

Saccharide Analysis of Corn Syrup Solids and Maltodextrins Using High-Performance Liquid Chromatography

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ABSTRACT

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Water-soluble saccharides from commercial samples of corn syrup solids and maltodextrins were characterized using a combination of high-performance liquid chromatography techniques. Saccharides consisting of 1-10 degrees of polymerization were analyzed using a plastic C₁₈ Resolve column compressed in a radial compression module. The overall molecular weight profile of each sample was evaluated by size-exclusion

chromatography using a two-column system packed with silica gel (E-HighÅ and E-500). Both procedures were conducted at room temperature. These methods should prove useful for rapidly monitoring the extent of hydrolysis during processing and for predicting the physicochemical properties of the final hydrolysate.

Starch hydrolysis products, such as glucose syrups, corn syrup solids, and maltodextrins, are widely used for their functional properties throughout the food industry. Dextrose equivalent (DE) values, which refer to the percentage of reducing sugars calculated as D-glucose, are typically used to categorize these products. This approach, however, possesses certain limitations. The physicochemical properties of glucose syrups and maltodextrins are dependent on the overall saccharide profile present in the final hydrolysate. Consequently, two products hydrolyzed by different methods may have the same DE yet different saccharide composition and properties (Dziedzic and Kearsley 1984).

High-performance liquid chromatography (HPLC) is a rapid and convenient method for separating and quantitating the saccharides present in glucose syrups and maltodextrins (Scobell et al 1977). Cation-exchange resins in the silver form (Scobell and Brobst 1981) and C₁₈-bonded silica columns (Cheetham et al 1981) have been developed to measure saccharides consisting of one through approximately 10 degrees of polymerization (DP) of anhydrous glucose units. Separation is based on chain length, and individual saccharides are expressed relative to their DP, i.e., DP 1 is glucose, DP 2 are disaccharides, etc. In addition, high-performance size-exclusion chromatography (HPSEC) has recently been used for determining the overall molecular weight ranges of purified starch components subjected to controlled enzymatic hydrolysis (Kruger and Marchylo 1985) and for quantitating the amylose and amylopectin levels present in corn and wheat starches (Kobayashi et al 1985).

The objective of the present study was to examine methods to characterize starch hydrolysis products using commercially available prepacked HPLC columns. A C₁₈-bonded silica column was utilized for measuring the DP 1-10 saccharide components of commercially available, low-DE corn starch products. The overall molecular weight profile of these hydrolysates was examined using HPSEC.

MATERIALS AND METHODS

Corn syrup solids (M365, M250, M200) and maltodextrins (M150, M100, M040) were obtained from Grain Processing Corp., (Muscatine, IA) and stored at room temperature. Dextran molecular weight standards ($M_w = 9,000, 74,300, 249,000, \text{ and } 488,000$), and α -D-glucose were purchased from the Sigma Chemical Co., St. Louis, MO. Polydispersity values for the molecular weight standards were not provided. Anthrone reagent was purchased from the J. T. Baker Chemical Co., Phillipsburg, NJ. All other reagents were obtained from Fisher Scientific,

Dallas, TX.

Each hydrolysate was solubilized according to the procedure of Warthesen (1984). Samples prepared for chemical analysis were assayed directly, whereas those intended for HPLC were filtered through 0.45 μm filters before injection.

Analytical Methods

Moisture values were determined by air-oven drying at 105°C for 24 hr, and all analytical values were expressed on a dry-weight basis. Reducing sugars were determined according to Nelson (1944), using D-glucose as standard. Total carbohydrate values were obtained using the modified anthrone-H₂SO₄ procedure of Brooks and co-workers (1986), and the values obtained were multiplied by 0.90 to convert from glucose equivalents to total carbohydrate or starch equivalents (McCready et al 1950). All analyses were performed in triplicate. DE values were determined by dividing the reducing sugar value by the total carbohydrate value and multiplying the quotient by 100 (Hyun and Zeikus 1985).

HPLC

The chromatographic system consisted of a model M-45 pump, a U6K injector, and a 740 integrator (Waters Associates, Milford, MA). Detection was performed using an Altex model 156 differential refractometer (Beckman Instruments, Berkeley, CA) attenuated at 256X for DP 1-10 determinations and 512X for HPSEC. All HPLC analyses were done at room temperature.

For measuring the DP 1-10 saccharides, an 8-mm i.d. Resolve C₁₈ 5- μm plastic cartridge installed in a RCM-100 radial compression module (Waters Associates) was used. The column was preceded by a guard column containing a Resolve C₁₈ Guard-Pak insert (Waters Associates). Water for the mobile phase was obtained immediately before use from a Milli-Q (Millipore Corp., Bedford, MA) water purification system that included a 0.22- μm filter and degassed under vacuum. Starch hydrolyzates and the D-glucose standard were solubilized to yield approximately 100 and 1.0 mg/ml, respectively. Injection volumes of 15 μl were eluted at a flow rate of 1.0 ml/min. All samples were assayed in triplicate and the mean values reported. Although it has been suggested that mobile-phase water be held with stirring at 70-80°C rather than ambient temperature to prevent gas formation or microbial growth (Anonymous 1984), no such difficulties were encountered in this study. For overnight or longer periods of storage, the column was flushed with at least 10 bed volumes of 20% acetonitrile/80% water and stored in the same solution.

For determining the overall molecular weight profile of the samples, E-HighÅ and E-500 $\mu\text{Bondagel}$ silica gel permeation columns (Waters Associates) were connected in series. Water containing 0.15M NaCl was used as the mobile phase. Injection volumes of 25 μl were eluted at a flow rate of 0.5 ml/min. Molecular weights were estimated by comparing sample peak retention times to a standard curve composed of the log weight average molecular weight of the dextran standards ($M_w 9,000-488,000$) versus retention time.

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TABLE I
Analytical Values for Corn Starch Hydrolysates

Sample	% Moisture	% Reducing Sugar ^a	Range	% Total Carbohydrate ^{a,b}	Range	Dextrose Equivalent ^c
M365	3.85	30.98	30.62–31.29	91.84	90.85–92.84	33.7
M250	3.61	22.42	22.17–22.50	93.50	92.23–94.35	24.0
M200	3.64	16.68	16.49–16.79	94.52	94.37–95.65	17.7
M150	2.75	11.80	11.70–11.91	95.14	94.06–95.99	12.4
M100	2.59	10.44	10.37–10.48	96.05	95.51–96.37	10.9
M040	2.82	4.57	4.55–4.58	94.63	93.00–96.92	4.8

^a Values expressed on a dry weight basis.

^b Values expressed on a starch equivalent basis (see text).

^c Values expressed on a total carbohydrate basis.

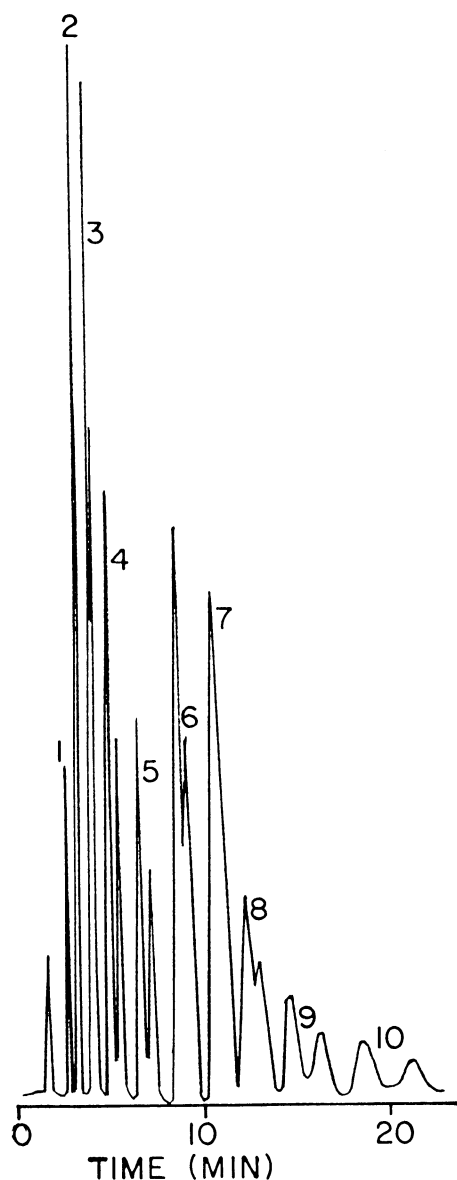


Fig. 1. Chromatogram of M150 maltodextrin using a C₁₈ Resolve column. Numbers refer to the degree of polymerization of the saccharides.

RESULTS AND DISCUSSION

Moisture, reducing sugar, total carbohydrate, and DE values are reported in Table I. In the total carbohydrate assay, the addition of water during hydrolysis of the sample to glucose resulted in a weight increase of up to 10% for pure starch. Therefore, multiplication of the glucose equivalent value by 0.90 was used to convert to total carbohydrate or starch equivalents (McCready et al 1950). Because the commercial corn syrup solids and maltodextrins used in this study were partially hydrolyzed starch,

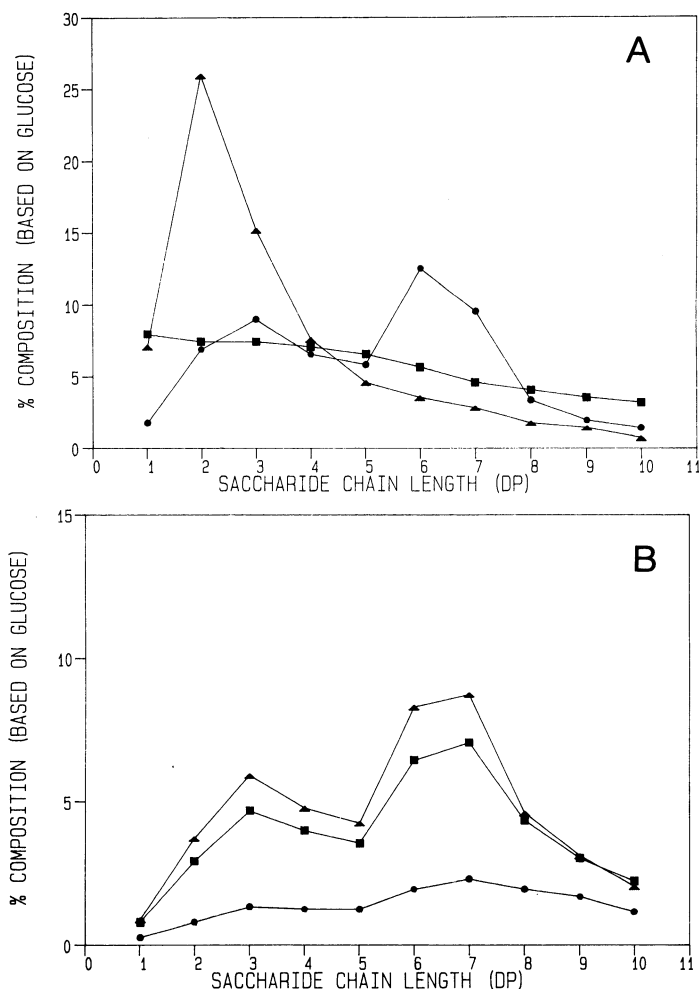


Fig. 2. DP 1–10 saccharide levels present in A: corn syrup solids M365 (▲), M250 (■), M200 (●), and B: maltodextrins M150 (▲), M100 (■), M040 (●).

total carbohydrate values expressed as starch equivalents would be expected to fall between 90 and 100%, in agreement with the values reported in Table I. DE values calculated according to Hyun and Zeikus (1985) ranged from 4.8 to 33.7.

A chromatogram for the analysis of M150 is shown in Figure 1. Approximately 20 min was required to resolve DP 1–10 at a flow rate of 1.0 ml/min. The pairs of peaks obtained for most components between DP 3 and 10 were attributed to the α and β anomers of these saccharides (Cheetham et al 1981).

Figures 2A and B illustrate the profile of DP 1–10 components that were present in the samples of corn syrup solids and maltodextrins, respectively. Quantitation by area normalization was not possible, because the higher molecular weight carbohydrate material was not eluted from the column using water. Consequently, because each saccharide reportedly possesses the same response factor (Scobell et al 1977), weight percent

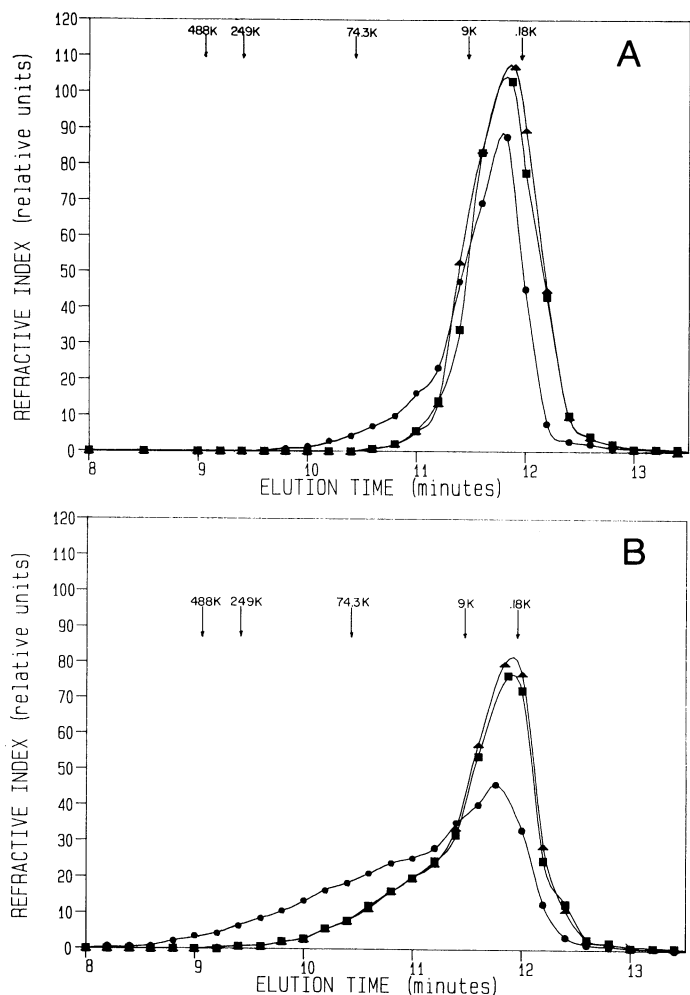


Fig. 3. High-performance size exclusion chromatography (HPSEC) of the water soluble saccharides present in **A:** corn syrup solids M365 (▲), M250 (■), M200 (●), and **B:** maltodextrins M150 (▲), M100 (■), M040 (●).

compositions were expressed relative to an external glucose standard. A precolumn, containing the same packing material, was used to extend the life of the analytical column (Anonymous 1984).

The corn syrup solids possessed decidedly different DP 1-10 patterns. The total contribution of these components to each sample was as follows: 70.75% for M365, 57.46% for M250, and 58.74% for M200. M365, a high-maltose product, showed a sharp decrease in component contribution between DP 2 and 10. The decrease from DP 1 to 10 for M250 was much more gradual and resembled that obtained largely from acid hydrolysis. In contrast, M200, which was similar to M250 in the weight percent of DP 1-10 components, had a clustering of products at DP 6-7 and DP 3. This pattern was similar to that expected for an enzyme-hydrolyzed product (Cheetham et al 1981, Scobell and Brobst 1981). The maltodextrins showed patterns similar to M200 except that DP 7 was the dominant saccharide rather than DP 6. The percent contribution of DP 1-10 components was 46.27, 38.82, and 13.92 for M150, M100, and M040, respectively.

HPSEC data of the samples are provided in Figures 3A and B. Each sample had a broad major peak region with an average molecular weight of less than 9,000. Average molecular weights of these regions could not be accurately determined because they were near or exceeded the lower limits of resolution for this column system (Anonymous 1980). Therefore, the elution time for a small molecule, glucose ($M_w = 180$), was included in each figure for additional comparison. M200 had a small leading shoulder with an average molecular weight of approximately 22,000, whereas both

M150 and M100 showed more pronounced shoulder regions in the range of 150,000. The lowest DE sample, M040, showed the most heterogeneity in its elution profile. A large portion of the soluble saccharides eluted over a wide region beginning before the elution of the 488,000 molecular weight dextran standard. As expected, the HPSEC data showed that as the DE of the hydrolysate increased, the amount of soluble high molecular weight saccharides decreased.

The use of a combination of HPLC-based separations allows rapid characterization of starch hydrolysates. The information obtained should permit an accurate prediction of the physicochemical properties of syrups or maltodextrins. For example, the proportions of low molecular weight components are known to influence sweetness, viscosity, fermentability, crystallization, and humectant properties (Cheetham et al 1981). High molecular weight components affect such properties as solubility and solution stability. HPSEC should be useful for quickly monitoring the progress of hydrolysis during processing as well as for determining the overall molecular weight profile of the final product. The C_{18} Resolve column permits the separation of the low molecular weight saccharides through DP 10. One advantage of this column is that, even at ambient temperature, baseline resolution is typically obtained between components, increasing the ease of quantitation. Further, at a constant flow rate of 1.0 ml/min, analyses are complete in less than 25 min. This eliminates the need for additional components, such as column heating units or programmable pumping systems, which are often required for these analyses. Finally, the columns are inexpensive to replace and, because the loading capacity is reported to be relatively high (Cheetham et al 1981), it could be also used for the isolation of material as standards or for identification purposes.

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