Anal. Found: C, 52.8, 53.1; H, 10.02, 10.05; Cl, 26.43, 26.46.

The ratio of carbon to hydrogen is too high for this compound to contain a benzene ring. When shaken with water the free base formed leaf-like crystals that melted slightly above room temperature. It also gave a picrate with a melting point of 155°.

Summary

It has been shown that pyrrole can be reduced easily to pyrrolidine in absolute alcohol–hydrochloric acid solution This method is more rapid and convenient than the glacial acetic acid method.

Reduction of N-phenylpyrrole yields N-hexahydrophenylpyrrolidine. The reduction cannot be stopped at the intermediate N-phenylpyrrolidine.

Bromobenzene does not react with pyrrolidine as with piperidine. Pyrrolidine is less stable and rupture of the ring appears to take place.

N-phenylpyrrolidine can be prepared in satisfactory yields by condensing tetramethylene chloride with aniline. The compound can also be prepared by dry distillation under reduced pressures of α,α'-dicarboxy-N-phenylpyrrolidine but the yields are very low.

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THE FATTY ACIDS ASSOCIATED WITH WHEAT STARCH

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The occurrence of fatty acids combined with carbohydrate in several natural starches is quite well known.[1] In two of these starches, corn and rice, the fatty acids have been determined qualitatively and quantitatively.[2] A review of the literature revealed that there is very little known about the non-carbohydrate constituents, if any, of wheat starch. Should fatty acids be found combined with carbohydrate in wheat starch, it is logical to assume that there are at least two components, α- and β-amylose,[3] comparable to those found in corn and rice starch and that the fatty acids constitute part of the α-amylose component.[3]

The work was accordingly carried out first with the object of establishing whether or not fatty acids occurred combined with carbohydrate. After this had been shown, the next thing was to determine the total amount of fatty material, "fat by hydrolysis,"[1b] which would give a means of comparison with other starches. A qualitative and quantitative analysis by means of iodine numbers of the fatty acids[2] present in the "fat by

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[1] (a) Sostegni, *Gazz. chim. ital.*, **15**, 376 (1885); (b) Taylor and Nelson, THIS JOURNAL, **42**, 1726 (1920); (c) Aoi, *J. Chem. Soc. Japan*, **44**, 755 (1923).

[2] (a) Taylor and Lehrman, THIS JOURNAL, **48**, 1739 (1926); (b) Lehrman, *ibid.*, **51**, 2185 (1929).

[3] Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

hydrolysis" would be important in that it would give additional information in the study of the starches.

As in previous work,[2] the probable absence of sterols and other substances that might occur in the starch and be present in the liberated fatty acids was shown; also a search for glycerol[2b] in the aqueous filtrate from the hydrolysis was negative, indicating that the fatty acids were not present extraneously in the starch. In the part of the work on the oxidation of the unsaturated fatty acids to hydroxy compounds by means of potassium permanganate in alkaline solution,[4] it was found that all of the more unsaturated (two double bond) fatty acid was changed before any of the less unsaturated (one double bond) fatty acid.

Experimental Part

Mixed Fatty Acids from Wheat Starch.—The wheat starch[4a] was extracted for several hours using petroleum ether and showed a negligible amount of extractable material. A total of twenty pounds, used in five-pound quantities, was required for the work. The starch was hydrolyzed using hydrochloric acid,[2b] five pounds yielding 22.26 g. of a light yellow colored fatty solid corresponding to 0.95% "fat by hydrolysis."

Examination of Filtrate for Glycerol.—The filtrate from the hydrolysis was extracted with chloroform and after the chloroform had evaporated an extremely small amount of brown solid, which smelled of glucose, remained. This brown solid was tested for glycerol[5] with negative results.

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,[2a] the insoluble magnesium soap was decomposed by heating with concentrated hydrochloric acid. After cooling, a fatty solid layer which was floating on top was removed, dried and dissolved in ether. The solution was dried over anhydrous calcium chloride together with some calcium carbonate in order to remove any hydrochloric acid that might be present. The ether was poured off and allowed to evaporate, leaving a very light yellow colored fatty solid. This was dissolved in alcohol, chilled in an ice-salt bath and the solid quickly filtered by means of suction. This process was repeated until a pure white solid was obtained which was then crystallized from alcohol, when it gave a melting point of 62°.

The phenylhydrazide was made[6] 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 the indicator.[8]

Anal. Calcd. for palmitic acid, $C_{16}H_{32}O_2$: mol. wt., 256.3. Mol. wt. found: (monobasic acid) 249. Calcd.: C, 74.91; H, 12.59. Found: C, 75.10; H, 12.48.

From the above data the presence of palmitic acid in the mixed fatty acids is shown.

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[4] Lapworth and Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

[4a] The author wishes to thank Stein, Hall and Co., Inc., New York City, for their kindness in supplying this material.

[5] Gettler, *J. Biol. Chem.*, **42**, 311 (1920).

[6] Brauns, THIS JOURNAL, **42**, 1480 (1920).

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

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

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[2a] was a light brownish colored oil. A 3-g. portion of this mixture was oxidized with potassium permanganate in alkaline solution.[4] The white solid oxidized acids were then extracted with chloroform in order to make a separation[2b] of the oxidized acids, if any. On evaporation of the chloroform a fatty material was obtained which was reoxidized and gave an oxidized product different from the one obtained in the first treatment.

The solid oxidized product (residue from the chloroform extraction) was dissolved by prolonged extraction with ether and the solvent allowed to evaporate. The residue was a white solid melting at 154–156°. This solid was repeatedly extracted with hot water and the solution allowed to cool slowly, whereupon silky white crystals were obtained. These crystals were filtered off, recrystallized from water and dried, giving a melting point of 154–155°. The analytical data indicated the presence of linolic acid in the mixture of unsaturated fatty acids.

Anal. Calcd. for tetrahydroxystearic acid, $C_{18}H_{36}O_6$: C, 62.02; H, 10.42. Found: C, 62.17; H, 10.27.

The product of the second oxidation was dissolved by extraction with anhydrous ether and after the solvent evaporated a white solid remained which gave a melting point of 126.5–127.5°. This was recrystallized from anhydrous ether, giving a melting point of 126–127°.

The barium salt was made[8] and gave a melting point of 216°, darkening at 214°.

The molecular weight of the oxidized acid was determined as previously in the case of palmitic acid.[8] The analytical results indicate the presence of oleic acid in the mixture of unsaturated fatty acids.

Anal. Calcd. for dihydroxystearic acid, $C_{18}H_{36}O_4$: mol. wt., 316.3. Found: 292.5. Calcd.: C, 68.29; H, 11.47. Found: C, 68.31; H, 11.12.

The fact that all the tetrahydroxystearic acid and none of the dihydroxystearic acid is found in the product of the first oxidation apparently indicates that all of the linolic acid is oxidized before any of the oleic acid. This is further shown by the absence of tetrahydroxystearic acid in the product of the second oxidation.

The filtrate from the first oxidation was now examined for higher hydroxy acids,[9] but the results were negative, indicating the absence of acids more unsaturated than linolic in the mixture of unsaturated fatty acids.

Another portion, 4 g., of the mixture of unsaturated fatty acids was oxidized in glacial acetic acid by perhydrol (30% hydrogen peroxide),[10] but no tangible results could be obtained.

B. Bromination.—A 2-g. portion of the mixture of unsaturated fatty acids was brominated,[11] and gave no ether-insoluble bromides, indicating the absence of acids more unsaturated than linolic in the mixture of unsaturated fatty acids, which bears out the results as obtained by oxidation. After evaporation of the ether, the residue was recrystallized from petroleum ether, yielding white crystals, m. p. 113–114°.

Anal. (Carius). Calcd. for tetrabromostearic acid, $C_{18}H_{32}O_2Br_4$: Br, 53.33. Found: Br, 53.24.

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

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[9] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," The Macmillan Company, New York, **1913,** 5th ed., Vol. I, p. 564.

[10] Hilditch and Lea, *J. Chem. Soc.*, 1580 (1928).

[11] Ref. 9, p. 573.

The petroleum ether from the recrystallization of the tetrabromostearic acid was allowed to evaporate, giving a dark brown, thick mass. A portion of this was boiled with concentrated nitric acid to which some solid silver nitrate had been added. On addition of water a heavy precipitate of silver bromide was obtained. This indicates the probable existence of dibromostearic acid, which in turn shows the presence of oleic acid in the mixture of 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,[2a] no unsaponifiable matter was noticed. The Liebermann–Burchard test for phytosterol[12] was negative. The test with 1% alcoholic digitonin[13] was negative. The method of Holde and Gorgas[14] also gave negative results for unsaponifiable matter.

The results given above show the presence of three fatty acids, that is, palmitic, oleic and linolic, and the probable absence of other substances in the fatty acid mixture obtained by extracting the solid material resulting from the hydrolysis of wheat starch.

Determination of Iodine Numbers and Amounts of the Fatty Acids.—Knowing what fatty acids were present, the amount of each one was calculated from the determinations of the iodine numbers[2a] of the mixed and unsaturated fatty acid portions.

TABLE I

RESULTS OF DETERMINATIONS

Fatty acid sample	Weight, g.	Iodine number
Mixed	0.2801	80.36
Mixed	.2098	81.66
Unsaturated	.1324	123.6
Unsaturated	.1350	124.8

TABLE II

RESULTS OF CALCULATIONS

Fatty acid	Percentage
Palmitic	35
Oleic	41
Linolic	24

Summary

The percentage of "fat by hydrolysis" from wheat starch has been determined.

It has been shown that in the oxidation by potassium permanganate in alkaline solution of a mixture of oleic and linolic acids, all the linolic acid is changed before any of the oleic acid is affected.

The fatty acids (saturated and unsaturated) liberated by the hydrolysis of wheat starch free from extraneous material have been identified and their amounts determined.

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[12] Ref. 9, p. 270.

[13] Ref. 9, p. 264.

[14] Holde and Gorgas, *Chem. Umschau Fette, Oele, Wachse Harze*, **32**, 314 (1925); **33**, 109 (1926).