CONDENSED TANNIN–RESORCINOL ADDUCTS AND THEIR USE IN WOOD-LAMINATING ADHESIVES: AN EXPLORATORY STUDY

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SYNOPSIS

The reaction of a tannin extract (containing about 30% carbohydrate) from loblolly pine (*Pinus taeda* L.) bark (two parts) and resorcinol (one part) at 120°C for 24 h with acetic acid catalyst gave a product containing predominantly oligomeric procyanidin-4-resorcinol adducts (39%), unreacted resorcinol (22%), carbohydrate (20%), the resorcinol adduct 2*R*,3*R*,4*S* 4-(2,4-dihydroxyphenyl)-flavan-3,3',4',5,7-pentaol (8%), its 2,3-*trans* isomer (4%), and catechin and epicatechin (7%). The above mixture was used as a resorcinol replacement in a conventional phenol–resorcinol–formaldehyde laminating adhesive as used in the manufacture of laminated wood beams. Preliminary gluing results suggest that, with some modification of adhesive formulation and resin synthesis conditions, room-temperature curing adhesives for wood-laminating purposes could be produced successfully using such condensed tannin–resorcinol adducts to replace more than 60% of the resorcinol requirement.

INTRODUCTION

The increasing cost and scarcity of resorcinol required for the synthesis of cold-setting wood-laminating adhesives prompted our consideration of the use of condensed tannins extractable from conifer barks as a source of inexpensive but highly reactive phenols. The condensed tannins in loblolly pine bark are polymeric procyanidins (1) that are composed predominantly of 2,3-*cis*-procyanidin units terminated with the 2,3,-*trans*-flavan-3-ol (+)-catechin (Fig.1) [1]. Both C(4)–C(6) and C(4)–C(8) interflavanoid bonds are present in these polymers [2,3]. Condensed tannins isolated from a broad spectrum of plants, including bark of the southern pines, exist as mixtures of procyan-

Journal of Applied Polymer Science: Applied Polymer Symposium 40, 79–90 (1984)
Published by John Wiley & Sons, Inc.

CCC 0570-4898/84/030079-12$04.00

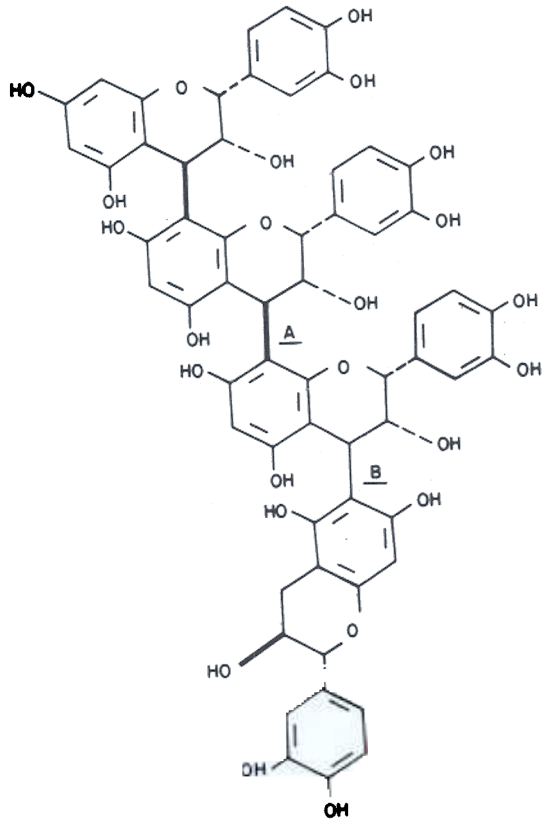

FIG. 1. Polymeric procyanidins (1) .A = 4β-8, 3 units, B=4β-6, 1 unit, $\overline{M}_n \sim 9$ flavan units.

idins of a comparatively broad molecular-weight distribution with number-average molecular weights centering on 2000–3500 (i.e., 7–12 flavanoid units) [1,4]. The condensed tannins in conifer barks have a phloroglucinol A-ring hydroxylation pattern so that they polymerize too rapidly on addition of formaldehyde for most wood adhesive applications [5].

If the molecular weight of these tannins could be reduced, the rate of gellation might be slowed sufficiently to permit the formulation of a cold-setting adhesive. An important feature of the chemistry of polymeric procyanidins is the lability of the interflavanoid bond to acid-catalyzed cleavage [6]. When reacted in the presence of a nucleophile such as a thiol or phloroglucinol, relatively high yields of monomeric flavan-4-sulfides or phloroglucinol adducts can be produced [7]. The products of this reaction with resorcinol would result from an equilibrium of both relative cleavage and condensation rates [6]. If the cleavage rate of a flavan-4-resorcinol adduct is sufficiently slow in comparison with the interflavanoid bond of procyanidins, the resorcinol adduct would accumulate despite the greater nucleophilicity of the phloroglucinol ring. It therefore seems possible that a reaction of con-

densed tannins with resorcinol at acidic pH could lead to low-molecular-weight procyanidin-4-resorcinol adducts that would be useful in the synthesis of cold-setting adhesives for the production of laminated wood timbers. Our initial exploration of this approach is described here.

EXPERIMENTAL

A loblolly pine bark acetone–water extract (10 g) and resorcinol (7 g) were added to ethanol (50 mL) and water (20 mL) to which acetic acid (5 mL) was added as the sample was purged with argon. The sample vial was sealed and heated at 100°C for 7 h. The product was diluted with water and extracted with ethyl acetate (six times at equal volume) to recover a red-brown ethyl acetate-soluble product (13.3 g) that was separated on a Sephadex LH-20 column (2.4 cm i.d. × 220 cm) by elution with ethanol and collection of 15 mL fractions. Elution of products from the column was followed by one-dimensional cellulose TLC (Schleischer and Schull, F 1440 plates, 10 × 10 cm) developed with 6% acetic acid and sprayed with vanillin–HCl. Combined fractions containing one or two products were examined by two-dimensional cellulose TLC by developing the plates in the first dimension with *t*-butanol–acetic acid–water [3:1:1 (v/v/v) TBA] and in the second dimension with 6% acetic acid. Fractions 20–40 contained unreacted resorcinol (6.4 g). Fractions 40–60 contained predominantly catechin with small amounts of epicatechin and a trace of resorcinol (0.64g). Fractions 60–80 contained two products suspected to be flavan-4-resorcinol adducts (0.43 g). Further elution with ethanol and then acetone–water [1:1 (v/v)] gave oligomeric products (3.1 g).

Flavan-3-ols

Fractions 40–60 were separated by reverse-phase HPLC on a DuPont Zorbax CN column (9.4 mm × 24 cm) by elution with methanol–water [30:70 (v/v)] flowing at 2.5 mL/min. Retention volumes were 24.5 mL for (+)-catechin and 35.5 mL for (−)-epicatechin. Comparison of the relative peak areas (UV, 254 nm) showed a catechin-to-epicatechin ratio of 4.5:1.

Epicatechin-4-Resorcinol (2)

The combined fractions 60–80 were separated by reverse-phase HPLC on a DuPont Zorbax CN column by elution with methanol–water [15:85 (v/v)] flowing at 5 mL/min, where the major component was collected at a retention volume of 90 mL. After freeze drying, it was recovered as a tan-colored amorphous solid. Found: C, 60.4; H, 4.7%; $C_{21}H_{18}O_8 \cdot 1H_2O$ requires C, 60.6; H, 4.8%. The phenol had cellulose TLC R_f values of 0.60 in TBA and 0.50 in 6% acetic acid dimensions where it gave a red-colored product with vanillin–HCl. The ^{13}C-NMR spectrum of the phenol in d_6-acetone-D_2O showed δ : 38.7 (C4), 70.3 (C3), 74.3 (C2), 94.9 (C8), 96.2 (C6), 101.6 (C3″), 102.9 (C4a),

106.7 (C5″), 114.8 (C2′), 115.7 (C5′), 118.9 (C6′), 121.6 (C1″), 130.5 (C1′), 131.3 (C6″), 144.3 (C4′), 144.6 (C3′), and a group of signals 155.4–157.4 (ArCOH). ^{1}H-NMR of the phenol in d_6-acetone-D_2O showed δ: 4.14 (1H,*d*,*J*=1.2 Hz,H3) and 6.09–6.95 (8 H,*m*,ArH), while other heterocyclic ring protons were obscured by OH.

Methylation (CH_2N_2) of (2) and preparative TLC [benzene–acetone, 9:1 (v/v), R_f=0.41] gave a white amorphous solid. Found: C, 66.7; H, 6.5%; $C_{27}H_{30}O_8$ requires C, 67.2; H, 6.2 for which El-MS showed M^+=482 (53) and fragmentation ions 327 (12), 317 (16), 303 (100), 285 (29), 271 (93), 180 (16), 167 (21), 151 (30), and 149 (11). The peracetate (acetic anhydride–pyridine, 1:1) of (2) was isolated by preparative TLC [benzene–acetone, 1:1 (v/v), R_f=0.53] as a white amorphous solid. Found: C, 60.8; H, 4.8%; $C_{35}H_{32}O_{15}$ requires C, 60.7; H, 4.6%, α_{578} + 28.3°, *c*= 0.59 ($CHCl_3$). ^{1}H-NMR $CDCl_3$ showed δ: 1.90–2.38 (21 H,*m*, OAc), 4.42 (1 H,*d*, *J*=3 Hz,H4), 5.07 (1 H,*br*,H2), 5.17 (1 H,*d*,H3) 6.6–7.3 (8 H,*m*,ArH). The CD spectrum of the peracetate (acetonitrile) showed positive Cotton effects at 234 and 277 nm.

Catechin-4-Resorcinol (3)

A second compound occurring in amounts smaller than (2) was isolated from the fraction 60–80 by preparative HPLC on the DuPont Zorbax CN column eluted with methanol–water[15:85 (v/v)] at a retention volume of 43 mL. The phenol (3) was isolated as a tan-colored amorphous solid. Found: C, 60.4; H, 4.7%; $C_{21}H_{18}O_8 \cdot 1H_2O$ requires C, 60.6; H,4.8%. The phenol had cellulose TLC R_f values of 0.70 in TBA and 0.55 in 6% acetic acid where it gave a red coloration with vanillin–HCl. ^{13}C-NMR in d_6-acetone-D_2O showed δ: 39.6 (C4), 75.5 (C3), 81.2 (C2), 94.5 (C8), 96.1 (C6), 102.0 (C3″), 103.9 (C4a), 106.5 (C5″), 114.2 (C2′), 114.8 (C5′), 118.9 (C6′), 121.3 (C1″), 128.0 (C1′), 129.7 (C6″), 143.8 (C4′), 144.0 (C3′), and 154.5–157 (ArCOH). ^{1}H-NMR in d_6-acetone-D_2O showed δ: 4.32 (1 H,*dd*, *J*=10 Hz and *J*=7 Hz,H3). Methylation of (3) and preparatory TLC gave an amorphous white solid for which El-MS showed M^+=482 and fragmentation similar to the methylated derivative of (2).

Acid-Catalyzed Cleavage of (2)

To compare the rates of acid-catalyzed cleavage of epicatechin-4-resorcinol (2) and the dimeric procyanidin B1 (4), they were each dissolved in ethanol (2 mL) and phenylmethanethiol (10 μL) and acetic acid (3 μL) was added as the samples were purged with argon. The reaction vials were sealed and heated at 90°C on a water bath. After heating periods ranging from 2 to 20 h, samples (5 μL) were withdrawn by syringe and applied to cellulose TLC plates which were developed in the first dimension with TBA and in the second dimension with 6% acetic acid. The plates were sprayed with vanillin–HCl, heated, and the extent of cleavage was estimated by visual comparison

of the relative spot intensities of the starting compounds and their cleavage products, epicatechin-4-benzyl sulfide and either resorcinol or catechin.

Preparation and Characterization of "Run A"

An acetone–water extract from the whole bark of loblolly pine (164 g) was combined with resorcinol (82 g) and dissolved in ethanol (190 mL) to which acetic acid (50 mL) was added. The solution was heated on a Parr autoclave at 120°C for 24 h. After cooling, the product was reduced in volume on a rotary evaporator and dispersed in water. An aliquot (70 mL) was taken for analysis. The remainder and a second reaction product prepared under similar conditions were freeze dried to obtain a red-brown solid (500 g) for evaluation in adhesive formulations ("Run A").

The 70 mL aliquot was diluted further with water and extracted six times with ethyl acetate to obtain ethyl acetate-soluble (18.2 g) and water-soluble (5.3 g) portions. The ethyl acetate-soluble portion was separated on Sephadex LH-20 and fractions containing unreacted resorcinol, flavan-3-ols, and flavan-4-resorcinol adducts were compared with the compounds described above by two-dimensional cellulose TLC. Two oligomer fractions (tubes 72–100 and 101–87) were collected by further elution with ethanol. A final oligomer fraction was obtained by elution with acetone–water.

Each of the ethanol eluted oligomer fractions (5 mg) were dissolved in ethanol (2 mL) after which phenylmethanethiol (two drops) and acetic acid (two drops) were added as the reaction vials were purged with argon. The vials were sealed and heated at 105°C overnight. Reaction products were examined by two-dimensional cellulose TLC in comparison with authentic compounds. The two ethanol eluted oligomers and the acetone–water eluted oligomers (75 mg each) were acetylated (acetic anhydride–pyridine, 1:1) and the peracetate derivatives recovered by precipitation from water and then from *n*-hexane to obtain off-white amorphous solids. These peracetates were examined for elemental composition and for number-average molecular weight by vapor pressure osmometry in $CHCl_3$. The ^{13}C-NMR spectra of the two ethanol eluted oligomers, the acetone–water eluted oligomer, and the water-soluble portion of the product after extraction with ethyl acetate were recorded in d_6-acetone-D_2O [1:1 (v/v)] at 20 MHz with a Varian FT-80A spectrometer.

Resin Preparation

A phenol–formaldehyde prepolymer was prepared by reacting 1 mol phenol with 1 mol formaldehyde in the presence of 6.6% sodium hydroxide, based on the weight of phenol. Water (64.2%), also based on the weight of phenol, was added as a diluent. The reaction was carried out at reflux temperature until a viscosity of 160 cP was reached. To 46.1 g of this prepolymer solution 30 mL water were added, the temperature of the mass brought to 60°C, and, while maintaining this temperature, 17.6 g material previously described as

"Run A" were added slowly under constant agitation. The addition was made in small increments because previous experiments had shown that the "Run A" material had a tendency to form lumps when mixed with the prepolymer. After this addition was complete, the temperature of the mass was raised from 60 to 100°C over a period of 10 min while agitation was continued. The reaction was continued under reflux (at approximately 100°C) for 1 h, the mass cooled to room temperature, and stored for further experiments. The viscosity at the end of the reaction period was 300 cP. This resin will be designated as "Resin A."

Adhesive Preparation

The first adhesive formulation examined was prepared by combining resin A (30 g), paraformaldehyde (4.5 g), and walnut shell flour (1.0 g). The ingredients were mixed and 9.7 g mixture were applied to a test board of Douglas fir (¾ × 6 × 8 in.). This is equivalent to a spread rate of 70 lb/1000 ft^2 of glue-line. After placing a second board on top, 20 min closed assembly time were allowed, followed by a clamp time of 22 h at 70°F. The remainder of the adhesive mix was allowed to stand at room temperature. The gel time was 165 min. The analogous mixture made with a conventional resorcinol–phenol–formaldehyde resin had a gel time of 135 min. After several days standing at room temperature, both compositions were hard and insoluble in water.

A second adhesive formulation was made by combining resin A (10 g), 50% sodium hydroxide (1.5 mL), and paraformaldehyde (1.5 g). Gluing conditions were the same as for the above adhesive except the glue spread was 7.5 g and the closed assembly time was reduced to 5 min. This mixture thickened rapidly, was stringy within 30 min, and gelled within 42 min. The adhesive remained partially water soluble after gellation and after storing for several days at room temperature.

The third adhesive formulation was made by combining resin A (10 g) and a 50% solution of formalin (3 g). After only 5 min of mixing the adhesive was applied and the laminate was put under pressure immediately. As pressure was applied, the squeeze-out began to gel. The gel time of the mixture was only 8–10 min. The adhesive was a hard solid, insoluble in water and common organic solvents (ketones, alcohols), after overnight storage.

Glue-Bond Specimen Preparation

A board of Douglas fir, flat grain, smoothly planed, ¾ × 6 × 8 in., was coated with the adhesive described before. A second ("identical") board was placed on top, the assembly allowed to stand for the assembly time given, then put under a pressure of 1035 kPa (150 psi). Pressure was maintained for several hours and the laminate aged for one week prior to cutting six shear specimens as per PS 56-73. Of these six specimens, two were sheared dry, two were sheared after vacuum pressure cycles as described for AITC

110 (PS 56-73) and then sheared, two were subjected to 2 h boiling in water, and then sheared wet.

RESULTS AND DISCUSSION

Products obtained from the reaction of loblolly pine bark tannins with excess resorcinol could be accounted for by acid-catalyzed cleavage of the interflavanoid bond of procyanidins and condensation of flavanyl carbonium ions with resorcinol and oligomeric procyanidins. No C2-substituted products as obtained from the reaction of catechin with resorcinol in the presence of mineral acid [8] were found. A number of different reaction conditions and bark extract types were examined in addition to those described above, but the relative yields of flavan-3-ols, flavan-4-resorcinol adducts, and oligomeric procyanidin derivatives did not differ substantially from the results described below. Variations in product yields between different types of extracts could be largely attributed to variations in the amounts of carbohydrates present in the extract.

The yields of flavan-3-ols varied in the range of 7–12% of the starting tannin. Since the number-average molecular weight of condensed tannins from loblolly pine bark generally centers on 2500–3500, the terminal flavan-3-ol units constitute about 8–12% of the polymer. The yields of flavan-3-ols obtained from these reactions therefore indicate that the terminal units were almost completely replaced by resorcinol. This was supported by ^{13}C-NMR and thiolytic cleavage studies of the oligomeric products. As expected from earlier studies of the structure of the condensed tannins in loblolly pine bark, the flavan-3-ols generated from the terminal unit were predominantly catechin with only small proportions of epicatechin.

The yields of the flavan-4-resorcinol adducts varied in the range of 12–20% of the starting tannin. The dominant isomer produced was the 4-resorcinol adduct of epicatechin as would be predicted from earlier study of the structure of the polymers. Since this compound has not been described previously, it was necessary to prove its structure. The constitution of (**2**) was evident from elemental analysis, ^{1}H- and ^{13}C-NMR, and EI-MS spectra of the phenol or its methylated or acetylated derivatives. A 2,3-*cis* configuration was shown by the ^{13}C-NMR chemical shifts of C2 and C3 (74.3 and 70.3 ppm, respectively) [9], as well as the small coupling constant for H3 in the proton spectra of the phenol and peracetate derivative [10,11]. A 3,4-*trans* configuration, shown by the upfield shift of the C2 carbon signal to 74.3 ppm [12] as well as the H-3 coupling in the proton spectrum, is consistent with all products obtained from 2,3-*cis*-procyanidins isolated to date. A 2*R*, 3*R*, 4*S* absolute stereochemistry demonstrated by the positive Cotton effect at the 234 nm band in the CD spectrum of the peracetate [13] is consistent with the product expected from the (−)-epicatechin upper units known to be present in natural loblolly pine bark tannins. Compound (**2**) is therefore 2*R*, 3*R*, 4*S*, 4-(2,4-dihydroxyphenyl)-flavan-3,3′,4′,5,7-pentaol.

The constitution of (**3**) is also evident from elemental analysis (see Fig. 2)

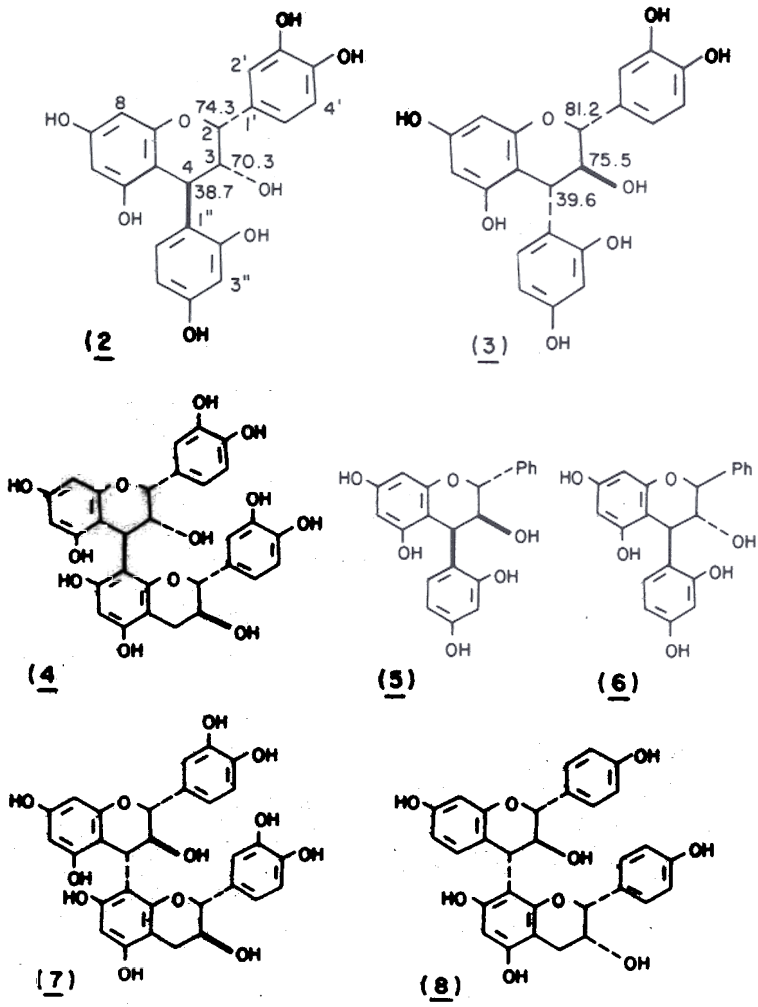

FIG. 2. Flavan-4-resorcinol adducts and related proanthocyanidins (2–8).

and ^{1}H- and ^{13}C-NMR and EI-MS spectra of the phenol or its methyl ether derivative. A 2,3-*trans* stereochemistry is shown by the chemical shifts of C2 and C3 (81.2 and 75.5 ppm, respectively) [9], and by the large coupling constant for H3 (J_{23} = 10 Hz). Both the 2,3-*trans*–3,4-*trans* and 2,3-*trans*–3,4-*cis* (5) isomers were obtained by Botha et al. [14] via reduction of (+)taxifolin with sodium borohydride followed by addition of resorcinol. The coupling constant of H3 (J_{34} = 7.0 Hz) found for the phenol (3) indicates that it is the 2,3-*trans*–3-4-*trans* isomer. The absolute stereochemistry of (3) has not yet been proven and is only tentatively assigned the 2*R*, 3*S*, 4*R* configuration recognizing that some of the product could be the *ent*-isomer (6) obtained by B-ring inversion of a 2,3-*cis*-procyanidin unit. The procyanidins

of loblolly pine bark do contain small proportions of the 2,3-*trans*-procyanidins analogous to the procyanidin B3 (7), however.

Ethanol-eluted oligomers were obtained in yields of 15–25% of the starting tannin. These compounds were divided into two fractions by chromatography on Sephadex LH-20. The fraction eluted first (tubes 72–101) was a mixture of products dominated by dimeric 2,3-*cis*-procyanidin-4-resorcinol adducts on the basis of its ^{13}C-NMR spectrum. The fact that these compounds were predominantly terminated with a resorcinol substituent was shown by the comparatively large signals at 70.3 and 74.3 ppm, representing the C3 and C2 of an epicatechin unit substituted at C4 with a resorcinol unit in comparison with the signals at 67.8 and 82.5 ppm for the C3 and C2 of a terminal catechin unit. This was also evident from the comparatively strong signal at 38.7 ppm for a flavan with a resorcinol substituent at C4 in comparison with the signal at 36.8 ppm for the corresponding C4 in procyanidins. Additional evidence supporting the conclusion that most of these compounds were terminated with a resorcinol unit was obtained by acid-catalyzed thiolytic cleavage which gave predominantly epicatechin-4-benzyl sulfide and epicatechin-4-resorcinol with only small amounts of catechin. Comparison of the signal intensity for C3 and C2 of epicatechin units substituted at C4 with resorcinol with the C3 and C2 carbon signals of the 2,3,-*cis*-procyanidins (i.e., 72.7 and 76.6 ppm) suggested that the number-average molecular weight of this fraction would be about that of a dimeric procyanidin-4-resorcinol adduct. This conclusion was supported by vapor pressure osmometry of the peracetate (found: C, 60.0; H, 4.7%; $C_{60}H_{54}O_{26}$ requires C, 60.5 and H, 4.5%) which showed an M_n of 1154 as compared to a required 1190 for the required peracetate. This fraction contained only small signals at chemical shifts expected for carbohydrates.

The ^{13}C-NMR spectrum of the ethanol-eluted oligomers in later fractions (tubes 101–187) also showed a mixture of oligomeric 2,3-*cis*-procyanidin-4-resorcinol adducts basically similar to the fraction described above. As in the previous fraction both ^{13}C-NMR and acid-catalyzed thiolytic cleavage showed that most of the components of this fraction were terminated with a resorcinol substituent at C4. Comparison of the C3 and C2 signals for an epicatechin unit substituted at C4 with resorcinol with those of 2,3-*cis*-procyanidin units, suggested that this fraction was dominated by trimeric procyanidins terminated with a resorcinol unit. Vapor pressure osmometry of the peracetate (found: C, 60.3, H, 4.7%; $C_{85}H_{77}O_{37}$ requires C, 60.4 and H, 4.6%) gave an M_n of 1822 as compared with 1689 required for the required peracetate.

The acetone–water-eluted oligomers were obtained in yields of 35–45% of the starting tannin. The ^{13}C-NMR spectrum of this fraction showed that it too was largely composed of oligomeric procyanidins terminated with a resorcinol unit. Elemental analysis of the peracetate (found: C, 60.0; H, 4.7%) was consistent with this general constitution. It was not possible to predict the number-average molecular weight of this fraction from the ^{13}C-NMR spectrum because of substantially greater line broadening as compared to the

earlier fractions. Vapor pressure osmometry of the peracetate showed an M_n of 3392, suggesting oligomeric products with an average of ca. 6 flavanoid units per chain. This molecular weight is comparable with that usually obtained from the natural tannin. Therefore only about half of the condensed tannin polymer was reduced in molecular weight by this reaction.

The residual water-soluble product which amounted to about 20% of the total product was shown to contain additional quantities of oligomeric procyanidin derivatives and large amounts of carbohydrates by its ^{13}C-NMR spectrum. The amounts of carbohydrate in the crude extract used for the reaction clearly determined the relative proportion of water soluble materials in the reaction products. No attempt was made to characterize this fraction further.

As observed in previous studies [6], the half-life of the procyanidin B1 (4) was about 4 h when heated at 90°C in the presence of excess phenylmethanethiol and acetic acid. A parallel reaction of epicatechin-4-resorcinol (2) showed only a trace of resorcinol and epicatechin-4-benzylsulfide after 20 h of heating. Patil and Deshpande [15], studying the structure of a procyanidin with a resorcinolic A ring in the upper unit and an epiafzelchin lower unit (8), also found little interflavanoid bond cleavage when reacting this compound with excess phenylmethanethiol and acetic acid in ethanol at reflux temperature. These results support the hypothesis that, because of the resistance of the flavan-4-resorcinol bond in comparison with the ease of cleavage of the interflavanoid bond of procyanidins, procyanidin-4-resorcinol adducts are produced in significant yield despite the fact that resorcinol is a poor nucleophile in comparison with the phloroglucinol A ring of the procyanidins.

The product used in the synthesis of the laminating adhesive, that is, "Run A" described below, can thus be summarized as: oligomeric-4-resorcinol adducts (39%), unreacted resorcinol (22%), carbohydrate (20%), flavan-4-resorcinol adducts (12%), and flavan-3-ols (7%).

It was expected that the product "Run A" would exhibit higher reactivity than resorcinol because of the higher reactivity of the phloroglucinol A rings of the procyanidin moieties as well as the much higher initial molecular weight of the product as compared with resorcinol. Three attempts at resin synthesis were required to reach the results described in the Experimental section. The first attempt at resin synthesis using "Run A" failed because it was added to the phenol–formaldehyde prepolymer too rapidly, which resulted in large lumps that could not be dispersed with a magnetic stirrer. The second attempt at resin synthesis failed because the polymer made using the "Run A" product gelled too rapidly. When preparing an equivalent resorcinol-modified phenolic wood-laminating adhesive, 17.6 g resorcinol are added to the prepolymer and the mixture is refluxed for approximately 4 h before the appropriate viscosity is reached. The resin gelled after only 1.5 h of reflux when the resorcinol was replaced with "Run A." The third batch (described more fully in the Experimental section) was therefore refluxed for only 1 h. Even this length of time is judged to be too long, based on the behavior of the resin during the

gluing experiments. Further experimentation is aimed at preserving this reactivity for release in the glue-line rather than during resin preparation.

The adhesives varied greatly in pot lives, depending apparently on pH and formaldehyde availability. Through the use of a variety of formaldehyde donors, such as, formalin, paraformaldehyde, and the various oxazolidines, etc., the availability of the crosslinking agent can be varied over wide ranges. Further experimentation is aimed at adjustment of the pot life and cure time in the press. From an overall handling viewpoint, the adhesive mixtures showed normal properties; for example, easily spreadable, reasonable flow, and penetration.

Strength properties and wood failure of the three adhesives when tested in dry shear, after vacuum-pressure water soak (AITC 110), and after a 2 h boil test shown in Table I indicate that, after only a limited amount of adhesive formulation work, bonds were obtained that passed the dry shear and 2 h boil tests. The poor results obtained in the AITC 110 test, of course, show that further development is required. However, the work described here is of exploratory nature. It took only three adhesive formulations, and even those with a poorly monitored resin preparation because of limited availability of material, to prepare laminates that meet two out of three major tests. We are therefore encouraged that further development can lead to a fully approved exterior-laminating adhesive system using a material like "Run A" material as a full replacement for resorcinol. For example, removal of the carbohydrates should result in glue-lines with better water resistance. Additionally, many opportunities exist to improve the bonds through variations in resin synthesis and adhesive formulation conditions. Therefore, research is continuing on this

TABLE I
Summary of Bond Test Results[a]

	Adhesive no.		
			3
(a) Dry shear			
Shear strength (kPa = psi)	9100	7830	9690
	1320	1140	1400
Wood failure (%)	0	80	95
(b) Vacuum pressure (AITC 110)			
Shear strength (kPa = psi)	2610	3390	110
	870	490	17
Wood failure (%)	12	18	0
(c)2 h boil			
Shear strength (kPa = psi)	10,420	5500	5340
	1510	800	780
Wood failure (%)	85	78	85

[a] All values are averages of (only) two specimens.

and related approaches to the development of resorcinol replacements from bark extracts.

The authors thank Dr. J. J. Karchesy, Department of Agricultural Chemistry, Oregon State University, Corvallis, Oregon, for some of the spectra reported in this paper.

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