The filtrate and washings were combined, the alcohol was removed under reduced pressure, and the residue distilled *in vacuo*. The product was colorless.

2-(3-Diethylaminopropylmercapto)-ethanol.[7] **Method C.**—To a stirred cooled solution (0°) of 11.5 g. (0.5 mole) of sodium in 500 cc. of ethanol was added 39 g. (0.5 mole) of 2-thiolethanol. To this solution was added dropwise at 0°, 74.8 g. (0.5 mole) of 3-diethylaminopropyl chloride during one-half hour. The mixture was stirred in the cold for 2 hours, refluxed four hours and then cooled. The sodium chloride was removed by filtration and washed with 2 × 50 cc. of ethanol. The filtrate and washings were combined, the alcohol was removed under reduced pressure and the residue was distilled *in vacuo*. The product was colorless.

N-(3-(3-Chloropropylmercapto)-propyl)-diethylamine.—To a stirred, cooled solution (0°) of 75 g. (0.366 mole) of 3-(3-diethylaminopropylmercapto)-propanol in 175 cc. of dry chloroform was added dropwise, in the absence of moisture, a solution of 43.5 g. (0.366 mole) of purified thionyl chloride in 175 cc. of dry chloroform, over a period of one hour. When the addition was complete the solution was stirred in the cold for one hour and refluxed for one hour. Most of the solvent was distilled off and to the cooled residue was added 90 cc. of ethyl acetate and 200 cc. of ether. A tan-colored, hygroscopic hydrochloride was obtained in quantitative yield.

The hydrochloride was dissolved in 500 cc. of water, the solution was made alkaline with 35% potassium hydroxide solution, saturated with sodium chloride and extracted with ether. The combined ethereal extracts were dried over anhydrous potassium carbonate, the solvent was removed under reduced pressure and the residue was distilled *in vacuo*. There was obtained 56.8 g. (69.4%) of water-white product, b. p. 80–82° at 0.025 mm., $n^{20}D$ 1.4875.

Anal. Calcd. for $C_{10}H_{22}ClNS$: C, 53.69; H, 9.84; N, 6.26. Found: C, 53.50; H, 10.01; N, 6.01.

The citrate crystallized as rosets of white needles from absolute ethanol, m. p. 85–89°.

Anal. Calcd. for $C_{10}H_{22}ClNS \cdot C_6H_8O_7$: N, 3.37. Found: N, 3.38.

2-(2-Chloropropylmercapto)-triethylamine Hydrochloride.—This compound was prepared by the above method, except that the initial temperature of the chlorination was −30°. The product was obtained as hygroscopic white platelets in 72% yield.

The free base was liberated in ice–water with 35% potassium hydroxide solution. The aqueous mixture was saturated with sodium chloride, extracted with ether, and the combined ethereal extracts were dried over anhydrous sodium sulfate. When this base was added to a solution of citric acid monohydrate in ether, the citrate separated as a fine white solid, m. p. 88–91°.

Anal. Calcd. for $C_9H_{20}ClNS$: C, 44.83; H, 6.97; N, 3.49. Found: C, 44.69; H, 6.55; N, 3.42.

Summary

The preparation of a series of dialkylaminoalkylmercaptoalkyl alcohols, chlorides, an amine and related compounds is described.

RENSSELAER, NEW YORK RECEIVED SEPTEMBER 26, 1946

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[7] *Cf.* Gilman and Tolman, THIS JOURNAL, **67**, 1847 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, PURDUE UNIVERSITY AGRICULTURAL EXPERIMENT STATION]

Partial Characterization of a Compound Involved in the Blackening of White Potatoes[1]

BY W. R. LEWIS AND D. M. DOTY

The development during cooking of grey or black discolorations of white potatoes (*Solanum tuberosum* L.) is of considerable commercial importance as well as of academic interest. Spangler[2] reported that 25% of 1,165 Chicago retailers listed tendency to cook black as either the first or second most objectionable defect of potatoes. Similarly it was shown to be the most common complaint of 880 retailers in the cities of Cleveland and Rochester.

Several investigators have studied causes and means of preventing blackening. Much of their time has been devoted to studies of environmental conditions which cause blackening. Tottingham,[3] *et al.*, studied the effect of mineral nutrition, of various soil moisture levels, and of high temperatures. They found no consistant correlation between blackening and any of these factors. Smith and Kelly[4] state that potatoes maturing at temperatures below 60°F. darken to a greater extent than those maturing at higher temperatures. However, after noting the above statement, Rieman,[5] *et al.*, say "... it has not been possible thus far to induce blackening with certainty under controlled experimental conditions by varying any environmental factor." Although these studies have made valuable contributions to the knowledge of the nutritional requirements of the potato plant, it is obvious that little is known concerning the fundamental cause of blackening.

The purpose of this investigation was, therefore, to characterize chemically the precursor of the black pigment so that a practical means of preventing the discoloration might be devised.

The concentration of a pigment precursor was greatly facilitated by the discovery that it showed a characteristic blue fluorescence. Partial characterization was effected in the following manner. The colorless fluorescent precursor was extracted from the fresh tubers with acidified alcohol. The

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[1] Journal Paper No. 271 of the Purdue University Agricultural Experiment Station.

[2] R. L. Spangler, "Retail Trade Practices and Preferences for Late-Corp Potatoes in Chicago and Suburbs and Quality Analysis of Potatoes Offered for Sale to Consumers, 1939–40," Agr. Marketing Service, U. S. D. A., 1940, 66 pages.

[3] W. E. Tottingham, R. Nagy and A. F. Ross, *Am. Potato J.*, **13**, 297 (1936).

[4] Ora Smith and W. C. Kelly, *Food Packer*, **25**, 32 (1944).

[5] G. H. Rieman, W. E. Tottingham and John S. McFarlane, *J. Agric. Research*, **69**, 21 (1944).

extract was concentrated and extraneous materials were removed by precipitation. Isobutyl alcohol was added to the fluorescent solution to permit the removal of water and ethanol by azotropic distillation. The fluorescent substance was precipitated by adding ether to the isobutyl alcohol solution. The fluorescent substance was converted to a black pigment by temperatures above 35° even in acid solution and in an atmosphere of carbon dioxide. The colorless fluorescent precursor instantly turned black in alkaline solution. It added bromine readily to form an insoluble non-fluorescent derivative. Fluorescence reappeared upon debromination.

The bromo derivative gave a positive Molisch test indicating the presence of a carbohydrate group. It failed to give a positive Millon test, which indicated the absence of tyrosine and tryptophan. The ninhydrin test was also negative, but after the bromo derivative was subjected to hydrolysis with 20% hydrochloric acid and the resulting solution neutralized, a positive ninhydrin test was obtained. Evidently an amino group or a carboxyl group was liberated by hydrolysis which suggests the presence of an amino acid or peptide unit.

The fluorescent substance reacted readily with 2,4-dinitrophenylhydrazine to form a nonfluorescent substance which indicated the presence of a free carbonyl group. Very limited solubility in solvents in which the substance was stable prevented further purification of this derivative.

The above data suggest that a precursor of a black pigment is an amino acid-sugar combination and may involve an aldehyde-amine condensation.

The fluorescent substance precipitated by ether was dissolved in acetone and adsorbed on a magnesium oxide chromatographic column. A black non-fluorescent band appeared at the top, and lower on the column four blue-fluorescent bands developed. However, when the same fluorescent preparation was adsorbed from an anhydrous ether-methanol solution only one blue fluorescent band developed. The difference in adsorption characteristics of the two solutions may be explained on the basis of alkalinity. The anhydrous ether-methanol in contact with magnesium oxide was only slightly alkaline, while the acetone solution, which contained traces of water, probably became distinctly alkaline on the column. The higher alkalinity could have led to the formation of new fluorescent compounds from the one originally present. The black band at the top of the column also indicated alteration of the pigment precursor from the acetone solution.

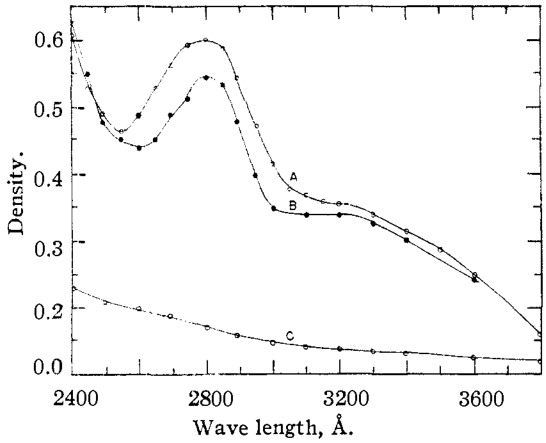


Fig. 1.—Absorption spectra: the fluorescing substance prepared by adsorption (A), and by precipitation (B), and its bromo derivative (C).

Absorption spectra of the fluorescent substance and its bromo derivative are shown in curves B and C of Fig. 1. The maximum at 2800 Å. suggests that there are three or more conjugated double bonds in the fluorescent compounds. The lower curve shows the elimination of this maximum when the substance was brominated.

Experimental

Concentration of the Fluorescent Compound.—Potato tubers were bisected and examined in the ultraviolet radiation from a 100-watt Mazda BH4 Mercury arc. Fluorescent portions of the tubers were cut off and dropped into a Waring blendor bowl. When approximately 250 g. of tissue was obtained, 400 ml. of 95% alcohol and 25 ml. of concentrated hydrochloric acid were added and the tissue was finely ground. About 30 g. of filter aid (Johns-Manville Hyflo Super-cel) was added and the slurry was filtered through a Büchner funnel. This procedure was repeated until 35 pounds of potatoes had been extracted. The residue in the funnel was repeatedly extracted until very little fluorescent material was obtained. The 15 liters of filtrate thus obtained was concentrated under reduced pressure in an atmosphere of carbon dioxide without allowing the temperature of the solution to exceed 30°. Non-fluorescent material which precipitated during the concentration was removed at intervals by centrifuging. When the volume of the solution reached 200 ml., a liter of *i*-butyl alcohol was added. A precipitate containing very little fluorescent material formed. It was removed by centrifuging and discarded. The remaining solution was placed in a distillation apparatus with an arrangement for continuous separation and return of the isobutyl alcohol from the azeotropic distillate. The apparatus was operated at reduced pressure in an atmosphere of carbon dioxide to remove the water completely without exposing the fluorescent materials to air or temperatures over 30°. The solution was concentrated to about 50 ml. Small increments of ethyl ether were added and the precipitate was removed by centrifugation after each addition until fluorescent material began to precipitate. The volume of the solution was then doubled by addition of ether which precipitated nearly all the fluorescent substance.

Preparation of the Bromo Derivative.—The bromo derivative was prepared by dissolving a portion of the fluorescent precipitate in absolute methanol and adding bromine dropwise until the fluorescence completely disappeared. The bromo derivative completely precipitated within a few minutes. Since solutions of the derivative invariably jelled when cooled, all attempts to crystallize this derivative failed. The precipitate was dissolved in absolute ethanol and purified by fractional precipitation with ether. The fractional precipitation was repeated three times. The preparation thus obtained was used for nitrogen and bromine determinations as well as for absorption curve C shown in Fig. 1. It contained 10.5% nitrogen and 13.3% bromine. Since constant composition was not attained, the analyses were of more qualitative than quantitative significance. The derivative charred at 180–190° without melting

Preparation of the 2,4-Dinitrophenylhydrazine Derivative.—The 2,4-dinitrophenylhydrazine derivative was obtained by adding a saturated alcoholic solution of 2,4-dinitrophenylhydrazine to an alcohol solution of the fluorescent substance. The derivative precipitated immediately. The derivative was so insoluble in all common inert solvents that it was not possible to redissolve it for crystallization. It charred without melting at 200–215°.

Adsorption on Magnesium Oxide.—A portion of the fluorescent substance obtained by precipitating with ether as previously described was dissolved in absolute methanol and diluted with 9 volumes of dry ethyl ether. This solution was put through a column of powdered magnesium oxide (2642 Micron Brand obtained from Westvaco Chlorine Products Corp.). After development with methanol a blue-green fluorescent band was found at the top of the column and several centimeters lower a well-defined band which showed the characteristic bright blue fluorescence. The lower band was eluted with methanol and used to obtain absorption curve A, Fig. 1.

Adsorption on Charcoal.—The fluorescent substance in aqueous potato extract at *p*H 1.0 may be adsorbed on Nuchar W or on Norite A and partially eluted with acetone, methanol, or ethanol. However, poor elution yields and the strongly oxidizing character of activated charcoals led to the abandonment of this means of purification.

Absorption Spectra.—All absorption measurements were made with a Beckman model DU spectrophotometer. The spectral region isolated varied between 20 and 40 A.

Summary

1. A colorless precursor of the pigment which causes some white potatoes to turn grey or black when they are cooked has been isolated.

2. The fluorescent pigment precursor is unsaturated, and contains a carbohydrate group and a nitrogenous group. The latter is probably an amino acid or a peptide.

3. Tyrosine and trytophan are not contained in the fluorescent pigment precursor.

4. The absorption curve of the precursor shows a maximum at 2800 Å.

LAFAYETTE, INDIANA RECEIVED SEPTEMBER 30, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

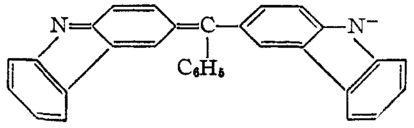
The Kinetics of the Reaction of Methanol with 3,3'-Dicarbazylphenylmethyl Ion in Alkaline Solution

BY GERALD E. K. BRANCH AND B. M. TOLBERT

The quinoidal derivatives of a diaminotriphenyl carbinol react with water or alcohols to form carbinols or ethers. Sidgwick and his co-workers,[1] working with very dilute aqueous solutions of *p,p'*-diaminotriphenylmethyl ion (Döbner's violet), and its tetramethyl and tetraethyl derivations (malachite green and brilliant green), found that in reactions at a fixed *p*H, the kinetics were those of reversible unimolecular reactions, but that the rate constants varied with the *p*H in ways that depended on the dye and the range of *p*H used. They satisfactorily explained these results by assuming rapid reversible reactions between the various quinoidal species possible, and similar reactions among benzenoidal species, and that each rate determining reaction was first order with respect to the quinoid or benzenoid involved. In such a setup, the distributions of the quinoid and benzenoid among their species depend on the *p*H and what species are possible for the particular dye.

In previous work on the kinetics of benzoidation of diaminotriphenylmethane dyes the quinoid has existed as Q^{++}, Q^{+} or Q. The present investigation goes one step further to the case in which the quinoid is distributed between the anhydrobase and its negative ion. The kinetics of the corresponding reactions of the negative ions of the closely related dihydroxytriphenylmethane dyes have been studied over a long period of time, especially by La Mer and his co-workers,[2] who find the rate determining reaction to be one between the negative ions of the dye and of the bleaching agent.

To obtain significant concentrations of the negative ion of a diaminotriphenylmethane dye with the negative charge on the nitrogen atoms rather than on an acidic side group, it is necessary to have exceedingly basic conditions or a dye made from an exceptionally acidic amine. For that reason, 3,3'-dicarbazylphenylmethyl chloride was chosen as the dye. It was synthesized from carbazol, an exceptionally acidic amine.[3] The formula of the negative ion is given below.



The negative of this dye is green and has a strong band in the neighborhood of 730 mμ[4]; while the anhydrobase has a violet red color with a strong band in the neighborhood of 500 mμ. One can, therefore, easily regulate the amount of alkali to obtain significant concentrations of both anhydrobase and negative ion, and the decay of both of these quinoids can be followed separately

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[1] Sidgwick and Moore, *J. Chem. Soc.*, **95**, 889 (1909), and Sidgwick and Rivett, *ibid.*, 899 (1909).

[2] For a list of examples, see Hochberg and LaMer, THIS JOURNAL, **63**, 3110 (1941).

[3] Branch, Tolbert and Lowe, *ibid.*, **67**, 1693 (1945).

[4] Tolbert and Branch, *ibid.*, **68**, 315 (1946).