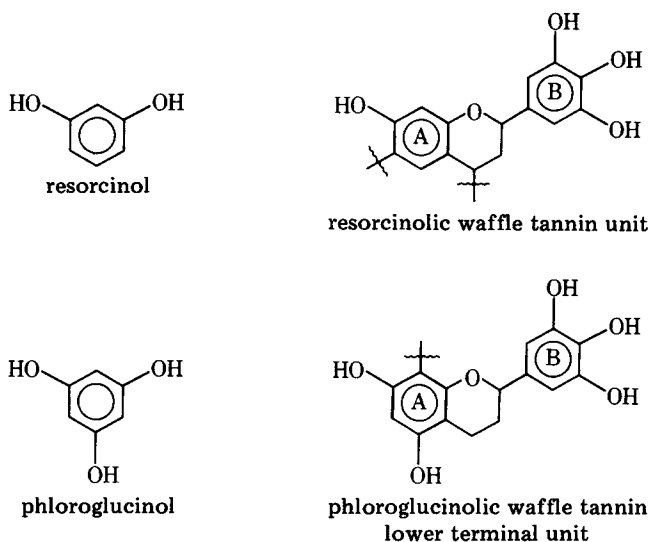


NOTES

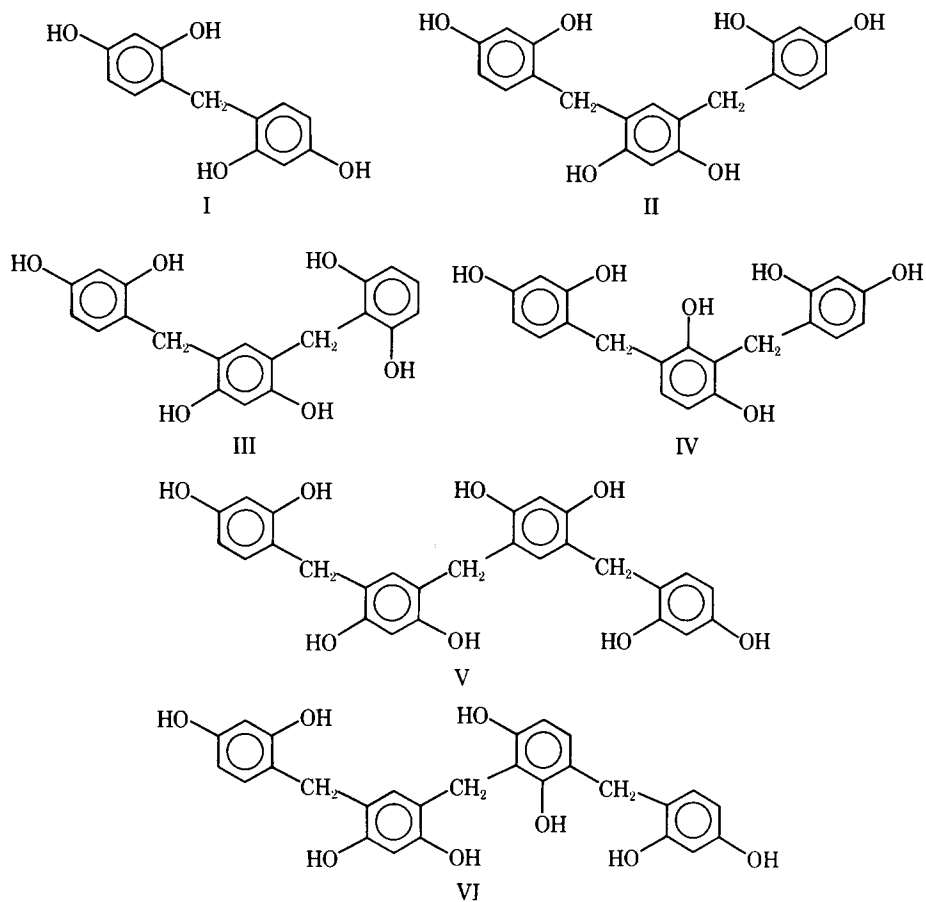
Condensates of Phenol, Resorcinol, Phloroglucinol, and Pyrogallol as Model Compounds of Flavonoid A- and B-Rings with Formaldehyde

INTRODUCTION

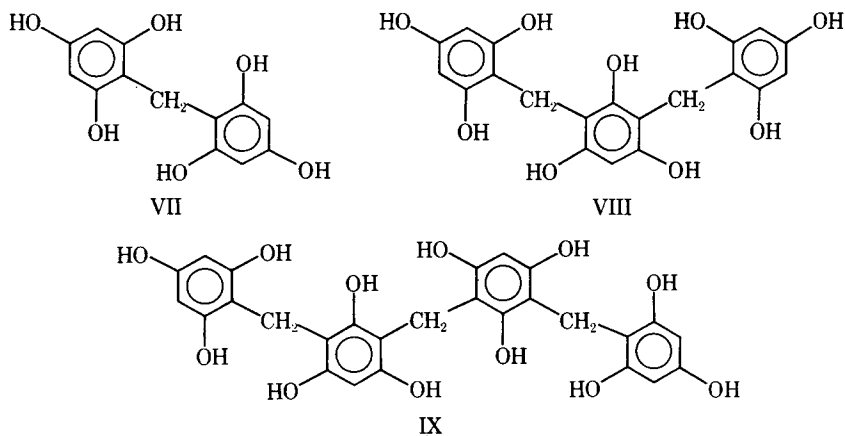
The reaction of polyflavonoid compounds such as wattle tannins with formaldehyde used to produce tannin-based wood adhesives⁵⁻⁷ can be understood more easily by studying the reaction of the constituent phenols with formaldehyde, especially considering that phenol/formaldehyde and resorcinol/formaldehyde condensates are also used as fortifiers for tannin-based adhesives for wood.^{1,5-7} The similarity between structure and reactivity of resorcinol and phloroglucinol with the A-rings and of pyrogallol with the B-rings of wattle tannin units indicates these three phenols as the most appropriate for this study. Particular emphasis was placed on phenol and resorcinol as they constitute the basis of fortifying resins for tannin-based adhesives^{1,5,6}:



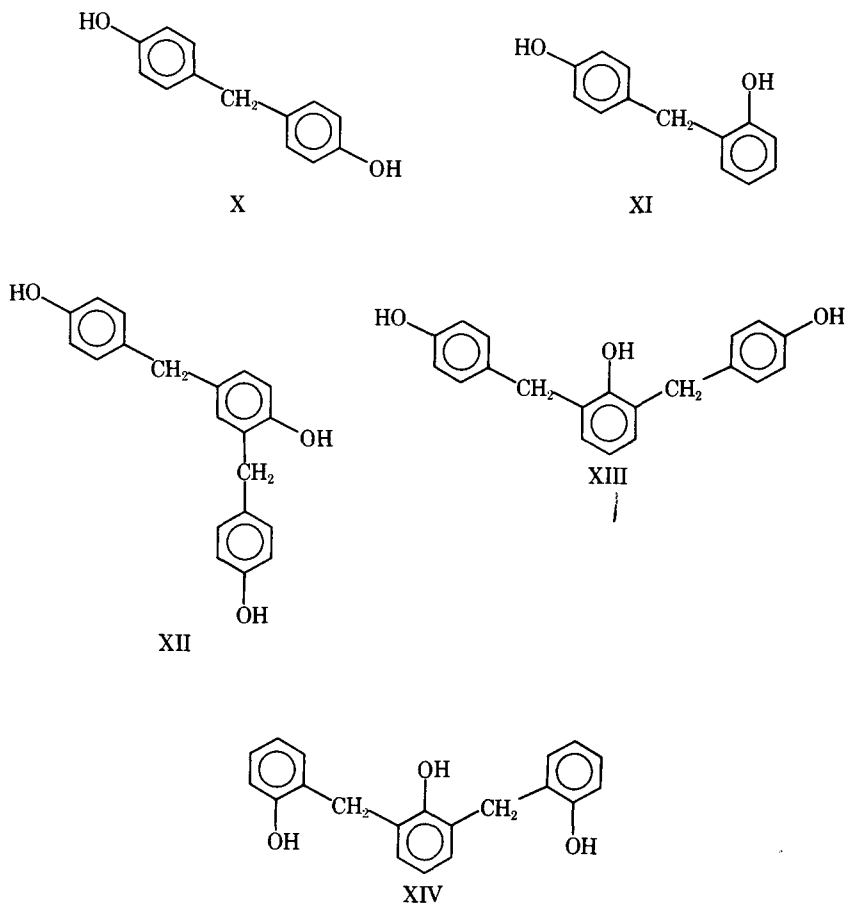
The individual reactions of resorcinol, phloroglucinol and phenol with formaldehyde, at a molar ratio 1:1, and at ambient temperatures, were examined in order to establish to what extent the degree of condensation could be limited to the formation of low molecular weight "oligomers" useful for crosslinking tannins. The reactions were carried out in aqueous methanol and the extent of condensation limited by restricting the amount of formaldehyde added in relation to the different phenols offered, and by applying relatively mild acid or alkaline conditions. In the case of resorcinol, the combination of mass and NMR spectrometry of methylated and unmethylated products permitted unambiguous interpretation of structures I-VI formed under both acid and alkaline conditions:



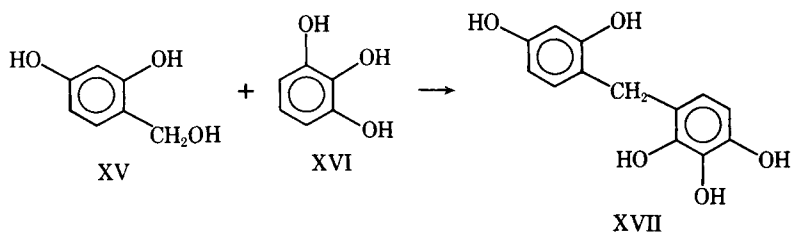
The same approach was repeated with phloroglucinol under acid conditions. Molar quantities of phloroglucinol and formaldehyde and catalytic quantities of trichloroacetic acid were used at ambient temperatures. Column chromatography of the reaction mixture yielded three new products (VII-IX) in addition to unreacted phloroglucinol and small quantities of higher polymers; structural evidence for these compounds was obtained by examination of their methylated derivatives:



The identical reaction with phenol,⁴ under acid conditions and at ambient temperature, proceeds with much greater difficulty (higher activation energy requirement). Due to the lower reactivity of phenol relative to phloroglucinol, mineral acid is necessary for condensation of the former with formaldehyde at ambient temperature. From such reaction only five compounds, two "diphenolic" (X, XI) and three "triphenolic" (XII, XIII, and XIV), could be isolated:



Considering that the basic flavonoid wattle tannin unit consists predominantly of resorcinol linked to either pyrogallol (ca. 70%) or catechol (ca. 30%), it is interesting to have a knowledge of the reactivity of a strong electrophile such as methylolresorcinol [XV, 4-(hydroxymethyl)resorcinol] with a weak nucleophile such as pyrogallol (XVI). By reacting resorcinol with formaldehyde under acid conditions in the presence of an excess of pyrogallol in the molar proportions 1:1:5, it is possible to judge that methylene-bridged condensates (XVII) other than resorcinol-CH₂-resorcinol are formed. Units of type XVII were detected by mass spectrometry:



EXPERIMENTAL

General Experimental Conditions

TLC substrate Kieselgel PF254; TLC spray reagent conc. $\text{H}_2\text{SO}_4:\text{HCHO}$ 38% solution 98:2 (v/v); magnetic mass spectrometer Varian BH5; NMR apparatus 60 MHz Varian.

Resorcinol/Formaldehyde Condensation Under Acid Conditions at Elevated Temperatures

Resorcinol (5.5 g) was dissolved in 80% methanol (25 ml), formaldehyde (40% w/v, 4 ml), and trichloroacetic acid (299 mg) and left for 30 min at 96°C. The reaction mixture was then placed into a separating funnel containing ether (250 ml) and sodium bicarbonate (32 mg). After the extraction the ether extract was washed with water (3×100 ml). After ether evaporation under reduced pressure at 60°C, column chromatography of the product (benzene:acetone 70:30 v/v) yielded 10 fractions. Apart from the two initial fractions which consisted almost entirely of resorcinol, all the others were methylated with diazomethane. The fully methylated fractions were separated by TLC in benzene:acetone (19:1 v/v). Some of the methylated fractions separated in two distinct bands and their R_f were as follows (in order of elution): R_f 0.47 (113 mg, 1 band), 0.47 (14 mg, 1 band), 0.42 (47 mg, 2 bands) 0.42 (87 mg, 1 band), 0.29 (108 mg, 2 bands), 0.42 (14 mg, 1 band), 0.34 (33 mg, 2 bands), 0.24 (11 mg, 2 bands), 0.31 (30 mg, 2 bands).

The different methyl ethers obtained were identified by mass and $^1\text{H-NMR}$ spectrometry as indicated below.

Resorcinol/Formaldehyde Condensation Under Alkaline and Acid Conditions at Ambient Temperatures

5.5 g Resorcinol and 4 ml 40% formaldehyde were treated with 300 mg trichloroacetic acid or with 1 g 40% sodium hydroxide solution, and the condensates obtained were separated by TLC with benzene:acetone (70:30 v/v). The mass and NMR spectra of the unmethylated compounds indicated that the condensates obtained were identical to those found in acid conditions at high temperature.

Identification of Bis(4,6-dimethoxyphenyl)methane

The band, R_f 0.47, cardinal red with the spray reagent, yields colorless needles from methanol. Empirical formula $\text{C}_{17}\text{H}_{20}\text{O}_4$ requires M288. Found: M^+ 288(100), m/e 273(21), 257(51), 241(18), 151(63), 150(27), 137(39), 121(67), $\delta(\text{CDCl}_3)$ 6.92(*d*, 2*x*(2)-H), 6.45(*d*, 2*x*(5)-H), 6.36(*d*. of *d.*, 2*x*(3)-H), 3.82(S, CH_2), 3.79, 3.75(S, 4*x*OMe). $\delta(\text{C}_6\text{D}_6)$, 7.10(*d*, 2*x*(2)-H), 6.50(*d*, 2*x*(5)-H), 6.42(*d*. of *d.*, 2*x*(3)-H), 4.15(S, CH_2), 3.47, 3.41(S, 4*a*OMe). The mass spectrum of the unmethylated condensate is in agreement with that of the methylated condensate. Unmethylated condensate found: M^+ 232(25), m/e 123(58), 110(69), 109(15).

Identification of 4,6-Bis(4'-dimethoxybenzyl)-di-O-methylresorcinol

The band, R_f 0.42, cardinal red with the spray reagent, yields colorless needles from methanol. Empirical formula $\text{C}_{26}\text{H}_{30}\text{O}_6$ required M438. Found: M^+ 438(100), m/e 407(10), 301(26), 288(60), 287(100), 271(10), 257(23), 241(13), 151(100), 150(43), 137(34), 121(72). $\delta(\text{CDCl}_3)$, 6.92(*d*, 2*x*(2')-H), 6.72(S, 5-H), 6.45(*d*, 2*x*(5')-H), 6.43(*d*, 2-H), 6.40(*d*. of *d.*, 2*x*(3')-H), 3.92(S, 2*x* CH_2), 3.85, 3.82, 3.77(S, 6*x*OMe). Mass spectrum of unmethylated compound show same fragmentation. Found: M^+ 354(5), m/e 244(7.5), 232(60), 123(81), 110(100).

Identification of 2,6-Bis(4'-dimethoxybenzyl)-di-O-methylresorcinol

The band, R_f 0.29, cardinal red with the spray reagent, yields colorless needles from methanol. Empirical formula $\text{C}_{26}\text{H}_{30}\text{O}_6$ requires M438. Found: M^+ 438(56), m/e 424(42), 407(7), 301(17), 288(33), 287(86), 273(20), 257(10), 255(16), 241(9), 152(100), 150(24), 138(56), 137(40), 121(43). $\delta(\text{CDCl}_3)$, 7.01(*d*. of *d.*, 5-H), 6.88(*d*, 2*x*(2')-H), 6.40(*d*, 2*x*(5')-H), 6.39(*d*, 4-H), 6.34(*d*. of *d.*, 2*x*(3')-H), 3.87(S, 1- CH_2), 3.82(S, 1- CH_2), 3.77, 3.75, 3.68, 3.65(S, 6*x*OMe). Mass spectrum of unmethylated compounds show identical fragmentation. Found: M^+ 354(2), m/e 232(15), 123(66), 110(54).

Identification of 6-[(4'6'-Dimethoxybenzyl)-2,4-dimethoxyphenyl]-di-O-methylresorcinol

The band, R_f 0.31, cardinal red with the spray reagent, yields colorless needles from methanol. Empirical formula $C_{26}H_{30}O_6$ requires M438. Found: M^+ 438(5.5), m/e 407(3), 301(17) 288(16), 287(87), 271(3), 257(3), 255(5), 241(5), 151(100), 150(22), 137(16), 121(49). δ ($CDCl_3$), 7.00(d , 5'-H), 6.88(d , 2'-H), 6.70(s , 5-H), 6.40(d , 2x(5')-H), 6.45-6.20(3'-H, 4'-H, 2-H, 3''-H, 4''-H), 3.80, 3.77, 3.75, 3.66, 3.61(s , 6xOMe).

Identification of Bis((4'6'-dimethoxybenzyl)-2,4-dimethoxyphenyl)methane

The band, R_f 0.34, cardinal red with the spray reagent, yields colorless needles from methanol. Empirical formula $C_{35}H_{40}O_8$ requires M588. Found: M^+ 588(22), m/e 452(16), 438(61), 424(4), 407(5), 301(31), 288(34), 287(100), 271(10), 257(6), 241(9), 152(100), 150(100), 150(35), 138(23), 137(21), 121(51). δ ($CDCl_3$), 6.87(d , 2x(2')-H), 6.69(s , 2x(6)-H), 6.42(d , 2x(5')-H), 6.40(d , 2x(3)-H), 6.33(d . of d ., 2x(3')-H), 3.87(s , 3x CH_2), 3.78, 3.75, 3.68, 3.65(s , 4a(2sOMe)).

Identification of ((4'6'-Dimethoxybenzyl)-2,4-dimethoxyphenyl)-[(4'6'-dimethoxybenzyl)-2,6-dimethoxyphenyl]methane

The band, R_f 0.24 cardinal red with spray reagent, yields colorless needles from methanol. Empirical formula $C_{35}H_{40}O_8$ requires M588. Found: M^+ 588(46), m/e 452(15), 438(61), 424(10), 407(8), 301(31), 288(32), 287(100), 271(10), 257(5), 241(7), 151(100), 150(31), 137(25), 121(50). δ ($CDCl_3$), 6.96(d , 4''-H), 6.85(d , 2x(2')-H), 6.77(s , 6-H), 6.43(s , 3-H), 6.40(d , 3''-H), 6.38(d , 2x(5')-H), 6.32(d . of d ., 2x(5')-H), 6.32(d . of d ., 2x(3')-H), 3.88, 3.78, 3.74, 3.67, 3.58(s , 2x(2xOMe) +4xOMe).

Phloroglucinol/Formaldehyde Condensation Under Acid Conditions

Phloroglucinol (6.48 g) was dissolved in 80% methanol (25 ml), formaldehyde (40% w/v, 3.24 ml) and trichloroacetic acid (63 mg) and stirred for 2 hr at room temperature. The reaction mixture was then placed into a separating funnel containing ether (250 ml) and sodium bicarbonate (32 mg). The ether extract was washed with water (3 \times 100 ml). After ether evaporation under reduced pressure at 60°C column chromatography (benzene:acetone 6:4 v/v) yielded four fractions: R_f 0.47 (unreacted phloroglucinol), 0.41 (1.7291 g, 16.4%), 0.36(0.9106 g, 5.6%) and 0.28(40 mg, 0.19%), all orange-yellow when sprayed with $H_2SO_4:HCHO$ 99:1 TLC reagent. The fractions R_f 0.41 (100 mg), 0.36 (100 mg) and 0.28 (40 mg) yielded after individual methylation with dimethyl sulfate and TLC separation (dichloroethane) the three methyl ethers R_f 0.60, 0.38, and 0.29 respectively. They were identified by mass and 1H NMR spectrometry.

Identification of Bis(2,4,6-trimethoxyphenyl)methane

The band, R_f 0.60, yellow brown with the spray reagent, yields colorless needles (107 mg, 81%) from ethanol mp 116.8°C. Found: C, 65.6; H, 7.1, M^+ 348,157. Empirical formula $C_{19}H_{24}O_6$ requires C, 65.6; H, 6.9%, M 348,157. Found: M^+ 348(36), m/e 317(11), 181(100), 167(41), 150(II), 149(79), 137(10), 136(12). δ ($CDCl_3$), 6.09(s , 2x(3-5)-H), 3.89(s , CH_2), 3.68, 3.74(d , 6 α OMe); δ (C_6D_6), 6.15(s , 2x(3-5)-H), 4.40(s , CH_2), 3.78, 3.75(s , 6xOMe).

Identification of 2,6-Bis(2',4',4'-trimethoxybenzyl)-tri-O-methylphloroglucinol

The band, R_f 0.38, yellow brown with spray reagent, yields light-yellow needles (119 mg, 90.8%) from ethanol, mp 152.5°C. Found: C, 66.1; H, 7.0, M^+ 528,234. Empirical formula $C_{29}H_{36}O_9$ requires C 65.9, H 6.8%, M528,236. Found: M^+ 538(54), m/e 362(15), 361(25), 348(10), 347(33), 316811), 136(10). δ ($CDCl_3$), 6.20 (s , 4-H), 6.10(s , 2x(3' + 5')-H), 3.87(s , 2x CH_2), 3.91(s , 1-OMe), 3.60(s , 8xOMe); δ (C_6D_6), 6.13(s , 4-H + 2x(3' + 5')-H), 4.33(s , 2x CH_2), 3.07(s , 1-OMe), 3.58, 3.40, 3.30(s , 5xOMe).

Identification of Bis(3-(2',4',6'-trimethoxybenzyl)-2,4,6-trimethoxyphenyl)methane

The band, R_f 0.29, yellow brown with spray reagent, yields white needles (27 mg, 51.5%), mp 184–185°C. Found: M^+ 708,315. Empirical formula $C_{39}H_{48}O_{12}$ requires M 708,315. Found: M^+ 708(26) m/e 615(16), 528(26), 527(22), 348(40), 347(15), 181(100), 180(40), 168(27), 167(19), 151(14), 136(10). δ ($CDCl_3$), 6.13(broad s, 6x Ar-H), 3.87, 3.80. 3.73, 3.71(s, 12x OMe + 6x CH_2).

Phenol/Formaldehyde Condensation Under Acid Conditions

Phenol (9.411 g) was dissolved in 80% methanol (25 ml), formaldehyde (40% w/v, 6.3 ml), and hydrochloric acid (10N, 10 ml) and stirred for 24 hr at ambient temperature. The reaction mixture was then placed into a separating funnel containing ether (250 ml) and sodium bicarbonate (8.8211 g). The ether extract was washed with water (3 \times 100 ml). After ether evaporation under reduced pressure at 60°C a column chromatography separation (benzene:acetone 9:1 v/v) yielded six fractions, R_f 0.65 (unreacted phenol, 0.60(1.6601 g, 8.3%), 0.51(1.215 g, 6.1%), 0.42(1.8096 g, 5.2%), 0.33(2.7492 g, 7.9%), and 0.19(1.7052 g, 4.9%). The fractions R_f 0.60, 0.51, 0.42, 0.33, and 0.19 yielded after individual methylation (100 mg per fraction) with dimethyl sulfate and TLC separation (benzene:hexane 8:2 v/v) and five methyl ethers R_f 0.59, 0.51, 0.48, 0.40, and 0.29, respectively.

Identification of Bis(4-methoxyphenyl)methane

The band R_f 0.59, pink with spray reagent, yields a light-brown oil (106 mg, 0.3%). Found M^+ 288,115. Empirical formula $C_{15}H_{16}O_2$ requires M 228,115. Found: M^+ 228(100), m/e 197(96), 166(16), 121(57), 107(5,8), 91(19). δ ($CDCl_3$), 7.07(*d*, 2 + (2' + 6')-H, *J* 8,6) 6.77(*d*, 2x(3' + 5')-H, *J* 8,6), 3.61(s, CH_2), 3.64(s, 2x OMe), (Plate 18). δ (C_6D_6) 7.05(*d*, 2x(2' + 6')-H, *J* 9,2), 6.8(*d*, 2x(3'5')-H, *J* 9,2), 3.75(s, CH_2), 3.53(s, 2x OMe).

Identification of 2,4'-Dimethoxydiphenylmethane

The band, R_f 0.51, pink with spray reagent, yields a light-yellow oil (99 mg, 86%). Found: M^+ 288,113. Empirical formula $C_{15}H_{16}O_2$ requires M 228,115. Found: M^+ 228(100), m/e 197(89), 166(10), 122(13), 121(69), 107(8.1), 91(19). δ ($CDCl_3$), 7.07(*d*, (2' + 6')-H, *J* 8.4), 6.73(*d*, (3' + 5')-H, *J* 8,4), 6.67–7.30(*m*, (3-4-5-5)-H), 3.9(s, CH_2), 3.7, 3.3(s, 2x OMe); δ (C_6D_6), 7.07(*d*, (2' + 6')-H, *J* 8,4), 6.98(*d*, (3' + 5')-H, *J* 8,4), 6.43–7.31(*m*, (3-4-5-6)-H, 4.00(s, CH_2), 3.30(s, 2x OMe).

Identification of 2,4-Bis(*p*-methoxybenzyl)anisole

The band, R_f 0.48, pink with spray reagent, yielded a light-yellow oil (98 mg, 86%). Found: M^+ 348,172. Empirical formula $C_{23}H_{24}O_3$ requires M 348,173. Found: M^+ 348(86), m/e 317(16), 286(10), 241(27), 229(88), 228(12), 121(100), 108(12), 107(14). δ ($CDCl_3$), 6.63–7.21 (*m*, 2x(2' + 3'5' + 6')-H), 7.08(*dd*, 5-H, *J* 8.0 and 3.2), 6.87&*d*, 3-H, *J* 3.2), 3.78(*d*, 6-H, *J* 8.0), 3.88, 3.81(s, 2x CH_2), 3.77(s, OMe); δ (C_6D_6) 6.47–7.23 (*m* 11x Ar-H), 4.00(s, CH_2 (I)), 3.73(s, CH_2 (II)), 3.4, 3.37, 3.35(s, 3x OMe).

Identification of 2,6-Bis(*p*-methoxybenzyl)anisole

The band, R_f 0.40, pink with spray reagent, yielded a light-yellow oil (101 mg, 88%). Found: M^+ 348,171. Empirical formula $C_{23}H_{24}O_3$ requires M 348,173. Found M^+ 348(57), m/e 317(12), 286(11), 241(41), 227(18), 121(100), 108(12), 107(21). δ ($CDCl_3$) 7.13(*d*, 2x(2' + 6')-H, *J* 8.2), 6.81(*D*, 2x(3' + 5')-H, *J* 8.2), 6.70–7.10(*m*, 4-H), 6.94(s, (3-5)-H). δ (C_6D_6), 7.11(*d*, 2x(2' + 6')-H, *J* 8,2), 6.77(*d*, 2x(3' + 5')-H, *J* 8,2), 6.66–2.6 (*m*, 4-H), 6.96(s, (3-5)-H).

Identification of 2,6-Bis(*o*-methoxybenzyl)anisole

The band, R_f 0.29 pink with spray reagent, yielded a light yellow oil (109 mg, 59.8%). Found: M^+ 348,172. Empirical formula $C_{23}H_{24}O_3$ requires M 348,173. Found: M^+ 348(47), m/e 317(11), 286(19), 241(39), 277(11), 228(13), 121(100), 108(11), 107(29). δ ($CDCl_3$), 6.63(*m*, 11x ArH), 3.83(s, 2x CH_2), 3.75(s, 3x OMe). δ (C_6D_6), 6.45–7.08(*m*, 11x Ar-H), 4.01(s, 2x CH_2), 3.37(s, 3x OMe).

Pyrogallol/Resorcinol/Formaldehyde Condensation Under Acid Conditions

Resorcinol (1.1 g) and pyrogallol (6.3 g) were dissolved in 80% methanol (25 ml), formaldehyde (40% w/v, 4 ml) and trichloroacetic acid (400 mg) and left for 16 hr at ambient temperature. The reaction mixture was separated by TLC(70:30 benzene:acetone v/v) and yielded bands of different R_f . With the exception of the unreacted resorcinol and unreacted pyrogallol bands two higher R_f bands were scraped off the TLC plate, washed with acetone, and dried on a rotary evaporator. The mass of the unmethylated compounds indicated one of the bands to be a resorcinol-CU₂-resorcinol oligomer already isolated in the resorcinol/formaldehyde condensation. The other R_f band condensate appeared to be a resorcinol-CU-pyrogallol condensate of empirical formula C₁₃H₁₂O₅ presenting the following mass spectrum: M⁺ 248(100); *m/e*, 231(55), 139(57), 125(23), 123(59), 122(62), 109(27), 106(66).

CONCLUSIONS

From the condensates formed it is notable that the reactivity of the two main sites (4 and 6) of resorcinol is reflected, leading to linear condensates only. However, reaction with the remaining reactive but sterically hindered site (2-position) between the hydroxyl functions is also observed (III, IV, and VI), and condensates involving all the types of reactive sites (2, 4, and 6) were isolated (VI). The trimers II, III, and IV could all originate from the dimer I, the symmetrical tetramer V from the predominant trimer II, and the unsymmetrical tetramer VI from either of the unsymmetrical trimers II and IV. In relation to the weights isolated and on a molar basis, the proportion of 4-plus 6-linkages relative to 2-linkages is of the order 10.5:1. Cognizance must however be taken of the fact that the first-mentioned pair represents two condensation sites relative to one. Difference in reactivity of the two types of reactive sites, i.e., 4- or 6-position relative to the 2-position is accordingly of the order of 5:1. Linear compounds appear to be formed in preference to branched compounds. Alternative structures with molecular mass identical to V and VI could be visualized as theoretically formed by attack on the central resorcinol ring of compounds III and IV. Such structures were not isolated. The reason for the preferred terminal attack lies in (i) the presence of two reactive nucleophilic centers on the terminal units as opposed to single centers of doubly bound units already in the chain, (ii) the greater steric hindrance and therefore lower reactivity of the available nucleophilic center of the doubly bound units (always 2-position; see III and IV) as opposed to the lower steric hindrance and therefore higher reactivity of at least one of the nucleophilic centres of the terminal units (a 4- or 6-position always available), and (iii) the lower mobility of doubly bound units imposing further limitations on their availability for reaction. The mixture of resorcinol/formaldehyde condensates of varying "short" chain lengths coupled with some unreacted resorcinol has proved invaluable in crosslinking wattle tannins in cold-setting applications,⁵⁻⁷ since different chain lengths would presumably be more effective in crosslinking reactive centers on tannins, thus meeting with the demands of different interatomic distances. The absence of methylol (HOCH₂-) groups on all the six compounds isolated reflects the reactivity of resorcinol under acidic conditions and the instability of the *p*-hydroxybenzyl alcohol groups and their conversion to *p*-hydroxybenzyl carbonium ions or quinone methides. This may explain the similar course of the condensations under both acid and alkaline conditions. Structural evidence for compounds I-VI was obtained by examination of their fully methylated derivatives.

In the case of phloroglucinol the electron-donating property through resonance of the three hydroxyl groups of the phloroglucinol ring placed meta to each other enhances the nucleophilic property of the unsubstituted positions of the ring, thus increasing its ease of attack by the protonated formaldehyde molecule. An alternative isomeric and symmetrical tetranuclear structure could be visualized, with molecular mass identical to IX, theoretically formed by attack on the central phloroglucinol ring of compound VIII. This structure was not isolated. The reason for the continued if somewhat surprising terminal attack lies in the observation that, as in the case of resorcinol, terminal units offer two highly reactive nucleophilic centers as opposed to single centers of doubly bound units already in the chain, and also the restraints of reduced mobility as suggested before. Thus, linear compounds appear to be found in preference to branched compounds. This is important, because such linear molecules may impart plasticity to adhesives resins. The isolation of these di-, tri-, and tetranuclear compounds (VII, VIII, IX) indicates that the phloroglucinol/formaldehyde condensation may be suitable for the formation of fortifiers for wattle-based adhesives, apart perhaps for cost considerations. The greater nucleophilic properties of phloroglucinol rather than resorcinol could severely bias the competitive reaction for formaldehyde between phloroglucinol/formaldehyde

condensates and wattle polyflavonoids A-rings which are mainly resorcinolic in nature. Competition for the free formaldehyde, during the adhesive curing process, could occur between phloroglucinol/formaldehyde condensates and the phloroglucinolic A-ring of the wattle polyflavonoid lower terminal unit. However, doubts should be expressed as regards the participation to this reaction of the resorcinolic A-rings of flavonoids other than the phloroglucinolic ones of the lower terminal units. Since in the case of wattle tannins resorcinolic A-rings outnumber phloroglucinolic A-rings by approximately 4 to 1, crosslinking will probably be achieved, but not to an extent sufficient to produce strong adhesives. Cold-setting wattle-based adhesives prepared by substituting phloroglucinol for resorcinol were proved to be weak.⁶

In the case of phenol, compound XIII could only arise from the bisphenol XI, whereas XII could originate from either XXI or XXII. Compound XX could not originate from any of the two bisphenols isolated. Because a tetranuclear compound apparently does not form, it is probable that the reaction accelerates after formation of the trinuclear condensate. Structural evidence for compounds XVI to XX was obtained by examination of their methylated derivatives. From the phenol/formaldehyde condensates obtained, it is possible to see that formation of resorcinol terminated phenol/formaldehyde fortifiers for tannin adhesives is not possible, as expected, in the acid field, contrary to what has been already found in alkaline-catalyzed reactions of the same type. This is due to the absence of methylol groups in acid-catalyzed phenol/formaldehyde condensates.

In the case of pyrogallol the compound identified by mass spectrometry is a pyrogallol/resorcinol/formaldehyde condensate of structure XVII. This is significant in relation to adhesives preparation because it indicates that also the less reactive B-rings of wattle tannin flavonoids should participate in the reaction with formaldehyde under mild acid or alkaline conditions, in contrast to the very drastic alkaline conditions recommended by previous authors for such a reaction.^{2,3}

The relative reactivities toward formaldehyde of resorcinol, phloroglucinol, and phenol give an indication of the probable behavior of the different reactive centers of flavonoid units in reacting with formaldehyde. The A-rings of the flavonoid lower terminal units, phloroglucinolic in nature, should be the first to react with formaldehyde followed by the resorcinolic A-rings of the other flavonoid units. Only a small amount of the pyrogallolic and catecholic B-rings should react with formaldehyde, and their contribution to the network crosslinking will be present, but limited.

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