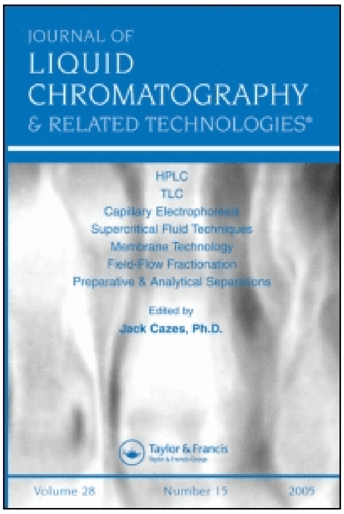

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FORMALDEHYDE CONDENSATION PRODUCTS OF MODEL PHENOLS FOR CONIFER BARK TANNINS

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ABSTRACT

Gel permeation chromatography of the condensation products of phenols and formaldehyde proved effective in understanding the reactions of condensed tannins with formaldehyde. Rates of condensation of phloroglucinols, resorcinols, catechols, (+)catechin, and (-)epicatechin were examined to determine if methylol-tannins from southern pine bark could be prepared as resin intermediates. The phloroglucinols (models for the A-ring of pine bark tannins) were so much more reactive than were the resorcinols (models for the A-ring of wattle tannins), that preparation of methylol-tannins from pine bark tannins seems unlikely even though this approach has been applied successfully to synthesis of resins from wattle tannins. The methylol content of catechin-formaldehyde condensation products was very low. The catechol B-ring was unreactive under conditions in which condensations of pine bark tannins could be controlled. Although there is much less steric hindrance of the A-ring of (-)epicatechin than of (+)catechin, differences in the rates of condensation of these isomers were not detected. GPC and H-NMR spectra of (+)catechin condensation products showed that a dimer formed rapidly and that further condensation occurred more slowly.

INTRODUCTION

Because of uncertainties in the price and availability of phenol, the forest products industry is interested in substituting condensed tannins, lignosulfonates, or Kraft lignins for significant portions of their phenol requirements for wood adhesives. Among the tannins, wattle extracts have been more successfully used in wood adhesive formulations than conifer bark extracts (1,2). Difficulty in controlling the condensation of conifer bark tannins in reaction with formaldehyde has been a major obstacle to using these abundant natural polymers in wood adhesives. Plomley (3) has shown that *Pinus radiata* bark tannins gelled 20 times as fast as wattle tannins when reacted with formaldehyde in aqueous solution at pH 6.0 and 60^{o}. Comparable differences in the gellation of southern pine bark tannins and wattle tannins have been observed in our laboratory. Roux et al. (1) reported that stable methylol-wattle tannins could be prepared by reaction with formaldehyde in alcohol solutions. Hillis and Urbach (4,5) have published the only detailed investigations of the reactions of conifer bark condensed tannins and (+)catechin with formaldehyde, and their work was done using dioxane-water solutions. This study was undertaken to determine if stable methylol-southern pine bark tannins could be prepared as resin intermediates. GPC offered a promising approach for examination of the condensation of these polymers.

EXPERIMENTAL

Model Compounds

Phloroglucinol (Aldrich) (6), 2, 4, 6-trihydroxytoluene (Pflatz and Bauer), resorcinol (Koppers), 4-ethylresorcinol (Pflatz and Bauer), and 4-methyl-catechol (Pflatz and Bauer) were used as purchased. Catechol (Aldrich) was recrystallized from benzene to give large needles (mp 104-105°, Lit. 105° (7); C = 65.7, H = 5.62, Calc. C = 65.4, H = 5.5%). For comparison of the rate of condensation of (+)catechin with phloroglucinol, resorcinol, and catechol models, where large quantities were required, (+)catechin (Sigma) was used without further purification. Where both H-NMR spectra and GPC were used to follow the condensation of (+)catechin, the amorphous powder was extracted with Et_2O to obtain 90% Et_2O-soluble material, resulting in a total yield of 85% of the purchased material as needles (mp 175-177°, Lit. 177°); $[\alpha]^{24}_{nm}$ c 0.4 in $(CH_3)_2CO:H_2O$ (1/1); 589 nm, +14.3°; 577nm, +16.2°; 546nm, +17.8°; 435nm, +29.0°; and 365nm, +40.9 (Lit. $[\alpha]_{Hg}$ +17.0°(8)); C = 61.6, H = 5.12, Calc. C = 62.0, H = 4.8%) after crystallization from H_2O. The pentaacetate (C = 60.2, H = 5.0; Calc. C = 60.0, H = 4.8) was crystallized from $EtOH:H_2O$ as large needles (mp 131-132°, Lit. 131-132°); $[\alpha]^{24}_{nm}$ c 0.4 in $CHCl_3$: 589nm, +32.2°; 577nm, +37.1°; 546nm, +47.2°; 435nm, +69.9° and 365 nm, +96.4° (Lit. $[\alpha]_{578}$ +39.7°(8)) without prior separations. For comparison of relative rates of condensation of (+)catechin and (-)epicatechin, (-)epicatechin (Aldrich) was used as purchased. This (-)epicatechin was an orange-tan crystalline material (mp 237-240, Lit. 240-242°; C = 61.4, H = 5.04, Calc. C = 62.0, H = 4.8%); $[\alpha]^{24}_{nm}$ c 0.4 in EtOH; 589nm, -51.2°, 577nm, -55.7°; 546nm, -62.8°; 435nm, -120.1°; and 365nm, -216° (Lit. $[\alpha_{578}]$ -57.6 (8)). The penta-acetate (C = 60.2, H = 5.0, Calc. C = 60.0, H = 4.8%) was crystallized from EtOH without prior separation as short needles (mp. 150-151°, Lit. 150-151° (7)); $[\alpha]^{24}_{nm}$ c 0.4 in $CHCl_3$: 589nm, -16.0°; 577 nm, -18.2°; 546nm, -19.0°; 435nm, and -37.4°; and 365nm, -63.1° (Lit. $[\alpha_{578}]$ -17.0° (8)).

Reaction Conditions

Reactions of model compounds with formaldehyde were made in $MeOH:H_2O$ (1:1) solutions at 10 percent solids (w/v) at initial pH conditions of 4.5, 6.0, and 7.5, at room temperature (24-25°). Preliminary studies had indicated that these conditions were suitable for examination of the rate of condensation of (+)catechin. Potassium hydrogen phthalate, potassium dihydrogen phosphate, and NaOH buffers were used to establish initial pH. The use of such high portions of alcohol is unusual in most resin syntheses. However, problems with solubility of the phenols and their condensation products, hopes of stabilizing the condensation as described by White and Knowles (9) and Roux (1), and consideration of the instability of (+)catechin in alkaline solution (10)led to examining the reactions in alcohol solution. Formaldehyde (37.8 percent solution) was added at mole ratios of 1.3 and 2.5 moles/mole of the phenol to solutions contained in small stoppered bottles. Solutions were sampled for several days after the addition of the formaldehyde.

Extent of Condensation

Aliquots (0.5 ml) were added to H_2O (5 ml), and the samples were frozen immediately. After freeze-drying, the samples were dissolved in pyridine (2 ml), and acetic anhydride was added periodically (1 ml to a total of 4 ml). The samples were stored overnight at room temperature. They were then added to ice water and the acetates were extracted with $CHCl_3$. The $CHCl_3$-soluble material was washed twice with HOAc (10%), twice with H_2O, and then evaporated under vacuum until dry. The samples were dissolved in THF or $CHCl_3$ in volumes sufficient to provide solution concentrations of ≈5 mg/ml. The acetates (25-50 μl of above solutions) were separated on a Waters Associates chromatograph equipped with a series of 0.25" ID. Microstyragel columns (1' of 10^3 Å, 2' of 500 Å, and 2' of 100 Å). Either THF or $CHCl_3$ solvents flowing at 1.5 ml/min (2,500-3,500 psi) were used. Both UV (254 nm) and RI detectors were employed, but results were reproduced from the UV detector response. Columns were calibrated using standard polystyrene and propylene glycols.

Formaldehyde Consumption

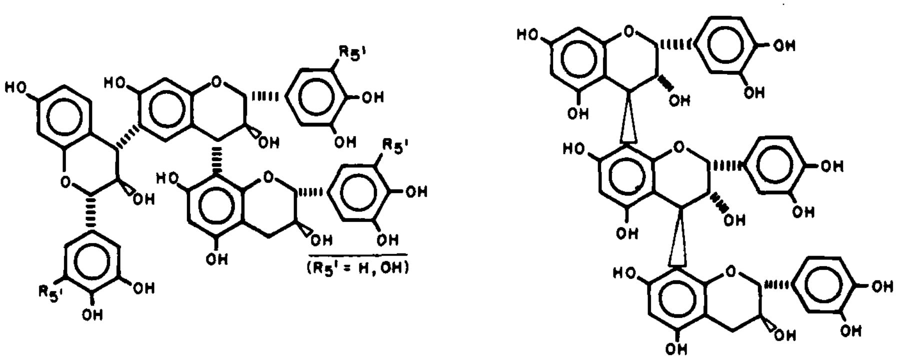
Residual formaldehyde was determined by the hydroxylamine-hydrochloride titration of samples heated to 60^o for 30 minutes, since residual formaldehyde was present as the hemiformal when large mole ratios of MeOH were present (11).

H-NMR Spectra of (+)Catechin Condensation Products

Formaldehyde (2.5 moles/mole of (+)catechin) was added to (+)catechin dissolved in $MeOH:H_2O$ (1:1) at 10 percent solids (w/v) at pH 7.5. Aliquots (1 ml) were withdrawn after addition of formaldehyde and periodically thereafter from solutions maintained at room temperature. After samples were dried and acetylated, portions (30-50 mg) were dissolved in $CDCl_3$, and H-NMR spectra were determined at 60MHz on a Perkin Elmer R24-B instrument using TMS internal standard. The following assignments for (+)penta-acetylcatechin (δ in $CDCl_3$):7.1-7.3 (3H,m,B-ring) 6.5-6.7 (2H,dd,A-ring), 5.3-5.4 (1H,m,H-2), 5.0-5.1 (1H,s,H-3), 3.1-3.4 (2H,m,H-4), 2.2-2.3 (12H,s,ArOAc), 1.95-2.0 (3H,s,Aliph.OAc) were identical to those reported by Thompson et al. (8). Methylene bridge protons (δ, 2.6-3.7) and methylol acetates ($ArC\underline{H_2}OAc$, δ, 4.5-5.2 and $ArCH_2O\underline{Ac}$, δ, 1.8-2.0) were broad bands, similarly described by Woodbrey et al. (12) and Steiner (13). No distinct signals in the methyl ether bridge region (δ, 4.2-4.5) were detected. Since the $ArC\underline{H_2}Ar$ signal overlapped the two C-4 protons, and the $ArC\underline{H_2}OAc$ protons overlapped the C-2 and C-3 protons of catechin, the total areas were integrated and, after normalization to a total of 15 $-O\underline{Ac}$ protons, reported as sums.

RESULTS AND DISCUSSION

Since wattle tannins have been much more successfully used in adhesive formulations than conifer bark tannins, particular emphasis was placed on comparing their structural differences. Wattle tannin is built up of (-)fisetinidin units linked C-4 to C-6, and (+)catechin appears in small proportions, generally as the terminal unit (fig. 1, I). Some (-)robinetinidin and (+) gallocatechin units are also present (1). Wattle tannins have a $\overline{Mn}$ of 1,250 (i.e., n = 4-5) with some molecules condensed as high as a mass of 3,000 (i.e., n = 10-11) (1). In contrast to wattle tannins, water-soluble tannins from southern pine bark (14, 15) are built up of (-)epicatechin and (+)catechin units (in ratios of approximately 5/1) linked C-4 to C-8, or possibly C-6 (fig. 1, II). GPC and VPO of methylated cold water-soluble tannins from loblolly pine outer bark (11) indicates that these polyflavonoids occur in a broad mass range (1,000-15,000) with a $\overline{Mn}$ of 1,250, a $\overline{Mw}$ of 4,100, and a UV detector elution maximum at a volume corresponding to that of a 2,800 molecular weight polystyrene (i.e., n = 8). Because of increased activation by the 5-hydroxyl of the catechin unit, condensation of pine bark tannins would be expected to occur faster than wattle tannins which are dominated by units containing



I

II

FIGURE 1

a resorcinol A-ring. Since we were unable to find data to permit assignment of how much differences in A-ring hydroxylation might influence the reactivity of these two types of tannins, we compared the condensation rates of phloroglucinol, 2,4,6-trihydroxytoluene, resorcinol and 4-ethylresorcinol. If there are to be good opportunities for crosslinking, it would be preferable to find conditions in which there was some condensation through the catechol B-ring. Therefore, we also compared the rates of condensation of catechol and 4-methylcatechol with the condensation of phloroglucinols and resorcinols. We also measured the rates of condensation of (+)catechin and (-)epicatechin after addition of formaldehyde under the same conditions.

Phloroglucinol and 2,4,6-Trihydroxytoluene

When only 1.3 moles of formaldehyde were added to phloroglucinol, formaldehyde consumption rapidly reached 0.8 mole/mole, and GPC showed that large proportions of phloroglucinol had not reacted, while the other portion had polymerized to high molecular weight. Gels were formed after 3-4 hours at pH 4.5 and 6.0 and after only 1.5 hours at pH 7.5. When phloroglucinol was reacted with 2.5 moles of formaldehyde at pH 4.5 and 6.0, formaldehyde consumption immediately reached 1.0 mole/mole and then increased to 1.4 moles/mole after 40 minutes and 1.6 moles/mole after 3 hours. Samples reacted at pH 4.5 and 6.0 gelled after 4 hours. GPC showed that the products were of high molecular weight after only 30 minutes. When reacted with 2.5 moles of formaldehyde at pH 7.5, 1.6 moles of formaldehyde were consumed immediately, and the samples gelled within 1 hour. These phloroglucinol condensation products were not sufficiently soluble to obtain high yields of acetates for GPC.

The 2,4,6-trihydroxytoluene is possibly a better model for the A-ring of catechin-based tannins. When reacted with 1.3 moles of formaldehyde per mole of phenol, 0.78-1.0 mole of formaldehyde was consumed after 5 hours at pH 4.5 and after only 1 hour at pH 7.5. Precipitates were noted after only 1 hour at pH 4.5, and GPC showed that most of the 2,4,6-trihydroxytoluene had polymerized to high molecular weight products after only 15 minutes (fig. 2). When reacted with 1.3 moles of formaldehyde at pH 7.5, precipitates were noted after only 15 minutes, and GPC

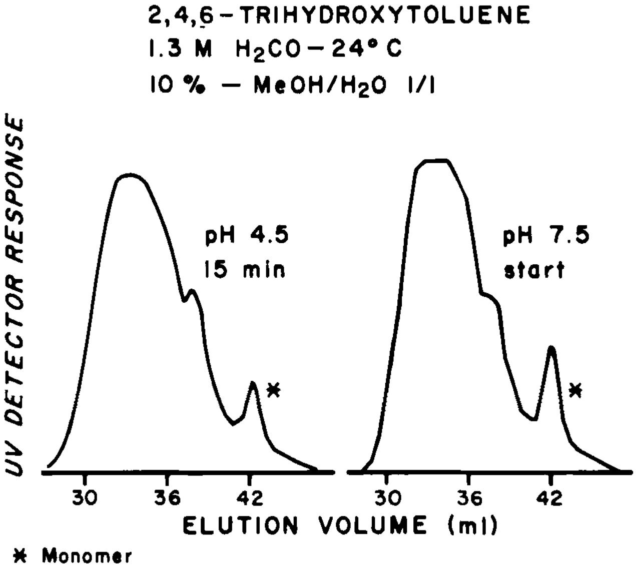


FIGURE 2

showed that high molecular weight products were dominant immediately after addition of the formaldehyde. When 2,4,6-trihydroxytoluene was reacted with 2.5 moles of formaldehyde, 0.8 mole was consumed after only 1 hour at pH 6.0, and at pH 7.5 formaldehyde consumption was about 1 mole/mole immediately. GPC of samples withdrawn after addition of formaldehyde showed extensive polymerization even at pH 4.5. All samples contained substantial portions of precipitates after 15-30 minutes at room temperature.

Resorcinol and 4-Ethylresorcinol

We expected resorcinols to react more slowly than phloroglucinols, but the magnitude of the differences between the rate of condensation of these phenols was greater than anticipated. When resorcinol was reacted with limited formaldehyde (1.3 moles/mole), formaldehyde consumption was not significant at pH levels of 4.5 and 6.0, and at pH 7.5 only 0.47 mole/mole of formaldehyde was consumed after 30 hours at room temperature. Throughout a reaction period of 90 hours, samples remained thin solutions. GPC of the condensation products showed that a substantial portion of the resorcinol remained unreacted, but the other portion polymerized to high molecular weight. When reacted with 2.5 moles of formaldehyde at pH 4.5, there was no consumption of formaldehyde, and at pH 7.5 only 0.83 mole of formaldehyde was consumed after 72 hours of reaction. GPC showed a wide range in molecular weight of the products.

GPC of the condensation products of 4-ethylresorcinol with formaldehyde indicated that polymerization was not significant for over 20 hours at pH 4.5 and 6.0. When reacted with either 1.3 or

2.5 moles of formaldehyde at pH 7.5, 4-ethylresorcinol began to polymerize after 1 hour, but there was still substantial unreacted phenol after 27 hours. To polymerize the majority of the phenol to high molecular weight material (fig. 3), 150 hours of reaction were required.

Catechol and 4-Methylcatechol

GPC of products obtained from the reaction of catechol with formaldehyde indicated that there was no significant condensation after 72 hours at pH 7.5. After several days of reaction, some material was eluted at volumes corresponding to high molecular weight species, but large proportions of catechol remained unreacted. There was also no significant formaldehyde consumption by 4-methylcatechol after 24 hours at room temperature. GPC of

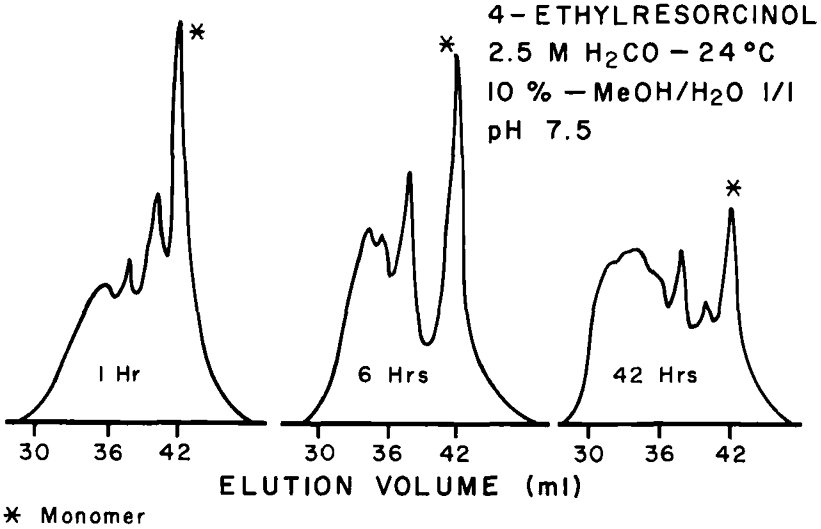


FIGURE 3

condensation products of 4-methylcatechol with formaldehyde (2.5 moles) at pH 7.5 also indicated that significant condensation occurred only after several days of reaction.

Catechin

Formaldehyde consumption by (+)catechin rapidly approached 0.9 mole/mole (1.5 hours at pH 7.5) when either 1.3 or 2.5 moles/mole were added but did not increase further even when reacted with 2.5 moles/mole at pH 7.5 for 20 hours. GPC indicated that catechin had polymerized to high molecular weight products after 4 hours under these conditions. The rate of condensation of catechin was midway between that of 2,4,6-trihydroxytoluene and 4-ethylresorcinol. The pH had a strong influence on the rate of condensation (fig. 4), and

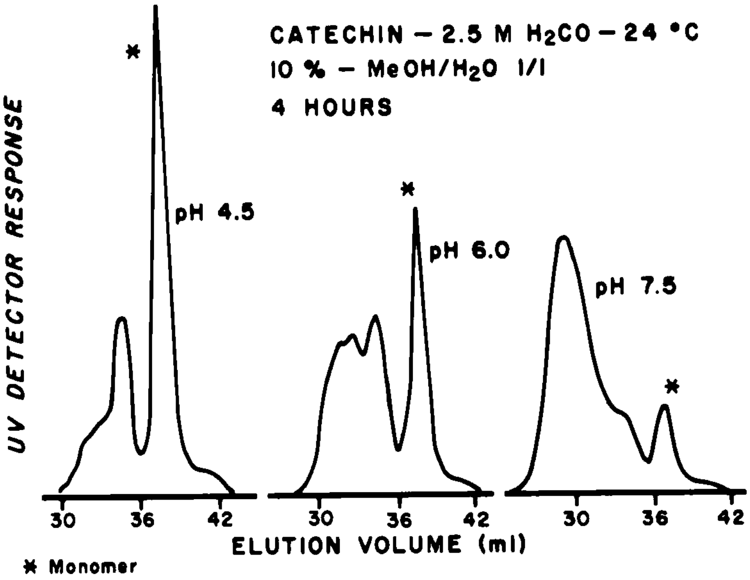


FIGURE 4

it appeared that the condensation might be controllable at pH conditions of 6.0. However, the condensation products precipitated from solution after 2.5 hours at pH 6.0. At pH 7.5, the condensation products remained in solution, and a friable gel which gave a weak solid was obtained when the solvent was allowed to evaporate slowly.

Wide differences in the ratio of (+)catechin and (-)epicatechin units in the polyflavonoids of western hemlock (1:1) (16), Douglas-fir (1:3) (17), and southern pine (1:5) (14,15) have been suggested by thioglycolysis products of bark extracts. There is a strong tendency for hydrogen bonding between the 3-hydroxyl and the pyran ether oxygen (18). In (+)catechin such bonding rotates the catechol B-ring into an axial position, crowding the spacing around the C-8 position. Similar hydrogen bonding in the (-)epicatechin isomer rotates the B-ring into an equitorial plane so that there is no crowding of the C-8 position of the A-ring. Consideration was accordingly given to possible differences in formaldehyde condensation rate associated with stereochemistry of the flavanol, but a comparison of rates of condensation of (+)catechin and (-)epicatechin by GPC or of their condensation products revealed no differences between these isomers.

When the H-NMR spectra of (+)catechin condensation products were measured against a constant total of 15 acetate protons/flavonoid unit, the A-ring proton signal rapidly decreased to about 1 proton/flavonoid unit and then decreased at a much slower rate to undetectable levels (fig. 5A). Catechol B-ring proton signals did not decrease even after 25 hours of reaction with 2.5 moles

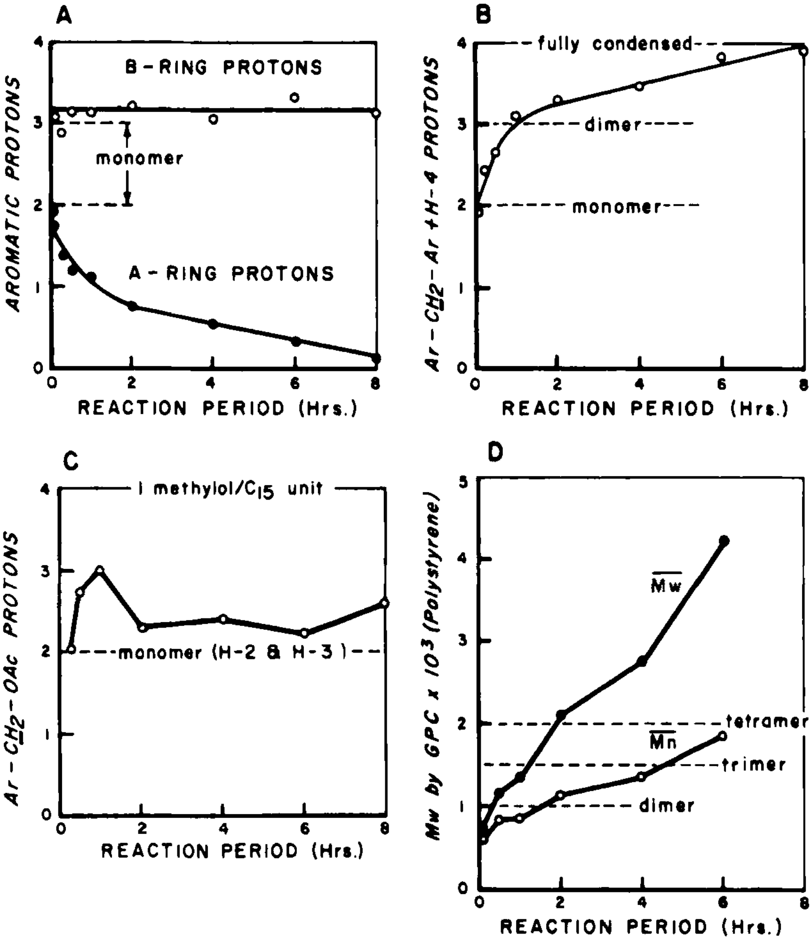


FIGURE 5

of formaldehyde at pH 7.5 when GPC of the condensation products suggested a $\overline{Mn}$ of 2,648 and a $\overline{Mw}$ of 10,600. The increase in the methylene bridge protons (fig. 5B) and estimation of the molecular weight by GPC (fig. 5D) also indicated that a dimer was formed within 1 hour and that further condensation occurred more slowly.

Although the bands were too broad to exclude ether linkages, no distinct signal was observed in this region (δ, 4.2-4.5). In the first hour of reaction, methylol proton signals increased to levels corresponding to 0.5 methylol groups/flavonoid unit but averaged only about 0.2 methylol groups/flavonoid unit later in the reaction (fig. 5C). The condensation products obtained at pH 7.5 appeared to be analogous to phenol-formaldehyde novolacs (H+ catalyzed) rather than resols (OH- catalyzed), where methylolation rather than condensation of methylol-phenols was rate-limiting. The ratio of aliphatic to aromatic acetate protons was generally higher than we expected, suggesting the occurrence of a side reaction. Of particular concern was a base catalyzed rearrangement to catechinic acid similar to that described by Sears et al.(10). Examination of the IR spectra of (+)catechin condensation products showed no significant absorbtion bands in the 1750-1700 cm^{-1} region, so rearrangement to catechinic acid (9) was not extensive.

Our results parallel those of Hillis and Urbach (4), who studied the consumption of formaldehyde by catechin in dioxane solutions. Hillis and Urbach (4) concluded that the 8-methylol-catechin derivative was the major initial reaction product. Roux et al. (1), studying the bromination of catechin, showed that the 8 position was much more reactive than the 6 position. These studies, together with our observations by GPC and H-NMR, indicate that a dimer was formed quickly by condensation via C-8 -- C-8, and that further condensation occurred much more slowly through C-6 -- C-6.

CONCLUSIONS

It seems unlikely that conditions can be found in which relatively stable methylol-tannin resin intermediates can be prepared from southern pine bark tannins. Even in reaction with formaldehyde at mild pH and temperature conditions in alcohol solvents, catechin polymerized to high molecular weight products containing low proportions of methylol groups.

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