acylglutamic acid anilides was essential since they tended to be gelatinous in nature and absorbed significant amounts of citrate. The above washing procedure served to remove acylamino acid impurities and to give products of correct intrinsic and mixed m. p.'s. The compounds were then weighed to the nearest milligram[13] and the melting points checked on a melting point block. All of the studies were repeated.

The proportions of reagents employed for the experiments in Table III were the same as in earlier runs as previously described except that the molar ratio of aniline to acyl-L-amino acid was 2:1 instead of 1:1 and the quantities of acylglycines were equimolar to that of the L-acids. The citrate buffer concentration was 1.0 *M* throughout. The total reaction volume of 10 ml. was made up in tubes of 12 × 100 mm. size. The results are averages of duplicates.

**Purification of Anilides.**—The accumulated yields of each of the anilides from many runs were pooled in order to obtain sufficient material for characterization and determination of melting points and rotation. In certain instances in which only small quantities of the materials were available, more was synthesized enzymatically by use of proportionally larger quantities of the reactants.

All of the acylated monoaminomonocarboxylic acid anilides were washed with 1 *N* sodium hydroxide (except the glutamic acid derivatives wlich were washed with water alone), then with water and dried prior to recrystallization. All were purified by dissolving in the minimum quantity of hot dioxane, treating the solution with a small quantity of decolorizing carbon (Darco G-60) and adding water to the hot filtrate to incipient crystallization. The recrystallization procedure was repeated with the omission of the carbon. The acylglutamic acid anilides were recrystallized twice from dioxane–hexane to constant m. p.

(13) As has been indicated, the carboallyloxyglycine was somewhat impure. The percentage of impurities based on the deviation of the nitrogen content from theoretical, however, was approximately within the limits of accuracy of the method used in conducting the anilide synthesis studies. No corrections in yield of anilide because of impurities in the reacting acid were therefore applied.

in a manner similar to that employed above. Hexane was used instead of water for these derivatives since the latter gave gels in the presence of water.

**Acknowledgments.**—The analytical services of Mr. Armand McMillan are gratefully acknowledged. Miss Janet Wilkerson performed a number of experiments of which Table III represents a typical set of results.

## Summary

The yields and *p*H optima, in 1.0 *M* and 0.1 *M* citrate buffer, for the papain-catalyzed formation of anilides from the benzoyl, *p*-nitrobenzoyl, carbobenzoxy and carboallyloxy derivatives of glycine, valine, leucine, and glutamic acid have been tabulated. The previously observed decreasing preferences for leucine, glycine and valine have been confirmed in this work for a total of four types of blocking groups, with a shift in order between glycine and leucine when carbobenzoxy, only, was the substituent. The more rapid and complete reaction in 1.0 than in 0.1 *M* citrate buffer has been confirmed for virtually all of these acylamino acids. Of the entire series of sixteen acylamino acids only carboallyloxyglutamic acid failed to yield an anilide.

The *p*H optima were lower in 0.1 than in 1.0 *M* citrate buffer. Accumulated observations indicate incompletely explained differences in *p*H optimum for different substrates.

The constants of the resultant new acylamino acid anilides are recorded.

AMES, IOWA RECEIVED JANUARY 18, 1950

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

# Chemical Interactions of Amino Compounds and Sugars. V.[1] Comparative Studies with D-Xylose and 2-Furaldehyde[2]

BY TZI-LIEH TAN,[3] M. L. WOLFROM AND A. W. LANGER, JR.[3]

It has been demonstrated[1,4] that the "browning" of sugar solutions, when heated in the presence or absence of amino acids at elevated temperatures, was accompanied by the formation of a small amount of furan bodies. These furan compounds, which decompose readily in the presence of mineral acids,[4b,5] amino acids[6] and other chemicals[5,6] to form color, have been considered as possible intermediates in the coloration or "browning" of various food products containing reducing sugars and amino acids. In the preceding paper[1] of this series, evidence was presented in favor of this supposition. To continue our studies on the role of furan compounds in the "browning" reaction, we have investigated and compared the reactions of glycine with a sugar, D-xylose, and with a furan compound, 2-furaldehyde. This paper describes the results of our study of coloration rates and some properties of the colored products formed in both systems.

(1) Previous communication in this series: M. L. Wolfrom, R. D. Schuetz and L. F. Cavalieri, THIS JOURNAL, **71**, 3518 (1949).

(2) This paper reports research undertaken in coöperation with the Quartermaster Food and Container Institute for the Armed Forces, and has been assigned number 300 in the series of papers approved for publication. The views or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the Department of the Army.

(3) Research Associate (T.-L. Tan) and Research Fellow (A. W. L.) of The Ohio State University Research Foundation (Project 366).

(4) (a) B. L. Scallet with J. H. Gardner, THIS JOURNAL, **67**, 1934 (1945); (b) B. Singh, G. R. Dean and S. M. Cantor, *ibid.*, **70**, 517 (1948); (c) C. D. Hurd, C. D. Kelso and E. Rondesvedt, Report to the Quartermaster Food and Container Institute for the Armed Forces, July to September, 1946; (d) R. G. Rice, *Abstracts Papers Am. Chem. Soc.*, **112**, 3A (1947); (e) S. Akabori, *Ber.*, **66**, 143 (1933); *Proc. Imp. Acad. (Tokyo)*, **3**, 362 (1927).

(5) J. J. Blanksma and G. Egmond, *Rec. trav. chim.*, **65**, 309 (1946).

(6) R. G. Rice, Z. I. Kertesz and E. H. Stotz, THIS JOURNAL, **69**, 1798 (1947).

We observed previously[1] that an aqueous solution of pure 2-furaldehyde containing glycine "browns" at a higher rate than that of D-xylose under the same conditions. The slow development of color, or induction period, in the sugar solution was interpreted as due to the time required for the formation of color precursors, of which one was suspected to be 2-furaldehyde. The concentration of the furan compound present at any one time in the D-xylose "browning" solution is very low. We have extended our studies to determine whether this small amount of 2-furaldehyde is a factor in the "browning" of the sugar–amino acid solution.

One approach consisted in heating equimolar (0.250 *M*) solutions of D-xylose and glycine, in which the sugar was replaced in different degree by 2-furaldehyde. Color formation in these solutions at various time intervals was measured at a selected wave length (490 mμ). The results (Fig. 1) show that the rate of coloration is increased with an increase in the initial amount of 2-furaldehyde in the solution. It appears probable that the color formed in each solution is merely a summation of that formed from D-xylose and that from 2-furaldehyde. Repetition of the experiment in a phosphate buffer (*p*H 4.9) led to similar results.

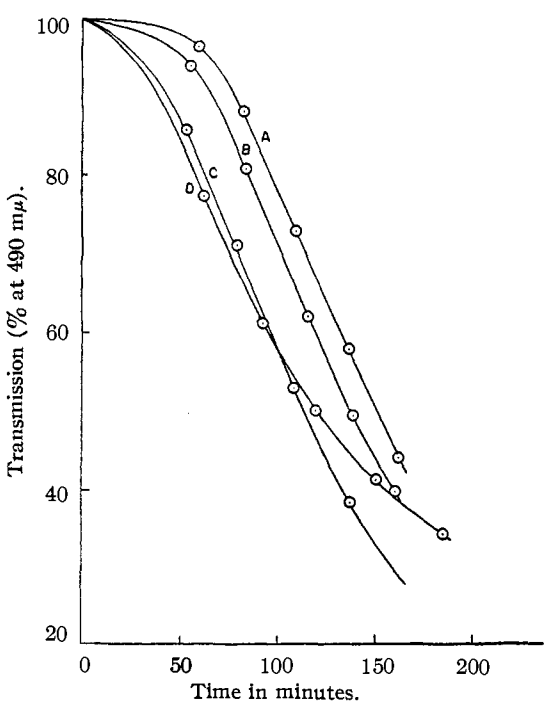



Fig. 1.—Effect of gradual substitution of 2-furaldehyde for D-xylose on the rate of coloration in the sugar solution: curve A, equimolar (0.250 *M*) solution of D-xylose and glycine at reflux temperature; B, 10% of D-xylose in A substituted by 2-furaldehyde; C, 50% substituted; D, 100% substituted. Lumetron (Model 402 E) photoelectric colorimeter. Essentially similar results were obtained by repeating this in a phosphate buffer at *p*H 4.9.

The rapid development of color with glycine in a 2-furaldehyde solution of low concentration was demonstrated by studying the coloration in such a solution over-layered with toluene. Since 2-furaldehyde was found to be more soluble in toluene than in water, this compound would be largely in the toluene layer, but as soon as its concentration in the water solution decreased, more 2-furaldehyde would enter from the toluene. This should resemble in some degree the "browning" solution, in which 2-furaldehyde is present only in small amount. Its removal by the formation of color could prompt a further conversion of the sugar into this furan compound. The result of heating and stirring continuously an aqueous solution of 2-furaldehyde (0.125 *M*) and glycine (1.250 *M*) which was covered with an equal volume of toluene solution is shown in Fig. 2 (curve A). For comparison, aqueous solutions of D-xylose (0.125 *M*) and glycine (1.250 *M*) which were covered with toluene were heated with and without stirring (Fig. 2, curves B and C). A large excess of glycine was used here to minimize the difference in total concentration of the

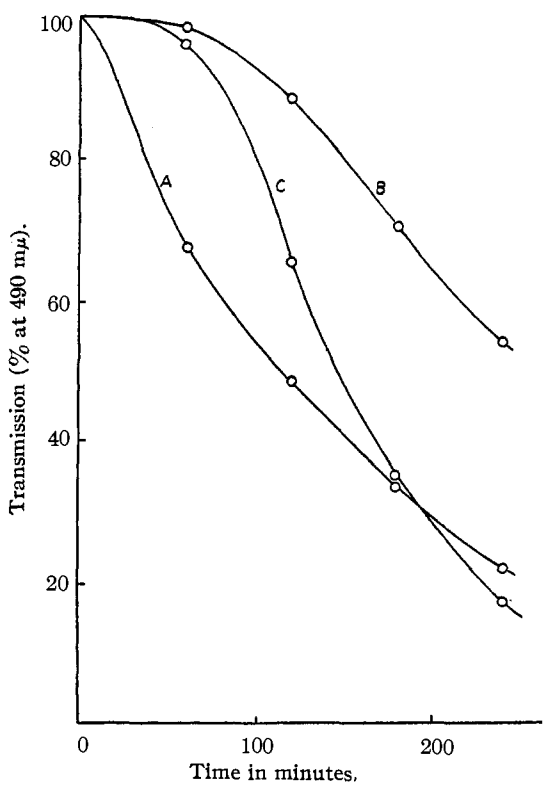



Fig. 2.—Rates of coloration in D-xylose and in 2-furaldehyde solutions covered with toluene: curve A, an aqueous solution of 2-furaldehyde (0.125 *M*) and glycine (1.250 *M*) covered with an equal volume of toluene, stirred and heated at 90–92°; B, the 2-furaldehyde in A was substituted by D-xylose; C, same as B without stirring. Lumetron (Model 402 E) photoelectric colorimeter. The distribution coefficient of 2-furaldehyde was found to be *ca.* 6:1 (toluene:water).

TABLE I

COLORED[a] MATERIALS PREPARED FROM D-XYLOSE AND 2-FURALDEHYDE

| Product[b] | G. in 200 ml. of water: D-Xylose (X) | Glycine (G) | Molar ratio, X:G | Temp., °C. | Time of heating, hr. | Isolation method[c] | Yield, g.[d] | Analyses, %[e] C | H | O[f] | N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3.7 | 18.7 | 1:10 | 95 | 23 | A | 0.7 | 54.4[g] | 6.40[g] | 32.15 | 7.05 |
| 2 | 30.0 | 15.0 | 1:1 | 95 | 50 | A | 0.3 | 55.2[g] | 6.89[g] | 32.13 | 5.78 |
| 3 | 7.5 | 3.8 | 1:1 | Reflux | 40 | C | 1.3 | 57.3 | 6.48 | 30.22 | 6.00 |
| 4 | 30.0 | 15.0 | 1:1 | 95 | 50 | C | 13.0 | 57.9 | 6.65 | 29.65 | 5.80 |
| 5 | 3.7 | 18.7 | 1:10 | 95 | 90 | B | 2.5 | 58.0[g] | 6.86[g] | 28.29 | 6.85 |
| | 2-Furaldehyde (F) | | F:G | | | | | | | | |
| 6 | 2.4 | 18.7 | 1:10 | 95 | 90 | E | 0.8 | 59.5 | 5.86 | 29.99 | 4.65 |
| 7 | 2.4 | 18.7 | 1:10 | 95 | 20 | A | .5 | 62.4[g] | 4.55[g] | 29.12 | 3.93 |
| 8 | 2.4 | 18.7 | 1:10 | 95 | 90 | D | .4 | 63.8 | 5.29 | 27.10 | 3.81 |
| 9 | 2.4 | 18.7 | 1:10 | 95 | 20 | D | .2 | 64.4 | 5.19 | 26.89 | 3.52 |
| 10 | 19.8 | 15.0 | 1:1 | 95 | 55 | C | 10.0 | 65.6 | 4.86 | 26.43 | 3.11 |
| 11 | 4.8 | 3.8 | 1:1 | Reflux | 40 | C | 1.0 | 66.7 | 4.99 | 25.22 | 3.09 |

[a] Brown. [b] All were very soluble in sodium hydroxide except 3, 4 and 10; products 1, 2, 5 and 6 gave a positive Folin [O. Folin and Vintila Ciocalteu, *J. Biol. Chem.*, **73**, 627 (1927)] phenol test. [c] Methods of isolation of the colored materials: A, precipitated from dialyzed solution with ethanol; B, precipitated from dialyzed solution with dioxane; C, collected by filtration; D, collected by centrifuging dialyzed solution; E, precipitated from the dialyzed and centrifuged solution with dioxane. See also experimental portion. All the products isolated were washed successively with ethanol, acetone and ether. [d] Technical yield expressed on the basis of the air-dried products. [e] Analytical samples were prepared by drying over phosphorus pentoxide at 56° and 1 mm. pressure for 20 hr. Microanalyses by Mrs. Elizabeth H. Klotz of this Laboratory. Each value represents the average of two determinations. [f] By difference. [g] About 0.1–1% residue left in the combustion boat.

reactants in the aqueous solutions. The results may be explained satisfactorily on the basis of the "furfural intermediate" theory. The immediate availability of 2-furaldehyde caused an earlier "browning" of the 2-furaldehyde solution (curve A), while the induction period required for the conversion of a certain amount of D-xylose into 2-furaldehyde resulted in a slow development of color in the sugar solution (curves B and C). Furthermore, due to the rapid removal of a part of the 2-furaldehyde formed, the D-xylose solution, stirred continuously with toluene, turned brown (curve B) at a slower rate than that without stirring (curve C). The retardation of color formation by stirring with toluene recalls the observations made by Rice and Kertesz[7] and by Stadtman and co-workers.[8] The latter group of workers has reported that continuous extraction of apricot concentrates with ethyl acetate may inhibit the "browning." Along with other carbonyl compounds, 2-furaldehyde has been found by these authors in the ethyl acetate extract. A similar result has been reported by the former group of workers who observed the inhibition of color formation in a D-xylose solution containing glycine by extracting continuously with benzene.

The above results merely indicate the possibility that 2-furaldehyde may be an important color precursor in the browning reaction. That the evidence is not quite definitive is apparent from the fact that the essential color precursor extracted by toluene may not be 2-furaldehyde and that the concentration of the 2-furaldehyde in the aqueous solution covered with toluene is probably thousands of times higher than that in the D-xylose–glycine solution. It may still be possible that the color formed from the decomposition of 2-furaldehyde in the browning reaction is not so significant as demonstrated in the artificial system.

To secure more information concerning the relationship of 2-furaldehyde to the browning reaction, effort was finally directed to a comparison of the colored products prepared under varied conditions from both D-xylose–glycine and 2-furaldehyde–glycine. The data of Table I summarize the reaction conditions, methods of isolation, yields and elementary analyses of the products. Products 1 and 7, 3 and 11, 4 and 10, likewise 5 and 6, are comparable in respect to reaction conditions and methods of isolation. The chemical analyses show that, although the products derived from the same reactants under different experimental conditions varied in their composition, those from 2-furaldehyde gave, in general, higher carbon and lower hydrogen and nitrogen analyses. Interestingly, one fraction (product 6 in Table I, water-soluble) formed by heating the furan compound in the presence of an excess of glycine, gave analyses approaching those of the products, especially 5, obtained from D-xylose under similar reaction conditions. This finding, which is in accord with the supposition that the 2-furaldehyde formed in small amount in the browning solution would be exposed to reaction with an excess of glycine, appears to support the "furfural intermediate" theory. The

(7) R. G. Rice and Z. I. Kertesz, Report to the Quartermaster Food and Container Institute for the Armed Forces, July to August, 1947.

(8) Victoria A. Haas, E. R. Stadtman, F. H. Stadtman and G. MacKinney, THIS JOURNAL, **70**, 3576 (1948).

chemical analyses obtained on products 10 and 11 may be attributed to a different type of decomposition occurring when 2-furaldehyde is present in abundance. Comparison of the data for products 1 and 5 with those for 7 and 6 demonstrates the fact that longer heating of glycine solutions with D-xylose yields products containing higher carbon values as a result of more extensive dehydration whereas longer heating of glycine with 2-furaldehyde gives products containing lower carbon and higher nitrogen values as a result of what is probably a more extensive hydration and nitrogen incorporation, likely involving ring opening.

The products prepared both from D-xylose and 2-furaldehyde are brown in color. All are very soluble in sodium hydroxide with the exception of products 3, 4 and 10. Products 1, 2, 5 and 6 exhibited a positive Folin phenol test.

Ultraviolet and visible absorption spectra of those products soluble in alkali were determined.

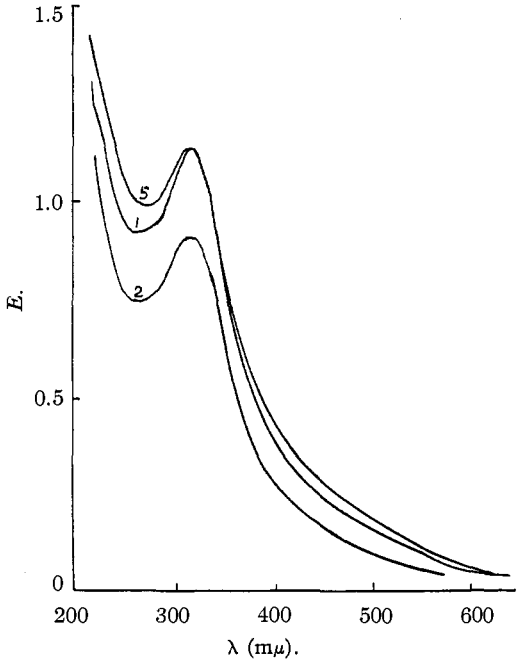



Fig. 3.—Ultraviolet and visible absorption spectra of the colored products from D-xylose (*cf.* Table I). Measured in 0.1 *N* NaOH (4 mg./100 ml. of NaOH). Beckman (model DU) spectrophotometer, 1 cm. cell.

The products from D-xylose (Fig. 3) invariably showed a band at 320 mμ, while those from 2-furaldehyde (Fig. 4) have a broad band in the region 280–320 mμ which undoubtedly consists of two or more component bands. Previous data[1] have demonstrated that neither component alone produces significant coloration under comparable conditions. D-Xylose slowly produces small amounts of 2-furaldehyde. D-Xylose and glycine alone exhibit only end absorption in the ultraviolet while the ultraviolet absorption spectrum of 2-furaldehyde is characteristic and shows major and minor maxima at 277 and 227 mμ, respectively.

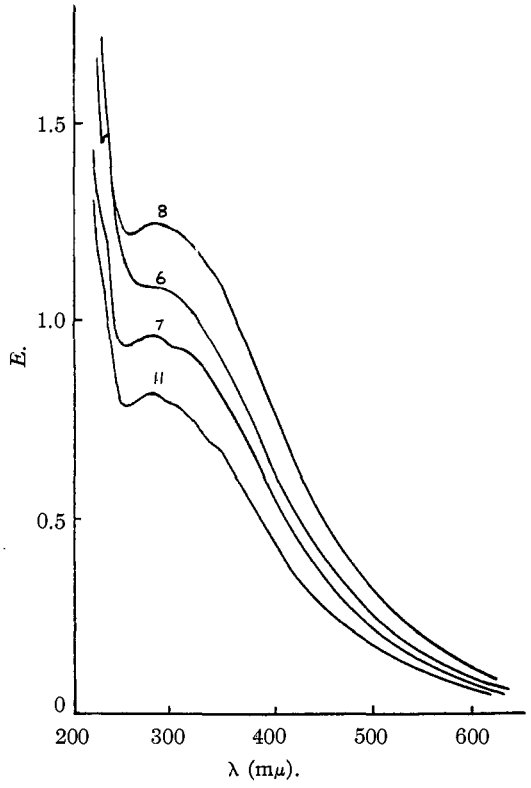



Fig. 4.—Ultraviolet and visible absorption spectra of the colored products from 2-furaldehyde (*cf.* Table I). Measured in 0.1 *N* NaOH (4 mg./100 ml. of NaOH). Beckman (Model DU) spectrophotometer, 1 cm. cell.

Infrared absorption spectra measurements[9] were carried out on several colored products. The insolubility of these substances in most organic solvents made it necessary to make the measurements in a paraffin hydrocarbon (Nujol) suspension. The absorption spectra (Fig. 5) of products 4–7 and 10 are characterized by an absorption band at 6.2 μ. A second band occurs at 5.9 μ in the spectra of products 6, 7 and 10—all from 2-furaldehyde. Absorption bands in the region 5.9–6.2 μ may be attributable to the motions of doubly bonded atoms.

To extend our comparative study, we investigated the behavior of the colored products toward bromine, employing the procedure of McIlhiney[10] which evaluates substitutive and additive bromine in one experiment. This method has been applied previously to the study of "humins" by Fuchs and Leopold[11] and to "melanoidins" by Enders and Theis.[12] The results of treating

(9) The infrared absorption spectra measurements were made by Messrs. Donald Timma and Harold Greenhouse of this Laboratory.

(10) P. G. McIlhiney, THIS JOURNAL, **21**, 1084 (1899).

(11) W. Fuchs and H. Leopold, *Brennstoff-Chem.*, **8**, 101 (1927).

(12) C. Enders and K. Theis, *ibid.*, **19**, 402 (1938).

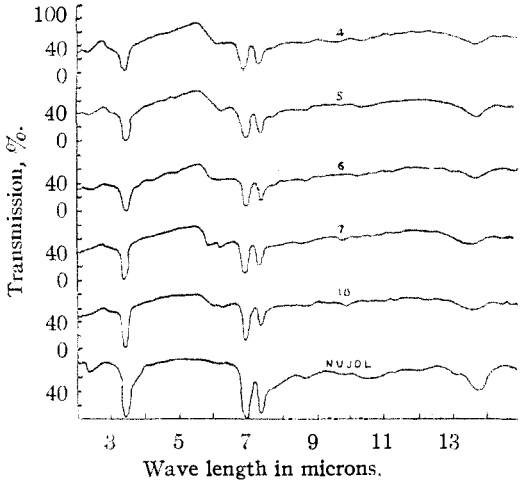



Fig. 5.—Infrared absorption[9] spectra of the colored products prepared both from D-xylose and from 2-furaldehyde (*cf.* Table I). Measured in a paraffin hydrocarbon (Nujol) suspension (100 mg./ml. of Nujol) using a cell with a thickness of 0.02 mm. The Nujol curve given for comparison was measured in a cell of 0.05 mm. length. Beckman IR-2 infrared spectrophotometer.

products 4–6 and 10 according to this procedure are shown in Table II. The values for total

TABLE II

BROMINATION STUDIES ON ISOLATED COLORED PRODUCTS

| Product[a] | Molar ratio, D-xylose: glycine | Procedure of McIlhiney[10] as modified by Fuchs and Leopold[11] Bromine consumed, mg. per 250-mg. sample Total | As HBr | As additive (by diff.) | Procedure of Fuchs[13] Bromine, % Cleavable | Residual[b] |
|---|---|---|---|---|---|---|
| 4 | 1:1 | 250 | 172 | 78 | 34.8 | 7.29 |
| 5 | 1:10 | 170 | 122 | 48 | 39.1 | 7.31 |
| | 2-Furaldehyde: glycine | | | | | |
| 10 | 1:1 | 386 | 252 | 134 | 29.0 | 17.0 |
| 6 | 1:10 | 200 | 136 | 64 | 33.1 | 8.52 |

[a] See Table I. [b] In the products treated with calcium acetate. Determinations by the Clark Microanalytical Laboratory, Urbana, Illinois.

bromine consumed for products 5 and 6 are close, while that of 4 is higher and that of 10 is highest. The bromine consumed may be substitutive or additive in nature. The bromine used for substitution may be calculated from the second titration data which represent the bromine present as hydrogen bromide, as it is understood that, with the replacement of one atom of hydrogen in the molecule by bromine, one atom of bromine is also consumed by combining with the replaced hydrogen to form one molecule of hydrogen bromide. The values of bromine present as hydrogen bromide are abnormally high in all four determinations. Twice the values, which represent the bromine used for substitution, exceed the total bromine consumed. A high substituted bromine value has previously been reported by Enders and Theis[12] in their study of "melanoidins." These authors attribute the abnormality to possible secondary reactions occurring during titration. The data of Table II show that products 5 and 6 are also similar in their determined proportion of "substitutive" and "additive" bromine. Although these results reveal no part of the intimate structures of the colored products, the resemblance of the titration data from products 5 and 6 may suggest their close relationship in structure, as it is not improbable that the secondary reactions may arise from a common cause. The values obtained by McIlhiney's method, while having little absolute significance, are of importance in these comparative studies and are in relative agreement with those obtained by the Fuchs procedure described below.

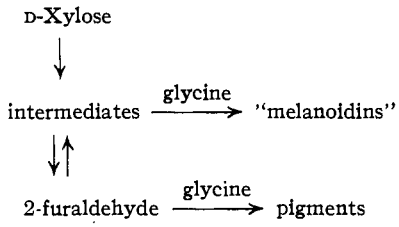
A second method of bromination employed for the present comparative study consisted in the bromination of the substance in carbon tetrachloride suspension and subsequent treatment with calcium acetate solution. This method has been used by Fuchs[13] to study, comparatively, cellulose, lignin, wood and coal, and later has been extended by Enders and Theis[12] to "melanoidins." The latter authors ascribe the bromine unattacked by the acetate solution to that attached to structures which are aromatic in nature. Products 4–6 and 10 were brominated by following the procedure of Fuchs. The brominated products were found to decompose slowly, even at room temperature, with evolution of hydrogen bromide. Therefore no attempt was made to determine the total bromine present in these products; the residual bromine found after treatment of the brominated products with calcium acetate was determined instead and the bromine removed by the acetate as bromide was assayed by titration with silver nitrate. Results of this study are shown in Table II. It can be seen that the data obtained on product 6 are quite similar to those found on the products from D-xylose (4 and 5). The brominated product 10 contains more bromine unremovable by treatment with calcium acetate.

The deductions from the bromination experiments are in accord with those made in the study of the elementary analyses. Product 6, formed from 2-furaldehyde under conditions which resemble roughly the browning reaction, gave analyses and bromination values which are similar to those of the products from D-xylose, indicative of a structural resemblance between them.

Our data show that the nature of the pigment from either the D-xylose–glycine or the 2-furaldehyde–glycine systems is a function of the reaction conditions. The products from the two systems approach each other in properties when the reaction conditions become more similar,

(13) W. Fuchs, *Brennstoff-Chem.*, **9**, 348 (1928).

as when 2-furaldehyde is reacted with a large excess of glycine. 2-Furaldehyde is undoubtedly a member of a complex system of the type shown




It is probable that the small amount of 2-furaldehyde present in the D-xylose–glycine system represents a by-product which may form pigmented products of its own type. It may also react by ring-opening to form intermediates in common with D-xylose and from these would be obtained "melanoidins" of similar structure. Such a view would be in accordance with the work of Akabori.[4e] For a hexose, as D-glucose, 5-(hydroxymethyl)-2-furaldehyde would play a role entirely analogous to 2-furaldehyde.[14]

## Experimental

**Materials.**—The colorless 2-furaldehyde required in this comparative study was obtained from a commercial sample (Baker Chemical Co.) that had been freshly twice-redistilled under diminished pressure. The D-xylose used was of C. P. grade (Pfanstiehl Chemical Co.).

**Preparation of Colored Products.**—Three general procedures were used.

**Procedure 1.**—A mixture of 3.7 g. (0.025 mole) of D-xylose (or 2.4 g. of 2-furaldehyde), 18.7 g. (0.250 mole) of glycine and 200 ml. of water was heated at 95° for a designated time. The contents were transferred into a cellophane bag (made of Osmosis Membrane 70160-B, a product of the Central Scientific Co., Chicago, Ill.) and dialyzed against distilled water until the solution in the bag gave negative ninhydrin and Molisch tests (three days). The dialyzed solution was concentrated (in the case of 2-furaldehyde, the solution was centrifuged before concentration to remove the water-insoluble colored product; insoluble products 8 and 9 of Table I were so separated from the soluble products 6 and 7, respectively) under reduced pressure to about one-third of the original volume and coagulated by adding five times the volume of dioxane (ethanol was used in several experiments; *cf.* Table I). The precipitate formed was collected by centrifuging, washed successively with ethanol, acetone and ether, and finally dried in the air (products 1 and 5–7 in Table I).

**Procedure 2.**—Thirty grams (0.20 mole) of D-xylose (or 19.8 g. of 2-furaldehyde), 15.0 g. (0.20 mole) of glycine and 200 ml. of water were mixed and heated at 95° for two days (*cf.* Table I). The reaction mixture was filtered under suction and the water-insoluble colored product washed with water, ethanol, acetone and ether (products 4 and 10 in Table I). The filtrate, in the case of D-xylose, was highly colored and was dialyzed and coagulated with ethanol as in procedure 1 (product 2 in Table I).

**Procedure 3.**—A solution containing 7.5 g. (0.05 mole) of D-xylose (or 4.8 g. of 2-furaldehyde), 3.8 g. (0.05 mole) of glycine and 200 ml. of water was heated under reflux for forty hours. The colored material formed was insoluble in water and was separated from the starting materials by filtration as in procedure 2 (products 3 and 11 in Table I).

(14) M. L. Wolfrom, R. D. Schuetz and L. F. Cavalieri, THIS JOURNAL, **70**, 514 (1948).

## Summary

1. A comparative study under definitive conditions has been made of the coloration of D-xylose–glycine and 2-furaldehyde–glycine solutions. The results indicate that 2-furaldehyde can be a color precursor in the "browning" of D-xylose solutions.

2. Brown materials have been prepared, under a variety of conditions, from glycine and D-xylose and compared with those formed from glycine and 2-furaldehyde. Their elementary composition, absorption spectra (ultraviolet, visible and infrared) and behavior toward bromine have been studied and compared.

3. The results show that the products obtained from 2-furaldehyde approach in properties those from D-xylose as their conditions of formation approach those of the latter.

COLUMBUS, OHIO RECEIVED APRIL 3, 1950

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[CONTRIBUTION FROM THE INSTITUTE FOR ENZYME RESEARCH, UNIVERSITY OF WISCONSIN, AND THE TEXAS RESEARCH FOUNDATION]

# Chemical Oxidation of Organic Acids. I. Some Observations on the Oxidation of Propionate by Alkaline Permanganate[1,2]

BY HENRY R. MAHLER AND AMMARETTE ROBERTS

In 1941 and 1942, Nahinsky, Ruben and coworkers published two papers[3] dealing with the oxidation of propionate by alkaline permanganate. They elucidated the mechanism of this reaction by means of $C^{11}$, a radioactive isotope of carbon of short half-life, and the only radiocarbon tracer then available for chemical experimentation Employing propionate-1-$C^{11}$, their most remarkable results were those obtained in a strongly alkaline medium. Under those conditions, the oxalate formed according to the equation

$$CH_3CH_2C^*O_2^- + 4MnO_4^- = C_2{}^*O_4^- + C^*O_3^- + 4MnO_2 + 2H_2O + OH^-$$

incorporated the bulk of the radioactivity, *i. e.*, 87%.

We have undertaken to re-investigate these experiments utilizing propionate-1-$C^{14}$. Two related aims prompted us to this endeavor: the

(1) The experimental work reported in this communication was carried out at the Texas Research Foundation, Renner, Texas.

(2) Presented before the Division of Physical and Inorganic Chemistry at the 117th meeting of the American Chemical Society at Detroit, Michigan, April 17, 1950.

(3) P. Nahinsky and C. N. Ruben, THIS JOURNAL, **63**, 2275 (1941); P. Nahinsky, C. N. Rice, S. Ruben and M. D. Kamen, *ibid.*, **64**, 2299 (1942).