Base-Catalyzed Sucrose Degradation Studies

Alkaline sucrose degradation at 100° C. yields hydroxyacetone, 2-hydroxy-3-methyl-2-cyclopenten-1-one, 2,5-dimethyl-4-hydroxy-3(2H)-furanone, and acetic, propionic, and lactic acids. These products probably arise by base-catalyzed hydrolysis of sucrose to hexoses that are further degraded. The relationship of this study to nonenzymic browning in sucrose-containing foods is discussed.

Alkaline degradation of a sucrose model system has been carried out as part of a continuing study of nonenzymic browning changes that occur during storage in foods such as dehydrated citrus juice powders (Berry and Tatum, 1965). In fruit juices, sucrose contributes to nonenzymic browning only after acid-catalyzed hydrolysis to the more reactive reducing sugars D-fructose and D-glucose (Talburt, 1961). Under alkaline conditions, sucrose is considered relatively unreactive because it lacks the unsubstituted hemiacetal grouping present in reducing disaccharides (Hassid and Ballou, 1957). However, Browne and Zerban (1941) noted that sucrose is slowly, but steadily, hydrolyzed by strongly alkaline copper reagents and thus can produce a reducing effect on these reagents.

Previous degradation studies involving fructose-acid (Shaw *et al.*, 1967), ascorbic acid (Tatum *et al.*, 1969), and fructose-base (Shaw *et al.*, 1968) model systems helped both in identifying browning products also present in stored, dehydrated orange powder (Tatum *et al.*, 1967) and in explaining the formation of these products. The current study reports results from alkaline degradation of a sucrose model system, including some of the compounds formed and possible mechanisms for their formation.

EXPERIMENTAL

Gas-liquid chromatographic (GLC) and thin-layer chromatographic (TLC) procedures were described by Tatum *et al.* (1967).

Spectrophotometric Methods. Infrared spectra were determined neat or in CS_2 on a Perkin-Elmer 137 spectrophotometer. Mass spectra were determined on a Bendix Time-of-Flight 3012 instrument. The pH measurements were made with a Beckman Zeromatic pH meter.

Sucrose Degradation. A solution of 240 grams of sucrose (certified ACS, Fisher Scientific Co., Fair Lawn, N. J.) in 440 ml. of water was treated dropwise with 50% sodium hydroxide solution until pH was 11.5. The solution was refluxed for 3 hours either open to the air or under nitrogen; a brown color developed gradually during this period. The pH remained above 10 during this heating period, as determined by periodic checking with alkacid test paper. The solution was cooled, acidified to pH 3 to 4, saturated with sodium chloride, and extracted with three 250-ml. portions of ether. The extracts were combined, dried over sodium sulfate, and concentrated to a small volume under reduced pressure. This amber-colored solution was used for GLC separation. When the solution was concentrated to dryness, there remained 0.26 gram of viscous, brown residue with a caramel odor.

Glucose Degradation. A solution of 240 grams of D-glucose in 440 ml. of water was adjusted to pH 11 with 50% sodium hydroxide solution and refluxed for 3 hours. Frequent addition of sodium hydroxide solution was needed to maintain strong alkalinity (pH > 9) during this heating period. The cooled reaction mixture was adjusted to pH 4 with dilute hydrochloric acid and extracted with ether, and the extract separated by GLC as described above for sucrose. Only the GLC peak corresponding to lactic acid was collected and it was identified by comparison of its infrared spectrum with that of an authentic sample.

Comparison Samples. 4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone was prepared by the method of Henry and Silverstein (1966). Hydroxyacetone and 2-hydroxy-3-methyl-2-cyclopentane-1-one were purchased from K and K Laboratories, Inc., Plainview, N. J., acetic and propionic acids from Fisher Scientific Co., Fair Lawn, N. J., and lactic acid from Merck and Co., Inc., Rahway, N. J.

RESULTS AND DISCUSSION

Base-catalyzed sucrose degradation has afforded the six ether-soluble products listed in Table I. Relative quantities of these products were the same whether or not air was excluded. In each case, the product was identified by GLC retention time and by comparison of infrared and mass spectra with those of an authentic sample. GLC retention times for all compounds were identical to those for authentic samples and all but acetic and propionic acids gave characteristic colors on thin-layer chromatograms.

Alkaline degradation of sucrose to reducing sugars is probably the first step in forming the products found in this study (Whistler and BeMiller, 1958). The hexoses thus formed could undergo further degradation, as suggested for D-fructose by Shaw *et al.* (1968). Five of the six products identified as fructose products in that study have been also found in this current study as products from sucrose degradation. Although lactic acid, the sixth product, was not found in that study, it was found when D-glucose was similarly treated with alkali. Montgomery (1949) noted that lactic acid is an expected product from alkaline sucrose degradation at temperatures of 100° and above. Since the reaction took the same course in a nitrogen atmosphere as in air, there was not likely to have been an initial air oxidation of sucrose to give an alkali-sensitive carbonyl derivative (Whistler and BeMiller, 1958).

Table I. Sucrose-Base Degradation Products

	GLC		TLC	
Compound	R_t	Odor	R_f	Color with spray
Hydroxyacetone	10	Rancid oil	0.47	Green-brown
Acetic acid	13	Pungent	...	...
Propionic acid	17	Pungent	...	...
2-Hydroxy-3-methyl-2-cyclopenten-1-one	35	Caramel	0.70	Yellow
2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone	50	Caramel	0.62	Brown
Lactic acid	59	Rancid oil	0.33	Blue

The small total yield (0.11%) of ether-soluble products isolated from this alkaline sucrose degradation illustrates the unreactive nature of sucrose with alkali. That alkali was actually necessary for the degradation was shown by repeating the reaction at pH 7.2. After the solution was refluxed for 6 hours, only a pale yellow color had developed. Extraction and GLC separation of the concentrated extract as above afforded no peaks comparable to those found when strong alkali was used. Fisher certified sucrose contains 0.05% invert sugar, but that invert sugar probably did not contribute appreciably to the quantity of ether-soluble products isolated. At least in our analogous studies with both fructose and glucose, the total ether-soluble products were isolated in <5% yield.

The products listed in Table I all have strong odors, but 2-hydroxy-3-methyl-2-cyclopenten-1-one and 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone are of special interest because they both have strong, caramel-like odors. Their presence in foods, even in small quantities, could contribute to odor and flavor changes that result from nonenzymic browning. This model study was conducted at a pH higher than that normally encountered when sucrose-containing foods are processed. When foods such as maple sap are heated under slightly alkaline conditions, the caramel flavors produced are believed to arise from degradation of the reducing sugars rather than from sucrose (Underwood *et al.*, 1961). The current study shows that degradation products with caramel-like aromas can be produced from alkaline sucrose degradation if conditions are severe enough.

LITERATURE CITED

Berry, R. E., Tatum, J. H., J. AGR. FOOD CHEM. **13,** 588 (1965).

Browne, C. A., Zerban, F. W., "Physical and Chemical Methods of Sugar Analysis," 3rd ed., p. 787, Wiley, New York, 1941.

Hassid, W. Z., Ballou, C. E., "The Carbohydrates," Ward Pigman, Ed., p. 481, Academic Press, New York, 1957.

Henry, D. W., Silverstein, R. M., *J. Org. Chem.* **31,** 2391 (1966).

Montgomery, R., "Chemical Production of Lactic Acid from Sugars," Sugar Research Foundation, New York, Sci. Rept. Ser. **11,** 1949; *C.A.* **43,** 3785e (1949).

Shaw, P. E., Tatum, J. H., Berry, R. E., *Carbohydrate Res.* **5,** 266 (1967).

Shaw, P. E., Tatum, J. H., Berry, R. E., J. AGR. FOOD CHEM. **16,** 979 (1968).

Talburt, W. F., "Fruit and Vegetable Juice Technology," D. K. Tressler, M. A. Joslyn, Eds., p. 432, Avi Publishing, Westport, Conn., 1961.

Tatum, J. H., Shaw, P. E., Berry, R. E., J. AGR. FOOD CHEM. **15,** 773 (1967).

Tatum, J. H., Shaw, P. E., Berry, R. E., J. AGR. FOOD CHEM. **17,** 38 (1969).

Underwood, J. C., Willits, C. O., Lento, H. G., *J. Food Sci.* **26,** 397 (1961).

Whistler, R. L., BeMiller, J. N., *Advan. Carbohydrate Chem.* **13,** 289 (1958).

Philip E. Shaw
James H. Tatum
Robert E. Berry

U. S. Fruit and Vegetable Products Laboratory
Southern Utilization Research and Development Division
Agricultural Research Service
U. S. Department of Agriculture
Winter Haven, Fla. 33880

Received for review December 9, 1968. Accepted February 10, 1969.