Carbon-13 Nuclear Magnetic Resonance Studies of Chemically Modified Waxy Maize Starch, Corn Syrups, and Maltodextrins. Comparisons with Potato Starch and Potato Maltodextrins

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Comparative studies of corn syrups, maltodextrins, chemically modified waxy maize starch, and corn starch were carried out by carbon-13 NMR techniques. Spectral assignments were made for all materials studied and were checked against independent assignments by proton–carbon correlation spectroscopy. Degrees of branching and polymerization were estimated for maltodextrins from corn starch and were compared with those of potato maltodextrins in relation to the observed difference in the gelling behavior and functionality of corn and potato maltodextrins, respectively. Chemical shifts were found to be similar among maltodextrins from corn and potato, as well as wheat amylopectin and amylopectin B. A comparison of solid-state ^{13}C NMR spectra of corn, wheat, and potato starches reveals their *polymorphism*, in terms of the number of glucose rings in the "unit cell" of the amylopectin crystalline regions of starch granules. Gelatinization causes changes in the symmetry of the crystalline regions of amylopectins inside waxy maize starch granules and/or increased mobility of branches in such regions. A broad band in the anomeric region of the solid-state ^{13}C NMR spectra of waxy maize starch is assigned to the disordered regions of amylopectin in the starch granule structure. Carbon-13 NMR is shown to be a valuable, noninvasive tool for comparative, structural studies of corn starches and products derived from starch. Structural details were obtained that are relevant to gelatinization and gelling mechanisms. For corn maltodextrins structural details were obtained concerning the degrees of branching and polymerization, as well as the anomers; such details were compared between corn and potato starch maltodextrins and found to be significantly different.

INTRODUCTION

Physical and chemical modifications of carbohydrates lead to differences in their behavior and their uses in a variety of processed foods. Whereas chemical analyses by destructive methods have been refined to a substantial degree, there have been very few, *comparative* studies of these important groups of materials by noninvasive, or nondestructive, techniques. Corn syrups, maltodextrins from corn starch, and starch are three important types of carbohydrate materials widely utilized in food products.

Our aim is to carry out a comparative study of these materials by a noninvasive technique, carbon-13 (^{13}C) nuclear magnetic resonance (NMR), and to relate the structural, chemical and physical, information obtained to previous results from X-ray diffraction of starches (Zobel, 1988a,b) and potato maltodextrins (Reuther et al., 1981). We have shown previously (Baianu and Förster, 1980) that it is possible to obtain solid-state NMR spectra of wheat starches and other related materials of great interest to the food industry without any modification of such materials. The technique is here applied to obtain additional, structural information for corn starch and to investigate some of the local, structural, and dynamic changes produced by gelatinization of hydrated starch granules. Differences between starches from different cereals and potatoes are of interest in this context and will also be considered.

In a recent paper (Mora-Gutierrez and Baianu, 1989), it was shown that corn maltodextrins and potato maltodextrins have different gelling behaviors, related to their distinct hydration properties. An attempt will be made to distinguish from ^{13}C NMR spectra those features—chemical or physical—that are responsible for such functional differences between maltodextrins from corn and potato. ^{1}H NMR relaxation studies of differences in the gelatinization behaviors of corn, wheat, and potato starches were also reported recently (Yakubu et al., 1990) and indicate that there are indeed significant differences not only between cereals and tuber starches but also between cultivars of the same plant. Although some of the structural differences between starches from different plant sources are known, the details of the changes occurring during gelatinization are still being debated. Solid-state NMR techniques are potentially an important source of information, complementary to X-ray diffraction, for the mechanism and structural details of the starch gelatinization process.

MATERIALS AND METHODS

Materials. Lo-Dex 5 maltodextrins, Amaizo Polar Gel 5, and Fro-Dex 55L corn syrup solids were kind gifts of American Maize Products Co. (Hammond, IN). The analytical data for these products are given in Table I.

Sample Preparations. Maltodextrins (Lo-Dex-5) (1.5 g) 1.0 g of chemically modified starch (Polar Gel 5) (1.0 g), and high-fructose corn syrup solids (Fro-Dex 55L) (1.25 g) were dissolved in H_2O–D_2O (2.5:2.5) and heated to 60 °C for 4 min before complete solubility was achieved. In the case of Polar Gel 5 a suspension was obtained instead. Three milliliters of solution was transferred into 10-mm high-resolution NMR tubes; these were shaken by a Fisher minishaker for complete mixing. Samples were allowed to stand at room temperature for 30 min before each measurement.

NMR Measurements. ^{13}C NMR spectra (50.3 MHz) were recorded in our laboratory with a Bruker CXP-200 multinuclear spectrometer operating at 4.7 T (Bruker Instruments, Inc., Billerica, MA). The number of scans required for adequate signal-to-noise ratio was ~100 for Lo-Dex 5 and Fro-Dex 55L and ~400 for Polar Gel 5.

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Table I. Chemical Analysis[a]

type of analysis	Lo-Dex 5	Fro-Dex 55L
DE	7	37.4
pH	4.2	4.4
% H_2O	6.1	1.88
% ash	0.32	0.30
carbohydrate composition, %	monosaccharides <1 disaccharide <2 trisaccharide <2 tetrasaccharides and higher ~95	fructose 10.4
oligosaccharide distribution, %	DP_1 = 0.70 DP_2 = 1.10 DP_3 = 2.50 DP_4 = 1.50 DP_5 = 1.15 DP_6 = 2.90	DP_1 (glucose) 10.6 DP_2 (maltose) 6.4 DP_3 (glucose) 7.0 DP_{4+} (glucose) 65.6

[a] Data from American Maize Co. (1984). [b] DP_n = n-unit polysaccharide (with anhydroglucose as the unit).

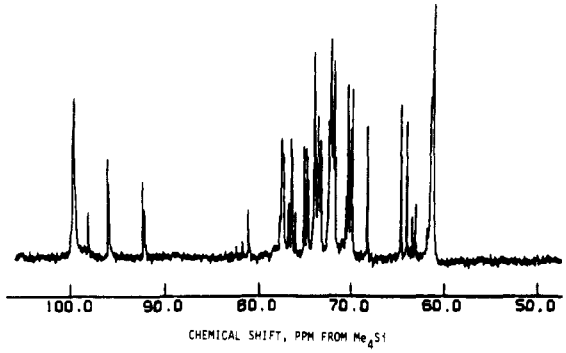

Figure 1. 50.3-MHz natural abundance ^{13}C NMR spectrum of a 25% Fro-Dex 55L solution in H_2O–D_2O (1:1) at 25 °C, recorded with proton broadband decoupling, 25-μs (60°) pulses, 100 scans, 1.5-s recycle time, 16k Fourier transform, 1.0-Hz line broadening by exponential multiplication, and 15-kHz bandwidth.

16K and 32K Fourier transforms were carried out on-line with a 24-bit Aspect 2000A computer. Other specific conditions are given in the legends to figures.

HPLC. Reverse-phase HPLC was carried out with a C-18 column, Microbondapack Series 410 (Perkin-Elmer). Fifty-microliter samples (2% w/v high-fructose corn syrups or Fro-Dex 55L) were injected, and chromatograms were recorded with a flow rate of 1 mL/min by monitoring continuously the refractive index at 890 nm.

RESULTS AND DISCUSSION

Fro-Dex 55L, a Corn Syrup. The carbon-13 NMR spectrum of a high-fructose syrup (Fro-Dex 55L) is shown in Figure 1. The main components of corn syrups are known to be glucose, maltose, oligosaccharides, and dextrins. The amounts of glucose and maltose vary with the degree of hydrolysis, which is measured by the reducing strength of the product expressed as dextrose equivalent (DE) (Table I). The assignments of the observed peaks (Table II) were made by comparison with the observed chemical shifts of amylopectin B (Dais and Perlin, 1982) and fructose (Pfeffer et al., 1979). The total integrated intensity of the carbon-13 NMR peaks of Fro-Dex 55L in the range ~70–80 ppm is significantly higher than the intensity of the other peaks. The 70–80 ppm region contains the C-2, C-3, C-4, and C-5 resonances assigned to fructose, oligosaccharides, and amylopectin B; oligosaccharides appear to be present in high proportion in this polysaccharide mixture. Glucose and maltose peaks overlap with the oligosaccharide peaks, making it impossible to quantitate the amounts of glucose and maltose.

Our reverse-phase HPLC data obtained with a C-18 column Microbondapack Series 410 (Perkin-Elmer) are consistent with the NMR data in regard to the high proportion of oligosaccharides.

Table II. ^{13}C Chemical Shifts of Corn Syrup Solids (Fro-Dex 55L) and Assignments

chemical shifts of ^{13}C resonance	resonance assignments
61.3; 61.4; 61.8	C-6 at the nonreducing end of oligosaccharides/large amylopectinfragments
63.0	C-6 of fructose (α-furanose)
63.5	C-6 of fructose (β-furanose)
63.9	C-1 of furctose (α- and β-furanose)
64.5	C-1 and C-6 of fructose (β-pyranose)
68.2	C-3 of fructose (β-pyranose)
69.6; 70.0	C-4 at the nonreducing end of oligosaccharides/large amylopectin fragments; C-3 and C-4 of fructose (β-pyranose)
70.4	C-3 of fructose (α-pyranose)
70.5	C-4 of fructose (β-pyranose); C-5 of oligosaccharides and amylopectin large fragments
71.8	C-2 of large amylopectinfragments
72.1	C-2 of large amylopectin fragments; C-5 of fructose (α-pyranose)
72.3; 73.2; 73.7; 73.9; 74.7; 74.9	C-3 of oligosaccharides and large amylopectin fragments
75.1	C-4 of fructose (β-furanose)
76.0	C-3 of fructose (α-furanose)
76.3	C-3 of fructose (β-furanose)
76.	C-5 of fructose (β-pyranose)
77.4	C-4 of the reducing end residues of oligosaccharides and large amylopectin fragments
81.1	C-6 of the reducing end residues of oligosaccharides and large amylopectin fragments
92.1; 92.5	C-1 at the α-reducing end of oligosaccharides
96.1; 96.3	C-1 at the β-reducing end of oligosaccharides
98.3	C-1 of the reducing end of terminal residues in trisaccharides (Gidley, 1985) and C-2 of fructose (β-pyranose)
99.8	C-1 of large amylopectin fragments (internal units)

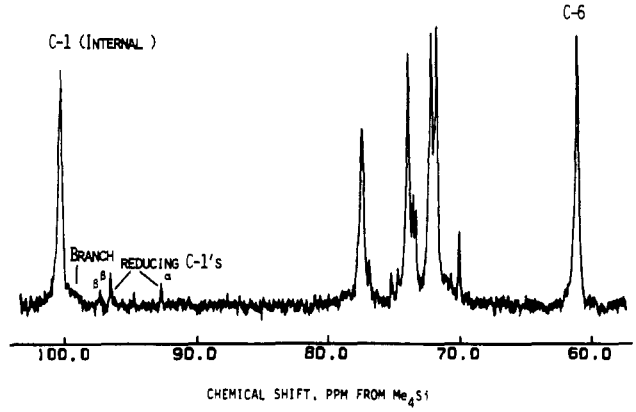

Figure 2. 50.3-MHz natural abundance ^{13}C NMR spectrum of a 30% Lo-Dex 5 solution in H_2O–D_2O (2.5:2.5) at 25 °C, recorded with proton broadband decoupling. The same conditions as in Figure 1 were used.

Maltodextrins. The ^{13}C NMR spectrum of Lo-Dex 5 maltodextrins is shown in Figure 2. This high molecular weight polysaccharide mixture exhibited 18 resolved resonances. Proposed assignments of these ^{13}C resonances are presented in Table III. On the basis of these peak assignments and the chemical analysis composition available from American Maize Co. (Table I), Lo-Dex 5 appears to mainly consist of oligosaccharides with molecular weights higher than tetrasaccharides that have D-glucose as the monomer. Maltodextrins derived from waxy maize starch, such as Lo-Dex 5, consist of branched oligosac-

Table III. ^{13}C Chemical Shifts and Assignments for Lo-Dex 5 Maltodextrins in Solution

chemical shifts, ppm	resonance assignments
61.4; 61.9	C-6 at the nonreducing end of oligosaccharides and large amylopectin fragments (I-1)[a]
70.1	C-4 at the nonreducing end of oligosaccharides and large amylopectin fragments (T-4)
70.7	C-5 of oligosaccharides and large amylopectin fragments (I-5); C-6 of $\alpha(1\rightarrow6)$ linkages
71.9	C-2 of oligosaccharides and large amylopectin fragments (I-2)
72.3; 73.6; 73.7; 74.1; 74.7; 75.2	C-3 of oligosaccharides and large amylopectin fragments (T-3)
77.0; 77.7	C-4 of oligosaccharides and large amylopectin fragments (I-4)
92.5	C-1 of the α-reducing end of oligosaccharides (α-1)
94.7	C-1 of oligosaccharides, involved in the $\alpha(1,6)$ linkages, or branching bonds (branch 1)
96.4; 97.3	C-1 of the β-reducing end of oligosaccharides (β-1)
100.3	C-1 at the nonreducing end of large fragments of amylopectin (I-1), or linear chain anomeric resonances

[a] Notations in parentheses are the corresponding 2D NMR assignments of McIntyre and Vogel (1990).

charides and low amounts of di-, tri-, and tetrasaccharides (Table I). Their gelling behavior appears to be significantly different (Mora-Gutierrez and Baianu, 1989a) from that of maltodextrins prepared in the laboratory from potato starch (Reuther et al., 1981; McIntyre et al., 1990). It is, therefore, of interest that the ^{13}C NMR spectra of Lo-Dex 5 (Figure 2) are more resolved than those of potato starch maltodextrins [Figure 4 on p 263 of McIntyre et al. (1990)], although the DE of the latter is 14, compared to the DE of 7 of Lo-Dex 5. The assignments of the ^{13}C resonances in Figure 2 are presented in Table III and are *in complete agreement* with the independent work on potato starch maltodextrins of McIntyre et al. (1990) and are also consistent with the assignments made from carbon–proton correlation spectra of potato starch maltodextrins and HMQC spectra [Figures 6a and 6b, respectively, on p 292 of McIntyre and Vogel (1990)]. The chemical shift values listed in Table III are also very close to those reported for wheat amylopectin (Dais and Perlin, 1982). It is interesting to compare further the branching degree, the degree of polymerization (DP), and estimated molecular weight averages for Lo-Dex 5 and potato starch maltodextrins (McIntyre et al., 1990). These parameters are important for the gelling behavior, as well as the utilization of such materials in foods. At present, Lo-Dex 5 is an established, commercial product, whereas the potato starch maltodextrins discussed above are a laboratory sample. From ^{13}C NMR spectra, such as that shown in Figure 2, one obtains a degree of branching of 2.4 ± 0.4% and a DP value of about 24 for Lo-Dex 5 (DE = 7), whereas the potato starch maltodextrins had a degree of branching of 3.1% (determined by ^{1}H NMR) and a DP of 12 (with a DE of 14).

Following the 60 °C heat treatment and cooling to 25 °C, the Lo-Dex 5 maltodextrin maintains a high mobility of the branches, whereas the potato starch maltodextrins (unheated) have lower branch mobility, in spite of their lower molecular weights. Furthermore, potato starch maltodextrins were reported to gel upon cooling after being heated to 70 °C (Reuther et al., 1981). The hydration

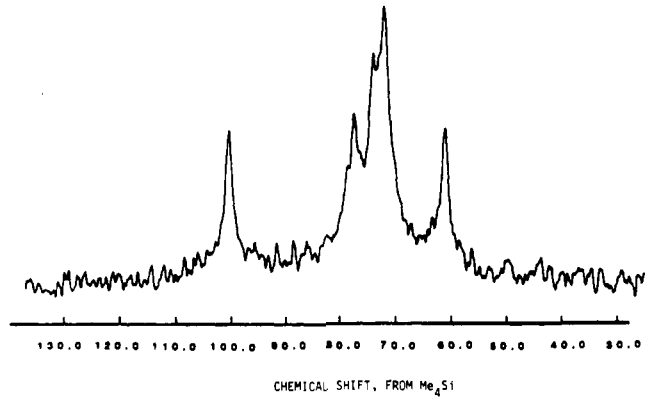

Figure 3. 50.3-MHz natural abundance ^{13}C NMR spectrum of a 20% Polar Gel 5 dispersion in H_2O–D_2O (1:1) at 25 °C. The same conditions as in Figure 1 were used.

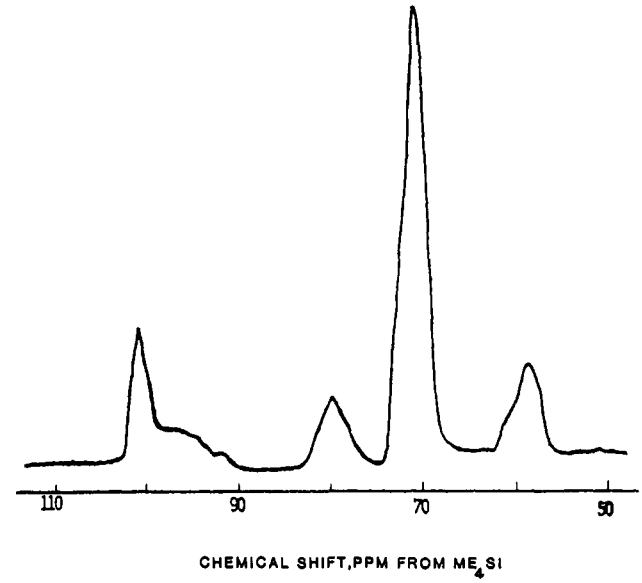

Figure 4. CP-MAS, ^{13}C NMR spectrum of gelatinized corn starch at 50.3 MHz recorded with 3-kHz spinning rate, 30-G decoupling radio frequency field, 500 scans, 5-Hz line broadening, 2.5-μs (90°) pulses, 15-kHz bandwidth, and 8k Fourier transform (4K data points).

properties of Lo-Dex 5 maltodextrins change dramatically upon heating to 60 °C followed by cooling to 25 °C (Mora-Gutierrez and Baianu, 1989), whereas those of potato starch maltodextrins change the opposite way—to increased water trapping caused by gelling (Reuther et al., 1981). For waxy maize maltodextrins, such as Lo-Dex 5, it is possible to obtain ^{13}C NMR results within a few minutes by employing 20 mm diameter sample tubes; this time-saving does not appear to be possible at present with potato starch maltodextrins (McIntyre et al., 1990) even at higher magnetic fields and for lower DP (lower average molecular weights).

Chemically Modified Corn Starch and Gelatinized Starch Compared with Unheated Waxy Maize Starch. The broadband proton decoupled carbon-13 NMR spectrum of a chemically modified starch (Polar Gel 5) is presented in Figure 3. Comparison of this spectrum with the CP-MAS spectrum of a gelatinized corn starch (Figure 4) shows that the chemically modified starch peaks of the internal, anomeric (100.9 ppm) and C-6 (61.6 ppm), carbons are similar in line width and chemical shift value to those of gelatinized starch. To improve the resolution in the carbon-13 NMR spectra of Polar Gel 5, one could use the cross-polarization (CP) NMR technique combined with magic-angle spinning (MAS), as we have done for gela-

Table IV. ^{13}C Chemical Shifts of Chemically Modified Waxy Maize Starch (Polar Gel 5)

chemical shifts, ppm	assignments of resolved ^{13}C resonances[a]	chemical shifts, ppm	assignments of resolved ^{13}C resonances[a]
61.6	C-6	77.9	C-4
72.4	C-2 and C-3	100.9	C-1
74.9	C-3		

[a]Amylopectin carbons only.

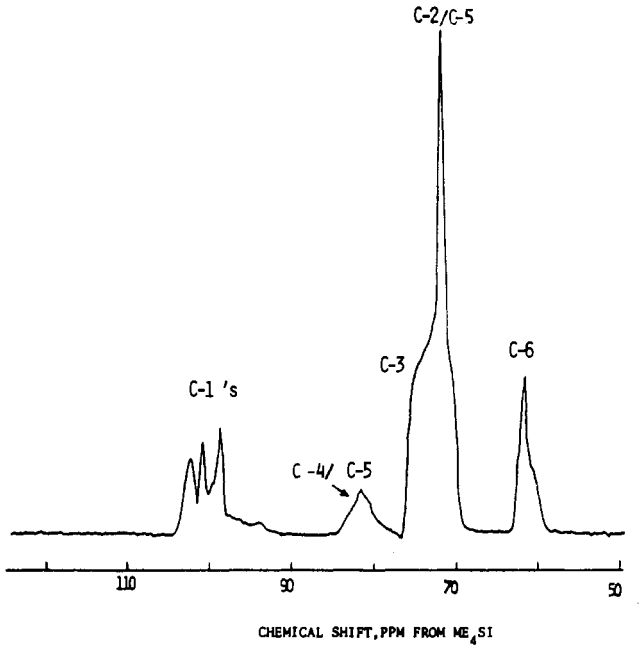

Figure 5. CP-MAS, ^{13}C NMR spectrum of nongelatinized corn starch at 50.3 MHz. Other conditions were as in Figure 4.

tinized corn starch. Since structural alterations by physical or chemical processing also modify the dynamics of specific sites in carbohydrate molecules, there are some significant differences in the region from 70 to 80 ppm between the CP-MAS spectra of gelatinized corn starch powders (Figure 4) and proton broadband decoupled ^{13}C NMR spectra of chemically modified corn starch in aqueous suspensions (Figure 3). The assignments of the observed peaks are summarized in Table IV. There is, however, a major difference between the CP-MAS, ^{13}C NMR spectra of gelatinized and nongelatinized corn starch in the anomeric carbon region (Dev et al., 1984; Marchessault et al., 1985; Mora-Gutierrez and Baianu, 1985) (Figures 4 and 5, respectively). The solid-state ^{13}C NMR spectrum in Figure 5 shows relatively sharp peaks in the hydrated (≳30% moisture w/w) waxy maize starch that correspond to the ordered, crystalline regions of amylopectin molecules in the starch granule; the *three* peaks of the anomeric carbon around 100 ppm are consistent with X-ray diffraction patterns which suggest that type A starch patterns originate from an asymmetric unit containing *three* D-glucose units. Underlying the three sharp peaks at about 100 ppm in Figure 5, there is a substantially broader peak that is most likely assigned to disordered amylopectin regions and has a wide distribution of chemical shift anisotropies corresponding to such disorder. Upon gelatinization, the three sharp peaks merge into one, indicating the transformation of the asymmetric unit into a symmetric one or alternatively the partial averaging of chemical shift anisotropy differences by fast molecular motions, as a result of gelatinization. The solid-state NMR spectrum in Figure 4 begins to resemble the low-power proton-decoupled spectrum of the starch suspension in Figure 3, although significant differences persist in the region from 70 to 80 ppm.

Our results in Figure 5 are in agreement with independent work by Veregin et al. (1986) and our previous report of solid-state ^{13}C NMR spectra of cereal starches (Baianu et al., 1990). In the latter, we have shown that dried starches from wheat do not exhibit any splitting of the anomeric carbon in the solid-state spectrum, although the peaks throughout the spectrum are sharp and correspond to a quasi-crystalline structure. In the case of potato starches, hydrated at the 30% level, there were only *two* peaks observed for the anomeric carbon in the solid-state NMR spectrum, consistent with an asymmetric unit containing only *two* glucose rings. These observations suggest that there is considerable *polymorphism* in the structure of the starch granules, depending upon hydration level, plant source, and amylopectin/amylose ratio. It is interesting that some of these differences are carried over to the maltodextrins prepared from such starches, as discussed under Maltodextrins. Such structural differences are also reflected in different functionalities of the maltodextrins and, therefore, in different utilizations/applications. In view of the short time required for recording solid-state NMR spectra of starches (of the order of a few minutes) and the fact that disordered structures, as well as crystalline regions, are readily detected by solid-state NMR, the technique is becoming increasingly important for the analysis of foods containing starches and the study of heat-processing effects on the starch structures. [For a review of the solid-state NMR techniques, the reader is referred to a recent paper (Baianu, 1989) and the references cited therein.]

Figure 6 shows expanded plots of the anomeric, C-1 region of corn syrups (Figure 6A), maltodextrins (Figure 6B), and chemically modified starch (Figure 6C). As expected, the average size of the polymer determines the line broadening. The broad component which is close to the baseline in Figure 6B is related to very high molecular weight components. On the other hand, the relatively small line widths of the sharp peaks at ~94–98 ppm (Figure 6A) are related to the units at the reducing ends which have increased mobility.

As the average size increases, broader peaks are observed (Figure 6) because the motional rate decreases with increasing average molecular size and the correlation time increases; in the case of Polar Gel 5, however, there are very fast, local chain motions, much faster than the tumbling rate of Polar Gel 5 particles. This is also likely to occur for many, but *not all*, amylopectin regions in gelatinized corn starch, where considerable chemical shift anisotropy remains (as in the anomeric region of Figure 4).

CONCLUSIONS

Comparative studies of corn syrups, maltodextrins, chemically modified waxy maize starch, and corn starch were carried out by ^{13}C NMR techniques. The results for corn maltodextrins and starches are compared with those for wheat starch, wheat amylopectin, amylopectin B, potato starch, and potato maltodextrins. Significant differences are found between the spectra of corn starch and corn maltodextrins and the corresponding spectra of potato starch and potato maltodextrins, respectively. Such differences for maltodextrins are concerned with the average degree of polymerization (DP), as well as the gelling properties of corn and potato maltodextrins. Chemical shift values for the various groups in these materials are

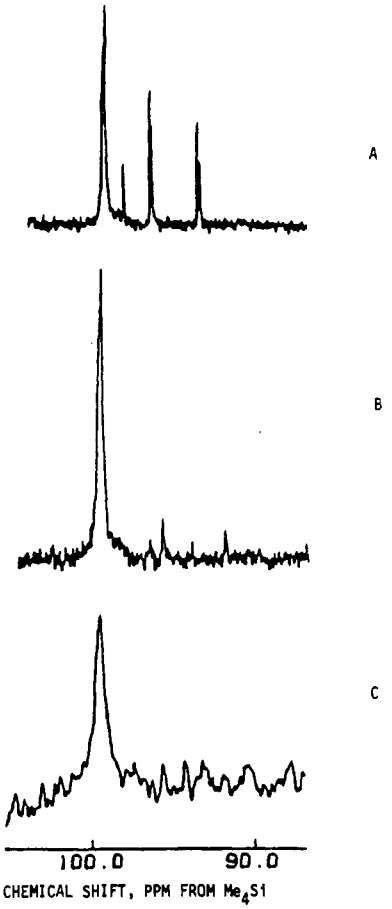

Figure 6. ^{13}C NMR expanded plots of the anomeric, C-1, region of the spectra of corn syrups (A), maltodextrins (B), and chemically modified starch (C), from Figures 1, 2, and 3, respectively.

very similar for materials from different sources (e.g., corn maltodextrins and potato maltodextrins). Carbon-13 NMR assignments are presented for all the materials discussed and are found to be in complete agreement with independent correlation spectra (2D NMR) assignments. Our ^{13}C NMR results are shown to be consistent with reverse-phase HPLC data for the lower molecular weight components and with analytical data presented for the maltodextrins and corn syrups.

Major structural changes are observed by solid-state ^{13}C NMR in the spectrum of corn starch. Such changes are interpreted to be due to the modification of the asymmetric unit of corn starch that contains three glucose rings in the crystalline regions of amylopectin in the corn starch granule. The noncrystalline, or disordered, regions of the amylopectin in the corn starch granule give a very broad band for the anomeric carbons, as expected for a wide distribution of chemical shift anisotropies of the anomeric carbons from the disordered regions. Upon gelatinization, the three anomeric carbon peaks merge into a single, sharp peak, suggesting that the asymmetric unit is replaced by a symmetric unit or else the increased molecular motion in such regions may be sufficient to average chemical shift anisotropy differences. A comparison with potato starch spectra indicates the presence of *polymorphism* in starch structures from different sources and/or at different hydration levels. Such interpretations are consistent with the analysis of X-ray diffraction patterns for starches (Zobel, 1988).

Technical improvements are suggested that would reduce the recording time of ^{13}C NMR spectra of corn maltodextrins to a few minutes, which is important for analytical and practical uses of ^{13}C NMR. This may not be possible, however, for potato maltodextrins, and in this case, ^{1}H NMR can be used (McIntyre et al., 1990; McIntyre and Vogel, 1990).

Carbon-13 NMR is a valuable tool for structural/comparative studies of starches and related or derived products. Structural details that are obtained about such materials concern degree of branching, degree of polymerization for maltodextrins, orientations of molecules and type of unit cell for the crystalline regions of starch, gelatinization, and gelling properties.

LITERATURE CITED

Amaizo Product Sheet, American Maize Co., 1984.

Aue, W. P.; Bartholdi, E.; Ernst, H. R. Two-dimensional spectroscopy. Applications to nuclear magnetic resonance. *J. Chem. Phys.* **1976**, *64*, 2229–2246.

Baianu, I. C. Solid-state NMR of Corn Starch Gelatinization and Retrogradation. Presented at the Starch Science and Technology Conference, Orlando, FL, 1985.

Baianu, I. C. High-resolution NMR studies of food proteins. In *Nuclear Magnetic Resonance in Agriculture*; Pfeffer, P. E., Gerasimowicz, W. V., Eds.; CRC Press: Boca Raton, FL, 1989; pp 167–218.

Baianu, I. C.; Förster, H. Cross-polarization, high-field carbon-13 NMR techniques for studying physicochemical properties of wheat grain, flour, starch, gluten and wheat protein powders. *J. Appl. Biochem.* **1980**, *2*, 347–354.

Baianu, I. C.; Kumosinski, T. F.; Bechtel, P. J.; Myers-Betts, P. A.; Yakubu, P. I.; Mora, A. Multinuclear spin relaxation and high-resolution nuclear magnetic resonance studies of food proteins, agriculturally important materials and related systems. In *NMR Applications in Biopolymers*; Finney, J., et al., Eds.; Plenum Press: New York, 1990; pp 361–389.

Bundle, D. R.; Smith, I. C. P.; Jennings, H. J. Determination of the structure and conformation of bacterial polysaccharides by carbon-13 nuclear magnetic resonance. *J. Biol. Chem.* **1974**, 2275–2281.

Dais, P.; Perlin, A. S. High field ^{13}C-NMR spectroscopy of β-D-Glucans, amylopectin and glycogen. *Carbohydr. Res.* **1982**, *100*, 103–116.

Dev, S. F.; Rha, C. K.; Burum, D. P. High-resolution CP-MAS and Solution NMR Studies of Polysaccharides. *Abstracts of Papers*, Starch 11th International Conference on Magnetic Resonance in Biological Systems, Chicago, IL, 1984; American Chemical Society: Washington, DC; p 114.

Doctor, V. M.; Echo, D. Studies by ^{13}C and ^{1}H NMR spectroscopy of polysaccharide structure following sulfation. *Carbohydr. Res.* **1983**, *121*, 312–315.

Dorman, D. E.; Roberts, J. D. Nuclear magnetic resonance spectroscopy. Carbon-13 spectra of some pentose and hexose aldopyranoses. *J. Am. Chem. Soc.* **1970**, *92*, 1355–1361.

Gidley, M. J. Quantification of the structural features of starch polysaccharides by n.m.r. spectroscopy. *Carbohydr. Res.* **1985**, *139*, 85–93.

Hall, L. D.; Sukumar, S.; Sullivan, G. R. Two-dimensional spectroscopy: ^{1}H NMR spectra of mono- and di-saccharides. *J. Chem. Soc. Commun.* **1979**, 292–294.

Marchessault, R. H.; Taylor, M. G.; Fyfe, C. A.; Veregin, R. P. Solid-state ^{13}C c.p.-m.a.s. n.m.r. of starches. *Carbohydr. Res.* **1985**, *144*, C1–C5.

McIntyre, D. D.; Vogel, J. H. Two-dimensional nuclear magnetic resonance studies of starch and starch products. *Starch* **1990**, *42*, 287–293.

McIntyre, D. D.; Clinton, H.; Vogel, J. H. One-dimensional nuclear magnetic resonance studies of starch and starch products. *Starch* **1990**, *42*, 260–267.

Mora-Gutierrez, A.; Baianu, I. C. NMR Relaxation Studies of Chemically Modified Starch Hydration and Structure of Polysaccharide Mixtures. Presented at the Starch Science and Technology Conference, Orlando, FL, 1985.

Mora-Gutierrez, A.; Baianu, I. C. ^{1}H NMR relaxation and viscosity measurements on solutions and suspensions of carbohydrates and starch from corn: The investigation of carbohydrate hydration, stereochemical and aggregation effects in relation

to ^{17}O and ^{13}C NMR data for carbohydrate solutions. *J. Agric. Food Chem.* **1989a**, *37*, 1459–1465.

Mora-Gutierrez, A.; Baianu, I. C. Hydration studies of maltodextrins by proton, deuterium and oxygen-17 nuclear magnetic resonance. *J. Food Sci.* **1989b**, *55*, 462–465.

Perlin, A. S.; Hamer, G. K. Characterization of carbohydrate polymers by carbon-13 NMR spectroscopy. In *Carbon-13 NMR in Polymer Science*; Wallace, M. P., Ed.; ACS Symposium Series 123; American Chemical Society: Washington, DC, 1979.

Perlin, A. S.; Casu, B.; Koch, H. J. Configurational and conformational influences on the carbon-13 chemical shifts of some carbohydrates. *Can. J. Chem.* **1970**, *48*, 2596–2606.

Pfeffer, P. E.; Valentine, K. M.; Parrish, F. W. Deuterium induced differential isotope shift ^{13}C NMR. I. Resonance reassignments of mono- and di-saccharides. *J. Am. Chem. Soc.* **1979**, *101*, 1265–1274.

Reuther, F.; Richter, M.; Schierbaum, F.; Anger, M. X-ray scattering by potato maltodextrins. *Abstracts of Papers*, 1st Bratislava Symposium on Saccharides, Smolence, Czecholovakia, 1981.

Seymour, F. R. Polysaccharide branching and carbon-13 NMR. In *Carbon-13 NMR in Polymer Science*; Wallace, M. P., Ed.; ACS Symposium Series 123; American Chemical Society: Washington, DC, 1979.

Veregin, R. P.; Fyfe, C. A.; Marchessault, R. H.; Taylor, M. G. ^{13}C cp.-m.a.s., n.m.r. of starch. *Macromolecules* **1986**, *19*, 1030–1034.

Yakubu, P. I.; Baianu, I. C.; Orr, P. H.; Bechtel, P. J.; Osman, E. Differences in the Physicochemical and Functional Properties of Corn, Wheat and Potato Starches. *Abstracts of Papers*, IFT National Meeting, Dallas, TX, 1991; American Chemical Society: Washington, DC.

Zobel, H. F. Molecules to granules: A comprehensive starch review. *Starch* **1988a**, *40*, 44–50.

Zobel, H. F. Starch crystal transformation and their industrial importance. *Starch* **1988b**, *40*, 1–7.

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