

The Syntheses of Polyhydroxybenzene Derivatives from Furfural. II¹⁾

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It is well-known that poison ivy and Japanese lac urushiol contain a mixture of four components which have the carbon skeleton of 3-pentadecylcatechol. One of these components has a completely reduced side chain (hydrourushiol). The other three contain one, two and three olefinic bonds respectively^{2,3)}. A number of investigators^{1,2,4-6)} have synthesized hydrourushiol. The mono-olefinic compound of urushiol and its homologs have also been synthesized by several investigators^{1,8,9)}.

Because of the absence of a general method for the preparation of 3-alkyl catechol and for the other reasons pointed out by Loev and Dawson^{9,10)}, none of di- or tri-olefinic catechols has heretofore been available, either from natural sources or by synthetic means. Consequently, there has been interest in the

development of a method of synthesizing such alkenylcatechols. The present paper's method of the syntheses of di- and tri-olefinic catechols (Fig. 1) is based on a route developed earlier¹⁾ by us for syntheses of 3-alkylcatechols. This paper also describes syntheses of 3-alkynylcatechol, as well as of 3-phenylcatechol, neither of which has ever been synthesized before.

Heptadecyl bromide, 1-bromo-8, 11-heptadecadiene and 1-bromo-8, 11, 14-heptadecatriene were prepared by Hunsdiecker reaction from the silver salts of stearic acid, linoleic acid and linolenic acid respectively. It is noteworthy that Hunsdiecker reaction is useful in the preparation of olefinic bromides.

The structures of I, II, III, IV and V were determined from the synthetic process, from analyses, from infrared spectra, and from their reduced products. All of these compounds gave dark blue color with ferric chloride and turned red when dilute aqueous alkali was added.

Heptadecol (I)^{2,11)}, one of the components of the Indochina lac tree (*Rhus succedanea*), was also obtained by the reduction of II and 3-(8'-heptadecenyl)catechol¹⁾.

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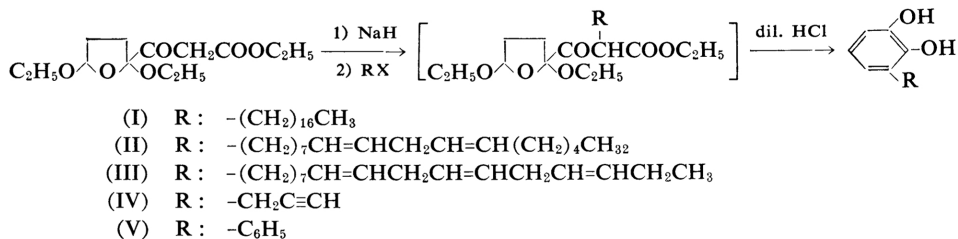


Fig. 1

It is known that a latex of the lac tree is polymerized by enzyme laccase on exposure to air at room temperature. A crude laccase, which had a specific activity of 4.1×10^2 at 25°C^{12} , was isolated from the latex of the Japanese lac tree (*Rhus vernicifera*). To each synthetic 3-alkylcatechol was added a small amount of crude laccase. It was shown that such 3-alkylcatechols as hydrourushiol, hydrolaccol, 3-propylcatechol, and 3-methylcatechol did not solidify as a hard thin film, while 3-olefinic catechol and 3-alkynylcatechol solidified as such a hard thin film when exposed to air at room temperature. The solidification rates are shown in the following comparison:

Latex of the Japanese lac tree < 3-allylcatechol < 3-(8'-heptadecenyl)catechol < II < III < IV.

Experimental

Heptadecyl Bromide.—This compound was prepared from a pure stearic acid according to the method described in the literature¹³.

1-Bromo-8, 11-heptadecadiene.—Into a mixture of 14.0 g. of pure linoleic acid in 300 ml. of hot water and 2.9 g. of potassium hydroxide in 50 ml. of hot water was added 8.5 g. of silver nitrate in 25 ml. of hot water with stirring. The precipitated silver salt was collected on a filter, washed with water and acetone, and dried in a vacuum at room temperature. This material was powdered and then dried in a vacuum at room temperature over phosphorus pentoxide. 37.5 g. (96.6%) of silver linoleate was thus obtained. Into a suspension of 22.8 g. of silver linoleate in 150 ml. of carbon tetrachloride (dried over phosphorus pentoxide) was added dropwise 9.0 g. of dry bromine with stirring at room temperature. After the evolution of carbon dioxide had ceased, the silver bromide was removed by filtration, and the filtrate was washed with a saturated sodium hydrogen carbonate solution and then with water and dried over magnesium sulfate. The carbon tetrachloride was distilled off under reduced pressure. The residue was crude 1-bromo-8, 11-heptadecadiene (a yellowish brown viscous oil) which was pure enough for subsequent purposes. The yield was 9.6 g. (52.0%).

Found: C, 64.03; H, 9.04; Br, 25.00. Calcd. for $\text{C}_{17}\text{H}_{31}\text{Br}$: C, 64.74; H, 9.91; Br, 25.34%.

1-Bromo-8, 11, 14-heptadecatriene.—The silver linoleate (a quantitative yield) was prepared from pure linolenic acid by the method described above for the preparation of the silver linoleate. A yellowish-brown viscous oil of 1-bromo-8, 11, 14-heptadecatriene was prepared from 26.5 g. of silver linoleate and 9.0 g. of dry bromine by the method described above for the preparation of 1-bromo-8, 11-heptadecadiene.

Found: C, 64.40; H, 9.21; Br, 25.78. Calcd. for $\text{C}_{17}\text{H}_{29}\text{Br}$: C, 65.15; H, 9.33; Br, 25.50%.

Hydrolaccol (I), 3-(8', 11'-Heptadecadienyl)-catechol (II), 3-(8', 11', 14'-Heptadecatrienyl)-catechol (III), 3-Propargyl Catechol (IV), and 3-Phenyl Catechol (V).—Each of these compounds was prepared from 1 mol. each of sodium hydride and of *n*-butyl ether in a three-necked flask with a mechanical stirrer, a dropping funnel, and a reflux condenser carrying a soda-lime tube. One mole of ethyl (2,5-diethoxytetrahydro)-furfuroylacetate was added dropwise to the stirred contents of the flask at room temperature for an hour, the corresponding alkyl bromide (iodobenzene was used for the preparation of IV) was added, and the reaction mixture was heated for 8 hr. After the reaction was over, the reaction mixture was acidified with acetic acid, and then *n*-butyl ether was removed by vacuum distillation. The residue was added to 100 ml. of 0.1 N hydrochloric acid and 200 ml. of dioxane and the mixture was allowed to stand at room temperature for a week; the solvent was then removed by vacuum distillation, and the residue was dissolved in ether. The ethereal solution was washed with saturated sodium hydrogen carbonate and with water and dried over magnesium sulfate. The ether was removed by distillation, and the residual oil was dissolved in ethanol and treated with the excess of an ethanolic solution of lead acetate trihydrate. The dense precipitate of lead salt was filtered off and washed with ether. The lead salt was suspended in ethanol and treated with hydrogen sulfide. The lead sulfide was removed by filtration, and the solvent was distilled off from the filtrate. The residual oil was distilled further.

The Reduction of II to Hydrolaccol.—0.51 g. of II in ethanol was reduced through the use of W-6 Raney nickel¹⁴ at room temperature for 10 hr. The product was then recrystallized from toluene; m. p., 63°C . The yield was 0.505 g. (87% yield).

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Compound	Molecular formula	M. p. or b. p.	Yield %	Calcd., %		Found, %	
				C	H	C	H
I	C ₂₃ H ₄₀ O ₂	m. p. 62~63°C	26.4	79.25	11.57	79.28	11.37
II	C ₂₃ H ₃₆ O ₂	212~221°C/0.03 mmHg	15.9	80.18	10.53	80.48	10.64
III	C ₂₃ H ₃₄ O ₂	209~217°C/0.022 mmHg	19.9	80.65	10.01	79.89	9.82
IV	C ₉ H ₈ O ₂	130~136°C/5 mmHg	11.8	72.96	5.44	73.22	5.91
V	C ₁₂ H ₁₀ O ₂	m. p. 57~59°C	7.82	77.40	5.41	77.38	5.40

This product was identified by mixed melting point determination and comparison with the infrared spectra of a sample which had been prepared from ethyl (2,5-diethoxytetrahydro)-furfuroylacetate and heptadecyl bromide.

Laccase.—Crude laccase was isolated from the latex of the Japanese lac tree (*Rhus vernicifera*) according to the method described in the literature¹²⁾.

The Action of Laccase.—Into each synthetic 3-alkylcatechol was added a small amount of crude

laccase with stirring, the mixture was then spread over a watch glass as thinly as possible at room temperature. A hard thin film adhered to the watch glass when solidification had been completed. The times required for this solidification were then compared.

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