

from the filtrate recrystallized from ligroin. Table I gives a summary of this work.

Orcinol and 1-nitro-2-naphthol reacted with great difficulty with the isocyanate and gave small yields of the urethans. The derivatives from *o*-aminophenol and methylamine were crystallized from alcohol, being too insoluble in hot ligroin. The derivatives from methylamine, ethylamine, dimethylamine and diethylamine were obtained from approximately 30% water solutions. The derivative from benzylamine was obtained from a 10% water solution. Nitrogen was determined by the Kjeldahl method.

Summary

1. α -Naphthylisocyanate proved to be a satisfactory reagent for phenols and primary and secondary aliphatic amines, forming well-crystallizing and sharply melting urethans. Polyhydroxy phenols do not react under the conditions used.
2. The reaction is catalyzed by tertiary aliphatic amines.
3. The reagent apparently can be used satisfactorily with oximes, as well as for acetamide and acetanilide.

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 513]

THE UNSATURATED FATTY ACIDS ASSOCIATED WITH CORN STARCH

BY T. CLINTON TAYLOR AND LEO LEHRMAN

RECEIVED MARCH 25, 1926

PUBLISHED JUNE 5, 1926

After the extraneous fat occurring in corn starch is removed completely by common fat-solvents and the whole starch subsequently hydrolyzed, 0.5 to 0.6% of fatty acids are liberated.¹ This fatty material has been shown to contain a saturated portion consisting almost wholly of palmitic acid¹ and an unsaturated portion of unknown composition. The fatty acids in this latter portion now have been identified and the amount to which they occur established. Further, it has been shown that sterols and other substances occurring with the natural fats are absent.

Recently in this Laboratory it was shown that corn starch could be separated conveniently into two parts, namely, α - and β -amylose, by either electrophoresis or ultrafiltration.² When these respective amyloses are hydrolyzed, only the alpha³ portion yields fatty acids,³ indicating that the source of the fatty acids in whole corn starch is in one definite component of it. With the data made available by this investigation and the knowledge that only one part of the corn starch carries these acids, it will be

¹ Taylor and Nelson, *THIS JOURNAL*, **42**, 1726 (1920).

² H. A. Iddles, *Dissertation*, Columbia, 1925.

³ Meyer, "Untersüchungen über die Stärkekörner," Gustav Fischer, Jena, 1895.

possible to proceed to the larger problem of determining the structure of what appears to be a carbohydrate fatty acid compound and to discover possibly the role of these compounds in characterizing the starch. The results of these investigations will be published within a short time.

Experimental Part

Separation of Unsaturated from Saturated Fatty Acids.—As a convenient source of raw material for the qualitative identification of the fatty acids, "refinery mud" was used. This is the solid filtered from the liquor remaining after the hydrolysis of corn starch in the process of making commercial glucose. The drying and handling of it were carried out exactly as given by Taylor and Nelson.¹ It will be shown later that the mixed fatty acids obtained from this source are identical with those obtained by the hydrolysis of pure corn starch under laboratory conditions.

In order to have the pure unsaturated material to work with, it was necessary to separate the palmitic acid from it. For this purpose the magnesium soap-alcohol method of Thomas and Yu⁴ proved very useful.

The insoluble magnesium palmitate was filtered off on an alundum cup using suction. The filtrate consisted of the soluble magnesium soaps of the unsaturated fatty acids in an excess of alcohol. This was distilled in a vacuum, the soaps were decomposed by warming with concd. hydrochloric acid and the resulting fatty acids extracted with petroleum ether. In order to remove moisture and hydrogen chloride, the ether extract was kept over calcium chloride and calcium carbonate in a desiccator for several hours. On distilling the ether in a vacuum a dark brown oil was left in the flask.

Identification of Unsaturated Fatty Acids.—A part of the unsaturated oil from the above treatment was oxidized with alkaline permanganate solution.⁵ The solids resulting from the oxidation were filtered off and extracted with ether. A part dissolved in this medium and the remainder was practically insoluble in the solvent. Several crystallizations of the soluble portion from ether and from alcohol gave a mass of white needles on evaporation of the solvent. The melting point of this substance was 128–129° which corresponds to that of dihydroxystearic acid.⁶

Anal. Subs., 0.1234, 0.1126: CO₂, 0.3094, 0.2812; H₂O, 0.1249, 0.1152. Calcd. for C₁₈H₃₆O₄: C, 68.34; H, 11.48. Found: C, 68.39, 68.11; H, 11.33, 11.37.

The presence of dihydroxystearic acid at this point indicates the presence of oleic acid in the original oil.

The ether-insoluble portion of the oxidized substances was boiled with water, the mixture filtered hot and allowed to cool slowly whereupon a silky white solid formed. This was filtered off, crystallized several times

¹ Thomas and Yu, *THIS JOURNAL*, **45**, 123 (1923).

⁵ Lewkowitsch, "Chem. Tech. and Anal. of Oils, Fats and Waxes," MacMillan Co., London, 1914, 5th ed., vol. 1, p. 564.

⁶ (a) Ref. 5, p. 288. (b) Nicolet and Jurist, *THIS JOURNAL*, **44**, 1139 (1922). (c) Reinger, *Ber. Pharm. Ges.*, **32**, 124 (1922). (d) Robinson and Robinson, *J. Chem. Soc.*, **127**, 176 (1925).

from water and dried. Examination under the microscope showed needles; m. p., 155–156°.

A tetrahydroxystearic acid is recorded in the literature with this melting point.⁷

Anal. Subs., 0.1056, 0.1148: CO₂, 0.2401, 0.2620; H₂O, 0.0971, 0.1066. Calcd. for C₁₈H₃₀O₈: C, 62.02; H, 10.42. Found: C, 62.00, 62.24; H, 10.22, 10.32.

This sativic acid must result from the oxidation of a linolic acid in the original material.

The filtrate from the mixture of hydroxy acids was examined for the presence of higher hydroxylated acids but the results were negative. Likewise a modified oxidation of the original fatty substances according to Fahrion^{7a} yielded only the two above-mentioned hydroxy acids.

An elaidin test made as recommended by Allen⁸ using freshly prepared mercurous nitrate gave a very positive test for oleic acid.

Bromination of Unsaturated Fatty Acids.—Treatment of the unsaturated fatty acid with bromine⁹ gave no ether-insoluble bromides, indicating the absence of acids more unsaturated than linolic. Evaporation of the solvent and several recrystallizations of the residue from petroleum ether gave white needles, m. p. 113°. This melting point and the results of the Carius bromine determinations show the compound to be tetra-bromolinolic acid.¹⁰

Anal. Subs., 0.1658, 0.1944: AgBr, 0.2071, 0.2439. Calcd. for C₁₈H₃₂O₂Br₄: Br, 53.33. Found: 53.15, 53.38.

Examination for Other Substances.—The result of a sodium fusion made in the usual way on the material containing both the saturated and unsaturated fatty acids was negative for nitrogen. A fusion of another sample of the above material with a mixture of sodium carbonate and nitrate gave negative results also for phosphorus.

During the alcoholic saponification of the original fatty material in the preparation of the magnesium soaps no unsaponifiable matter was noticed. Nevertheless the method of Kerr and Sorber¹¹ for detecting phytosterol was applied but again the results were negative. The Liebermann-Burchard¹² test for phytosterol was also negative.

In order to be sure that all of the fatty acids had been liberated from amylose and that no unhydrolyzed compounds of any sort remained, separate portions of "mud" were boiled up successively with 10% aqueous

⁷ (a) Fahrion, *Chem. Umschau Fette, Oele, Wachse Harze*, **27**, 58, 201 (1920); **28**, 5, 20 (1921). (b) Nicolet and Cox, *THIS JOURNAL*, **44**, 144 (1922). (c) Ref. 5, p. 232.

⁸ Allen, "Commercial Org. Anal.," Blakistons, 1909, vol. 2, pt. 1, p. 39.

⁹ Ref. 5, p. 573.

¹⁰ Ref. 5, p. 198.

¹¹ Kerr and Sorber, *J. Assoc. Official Agr. Chem.*, **8**, 90 (1924).

¹² Ref. 5, p. 270.

caustic alkali solution and 10% aqueous hydrochloric acid for 45-minute intervals. The iodine numbers of the original dried material and the separated fatty acids were practically the same as that of the corresponding material before this special treatment, showing that no acids were liberated during the hydrolysis.

The original fatty material was methylated¹³ and distilled under a pressure of 1 to 2 mm. The first distillate solidified in the condenser but the esters that distilled over above 155° were liquid. The highest temperature reached was 175° at which everything had distilled. Examination of these esters showed only the presence of palmitic, oleic and linoleic acids. Although no quantitative separation was accomplished¹⁴ among the above-mentioned acids, the absence of other materials confirms results of the other tests.

Having established the presence of the three fatty acids and the probable absence of other substances, the next step was to determine the iodine numbers of the original and unsaturated portions and so indirectly fix the amount of each acid present.

In these determinations the fat liberated upon hydrolysis of ten pounds of a special alkali-washed corn starch¹⁵ was used. The unsaturated fatty acids were separated this time by Holde's¹⁶ thallium soap-alcohol method, resulting in a light yellow oil instead of a dark brown portion as before.

Determination of Iodine Numbers.—The method of Hanus¹⁷ was used with the time of contact between oil and iodine changed to 60 minutes. This was done because results were concordant and checked with theory on a sample of pure oleic acid.

Pure oleic acid was separated by the magnesium-soap method⁴ from a sample of c. p. oleic acid, $d^{22}_4 = 0.893$ and $n^{22}_D = 1.461$ (Abbé refractometer). Solutions were standardized against resublimed iodine, and the time of contact between reagent and oil was 60 minutes.

I No. Subs., 0.1765, 0.1842. Calcd. for oleic acid: *I No.*, 90.07. Found: 90.1, 90.3.

In Table I are recorded the iodine numbers of the original and of the unsaturated portions of the fatty acids liberated upon hydrolysis of corn starch.

TABLE I
IODINE NUMBERS

Sample	Wt.		Iodine number	
Orig. fatty acids from dried "Refinery Mud"	0.1898	0.2079	98.54	98.78
Unsat. fatty acids from "Refinery Mud"1966	.1386	132.90	133.56
Orig. fatty acids from pure starch1753	.2620	101.5	101.4
Unsat. fatty acids from pure starch1490	.1336	133.3	133.6

¹³ Jamieson and Baughman, *THIS JOURNAL*, **42**, 1200 (1920).

¹⁴ Brown with Beal, *ibid.*, **45**, 1289 (1923).

¹⁵ This special starch containing only 0.02% of directly extractable material was furnished by the Corn Products Refining Company to whom our thanks are due.

¹⁶ Holde, Selim and Bleyberg, *Z. deut. Ol- Fett-Ind.*, **44**, 277, 298 (1924).

¹⁷ Woodman, "Food Analysis," McGraw-Hill Book Co., New York, 1915, p. 164.

It can be seen that the fatty acids in "refinery mud" are the same as those liberated from pure starch. Since the unsaturated portion contains only oleic and linolic acids, their amounts can be determined by solving the following equations; $x + y = 100$; $90.07x/100 + 181.42y/100 = 133.5$; x is the percentage of oleic acid and y the percentage of linolic acid; 90.07 and 181.42 are their respective theoretical iodine numbers and 133.5 is the actual experimental iodine number of the mixture of unsaturated fatty acids: whence $x = 52\%$; $y = 47\%$. Assuming that the saturated portion is entirely palmitic acid and that its iodine number under the above conditions is zero, we have: $W + Z = 100$; $133.5Z/100 = 101.5$, where W is the amount of palmitic acid in the original fatty material and Z is the combined amounts of oleic and linolic acids, the whole mixture having an iodine number of 101.5; whence $W = 23\%$; $Z = 76\%$.

From these results it may be concluded that the fatty acids liberated upon hydrolysis of corn starch (alpha amylose) consist of approximately 24% of palmitic acid, 40% of oleic acid and 36% of linolic acid.

Summary¹⁸

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

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS

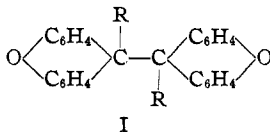
III. THE EFFECTIVENESS OF SECONDARY ALKYL GROUPS IN PROMOTING DISSOCIATION

BY J. B. CONANT, L. F. SMALL¹ AND A. W. SLOAN

RECEIVED MARCH 27, 1926

PUBLISHED JUNE 5, 1926

In previous papers of this series,² it has been shown that while dixanthyl itself ($R = H$, Formula I) shows none of the characteristic properties of a



¹⁸ The work embodied in this paper is taken from the first part of a thesis presented by Leo Lehrman to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

¹ Du Pont Fellow in Chemistry 1925-26.

² Conant and Sloan, *THIS JOURNAL*, **47**, 572 (1925). Conant and Small, *ibid.*, **47**, 3068 (1925).