[Contribution from the Oregon Forest Products Laboratory and
Department of Chemistry, Oregon State College]

THE ISOLATION AND PROPERTIES OF CATECHOL FROM WHITE FIR BARK

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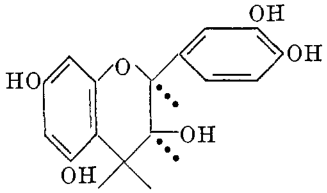
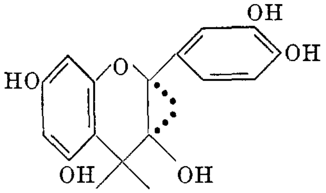
Previous investigations at this Laboratory have indicated that the bark of certain conifers is a good source of flavonoids (1, 2, 3). This paper describes part of a study of the bark of white fir (*Abies concolor*, Lindl. and Gord.), a major pulpwood and lumber species in the western United States.

The ethyl ether extract of white fir bark, which had been previously extracted with benzene to remove waxes, was evaporated to dryness and dissolved in hot water. Upon cooling the solution, a voluminous, pink precipitate was obtained. Color reactions indicated the material to be a polyphenol with a phloroglucinol nucleus. After recrystallization from hot water, the compound was found to be identical with the *d*-catechol, 3,3′,4′,5,7-pentahydroxyflavan (I) obtained from the wood and leaves of *Uncaria gambir* (4, 5). The mother liquor and filtrates from the recrystallization of I yielded small amounts of a second crystalline compound, *l*-epicatechol (II), which has previously been isolated from the wood of *Acacia catechu* (6, 7) and is stated to be the *cis* modification of I (8).



I



II

White fir bark from trees of different ages was mechanically separated into cork, bast fiber, and inner bark fractions. The yield of crude ether-soluble *d*-catechol and *l*-epicatechol both from these fractions and from white fir wood is shown in Table I. Inasmuch as white fir bark is readily available and the yields were relatively good, a further study of the properties of *d*-catechol and *l*-epicatechol appeared to be of importance. Although considerable work has been done on these compounds in the past, many discrepancies appear in the literature. One of these is concerned with the m.p. of *d*-catechol. Zwenger (9) reported the m.p. of gambir catechol (*d*-catechol) to be 217°, while Gautier (10) reported the isolation of three gambir catechols melting at 163°, 176–177°, and 204–205°. Perkin (4) indicated that gambir catechol sintered at 145–150° and then melted at 175–177°. Clauser (11) stated that catechol normally melted at 96°, but if dried over sulfuric acid it then melted at 176°; further drying at 100° raised the m.p. to 210°. Perkin (12) later stated that he was unable to obtain a m.p. higher than 177°. This was confirmed by Freudenberg (13), whose work suggests (14) that Clauser's high m.p. was due to racemization during drying at high temperature. Recently, Keller and Berger (15) reported a dimorphic form of *d*-catechol, m.p. 210–213°, obtained by extracting unwashed gum gambir.

We have found that the source of these discrepancies lies in the occurrence of two crystalline modifications of *d*-catechol. The high-melting modification is obtained by crystallizing from an aqueous solution saturated at the boiling point and vacuum-drying over P_2O_5 at 110°. This form melts sharply at 219°. The low-melting form is obtained by crystallization from a large volume of water; it sinters at 145–155° and melts at 176–177°, in agreement with previous investigators. The infrared spectra of both forms are identical, but the x-ray diffraction patterns differ. Both forms show the same optical rotation and give identical pentaacetate derivatives, indicating that racemization is not responsible for the high melting point. The form reported by Keller and Berger (15) is apparently a mixture and not a result of using unwashed gambir as they have suggested, but rather a function of the concentration of the solution from which crystallization takes place.

TABLE I

YIELD OF CRUDE, ETHER-SOLUBLE *d*-CATECHOL AND *l*-EPICATECHOL

SOURCE	AGE OF TREE[a]	YIELD,[b] %
White fir wood	145	0.12
Whole bark	209	3.80
Inner bark	209	0.07
Outer bark[c]	209	1.28
Cork	209	8.98
Cork	152	5.93
Cork	241	16.62

[a] Average age of three tree samples. Samples obtained 3′ from base of tree. [b] Percentage of oven-dry weight of material. [c] Excluding cork.

A further difficulty is involved in the removal of the water of crystallization, since it apparently cannot all be removed without degrading the molecule. Even *d*-catechol which has been vacuum dried at 115° over P_2O_5 for two weeks still contains water, as evidenced by the persistence of the 1627–1635 $cm.^{-1}$ band[1] in the infrared spectrum (see Figure 1). This difficulty was not observed in the examination of *l*-epicatechol.

Another discrepancy pertains to the relation of *d*-catechol to *l*-epicatechol. Nierenstein and his coworkers believed that the two compounds are structural isomers (14) while Freudenberg has stated that they are optical isomers (5), epicatechol having a *cis* configuration and catechol a *trans* configuration. This latter view is now generally accepted (8).

We have examined the infrared spectra of the catechins and compared them with *d*-3, 3′,4′,5,7-pentahydroxyflavanone (dihydroquercetin) (III), a natu-

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[1] Unpublished work. Because of its intensity, this band may obscure bands from carbonyl groups, ethylenic double bonds, etc. in natural products which are hygroscopic, hence great care must be exercised in the drying of compounds before measuring their infrared spectra.

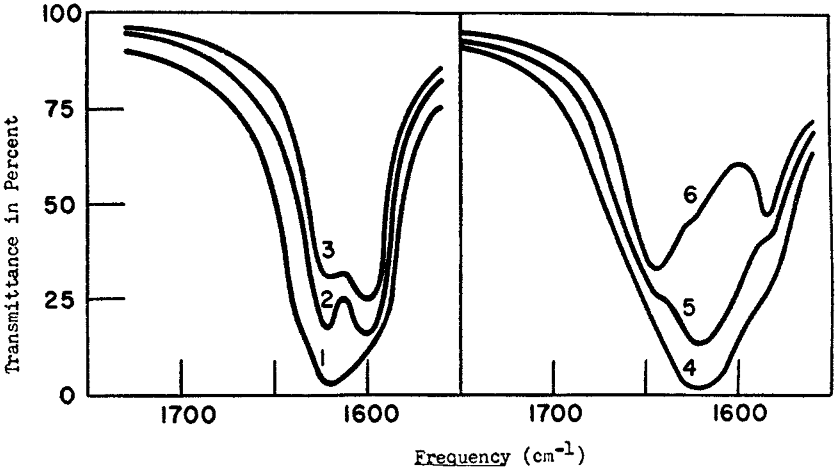


FIG. 1. INFRARED SPECTRA OF [1] *d*-CATECHOL, AIR-DRIED; [2] *d*-CATECHOL, vacuum-dried over P_2O_5 at 56°; [3] *d*-catechol, vacuum-dried over P_2O_5 at 110° for seven days; [4] *d*-dihydroquercetin, air-dried; [5] *d*-dihydroquercetin, vacuum-dried over P_2O_5 at 56°; [6] *d*-dihydroquercetin, vacuum-dried over P_2O_5 at 110°. All samples are solids mulled in Nujol.

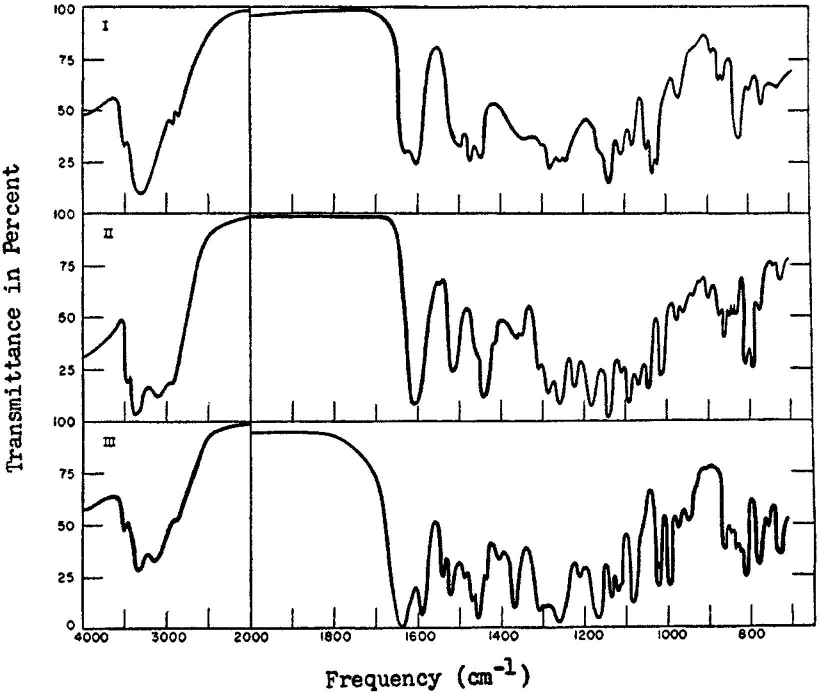


FIG. 2. INFRARED SPECTRA (solid mulls) OF (I) *d*-CATECHOL; (II) *l*-EPICATECHOL; (III) DIHYDROQUERCETIN.

rally occurring compound which differs from the catechols by having a carbonyl group in the 4 position. The spectra of these compounds and their pentaacetate

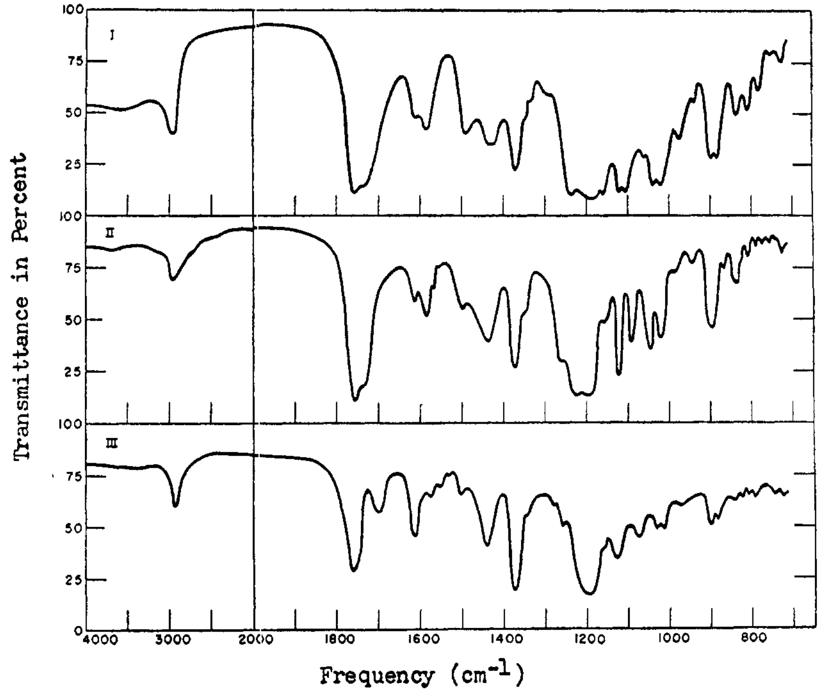
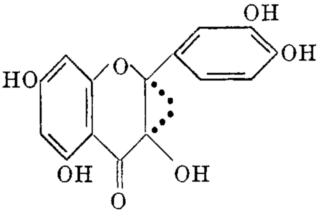


FIG. 3. INFRARED SPECTRA (solid mulls) OF (I) *d*-CATECHOL PENTAACETATE; (II) *l*-EPICATECHOL PENTAACETATE; (III) *d*-DIHYDROQUERCETIN PENTAACETATE.

derivatives are shown in Figures 2 and 3. The probable band assignments are given in Table II.



III

Examination of Figure 2 indicates that the infrared spectrum of *l*-epicatechol closely resembles that of *d*-dihydroquercetin, especially in the appearance of the two sets of strong bands at 1000–1050 cm.$^{-1}$ and 775–825 cm.$^{-1}$, and the series of four weak bands at 825–860 cm.$^{-1}$. However, the spectra of the two catechols do not closely resemble each other. This dissimilarity is not nearly so marked in the case of the pentaacetate derivatives, in which a closer resemblance between the catechol derivatives may be noted. Even in this case, *l*-epicatechol pentaacetate shows a close relationship to dihydroquercetin pentaacetate. The wide divergence between the infrared spectra of *cis*- and *trans*-isomers is well known and would seem to be a reasonable explanation for the differences observed here.

The close spectral relationship between dihydroquercetin and epicatechol suggested that the former should also have a *cis* configuration and that reduction of dihydroquercetin should therefore yield epicatechol rather than catechol. Attempts to reduce dihydroquercetin by a Clemmensen reduction were unsuccessful, inasmuch as both I and II are very unstable in an acid medium. However, a modified Clemmensen reduction of the pentamethyl derivative of dihydroquercetin gave the expected pentamethyl epicatechol. Since the constitution of epicatechol is well established (16), this synthesis provides further proof of the structure of dihydroquercetin.

TABLE II

TENTATIVE INFRARED FREQUENCY ASSIGNMENTS

ASSIGNMENT	ABSORPTION MAXIMUM, cm.$^{-1}$		
	d-catechol	*l*-epicatechol	*d*-dihydroquercetin
Hydroxyl stretching	3475, 3318	3486, 3409, 3162	3510, 3355, 3150
C—H stretching	2938, 2869	2935	2875
Conjugated carbonyl*			1642
Phenyl ring	1601, 1500	1603, 1516	1593, 1541, 1524
C—H bending	1451, 1347	1442, 1352	1458, 1369

ASSIGNMENT	*d*-catechol pentaacetate	*l*-epicatechol pentaacetate	*d*-dihydroquercetin pentaacetate
Aromatic ester carbonyl	1756	1758	1764
Aliphatic ester carbonyl	1737	1738	
Conjugated carbonyl*			1703
Phenyl ring	1612, 1584, 1487	1613, 1583, 1570	1613, 1573, 1553
		1505	1505
C—H bending	1434, 1347	1437, 1350	1438, 1346
Acetyl CH_3	1371	1373	1372
Acetyl C—O	1195–1185	1207–1190	1200–1184

* The frequency of this band is influenced by conjugation with the aromatic ring and chelation with the 5 hydroxy group. Chelation is obviously impossible in the case of the acetate derivative, consequently the frequency is higher. The problem is discussed by Hergert and Kurth, *J. Am. Chem. Soc.* **75**, 1622 (1953).

EXPERIMENTAL

White fir bark. White fir bark and wood were procured from a mixed stand of fir and pine near Fort Klamath, Oregon, in July, 1950. White fir bark is scaly and ranges from one to six inches in thickness. The inner bark ranges from ¼ to 1½ inches in thickness and is composed of sieve cells, phloem parenchyma, and bast fibers. The outer bark consists of salmon-colored, corky layers interspersed with areas of dark red, phloem tissue. The inner bark was separated from the outer bark by a band saw and then ground in a Wiley mill to pass a 20-mesh sieve. The outer bark was ground in a Mitts and Merrill hog fitted with a ½-inch screen and then dried to about 7% moisture content. The fraction retained on a 20-mesh (about 35% by weight of the whole bark) was found to be mostly cork. It was then refined in accordance with a previously described procedure (2). The portion passing through a 20-mesh screen was practically cork-free and consisted of broken and crushed phloem tissue.

Isolation of d-catechol. One-kg. samples of the various bark fractions were extracted with benzene in a large, borosilicate glass, Soxhlet-type extractor. The benzene-extracted bark was then extracted with diethyl ether for 24 hours. The ether extract was evaporated to dryness and weighed. The yields of crude materials thus obtained are reported in Table I.

It was later found that *d*-catechol and *l*-epicatechol could be more readily obtained by directly leaching the cork fraction with hot water. The hot water extract was concentrated to about 1% total solids and then placed in a porcelain bowl. A small amount of sodium bisulfite (2 parts to 100 parts of solid extract) was added to prevent the tannin from acting as a colloidal dispersant. After several days, crystals began to appear. These were filtered off and the filtrate was discarded.

Low melting form of d-catechol. The crude crystalline material was recrystallized several times from hot water and then decolorized with a little charcoal. The white crystals thus obtained were recrystallized from a dilute aqueous solution (1 g. in 40 cc. of water). After filtration, they were air-dried for 24 hours and then dried for 3 days over P_2O_5 at 105° *in vacuo*. The crystals (I) sintered at 150° and melted at 176–177° (all melting points were taken on a Fisher-Johns melting point block and are corrected); $[\alpha]^{25}_{D}$ +16.6° (1:1 acetone-water, *c*, 5.49), ±0.0° (100% ethanol, *c*, 2.0); [reported (5) $[\alpha]_{5780}$ +17.1° in acetone-water, ±0° in alcohol]. The m.p. was undepressed when I was mixed with an authentic sample of *d*-catechol from *Uncaria gambir* (furnished by the S. B. Penick Co. and further purified by repeated recrystallization from water).

Acetylation of I with pyridine-acetic anhydride (12) for 24 hours at room temperature gave colorless prisms from acetone-alcohol, m.p. 132–133°; $[\alpha]^{25}_{D}$ +39.1° (chloroform, *c*, 4.32) [reported (5), m.p. 131–132°, $[\alpha]_{5780}$ + 40.6°].

Anal. Calc'd for $C_{15}H_9O_6(CH_3CO)_5$: CH_3CO, 43.0. Found: CH_3CO, 42.7.

High melting form of d-catechol. Pure I was dissolved in boiling water until a saturated solution was obtained. The crystals (Ia) formed upon cooling were filtered off and dried *in vacuo* for 5 days over P_2O_5 at 105°, m.p. 219°; $[\alpha]^{25}_{D}$ +16.4° (1:1 acetone-water, *c*, 5.2). This higher melting form did not sinter at 145–155°, in contrast to the low-melting form. Acetylation of Ia with acetic anhydride-pyridine gave white crystals, m.p. 132–133°. This m.p. was undepressed by admixture with the pentaacetate of I.

Isolation of l-epicatechol. The mother liquor and filtrates from the recrystallization of I were combined and slowly evaporated at room temperature by placing the solution in a large porcelain bowl and blowing air across the surface. Pink crystals were formed after two or three days. When the solution had been evaporated to about 50 ml., the mixture was filtered. The crude crystalline material was washed with warm (30–35°) water to remove any residual *d*-catechol, and then recrystallized from hot water; yield 9% of the original crude extract. The purified material (II) melted at 245° [reported (6), m.p. 237–239° uncorr.]; $[\alpha]^{25}_{D}$ −58.9° (1:1 acetone-water, *c*, 1.22); $[\alpha]^{25}_{5780}$ −60.5° (acetone-water, *c*, 1.22) [reported (6), $[\alpha]^{20}_{D}$ −58°]. Admixture with authentic *l*-epicatechin (prepared by Dr. Chas. Horton and obtained from Dr. S. H. Wender of the Univ. of Okla.) did not depress the m.p.

Acetylation with pyridine-acetic anhydride gave the acetate derivative, m.p. 152–153° [reported (6), m.p. 151–152°]; $[\alpha]^{25}_{D}$ −15.6° (chloroform, *c*, 1.54), [reported (6), −14.3° to −15.0° in $C_2H_2Cl_4$].

Isolation of d-dihydroquercetin. Douglas fir bark cork was used as a raw material for the extraction of *d*-dihydroquercetin (2) (III), m.p. 241–243°, $[\alpha]^{25}_{D}$ +44.2° (1:1 acetone-water, *c*, 3.5). Acetylation with pyridine-acetic anhydride gave the acetate derivative, m.p. 128–129°, from methanol.

Pentamethyl dihydroquercetin. d-Dihydroquercetin (30.0 g.) was dissolved in 300 cc. of acetone. Over a period of two hours, 100 ml. of methyl sulfate and 60 g. of KOH (in water to make 100 cc. of solution) were added in small quantities, with stirring. The temperature was not allowed to exceed 10° during the reaction. An additional 60 g. of KOH and 100 ml. of dimethyl sulfate were added over another two-hour period. Then 100 ml. of water was added to the mixture and the mixture was placed in an icebox. After standing 24 hours, the crystalline precipitate was filtered off, washed with cold 80% ethanol, and dried. Two recrystallizations from 95% ethanol gave colorless prisms, m.p. 134–135°, yield 26.5 g. (72%).

The basic mother-liquor was acidified, and the precipitate was filtered off and remethylated as above. An additional 4.4 g. (12%) was obtained. The compound was insoluble in base.[2]

Anal. Calc'd for $C_{15}H_7O_2(CH_3O)_5$: CH_3O, 41.44. Found: CH_3O, 41.32.

Synthesis of pentamethyl epicatechol. Pentamethyl dihydroquercetin (5 g.) was dissolved in 75 cc. of toluene and added to 10 g. of amalgamated zinc (17), 20 cc. of water, and 10 cc. of conc'd HCl. The mixture was slowly brought to reflux temperature over a period of 8 hours with constant stirring and then refluxed for an additional 40 hours. During this time, an additional 10 cc. of conc'd HCl was added in 4 portions. The two layers that formed were then separated. The aqueous portion was extracted with four 25-cc. portions of ether. The

TABLE III

INTERPLANAR SPACINGS AND INTENSITIES OF CATECHOL AND DIHYDROQUERCETIN

l-EPICATECHOL PENTAACETATE	*l*-EPICATECHOL	*d*-CATECHOL (*low melting*)	*d*-CATECHOL (*high melting*)	*d*-DIHYDROQUERCETIN (*anhydrous*)
16.1 [100]	9.60 [3]	11.47 [29]	11.47 [27]	13.6 [5]
12.6 [28]	6.28 [13]	10.77 [12]	9.90 [4]	8.34 [27]
10.8 [10]	6.02 [20]	9.60 [41]	7.89 [13]	6.91 [25]
10.0 [11]	5.50 [29]	8.11 [15]	7.49 [8]	6.28 [72]
9.50 [18]	4.90 [100]	7.37 [15]	5.79 [100]	4.92 [26]
8.50 [17]	4.57 [25]	6.32 [59]	5.01 [5]	4.72 [99]
7.49 [7]	4.23 [7]	5.79 [88]	4.60 [19]	4.11 [51]
6.60 [13]	3.86 [27]	5.37 [100]	4.44 [28]	3.93 [25]
6.28 [19]	3.74 [32]	5.01 [29]	4.11 [64]	3.55 [100]
5.71 [13]	3.56 [70]	4.53 [59]	3.97 [60]	3.26 [42]
5.43 [18]	3.35 [3]	4.31 [37]	3.80 [45]	3.05 [22]
5.18 [15]	3.25 [7]	4.11 [71]	3.66 [39]	3.00 [35]
5.04 [10]	3.14 [38]	4.02 [49]	3.60 [35]	2.88 [16]
4.90 [15]	3.07 [38]	3.83 [39]	3.46 [44]	2.75 [10]
4.74 [12]	2.98 [4]	3.70 [34]	3.34 [19]	2.55 [9]
4.53 [15]	2.74 [4]	3.57 [34]	3.25 [11]	2.44 [10]
4.31 [21]	2.68 [9]	3.42 [71]	3.08 [13]	2.27 [7]
4.21 [27]	2.62 [2]	3.23 [22]	2.96 [8]	2.18 [6]
3.98 [16]	2.57 [3]	3.09 [24]	2.70 [8]	2.07 [15]
3.81 [13]	2.43 [3]	2.95 [7]	2.48 [7]	1.95 [6]
3.62 [33]	2.34 [3]	2.78 [5]	2.43 [7]	
3.40 [12]	2.21 [5]	2.69 [5]	2.34 [9]	
	2.14 [3]	2.50 [12]	2.10 [3]	
	2.07 [6]	2.42 [5]	2.07 [8]	
	2.01 [2]	2.38 [7]	2.00 [4]	
	1.93 [6]	2.30 [5]	1.81 [4]	
	1.86 [1]	2.27 [5]	1.76 [3]	
	1.79 [2]	2.22 [12]		
	1.71 [3]	2.10 [5]		
		2.07 [5]		
		2.00 [5]		

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[2] When methylation is carried out at elevated temperatures, the yield of pentamethyl dihydroquercetin is very low. Several other products are obtained which appear to be the result of a benzilic acid rearrangement of the chalcone formed from the opening of the pyran ring. These products will be described in detail in a subsequent publication.

ether and toluene solutions were combined, washed with aqueous Na_2CO_3 solution, and dried over Na_2SO_4. The solution was evaporated to dryness *in vacuo* and the residues extracted with CCl_4. This solution was evaporated nearly to dryness and ethanol was added. After one week, crystals of pentamethyl *d, l*-epicatechol were obtained. These were recrystallized from 95% ethanol, m.p. 110–113° [reported (5) m.p. 113–114°]; $[\alpha]_D^{25}$ +0.3° (chloroform, *c*, 0.75). Yield, 0.7 g. (14%).

Anal. Calc'd for $C_{15}H_9O(OCH_3)_5$: CH_3O, 43.06. Found: CH_3O, 42.81.

X-ray diffraction patterns. Powder diffraction patterns were obtained by using a North American-Phillips x-ray spectrometer with a Geiger-tube detector. Cu radiation with a Ni filter was used as a source. The samples were ground to pass through a 300-mesh screen. They were then pressed into a depression in an aluminum plate to form a layer about ⅛″ thick, ½″ wide, and ¾″ long. The interplanar spacings and intensities of catechol and dihydroquercetin are shown in Table III. The intensities are expressed as a percentage of the intensity of the strongest line of each pattern. The interplanar spacings of *l*-epicatechol pentaacetate have previously been reported by Bradfield and Penny (18) and are in reasonably good agreement with those reported here. The values reported for dihydroquercetin from Douglas-fir heartwood (19) do not agree with those reported here. They may have been obtained from dihydroquercetin which contained water of crystallization.

Infrared spectra. The instrument used to obtain infrared spectra was a model 12C Perkin-Elmer spectrometer fitted with a Brown Recorder and adapted to automatic double-beam operation by the method of Savitsky and Halford (20). A lithium fluoride prism was used in the 4000–2500 cm.$^{-1}$ region and a sodium chloride prism in the 2500–600 cm.$^{-1}$ region. The compounds were mulled in mineral oil (Nujol). The mull was placed between two salt plates. Two salt plates containing a layer of Nujol (equivalent to the amount in the sample) served as a blank. Perfluoro-kerosene mulls were used in the region where Nujol interferes. The spectra in Figures 2 and 3, therefore, represent only bands due to the sample.

Acknowledgement. We wish to express our appreciation to Mr. D. Mortimore for obtaining the x-ray diffraction patterns.

SUMMARY

1. Good yields of *d*-catechol and *l*-epicatechol were obtained by ether or hot-water extraction of white fir (*Abies concolor*) bark.

2. Two crystalline forms of *d*-catechol were obtained, depending upon the concentration of the solution from which crystallization took place.

3. Pentamethyl epicatechol was obtained by a modified Clemmensen reduction of pentamethyl dihydroquercetin.

4. The infrared spectra of catechol and its derivatives are presented and interpreted.

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