TABLE I (*Concluded*)

Compound	Mole equivalents of $Pb(OAc)_4$ consumed	Time,[a] hr.	Oxidation product identified
Blank determinations			
1-Propanol	0	168	
2-Propanol	0	168	
Trimethylene glycol	0	72	
Triethylamine	0.5	120	
Triethylamine + 1-propanol	*ca.* 1	120	Diethylamine[b]

[a] Time is approximate since titrations were run at six-hour intervals. [b] Isolated in small yield.

piperidino)-ethanol resulted in the production of piperidine in similar yield. The base was likewise isolated and identified as the picrolonate which melted, with decomposition, at 245-246° (uncor.) and gave no depression of melting-decomposition point when mixed with an authentic sample of piperidine picrolonate. Glyoxal *p*-nitrophenylosazone was also isolated after treatment of the oxidized solution with *p*-nitrophenylhydrazine, just as in the case with 2-diethylaminoethanol. From the oxidation of both 3-diethylamino-1-propanol and 4-diethylamino-1-butanol, diethylamine—as the picrolonate—was obtained in small yield, as it was from the oxidation of a mixture of triethylamine and 1-propanol.

Summary

1. Aminoalcohols containing contiguous hydroxyl and tertiary amino groups have been found to undergo oxidative cleavage with lead tetraacetate in glacial acetic acid at 60°, with one mole of aminoalcohol requiring approximately one mole of lead tetraacetate.

2. Diethylamine has been isolated and identified as one of the products of lead tetraacetate oxidation of 2-diethylaminoethanol, 1-diethylamino-2-propanol and 1-diethylamino-2-methyl-2-propanol. Piperidine has been isolated from the oxidative cleavage of 2-(1-piperidino)-ethanol. The formation, in the degradation of the two aminoethanols, of glyoxal *p*-nitrophenylosazone indicates that the other product of cleavage of these two compounds is glycolaldehyde.

3. Lead tetraacetate in glacial acetic acid at 60° is evidently not specific for the 1,2-aminoalcohols, since 3-diethylamino-1-propanol, 4-diethylamino-1-butanol and a mixture of triethylamine and 1-propanol were oxidized, although more slowly.

4. A possible mechanism for the oxidation of the tertiary 1,2-hydroxyamines has been proposed on the basis of the products isolated.

URBANA, ILLINOIS RECEIVED OCTOBER 2, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Changes in Autoclaved Glucose

BY D. T. ENGLIS AND DONALD J. HANAHAN

As one phase of a study of the causes of discoloration of corn sirup, attention was directed to certain changes which take place upon the heating of pure glucose in the presence of small amounts of other substances. Among the factors which are said to be responsible for the discoloration of commercial glucose, or corn sirup, are[1,2,3] the presence of inorganic salts, nitrogenous and other non-sugar substances, as well as the changes in the carbohydrates themselves as a result of heat treatment and *p*H effects. It is possible, too, that oxidation[4] may contribute to the degree of discoloration.

In studying the browning of autoclaved milk Kass and Palmer[5] observed that when lactose solutions were heated with various buffers the discoloration was accompanied by a development of acidity, pronounced fall of optical activity, comparatively slight loss of copper reducing ability and an appreciable, but constant, conversion of lactose to ketoses, or substances not oxidized by sodium hypoiodite. In following the changes taking place, these investigators employed the reduction in optical rotation as the principal index of the degree of transformation of the lactose, although in a few cases this was supplemented with the estimation of aldoses by iodometric method. The loss of optical activity and production of discoloration was found to be a complex function of the buffer concentration and duration of heating and was directly proportional to the initial concentration of lactose. Increased conversion of lactose was observed with increase in the concentration of a phosphate buffer at approximately constant *p*H.

In the usual commercial processing of corn sirup, the *p*H of the material is always on the acid side. Furthermore, the salt content is very low and conditions are generally favorable to stability of the sirup. However, traces of phosphate are present and it is possible that some of the reactions which are characteristic of the constituents in a sirup mixture of higher salt concentration may take place at a slower rate and to a lesser degree upon processing and aging. Since glucose, the simplest and perhaps the most active sugar constituent in the corn sirup, is an aldose sugar, it is to be expected that it will show the same general

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(1) Kröner and Kothe, *Z. Spiritusind*, **60**, 191, 199, 207 (1937); *Chem. Abs.*, **33**, 2361 (1939); *ibid.*, **62**, 191, 197, 205, 245, 253; *ibid.*, **34**, 3941, 3942 (1940); *ibid.*, *Vorratspflege u. Lebensmittelforsch*, **2**, 299 (1939); *Chem. Abs.*, **35**, 3843 (1941).

(2) Kröner, *Forschungdienst*, **9**, 538 (1940); *Chem. Abs.*, **36**, 5377 (1942).

(3) Porst, Orig. Comm. 8th Int. Cong. Appl. Chem., **13**, 205-212 (1912).

(4) Frankenhoff, *Ind. Eng. Chem.*, **34**, 987 (1942).

(5) Kass and Palmer, *Ind. Eng. Chem.*, **32**, 1360 (1940).

Table I

Analysis of Dextrose Samples

Series A: autoclaved thirty minutes at 15 lb./sq. in. (1 kg. per sq. cm.) g./100 ml.

Expt.	Added constituents	Lane and Eynon reducing sugars	Residual glucose (by optical method)	Iodometric aldoses	Ferri-cyanide ketoses	Total	*p*H Before	*p*H After	Color
1	None	3.96	3.95	3.98	..	3.98	5.3	3.5	None
2	0.1 g. NH_4Ac	40.5	39.4	38.8	0.37	39.2	6.4	5.2	Brown tinge
3	0.1 g. glycine	39.9	40.5	38.9	0.62	39.5	6.5	4.8	Brown tinge
a	0.7 g. KH_2PO_4	4.00	3.10	3.69	0.32	4.01	6.5	6.4	Light brown
b	0.7 g. KH_2PO_4	3.90	2.37	3.24	0.65	3.89	6.5	6.4	Light brown
4c	0.7 g. KH_2PO_4	3.94	2.57	3.39	0.42	3.81	6.5	6.4	Light brown
d	0.7 g. KH_2PO_4	3.94	2.34	3.40	0.65	4.05	6.5	6.4	Light brown
e	0.7 g. KH_2PO_4	4.05	2.39	3.27	0.67	3.94	6.5	6.4	Light brown
a	0.7 g. KH_2PO_4	39.9	32.2	36.6	2.81	39.4	6.4	5.7	Brown
b	0.7 g. KH_2PO_4	36.8	26.8	32.6	4.25	36.8	6.4	5.7	Brown
5c	0.7 g. KH_2PO_4	39.2	28.7	36.1	3.06	39.2	6.4	5.7	Brown
d	0.7 g. KH_2PO_4	39.2	29.0	36.0	4.78	40.8	6.4	5.7	Brown
e	0.7 g. KH_2PO_4	40.9	26.4	34.2	5.59	39.8	6.4	5.7	Brown
a	0.7 g.	39.8	31.8	37.2	2.81	40.0	6.4	5.6	Brown
b	KH_2PO_4	37.3	28.6	32.4	3.78	36.2	6.4	5.6	Brown
6c	trace	39.5	29.1	36.0	3.43	39.4	6.4	5.6	Brown
d	of NH_4Cl	39.5	29.4	35.9	4.25	40.2	6.4	5.6	Brown
e	in each	40.9	30.3	35.1	5.23	40.4	6.4	5.6	Brown

Series B: autoclaved sixty minutes at 15 lb./sq. in. (1 kg. per sq. cm.) g./100 ml.

Expt.	Added constituents	(a) Lane and Eynon reducing sugars	(b) Residual glucose (by optical	(c) Converted glucose method)	(d) Iodometric aldoses	(e) Ferricyanide ketoses	(f) (d + e) Total	*p*H Before	*p*H After	Color
8a	0.7 g. KH_2PO_4	41.1	24.9	16.2	34.1	6.75	40.8	6.6	5.5	Red brown
b	0.7 g. KH_2PO_4	41.3	25.4	15.9	34.3	6.69	41.0	6.6	5.5	Red brown
10a	0.7 g. KH_2PO_4									
b	0.01 g. SO_2	40.9	26.1	14.8	33.9	6.63	40.5	6.6	5.2	Light yellow
11a	(as $NaHSO_3$)	40.8	25.7	15.1	34.5	6.79	41.3	6.6	5.1	Light yellow
b	in each	41.1	25.6	15.5	34.0	6.44	40.0	6.6	5.4	Light yellow
		41.5	25.3	16.2	35.2	6.89	42.2	6.6	5.3	Light yellow
12a	0.7 g. KH_2PO_4									
b	0.1 g. SO_2	41.0	25.5	15.5	34.0	6.68	40.0	...	...	Light yellow
13a	(as $NaHSO_3$)	41.0	25.8	15.2	33.6	...	..	...	...	
b	in each	41.1	24.3	16.8	34.0	6.96	41.0	...	...	
		41.1	24.8	16.3	33.6	...	..	...	...	
14	10 g. KH_2PO_4	38.6	0.38	38.2	27.3	14.6	41.9	6.6	5.8	Dark red

conduct as Kass and Palmer have observed for lactose.

The addition of a small amount of sulfite to inhibit discoloration is a common practice in the manufacture of many sirups. In this connection, it is of interest that Tomado and Taguchi[6] have shown that in the presence of bisulfite an addition product of glucose is formed which has negligible optical activity, while fructose is scarcely affected. The quantity of sulfite necessary to render the glucose inactive is quite large, but it appeared probable that even small amounts might influence the glucose transformation in the process of autoclaving.

In the present investigation, the major attention was directed to a study of the effect of a phosphate buffer at a *p*H slightly below the neutral point. To establish a more complete balance sheet for the changes observed, direct determinations of both aldoses and ketoses were included along with the estimation of total reducing sugars, optical activity and *p*H.

Experimental

The same procedure was followed in all experiments. The required amount of c. p. anhydrous dextrose was weighed out and transferred to a 100 ml. volumetric flask. To this was added a solution of the substance whose action on the sugar was to be investigated and enough distilled water to make approximately 90 ml. In the case of the more concentrated sugar solutions, it was necessary to warm them on the steam-bath for a short time to effect rapid solution. The mixtures were autoclaved for the specified length of time at 15 lb. per sq. in. (1 kg. per sq. cm.). The period of heating was thirty minutes in the first series of experiments and sixty minutes in the second series. At the end of the heating period, each sample was cooled to room temperature and then diluted to 100 ml. Aliquots of these samples were analyzed for total reducing sugars (as glucose) by the copper-reduction method of

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(6) Tomado and Taguchi, *J. Chem. Soc. Japan*, **33**, 434 (1930).

Lane and Eynon,[7] aldose sugars by the hypoiodite method of Cajori[8] and ketoses (as fructose) by the selective alkaline ferricyanide oxidation process of Becker and Englis.[9] The acidity, before and after heating, was measured with a Beckman Industrial Model *p*H meter, employing a glass electrode. Optical activity of the solutions was determined with a Schmidt and Haensch double wedge saccharimeter using a two-decimeter polarimeter tube. The results are given in Table I.

Discussion of Results

The analysis of the first series of samples, which had been autoclaved for thirty minutes, showed that the sum of the aldoses and ketoses agreed quite well with the values for total reducing sugar and indicated that the analytical methods were satisfactory. However, the extent of conversion found for duplicate samples was not in good agreement. Since the samples were placed in the autoclave at room temperature and then heated for only thirty minutes, it was apparent that there must have been considerable variation in the average temperature conditions. To lessen this variation the period of autoclaving was increased to one hour and the agreement between duplicates was improved in the second series.

Although the drop in optical rotation may be proportional to the alteration of the glucose, a calculation of the amount of the sugar remaining upon the basis of the residual optical value gives a quantitative estimation only if the product formed is inactive. If it is assumed that glucose has been changed to fructose alone, the change in rotation is 1.39 angular degrees (+0.525 to −0.869) for the D line at 30° for each gram per 100 ml. of glucose transformed; if the glucose is just rendered optically inactive the change will be only 0.525° per gram. Hence, any calculation based on the second assumption gives an apparent glucose change of the magnitude 1.39/0.525 or 2.65 times that which may be actually characteristic of the reaction. This is evident by comparing in the table the values in column (c) with those of column (e) in which the ketose has been estimated directly. The average of the ratio of (c)/(e) is 2.34, which is slightly less than the theoretical 2.65. This seems to indicate that a small amount of some ketose other than fructose, with dextro or less levo rotation than fructose, has been produced. Phosphates are common constituents of many nutrient solutions and the sterilization by autoclaving may give rise to small amounts of non-fermentable sugars which may bring into question previous conclusions regarding the characteristics of the organisms under examination. The same may be said of the results of certain biological methods of sugar analysis which include such a treatment.

The presence of the small amount of sulfite employed in these experiments has no apparent effect upon the extent of conversion, but does inhibit the discoloration. It is probable that most of the sulfur dioxide is lost in the process of autoclaving. It was feared that the addition of sulfite might have affected the analytical results so in experiments 10b, 11b, 12b, and 13b, portions of the treated solutions were taken and air bubbled through them for some time at room temperature before analysis. The variations observed are within experimental error and confirm the belief that most, if not all, of the sulfur dioxide was lost in the heating process.

Maintaining the *p*H constant and increasing the amount of phosphate (Expt. 14), markedly increased the amount of glucose conversion and the discoloration. Two other buffers, glycine and ammonium acetate (Expt. 2 and 3), in solutions of approximately the same *p*H are not nearly so effective as phosphate in bringing about a conversion of glucose to fructose; hence, the effect is not one of *p*H alone. Upon the basis of polarimetric evidence this same fact was indicated by Kass and Palmer for the conversion of lactose to ketoses or other products.

In surveying the effect of alkalies upon various sugars, Kusin[10] has pointed out that in the numerous papers which have appeared since the early observations of Lobry de Bruyn and Alberda Van Ekenstein[11] it has been generally assumed that the cation is of negligible consideration and in most instances the significant effect is assigned to the hydroxyl ion. His experimental results indicated that calcium and sodium hydroxides had markedly different action upon glucose; the first gave considerable mannose and little fructose, while the latter gave considerable fructose but little mannose.

Wolfrom and Lewis[12] have shown that lime water produced large amounts of ketoses from D-glucose when the reaction was allowed to reach equilibrium. This stage was attained after ten days at 35°. The experiments of Kusin, in most instances, involved a reaction period of about twenty-four hours at room temperature and the results he observed would seem to be characteristic only of early stages of the reaction.

In the case of calcium hydroxide, Kusin believes the pyranose ring is not ruptured and the effect is such that after enolization when water adds to the molecule again the hydroxyl is directed to the end carbon thus favoring aldose formation. On the other hand, with sodium hydroxide, the ring is hydrolyzed and the nature of the saccharate compound causes the addition of the hydrogen to the acyclic enol on the terminal carbon and the hydroxyl goes to the adjacent carbon so that fructose formation is favored.

Previous work on an alkaline medium has indicated then that the *p*H, temperature, time and nature of the cations present influence sugar transfor-

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[7] Lane and Eynon, *J. Soc. Chem. Ind.*, **42**, 32T, 143T, 463T (1923).

[8] Cajori, *J. Biol. Chem.*, **54**, 616 (1922).

[9] Becker and Englis, *Ind. Eng. Chem., Anal. Ed.*, **13**, 15 (1941).

[10] Kusin, *Ber.*, **69B**, 1041 (1936).

[11] Lobry de Bruyn and Alberda Van Ekenstein, *Rec. trav. chim.*, **14**, 156 (1895).

[12] Wolfrom and Lewis, THIS JOURNAL, **50**, 837 (1928).

mations. In the present work with mixtures which are slightly acid, it is apparent that the anions, particularly phosphate, have a significant effect.

In agreement with many previous workers, it was observed that there was little or no discoloration of the pure sugar on heating. The formation of small amounts of acid substances from the sugar lowered the *p*H to a greater degree than in the cases where buffers were present and the increase in acidity may be partly responsible for the increased stability to color change. In the low concentrations employed, neither the ammonium acetate nor glycine buffers showed much difference from phosphate of the same *p*H as regards the yellowing tendency.

Summary

Autoclaving of glucose solutions in the presence of a phosphate buffer at an initial *p*H of 6.4–6.6 gives a considerable conversion to ketoses. From polarimetric and chemical analytical data, D-fructose appears to be the major product, but small amounts of other ketoses may be formed. Two other buffers of similar *p*H are less effective. Increase in the amount of phosphate increases the conversion at the same *p*H. A small amount of bisulfite does not alter the extent of conversion. In the absence of sulfite the degree of discoloration is mainly a *p*H effect.

URBANA, ILL. RECEIVED SEPTEMBER 18, 1944

[CONTRIBUTION FROM NORTHERN REGIONAL RESEARCH LABORATORY,[1] PEORIA, ILL.]

The Preparation of 1,3- and 1,4-Pentadienes from Furfural

BY L. E. SCHNIEPP[2] AND H. H. GELLER[3]

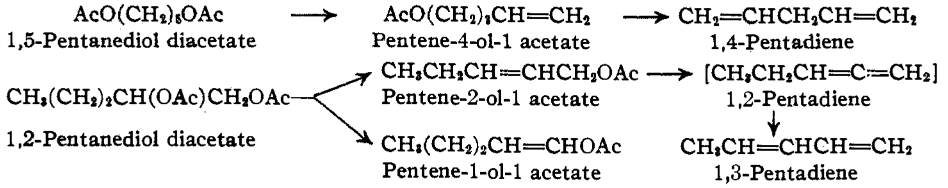
Catalytic conversion of 1,4- and 1,5-pentanediols to 1,3-pentadiene has been reported by Beati and Mattei.[4] The preparation of the pure 1,4-pentadiene has proven to be much more difficult because of its tendency to rearrange. The procedure of Shoemaker and Boord[5] is the best of the previously reported synthesis methods.

Pyrolytic decomposition of the diacetates of 1,2- and 1,5-pentanediols offers a new and convenient method of preparing the pure 1,3- and the 1,4-pentadienes from furfural hydrogenation products.

The formation and isolation of the 1,4-pentadiene as a pyrolysis product from the 1,5-diol diacetate is in general agreement with the findings of Van Pelt and Wibaut,[6] who found that double bond displacement did not normally occur when acetates of mono- and di-hydroxy compounds were converted to olefins by pyrolysis. This generalization does not apply, however, in the case of the 1,2-diol diacetate since only the 1,3-pentadiene was obtained as the pyrolysis product. The 1,2-diene, which is probably the initial reaction product, would be expected to rearrange to the 1,3-isomer under the influence of heat, as has been shown to be the case with 3-ethyl-1,2-pentadiene.[7]

The pyrolytic decomposition of the 1,5-pentanediol diacetate presents an attractive method of preparing 1,4-pentadiene. The pure diene was obtained in yields of 90–96% by pyrolyzing the diacetate at 575 ± 5°. Since the intermediate pyrolysis product, pentene-4-ol-1-acetate, which was isolated and identified, also yields 1,4-pentadiene on pyrolysis, nearly quantitative yields may be obtained by recycling the pyrolysis liquors until all of the acetates have been converted.

The conversion of 1,2-pentanediol diacetate to 1,3-pentadiene averaged 60–65% of the theoretical. The pentenol acetates remaining in the pyrolysis liquors did not yield any appreciable amount of diene on repyrolysis. The only intermediate isolated from these liquors was identified as the acetate of pentene-1-ol-1, since on hydrolysis it is converted to *n*-valeraldehyde and acetic acid. It appears, therefore, that the pyrolysis of 1,5- and 1,2-pentanediol diacetates proceeds by the routes



Experimental

1,2- and 1,5-Pentanediols.—Crude tailings from the commercial manufacture of tetrahydrofurfuryl alcohol were fractionally distilled under reduced pressure. The fraction boiling over the range of 90–150° (6 mm.) was collected and refractionated under atmospheric pressure. The fraction boiling at 205–211° was practically pure 1,2-pentanediol. The 1,5-pentanediol fraction was collected at 234–

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[4] Beati and Mattei, *Ann. Chim. Applicata*, **30**, 21 (1940).

[5] Shoemaker and Boord, THIS JOURNAL, **53**, 1505 (1931).

[6] Van Pelt and Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

[7] Mereschkovski, *J. Russ. Phys.-Chem. Soc.*, **45**, 1940 (1913).