This is due to the increased rate of conversion through the intermediates to 5-(hydroxymethyl)-2-furaldehyde. This is shown by curves 1 in Figs. 1, 3, 4, and curve 3 in Fig. 4.

To explain these absorption curves we can postulate that D-glucose, represented by I (other anomers and ring structures than I are possible), is transformed first into II or its aldehydrol. The intermediate III then results from II by loss of water, producing a conjugated enal. Evidence for III is found in both the region and the magnitude of absorption shown in curve 4, Fig. 1. Evans and Gillam[8] have demonstrated that α,β-unsaturated aldehydes (R—CH=CR'CHO) show high absorption in the general region of 230 mμ. In this intermediate (III), R is $(CHOH)_2CH_2OH$ and R' is the hydroxyl group. A similar type of intermediate was shown to be present in the conversion of 2,3,4,6-tetramethyl-D-1,2-glucoseen into 5-(methoxymethyl)-2-furaldehyde[9] in acid solution. There the 6-methyl ether of the conjugated enonal VII was established as an intermediate in this conversion by isolation as its crystalline phenylosazone.

The postulated intermediate III could produce IV by cyclic dehydration. The 5-(hydroxymethyl)-2-furaldehyde (V) could result from IV by a final dehydration producing a third double bond in conjugation with the two already present. The mechanism proposed here for the conversion of D-glucose to 5-(hydroxymethyl)-2-furaldehyde through the intermediates II, III and IV, is based upon that originally suggested by Hurd and Isenhour,[10] who, however, offered no experimental evidence to support it. The route through the intermediates VI, VII and VIII receives experimental support in the work of Wolfrom, Wallace and Metcalf.[9] The dehydrations postulated are the well-established ones of an hydroxyl group in the β position to a carbonyl. The resulting dehydrated products are α,β-unsaturated carbonyl compounds and we offer spectroscopic evidence for such intermediates.

(8) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

(9) M. L. Wolfrom, E. G. Wallace and E. A. Metcalf, THIS JOURNAL, **64**, 265 (1942).

(10) C. D. Hurd and L. L. Isenhour, *ibid.*, **54**, 317 (1932).

Experimental

Materials.—The D-glucose used in this work was a very pure grade of the monohydrate.[11] It was crystallized from triply distilled water.

Absorption Measurements.—The D-glucose was weighed into a 500-ml. round-bottom Pyrex flask with a ground glass joint and connected to a reflux condenser. The solvent was added, and in the experiments where hydrochloric acid was used, the *p*H was adjusted at this point. The aqueous D-glucose solutions were refluxed by means of a Glas-col type electric heater. At definite time intervals aliquots were removed, cooled rapidly to room temperature, and immediately read in the spectrophotometer.

Acknowledgment.—The assistance of Clare B. Spitler and Doris K. Cavalieri is gratefully acknowledged.

Summary

The course of the formation of 5-(hydroxymethyl)-2-furaldehyde from D-glucose in the absence and presence of hydrochloric acid has been followed by ultraviolet absorption spectra measurements and on the basis of this, structures are proposed for several intermediates.

COLUMBUS, OHIO RECEIVED[12] OCTOBER 4, 1947

(11) We are indebted for this material to Dr. S. M. Cantor of the Corn Products Refining Co., Argo, Illinois.

(12) The original manuscript with all essential data was received on September 23, 1946.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF CORN PRODUCTS REFINING COMPANY]

The Role of 5-(Hydroxymethyl)-furfural in the Discoloration of Sugar Solutions

BY BHAGAT SINGH,[1] G. R. DEAN AND SIDNEY M. CANTOR[2]

The acid catalyzed hydrolysis of starch at elevated temperature for the commercial production of D-glucose results in the formation of considerable coloring matter.[3] Under the same conditions of temperature and concentration the decomposition of pentoses to yield furfural and of hexoses to yield 5-(hydroxymethyl)-furfural (hereafter abbreviated in most cases to HMF) and levulinic and formic acids are well known phenomena. Various hypotheses have been advanced for the mechanism of color formation. Porst[4] believed that the color change might be due to furfural derived from the sugars and to traces of phenols and other derivatives which come from the decomposition of the small amount of protein contained in the starch. The possible participation of furfural and levulinic acid to form coumarone has been suggested as the cause of "humins" and color by Meunier.[5] The

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(3) During the course of this investigation this laboratory became associated with the coöperative project on non-enzymatic browning sponsored by the Committee on Food Research of the Quartermaster Corps of the U. S. Army. The relationship between this work and the general problem of color development in sugar containing systems was called to the attention of other laboratories in the project and a portion of the data was presented in the symposium on Non-Enzymatic Browning of the Division of Food and Agricultural Chemistry at the Chicago Meeting of the American Chemical Society in September, 1946, in an introductory paper entitled, "A Review of Some Sugar Reactions which Give Rise to Color," by Sidney M. Cantor and Charles D. Hurd.

(4) Porst, Orig. Com. 8th Intern. Congr. Appl. Chem., **13**, 205 (1912).

(5) Meunier, *Chemie et Industrie*, Special No. 583, February (1929).

literature on this subject has been reviewed recently.[6] Experience in this Laboratory had indicated that the major portion of the coloring matter arises from decomposition of the glucose molecule and that HMF is the precursor of coloring matter in starch hydrolyzates. It has been postulated that HMF polymerizes to give colored products of varying degrees of solubility.[7] The HMF molecule, arising from the dehydration of glucose, has a triene structure and shows absorption in the ultraviolet. It seems reasonable to suppose that polymerization (condensation) of this molecule might give rise to a molecule possessing the requisite number of conjugated double bonds for the selective absorption in the visible region. Modern concepts concerning the color of linear conjugated systems show that the presence of six to eight double bonds in a molecule gives rise to color.[8] This work was undertaken to make a quantitative spectrophotometric[9] study of (1) the destruction of glucose as a function of concentration, time and *p*H value of the system, (2) the role of HMF and levulinic acid in color formation, and (3) the possibility of condensation between glucose and amino acids under conditions employed for the commercial hydrolysis of starch, and its relation to the total color of the system.

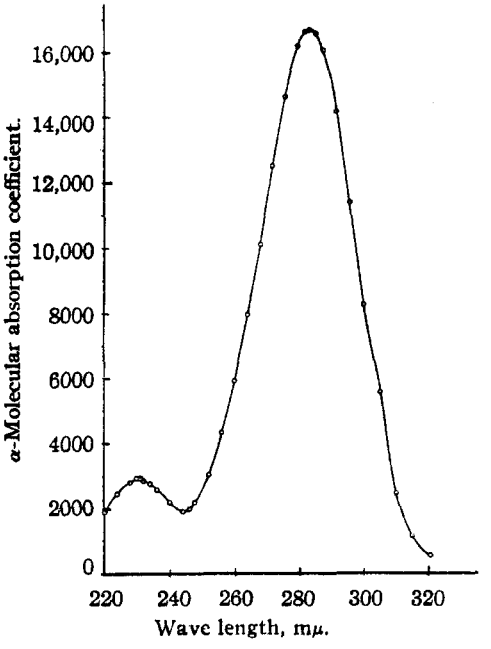

Fig. 1.—The molecular absorption coefficient of 5-(hydroxymethyl)-furfural.

(6) Hanahan, Thesis (M.S. in Chemistry), University of Illinois, 1942.

(7) Tanaka, "Sexagint Y. Osaka Chem. Inst. Dept. Science, Kyoto Imp. Univ.," 1927; 13-26; Blanksma and Egmond, *Rec. trav. chim.*, **65**, 309 (1946).

(8) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939); Brooker, "Nuclear and Theoretical Organic Chemistry," Interscience Publishers, New York, N. Y., 1943, p. 89.

(9) The polarographic determination of 5-(hydroxymethyl)-furfural is the subject of a forthcoming paper.

Experimental

Dextrose.—Bureau of Standards D-**glucose** no. 41 or a sample of equivalent purity,[10] was used in all the experiments. Absence of absorption in the ultraviolet was used as a criterion of purity.

5-(Hydroxymethyl)-furfural.—HMF was prepared from sucrose by using the procedure of Middendorp.[11] The light yellow material was twice distilled under high vacuum (m.p. 31.5–32.0°, uncor.).

Levulinic Acid.—The white, crystalline solid (m.p. 32°, uncor.) was obtained after four recrystallizations of technical grade material.

Leucine (C. P. Pfanstiehl).—A Beckman Spectrophotometer (model DU) was used in this work for the examination of the ultraviolet and the visible spectra. The instrument was calibrated by using purified potassium chromate as an absorption standard and the performance compared with that recorded in the literature.[12] High temperature experiments were conducted in sealed tantalum bombs of approximately 20 ml. capacity. These bombs are test-tube shaped and are equipped with tantalum lined closures which are sealed by means of a screw and nut collar device. They were fabricated to specification by the Fansteel Metallurgical Corp.

All solutions were made up using doubly distilled water.

The results are given in optical density (log I_0/I) *versus* wave length in millimicrons (mμ) except in cases where pure compounds, such as HMF and levulinic acid, were examined. For HMF and levulinic acid the molecular absorption coefficient, α, was calculated from Beer's law. Two centimeter fused silica cells were used for the ultraviolet region and one centimeter glass cells for the visible region.

All HMF values were determined in dilutions that gave an optical density between 0.5 and 1.0 at 284 mμ (slit width = 0.34 mm.). Color readings were obtained by integration of transmission curves throughout the visible spectrum range.

An arbitrary unit of color was used equal to 2.5 sq. in. of area under the curve.

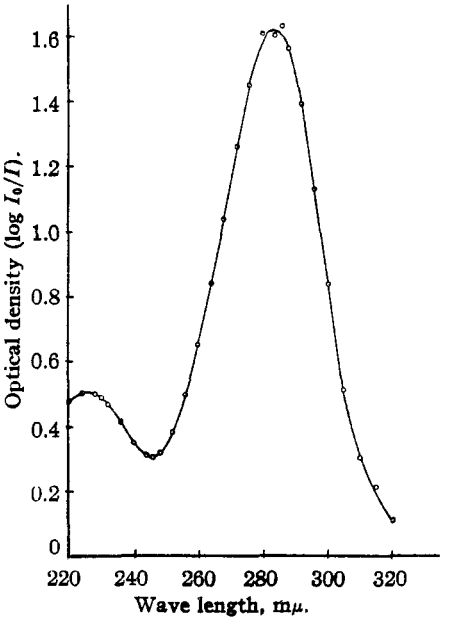

Fig. 2.—The ultraviolet spectrum of neutralized starch hydrolyzate: *p*H, 4.3; concn. 18%; diluted 1:100; 2-cm. cells.

(10) "Polarimetry, Saccharimetry and the Sugars," Circular C 440, National Bureau of Standards, p. 390.

(11) Middendorp, *Rec. trav. chim.*, **38**, 16 (1919).

(12) Hogness, Scheile and Sidwell, *J. Phys. Chem.*, **41**, 379 (1937).

Results

The absorption spectrum of pure HMF is shown in Fig. 1 and that of a dilute solution of a starch hydrolyzate in Fig. 2. The HMF spectrum shows two maxima, a major peak at 284 mμ and a minor one at 230 mμ.[13]

The molecular absorption coefficients compared with similar constants from other researches are shown in Table I.

TABLE I

MOLECULAR ABSORPTION COEFFICIENT OF 5-(HYDROXYMETHYL)-FURFURAL

Source	λ(max), mμ	(Liters mole^{-1} cm.$^{-1}$)	M. p., °C.
Scallet and Gardner[a]	283	14,330	
This paper	230, 284	3080, 16,700	31.5–32.0 (uncor.)
Schuetz and Wolfrom[b]	285	16,500	33.3–33.5 (cor.)

[a] Scallet and Gardner, THIS JOURNAL, 67, 1934 (1945).
[b] Schuetz and Wolfrom, *ibid.*, 70, 514 (1948).

The band around 280 mμ is usually taken as evidence for the carbonyl group; the intensity of this transition is determined partly by conjugation.

An estimate of the extent of destruction products in starch hydrolyzates was obtained by hydrolysis of a suspension of defatted corn starch. Conditions for hydrolysis were: starch concentration, 17.0% by weight; temperature, 145°; time, thirty minutes; acid concentration, 0.03 *N* HCl. After thirty minutes of reaction time 0.068% HMF (g./100 g. solution) was present and the color of the solution was 5.6 units. The final solution contained 18.5% of dry solids (approx. 16.7% D-glucose).

The ultraviolet spectra of heated 16% glucose solutions (0.03 *N* HCl, 145°) for the first ten minutes are shown in Figs. 3 and 4. There is evidence first of a band around 280 mμ and later a band around 230 mμ appears. The data are summarized in Table II.

TABLE II

DESTRUCTION OF D-GLUCOSE AS A FUNCTION OF TIME (16% GLUCOSE, 0.03 *N* HCl, 145°)

Time, minutes	Per cent. HMF (g./100 g. solution)	Color (arbitrary units)
2	Evidence for carbonyl groups[a]	No color
4	0.0005	No color
6	.0019	No color
8	.0044	0.3
10	.0075	0.6
12	.0122	1.0
14	.0187	1.5
20	.0332	3.2
30	.0635	5.6

[a] An absorption band around 280 mμ appears.

TABLE III

DESTRUCTION OF D-GLUCOSE AS A FUNCTION OF CONCENTRATION (0.03 *N* HCl, 145°, 30 MINUTES)

Per cent. glucose	Per cent. HMF (g./100 g. solution)	First order rate constant	Color
1	0.0039	1.3×10^{-4}	0.32
5	.0170	1.1×10^{-4}	2.17
10	.0360	1.2×10^{-4}	3.91
16	.0635	1.3×10^{-4}	5.59

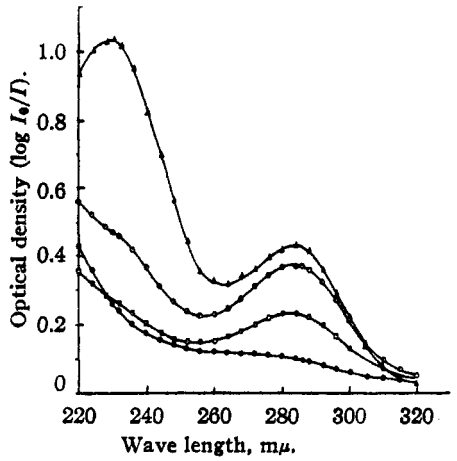

Fig. 3.—Effect of reaction time on the ultraviolet spectra of D-glucose destruction products; conditions: 16% D-glucose, 0.03 *N* HCl, 145.5°; 1% D-glucose, 0.03 *N* HCl, 145.5°; 2 cm. cells: ●, 1 minute, 16% glucose; ⊙, 2 minutes, 16% glucose; △, 2.3 minutes, 16% glucose; ⊡, 2 minutes, 1% glucose.

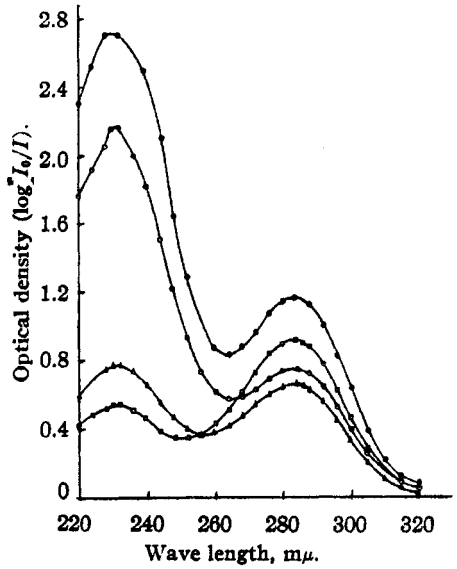

Fig. 4.—Effect of reaction time on the ultraviolet spectra of D-glucose destruction products; conditions: 16% D-glucose, 0.03 *N* HCl, 145.5°; 2 cm. cells: ⊙, 3 minutes; ●, 4 minutes; △, 6 minutes, diluted 1:10; ⊡, 10 minutes diluted 1:25.

The results of destruction of glucose as a function of concentration are summarized in Table III.

A study was made of the stability of the glucose molecule as a function of the *p*H value of the medium. Dilute hydrochloric acid was the only catalyst used for obtaining various *p*H levels. The results are summarized in Table IV and Fig. 5.

A comparative study of destruction as a function of *p*H using sucrose, D-fructose and L-ascorbic acid was also made. The results are given in Table V.

The destruction of pure HMF in water solution was studied at three different concentrations under conditions

(13) The authors are grateful to Prof. R. S. Mulliken of the University of Chicago for pointing out to them that a molecule containing a carbonyl group attached to a linear conjugated chain can have more than one electronic transition, one usually more intense than the other. See also McMurry, *J. Chem. Phys.*, 9, 241 (1941).

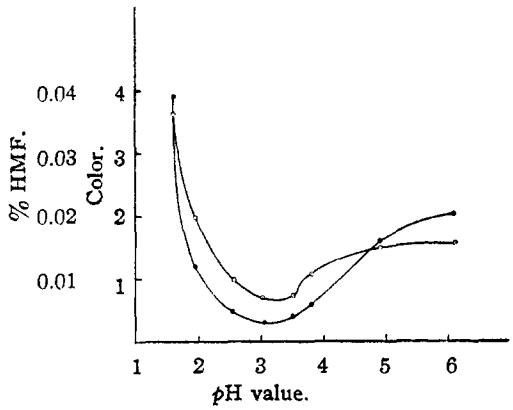

Fig. 5.—Effect of *p*H value on the formation of 5-(hydroxymethyl)-furfural and color in the D-glucose destruction reaction; conditions: 10% D-glucose; 145.5°; 30 minutes: ⊙, % 5-(hydroxymethyl)-furfural; ●, color in arbitrary units.

TABLE IV

DESTRUCTION OF D-GLUCOSE AS A FUNCTION OF *p*H VALUE (10% GLUCOSE, 145°, 30 MINUTES)

*p*H value		Per cent. HMF	
Before heat	After heat	(g./100 g. solution)	Color
1.60	1.60	0.0360	3.91
1.95	1.90	.0196	1.17
2.55	2.60	.0097	0.46
3.00	2.90	.0071	.30
3.53	3.58	.0072	.39
3.80	3.78	.0105	.61
4.92	4.30	.0148	1.56
6.10	4.30	.0156	2.02

TABLE V

DESTRUCTION OF SUCROSE, D-FRUCTOSE AND L-ASCORBIC ACID AS A FUNCTION OF *p*H VALUE (10% SOLUTIONS, 145° 30 MINUTES)

	Sucrose		D-Fructose		L-Ascorbic acid[a]	
*p*H value	Per cent.	HMF Color	Per Cent.	HMF Color	Per cent. furfural	Color
1.7	1.0	11.8	2.5	11.9	2.1	12.1
2.7	0.16	2.9	0.3	4.5		
3.9	.02	1.9	0.08	4.4	2.3[b]	11.4
6.0	.004	1.3	0.07	5.3		

[a] Furfural determined at 278 mμ (slit width 0.35 mμ). Purified furfural was supplied through the courtesy of the Quaker Oats Company. The furfural spectrum coincides with that of HMF except that maximum absorption occurs at 278 mμ (α = 14,600). [b] *p*H value 3.5.

prevalent in commercial starch hydrolysis (0.03*N* HCl, 145°, 30 minutes). The data are shown in Table VI.

TABLE VI

DESTRUCTION OF HMF UNDER HYDROLYSIS CONDITIONS (0.03 *N* HCl, 145°, 30 MINUTES)

Per cent. HMF in solution				
Before destruction	After destruction	Per cent. HMF destroyed	Specific reaction rate *k*, minutes^{-1}[a]	Color (arbitrary units)
0.098	0.075	24.0	0.0089	2.75
.197	.150	24.8	.0091	3.93
.393	.305	22.4	.0085	6.34

[a] *k* = first order reaction rate constant.

The stability of HMF as a function of *p*H value is shown in Table VII.

TABLE VII

STABILITY OF HMF AS A FUNCTION OF *p*H VALUE (0.35% HMF SOLUTION, 145°, 30 MINUTES)

*p*H value			
Before heating	After heating	% HMF decomposed	Color (arbitrary units)
1.75	1.77	24	6.0
2.28	2.28	12	3.8
2.88	2.90	12	2.6
3.95	4.13	0	1.5

A 0.27% water solution of pure levulinic acid (*p*H 3.14) was subjected to hydrolysis conditions (145° for thirty minutes). The ultraviolet spectra before and after heating are shown in Fig. 6.

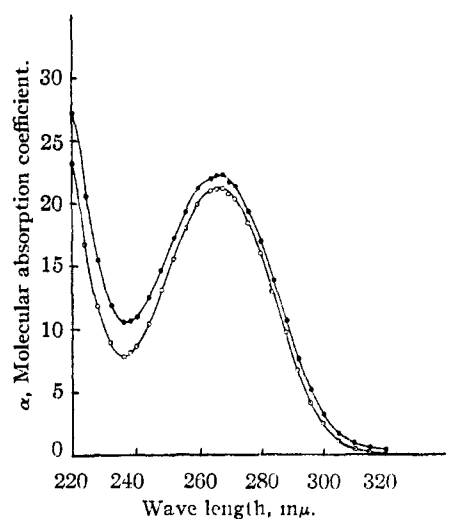

Fig. 6.—The ultraviolet spectrum of levulinic acid, effect of heating: concn., 0.27%; time, 30 minutes; temp., 145.5°; *p*H 3.14: ⊙, before heating; ●, after heating.

To determine the importance of the functional grouping attached to the number one carbon atom in glucose, 10% solutions of glucose and methyl α-D-glucoside were subjected to identical conditions (*p*H 6, 145°, thirty minutes). The results are given in Table VIII and Fig. 7.

TABLE VIII

DESTRUCTION OF GLUCOSE AND METHYL α-D-GLUCOSIDE UNDER HEAT (10% SOLUTIONS, 145°, 30 MINUTES)

	*p*H value			
	Before heat	After heat	% HMF (g./100 g. soln.)	Color
Glucose	6.10	4.30	0.0156	2.0
Methyl α-D-glucoside	6.0	5.95	No evidence	No color

Since starch hydrolyzates contain a small amount of nitrogenous substance (about 0.09% nitrogen on dry substance basis), the possibility of a glucose–(amino acid) condensation product was investigated. Of the two amino acids, glutamic acid and leucine, present in corn gluten in large amounts, leucine, the simpler of the two, was chosen for this study. The ultraviolet spectral data of 10% glucose (*p*H 5) and 10% glucose plus 0.4% leucine (*p*H 6), refluxed for three hours at 100°, are shown in Fig. 8.

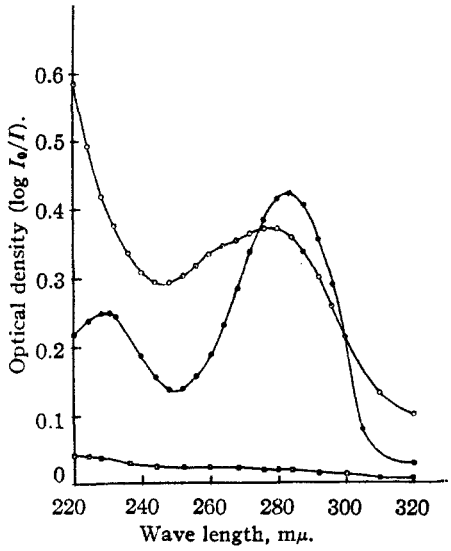

Fig. 7.—Ultraviolet spectra of destruction products of D-glucose and methyl α-D-glucoside; conditions: 145.5°, 30 minutes, *p*H 6 (2-cm. cells): ⊙, 10% methyl α-glucoside after heating; ●, 10% glucose (diluted 1:100) after heating; ⊡, 5% methyl α-glucoside before heating.

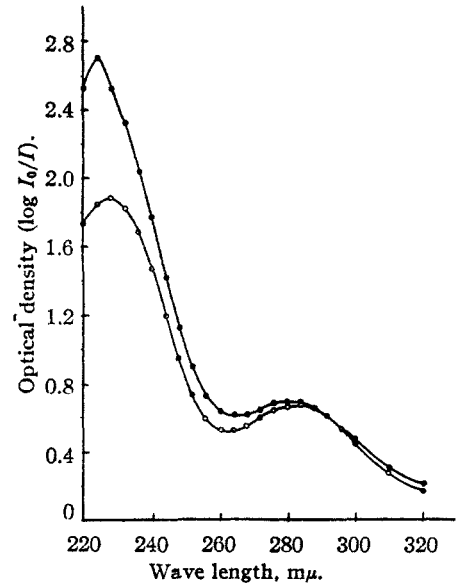

Fig. 8.—Ultraviolet spectra of heated D-glucose solution and D-glucose + leucine solution; conditions, refluxed 3 hours at 100°: ⊙, 10% D-glucose solution, *p*H 5; ●, 10% D-glucose + 0.4% leucine, *p*H 6.

Discussion

The results of hydrolysis of defatted corn starch indicate that a satisfactory definitive mechanism for the extent of the destruction reaction in starch hydrolyzates must be able to account for the presence of HMF (0.068%) and color (5.6 units). Solutions of 16% glucose heated under the same conditions contained 0.064% HMF and 5.6 units of color (Table II). Although the concentration of glucose during starch hydrolysis is variable (increases from zero to 16.7% in thirty minutes), nevertheless it is quite clear that the major portion of HMF and coloring matter in starch hydrolyzates can be accounted for by the destruction of the glucose molecule.

The destruction of glucose as a function of time (Fig. 3) shows first the appearance of a molecule containing the carbonyl group (absorption band around 280 mμ). That this substance is not HMF is apparent from the fact that the minor peak around 230 mμ is missing. The concentration of the substance, calculated as HMF, is 0.00145 g. per liter. HMF solutions of this order of concentration show two peaks. Shortly thereafter the spectrum of an HMF-like molecule appears in the sense that the absorption spectrum shows the two characteristic peaks at 285 mμ and 230 mμ. The changes in the relative heights of these peaks, however, suggest the presence of other substances besides HMF. Presumably, the first reaction is the opening of the pyranose ring and the development of the carbonyl group followed by dehydration. The ultraviolet spectral evidence for the first ten minutes (Fig. 4) shows the presence of HMF alone and then the rapid development of coloring matter. Such an induction period in the formation of coloring matter has been observed in other systems and has been attributed to some autocatalytic mechanism. However, the appearance of HMF during this induction period, together with the demonstration that coloring matter is formed from pure HMF as starting material, support the theory that HMF is the precursor of coloring matter during the acid decomposition of hexose-containing carbohydrates.

Table III shows that the rate of destruction of glucose with formation of HMF is independent of the glucose concentration, indicating a first order mechanism for the reaction. A slight rise in the first order rate constant might be anticipated in more concentrated glucose solutions because of the effect of glucose in increasing the hydrogen ion activity of the solution.[14] The destruction of glucose as a function of *p*H value[15] (Fig. 5) demonstrates the surprising stability of the glucose molecule in the neighborhood of a *p*H value of three where only one-fifth as much HMF and one-thirteenth as much coloring matter is produced as at *p*H 1.6. Ring stability appears to approach a maximum at this point.[16] The results seem to follow the concepts of prototropy developed by Lowry[17] and are reminiscent of the catalytic catenary of Dawson[18] connecting the velocity of a hydrolytic reaction in water with the corresponding *p*H value. Dawson studied the enolization of acetone (followed by rapid substitution of iodine) and the hydrolysis of ethyl acetate. The velocity

(14) Moelwyn-Hughes, *Trans. Faraday Soc.*, **24**, 321 (1928).
(15) Kroner and Kothe, *Ind. Eng. Chem.*, **31**, 248 (1939).
(16) Cantor and Peniston, THIS JOURNAL, **62**, 2113 (1940).
(17) Lowry, *J. Chem. Soc.*, **123**, 828 (1923).
(18) Dawson and Lawson, *ibid.*, 393 (1929).

of mutarotation of glucose[19] as a function of *p*H goes through a similar minimum. With sucrose and D-fructose there is no such minimum and the destruction is much greater than in glucose. As might be anticipated,[20] L-ascorbic acid undergoes extensive destruction under the conditions of the experiment (Table V).

The reaction in HMF solutions of different concentrations under starch hydrolysis conditions to produce coloring matter shows that about the same percentage of HMF is destroyed indicating a first order reaction (Table VI). Teunissen[21] has shown that the rate of decomposition of HMF at 100°, as followed by titration of organic acid decomposition products, follows a first order mechanism. No change occurred in levulinic acid solution on heating except a slight increase in ultraviolet absorption (Fig. 6). This is another demonstration of the fact that HMF is the sole precursor of coloring matter and that levulinic acid plays no part in this process.[22] The importance of the functional grouping on the aldehydic carbon atom of the glucose molecule to the destruction reaction is evident from the data on methyl α-glucoside under identical conditions (Table VIII and Fig. 7). Methyl α-glucoside shows a slight hydrolysis with subsequent destruction of the glucose formed (as evidenced by the development of the carbonyl group (Fig. 7)) while glucose gives rise to HMF and coloring matter.

The possibility of glucose–(amino acid) condensation is rather remote under the specified conditions (Fig. 8). Although the glucose solution containing leucine shows a slightly greater absorption in the far ultraviolet, the two spectra coincide around 280 mμ. Evidently about the same amount of HMF is produced in the two cases. Similarly, under these conditions no difference in HMF or color content could be noted between glucose solutions with or without leucine. Moreover, these experiments indicate no specific catalytic action of leucine in small concentration on formation of either HMF or coloring matter. Any such catalytic action at relatively high concentrations of amino acids is probably due to contribution either to the total ionic strength of the reacting system or to the hydrogen ion activity.

The results of this study suggest the importance of HMF, and consequently of hexoses, to the color problem. A recent report has indicated that furfural or HMF is partially responsible for color development in certain dried fruits.[23] Heretofore considerable attention has been devoted to the reaction between reducing sugars and amino acids or polypeptides (the Maillard[24] reaction) as the cause of browning in various foodstuffs, but this conclusion has been drawn only on the basis of model reactions between amino acids and aldoses and the presence of these substances in foodstuffs. It would now appear that the *p*H value of the food system in addition to the specific constituents of the system is an important factor in determining the course by which colored bodies are formed.

(19) Hudson, THIS JOURNAL **29**, 1572 (1907); Lowry, *Chemistry and Industry*, **42**, 43 (1923).

(20) Seaver and Kertesz, THIS JOURNAL, **68**, 2178 (1946).

(21) Teunissen, *Rec. trav. chim.*, **49**, 784 (1930).

(22) Peniston (unpublished results) showed that even under conditions similar to those employed here (*p*H 1.6) the levulinic acid molecule does not break down.

(23) Stadtman, A. C. S. Meeting, Chicago, Illinois, September, 1946.

Summary

It is shown that a major portion of 5-(hydroxymethyl)-furfural and coloring matter in starch hydrolyzates comes from the destruction of the glucose molecule.

The absorption spectrum of 5-(hydroxymethyl)-furfural has been studied and it is found that there are two peaks, a major one around 284 mμ and a minor one around 230 mμ.

In the destruction of the glucose molecule on heating in an acid medium there is evidence first of an absorption band around 280 mμ and later a band around 230 mμ appears. It is postulated that the first reaction is the opening of the pyranose ring, development of the carbonyl group followed by dehydration. Later, color develops in the solution for which 5-(hydroxymethyl)-furfural is the precursor.

Solutions of different concentrations of 5-(hydroxymethyl)-furfural on heating in an acid medium show development of color and about the same percentage of destruction indicating a first order reaction. Levulinic acid in solution shows no apparent destruction on heating.

The glucose destruction reaction as a function of *p*H goes through a minimum around a *p*H value of 3. No such minima were found for D-fructose and sucrose. The extent of destruction for sucrose and D-fructose as compared with glucose is greater in acid media.

The importance of the functional grouping on the number one carbon atom in glucose is shown by the comparative destruction of glucose and methyl α-glucoside under comparable conditions. Glucose solutions produce 5-(hydroxymethyl)-furfural with consequent color while no destruction takes place in methyl α-glucoside solutions.

No evidence was found for condensation between glucose and leucine under the conditions of this study.

It is suggested as a result of the study that a similar mechanism may be partially responsible for the color which develops in certain natural products containing reducing sugars.

ARGO, ILLINOIS RECEIVED JULY 25, 1947

(24) Maillard, *Compt. rend.*, **154**, 66 (1912); *Ann. chim.*, **5**, 258 (1916).