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

The Extraction of Fat and Phosphorus from Wheat Starch

BY LEO LEHRMAN

The presence in some starches, in particular the common cereal and tuber starches (except potato), of fat which is not extracted by the usual fat solvents, such as ether and carbon tetrachloride, is well known.[1] Lately it was reported that this fat can be removed by extraction with certain fat solvents containing hydrophilic groups, such as methanol, dioxane and the cellosolves.[2] The non-extractable fat occurring in starch subsequently was shown to be held by adsorption.[3] In the case of corn starch it was stated that the fat is bound by associative forces as indicated by the ease of its removal after the starch granules are disintegrated.[4]

The conclusion has been made that the fatty material in wheat starch is present as a phospholipid on the basis that fat and substantially all the phosphorus are simultaneously extracted, this extracted lipid material containing a relatively high per cent. of phosphorus.[5] However, in the work just referred to, no figures are given for the amount of phosphorus present in the extracted wheat starch with the lowest fat content. Furthermore, the sample with the smallest phosphorus content (nearly 15% of the original amount) still had some fat in it. From these data one cannot conclude that the phosphorus content of starch would be zero if all the fat were removed.

In this paper it is shown, in agreement with Schoch, that in wheat starch there is some relation between the fat and phosphorus, on the basis of the amounts of these that are extracted with methanol. Furthermore, by first disintegrating the granules[6] it is possible to extract all the fat, but some phosphorus, small in amount (5% of original content), still remains in the starch. This indicates that a small amount of phosphorus is present not as a phospholipid, but possibly linked in some way with the starch.

It has also been stated that the phosphorus in wheat starch occurs largely as a phosphatide[7,8] adsorbed to a large extent on the starch.[7] That the phosphatide is loosely bound is seen from the fact that while alcohol extracts most of the phosphorus from wheat starch when it is pasted or treated with alkali,[9] this gelatinization making the phosphorus more accessible to the solvent, no phosphorus is removed from intact granules.[10]

The results in this paper not only give additional evidence that the wheat starch phospholipid, as it becomes more available through the use of better penetrating solvents or by disintegration of the starch granules, is increasingly removed by extraction, but that a small amount of the phosphorus is present in other than phospholipid form. It is significant that the extracted starch is more nearly free of phosphorus than any starch previously reported in the literature.[11]

Experimental

Raw wheat starch[12] and wheat starch disintegrated by use of a Waring Blendor[13] and precipitated with ethanol, were extracted in an all glass Soxhlet extractor with methanol for ten weeks. Portions of the starches were removed at intervals, dried and the amount of "fat by hydrolysis"[14] and phosphorus[15] were determined. The results are listed in Table I.

TABLE I

EXTRACTION OF WHEAT STARCH WITH METHANOL

Duration of extraction	Raw wheat starch[a] % "Fat by hydrolysis" in extracted starch	% P in extracted starch	Disintegrated starch % "Fat by hydrolysis" in extracted starch	% P in extracted starch
0	0.49[b]	0.055	0.30[c]	0.034[c]
2 hours	.45			
1 day	.39			
2 days	.30			
3 days	.28			
4 days	.27			
1 week	.25			
2 weeks	.18		.08	.017
4 weeks	.15		.04	.016
6 weeks	.13			
8 weeks	.12	0.018	.04	.016
10 weeks	.12	.018		

[a] Raw wheat starch has negligible extraneous extractable material using petroleum ether. [b] All quantitative data are the averages of duplicate analyses that agreed well. [c] It is interesting to note that ethanol, used in precipitating the disintegrated starch, removed some of the fat and phosphorus from the starch.

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

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

(3) (a) Lehrman, *ibid.*, **61**, 212 (1939); **64**, 2144 (1942).

(4) Whistler and Hilbert, *ibid.*, **66**, 1721 (1944).

(5) Schoch, *ibid.*, **64**, 2954 (1942).

(6) Whistler and Hilbert, *ibid.*, **66**, 1721 (1944).

(7) Nottbohm and Mayer, *Z. Unters. Lebens.*, **67**, 369 (1934).

(8) Posternak, *Helv. Chim. Acta*, **18**, 1351 (1935).

(9) Samec and Beniger, *Kolloid-Beihefte*, **33**, 95 (1931).

(10) Posternak, *Helv. Chim. Acta*, **18**, 1351 (1935); Waldschmidt-Leitz, Samec and Mayer, *Z. physiol. Chem.*, **250**, 193 (1937); Samec and Blinc, *Kolloid-Beihefte*, **47**, 371 (1938).

(11) Kerr, "Chemistry and Industry of Starch," Academic Press, Inc., New York, N. Y., 1944, p. 156.

(12) The author wishes to thank Stein, Hall and Co., Inc., New York, N. Y., for its kindness in supplying this starch.

(13) Whistler and Hilbert, THIS JOURNAL, **66**, 1721 (1944).

(14) "Fat by hydrolysis" was determined by acid hydrolysis of a 10-g. sample of the starch and recovering the fatty acids as described in a previous paper [Lehrman, THIS JOURNAL, **64**, 2144 (1942)]. This method has the advantage of not extracting non-fatty material.

(15) Phosphorus was determined by first ashing 1 g. of the starch with 1 g. of magnesium carbonate in a platinum crucible [Howk and De Turk, *Ind. Eng. Chem., Anal. Ed.*, **4**, 111 (1932)]. The residue was dissolved in 3 *M* sulfuric acid, making the solution just acid to phenolphthalein and determining the amount of phosphorus colorimetrically using a Klett-Summerson photoelectric colorimeter with a Pyrex red filter [Briggs, *J. Biol. Chem.*, **59**, 255 (1924)].

Disintegrated wheat starch was extracted in a rubber type Soxhlet extractor with 80% dioxane-water solution (constant boiling mixture). After one and two week periods the starch was dried and analyzed for "fat by hydrolysis" and phosphorus. The results were as follows: fat 0.015 and 0.000%, respectively; phosphorus, 0.004 and 0.003%, respectively.

Summary

Extraction of raw and disintegrated wheat starch with methanol removes most of the fat and phosphorus. Extraction of disintegrated wheat starch with 80% dioxane-water solution (constant boiling mixture) removes all the fat but not all the phosphorus. This shows that a small amount of the phosphorus is present not as a phospholipid, but possibly linked in some way with the starch. The extracted starch is more nearly free of phosphorus than any starch previously reported in the literature.

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The Binary System Stearonitrile–Palmitonitrile

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Binary systems of long-chain compounds have been the subject of numerous investigations. The saturated acids have received the most attention,[1] while binary systems involving the ethyl and methyl esters,[2-5] the alcohols[2,3,6] the alkyl iodides,[7] the amides and related compounds,[5] and also the hydrocarbons[6,7] have been studied. These investigations have been rendered rather complex by the existence of various polymorphic forms, and in many instances complete phase diagrams have not been obtained.

Smith[2] found two forms of ethyl stearate and ethyl palmitate although he was unable to obtain the high melting form for compositions very far removed from the pure components, the lower-melting modifications forming a continuous series of solid solutions without minimum or maximum. The portions of the curve obtained for the high melting form indicated that they were part of a system with a minimum melting point. Mumford and Phillips[4] obtained similar results for the systems ethyl myristate–ethyl palmitate and ethyl laurate–ethyl myristate. With decreasing molecular weight of the components, larger portions of the upper curve (high melting modification) and smaller portions of the lower curve (low freezing modification) were found until, for the system ethyl decoate–ethyl laurate, only the melting curve for the higher modification was shown. In this case, the minimum melting point is definitely indicated. Guy and Smith[5] showed that methy, palmitate and methyl stearate are polymorphousl yielding transparent (metastable) and opaque crystals. In mixtures, the transparent form is stabilized. The evidence for compound formation was inconclusive according to these authors. Smith[2] showed that the system hexadecyl alcohol–octadecyl alcohol forms a continuous series of solid solutions with a minimum.

Investigation of the system octadecyl iodide–hexadecyl iodide[7] showed that some change took place in the crystals soon after formation although there was no evidence of polymorphism in the cooling curves. Except near the extreme compositions, the mixtures crystallized slowly, and it was difficult to obtain concordant values of the freezing points. The amides and anilides of palmitic and stearic acids[5] yield mixed melting point curves similar to the curves for the corresponding acids, although there is less depression of the melting point. An equimolecular compound is formed in each case.

Phillips and Mumford[8] found no evidence of polymorphism in pure hexadecane, but Smith[7] showed that about 5% of octadecane is required to stabilize the metastable (transparent) form. This is similar to the result obtained for the system ethyl palmitate–ethyl stearate.[2] A mixture containing 2 mole per cent. of octadecane cools to 16.11°, and the temperature remains constant while the transparent form separates. These crystals can be kept for several minutes, but if they are pressed with a thermometer (or stirred), they immediately become opaque, and the temperature rises 1.2°. The transparent form can be kept for several hours if the composition is near that of the minimum freezing mixture (5.3 mole per cent. octadecane). Meyer and Reid[9] made similar observations in their study of octadecyl acetate. This behavior was also observed in the present investigation in the vicinity of the minimum freezing composition.

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(1) W. Heintz, *Pogg. Ann.*, **92**, 588 (1854); L. E. O. de Visser, *Rec. trav. chim.*, **17**, 182, 346 (1898); E. Carlinfanti and M. Levi-Malvano, *Gazz. chim. ital.*, **39**, II, 353 (1909); G. T. Morgan and A. R. Bowen, *J. Soc. Chem. Ind.*, **43**, 346T (1924); N. N. Efremow, *Ann. inst. polytech. Oural*, **6**, 155 (1927); R. L. Shriner, J. M. Fulton and D. Burks, Jr., THIS JOURNAL, **55**, 1494 (1933); R. N. Wenzel, *Ind. Eng. Chem., Anal. Ed.*, **6**, 1 (1934); R. Ashton, R. Robinson and J. C. Smith, *J. Chem. Soc.*, 283 (1936); J. C. Smith, *ibid.*, 625 (1936); H. A. Schuette and H. A. Vogel, *Oil and Soap*, **17**, 155 (1940); H. A. Schuette, R. N. Christenson and H. A. Vogel, *ibid.*, **20**, 263 (1943).

(2) J. C. Smith, *J. Chem. Soc.*, 802 (1931).

(3) P. C. Carey and J. C. Smith, *ibid.*, 635 (1933).

(4) J. W. C. Phillips and S. A. Mumford, *Rec. trav. chim.*, **52**, 175, 181 (1933).

(5) J. B. Guy and J. C. Smith, *J. Chem. Soc.*, 615 (1939).

(6) P. C. Carey and J. C. Smith, *ibid.*, 1348 (1933).

(7) J. C. Smith, *ibid.*, 737 (1932).

(8) J. W. C. Phillips and S. A. Mumford, *ibid.*, 1735 (1931).

(9) J. D. Meyer and E. E. Reid, THIS JOURNAL, **55**, 1574 (1933).