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THE ROLE OF SUGARS IN WOOD ADHESIVES BASED ON AMMONIUM SPENT SULFITE LIQUOR

by

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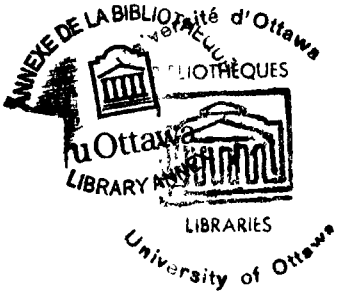

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PREFACE

Ammonium based spent sulfite liquor (ammonium lignosulfonate, NH_4SSL) is a waste by-product from pulp mills which contains 20 to 30% of hydrolyzed carbohydrate. Prior research and development work has demonstrated the possibility of using this pulping residue as an adhesive for wood. The carbohydrate portion of ammonium based spent sulfite liquor is thought to be partly responsible for its adhesive properties. Although studied intensively, the mechanism of the polymerization and condensation processes which are responsible for these adhesive properties of carbohydrates is still not completely understood. Commercialization of the ammonium sulfite liquor adhesive is not progressing as rapidly as anticipated, partly because of the lack of understanding of the chemical reactions involved. The aim of this thesis is to identify the functional groups and reactive species responsible for the adhesive properties of the carbohydrate portion of ammonium based spent sulfite liquor adhesives. Based on this information it may be feasible to formulate an ammonium based spent sulfite liquor with improved adhesive properties. This is a prerequisite to further commercial implementation of this adhesive.

LIST OF ABBREVIATIONS

^{13}C-NMR	Carbon - 13 Nuclear Magnetic Resonance
CP-MAS	Cross Polarization - Magic Angle Spinning
CaSSL	Calcium Based Spent Sulfite Liquor
DP	Degree of Polymerization
FAB	Fast Atom Bombardment
GC	Gas Chromatography
GC-MS	Gas Chromatography - Mass Spectrometry
HPLC	High Performance Liquid Chromatography
HMF	5-(Hydroxymethyl)-2-Furaldehyde
HP	Hewlett Packard
IB	Internal Bond
IR	Infrared
LC	Liquid Chromatography
MW	Molecular Weight
$\bar{M}_n$	Number-Average Molecular Weight
M/Z	Mass/Charge
NaSSL	Sodium Based Spent Sulfite Liquor
NH_4SSL	Ammonium Based Spent Sulfite Liquor
NMR	Nuclear Magnetic Resonance
PF	Phenol-Formaldehyde
PTLC	Preparative Thin Layer Chromatography
SSL	Spent Sulfite Liquor
TS	Torsion Shear
UV	Ultraviolet

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ABSTRACT

Monosaccharides are known to be active ingredients contributing to the adhesive properties of ammonium-based spent sulfite liquor. In order to achieve a better understanding of the involvement of low molecular weight sugars in the adhesion process, glucose - a representative sugar in NH_4SSL - was reacted under heat and pressure conditions similar to those used in the pressing of waferboard panels. The products collected at various reaction times were analyzed by analytical high performance liquid chromatography (HPLC). The reactions were conducted with and without the presence of catalysts, lignin, cellulose and wood. Representative fractions were collected by preparative HPLC. Each fraction was freeze-dried and analyzed by spectroscopic methods. The reactivity of each fraction and other related chemicals was evaluated by techniques especially devised for the examination of the adhesive properties of small quantities of material. treated carbohydrate fractions in the presence of a phenol-formaldehyde copolymer was evaluated.

Results indicate that polycondensation of the D-glucose molecules via formation of glucosidic linkages is the main initial reaction. It is a reversible process affected by variables such as oligomer molecular weight, alpha or beta glucosidic linkages, acid or small quantities of ammonium lignosulfonate catalysts, and press temperature and pressure. 1,6-Anhydro-D-glucose, 5-hydroxymethyl-2-furaldehyde and 2-furaldehyde are minor reaction products. Upon further heating the thermal polymer decomposes and dehydrates with formation of carbon-carbon double bonds and carbonyl functionalities which could

crosslink with participation of hydroxyl functionalities. Indirect evidence was obtained for the condensation of D-glucose with cellulose. Further studies with glass fibers showed that alternate mechanisms are also possible depending on the conditions of the reaction and the environment which is provided.

When used alone as an adhesive, D-glucose was the most reactive species studied while in the presence of phenol-formaldehyde (PF), 2-furaldehyde was more reactive.

A new adhesive system resin dispersion was obtained by simply blending ammonium spent sulfite liquor, an alkaline phenolic and, when required an acid catalyst. The curing properties of the NH_4SSL-PF resin depended on the composition of NH_4SSL, the amount of PF resin and the resin pH. A NH_4SSL-PF resin containing up to 50 percent NH_4SSL solids had curing and adhesive properties similar to a commercial phenol-formaldehyde resin currently used in the manufacture of waferboards.

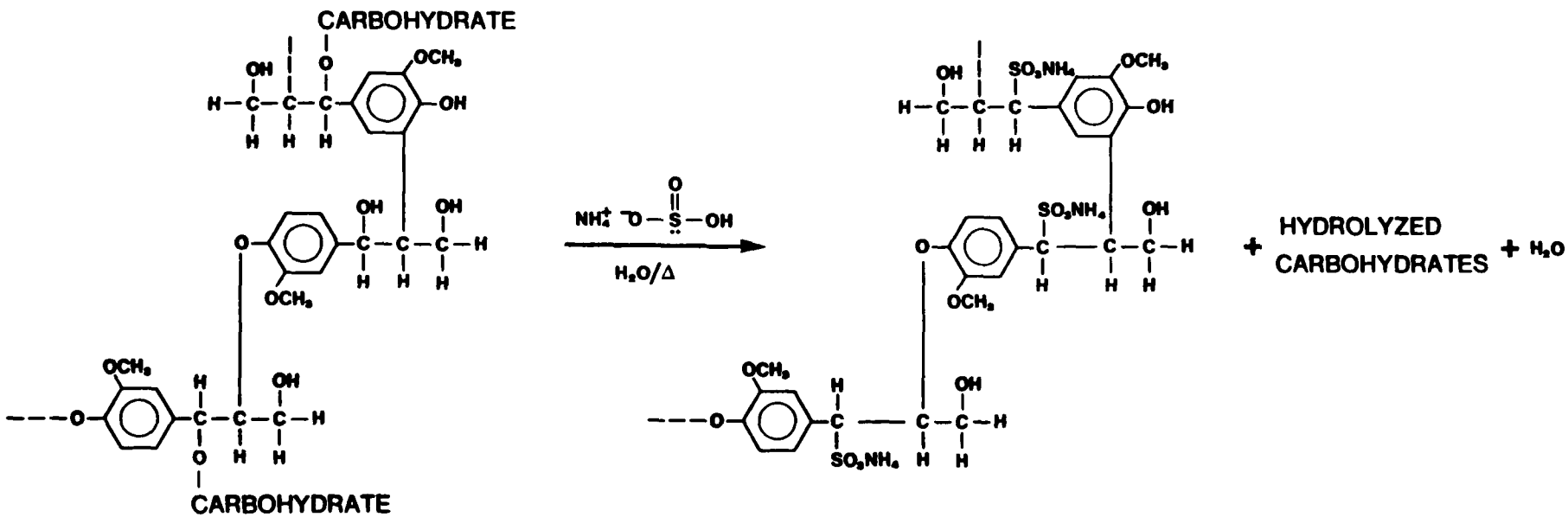
INTRODUCTION

Three natural polymer types are present in wood; cellulose 40 to 60%, lignin 20 to 30% and hemicelluloses 10 to 25% (by weight) varying with the species. It also contains small quantities of extractives and inorganics, generally less than 10% (1). Cellulose and hemicelluloses are carbohydrate polymers while lignin contains both aromatic and aliphatic groups. In the manufacture of wood pulp by the acid sulfite process, wood is heated under pressure in a solution of calcium, magnesium, sodium or ammonium bisulfite containing an excess of sulfur dioxide. The bond between lignin and carbohydrate is hydrolyzed and the lignin molecule is cleaved into smaller polymers and solubilized by transformation into its sulfonic acid salt (Scheme 1). Most cellulose remains unchanged and is recovered for the manufacture of paper. Some polysaccharides (mostly hemicellulose oligomers) are hydrolyzed into monosaccharides and other water-soluble substances. These are recovered in the raw cooking liquor along with soluble lignosulphonates. In general, spent sulfite liquor (SSL) contains approximately 65% lignin, 25% reducing sugars, and 10% inorganic materials on a solid basis. In North America, over 50 pulp and paper mills produce approximately 4 million metric tonnes of SSL (2) every year, most of which is burned at a low energy recovery cost or disposed of at great expense.

The fact that lignin is known as a natural binding agent in wood and has a chemical structure similar to phenol-formaldehyde resin frequently used as a wood adhesive has encouraged efforts in developing wood adhesives from SSL and other lignin sources. The literature

Scheme 1

Ammonium Based Acid Bisulfite Pulping of Lignocellulosic Material



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contains an impressive number of patents related to the utilization of lignin (3). Most of these have not been commercialized.

A few years ago, it was discovered that crude NH_4SSL could be used without any modification as a thermosetting adhesive in the replacement of conventional phenol-formaldehyde resin adhesive employed for the manufacture of waferboard, a wood-composite product of exterior grade quality (4,5). The potential of this new resin is enormous since 10% PF replacement with NH_4SSL could result in a saving of several million of dollars for the North American wood composite industry. Unfortunately, crude NH_4SSL requires high energy (high temperature and/or long press times) to achieve a level of cure comparable to PF. This would result in reduced mill capacity and make the process less attractive for industrial uses. This adhesive has been developed based on empirical considerations only with minimal understanding of the chemistry involved during the polymerization and bonding of NH_4SSL. A better understanding of the chemistry involved appears to be a prerequisite to further development and implementation of this technology.

The thermosetting and binding properties of SSL has commonly been considered to be a lignin polymerization reaction (6-11). Minimal importance was attached to the carbohydrates which are minor constituents of the SSL. In previous work on crude NH_4SSL (12, 13), we have demonstrated that the carbohydrate portion of NH_4SSL was responsible for part of its adhesive properties. In fact, under our experimental conditions, purified lignosulfonate with low sugar content when used alone as a wood binder, failed to bind wood while a simple carbohydrate such as D-glucose provided a durable bond (13). Optimum results were

obtained when the ammonium lignosulfonate to carbohydrate solid weight ratio was adjusted to 1:1. It was suggested that the ammonium lignosulfonate salt, which is a weak acid, catalyzed the dehydration of the carbohydrates (13).

The development of thermosetting adhesives from carbohydrates is not new. From the beginning of the century up to the present, parallel to the work on lignin adhesives, many research activities have examined the potential of carbohydrates in the formulation of thermosetting resin adhesives (13-22). Replacement of part or all of phenol-formaldehyde resin with carbohydrates has been reported on a number of occasions (15, 16, 17, 18-23). However most of this technology has not been pursued. Although the chemistry of thermal polymerization and degradation of carbohydrates has been studied intensively as judged by the vast literature available on the subject, including the interesting work of Shafizadeh et al. (24), Houminer (25), van der Kaaden et al. (26) and many others (for reviews see Ref. 27, 28, 29), the mechanism of polymerization and adhesion of carbohydrate is still not completely understood (13, 21, 22, 30-32). At the present, very little work has been done to identify the reactive species responsible for the adhesive properties of polymerized carbohydrates (13, 23, 33-35). Research on the thermal treatment of carbohydrate has been directed toward other goals (24, 36).

REVIEW OF CURRENT KNOWLEDGE

The Phenomenon of Adhesion

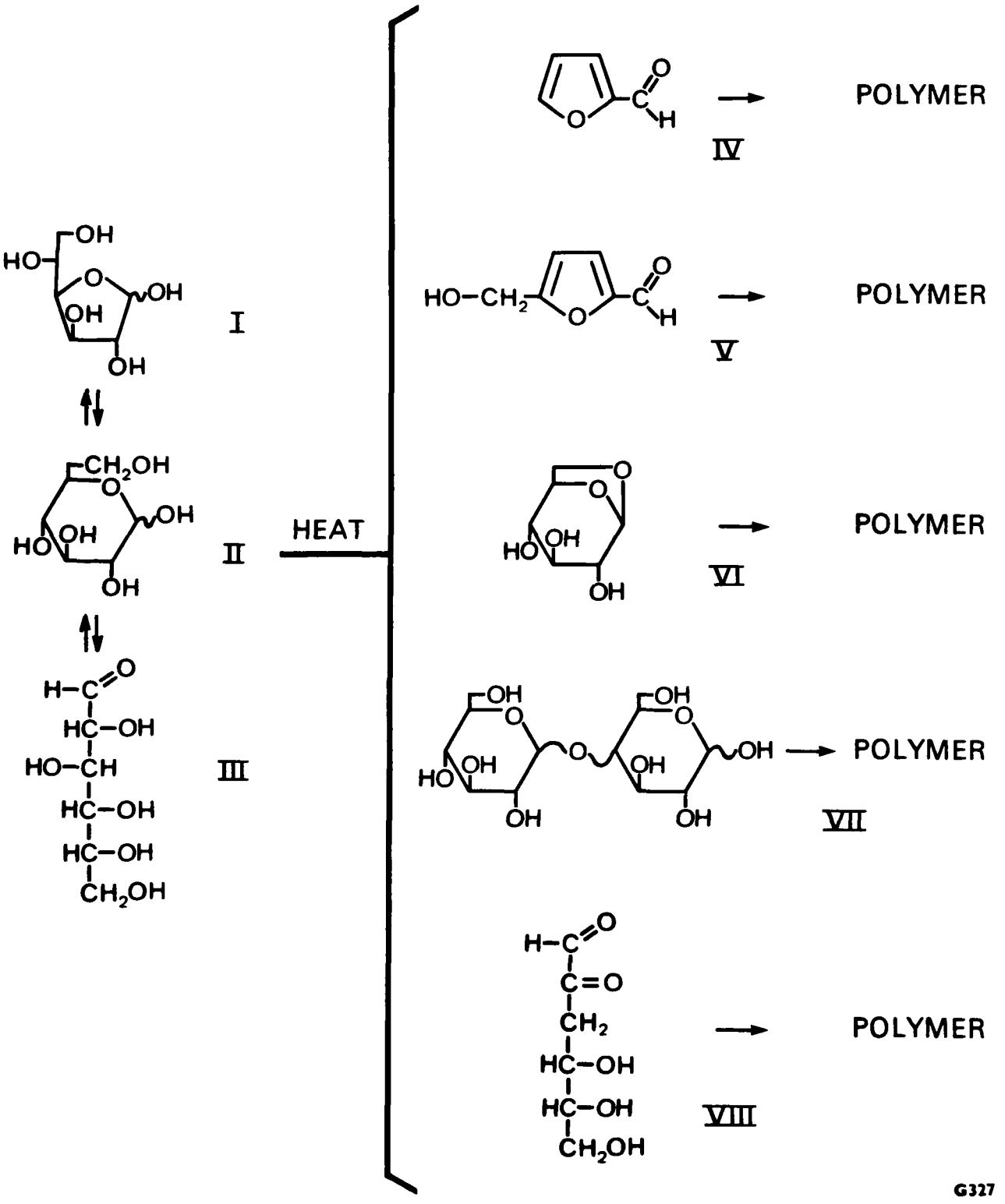
Over the years, several theories have been suggested to explain the phenomenon of adhesion (37-40); these include mechanical interlocking, diffusion, electronic- and adsorption-based mechanisms. Although none of these approaches alone completely explains the phenomenon, the adsorption theory is most widely accepted (37, 41, 42). This theory is based on the fact that a strong joint can be obtained between two ideal planar surfaces when brought into an intimate contact (43). Formation of a strong joint ensues due to the small but additive forces acting between the atoms on the two surfaces, the most common forces being van der Waals forces (37). When two rough surfaces are assembled - two pieces of wood for example - the area of contact is small and a very weak bond is obtained. An adhesive is required to wet or conform to the surface and provide a continuum. When the adhesive solidifies, a strong joint can be obtained. In the case of phenolic resins, solidification occurs through polymerization by condensation of phenol with formaldehyde. This is generally achieved by heating in the presence of a catalyst producing an insoluble and infusible crosslinked polymer. A strong durable joint, resistant to water hydrolysis, suitable for exterior applications is obtained. Although calculations show that van der Waals forces are sufficient to provide a strong joint (42), some researchers are of the opinion that an actual chemical bond between the substrate and the adhesive is required to provide a durable joint (37, 41, 42). Resin adhesives such as isocyanate or PF are believed to react with wood components during the manufacture of wood composites (44-46).

Carbohydrate Thermosetting Adhesives

Simple carbohydrates such as D-glucose, with or without the presence of acid (13, 18, 47) or phenolic copolymers (16, 19, 29, 35) can be used as a thermosetting adhesive for wood, producing a relatively strong durable bond. According to the adsorption theory, the carbohydrates may operate by wetting the wood substrate, then solidifying through self-polymerization into an insoluble and infusible mass. However, carbohydrates may also react with the wood, producing a durable joint. The problem with carbohydrates is the relative complexity of the molecule which can exist in various tautomeric forms in equilibrium either in water solution or in the molten state. For example, D-glucose may exist as an open chain (III) containing five hydroxyls and one aldehyde group or as a cyclic hemiacetal with pyranose (II) or furanose (I) structure (Scheme 2). The thermal polymerization of sugars is complex because various products have been obtained depending on the experimental conditions which have been employed. For example, when heated in vacuo, the main product of dehydration of glucose is levoglucosan or 1,6-anhydro-β-D-glucopyranose (VI) (48). If glucose is subjected to heat in an acid solution under controlled conditions or to high temperatures for a short period of time, 5-(hydroxymethyl)-2-furaldehyde or HMF (V) and 2-furaldehyde (IV) are the major reaction products (29, 49-51). An important intermediate to HMF formation is 3-deoxy-D-erythro-hexosulose or 3-deoxy-D-glucosone (VIII) (52-54). Alternatively, if glucose is heated at a lower temperature for a longer period of time, polycondensation of glucose occurs (VII) (55-58). All of these (IV, V, VI, VII and VIII) are known to polymerize and form high molecular weight material under the action of heat (25, 52, 54, 56-64).

Scheme 2

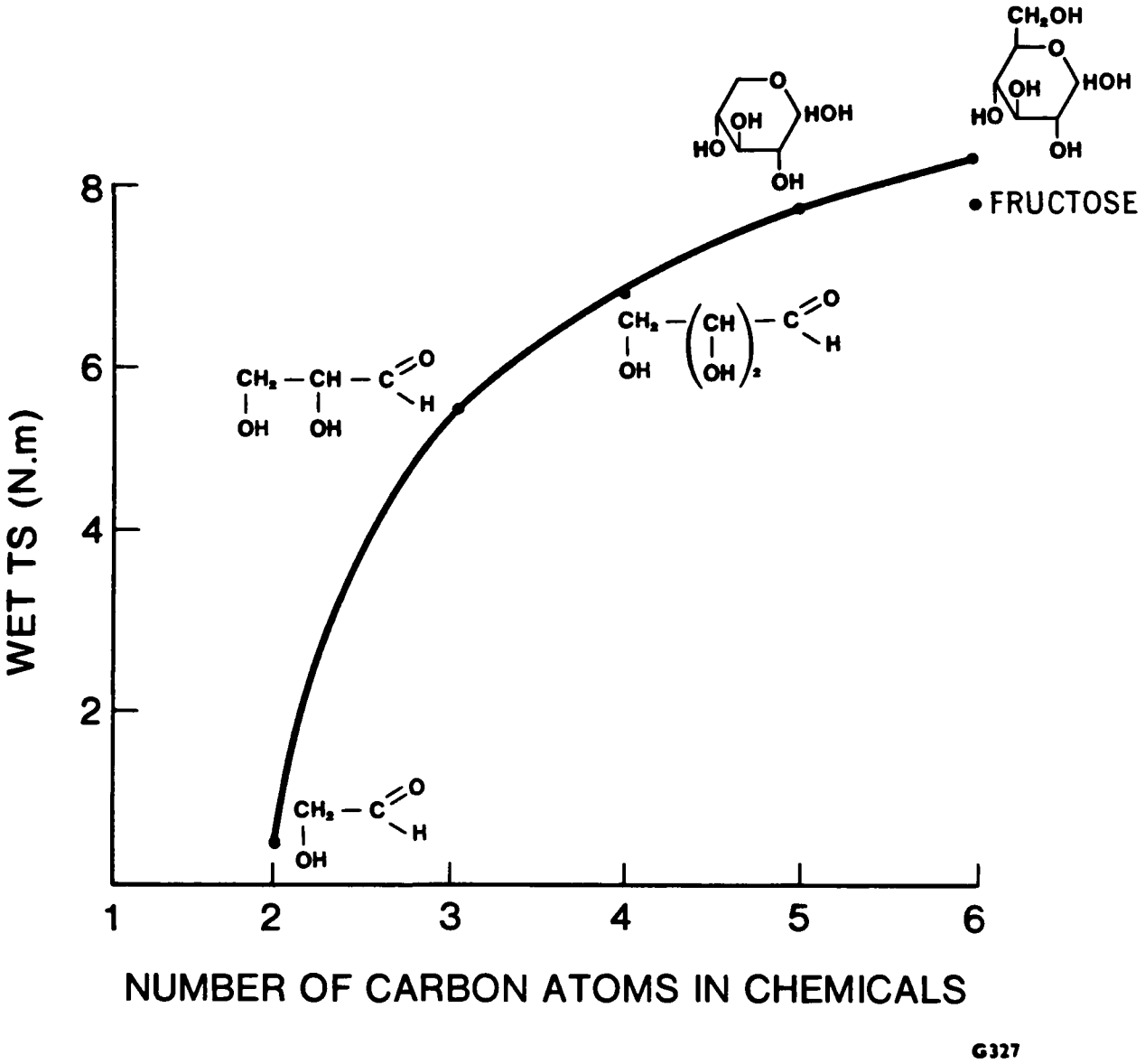
Possible intermediates in D-glucose thermal polymerization



From early work (14) up to the present (16, 18-20, 23), furan compounds have generally been assumed to be the reactive intermediates in carbohydrate adhesion. Under heat and pressure, the carbohydrate is transformed into a furan derivative which is then converted into a thermosetting resin with (14, 16, 19, 20, 23) or without (18, 20, 65) the presence of phenol and formaldehyde. The evidence for this process is based in part on the well known high reactivity of furans (62, 64, 66), which possess aromatic character and an aldehyde group similar to phenol and formaldehyde. In a recent study, it has been demonstrated that 2-furaldehyde or HMF could provide a strong joint (13). However, all the furaldehyde derivatives tested (alone, without copolymer) were surprisingly found to be less reactive than D-glucose. When a series of molded wood products were bonded with carbohydrates of different chain lengths, even glyceraldehyde, a three-carbon sugar, provided some bonding. The relationship between chain length and bonding efficiency (Torsion Shear or TS test) for small carbohydrates is reproduced in Figure 1. In addition a sample of 2-furaldehyde was still soluble in acetone after heating under pressure 16 hours at 175° C (13). These simple experiments indicate that furan may not be the only species contributing to the adhesive properties of carbohydrates (13). In fact, the real importance of furan in carbohydrate polymerization and in wood bonding remains unresolved. In recent studies related to the mechanism of condensation and bonding of carbohydrates, using modern chromatography and spectroscopy techniques, Christiansen and Gillespie (21) as well as Viswanathan et al. (67) reported that furan compounds could not be identified as reactive intermediates.

Figure 1

Influence of carbohydrate chain length on torsion shear
(from Ref. 13)



Carbohydrate thermosetting adhesives have generally been formulated based on empirical considerations only. An important part of carbohydrate thermal or pyrolytic studies relates to the depolymerization of cellulosic materials to produce useful chemicals (24, 36, 68-70) or to identifying the factors involved in flame propagation in connection with the problem of rendering cellulosics flame-resistant (71-75). The studies have often been carried out at temperatures of 300°C or above under a low pressure environment (24, 68-75). The low molecular weight materials or the tars have generally been partly characterized (24, 68-75), but little is known about the non-volatile, higher molecular weight, often highly crosslinked materials which are formed (76, 77). Other carbohydrate thermal studies conducted at lower temperatures often relate to the production of specific chemicals from carbohydrates such as HMF, 2-furaldehyde (29, 50-52, 78, 79) or even aromatic derivatives which would be responsible in part for the coloring of carbohydrate materials upon storage (80). Relatively few studies have addressed the mechanism of polymerization of simple carbohydrates such as D-glucose at temperatures below 300 C and these have generally been conducted at or below atmospheric pressure (54, 56-58, 81-86). Although the low molecular weight oligomers and carbohydrate dehydration products formed under these conditions have been partly identified and characterized (54, 56, 59, 63) very little is known about their relative reactivities (85), and their thermosetting and adhesive properties. How carbohydrates crosslink under heat and pressure to an insoluble, infusible mass is still not known.

AIMS OF THIS RESEARCH

The aim of this research has been to identify the functional groups and reactive species responsible for the polymerization and adhesive properties of the carbohydrate portion of NH_4SSL while studying the polymerization mechanism. It was anticipated that these results might be useful in formulating an improved adhesive. The possibility of improving the reactivity of NH_4SSL by copolymerization with a PF copolymer was also evaluated.

APPROACH

The approach selected for this study was to subject a carbohydrate model, D-glucose, to temperature and pressure conditions similar to those employed during the manufacture of waferboards. The reaction was to be conducted with or without the presence of a catalyst, lignin, or cellulose, and would be monitored externally by high performance liquid chromatography (HPLC) and other modern spectrometric methods. The heat-treated carbohydrate dehydration and polymerization products would be separated and collected using suitable fractionation techniques. It should then be possible to establish a correlation between the reactivity of each fraction and its chemical composition. The most reactive fraction would be identified and optimized if required. Based on these results, formulations of an ammonium lignosulfonate resin with improved reactivity may be feasible.

Since this work was performed within the context of a study on adhesives for wood composites, it is important that the ammonium lignosulfonate adhesives possess curing and bonding properties similar to those of conventional phenol-formaldehyde resins. The addition of a phenolic copolymer to ammonium spent sulfite liquor may be required to further improve its adhesive properties, resulting in partial rather than total replacement of PF resins in adhesive formulations. In the second part of the study, the reactivity of the heat-treated carbohydrate fractions in the presence of phenol-formaldehyde resin was to be evaluated. It may then be feasible to formulate an NH_4SSL-PF resin with adhesive properties similar to existing commercial PF used in the manufacture of wood composites.

METHODS OF FRACTIONATION

Various methods which have been used for the fractionation and purification of carbohydrates and their derivatives (53, 75, 81, 87-102), together with some of their advantages and disadvantages, are summarized in Table 1. Although gas chromatography (GC) is useful for the separation of carbohydrates, it requires derivatization and high temperature volatilization of the carbohydrate derivative (75, 91, 92). This may present some difficulties with heat-sensitive material (92) or materials of higher molecular weight. In comparison, liquid chromatography (LC) avoids these two problems (88, 94-102). Thus, materials of different molecular weight can theoretically be separated provided that a suitable 'stationary bed' (column packing) and mobile phase (eluant) has been selected, the limit being the solubility of the materials in the liquid phase. Solubility problems with substances of high molecular weight are not uncommon.

Various column packing materials were found suitable for the separation of carbohydrates. Activated carbon and Celite are some of the earliest materials used successfully for the chromatographic separation of homologous oligosaccharides (87). More efficient packings have been developed recently. For example, fractionation of oligosaccharides up to a degree of polymerization (DP) of 60 was reported using polyacrylamide gel (94). Unfortunately the gel is not suitable for high performance liquid chromatography (HPLC) where a relatively high pressure is used to force the eluant through a bed made of very small (3-50 m) particles (100). Also, similar to activated carbon and Celite, the gel would be less suitable for the separation of low molecular weight carbohydrate and dehydration products (81, 103). Amine-modified silica packing could

Table 1

Selected methods of fractionating carbohydrates and derivatives

Fractionation Technique	Membrane or Column Packing - Material	Eluant	Advantages/Disadvantages
Ultrafiltration/ Reverse Osmosis	Aromatic Polymer[1]	H_2O	Fast/poor separation of low molecular weight material
Column-Gas Chromatography	Crosslinked Dimethyl Silicone	N_2	Fast/good separation Needs derivatization
Column-Liquid Chromatography	Activated Carbon-Celite	H_2O/Alcohol	Slow/good separation Organic eluant
	Alkylated Silica Gel	H_2O	Fast/good separation/Degenerates rapidly under experimental condition
	Sulphonated Divinyl-Benzene-Styrene Cation Exchange Resin	H_2O	Fast/good separation Could be regenerated
	Polyacrylamide Gel	H_2O/Buffer	Slow/Good Separation Does not withstand high pressure
	Amine-Modified Silica	H_2O/Acetonitrile	Fast/Good Separation Organic eluant

[1] Anisotropic membrane with high hydraulic permeability.

provide an excellent separation in a short period of time (96-99). Unfortunately, it is usually used with a water-acetonitrile elution gradient. Using an expensive organic solvent and an elution gradiant system which requires extra manipulations may not be practical for the separation of large quantities of material. In a preliminary screening study, alkylated silica packing was evaluated for the fractionation of heat-treated D-glucose. As expected from previous work, acceptable separation was obtained (96-99). Unfortunately the silica column was found to lose its resolution on repetitive separations and was difficult to regenerate. Carbohydrates can also be fractionated using a sulphonated divinylbenzene-styrene cation exchange (ion-exchange resin) packing material (100-103). This ion exchange resin bears groups that are capable of both polar (the sulfonic acid moiety) and non-polar (the aromatic backbone) interactions (102). This ion exchange resin material has been found suitable for the fractionation of both carbohydrate oligomers and carbohydrate dehydration products (102-104). Similar to the silica packing, the ion-exchange resin is available in different particle sizes and price ranges and thus could thus be tailored for both analytical and preparative work. Chromatography through an ion-exchange resin, using water as a eluant, was used for most of the preparative and analytical separations of heated carbohydrates and derivatives in this study. The analytical work was performed using two pre-packed columns from Bio-Rads laboratories in series in the following order: (A) Aminex HPX-87P (lead) and (2) Aminex HPX-42A (silver).

The preparative work was performed using columns hand-packed with AG 50W-X4 cation (Ca^{++}) exchange resin. A less expensive packing of larger particle sizes (see Experimental) was found to be adequate. For

comparison, the heated carbohydrate material was also fractionated by ultrafiltration. This technique was also used to fractionate NH_4SSL to different molecular weight ranges. Fractionation was accomplished by using membranes of different pore sizes. The membranes are permeable to low molecular weight solvents but retain polymeric materials which have molecular dimensions larger than a critical size; corresponding to the 'cut off level of the membrane'. Membranes with a molecular weight cut off level of 500 and over were used for this study. This technique has been used successfully in the past for the fractionation of ammonium lignosulfonate (12, 13).

METHODS OF EVALUATION OF CARBOHYDRATE REACTIVITY

Carbohydrates can be used as heat-hardening resins. A simple method for investigating the curing rate of a thermosetting resin is to subject the resin to different thermal treatments and measure the change in its molecular weight (105, 112) or its rate of insolubilization (106). Liquid chromatography is a useful tool to accomplish the former task (107). Size exclusion chromatography is a well known technique often employed for the characterization of adhesive polymers (108-112). Although the fractionation through the sulphonated divinylbenzene-styrene cation exchange packing material is obtained through a complex sample/packing interaction (ion exchange, ion exclusion, normal phase partition, size exclusion, ligand exchange and reverse phase partition) size exclusion is believed to be the primary mechanism involved in the separation of oligosaccharides (102). Size exclusion is based on the physical exclusion from the interparticle volume, of molecules too large to penetrate the effective pore structure of the resin. The high

molecular weight carbohydrate is thus eluted first followed by the lower molecular weight material. In this study, analytical HPLC with ion-exchange resin packing was used to obtain a profile of the molecular weight distribution of the water soluble portion of carbohydrates, heat-treated under various conditions. In addition to the analytical work, preparative liquid chromatography involving an ion-exchange resin was employed for the purification and collection of various heated carbohydrate fractions, which could be characterized for the relative rate of insolubilization concomitant with change in molecular weight. This was accomplished by subjecting selected fractions to further heat treatments and analysis of the heated material by analytical HPLC.

Another simple method for investigating the relative rate of cure of thermosetting resins is to heat the resin under pressure until it reaches the crosslinked, insoluble and infusible stage. The time required, at a given temperature, to reach this crosslinked stage is directly related to the reactivity of the material being studied. Since the bonding properties of a material are related to its ability to crosslink, an indirect measurement of the extent of crosslinking can be obtained from the measurement of adhesive strength in the mechanical torsion shear (TS) test (13, 113). In practice (see experimental section), wood particles were coated with a few percent of the substance whose adhesive properties were being investigated. The adhesive-coated particles were placed in a paper mold and consolidated in a press with heat and pressure to set the adhesive (see Figure 2). Small 'particleboard' specimens were then immersed in boiling water to eliminate any uncured resin adhesive, and wet torsion shear (TS) strength measurements were conducted.

Figure 2

The press used to produce particleboard

The main advantage of this test, requiring only a small sample of the material, is its reproducibility. Also, the results can be correlated easily to accepted standard tests: Internal Bond Test CAN3-0188.1-M78 (114).

RESULTS AND DISCUSSION

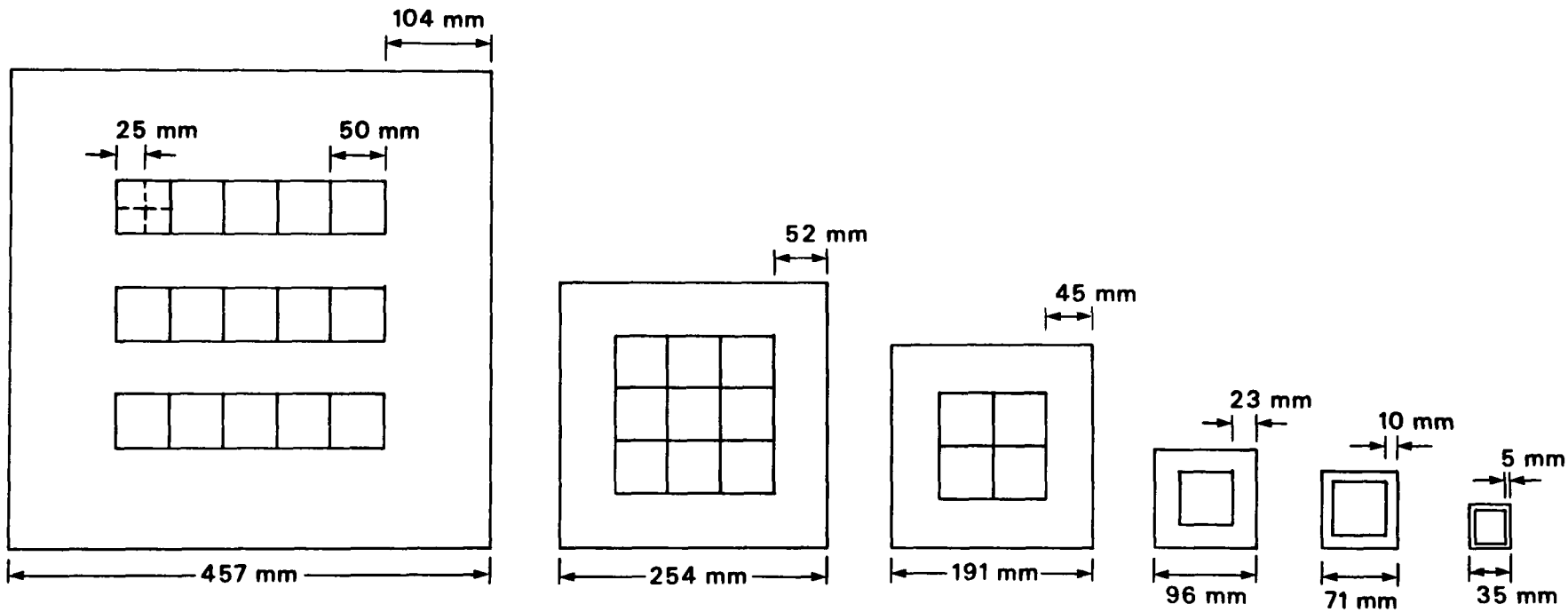
PART I. CHOICE OF METHOD FOR EVALUATING SMALL SAMPLE OF ADHESIVE

A basic study on adhesives usually involves the evaluation of the adhesive properties of small samples of material which may take months to collect and prepare. Various techniques for evaluating small quantities of adhesives have been proposed in the past (13, 115, 116). Although promising results were obtained with some of these techniques, none was fully satisfactory because of the difficulty in relating results obtained from tests of non-standard assemblies, such as 40-mm diameter molded disks (13), to those obtained for standard 457 x 457-mm laboratory panel assemblies.

In this study, small particleboard panels were produced under conditions similar to those used for the manufacture of larger panels. To demonstrate the relationship, a series of 11.1-mm thick particleboard panels were prepared with dimensions varying from 35 x 35 mm to 457 x 457 mm (Figure 3). Phenolic resin content was 6% and pressing time was 8 minutes. As indicated in Figure 4, both internal bond (IB) and torsion shear (TS) results were found to be practically independent of panel size. For the remainder of the study 35 x 35-mm panels, which required only 0.9 g of adhesive for each test, were prepared. Use of a paper mold to maintain the wood particles in place during handling and pressing helped to provide a panel with tight and uniform edges (Figure 2). Reproducible test results were obtained using this technique. Subsequently wet TS tests were used exclusively for comparing the reactivity of adhesives. Wet TS provides information similar to wet IB (Figure 4) and less time and material are required.

Figure 3

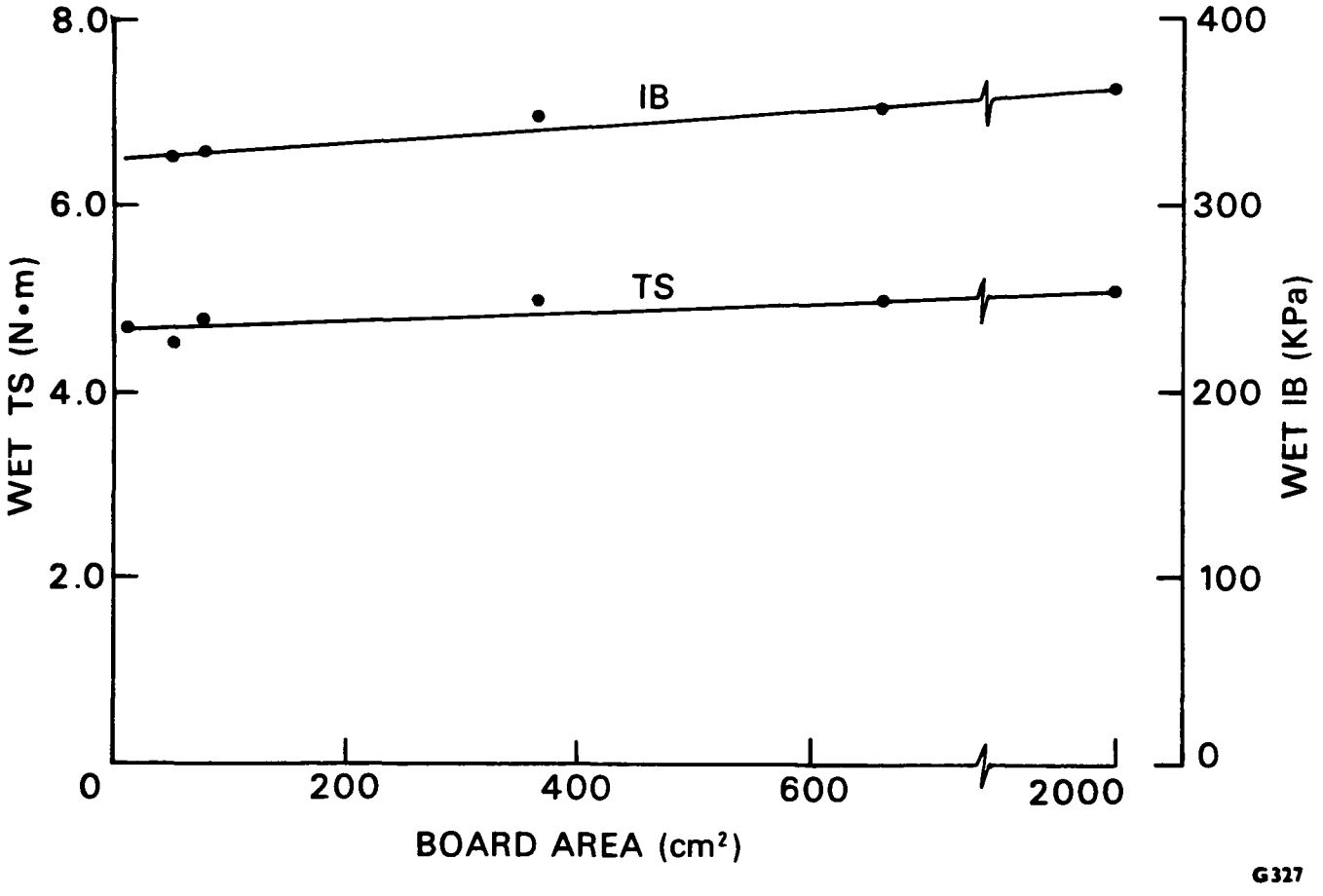
Cutting pattern of the various particleboards [1]



1 Adhesive requirements for 457 x 457-mm and 35 x 35-mm particleboards are 120g and 0.9g respectively.

Figure 4

Relation of panel size to wet internal bond and torsion shear



Identifying a good adhesive and following its rate of cure is possible using small particleboards and the TS test technique. This is illustrated in Figure 5, which shows the relationship between wet TS and length of press cycle, for 35 x 35-mm panels bonded with 6% PF. The sharp increase in wet TS strength between 4-and 6-minute press cycles clearly indicate the cure time for this particular resin.

CHOICE OF CARBOHYDRATE THERMOSETTING STANDARD

The adhesive properties of the major constituents of NH_4SSL were evaluated for TS strength in particleboard panels (Table 2). As expected from results of previous work (12, 13), purified lignosulfonate with low reducing sugar contents failed to bond wood. However, the monosaccharides present in the NH_4SSL pulping effluent do contribute to the bonding. Mannose produced boards with the highest TS values, with 6.1 N.m, while arabinose was the lowest, with 2.9 N.m. In general, the six carbon sugars (mannose, glucose and galactose) produced a better particleboard when pressed 15 minutes at 230°C than did the five-carbon sugars (arabinose, xylose). These results confirm those of a previous study which also indicated that the six-carbon sugars produced a stronger bond when used alone as a wood adhesive (13). Since most of the work reported in the literature on thermal polymerization of carbohydrates involved a glucose monomer or polymer as substrate (15-36, 48-53, 55, 57, 58, 68, 69, 71-86), this compound was selected for this study.

Figure 5

Effect of press cycle on TS for 35 x 35-mm particleboards pressed at 175°C with 6% PF

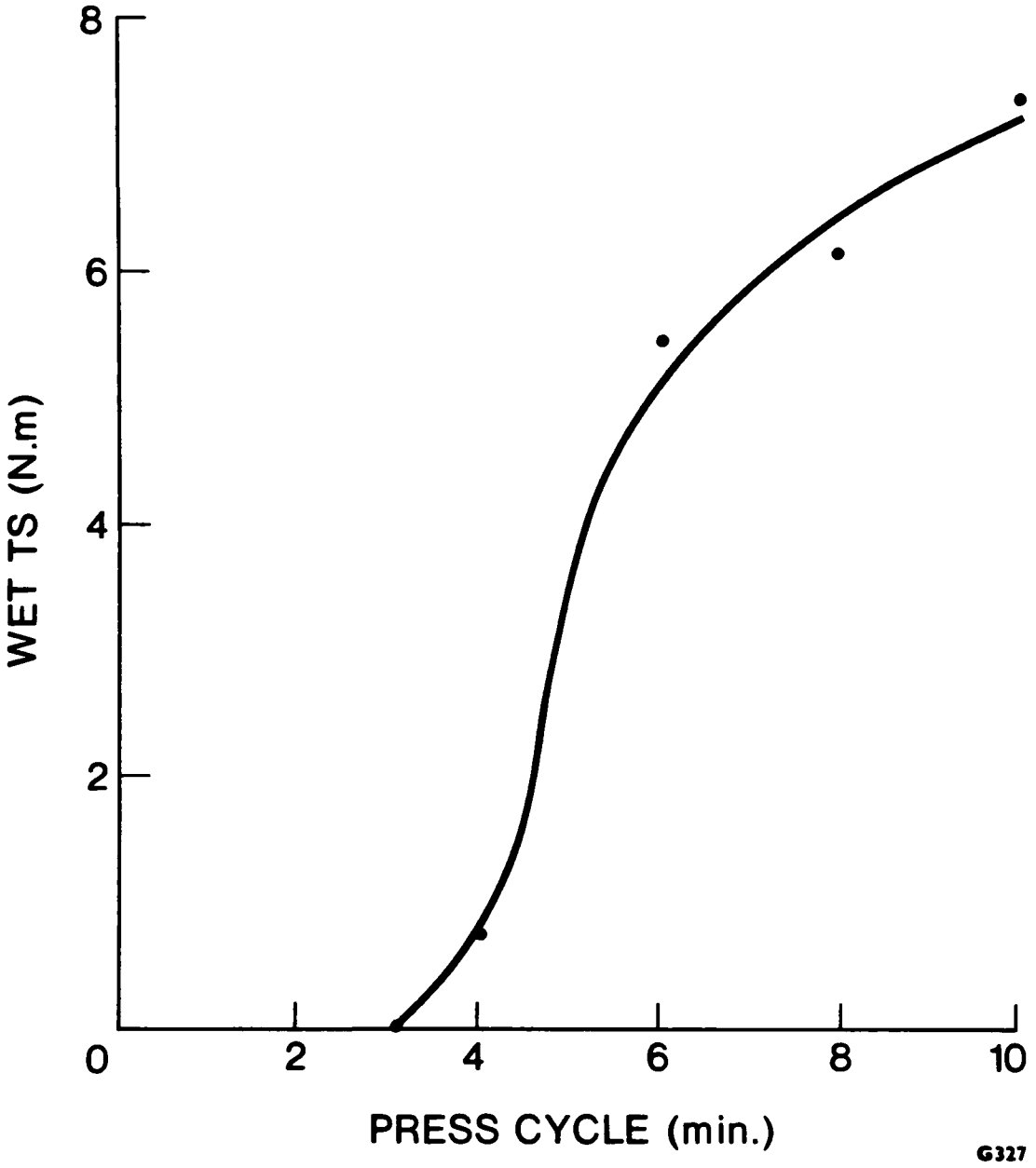


Table 2

Evaluation of adhesive properties of major constituents of NH_4SSL

Constituents	Content in NH_4SSL[1] (Solid Weight %)	230°C - 15 min. TS (N.m)
Monosaccharide		
Mannose	8.1	6.1
Xylose	3.6	3.0
Glucose	3.3	4.2
Galactose	3.2	5.4
Arabinose	1.4	2.9
Lignin		
Ligno-SO_3NH_4 (MW>5,000)[2]	52.8[3]	0

1 Monosaccharide contents are results of HPLC obtained from the laboratory of Tembec Inc., Temiscaming, Quebec.

2 NH_4SSL sample diafiltrated and washed twice with water through a Diaflo YM-5 ultrafiltration membrane having a nominal molecular weight (MW) cut-off of 5,000.

3 Lignin content determined from ultraviolet (UV) spectra, the corresponding total monosaccharide content as measured by HPLC was 7%.

ANALYTICAL HPLC CHROMATOGRAMS OF HEATED D-GLUCOSE

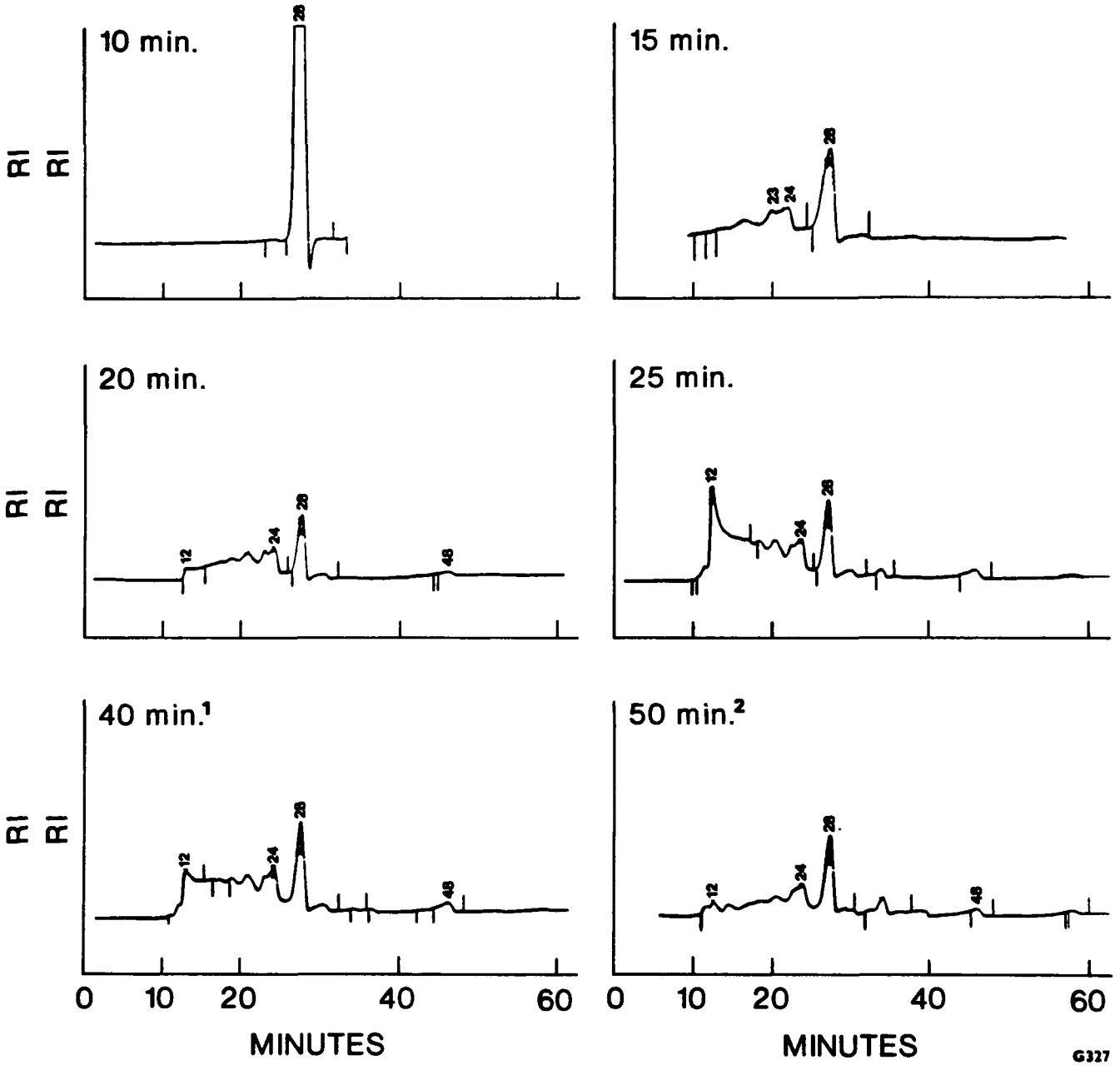
Although miniature particleboards and TS tests generated useful information on the reactivity of resin adhesives, information on the mechanism of resinification was desired. For this purpose, liquid chromatography of carbohydrates, subjected to various thermal treatments under conditions similar to particleboard manufacture, was utilized.

During the pressing of particleboards, the resin coated wood particles are subjected to heat and pressure. Since wood is a good insulator, the heat is transmitted slowly from the surface of the panel to its centre. To simulate pressing conditions, anhydrous glucose was placed in a pressure reactor under 2.8 MPa of nitrogen gas (N_2) and the reactor was immersed in a oil bath at 230°C for various periods of time. This technique permits treatment of relatively large quantities of material at one time. Also, due to the relatively high N_2 pressures employed, practically no sample loss was recorded during the 0-50 minutes of treatment. Thus, only one component (the residue) required analysis.

The HPLC chromatograms showing the transformation of heated glucose with time are shown in Figure 6. At ten minutes in the pressure vessel, only one HPLC peak, the starting material (glucose - 28 minutes retention time), was recorded. After 15 minutes of heat treatment, new peaks were observed on both sides of the starting material indicating that the glucose had started to dehydrate and polymerize. The gradual formation of material with short elution times - high molecular weight material - can be observed at 20 and 25 minutes of heat treatment. Only the water-soluble fraction of the treated sugar is recorded on the HPLC chromatogram. Upon further heating insoluble material began to form (see footnote, Figure 6) and as expected, the peak representing the higher

Figure 6

Analytical HPLC Chromatograms of glucose heated in a pressure vessel at 230°C with 2.8 MPa (N_2)



1 Sample 1% insoluble in hot water.

2 Sample 80% insoluble in hot water.

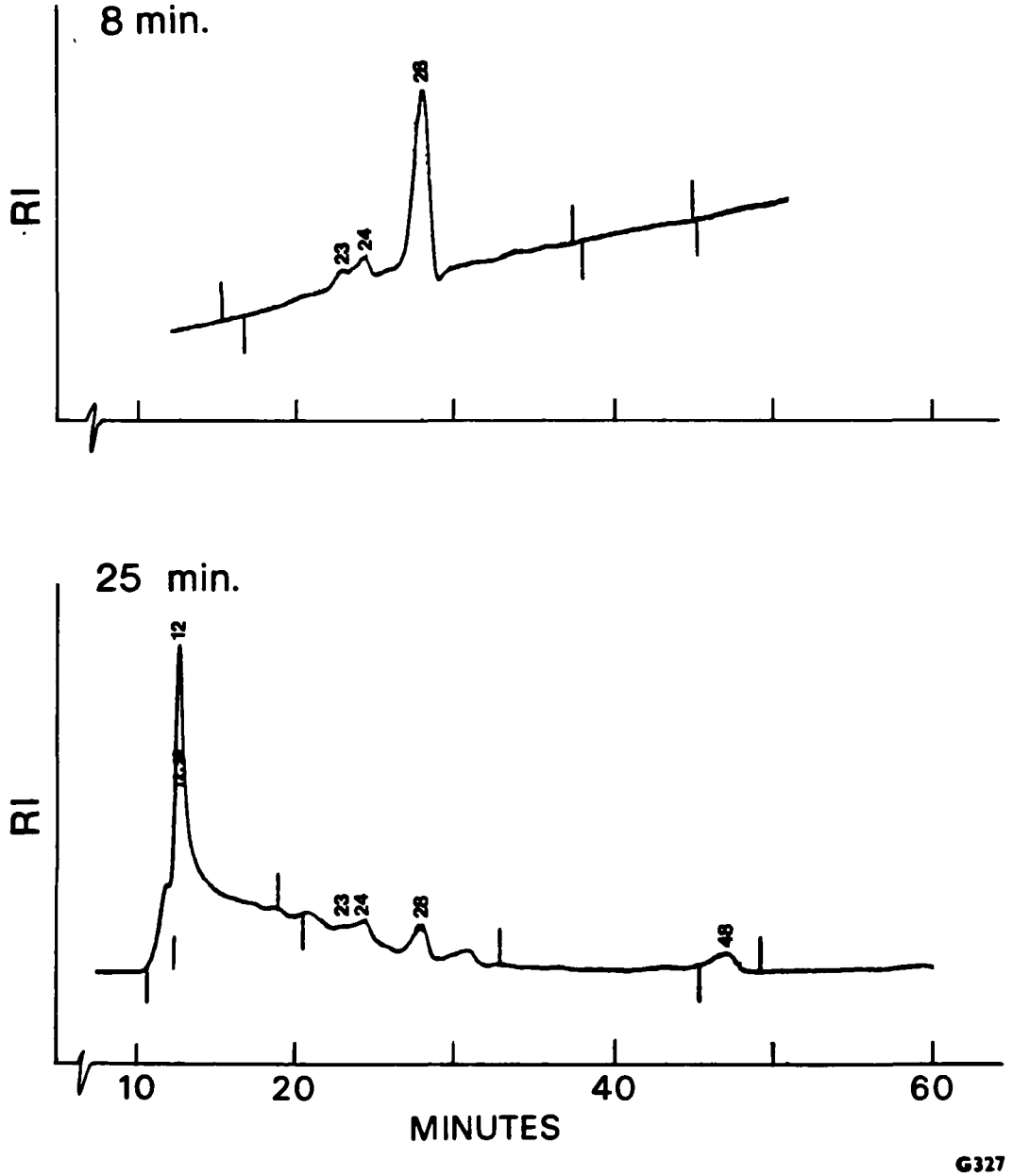
molecular weight material (12 min. elution) started to decrease in intensity.

After 50 minutes of heat treatment, most of the material eluting before glucose had disappeared. These results indicate that, upon heating, glucose is slowly transformed into an insoluble, high molecular weight material.

In order to verify if the pressure vessel technique was representative of what occurs during the manufacture of particleboard, glucose was pressed at the centre of a particleboard between two Teflon sheets (see Experimental, p. 126). This technique is less practical for the preparation of large quantities of material since glucose melts during pressing and a large percentage is lost, as it flows out of the teflon sheets. Nevertheless, both techniques, pressure vessel and Teflon sheets yielded similar chromatograms. For example the chromatograms corresponding to 8 minutes pressing between Teflon sheets (Figure 7) and 15 minutes in the pressure vessel (Figure 6) are nearly identical. The chromatogram corresponding to 25 minutes in the press between Teflon sheets displays a larger concentration of high molecular weight material than the equivalent chromatogram for the pressure vessel treatment. In a separate experiment with the pressure vessel, it was observed that the proportion of high molecular weight material increased with decreasing N_2 pressure. Since the press is effectively open on the sides and closed to metal stops (see Experimental, p. 126), the actual pressure on the sample between the Teflon plates is less than the measured press pressure. Reduced pressure is known to favour the formation of high molecular weight polymers from D-glucose (25).

Figure 7

Analytical HPLC chromatograms of glucose heated in a press (230°C, 6.9 MPa) between two teflon sheets at the center of a particleboard panel



To ascertain whether similar reactions would occur in the presence of wood, composites comprised of pre-extracted wood particles (see Experimental, p. 127) were pressed for 8 and 25 minutes with 6% glucose and the resulting specimens were each extracted with water for 3 hours in a Soxhlet extractor. The water-soluble fractions were analyzed by HPLC. As indicated in Figure 8 (wood, 25 minutes), pre-extracting the wood for 16 hours with hot water (see Experimental, p. 127) did not eliminate the large peak at a 12-minute retention time. Comparing the chromatogram of Figure 8 (8 minutes press) with those of Figure 7 (8 minutes press, Teflon) and Figure 6 (15 minutes press. vessel) suggests that a similar reaction is occurring when wood is present; at least at the beginning of the polymerization. The glucose peak at 28 minutes retention time can be recognized along with the characteristic double, skew peak of higher molecular weight material at elution times of 23 and 24 minutes, respectively. These peaks could also be recognized as the D-glucose samples heated 25 minutes in the press in the presence (Figure 8) or absence (Figure 7) of wood.

ANALYSIS OF D-GLUCOSE THERMAL REACTION PRODUCTS

Figure 9 compares the analytical HPLC chromatograms of a standard solution of acid-hydrolyzed starch (corn syrup) with the chromatogram of heated glucose. Cellobiose, fructose, mannose, 1,6-anhydro-D-glucose, HMF and 2-furaldehyde were added to the standard solution of corn syrup as references. The two Aminex cation exchange resins used in series (see Experimental; p. 123) provided an acceptable separation of corn syrup oligomers up to a degree of polymerization (DP) of 8. Also good separation of stereoisomers and glucose dehydration

Figure 8

Analytical HPLC chromatograms of water extracted wood particles pressed at 230°C with and without 6% D-glucose

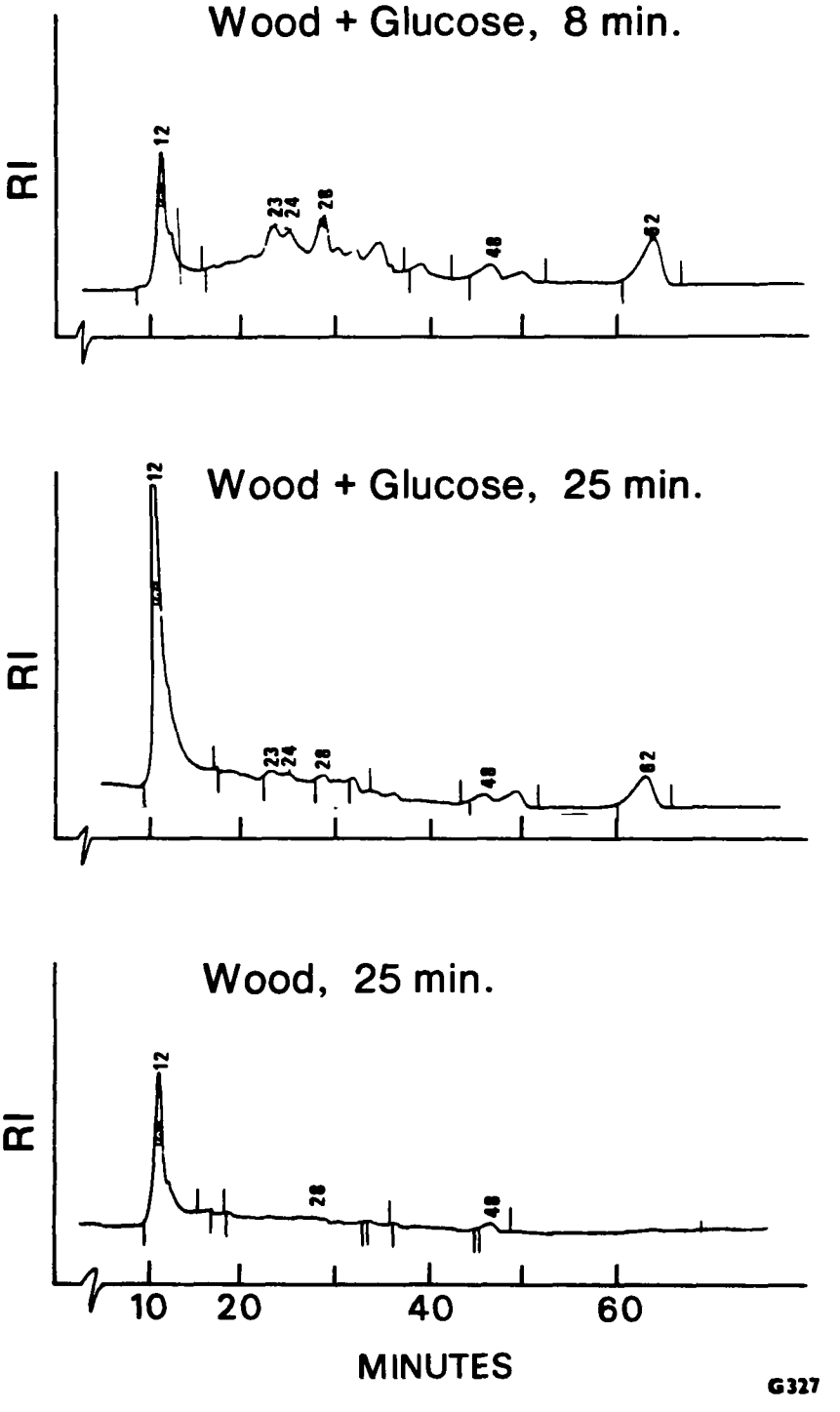
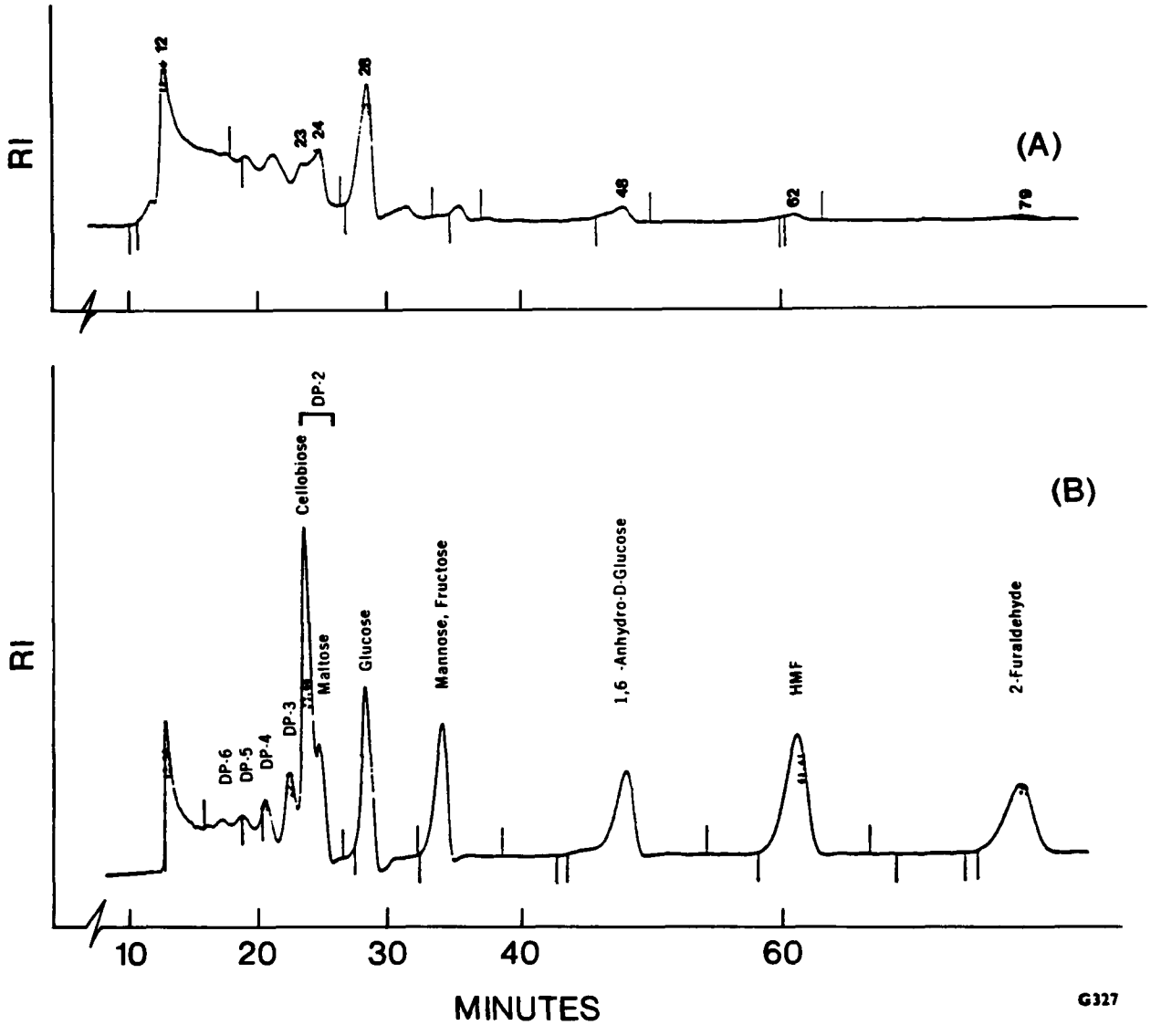


Figure 9

Comparison between analytical HPLC chromatograms[1] of heated sugar (A) and corn syrup with selected additives (B)[2]



1 Pre-packed columns: Aminex HPX-87P and Aminex HPX-42A.

2 References: cellobiose, D-mannose, DL-fructose, 1,6-anhydro-D-glucose, HMF and 2-furaldehyde added to a standard solution of corn syrup.

products was observed with the exception of D-mannose and D-fructose which were eluted as one peak. The similarity between the chromatograms of heated sugar and hydrolyzed corn syrup suggests that the main initial reaction occurring during heating of D-glucose in a pressure vessel or in a wood composite is a conventional polycondensation between glucose molecules with the formation of glucosidic linkages (acetals of D-glucose with alcohol are called glucosides, see example VII in Scheme 2). Upon heating, two molecules condense with the loss of water forming disaccharide molecules (example maltose, retention time 24 minutes, cellobiose 23 minutes) which condense further to form trisaccharides and finally higher oligosaccharides. This type of sugar polymerization has been studied previously (55, 57, 58, 83, 85, 86, 117, 118) and the structure of the water soluble polymers are relatively well known (55-58, 118). Isolative and periodate oxidation studies have indicated that the products consist of highly branched glucose polymers with all possible glucosidic linkages, but with a predominance of 1,6 - followed by 1,4-glucosidic bonds (25, 55, 58, 81, 119, 120). Upon heating, D-glucose could rearrange into various tautomeric forms (Scheme 2) including the formation of D-glucofuranose that condenses and is incorporated into the polymer (58, 118). According to Dutton and Unrau, at least 15% of the D-glucose units would be of the furanose type (58). Optical rotation studies of the polymer indicated the presence of both α-and β-glycosidic linkages with a predominance of the α-linkage (58, 118, 119). This was verified later by Sugisawa and Edo from isolation of various disaccharides and trisaccharides from D-glucose heated at 150°C without a catalyst, although some of the disaccharides isolated showed the presence

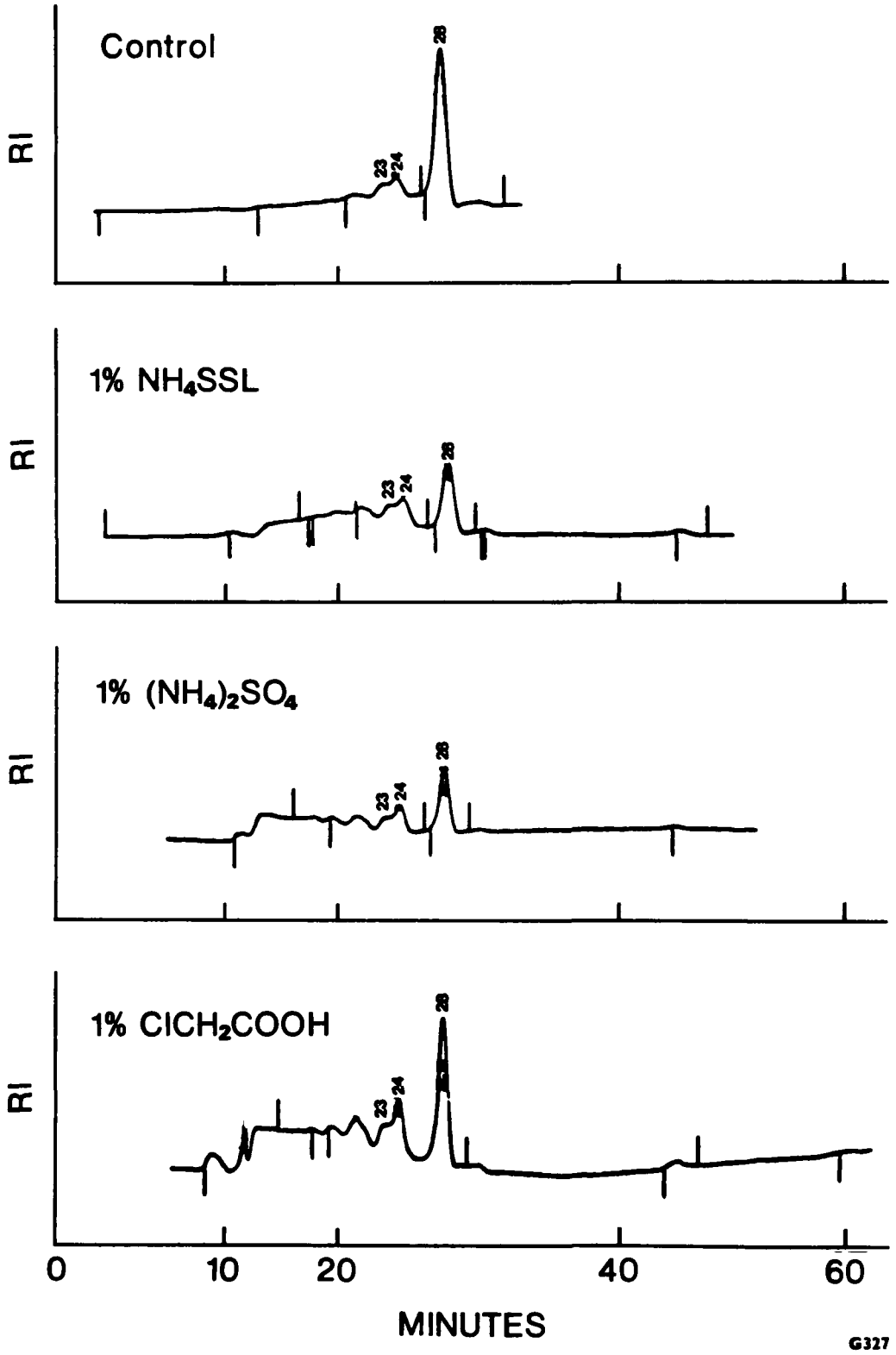
of β-linkages (81). It should be added that HPLC thermograms similar to those of heated sugar were also obtained by Bonn during the thermolysis of wood (104, 121). However the reactions which occur during the final thermosetting of a carbohydrate are not as well known. Although the structures of the various oligomers being formed during the heating of D-glucose have been elucidated in part (81), the main interest of this study was the identification of the reactive species and the mechanism of adhesion of the carbohydrate portion of NH_4SSL.

Effect of NH_4SSL on Glucose Condensation

It is well known that acid catalyzes the dehydration and condensation reactions of sugar (13, 25, 27, 52, 55, 119). In a previous study (13), it was suggested that ammonium lignosulfonate might act as a weak acid catalyzing the polymerization of glucose. Analytical HPLC chromatograms in Figure 10 appear to confirm this, based on the formation of high molecular weight material. These chromatograms represent D-glucose heat-treated in a pressure vessel for 10 minutes separately with or without (control) additions of 1% NH_4SSL ($MW > 5,000$; see Table 2), $(NH_4)_2SO_4$ and $ClCH_2COOH$. The polymerization of glucose is catalyzed in a similar fashion by all three additives. In fact, the chromatogram of glucose heated 10 minutes with 1% NH_4SSL (Figure 10) is similar to that which is obtained when glucose was heated alone for 20 minutes (Figure 6).

Figure 10

Effect of catalyst addition on sugar polymerization



Fractionation of Heated Sugars

Unless the relative proportions of dehydration products obtained from high- and low-molecular weight sugars are known, their relative contribution to bonding cannot be evaluated. In order to identify the most reactive compounds, heated sugar must be fractionated into its various components. Unfortunately analytical HPLC separation provides only microgram portions of the material which are insufficient for adhesive testing.

The first approach was to fractionate the heated sugar by gravity column chromatography on a 297-micron AG 50W-X4 (Ca^{++}) resin. The same material (D-glucose heated 25 minutes at 230°C in a pressure vessel, see Figure 6) was also fractionated by hyperfiltration using a membrane with a low molecular weight cut-off (500 MW). Figure 11 presents the HPLC chromatograms of the high- and low-molecular weight material obtained by fractionation with the gravity column. Similar chromatograms were obtained from fractionation by ultrafiltration. Both methods were successful in separating the high molecular weight material, with 12 minute retention time, from the remaining heated sugar material. The infrared (IR) spectrum of the high molecular weight fraction obtained by fractionation with the gravity column is shown in Figure 12, along with that of maltopentaose. The similarity between the IR spectra suggests that the high molecular weight fraction was a polyglucose type of material. Hydrolysis of the high molecular weight fraction in boiling 0.1 N HCl, for 16 hours, produced only glucose, leaving a residue of

Figure 11

HPLC chromatograms of heated D-glucose fractionated by gravity chromatography ion exchange resin

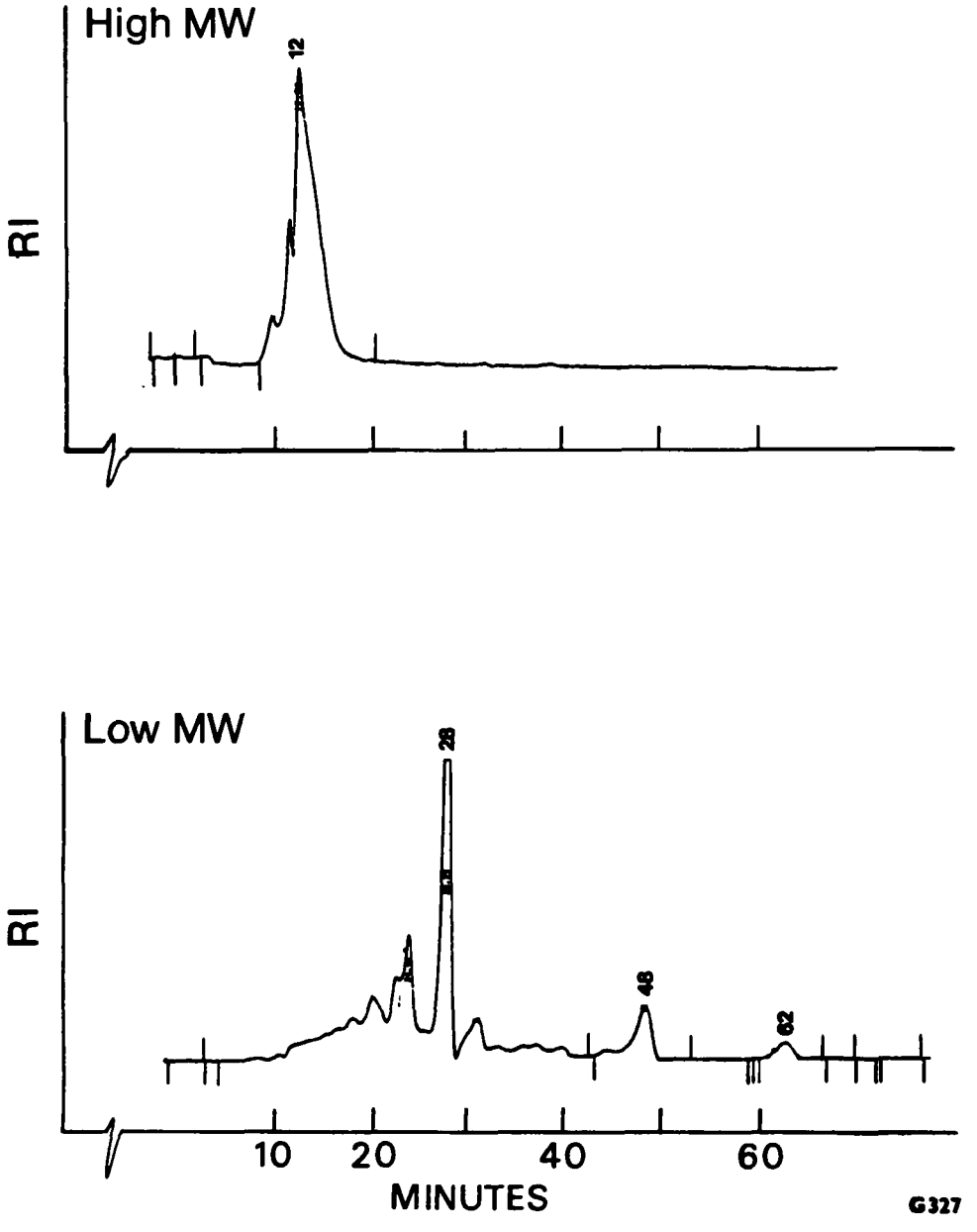
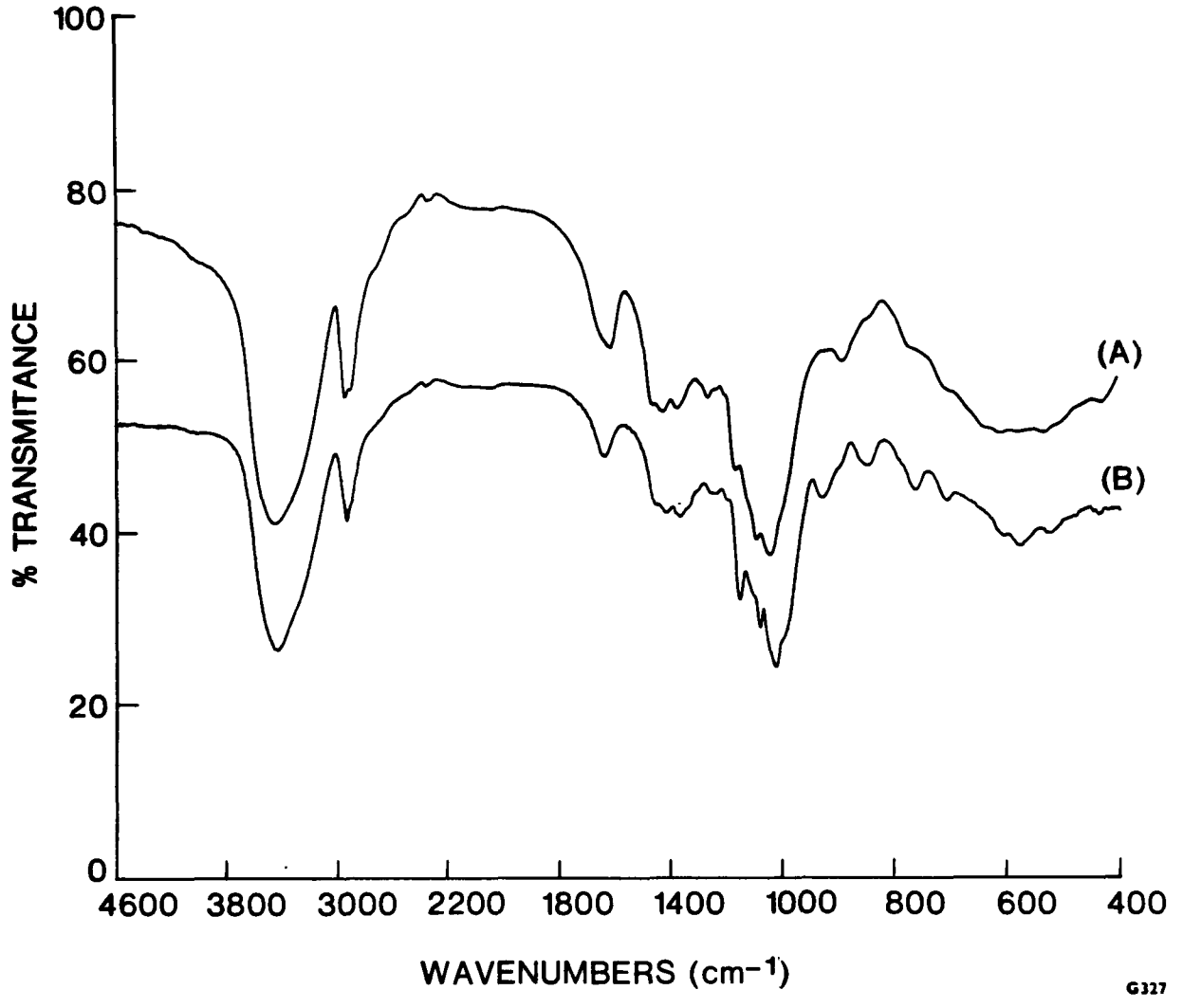


Figure 12

Infrared spectra of heated glucose high-molecular-weight fraction obtained by gravity column chromatography (A) and maltopentaose (B)



10.1%. Shafizadeh and Lai (118) encountered similar results in studying the thermal rearrangement of cellobiose and trehalose. They suggested that additional reactions, beyond glycosidic linkages, were necessary to explain the presence of non-hydrolyzable polymeric material. These could involve the incorporation of acyclic 3-deoxyglycosulose molecules in the polymer or the dehydration and rearrangement of glycosyl units.

Long-chain carbohydrates, especially those containing the beta type of linkage such as cellulose, are not readily hydrolyzed. For comparison, the high molecular weight heated sugar fraction was also subjected to hydrolysis in concentrated sulfuric acid (72%) according to a method employed for hydrolysis of cellulose and hemicellulose from wood (122,123). Under these conditions, 10.6% of the high MW material could not be hydrolyzed. The similarity of the results confirm that both methods are suitable for hydrolysis of the hydrolyzable material from D-glucose heated polymers. The concentrated sulfuric acid method was employed for the remainder of the study.

As shown in Table 3, the first fraction from the gravity column or the retentate from hyperfiltration represented 10 to 12% by weight of the starting material and had a number-average molecular weight ($\bar{M}_n$) of 1220 to 1340. As expected, this material insolubilized faster than the corresponding low molecular weight fraction with a mild heat treatment (Table 3). Particleboards made with the high-molecular-weight materials resulted in lower TS values than those made with lower-molecular-weight material. Evidently, the rate of insolubilization of polymers cannot be used as the only criterion to evaluate the reactivity of an adhesive. Producing a bond and testing it appears to be the ultimate test. The HPLC chromatogram of the low molecular fraction, shown in Figure 11,

Table 3

Effect of fractionation on adhesive properties of treated sugar1

Method of Fractionation	Treated Sugar (WT %)	Osmometry ($\bar{M}_n$)	Solubility After Further Heat Treatment2	232°C-15 Min. TS (N.m)
Gravity Chromatography Ion-Exch. Resin	11	1220	Insoluble	2.0
	85	300	Soluble	4.8
Hyperfiltration	12	1340	Insoluble	1.6
500 MW Cut-Off	88	290	Soluble	5.0

1 Sample pre-heated at 230°C for 25 minutes at 2.8 MPa of N_2 before fractionation.

2 Fractionated sample post-heated at 230°C for 20 min. at 2.8 MPa of N_2.

indicates the presence of various components (several peaks). Further fractionation of the heated D-glucose material was required to identify the reactive species.

Preparative HPLC

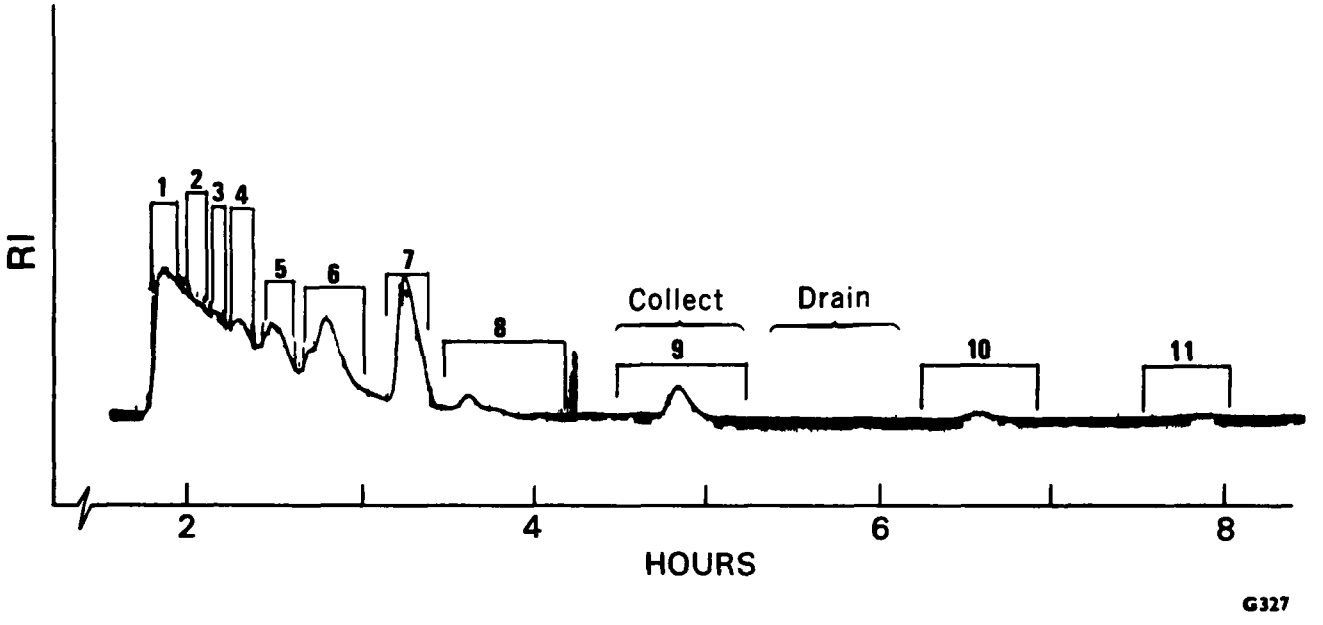
The analytical HPLC columns packed with 10-25 micron ion-exchange resin provided excellent separation of the heated sugar components (Figure 6-11). However, packing of a preparative column with 4 kg of 20-micron Aminex 50W-X4 resin would cost approximately $40,000. Acceptable separation was obtained with the 38-micron equivalent AG 50W-X4 (Ca^{++}) resin which costs only $1,000 for 4 kg. Figure 13 shows the type of chromatogram obtained when 6 g of heated sugar solution at 50 percent solids was injected into the preparative column packed with this resin. The separation was not as good as with the two analytical columns in series (compare Figure 6 and 13) but at least the major peaks could be recognized and collected. An interesting aspect of the (Ca^{++}) ion exchange resin was the ease of regeneration with nitric acid. A disadvantage was that pressure limitations precluded high flow speeds. The analytical HPLC chromatograms for the various individual fractions collected with the preparative columns are shown in Figure 14. All fractions were relatively pure (single peaks) except for fraction 8 which contained several compounds.

Characteristics of the Various Fractions Collected

Fractions 1 to 7 accounted for 87.2% by weight of the material collected by preparative HPLC and represented the principal products when glucose is heated under these experimental conditions (Table 4). The IR

Figure 13

Preparative HPLC chromatogram of heated D-glucose with indication of collection mode [1]



[1] Sample pre-heated in pressure reactor for 25 minutes at 230°C and 2.8 MPa of N_2.

Figure 14

Analytical HPLC chromatogram of each fraction collected with preparative column

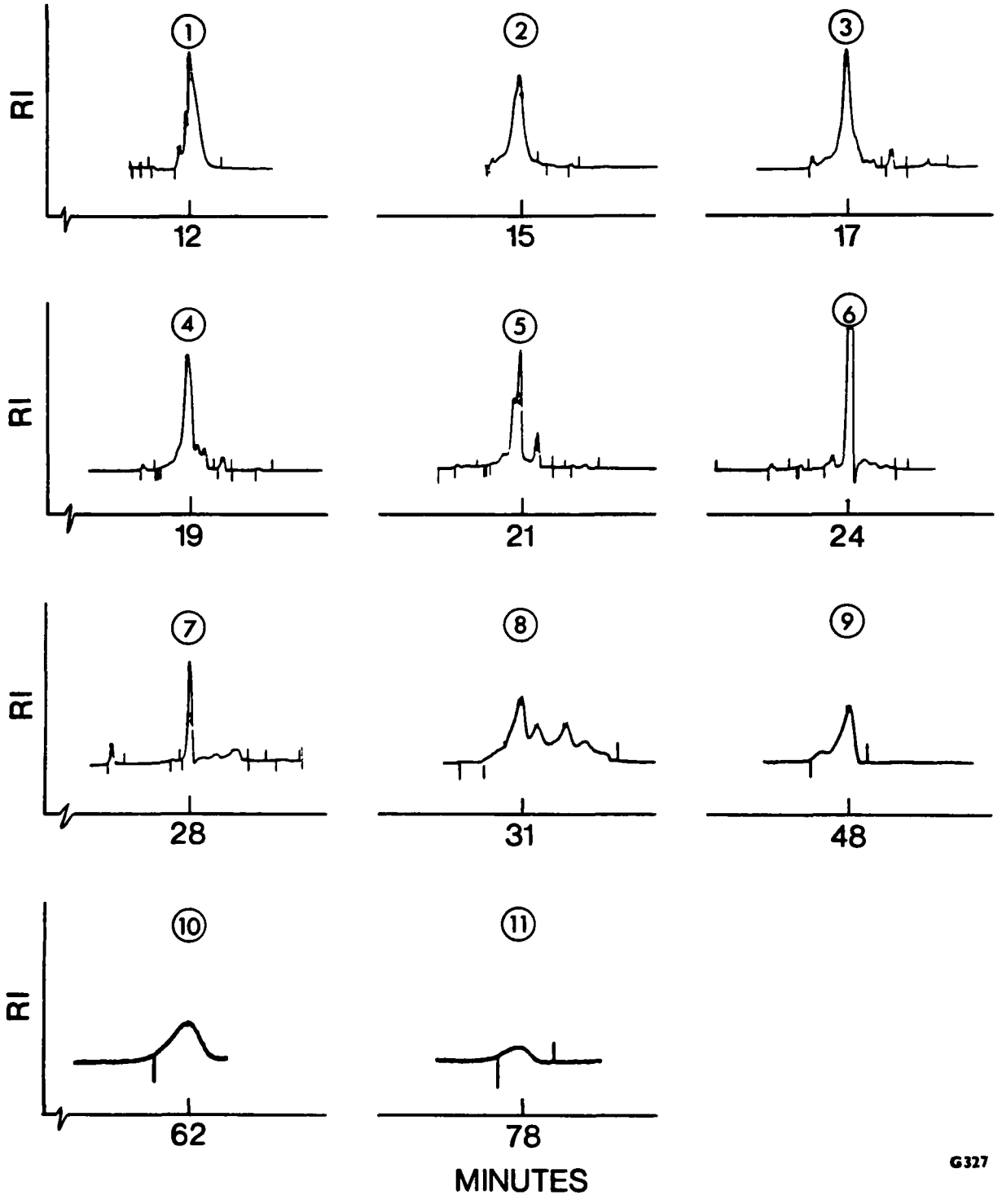


Table 4

Evaluation of the adhesive properties of the various fractions collected

Fraction No.	HPLC Retention Time[1] (Min.)		Heated Sugar (WT %)	40% Soln. pH	Initial Melt (°C)	Osmometry ($\bar{M}_n$)	230°C 12 Min. TS (N.m)	230°C 15 Min. TS (N.m)
1	12		19.2	3.2	240	1,170	0	0.1
2	15		9.8	-	192	980	0	0.2
3	17	87.2%	8.8	3.7	184	750	0	0.2
4	19		6.6	-	167	520	0	0.2
5	21		8.0	3.7	154	350	0	2.0
6	24		11.6	-	120	200	2.1	4.5
7	28		23.2	4.8	73	190	3.1	4.2
8	31		8.3	3.8	68	-	2.9	5.0
9	48		3.0	2.6	63	-	0	2.1
10	62		1.4	-	31	-	0	0
11	78		0.1	3.4	-	-	-	0
Ref. D-Glucose	28		-	5.3	153	190	2.8	4.2
HMF	62		-	-	35	-	0	1.0
2-Furaldehyde	78		-	-	-	-	0	0
2-Furaldehyde[2]	78		-	-	-	-	2.2	4.1

[1] Retention time of major peak only, see Figure 14.

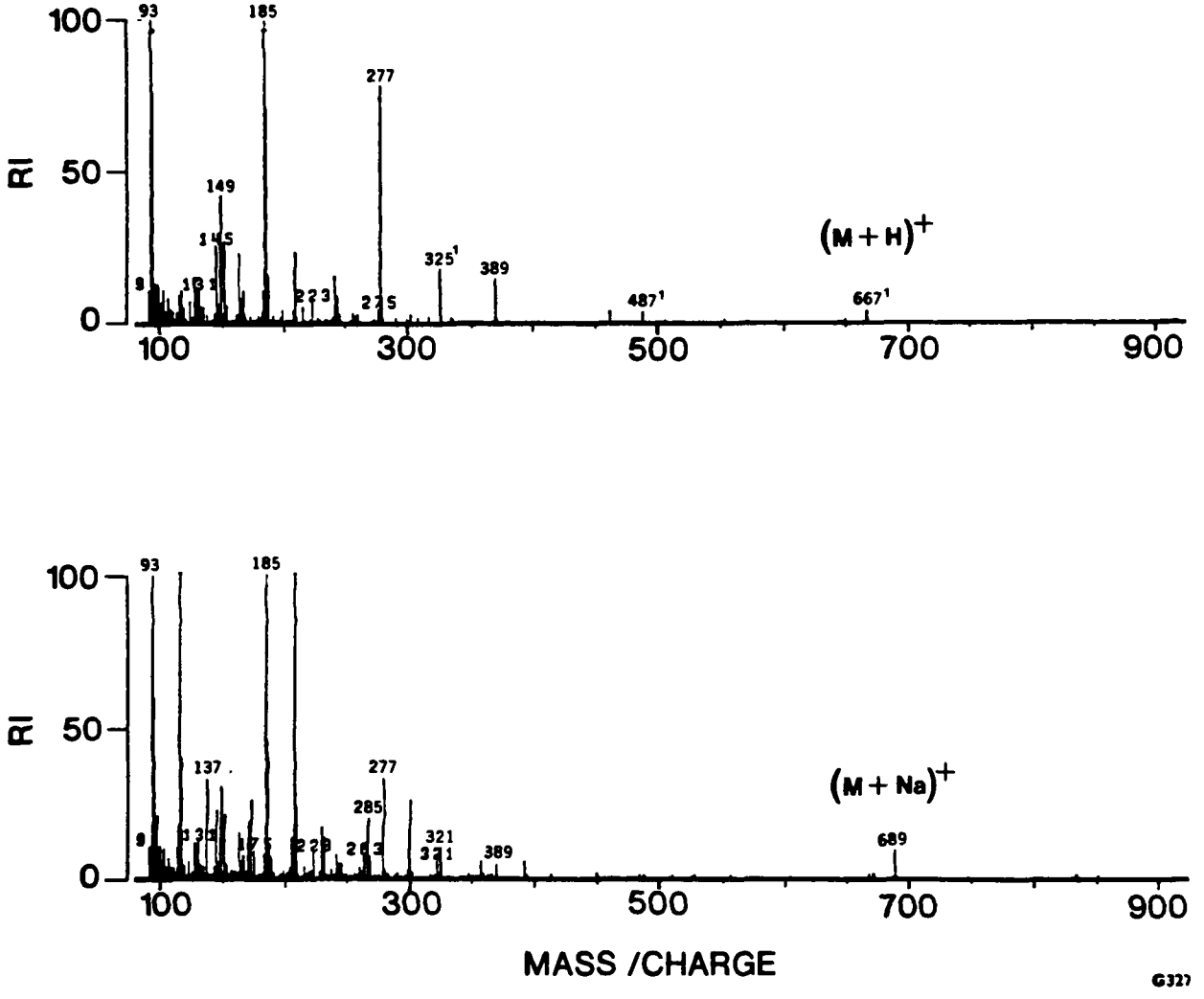
[2] Wood macerated in acetic-furfural 2 hours at 80°C (13).

spectra of fractions 1 to 6 were similar and could be superimposed on the spectra of glucose oligomers such as the spectrum of maltopentaose shown in Figure 12. The number-average molecular weights determined by vapour pressure osmometry increased gradually up to 1,170 for fraction 1 and as expected, initial melting temperature of the sugar fractions increased with molecular weight. Fraction 3, when subjected to hydrolysis in concentrated H_2SO_4, reverted 100% to glucose without an insoluble residue. The fast-atom bombardment (FAB) mass spectra shown in Figure 15 confirmed that fraction 3 is a low molecular weight carbohydrate oligomer. The $(M + H)^+$ ion present in the FAB spectrum at mass/charge 667 (M/Z 667) corresponded to the formula weight of a tetrasaccharide such as maltotetraose (see footnote in Figure 15). Molecular-ion species present at M/Z 487 (M/Z 505 - H_2O) and M/Z 325 (M/Z 343 - H_2O) correspond to trisaccharides and disaccharides such as maltotriose and maltose, respectively. The FAB spectrum of fraction 3 in the presence of NaCl showed the presence of M/Z 689 $(M + Na)^+$ which also corresponded to the formula weight of maltotetraose plus sodium.

Fraction 1 in concentrated H_2SO_4 hydrolyzed to D-glucose except for a 10% water insoluble residue. Similar results were obtained with the HMW sugar fraction isolated previously by gravity column chromatography. As shown in Figure 16, the ^{13}C-NMR spectrum of fraction 1 is similar to the spectrum of the D-cellobiose (4-β-D-glucopyranosyl-D-glucopyranose) reference which confirms that it is a glucose type of oligomer. The similarity of fraction 1 with cellobiose is interesting because the latter contains a β type of linkage. Previous studies based on optical rotation had suggested that heated glucose polymers would consist mainly of α-glucosidic linkages (58, 118, 119). The peak at

Figure 15

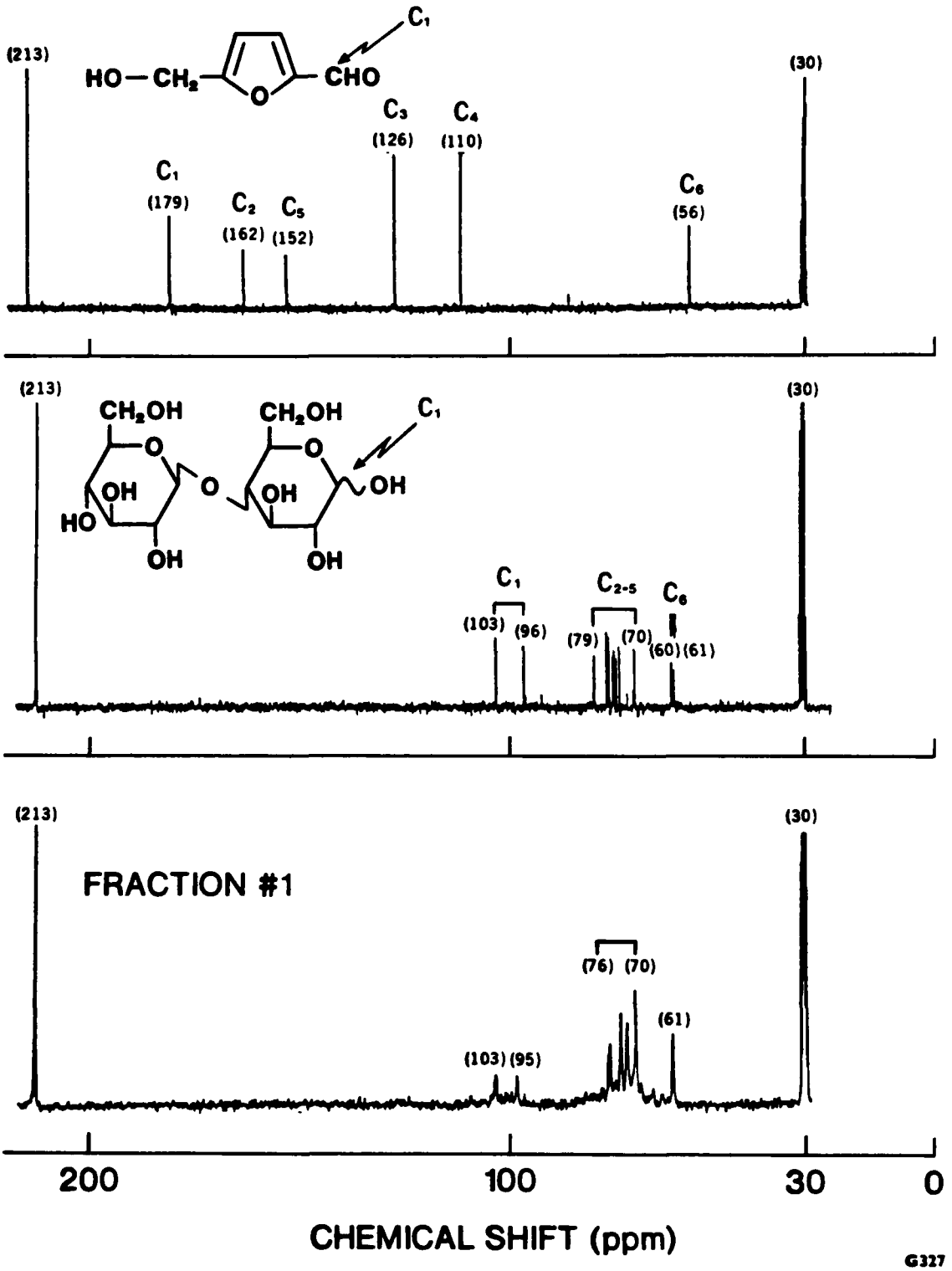
Positive ion fast atom bombardment mass spectrum of
Fraction 3 in glycerol



1 Formula weight for maltotetraose is 666.7g, maltoltriose less H_2O is 486.4g, maltose less H_2O is 324.3g.

Figure 16

Comparative liquid-state ^{13}C-NMR spectra [1] of HMF, cellobiose and Fraction 1 [2]



1 Solvent: Water-acetone in 1:1 volume ratio.

2 Heated D-glucose fractionated by preparative HPLC.

103 ppm is in a relatively low field area of the spectrum which could correspond to a β-glucosidic linkage. However, peaks in the 102-103 ppm area are also reported in the literature for α-linked glucose polymers (124, 125).

Figure 16 also shows the spectrum of the HMF reference with typical signals for α , β-unsaturated carbon at 162, 152, 126 and 110 ppm. Non-hydrolyzable material in heated sugar may be due to unsaturated groups in the polymer (118). The ^{13}C-NMR spectrum of fraction 1 is not similar to the spectrum of HMF and showed no signal corresponding to the presence of an unsaturated group in the polymer. However fraction 1 is a relatively low molecular weight, water-soluble oligomer. Unsaturation may occur upon further heating.

With regard to other fractions collected by preparative HPLC (Table 4), IR and HPLC retention times of peaks 9 and 10 correspond to those of 1,6-anhydro-D-glucose and HMF respectively, whereas the retention time of peak 11 corresponds to that of 2-furaldehyde. The main peak of fraction 8 was isolated by reinjecting this fraction into the preparative column. The IR spectrum of the principal peak was similar to the spectrum of mannose. However, gas chromatography-mass spectroscopy (GC-MS) suggested that the acetylated material consisted of a mixture of several monosaccharides including mannose. Mannose is known to be a product of isomerization of glucose (84, 126, 127). As shown in Table 4, the pH of the various fractions collected by preparative HPLC did not vary significantly. 1,6-anhydro-D-glucose (peak 9) had a low pH of 2.6.

The test results for particleboard bonded with each of these fractions are shown in Table 4. Based on TS results, none of the fractions had an adhesive reactivity superior to that of D-glucose.

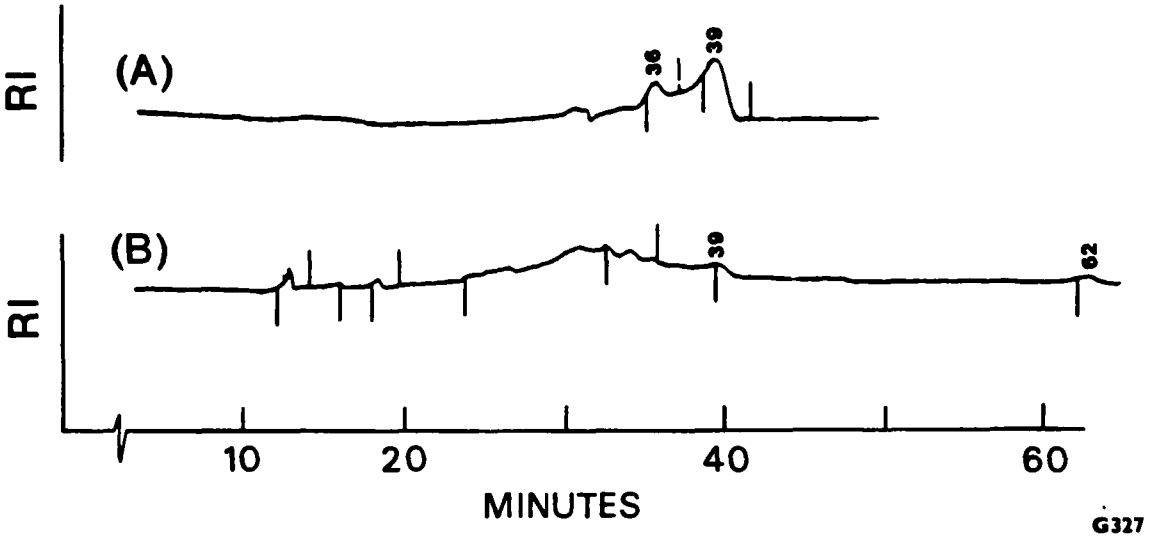
Fractions 6, 7 and 8 possessed equivalent reactivity. The larger sugar molecules, or sugars with $\bar{M}_n$ above 200 (fractions 1 to 5) were less reactive than glucose. Fraction 7 ($\bar{M}_n$ 190) yielded a TS strength of 4.2 N.m for a 15-minute press time, fraction 5 ($\bar{M}_n$ 350) had a TS of 2.0 N.m. TS values of 0.1-0.2 N.m were observed for higher molecular weight fractions ($\bar{M}_n$ 520 to 1,170) and fractions 9, 10 and 11 provided TS strength results of 2.1, 0 and 0 N.m, respectively. If D-glucose alone was used as an adhesive, there would be no reason to promote the formation of these compounds which are less reactive than D-glucose itself.

Polymerization of Glyceraldehyde

In a previous study (13), DL-glyceraldehyde was observed to bind wood. The IR spectrum of the polymerized glyceraldehyde was very similar to that of polymerized D-glucose. A study was undertaken to determine if glyceraldehyde would polymerize through the same intermediates as glucose (13). Figure 17 shows a HPLC chromatogram of DL-glyceraldehyde heated in a pressure vessel 15 minutes at 230°C. The heated product was still 99 percent soluble in water at 55°C. As observed in Figure 17, the chromatogram of heated glyceraldehyde is quite different from that obtained previously for glucose, indicating a different type of intermediate. Interestingly, a small quantity of material with a retention time identical to HMF was detected. The generally accepted path of glyceraldehyde interconversion/dehydration is shown in Scheme 3 (128 - 130). The adhesive properties of the main intermediate 1,3-dihydroxy-2-propanone and methyl glyoxal (pyruvaldehyde) along with glyceraldehyde starting material were evaluated (Table 5). As

Figure 17

Analytical HPLC chromatograms of DL-glyceraldehyde before (A) and after (B) heat treatment (230°C, 15 min.)



Scheme 3

Glyceraldehyde interconversion/dehydration, (128,130)

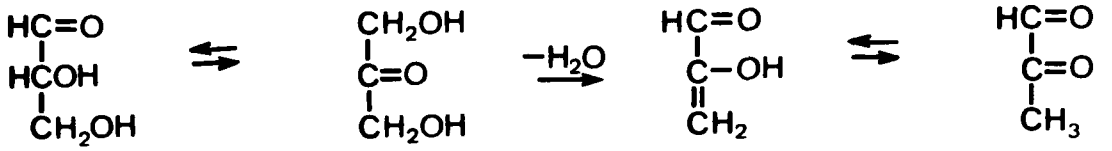


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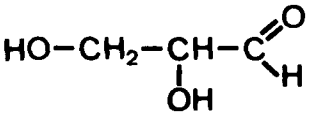
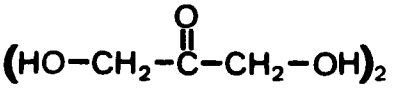
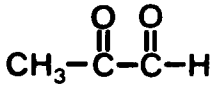
Table 5

Adhesive properties of glyceraldehyde and related interconversion/dehydration products

Compound	Formula	Boiling Point (131) (°C)	230°C - 15 Min. TS (N.m)
D-Glyceraldehyde		150[1]	2.9
1,3-Dihydroxy-2-Propanone (Dimer)		-	0
Methyl Glyoxal		72 [2]	0

1 at 0.8 mm Hg.

2 at 760 mm Hg.

was the case for observations made with glucose, the starting material (glyceraldehyde in this case) was again found to be the most reactive compound. The sugar interconversion and dehydration products were not as effective as wood binder since particleboards pressed with these chemicals disintegrated in boiling water.

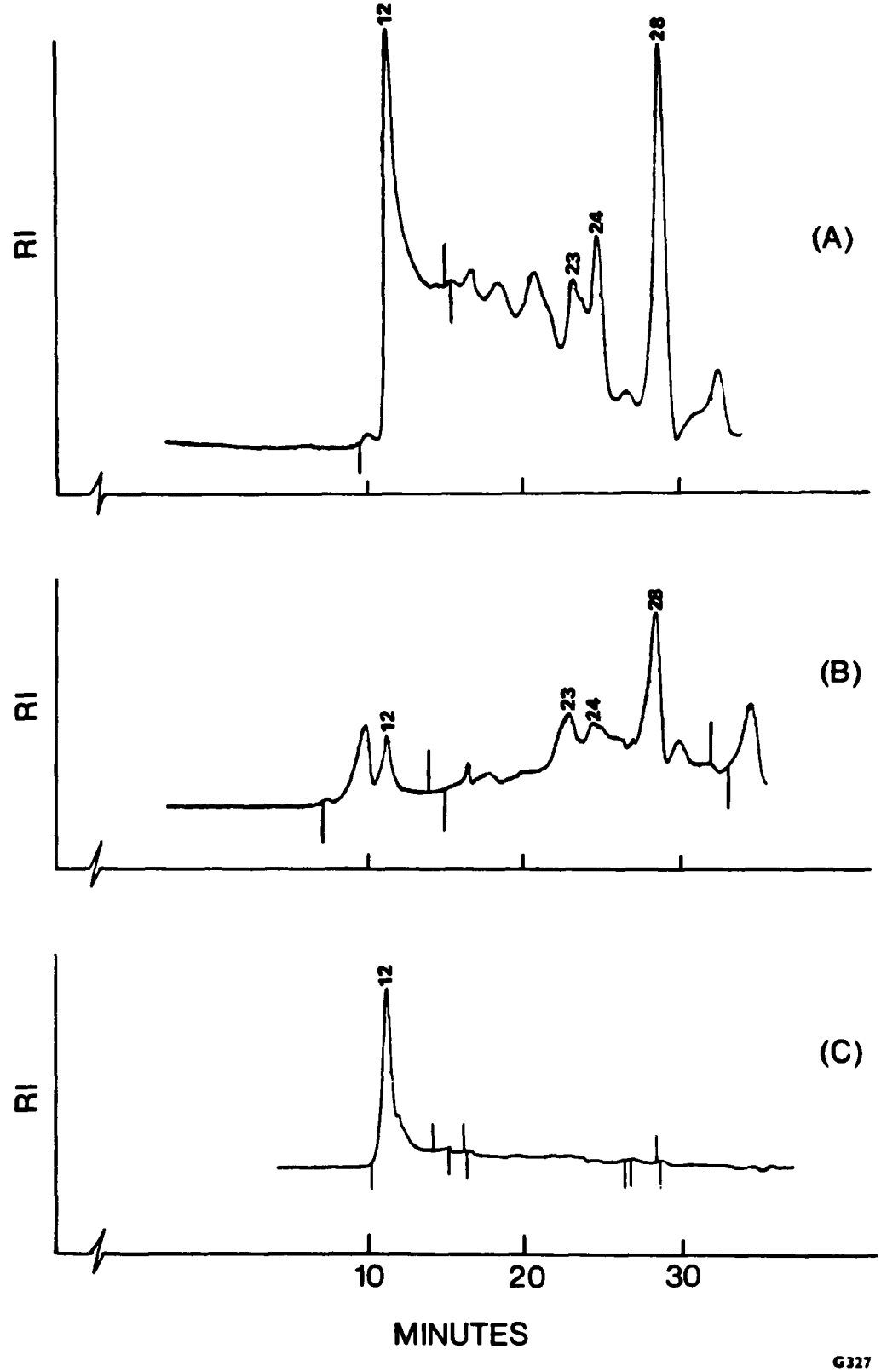
Condensation of D-Glucose with Wood

When D-glucose was pre-polymerized or dehydrated prior to wood bonding, a less reactive adhesive resulted. The fact that the starting material (D-glucose or DL-glyceraldehyde) was the most reactive compound suggested that it may be reacting directly with wood. 2-Furaldehyde, used alone as binder, provided a good bond only if macerated with wood under heat and pressure in the presence of an acid prior to bonding (13). Perhaps the initial steps in wood bonding with 2-furaldehyde or D-glucose is the condensation of the active aldehyde group with wood.

To assess whether wood influences the polymerization of D-glucose, a wood sample coated with D-glucose was placed in a pressure vessel and heated, for 20 minutes at 230°C under 2.8 MPa (N_2), together with suitable controls. After treatment, the samples were extracted with water for 3 hours. The water fractions were then analyzed using HPLC. The HPLC chromatograms for heat-treated glucose, heat-treated glucose on wood, and heat-treated wood are shown in Figure 18. Different HPLC chromatograms were obtained for each substance. Glucose heated alone produced large peaks (large concentration of water soluble material) whereas only small peaks were detected for the heat treated glucose-wood mixture (less material soluble in water or more bonded to the wood). The

Figure 18

Analytical HPLC of (A) heat-treated glucose, (B) heat-treated glucose on wood and (C) heat-treated wood [1]



[1] Samples heated in pressure reactor for 20 minutes at 230°C under 2.8 MPa (N_2) then extracted in Soxhlet extractor for 3 hours in water.

heat-treated glucose appeared to remain attached to wood instead of dissolving into water.

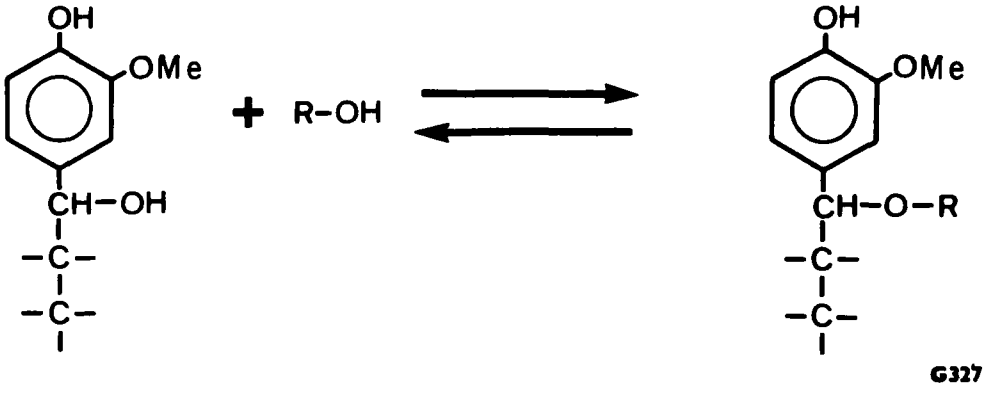
Condensation of D-Glucose with Cellulose or Lignin

The two major constituents of wood are cellulose and lignin. When glucose is heated in a pressure vessel in the absence of wood, the predominant initial reaction is polycondensation of the glucose molecules through glucosidic linkages, with the elimination of water and the formation of glucosidic linkages. Since cellulose is a polyglucose polymer with C-2, C-3 and C-6 hydroxyls free for glucosidic bond formation, glucose may condense directly with the cellulose in wood upon heating. Alternatively, D-glucose may react with lignin, the other major component of wood (132). The lignin-glucose condensation would be expected to occur at the α-position of the lignin phenylpropane unit as indicated in Scheme 4. D-Glucose might possibly also react with other functional groups of lignin including free phenolic hydroxyls (133).

To clarify this point, a sample of glucose applied to cellulose and a sample of glucose mixed with lignin extracted from hydrolyzed wood were placed separately in a pressure vessel and heated at 230°C for 20 minutes at 2.8 MPa (N_2). A sample of cellulose without glucose was included for comparison. After treatment, the samples were extracted with water for 3 hours and analyzed with HPLC. The HPLC chromatograms of each water fraction are shown in Figure 19. A comparison between Figure 18 and Figure 19 indicates that under these experimental conditions glucose did not react with lignin but might have reacted with the cellulose constituent of wood. The experiment was repeated for increasing reaction times. In each case, as demonstrated in Figure 20,

Scheme 4

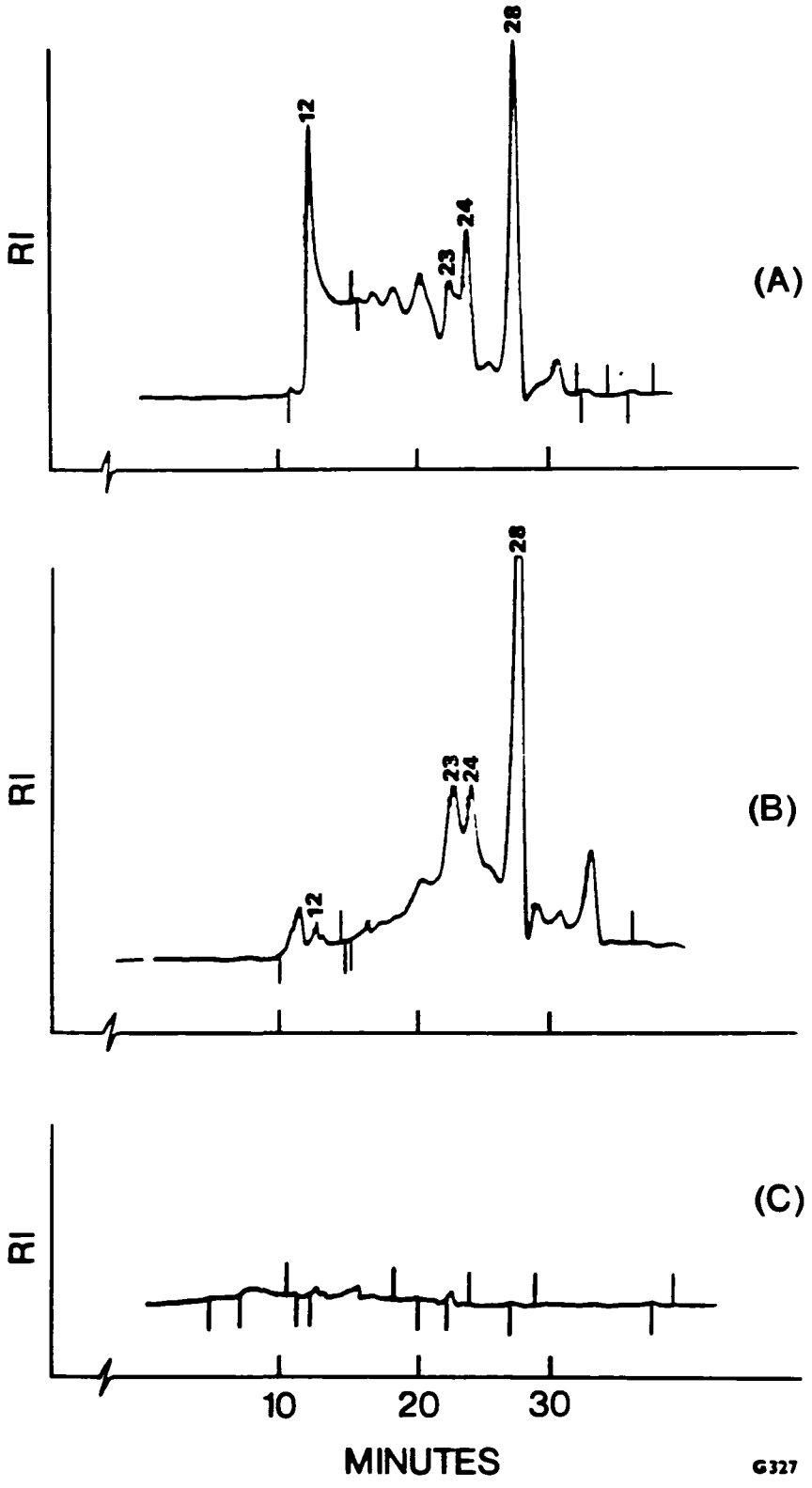
Reaction of glucose with lignin model compound [1] (132)



[1] R-OH represents glucose

Figure 19

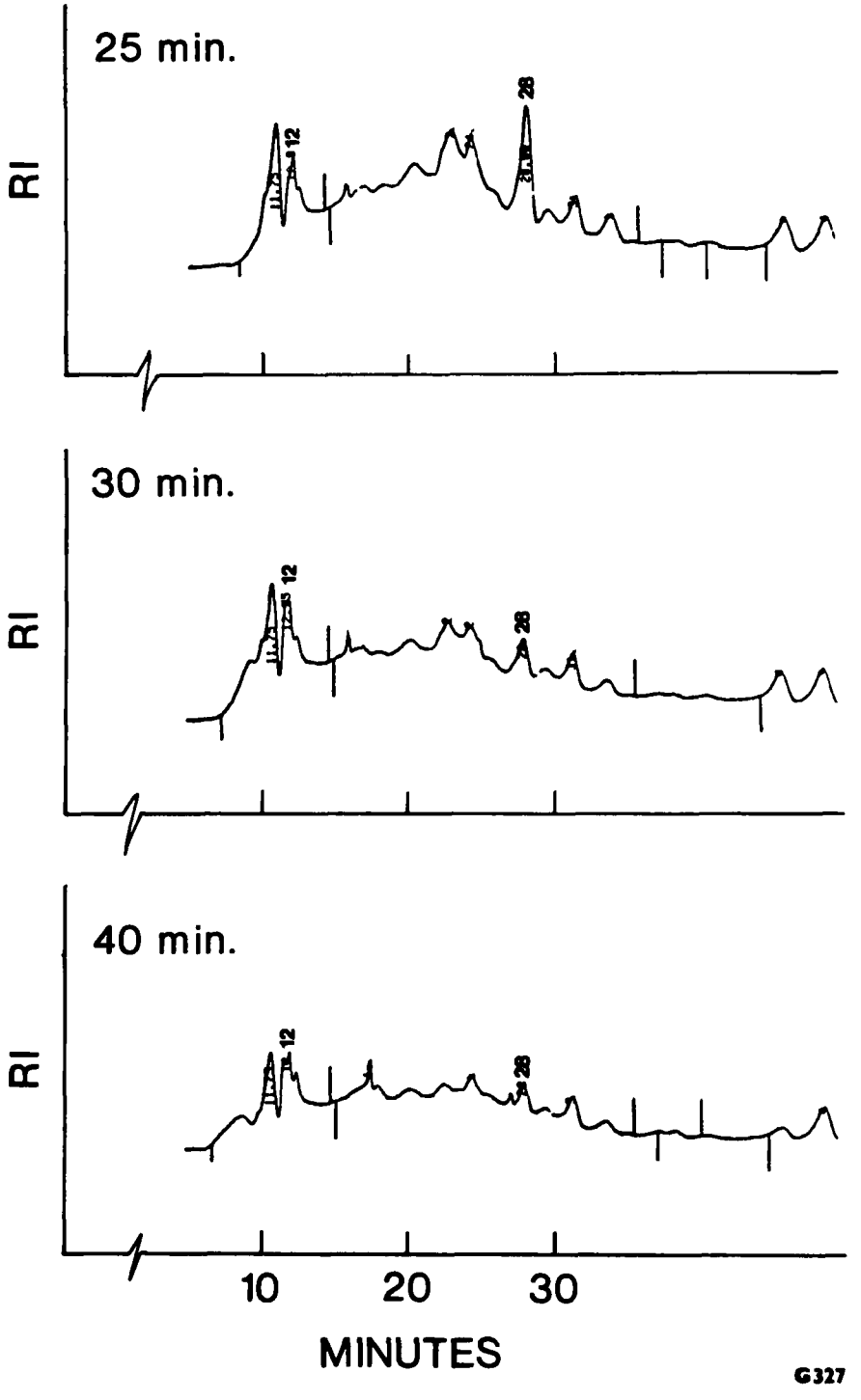
Analytical HPLC of (A) heat-treated glucose on lignin (B), heat-treated glucose on cellulose and (C) heat-treated cellulose [1]



[1] Sample heated in pressure reactor for 20 minutes at 230°C under 2.8 MPa (N_2) then extracted in Soxhlet extractor for 3 hours in water.

Figure 20

Analytical HPLC of heat-treated glucose on cellulose at 230°C for various periods of time [1]



[1] Sample heated in pressure reactor under 2.8 MPa (N_2) then extracted in Soxhlet extractor for 3 hours in water.

most of the heated sugar material could not be extracted from cellulose. This was confirmed by measuring the weight of D-glucose retained on cellulose after various heat treatments. The results summarized in Table 6 indicate that up to 30% of heated D-glucose residues could not be extracted from cellulose with water after a 40 minute heat treatment while D-glucose (0.2 g) heated alone under similar conditions was soluble in water. Upon mild acid hydrolysis of the extracted '40 minute' sample with 1 N HCl, only a small quantity of D-glucose was detected in the solute by HPLC.

Condensation of D-Glucose with Ethylene Glycol

When heated in a pressure vessel in the presence of cellulose which contains a large concentration of free hydroxyl groups, D-glucose will not only condense with itself to form a polymer but may also readily condense with cellulose. Similar types of reactions were observed when D-glucose was heated for 20 minutes at 230°C and 2.8 MPa (N_2) in a pressure vessel in the presence of ethylene glycol instead of cellulose. Figure 21 shows HPLC chromatograms of glucose and ethylene glycol before and after the heat treatment. After the heat treatment, four new peaks appeared on the chromatogram at 23, 25, 27 and 30 minutes retention time. The fractions corresponding to each of these peaks (see Figure 21) were collected using the preparative HPLC column and freeze-dried. NMR analysis and mass spectrometry indicated that fraction 3 and 4 would correspond to a 1:1 molar condensation product of ethylene glycol with glucose while fraction 1 and 2 would correspond to the condensation of 2 moles of glucose with one mole of ethylene glycol, as illustrated by Scheme 5.

Table 6

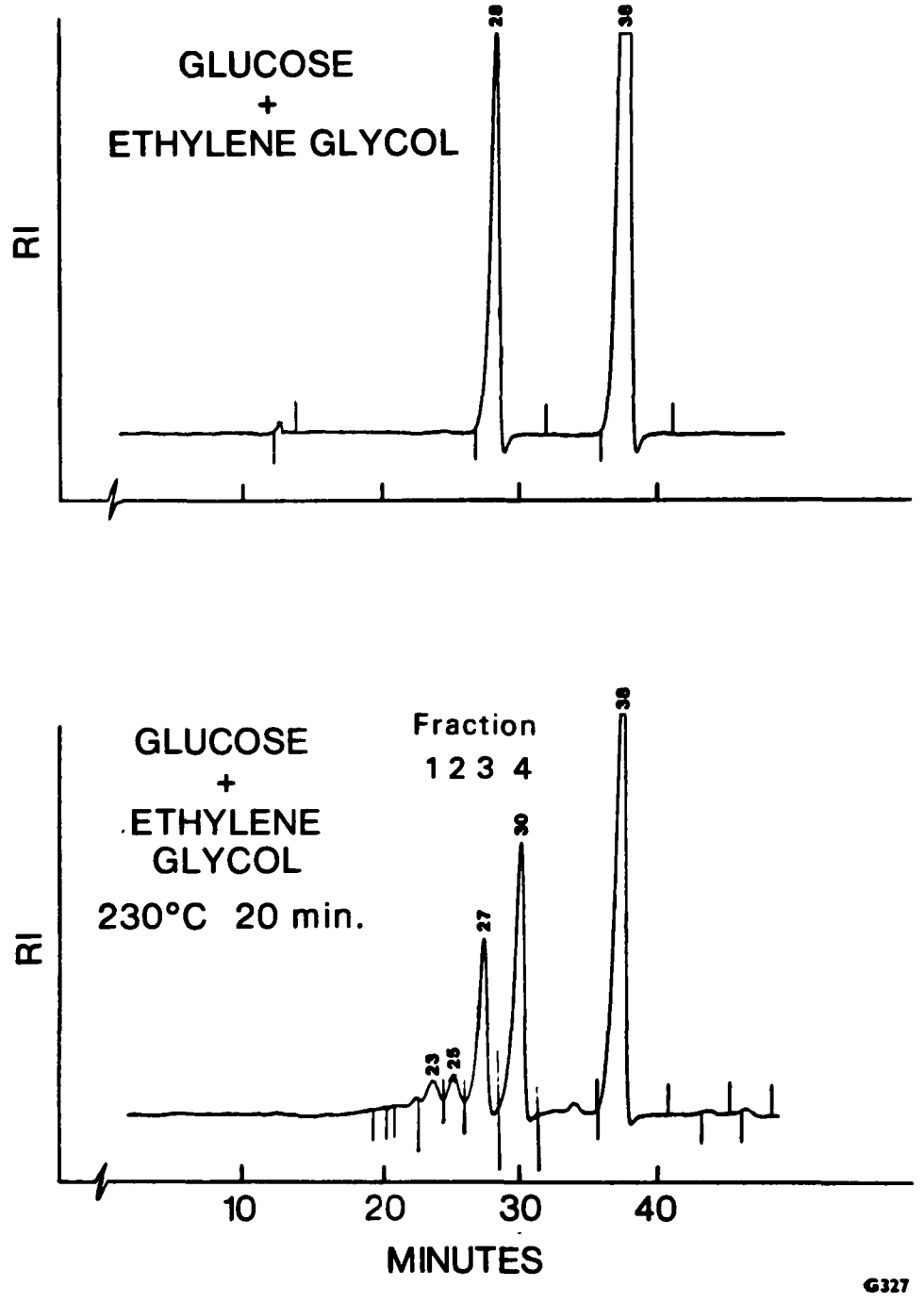
Glucose retained in heated glucose-cellulose mixture after 3 hours soxhlet extraction

Cellulose Initial Weight (g)[1]	Cellulose + Glucose Initial Weight (g)	Thermal Treatment 230°C-2.8 MPa (Min.)	Cellulose After Extraction Weight (g)	Cellulose + Glucose After Extraction Weight (g)	Glucose Retained (%)[1]
0.405	0.600	20	0.403	0.409	3.1
0.396	0.591	25	0.394	0.407	6.7
0.396	0.597	30	0.394	0.422	13.9
0.397	0.592	35	0.395	0.441	23.6
0.428	0.627	40	0.425	0.488	31.7
Cellulose Ref. 0.388		35	-	0.386	-
	Glucose Ref. 0.200	35	-	-	0.0

[1] Each result average of two measurements.

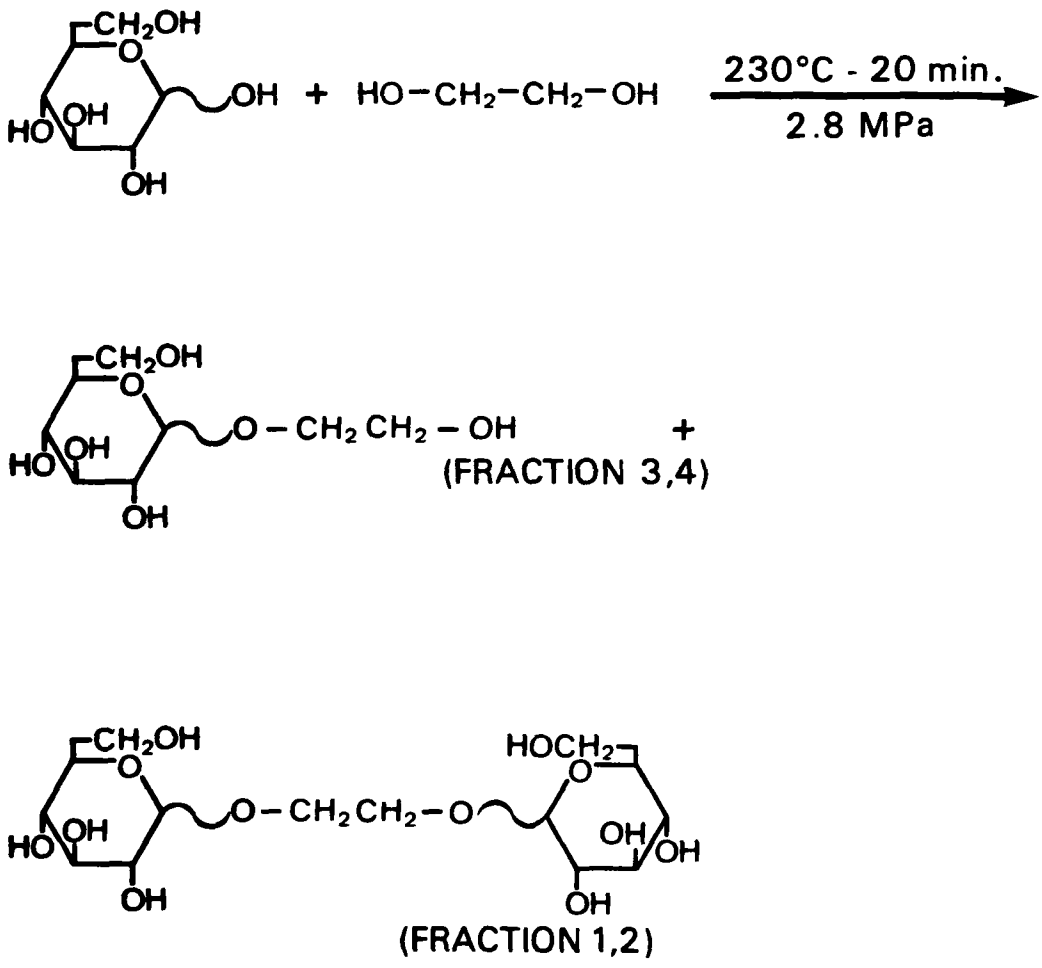
Figure 21

Analytical HPLC chromatograms of glucose and ethylene glycol before and after heat treatment in a pressure vessel under 2.8 MPa (N_2)



Scheme 5

Possible reaction of glucose with ethylene glycol



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The possibility that wood bonding can involve a chemical reaction between the adhesive and free hydroxyls of wood is not a new concept. Rudkin in 1950 suggested that the hydroxyl groups of wood were important for bonding since acetylation of these groups caused a marked decrease in bond strength when urea-formaldehyde was used as an adhesive (134). Chow in 1969 indicated that only half the energy was required for phenol-formaldehyde (PF) resin-wood bonds as for a resin-resin bond (44). Current results suggest that during the heating of D-glucose in the presence of wood or pure cellulose, an initial reaction is the formation of glucosidic linkages between cellulose and D-glucose.

It is also possible that when heated on cellulose D-glucose dehydrates to an insoluble polysaccharide at a faster rate. It has been stated that the presence of salt or the geometry of the heat-treated sample (for example, bulk versus thin layer) could affect the thermal degradation process (25, 54, 135). On cellulose, D-glucose may flow in a thin layer which would facilitate its dehydration. Dehydration may also be catalyzed by salt present in cellulose, although not likely, as the ash content was found to be only 0.01%. D-Glucose may dehydrate and polymerize through a different process than any of the foregoing, when heated on cellulose (although mild acid hydrolysis yielded only D-glucose). For example, fructose dehydrates to HMF more rapidly when heated in the presence of polyethyleneglycol rather than water (136).

The difficulty in examining the bonding reaction of the glucose-cellulose system is that cellulose is a polyglucose linked with a glucosidic bond. IR and ^{13}C-NMR of D-glucose heated on cellulose are similar to those of pure cellulose. Direct evidence for the formation of

a new glucosidic linkage under these conditions, is difficult to obtain.

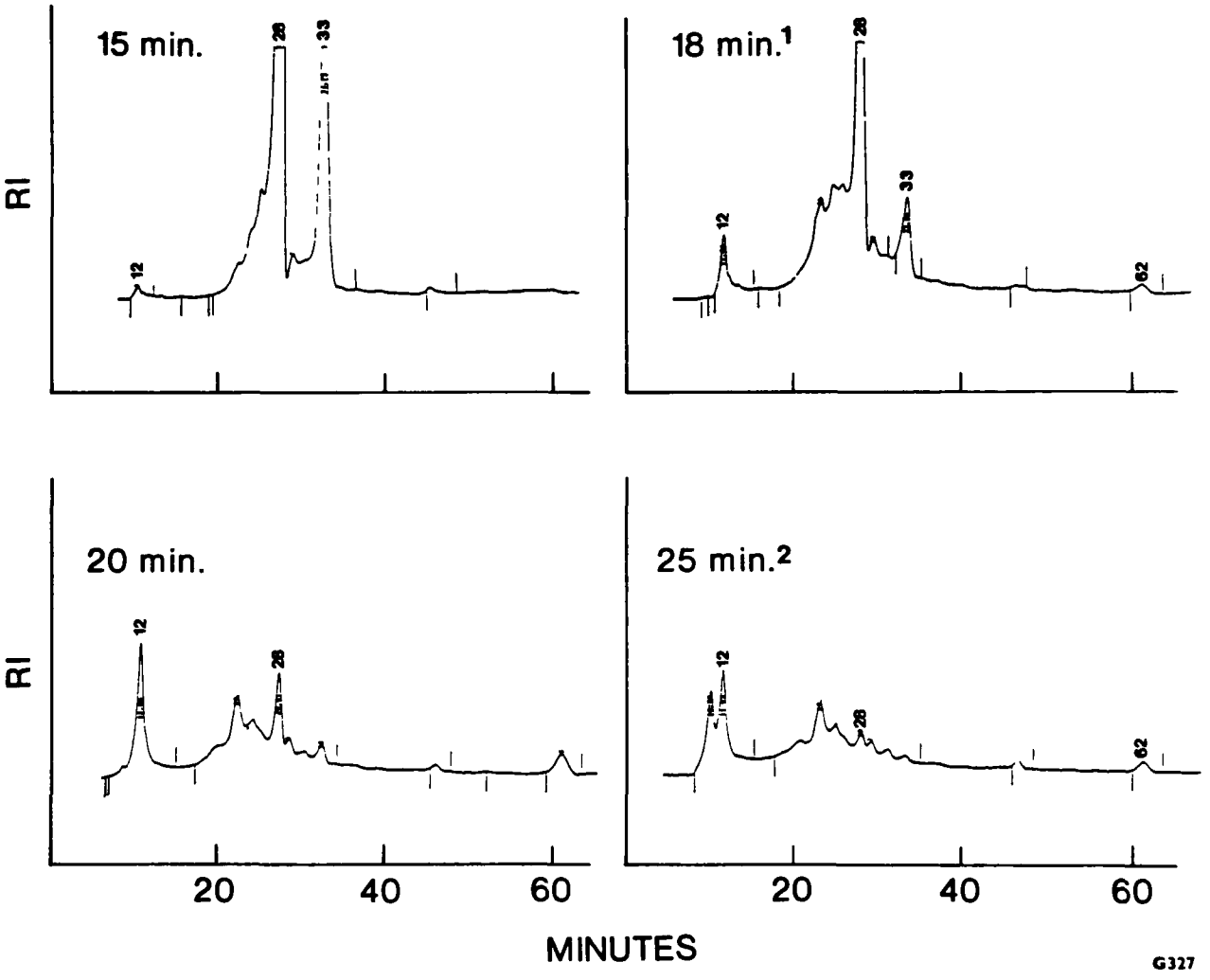
Reacting D-Glucose on Glass Fibers

In order to assess the effect of the treating medium (solid support) on D-glucose polymerization, D-glucose samples were applied to Corning Pyrex glass fibers, then subjected to heat treatment of 15 - 25 minutes in a pressure vessel at 230°C. The heated material was then extracted in a Soxhlet extractor for 3 hours with water. HPLC chromatograms similar to the previous ones obtained for treatment on cellulose or wood were obtained, except for the 15 minute heat treatment chromatograms which showed a large concentration of a peak with a retention time of 33 minutes (compare Figure 18 and 19, example B with examples in Figure 22). Insolubilization occurred at a faster rate on glass fibers than was the case for heating D-glucose on cellulose. Up to 37% of the heated carbohydrate material could not be extracted from the glass after heat treatment for 25 minutes (footnote, Figure 22), which compares with 6.7% for D-glucose heat-treated for 25 minutes on cellulose (Table 6). As is the case for cellulose, glass has free reactive hydroxyl groups at its surface which could potentially react with D-glucose. IR spectroscopy has been used successfully in the past to study the condensation reaction of glass silanol groups with various organic compounds (137, 138). The IR spectra of D-glucose heated on glass did not provide any evidence to support a condensation reaction of D-glucose with the glass surface.

To gain further insight into D-glucose polymerization on glass, the water-soluble extract from the 18-minute heat treatment (Figure 22) was fractionated according to the scheme given in Figure 23. The

Figure 22

Analytical HPLC chromatograms of D-glucose heated on Pyrex glass fiber in a pressure vessel at 230°C with 2.8 MPa (N_2)

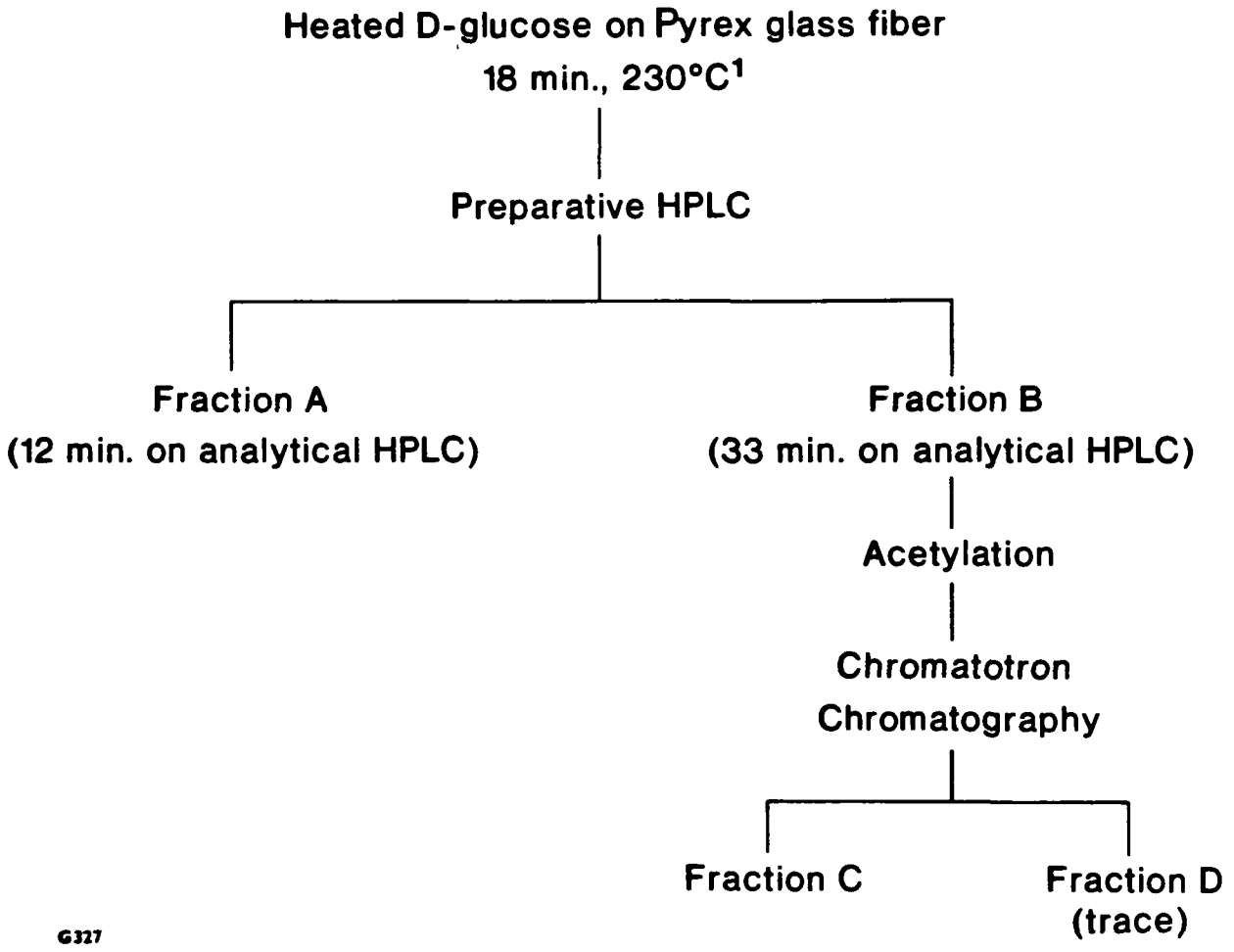


1 D-glucose 7% retained on glass fiber.

2 D-glucose 33% retained on glass fiber.

Figure 23

Fractionation of water-soluble extract from 18-minute heat treatment of D-glucose on glass



1 See analytical HPLC chromatogram in Figure 22.

fractions corresponding to the analytical HPLC peaks at 12-minutes (fraction A) and 33-minutes (fraction B) retention time were collected. Fraction B was acetylated and separated by chromatography on a chromatotron (rotating preparative thin layer chromatography) into fractions C and D which were obtained in a 16:1 solid weight ratio. The gas chromatography elution profile of fraction C is shown in Figure 24. The mass spectra for the components of fraction C appearing at 17.48, 17.56, 17.59 and 17.64 minutes on the gas chromatography elution profile are shown in Figure 25. The similarities between the mass spectra suggest that fraction C or the peak appearing at 33 minutes retention time in Figure 22 is mainly a mixture of 4 isomers. Comparison of these mass spectra with those found in the literature for β-D-fructopyranose pentaacetate (139) and keto-D-fructose pentaacetate (140) (see Figures 25 and 26) indicated that the material was composed mainly of isomers of D-fructose. This was also verified by comparison with D-fructose and acetylated D-fructose from commercial sources.

Upon heat treatment on glass fiber, D-glucose did not react with the hydroxyl groups of glass but first isomerized into D-fructose which then dehydrated and polymerized. This type of aldose-ketose isomerization is generally strongly catalyzed by the presence of alkali (141-144). The Pyrex glass fiber was assumed to be neutral while in reality it was slightly alkaline. The pH of distilled water increased from 6.5 to 8.0 upon addition of the Corning Pyrex glass fiber. The slight alkalinity of the glass fiber material may have catalyzed the formation of D-fructose which explains the large peak at 33 minute retention time for D-glucose heat treated 15 minutes on glass fibers.

Figure 24

Gas chromatography elution profile of Fraction C
(see Figure 23)

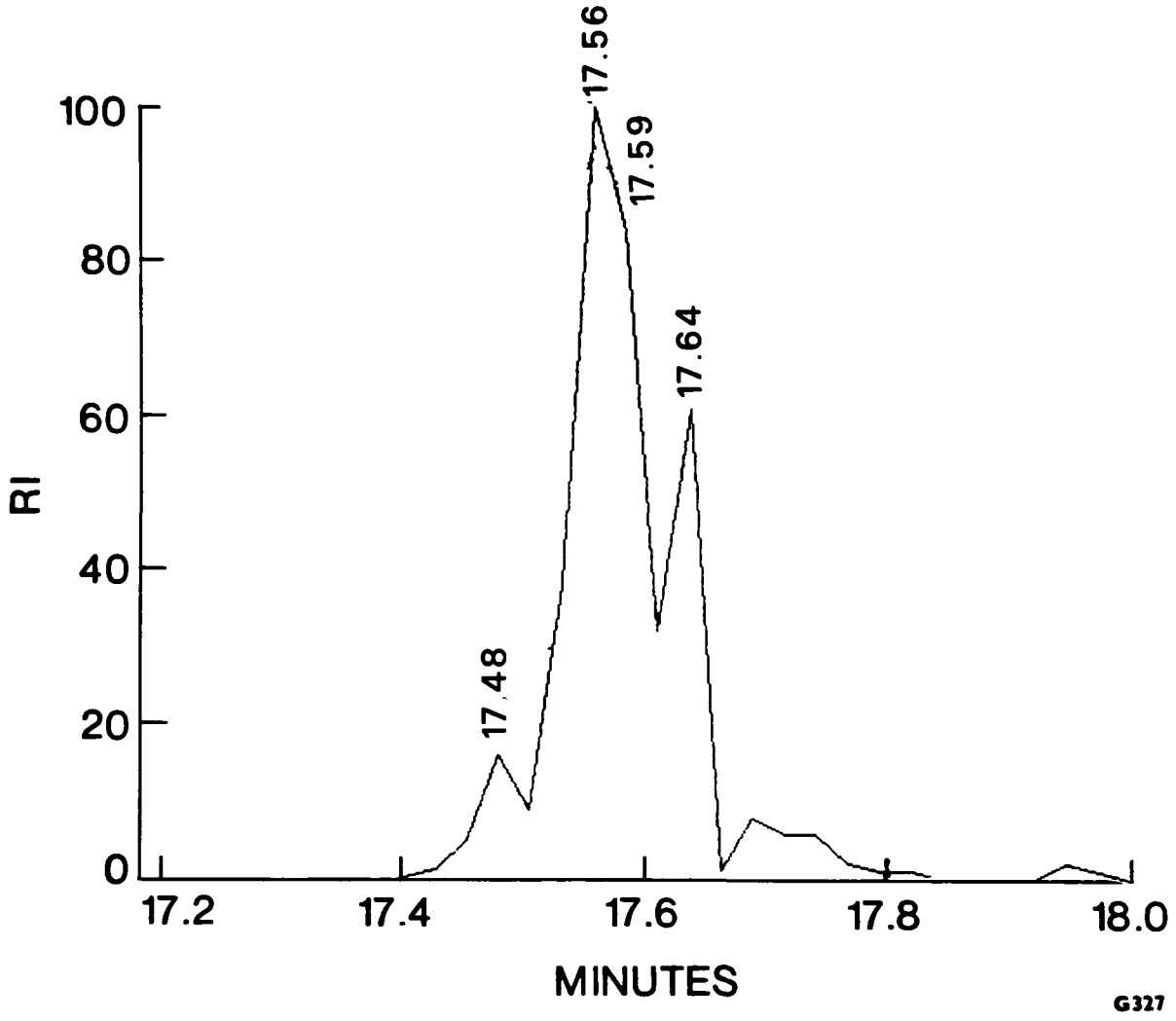


Figure 25

Mass spectra of Fraction C obtained at various elution times
(see GC elution profile on Figure 23)

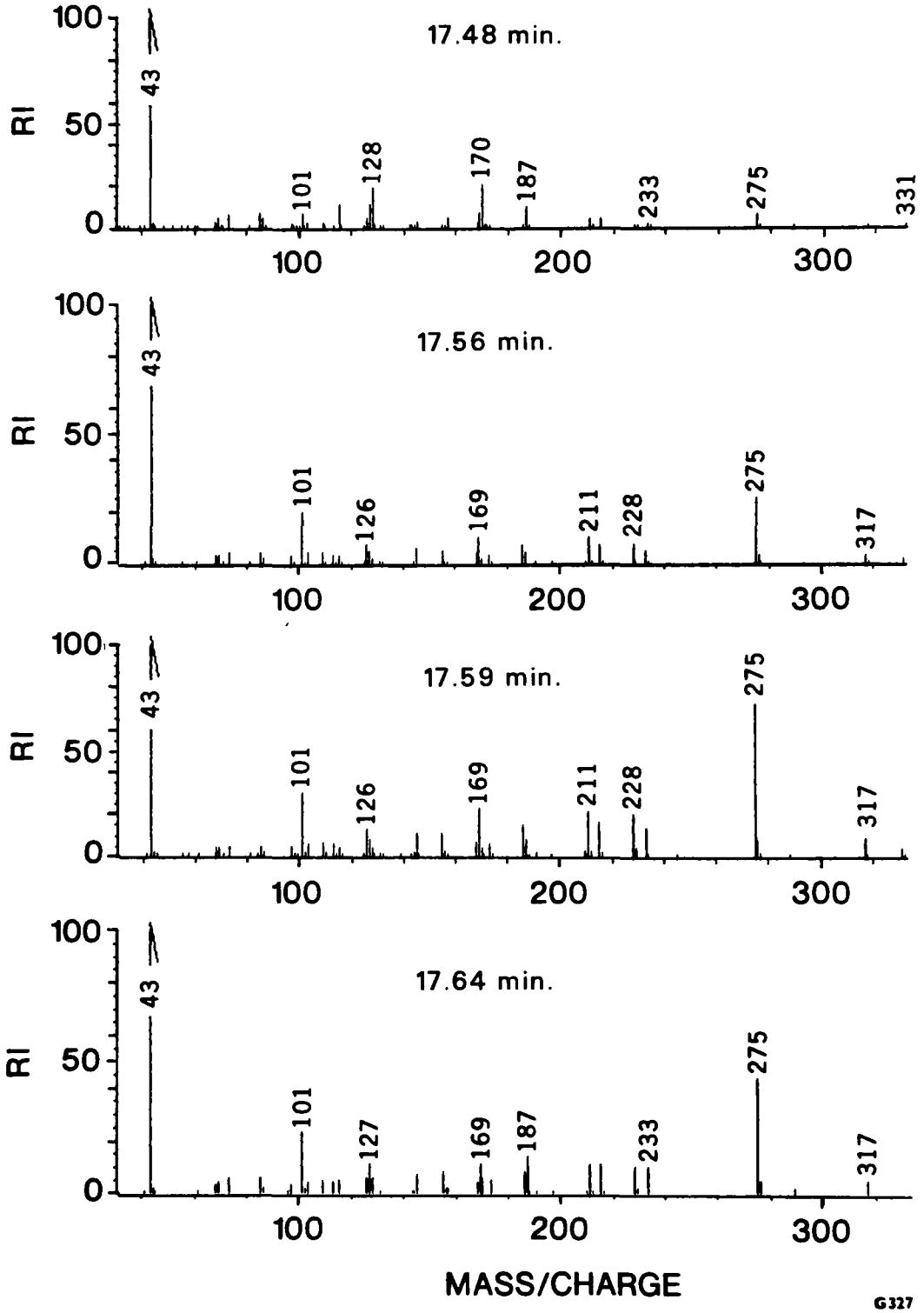
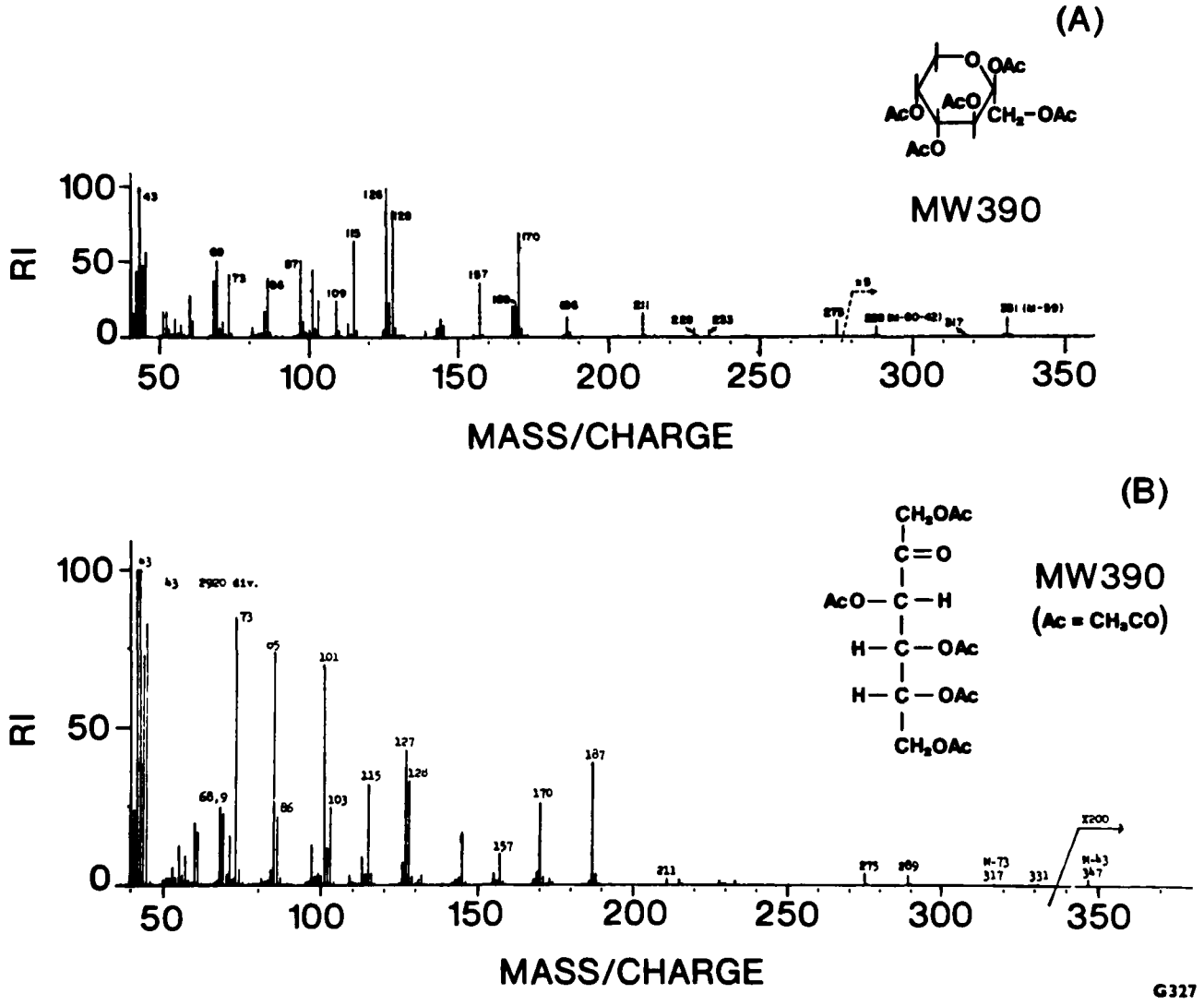


Figure 26

Mass spectra of β-D-fructopyranose pentaacetate (A) and keto-D-fructose pentaacetate (B) obtained from ref. 139 and 140, respectively



The presence of alkali may also have catalyzed the dehydration and the production of insoluble material.

The formation of D-fructose from D-glucose under alkaline conditions generally occurs through the formation of an enediol intermediate as shown in Scheme 6. This enediol would dehydrate into 3-deoxy-D-erythro-hexosulose and 3,4-dideoxy-D-glycero-hex-3-ene-osulose which are important intermediates in the formation of HMF (29, 53, 144, 145). These intermediates are reactive and will decompose and polymerize under the action of heat (54, 144). It was anticipated that these materials should be present only in small proportions within the fraction collected at 33 minutes retention time. Gas chromatography-mass spectrometry (GC-MS) analysis of fraction D, which is the minor component of peak 33 (Figure 23), showed this fraction to be a mixture of several components (Figure 27). The mass spectra of the components corresponding to the peaks appearing at 10.57, 14.70 and 15.14 minutes retention times on the gas chromatography elution profile in Figure 27 are reproduced in Figure 28 along with the mass spectrum of aldehydo-D-arabinose tetraacetate obtained from the literature (140). The similarity between the mass spectrum for the component at 15.14 minutes and the mass spectrum of acetylated arabinose indicate that it is a 5-carbon monosaccharide. The production of a 5-carbon sugar from a reverse aldolization and thermal degradation of sugar under alkaline conditions is known (146). The interpretation of the mass spectra for the peaks at 10.57 and 14.70 min. is given in Table 7, which corresponds to the fragmentation of acetylated 3,4-dideoxy-D-glycero-hex-3-ene-osulose and 3-deoxy-D-erythro-hexosulose, respectively.

Scheme 6

Formation /hydration of HMF

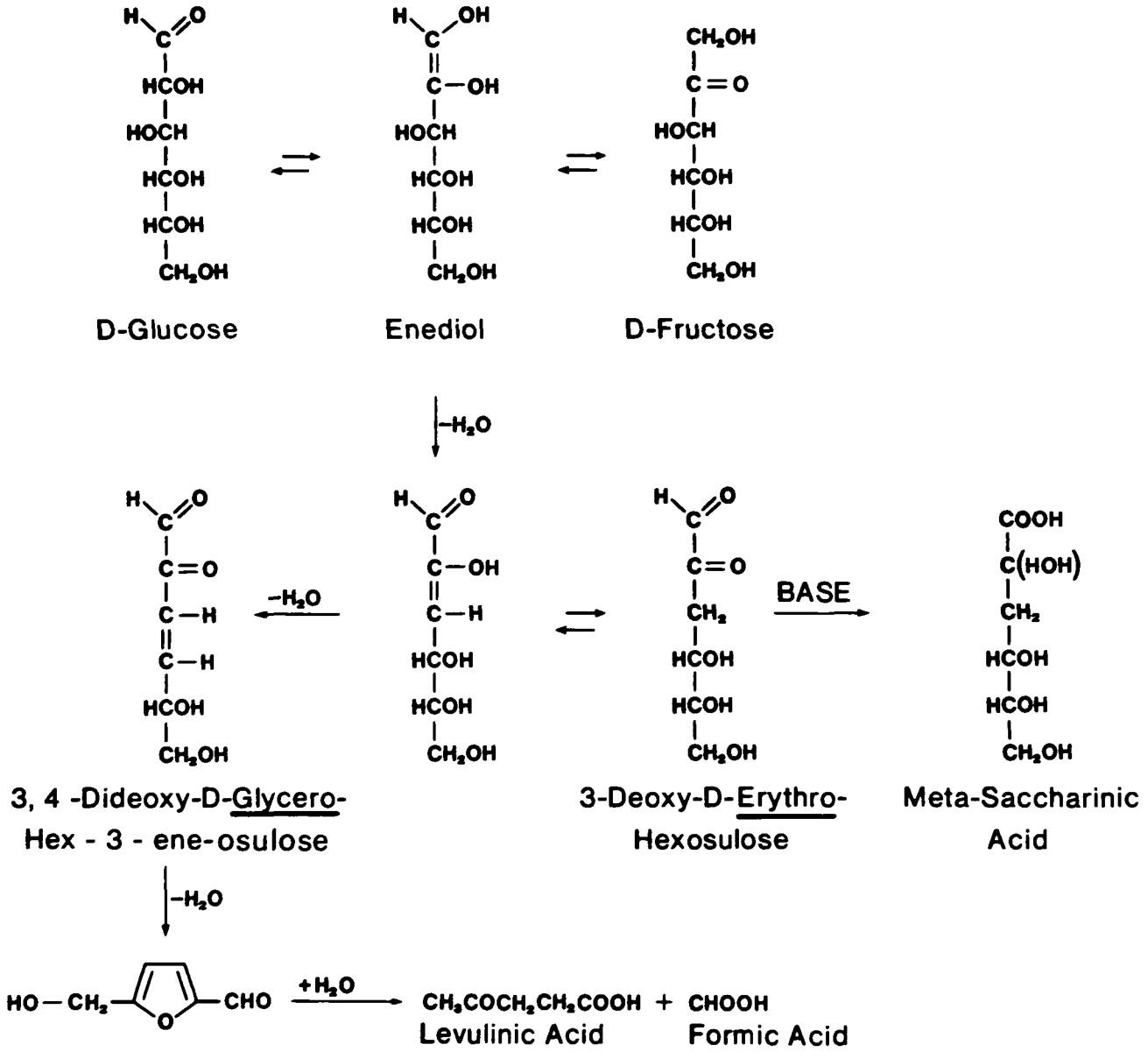


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Figure 27

Gas chromatography elution profile of Fraction D

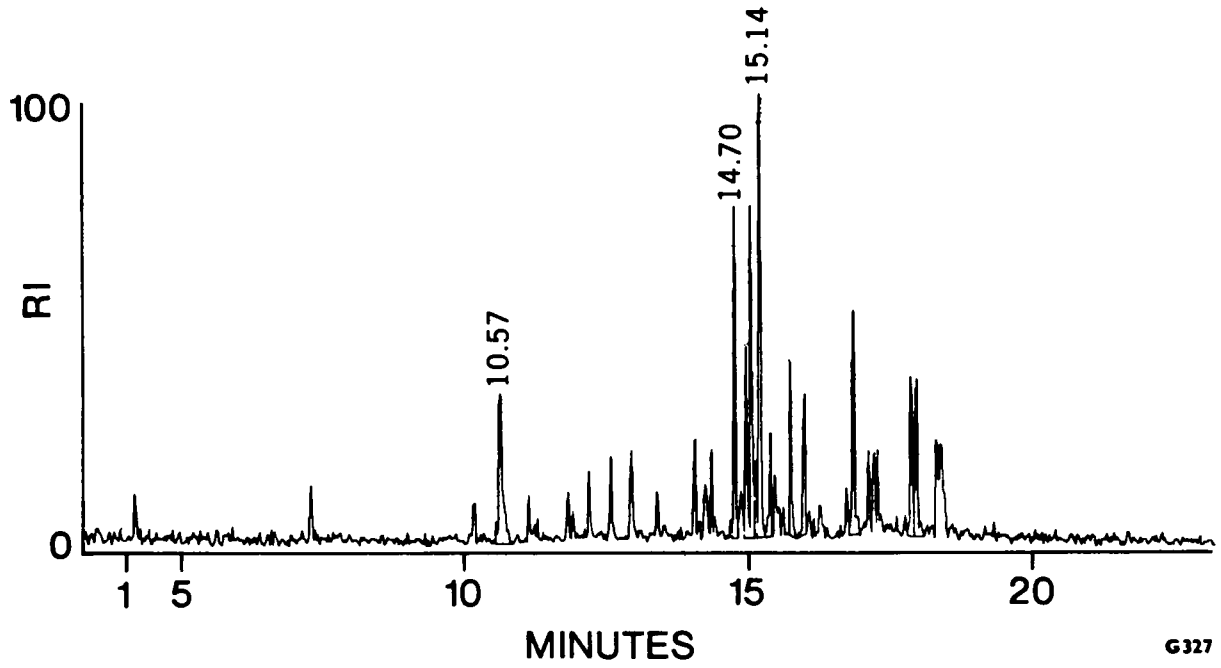


Figure 28

Mass spectra of Fraction D obtained at various elution times by GC-MS along with aldehydo-D-arabinose tetraacetate reproduced from ref. 140

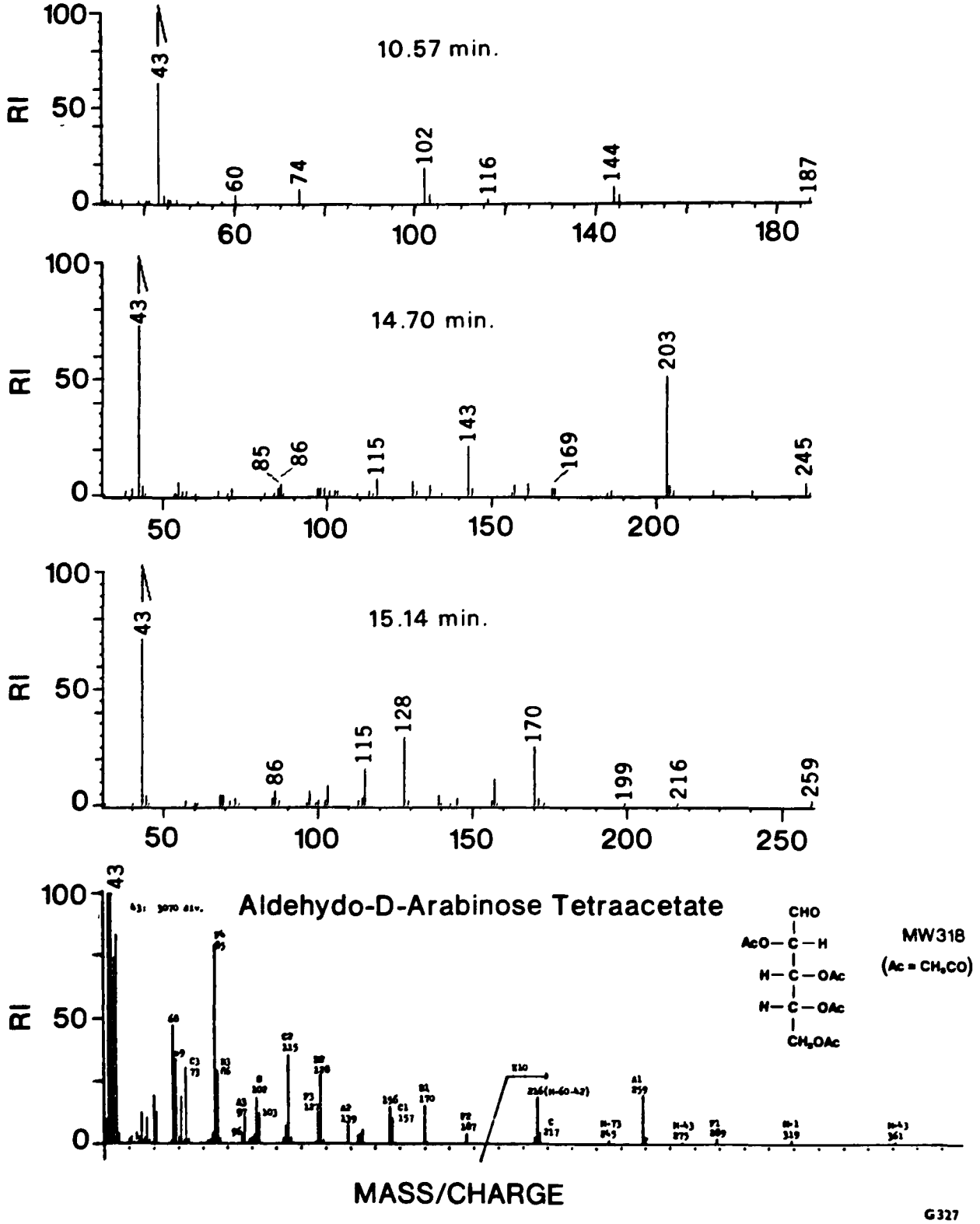
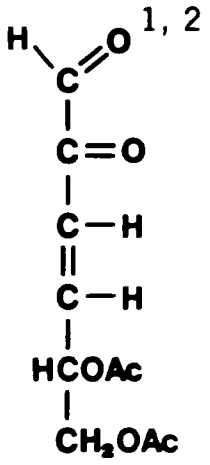
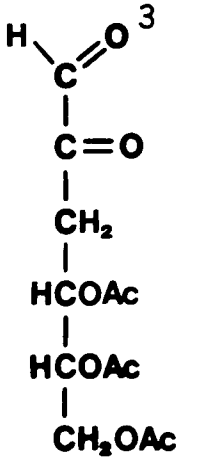


Table 7

Tentative interpretation of mass spectra for peaks at 10.57 and 14.70 minutes (see Figure 27 and 28)

GC-Elution Time (Min.)	Compound Formula	Mass / Charge	Interpretation
10.57	 [1, 2]	228	(M^+) Non Visible
		185	($M^+ - 43, CH_3-C\equiv O^+$)
		144	(185 + 1 - 42, $CH_2=C=O$)
		116	(144 + 1 - 29, $H-C\equiv O^+$)
		85	(116 - 31, $\cdot CH_2OH$)
14.70	 [3]	288	(M^+) Non Visible
		245	($M^+ - 43, CH_3-C\equiv O^+$)
		203	(245 - 42, $CH_2=C=O$)
		143	(203 - 60, CH_3COOH)
		115	(143 + 1 - 29, $H-C\equiv O^+$)
		85	(115 - 30, CH_2O)

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1 Ac = $COCH_3$
2 Acetylated 3,4-dideoxy-D-glycero-hex-3-ene-osulose.
3 Acetylated 3-deoxy-D-erythro-hexosulose.

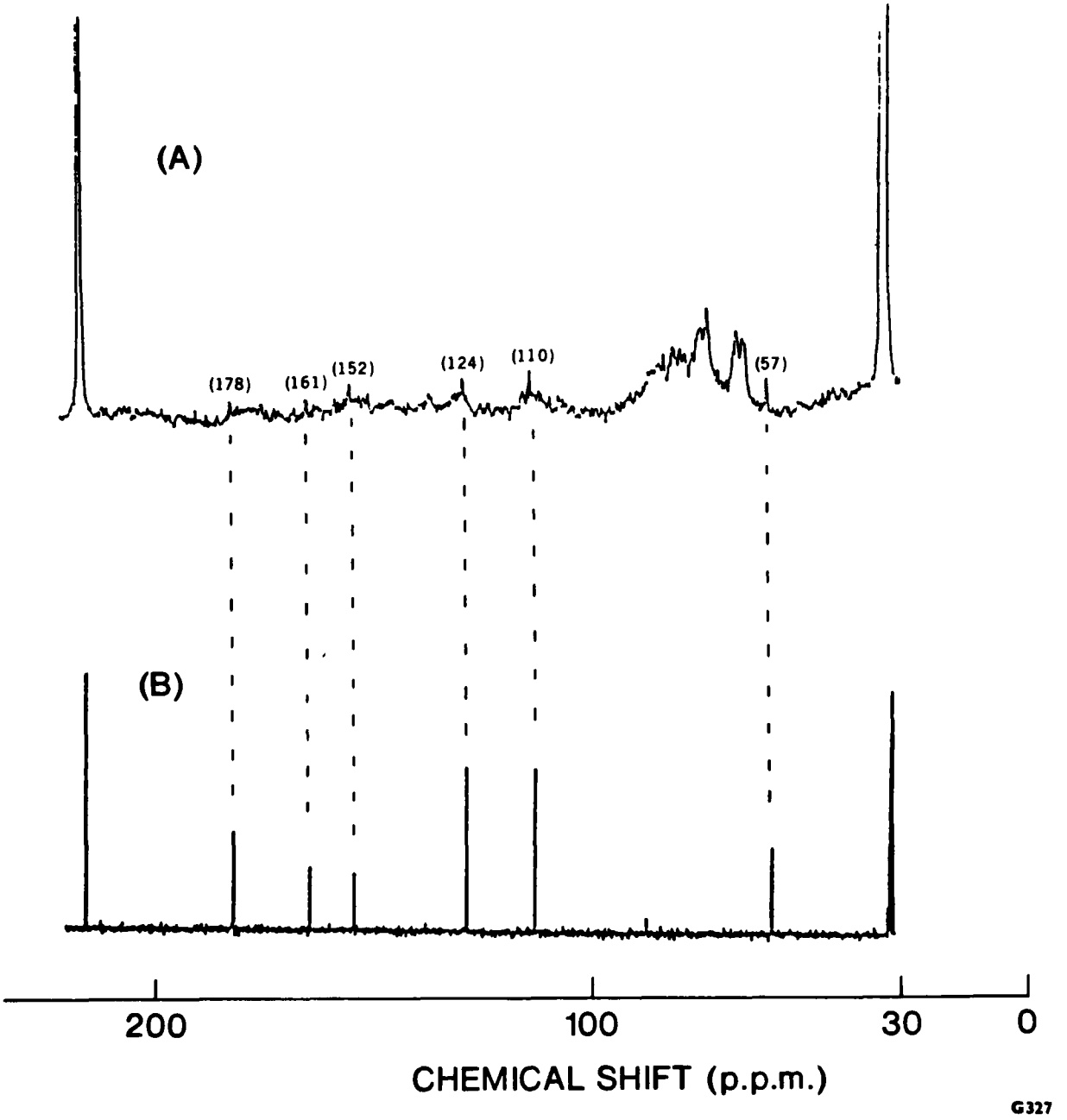
Alkali is known to cause the degradation of reducing sugars (143, 144, 146, 147) in contrast to acid which catalyzes their polymerization (25, 55, 84, 117, 119, 120) and enhances their adhesive properties (4, 5, 12, 13, 18). This is illustrated in part in Figure 29 which shows the ^{13}C-NMR spectrum of fraction A. Fraction A is the high MW material obtained at 12 minutes retention time by analytical HPLC from D-glucose heated on alkaline glass fiber, as shown on Figure 23. Although the general backbone of a carbohydrate can be recognized, bands of low intensity are obtained between 60 to 76 ppm and the peaks for the anomeric carbon which lie between 95 to 103 ppm were not detected. Interestingly, the ^{13}C-NMR spectrum shown in Figure 29 indicates the presence of a small quantity of HMF in high molecular weight fraction A. No trace of HMF was found previously in the ^{13}C-NMR spectrum of fraction 1 derived from heat-treated D-glucose (Figure 16).

The insoluble material formed on glass fiber may be due to the homopolymerization of HMF, which can be produced in high yield by dehydration of D-fructose (52, 78, 79, 136). However, HMF heated for 25 minutes at 230°C on the Pyrex glass fiber could be recovered by extraction with organic solvent but not from the D-glucose residue. The extracted HMF material had a ^{13}C-NMR spectrum similar to that of the starting material (Figure 16).

This portion of the study relating to behavior of D-glucose under alkaline conditions was not originally planned. However the chemistry involved in heating D-glucose as a thin solid layer on an alkaline glass support in a pressure vessel agreed generally with the literature information describing the transformation of D-glucose under alkaline conditions (141-147). In the presence of an alkaline catalyst,

Figure 29

Comparative liquid-state ^{13}C-NMR spectra of Fraction A [1], [2] from heated D-glucose on Pyrex fibreglass (A) and HMF reference (B)



1 Solvent: acetone-water in 1:1 volume ratio.

2 See Figure 23.

D-glucose isomerizes and dehydrates into known intermediates independently of the presence of the solid glass support. Similar conclusions may also be made concerning cellulose.

D-glucose may be condensing with cellulose under acidic conditions through formation of a glucosidic linkage, but as illustrated in Scheme 7, this is not sufficient to explain the formation of a durable bond between two lignocellulosic units. This type of condensation reaction is known to be reversible (25, 29, 84, 117). A second step is required in order to achieve durable bonding of two cellulose units.

Reactivity of Selected D-Glucose Derivatives

A series of D-glucose derivatives were evaluated for their ability to polymerize under a combination of heat and pressure and produce a 'boil proof bond'. In addition, some of these D-glucose derivatives were subjected to heat and pressure treatment in a pressure vessel and the thermal reaction was monitored externally by HPLC. The TS test results are summarized on Table 8 while the HPLC chromatograms are shown in Figure 30 and 31.

Previous results (Table 4) for heated D-glucose fractions had suggested that low MW D-glucose oligomers would be less reactive than D-glucose. However these current results show similar TS test results for maltose, maltotriose and D-glucose. Of the di- and trisaccharides which were evaluated, only cellobiose which melts at 225°C and possesses a non-reducing β linkage, was found to be less reactive than D-glucose. With cellobiose, a low TS test result of 2.0 N.m was obtained at a 15 minute press cycle, compared to 4.2 N.m for D-glucose. The HPLC chromatograms shown in Figures 30 and 31 confirmed that the β-linked disaccharide

Scheme 7

Possible glucose-cellulose condensation

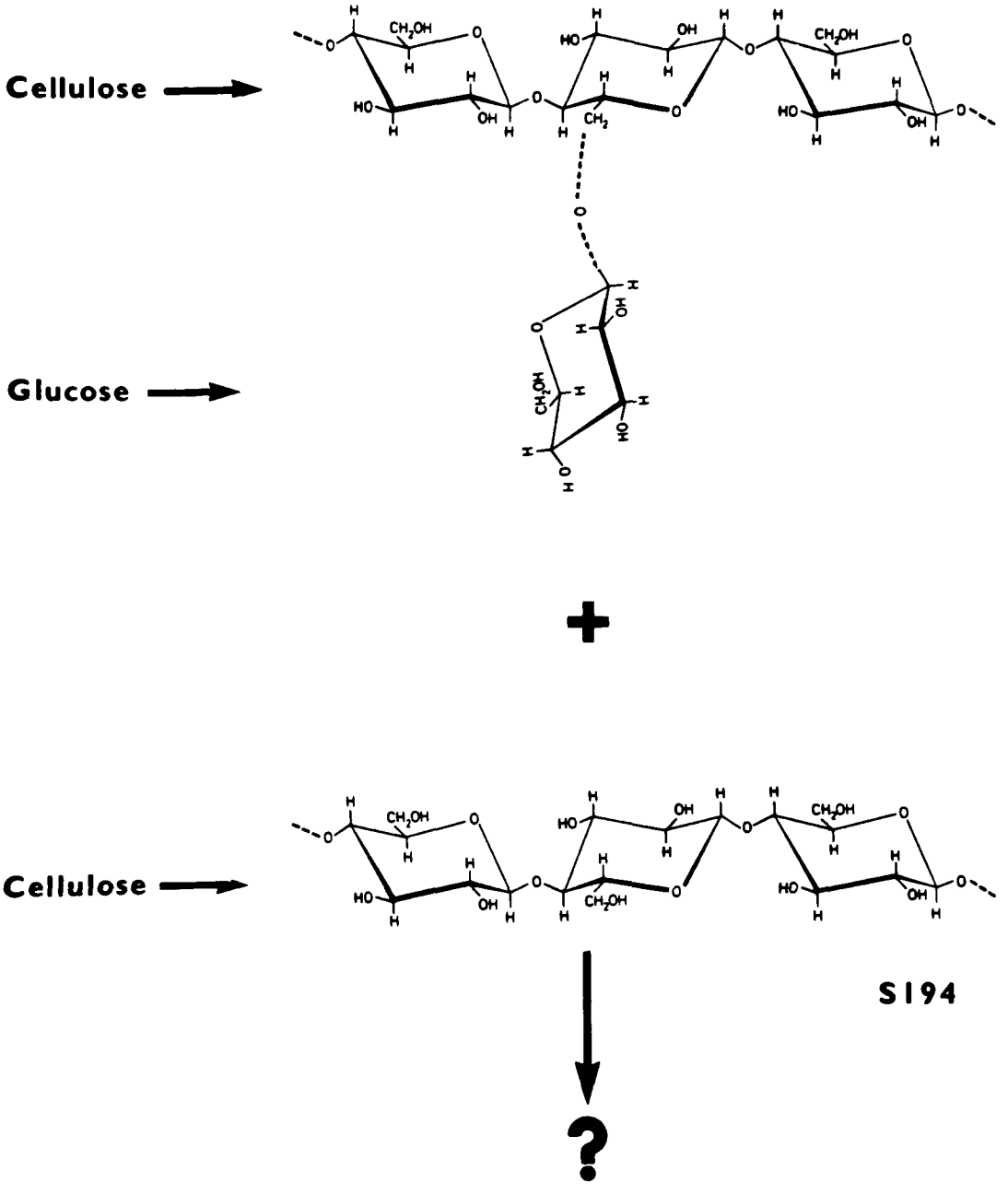


Table 8

Evaluation of adhesive properties of selected D-glucose derivatives

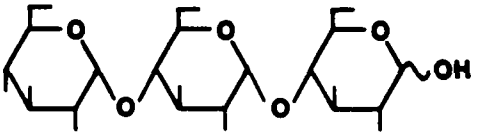
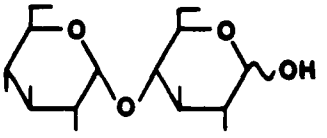
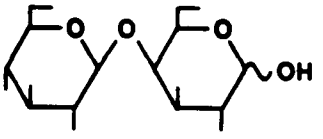
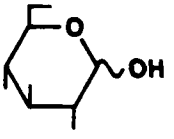
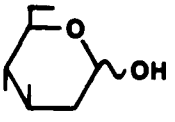
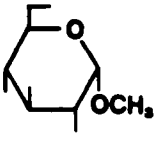
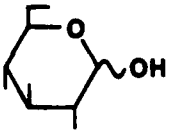
Compound	Formula	Melting Point (°C)	230°C 15 Min. TS (N.m)	230°C 30 Min. TS (N.m)
Maltotriose		133	4.4	8.3
Maltose (Monohydrate)		102	4.6	8.5
Cellobiose		225	2.0	7.9
Glucose Plus 5% Hydroquinone		146	3.8	7.2
2-Deoxy-Glucose		147	0	2.5
Methyl α-D-Glucoside		170	0.3	1.1
D-Glucose		146	4.2	7.9

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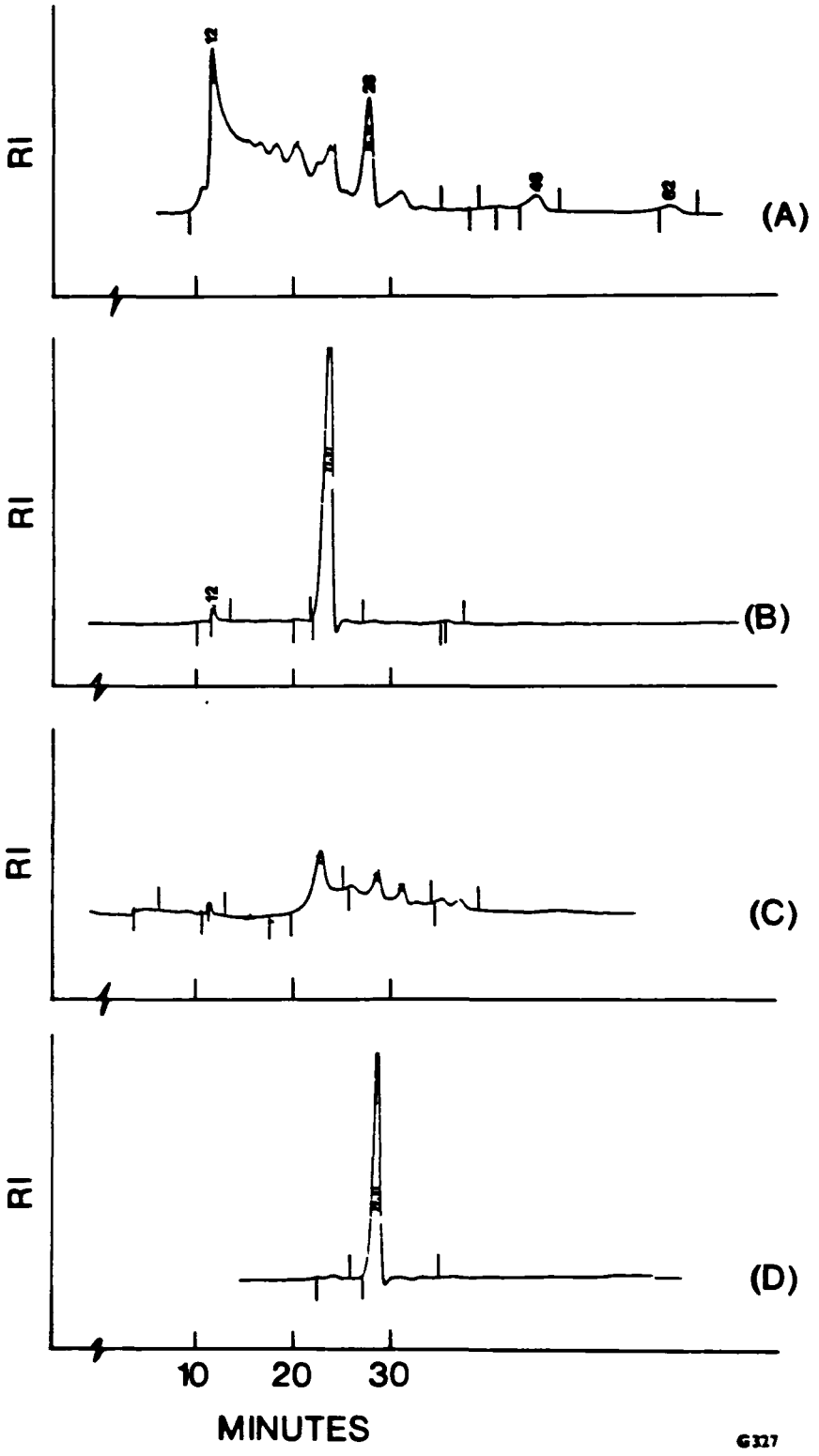
Figure 30

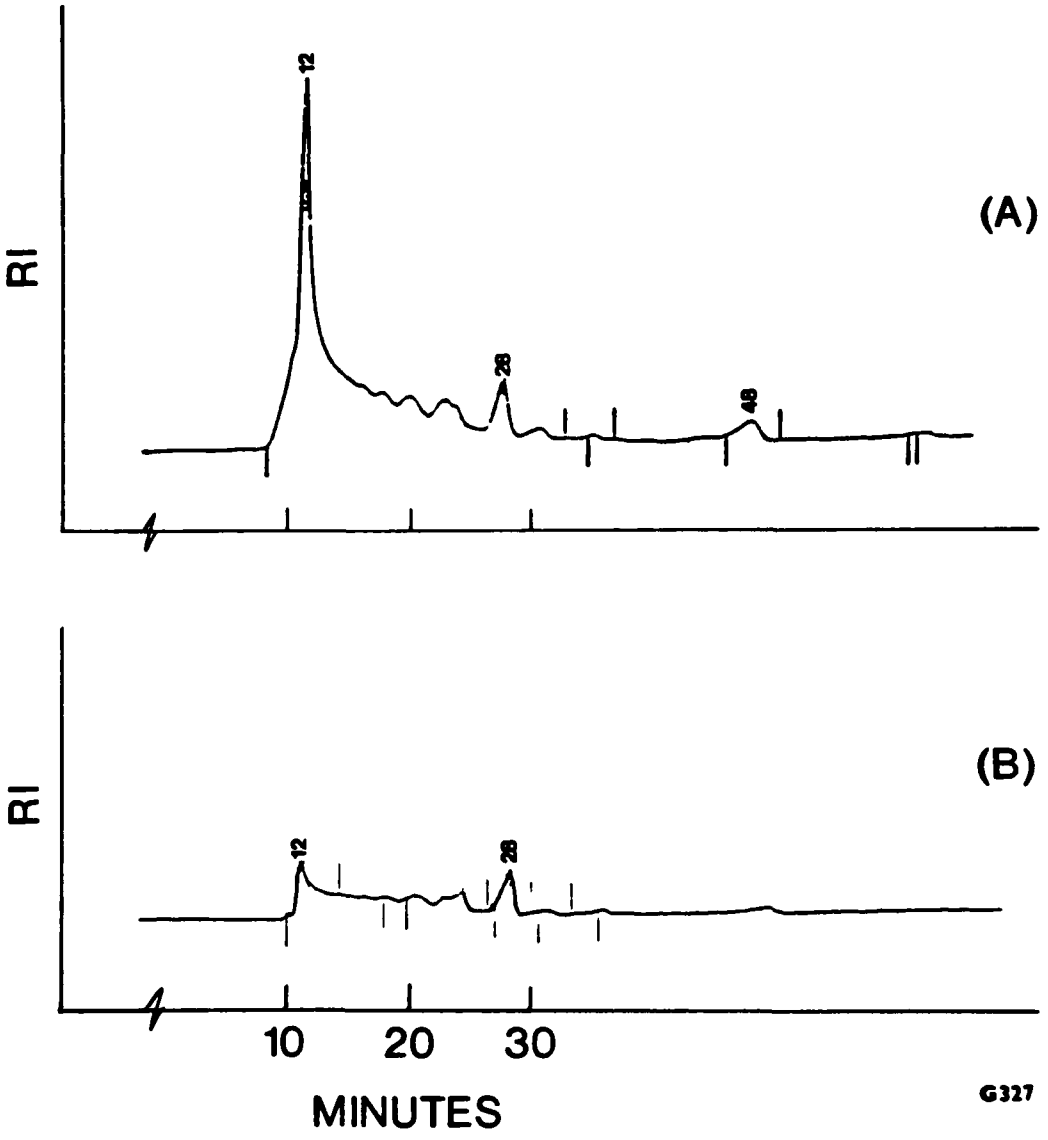
Analytical HPLC chromatograms of D-glucose derivatives heated in a pressure vessel 25 minutes at 230°C with 2.8 MPa (N_2)



[1] Maltotriose (A), cellobiose (B), 2-deoxy-glucose (C), methyl α-D-glucoside (D).

Figure 31

Analytical HPLC chromatograms of cellobiose (A) and methyl α-D-glucoside (B) heated in a pressure vessel 40 minutes at 240°C with 2.8 MPa (N_2)



(cellobiose) is more stable thermally than to the α-linked oligosaccharide (maltotriose). While heating at 230°C was sufficient to decompose and polymerize maltotriose (Figure 30), heating at 240°C was required to decompose and polymerize cellobiose (Figure 31). The HPLC chromatograms for polymerized cellobiose, maltotriose and D-glucose (Figure 6, 25 minutes) were comparable indicating that similar thermal chemical reactions had occurred. Peaks at 28, 48 and 62 minutes retention times were apparent indicating the presence of D-glucose, 1,6-anhydro-D-glucose and HMF (compare example I of Figure 9, 18 and 19). Formation and cleavage of glycosidic bonds are competitive chemical reactions under such experimental conditions. These results are in agreement with current findings from the literature which report that condensation polymerization of carbohydrate with glucosidic bond formation is an equilibrium process (25, 29, 84, 117) as shown in Scheme 8.

Scheme 8. Polycondensation of Sugars

$$n\ C_6H_{12}O_6 \rightleftharpoons C_6H_{11}O_5 - (C_6H_{10}O_5)_{n-2} - C_6H_{11}O_6 + (n-1)H_2O$$

The generation of free radicals upon heating carbohydrates is well documented (27, 28, 54, 75, 76, 146, 148, 149). However, free radicals would initially not play an important role in the mechanism of condensation (25, 146, 148, 149) and adhesion of carbohydrates. The addition of a radical scavenger such as hydroquinone had no effect on the adhesive properties of D-glucose (Table 8).

The presence of a free anomeric hydroxyl (aldehyde) is essential for the condensation (67, 149) and adhesion (13) of carbohydrates. The low TS strength of 1.1 N.m for the particleboard bonded 30 minutes at 230°C with methyl α-D-glucoside indicates that this extended press cycle was not sufficient to release its free anomeric hydroxyl. Comparison of HPLC chromatograms in Figure 30 and 31 indicate that a heat treatment of 240 C in a pressure vessel was required to decompose and polymerize the methyl α-D-glucoside.

The poor adhesive result obtained with 2-deoxy-glucose was unexpected as this compound possesses a free anomeric hydroxyl for polymerization. However the HPLC chromatograms in Figures 30 and 31 show that this compound does not polymerize similarly to D-glucose but instead seems to decompose to lower molecular weight materials under the action of heat. These data illustrate the usefulness of HPLC chromatograms in interpreting TS test results and for studying the mechanism of carbohydrate condensations.

From the carbohydrate derivatives tested, only those which decomposed to D-glucose and then polymerized when treated at 230°C in a pressure vessel provided a particleboard with TS test above 3.8 N.m for a press cycle of 15 minutes at 230°C. This is consistent with previous results which indicated that D-glucose was the most reactive species.

Except for 2-deoxy-glucose, all polymerized in a manner similar to D-glucose, presumably through glucosidic bond formation. The results obtained with maltose and maltotriose, compared to cellobiose, indicate that the type of glucosidic linkage has an influence on the adhesive properties of low molecular weight carbohydrates. The α-linked disaccharide and trisaccharide tested melted, decomposed and polymerized at a lower temperature in comparison to the β-linked one. The presence of β-linkage in the fractionated heated sugar oligomer (Figure 16) could be responsible in part for its lower reactivity (Table 4). Branching and the presence of non-reducing end groups (118, 150) could also be responsible for the lower reactivity of the heated sugar oligomers.

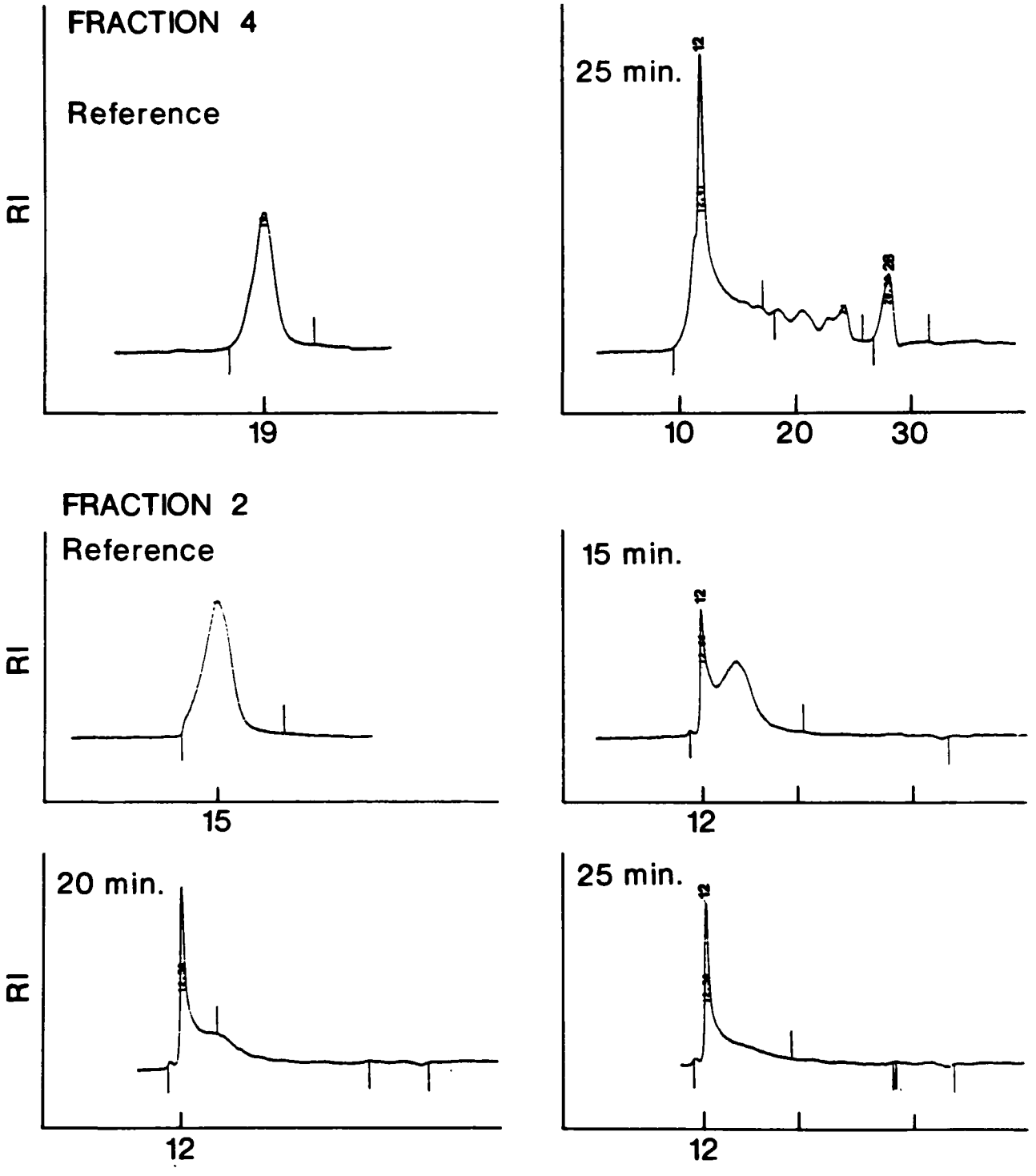
Condensation with the formation of glucosidic bonds may play an important role in the mechanism of adhesion of D-glucose. Unfortunately, this is an equilibrium process (Scheme 8). While glucose is the most reactive species, which polymerizes rapidly under mild conditions through glucosidic linkages, it also exists as an acyclic form which can dehydrate into reactive conjugated aldehyde species (Scheme 6). Since the carbohydrate derivatives which yielded satisfactory test results, decompose to D-glucose upon heating, their role in adhesion cannot be evaluated from these data.

Bonding Through Glucosidic Polymerization

Based on results obtained with carbohydrate models, it was anticipated that the heated sugar oligomers (fraction 1-6 from Table 4) would also decompose and polymerize upon heating in a manner similar to maltotriose or cellobiose. Fraction 2 and 4 were subjected to various heat treatments in a pressure vessel and analyzed by HPLC (Figure 32).

Figure 32

Comparison between chromatograms of Fraction 2 and Fraction 4 heated in a pressure vessel at 230°C with 2.8 MPa (N_2)



Fraction 4 with a $\bar{M}_n$ of 520 (Table 4), both decomposed and polymerized upon heating, producing an HPLC chromatogram (Figure 32) similar to that of heated D-glucose. In contrast, when fraction 2 ($\bar{M}_n$ of 980) was subjected to a similar heat treatment, resulting HPLC chromatograms indicated only the formation of higher molecular weight material (Figure 32). Polymerization reactions predominated over decomposition ones; the resulting polymer eventually becoming insoluble.

This particular high MW heated sugar fraction was selected for further study to verify if this type of polymerization, without initial decomposition to lower MW material, could eventually produce bonding. A new set of particleboard panels was prepared using fraction 2 as adhesive. The press conditions were identical to those employed for the preparation of samples shown in Table 4 except for an extended press cycle of 30 minutes at 230°C instead of 15 minutes. Under these conditions, a TS strength of 6.3 N.m was obtained for fraction 2 which compared to 7.9 N.m for D-glucose (see Table 8 for D-glucose test value). It thus appears that this type of carbohydrate polymeric material could produce a good bond if an extended press cycle was used.

The possibility of binding polar surfaces like cellulose with polysaccarides such as insoluble starch is known. Gelatinized starch (starch granules ruptured with live steam) is applied as a water dispersion (151) and upon evaporation of the solvent, a strong bond is obtained. Mechanical interlocking and the interaction of secondary forces (van der Waals and hydrogen bonding) are thought to be responsible for the adhesion (151). This type of bond is strong but possesses very limited water-resistance. It remained to be determined if simple insolubilization through formation of glucosidic linkages (α or β type)

between several molecules of D-glucose, or D-glucose and cellulose, would be sufficient for the production of a durable bond.

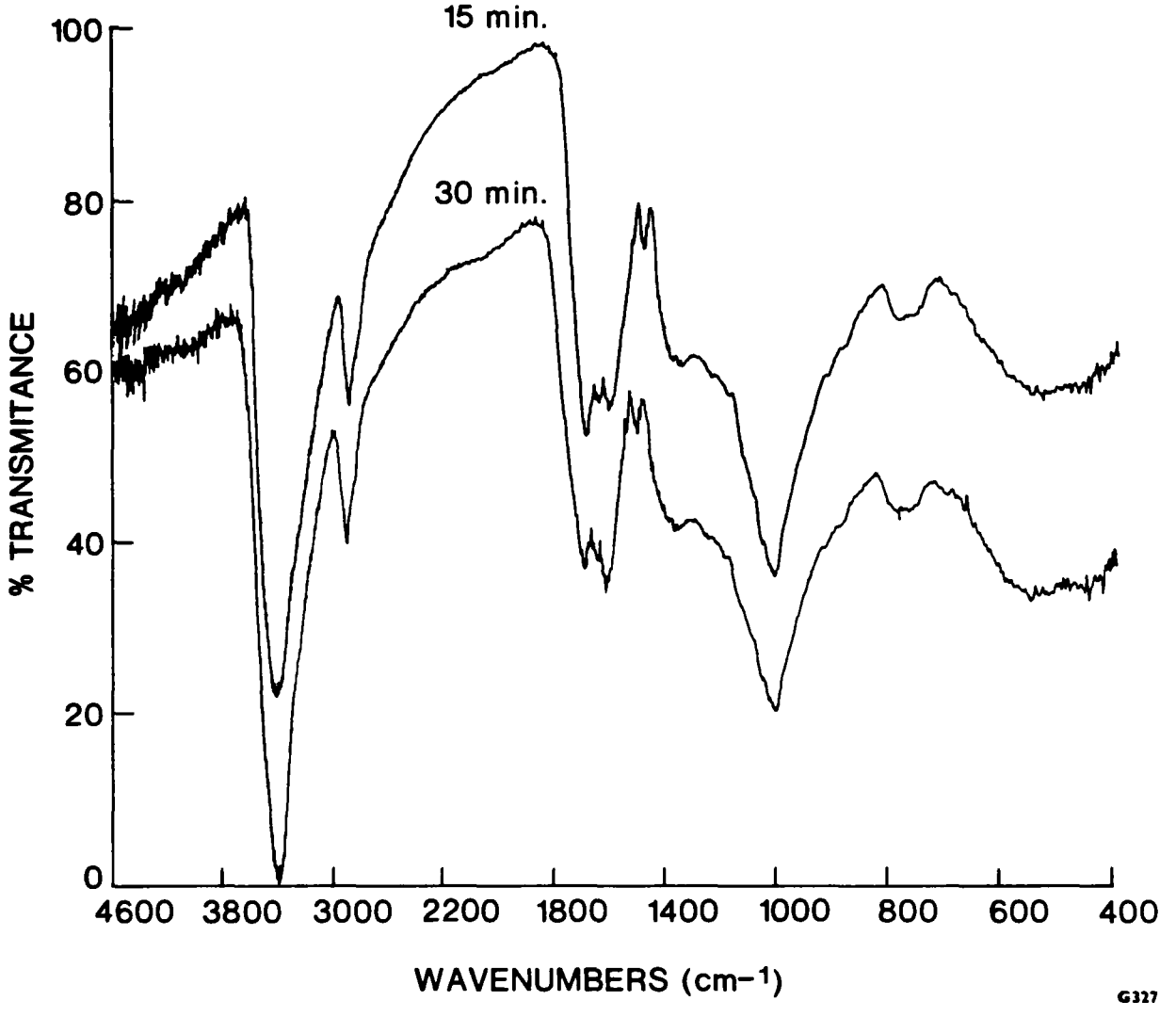
IR and ^{13}C-NMR of Post-Heated Fraction 2

In the work described up to this point, only the water-soluble heated sugar oligomers were characterized for functional groups and adhesive properties. Spectroscopic analysis of the water-insoluble, high MW, carbohydrate products may provide additional information. Samples of Fraction 2 (water soluble) which would not decompose to D-glucose upon heating in a pressure vessel (Figure 32) were placed between Teflon sheets in the middle of a 11.1-mm particleboard mat and heated in a press at 230°C and 6.9 MPa for 20 and 40 minutes, respectively. Heating in the press resulted in a more severe treatment than in the pressure vessel as both samples were found to be insoluble in warm water.

If fraction 2 polymerizes further through the formation of glucosidic linkages the IR spectra of these additionally heated sugar samples should be similar to that of the starting material or maltopentaose (Figure 12). However, the IR spectra of post heated fraction 2 (Figure 33) show the presence of new bands, including those at 1630 and 1710 cm^{-1}. These are characteristic of high molecular weight carbohydrate polymers obtained by thermal polymerization (77, 118). Similar IR spectra were obtained upon thermal polymerization of DL-glyceraldehyde and D-glucose in a press (13) and during the pyrolysis of cellulose (77, 152-154). The band at 1710 cm^{-1} has generally been assigned to C=O stretching vibration (77, 152-154) whereas the band at 1630 cm^{-1} has been assigned both to C=C vibration and O-H stretching of absorbed water (152-154). Information in the literature concerning the

Figure 33

Infrared spectra of heated glucose Fraction 2 post-heated in a press at 230°C [1]



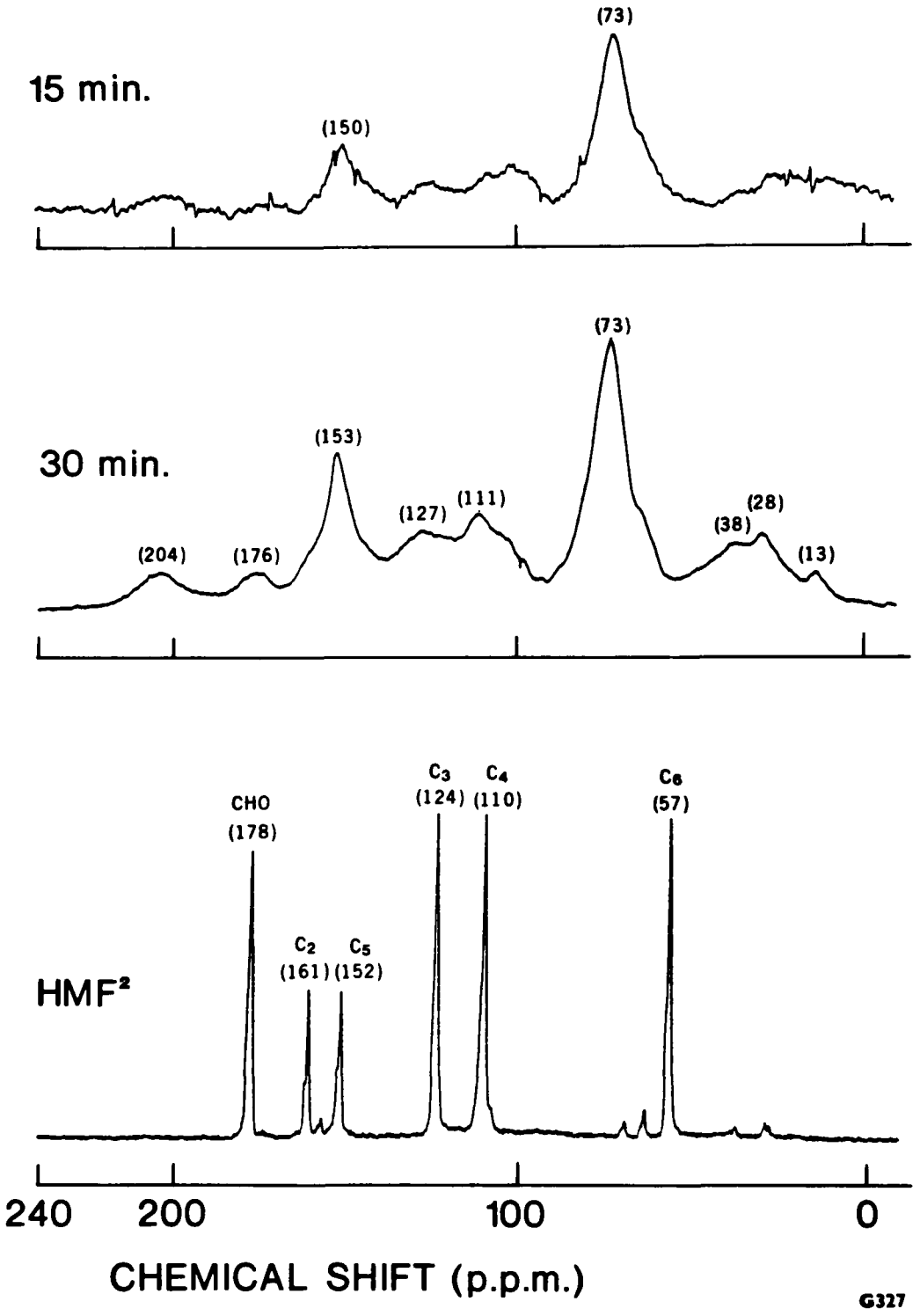
[1] Samples heated between Teflon sheets placed in the middle of 11.1 mm thick particleboard mat.

nature of these bands can be confusing. Through the years, these bands have been attributed to the presence of various compounds or functional groups including: the presence of keto-enol group (152, 153) or the incorporation of acyclic 3-deoxyglycosulose in the polymer (118), the formation of HMF or the presence of levulinic acid from hydration of HMF (23, 35). The presence of the carbon-carbon double bond in the IR spectra of carbohydrate pyrolytic products has been supported by results of bromine addition tests (155), by the increase of the water content in the distillate (36, 156) and by comparative elemental analysis of the starting material and end product (13).

IR spectra of complex high molecular weight polymers often result in overlapping peaks which are difficult to interpret. The availability of CP-MAS probe units for ^{13}C-NMR of solids (solid state ^{13}C-NMR) has facilitated the analysis of complex high MW natural polymers such as lignin (157, 158), cellulose (159, 160) and starch (124). This technique was employed for the characterization of the insoluble carbohydrate polymer obtained by thermal polymerization. The solid state ^{13}C-NMR spectra of post-heated fraction 2 are shown in Figure 34. These are different from those of simple D-glucose oligomers shown in Figure 16. The spectrum of the 15-minute, post heated Fraction 2 appears to confirm the early formation of carbon-carbon double bonds, most likely conjugated. This is indicated by the presence of a broad peak or absorption of high intensity centered at 150 ppm. Upon further heating, new absorption peaks (or stronger ones) appear at 13-38, 111, 127, 176 and 204 ppm. The appearance of these peaks indicates that a major modification of the carbohydrate polymer is taking place. The large absorption at 60-80 ppm due to carbon bearing oxygen indicates however

Figure 34

Comparative solid-state ^{13}C-NMR spectra of heated glucose Fraction 2 post-heated in a press at 230°C [1] and HMF reference [2]



1 Samples heated between Teflon sheets placed in the middle of 11.1 mm thick particleboard mat.

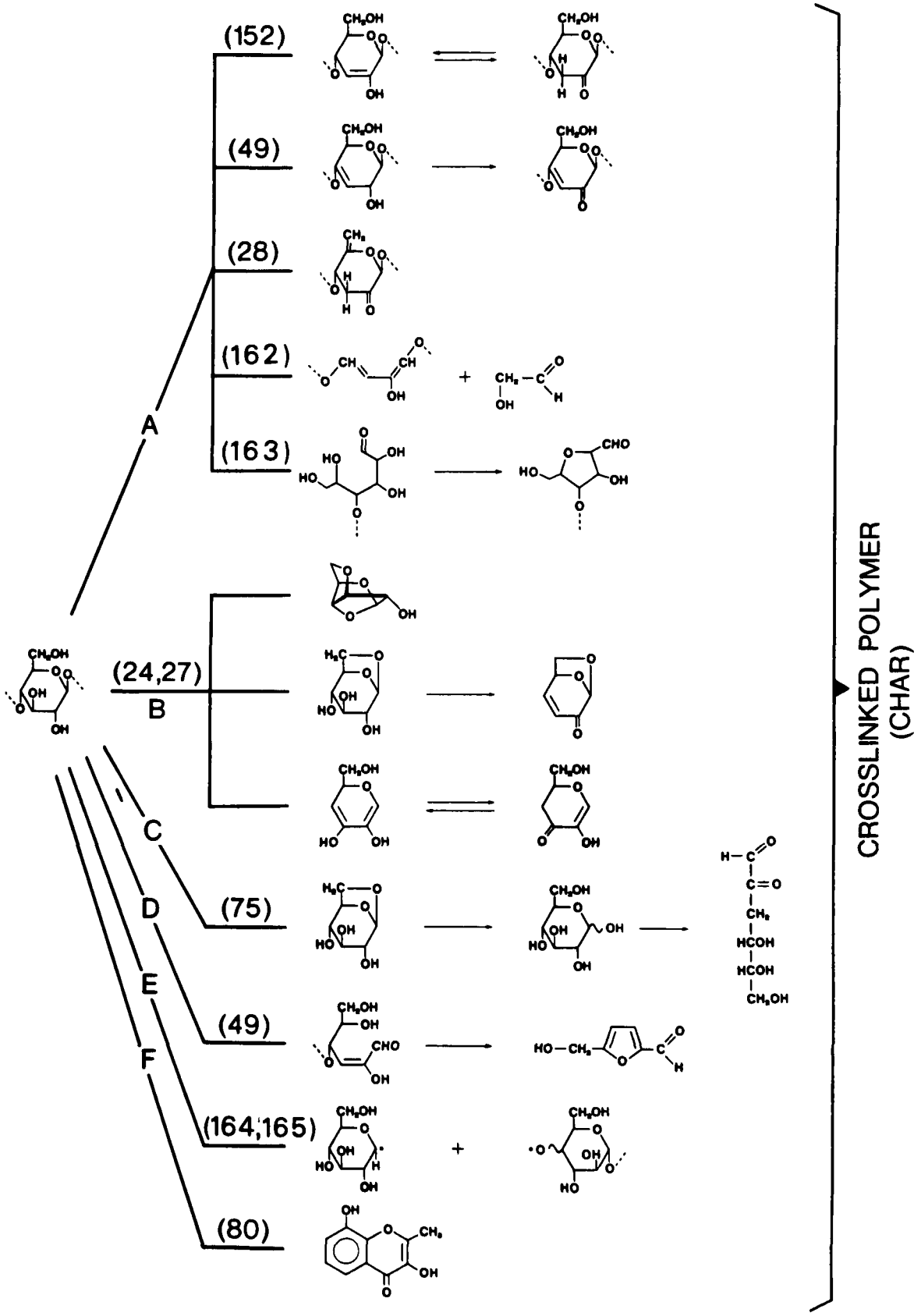
2 Liquid HMF reference (starting material) spectrum obtained under conditions identical to solids (in CP-MAS probe, without adjusting for homogenity of magnetic field).

that part of the saccharide backbone is still present after the 30-minute press cycle (compare Figure 16 and 34). The absorption bands at 13-40 ppm are generally an indication of $-\overset{|}{\underset{|}{C}}-CH_2-\overset{|}{\underset{|}{C}}-$ and $-\overset{|}{\underset{|}{C}}-CH_3$ bonds which suggest that partial decomposition of the polymer had occurred. Of course, the production of $-\overset{|}{\underset{|}{C}}-CH_2-\overset{|}{\underset{|}{C}}-$ bonds may also originate from condensation of carbon-carbon double bonds. The absorption at 176 and 204 ppm may be due to the presence of a carbonyl-carbon, probably aldehyde and ketone, although carboxylic acid-carbonyl resonances can also be found in the range 165 to 185 ppm (161). The broad peaks centered at 111 and 127 ppm might suggest the presence of a furan ring. These would correspond to the less reactive unsaturated carbon of HMF for example. However, the peaks at 152 - 161 ppm for HMF are generally of lower intensity than those at 110 - 124 ppm which is not the case for the post heated carbohydrate samples (see Figure 34). In fact, these absorptions could correspond to some of the various carbohydrate degradation products shown in Scheme 9. These have been proposed to account for the thermal degradation of cellulose. The reference for each degradation pathway proposed is indicated in Scheme 9. This information on cellulose degradation, may apply in part to the lower molecular weight polyglucose material which are most likely produced under the experimental conditions used in this study.

As indicated in Scheme 9, a considerable amount of information is available on the thermal degradation of cellulose. Cellulose may depolymerize and dehydrate with the formation of pyran (pathway B) or furan (pathway D), aromatic (pathway F) and acyclic (pathway C) or radical components (pathway E) (Scheme 9). Intramolecular dehydration may also occur with the formation of unsaturated carbon-carbon double

Scheme 9

Thermal degradation of cellulose



bonds in the polymer (pathway A). Of course, all of these could further rearrange and recondense producing a large highly crosslinked polymer often designated as char. For example, depending on the experimental conditions, levoglucosenone or 1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranos-2-ulose could undergo a Diels-Alder reaction (166), or be subjected to a Michael - addition (167), or decompose to a very reactive 3 - oxidopyrylium ion (168) or dehydrate to HMF (70). To summerize, cellulose may depolymerize through a variety of mechanisms (pathways B, C, D, E, F) or dehydrate without complete initial depolymerization (pathway A) and then condense. Recent calorimetric data by Mok and Antal (169) support these competitive pathways.

Based on our own results and literature information (55-60, 118, 169), the mechanism of condensation and adhesion of D-glucose, under conditions similar to those employed in the production of particleboard might be as follows: under a combination of heat and pressure, D-glucose melts and flows in a thin layer on the lignocellulosic material. The carbohydrate thus wets and forms a continuum between the surfaces to be assembled. Melting occurs with concurrent thermal anomerization (29,118, 148). This is followed by a condensation process which involves glucosidic bond formation, the low molecular weight sugar being the most reactive components. At low temperature, this condensation is reversible for the lower molecular weight oligomers. Intramolecular dehydration and isomerization of the free D-glucose also occurs to a small extent. These dehydration and isomerization products also homopolymerize or condense with the D-glucose thermal polymer. At this point, a strong but non-durable bond is obtained. Upon further heating, the D-glucose thermal polymer eventually decomposes (solid state ^{13}C-NMR spectra shown in

Figure 34 indicates the formation of $-\overset{|}{\underset{|}{C}}-CH_3$ and $-\overset{|}{\underset{|}{C}}-CH_2-\overset{|}{\underset{|}{C}}-$ bonds) and dehydrates with the formation of unsaturated groups including highly reactive α,β-unsaturated aldehydes and ketones (Scheme 9 and reference 13). Condensation occurs with participation of hydroxyls, ketones, aldehydes and carbon-carbon double bond functionalities.

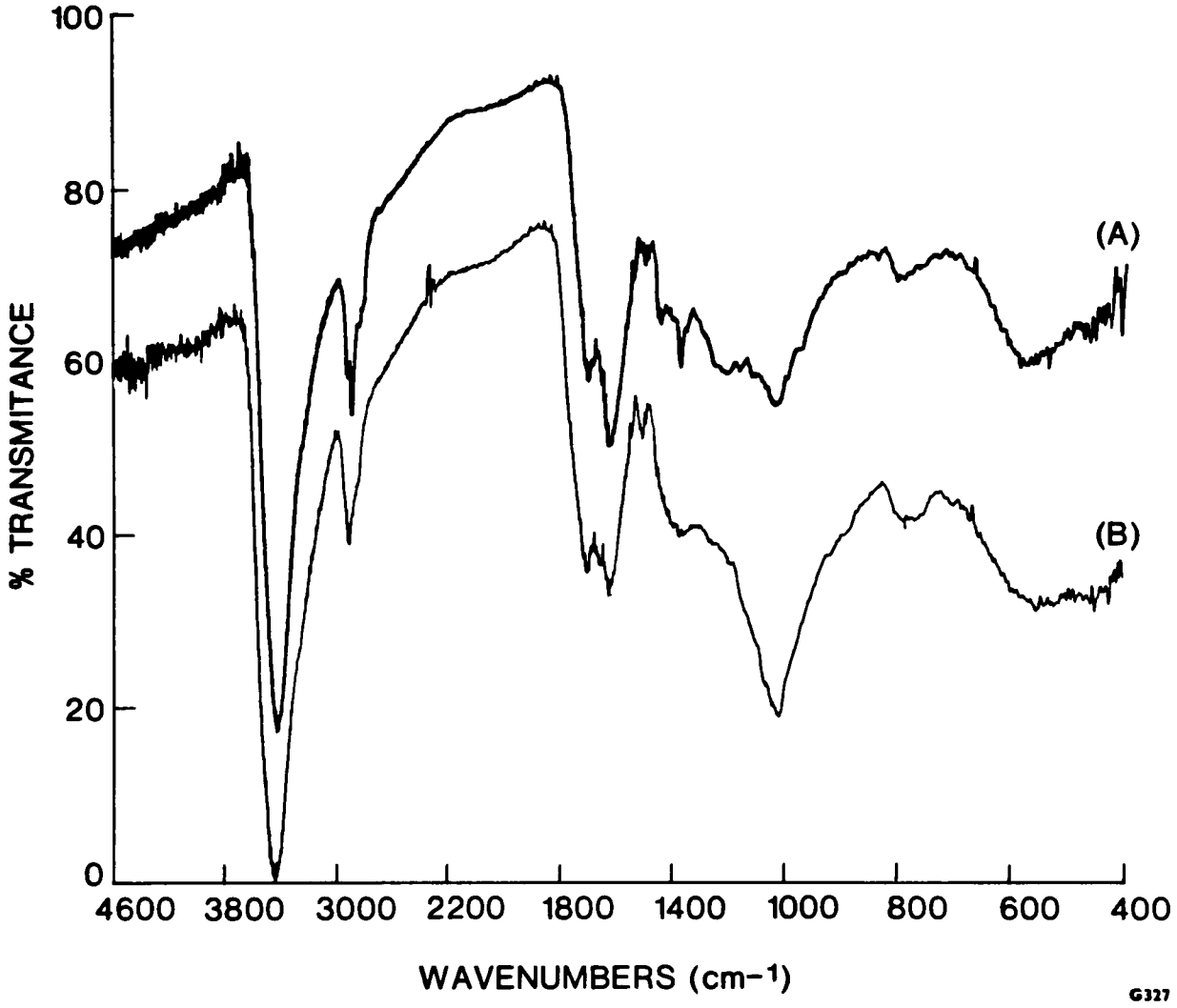
Effect of Cellulose on D-Glucose Polymerization

Insolubilization of D-glucose has been shown to occur more rapidly if it is heated in contact with cellulose fibers (Table 6). There exists a possibility that D-glucose reacts differently in the presence or absence of cellulose. To verify this point, D-glucose was coated onto cellulose and heated in a press. The resulting material was then hydrolyzed in concentrated acid. This treatment should remove hydrolyzable components of the cellulose which mask the IR and 13C-NMR spectra of the heated (crosslinked) D-glucose polymer. Figure 35 compares the IR spectrum of the insoluble non-hydrolyzable material to the spectrum of post heated fraction 2. The similarity between the IR spectra suggests that the same type of polymer or functional groups are being formed whether cellulose is present or not.

Figure 36 compares the solid state 13C-NMR spectra of the cellulose reference (A), glucose heated on cellulose followed by 3 hours water extraction (B), non-hydrolyzable glucose heated on cellulose (C) and post heated fraction 2 (D). The spectrum of D-glucose heated on cellulose followed by water extraction, shows the presence of a small peak at 152 ppm which indicates the formation of a carbon-carbon double bond. When the hydrolyzable material was removed, a spectrum similar to

Figure 35

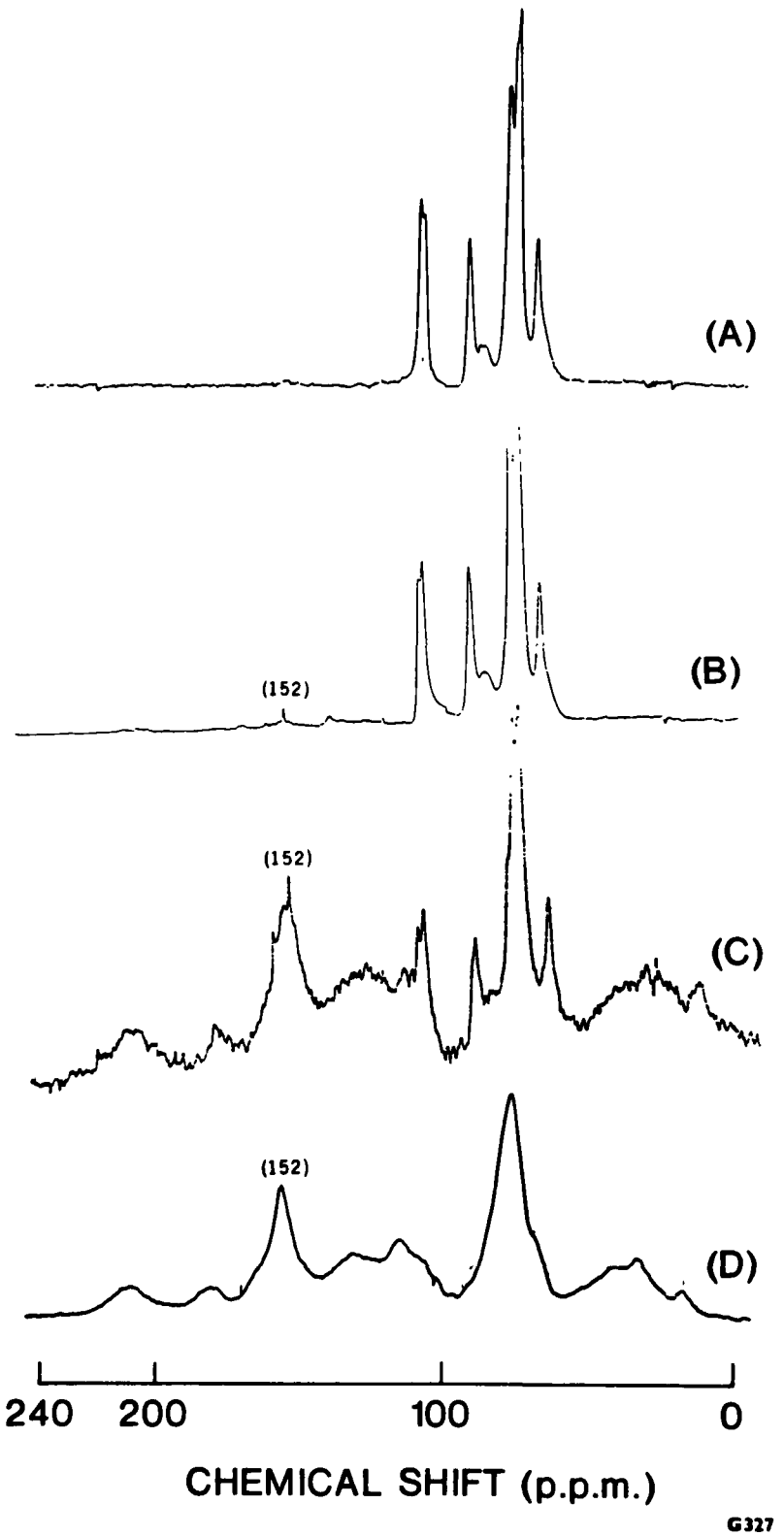
Comparison between infrared spectra of non-hydrolyzable heated glucose on cellulose (A) and post-heated glucose fraction 2 (B) [1]



[1] Fraction 2 post-heated 30 minutes at 230°C between Teflon sheets placed in the middle of 11.1 mm thick particleboard mat.

Figure 36

Comparison between solid state ^{13}C-NMR of heat-treated cellulose (A), extracted heated glucose on cellulose (B), non-hydrolyzable glucose on cellulose (C) and post-heated Fraction 2 (D) [1]



1 The sample was post-heated in a press 30 minutes at 230°C between Teflon sheets placed in the middle of 11.1-mm thick particleboard mat.

post heated fraction 2 was obtained (compare spectra C and D from Figure 36). This confirms the previous conclusion deduced from the IR spectra (Figure 35). Spectrum C from Figure 36 shows absorption peaks for non-hydrolyzed cellulose. This may be an indication that cellulose is simply more difficult to hydrolyze when heat treated with D-glucose. It might also be interpreted as evidence for the thermal condensation of D-glucose with cellulose.

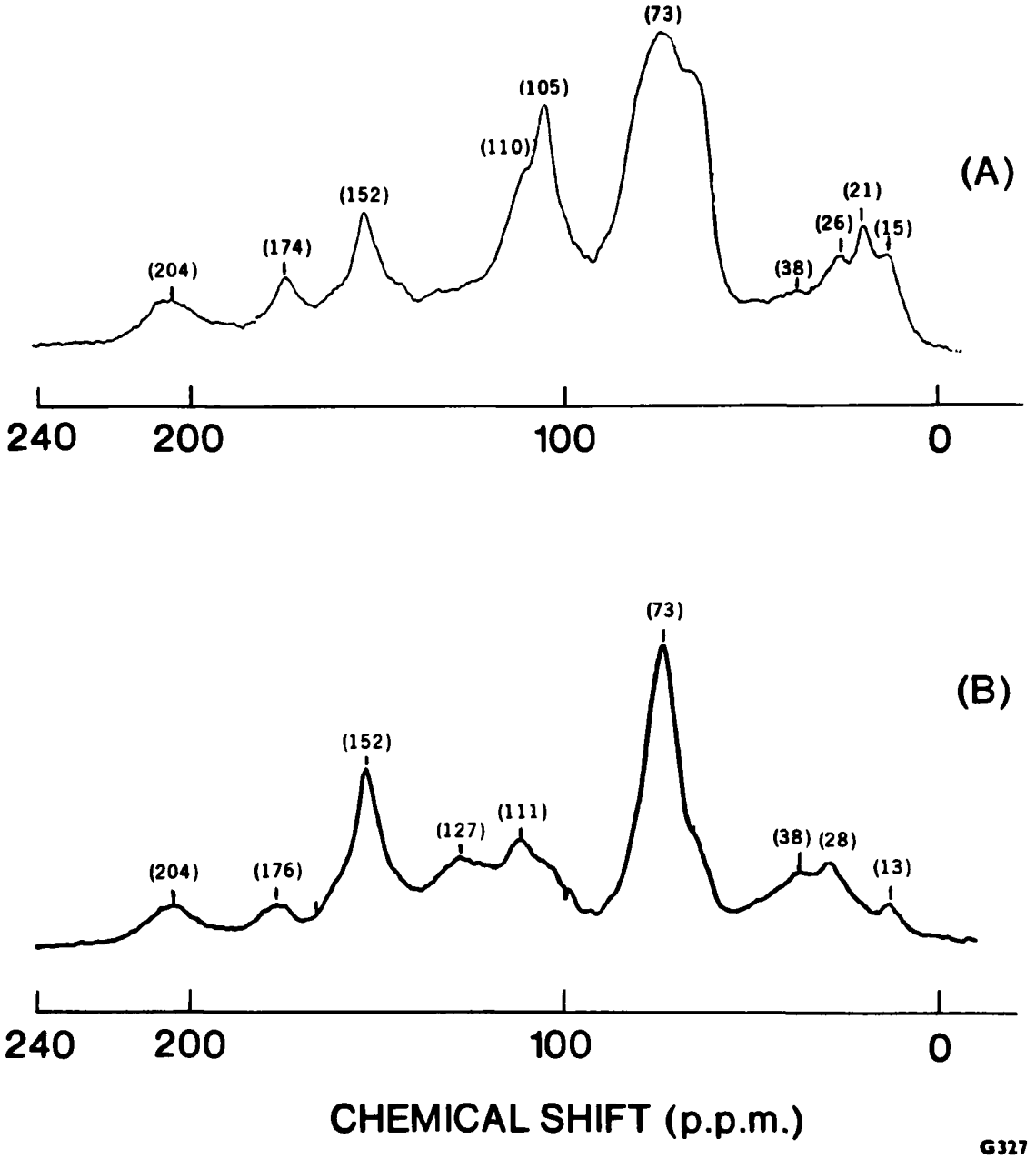
Thermal Polymerization of DL-Glyceraldehyde

Heyns and Klier (170) have reported that glyceraldehyde decomposes in a manner which is different to that of higher molecular weight sugars when subjected to similar heat treatments. HPLC chromatograms of water soluble polymers of D-glucose and DL-glyceraldehyde obtained by thermal polymerization in a pressure vessel were found to be different (Figure 9 and 17). However the IR specta of D-glucose and DL-glyceraldehyde polymers obtained by thermal polymerization for 10 minutes between Teflon sheets in a press at 200 C and 13.8 MPa were very similar (13). Both D-glucose and DL-glyceraldehyde monomers produced a boil-proof bond (13). These experimental observations appear to be contradictory.

A sample of DL-glyceraldehyde was placed between Teflon sheets in the middle of a 11.1-mm particleboard mat and heated 40 minutes at 230°C and 6.9 MPa. Figure 37 shows the solid state 13C-NMR spectrum of the polymerized DL-glyceraldehyde. The spectrum of post-heated fraction 2 was added for direct comparison. The similarity between the two spectra indicates that both polymers contain similar functionalities. This is particularly obvious for the absorption peaks at 204, 174, 152

Figure 37

Comparison between ^{13}C-NMR of heat-treated DL-glyceraldehyde (A) and post-heated Fraction 2 (B) [1]



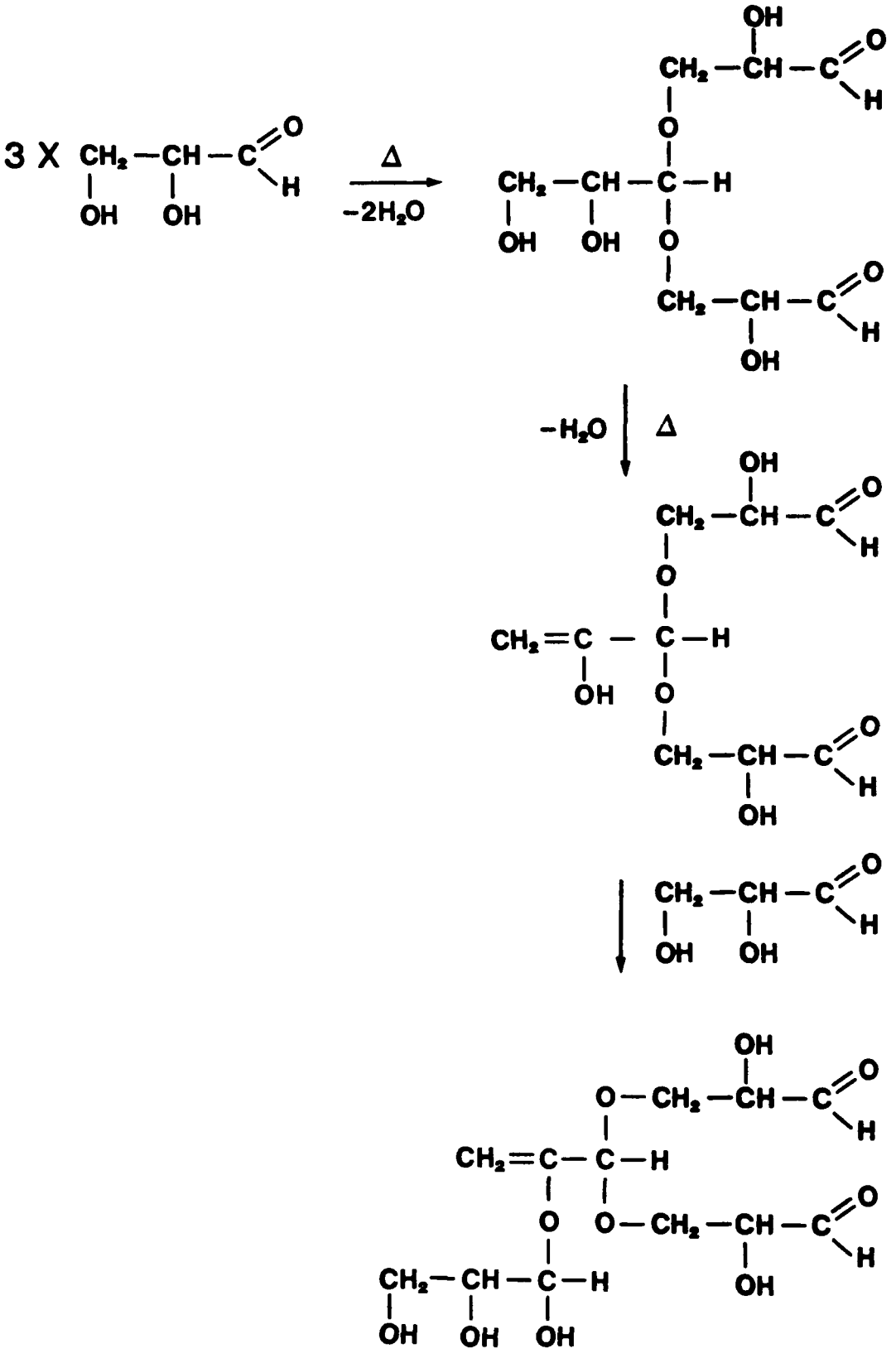
[1] Both samples were heated in a press 40 minutes at 230°C and 6.9 MPa between Teflon sheets, in the middle of 11.1-mm thick particleboards.

and 73 ppm. These are consistent with the interconversion - dehydration products of glyceraldehyde presented in Scheme 3 and Table 5. Again, the absorption at 175 and 204 ppm could indicate the presence of a carboxylic carbon from ketone or aldehyde, peak at 152 the presence of conjugated carbon-carbon double bond such as the enolic form of pyruvaldehyde (methyl glyoxal) shown in Scheme 3 and Table 5. The absorption at 73 ppm would indicate the presence of an oxygen bearing carbon. The methyl group from pyruvaldehyde would be expected to absorb in the higher field of the spectrum along with $-\overset{|}{\underset{|}{C}}-CH_2-\overset{|}{\underset{|}{C}}-$ bonds from carbon-carbon double bond condensation (15-38 ppm).

Although DL-glyceraldehyde, unlike D-glucose, cannot form a monomeric cyclic furanose or pyranose isomer (171), different molecules can condense through formation of acetal linkages. The absorption at 105-110 ppm could indicate the presence of an acetal carbon due to the self-condensation of DL-glyceraldehyde molecules. Non-conjugated double bonds also absorb in this area of the spectrum. These could originate from the dehydration of the self-condensation products of glyceraldehyde as illustrated in the simplified model of Scheme 10. Both HMF and post heated fraction 2 show a definite absorption centered at 127 ppm (Figure 34). This adsorption does not seem to be present in the ^{13}C-NMR spectrum of the DL-glyceraldehyde polymer (Figure 37). This may be an indication that DL-glyceraldehyde polymerizes primarily into an acylic type of polymer while the D-glucose crosslinked thermal polymer contains more pyran and furan rings similarly to cellulose pyrolytic condensation products (Scheme 2 and 9). The fact that high MW thermal polymers of DL-glyceraldehyde and D-glucose decompose in a different manner, as observed by Heyns and Klier (170), is most likely related to the higher proportion

Scheme 10

Dehydration of self condensation products of DL-glyceraldehyde



of pyranoid and furanoid rings in the high MW D-glucose thermal polymer (Scheme 9).

In a press, DL-glyceraldehyde is subjected to a temperature gradient. By analogy to D-glucose, the condensation of DL-glyceraldehyde under conditions similar to particleboard production may occur as follows: DL-glyceraldehyde first melts and isomerizes into 1,3-dihydroxy-2-propanone via an ene-diol intermediate or a 1,2-hydride-shift mechanism (128-130). Condensation between hydroxyl and carbonyl groups of the different molecules present in the melt occurs with the formation of hemiacetal and acetal bonds. The HPLC chromatograms of these low molecular weight DL-glyceraldehyde oligomers are shown in Figure 17. A second step is required for the formation of a 'boil proof' bond. Upon further heating, partial decomposition and dehydration of the polymer occurs with the formation of conjugated (Scheme 3) and non-conjugated (Scheme 10) carbon-carbon double bonds and carbonyl functionalities. Condensation into an insoluble, infusible mass then occurs via participation of carbon-carbon double bonds, carbonyl and hydroxyl functionalities. Hydroxyls can form ether bonds by electrophilic addition to double bonds. The addition of alcohol to a double bond is catalyzed by acids (scheme 6) or bases and follows Markovnikov's Rule (172). In this study, heating of carbohydrates resulted in a slight decrease in pH.

Thermal polymerization of carbohydrate thus result in a highly crosslinked polymer with water resistant carbon-carbon and carbon-oxygen-carbon bonds. High temperatures and long press cycle are however required to achieve curing.

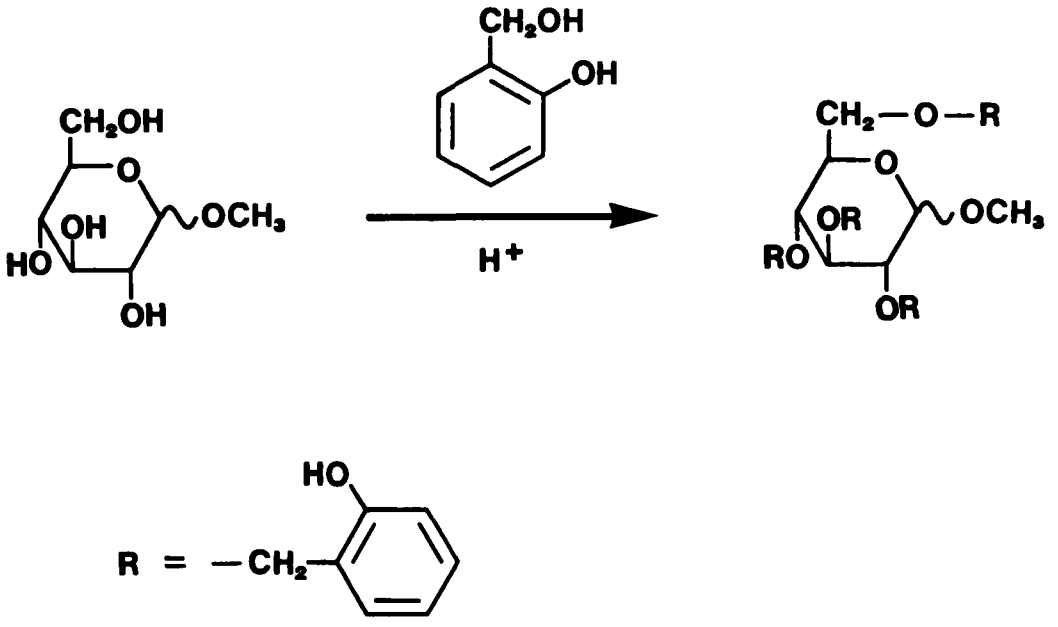
PART II. COPOLYMERIZATION OF GLUCOSE FRACTIONS WITH PHENOL-FORMALDEHYDE RESINS

In the first part of this study, D-glucose heated in a pressure vessel was separated into 11 fractions which were collected by preparative chromatography (Figure 14). Miniature particleboards were prepared from each of these fractions and their adhesive properties were evaluated by the measurement of adhesive strength through a mechanical torsion shear (TS) test (Table 4). D-glucose, the starting material (fraction 7) was found to be more reactive than its polymers (fraction 1 to 6) or dehydration products (fraction 8 to 11). These results were obtained without copolymerization with a phenol-formaldehyde resin. In the presence of a PF copolymer different results are to be expected.

The possibility of incorporating carbohydrate into phenolic resins has been confirmed recently by Conners (33). Using model compounds, it was demonstrated that phenol-formaldehyde could condense with non-reducing carbohydrate hydroxyls with the formation of ether bonds as illustrated in Scheme 11. This reaction would be responsible in part for the compatibility of carbohydrates with phenol-formaldehyde resin. Alternatively, as indicated in Scheme 12, 2-furaldehyde (furfural) - a carbohydrate dehydration product - could also condense with phenol-formaldehyde resin in various ways. The possibility of using phenol-formaldehyde-furfural resin as a binder for foundry sand molds and friction materials is well known (173, 174, 175). The utilization of phenol-formaldehyde-furfural resin for the manufacture of wood composites has also been proposed in the past (176). From this background the relative reactivity of the carbohydrate polymers or dehydration products in the presence of a PF copolymers, is difficult to predict.

Scheme 11

Methylglucoside phenol-formaldehyde condensation



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Scheme 12

Possible condensation of 2-furaldehyde with phenol-formaldehyde model

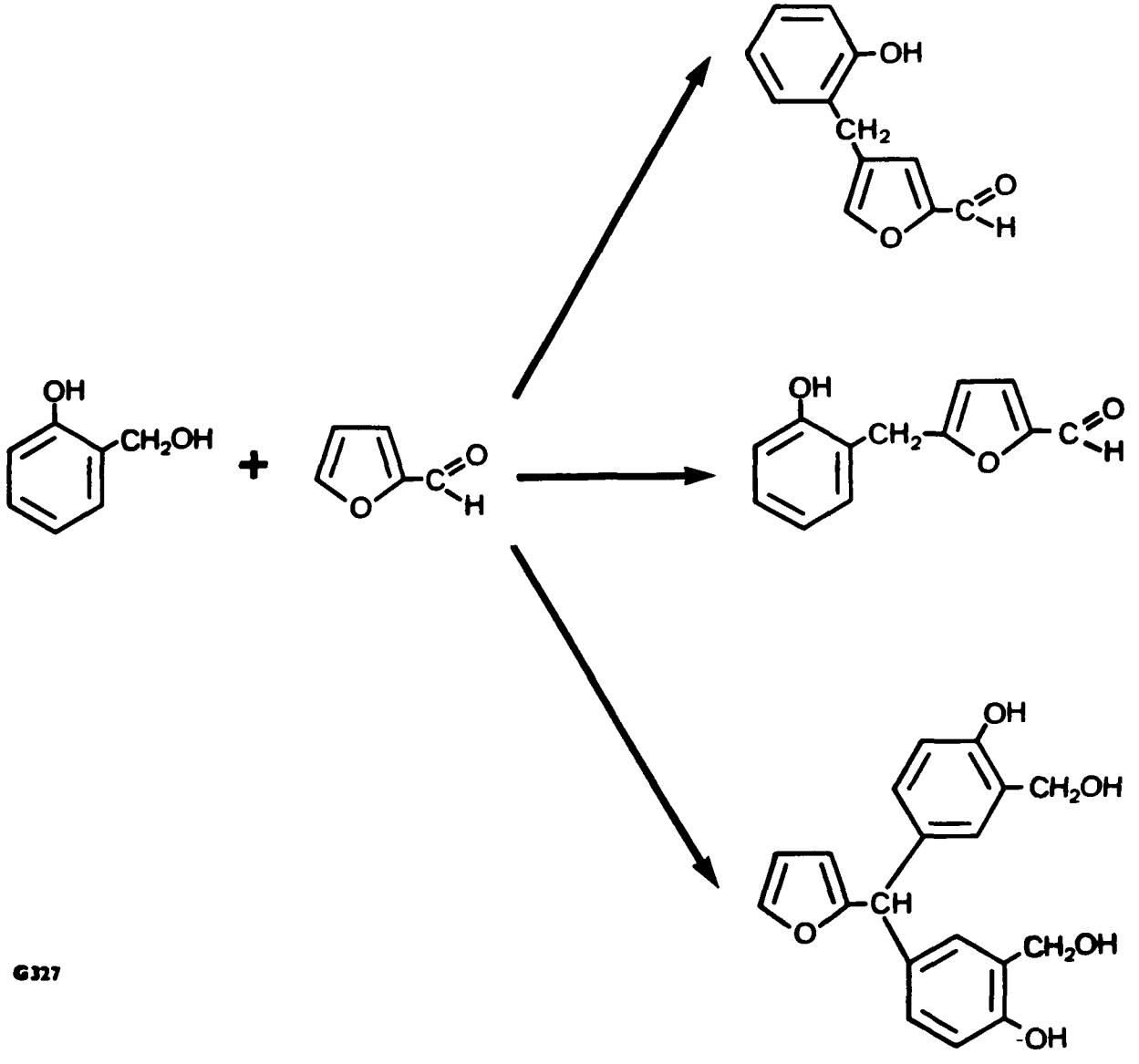


Table 9 summarizes the TS test results obtained when particleboards were bonded with the representative heated fractions 1, 4, 7, 10 and 11 (from the first part of the study; see Table 4 and Figure 14) in the presence of a commercial PF copolymer (W31-54E). The two adhesives were incompatible, in that carbohydrates decompose or fragment when heated under alkaline conditions (143, 144, 146, 147) while the liquid PF resin precipitated out under acidic conditions. To avoid this problem, the acid which is required to neutralize the alkaline PF copolymer was added onto the wood separately.

Particleboards were bonded by heating in a press for 5 minutes at 210°C instead of the 15-30 minutes at 230°C used previously when carbohydrates were used alone as binders. Under these conditions, 2-furaldehyde (fraction 11) clearly produced a better bond as indicated by a wet TS test result of 4.0 N.m compared to 2.6 to 2.7 N.m for the other fractions (Table 9).

The Reactivity of NH_4SSL with Addition of 2-Furaldehyde

2-Furaldehyde is more expensive than PF while SSL is available at a fraction of PF cost. Heating SSL in the presence of an acid in order to transform the carbohydrate portion into furfural derivatives and then using the resulting product as a PF extender for wood bonding has been proposed (177). Fractionated high molecular weight NH_4SSL with a low carbohydrate content (9% reducing sugars) was mixed with 2-furaldehyde and phenol-formaldehyde resin in a 0.5:0.5:1.0 weight ratio. Miniature particleboards were produced with this resin and with unfractionated NH_4SSL (26% reducing sugar content) mixed with phenol-formaldehyde in a 1:1 ratio.

Table 9

Adhesive properties of heated glucose fractions (HPLC) copolymerized with 50% phenolic resin by weight

Fraction No.	HPLC Retention Time (Min.)	Osmometry ($\bar{M}_n$)	210°C - 5 Min. TS (N.m)
1	12	1,170	2.6
4	19	520	2.7
7	28	190	2.6
10 (HMF)	62	-	2.6
11 (2-Furaldehyde)	78	-	4.0
Ref. PF (100%)	-	-	4.2

The wet TS test results for panels prepared with the NH_4SSL-PF and NH_4SSL-furfural-PF resins are summarized in Figure 38 as well as for panels prepared for the furfural-PF resins at different weight ratios. These preliminary data indicate no significant advantage from replacing the carbohydrate in NH_4SSL with 2-furaldehyde.

TS test results for particleboards bonded with NH_4SSL-PF resin (3.0 - 3.2 N.m) were slightly better than those for panels bonded with the heated D-glucose fractions 1, 4 or 7 (Table 9) blended with PF (2.6-2.7 N.m). These results suggest that factors other than the carbohydrate component, such as lignosulfonate content of NH_4SSL, may contribute to the adhesive properties of NH_4SSL-PF resin.

During studies with NH_4SSL-PF resins, it was discovered that it was not necessary to add the required acid to the wood particles prior to blending with the resin (178). Acidic NH_4SSL could be blended with alkaline PF to provide a fine dispersion, the pH of which could then be adjusted and the dispersion sprayed directly on wood. This new approach avoided any acid corrosion problems and enhances any industrial applications.

NH_4SSL/Phenol-Formaldehyde Adhesive Properties as Affected By:

Lignin - Carbohydrate Ratio

NH_4SSL was fractionated by ultrafiltration to prepare samples with increasing proportions of lignin. These were blended with 50 percent PF-resin and employed for the manufacture of particleboards. As shown in Table 10, the low molecular weight NH_4SSL fractions containing a higher proportion of carbohydrate (45% reducing sugars) produced stronger panels than the starting material (27% reducing sugars) or the more

Figure 38

Effect of phenolic resin replacement with
2-furaldehyde on wet TS strength of particleboard

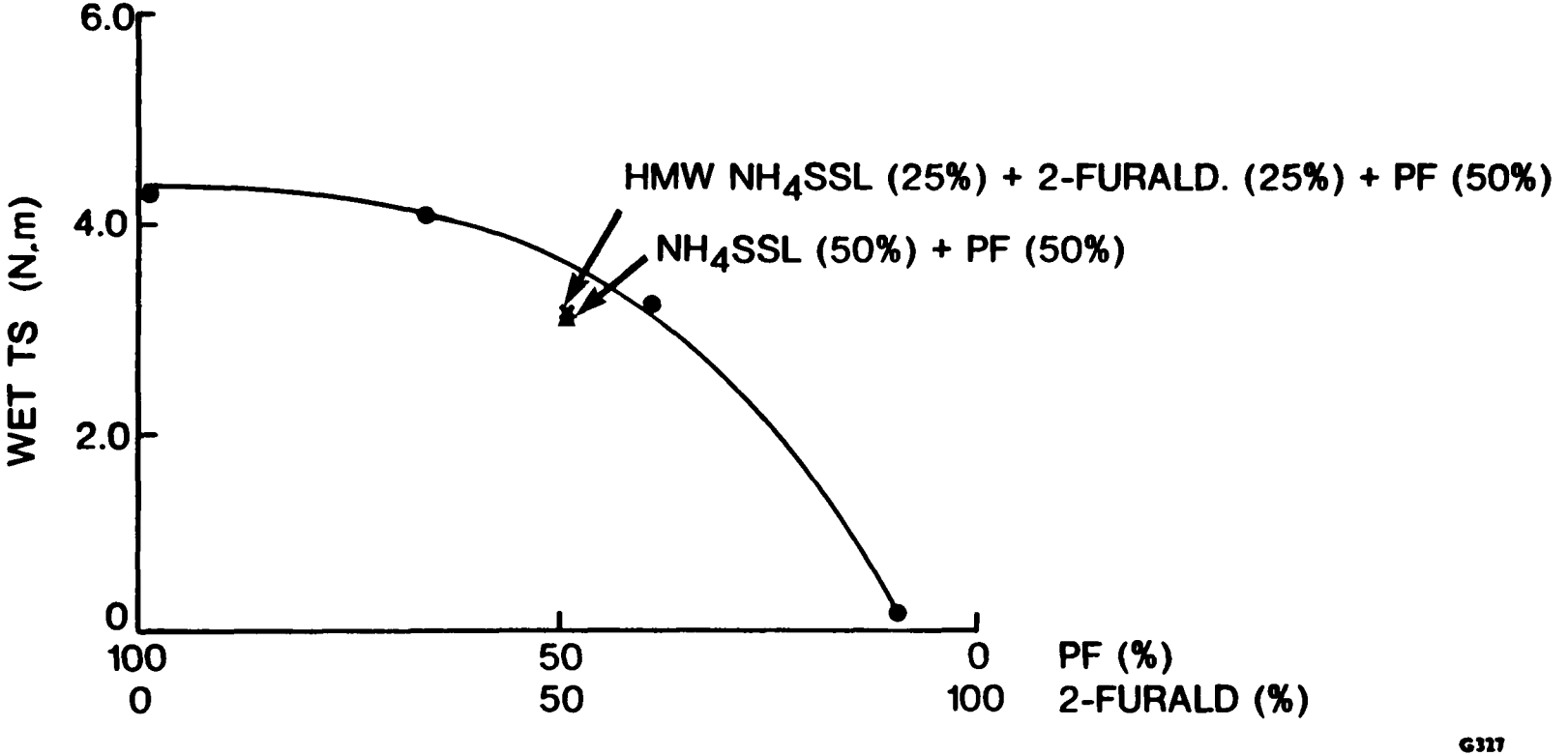


Table 10

Effect of lignin reducing sugars content and lignin molecular weight on adhesive properties of copolymerized ammonium SSL resin [1]

NH_4SSL Fractions (MW)	Lignin (UV) (%)	Reducing Sugars(%)	210°C - 5 Min. TS (N.m)
0-5000 YM-5[2]	26	45	3.8
Unfractionated	60	27	3.6
>5,000 YM-5	76	20	2.9
>5,000[3] YM-5	83	14	2.2
>100,000[4] XMA-100	86	12	2.7
Reference D-Glucose	0	100	1.9

1 Resin: NH_4SSL (50%) - PF (50%).

2 YM-5 and XMA-100 are the manufacturers names for ultrafiltration - membranes with nominal molecular weight cut-off of 5,000 and 100,000 respectively.

3,4 Retentate after 2 washings with water.

highly purified lignosulfonate (12-14% reducing sugars). Similar to previous results using only NH_4SSL without PF (12,13), both lignin and carbohydrates are believed to contribute, since panels made with glucose-PF resin resulted in lower TS values. The use of high molecular weight NH_4SSL (MW above 100,000) did not improve board properties, a result which is somewhat surprising since it has been claimed that higher molecular weight SSL has a higher reactivity (179, 180).

SSL Cooking Base

When heated in a press, together with lignocellulosic materials at temperatures above 170°C, crude or low molecular weight NH_4SSL decomposes into lignosulfonic acid and ammonia gas, whereafter the lignosulfonic acid condenses and polymerizes providing the adhesion necessary for an exterior grade wood composite product (5). Unlike NH_4SSL, calcium SSL (CaSSL) and sodium SSL (NaSSL) do not decompose at the temperatures which are normally used for the manufacture of wood composites and do not produce an exterior type bond (4, 5). Results comparing NH_4SSL with SSL of other cooking bases used in combination with a PF co-reactant under acidic conditions are summarized in Table 11. Similar dry strengths were obtained with NaSSL-PF, CaSSL-PF, and NH_4SSL-PF, but only the ammonium-based resin system produced panels with acceptable wet strengths under these experimental conditions. For example, when pressed under identical conditions, panels bonded with NaSSL-PF disintegrated in boiling water while those bonded with CaSSL-PF had a low TS of 0.3 N.m compared to a TS value of 3.6 for the resin prepared from NH_4SSL. The higher reactivity of NH_4SSL is related to the ammonium lignosulfonate functionality since a particleboard panel with

Table 11

Effect of SSL cooking base on PF (30%) - SSL (70%) adhesive properties

Resins[1]	210°C - 5 Min. TS (N.m)
NH_4SSL - PF	3.6
NaSSL - PF	0
CaSSL - PF	0.3
NH_3 + HSSL[2] + PF	3.2

1 SSL-PF resin dispersion adjusted to pH 5.0.

2 CaSSL de-ionized by ion-exchange, then neutralized with ammonia.

3.2 N.m wet TS strength was obtained when CaSSL was transformed into NH_4SSL. Lignin may condense with methylolated phenol through electrophilic condensation at the aromatic ring as indicated in Scheme 13. Allan (181) and later Mathur (182) have demonstrated that NH_4SSL could condense directly with phenol at temperatures of 150°C and higher. Mathur's data suggest that phenol condensation occurs mainly at the alpha carbon position of the ammonium lignosulfonate phenyl propane unit as shown in Scheme 13. Interestingly, the same data show that NH_4SSL is far more reactive towards phenol condensation than magnesium SSL and that this type of reaction is acid catalyzed.

pH of Resin

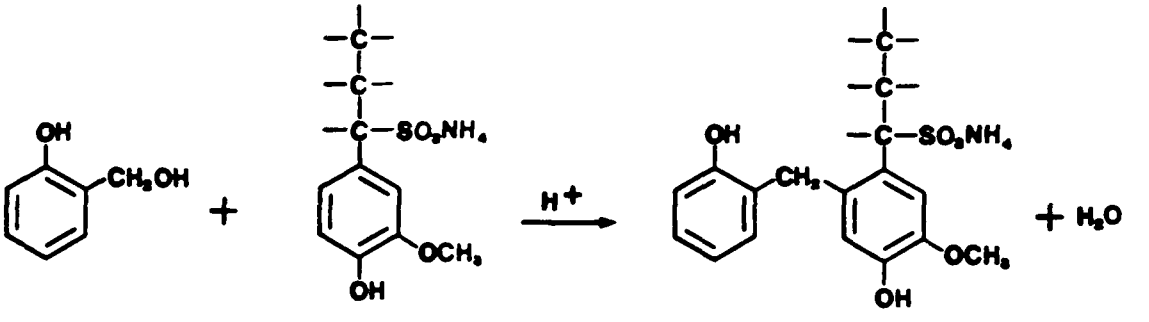
The effect of the pH of the NH_4SSL-PF resin dispersion on curing properties is illustrated in Table 12. The results clearly indicate a trend towards increasing TS strength with decreasing pH. For example, at pH 11, the wet TS strength was 1.9 N.m as compared to 3.6 N.m at pH 3.0. The acid probably catalyzes the condensation of phenol with formaldehyde and the condensation of PF with the lignin and the carbohydrate constituents of NH_4SSL.

Under strongly acidic (below pH 4.0) conditions the methylol groups of the phenol-formaldehyde resin are very unstable, producing carbonium ions (173). These could then react with the phenolic, carbohydrate or lignin constituents of the resin. The good result at pH 6 with NH_4SSL-PF resin is however more surprising since the PF resole component of the resin is generally believed to be less reactive between pH 4-6 (173, 183).

Scheme 13

Representative reactions that can occur between ammonium lignosulfonate and phenolics

METHYLOL-LIGNIN CONDENSATION



PHENOL-LIGNIN CONDENSATION

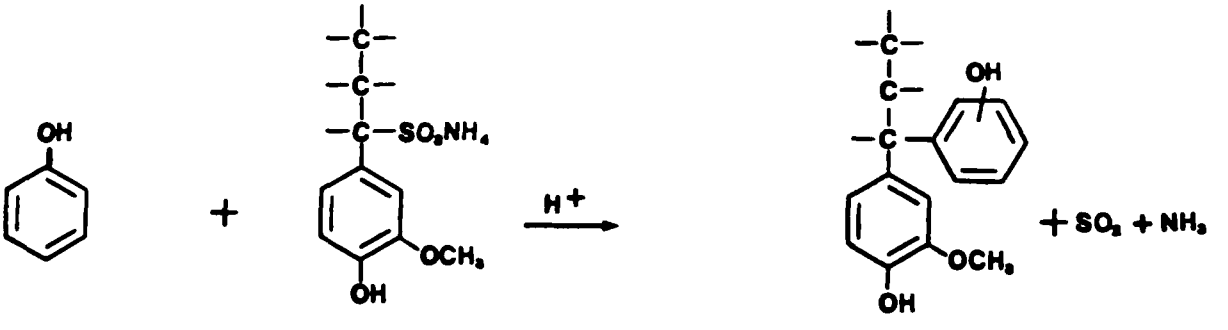


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Table 12

Effect of acid catalyst on adhesive properties of NH_4SSL-PF resin

NH_4SSL (50%)-PF (50%) pH	210°C - 5 Min. TS (N.m)
11.0	1.9
8.0	2.9
6.0	3.4
3.0	3.6

Various attempts have been made in the past to crosslink NH_4SSL with PF in order to produce a wood adhesive. These include Herschler's report on the use of an acid-tolerant resin (184) as well as other interesting approaches (185, 186) to avoid precipitation problems. More recently, in 1978, Allan (181) developed a process for making a phenol-formaldehyde resin in which a portion of the phenolic ingredients were replaced with a phenol-ammonium lignosulfonate, high temperature, condensation product.

The NH_4SSL-PF resin dispersion developed herein is produced in a simple one-step operation without filtration, added alkali, high temperature and pressure equipment. In contrast to the work of Roffael and Rauch or Wiegand and Cadopte (185, 186) this adhesive system was found to be more reactive under acidic (pH 3-7) than under alkaline conditions.

Comparisons Between Experimental and Commercial Resins

Table 13 compares the adhesive properties of NH_4SSL-PF at different SSL to PF ratios (30:70, 50:50 and 70:30) with commercial face and core PF resins presently used for manufacturing waferboard in Canada. The industry makes a three-layer panel with a faster curing adhesive in the centre layer which is further away from the heating source. A slower curing resin is used for the face layers to avoid 'pre-curing' of the resin before the full pressure is applied. The results summarized in Table 13 indicates that the test formulation containing 30 percent NH_4SSL yielded panels at both 3 and 5 minute press cycles, equivalent to the commercial face phenolic resin in terms of bond strength and speed of cure. Increasing the proportion of NH_4SSL resulted in inferior

Table 13

Comparison between TS test results for commercial and experimental resins

Resin Type	210°C	
	3 Min. TS (N.m)	5 Min. TS (N.m)
NH_4SSl (30%) + PF (70%)	1.7	3.5
NH_4SSL (50%) + PF (50%)	0.6	4.0
NH_4SSL (70%) + PF (30%)	0	1.3
Commercial Face PF	1.3	3.8
Commercial Core PF	4.1	5.0

mechanical properties albeit at a 5-minute press cycle, the 50:50 formulation and the commercial face PF resin gave similar TS data. At three minutes press cycle resin undercuring was however apparent. Torsion shear, after a boiling water treatment, relates to the mechanical strength properties at the centre layer of the panel, where undercuring generally occurs. As a follow-up to this work, the NH_4SSL-PF resin dispersion was tested successfully for the production of laboratory waferboards (187).

CONCLUSIONS

The principal initial reaction occurring during heating of D-glucose in a pressure vessel under conditions similar to those used in the formulation of wood composites is the polycondensation of glucose molecules through glucosidic linkages. The reaction can be catalyzed by acid or small quantities of ammonium lignosulfonate. Reduced pressure favours the formation of high-molecular-weight material. 1,6-anhydro-D-glucose, HMF and 2-furaldehyde are minor reaction products. The thermal stability or resistance to hydrolysis of the polyglucose polymer is influenced by the molecular weight of the carbohydrate polymer and the presence of α and β linkages. Dissacharides are formed first, followed by trisaccharides, higher oligosaccharides and, finally, insoluble products. Upon further heating and pressure treatment, dehydration and partial decomposition of the polymer occurs with the formation of C=C, C=O, $-\overset{|}{C}-CH_2-\overset{|}{C}-$, $-\overset{|}{C}-CH_3$ groups including highly reactive α, β-unsaturated aldehyde. These may readily polymerize to the infusible stage with participation of unsaturated, carbonyl and hydroxyl functionalities. Similar chemical reactions occur regardless of whether wood is present or not. D-Glucose reaches the insoluble stage at a faster rate, under heat and pressure treatments, when spread as a thin layer on wood or cellulose. There is also indirect evidence for the formation of a chemical bond between D-glucose and cellulose.

DL-Glyceraldehyde may also polymerize with formation of acetal linkages followed by dehydration and presumably partial decomposition of the polymer with formation of C=C, C=O, $-\overset{|}{C}-CH_2-\overset{|}{C}-$ and $-\overset{|}{C}-CH_3$ groups including α, β-unsaturated aldehyde, similarly to D-glucose. In

contrast to DL-glyceraldehyde, high molecular weight D-glucose polymers would contain more pyranoid and furanoid rings.

In the presence of alkali, D-glucose is isomerized first to D-fructose. The alkali strongly catalyzes dehydration and decomposition of D-fructose into water-insoluble materials including condensed 5-(hydroxymethyl)-2-furaldehyde. HMF formation would occur through the expected 3,4-dideoxy-D-glycero-hex-3-ene-osulose and 3-deoxy-D-erythro-hexosulose intermediates.

When used alone as an adhesive, without addition of catalyst or copolymer, D-glucose was more reactive than its polymers or degradation products, identified as resulting from heat-pressure treatment. The heated D-glucose oligomers, 1,6-anhydro-D-glucose, HMF and 2-furaldehyde had no special adhesive properties under the experimental conditions studied.

The addition of a phenol-formaldehyde resin copolymer reduced significantly the curing requirements of both carbohydrate and ammonium spent sulfite liquor. In the presence of PF copolymers, 2-furaldehyde was clearly more reactive than any of the other carbohydrate dehydration and polymerization products tested. NH_4SSL had a reactivity intermediate between D-glucose and 2-furaldehyde.

A new adhesive resin dispersion was developed by simply blending together ammonium spent sulfite liquor, an alkaline phenolic resin and, in some cases, an acid catalyst. The curing properties of the NH_4SSL-PF resin dispersion are dependent on the lignin and carbohydrate contents of NH_4SSL, the amount of PF resin incorporated into the formulation, and the resin pH. This study indicates that an economical NH_4SSL-PF resin containing up to 50 percent NH_4SSL show good potential

for replacing some of the phenolic resin adhesive used for the manufacture of wood composites such as waferboards.

EXPERIMENTAL

METHOD OF ANALYSIS

1. Solids contents were determined by Tappi Standard Method T 629 wd-80(188) with results expressed on a weight basis.

2. pH values were determined in water at 40% concentration of adhesive solids.

3. Lignin was determined in aqueous solutions based on absorbance at 280 nm, using a Pye Unicam UV spectrophotometer model SPG-400. A calibration curve was prepared using a pure sample of spruce lignosulfonate (Identified as RAS II in reference 189) supplied by Dr. W.Q. Yean from the Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill Univeristy, Montreal, Quebec.

4. Reducing sugars were determined by the Swedish Method CCA-11 as suggested by Yorston (190, 191).

5. Monosaccharide analyses of NH_4SSL were supplied by Tembec Inc., Temiscaming, Quebec.

6. Polymerized carbohydrates were hydrolyzed according to Tappi Standard Method T222 os-74 (192). This method is generally used for the determination of lignin in wood and pulp.

Carbohydrate samples were dissolved for 2 hours in 72% H_2SO_4, and the solutions were then boiled under reflux for 3 hours in 12% H_2SO_4. Where indicated in the text, hydrolyses of polymerized carbohydrates were carried out in 1N HCl at 100°C for 16 hours (118).

7. Molecular weights were determined in a Wescor Vapor Pressure Osmometer Model 5100C.

8. Ash contents were determined on cellulose (bulk cotton linter pulp, Buckeye Cellulose Corp., Memphis, Tenn.) ignited in a crucible at 800°C for 16 hours.

9. Infrared spectra were recorded with a Nicolet 5 DXB FT-IR spectrometer.

10. Liquid and solid state ^{13}C-NMR spectra were recorded at 75:43 MHz using a Varian XL-300 spectrometer. For the liquid state ^{13}C-NMR spectra the solvent was acetone-water in a 50:50 volume ratio. A CP-MAS probe from Doty Scientific Inc. was used for solids.

11. Fast-atom-bombardment mass-spectrometry was performed with a VG 7070E mass spectrometer. The spectra were obtained from carbohydrate samples dissolved in glycerol with and without addition of NaCl.

12. Gas chromatography-mass spectrometry (GC-MS) was performed using a Hewlett Packard (HP) 5890A gas chromatograph with HP-1 high performance capillary columns (12 m x 0.2 mm x 0.33 m). The injector port was at 250°C, the detector 280°C and the column temperature was programmed to increased from 70°C to 230°C at a rate of 10°C per minute, using helium carrier gas at 0.8 ml/min. The GC was coupled with a HP 5970B mass selective detector with a 70eV electron impact source.

13. Analytical HPLC used a Waters high performance liquid chromatograph with an integrated data module system, auto-injector, M45 solvent delivery module, column compartment and 401 RI detector. Two pre-packed columns from Bio-Rad Laboratories (Richmond, CA, U.S.A.) were used in series in the following order: (A) Aminex HPX-87P (lead) and (2) Aminex HPX-42A (silver). Water was the eluant and the columns were maintained at 85 C. Samples were dissolved by stirring them in water for 1 hour at 55°C. Prior to HPLC analysis, acidic material was neutralized with 0.1 N NaOH and the salt removed with a mixed ion exchange resin bed: Amberlite IRC-50(H) and Amberlite R-45(OH).

SOURCE OF ADHESIVE

Three softwood sulfite lignins (SSL) (50% solids) were obtained for the study: ammonium-based SSL from the Temfibre dissolving pulp production facilities in Temiscaming, Quebec, Canada; calcium-based SSL derived from bisulfite pulping, from Lignosol, Quebec City, Quebec, Canada; and sodium-based SSL derived from dissolving pulp, provided by ITT Rayonier, New York, NY, U.S.A.

Calcium SSL was transformed into its ammonium salt by elution through an ion-exchange resin (Rexin 101-H from Fisher) and adjusted to pH 2.0 with concentrated ammonium hydroxide.

Water-insoluble lignin was prepared at Forintek from hydrolysed hardwood by extraction with alkali. This lignin was further washed with water for 3 hours in a Soxhlet extractor.

Carbohydrates and derivatives were obtained from various chemical suppliers. A liquid phenol-formaldehyde resin (W31-54E), 48% solids content was provided by Borden Chemical Company (Canada) Limited. For control purposes, two commercial phenolic powders were collected directly from the production line of a waferboard mill.

ADHESIVE FORMULATION

Liquid formulations were used except for the study described in Table 13 (p. 116) where commercial PF powders and freeze-dried NH_4SSL-PF powder were employed. The adhesive was dissolved in water or methanol at 40% solids content and the desired quantity of catalyst or PF copolymer (calculated on the binder weight) was added to the solution with stirring.

NH_4SSL-PF dispersions were prepared at 30, 50 and 70% phenolic solids replacement, by simple addition of dilute acid and NH_4SSL liquid to the binary phenolic resin kept under vigorous stirring (178). At 50% phenolic replacement, a typical NH_4SSL-PF resin dispersion at pH 5.0 and 40 percent solids had a Brookfield viscosity of 140 centipoise. The pH of the resin was adjusted to the desired value by the addition of hydrochloric acid or sodium hydroxide.

PARTICLEBOARD PREPARATION AND TESTING

The adhesive was evaluated by production and evaluation of particleboard as follows: Poplar wood particles were obtained by hammermilling veneers. The fraction which passed through a 4.75 mm Tyler sieve but was retained on a 1.00-mm sieve was used for the study. The wood particles (15 g) were sprayed in a miniature blender with 0.9 g of adhesive (6% adhesive solid based on dry wood), diluted to 40 percent concentration in water. Where powder adhesive were used, the powder was simply added to the wood furnish before blending. The moisture content of the resin-coated particles was adjusted to 3% by hot air drying. The resin-coated particles were then hand-felted into a 35 x 35 mm paper mold and pressed in an electrically heated press to 11.1-mm stops at 175 to 230°C as desired for pre-selected periods of time. The press closing pressure was 6.9 MPa. The target density was 800 kg/m3. Two boards 35 x 35 x 11 mm, were pressed simulataneously, one containing the adhesive to be evaluated and the other a standard D-glucose or PF as a reference. Replicates of each panel were produced. The cure of the adhesive was evaluated through torsion-shear (TS) tests. TS was evaluated from 25-x 25-x 11.1-mm specimens cut from the centre of each panel. The specimens

were immersed in boiling water for 30 minutes, cooled for 30 minutes in water at 20°C and tested wet (13).

Results reported in this study all pertain to 35-x 35-mm boards except as specified in Figure 3 and 4. As shown in Figure 3 particleboard of 6 different dimensions were produced: 457 x 457 mm (two); 254 x 254 mm (four); 191 x 191 mm (ten); 96 x 96 mm (ten); 71 x 71 mm (ten); 35 x 35 mm (five). Both wet TS and wet internal bond (IB) strengths were determined. IB strength which also relate to the degree of curing of the adhesive were determined on 50-x 50-x 11.1-mm specimens (193). These were subjected to a 2-hour boiling water treatment, cooled for 30 minutes in water and dried for 16 hours in a convection oven at 65°C prior to testing.

THERMAL TREATMENTS IN PRESSURE VESSELS

The adhesive samples (20g, unless otherwise indicated in the text) were placed in a pressure vessel and flushed with dry nitrogen for 5 minutes. The samples were then pressurized to 2.8 MPa with nitrogen and the pressure vessel submerged in an oil bath maintained at desired temperatures (230°C, 240°C) for a pre-determined period of time. At the end of the treatment, the pressure vessel was cooled by immersion in cold water, and the sample was removed and stored for further analysis.

THERMAL TREATMENT IN A PRESS

The adhesive samples (1 g) were placed between two 20 x 20-cm Teflon sheets. The Teflon sheets were themselves placed in the middle of a particleboard mat and pressed at 230°C and 6.9 MPa for pre-determined periods of time.

For comparison, particleboard specimens bonded with D-glucose were prepared from wood particles previously extracted 16 hours with boiling water in a Soxhlet extractor. The wood particles, free of most water-soluble extractibles, were bonded with 6% D-glucose (based on dry weight of the wood) at 230°C for 8 or 25 minutes. From each panel, 4 mm were removed from each surface layer and the inner 3.1 mm of core material was extracted in a Soxhlet extractor for 3 hours with water. The water fraction containing the unreacted D-glucose material was then analyzed by HPLC.

FRACTIONATION BY ULTRAFILTRATION

The NH_4SSL was fractionated with an amicon TC5E thin channel ultrafiltration system fitted with a Diaflo YM-5 membrane having a nominal molecular weight cut off of 5,000. For example, 20 kg of NH_4SSL at 10% concentration was diafiltrated and washed twice with 20 kg of water through a YM-5 membrane. The permeate and samples of the retentate after each washing were transformed into powders separately by freeze-drying. Fractionation of NH_4SSL starting material was repeated using a XMA-100 membrane with nominal molecular weight cut off of 100,000.

Thermally treated D-glucose (25 minutes at 230°C and 2.8 MPa (N_2) in the pressure vessel) was fractionated by reverse phase osmosis at the Pulp and Paper Research Laboratories in Montreal, Quebec. In a typical experiment, 0.3 kg of a treated sample at a 5% concentration was hyperfiltrated and washed with 30 kg of water through a HMX 65PP membrane (500 molecular weight cut-off) fitted on a Module 20-LAB DDS RO system. The retentate, having a nominal molecular weight greater than 500 (1/5 of

total) and the permeate (4/5 of total) having a nominal molecular weight less than 500, were separately transformed into powders by freeze drying.

GRAVITY COLUMN FRACTIONATION

D-glucose (3.0 g) treated for 25 minutes at 230°C and 2.8 MPa (N_2) in a pressure vessel (see above) was fractionated by gravity column chromatography. The sugar 'caramel' at 50% solids was chromatographed on a glass column (1500- x 56-mm internal diameter) packed with 297 micron AG 50W-X4 cation (Ca^{++}) exchange resin, at room temperature. Thirty fractions were collected and analyzed by analytical HPLC. The first 10 fractions and the last 20 fractions, which represented 11 and 84% respectively, of the starting material were then combined separately and freeze-dried.

PREPARATIVE HPLC FRACTIONATION

The preparative HPLC system consisted of a Waters V6K injector, M-45 pump, 401 Refractive Index Detector, 201 Gibson collector and a large stainless steel column (2200- x 56-mm internal diameter), kindly supplied by Laval University, St-Foy, Quebec. The column was packed with 38 micron AG 50W-X4 cation (Ca^{++}) exchange resin. A 6.0 g sample of D-glucose (50% concentration), pre-treated 25 minutes at 230°C and 2.8 MPa (N_2), was injected at one time into the column, which was maintained at 85°C. The fractionation was achieved with water as a solvent at a flow of 10 ml/min. over a 7 hour period. In order to obtain enough material to evaluate the adhesive properties of each fraction collected, a total of 30 injections were made. From these a total of eleven different fractions were collected and freeze-dried.

D-GLUCOSE REACTION WITH WOOD COMPONENTS

Wood particles (0.4 g), pre-extracted 16 hours with water in a Soxhlet extractor, were coated with 0.2 g of D-glucose dissolved in 0.8 g of water. The coated sample was oven-dried at 65°C and heat-treated in a pressure vessel at 230°C for 20 minutes under 2.8 MPa (N_2). The treated sample was then extracted with water for 3 hours in a Soxhlet extractor. The water-soluble fraction containing D-glucose and/or derivatives which were not bonded to the wood was then analyzed by HPLC. D-Glucose and pre-extracted wood particles without D-glucose were also treated for 20 minutes in the pressure vessel, extracted with boiling water, and analyzed by HPLC. This experiment was repeated using water-insoluble lignin (lignin extracted from hydrolyzed wood) and purified cellulose (cotton linter pulp, Buckeye Cellulose Corp., Memphis, Tenn.), instead of wood. In addition, a series of cellulose samples (0.4 g) coated or uncoated with D-glucose (0.2 g), were treated in the pressure reactor for various periods of time (20 to 40 minutes) and then extracted for 3 hours with water, as described above. The oven-dry weight of each sample was determined after the water extraction, and the percentage of D-glucose left on the cellulose was calculated.

In order to determine if the D-glucose and/or its derivatives left on cellulose after extraction, could be hydrolyzed with acid, the 40-minute D-glucose on cellulose sample (D-glucose heated in pressure reactor 40 minutes at 230°C under 2.8 MPa (N_2) and then extracted 3 hours in a soxhlet extractor) was subjected to acid hydrolysis according to the two methods described previously (i.e., 1 N HCl and 72% H_2SO_4). In each case, the acid was neutralized and the remaining salt removed by

precipitation followed by ion exchange resins. The water soluble material was analyzed by HPLC. The residue after hydrolysis in concentrated H_2SO_4 was examined by solid state ^{13}C-NMR, along with a cellulose reference.

D-GLUCOSE REACTION WITH ETHYLENE GLYCOL

A sample of D-glucose (0.5 g) was mixed with an excess of ethylene glycol (2.0 g) and heated in the pressure vessel at 230°C for 20 minutes under 2.8 MPa of nitrogen. The heat-treated sample, and an untreated reference, were analyzed by analytical HPLC. The heat-treated sample (D-glucose-ethylene glycol) was further fractionated by preparative HPLC. A sample of each reaction product was collected and freeze-dried. NMR and mass spectra for each fraction were recorded.

D-GLUCOSE REACTION ON GLASS FIBRE

Lead-free borosilicate glass fibers, 0.006 mm diameter, were obtained from Sargent-Welch Laboratory (Pyrex Brand Glass No. 7220). A series of glass fiber samples (0.4 g) were coated with 0.2 g of D-glucose and placed in the pressure vessel at 230°C and under 2.8 MPa of nitrogen for various periods of time (15 to 25 minutes) and then extracted for 3 hours with water in a Soxhlet extractor. The water-soluble fractions were analyzed by analytical HPLC.

The water-soluble material from the 18-minute heat treatment (4.1 g solid obtained from repetitive treatments and extractions) was further fractionated by preparative HPLC (see Figure 23, p. 65). Fractions at 12 (Fraction A) and 33 minutes (Fraction B) retention time

(analytical HPLC) were collected and freeze-dried. The liquid state ^{13}C-NMR spectrum of fraction A was recorded along with pure HMF used as reference. The proportion of this fraction A hydrolyzable in H_2SO_4 (see method of analysis) was determined. The first fraction obtained previously from the fractionation of heat treated D-glucose (see experimental-preparative HPLC fractionation, p. 128) was also hydrolyzed in 72% H_2SO_4.

Fraction B (800 mg) was acetylated in pyridine-acetic anhydride. The acetylated material was purified by standard preparative thin layer chromatography (PTLC) techniques with elution through a silica gel bed using hexane: ethyl acetate as a solvent in a 1:1 volume ratio. The purified material was further fractionated with a chromatotron into acetylated fractions (C; 500 mg and D; 30 mg). GC-MS spectra of each fraction were recorded.

A glass fiber sample (0.4 g) was coated with 0.2 g of HMF and heated in the pressure vessel for 25 minutes at 230°C and 2.8 MPa. The sample-insoluble in water-was extracted with acetone. The liquid-state ^{13}C-NMR spectrum of the extracted sample was determined.

RECOMMENDATIONS FOR FURTHER WORK

As a follow-up to this work, the NH_4SSL-PF resin dispersion was tested successfully for the production of laboratory waferboards. A Canadian PF resin producer and an SSL producer have shown interest in the commercialization of a SSL-PF resin for waferboard applications. It has been recommended that the NH_4SSL-PF resin system be tested in the industrial production of waferboard.

Information concerning the contribution of the lignin fraction to the adhesive properties of NH_4SSL is still incomplete. Further development and commercial implementation of new adhesive systems would be greatly facilitated with a better understanding of the lignin chemistry involved. A basic study on lignin-PF thermal reactions should be initiated.

A better understanding of the chemistry involved during the thermosetting of carbohydrate at high temperature has been developed. Attempts should be made to apply this information to the development of low cost adhesives with improved reactivity.

CLAIMS TO ORIGINAL WORK

1. D-Glucose was heated under conditions similar to those employed in waferboard production, and products were analyzed by analytical HPLC. The reaction was conducted in the presence or absence of acid, base, cellulose, lignin or wood.
2. Fractionation of D-glucose heated under pressure was accomplished by ultrafiltration and preparative HPLC. The fractions were characterized for molecular weight and analyzed by spectroscopy.
3. Polycondensation of D-glucose with formation of glucosidic linkage was shown to be the main initial reaction when D-glucose was heated under the selected conditions.
4. Polycondensation of D-glucose is catalyzed by the presence of small quantities of ammonium lignosulfonate.
5. The higher molecular weight D-glucose oligomers are more stable to thermal decomposition than lower molecular weight oligomers. Continued heating resulted in formation of higher molecular weight material.
6. ^{13}C-NMR of heated D-glucose oligomers suggests the presence of non-glucosidic beta linkages.
7. Thermal polymerization of D-glucose to the infusible stage occurs with partial decomposition of the polymer and formation of C=C, C=O, $-\overset{|}{\underset{|}{C}}-CH_2-\overset{|}{\underset{|}{C}}-$ and $-\overset{|}{\underset{|}{C}}-CH_3$ groups.
8. D-Glucose subjected to heat and pressure insolubilizes at a faster rate when in contact with cellulose fibers.

9. The same types of functional groups are formed when D-glucose is subjected to heat and pressure, whether cellulose is present or not.

10. D-Glucose subjected to heat and pressure in the presence of alkali isomerized first to D-fructose before dehydration, polymerization and degradation.

11. D-Glucose and DL-glyceraldehyde polymerize under heat and pressure with the formation of similar functional groups.

12. The difference between ^{13}C-NMR spectra for D-glucose and DL-glyceraldehyde polymers was attributed to the presence of furanoid and pyranoid rings in the D-glucose polymer.

13. The thermosetting and adhesive properties of each of the heated D-glucose fractions collected by preparative HPLC was evaluated using miniature particleboards and torsion shear tests.

14. The thermal stability and adhesive properties of low molecular weight sugars is influenced by the presence of alpha and beta glucosidic groups.

15. A mechanism of adhesion of carbohydrates through acetal bond formation, partial decomposition, recondensation with participation of C=C, C=O and OH functionalities was proposed.

16. D-Glucose thermal polymerization and dehydration products had no special adhesive properties when used alone as adhesives.

17. In the presence of PF copolymers, 2-furaldehyde was more reactive than other carbohydrate, dehydration and polymerization products tested. The reactivity of NH_4SSL was intermediate between D-glucose and 2-furaldehyde.

18. A new NH_4SSL-PF resin dispersion was obtained by simply blending, together NH_4SSL, PF and an acid.

19. The new NH_4SSL-PF resin had cure properties similar to the PF resin used in the manufacture of waferboard.

20. The NH_4SSL-PF resin cure properties were dependent on the lignin and carbohydrate contents of NH_4SSL, the proportion of PF in the resin and the resin pH.

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