

rapid decrease in viscosity and a gradual decrease in optical rotation. Unlike other amylases, the *macerans* amylase does not increase the reducing power of whole starch to any noteworthy extent.

The Schardinger dextrans have been prepared from potato starch by means of the *macerans* amylase in a maximum yield of 55%. The relative proportions of alpha and beta dextrans in the product have been shown to vary greatly with different digestion conditions; the factors involved in this behavior are receiving further study. Beta dextrin is stable toward *macerans* amylase at 20°, whereas the alpha dextrin is converted, at least in part, to higher rotating material which exhibits

slight reducing properties and contains no beta dextrin.

The rotations of carefully purified alpha and beta dextrans have been found to be  $+150.5 \pm 0.5^\circ$  and  $+162.5 \pm 0.5^\circ$ , respectively, instead of  $+148^\circ$  and  $+158^\circ$ , as previously reported. The new value for beta dextrin was confirmed by preparing its acetate (rotation  $+125.5^\circ$  in chloroform; m. p. 196–196.5° (cor.)), from which the original high rotating beta dextrin was regenerated. The same beta dextrin acetate was produced when either pyridine or zinc chloride was used as the acetylation catalyst.

BETHESDA, MARYLAND

RECEIVED MAY 28, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

## The Nature of the Fatty Acids Associated with Starch. The Adsorption of Palmitic Acid by Potato and Defatted Corn and Rice Starches

BY LEO LEHRMAN

It is well known that starches, with the exception of potato, have associated with them small amounts of fatty material which is not extracted by the usual fat solvents, such as ether or carbon tetrachloride.<sup>1</sup> Acid hydrolysis is usually employed to liberate this fatty material, which is therefore termed "fat by hydrolysis" to distinguish it from the fatty material which can be extracted by ether or carbon tetrachloride. The fatty material that can be extracted from raw starches by ether or carbon tetrachloride is usually referred to as extraneous extractable fatty matter. Recently Schoch reported that fat solvents having hydrophilic groups, particularly methanol, the cellosolves and 80% dioxane, extract practically all the fatty acids in three cereal starches.<sup>2</sup> He further reported that the defatted starches retain a number of the usual properties of the original starches. In addition, fatty acid can be introduced into the defatted starches and cannot be removed by extraction with the usual fat solvents, such as ether or carbon tetrachloride. On the basis of these results, Schoch concluded that free fatty acid is present in starch as an extraneous impurity.

(1) (a) Sostegni, *Gazz. chim. ital.*, **15**, 376 (1885); (b) Taylor and Nelson, *THIS JOURNAL*, **42**, 1726 (1920); (c) Taylor and Lehrman, *ibid.*, **48**, 1739 (1926); (d) Lehrman, *ibid.*, **51**, 2185 (1929); **52**, 808 (1930); **54**, 2527 (1932); **55**, 850 (1933); **59**, 1050 (1937).

(2) Schoch, *ibid.*, **60**, 2824 (1938).

This author submitted a comment which stated his reasons for disagreeing with this conclusion and suggested the possibility of the fatty acids being adsorbed by starch.<sup>3</sup> Lately, it has been shown that the amount of fatty material extracted by methanol from corn starch ground in a rod mill is the same as that extracted from the unground corn starch. From this observation the conclusion has been drawn that the fatty acids are not present extraneously.<sup>4</sup> Adsorption has been mentioned in connection with the occurrence of fatty acids in starch but the evidence is meager.<sup>5</sup>

Potato starch has been shown not to contain any "fat by hydrolysis"<sup>6</sup> and, therefore, could be used like a defatted starch. Oleic acid was introduced into potato starch, though only in a small percentage, by refluxing with a methanol solution of the fatty acid.<sup>7</sup> In order to determine how a fatty acid combines with starch, varying concentrations of palmitic acid in a hydrophilic solvent (methanol) were refluxed with potato starch. Palmitic acid was chosen because it occurs in the "fat by hydrolysis" of all starches; it is saturated and, therefore, no special precautions are neces-

(3) Lehrman, *ibid.*, **61**, 212 (1939).

(4) Evans and Briggs, *Cereal Chem.*, **18**, 447 (1941).

(5) (a) Schoch, *ibid.*, **18**, 124 (1941); (b) ref. 4, p. 453; (c) Evans and Briggs, *ibid.*, **18**, 467 (1941).

(6) Lehrman and Kahat, *THIS JOURNAL*, **55**, 850 (1933).

(7) Schoch, private communication.

sary to prevent oxidation; and finally, it is taken up by corn starch in preference to unsaturated fatty acids.<sup>8</sup> After removing the excess palmitic acid by extraction with carbon tetrachloride, the "fat by hydrolysis" was determined.

A graph of the results of these experiments is a typical Freundlich isotherm indicating that the palmitic acid was probably adsorbed by the potato starch. The experimental work was carried out with defatted corn and rice starches to determine whether a similar Freundlich isotherm would be obtained.

### Experimental

**Preparation of Defatted Corn and Rice Starch.**—Corn and rice starch<sup>9</sup> having negligible extraneous fatty material and 0.65 and 0.69% "fat by hydrolysis," respectively, were extracted in a Soxhlet extractor with methanol for two weeks. Though the "fat by hydrolysis" in each starch had decreased to 0.03%, further extraction had no effect. This result agrees with that found by others.<sup>10</sup> That the methanol extraction of the fat from the starches cannot be due to hydrolysis has already been shown.<sup>11</sup>

**Introduction of Palmitic Acid into the Fat-Free Starches.**—Ten-gram samples of potato (negligible extraneous fat) and defatted corn and rice starches separately, were refluxed while stirring with 1–20 g. of pure palmitic acid dissolved in 50 ml. of pure methanol for five hours. It was found that longer heating did not increase the amount of palmitic acid taken up by the starches. The mixtures were filtered, the residues washed with carbon tetrachloride and allowed to dry. The residues then were extracted for three hours with hot carbon tetrachloride in a rubber extractor and allowed to dry. The dry starch products were hydrolyzed with dilute hydrochloric acid, cooled, filtered through petroleum ether extracted filter papers, the papers and fatty acids washed several times with distilled water and allowed to dry. The filter papers and fatty acids then were extracted with petroleum ether, the extracts allowed to evaporate in weighed beakers and the residues weighed. Figure 1 is the graph obtained by plotting these values.

### Discussion

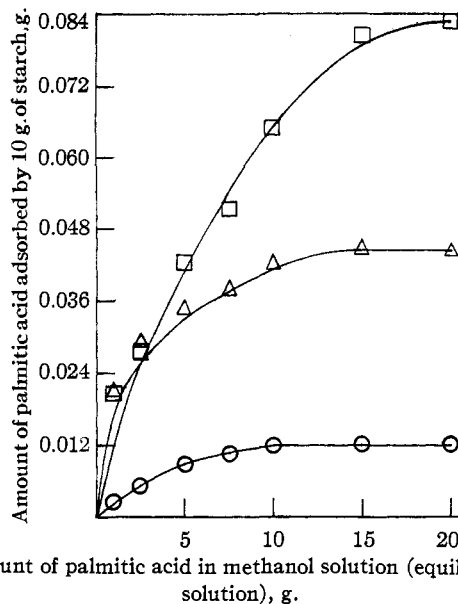
The fact that the palmitic acid taken up by the starches follows a typical Freundlich isotherm indicates either adsorption or solid solution. While X-ray diffraction patterns would be necessary to decide which phenomenon took place, from the generally accepted amorphous state of starch, adsorption is the more probable. It has already been noted that defatted starches have a number

(8) Ref. 4, p. 454; ref. 5c.

(9) The author wishes to thank Stein, Hall and Co., Inc., New York City, for their kindness in supplying these starches.

(10) (a) Schoch, private communication; (b) ref. 4, pp. 447, 448.

(11) (a) Ref. 10a. In this communication Schoch states that from his experimental data none of the fatty acids in corn, wheat or rice starch is esterified with carbohydrate; (b) ref. 4, p. 451.



Amount of palmitic acid in methanol solution (equilibrium solution), g.

Fig. 1.—Adsorption isotherms of palmitic acid with potato and defatted corn and rice starches; O, potato starch; Δ, defatted corn starch; □, defatted rice starch.

of the usual physical properties of the original starches. This is to be expected if the fatty acids are adsorbed on the starch. The fact that a starch component is electrically charged only when it contains fatty acid (fat by hydrolysis)<sup>12</sup> can be accounted for on the basis of an adsorption of the fatty acid. There would be no electrical charge if the fatty acid were chemically combined with carbohydrate (such as by esterification or etherification). It is interesting to note that potato starch, which has no fatty acid associated with it, has practically no charged component.<sup>13</sup>

The amount of fatty acid taken up by each starch gives additional weight to the case for adsorption. Thus, potato starch, known to have no fatty acid, adsorbs only a very small amount of palmitic acid compared with defatted corn and rice starches. Furthermore, defatted rice starch, which in its original condition has a higher percentage of "fat by hydrolysis" than corn starch, adsorbs more palmitic acid than defatted corn starch.

It has already been shown that corn starch takes up (adsorbs) saturated fatty acid in preference to unsaturated fatty acid.<sup>8</sup> It is difficult to explain on this basis, however, why defatted corn starch adsorbs less than its original fatty acid content, while defatted rice starch adsorbs more, or that potato even adsorbs any. It does show that these

(12) Taylor and Wertz, *THIS JOURNAL*, **49**, 1584 (1927).

(13) Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926).

three starches are different in their surface effects.

All these data are consistent with the conclusion that the fatty acids associated with starch are adsorbed.

### Summary

1. Potato and defatted corn and rice starches

take up palmitic acid from a methanol solution probably by adsorption.

2. A discussion of known facts leads to the conclusion that fatty acids associated with starch are probably adsorbed.

NEW YORK, N. Y.

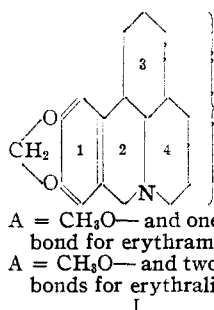
RECEIVED JUNE 1, 1942

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MERCK & CO., INC.]

## Erythrina Alkaloids. XIII. Studies on the Constitution of Erythraline, Erythramine, and Erythratine

BY KARL FOLKERS, FRANK KONIUSZY AND JOHN SHAVEL, JR.

Studies<sup>1</sup> on the constitution of erythramine and erythraline led to the formulation of the partial structure I with the comment that the presence of

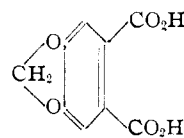


A = CH<sub>3</sub>O— and one double bond for erythramine  
A = CH<sub>3</sub>O— and two double bonds for erythraline

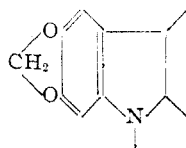
one five-atom nucleus was not excluded. The initial studies<sup>2</sup> showed that erythramine, C<sub>18</sub>H<sub>21</sub>NO<sub>3</sub>, contains a methylenedioxy group, a methoxyl group, a tertiary nitrogen atom probably common to two nuclei, and an ethylenic double bond, besides one aromatic nucleus. It consists apparently of four nuclei (exclusive of the methylenedioxy bridge), three being partially or completely saturated and one aromatic. Erythraline, C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>, differs only in having one more ethylenic double bond since dihydroerythramine and tetrahydroerythraline were found to be identical when the free bases and hydriodides were compared. Ring 1 of the partial structure was established by the formation of hydrastic acid (II) by oxidation of erythraline methoxyhydroxide; and rings 1 and 2 were strongly indicated by the very close similarity between the ultraviolet absorption spectra of dihydroerythramine and 6,7-methylenedioxy-1,2,3,4-tetrahydroisoquinoline hydrobromides. The hydroindole formulation (III) which might be anticipated because of the accompanying

hypaphorine, which is so widely distributed in seeds of species of *Erythrina*, was excluded by the formation of hydrastic acid. Rings 3 and 4 were indicated tentatively because of the tertiary nitrogen atom. It was of interest that these two alkaloids and lycorine and tazettine, of the *Lycoris* alkaloids, possess methoxyl and hydroxyl groups on hydroaromatic nuclei of structures identical for rings 1 and 2.

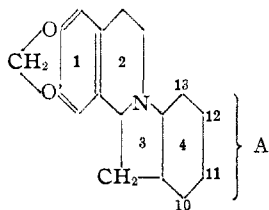
Recently,<sup>3</sup> new structural studies were presented including experiments performed on  $\beta$ -erythroidine, which led to the isolation of indole from the products of potassium hydroxide fusion. Although  $\beta$ -erythroidine appears to differ considerably from erythraline and erythratine in functional groups and nuclear formulation, it was of interest to examine the products from the fusion of erythraline with potassium hydroxide for the presence of indole. By a modified procedure which involved adding erythraline hydriodide in portions to the molten alkali, pure indole picrate, identical with an authentic specimen, was obtained by appropriate technique. Interpretation of the indole formation suggests erythraline and erythramine actually do



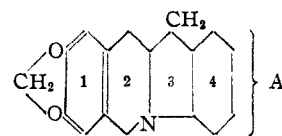
II



III



IV



V

A = CH<sub>3</sub>O— and >C=C< for erythramine

A = CH<sub>3</sub>O— and 2 >C=C< for erythraline

A = CH<sub>3</sub>O— and HO— and >C=C< for erythratine

(1) Folkers and Koniuszy, *This Journal*, **62**, 1673 (1940).

(2) Folkers and Koniuszy, *ibid.*, **61**, 3053 (1939).

(3) Folkers, Koniuszy and Shavel, Jr., Abstracts of Papers, meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1941, Division of Organic Chemistry, page 30.