishing them as Principes, the princes or rulers, whereas certain other groups were merely plebeians, patricians, and so forth. It is interesting to note that this term, Principes, continues to appear from time to time in publications as a synonym for the family name of the palms (Palmae or Palmaceae). Although Linnaeus only know 15 species whereas at the present time the family includes from 1,600 to 5,000 kinds of palms, the discovery of new species has in no way minimized his estimate of their "social" prominence." Copernicia cerifera, Mart., (Corypha cerifera, Virey, Arrudlaria cerifera, Macedo) sometimes known as the "Universal Provider", probably ranks first also in economic value[4] principally

because of its being the source of carnauba wax. The plant's most common name is the Carnauba Wax-bearing Palm.

References:

1 Greene, L., Oil and Soap, 16, p. 107 (1939).
Oil, Paint, and Drug Reporter, Aug. 22 (1932).

2 Worton, A., Kempf, P., and Bibbins, F., Journ. Am. Pharm. Assoc., 27, p. 21 (1938).

3 Bombard, M. L., Annual Report of the Board of Regents of the Smithsonian Institution, p. 505 (1956).

4 Franck, H., Pharm. J., p. 406 (1922).

Scientific Names

G. Piso in 1648[1] as well as Raii in 1688[2] used the name Carnaiba for the plant's designation in their descriptions. In 1810 Arruda[3] gave the plant the binomial name Corypha cerifera. Von Martius[4] towards 1819[5], independent of Arruda, christened the plant Copernicia cerifera. De Macedo[6] in 1867 correlated the work of Arruda and von Martius, and took the privilege of renaming the plant Arrudaria cerifera. Macedo based his judgment on the priority of Arruda's discovery and recognition of the plant. However, the latter name gained no favor among botanists and writers as shown by its infrequent occurrence in the literature. Although there seems to be no particular favor by botanists to either of the other names, the Index Kewensis includes both Copernicia cerifera[7] and Corypha cerifera[8] but lists the latter as a synonym for Copernicia cerifera. B. Dahlgren[9] in his Index of American Palms does likewise. Dahlgren gives Caranaiba[10] as the plant's pre-Linnean name and cites Piso as his reference. However Piso's original article shows the name to be Carnaiba.[11]

References:

[1]Piso, G., Hist. Nat. and Med., Lib. 4, p. 125 (1648).

[2]Raii, J., Hist. Plant., v. 2, p. 1568 (1688).

[3]Arruda, M., Cent. Plant. Pern., p. 51, (1810).

[4]von Martius, K., Flora Brasiliensis, Pars II, v. 3, p. 547 (1862).

[5]de Macedo, M., Notice sur le Palmier Carnauba, p. 6 (1867).

[6]Ibid., p. 5.

[7] Hooker, J., and Jackson, B., Index Kewensis, part 1, p. 611 (1895).

[8] Ibid., p. 528.

[9] Dahlgren, B., Index of American Palms, v. 14, p. 127 and p. 151 (1936).

[10] Ibid., p. 528.

[11] Piso, G., loc. cit., p. 126.

Etymology

The genus name Copernicia was given in honor of the famous investigator, Copernicus.[1]

Cerifera, the species name, is derived from the Latin word cerifer (cera + -fer) meaning wax-bearing.[2] It refers to the carnauba wax which is deposited upon the exposed parts of the plant, especially the leaves.

References:

1 Hahmann, C., Arch. der Pharm., 259, p. 176 (1921).

2 Murray, A., New English Dictionary, v. 2, p. 252 (1893).

Synonyms and Common Names

The following is a list of synonyms and common names of the plant Copernicia cerifera occurring in the literature:

Black Palm[1]

Caranahiba[2,3]

Caranahyba[2,3]

Caranaiba[3]

Caranasive[3]

Caranatriba[4]

Caranauba[3]

Caranauve[3]

Caranauva[3]

Caranda[1,2,4,5,6]

Carandhi[4,5]

Caranday[1,4,5]

Carandeuba[3]

Caranhyba[5]

Carandahiba[3]

Carnabuba[4,5]

Carnahuba[1,3]

Carnahyba[3,4,5]

Carnahubelra[3]

Carnhypa[4]

Carnaiba[2,4,5,7]

Carnaubahyba[2,5]

Carnauba[5]

Carnauba Palm[4]

Carnauba wax palm[4]

Carnaubeira[3]

Carnaulia[5]

Carnauva[3]

Carnauve[4]

Crindeuba[3]

Grundeuba[3]

Palma negra[4,5]

Palmen negra[4]

References:

1 Morong, T., Bull. Pharm., 6, p. 19 (1892).

2 Dahlgren, B., Index of American Palms, v. 14, p. 529 (1936).

4 Grimme, C., Pharm. Zentrahl., 62, p. 249 (1921)..

5 Hahmann, C., Arch. der Pharm., 259, p. 176 (1921).

6 von Martius, K., Flora Brasiliensis, Pars II, v. 3, p. 547 (1882).

7 Piso, G., Hist. Nat. and Med., Lib. 4, p. 125 (1648).

8 Wood, G., and Bache, F., U. S. Dispensatory, 16 ed., p. 1742 (1892).

Description of the Plant

Arruda[2] described the plant as reaching a height of thirty feet or more. The green fruits are of the size of small olives which they resemble in shape as well as in color. The ripe fruits are black and shiny and of the size of a dove's egg. The seed is covered with a sweet flesh. The leaves of this plant are about two feet in length folded like a fan when young, later however, opening and developing to its full size of a little more than two feet. In a recent expedition to the source of the Carnauba palm Steinle[3] describes the tree as that of the fan-leaf type and grows to a height of forty feet or more. The uncut trees are crowned with a beautiful ball of green leaves. The plant[3] shows leaf scars on the stems, containing more markings than any other useful plant. The markings exist as the remains of thick spiral-like petioles pressed together on the stems, but they occur only up to a certain height. Raii[4] has pointed out that there are higher and longer markings at first, becoming shorter and finally falling from above, so that the stems exhibit a smooth upper half.

Martius[5] describes the plant as:

Caudex speciosus parte basilari gibboso-armata superiore denutata dein sub vertice petiolorm basibus persistentibus vestita, coma exacte fere sphaeroidea, foliis longe petiolatis petiolo diametrum laminae aequante vel superante, lamina fere orbiculari modo ad imam basin eccisa in lacinias undiqua radiantes plrq. usque ad medium incisa ceraceo-albida. Spadix longissime pedunculatus folia excedens, pedunclo rhachin gracillime elongatam laxe et reulariter ramificatam superante, ramulis floriferis dense velutino-sericeis denique calvescentibus flores per spicas nemutas paucas conglomeratos vel as apicem ramulorum solitarios laxe sparsos

evolventibus, floribus paros albidis, baccis ellipsoideis solitaris ad ramulos sparsis pendulis.

Caudex plrq. 10-15 m. altus diametro spithamea vel amjore, gibis inferne armatus oblique erectus 4-6 cm. altis et 2-5 cm. crassis per spiram densam secus foliorum dispositionem congestis. Folia plurima dense congesta 1.5-2 m. lg. undique patentia, vetustiora reflexa, juniora erecta, itaque omnia caput globosum caudicis verticem occultans formantia; petiolus 1-1.5 m. lg. aculeis validissimis praesertim supra vaginam armatus in parte superiore rarius aculeatus ad apecem saepe fere inermis; lamina 8-10 dm. in diam. floccis ceraceis albis dise adspeisa, sed in facie superiore glabrescens, plrq. ultra dimidium in lacinias 55-55 aetate provectiore ad apicem fifidas pungentes incisa, mediano inferne valide prominente et nervis II. multis temussimis et nervis III. oblique reticulatis conspicius. Spadices 2-5 m. lg. pedunculo spathis multis incomletis tubuloso-vaginantibus vestito, rhachi spathis eisdem ramos in axillis gifnentibus instructa, ramis aeque ramificatis et spathellas (ramilas paniculatos suffulcientes) - gerentibus, spicis floriferis 0.5-1 cm. lg. in parte inferiore spiculas paucifloras quasi glomerulatas et apicem versus flores solitarie spasos evolventibus. Flores androeceum et gynaeceum untrumque plrg. fertile evolventes, interdum unisexules alterius sexus organis sterilibus fertilia aemulantibus, calyce viridescente, corollam longatam dimidiam subaequante vel superate, filamentis tubi lobis y brevissime insidentibus, berimine tridymo ad apicem connato intus inter ovaria 5 rima profunda rtipartito. Baccae 2 cm. altae plrq. ellipsoideae (cf. iconem nostram) rarius minores fere globosae colore cinereo-coerulescente.

References:

1 Piso, G., Hist. Nat. and Med., Lib. 4, p. 125 (1648).

2 Steinle, J., Ind. Eng. Chem., 28, p. 1005 (1936).

3 Engler, A., and Prantl, K., Die Nat. Pflanzenfamilien, Teil 2, v. 3, p. 37 (1887-1889).

4 Raii, L., Hist. Plant., v. 2, p. 1568 (1688).

5 von Martius, K., Flora Brasil., Pars II, v. 3, p. 547 (1862).



An Uncut Carnauba Palm in Full Foliage;
This Specimen is About 25 to 50 Years Old

Habitat

Copernicia cerifera is indigenous to Brazil. The plant is wide-spread on the Varzeas or the low lands upon the borders of the rivers and the rivulets of Pernambuco, Paraiba do Norte, Seará, and Piauhy and principally the banks of the rivers Jaguaribe, Apdi, Mossora, and Acu.[1] The centers of the Carnauba country lie within what is commonly described as the "shoulder of Brazil."[2] The growth is almost equally divided between the states of Ceará and Piauhy with some in the neighboring states of Maranhao, Rio Grande do Norte, Pernambuco, and Parahyba. The country consists of arid, alluvial plains dotted with hills and small mountains. During the dry season the sparse vegetation, with the exception of the palm trees, takes on a gray dusty look. The soil, although analysis shows it to be extremely fertile, appears sandy and is baked hard by the hot sun. All but the largest rivers are completely dry. A notable example is the Jaguaribe. In the rainy season this is a mighty torrent about 300 miles in length. During a few weeks in the early part of the year this region is subject to torrential rains. All of the lowlands are completely flooded at this time, and the dry thirsty plants soak up the water which they may not receive for a year or sometimes two.[3] In a general way the area of distribution of the Carnauba palm coincides with the drought-afflicted area of the northeastern states of Brazil, thus being most abundant in the state of Ceará and in the neighboring states, Rio Grande do Norte '

and Paraiba on the east and Piauhy on the west. In this region the stands of Carnauba palms are found principally on the alluvial ground of the flood plains of the largest rivers, chiefly in their lower courses well toward the coast, but also in the interior where some peculiarity of the terrain produces a similar formation. Attempts that have been made to introduce the Carnauba palm elsewhere for commercial purposes have been failures to date. Attempts to grow the plant in other places, especially Ceylon, have showed that the plant will flourish in almost any warm place, especially in humid localities, but it yields no wax outside its native habitat.[4]

References:

1 Koster, H., Travels in Brazil, v. 1, p. 209 (1816).

2 Steinle, J., Ind. Eng. Chem., 28, p. 1008 (1936).

3 Ibid.

4 _____, Amer. Drug., 74, p. 58 (1926).

Therapeutic Uses

Although Copernicia cerifera has not generally been listed in the popular materia medica, the plant has found wide use among the natives of its habitat. Like most medicinal plants its uses are many and varied. Of all the uses that will be cited, most bear on its being a substitute for sarsaparilla.

The root first attracted attention in the civilized world when in 1875 two bales of carnauba root were imported into Liverpool with the following remarks: "The root is recognized by the profession as an excellent purifying agent successfully applied in the cure of various diseases arising from impurity of the blood. We are indeed astonished that it is not more widely known as its therapeutic qualities, which are worthy of full credence, rival those of sarsparilla. The carnauba root likewise has diuretic power and possesses unusual efficacy in the cure of chronic blennorrhoeas. It is very cooling and displays a vigorous action in purifying the blood."[1]

The United States Dispensatory includes the root as a diuretic.[2]

Others have commented on the therapeutic value of the roots. Franck[3] has pointed out that it was used as a purgative. Peckolt[4] has reported that a decoction of the roots has been used by the natives against syphilitic diseases, skin diseases, and rheumatism. He also points out that the chief use of the root serves the Indians and inhabitants as an ash preparation prepared by lixiviation and

mixed with salt and is valued as a panacea. Many Brazilians insist that it is a valuable blood purifier.[5]

References:

1 Symes, C., Pharm. Journ., 34, p. 661 (1875).

2 Wood, G., and Bache, F., U. S. Dispensatory, 16 ed., p. 1742 (1892).

3 Franck, H., Working up from Patagonia, p. 419 (1922).

4 Peckolt, T., Pharm. Rund., 7, p. 261 (1889).

5 Jaeger, R., The United States of Brazil, p. 9 (1925).

Previous Chemical Investigation

Although no work upon the leaves of Copernicia cerifera has been reported, some work has been done on other parts of the plant. Cleaver[1] in 1875 reported that he found traces of an alkaloid, an acrid resinous body, a red coloring matter, a variety of tannic acid, and probably a small portion of volatile oil in the roots. Glucose and a fatty oil were found in the fruit by Grimme[2], while Peckolt[3] pointed out that the seeds contain a red coloring matter and a resin.

References:

[1] Cleaver, E., Pharm. Journ., 54, p. 965 (1875).

[2] Grimme, C., Pharm. Zentralh., 62, p. 249 (1921).

[3] Peckolt, T., Pharm. Rund., 7, p. 265 (1889).

Experimental

Material

The leaves used in this preliminary investigation were obtained from Dr. J. V. Steinle of the S. C. Johnson and Son Company who in turn obtained them from their laboratory in the Carnauba palm country.

As much of the wax as possible was scraped and shaken from the air-dried leaves and then milled until the material passed through a No. 40 mesh sieve. All of the determinations were carried out on this material.

Moisture Determinations

The moisture content of the finely ground air-dried leaves were determined by the xylene method[1] using a Dean-Stark apparatus and the results are given herewith:

Sample I. 4.6 per cent
II. 4.5 per cent
III. 4.5 per cent

Ash Determinations

The ash content[2] of the finely ground material was determined, and the following results are expressed in per cent:

	Sample I	Sample II
Total ash	4.80	4.95
Water-soluble ash	2.66	2.75
Water-insoluble ash	2.14	2.20
Acid-soluble ash	2.76	3.00
Acid-insoluble ash	1.15	1.20

Tannin Determination

The percentage of tannin contained in the leaves used in these studies was determined according to a method described by Villavecchia.[3] The results of three determinations are as follows:

Sample I. 5.24 per cent
II. 5.50 per cent
III. 5.65 per cent

Extraction with Selective Solvents

Two portions of the milled leaves, each weighing 50 grams, were exhausted with selective solvents according to a modified method of Rosenthaler.[4] For the extraction a Soxhlet extractor was employed. The results are as follows:

Solvent	Per cent of Extract I.	II.
Petroleum Ether (B. pt. 55°-40°)	0.88	0.96
Petroleum Ether (B. pt. 65°-68°)	0.97	0.91
Ether	2.60	2.55
Chloroform	1.25	1.20
Alcohol (95%)	17.72	17.81
Marc	76.46	76.70
Totals	99.88	99.93

Description and Comparison of the Extracts

Petroleum Ether (B. pt. 55°-40°). This extract was light green in color, brittle and quite waxy. It had very little odor or taste. It was probably most of the wax that was left on the leaves.

Petroleum Ether (B. pt. 65°-68°). This extract was distinctly fatty in appearance and possessed a marked odor of the plant and had a very biting peppery taste. It was semi-solid and very sticky and was dark green.

Ether Extract. The ethereal extract was dark green and slightly aromatic. It was hard and grainy.

Chloroform Extract. The extract was very much like the ether extract in appearance.

Alcoholic Extract. This material was almost black in color, gummy and resinous. It has a sweet taste and an odor resembling that of prunes.

Marc. The dried marc remaining after these extractions was light in color, odorless and tasteless.

Sucrose Determination

The sucrose contents of the finely milled leaves was determined and the following are the results obtained:

Sample I. 0.45 per cent
II. 0.71 per cent

Pentosan Determination

The pentosan contents of the leaves was determined. The following are the results:

Sample I. 12.19 per cent
II. 12.47 per cent

Pentose Determination

The pentose content[7] of the leaves was determined by calculation from the pentosan content and the results are herewith given:

Sample I. 14.05 per cent
II. 14.72 per cent

Reducing Sugars Determination

The reducing sugars[8] were determined and calculated as dextrose. The following are the results:

Sample I. 2.56 per cent
II. 2.20 per cent

Crude Fiber Determination

The crude fiber content[9] was determined on the marc obtained from the selective solvent extraction and calculated as of the air-dried ground leaves. The results are as follows:

Sample I. 54.49 per cent
II. 55.64 per cent

Starch Determination

The starch content[10] of the leaves was determined and the results below are those obtained:

Sample I. 0.54 per cent
II. 0.74 per cent

References:

1. United States Pharmacopoeia, Eleventh Revision, p. 475 (1936).

2. Woodman, A., Food Analysis, 3 ed., p. 29 (1951).

3. Villavecchia, V., Treatise on Applied Analytical Chemistry, v. 2, 3 ed., p. 542 (1918).

4. Rosenthaler, L., Nachweis Organischer Vergindungen, 2 ed., p. 512 (1923).

5. Official Methods, 4 ed., p. 154 and p. 479 (1935).

6. Ibid., p. 544, and p. 479.

7. Ibid.

8. Ibid., p. 542 and 479.

9. Ibid., p. 540.

10. Ibid., p. 542 and 479.

Derivation of Carnauba

The literature contains two possible derivations for the name of carnauba wax. The first[1] is that it appears to be a shortening of the Portuguese word Carnahuba, employed to designate the tree in Brazil. It is derived from two words common to Portuguese and Spanish, Carne meaning flesh, and uva meaning grape, in allusion to the fleshy berries which bear some similarities to the grape. The other version[2] is as follows: The southern Brazil tree Caranda or Carana had frequently been confused with the Carnauba palm; however, it yields no wax. The southern Caranda has, however, given its name to its northern relative, for the word Caranda, of the Guarny Indian tongue, signifying a stand of palms, has in the north been transformed to Carnauba by shortening and by the addition of the suffix uba which in the tupy language means tree.

References:

1 Morong, T., Bull. Pharm., 6, p. 19, (1892).

2 Anonymous pamphlet.

Common Names

Carnauba wax is known by several names in the literature as well as in its native habitat and on the market. The following is a list of those found:

Brasil Wax[1]

Canaiba[2]

Canauba[3]

Caranaiba[4]

Caranda[3,6]

Caranda wachs[6]

Carandawachs[6,7]

Caranauve[3,4]

Carauba-wachs[6]

Carnahuba[5,9,10]

Carnahubawachs[6,7]

Carnahyba[3,5]

Carnauba[5,7]

Carnauba wachs[6]

Carnaubawachs[10,11]

Carnaubeira[12]

Cearawachs[3,6;11,12]

Ceara-wachs[7]

Cera Carnauba[6,7]

Cera de Carnauba[6]

Cera foliorum[6,7]

Cera palmarum[6,7]

Cira de carnahuba[6,7]

Cire de Carnauba[3,6,7,11]

Palma negra-wachs[6]

Palma negra wachs[6,7]

Palmenwachs[6,7]

References.

1 Kebler, L., Am. Journ. Pharm., 65, p. 585 (1893).

2 _____, Proc. Am. Pharm. Assoc., 17, p. 187 (1869).

3 Tschirch, A., Handb. der Pharmacog., v. 2, p. 734 (1912).

4 Virey, J., Journ. de Pharm. et Chim., 25, p. 112 (1834).

5 von Martius, K., Flora Brasil., Pars 2, v. 3, p. 547 (1869).

6 Grimme, C., Pharm. Zentrahl., 62, p. 249 (1921).

7 Hahmann, C., Arch. der Pharm., 259, p. 176 (1921).

8 Herberger, J., Buch. Rep. de Pharm., 49, p. 259 (1834).

9 Berard, P., Bull. Soc. Chem., (2) 9, p. 41 (1868).

10 Brannt, W., Animal and Veg. Fats and Oils, 2 ed., v. 2, p. 144 (1896).

11 Lewkowitsch, J., Chem. Tech. Anal. Oils, Fats and Waxes, 5 ed., v. 2, p. 872 (1904).

12 Benedict, R., and Ulzer, F., Analyse der Fette und Wachsarten, 5 ed., p. 1045 (1908).

13 Higgins, E., Am. Journ. of Pharm., 92, p. 184 (1919).

History of the Discovery of Carnauba Wax

De Macedo[1] made the claim that it was his kinsman, Manoel-Antonio de Macedo, who, at the beginning of the eighteenth century discovered carnauba wax. It seems odd that neither Piso[2] nor Raii[3] nor even the Very R. P. M. Fr. José Marianno da Conceiceo Veloso who in 1797[4] informed Arruda of the plant did not notice the wax formation on the leaves of the carnauba palm.

Authorities of Brasil were quick to recognize this discovery because Brande[5] in a paper written to the Royal Society of London, May 9, 1811, concerning a chemical investigation of carnauba wax, stated the following:

"It (wax) was transmitted to Lord Grenville from Rio de Janeiro, by Comte de Galveas, as a new article lately brought to that city from the northern-most parts of Brasilian dominicans, ... When the Comte wrote Lord Grenville in July last, orders had been sent to the governors of the districts where it grows, requiring them to report more particularly, on the nature and qualities of this interesting tree; we may therefore hope that information will soon be obtained, whether the article can be procurred in abundance and at a reasonable price, in which case it will become a valuable addition to the comforts of manking, by reducing the price and improving the qualities of candles, flambeau, ..."

Although the wax resembles that described by Humboldt[6] in 1815 it is not the same, as Humboldt's wax was collected from Ceroxylon andicola which grows on high mountains on the edge of

regions of perpetual snow in Brazil. The Carnauba palm, however, was not entirely unknown to Humboldt, for it appears from his book, that M. Correa had informed him that a palm called Carnauba by the natives of Brazil, produced a wax from its leaves.

Another early reference to the use and discovery of carnauba was is related by Koster[7] in his account of his travels in Brazil sometime before 1816. He states, "During my stay at Natal, the governor shewed me a species of wax which is produced from the leaves of the Carnauba, a tree I have frequently mentioned. A quantity of this wax was sent by him to Rio de Janeiro. It is mentioned in one of Dr. Arruda's publications, and a sample of it found its way to England, and has been taken notice of by the Royal Society. The Governor, in one of his journies through his province passed the night, as often happened, in a peasant's cottage. A wax candle was lighted and placed before him, which was rudely made, but afforded a good light. He was somewhat surprised at this, because oil is generally used. On making inquiry, he found that the wax dropped from the leaves which covered the cottage, during the heat of the day. I suppose the cottage had been newly built or that a fresh covering of leaves had been on to it. He afterwards made the experiment himself; tried some of the candles; and became confident of the importance of the vegetable wax."

Carnauba wax apparently gained no favor until the beginning of 1846.[1] However, in the early part of the eighteenth century the government of Brazil offered a prize of 6000 francs to the discoverer, Macedo. The authorities were ignorant of Macedo's whereabouts;

consequently the prize was never awarded. However, Macedo was somewhere in the province of Ceará and spent the rest of his life in a state bordering on poverty.

The younger Macedo took great interest in the commercial possibilities of carnauba wax. He states[8] that in 1836 he had great difficulty in being able to bring a half a kilogram of the wax to Paris, thus emphasizing the rareness of the wax. He took this wax in 1837 to M. Barruel, laboratory assistant in the course in chemistry at Sorbonne. M. Barruel, without subjecting the sample to a regular wax analysis, limited his observations by saying that he predicted that this material in a suitable state could be used for waxing the floors of apartments. Macedo[9] in 1856 also tried to get several Frenchmen interested in buying some land in Ceará to produce carnauba wax and start a candle factory in Paris, but unfortunately he was not successful.

From the following statistics in the province of Ceará it is possible to gain an appreciation of the progress which was made in this industry once it got started in 1845-1846.[10]

(See next page.)

Exportation of Carnauba Wax
from the Port of Ceara.

Year	Quantity in Kilograms	Official Value in Francs f	c
1845-1846	26,208	17,546	59
1846-1847	1,888	672	60
1847-1848	464	104	40
1848-1849	10,944	4,288	20
1849-1850	—	—	—
1850-1851	5,504	1,497	97
1851-1852	1,088	816	00
1852-1853	4,488	5,556	05
1853-1854	23,296	19,518	10
1854-1855	16,000	15,000	15
1855-1856	41,904	51,871	71
1856-1857	10,256	15,117	99
1857-1858	26,112	34,242	34
1858-1859	51,808	44,142	44
1859-1860	68,096	84,284	81

Exportation of Carnauba Wax
from the Port of D'Aracati

Year	Quantity in Kilograms	Official Value in Francs f	c
1856-1857	538,568	879,429	69
1857-1858	562,160	951,584	57

References:

1 De Macedo, M. A., Notice sur le Palmier Carnauba, p. 16 (1867).

2 Piso, G., Hist. Nat. and Med., Lib. 4, p. 125 (1648).

3 Raii, J., Hist. Plant., v. 2, p. 1368 (1688).

4 Arruda, M., Cent. Plant. Pern., p. 51 (1810).

5 Brande, W., Phil. Trans. Roy. Soc. London, Part I, p. 261 (1811).

6 Ibid.

7 Koster, H., Travels in Brasil, v. 1, p. 209 (1816).

8 De Macedo, M., loc. cit., p. 24.

9 Ibid., p. 25.

10 Ibid.

Production of Carnauba Wax.[1]

The actual production of carnauba wax is exceedingly crude. The original native methods of production have been little improved. The harvesters go forth into the carnaubal armed with a sharp sickle-like knife fastened to the end of a long pole. With this long-handled knife they cut the desired number of leaves from each tree. Harvesting takes place from about July to January; the time varies in different localities, depending primarily on rainfall. A maximum of about twenty leaves can be cut from one tree during the season. This is generally done in about three cuttings, ten leaves on the first cutting and five on each of the subsequent two. The leaves are cut only from the upper half of the foliage ball because, when the leaves pass below the horizontal, they have lost a goodly quantity of their wax-coating. A few leaves from each tree are cut from the so-called cabbage of the ball before they have actually opened. From these closed leaves the lighter colored grades of wax are obtained. As the leaves fall to the ground after being cut, workers gather them together, slash off the long stems, and divide them at the same time into two groups — the open leaves or palhos, and the closed leaves or olhos. These freshly cut leaves are now transported, usually on the back of a patient donkey, to a natural open area where the drying field is located.

At the end of the day, the leaves are spread out in the drying field in neat rows, the olhos in one section and the palhos in another. Under the intensely hot sun the leaves are thoroughly

dried in about three days. As the leaves dry, the fibrous cells shrink, but the wax coating on the surface does not, and therefore loosens from the leaf. The constant winds blowing in from the ocean not only help to dry the leaves but also to blow off and dissipate a considerable proportion of this powdery wax coating. After the third day the leaves are thoroughly dry, and the laborers gather them carefully together, tie them into bundles, and transport them to an out-building near the main farm-house.

In a closed shed or hut which, when the door is closed, has no opening other than a small 8-inch-square hole to admit a little light and air, the wax-beaters work. These men, stripped to the waist, perform the most arduous task in connection with the production of carnauba wax. On a bench or stand in the middle of the room are mounted a half-dozen or more sharp knives pointing upward between two curved brackets. The beater takes a handful of leaves, two or three at the most, and draws them between the brackets through the maze of knives. This operation is repeated until the palm leaves are thoroughly slit. He then takes a short stick and pounds the leaves until all the loose wax is removed. The cutting operation is necessary to open the closed portion of the leaves from which a great deal of wax is obtained. The spent leaves are generally thrown out of the hut through the ventillating opening, and the powdery wax is allowed to accumulate on the floor.

At the end of the day the powdered wax is gathered into baskets and tins and removed to the melting room. Here, in a

thatched hut and over an open fire, the powdery wax is melted. Often an old five gallon gasoline can from which the top has been removed is used as the melting vessel. A full five gallon can of powder will melt down to less than a quart of molten wax. The wax is slowly melted over the fire, being stirred constantly during the operation. If a chalky wax, called arenosa is desired, a cup of water is added to the wax while it is being melted. When no water is added, the regular gorduroso or north country wax is produced. (In the production of the light No. 1 or 2 wax, the wax powder is beaten from the young, unopened leaves or olhos is employed.) The molten wax, containing a great deal of leafy fiber, is quickly poured into a cheesecloth held by two natives and is filtered. To obtain most of the wax from the residue, the ends of the cloth are twisted, and the center mass is squeesed with a pair of large wooden scissors. Some of the more modern establishments use a crude type of filter press. The cheesecloth containing the molten wax is placed in a cavity over a log over the bottom of which strong fibers have been stretched. A block is placed on top of the folded cheesecloth, and a long heavy pole is used as a lever to express the wax from the cake. The molten wax is caught in an earthen pan and allowed to cool, and the broken pieces of wax thus obtained are now ready for the market.

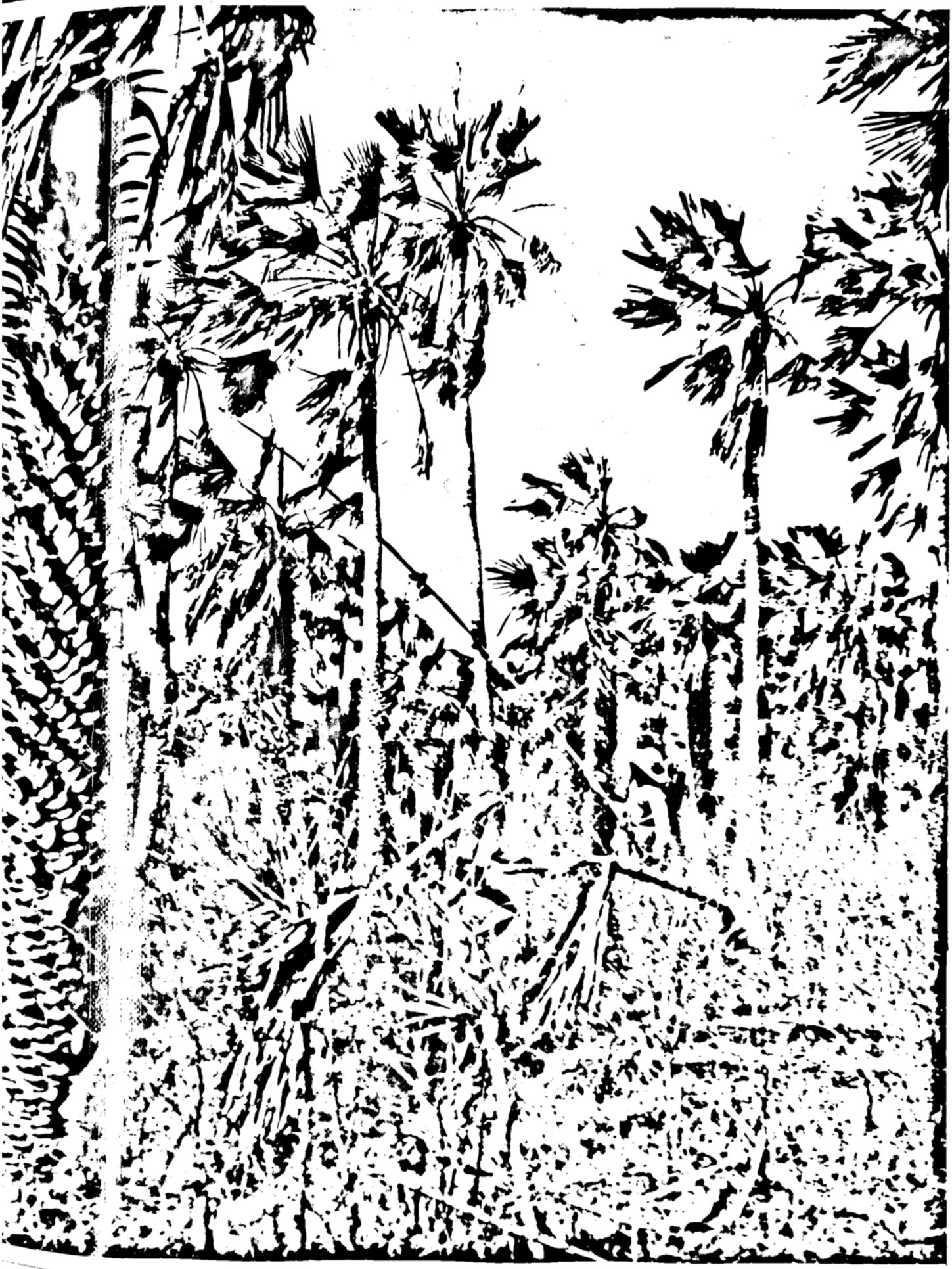
This procedure of harvesting and wax recovery is commonly used in the state of Ceará. In Piauhy a slight variation is employed. Here scattered rainfall is more frequent, and, if an unexpected

rain should occur while the leaves are in the drying field, the entire yield from the cutting would be lost. Therefore, in order to reduce the drying time to one day, the freshly cut leaves are carefully slit before they are spread in the drying field. The women and children of the worker's family sit about with long sharp knives with which they deftly slit the green leaves into fine shreds which still remain attached to the butt end of the leaf. The remainder of the operation is similar to that already described, except greater care must be exercised in gathering the dried leaves since the powdery wax is even less firmly attached to these slit leaves than to the dry whole leaves.

The yield of wax per leaf varies with the age of the tree, the locality, and the amount of rainfall which has preceded the harvest. On an average, however, a leaf will yield about five grams of wax. Considering the maximum cutting of about twenty leaves from a tree, five carnauba palms will produce about one pound of carnauba wax a year. One native can handle about a thousand leaves through the complete process in a day.

References

1 Steinle, J., Ind. Eng. Chem., 28, p. 1004 (1936).



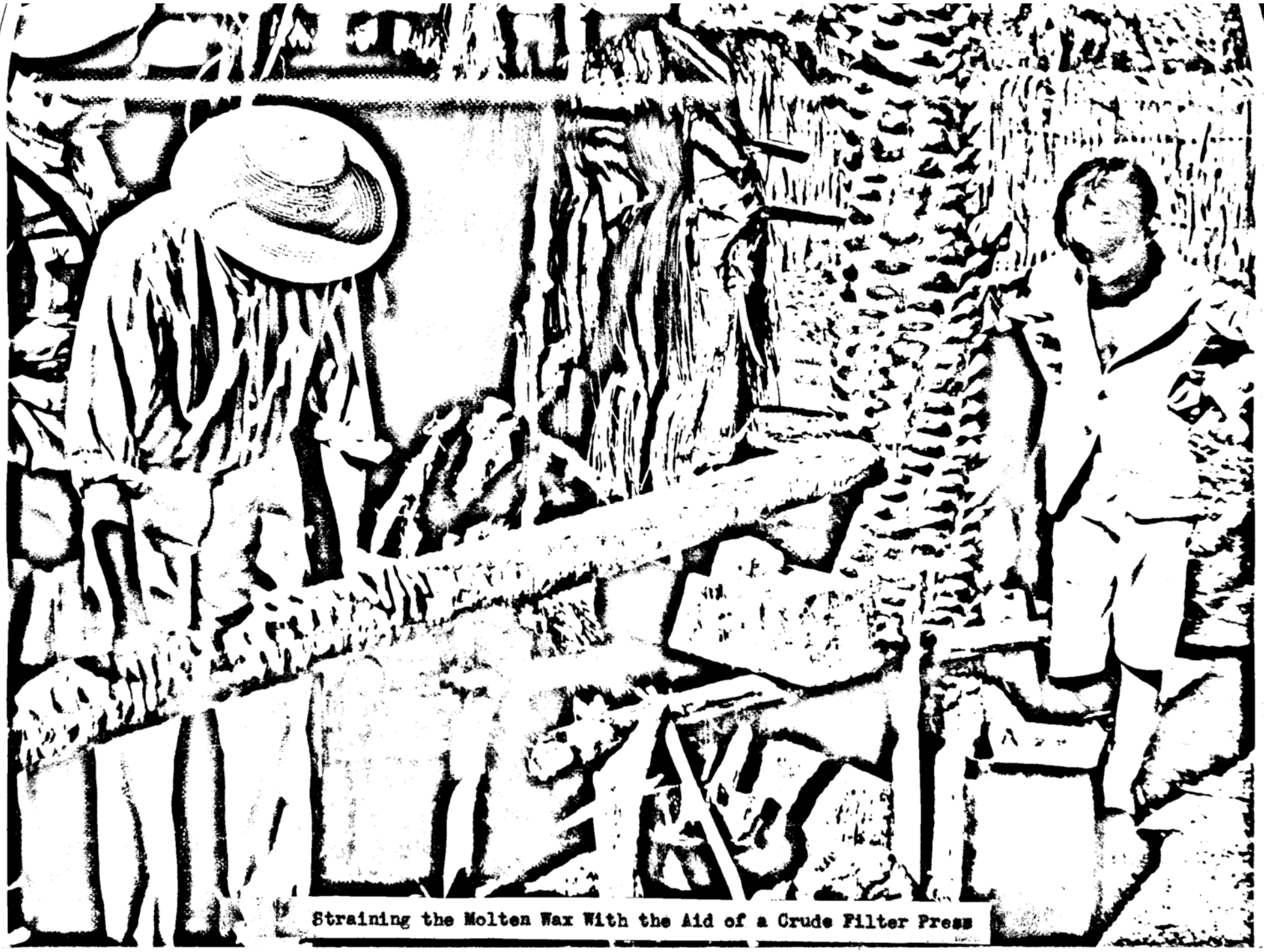
Cutting Leaves from the Trees
With a Sharp Sickle-Like Knife Mounted on a Long Pole



Freshly Cut Leaves, After Removal of the Stems,
Are Transported to the Drying Field



After Drying for 3 Days in the Sun,
The Leaves are Carefully Gathered into Bundles for Beating



Straining the Molten Wax With the Aid of a Crude Filter Press

Etymology and Early Use of the Word Wax

The word wax (waeks) outside of the Teutonic occurs as the Lithuanian word waskas (vasku) but is probably adopted from the Teutonic. The root may be identical with the Teutonic waxs (wax v') meaning to grow. It does not seem impossible that the etymological sense may have been "that which grows (in the honeycomb)". The view most in favor refers the word to the Indogermanic root weg, to weave, found in the old Irish figim, to weave, Lithuanian, velvum, veil, sail (believed to be from the prehistoric veg-slom), and in certain Teutonic words. The advocates of this etymology appeal to the apparent semisiological parallel of the German wake, honeycomb, presumed to be from the root of weben, to weave.

Murray's dictionary includes the following quotations involving the early uses of the word wax.

1200. Trin. Coll. Homer., 47. "alse wex on be candele sene, be welke wioinnen."

1568. Chaucer, Cant. Tales, Prol. 675. "This Pardoner haddle beer as yelow as wex."

1398. Trevisa Barth. "Wexe is the drastes of honey."

Reference:

1 Murray's English Dictionary, part 2, sec. I, v. 10, p. 194 (1895).

Definition of the Term Wax

The word wax is a generic term designating a certain class of substances. Like many other generic terms designating a group of naturally occurring products, the word was adopted from the name given to the first known member of this group, that is the "wax par excellence", beeswax. That beeswax was the first known wax is shown in its etymology, for the word is derived from the Teutonic waxs meaning "that which grows (in the honeycomb)." Thus as a new substance that resembled beeswax was found, it too was called a wax. These resemblances were not based on chemical likeness, but rather on physical properties, such as waxiness to the touch, insolubility in water, a density less than water, combustibility, etc. Thus, a wax in a generic sense really means "a substance like beeswax."

Today, Webster[1] defines the term, wax, as "any of a class of substances of plant or animal origin. They contain esters, and often in addition, alcohols and fatty acids and hydrocarbons. Usually 'True' waxes are distinguished chemically from fats (which are esters of glycerol) as containing chiefly esters of higher monohydroxy alcohols. On this basis certain oils, as sperm oil, are called liquid waxes." Chibnall[2] attempts a more rational definition, "A wax is a product containing long chain aliphatic compounds, hard or becoming hard by hydrogenation, fat soluble and containing no glycerides."

A survey of the definitions of the term wax from authoritative

sources beginning with the early period of modern chemistry proved interesting. The following is a list arranged in chronological order depicting what was understood as a wax from the earlier times to the present.

1767[3] "A wax is a concrete fatty material which is obtained from bees or plants."

1799[4] "The matter of wax, as forming an ingredient in many vegetables, is discoverable, partly from certain flexibilities in such bodies."

1803[5] "The light matter which is called the down of fruits, which silvers the surface of prunes and other fruits, is wax."

1815[6] "Wax exists also as a vegetable product and may in this point of view be regarded as a concrete fixed oil."

1862[7] "Waxes or those closely related substances are generally widely distributed in the plant kingdom. It occurs mostly with chlorophyll, many times also in other plant parts and chiefly as a coating. These wax substances of the plant kingdom are different from fatty substances in that on treatment with potassium hydroxide no glycerin is formed and no yielding of acrolein on dry distillation (except a species of Japanese wax); only from a few plants can these be obtained with profit."

1875[8] "Vegetable wax. An excretion from certain plants, having the consistency and appearance of wax. It occurs sometimes on the surface of leaves and fruit. It is sometimes obtained by bruising and boiling the plant, or parts of it in water, when it floats on the surface on cooling."

1895[9] "Any of a class of substances, found in nature in greater or less purity, including beeswax and other compounds resembling it in general properties (more or less) in chemical composition. In chemistry it is properly restricted to those 'waxes' of animal and vegetable origin which, like beeswax, are composed of fatty acids and alcohols. The mineral 'waxes' are hydrocarbon."

1918[10] "The terms 'fatty oils, fats and natural waxes' are used to designate those oils, fats and waxes which are the products of animals and plants as distinguished from those of oils and waxes which result from the treatment of certain mineral products. Natural waxes are those derived from animal and vegetable sources."

1921[11] "The term wax, when used in the chemical sense, has reference to this particular type of ester rather than to any special physical properties which the compound possesses, and both solid and liquid waxes are known."

1929[12] "Wax (waks). One of a group of plastic substances obtained from plants or deposited from insects which consist of esters of fatty acids with high atomic alcohol radicals: as

beeswax: .... Myricyl palmitate $C_{30}H_{61}\cdot C_{15}H_{31}O_2$

spermaceti .. Cetyl palmitate $C_{16}H_{33}\cdot C_{15}H_{31}O_2$.

Waxes differ from fats in that they are esters of monohydric high atomic alcohols; whereas, fats are the esters of trihydric, low atomic alcohols (as glycerol)."

1955[13] "Waxes. The term 'wax' is applied to natural products of which beeswax is the best known, having properties similar to those of fats. In organic chemistry it is applied specifically to natural products consisting principally of esters which may be thought of as fat in which glycerol is replaced by other alcohols. Most of these alcohols have a relatively high molecular weight and a single OH group."

1956[14] "The term wax is frequently used as generic name for a number of solid hydrocarbons."

[15] "Waxes are esters formed by combination of mono- or dihydric alcohols with higher fatty acids."

[16] "The term pure 'wax' applies to esters isolated from natural sources or prepared synthetically. Examples, cetyl palmitate, cetyl stearate, etc."

[17] "Liquid waxes have so far only been found in animals and are so nearly related to each other that it is impossible to distinguish between them by chemical means."

1937[18] "Esters of higher acids and higher alcohols are waxes."

1939[19] "Waxes. The various kinds of wax consist predominantly of esters of the higher mono-basic carboxylic acids with the higher monohydric (seldom dihydric) alcohols. In addition they always contain some free acids, some free alcohols, and often hydrocarbons."

References:

1 Webster's Dictionary, p. 2888 (1937).

2 Taken from a lecture delivered by Prof. Chibnall in 1938.

3 Macquer, P., Dictionnaire de Chymie, p. 501 (1767).

4 Murray's New English Dictionary, v. 10, part 2, sec. I, p. 194 (1893).

5 Ibid.

6 Ibid.

7 Doebereiner, F., Chem. Schule d. Pharm., p. 725 (1862).

8 Sweringen, H., Pharm. Lexicon, p. 409 (1875).

9 Murray, op. cit.

10 Fryer, F., and Weston, F., Tech. Handb. Oils, Fats, Waxes, v. 1, p. 5 (1918).

11 Thatcher, R., The Chem. of Plant Life, 1 ed., p. 140 (1921).

12 Bailey, D., and Bailey, K., An Etymological Dict. Chem. and Mineralogy, p. 299 (1929).

13 Harrow, R., and Sherwin, C., Textbook of Biochem., p. 121 (1935).

14 Lewkowitsch, L., Chem. Tech. and Anal. Oils, Fats, and Waxes, 6 ed., v. 1, p. 4 (1936).

15 Ibid., p. 66.

16 Ibid.

17 Ibid., p. 69.

18 Whitmore, F., Organic Chemistry, p. 546 (1937).

19 Karrer, P., Organic Chemistry, p. 190 (1938).

Classification of Waxes

In order to bring order into members of the "lumber chamber" a rational classification is necessary. The usual classifications for these classes of substances are based upon chemical properties. The chemical properties of a single product vary to such a large degree that it would be impossible to classify one substance, to say nothing about classifying a whole group of substances. A classification based upon chemical properties will sooner or later end in chaos. A reclassification of waxes according to "source" regardless of properties would solve the problem.

Chibnall's[1] classification which he has called "Occurrences of Waxes" comes closest to a rational classification.

Epidermal Excretions.
- Candelilla wax
- Carnauba wax
- Apple peel wax

Secretion.

Insect waxes of uncertain origin.
- Beeswax
- Lac-wax
- Cochineal wax

Leaf waxes (Not epidermal excretions, but an integral part of the protoplasm of mesophyll.)
- Cabbage
- Brussells sprouts
- Lucerne
- Wheat
- Cocksfoot

Other kinds.
- Sperm
- Bird (feathers).

Lewkowitsch[2] says the following regarding classification: "In classification of waxes we can, in our present state of knowledge, adopt the iodine value only as a basis for subdivision, as it is not yet possible to establish a distinction, based on chemical properties, between vegetable and animal waxes. Although a phytosterol has been shown to occur in flax wax and cholesterol in wool wax, definite proof is still wanting that a vegetable and animal wax can be differentiated in a similar manner as in the case of vegetable fats by the presence of these two alcohols.

"For the sake of uniformity, it is convenient to carry the classification on the same lines as for fats."

The following is the classification Lewkowitsch offers for waxes:

I. Liquid waxes

II. Solid waxes
- A. Vegetable
- B. Animal

The classification above is not a solution to the problem since we are no better off than when we started. Fryer and Weston[3] offer the following classification:

1. Animal and Vegetable waxes.
2. Mineral waxes.
   - A. Waxes obtained in a more or less pure condition from the earth, e.g.
     1) Ozokerite.
   - B. Waxes obtained by extraction of mineral products with suitable solvents, e.g.
     1) Montan wax from brown coal.
     2) Bitumen wax from bitumen.
     3) Beat wax from bitumen.
   - C. Waxes obtained by destructive distillation of mineral products, e.g.
     1) Shale waxes from shale.

To complicate matters another class of compounds also known as waxes is the new type of substance called Etholides. Lewkowitsch[4] says the following: "Etholides: A name given to a new class of vegetable waxes obtained from the leaves of coniferous plants (Juniperus Sabini, J. communis, Thuja occidentalis, etc.). They do not contain an alcohol constituent. It is believed to be hydroxy acids with the formation of esters between two of these compounds, compared with formation of peptides from amino acids."

The question arises, "Where would this new wax fall into a classification?" Since it has been shown that some waxes contain small amounts of hydroxy acids, a proper classification based on properties would require a reclassification every time a new wax is found.

References:

1 Taken from a lecture delivered by Prof. Chibnall (1938).

2 Lewkowitsch, L., Chem. Tech. Anal. Oils, Fats, Waxes, 6 ed., v. 1, p. 5 (1956).

3 Fryer, P. and Weston, F., Tech. Handb. Oils, Fats, Waxes, v. 1, p. 5 (1918).

4 Lewkowitsch, loc. cit. p. 70.

Previous Work on Carnauba Wax

William Thomas Brande[1] in 1811 published the first experimental work on carnauba wax. Although Brande did not attempt to investigate the composition of the wax, he did report many experiments concerning the physical properties and behavior of the wax to acids, destructive distillation, descriptions of various solutions of the wax, attempts to bleach the wax, and many experiments showing its unlikeness to other waxes. The chemical composition of this important vegetable wax was unknown until 1876 when several publications revealing its chemical nature appeared. The standard classical work of Sturche[2] appearing in 1884 is still held as authoritative today by most writers. The present status of the chemical composition of carnauba wax is also the result of facts brought forth by Heiduscka and Gareis[3] in 1919, Gottfried and Ulser[4] in 1926, and Francis[5] in 1950.

Sturche's paper not only included his own researches on carnauba wax but a summary of other recent accomplishments. Berard[6] centered his work upon cerotic acid which he obtained from carnauba wax, while Story Maskelyne[7] and von Pieverling[8] studied myricyl alcohol from the same source. Sturche's work represented isolation of constituents wholly by fractional extraction and crystallisation of the saponified wax and further separation by the same means he obtained the different acids. This method of isolation of wax constituents represents a precedent of tedious and painstaking work never equalled, either before or after. The results of this investigation

are as follows:

1) A hydrocarbon, melting point 59-59.5°.

2) An alcohol, $C_{26}H_{53}CH_2OH$, melting point 76°.

3) Myricyl alcohol, $C_{29}H_{59}CH_2OH$, melting point 85.5°.

4) A distomic alcohol, $C_{33}H_{66}(CH_2OH)_2$, melting point 105.5 to 105.8°.

5) An acid $C_{23}H_{47}COOH$, melting point 72.5, identical or isomeric with lignoceric acid.

6) An acid $C_{26}H_{53}COOH$, melting point 79°, identical or isomeric with cerotic acid.

7) An acid $C_{19}H_{38}(CH_2OH)(COOH)$, or its lactone $C_{19}H_{38}(CH_2)(CO)$, melting point 105.5°.

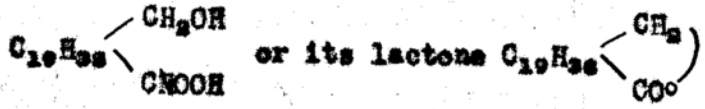
Gottfried and Ulser[9] verified the existence of a hydrocarbon and identified it as being n-heptacosane. These workers also pointed out the existence of ceryl alcohol which is probably the same compound that Stursche represented as $C_{26}H_{53}CH_2OH$. Both the above mentioned men and Heiduschka and Gareis[10] isolated and characterized melissyl and myricyl alcohols to further verify the alcohols Stursche reported. Francis[11] in 1950, using the newer methods of X-ray analysis, examined the alcohols of carnauba wax. He not only found those alcohols already reported, but apparently two alcohols containing 32 and 34 carbon atoms respectively. Francis also examined the "cerotic acid" from carnauba wax and obtained evidence for the existence of C_{24}, C_{26}, C_{28}, C_{30}, (and in one case probably C_{27} acid) acids.

The following is a summary of the present status of the constituents of carnauba wax:

1) Hydrocarbons.
   n-heptacosane
   unknown hydrocarbon, melting point 59°, probably identical with n-heptacosane.

2) Acids.
   tetra-cosanoic acid
   $C_{24}H_{47}COOH$, probably identical with tetra-cosanoic.
   hexa-cosanoic acid
   $C_{26}H_{43}COOH$, probably identical with hexa-cosanoic
   heptacosanoic acid (?)
   octacosanoic acid
   triacontanoic acid

3) Hydroxy acid.



$C_{19}H_{38}$ (CH$_2$OH, CHOOH) or its lactone $C_{19}H_{38}$ (CH$_2$, CO°)

4) Alcohols.
   ceryl alcohol, hexacosanol.
   $C_{26}H_{53}CH_2OH$, probably identical with ceryl alcohol.
   melissyl alcohol, triacontanol.
   an alcohol with 32 carbon atoms.
   an alcohol with 34 carbon atoms.
   a diatomic alcohol, $C_{33}H_{66}$ (CH$_2$OH, CH$_2$OH).

References:

1 Brande, W., Phil. Trans. Roy. Soc. London, 1811, part I, p. 261 (1811).

2 Sturche, H., Annalen, 225, p. 285 (1884).

3 Heiduscka, A., and Garais, M., Journ. prakt. Chem., 99, p. 295 (1919).

4 Gottfried and Ulzer, Chem. Umschau., , p. 141 (1926).

5 Francis, F., Proc. Roy. Soc., A., 128, p. 214 (1930).

6 Berard, P., Bull. Soc. Chem., 9 (2), p. 41 (1868).

7 Maskelyne, N., J. Chem. Soc., 7, p. 87 (1869).

8 von Pieverling, L., Annalen, 185, p. 344 (1876).

9 Gottfried and Ulzer, op. cit.

10 Heiduscha and Garais, op. cit.

11 Francis, op. cit.

Physical and Chemical Constants.[1]

Specific Gravity	Melting Point	Optical Refraction Refractive Index
0.990-0.999	80° - 86°	1.472 (40°)

Viscosity (Ostwald)	Saponification Value	Acetyl Value
42-45 (100°)	79-88	51-60

Iodine Value	Acid Value
8-13.6	0.5 - 13.6

References

Grun, A. and Halden, W., Analyse der Fette und Wachse, v. 2, p. 529 (1929).

Introduction to the Experimental Part

In the isolation, purification, and identification of natural products the goal of the investigator must be that of obtaining the compounds in the condition in which they existed in the original state. However investigations upon fats and waxes, with the exception of the recent work of Boemer and others,[1] have proceeded after saponification and separation into its saponifiable and non-saponifiable fractions. Of course, this does not elucidate the exact structure of the original naturally occurring substance. Since no methods of separating the constituents of waxes without a chemical change are known at this time, the conventional procedure was used in this work. Thus, this investigation began with the saponification of the wax with alcoholic potassium hydroxide, removal of the alcohol, and resolving the whole into soaps and non-soap portions. This separation was accomplished by the preferential solubility of the non-soap portion in Skellysolve B.

The isolation of unitary substances from natural fatty acids has been shown to be very difficult. Up until about the last decade the general method of separating fatty acids was based on fractional crystallisation. In 1898 de Visser[2] at the Apollo Candle Works, Schiedam, crystallized stearic acid 51 times and palmitic acid 56 times from alcohol. Actually such a procedure was not sufficiently varied, and his products were slightly contaminated with each other and with traces of ethyl esters: but de Visser set a standard which has not often been approached. The main difficulty lies in separating

substances from the homologues with which they are usually associated and with which they form solid solutions. Another factor is that the depressions of melting points by admixture with homologues are small. Carboxylic acids show relatively large depressions, yet one per cent of palmitic acid lowers the melting point of stearic acid by only 0.24°[3]; as an extreme example the addition of 20 moles per cent of tetracosanoic acid to tricosanoic acid lowers the melting point by only 0.45°[4].

The purification of materials by crude crystallization is easy if the chief and by-products possess very different solubilities in a certain solvent. If the solubilities are not very different one must follow the path of fractional crystallization.[5] The more difficultly soluble substances separate out first, while the more soluble portions for the time being remain in the filtrate and can be obtained by concentration. One factor must not be over-looked and that is that one substance may possess an influence on other substances either keeping them in solution or throwing them out.[6]

Generally, the separation of homologues of fatty acids is best attained by fractional distillation of either their methyl or ethyl esters at low pressures through an efficient column.[7] Longenecker[8] has prepared a review of the use of fatty acid ester distillation methods in fat analysis. He states that as early as 1877 Krafft[9] attempted the distillation of castor oil but succeeded only in cracking the oil. Haller and Youssoufian[10] described the fractional distillation of methyl esters of coconut oil fatty acids

in 1906. Bull[11] contributed materially to the problem of ester distillation is 1906. He carried out a fractionation of the methyl esters of cod liver oil fatty acids with a heated column provided with a total reflux. Crowther and Hynd[12] in 1917 and Channon, Drummond and Golding[13] in 1924 made extensive studies on the fatty acids of butter fat through the distillation of the methyl esters.

Two factors unquestionably facilitated research with the ester distillation methods. First, the introduction into the distillation system of vacuum pumps capable of continuously evacuating laboratory distillation apparatus to 1 mm. or less of mercury made the process of fractionation of high boiling acids or their esters much less difficult than with the older high vacuum technic. Second, the fractionation equipment available for ester distillations was quite simple until the last decade. However, the rapid concurrent development of theoretical knowledge of the fundamental principles involved in fractional distillations has brought about the construction of entirely new types of distillation equipment.

Analysis of a fat for its constituents by the ester distillation method requires a maximum resolution of mixed esters into samples containing not more than two adjacent groups of homologous series, e.g. C_{16} and C_{18}, not C_{14}, C_{16} and C_{18}. Jantzen and Tiedche[13] in 1930 described a packed distillation column with which they separated the methyl esters of n-eicosanoic, n-docosanoic, and n-tetracosanoic acids in pure state. Single turn glass helices[14] were shown to be particularly desirable for fatty acid ester distillations.

Since 1954 Longenecker and others[15,16,17,18,19] have used a column in which these refinements are combined. The main features of the column are (a) the use of single turn glass helices for the packing, (b) electrical heating of the column which may be regulated to control equilibrium conditions between the liquid and vapor phases, (c) direct measurement of boiling points, (d) total condensation of the vapor, and (e) adjustment of the distillation rate so as to maintain a high reflux ratio (ratio of the vapor condensate returned to the column to that collected as distillate).

Schuette and Vogel[20] have shown that one can calculate the amount and character of acids in a mixture by means of their binary mixture curves, providing the mixture contains only two acids, one acid differing from the other by two carbon atoms, if one knows the mean molecular weight and the solidification point.

A high vacuum distillation apparatus and column (see description p. 54) was used to fractionate the methyl esters of the fatty acids of carnauba wax. Preliminary experiments on the distillation of the methyl esters of the acids of carnauba wax showed that it was very difficult to fractionate the material into definite fractions. Thus, it was not possible to obtain clear-cut fractions. Francis et al[21], in an attempt to obtain pure arachidic acid from a preparation obtained from peanut oil, made a systematic fractional distillation of its ethyl ester and finally obtained several fractions. From the corresponding acids which were repeatedly recrystallized they obtained X-ray data. They obtained no separation of pure individual

esters. Holde,[22] after describing the results of fractionations of the ethyl esters of montanic acid, concluded that separation was not possible. With this in mind an attempt was made to make a systematic fractional distillation in order to obtain fractions most likely to contain only two acids so that Schuette and Vogel's curves could be utilized.

Preliminary experiments also showed that about half of the methyl esters of acids of carnauba wax would not distill without decomposition. Thus, the work that was done on the acids was solely that of the distillable portion. The following is an outline of the method used:

1. Saponification of the crude wax.
2. Separation of the soap from the non-soap portion.
3. Preparation of the methyl esters from the acids obtained from the soaps.
4. Distillation of the crude methyl esters into distillable and non-distillable fractions.
5. Fractionation of the distillable portion into like-boiling fractions.
6. Division into ten degree distilling fractions.
7. Division into five degree distilling fractions.
8. Saponification of the methyl esters into the corresponding acids.
9. Repeated recrystallization, determinations of neutral equivalents, and solidification points until definite results were obtained from Schuette and Vogel's curves.
10. Admixture of definite amounts of pure acids to each fraction so as to change its composition to a known amount and check its solidification point with its theoretical equivalent obtained from the curves.

References:

1 Boemer, A., Brehm, F., Z. Unters. Nahr. Genuss., 72, p. 1 (1936). Brown, J., Oil and Soap, 15, p. 102 (1938).

2 de Visser, L., Rec. Trav. Chim., 17, p. 182 (1892).

3 Ibid.

4 Ashton, R., Robinson, R., Smith, J., J. Chem. Soc., 1936, p. 283 (1936).

5 Orthner, L., Reichel, L., Organische-Chemisches Praktikum, p. 29 (1929).

6 Ibid.

7 Ashton, R. loc. cit.

8 Longenecker, H., Oil and Soap, 17, p. 55 (1940).

9 Krafft, F., Ber., 10, p. 2054 (1877).

10 Haller, A. and Youssoufian, Compt. rend., 145, p. 803 (1908).

11 Bull, H., Ber., 39, p. 3570 (1906).

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13 Channon, H., Drummond, J., and Golding, J., Analyst, 49, p. 511 (1924).

14 Jantzen, E., and Tiedche, C., J. pr. Chem., 127, p. 277 (1930).

15 Longenecker, H., J. Soc. Chem. Ind., 56, p. 199T (1937).

16 Hilditch, T. and Longenecker, H., Biochem. J., 31, p. 1806 (1937); J. Biol. Chem., 122, p. 497 (1937-38); Longenecker, H. and Hilditch, T., Biochem. J., 32, p. 784 (1938).

17 Hilditch, T. and Jasperson, H., Soc. Chem. Ind., 57, p. 84 (1938).

18 Longenecker, H., J. Biol. Chem., 128, p. 645 (1939); Ibid., 129, p. 15 (1939); ibid., 130, p. 167 (1939).

19 Smith, J., and Dastur, N., Biochem. J., 32, p. 1868 (1938).

20 Private communication.

21 Francis, F. Piper, S. and Malkin, T., Proc. Roy. Soc., A. 128, p. 214 (1930).

22 Ibid.

Experimental

Material

The material used in this investigation was the "chalky" grade of carnauba wax obtained from a large commercial shipment made to the S. C. Johnson and Son Company. All of the material used was processed as follows:[1] The large lumps of wax were broken by placing them in a thick cloth bag and by pounding with a hammer until the material was reduced to smaller pieces. Then the wax was placed in a large iron mortar and with the aid of a heavy pestle pulverized to a fine powder.

Reference.

[1] McLoud, E., Investigations on Carnauba Wax, Master's Thesis, U. W., p. 7 (1955).

The Apparatus

Figure 1 represents the soda-lime, sulfuric acid, and freezing traps. A mixture of powdered dry ice and acetone was used as the freezing medium.

Figure 2 shows the distilling head in actual size. This head was used in the distillation of the crude methyl esters. The apparatus was connected to the distilling flask and a thermometer inserted in the top of the head and stoppered with rubber tubing.

Figure 3 shows the combination column and receiver[1]. The packing in the column is a single turn glass helix. The distillate was collected in an 8 inch test tube and the opening closed with a rubber stopper. The column was heated with an outside heating jacket similar to those used with a Widmer column.

The system was evacuated over night before distillation was started. A Cenco-Hyvac pump was used for evacuation and a modified McLeod gauge for measuring pressures. Before any distillation was started a pressure of 0.01 mm. of mercury was obtained. Whenever a new fraction was placed in the distilling flask it was necessary to evacuate the system over night before distillation was continued. When fractions were cut the vacuum was released up to the point of the three-way stopcock, the rubber stopper removed, the fraction replaced by a new tube, restoppered with a fresh rubber stopper and evacuated again. About five minutes was necessary for the foregoing operation.

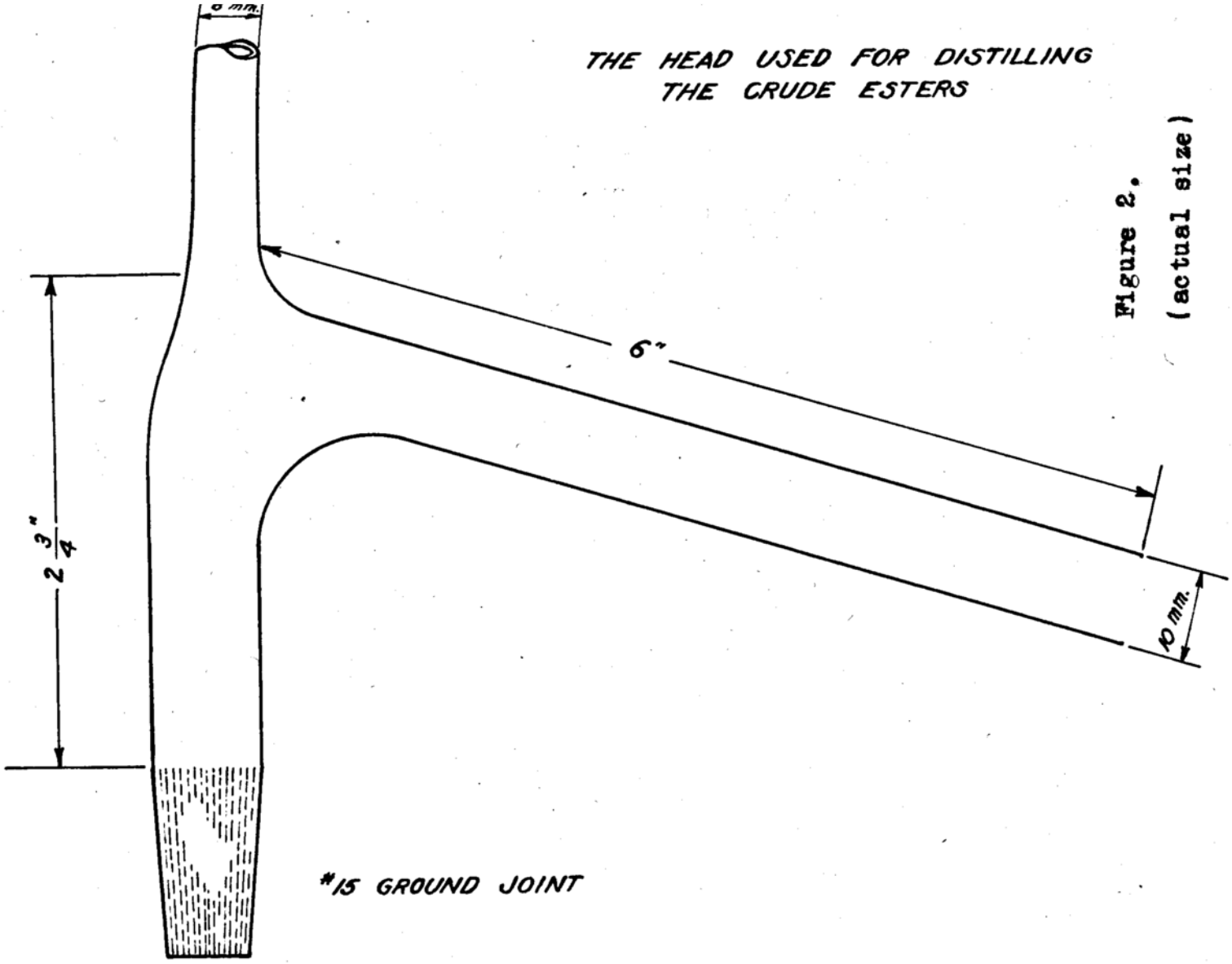
References

Bloom, E., Hydrogenation of Lignin, Ph. D. Thesis, University of Wisconsin, p. 15a (1939).

Figure 1.

Traps

(one-third actual size)



THE HEAD USED FOR DISTILLING
THE CRUDE ESTERS

Figure 2.
(actual size)

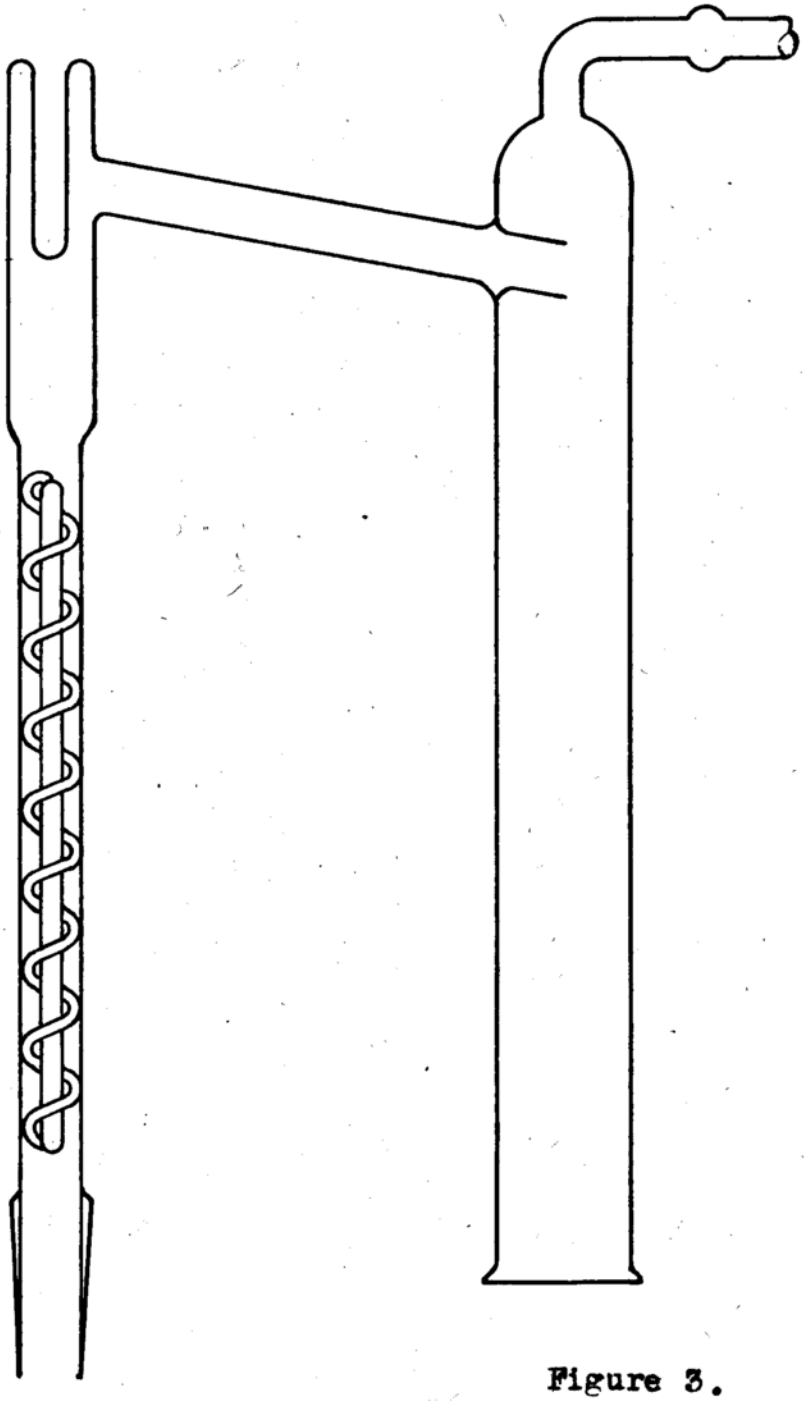


Figure 3.

Column

(one-half actual size)

Solidification Points.

The method of determining the solidification temperature of fractions of methyl esters and free fatty acids was that of Schuette and Vogel[1]. The method is as follows: The material was prepared for the determination by weighing up 0.7 gram in a 5-inch test tube. The tube was placed in a cotton-seed oil bath so that two-thirds of the tube is immersed in the oil. The temperature of which was easily controlled by an internal heating coil which had variable resistances in series with it outside the bath. When the sample was melted a thermometer with graduations of 0.2 degrees was placed in the tube so that the liquid sample completely covered the bulb of the thermometer. The outside resistance was then increased until the oil bath as a whole and the sample in it decreased in temperature at a rate of approximately 0.8 degrees per minute. During the slow cooling the test tube was rotated by means of a belt attached to a rotary stirrer and passing around the top of the test tube, which was held in place by a glass ring so that it was free to rotate. The slow rotation provided some degree of stirring so that the sample was completely mixed and homogeneous. The stirring also kept the amount of super-cooling within a reasonable range, although stirring was purposely not sufficient to entirely eliminate the supercooling effect. This effect is desirable here since it marks a certain index of the approach of solidification and when the super-cooling is released the temperature will quickly rise to a constant reading until total solidification has taken place. When super-cooling is

entirely dispensed with by means of very rapid stirring the temperature will slowly drop and level off at the solidification temperature, but the reading will not be constant at any one particular temperature since we deal here with solid solutions in which the temperature can change during the process of slow solidification, whereas in rapid solidification (such as is obtained when we have super-cooling present) the change in temperature is so small as to be imperceptible on a thermometer.

The solidification temperatures recorded in this work fall within the range of 40°-85° and in this range it was found satisfactory to use as a cooling medium for temperatures of 40°-60° room temperature and 60°-85° about 45° so that the oil bath always had some heating current in the higher melting materials. The amount being regulated so that the loss of heat to the atmosphere exceeded the heat input by enough to give the desired rate of cooling of 0.8 degree per minute anywhere within the range given above.

[1] Private Communication.

Melting Points and Resolidification Points.

For the determination of melting points and resolidification points the general method of Francis and Collins[1] was used, however, with a modification of the apparatus.[2] The thermometer was graduated in 0.2 degrees and calibrated by immersion to 2.5 cm. A fraction of a milligram of substance was fused into a 1 mm. capillary tube sealed at one end. A small light, suitably screened, illuminated both the bath and the thermometer. A magnifying glass was used to observe the points and to read the temperature. The approximate melting point is first determined by raising the temperature rapidly in the ordinary way. The material is then allowed to cool very slowly and at the point when the molten mass just began to solidify was taken as the resolidification point. The temperature was allowed to drop about four degrees below this and then the accurate melting point obtained by raising the temperature to one degree below that point and then raised 0.1 degree in two minutes, until a clear liquid first appears on the surface of the solid.

[1] Francis, F., and Collins, F. J. E., J. Chem. Soc., p. 157 (1936).

[2] A modified apparatus was used for convenience because exact and precise melting points such as Francis and Collins obtained were not essential in this work.

Titrimetric Determination of the Mean Molecular Weights of the Acid Fractions.

The mean molecular weights of the acid fractions of carnauba was were obtained through their neutralization equivalents. Seven-hundredths normal aldehyde-free alcoholic potassium hydroxide was used. This was standardized against potassium acid phthalate under exactly the same conditions as the actual neutralization equivalents were taken. Sample weight of one-tenth gram was used and determinations carried out until checks of plus or minus two units were obtained. The determination was executed in a 250 cc. Erlenmeyer flask using a 10 cc. buret graduated to 0.05 cc. Alcohol (95 per cent) brought to the light pink of phenolphthalein with fiftieth normal potassium hydroxide at 50 degrees was used as the solvent. The determination is as follows: The sample was dissolved in exactly 25 cc. of neutral alcohol with the aid of heat. The titration was carried out at 50°-55°, adding the alkali slowly with continuous shaking, using phenolphthalein as indicator (3 drops of a 1 per cent solution in water). When five-tenths of a cc. from the end point was reached, 50 cc. of distilled water was slowly added. The first appearance of a permanent light pink was taken as the end-point. The neutralisation equivalent was calculated from the following formula:

$$\text{Neut. Equiv.} = \frac{\text{Weight of substance} \times 1000}{\text{No. of cc. N alkali used.}}$$

Determination of Constants

Melting Point

The melting point[1] was taken as the temperature at which the material, which had been previously drawn into a capillary tube and allowed to solidify, was observed to rise in the capillary tube. The melting point was observed to be 76°-78°.

Specific Gravity

The specific gravity of the wax was found to be 0.9897 according to the method for Cera Flava of the United States Pharmacopoeia[2].

Saponification Value

This constant was also determined according to the method outlined for Cera Flava.[3] The results are herewith given:

I. 68.5
II. 68.8

Acid Value

The method for Cera Flava[4] was used. The results are as follows:

I. 5.2
II. 6.0

Ester Value

The ester value given below is the difference between the saponification and acid values.

I. 62.8
II. 65.1

Iodine Value

The iodine value was determined according to the method of Hanus[8]. The results are as follows:

I. 10.4
II. 10.5
III. 10.6

Total Ash

The total ash was determined by slow burning to constant weight of a two gram sample of the wax. The results are given below.

I. 1.15 per cent
II. 1.14 per cent

Moisture Determination

The moisture content of the wax was determined according to the xylene method[9] using a Dean Stark apparatus. The following are the results:

I. 4.7 per cent
II. 4.8 per cent

Solubility

Solubilities were determined at room temperature. Saturated solutions of the wax in various solvents were prepared by shaking in the presence of an excess of finely powdered wax for 15 hours. The solutions were filtered and 10 cc. of the filtrate evaporated to dryness.

The table below expresses the relative solubilities.

Solvent	Grams soluble in 100 cc.
Alcohol	0.107
Chloroform	0.701
Ether	0.199
Skellysolve B	0.128
Ethyl Acetate	0.175
Benzene	0.547
Acetone	0.195
Water	0.061

References

1 The United States Pharmacopoeia, Eleventh Revision, p. 457 (1936).

2 Ibid., p. 114.

3 Ibid.

4 Ibid.

5 Ibid., p. 445.

6 Ibid., p. 473.

Saponification

The crude powdered wax was saponified with alcoholic potassium hydroxide using an excess of 20 per cent of alkali. For convenience the wax was divided into five portions as indicated below.

1.	855 g.	wax	.....	100 g.	KOH	.....	1500 cc.	alcohol
2.	645 g.	"	.....	85 g.	"	.....	" cc.	"
3.	790 g.	"	.....	100 g.	"	.....	" cc.	"
4.	860 g.	"	.....	100 g.	"	.....	" cc.	"
5.	1000 g.	"	.....	120 g.	"	.....	" cc.	"

Each portion of wax, alkali and alcohol was placed in a three liter round bottom flask and refluxed on a steam bath for ten hours.

After saponification was complete the alcohol was recovered at about 17 mm. pressure. Although the flasks were completely immersed in a boiling water bath, 56 hours were necessary to remove the last traces of alcohol. It was necessary to remove every trace of alcohol in order to avoid gel formation in subsequent extractions. The material was removed from the flasks and reduced to a fine powder by pulverizing in a large iron mortar.

Extraction of the non-soap portion from the soaps

Two to three hundred gram portions of the powdered saponified product were boiled under a reflux with 2 liters of ethylene dichloride for one hour and immediately strained through cheese cloth while hot. The solvent was recovered in the same manner as the alcohol above and the residue taken up in 2 liters of boiling Skellysolve B* and filtered while hot on a plaited filter using a

*The Skellysolve B used throughout this work was petroleum ether, B. Pt. 65-68°.

hot water funnel. The ethylene dichloride and Skellysolve residues were combined and the solvent from the filtrate was recovered. At this point a crude separation had been effected: i. e. the residue was the soap portion and the soluble fraction the non-soap portion.

The complete separation of soaps from non-soaps was carried out as follows: The crude soaps were extracted with boiling Skellysolve B until the material was completely free from soluble compounds. This was followed by the same treatment with boiling acetone. During the extraction with acetone a portion of the soaps became too finely divided to be handled in this manner, so the material was packed in a modified Soxhlet apparatus and the extraction carried to completion by means of continuous percolation.

The results of the saponification and separation of the soaps and non-soaps are herewith given:

Amount of wax in grams	Amount of soaps in grams	Amount of non-soaps in grams
4150	1500*	2200

The soap portion was powdery and light yellow in color, while the non-soaps were very light and crumbly, orange brown in color and had a melting point of 75° - 77°.

Preparation of the free fatty acids

The free fatty acids were prepared from the soaps by heating 200 gram portions with one liter of a 10 per cent aqueous solution

*A portion of soaps were lost due to an accident.

of hydrochloric acid to 85° and stirring with a mechanical stirrer for 15 minutes to one-half an hour. The conversion of the soaps to the acids was indicated by the melting of the product. After cooling, the cake of fatty acids was removed and washed with hot water until free from mineral acid. The solid cake of acids was taken up in hot Skellysolve B and adhering water removed in a separatory funnel. The solvent was recovered and the acids taken up in a large volume of boiling acetone and filtered. A residue of 52 grams which after continuous acid treatment remained acetone insoluble was obtained. The material was dark brown and melted at 94°. This was set aside. Nine hundred grams of wax acids melting at 68° - 72° resulted.

For further purification of the acids ether solutions at room temperature were prepared. A 10 per cent aqueous solution of sodium hydroxide was gradually added with constant stirring and the insoluble sodium soaps extracted with ether and Skellysolve B. When extraction was complete, the soaps were decomposed in the same manner as above. There resulted 850 grams of pure acids.

Preparation of the methyl esters

Seven hundred grams of the acids were divided into three portions and placed in a three liter round bottom flask and esterified by boiling with 2000 cc. of absolute methyl alcohol saturated with dry hydrochloric acid for 24 hours. At the end of this period the methyl alcohol was removed and the residue was covered with two

liters of water. The mixture was stirred with a mechanical stirrer while a dilute aqueous solution of sodium bicarbonate was added. When frothing ceased 200 cc. of 5 per cent sodium carbonate was added and stirred for half an hour, heated to the melting point of the esters and allowed to cool. The cake of crude esters were collected and dissolved in a large volume of Skellysolve B, the water separated by means of a separatory funnel, filtered while hot and the filtrate refluxed with animal charcoal for one hour. The decolorising solution was filtered until clear, cooled in a salt ice mixture, the esters were precipitated and collected on a Buchner funnel. The mother-liquor was reduced to a small volume, cooled, and the precipitate collected and added to the first crop.

From the 700 grams of acids started with there resulted 420 grams of crude esters melting at 68° - 69° and resolidifying at 67.6°.

Distillation of the Crude Methyl Esters

The brownish-black crude methyl esters (420 grams) were divided into four parts and each distilled through a short distilling head as shown in figure [1] . The material was distilled from a 250 cc. flask packed to half its capacity with glass wool. Ideal distilling conditions could not be maintained when the operation was carried out on a larger scale. The distillation was carried out under the following conditions: distilling temperature of 150 to 220 degrees, a Wood's metal bath heated with a free flame at temperatures of 219 to 550 degrees, pressure of about 0.05 mm. The

distillation was stopped when the pressure began to rise steadily, indicating decomposition.

A yield of 205 grams of distillate was obtained. The material was light yellowish-white in color, waxy in appearance, and had a melting point of 65.5°. The residue was removed from the flask while hot by pulling the glass wool from the flask with the aid of a wire hook, the residue adhering to the wool. The material was removed from the glass wool with boiling water. This non-distillable fraction of the crude esters was almost black in color and quite brittle. It was set aside.

The distillate was redistilled, yielding 195 grams of white waxy material almost free from any odor.

Determination of the Mean Molecular Weight of the Esters

In order to learn the nature of the esters obtained by distillation the saponification equivalent was determined. The determination was carried out by refluxing a 0.2 gram sample of the methyl esters with 25 cc. of half-normal alcoholic potassium hydroxide for four hours and titrating the residual alkali with tenth-normal hydrochloric acid with phenolphthalein as indicator. The titration was carried out at 60° to keep the material in solution. Good checking results were not obtained; however, the mean molecular weight was found to lie between 350 and 400. This indicates that the corresponding acids have approximately 22 to 26 carbon atoms.

Fractional Distillation of the Esters into Smaller Like-Boiling Fractions

Before the material representing a mixture of methyl esters of fatty acids of high carbon content could be fractionated in a rational manner, the whole had to be reduced into smaller like-boiling mixtures. The esters were divided into two portions and each handled in like manner. The esters were distilled from a 250 cc. flask packed to half its capacity with glass wool. The column described in figure 3 was used. Fractions were cut at the most uniform distilling points; however, there was constant variation in distilling temperatures. A Wood's metal bath served as source of heat.

There resulted five fractions from this fractionation. The corresponding fractions in both operations were combined and reported as one fraction. Below are two tables, one the distillation data, and the other a summary of this data.

Distillation Data

Time	Dist. Temp.	Bath Temp.	Heater Temp.	Press.	Fraction
8:12	86	219	161	.02	
8:17	114	217	161	.02	
8:26	159	246	162	.02	
8:32	147	238	165	.02	
8:38	139	239	165	.02	
8:44	159	241	165	.02	
8:48	140	240	165	.02	
8:55	158	240	165	0.018	
9:00	156	238	165	0.018	
9:05	152	238	165	0.018	
9:11	155	248	163	0.018	
9:20	145	254	164	0.018	Fraction I

Time	Dist. Temp.	Bath Temp.	Heater Temp.	Press.	Fraction
9:25	145	259	168	0.025	
9:28	155	259	169	0.025	
9:32	156	254	169	.022	
9:38	152	262	169	.022	Fraction II
9:45	160	265	169	.022	
9:48	155	265	175	.05	
9:50	161	261	175	.026	
9:55	165	261	175	.026	
10:00	160	264	176	.025	
10:05	164	267	177	.024	
10:12	165	265	177	.025	
10:22	157	274	177	.025	
10:26	168	280	177	.025	
10:30	172	280	177	.025	Fraction III
10:34	161	278	179	.05	
10:35	164	279	179	.05	
10:38	167	280	179	.05	
10:45	170	281	179	.05	
10:47	172	282	179	.029	
10:50	175	284	187	.029	
		Stopped			
1:15	165	290	188	.025	
1:15	174	290	188	.025	
1:19	180	290	188	.025	Fraction IV
1:22	172	285	191	.05	
1:30	172	300	198	.05	
1:32	197	305	184	.05	
1:34	195	308	200	.055	
1:38	197	315	202	.052	
1:45	195	322	205	.052	
1:50	184	327	205	.052	
2:02	176	339	207	.054	
2:06	176	341	207	.054	
2:12	172	344	207	.054	
2:20	170	347	207	.052	Fraction V

Summary of the Distillation Data

Fraction	Wt. in g.	M. pt.	S. pt.	R. pt.	B. pt. range	Av. pressure
1	17.2	41.2°	41.4°	40.8°	159-145°	0.02 mm.
2	59.1	48.5	49.0	48.4	145-152	0.025
3	50.5	56.4	56.7	55.8	160-172	0.025
4	55.8	58.0	58.2	57.4	170-180	0.05
5	42.2	64.9	65.1	65.8	180-195	0.05

Fractionation into Ten Degree Distilling Range Fractions

Each of the five fractions obtained in the foregoing fractionation were carefully separated into fractions distilling within 10 degree ranges. The fractionation started with fraction 1 distilled from a 100 cc. flask packed to half of its capacity with glass wool. When this fraction had been fractionated, fraction 2 was added to the same flask and this treated in the same manner. This procedure was continued until all of the fractions had been separated into those of ten degree distilling ranges. A bath containing Primex (hydrogenated vegetable fat) heated with a coil of nichrome wire and controlled with a rheostat was used for the lower temperatures and a Wood's metal bath heated with a free flame was substituted for higher temperatures.

Tabulated below is the distillation data and a summary of the results of this fractionation.

Time	Dist. Temp.	Bath Temp.	Heater Temp.	Pressure	Fraction
8:45				.01	
10:00	74	164	119	.01	
10:20	76	170	119	.012	
10:30	79	175	121	.012	
10:48	82	185	122	.012	
11:00	85	195	126	.012	
11:10	89	202	150	.012	
11:25	92	209	155	.014	Cut No. 1
11:30	95	212	158	.015	
11:41	95	215	140	.018	
11:50	98	220	140	.02	
11:56	102	224	142	.02	
12:05	105	227	159	.02	Cut No. 2
12:10	105	228	159	.02	
1:20	100	251	154	.02	
1:20	100	251	154	.02	
1:22	105	254	155	.02	
1:36	110	228	157	.02	
1:55	112	250	157	.02	
2:15	112	250	158	.022	
2:42	115	256	159	.025	Cut No. 3
2:52	117	245	142	.02	
5:15	125	250	147	.025	Cut No. 4
	Fraction No. 2 put in				
4:05	118	218	167	.02	
4:10	122	222	160	.02	
4:30	129	228	159	.02	
4:48	151	231	160	.025	
5:00	152	252	160	.025	
5:15	152	254	161	.025	
	Heat removed and evacuated over night				
9:15	115	226	156	.02	
9:18	121	227	158	.02	
9:29	128	250	160	.02	
9:55	150	255	162	.02	
10:26	151	258	160	.025	
10:55	150	257	159	.025	
11:15	129	258	160	.025	
11:55	151	241	161	.025	
11:45	151	242	162	.025	
2:09	120	251	162	.025	
2:42	150	246	161	.025	
2:50	154	245	165	.025	Cut No. 5

Time	Dist. Temp.	Bath Temp.	Heater Temp.	Pressure	Fraction
2:59	115	242	156	.025	
3:10	128	245	159	.025	
3:52	132	252	161	.025	
3:56	135	254	163	.025	
	Heat removed and evacuated over night.				
9:00	135	256	172	.025	
9:07	145	259	174	.025	
9:17	136	250	168	.025	
9:35	134	255	162	.025	
9:55	137	259	163	.025	
10:22	135	259	167	.025	
10:45	152	259	156	.025	
	Fraction No. 5 put in flask.				
2:33	125	257	157	.025	
2:37	130	257	164	.025	
2:42	138	259	165	.025	
2:46	141	259	165	.025	Cut No. 6
3:01	146	262	165	.05	
3:10	153	262	180	.027	
3:23	153	262	180	.025	
3:45	148	261	179	.025	
4:20	150	264	180	.025	
	Heat removed and evacuated over night.				
8:00				.01	
10:50	127	265	170	.02	
10:55	155	264	171	.022	
11:02	145	265	175	.022	
11:07	149	266	180	.025	
11:14	152	267	181	.025	
11:21	154	268	181	.025	
11:45	152	268	181	.022	
12:05	153	270	182	.022	
12:35	154	270	182	.022	
12:55	150	270	181	.02	
1:15	149	270	181	.02	
1:27	145	270	179	.02	
1:45	140	269	178	.015	
2:00	140	269	178	.015	
	Fraction No. 4 put in and evacuated over night.				

Time	Dist. Temp.	Bath Temp.	Heater Temp.	Pressure	Fraction
8:00				.005	
9:00	145	261	179	.025	
9:02	145	261	179	.025	
9:22	150	263	180	.025	
10:00	151	264	181	.025	
10:45	151	263	181	.025	
11:45	154	270	185	.022	
1:30	144	268	178	.02	
2:15	149	270	180	.02	
3:05	149	271	181	.02	
3:55	145	273	180	.018	
4:20	155	279	182	.02	
4:25	158	277	182	.02	
	Heat removed and evacuated over night.				
1:00	154	279	184	.02	
1:30	155	280	185	.02	
2:25	149	280	185	.02	
2:34	155	282	185	.02	
2:50	155	289	184	.02	
3:22	148	291	185	.02	Cut No. 7
4:17	149	296	184	.02	
	Oil bath removed and Wood's metal substituted. Evacuated over night.				
9:11	144	275	190	.025	
9:18	150	279	192	.05	
10:00	150	285	185	.05	
10:05	156	284	186	.05	
10:26	159	279	186	.05	
10:50	158	285	186	.05	
1:48	145	286	180	.055	
1:50	150	286	182	.055	
1:55	156	285	182	.055	
2:15	156	288	186	.055	
2:21	166	289	190	.055	
2:30	177	289	202	.055	
2:38	162	289	177	.055	
2:45	165	290	180	.055	
2:52	165	289	180	.055	
3:05	165	292	179	.055	Cut No. 8
	Evacuated over night.				
1:59	180	295	182	.04	
2:01	190	297	184	.04	
2:10	190	297	182	.04	
3:20	192	325	228	.04	Cut No. 9

Summary of the Distillation Data

Fraction	Wt. in g.	M. pt.	S. pt.	R. pt.	B. pt. range	Av. pressure
1	0.55	—	—	—	95°	0.012 mm.
2	0.94	—	—	—	95-105	0.02
3	2.51	27.4	27.50	27.7	105-115	0.02
4	1.16	37.9	—	38.2	115-125	0.025
5	27.29	41.6	42.10	41.8	125-135	0.025
6	8.79	46.8	47.95	47.5	135-145	0.022
7	85.52	56.9	57.25	57.2	145-155	0.022
8	11.60	60.4	61.10	60.5	155-165	0.05
9	44.65	62.2	65.90	64.4	over 165	0.055

Fractions 1 and 2 were almost liquid and yellowish in color and so small in amount they were set aside. Fraction 3 was set aside as a finished fraction to be included among the five degree range fractions. Fraction 4 was set aside for the same reason as fractions 1 and 2.

Separation into Five Degree Distilling Range Fractions

The ten degree fractions were fractionated into their corresponding two five degree fractions. One fraction at a time was fractionated in the same manner as was done in the preparation of the ten degree fractions.

Below is a table of the distillation data and a summary of the results.

Distillation Data

Time	Dist. Temp.	Bath Temp.	Heater Temp.	Pressure	Fraction
	Fractions No. 4 and 5 put in flask.				
8:00				.01	
9:00	115	218	167	.025	
10:00	154	245	165	.025	
11.42	107	210	154	.015	
11:50	114	214	159	.015	Cut No. 1
1:00	119	208	164	.02	
1:30	118	211	165	.015	
1:40	119	212	165	.015	
2:00	120	215	164	.015	Cut No. 2
2:05	122	215	164	.025	
2:11	121	214	164	.02	
2:55	121	215	164	.02	
3:20	120	219	165	.02	
4:00	120	224	165	.02	
4:55	118	225	161	.02	
	Fraction No. 6 put in flask and evacuated over night.				
10:00	121	225	168	.02	
10:35	125	258	170	.02	Cut No. 3
10:42	129	245	172	.025	
10:45	130	245	172	.025	
	Evacuated over night.				
9:54	105	235	164	.02	
9:45	130	241	180	.02	
9:51	135	245	175	.02	
9:53	135	247	175	.02	Cut No. 4
10:00	136	252	178	.05	
10:02	140	252	178	.05	
10:05	142	254	178	.025	
10:30	141	260	178	.025	
10:40	145	265	185	.025	
10:43	144	265	184	.025	
10:45	142	267	179	.025	
10:55	144	270	198	.025	Cut No. 5

Time	Dist. Temp.	Bath Temp.	Heater Temp.	Pressure	Fraction
		Fraction 7 placed in flask.			
10:17	147	254	188	.025	
10:35	150	260	182	.025	Cut No. 6
10:42	155	262	185	.035	
10:55	159	264	178	.03	
11:22	155	266	182	.03	
11:45	154	268	182	.025	
12:50	149	272	182	.022	
2:20	151	276	210	.022	Cut No. 7
		Wood's metal bath substituted for Primex. Fraction 8 put in.			
2:53	142	510	184	.035	
3:30	151	514	186	.03	
3:45	155	525	185	.03	Cut No. 7a
3:53	157	528	178	.035	
4:10	155	542	184	.05	
4:17	158	526	181	.04	
4:36	152	536	186	.04	
4:45	155	537	186	.04	
5:00	153	540	188	.04	
5:30	165	510	185	.03	Cut No. 8
		Evacuated over night.			
10:05	160	275	186	.035	
10:45	137	275	185	.03	
10:55	160	290	200	.035	
10:58	168	290	197	.035	
11:00	172	292	197	.035	
11:01	175	292	197	.035	Cut No. 9
		Fraction 9 put in flask.			
11:04	185	295	196	.045	
11:08	188	295	196	.045	
11:12	188	295	197	.04	
11:16	189	295	198	.04	
11:24	187	297	196	.04	
11:29	185	298	197	.045	
11:35	183	299	199	.045	
11:42	182	300	200	.045	
11:45	179	300	200	.045	
11:48	177	299	200	.045	Cut No. 10

Time	Dist. Temp.	Bath Temp.	Heater Temp.	Pressure	Fraction
1:15	165	299	200	.04	
1:40	176	209	215	.04	
1:55	181	310	219	.04	
2:00	176	309	219	.04	

Heated and remainder collected as Cut No. 11.

Summary of the Results Obtained

Fraction	Wt. in g.	M. pt.	S. pt.	R. pt.	B. pt. range	Av. pressure
1*	2.5[illegible]	27.4°	27.50°	27.7°	105-115°	0.012 mm.
2	6.40	40.2	40.10	39.8	115-120	0.02
3	9.24	42.2	42.70	42.1	120-125	0.02
4	2.14	44.9	44.82	45.0	130-135	0.02
5	6.75	50.0	49.96	49.8	140-145	0.025
6	9.01	50.7	51.69	51.1	145-150	0.025
7	69.70	54.4	56.20	54.4	150-155	0.03
8	5.15	57.1	58.18	57.5	160-165	0.04
9	1.48	58.6	58.28	58.9	170-175	0.055
10	16.71	61.4	62.65	62.2	185-190	0.04
11	28.21	65.0	65.17	64.0	over 190	0.04

*Fraction 1 is fraction 3 carried over from the ten degree range fractions.

This concluded the fractionations.

Saponification of the Methyl Esters to the Corresponding Acids

The recovery of the fatty acids from their methyl esters was accomplished by saponification with alcoholic potassium hydroxide. Twenty per cent excess of alkali calculated on a mean molecular weight of 400 together with enough alcohol to keep the material in solution was used. The solution of esters, alkali and alcohol was refluxed in an appropriate sized round bottom flask for four hours.

After saponification had taken place the alcohol was removed by vacuum distillation leaving a dry cake of crude soaps. Care was taken to remove the last traces of alcohol since any remaining alcohol interferes with subsequent extractions. The dry soaps were extracted twice with Skellysolve B with intermediate filtering in the hot. This extraction was followed by an ether extraction, and finally the soaps were dried in the air. The dry potassium salts of the fatty acids were placed in a large beaker and covered with a large volume of 10 per cent sulfuric acid, heated to 85° and stirred with a mechanical stirrer until the fatty acids were liberated. The decomposition of the soaps was indicated by the fusing of the liberated fatty acids. On cooling the acids were removed as a solid cake. The mineral acid was removed by washing with several portions of hot water until the washings were neutral to litmus.

The neutral cakes of fatty acids were dried between filter paper and taken up in a large volume of Skellysolve B, refluxed with animal charcoal for one hour and filtered through a hot water funnel using a plaited filter paper. Enough solvent was added to keep the

material in solution at room temperature. The solutions were shaken several times with anhydrous sodium sulfate, then filtered through a cone of the sodium sulfate on a plaited filter. The solutions were concentrated to one-third volume and placed in a salt-ice bath for two hours. The deposited material was collected on a Buchner funnel with the aid of suction. The mother liquors contained a negligible amount of fatty acids. The fractions were dried in a vacuum oven at 48° for eight hours at a pressure of 5 mm.

The following is a tabulation of some of the physical constants of the fatty acids obtained from their corresponding fractions of methyl esters:

Fraction	Wt. in g.	M. pt.	S. pt.	R. pt.	Molecular weight
1	1.60	60.2	60.78	60.2	294
2	5.75	69.0	69.52	69.2	291
3	6.76	71.4	71.48	71.4	298
4	1.11	66.1	68.01	67.0	520
5	5.56	72.8	74.51	75.7	550
6	5.51	71.5	71.46	71.2	558
7	58.70	78.6	78.78	78.2	549
8	5.45	76.1	77.51	77.2	575
9	0.84	77.4	77.18	77.9	588
10	11.86	80.2	80.92	79.4	599
11	24.95	84.0	85.62	84.6	424

After application of the above data to the proper binary mixture curves of Schuette and Vogel, it was seen that the fractions

were not binary mixtures. Thus, recrystallization procedure was the next step. Each fraction was recrystallized twice from Skellysolve B and twice from acetone in alternate order. One hundred cc. of solvent was used per gram of fraction and allowed to cool for one hour in an ice chest at 12°, the deposited material collected on a filter with the aid of suction and dried in a vacuum oven at 48° for 8 hours at a pressure of 5 mm.

Below is a tabulation of the status of each fraction after four recrystallizations.

Fraction	Wt. in g.	M. pt.	S. pt.	R. pt.	Molecular weight
1	1.60	60.2	60.78	60.2	294
2	2.55	72.8	72.67	72.4	502
3	5.05	72.9	72.77	72.5	504
4	0.40	66.2	—	66.1	521
5	5.45	75.1	75.05	74.9	527
6	4.38	72.9	72.99	72.7	555
7	56.00	79.4	79.20	79.3	559
8	2.59	77.9	78.06	78.2	585
9	0.55	78.1	—	78.0	590
10	9.70	81.4	81.24	81.1	411
11	22.10	84.6	84.50	84.5	421

The composition of the fractions was determined by the use of solidification point curves of binary fatty acid mixtures of

Schuette and Vogel.* From the observed mean molecular weight the proper curve is selected. The position of the solidification point of a fraction on the curve is noted. Two such positions are usually found. However, the observed mean molecular weight indicates which of these two positions is the correct one. If there is no coordination between the observed and calculated mean molecular weights, it may be assumed that the fraction is not a binary mixture. In this event further recrystallisations are necessary.

The following is a summary of the conclusions drawn from the data obtained by application of each fraction to their respective curves:

Fraction 1: The observed mean molecular weight placed this fraction in the C_{18}-C_{20} binary system. However, the solidification point was far below the range of this curve. The solidification point of its methyl ester was very close to that of palmitic acid. Since this fraction was small no further work was advisable.

Fraction 2: This fraction also fell in the C_{18} - C_{20} system. The solidification point indicated from the curve a mixture of 6 mol per cent of C_{18} acid and 94 mol per cent C_{20} acid. But since the observed mean molecular weight was 502 and the calculated 510.8, this fraction evidently contained a third constituent.

Fraction 3: This fraction also fell in the C_{18} -C_{20} system. Application of the solidification point to this curve indicated about the same composition as fraction 2. But also in this fraction some discrepancy existed between the observed mean molecular weight and the

*The solidification points of a number of binary mixtures of known composition are determined. From these a curve is plotted with the solidification points as the ordinate and composition expressed in mol-per cents as the abscissa.

calculated. The observed molecular weight was 504 and calculated 510.8.

Fraction 4: The observed mean molecular weight of this fraction placed it on the C_{20} - C_{22} curve. The composition was 75 mol per cent C_{20} and 25 mol per cent C_{22} acids. The observed mean molecular weight was 521 and the calculated 519.5. This difference is clearly within the limits of experimental error and is definite proof that the mixture is what is indicated above.

Fraction 5: An observed mean molecular weight of 527 placed this fraction in the binary system of C_{20} - C_{22}. The solidification point indicated that this fraction contained 20.7 mol per cent of C_{20} and 79.3 mol per cent of C_{22}, but the calculated molecular weight of 554.1 does not agree closely enough with the observed.

Fraction 6: Although this fraction belonged to the C_{22} - C_{24} binary system, the solidification point did not fall on this curve. Evidently a considerable amount of another acid was present.

Fraction 7: Although the solidification point of this fraction was very close to pure docosanic acid (S. pt. 79.70°) the observed mean molecular weight and the solidification point indicated it to be 21.5 mol per cent of C_{22} and 78.5 mol per cent C_{24} acids. The observed molecular weight was 559 and calculated 563, which is good proof for the fraction to be close to what is shown above.

Fraction 8: By interpolation this fraction was 47 mol per cent C_{24} and 53 mol per cent C_{22} acids. The observed and calculated mean molecular weights agreed.

Fraction 9: Also by interpolation this fraction was 30 mol per cent C_{24} and 70 mol per cent C_{26} acids. The calculated mean molecular weight was 387.9 and observed was 390.

Fractions 10 and 11: Although curves were not available for acids for molecular weights in this group and since interpolation was not reliable at this point, C_{26}, C_{28}, and possible C_{30} acids were indicated. Although the mean molecular weight observed was close to C_{28} acid, the solidification point was about 5 degrees low. Many recrystallisations did not raise either the molecular weight or the solidification point of these two fractions. The molecular weight of both fractions might indicate only the C_{26} and C_{28} acids but the depression of the solidification points of these higher binary systems are not as great those observed for these fractions. Thus there is good evidence of C_{30} being present, and the presence of the C_{26} and C_{28} acids can not be doubted.

Fraction 4 appeared to be the only fraction that was definitely a binary system, while all of the others although not in perfect agreement with the facts, without question contain the acids assigned to them.

In order to obtain better evidence as to the composition of all of the fractions, each was carried through the same process of recrystallizations as before. However, since fractions 2 and 3 were practically the same in composition, these were combined; and since fractions 8 and 9 were small and so much alike these were combined also. With the exceptions of fractions 1 and 4 all were further recrystallized. The solvent from the mother liquors was removed and

the residues collected. The combined residues of Fraction 2 were combined and included in the general scheme as Fraction 2a.

The following is a tabulation of the constants of the fractions at this point:

Fraction	Wt. in g.	S. pt.	Molecular Wt.
1	1.60	80.78	294
2a	0.75	85.66	508
2 3	4.55	75.58	511
4	0.40	71.46	520
5	2.75	75.12	546
6	5.26	75.90	555
7	----	80.62	565
8 9	1.55	78.58	591
10	7.60	81.95	410
11	18.65	85.07	422

The above fractions were studied in the same manner as the foregoing system. The following is an analysis of each fraction:

Fraction 2a: By application of the data for this mixture to the curve it was found that this fraction was composed of 31.5 mol per cent of C_{18} and 68.5 mol per cent of C_{20} acids. The observed mean molecular weight and calculated, 508 and 505.7, were in fairly good agreement.

Fraction 2 and 3: This fraction was changed to a composition of 3 mol per cent C_{18} and 97 mol per cent C_{20} acids. The observed and calculated molecular weights of 311 and 311.3 were in good accord.

Fraction 5: This fraction was now a mixture of 86.7 mol per cent of C_{22} and 13.3 mol per cent C_{24} acids. The observed molecular weight was 346 and calculated 343.3.

Fraction 6: This was a mixture of 67 mol per cent of C_{22} and 33 mol per cent of C_{24} acids. The observed molecular weight of 353 and calculated 349.9.

Fraction 7: The composition of this fraction was 14.3 mol per cent of C_{22} and 85.3 mol per cent of C_{24} acids. Theory for the molecular weight was 364.3 and found was 365.

Fraction 8 and 9: By interpolation this fraction was 44 mol per cent C_{24} and 56 mol per cent of C_{26} acids. Theory for the molecular weight was 384.3, found 391.

Fraction 10 and 11: The status of these two fractions remains unchanged.

Although there seems to be no question concerning the conclusions drawn from the application of data to the solidification point curves, one can employ a further medium by which the curves themselves will verify their own accuracy.

These solidification point binary mixture fatty acid curves have the form of a W.[1] With increasing molecular weight the break in the center becomes flatter. For example, the $C_{22} - C_{24}$ acid

[1]Schuette, H., and Vogel, H., Oil and Soap, 16, p. 16 (1939).

system has a plateau involving a composition of 30 to 70 per cent of C_{22} acid. Obviously, if the solidification point falls upon this plateau, it is impossible to calculate the composition of the mixture. Greatest accuracy can be obtained when the solidification point falls upon the most perpendicular portion of the curve.

Since the solidification points are very definite and the shape of the curve is also definite, a change in composition of any mixture in a definite system can be detected by a change in the solidification point. This change can be affected by the admixture of a definite amount of the proper pure synthetic acid. From this one can compare the solidification points of the new mixture with that calculated for it. If the two points compare, the original composition could be none other than what it indicated to be in the first instance.

Fractions 2a to 7 inclusive were examined by the admixture of the proper pure synthetic acid and the observed and calculated solidification points compared. The results in each case proved the initial conclusions to be correct. Hence, the presence of all of the acids from C_{18} to C_{26} and a good indication for C_{20} has been verified.

The plausibility of the existence of these acids mentioned above can also be seen in the table given below.

Fraction	Composition
2a	31.5 mol per cent C_{18}; 68.5 mol per cent C_{20}
2 and 3	3.0 mol per cent C_{18}; 97.0 mol per cent C_{20}
4	75.0 mol per cent C_{20}; 25.0 mol per cent C_{22}
5	86.7 mol per cent C_{22}; 13.3 mol per cent C_{24}
6	67.0 mol per cent C_{22}; 33.0 mol per cent C_{24}
7	14.3 mol per cent C_{22}; 85.3 mol per cent C_{24}
8 and 9	44.0 mol per cent C_{24}; 56.0 mol per cent C_{26}
10	Definitely C_{24} and C_{26} present.
11	Definitely C_{24} and C_{26} present and possibly C_{28}.

Separation of the Non-Soap Portion into One Fraction of Primary Alcohols and the Rest of the Material into a Second Fraction.

The separation was carried out according to the procedure of Chibnall et al.[1] One hundred grams of the non-soap fraction was decolorized with animal charcoal from Skellysolve B. The resultant white very light powder was heated with 100 grams of phthalic acid anhydride for 18 hours with 40 cc. of pyridine at 120 degrees. An oil bath was used and the reaction carried out in a 500 cc. three-necked flask with an efficient stirrer and condenser. The pyridine was removed by pouring the molten mixture into 10 per cent hydrochloric acid and stirred while the mixture was heated to the boiling point. After cooling the solid layer of phthalates was separated and heated with successive quantities of water to remove residual phthalic acid anhydride. The mixture was allowed to cool and the solid cake of esters was collected and pulverized in a mortar, and then placed into 5000 cc. of warm ether. The mixture was warmed continuously and shaken vigorously and allowed to stand over night. Not all of the material went into solution. The solvent was decanted, about half of the solvent removed and the residue treated with ether again and again until no more went into solution. The ether solutions were combined and the residue (20 grams) put aside.

The light brown ether solution of crude esters was cautiously agitated with 10 per cent warm aqueous solution of sodium carbonate which caused the separation in the aqueous phase of the insoluble white sodium salts of the primary phthalic esters. The lower layer, which was an emulsion of water, ether and suspended solid

matter was separated from the supernatant ether. This emulsified portion was refluxed with xylene until two distinct layers appeared, aqueous on the bottom and xylene on the top. The xylene layer contained the sodium salt of the phthalic esters of the primary alcohols. The whole solution was transferred to a separatory funnel while hot and the two layers separated. The aqueous phase was extracted with hot xylene until free from soluble material. The xylene solution was cooled in an ice-salt bath and filtered with suction and the white fluffy residue was dried on porous plates in a vacuum drying oven at 60 degrees. Ninty-five grams of primary phthalate was obtained at this point. The dried material was extracted with anhydrous ether in a modified soxhlet extractor until exhaustion. The ether extractive was added to the original ether soluble portion and the solvent removed. There resulted about 10 grams of a brown gummy substance. This material was added to the original ether insoluble matter and the whole put through the phthalic acid anhydride treatment. There resulted again the same ether insoluble substance and no yield of primary alcohol half esters of phthalic salts. The ether insoluble portion was put aside and the solvent removed from the ether soluble sodium salts representing any non-soap constituents with the exception of primary alcohols and this put aside also.

Primary Alcohols:

The sodium salts of the primary phthalates were hydrolyzed by boiling in 2000 cc. of benzene and sodium ethoxide added (50 grams of sodium in 700 cc. of alcohol). It was heated and boiled for 5

minutes and allowed to stand for two hours. Warm water (1000 cc.) was added and shaken and separated in a separatory funnel. The aqueous solution was extracted with benzene repeatedly. The benzene solutions were combined and solvent removed by distillation and the residue extracted with acetone, then ether. The material was removed from the solvent by cooling in ice-salt bath and filtered with suction. There resulted a very light cake of white primary alcohols weighing 62 grams having a melting point of 87 degrees.

[1] Chibnall, A., Piper, S., Pollard, A., Smith, J., and Williams, E., Biochem. J., 25, p. 2095 (1931).

The Emulsifying Power of Carnauba Wax Alcohols and Their Acetates

The absorption of water by ointment and cosmetic bases has been studied by many investigators.[1] Among the more widely used emulsifying agents for this purpose are waxes such as lanolin, spermaceti and beeswax; polycyclic alcohols such as sterols; and aliphatic alcohols of high molecular weight, some of which are components of certain waxes.[2] Of these, lanolin and waxes were used by the ancients.[3] More recently ointment bases of high water absorptive power have been introduced, and are usually incompletely described as consisting of certain alcoholic components of lanolin combined with petrolatum.[4] In 1909 Blatz[5] showed that cetyl alcohol when mixed with petrolatum produced an ointment base capable of absorbing 60 to 70 per cent of water.

The physiological activity of the water contained in an ointment base appears to be an open question. Whitehouse and Ramage[6] have shown that human skin is permeable to water under physiological control, partially regulating body temperature. Salts and colloidal substances do not appear to diffuse through the epidermis; thus in this respect the skin plays the part of a semi-permeable membrane. Gershenfeld and Miller[7] in 1935 pointed out the varying bactericidal efficiency of two per cent phenol ointment and recommended water miscible vanishing creams as bases for this and other bactericidal agents. Lee and Dekay[8] in 1952 in a discussion of an ointment base

for official ointments made the following statement: "The criticisms of the official ointments are in a measure traceable to their bases. The usual story about them is that they become rancid or grainy or too stiff or too soft ... An ideal ointment base is, of course, a pharmaceutical dream that has never come true and perhaps never will."

However, experiments of Bliss[9] on skin absorption resulted in the conclusion that the properties and powers of the drug rather than those of the base are the major factors in the absorption into the skin.

Lifschutz[10] has shown, semi-quantitatively, the influence of certain alcoholic components of lanolin as water-in-oil emulsifying agents when used with petrolatum. Lifschutz[11] has also pointed out that lanolin as an ointment base possesses chemical and physical disadvantages, and that its water-absorptive properties are due to the presence of from 5 to 8 per cent of free alcohols. He recommends a mixture of 5 per cent of these alcohols with petrolatum as an ointment base which will absorb from 300 to 400 per cent of water. Powers and co-workers[12] have investigated the relative efficiencies of certain components of lanolin and have found that the emulsifying efficiency of cholesterol is much less than that of mixtures of cholesterol and cholesterol esters when used with petrolatum. These workers were able to emulsify as much as 800 per cent of water in petrolatum by means of the admixture of 5 per cent of each of cholesterol and cholesteryl stearate.

Casparis and Meyer[18] have determined the maximum amount of water which mixtures of several different waxes and alcohols with petrolatum and lard are capable of absorbing. They designated as "water number" the maximum quantity of water capable of being held at ordinary temperatures (20°C.) by 100 grams of water-free base.

A preliminary investigation was undertaken to ascertain the water absorbing power of the non-soap portion of saponified carnauba wax. This non-soap portion consists chiefly of higher molecular weight aliphatic alcohols. Besides this product the acetates were prepared and their water absorptive power determined.

Experimental

The carnauba wax alcohols were obtained after saponification of the wax according to the method described on page 60 of this thesis. The product in Skellysolve B solution was decolorized by refluxing with animal charcoal and yielded a white crystalline material melting at 87°.

Preparation of Acetates from the Carnauba Wax Alcohols[14]

The white crystalline alcohols (17 g.) were refluxed for 24 hours with 20 g. of fused sodium acetate and 250 cc. of acetic anhydride. The reaction mixture was poured into a large volume of hot water, stirred with a mechanical stirrer during one hour. On cooling, the solid acetates were collected, taken up in methyl alcohol and boiled with decolorising charcoal for one hour and filtered while hot. The methyl alcohol solution was cooled in a salt-ice mixture and the precipitated acetates collected on a Buchner funnel. The product was recrystallised from Skellysolve B. There resulted 12 grams of white matted crystalline acetates melting at 82°.

Determination of the Emulsifying Power.

The emulsifying power of all of the preparations were determined according to the method of Chang.[18] The procedure is as follows: The melted preparation is placed in a warm deep wedgewood mortar and distilled water added in increasing amounts with constant trituration until the maximum amount of water is emulsified. The

mass is placed in an ice chest for 24 hours at a temperature of 12°. At the end of this time the major portion of the excess water is removed by kneading and the remaining adhering water separated by placing the material on a pill tile and the globules of water expressed with a spatula and absorbed with filter paper.

The amount of water absorbed was determined on 20 to 30 gram samples in the same manner as the pharmacopoeial moisture determination method using a Dean Stark apparatus. Foaming was minimized by adding a small amount of powdered rosin to the xylene mixture.

In the tabulation that follows are reported the composition of the preparations studied, their water numbers and the melting points of the water-free bases.

Tabulation of the Emulsifying Power of Some Water-in-Oil Emulsifying Agents with Petrolatum*

Emulsifying Agent in White Petrolatum	Water Number	Melting Point of Water-free Base
Carnauba wax alcohols 1 %	18.0	58
" " " 3 %	18.7	60
" " " 5 %	24.3	65
" " " 7 %	22.3	69
" " " 9 %	24.3	71
Carnauba wax alcohol-acetates 1 %	18.6	49.0
" " " " 3 %	34.8	50.0
" " " " 5 %	45.1	51.0
" " " " 7 %	48.3	51.3
" " " " 9 %	47.3	52.0

It is seen from the data above that the acetates of the carnauba wax alcohols have almost twice the emulsifying properties that the alcohols themselves possess. Also it is remarkable that as low as one per cent of the acetates will depress the melting point of the petrolatum from 55° to 49°. The increase in melting point is not as marked as that of the alcohol admixtures. In the two groups of mixtures three per cent of emulsifying agent has the most effect. This is in agreement with the results which Powers and his co-workers[10] obtained on constituents of lanolin.

References

[1] Chang, C., Hydrogenated Oils as Ointment Bases, B.S. Thesis, U.W. (1939).

[2] Powers, J., Leask, H. and Warner, R., J. Am. Pharm. Assoc., 29, p. 14 (1940).

[3] Schelenz, H., Geschichte der Pharmazie, p. 105 (1904).

[4] Unna, E., Chem. Abstr., 7, p. 925 (1913).

[5] Slats, F., Apoth. Zeit., 24, p. 525 (1909).

[6] Whitehouse, A., and Ramage, H., Proc. Roy. Soc. London, 115, p. 42 (1933).

[7] Gershenfeld, L., and Miller, R., Am. Journ. Pharm., 105, p. 186 (1933).

[8] Lee, C., and Dekay, H., J. Am. Pharm. Assoc., 21, p. 1022 (1932).

[9] Bliss, A., Drug. Cos. Ind., 37, p. 750 (1935).

[10] Lifschutz, I., Z. physiol. Chem., 114, p. 108 (1921).

[11] Lifschutz, I., Pharm. Zentralhalle, 65, p. 505 (1925).

[12] Powers, J. et al., loc. cit.

[13] Casparis, P., and Mayer, E., Pharm. Acta Helv., 10, p. 165 (1935).

[14] Pollard, A., Chibnall, A., and Piper, S., Biochem. Journ., 25, p. 2111 (1931).

[15] Chang, C., loc. cit.

[16] Powers, J., et al., loc. cit.

* The brand of petrolatum used in this work was White Stanolind. The petrolatum had a water number of 6 and a melting point of 55°.

LIST OF BOOKS CONSULTED.

Brannt, W., Animal and Vegetable Fats and Oils, v. 2, 2 ed., 1896.

Cowan, T., Wax Craft, 1 ed., 1908.

Grün, A., and Halden, W., Analyse der Fette und Wachse, v. 2, 1929.

Hopkins, E., The Oil-Chemist's Handbook, 1 ed., 1900.

Kitt, M., Die Jodzahl der Fette und Wachsarten, 1902.

Jolles, A., Die Fette vom Physiologisch-chemischen Standpunkte, 1907.

Leathes, J., The Fats, 1910.

Leathes, J. and Roper, H., The Fats, 2 ed., 1925.

Lewkowitsch, J., Chemical Technology and Analysis of Oils, Fats, and Waxes, v. 3, 3 ed., 1904; v. 3, 4 ed., 1909; v. 3, 5 ed., 1914; v. 3, 6 ed., 1923.

Lüdecke, C., Die Wachse und Wachskörper, 1926.

Sedna, L., Das Wachs, 2 ed., 1902.

Tschirch, A., Handbuch der Pharmacognosie, v. 2, 1 ed., 1912.

Ulzer, F., and Pastrovich, P., and Eisenstein, A., Analyse der Fette und Wachsarten, 3 ed., 1908.

Wehmer, C., Die Pflanzenstoffe, v. 1, 2 ed., 1929.

Wright, A., The Analysis of Oils and Allied Substances, 1905.

LIST OF JOURNALS CONSULTED.

Am(erican) Drugg(ist), v. 15-21; 1884-1892.

Am(erican) Drugg(ist and Pharmaceutical Record), v. 22-72; 1893-1924.

Am(erican) Drugg(ist), v. 75-95; 1925-1959.

Am(erican) Journ(al of) Pharm(acy), v. 1-111; 1829-1959.

Bull(etin of the) Am(erican) Pharm(aceutical) Assoc(iation), v. 1-6; 1906-1911.

Chem(ical) Abstr(acts), v. 1-53; 1907-1959.

Chem(ist and) Drugg(ist), v. 1-55; 1859-1899.

Journ(al of the) Am(erican) Pharm(aceutical) Assoc(iation), v. 1-28; 1851-1939.

New Remedies, v. 1-12 (2 and 5 missing); 1872-1882.

Pharm(aceutical) Era, v. 1-67; 1887-1950.

Pharm(aceutical) Journ(al), v. 1-155; 1841-1955.

Pharm(aceutical) Journ(al and) Trans(actions), v. 1-141; 1842-1958.

Pharm(aceutical) Record, v. 5-15; 1885-1895.

Proc(eedings of the) Am(erican) Pharm(aceutical) Assoc(iation), v. 1-59; 1851-1911.

Y(ea)rb(oo)k (of the) Am(erican) Pharm(aceutical) Assoc(iation), v. 1-27; 1912-1938.

Y(ea)rb(oo)k of Pharm(acy), 1870-1958.

Piso, G. 1648

Palmae Brasiliensis.

Hist. Natural and Medic., Lib. IV, p. 125.

A description of the plant at this early date with pictures.

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Raii, ___ 1688

Historia Plantarum, v. 2, p. 1568 (Journ. de Pharm. Chim., 26, p. 112.)

Supposedly a description of the carnauba tree written in Latin in 1688.

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de Camara, Arrudo. 1810

Carnauba ou Carnaiba. Corypha Cerifera.

Cent. Plant. Pern., p. 51.

A description of the plant, habitat, and history.

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Brande, W. 1811

An Account of a Vegetable Wax from Brazil.

Royal Soc. Trans. 1811, p. 261 (Canstatt's Jah. Bericht Pharm., 1842, p. 255; Trans. Journ. d'Pharm., 25, p. 435; Buch. Rep. de Pharm., 18, p. 190; Ibid., 49, p. 259.)

The first original research on carnauba wax including results.

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Koster, H. 1816

Travels in Brazil, v. 1, p. 209.

A description of carnauba wax is given in connection with Koster's experiences in Brazil while visiting the governor, in regard to ideas concerning the economic importance of the wax.

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(Editor.) 1824

Repertorium fur die Pharmacie, 18, p. 190.

Under miscellaneous items it is mentioned that a new plant wax has been obtained from an unknown tree in Brasil and is called carnauba.

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Virey, J. 1834

Recherches
D'historie Naturelle et de Chemie sur la Matiere cireuse du Carnauba (palmier).

Journ. de Pharm. et Chim., 26, p. 112.

Description, history, botanical source and general information concerning the carnauba plant and wax.

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(_____) 1854

Das Carnauba-Wachs.

Buch. Rep. de Pharm., 49, p. 259.

A description of carnauba wax and its history discussed in connection with the work of Arruda, von Martius, Brandes, and Virey.

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von Wiggers, __. 1845

Carnauba-Palmwachs.

Yahresbericht, 5, p. 181.

A short paragraph describing carnauba wax with also a list and description of several others.

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Brodie, B. 1848

Untersuchung über die Chemische Natur des Wachses.
I. Ueber eine neue Säure, Cerotinsaure im Bienwachs.

Annalen der Chem., 67, p. 180 (Ibid., 71, p. 144.)

A long article upon the results of research on the chemical constituents of waxes.

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Brodie, B. 1849

Untersuchung über die Chemische Natur des Wachses.
III. Ueber das Myricin.

Annalen der Chem., 71, p. 144 (Ibid., 225, p. 284.)

A long report on the chemical research on waxes concerning their constituents.

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Abi, —. 1855

Zur Pharmacognosie Ueber Thier-Wachs, Pflanzen-Wachs und Erd-Wachs.

Prakt. Pharm., 4, p. 1.

Several waxes described pharmacognostically including carnauba wax.

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von Wiggers, __. 1860

Melissyl-alcohol.

Jahresbericht, 19, p. 148.

A description, properties and a study of Melissyl alcohol.

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Procter, B. 1865

Substitutes for Wax.

Chem. and Drugg., 4, p. 214 (Amer. Journ. Pharm., 55, p. 527.)

The relative merits of various substances suitable for substitutes of wax medicinally with carnauba wax included in discussion.

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de Macedo, M. 1867

Notice sur le Palmier Carnauba.

A long pamphlet with a good historical account of the carnauba plant and wax together with a description of the plant and wax with general, chemical and economical discussions of each.

- - - - - - - - - - - - - - - - -

Berard, P. 1868

Note sur la cire Carnahuba.

Bull. Soc. Chim., 9 (2), p. 41.

A short article concerning the chemistry of carnauba wax and its constituents.

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(_____) 1868

(Copernicia cerifera.)

N. Rep. Ph., 17, p. 248 (Proc. Am. Pharm. Assoc., 16, p. 202.)

(The habitat, method of collection, and the uses of different parts of the carnauba plant are given.)

The original was not available.

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(_____) 1868

(Die Carnaubapalme.)

Regensburger Flora, Nr. I, p. 44 (Arch. der Pharm., 184, p. 259.)

(A description of the plant is given along with its botany and history.)

The original was not available.

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Maskelyne, N. 1869

On an Alcohol in the Wax of the Copernicia cerifera.

J. Chem. Soc., 7, p. 87 (Chem. News, Jan. 29, 1869; Amer. Journ. Pharm., 41, p. 206.)

From a letter written to Brodie telling how he isolated Melissyl alcohol with a short description.

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(_____) 1869

Carnaüba - Wachs.

Jahresbericht, 29, p. 545.

A description of the wax and the method of obtaining it together with a discussion of its chemical constitution.

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(Editor.) 1869

Proc. Am. Pharm. Assoc., 17, p. 187.

Slight description of carnauba wax with the name Canaüba used.

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(_____) 1869

Carnauba Wax.

Journ. Chem. Soc., (2) 7, p. 87 (Journ. f. Prakt. Chemie, 107, p. 62; Arch. de Pharm., 192, p. 84; Proc. Am. Pharm. Assoc., 19, p. 508.)

The source, description, and incomplete chemical composition of the wax are given together with some technic and methods of analysis.

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(_____) (1869)

(Das Carnaubawachs.)

Journ. f. prakt. Chem., 107, p. 62 (Proc. Am. Pharm. Assoc., 19, p. 508; Arch. der Pharm., 192, p. 84.)

(The source, method of collection and some chemical properties of carnauba wax are given.)

The original was not available.

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Cleaver, E. 1875

The Chemical Examination of Carnauba Root.

Pharm. Journ., 54(v), p. 985 (Yrbk. Pharm., 5, p. 254; Proc. Am. Pharm. Assoc., 23, p. 129.)

A description of the carnauba root and its chemical examination.

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(Editor.) 1875

Ceara odor Carnaubawachs.

Jahresbericht, 55, p. 286.

A report that 5 million pounds of carnauba wax are exported yearly.

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Symes, C. 1875

Carnauba Root.

Pharm. Journ., 54 (v) p. 661 (Yrbk. of Pharm., 15, p. 241.)

Value of carnauba root medicinally is given and compared to sarsaparilla.

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(_____) 1875

(Carnauba Root (Corypha cerifera).)

Pharm. Journ. and Trans., ___, p. 661 (?) (Proc. Am. Pharm. Assoc., 25, p. 129.)

(A description of the root, the chemical composition and some properties.)

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(Editor.) 1876

Fossil and Vegetable Wax.

New Remedies, 5, p. 38.

A short article describing fossil and vegetable waxes as to source, collection, use, and amount exported with carnauba wax included.

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Guyot, M. (P). 1876

Note sur deux cires Vegetales.

Rep. de Pharm., 4, p. 710 (Proc. Am. Pharm. Assoc., 25, p. 282; New Rem., 1877, p. 109.)

Various characteristics by which carnauba and myrtle waxes can be distinguished.

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Morgan, C. 1876

The Carnauba Tree.

Pharm. Journ. and Trans., 55, p. 745 (Yahresbericht, 56, p. 90.)

A report on the trade and commerce of Brazil read before Parliament in which the carnauba tree is discussed from the angle of use, products and description.

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von Pieverling, L. 1876

II. Ueber Melissylalcohol und einige seiner Umsetzungsproduct.

Annalen, 185, p. 344 (Jahresbericht, 38, p. 558.)

A dissertation upon the research of melissyl alcohol and melissic acid in detail.

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(Editor.) 1877

The Brasilian Wax-Palm.

New Remedies, 6, p. 259 (Proc. Am. Pharm. Assoc., 25, p. 185.)

An interesting story about the carnauba palm tree giving a good description of the plant and all of its parts and their uses.

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(Editor.) 1878

Carnauba Root.

Proc. Am. Pharm. Assoc., 26, p. 185.

The physical and chemical properties and a list of the chemical constituents listed together with pictures of a branch of the palm and of the fruit.

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Meyer, A. 1879

Ueber den Japantalg.

Arch. der Pharm., 215, p. 97 (New Remedies, 8, p. 327.)

A discussion of Japan wax, carnauba wax also included.

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Hirscholn, E. 1880

Contributions to the Chemistry of Several Varieties of Wax.

Pharm. Journ. and Trans., 59, p. 749.

Seventeen varieties of vegetable waxes listed with reactions to various tests with carnauba wax included.

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(_____) 1880

(Vegetable Waxes)

Journ. of Applied Science, __, p. __ (Drugg. Circ., 24, p. 62.)

(Many waxes are described as to source and physical constants including carnauba wax.)

The original was not available.

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von Martius, K. 1882

Copernicia Cerifera Mart.

Flora Brasiliensis, Pars II, vol. III, p. 547.

A botanical classification of the plant, description, habitat, synonyms and the early men involved with the plant.

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Heinner, O. 1885

On the Analysis of Beeswax.

Analyst, 8, p. 16.

A detailed report upon the research of beeswax with special interest in cerotic acid and myricyl alcohol, also carnauba wax.

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Hübl, A. (1885)

(Zur Prüfung des Bienenwachses.)

Dingler Polytech. Journ., 249, p. 338 (Proc. Am. Pharm. Assoc., 35, p. 200; Am. Journ. Pharm., 56, p. 479.)

(Investigation of beeswax with remarks on carnauba wax and others.)

The original was not available.

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(Editor.) 1884

Notes on Drugs and Chemicals.

Am. Drugg., 15, p. 211.

A compilation of notes on various drugs and chemicals in which the shipping and bleaching of carnauba wax is mentioned briefly.

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(Editor.) 1884

Carnauba-Wachs.

Yahresbericht, 44, p. 629.

Formulas for varying the melting point of various mixtures of carnauba wax with a description of carnauba wax.

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(Editor.) 1884

The Month.

Pharm. Journ. and Trans., 45, p. 1045.

The highlights of the month are given and contains a report on the chemistry of carnauba wax accomplished by Sturche.

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Sigaud, __, 1884

Note sur deux especies de cire vegetale du Bresil.

Journ. de Pharm., 58, p. 154 (Journ. of Pharm., 16, p. 151; The Chem. Gaz., 2, p. 127.)

Discussion of the history of carnauba wax and its source.

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Sturche, H. 1884

Ueber die Chemischen Bestandtheile des Carnaubawachses.

Annalen, 225, p. 285.

A very detailed chemical report on the results of research accomplished on carnauba wax.

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Valenta, E. (1884)

(Zum Nachweis von Carnaubawachs.)

Zeitschr. f. landw. Gew., __, p. __ (Pharm. Centralhalle, 24, p. 417; Zeit. anal. Chem., 25, 257.)

(A discussion of various mixtures of Carnauba wax and other waxes to alter the melting point, consistency, etc.)

The original was not available.

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Liebermann, C. 1885

Ueber das Wachs und die Fette der Cochenille.

Berichte, 18, p. 1979.

Chemistry of cochenille wax and also comparison to carnauba wax and others.

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Allen, A. H. 1886

Yahresberichte, 46, p. 187.

A table of constants given for several waxes including carnauba wax, also procedures for determinations given.

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(Editor.) 1886

Semi-annual Report on Drugs and Chemicals.

Am. Drugg., 15, p. 115.

In a long list of notes on various drugs and chemicals carnauba wax is included with a note about its importation at Hamburg.

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Schwalb, F. 1886

Ueber Wachsuntersuchungen
IV. Die nichtsauren Bestandtheile des Bienwachses.

Annalen, 254, p. 106 (Journ. chem. Soc., 1887, 124; Amer. Journ. Pharm., 59, p. 196; Jahresbericht, 46, p. 186.)

Research on the non-acid constituents of beeswax in which myricyl alcohol is studied in conjunction with carnauba wax.

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Horn, F. M. 1888

Estimation of Resin in Wax.

Chem. and Drugg., 32, p. 85.

The method is based on solution of resin in alcohol and testing for resin according to Donath's process.

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Pecholt, T. 1889

Nutzenpflanzen Brasiliens.

Pharm. Rund., 7, p. 261 (Pharm. Ztg., 54, p. 782.)

A general description of the carnauba plant and wax with uses, synonyms and chemistry of the wax.

- - - - - - - - - - - - - - - - - -

Kossel, A. and Obermüller, K. 1890

(A New Method for the Saponification of Fats, Waxes, etc.)

Ztschr. f. Physiol. Chem., 1890, p. 597 (Amer. Journ. Pharm., 62, p. 490.)

An ether solution of the fat or wax treated with an alcoholic solution of sodium ethylate used with details.

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Gawalowski, A. 1890

Eine Methode zur Bestimmung des Specifischen gewichtes von Wachsarten, Harzen und harten Fetten durch Titruen.

Pharm. Zeit., 55, p. 427 (Irbk. Pharm., 1891, p. 228.)

A very detailed method given for the determination of the specific gravity of waxes, etc.

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Morong, T. 1892

Copernicia Cerifera, Mart.

Bull. of Pharm., 6, p. 19 (Proc. Am. Pharm. Assoc., 40, p. 812; Pharm. Journ. and Trans., 51, p. 675; Yahresbericht, 52, p. 136.)

The botany and Materia Medica of the plant described.

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(_____) 1892

(Tests for Vegetable Waxes.)

Am. Drugg., ___, p. __ (Pharm. Journ., 52, p. 125.)

(Various tests in some detail for ten different waxes including carnauba wax.)

The original was not found.

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(_____) 1892

La Cire de Carnauba.

Bull. Soc. Roy. Pharm., de Bruxelles, 56, p. 346.

The description, source, chemistry of, and uses of carnauba wax.

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Kebler, L. 1895

Notes on the Examination of Beeswax.

Amer. Journ. Pharm., 65, p. 585 (Proc. Am. Pharm. Assoc., 44, p. 658.)

Origin of beeswax, comb foundation, fraud in the trade, adulteration in England and short description of carnauba wax are given.

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Villon, A. 1895

La Cire de Carnauba.

Bull. Soc. Chem., 9 (Ser. 3), p. 1046 (Pharm. Era, 12, p. 248.)

A description of the chemical properties and uses of carnauba wax.

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(_____) (1894)

(Uses of Carnauba Palm.)

Am. Drugg., __, p. __ (Proc. Am. Pharm. Assoc., 45, p. 870.)

(A discussion of the economic value of the carnauba palm together with some data.)

The original was not found.

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Kebler, L. F. 1895

Beeswax and its Adulterants.

Amer. Drugg. and Pharm. Record, 27, p. 4.

Carnauba wax described and mentioned as an adulterant of beeswax along with many others.

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Brannt, W. 1896

Palmae (Spadiciflorae).

Animal and Vegetable Fats and Oils, 2 ed., v. 2, p. 144.

The source, method of collection, general information and chemical constituents, constants and uses of carnauba wax are given.

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Dietrich, K. (1897)

(Examination of Waxes by the Hot and the Cold Methods.)

Haefenberger Annalen, ___, p. ___ (Am. Drugg. and Pharm. Record, 32, p. 315.)

(General conclusions are given on examination of waxes in the cold with carnauba wax included.)

The original was not available.

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Blits, ___ 1898

(To Determine the Melting Point of Waxes, Fats, etc.)

Neder. Tydsch. Phar. II (Am. Drugg. Pharm. Record, 32, p. 312.)

(A new method of determining melting points of fats and waxes using mercury.)

The original was not available.

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Lewkowitsch, L. 1898

The Meaning of the Acetyl Value in Fat Analysis.

Analyst, 24, p. 319.

Discussion of acetyl value with tables of values in which carnauba wax is included.

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Werder, J. (1898)

(Examination of Wax with the Refractometer.)

Chem. Zeit., 22, p. 58 and p. 59 (Analyst, 23, p. 96.)

(The Zeiss butter refractometer is advantageously employed in examination of waxes, especially when small amounts of materials are only available.)

The original was not available.

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(_____) 1898

Refractive Power of Different Kinds of Wax.

Analyst, 23, p. 97.

A total of 30 waxes are listed in a table giving their refractive powers with carnauba wax included in the list.

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Eickhorn, O. 1900

Ueber eine neue Modification der Hübl'schen Methode zur Bestimmung der Saure und Verseifungszahlen von Wachs.

Zeit. Anal. Chem., 39, p. 640.

Technic and chemical methods given for determination of acid and soap parts of wax.

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Hopkins, E. 1900

Adulteration of Oils, Fats, and Waxes.

The Oil-Chemists Handbook, 1 ed., p. 17.

Several adulterants listed which are used to adulterate various products.

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Hopkins, E. 1900

Constants.

The Oil-Chemists Handbook, 1 ed., p. 58.

Constants for carnauba wax and other waxes.

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Hopkins, E. 1900

The Oil-Chemists Handbook, 1 ed., p. 8.

Source, process of manufacture, color, taste, characteristic tests, adulterants, etc. given for carnauba wax.

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Hopkins, E. 1900

Solubility of the Oils, Fats, and Waxes.

The Oil-Chemists Handbook, 1 ed., p. 15.

Solubility of carnauba wax in various solvents.

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Wiesner, J. 1900

Copernicia cerifera Mart (= corypha cerifera Virey).

Die Rohstoffe des Pflanzenreiches, 2 ed., v. 1, p. 525, 550.

Besides many references several pages are devoted to the chemistry of carnauba wax and synonyms.

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(Editor.) 1901

Pharm. Era, (Price List Supplement), 24, p. 46.

Prices of the various grades of carnauba wax are given.

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(_____) 1901

The Carnauba Palm.

Pharm. Journ., 66, p. 710.

A general description of the palm and of the wax obtained from it.

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(Editor.) 1902

Waxes Used in Pharmacy.

Pharm. Journ., 68, p. 19.

Many waxes used in Pharmacy are described in which carnauba wax is included.

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(Editor.) 1902

Carnauba Wax.

Pharm. Era, 28, p. 250.

The source, description, physical properties, uses and general information given on carnauba wax.

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Kitt, M. 1902

Die Jodzahl der Fette und Wachsarten, p. 62.

Constants and general methods of technic for carnauba wax and allied products given.

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Sedna, L. 1902

Das Carnaubawachs auch Cereawachs (Cearawachs).

Das Wachs, 2 ed., p. 26.

The source, method of obtaining, dates of early shipments to Europe, description and chemistry of carnauba wax are discussed.

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Barclay, J. 1905

Notes on Crude Drugs, Fixed Oils, Waxes, etc.

Pharm. Journ., 76, p. 97.

Various constants for carnauba wax are included.

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Kraemer, __. and Sorthau, __. (1905)

(Determining the Melting Point of Resins and Waxes.)

Nouv. Remedes, 19, p. 527 (Pharm. Journ., 71, p. 402.)

(Detailed explanation of method of determining melting points of resins and waxes.)

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Wright, A. 1905

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The Analysis of Oils and Allied Subst., 5 ed., p. 19.

Physical and chemical properties of cerotic acid obtained from carnauba wax.

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Wright, A. 1905

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The Analysis of Oils and Allied Subst., 5 ed., p. 50.

Properties of ceryl and myricyl alcohol obtained from carnauba wax.

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Wright, A. 1905

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The Analysis of Oils and Allied Subst., 5 ed., p. 66.

Tables giving physical properties of carnauba wax and others.

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Wright, A. 1903

The Analysis of Oils and Allied Subst., 5 ed., p. 102.

Chemical constants of carnauba wax and many other waxes.

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Wright, A. 1903

The Analysis of Oils and Allied Subst., 5 ed., p. 145.

Free alcohols from waxes including carnauba wax with tables of acetyl values.

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Wright, A. 1903

The Analysis of Oils and Allied Subst., 5 ed., p. 229.

General description and uses of carnauba wax given.

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(Editor.) 1904

(Carnauba Wax.)

Pharm. Weekblad, 4, p. 78 (Pharm. Journ., 72, p. 246.)

(The source, method of obtaining, description and various uses of carnauba wax, together with export channels of the wax.)

The original was not available.

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(Editor.) 1904

Carnauba Wax.

Pharm. Era, 31, p. 280.

Source, method of obtaining, principle exports, uses etc. are cited.

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Lewkowitsch, L. 1904

Carnauba Wax.

Chem. Tech. and Anal. of Oils, Fats, and Waxes, 5 ed., v. II, p. 872.

Synonyms, description and collection of the wax, tables of physical and chemical constants, and chemical composition are given.

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(_____) (1904)

(Carnauba Wax.)

Pharm. Weekblad, 4, p. 78 (Yrbk. Am. Pharm. Assoc., 52, p. 909; Pharm. Journ., 72, p. 246.)

(General information on the source, use, and commercial aspects are given on carnauba wax.)

The original was not available.

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(Editor.) 1905

Gramophone Wax.

Pharm. Journ., 74, p. 542.

In a column for correspondents a formula is given for phonograph records which contains carnauba wax.

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Lothian, J. 1905

Vegetable Wax Found on the Shetland Coast.

Pharm. Journ., 75, p. 862 (Proc. Am. Pharm. Assoc., 54, p. 726.)

The identification of a wax found on Shetland coast to be carnauba wax coming from a passing ship. Also source, use and properties are given.

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Engler, C. 1906

Zur Frage der Entstehung des Erdöls.

Chem. Zeit., 30, p. 711.

A discussion of petroleums in which fatty oils, fats and waxes are described as the mother-substances of the earth —— carnauba wax included.

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Radcliffe, L. 1906

A Redetermination of the Constants of Carnauba Wax.

Pharm. Journ., 77, p. 596 (Proc. Am. Pharm. Assoc., 55, p. 760; Journ. Soc. Chem. Ind., 25, p. 214; Yrbk. Pharm., 1906, p. 19; Chem. Abstr., 1, p. 766.)

Some technics given for the determination of constants together with the results for carnauba wax.

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(Editor.) 1907

Carnauba Wax.

Pharm. Journ., 78, p. 484.

In a column for correspondents carnauba wax along with others in a method for incorporating the wax with fats.

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(Editor.) 1907

Carnauba Wax.

Southall Reports, 1907, p. 8 (Yrbk. of Pharm., 1907, p. 52.)

A drug company's report on the physical and chemical constants of carnauba wax.

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(Editor.) 1907

Wachs (Hamburg) - Carnaubawachs.

Chem. Zeit., 25, p. 1336.

A report on the status of the market concerning Carnauba wax and also the price.

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von Zimmermann, A. 1907

Die Wachspalme (Cop. cer.)

Pflanzer, Bd. 3, p. 191 (Chem. Rep., 1907, p. 95; d. Oel-u-Fette-Ztg., 1908, p. 47; Pharm. Zentralh., 49, p. 453; Irbk. Pharm., 1908, p. 229.)

A general description of the carnauba tree is given including also descriptions of plant parts and method of obtaining the wax.

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Cowan, T. W. 1908

Carnauba Wax.

Wax Craft, 1 ed., p. 100.

A description and method of collection of the wax together with its physical and chemical properties.

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Benedict, R., and Ulzer, F. 1908

Carnaubawachs.

Analyse der Fette und Wachsarten, 5 ed., p. 1045.

Synonyms, table of constants, source, chemical constituents and men who worked on carnauba wax are given.

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(Editor.) 1908

Mitteilungen über einige Arzneimittel und Drogen.

Pharm. Ztg., 53, p. 512 (Proc. Am. Pharm. Assoc., 56, p. 161.)

In a list of drugs appears carnauba wax described as to general description.

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Wittels, ___. and Welwart, ___. 1908

Uber verfalschtes Karnaubawachs.

Seifensieder-Zeitg., 35, p. 1442 (Chem. Abstr. 4, p. 2055; Chem. Centrahalle, 1909 (1), p. 692.)

The detection of paraffin in carnauba wax is reported by saponification.

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Berg, R. 1909

Die Verseifung von Carnaubawachs.

Chemiker-Zeitung, 33, p. 885.

A very good article on the saponification of carnauba wax dealing with methods, technic, and problems.

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(Editor.) 1909

Chem. Abstr., 6, p. 3295.

A German patent by C. Mähler on the manufacture of carnauba wax-leather cream free with turpentine together with the method.

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Lewkowitsch, L. 1909

Carnauba Wax.

Chem. Tech. and Anal. of Oils, Fats, and Waxes, 4 ed., v. II., p. 756.

Synonyms, tables of physical and chemical constants, chemical composition and general information concerning carnauba wax.

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Wagenaar, W. 1909

(Reactions for Fat in Beeswax, Paraffin, Cetaceum, Carnauba Wax, and Wool Fat.)

Pharm. Weekblad, 48, p. 479 (Chem. Abstr., 5, p. 2502.)

(The procedures are given for tests for fats in various waxes.)

The original was not available.

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(_____) (1909)

(Characteristics of and Tests for Vaselines and Paraffins.)

Indust. Chim., 10, p. 217 (Indust. Sap. 1909, p. 141, 147; Chem. Abstr., 4, p. 3296.)

(Tests for "natural" and "artificial" vaselines, paraffins, ceresins, and carnauba wax.)

The original was not available.

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Leathes, J. B. 1910

Alcohols that Occur in Waxes.

The Fats, p. 55.

Principal wax alcohols given including those obtained from carnauba wax.

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(_____) 1910

(Carnauba Wax.)

Evan's Analyt. Report, 1910, p. 20 (Yrbk. of Pharm., 1911, p. 95.)

(A few constants for carnauba wax are given.)

The original was not available.

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Wichmann, A. 1911

Vereinfachtes Verfahren für die Bestimmung von Säure und Verseifungszahl im Wachs.

Pharm. Centralhalle, 52, p. 565 (Chem. Abstr., 5, p. 2192.)

A detailed procedure on how to take acid and saponification values of waxes with carnauba wax included.

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Leys (Leijs), A. 1912

Cires d'abeilli et de Carnauba.
Methode d'analyse, dosage des hydrocarbures estrangers.

Journ. der Pharm. Chim., 5, p. 577 (Ser. 7) (Yrbk. Am. Pharm. Assoc., 1, p. 252; Pharm. Ztg., 57, p. 574; Yrbk. Pharm., 1912, p. 110; Ann. Chem. Anal., 17, p. 334; Mat. Grasses, 5, p. 2887; Chem. Abstr., 7, p. 909; Ibid., p. 3041.)

The technic and special apparatus is shown for a new method of distinguishing between carnauba and beeswax.

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Tschirch, A. 1912

Carnaubawachs.

Handbuch der Pharmakognosie, v. II., 1 ed., p. 754.

Synonyms, general appearance, method of obtaining the wax, illustrations of the plant and its parts and also the chemistry of the wax.

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Kleine, E. 1914

Carnauba or Carnahuba Wax.

Drugg. Circ., 58, p. 524 (Yrbk. Am. Pharm. Assoc., 5, p. 204.)

Source, method of collection, uses, description of carnauba wax given.

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Lewkowitsch, J. 1914

Carnauba Wax.

Chem. Tech. and Anal. of Oils, Fats and Waxes, 5 ed., v. ii, p. 875.

Tables, chemical and physical properties and general information are given.

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Ljubowsky, S. (1914)

(Cable Wax.)

Seifensieder Ztg., 40, p. 1174 (Chem. Abstr., 8, p. 589.)

(Formulas given containing carnauba wax for insulating cables and wires.)

The original was not available.

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Ludecke, C. (1914)

(Carnauba Wax.)

Seifensieder Ztg., 40, p. 1257 (Chem. Abstr., 8, p. 589.)

(Methods of testing for detection of adulteration of carnauba wax.)

The original was not available.

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Lach, B. (1915)

(Bleaching of Carnauba Wax.)

Chem. Rev. Fett., Hars, Ind., 22, p. 40, 49 (Chem. Abstr. 9, p. 2522.)

(Procedure and apparatus for bleaching process.)

The original was not available.

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(Editor.) 1916

The Exports of Carnauba Wax.

Chem. and Drugg., 88, p. 975 (Yrbk. Am. Pharm. Assoc., 5, p. 188.)

A note on the exports and values of carnauba wax from Brazil during 1915.

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(Editor.) 1918

Referaten.

Pharm. Weekblad, 55, p. 684 (Yrbk. Am. Pharm. Assoc., 7, p. 314)

A list of the constants of various waxes including carnauba wax.

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(Editor.) 1919

Carnauba Wax.

Chem. and Drugg., 90, p. 1057 (Yrbk. Am. Pharm. Assoc., 7, p. 253.)

A comparison of the exports from Brazil between 1917, 1916, and 1915.

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Eguchi, M. (1919)

(Variation of Electrical Conductivity of Oils and Waxes.)

Proc. Phys. Math. Soc. Japan (3) 1, p. 320 (Chem. Abstr., 14, p. 2577.)

(Curves are given for certain waxes including carnauba wax concerning the electrical conductivity especially during solidification.)

The original was not available.

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Heiduscha, A., and Gareis, M. 1919

Beitrage zur Kentnis des Melissyl Alcohol und der Melissinsaure.

Journ. prakt. Chem., 99, p. 295 (Chem. Abstr., 14, p. 955; Amer. Chem. Soc., 14, p. 955; Yrbk., Pharm., 1920, p. 78.)

A comparative study, in detail, concerning the identity of the melissyl alcohol from beeswax and with that from carnauba was with many derivatives.

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Higgins, E. (1919)

(Medicinal Plants in Bahia.)

Commercial Reports, 1919 (Amer. Journ. Pharm., 92, p. 184; Pharm. Era, 55, p. 51.)

(Source and medicinal value of carnauba wax included in long list of other plants.)

The original was not available.

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(Editor.) 1920

Carnauba Wax: Montan Wax.

Pharm. Era, 52, p. 78.

A discussion over the possibility of the composition of "Carnaumontine" wax and is believed to be a mixture of carnauba and montan wax.

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Fryer, P. and Weston, F. E. 1920

Natural Waxes.

Tech. Handbook of Oils, Fats, and Waxes, 1, p. 182.

Physical and chemical constants, composition, adulteration, source yield, grades, and method of refinement of carnauba wax is given.

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Grimme, C. 1921

Uber die Ausnutzung der Carnauba-wachs Palme.

Pharm. Zentralh., 62, p. 249 (Yrbk. Am. Pharm. Assoc., 10, p. 221.)

Descriptions, synonyms, habitat, uses, appearance, and composition of various parts of the carnauba plant are given.

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Hahmann, C. 1921

Die Verwendung der Copernicia cerifera Mart., mit einem Beitrag zur anatomischen Kentnis von deren Wursel, Frucht und Samen.

Arch. der Pharm., 259, p. 176 (Yrbk. Am. Pharm. Assoc., 10, p. 251.)

Structure of root, seed, and fruit described with pictures, synonyms, and uses of various parts of the plant.

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Franck, H. (1922)

(The Carnauba as a "Universal Provider".)

Working Up from Patagonia, p. 419 (Pharm. Journ., 109, p. 406.)

(A survey of the many uses of the different parts of the plant with a description of the plant.)

The original was not available.

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Ludmor, F. 1922

(Carnauba Wax Palm. Die Carnauba-wachs-Palme.)

Ztschr. D. Öl und Fett-Ind. Nr. 35 (Yrbk. Am. Pharm. Assoc., 12, p. 245; Pharm. Ztg., 68, p. 166.)

(A description and uses of the various parts of the plant including the wax are given together with the commercial forms.)

The original was not available.

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Reutter, L. 1924

(A New Method for the Analysis of Fats and Vegetable Oils.)

Schweiz. Apoth. Ztg., 62, p. 486 (Chem. Abstr., 19, p. 2139.)

(A detailed account of the systematic separation of each chemical constituent of oils with carnauba wax and others.)

The original was not available.

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Grün, A. Halden, W. 1925

Analyse der Fette und Wachse, v. 1, p. 112.

Boiling points of many wax acids.

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Grün, A. and Halden, W. 1925

Analyse der Fette und Wachse, v. 1, p. 59.

One of cleavage products of carnaubon is carnaubic acid (identical with lignoceric acid).

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Grün, A. and Halden, W. 1925

Analyse der Fette und Wachse, v. 1, p. 15.

Relationship of melissic acid of beeswax and carnauba wax.

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Jaeger, R. 1925

The United States of Brazil, p. 9.

In a story concerning the resources, wealth and future of Brazil, carnauba wax and the plant from which it is obtained is described as to use and future developments.

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Leathes, J. B. and Roper, H. S. 1925

Carnauba or Melissyl Alcohol.

The Fats, 2 ed., p. 44.

Discussion of melissyl alcohol, properties and relationship to other waxes, also coceryl alcohol.

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Rousseau, R. 1925

Les Cires et en Particulier les Cires Vegetales.

Travaux du Laboratoire de Mat. Med., 16, pt. 5, p. 1.

A long article on vegetable, animal and mineral waxes, especially vegetable in regard to source, method of collection, constants, chemistry, etc. with carnauba wax included.

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Berg, R. 1926

Wachse.

Handbuch der Chem. u. Tech. der Öle und Fette, Hartmann and others, v. iv, p. 454.

Synonyms, botany, methods of obtaining, description, chemical discussion, table of constants, constituents, methods of bleaching, methods of raising the melting point, and commercial aspects of carnauba wax.

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Gottfried, __., and Ulzer, __. 1926

(_____)

Chem. Umschau, 1926, p. 141 (Thorpe, J., Dict. of Applied Chem., Supp., v. 2, p. 692 (1935).)

Isolation from carnauba wax of n-heptacosane ceryl alcohol and melissyl alcohol.

(The original was not available.)

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Ludecke, C. 1926

Carnaubawachs.

Die Wachse und Wachskorper, p. 35.

General information given including source, method of collection, chemistry, methods of isolation of constituents and tests.

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(_____) 1926

(Carnauba Wax in Brazil.)

Commerce Reports, ___, p. __ (Am. Drugg., 74, p. 86.)

(A general description of the source, habitat of the plant, and uses of the wax.)

The original was not available.

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Charliers, M. 1927

(Detection and Determination of Waxes Mixed with Fats in Foods.)

Chimie et industrie, Special No., p. 699 (May, 1927) (Chem. Abstr., 21, p. 3398.)

(Determinations made by taking constants and comparing them to actual waxes, carnauba wax included.)

The original was not available.

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(Editor.) 1927

Making Cakes of Stearic Acid, Carnauba Wax, etc.

Chem. Abstr., 28, p. 1147.

A German patent 536,566, October 30, 1927 containing details of the apparatus used.

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(Editor.) 1927

Refining Vegetable Waxes.

Chem. Abstr., 27, p. 1226.

A German patent on a method of refining carnauba wax.

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(Editor.) 1927

Aqueous Emulsion of Carnauba Wax Dispersed with Sodium and Potassium Stearates.

Chem. Abstr., 21, p. 5138.

An U. S. patent by L. Davis and E. Bennett which describes the preparation of an emulsion to be used in treatint thread for sewing shoes.

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Mailhe, A. 1927

(The Decomposition of Carnauba and Japan Waxes.)

J. usines Gaz., 51, p. 129 (Chem. Abstr., 21, p. 2074.)

(Certain data is given in the original article for the products formed by the distillation of these waxes in the presence of zinc chloride.)

The original was not available.

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Mailhe, A. 1927

Sur la Decomposition des Cires Vegetales.

Bull. Soc. Chem., (4), 41, p. 1056 (Chem. Abstr., 21, p. 4082.)

Chemical methods in length are given for the decomposition of vegetable waxes including carnauba wax along with tables.

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Buchner, G. 1928

Verhalten des Bienwachses gegen Trichloräthylen bei Gewohnlicher Temperatur.

Chem. Ztg., 52, p. 519 (Chem. Abst., 22, p. 2478.)

Behavior of beeswax with trichlorethylene at ordinary temperature with technic, procedure, etc. is given together with behavior of other waxes including carnauba wax.

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(Editor.) 1928

Carnauba Wax.

Chem. Abstr., 22, p. 1246.

An U. S. patent by W. Sprague on the method of preparing fine-grained cakes of carnauba wax.

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(_____) 1928

Solvents for Carnauba Wax.

Pharm. Journ., 120, p. 490.

A list of solvents for carnauba wax including oil of turpentine, amyl alcohol, kerosene, acetone and others.

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(Editor.) 1929

Hydrogenation and Saponification of Fatty Oils.

Chem. Abstr., 26, p. 4129.

A British patent for hydrogenation of fats and waxes which includes carnauba wax.

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Grün, A. and Halden, W. 1929

Analyse der Fette und Wachse, v. 2, p. 528.

Tables of all data of carnauba wax including source, habitat, description, etc.

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Meyer, J. 1929

(Substitutes for Carnauba Wax.)

Kunststoffe, 19, p. 82 (Chem. Abstr., 24, p. 4178.)

(Several substitutes employed in Germany are described.)

The original was not available.

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Peckett, O. 1929

Solvents for Waxes.

Ind. Eng. Chem., 21, p. 767 (Chem. Abstr., 25, p. 4585.)

Various solvents for waxes including carnauba wax with curves, tables and procedures given.

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Sanderson, J. (1929)

(The Waxes of Industry.)

Chemical Markets, __, p. __ (Amer. Journ. Pharm., 101, p. 214.)

(A discussion of waxes in general with common uses emphasized including carnauba wax.)

The original was not available.

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Vesely, V. (1929)

(Residues from the Refining of Carnauba Wax.)

Chim. and Industrie (Special No.), p. 554 (Feb. 1929) (Chem. Abstr., 25, p. 4091.)

(Some figures given for the analysis of 5 samples of crude carnauba wax, 2 samples of bleached and 5 of residue.)

The original was not available.

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Wehmer, C. 1929

Copernicia Cerifera Mart.

Die Pflanzenstoffe, v. I., 2 ed., p. 121.

Source, chemical constituents of carnauba wax and percentage of each constituent in the wax.

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(_____) (1929)

(Carnauba Wax.)

Revista Commerc-italo-brasil, 12, p. 55 (Prog. ind. tintori e tessili, 19, p. 27; Chem. Abst., 24, p. 2001.)

(Several constants obtained from analysis of carnauba wax, Japan wax, and candelilla wax are given.)

The original was not available.

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Francis, F., Piper, S., and Malkin, T. 1950

The n-Fatty Acids.

Proc. Roy. Soc., A., 128, p. 214.

The results of investigations in length on methods of preparation, melting and setting points of pure acids and of mixtures of known composition, large crystal spacings of pure acids and of mixtures of known composition, fatty acids from the oxidation of paraffin wax, fatty acids from natural sources and fatty acids from the oxidation of alcohols present in Chinese wax and carnauba wax.

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Katrakis, C. and Megalockonomos, J. (1950)

("Aniline Point" as Constant for Waxes.)

Practika (Alsod. Athenon) 5, p. 5111 (Chem. Abstr., 27, p. 2525.)

(Several values given in which carnauba wax is 78.)

The original was not available.

Watson, L. (1930)

(Detection of Carnauba Wax in Beeswax.)

Am. Bee J., 70, p. 118, and p. 146 (Chem. Abstr., 24, p. 2908.)

(A method is given for the detection of carnauba wax in beeswax.)

The original was not available.

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(Editor.) 1931

Waxes.

Chem. Abstr., 26, p. 1820.

A French patent on the waxy substances obtained by hydrolysis with lime and treatment with sulfuric acid.

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Bennett, H. (1932)

(Emulsification of Carnauba Wax.)

Melliand Textile Monthly, 4, p. 297 (Chem. Abst., 27, p. 5555.)

(Directions, in brief, are given for the preparation of wax polishes by emulsification in water.)

The original was not available.

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(Editor.) 1932

Refining Carnauba Wax etc.

Chem. Abstr., 26, p. 1820.

An U. S. patent by F. Zschach and Rodrian in which a method is given for refining carnauba wax by dissolving the wax in an oxygenated solvent and boiling with charcoal.

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Gray, W. 1932

Exhibits.

Pharm. Journ., 128, p. 94.

A short article on an exhibit of specimens of carnauba wax found near the Shetland Islands.

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Ivanovsky, L. (1932)

(The Retention of a Solvent as a Constant for Waxes.)

Chem. Listy, 26, p. 552 (Chem. Abstr., 26, p. 6170.)

(The retention numbers (R_g) explained and tells what is depended on together with comparison of numbers of many waxes including carnauba wax.)

The original was not available.

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Radley, J. 1932

The Fluorescence Analysis of Waxes.

Analyst, 57, p. 826 (Chem. Abstr., 27, p. 202.)

Methods of analysis by fluorescence are given with its meaning, and ability to detect specific waxes and amounts in mixtures.

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Schneider, G. and Folgner, R. (1932)

(Use of the I.G. Brands of Synthetic Waxes.)

Chem. Umschau Fette Öle, Wachse Harze, 39, p. 175 (Chem. Abstr., 26, p. 6170.)

(New synthetic waxes used for hardening soft waxes used as a substitute for carnauba wax.)

The original was not available.

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Waterman, H., de Kok, P. and Tulleners, A. 1932

Preparation of Paraffins from Carnauba Wax by Means of Catalytic Hydrogenation.

J. Inst. Petroleum Tech., 18, p. 1007 (Chem. Abstr., 27, p. 1494.)

Experimental data is given concerning the preparation of paraffins from carnauba wax by means of catalytic hydrogenation yielding 70% paraffin.

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(_____) 1932

(Carnauba Wax.)

Oil, Paint and Drug Reporter, August 22, p. __.

A long varied list of the uses of carnauba wax in industry.

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(Editor.) 1933

Impregnating Materials such as the Treatment of Telephone Cords with Carnauba Wax and Paraffin.

Chem. Abstr., 27, p. 4860.

An U. S. patent by B. Ford and M. Lomme which describes a method of impregnating wire with carnauba wax and paraffin.

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(Editor.) 1933

Wax Conversion Products.

Chem. Abstr., 28, p. 925.

A French patent on the products obtained by treating the wax with amines making them more easily immersible in water.

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(Editor.) 1933

Carnauba Wax.

Chem. Abstr., 27, p. 5207.

A German patent by E. Christmann describing a white or light yellow product obtained by saponifying and neutralizing the soaps of carnauba wax.

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Leaper, J. (1933)

(A Method for Determination of Saponification Number of Fats and Waxes.)

Dyer, Calico Printer, Bleacher, Finisher, 70, p. 455 (Pharm. Monatshefte 15, p. 196; Amer. Journ. Pharm., 106, p. 456.)

(Instead of using KOH, diethyleneglycolethylether is used in carbitol solution, details are given.)

The original was not available.

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Ivanovszky, L. (1934)

(Carnauba Wax, In Particular its Refining, Examination, and Evaluation.)

Seifensieder-Ztg., 61, p. 465, 481 (Chem. Abstr., 28, p. 7047.)

(Source, short description of the chemical means of refining, and a discussion of viscosity is given.)

The original was not available.

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von Schneider, G. and Folgner, R. 1934

Weisses Carnaubawachs.

Fettchemische Umschau, 41, p. 1.

A method is given for obtaining a white carnauba wax without bleaching.

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Ivanovszky, L. 1935

Wachse.

Ozokerit und Verwandte, v. 1, p. 269.

Classification of grades of carnauba wax with physical constants.

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Ivanovsky, L. 1935

Das Zerefin.
A. Die Rohstoffe zur Serefin-Erzeugung.

Ozokerit und Verwandte Stoffe, V. 1, p. 176.

General comparison of carnauba wax and many others, such as paraffin, montan wax, stearin, etc.

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Welwart, ___. (1935)

(The Constants of Carnauba Wax Residue.)

Seifensieder Ztg., 62, p. 264 (Chem. Abstr., 29, p. 5868.)

(Constants of Carnauba wax are given and also what residues probably are.)

The original was not available.

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Dahlgren, B. 1936

Index of American Palms, v. 14, p. 151.

Genera and species of Corypha cerifera.

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Dahlgren, B. 1936

Index of American Palms, v. 14, p. 127.

Genera and species, Copernicia cerifera.

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Dahlgren, R. 1936

Index of American Palms, v. 14, p. 506.

Prelinnean names of Carnauba.

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Dahlgren, R. 1936

Index of American Palms, v. 14, p. 528.

A list of vernacular names of carnauba.

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(Editor.) 1936

Carnauba Wax.

Industrial Finishing, May, 1936, p. 56.

A short review of the important part carnauba wax plays in polishes is given. It is pointed out that the demand for the wax is becoming greater than the output, consequently synthetic waxes are being worked out.

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Johnson, H. (Jr.) 1936

Carnauba.

Am. Painter and Decorator, 1936, p. 1.

A very complete story of the production of carnauba wax with descriptions of the locale, plant, people and uses of the wax.

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Steinle, J. 1936

Carnauba Wax. An Expedition to its Source.

Ind. Eng. Chem., 28, p. 1004.

A Story of an expedition to the source of carnauba wax, with details of findings and general information about the plant and the wax.

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(Editor.) 1937

Symposium Over Oppervlakte-spanning en Spreiding.

Chem. Weekblad, 34, p. 707.

On pages 716-19 is a chapter by H. Limburg using carnauba wax surface in a study of wetting phenomena. He determined the variation with time in the angle formed by a drop of a 0.1% solution of a wetting agent.

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(Editor.) 1938

Bleaching Wax.

Chem. Abstr., 32, p. 6490.

A German patent 658,749 by W. Schrauth on bleaching wax accomplished by treating the crude carnauba wax with alkali metal in presence of butyl alcohol at a raised temperature.

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Koch, J., Hable, G. and Wrangell, L. 1938

Melting Point Studies of Binary and Trinary Mixtures of Commercial Waxes.

Ind. Eng. Chem., Analyt. Ed., 10, p. 166.

Binary and trinary mixtures with melting point systems recorded on graphs so that one can prepare mixtures of any melting point. Systems used were paraffin, carnauba, beeswax, candelilla, ozokerite, Chinese insect wax and montan wax. A new method for taking these melting points is recorded.

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Worton, A. and Kempf, P. and Bibbins, F. 1938

A New Enteric Coating and a Laboratory Method for its Control.

Journ. Am. Pharm. Assoc., 27, p. 21.

Together with a general review of enteric coatings a new enteric coating is reported which has carnauba wax as an ingredient.

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Greene, L. 1939

The Animal and Vegetable Waxes in 1938.

Oil and Soap, 16, p. 107.

An extensive review of the status of waxes in 1938 including animal, vegetable and synthetic waxes, extraction and refining, properties, products derived from waxes, emulsification, analysis, and uses.

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Taub, H., and Zweig, S. 1939

Microscopy of Waxes and Wax Constituents.

Journ. Am. Pharm. Assoc., 28, p. 155.

An aim for developing a method for identification and determination of adulterated waxes. Details of the experimental work are given which is based upon obtaining crystals from various solvents and examining the crystals.

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Zweig, S., and Taub, A. 1940

Identification of Commonly Used Waxes in Admixture.

Ind. Eng. Chem., Analyt. Ed., 12, p. 9.

The identification of commonly used waxes such as spermaceti, beeswax, carnauba, candelilla and montan in preparations containing them. This is based on a schematic outline on a semiquantitative basis involved in the isolation of an ethanol soluble fraction of fatty acids of high and low molecular weight, hydrocarbons and fatty alcohols of high and low molecular weights.

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