Summary.

Pancreatic and malt amylase and that of *Aspergillus oryzae* were selected as representative of the starch-splitting enzymes of the higher animals, higher plants, and of the fungi, respectively.

By the use of the Clark cell and rocking electrode the findings of Sherman and Thomas on the optimum hydrogen-ion concentration for malt amylase were confirmed and the optimum for pancreatic amylase was much more sharply defined than had been possible in previous work.

The optimum hydrogen-ion concentration for the amylase of *Aspergillus oryzae* resembles that of malt rather than that of pancreatic amylase.

Pancreatic amylase was active between the limits of P_H 4 to 10 with optimum activity at about 7, the solutions commonly considered neutral showing under similar conditions a P_H value of 5.8.[1]

Malt amylase was active between P_H 2.5 and P_H 9 with optimum activity at 4.4 to 4.5.

The amylase of *Aspergillus oryzae* showed activity from P_H 2.6 to 8 with optimum at about P_H 4.8.

The activities of the three amylases throughout the range of hydrogen-ion concentration in which activity was found are summarized by means of curves (Fig. 1).

The influence of concentration of electrolyte, as distinguished from concentration of hydrogen ion alone, appeared greatest in the case of pancreatic amylase and least in the case of the amylase of *Aspergillus oryzae*.

We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

NEW YORK.

THE NITRATION OF SUCROSE: SUCROSE OCTANITRATE.[2]

BY E. J. HOFFMAN AND V. P. HAWSE.

Received November 16, 1918.

The product of the action of nitric-sulfuric acid on cane sugar has hitherto proved of little practical value as an explosive on account of its extreme sensitiveness and liability to spontaneous decomposition. Among the explosive mixtures[3] containing this substance which have been proposed, may be mentioned "glukodine," an intimate mixture of nitroglycerin and "nitrosaccharose" prepared by the nitration of a saturated solution of cane sugar in glycerin, and Bjorkmann's explosive consisting of glukodine mixed with sugar, sodium nitrate and nitrocellulose or carbon. As a constituent of low-freezing dynamites it has likewise received some attention.

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[1] Compare Fales and Nelson, THIS JOURNAL, **37**, 2769 (1915).

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] L. Gody, "Matière Explosives," **1907**, p. 398.

The investigation which is the subject of this paper had for its object primarily the development of an optical method for the determination of nitrated sugar in mixtures of this with other explosive materials, particularly nitroglycerin; and, although further work is required to render the method capable of more than a limited application, the obviously necessary preliminary investigation of the preparation and properties of nitrated sucrose itself has led to results which appear to be of sufficient interest and value to present at this time.

The earlier investigators[1] of the product of the action of conc. sulfuric and nitric acid mixtures upon cane sugar describe it as a tough, viscous, transparent, colorless mass, which on cooling sufficiently becomes hard and brittle and can be pulverized. It explodes violently on impact or heating, and on this account was designated by Sobrero as fulminating sugar. Sobrero considered the substance to be sucrose tetranitrate. None of these investigators, with the apparent exception of Reinsch, succeeded in obtaining a crystalline product. The latter, by the spontaneous evaporation of the alcoholic solution of the white powder dried at 38°, obtained star-shaped, transparent crystals, but gives no analytical data regarding these.

Later, "nitro-saccharose" was prepared and examined by Elliott,[2] who describes it as a soft, viscous, wax-like, sticky substance, silky in appearance, which is soft enough at 30° to flow like molten pitch. Although washed with hot water and with a one % solution of sodium carbonate, the mass could not be freed entirely from acid, and it decomposed slowly with a faint odor of hydrocyanic acid. Heated on a water bath decomposition was accompanied by evolution of red fumes. Several reduction experiments gave results which were taken as indicating a composition approximating that of saccharose octanitrate.

According to Will and Lenze,[3] careful nitration of cane sugar yields the so-called octanitrate. The preparation of this substance was conducted as follows: The purest, thoroughly dry and finely pulverized sugar was dissolved in nitric acid of specific gravity 1.52 cooled to 0°, and to this was added gradually cold conc. sulfuric acid, the reacting mixture

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[1] Ascagne Sobrero, "Sur plusieurs composés détonants produits avec l'acide nitrique et le sucre, la dextrine, la lactine, l a mannite et la glycérine," *Compt. rend.*, **24**, 247 (1847); C. F. Schoenbein, "Ueber eine eigenthümliche Veränderung des Zuckers, durch Salpeter-Schwefelsäure bewerkstelligt," *Ann. Physik. Chem.* (Pogg.), **70**, 100 (1847); L. Svanberg, "Verbindung von Zucker mit Salpetersäure," *Jahresb.*, **27**, 389 (1847); (review of *Öfversigt of Vetelens Akad.*, **4**, 51); H. Reinsch, "Uber einige explosive Substanzen," *J. prakt. Chem.*, **47**, 477 (1849); H. Vohl, "Ueber die Löslichkeit der Schiessbaumwolle in Aether," *Ann.*, **70**, 360 (1849). Ad. u. W., Knop, "Ueber das Verhalten der nitrirten Zuckerverbindungen zu reducirenden Mitteln," *J. prakt. Chem.*, **56**, 334 (1852).

[2] A. H. Elliott, "On Nitro-saccharose," THIS JOURNAL, **4**, 147 (1882).

[3] W. Lenze, F. Will, "Nitrirung von Kohlenhydraten," *Ber.*, **31**, 68 (1898).

being kept cool by means of ice water. For each gram of sugar 10 cc. nitric acid and 20 cc. sulfuric acid were used. The resultant product was pressed out under ice-water to free from acid and was then taken up several times in alcohol and separated fractionally. When an alcoholic solution of the product was evaporated at about 0°, solid separated in the form of small spheres arranged in dendrite formation which had a crystalline appearance, but which on more careful examination were found to be amorphous. All attempts to obtain a crystalline product were unsuccessful. The product melted indefinitely at 28 to 29°. Nitrogen was determined by the Lubarsch modification of Lunge's method.

Calc. for $C_{12}H_{14}O_{11}(NO_2)_8$: N, 15.95. Found: 15.87, 15.72 $[\alpha]_D^{20}$ in a 3.4% alcoholic solution, 52.2°.

The nitric acid ester of cane sugar was unstable; allowed to stand at 50° it quickly decomposed. In three days there was a loss of 11%. It was also very unstable in contact with acid.

EXPERIMENTAL.

Method of Preparation and Purification.

Preliminary experiments showed that a product answering the description of previous investigators could readily be prepared by the addition of sugar, a little at a time, to mixtures of conc. sulfuric and nitric acids of varying strengths and proportions. But we were unable by repeated washing of the solid or semi-solid mass with water and dilute sodium hydrogen carbonate to obtain a product entirely free from acid; and the soft, waxy mass, or the white powder obtained by pulverizing the hard mass under ice-water, was very unstable and decomposed on exposure to the air.

The method of nitration and subsequent purification finally adopted as most satisfactory is indicated in the following experiments. The slight variations in detail are pointed out under each experiment. Nitric acid of sp. gr. 1.52, and sulfuric acid of sp. gr. 1.84 were used in the same proportions as by Will and Lenze. The sugar nitrated was Bureau of Standards C. P. sucrose.

Experiment 1.—Ten g. of the sucrose was dissolved in 100 cc. of nitric acid cooled to —3°. To this solution in a beaker kept cold by means of ice-salt mixture, and constantly agitated by means of a mechanical stirrer 200 cc. of sulfuric acid cooled to 8° was added slowly from a dropping funnel. During this operation extending over 1.5 hours the temperature of nitration varied between —2° and +4°. The stirring was discontinued one-half hour after all the sulfuric acid had been added. The solid nitrated product was then quickly removed from the acids and dumped into a large volume of ice-water under which it was pressed out well. The washing was repeated at least 5 or 6 times with fresh water at a temperature at which the product remained stiff but plastic enough to be kneaded well. In the final washings distilled water was used. Exposure of the mass to the air was avoided as much as possible.

The product thus washed was dissolved in ether (C. P., dried over sodium) in which it was readily soluble. The solution was transferred to a small, elongated, separatory funnel in which most of the water and impurities contained therein collected below and were drawn off. The solution, after several washings with cold distilled water, was washed several times with a one % solution of sodium hydrogen carbonate, and this treatment was followed by further washing with water until neutrality. After standing overnight in the funnel, the water collected was drawn off and the ether solution was transferred to small beakers. The ether was removed by evaporation under bell-jars in a current of dry air, followed by evaporation under diminished pressure in large vacuum desiccators containing conc. sulfuric acid. When most of the ether had been removed in this way, the mass had a semi-transparent vitreous appearance. Evacuation repeated at frequent intervals over periods of 5 to 7 days reduced the residual ether to from 0.6 to 1.7% in the case of quantities of 5 to 8 g. By still longer treatment this could be reduced to as low as 0.3%. With small quantities of material it was possible to remove practically all this residual solvent, but in the case of 10 to 12 g. lots it required much longer to remove the ether. Reference will be made later to this residual solvent and the means employed to estimate it very closely. No determination of yield was made in this experiment, the crude product of which is designated below as A.

Experiment 2.—This experiment was performed as was Expt. 1. 16 g. of sucrose dissolved in nitric acid at —8° was treated with sulfuric acid cooled to 0°. The duration of the operation was 2 hours, at temperatures lying between 0 and —10°. The purified crude product, designated as B, amounted to approximately 1.2 g. for each gram of sucrose treated.

Experiment 3.—In this, 15 g. of sucrose dissolved in nitric acid at —6° was treated with sulfuric acid cooled to 0°. The temperature of nitration was 0° to —4° over a period of 2 and $^5/_6$ hours. The yield of nitrated product, designated as C, was about 1.06 g. per gram of sugar.

Experiment 4.—This experiment differed from the foregoing in that the nitric acid employed was freshly prepared by distilling 150 cc. from a mixture of 300 cc. fuming nitric (sp. gr. 1.5) and 600 cc. conc. sulfuric acid. It probably contained less oxides of nitrogen than the acid previously used. 15 g. of sucrose was added in small portions to the nitric acid at —7° to 0° with constant stirring. The sulfuric acid cooled to —7° was then run in as before. During the nitration, 2 and $^1/_6$ hours, the temperature ranged from 0° to —6°. Purification of the product was accomplished as in the other experiments, the following difference in behavior being noted.

From the purified ether solution allowed to stand overnight in the funnel a considerable quantity of crystals separated and deposited on the glass surfaces. After drawing off the ether solution, these crystals were detached from the funnel by shaking with fresh ether and collected in a separate beaker. The main product contained in the ether solution is designated below as D, while the crystals separated from ether solution are referred to as D 2. Combined yield of nitrated product recovered was 1.7 g. per gram of sucrose.

Experiment 5.—This experiment had for its object the determination of the effect of nitration at slightly higher temperatures. 1.5 g. of sucrose was dissolved in nitric acid at 4° and treated with sulfuric acid cooled to 0°. During the addition of sulfuric acid, time 1 and $^1/_3$ hours, the temperature was allowed to rise to 10°. During the succeeding 1 and $^1/_4$ hours the cooling bath was removed and the temperature allowed to increase slowly to 20°. The product of this experiment was removed from the acids as a heavy liquid, and this was purified by washing at about 10°. The yield was low, approximately 0.7 g. from one g. of sucrose. It is designated below as E.

Investigation of the Crude Products.

The nitrated sucrose of Expts. 1 to 4, after removal of moisture and ether as far as practicable by evacuation, was a tough, viscous, semitransparent, colorless mass. Its viscosity varied somewhat with the different lots. Cooled to hardness and pulverized, it yielded a sticky, white powder. No definite solidification temperature could be established. A 5 g. sample was warmed to 54° and allowed to cool slowly. At 40° it flowed sluggishly and at 8° it became very hard and brittle. Between these temperatures the change from fluid to solid condition was very gradual.

Hygroscopicity and Stability.—A sample containing 1.7% residual solvent, exposed to the air at 24° absorbed in 53 hours only 0.3% moisture. Afterwards heated at 51° for 18 hours it lost 0.84% in weight exclusive of the absorbed moisture, while in 54 hours the total loss was 2.98%. Another sample containing 0.71% residual solvent, heated at 51°, lost in weight in 18 hours 0.50, in 41 hours 0.88 and in 62 hours 1.69%. Aside from loss in weight, no indications of decomposition were observed. But on continuing the heating for 24 hours the total loss was increased to 4.10% and decomposition was evident from the odor of oxides of nitrogen and the formation of green spots in the mass. A third sample heated at 32 to 33° in a small test tube after the manner of the Abel stability test began to decompose in 6 minutes as indicated by the brownish color formed on a strip of starch-iodide paper suspended above. It thus appears that the crude nitrate decomposes on heating at comparatively low temperatures, this decomposition becoming more rapid after long heating. But the author's experience has been that at room temperature (maximum 26°), when acid-free, the products are fairly stable and can be kept for weeks without any appreciable change in appearance or loss in nitrogen content.

Heated on platinum foil in a gas flame, the nitrated sucrose sputters, ignites and burns with a yellow flame. It is very sensitive to friction or impact.

Nitrogen Determinations.—Nitrogen was determined by the Lunge method in the modified Lunge nitrometer carefully calibrated to read percentage nitrogen directly. On account of their nature the samples to be analyzed could not be introduced alone into the nitrometer, but inasmuch as it was anticipated that in practice analyses would be required of mixtures of sucrose nitrate and nitroglycerin, this difficulty was easily overcome by first dissolving a given weight of the substance in approximately an equal weight of pure nitroglycerin, in which it was very soluble. Before analysis this solution was subjected to suction in a vacuum desiccator over sulfuric acid, as it was discovered that by this means the small residue of ether remaining absorbed in the sucrose nitrate could be readily removed. Its removal was indicated by the escape of bubbles from the solution. The first evacuation was continued only so long as such evolution was visible. Evacuation was repeated to constant weight, the total time required being usually only a few minutes. Sometimes a loss in weight occurred during the preparation of the solution and no further loss took place under suction. The nitroglycerin alone was subjected to the same treatment, but no appreciable volatilization was observed. Tests were made also to detect any decomposition of the mixture; in no instance was there any evidence of decomposition. The total loss in weight was, therefore, deducted from the original weight of the sucrose nitrate, this correction varying with the 5 different lots of crude product from 0.77 to 2.78%. A sample of the nitroglycerin solution was transferred to the thoroughly cleaned funnel of the nitrometer, care being taken that no spattering of the liquid occurred on the sides of the funnel. The weight of the mixture taken for analysis was determined by weighings before and after removal of the sample. The sample was then drawn into the nitrometer as completely as possible without the addition of any sulfuric acid, after which the residue of the sample adhering to the funnel was quickly washed in with the conc. sulfuric acid. The remainder of the operation was carried out in the usual manner. Having determined the total nitrogen, and having determined previously the nitrogen content of the nitroglycerin used, a sample calculation gave the nitrogen in the sucrose nitrate.

As a check on the analyses by this method determinations of nitrogen in one lot were made by the Dumas method. The copper oxide used for the combustion was previously treated as recommended by Fieldner and Taylor.[1]

ANALYSES.

	Nitrogen by nitrometer.		Nitrogen by Dumas method.	
Sample.	Individual determinations.	Av.	Individual determinations.	Av.
A.....	15.02, 15.33, 15.12	15.16		
B.....	15.13, 14.77, 15.08	14.99		
C.....	14.84, 14.86	14.85		
D.....	14.94, 15.04	14.99	15.27, 15.35, 15.35, 15.26	15.31
E.....	14.56, 14.64, 14.67, 14.63	14.63		

The nitrogen values by Dumas method are higher, as was to be expected from the well established fact that even after the most careful preparation of the copper oxide used for the combustion the method may give results too high, due to the adsorption of nitrogen in the fine oxide.[2] Under the same conditions as in the determination of nitrogen in D by Dumas method, the nitrogen in pure picric acid was determined as 18.63%; calc., N = 18.34%. The nitrogen by Dumas method thus appears to be nearly 0.3% too high. This correction, applied to the above determinations by Dumas method, would bring the results by the two methods into very close agreement.

The remarkably close agreement of the nitrogen as determined with that calculated for sucrose heptanitrate led to several molecular-weight determinations by the freezing-point method. The results obtained showed that the products examined were mixtures of nitrated products and impurities rather than any definite chemical compound. The subsequent separation and identification of crystalline sucrose octanitrate (molecular weight 702) fully established this fact. The determinations were as follows:

B (in glacial acetic acid), 428.9; C (in benzene), 557.1, and (in nitrobenzene), 565.2; D (in benzene), 536.3, and (in nitrobenzene), 505.4.

Optical Activity.—The specific rotatory power of the several products was determined in absolute ethyl alcohol solution. Several determinations were made with solutions containing also nitroglycerin to show the possible effect of the latter on the results. All solutions were made up to volume in calibrated measuring flasks at 17.5° and polarized at 20° except in two determinations reported. Constant temperature was maintained during the observations by means of running water surround-

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[1] A. C. Fieldner, and C. A. Taylor, "The Determination of Nitrogen in Coal," Bur. Mines., *Tech. Paper* 64, 15–19 (1915); see also, W. C. Cope and G. B. Taylor, "The Determination of Nitrogen in Substances used in Explosives," Bur. Mines., *Tech. Paper* 160, 5–14 (1917).

[2] A. C. Fieldner and C. A. Taylor, "The Determination of Nitrogen in Coal," Bur. Mines, *Tech. Paper* 64, 15–19 (1915); see also, W. C. Cope and G. B. Taylor, "The Determination of Nitrogen in Substances used in Explosives," Bur. Mines, *Tech. Paper* 160, 14 (1917).

ing the 2 dcm. polarization tube used. The scale of the polariscope was carefully tested over the range used by means of solutions of standard C. P. sucrose. The source of illumination was a frosted tungsten lamp, the light from which was filtered through 6% bichromate solution. The results were as follows:

Product.	Weight of sample in 100 cc. at 17.5°. G.	Correction for ether content. %.	Corrected weight per 100 cc. G.	Nitroglycerin content. G.	Temperature of polarization. Degrees C.	Angle of rotation. Degrees.	α.	Average. α.
A.	2.7308	2.45	2.6642	. . .	24	3.16	59.30	. . .
	1.1232	2.45	1.0956	2.3574	26	1.25	57.05	. . .
B.	3.2950	1.68	3.2396	3.3248	20	3.67	56.64	. . .
	1.1716	1.68	1.1520	. . .	20	1.30	56.42	. . .
	2.7896	1.68	2.7450	. . .	20	3.09	56.29	. . .
	1.3804	1.14	1.3648	5.9904	20	1.54	56.42	. . .
	2.6780	1.14	2.6436	10.6696	20	2.97	56.09	56.37
C.	1.7784	0.77	1.7648	. . .	20	1.98	56.10	. . .
	2.4984	0.63	2.4828	. . .	20	2.86	57.60	. . .
	1.6632	0.77	1.6504	. . .	20	1.875	56.80	. . .
	3.0040	0.71	2.9820	. . .	20	3.43	57.51	57.00
D.	2.6748	2.78	2.6004	. . .	20	2.95	56.72	56.72
E.	2.4060	0.98	2.3824	. . .	20	2.75	57.72	. . .

The average of 10 determinations of $[\alpha]^{20}$, exclusive of A and E, is 56.66. Determinations for A were made at temperatures other than 20°, and E was prepared by nitration at higher temperatures than A to D.

Sucrose Octanitrate.

Reference has been made above to the separation of crystals from some of the crude products. All attempts to obtain crystalline products from B and C by evaporation of the alcoholic solutions at zero and below were unsuccessful. Sometimes the solid separated in this way had the appearance of crystals, but after filtration this softened and again assumed the appearance of the original waxy material on warming to room temperature. It was, however, possible by slow evaporation of the alcohol solution at room temperature to obtain a separation of crystals. From 5 g. of B approximately 30% of solid substance was recovered in fractions of varying degrees of purity, but from this amount less than one g. of crystals could be collected of sufficient purity for analysis, by repeated washing with alcohol. These crystals melted at about 82.7 to 85.3°. In a similar manner the crystalline content of C was estimated at 23%.

Several lots of the impure crystals obtained from B and C were combined and purified by pulverizing under alcohol, decanting and repeatedly washing with fresh alcohol until about 0.5 g. was finally obtained which melted at 83.7 to 85.3°. One molecular-weight determination in nitrobenzene gave a value of 707.3.

An excellent yield of crystals was obtained from D, the crude product prepared as stated above by the use of freshly distilled nitric acid. The crystalline deposit from the conc. ether solution already referred to and designated as D 2 amounted to 1.38 g. These crystals were purified by several washings with cold alcohol in which they were difficultly soluble. The purified crystals melted at 84.3–86.3°.

The main product D was a stiff, opaque mass. This was only partially soluble in ethyl alcohol. Several treatments of 11.4 g. of D with absolute alcohol yielded 5 g. of insoluble, white crystals which melted indefinitely between 75 and 84°. Further purification gave 4.5 g. of crystals, D 1, which melted completely at 82.3–84.3°. Recrystallization from methyl alcohol yielded crystals melting at 85.5°, which is no doubt very close to the true melting point of the purest sucrose octanitrate.

The crystals are difficultly soluble in ethyl alcohol, slightly more soluble in benzene, almost insoluble in xylene and insoluble in petroleum ether. They are very soluble in ether, methyl alcohol and nitrobenzene, the solubility on these solvents increasing in the order named. A mixture of methyl alcohol and ether is a better solvent than either alone, while nitrobenzene was found to be the very best solvent for the crystals.

Stability.—The crystalline nitrate is very stable even up to temperature of fusion. A sample of D 1 was tested in a manner similar to that followed in the Abel stability test for explosives. Heated gradually from 33° up to 87° over a period of nearly two hours, it showed absolutely no signs of decomposition, although kept for nearly one hour in the fused condition.

The octanitrate behaves like the crude nitrated product with respect to heating in a flame, and to friction; but it is less sensitive to impact.

Nitrogen Determinations.—Duplicate determinations of nitrogen in D 1 were made by the Lunge nitrometer method. The procedure followed was the same as for the crude products, *i. e.*, the analysis of the nitroglycerin solution. No loss in weight of the solution occurred on the evacuation treatment. However, this procedure proved very unsatisfactory in the case of the crystals because it was very difficult to dissolve these in nitroglycerin in proportions suitable for analysis, and after transfer to the nitrometer the addition of the sulfuric acid caused at least a partial precipitation of the dissolved crystals which rendered the reaction slow and liable to incompleteness.

Calc. for $C_{12}H_{14}O_3(NO_3)_8$: N, 15.95. Found: 15.73, 15.68.

Nitrogen by Dumas method gave higher results: 16.23 and 16.23%. Nitrogen in D 2 by the same method was 16.22%. For picric acid it was 18.63% against the calculated content of 18.34%, an error of 0.29%. Applying a correction for corresponding errors in the nitrogen determinations for the crystals by Dumas method, due to adsorbed nitrogen in the copper oxide used, the nitrogen as determined by this method becomes almost identical with that calculated for sucrose octanitrate.

Two determinations of the molecular weight of the crystals in nitrobenzene gave the following values:

Calc. for $C_{12}H_{14}O_3(NO_3)_8$: M. W., 702. Found: 704.6, 695.8, mean 700.2.

Optical Activity.—The specific rotatory power of the octanitrate was determined in methyl alcohol solution and in an ethyl alcohol solution containing 7 cc. nitrobenzene per 100 cc., as follows:

Crystals.	Weight crystals in 100 cc. at 17.5°. G.	Solvent used.	Temperature of polarization. Degrees C.	Angle of rotation. Degrees.	$[\alpha]^{20}$.	Mean $[\alpha]^{20}$.
D 1........	2.4768	Methyl alcohol	20	2.77	55.92	...
D 2........	1.2012	Ethyl alcohol containing 7 cc. nitrobenzene	20	1.35	56.19	56.05

Crystallography and Photomicrography.—The authors are indebted to Mr. Herbert Insley of the Bureau of Standards for the crystallography of the sucrose octanitrate, and to Dr. R. Thiessen, of the Bureau of Mines, for the accompanying photomicrographs of the crystals.

The crystals belong to either the orthorhombic or monoclinic system, more probably to the latter. They are all elongated, needle-like forms, but it is impossible to say in what crystallographic direction they are elongated. Sometimes individual crystals are found massed together in a radiating group. They show the following optical properties: Optical character, positive; optic axial angle small, probably not more than 20°; plane of optic axes parallel to elongation direction. The great majority of individuals examined showed parallel extinction, but other forms showed inclined extinction varying from 6° to 20°. This would lead one to believe that the crystals are monoclinic. Double refraction is fairly high. Figs. 1 and 2 are the photomicrographs of the crystals at magnifications of 10 and 20 diameters, respectively. These show the octanitrate as it was crystallizing in methyl alcohol in the form of rosets. Figs. 3, 4 and 5

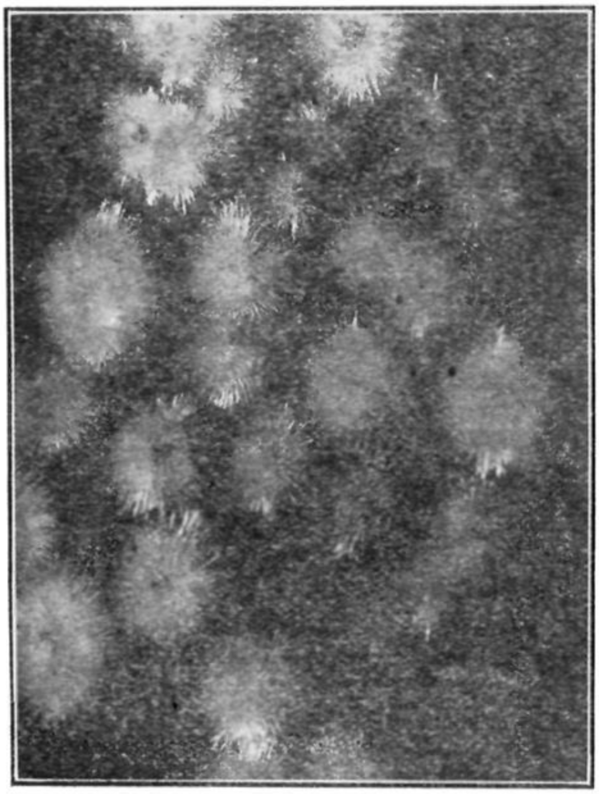

Fig. 1.

are photomicrographs taken at a magnification of 200 diameters. which indicate the appearance and form of individual crystals.

Application of the Results to the Determination of Sucrose Nitrate in Explosives.

Obviously the application of the polariscope to the analysis of mixtures of soluble organic constituents of explosives, including nitrated sucrose and at least one other nitrogen-containing constituent from which previous separation cannot be effected, is dependent on a knowledge of the specific rotation and the nitrogen content of the sucrose nitrate. Assuming no other optically active substance present, the determination of the sucrose nitrate itself would require only a knowledge of the specific rotatory power of that particular nitrated product. Given the two above-mentioned factors, the presence of nitrated sucrose in the mixture to be analyzed should not add appreciably to the difficulties incident to the analysis of explosive mixtures which do not contain this constituent. If the nitrogen content and specific rotation of the products obtained by the nitration of sugar under different conditions were only approximately the same, the results of the application of this method of analysis would still be sufficiently accurate to recommend the method. Further investigation is required to determine how greatly these values vary.

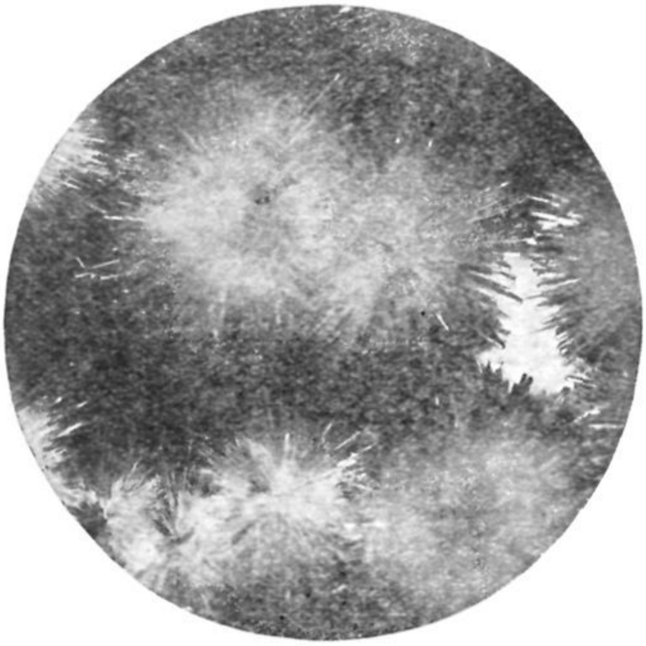

Fig. 2.

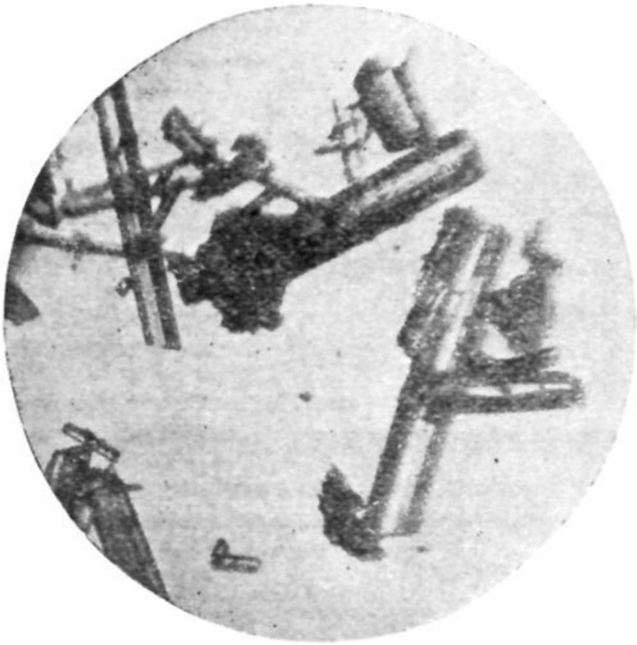

Fig. 3.

One example of variation is afforded by product E of Expt. 5 of this paper. If this product contained any sucrose octanitrate, the latter was evidently present in a much smaller proportion than in the products of the preceding 4 experiments, for all attempts to separate crystals from it were unsuccessful, and its nitrogen content was lower than that of any of the other products. One determination of the specific rotation of E gave $[\alpha]^{20} = 57.72$, which is higher than the mean value 56.66, from the other products. The solution for which this value was determined contained 2.3824 g. sucrose nitrate per 100 cc.; the angle of rotation (a) was 2.75°. Using $[\alpha] = 56.66$, $a = 2.75°$; from c (concentration) $= a/2\alpha$, we obtain $c = 0.02468$ instead of 0.023824, a difference of 1.86%.

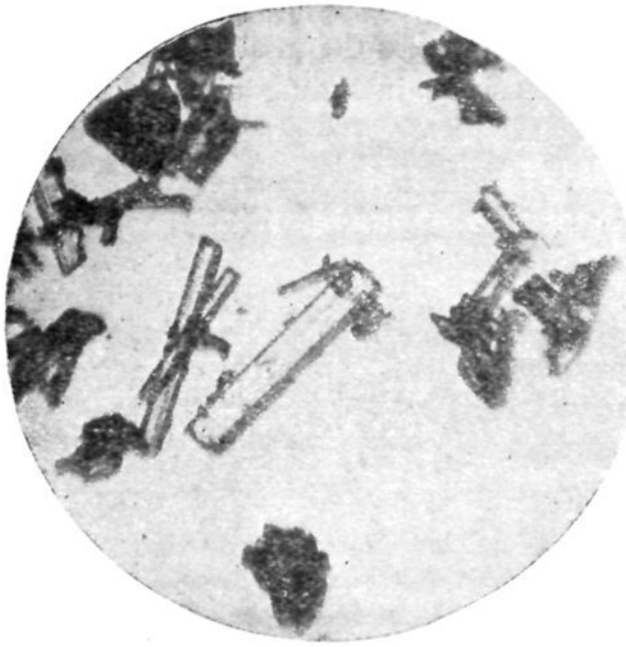

Fig. 4.

How closely it may be possible to estimate sucrose nitrate in the product of the simultaneous nitration of glycerin and sucrose is indicated by the following experiment: A mixture of 10.2 g. of glycerin and 3.12 g. of sucrose was nitrated. The sugar was not soluble in the cold glycerin, but was kept in suspension by frequent shaking. The mixture was added slowly to 100 cc. of mixed acid of the strength employed in the nitration of glycerin. Initial temperature of nitration was 7°, final 16°. The yield of product after washing free from acid was about 14.5 g. 10.65 g. of the dried mixture in 100 cc. of alcohol solution gave $a = 3.07°$, from which, taking $[\alpha] = 56.66$, the sucrose nitrate content was determined as 25.44% The mixture had a total nitrogen content of 17.67%, by analysis. Taking 15% as the nitrogen value for sucrose nitrate, and 18.50% for nitroglycerin, by calculation we obtain sucrose nitrate = 23.71%. The difference between the two results is seen to be 1.73%.

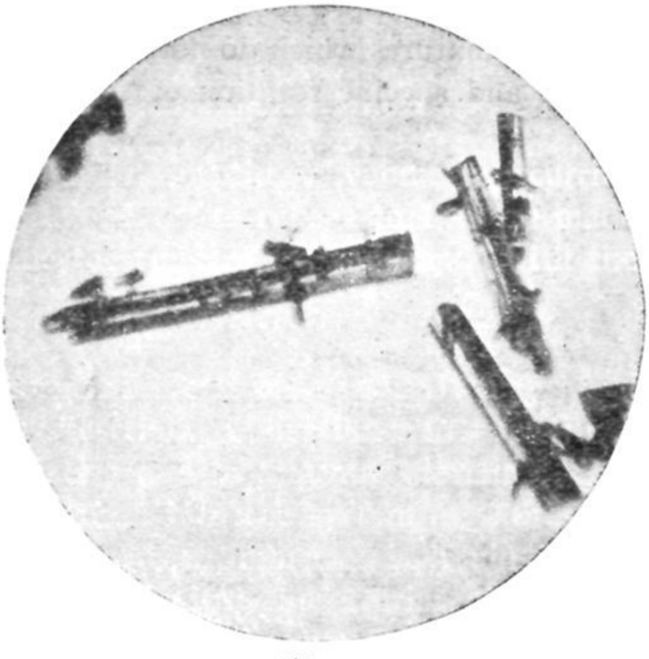

Fig. 5.

A further comparison of the results of the determination of sucrose nitrate mixed with nitroglycerin by the optical method and by calculation from total nitrogen was afforded by the examination of a manufacturer's sample of such a mixture, the method of preparation of which was not known to the authors. By the optical method, the sucrose nitrate was determined as 15.52%; calculated from the nitrogen determination the percentage of the sucrose nitrate was 16.86. The mixture probably contained other constituents, possibly some stabilizing material which would affect the results by the latter method.

Summary.

1. The crude product of the nitration of sucrose under the conditions above described is a tough, viscous, semi-transparent mass, which can be pulverized on cooling to hardness. It has no definite solidification temperature and is unstable above 30°. It contains an average nitrogen content of 15%, and has an average specific rotatory power of 56.66°.

2. Sucrose octanitrate has been separated from the crude nitration product and identified as well-defined crystals belonging to the orthorhombic or monoclinic system, more probably the latter. It melts at 85.5° and is very stable. Nitrogen and molecular-weight determinations gave values which are practically identical with those calculated for sucrose octanitrate. Its specific rotatory power was determined as 56.05°.

3. Sufficient data have been accumulated for a limited application of the polariscope to the analysis of explosive mixtures containing nitrated sucrose, and these form a basis for the further development of the method.

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ALKALI-INSOLUBLE PHENOLS.

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Solubility in aqueous alkalies is a general property one expects all phenols to possess. Nevertheless, many of them which do not have this property have been described. Some of these appear to be isolated examples while others seem to fall into classes such as the pseudo phenols of Zincke, the *o*-azophenols studied by Liebermann and others and the phenylhydrazones of certain *o*-hydroxyaldehydes and ketones investigated by Anselmino, Torrey and the author of this paper. The object of the present

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[1] The subject of this investigation was suggested by H. A. Torrey, and the work in this field was begun under his direction and published in *Ber.*, **43**, 3227 (1910). The continuation of the research, however, which is described in this publication was deprived of the benefit of his supervision by his early death in February, 1910. Although the views put forward in this communication do not agree with those held by Dr. Torrey, I feel that anything of value which may be contained therein is due to his encouragement and guidance in the beginning.