

Formation of Sucrose Pyrolysis Products

R. R. Johnson,¹ E. D. Alford,¹ and G. W. Kinzer²

The volatile products from sucrose pyrolysis and from an aqueous acid-stannous chloride degradation of glucose are similar in composition, which suggests some similarity in reaction mechanisms. A number

of products³ have been isolated from one or both of the product mixtures and conclusively identified. Three represent previously unreported carbohydrate pyrolysis products.

Parks *et al.* (1955) proposed that the thermal degradation of cellulose involves initial formation of levoglucosan (1,6-anhydro- β -D-glucopyranose) followed by fragmentation of this intermediate to form more volatile products. Glassner and Pierce (1965) subsequently provided substantiating evidence for this theory by showing a close similarity between gas chromatograms of pyrolysis products from levoglucosan and cellulose. More recently, Gardiner (1966) examined the products from vacuum pyrolysis of some hexoses and hexose-derived polysaccharides by gas chromatography of the trimethylsilyl ethers. He found that levoglucosan was the major product from glucose and glucose-derived polysaccharides and that these also gave the same minor products. Since these products are also formed by acid-catalyzed reactions of the same hexoses in solution, Gardiner (1966) suggested that the reactions proceed by similar mechanisms.

This communication illustrates another correlation of product mixtures, which suggests that the more volatile products from hexose pyrolysis are formed by reactions similar to those operative in a strongly reducing aqueous acid system. Conclusive evidence is presented for the identification of several new sucrose pyrolysis products.

EXPERIMENTAL

5-Methylfurfural Preparation from Glucose. A solution containing 4 liters of aqueous 12% sulfuric acid, 2.5 kg. of sodium chloride, and 625 grams of stannous chloride was heated to boiling in a 12-liter flask. A solution of 1.0 kg. of glucose in 1.25 liters of warm water was slowly added. Volatile products were steam-distilled from the reaction

mixture as they were formed and 3 liters of distillate was collected. The acidic distillate was neutralized with sodium carbonate, saturated with sodium chloride, and extracted with three 700-ml. portions of diethyl ether. After removal of the ether at 20° C. and 10 mm., the residual products were vacuum-distilled through a spinning-band column with gradually decreasing pressure. Distillation cuts were combined into major fractions on the basis of analyses by gas-liquid partition chromatography (GLPC). The first fraction (5.05 grams, 25° to 71°, and 24 mm.) was predominantly 2-methyl-2-cyclopenten-1-one (III); fraction 2 (2.53 grams, 71° and 24 mm. to 74° and 15 mm.) was a mixture of III, furfural, 2-acetofuran, and 5-methylfurfural (I); fraction 3 (10.5 grams, 74° and 15 mm. to 69° and 11 mm.) was predominantly 5-methylfurfural; and the highest boiling cuts comprising fraction 4 (2.71 grams, 69° to 86° and 11 mm.) contained 5-methylfurfural and 2-hydroxy-3-methyl-2-cyclopenten-1-one (II) as the major constituents.

The residue from the fractional distillation was distilled at 20° and 0.01 mm. for 16 hours, the distillate being collected in a dry ice-cooled receiver. Recrystallization of the solid distillate from toluene gave approximately 2 grams of II with melting point 102-4° (m.p. = 106-7°, Erickson and Collins, 1965).

Pyrolysis of Sucrose. About 10 grams of sucrose was placed in a 250-ml. distilling flask which was incorporated into an all-glass distillation assembly followed by a glass spiral trap at -80°. The distillation flask was heated with a gas burner until the evolution of aerosol ceased, at which time another 10- to 20-gram portion of sucrose was added and heating was resumed. A total of 200 grams of sucrose was pyrolyzed in this manner, using several pyrolysis flasks.

Products collected in the receiver (118 grams) and in the dry ice trap (5 grams) were combined (123 grams, 61%) and extracted three times with a total of 600 ml. of chloro-

¹ Research Department, Brown & Williamson Tobacco Corp., Louisville, Ky. 40201

² Organic Chemistry Department, Battelle Memorial Institute, Columbus Laboratories, Columbus, Ohio

form. The combined chloroform solutions were concentrated at 60° and 10 mm. to give residual products (25 grams, 12.5%), which were then vacuum-distilled into dry ice traps. A first fraction (9.8 grams, 4.9%) was obtained at 20° and 0.03 mm. in 5 hours and a second fraction (5.9 grams, 2.9%) at 60° and 0.01 mm. in 17 hours. The first fraction was dissolved in diethyl ether and rapidly extracted with two equal portions of saturated aqueous sodium bisulfite solution and one portion of saturated aqueous sodium chloride solution. Concentration of the ether solution gave products from which almost all of the aldehydes had been removed. The sodium bisulfite extracts were combined and treated with excess sodium carbonate solution to recover the aldehydes.

RESULTS

One convenient 5-methylfurfural synthesis by Scott and Johnson (1932) involves slow addition of fructose or sucrose to a boiling mixture of aqueous sulfuric acid and stannous chloride. Volatile products are steam-distilled from the mixture as they are formed and the odor of hydrogen sulfide is apparent. In addition to 5-methylfurfural, the synthesis from sucrose gives a number of by-products in significant yield. The use of glucose in this synthesis results in a product mixture containing increased yields of the by-products and less 5-methylfurfural.

Isothermal GLPC on a 40,000-theoretical-plate capillary column (Igepal CO-880) was used to compare the synthetic product mixture from glucose with pyrolysis products from invert sugar. The chromatogram of the chloroform-soluble pyrolysis products from invert sugar had 27 significant peaks, while 26 were found in the chromatogram of the glucose-derived synthetic mixture; 21 of these peaks appeared to be common to both chromatograms. The 2-acetofuran peak in both chromatograms was used to calculate relative retention times for these comparisons. A Perkin-Elmer Model 226 flame ionization gas chromatograph was used in these investigations with a 200-foot × 0.02-inch i.d. stainless steel capillary column coated with Igepal CO-880. Under isothermal conditions, 21 analyses for four compounds over a period of a week gave relative retention times with relative standard deviation of 0.15 to 0.24%. In this study, the relative retention times had to agree within 0.5% for a constituent to be considered common to both mixtures. The high degree of correlation found suggested that the synthetic product mixture would be an attractive source from which probable hexose pyrolysis products could be isolated for identification purposes. This attractiveness is due principally to the occurrence of high concentrations of some of the minor pyrolysis products in the synthetic mixture.

As a result of the correlation of GLPC peaks, a program was initiated to isolate and identify the products from the glucose-derived synthetic mixture and then to search for these in the pyrolysis products from sucrose. Sucrose was selected for preparative pyrolysis, since capillary column GLPC indicated that it gave the same products as glucose and fructose, and in intermediate yields. To a large degree the experimentation on pyrolysis products was devoted to the higher boiling compounds. Table I shows the compounds which were isolated in both studies and presents the criteria used for each identification.

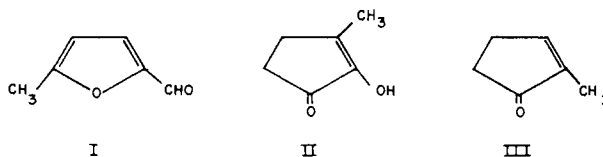
Table I. Identified Synthetic and Pyrolysis Products

	Identification Criteria	
	Synthetic product	Pyrolysis product
Acetone	IR, MS	IR
γ -Butyrolactone		IR
2-Butanone	IR, MS	IR
Furfural	IR, NMR	IR
2-Cyclopenten-1-one	IR, MS	
5-Methyl-2,5 <i>H</i> -furanone	IR, MS, NMR	IR, NMR
γ -Valerolactone	IR, MS, NMR	
2,3-Pentanedione	IR, MS	
Phenol		IR, NMR
2-Acetofuran	IR, NMR	IR, NMR
5-Methylfurfural	IR, NMR	IR, NMR
5-Hydroxymethylfurfural		IR, NMR
3-Hydroxy-2-methyl-4-pyrone (Maltol)		IR
2,5-Dimethylfuran	IR, MS	IR, NMR
2-Methyl-2-cyclopenten-1-one	IR, NMR	IR
2-Methyl-4-cyclopenten-1-one ^{a,b}	IR, MS, NMR	
2-Hydroxy-3-methyl-2-cyclopenten-1-one	IR, NMR	IR
3-Hexen-2-one ^a	IR, MS	
<i>cis</i> -4-Hexen-2-one ^a	IR, MS	
<i>trans</i> -4-Hexen-2-one ^a	IR, MS, NMR	
5-Hexen-2-one	IR, MS	
2-Methylcyclopentanone	IR, MS, NMR	
3-Methylcyclopentanone	IR, MS	
2,5-Hexanedione	IR, MS, NMR	
2,5-Dimethyl-3-oxotetrahydrofuran ^a	IR, MS, NMR	
5-Ethyl-3-oxotetrahydrofuran ^a	IR, MS, NMR	

^a All material except these were identified by GLPC and indicated spectral comparisons with authentic samples.

^b Reduces to 2-methylcyclopentanone.

Products from 5-Methylfurfural Synthesis. In a typical synthesis with 1.0 kg. of glucose, a 20.8-gram yield was obtained of chloroform-soluble products of intermediate volatility. The major components were 5-methylfurfural (I), 2-hydroxy-3-methyl-2-cyclopenten-1-one (II), and 2-methyl-2-cyclopenten-1-one (III). The relative yields of I, II, and III were, respectively, about 3:1:1.



With one exception, samples of the products were isolated for identification by GLPC on packed columns having Carbowax 20M, ethylene glycol succinate, or diethylene glycol succinate on Chromosorb W. The exception was 2,5-hexanedione, which was isolated by thin-layer chromatography.

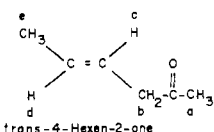
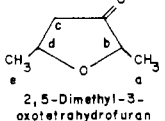
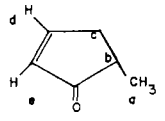
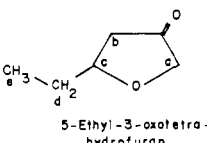
Authentic samples were not available to confirm the structures proposed for six of the isolated products. However, interpretation of the spectral data allows only the proposed structure in each instance. Infrared and mass spectral characteristics for these six compounds are presented in Table II. The results from nuclear magnetic resonance studies on four of the compounds are contained in Table III. Further confirmation of 2-methyl-4-cyclopenten-1-one was provided by hydrogenation of the sample to 2-methylcyclopentanone.

Table II. Infrared and Mass Spectrographic Characteristics of Isolated By-Products

	IR Absorption in CS ₂ , Cm. ⁻¹	Molecular Weight	Mass Spectrum ^a				
			Pk 1	Pk 2:I	Pk 3:I	Pk 4:I	Pk 5:I
<i>trans</i> -4-Hexen-2-one	1720, 965	98	43	98:16	55:14	83:4	
<i>cis</i> -4-Hexen-2-one	1720	98	43	98:12	55:11	83:4	
3-Hexen-2-one	1686, 1678, 1625, 975	98	83	43:61	55:58	98:31	69:6
2,5-Dimethyl-3-oxotetrahydrofuran	1760	114	42	45:89	57:26	114:23	71:22
2-Methyl-4-cyclopenten-1-one	1705	96	96	81:90	53:50	39:34	67:30
5-Ethyl-3-oxotetrahydrofuran	1755	114	56	41:91	114:56	85:52	72:16

^a Mass (*m/e*) of most significant peaks (Pk) of spectrum listed in order of decreasing intensity (I) as *m/e*:I. Intensity expressed as percentage of most intense or base peak (Pk 1). Spectra obtained on an AEI MS-9 high-resolution mass spectrometer.

Table III. NMR Data on By-Products from 5-Methylfurfural Synthesis^a

Structure	Proton Identification	Chemical Shift (ppm)
	a. 126 b. 183 (multiplet) c. 331 (multiplet) d. " e. 101 (multiplet)	
	a. 81 (doublet, J = 6 cps) b. 268 (quartet) c. 127 and 158 d. 243 (quartet) e. 74 (doublet, J = 8 cps)	
	a. 119 (doublet) b. 140 c. 142 (multiplet) d. 368 (multiplet) e. 359 (multiplet)	
	a. 235 (multiplet) b. 139 (doublet) c. 250 (complex multiplet) d. 99 e. 59	

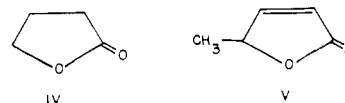
^a NMR spectra obtained on a Varian Associates HA-60-I spectrometer in deuteriochloroform solutions. Chemical shifts reported in Hz downfield from internal tetramethylsilane at 60 MHz/sec.

Products from Sucrose Pyrolysis. Pyrolysis of sucrose at atmospheric pressure gave a 7.8% yield of volatile, chloroform-soluble products, which were obtained in two distillate fractions. 5-Hydroxymethylfurfural was by far the major constituent of the higher boiling fraction and furfural was the major component of the lower boiling products.

Individual products were isolated by GLPC with columns containing Carbowax 20M on Haloport F and purified when necessary on packed columns with a more active support. In addition to the identified products in Table I, a mixture of *m*- and *p*-cresols was isolated and identified.

DISCUSSION

Three of the sucrose pyrolysis products identified in this study have not previously been cited as pyrolysis products from carbohydrates: 2-methyl-2-cyclopenten-1-one (III), γ -butyrolactone (IV), and 5-methyl-2,5H-furanone (V).



Nine of the 26 compounds in Table I were isolated from both the synthetic and the pyrolysis products and conclusively identified by spectral and GLPC comparisons with authentic samples. Two of the synthetic products, 2-cyclopenten-1-one and 2,3-pentanedione, were identified by Heyns *et al.* (1966) in a detailed study of glucose pyrolysis products. In addition, 5-hydroxymethylfurfural is presumed to be the precursor of 5-methylfurfural in the synthesis. Thus, the correlation of products can be extended to 12 of the 26 found. Further composition investigations would extend the number of common products.

The results of this study reinforce the hypothesis that many hexose pyrolysis products are formed by reactions similar to those occurring in a strongly reducing aqueous acid system. Other mechanistic routes are obviously required to explain many of the other hexose pyrolysis products such as phenols.

ACKNOWLEDGMENT

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LITERATURE CITED

- Erickson, J. L. E., Collins, F. E., Jr., *J. Org. Chem.* **30**, 1050 (1965).
 Gardiner, D., *J. Chem. Soc.* **1966**, 1473.
 Glassner, S., Pierce, A. R., III, *Anal. Chem.* **37**, 525 (1965).
 Heyns, K., Stute, R., Paulson, H., *Carbohydrate Res.* **2**, 132 (1966).
 Parks, W. G., Esteve, R., Lollis, M., Guercia, R., Petrarca, A., Abstracts, Division of Cellulose Chemistry, 127th Meeting, ACS, Cincinnati, Ohio, April 5, 1955.
 Scott, E. W., Johnson, J. R., *J. Am. Chem. Soc.* **54**, 2553 (1932).

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