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Studies of Japanese Lacquer: Isolation of a Diphenyl Dimer of Urushiol

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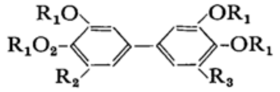
It is well known that Japanese lacquer oxidatively polymerizes under the action of laccase to form dried films with excellent properties. Previously, in order to elucidate the behavior of urushiol in the drying process, we have separated by thin-layer chromatography (TLC) three unknown components (with R_f 0.37, 0.27 and 0.20; 1 : 1 : 0.5 by wt, respectively) from a mildly-oxidized sap of the Japanese lacquer tree (*Rhus vernicifera* D. C. in Japan).[1]

It is the aim of the present paper to clarify the point that the component with R_f 0.20 (designated as D) is a diphenyl derivative (Ia) of urushiol. This has been proved by the separation of the hydrogenated D (Ib; 3,4,3′,4′-tetrahydroxy-5,5′-dipentadecyldiphenyl) from the hydrogenated polymeric urushiol by TLC and by its derivation to the acetyl derivative (Ic). The identification of (Ic) was performed as follows: It is evident that the acetyl derivative of the hydrogenated D was a derivative of a dimeric urushiol on the basis of the results of elemental analysis and molecular weight measurement. The diphenyl structure was confirmed by the UV spectral absorption (λ_{max}^{EtOH} 256 mμ, ε 2.15×10^4).[2] Among the possible six isomers the identity of the compound with Ic was established by the NMR spectrum of the phenyl protons. A quartet (4H, $J=2$ cps) characteristic of the AB system[3] was observed in the region of τ 2.5—2.8. The small J-value indicates that two protons in the AB system were present in the meta position.[3]



(I)

a: $R_1=H$; R_2, R_3=arbitrary side chain of urushiol
b: $R_1=H$; R_2, $R_3=C_{15}H_{31}$
c: $R_1=COCH_3$; R_2, $R_3=C_{15}H_{31}$

It is already known that tetrahydroxydiphenyl is formed in the reaction of *o*-quinone with cate-

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[1] T. Kato and J. Kumanotani, *J. Polymer Sci.* Part A-1, accepted, "Studies of Japanese Lacquer: Urushiol Dimerization by the Coupling Reaction between Urushiol Quinone and a Triolefinic Component of Urushiol."

[2] K. Hirayama, "Handbook of Ultraviolet and Visible Absorption Spectra of Organic Compounds," Plenum Press Data Division, A Division of Plenum Publishing Corporation, New York (1967), p. 113.

[3] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N.Y. (1967), pp. 118, 145.

chol in an aqueous medium,[4,5] and that urushiol quinone is formed[6] at an early stage of the oxidative polymerization of the sap of the Japanese lacquer tree. It seems, therefore, reasonable to assume that D (Ia) was formed by the reaction between urushiol and urushiol quinone.

Experimental[7]

Separation of a Diphenyl Dimer of Urushiol. The polymeric urushiol was obtained by the method reported previously[1] from a mildly-oxidized sap of the Japanese lacquer tree. The polymeric urushiol was hydrogenated at room temperature under an atmospheric pressure of hydrogen over 5% Pd-on-charcoal. The hydrogenated polymeric urushiol was dissolved in chloroform and applied as a spot on the silica-gel layer (thickness, 0.25 mm), which was made from Silica Rider (silica-gel with 12—14% calcium sulfate, purchased from the Daiichi Pure Chemicals Co.) and activated at 105°C for 1.5 hr. It was then chromatographed in a chloroform - ethyl acetate (87 : 13 v/v) solvent tank using the ascending technique. The developing distance was 12—14 cm. A filter paper (20×20 cm) impregnated with the developing solvent was inserted into the tank in order to saturate the atmosphere with the solvent-vapor. The chromatogram gave, when sprayed with a methanol-1% $FeCl_3$ solution, spots with R_f values of 0.50 (urushiol, dark violet), 0.37 (dark brownish green), 0.27 (dark violet) and 0.20 (dark violet), and others with smaller R_f values including a spot of the starting point. The compound with R_f 0.20 (the hydrogenated D) was then collected by TLC in the same manner as that described previously.[1] About 0.1 g of the purified, hydrogenated D which gave only one spot (with R_f 0.20) in its TLC, was obtained from 4 g of the hydrogenated polymeric urushiol. The hydrogenated D (91 mg) was acetylated at 50—60°C for 1 hr in a mixture of acetic anhydride (5 m*l*) and phosphoric acid (0.1 m*l*) under stirring, and the solution was further allowed to stand overnight at room temperature. The reaction mixture was shaken well with water (50 m*l*, *ca.* 60°C), and extracted with benzene (50 m*l*). The benzene extract was then washed with water (50 m*l*×3), and dried over calcium chloride. An oily material was obtained by the removal of the benzene in vacuum. It was examined by TLC (Silica Rider: thickness, 0.25 mm; developing solvent, chloroform - *n*-hexane, 3 : 2 v/v). The spots were detected by spraying with an aqueous sulfuric acid solution (1 : 1) and by heating at 150°C for 30 min, and the compound with R_f 0.26 was found to be a major product. It was collected by TLC using two silica-gel plates (1 mm thick). The separated material was crystallized from *n*-hexane - ether, and a white crystal (20 mg) was obtained, mp 99—100°C (corr.). UV λ_{max}^{EtOH} 256 mμ (ε 2.15×10^4); IR ν(KBr) 2920 (vs), 2860(s), 1770 (vs), 1599(w), 1478(s), 1378(s), 1259(m), 1208(vs), 1175(vs) 1113(w), 1030(m), 1014(m), 900(m), 873(w), 826(w), 775(w) and 720 cm^{-1} (w); NMR ($CDCl_3$) τ 2.5—2.8 (4H, quartet, $J=2$ cps, phenyl protons), 7.42 (4H, triplet, $J=7$ cps, protons of methylenes adjacent to benzene ring), 7.65 and 7.70 (each 6H, singlet, acetyl protons), 8.1—8.9 (52H, methylene protons), 9.11 (6H, triplet, $J=5$ cps, methyl protons).

Found: C, 74.48; H, 10.46%; mol wt, 760. Calcd for $C_{50}H_{78}O_8$: C, 74.40; H, 9.74%: mol wt, 807.2.

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4) E. J. Grossman, Dissertation Columbia Univ., 1960, Mic 60-3076, Univ. Microfilms, Inc., Ann Arbor, Michigan.

5) W. G. C. Forsyth and V. C. Quesnel, *Biochim. Biophys. Acta,* **25**, 155 (1957).

6) J. Kumanotani, T. Kato and A. Hikosaka, paper presented at International Symposium on Macromolecular Chemistry, Tokyo and Kyoto, 1.5.01, 1966; *J. Polymer Sci.* Part C, in press.

7) The infrared spectra were obtained with a Nihon-Bunko IR-spectrophotometer, Model IR-S. The ultraviolet spectra were taken with a Hitachi spectrophotometer, EPS-2. The NMR spectra were determined with a Nihon-Denshi NMR spectromteter, JMN C-60. The chemical shifts are described in τ values relative to tetramethylsilane as an internal standard. The molecular weights were measured in methyl ethyl ketone with a vapor pressure osmometer, Model 301-A, Mechrolab., Inc.