

The Fatty Acids of Carnauba Wax^{*,†}

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Although the Carnauba palm (*Copernicia cerifera* Martius, Fam. *Palmæ*) was first described by Piso (1) in 1648 and further described by Raii (2) in 1688, Arruda (3) who published his description of the plant in 1810 is usually credited with its discovery. The leaves of the Carnauba palm yield carnauba wax, a valuable product which plays an important role in industry (4) and which is beginning to find its way into the art of pharmacy (5). Carnauba wax was discovered in the beginning of the eighteenth century by de Macedo (6). Steinle (7) has described the plant and wax in respect to its source and method of production.

Brande (8), in 1811, published the first experimental work on carnauba wax which consisted of a preliminary physical and chemical investigation. The work of Sturche (9), in 1884, with the exception of a few scattered reports (10, 11, 12, 13, 14, 15), has served as the only source of knowledge of the composition of the wax. Previous work suggested the following composition: *n*-heptacosane, all of the normal straight chain fatty acids containing an even number of carbon atoms, of from 24 to 30, a hydroxy acid with 24 carbon atoms, normal primary alcohols with an even number of carbon atoms of from 26 to 34, and a dihydric alcohol with 24 carbon atoms.

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 (16, 17), have proceeded according to the time-honored method of the separation of the wax or fat 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 Skelly-solve B and ethylene dichloride.

The isolation of unitary substances from natural fatty acids has been shown to be very difficult. Until about the last decade the general method of separating fatty acids was based on fractional crystallization. The multiple crystallization method employed by de Visser, in 1898 (18), was shown to be incapable of yielding a pure compound (19, 20).

Generally, the separation of homologs of fatty acids is best attained by fractional distillation of either their methyl or ethyl esters at low pressures through an efficient column (21). Longenecker (22) has prepared a review of the use of fatty acid ester distillation methods in fat analysis. He states that as early as 1877 Krafft (23) attempted the distillation of castor oil but succeeded only in cracking the oil. Bull (24) contributed materially to the problem of ester distillation in 1906. The introduction into the distillation system of vacuum pumps capable of continuously evacuating laboratory distillation apparatus to 1 mm. or less of mercury and the evolution of entirely new types of fractional distillation equipment have caused a rapid advance in ester distillation methods. Single turn glass helices (25) were shown to be particularly desirable for fatty acid ester distillations. Since 1934, Longenecker and others (26, 27, 28, 29, 30, 31) have used systems resulting from the development of theoretical knowledge of the fundamental principles involved in fractional distillations.

Schuette and Vogel (32) have shown that from the solidification points of a number of binary mixtures of fatty acids of known com-

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position one can plot a curve that is definite for every system of two acids. If one has a mixture of maximum resolution and if the mean molecular weight and solidification point are known, it is possible to calculate the composition of this mixture by means of the above curves. With this in mind a systematic rational fractionation of the methyl esters was made by means of ester fractional distillation and repeated recrystallization.

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. Francis *et al.* (33), 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. No pure individual substances were obtained. Francis (34) reported that a complete separation of fatty acids by ester distillation methods was not possible. With this in mind an attempt was made to make a systematic fractional distillation 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 the acids of carnauba wax would not distil 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.

EXPERIMENTAL

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.

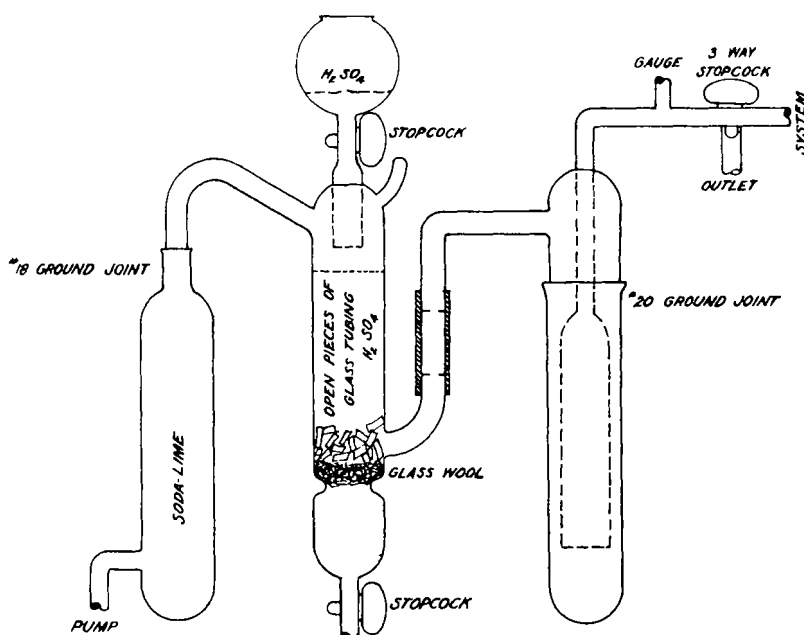


Fig. 1.—Soda Lime, Sulfuric Acid, Freezing Traps.

Figure 2 shows the combination column and receiver (35). 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 similar to those used with a Widmer column.

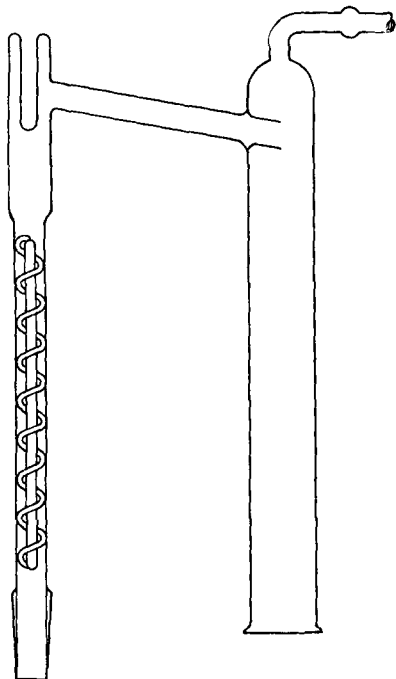


Fig. 2.—Combination Column and Receiver.

The system was evacuated over night before distillation was started. A Cenco-hyvac pump was used for evacuation and a modified McLeod gage 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 fractions replaced by a new tube, restoppered with a fresh rubber stopper and evacuated again. About five minutes was necessary for the foregoing operation.

Solidification Points.—The method of determining the solidification temperature of fractions of methyl esters and free fatty acids was that of Schuette and Vogel (36). In the tables the solidification point is designated as S. Pt.

Melting Points and Resolidification Points.—For the determination of melting points and resolidification points the general method of Francis and Collins (39) was used. The melting point is designated as M. Pt. and resolidification point as R. Pt. in the tables.

Titrimetric Determination of the Mean Molecular Weights of the Acid Fractions.—The mean molecular

weights of the acid fractions of carnauba wax 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 those under which 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 with a 250-cc. Erlenmeyer flask and a 10-cc. burette 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 was 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, with 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, 30 cc. of distilled water was slowly added. The first appearance of a permanent light pink was taken as the end-point. The neutralization equivalent was calculated from the following formula:

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

Determination of Constants.—The chemical and physical constants of the wax were determined according to the Pharmacopœial methods for *Cera Flava* (37).

Table I.—Chemical and Physical Constants of Carnauba Wax

M. pt.	76–78°
Sp. gr.	0.9897
Sap. no.	68.5
Acid no.	5.6
Ester no.	62.9
Iodine no.	10.5
Total ash	1.15 per cent
Moisture	4.8 per cent

Saponification of the Wax.—The crude powdered wax was saponified with alcoholic potassium hydroxide using an excess of 20 per cent of alkali. Four thousand one hundred and fifty grams of wax were divided into five portions and each refluxed for ten hours. After saponification the alcohol was removed completely at 17 mm. pressure. The dry material was removed from the flasks and powdered.

Extraction of the Non-Soap Portion from the Soaps.—Two to three hundred gram portions of the powdered saponified product were extracted with ethylene dichloride and Skelly-solve B. The extraction with the latter solvent was continued until completion and followed with acetone extraction. This extraction yielded the non-soaps as the soluble fraction and the soaps as the residue. The results of the saponification and separation of the soaps and non-soaps are herewith given:

Table II.—Proportion of Soaps and Non-Soaps

Amount of wax in grams	4150
Amount of soaps in grams	1300 ^a
Amount of non-soaps in grams	2200

^a A portion of soaps was lost due to an accident.

Preparation of the Free Fatty Acids.—The free fatty acids were prepared from the soaps by heating 200-Gm. portions with one liter of a 10 per cent aqueous solution of sulfuric acid at 85° and stirring for fifteen to thirty minutes. The conversion 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 Skelly-solve B, water removed in a separatory funnel, filtered, the filtrate cooled and the deposited material collected. Nine hundred grams of wax acids melting at 68–72° were obtained.

For further and final purification of the acids, ether solutions at room temperature were prepared and the dissolved acids precipitated with a 10 per cent solution of sodium hydroxide. The sodium soaps were extracted with ether and Skelly-solve B. The acids were recovered as above and there resulted 850 Gm. of pure fatty acids.

Preparation of the Methyl Esters.—Seven hundred grams of acids were divided into three portions and esterified by refluxing with absolute methyl alcohol saturated with dry hydrogen chloride for 24 hours. The esters were recovered from the reaction mixture by removing the methanol, mixing the residue with a large volume of water, and alkalizing with a dilute sodium bicarbonate and sodium carbonate solution. The mixture was heated to the melting point of the esters and stirred for a half an hour before cooling. The cake of crude esters was removed and extracted with Skelly-solve B. The Skelly-solve solution was refluxed with decolorizing charcoal, filtered, cooled in an ice-salt mixture and the precipitated esters collected on a Büchner funnel. There resulted 420 Gm. of crude esters melting at 68–69°.

Distillation of the Crude Methyl Esters.—The methyl esters were divided into four parts and each distilled through a short distilling head. The material was distilled from a 250-cc. flask packed to half its capacity with glass wool. 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 350 degrees, pressure of about 0.03 mm. of mercury. The distillation was stopped

when the pressure began to rise steadily, indicating decomposition. A yield of 205 Gm. of distillate was obtained. The distilled esters were almost white in color, waxy in appearance and had a melting point of 63.5°. The corresponding acids had a carbon content of 22 to 26 carbon atoms as shown by the saponification equivalents of the esters.

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 distillation was carried out in a 250-cc. flask packed to half its capacity with glass wool and connected to the column described in Fig. 2. Fractions were cut at the most uniform distilling points; however, there was constant variation in distilling temperatures. A Wood's metal bath served as a source of heat.

Table III gives the data for the five fractions collected:

Fractionation into Ten-Degree Distilling Range Fractions.—Each of the five fractions obtained in the foregoing fractionation was carefully separated into fractions distilling within 10-degree ranges. The fractionation started with Fraction 1 distilled from a 100-cc. flask packed to half 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) electrically heated with a coil of nichrome wire was used for the lower temperatures and a Wood's metal bath for the higher temperatures.

Table IV gives a summary of the results of the fractionation:

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 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. See Table V.

Table III.—Constants of Five Fractional Distillates

Fraction	Wt. in Gm.	M. Pt., Degrees	S. Pt., Degrees	R. Pt., Degrees	B. Pt. Range, Degrees	Av. Pressure, Mm.
1	17.2	41.2	41.4	40.8	139–143	0.02
2	39.1	48.5	49.0	48.4	145–152	0.025
3	30.3	56.4	56.7	55.8	160–172	0.025
4	55.8	58.0	58.2	57.4	170–180	0.03
5	42.2	64.9	65.1	63.8	180–195	0.03

Table IV.—Constants of Refractionated Distillates

Fraction	Wt. in Gm.	M. Pt., Degrees	S. Pt., Degrees	R. Pt., Degrees	B. Pt. Range, Degrees	Av. Pressure, Mm.
1	0.55	95	0.012
2	0.94	95-105	0.02
3	2.51	27.4	27.3	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	83.32	56.9	57.23	57.2	145-155	0.022
8	11.60	60.4	61.10	60.5	155-165	0.03
9	44.63	62.2	63.90	64.4	Over 165	0.035

Table V.—Constants of Refractionated Distillates of Ten-Degree Fractions

Fraction	Wt. in Gm.	M. Pt., Degrees	S. Pt., Degrees	R. Pt., Degrees	B. Pt. Range, Degrees	Av. Pressure, Mm.
1 ^a	2.51	27.4	27.30	27.7	105-115	0.012
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	6.73	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	58.16	57.3	160-165	0.04
9	1.48	58.6	58.28	58.9	170-175	0.035
10	16.71	61.4	62.63	62.2	185-190	0.04
11	28.21	63.0	65.17	64.0	Over 190	0.04

^a 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. Together with a 20 per cent excess of alkali and enough alcohol to keep the material in solution, the mixture was refluxed for four hours. The alcohol was removed completely and the soaps extracted with Skelly-solve B, followed by ether extractions. The acids were liberated from the soaps in the same manner as before. Skelly-solve B solutions of the free acids at room temperature were shaken several times with anhydrous sodium sulfate and filtered. The solutions were concentrated to a small volume and decolorized with animal charcoal. The acids were obtained by freezing out in an ice-salt bath and dried in a vacuum oven at 48 degrees for eight hours at a pressure of 5 mm.

Table VI is a tabulation of some of the physical constants of the fatty acids obtained from the corresponding fractions of methyl esters:

Table VI.—Physical Constants of Fatty Acids Obtained from Methyl Ester Fractions

Fraction	Wt. in Gm.	M. Pt., Degrees	S. Pt., Degrees	R. Pt., Degrees	Mol. Wt.
1	1.60	60.2	60.78	60.2	294
2	3.75	69.0	69.32	69.2	291
3	6.76	71.4	71.46	71.4	298
4	1.11	66.1	68.01	67.0	320
5	5.36	72.8	74.51	73.7	330
6	5.51	71.3	71.46	71.2	338
7	58.70	78.6	78.78	78.2	349
8	3.45	76.1	77.51	77.2	375
9	0.84	77.4	77.18	77.9	388
10	11.86	80.2	80.92	79.4	399
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 Skelly-solve B and twice from acetone in alternate order. One hundred cc. of hot solvent were used per Gm. of fraction; the solutions were allowed to cool for one hour in an ice chest at 12°, after which the deposited material was 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.

The fractions obtained still did not give favorable results. However, Fractions 2 and 3 became practically the same in composition, as did Fractions 8 and 9. Thus, these fractions were combined, respectively. Each fraction was carried through the same recrystallization process as above. The solvent of 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.

Table VII is a tabulation of the constants of the fractions at this point:

Table VII.—Constants of Fractions Obtained by Crystallization

Fraction	Wt. in Gm.	S. Pt., Degrees	Mol. Wt.
1	1.60	60.78	294
2a	0.75	65.66	308
2}	4.35	73.38	311
3}			
4	0.40	71.46	320
5	2.75	75.12	346
6	3.26	73.90	353
7	..	80.62	363
8}	1.53	78.58	391
9}			
10	7.60	81.95	410
11	18.65	85.07	422

The composition of the fractions was determined by the use of solidification point curves of binary fatty acid mixtures of Schuette and Vogel (39).¹ These are used as follows:

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 recrystallizations are necessary.

SUMMARY

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 but the mean molecular weight did not coincide. Since this fraction was small no further work was advisable.

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 the calculated, 308 and 303.7, were in fairly good agreement.

Fractions 2 and 3.—This fraction had 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 311.5 were in good accord.

Fraction 5.—This fraction was 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 the 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 was 353 and the calculated 349.9.

Fraction 7.—The composition of this fraction was 14.5 mol per cent of C_{22} and 85.5 mol per cent of C_{24} acids. Theory for the molecular weight was 364.5, found 363.

Fractions 8 and 9.—By interpolation this fraction was 44 mol per cent C_{24} and 46 mol per cent of C_{26} acids. Theory for the molecular weight was 384.3, found 319.

Fractions 10 and 11.—Although curves were not available for acids of 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 of Fraction 11 was close to C_{28} acid, the solidification point was five degrees low. Many recrystallizations did not raise either the molecular weight or the solidification point of either of these two fractions. The molecular weight of both fractions might indicate only C_{26} and C_{28} acids but the depression of the solidification points of higher binary systems are not as great as those observed for these fractions. Thus there is good evidence of C_{30} being present and the presence of C_{26} and C_{28} acids can not be doubted.

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 curves have the form of a "W" (40). With increasing molecular weight the break in the center becomes flatter. For example, the C_{22} – C_{24} acid system has a plateau involving a composition of 30 to 70 per cent of C_{22} acid. Obviously, if the solidification point falls upon the 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 produced by the admixture of a definite amount of the proper pure synthetic acid. From this one can

¹ 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.

compare the solidification points of the new mixture with that calculated for it. If the two points coincide, the original composition could be none other than what it was indicated to be in the first instance.

Fractions 2a and 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 C₁₈ to C₂₈ and a good indication for C₃₀ has been verified.

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

Table VIII.—Composition of Acid Fractions

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 ₂₀
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	14.5 mol per cent C ₂₂ ; 85.5 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 ₂₆ and C ₂₈ present
11	Definitely C ₂₆ and C ₂₈ present and possibly C ₃₀

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Book Review

Chemical Publications, by M. G. MELLON. 2nd Edition. 284 pages. International Chemical Series. McGraw-Hill Book Co., Inc., New York, N. Y., 1940. Price, \$2.75.

This is the second edition of the book by this title, the first edition of which appeared in 1928. The first chapter is given over to the introduction and general outline. This is followed by four chapters which deal with the original sources of published chemical information. The first subdivision of this class of material discussed is periodicals, the second is institutional publications. The next portion of the book covers secondary sources and includes a thorough treatment of index and review serials and abstract journals. The technique of making searches in the chemical literature is next considered and as a conclusion nineteen library problems are presented.—A. G. D.