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The Phenolic Extractives in Southern Red Oak (*Quercus falcata* Michx. var. *falcata*) Bark

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Summary

The bark of southern red oak (*Quercus falcata* Michx. var. *falcata*) is a rich source of quercitrin (quercetin-3-rhamnoside). It contains only low concentrations of (+)-catechin and no significant amounts of epicatechin or gallocatechin. The three major dimeric proanthocyanidins present are epicatechin-(4β→8)-catechin, catechin-(4α→8)-catechin and the 3-gallate ester of epicatechin-(4β→8)-catechin. No biphenyl-linked dimers and no flavan-3-ol- or proanthocyanidin-glycosides are evident. The higher molecular weight acetone-water soluble tannins are polymeric procyanidins predominantly made up of 2,3-*cis* chain extender units and terminated with the 2,3-*trans* (+)-catechin. The polymers contain only small amounts of 2,3-*trans* procyanidins chain extender units and only traces of prodelphinidin units. Although a gallate ester of a dimer is present in significant amounts, neither gallate esters of higher molecular weight procyandins nor hydrolysable tannins are detectable through reaction products or IR and ^{13}C-NMR spectral studies.

Introduction

Southern red oak (*Quercus falcata* Michx. var. *falcata*) is the most important species of the red oaks in the forests of the southern United States. It constitutes approximately 8.1% (amounting to 4 billion cubic feet) of the total hardwood volume on upland sites being surpassed in volume only by sweetgum (*Liquidambar styraciflua* L.) (13.2%), white oak (*Quercus alba* L.) (12.3%) and hickory (*Carya* sp.) (8.5%) (Koch 1985). The bark content of southern red oak trees 5–22 inches in diameter growing in Tennessee averaged 19% of the green weight and 22% of the dry weight of the total tree (Clark, Phillips, and Hitchcock 1980). The anatomy of southern red oak bark has been studied by Howard (1977), Nankano and Cote (1980), as well as by Manwiller (1977). The tannin content in the bark of southern red oak has been variously reported over a range of 6.4 to 11.2% (Rowe and Conner 1979, Schroeder 1978).

Extracts from barks of the red oaks (principally *Quercus tinctora*) were historically very important exports from the American colonies to England where they were used to make a yellow dye called quercitrin (quercetin-3-rhamnoside, Fig. 1, 1) (Ryan 1971). Red oak bark extracts have been used to treat sore throat and burns (Krochmal, Walters and Doughty 1969), dysentery, pulmonary and uterine hemorrhage, and fever (Morton 1973). Oral ingestion of these extracts, as other high tannin content preparations, has been linked to esophageal cancer (Morton 1973). Extracts from the barks of red oaks generally are reported to contain gallic acid, (+)-catechin (2), (+)-gallocatechin, leucopelargonidin, leucocyanidin, leucodelphinidin, and condensed tannins based on catechin-gallocatechin polymers (Fig. 1, 3) (Rowe and Conner 1979). In the red oaks, condensed tannins are normally found in the bark while hydrolysable tannins are found in the wood of the same species. However, Mayer and Loebich (1965) have reported the presence of a hydrolyzable tannin, hamamelitannin, in the bark of *Quercus rubra*.

The tannins of southern red oak bark are of renewed interest because increasing amounts of oaks are being pulped in the southeastern United States. Substantial amounts could become available at wood hydrolysis plants such as the Tennessee Valley Authority's pilot plant in Muscle Shoals, Alabama, should wood hydrolysis become commercially viable (Strickland 1986). The phenolic extractives in southern red oak bark have not been described in any detail.

Experimental Section

Thin layer chromatography

The elution of compounds from the Sephadex**) columns was monitored by cellulose thin-layer chromatography (TLC) on Bakerflex-Cellulose F plates developed in one dimension with 6% acetic acid (6HA). Two-dimensional chromatography (2D-TLC) was used to test the purity of the isolate by developing the plates (10 × 10 cm) first with t-BuOH-acetic acid-water (3:1:1, v/v/v; TBA) and then in

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the second dimension with 6HA. Compounds were visualized by spraying the plates with vanillin-HCl and heating, with diazotized sulfanilic acid, or with ferric chloride-potassium ferricyanide. Preparative TLC of acetate derivatives was performed using thick (0.75 mm) Si-gel (Baker 7G) developed with benzene-acetone (9:1, 8:2 or 7:3, v/v).

^{1}H- and ^{13}C-NMR spectra

Spectra of the phenolic isolates were recorded in acetone-d_6-D_2O (ca. 1:1, v/v) or methanol-d_4 using either a Varian FT-80A or a Bruker WM-250 spectrometer. ^{1}H- and ^{13}C-NMR spectra of acetate derivatives were recorded in chloroform-d using a Varian FT-80A spectrometer.

IR Spectra

IR spectra of KBr disks containing 1 to 2% of the tannin isolates were recorded using a Perkin Elmer 1420 spectrometer.

Extraction and isolation of compounds

Extraction of the finely ground whole bark collected from three southern red oak trees with acetone-water (70:30, v/v) at ambient temperature for several days gave a red-brown solid in a yield of 10.2% of the bark dry weight. Other samples of inner, middle, and outer bark were isolated by scraping the bark off in the rough, dark colored layer as outer bark, a transition zone as middle bark, and the light colored bark down to the cambium as inner bark. Air-dried samples of inner, middle, and outher bark were soaked in acetone-water (1:1, v/v) for several days and the extract was recovered by filtration. A purified isolate of the water-soluble tannin was prepared from each extract by dispersing the crude acetone-water extract in methanol-water (1:1, v/v), filtering off a yellow amorphous solid, and separating on a Sephadex LH-20 column (2.5 × 80 cm) by eluting with methanol-water until the eluate was colorless and then eluting the absorbed tannins from the column with acetone-water (1:1, v/v). The fractions were freeze-dried and weighed. In addition, the acetone-water soluble extracts were partitioned between ethyl-acetate and water to isolate further low molecular weight proanthocyanidin oligomers.

The product obtained from the methanol-water eluate (about 2 gm portions) was separated by chromatography on Sephadex LH-20 (2.5 × 80 cm) columns eluted with ethanol. Fractions (ca. 7 mL) were collected and those containing predominantly one compound were combined and rechromatographed on a Sephadex LH-20 column (1.5 × 80 cm) eluted with ethanol-water (1:1, v/v). Several of these separations were performed in order to obtain sufficient quantities of the dimeric procyanidins. Typically, the yellow pigment (quercitrin) was collected in fractions 14-20, catechin was collected in fractions 21-32, a mixture of proanthocyanidins was collected in fractions 45-70, and higher molecular weight oligomers were eluted in fractions 72-110. No other vanillin-HCl reactive compounds were detected by cellulose TLC.

The isolates of fraction 45-70 containing compounds (4) and (5) were combined (1.395 gm) and separated on a Sephadex LH-20 column (1.5 × 80 cm) by elution with ethanol-water (1:1, v/v). After repeated separations, with the dimer (4) eluting typically from fractions 35-50 and the dimer (5) in fractions from 50-70, pure compounds were obtained.

The compound (6) was isolated from the ethyl acetate-soluble fraction of the acetone-water eluate. Chromatography on a Sephadex LH-20 column (2.5 × 80 cm) by elution with ethanol gave a pure isolate in fractions 160 to 200.

Compound (1)

A sample of the inner bark was extracted with acetone-water (70:30, v/v) and the crude extract, when redissolved in methanol-water, gave large amounts of a yellow precipitate. The precipitate was collected by filtration and reprecipitated from ethanol-water. Chromatography (2D-TLC) showed a yellow spot at Rf 0.80 and 0.25 that gave a yellow reaction with sulfanilic acid and a blue reaction with ferric chloride-potassium ferricyanide. ^{13}C-NMR in dimethylsulfoxide-d_6 showed δ: 17.6 (C-6r*), 70.0 (C-5r), 70.3 (C-2r), 70.5 (C-3r), 71.3 (C-4r), 101.8 (C-1r), 93.5 (C-8q), 98.6 (C-6q), 104.1 (C-10q), 115.4 (C-2'q), 115.7 (C-5'q), 120.9 (C-1'q), 121.0 (C-6'q), 134.3 (C-3q), 145.1 (C-3'q), 148.3 (C-4'q), 156.4 (C-9q), 157.1 (C-2q), 161.2 (C-5q), 164.1 (C-7q), 177.6 (C-4q). This spectrum is consistent for quercetin-3-rhamnoside (Fig. 1, 1), by comparison to chemical shifts reported in the literature (Markham 1982).

Compound (4)

A tan-colored product with Rf values of 0.41 in TBA and 0.56 in 6HA on 2D-TLC was isolated as described above. ^{13}C-NMR in methanol-d_4 showed δ: 27.4 (C-4b*), 37.1 (C-4t), 68.5 (C-3b), 73.1 (C-3t), 77.0 (C-2t), 82.3 (C-2b), 95.9 (C-8t), 96.3 (C-6t), 97.0 (C-6b), 101.3 (C-10t, b), 108.0 (C-8b), 115.0 and 115.3 (C-2't, b), 116.0 and 116.1 (C-5't, b), 119.4 and 119.9 (C-6't, b), 132.2 and 132.7 (C-1't, b), 145.4 and 145.7 (C-3' and C-4') and a group of signals from 155.5 to 158.2 (C-5, C-7, and C-9). The acetate was made by reaction with acetic anhydride in pyridine. After preparative TLC on Si-gel with benzene-acetone (8:2, v/v; Rf 0.47) a white amorphous solid was obtained: Found C = 59.97, H = 4.86; $C_{50}H_{46}O_{22}$ requires C = 60.1, H = 4.65%. ^{13}C-NMR in chloroform-d showed δ: 20.4 (acetate CH_3), 27.0 (C-4b), 34.0 (C-4t), 68.4 (C-3b), 70.9 (C-3t), 73.6 (C-2t), 78.3 (C-2b), 107.1 (C-8t), 108.5 (C-6t), 110.6 (C-6b), 111.4 and 113.4 (C-10t, b) and 117.0 (C-8b) a group of signals from 122.2 to 125.3 (C-2', C-5' and C-6'), 134.45 and 136.3 (C-1'), 141.8-155.4 (C-5, C-7, C-3', C-4' and C-9), 167.6-169.6 (acetate C = O). The spectra of both the phenolic and acetate forms of this compound were consistent for the procyanidin dimer, epicatechin-(4β->8)-catechin (Fig. 1, 4) (Hemingway, Foo and Porter 1982, Hemingway *et al.* 1983). The ^{1}H-NMR spectrum was identical with that published previously (Weinges, Goritz and Nader 1968), the more improtant features being the pattern of the heterocyclic ring protons at δ 4.1 to 5.4 ppm which shows $J_{2,3} < 2$ Hz for the top unit and $J_{2,3} \sim 10$ Hz for the bottom unit.

Compound (5)

A tan colored product (Rf 0.41 in TBA and 0.44 in 6HA; 2D-TLC) was isolated as described above. ^{13}C-NMR in methanol-d_4 showed δ: 28.3 and 28.6 (C-4b, two rotamers), 38.5 (C-4t), 68.5 and 68.8 (C-3b, two rotamers), 73.6 (C-3t), 82.3 and 82.8 (C-2b, two rotamers), 83.8 (C-2t), 96.2 (C-8t), 96.9 (C-6t), 97.4 and 97.6 (C-6b, two rotamers), 102.2 and 107.2 (C-10t, b), 108.1 (C-8b), 115.1-116.3 (C-2' and C-5'), 119.9-121.0 (C-6'), 131.8-132.5 (C-1'), 145.5-145.9 (C-3' and C-4') and 154.7-158.5 (C-5, C-7 and C-9). The peracetate was isolated by preparative TLC on Si-gel by development with benzene-acetone (7:3 - Rf 0.55) to give a white amorphous solid: Found C = 59.98, H = 4.72; $C_{50}H_{46}O_{22}$ requires C = 60.11, H = 4.65%. The ^{13}C-NMR spectrum of the acetate derivative recorded in chloroform-d showed d: 20.4 (acetate CH_3), 25.7 (C-4b), 36.7 (C-4t), 68.4 (C-3b), 70.5 (C-3t), 78.1 (C-2b), 79.0 (C-2t), 108.1 (C-8t), 109.5 (C-6t), 109.9 (C-6b), 111.5 and 115.0 (C-10t, b), 116.9 (C-8b), a complex group of signals from 121.9-124.9 (C-2', 2-5' and C-6'), 135.2 (C-1'), 141.6-142.1 (C-3' and C-4'), a group of signals at 149.0 to 149.6 (C-5, C-7 and C-9) and acetate C = O 167.6. The ^{13}C-NMR spectra of both the phenol and acetate derivative were consistent with previously reported data for catechin-(4α->8)-catechin

*) The notations of r and q denote the rhamnose and quercetin functions and t and b denote top and bottom units of proanthocyanidins.

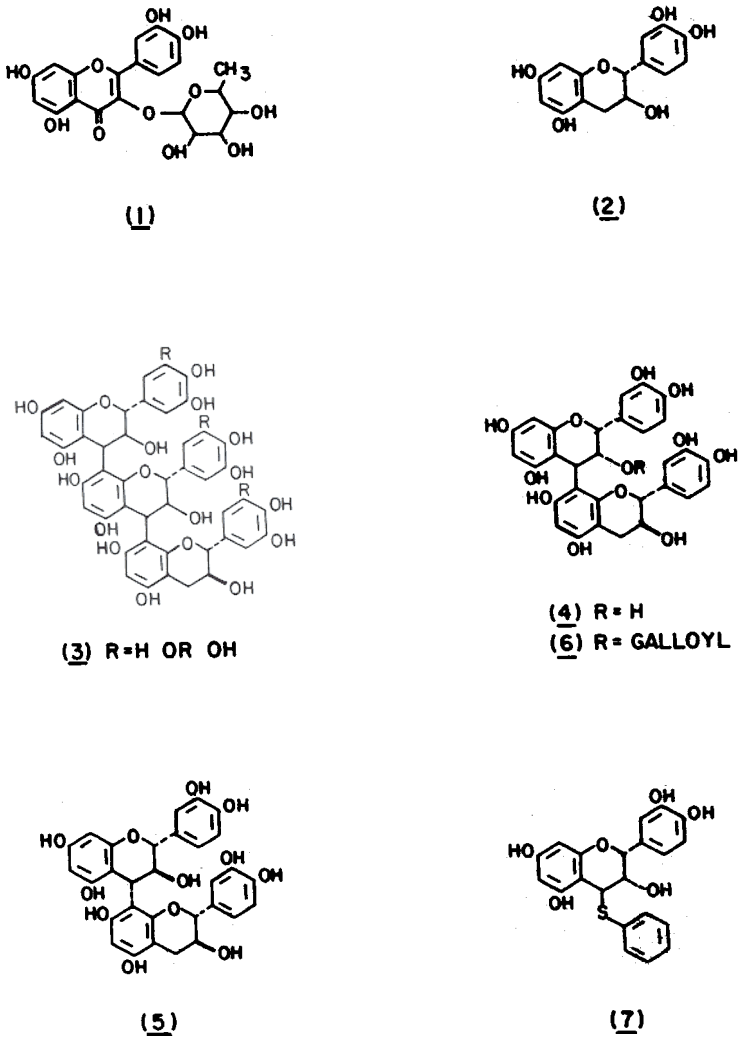

Fig. 1. Compounds isolated from the bark of southern red oak and their reaction products.

(Fig. 1, 5) (Hemingway, Foo and Porter 1982, Hemingway *et al.* 1983). The proton spectrum of the peracetate derivative was also superimposable on the spectrum published by Weinges *et al.* (1968).

Compound (6)

The third dimeric procyanidin was a tan colored solid that had Rf values of 0.59 in TBA and 0.37 in 6HA. The ^{13}C-NMR spectrum in methanol-d_4 showed δ: 28.5 (C−4b), 34.7 (C−4t), 68.6 (C−3b), 75.1 (C−3t), 75.9 (C−2t), 82.7 (C−2b), 95.8 (C−8t), 96.2 (C−6t), 97.0 (C−6b), 101.6 and 102.8 (C−10t, b), 107.5 (C−8b), 110.3 (C−2″ and C−6″ of galloyl group), 115.1−116.0 (C−2′ and C−5′), 119.4−121.5 (C−6′ and C−1″ of galloyl group), 131.8 (C−1′), 140.0 (C−4″ of galloyl group), 145.6−146.1 (C−3′ and C−4′ of catechol group and C−3″ and C−5″ of galloyl group), 155.0−157.4 (C−5, C−7 and C−9). The peracetate, isolated by preparative TLC on Si-gel with benzene-acetone (7:3, v/v; Rf 0.54) was a white amorphous solid: Found C = 59.08, H = 4.58; $C_{61}H_{56}O_{29}$ requires C = 59.3, H = 4.42%. The ^{13}C-NMR spectrum of the acetate derivative recorded in chloroform-d showed δ: 27.1 (C−4b), 34.4 (C−4t), 68.4 (C−3b), 72.5 (C−3t), 73.9 (C−2t), 78.5 (C−2b), 107.2 (C−8t), 109.0 (C−6t), 110.7 (C−6b), 111.5 and 113.6 (C−10t, b), 116.8 (C−8b), a complex group of signals at 123.2−125.6 (C−2′, C−5′ and C−6′) with a particularly strong signal at 122.2 (C−2″ and C−6″ of galloyl group), and a number of signals in the 133.8−156 ppm that were not assigned. Acetate C = O signals appeared centered at 167.8 and at 169.5 ppm. The ^{1}H-NMR spectrum was very similar to that obtained from epicatechin-(4β−>8)-catechin in the coupling of heterocyclic ring protons where the coupling constant $J_{2,3}$ <2 Hz for the upper unit indicating a 2,3-*cis*-3,4-*trans* stereochemistry while those for the lower unit were large (ca. 10 Hz) also indicating a 2,3-*trans* or catechin terminal unit. Changes in the chemical shifts of the C−2 and C−3 of the upper unit indicate that this compound is the 3−galloyl ester of (4) (Fig. 1, 6), as was found in *Polygonum multiflorum* (Nonaka, Miura and Nishioka 1982).

Isolation of Tannin

Finely-ground, air-dried whole bark was suspended in acetone-water (7:3, v/v) at ambient temperature for three days and the suspension was filtered to recover the extract. Acetone was removed on a rotary evaporator and the aqueous solution was freeze-dried and weighed to estimate the extract yield. The extract was redissolved in water and extracted 4−5 times with equal portions of ethyl acetate. The ethyl acetate-soluble fraction was dried on a rotary evaporator and the water-soluble portion was freeze-dried. After extraction with ethyl acetate, the water-soluble fraction was dissolved in MeOH-H_2O (1:1, v/v) and applied to a LH−20 Sephadex column (2.5 × 80 cm). The column was eluted with MeOH-H_2O

until the eluate was clear and then eluted with acetone-water (1:1 v/v) to recover approximately 42% of the extract as an acetone-water soluble tannin. To test for the presence of prodelphinidin (3, 5, 7, 3', 4', 5'-hexahydroxyflavan) units in the polymer, a sample (10 mg) of the acetone-water soluble tannin was dissolved in 10 mL of 2-propanol and 1 mL of concentrated HCl was added. The solution was heated at reflux for 1 hour and then examined by paper chromatography using Forestal solvent. The major product was cyanidin chloride by comparison of Rf and color with the authentic compound.

Thiolysis of the Tannin

The acetone-water soluble tannin (3 g) was dissolved in 50 ml of ethanol after which benzenethiol (3.5 mL) and glacial acetic acid (1.5 mL) was added. The sample was purged with argon and placed in a 105°C oven overnight. The reaction product was dried under a stream of N_2, added to water, and extracted into diethyl ether. Separation of the ether-soluble product on a Sephadex LH−20 column (1.5 × 80 cm) by eluting with chloroform-ethanol (4:1, v/v) gave two major products.

Compound (7)

A partially purified isolate (273 mg) was collected in fractions 41−57. This compound (150 mg) was acetylated with acetic anhydride-pyridine (1:1, v/v) at ambient temperature for two days. The acetate was extracted into dichloromethane an purified on preparative Si-gel plates developed with acetone-benzene (1:9, v/v) ^{1}H-NMR showed δ: 1.80−2.20, 15H, acetate CH_3; 4.53, 1H, d, J~2 Hz, H−4; 5.22, 1H, br-s, H−3; 5.62, 1H, br-s, H−2; 6.68, 2H, s, epicatechin H−6 and H−8; 7.17−7.61, 8H, m, B-ring of epicatechin + phenylsulfide ArH. This spectrum and chromatographic properties are fully consistent with those of the peracetate of epicatechin-4β-phenylsulfide (Fig. 1, 7) obtained previously from thiolytic cleavage of southern pine bark tannins (Hemingway, Foo and Porter 1982, Hemingway *et al.* 1983).

Compound (2)

A partially purified isolate (190 mg) of the compound obtained in next highest yield was obtained by collection of fractions 73−115. This product (100 mg) was acetylated and the acetate recovered by preparative Si-gel TLC. ^{1}H-NMR in chloroform-d showed δ: 1.82−2.27, 15H, acetate CH_3; 2.60−2.80, 2H, dd, H−4; 5.00−5.30, 2H, m, H−2 and H−3; 6.50−6.60, 2H, dd, H−6 and H−8 of catechin; 7.05−7.20, 3H, m, B-ring ArH. This spectrum and chromatographic properties are fully consistent with that of the penta-acetate of (+)-catechin (2) prepared by thiolysis of southern pine bark tannins (Hemingway, Foo and Porter 1982, Hemingway *et al.* 1983).

Results and Discussion

Comparison of the extract yields from inner, middle, and outer bark, as well as the proportions of the extract eluted from Sephadex LH−20 with methanol-water, and acetone-water are shown in Table 1. These results show a slight decline in extract yield going from inner to outer bark but the gross composition of the extracts did not change much. Large amounts of quercitrin (quercetin-3-rhamnoside) (1) were present in the extracts obtained from the inner bark. It precipitated as a yellow solid in a surprisingly pure form simply by suspending the extract in methanol-water. It was also present in high proportions in extracts from the whole bark.

Table 1. Extract yields and gross composition of extracts from the bark of southern red oak.

	Inner	Middle Bark	Outer
	Percent of Dry Weight		
Acetone-water Extract	10.7	14.8	5.5
Methanol-water Eluate	6.0	8.1	3.2
Acetone-water Eluate	3.3	5.9	1.8

The crude extract, obtained after precipitation of most of the quercetin-3-rhamnoside, was redissolved in water and extracted four to five times with an equal volume of ethyl acetate to recover 40% of the extract as ethyl acetate-soluble and 46.4% as water-soluble products. The 2D-TLC of the ethyl acetate-soluble fraction showed that the dominant flavan-3-ol present was (+)-catechin (2), only traces of epicatechin could be detected by thin layer chromatography, and no gallocatechin was evident from co-chromatography with the authentic compound.

The three major dimeric proanthocyanidins isolated were epicatechin-(4β−>8)-catechin (4), catechin-(4α−>8)-catechin (5), and the 3-gallate ester of epicatechin-(4β−>8)-catechin (6). Prodelphinidin dimers were not found in extracts from southern red oak although they are major constituents of *Quercus dentata* bark (Sun, Wong and Foo 1987).

We also were not able to isolate any flavan-3-ol- or procyanidin-glycosides from this bark as were found by Ishimura *et al.* (1987) in *Quercus miyagii* even though large quantities of quercetin-3-rhamnoside were present. If these compounds were major constituents of the methanol-water eluate they should have been readily detected by 2D-TLC on cellulose. We did isolate the 3-gallate of epicatechin-(4β−>8)-catechin, a compound also found in *Quercus miyagii* bark (Ishimura, Nonaka and Nishioka 1987) and analogous to the 3-O-galloyl-epigallocatechin-(4β−>8)-catechin found in *Quercus dentata* by Sun *et al.* (1987).

The water-soluble fraction was separated on LH-20 Sephadex, as has been used previously to isolate pure polymeric proanthocyanidins from a wide variety of plants. Reaction of the acetone-water eluted "tannin" fraction with HCl at reflux gave predominantly cyanidin cholride. Only very small amounts of delphinidin chloride were detectable. The ^{13}C-NMR spectrum of the acetone-water-soluble tannin was also consistent with a polymeric procyanidin; the major difference from spectra obtained from southern pine bark tannins being a very complex group of signals in the 70−80 ppm range, suggesting presence of carbohydrates that are usually readily removed by the above LH−20 Sephadex column separation and/or greater

heterogeneity in the stereochemisty of the procyanidin units (Hemingway, Carter and Parker 1982). We did not isolate any oligomeric proanthocyanidin-glycosides from the methanol-water soluble fraction even though their presence should be readily detected with the procedures used. These compounds have been described in extracts from a number of plants (Porter, Foo and Furneaux 1985; Nonaka *et al.* 1983; Nonaka *et al.* 1981) and rhamnosides have been isolated from *Quercus miyagii* bark so this aspect deserves further attention.

The thiolysis products confirmed the conclusions reached from interpretation of the ^{13}C-NMR spectrum. The two dimensional TLC of the ether-solube thiolysis product showed large amounts of catechin (2) from the terminal unit, a large amount of epicatechin-4β-phenylsulfide (7) from the chain extender units. In addition, two dimensional cellulose TLC suggested the presence of small amounts of products with appropriate Rf values for catechin-4α-phenylsulfide and the dimeric thioether derivatives described previously as reaction products from southern pine bark (Hemingway, Foo and Porter 1982, Hemingway *et al.* 1983). Only trace amounts of epicatechin were evident. Coumpunds (7) and (2) were isolated from the thiolysis products and their identity was verified by ^{1}H-NMR of their acetate derivatives.

An infrared spectrum of the tannin was also examined to search for carbonyl resonances that might indicate the presence of some hydrolysable tannin and to provide another estimate of the relative amounts of procyanidin and prodelphinidin units in the condensed tannin (Foo 1981). There was not a prominent carbonyl absorption, indicating that the extract contained little if any gallic or hexahydroxydiphenic acid esters. The aromatic skeletal signal at 1515 cm^{-1} was prominent and there was only weak absorbance at 1530 cm^{-1} consistent with results expected of a procyanidin polymer. Comparatively strong signals were present at 765 and 820 cm^{-1} with only a very weak absorption at 730 cm^{-1} also indicating that there was little if any prodelphinidin structure in the polymer.

Therefore, the main features of the polymer are: mainly 2,3-*cis*- with a smaller amount of 2,3-*trans*-3,5,7,3′,4′-pentahydroxyflavan chain extender units and termination of the polymer with 2,3-*trans*-3,5,7,3′,4′-pentahydroxyflavan, very similar to the structure of condensed tannins in southern pine bark (Hemingway, Foo and Porter 1982, Hemingway *et al.* 1983).

No gallic acid was detectable. This result is in contrast to the isolation of gallic acid from extracts of the bark of *Quercus dentata* (Sun, Wong and Foo 1987). No hydrolyzable tannins were found in the bark of southern red oak. This is in contrast to the isolation of hamamlitannin from the bark of *Quercus rubra* bark by Mayer *et al.* (1965). The tannins in southern red oak bark also differ markedly from those isolated from *Quercus dentata* primarily because of the absence of significant proportions of prodelphinidin units and in absence of significant proportions of hydrolysable tannins (Sun, Wong and Foo 1987). The tannins in southern red oak are more closely related to those in *Quercus miyagii* (Ishimura, Nonaka and Nishioka 1987) that also contains the dimeric procyanidins (4, 5, and 6) in addition to 3-O-rhamnosyl-catechin-(4α−8)-catechin, catechin-(4α−>6)-catechin, epicatechin-(4β-6)-catechin and gallocatechin-(4α−>8)-catechin. Although we did not isolate any procyanidin rhamnosides analogous to those obtained by Ishimaru *et al.* (1987), the presence or absence of these compounds deserves further study.

Another question of considerable interest is whether or not the condensed tannins contain significant proportions of biphenyl linkages as reported in oligomers isolated from the bark of *Quercus robur* by Ahn (Ahn and Gstirner 1971, Ahn 1974). These oxidative coupling products are considered to be produced from flavan-3-ols by phenol-oxidase enzymes as described by Hathway (Hathway 1959). We did not isolate any biphenyl linked oligomers from the extracts of southern red oak bark. These compounds were not reported in the tannin extracts of *Quercus dentata* or *Quercus miyagii* either (Sun, Wong and Foo 1987, Ishimura, Nonaka and Nishioka 1987). However, yields of thiolysis products from the higher molecular weight tannins were low and additional work to search for biphenyl linkages in the polymers might prove fruitful.

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