

2. The phenylstearic acid of Nicolet and deMilt has been compared with 9- and 10-phenyloctadecanoic acids and it has been found to be a mixture of approximately equal parts of these isomers.

3. A number of intermediate compounds used in the preparation of these compounds have been characterized.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF THE CITY OF NEW YORK]

THE FATTY ACIDS ASSOCIATED WITH CASSAVA STARCH

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Some of the common cereal starches (corn, rice and wheat) have been shown to have fatty acids combined with carbohydrate in the α -amylose component.¹ The individual fatty acids found in each of these starches are the same though the amounts are different. Two tuber starches, cassava and potato, also contain combined fatty acids,² but in a much smaller percentage. Beyond this meager information no tuber starch has been investigated from the point of view of the combined fatty acids occurring in it. It would be important to know whether the fatty acids in a tuber starch such as cassava are the same as those found in the common cereal starches.

As in the investigations on the cereal starches a search for sterols and other substances that might occur in the starch and then be present in the liberated fatty acids must be made. This is necessary if there is to be any comparison of the fatty acids found in the different starches. It is also requisite to investigate the aqueous filtrate from the hydrolysis of the starch for glycerol to be sure that the fatty acids are not present in the starch as extraneous glycerides.

Experimental Part

Mixed Fatty Acids from Cassava Starch.—A sample of the cassava starch³ was extracted with petroleum ether for several hours and showed a negligible amount of extractable material. The starch was hydrolyzed by hydrochloric acid^{1b} in 2000-g. portions, a portion yielding 2 g. of a light yellow fatty semi-solid, equal to 0.1% "fat by hydrolysis" and having an iodine number of 78.8.^{1a}

Examination of Filtrate for Glycerol.—Four liters of filtrate, dark brown in color, from the hydrolysis, was evaporated to 400 cc. of a thick sirupy liquid. As there is a great deal of frothing during the evaporation it was necessary to heat a volume not ex-

¹ (a) Taylor and Lehrman, THIS JOURNAL, 48, 1739 (1926); (b) Lehrman, *ibid.*, 51, 2185 (1929); (c) 52, 808 (1930).

² Taylor and Nelson, *ibid.*, 42, 1726 (1920).

³ The author wishes to thank Stein, Hall and Co., Inc., New York City, for their kindness in supplying this material.

ceeding 500 cc. in a 2-liter beaker. To the thick sirupy liquid an equal volume of alcohol was added, stirred well and filtered. The dark brown filtrate was evaporated to dryness on the steam-bath. The residue was ground up, alcohol added, the mixture stirred well and filtered. The filtrate was again evaporated to dryness on the steam-bath. This procedure was repeated several times until a small amount of residue, dark brown in color, completely soluble in alcohol, was obtained. This solution gave a negative test for glycerol.⁴

Isolation and Identification of Saturated Fatty Acid.—In the course of the separation of the unsaturated fatty acids from the saturated by means of the magnesium soap-alcohol method,⁵ the insoluble magnesium soap was decomposed by heating with concentrated hydrochloric acid. The liberated fatty material on purification¹⁰ yielded a white solid melting at 62°. The phenylhydrazide was made⁶ and gave a melting point of 110°. ⁷

The molecular weight of the acid was determined by dissolving a weighed amount in methyl alcohol and titrating with a standardized solution of barium hydroxide in methyl alcohol, using phenolphthalein as an indicator.⁸

Anal. Calcd. for palmitic acid, $C_{16}H_{32}O_2$: mol. wt., 256.3. Mol. wt. found (monobasic acid), 248.

Anal. Calcd. for palmitic acid, $C_{18}H_{32}O_2$: C, 74.91; H, 12.59. Found: C, 75.15; H, 12.44.

The above data indicate the presence of palmitic acid in the mixed fatty acids.

Identification of Unsaturated Fatty Acids. A. Oxidation.—The mixture of unsaturated fatty acids separated from the saturated fatty acid by means of the magnesium soap-alcohol method was a yellow oil having an iodine number of 100.6.^{1a} When a solution of these unsaturated fatty acids in petroleum ether is chilled with an ice-salt mixture a small amount of solid forms. This was filtered off by suction while cold, washed with cold petroleum ether and allowed to dry. The dried solid has a cream color and melts at 70–71°. On account of the small amount no other data could be obtained.

A 2-g. portion of the unsaturated fatty acids was oxidized by potassium permanganate in alkaline solution.⁹ The white solid oxidized acids, after being filtered off and allowed to dry, were extracted with chloroform in order to make a separation^{1b} of the oxidized acids, if any. On evaporation of the chloroform a fatty material was obtained which was re-oxidized and gave a product different from the one obtained in the first treatment.

The solid oxidized acid (residue from the chloroform extraction) was extracted with hot water. The silky white solid obtained when the water cooled was redissolved in hot water and the solid allowed to crystallize out. This solid was filtered off and dried and gave a melting point of 155–156°.

Anal. Calcd. for tetrahydroxystearic acid, $C_{18}H_{36}O_8$: C, 62.02; H, 10.42. Found: C, 62.20; H, 10.23.

The data indicate the presence of linolic acid in the unsaturated fatty acids.

The product of the second oxidation was completely soluble in chloroform, showing the absence of tetrahydroxystearic acid. The chloroform solution was allowed to evaporate, yielding a white solid mixed with a small amount of fatty material. The

⁴ Kolthoff, *Pharm. Weekblad*, **61**, 1497 (1924).

⁵ Thomas and Yu, *THIS JOURNAL*, **45**, 123 (1923).

⁶ Brauns, *ibid.*, **42**, 1480 (1920).

⁷ J. van Alphen, *Rec. trav. chim.*, **44**, 1064 (1925).

⁸ Escher, *Helv. Chim. Acta*, **12**, 103 (1929).

⁹ Lapworth and Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

fatty material was removed with a little ether and the white residue dissolved by extraction with chloroform. On evaporation of the chloroform a white solid, m. p. 123–124°, was obtained.

Anal. Calcd. for dihydroxystearic acid, $C_{18}H_{36}O_4$: C, 68.29; H, 11.47. Found: C, 68.39; H, 11.36.

These data indicate the presence of oleic acid in the unsaturated fatty acids.

The fact that no tetrahydroxystearic acid is found in the product of the second oxidation apparently indicates that it had been completely oxidized before the oleic acid.

The filtrate from the first oxidation was examined for higher hydroxy acids¹⁰ but the results were negative, indicating the possible absence of acids more unsaturated than linolic in the mixture of unsaturated fatty acids.

B. Bromination.—One and one-half grams of the unsaturated fatty acids was brominated,¹¹ yielding a white precipitate in the cold anhydrous ether. After washing with cold anhydrous ether and drying, the white brominated derivative gave a melting point of 175–176°.

The cold ether solution after the removal of free bromine was evaporated and the residue refluxed with hot petroleum ether. A white solid, insoluble in the hot petroleum ether, was filtered off, washed and dried. It gave a melting point of 170–172°. This solid was mixed with the precipitate obtained in the bromination above, extracted with hot petroleum ether and the petroleum ether extract combined with the same solution above. The residue of this extraction gave a melting point of 180–181°.

Anal. (Carius). Calcd. for hexabromostearic acid, $C_{18}H_{30}O_2Br_6$: Br, 63.34. Found: Br, 63.25.

These data indicate the presence of linolenic acid in the unsaturated fatty acids. It is interesting to note the detection of this acid as its bromide and the failure to find it as the oxidized product, hexahydroxystearic acid. This apparently shows that bromination is a more delicate method for detecting linolenic acid than oxidation.

When the petroleum ether from the above cooled, white crystals deposited. These were filtered off, redissolved in hot petroleum ether, allowed to crystallize and filtered. The white crystals obtained gave a melting point of 113–114°.

Anal. (Carius). Calcd. for tetrabromostearic acid, $C_{18}H_{32}O_2Br_4$: Br, 53.33. Found: Br, 53.23.

These results are additional evidence of the presence of linolic acid in the unsaturated fatty acids.

Examination for Other Substances.—The result of a sodium fusion on the mixed fatty acids showed the absence of nitrogen, sulfur and halogens. A fusion of another sample of the mixed fatty acids with a mixture of equal parts of sodium carbonate and sodium nitrate showed the absence of phosphorus.

During the alcoholic saponification of the mixed fatty acids necessary in the preparation of the magnesium soaps for the separation of unsaturated fatty acids from the saturated, no unsaponifiable matter was noticed. The Liebermann–Burchard test for phytosterol¹² was negative. The test with 1% alcoholic digitonin¹³ was also negative.

The results show the presence of four fatty acids—palmitic, oleic, linolic and linolenic—and the probable absence of other substances in the fatty acid mixture obtained by extracting the solid material resulting from the acid hydrolysis of cassava starch.

¹⁰ Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," The Macmillan Co., New York, 1913, 5th ed., Vol. I. p. 564.

¹¹ Ref. 10, p. 573.

¹² Ref. 10, p. 270.

¹³ Ref. 10, p. 264.

Summary

The fatty acids liberated by the hydrolysis of cassava starch free from extraneous fatty material have been found to be palmitic, oleic, linolic and linolenic.

The detection of small amounts of linolenic acid in the presence of oleic and linolic acids by bromination is a more delicate method than by oxidation.

This is the first time that linolenic acid has been found in a starch.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

FURAN REACTIONS. I. THE PYROLYSIS OF FURAN

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Two possibilities of pyrolysis suggest themselves in the pyrolysis of furan. Either it should yield difuryl, a change analogous to the transformation of benzene into diphenyl, or it should break into carbon monoxide and gaseous hydrocarbons. Since no difuryl was found, the C-H union must be stronger than the C-O bond. Actually, the products formed were carbon monoxide and hydrocarbons. Because of the high temperature required (about 700°) it is interesting that methylacetylene was identified and that evidence was also obtained for cyclopropene: $C_4H_4O \longrightarrow CO + C_3H_4$. In addition, acetylene, ethylene, propylene, methane and butadiene were identified.

Preliminary work¹ in this Laboratory demonstrated the stability of furan at 600° if the hot contact time was less than one second. This is higher than the value of 450-490° reported by Sinkinson² as the "initial conducting temperature." It may be noted³ that with a nickel catalyst (nickel on pumice, the oxide being reduced in a hydrogen stream at 280°) furan started to decompose at 360° when the contact time was thirteen to twenty seconds.

Furan was forced by displacement with mercury into an unpacked quartz tube (43 × 2 cm.) which was heated electrically for 32 cm. of its length. Within the tube was a glass-encased thermocouple. To condense the vapors, two empty flasks, cooled to -15°, were connected to the exit end of the tube, following which was a condensing coil at -80°.

Using 31-33 g. samples of furan it was found that by changing the duration of the experiment from 405 minutes to 110 minutes (a change of 59 to 15.6 sec. contact time) the percentage decomposition at 670-680°

¹ With F. D. Pilgrim.

² Sinkinson, *Ind. Eng. Chem.*, **17**, 31 (1925).

³ From results obtained with John W. Garrett.