ORIGINAL

Synthesis of 3-[(8*Z*,11*E*,13*Z*)-8,11,13-pentadecatrienyl]catechol and Analysis of the Triene Urushiol Fraction of the Sap of *Rhus vernicifera*

Noriyasu NIIMURA*, Yukio KAMIYA, Takahiro SATO,
Ichirou KATANO, and Tetsuo MIYAKOSHI
Department of Industrial Chemistry, Meiji University
(1-1-1, Higashimita, Tama-ku, Kawasaki-shi 214-8571)

Abstract : An efficient method for synthesizing 3-[(8*Z*,11*E*,13*Z*)-8,11,13-pentadecatrienyl]catechol, the main component in urushiol, was established. Good yield was attained via the Wittig reaction of ylides derived from (3*E*, 5*Z*)-3,5-heptadienyltriphenylphosphonium iodide with 3-(8-oxo-1-octyl)catechol diacetate in a stepwise procedure of repeated protection and deprotection of the hydroxyl group of catechol. Quantitative analysis of the triene urushiol of saps from of different origin was conducted for comparison with the synthesized triene urushiol as reference. In this manner, sap performance could be assessed best, since each sap with good performance as lacquer coating material was high in triene urushiol content. This content was found to depend on the growing conditions of the *Rhus vernicifera* tree and on the particular seasons for obtaining sap.

Key words : synthesis of urushiol, sap, lacquer, triene, urushiol

1 Introduction

The sap from *Rhus vernicifera* has been used as a surface coating material for wood, porcelain and metalware for thousands of years in Japan, because it dries into a tough and brilliant film^{1),2)}. These saps are latex composed of urushiol (60~65%), water (20~25%), plant gum (5~7%), glycoprotein (2~5%), and laccase enzyme (1%)^{3)~6)}. The composition of urushiol has been investigated using gel permeation chromatography (GPC), high performance liquid chromatography (HPLC) and nuclear magnetic resonance (NMR) spectroscopy^{7)~10)}. Most components of urushiol have unsaturated side chains. The components with an unsaturated side chain are important contributors to the industrially useful polymerization properties of these natural products^{2),11)}. The triene urushiol is shown in **Table 1**.

In this paper, an efficient synthesis of 3-[(8*Z*,11*E*,13*Z*)-8,11,13-pentadecatrienyl]catechol (1), which is the main component of urushiol, is described. Protection of the hydroxyl group of catechol as methyl ether is now widely used, and the protected form is very stable under various basic conditions¹²⁾. However, deprotection cannot be carried out in acid-sensitive molecules such as urushiols having a pentadecatrienyl side chain¹³⁾. On the other hand, protection of the hydroxyl group of catechol as acetyl ether has been also used. Deprotection of this group can be carried out without any damage to trienyl side chain, but the protected form is not stable in alkaline solution. This is problem in the alkylation of the aromatic

* Corresponding author : Noriyasu NIIMURA

Present address : Application and Research Center, Analytical Instruments Division, JEOL Ltd, (3-1-2 Musashino Akishima-shi, Tokyo 196-0021)

* 連絡者 : 新村典康

現在所 : 日本電子分析機器技術本部応用研究センター (〒196-0021 東京都昭島市武蔵野 3-1-2)

Table 1 The triene urushiol (1)~(3)

R=

- (1) 8(Z),11(E),13(Z)-C₇H₁₄CH=CHCH₂CH=CHCH=CHCH₃
 (2) 8(Z),11(E),13(E)-C₇H₁₄CH=CHCH₂CH=CHCH=CHCH₃
 (3) 8(Z),11(E),14-C₇H₁₄CH=CHCH₂CH=CHCH₂CH=CH₂

ring. In this study, protection of the hydroxyl group of catechol as methyl ether was used at the alkylation of the aromatic ring and that of catechol as acetyl ether was done after the alkylation. Urushiol was synthesized in good yields by this stepwise procedure based on repeated protection and deprotection of the hydroxyl group of catechol using these groups¹⁴⁾. At the first step of the synthesis, 3-(8-oxo-1-octyl)catechol diacetate (8) was produced according to the synthetic pathways shown in Scheme 1. 1 was synthesized via the Wittig reaction of ylides derived from (3*E*,5*Z*)-3,5-heptadienyltriphenylphosphonium iodide (18) with 8 as shown in Scheme 2.

Furthermore, a number of saps from different origins were analysed using GPC and gas chromatography/mass spectrometry (GC/MS). The performance of saps is discussed in terms of the content of the olefinic urushiol components in comparison with the standard triene urushiols, which have been accurately synthesized here.

2 Experimental

The saps of *Rhus vernicifera* from Xi'an in China, Woochum and Wonju in Korea and Iwate in Japan were analysed. Native sap was mixed with acetone and the mixture was filtered. The filtrate was evaporated to get a crude urushiol preparation as a residue. The residue was dissolved in chloroform and the solution was applied onto GPC columns (TSK gel G 1000 HR 21.5 mm i.d. × 600 mm, × 2) with chloroform. The monomeric fraction was collected and applied onto the GC/MS. GC/MS measurements were carried out using a HP 5890 series II (HP Ltd.) gas chromatograph and a JMS-DX 300 (JEOL Ltd.) mass spectrometer. A fused-silica capillary column (0.32 mm i.d. × 30 m) coated with 0.25 μm of DS-1 was used for separation. The mass spectrometer ionization energy was 70 eV (EI/MS).

All ¹H NMR spectra were taken in chloroform-*d* or carbon tetrachloride with tetramethylsilane as an internal standard on a JNM-GSX 270 NMR spectrometer (JEOL Ltd). All ¹³C NMR spectra were recorded on a JNM-GSX 270 NMR spectrometer operated at 67.9 MHz. HPLC was performed on a Gilson liquid chromatography with GPC (TSK gel, G 1000 H₈ 22 mm i.d. × 600 mm, × 2, eluent: chloroform, flow rate, 4.0 ml min⁻¹) and silica gel (Develosil

Scheme 1 Reagents : a ; Br(CH₂)₈Br, *n*-BuLi b ; BBr₃, CH₂Cl₂ c ; (CH₃CO)₂O, pyridine d ; NaI, acetone e ; DMSO, NaHCO₃

Scheme 2 Reagents : a ; DHP, H^+ b ; EtMgBr , HCHO c ; LiAlH_4 d ; PDC (12) e ; EtPPH_3Br , $n\text{-BuLi}$ f ; H^+ , CH_3OH g ; PPh_3 , CBr_4 h ; KI , acetone i ; PPh_3 , CH_3CN j ; 3-(8-Oxo-1-octyl)catechol diacetate (8) k ; LiAlH_4 , $t\text{-BuOH}$

10 mm i.d. $\times$ 250 mm, $5\ \mu\text{m}$, eluent : hexane-ethyl acetate=96:4, flow rate, $1.5\ \text{ml min}^{-1}$).

3-(8-Bromo-1-octyl)veratrole (4). Butyllithium 66.2 ml (1.5 M in hexane, 99.3 mmol, 1 M=1 moldm $^{-3}$) was added to a stirred solution of veratrole (41.1 g, 0.298 mol) in 1300 ml of dry THF at 0°C under nitrogen atmosphere. After stirring for 2 h at room temperature, a solution of 1,8-dibromooctane (27.0 g, 99.3 mmol) in 50 ml of dry THF was added, and the mixture was refluxed for 5 h. A saturated NH_4Cl solution was added to the mixture at room temperature. The mixture was poured into a saturated NH_4Cl solution and extracted with ethyl acetate. The ethyl acetate solution was washed with brine, dried (K_2CO_3), and concentrated in vacuo to yield crude products. The remaining veratrole was taken off under reduced pressure (5 Torr, 1 Torr=133.322 Pa) at 70°C . The residual oil was chromatographed over silica gel eluting with hexane to remove 1, 8-dibromooctane, and then with benzene to give **4** (27.5 g, 84% yield). $R_f=0.56$ (benzene) ; IR (neat) : 1010,780,745,640 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ =1.10–2.00 (m, 12H, CH_2), 2.54 (t, $J=7\ \text{Hz}$, 2H, CH_2Ar), 3.31 (t, $J=7\ \text{Hz}$, 2H, CH_2Br), 3.73 (s, 3H, OMe), 3.77 (s, 3H, OMe), 6.64 (m, 3H, ArH) ; EI-MS m/z (rel intensity, %) 330 (M^+ , 57), 328 (M^+ , 57), 152 (84), 151 (94), 137 (65), 136 (100), 121 (33), 91 (62).

3-(8-Bromo-1-octyl)catechol (5). A solution of boron tribromide (25.0 g, 99.6 mmol) in 50 ml of methylene chloride was added dropwise to a stirred solution of **4** (23.1 g, 70.2 mmol) in 150 ml of methylene chloride for 30 min at 0°C . The mixture was allowed to warm up slowly to room temperature over 12 h. The mixture was treated with water, and the methylene chloride layer was treated with brine, dried (MgSO_4), and concentrated in vacuo. The residual oil was chromatographed (benzene-ethyl acetate=1:1 as eluent) to give **5** as an oil (19.4 g, 92%). $R_f=0.58$ (benzene-ethyl acetate=1:1) ; IR (neat) : 3500,1600,1500,780,730, 640 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ =1.1–2.0 (m, 12H, CH_2), 2.53 (t, $J=7\ \text{Hz}$, 2H, CH_2Ar), 3.33 (t, $J=7\ \text{Hz}$, 2H, CH_2Br), 5.22 (br. s, 2H, OH, D_2O exchangeable), 6.62 (br. s, 3H, ArH) ; EI-MS m/z (rel intensity, %) 302 (M^+ , 12), 300 (M^+ , 12), 180(21), 179(25), 136(7), 124(89), 123 (100).

3-(8-Bromo-1-octyl)catechol Diacetate (6). A solution of **5** (16.8 g, 55.8 mmol), acetic anhydride (17.1 g, 0.168 mol), and pyridine (0.89 g, 11.3 mmol) was stirred at 100°C for 4 h, added to water, and extracted with ethyl acetate. The extract was washed with dil aq HCl and then neutralized with dil aq NaOH. The extract was dried (K_2CO_3) and concentrated in vacuo. The residue was chromatographed to afford **6** (16.3 g, 76%) as an oil. $R_f=0.37$ (benzene-ethyl acetate=9:1) ; IR (neat) 1780,1600,1500,1220 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ =1.1–2.0 (m,

12H, CH₂), 2.27 (s, 3H, CH₃CO), 2.31 (s, 3H, CH₃CO), 2.51 (t, J=7 Hz, 2H, CH₂Ar), 3.33 (t, J=7 Hz, 2H, CH₂Br), 7.04 (m, 3H, ArH) ; EI-MS m/z (rel intensity, %) 386(M⁺, 3), 384(M⁺, 3), 302(99), 300 (100), 124 (54), 123 (75).

3-(8-Iodo-1-octyl)catechol Diacetate (7). After a mixture of **6** (5.3 g, 13.7 mmol) and NaI (3.1 g, 20.5 mmol) in 50 ml of acetone was stirred at 60°C for 3 h, the resulting mixture was poured into a saturated sodium chloride solution, and the product was extracted with ethyl acetate. The extract was washed with Na₂S₂O₃, dried over MgSO₄, and concentrated in vacuo. Purification of the crude oil by column chromatography on silica gel (benzene-ethyl acetate=98:2 as eluent) afforded **7** (5.21 g, 88%) as an oil. R_f=0.40 (benzene-ethyl acetate=98:2) ; IR (neat) 1780,1600,1500,1220 cm⁻¹ ; ¹H NMR (CCl₄) δ=1.1-2.0 (m, 12H, CH₂), 2.27(s, 3H, CH₃CO), 2.31 (s, 3H, CH₃CO), 2.51 (t, J=7 Hz, 2H, CH₂Ar), 3.05 (t, J=7 Hz, 2H, CH₂I), 6.92(m, 3H, ArH) ; EI-MS m/z (rel intensity, %) 432(M⁺, 3), 390(15), 348(60), 263(4), 222 (4), 207(8), 123(100).

3-(8-Oxo-1-octyl)catechol Diacetate (8). A mixture of **7** (18.5 g, 42.8 mmol), 200 ml of DMSO, NaHCO₃ (7.1 g, 84.5 mmol), and 200 ml of benzene was stirred at 90°C for 4 h under nitrogen atmosphere. The mixture was then poured into water and extracted with benzene. The combined extracts were dried over MgSO₄, filtered, and evaporated. Column chromatography (gradient elution, benzene-ethyl acetate=9:1-3:1) gave **8** as a colorless oil (9.7 g, 71%). R_f=0.33 (benzene-ethyl acetate=9:1) ; IR (neat) 2720,1780,1730,1600,1500, 1220 cm⁻¹ ; ¹H NMR (CCl₄) δ=1.1-1.8 (m, 10H, CH₂), 2.27 (s, 3H, CH₃CO), 2.31(s, 3H, CH₃CO), 2.35 (t, J=7 Hz, 2H, CH₂CO), 2.50 (t, J=7Hz, 2H, CH₂Ar), 6.97 (m, 3H, Ar), 9.63 (br. s, 1H, CHO) ; EI-MS m/z (rel intensity, %) 320(M⁺, 2), 278(14), 236(100), 218(9), 124(31), 123(44).

2-(3-Butynyloxy)tetrahydro-2H-pyran (9). **9** was derived from 3-butyne-1-ol by a known procedure (89% yield)¹⁵. R_f=0.44 (benzene) ; IR (neat) : 3300,1120,630 cm⁻¹ ; ¹H NMR (CCl₄) δ=1.33-2.03 (m, 6H, CH₂ in pyran), 1.88 (t, J=2.4 Hz, 1H, HC≡C), 2.40 (dt, J=3.0 Hz, 2H, C≡C-CH₂), 3.28-3.97 (m, 4H, CH₂-O), 4.57 (br. s, 1H, O-CH-O) ; CI-MS (i-butane) m/z (rel intensity, %) 155 (MH⁺, 100).

5-(2-Tetrahydropyran-2-yloxy)-2-pentyn-1-ol (10). **10** was derived from **9** (90% yield) in a similar manner as described in our previous paper¹⁵. R_f=0.39 (benzene-ethyl acetate=1:1) ; IR (neat) : 3400,2200,1120 cm⁻¹ ; ¹H NMR (CCl₄) δ=1.33-2.03 (m, 6H, CH₂ in pyran), 2.47 (m, 2H, C≡C-CH₂), 3.30 (br. s, 1H, OH), 3.28-3.97 (m, 4H, CH₂-CH₂-O), 4.10 (br. s, 2H, HO-CH₂-C≡C), 4.60(br. s, 1H, O-CH-O) ; CI-MS (i-butane)m/z (rel intensity, %) 185(MH⁺,100), 167(19).

(2E)-5-(2-Tetrahydropyran-2-yloxy)-2-penten-1-ol (11). **11** was derived from **10** by a known method (78% yield)¹⁵. R_f=0.43 (benzene-ethyl acetate=1:1) ; IR (neat) : 3400,1120,970 cm⁻¹ ; ¹H NMR (CCl₄) δ=1.29-1.98 (m, 6H, CH₂ in pyran), 2.23 (m, 2H, C=CH-CH₂), 2.97-3.83 (m, 5H, CH₂-CH₂-O and OH), 3.90 (br. s, 2H, HO-CH₂-CH=C), 4.47 (br. s, ¹H, O-CH-O), 5.33-5.78 (m, 2H, CH=CH) ; CI-MS (i-butane) m/z (rel intensity, %) 187 (MH⁺, 100), 169 (18).

Pyridinium dichromate (PDC) (12). A solution of chromium trioxide (12.0 g, 0.120 mol) in 30 ml of water was added dropwise to pyridine (19.0 g, 0.240 mol) while stirring for 10 min at 0°C. The mixture was then stirred for 1 h at room temperature. Next, 250 ml of acetone was added to the mixture at 0°C. After 3 h, the mixture was filtered. The solid was washed with acetone and dried to give **12** (29.5 g, 65%).

(2E)-5-(2-Tetrahydropyran-2-yloxy)-2-pentenal (13). A solution of **11** (8.5 g, 45.7 mmol) in methylene chloride was added to a solution of **12** (6.0 g, 16.0 mmol) in 50 ml of methylene chloride while stirring for 6 h at room temperature. The alkanal **13** (71%) was obtained as an oil. R_f=0.57 (ether) ; IR (neat) : 1690,1640,1130,975 cm⁻¹ ; ¹H NMR (CCl₄) δ=1.23-1.91 (m, 6H, CH₂ in pyran), 2.56 (m, 2H, C=CH-CH₂), 3.00-3.93 (m, 4H, CH₂-O), 4.48 (br. s, 1H, O-CH-O), 6.03 (ddt, J=15.6, 7.5, 1.3 Hz, 1H, OHC-CH=C), 6.10 (dt, J=15.6, 6.4 Hz, 1H, OHC-CH=CH), 9.36 (d, J=7.5 Hz, 1H, CHO) ; CI-MS (i-butane) m/z (rel intensity, %) 185

(MH⁺, 100), 167 (28).

(3E,5Z)-1-(2-Tetrahydropyranyloxy)-3,5-heptadiene (14). 14 (cis-trans isomer : trans-trans isomer=7:3) was derived from the reaction between 13 and ethyltriphenylphosphonium bromide using the conventional method (88% yield)¹⁵. R_f=0.44 (benzene) ; IR (neat) : 1120, 980, 940 cm⁻¹ ; ¹H NMR (CCl₄) δ=1.13-2.00 (m, 6H, CH₂ in pyran), 1.71 (d, J=6.0 Hz, 3H, C=CH-CH₃), 2.33(m, 2H, C=CH-CH₂), 3.00-3.93(m, 4H, CH₂-O), 4.48 (br. s, 1H, O-CH-O), 5.10-6.50 (m, 4H, CH=CH-CH=CH) ; EI-MS m/z (rel intensity, %) 196 (M⁺, 7), 94(20), 85(100), 67(30).

(3E,5Z)-3,5-Heptadien-1-ol (15). 15 (cis-trans isomer : trans-trans isomer=7:3) was derived from 14 by the modified procedure (80% yield)¹⁵. R_f=0.57 (benzene-ethyl acetate=95:5) ; IR (neat) : 3350, 1040, 980, 940 cm⁻¹ ; ¹H NMR (CDCl₃) δ=1.73 (d, J=6.9 Hz, 3H, C=CH-CH₃), 2.07-2.67 (m, 3H, C=CH-CH₂ and OH), 3.61 (t, J=6.6 Hz, 2H, CH₂-O), 5.17-6.57 (m, 4H, CH=CH-CH=CH) ; ¹³C NMR (CDCl₃) δ=13.1(C-7), 36.0(C-2), 61.7(C-1), 124.7(C-6), 127.7 (C-4), 129.0 (C-5), 129.5 (C-3) ; EI-MS m/z (rel intensity, %) 112 (M⁺, 29), 94 (2), 81 (100), 67 (28).

(3E,5Z)-1-Bromo-3,5-heptadiene (16). 16 (cis-trans isomer:trans-trans isomer=7:3) was derived from 15 in a similar manner as described in our previous paper¹⁵. R_f=0.47 (hexane) ; IR (neat) : 980, 940, 640 cm⁻¹ ; ¹H NMR (CDCl₃) δ=1.73 (d, J=6.3 Hz, 3H, C=CH-CH₃), 2.63 (m, 2H, C=CH-CH₂), 3.32 (t, J=7.4 Hz, 2H, CH₂-Br), 5.17-6.53 (m, 4H, CH=CH-CH=CH) ; ¹³C NMR (CDCl₃) δ=13.4 (C-7), 32.2 (C-2), 36.2 (C-1), 125.9 (C-6), 128.8 (C-4), 129.6 (C-5), 131.0 (C-3) ; EI-MS m/z (rel intensity, %) 176 (M⁺, 18), 174 (M⁺, 19), 95(100), 81(45), 67(40).

(3E,5Z)-1-Iodo-3,5-heptadiene (17). 17 (cis-trans isomer : trans-trans isomer=7:3) was derived from 16 by the conventional procedure (67% yield)¹⁵. R_f=0.50 (hexane) ; IR (neat) : 980, 940, 640 cm⁻¹ ; ¹H NMR (CCl₄) δ=1.74 (d, J=6.0 Hz, 3H, C=CH-CH₃), 2.67 (m, 2H, C=CH-CH₂), 3.18 (t, J=6.9 Hz, 2H, CH₂-I), 5.41-6.46 (m, 4H, CH=CH-CH=CH) ; ¹³C NMR (CDCl₃) δ=5.6 (C-1), 13.5 (C-7), 37.0 (C-2), 125.8 (C-6), 128.0 (C-4), 128.9 (C-5), 131.5 (C-3) ; EI-MS m/z (rel intensity, %) 222 (M⁺, 42), 95 (100), 67(44).

(3E,5Z)-3,5-Heptadienyltriphenylphosphonium Iodide (18). 18 (cis-trans isomer : trans-trans isomer=7:3) was derived from 17 by a known procedure(81% yield)¹⁵. ¹H NMR(CDCl₃) δ=1.70 (d, J=6.0 Hz, 3H, C=CH-CH₃), 2.16-2.72 (m, 2H, C=CH-CH₂), 3.50-4.16 (m, 2H, CH₂-Br), 5.05-6.47 (m, 4H, CH=CH-CH=CH), 7.70 (m, 15H, PPh₃) ; ¹³C NMR (CDCl₃) δ=13.1 (C-7), 23.1(C-1), 25.4(C-2), 116.7 (P-CH₂×3), 126.0 (C-6), 127.6 (C-4), 127.9 (C-5), 128.7 (C-3), 131.1, 133.1, 134.9 (Ph×3).

3-[(8Z,11E,13Z)-8,11,13-Pentadecatrienyl]catechol Diacetate (19). Butyllithium (4.1 ml, 1.55 M in hexane, 6.36 mmol) was added to a suspension of 18 (cis-trans isomer : trans-trans isomer=7:3, 2.8 g, 6.36 mmol) in 50 ml of dry benzene at 20°C under nitrogen. The resulting reddish solution was stirred for 1 h. The upper layer of the phosphorane solution was removed by a syringe and added to a stirred solution of 8 (1.4 g, 4.24 mmol) in 10 ml of dry benzene over 3 h at 25°C. The mixture was extracted with benzene and dried over K₂CO₃. The solvent was distilled under reduced pressure and the residue was extracted with hexane. The concentration of the hexane solution under reduced pressure gave a crude product. The crude product was chromatographed over silica gel with benzene-ethyl acetate (98:2) as eluent. The residue was purified by HPLC to give 19 (0.56 g, 50%) as an oil. R_f=0.45 (benzene-ethyl acetate=9:1) ; IR (neat) 3016, 2927, 1770, 1468, 1371, 1258, 1209, 1170, 988, 947, 909, 788, 724 cm⁻¹ ; ¹H NMR (CDCl₃) δ=1.33 (m, 6H, 3,4,5-CH₂), 1.57 (m, 4H, 2,6-CH₂), 1.73 (m, 3H, 15-CH₃), 2.03 (m, 2H, 7-CH₂), 2.29 (s, 3H, CH₃COO), 2.33 (s, 3H, CH₃COO), 2.51 (t, J=8.2 Hz, 2H, CH₂ Ar), 2.82 (m, 2H, 10-CH₂), 5.32-5.50 (m, 3H, 8,9,14-C=CH, J_{8,9}=10.5, J_{13,14}=10.5), 5.58-5.74 (dt, 1H, 11-C=CH, J_{11,12}=15.0), 5.87-6.07 (ddq, 1H, 13-C=CH, J_{12,13}=11.0), 6.23-6.40 (ddd, 1H, 12-C=CH), 6.98-7.23 (m, 3H, ArH) ; ¹³C NMR (CDCl₃) δ=13.2 (C-15), 27.1 (C-7), 29.0-29.7

(C-1~6), 30.5 (C-10), 120.8.0 (ArC-6), 124.2(C-14), 125.5 (C-12), 126.1 (ArC-4), 126.8 (C-9), 129.6 (ArC-3), 127.2 (ArC-5), 129.3 (C-13), 129.8 (ArC-3), 130.9 (C-8), 132.2 (C-11), 140.5 (ArC-2), 142.4 (ArC-1); EI-MS m/z (rel intensity, %) 398 (M^+ , 27), 355 (24), 313 (10), 123 (100).

3-[(8*Z*,11*E*,13*Z*)-8,11,13-Pentadecatrienyl]catechol (1). A solution of $LiAlH_4$ (4 mg, 0.12 mmol) in 5 ml of dry THF was added to a solution of tert-butyl alcohol (27 mg, 0.36 mmol) in 5 ml of dry THF at 0°C. The mixture was stirred for 10 min. A solution of 19 (5 mg, 0.013 mmol) in 5 ml of dry THF was added to the resulting mixture at -50°C, and the mixture was stirred for 1 h. Methanol (1 ml) was added to the mixture at -50°C. After warming to room temperature, the mixture was poured into an aq saturated NH_4Cl solution, and the product was extracted with benzene. The organic layer was dried over Na_2SO_4 and concentrated in vacuo below 25°C. The residue was chromatographed over silica gel (benzene-ethyl acetate=9:1 as eluent) to give the mixture of 1 and 19 (1:3) as an oil (3.7 mg, 90.0%). R_f =0.34 (benzene-ethyl acetate=95:5); IR (neat) 3480, 3030, 2940, 1625, 1475, 1375, 1270, 1230, 1178, 980, 945, 825, 770, 730 cm^{-1} ; 1H NMR ($CDCl_3$) δ =1.44 (m, 6H, 3,4,5- CH_2), 1.72 (m, 4H, 2,6- CH_2), 1.87 (d, 3H, 15- CH_3), 2.15 (q, 2H, 7- CH_2), 2.71 (t, 2H, CH_2Ar), 2.97 (t, 2H, 10- CH_2), 5.46-5.62 (m, 5H, 8,9,14-C=CH, $J_{8,9}$ =10.5, $J_{13,14}$ =10.4, OH $\times$ 2), 5.70-5.81 (dt, 1H, 11-C=CH, $J_{11,12}$ =14.2), 6.10-6.15 (ddq, 1H, 13-C=CH, $J_{12,13}$ =10.4), 6.42-6.52 (ddd, 1H, 12-C=CH), 6.82 (s, 3H, ArH); ^{13}C NMR ($CDCl_3$) δ =13.4 (C-15), 27.2 (C-7), 29.3-29.8 (C-1~6), 30.7 (C-10), 113.0 (ArC-6), 120.2 (ArC-4), 122.1 (ArC-5), 124.4 (C-14), 125.6 (C-12), 126.9 (C-9), 129.5 (C-13), 129.6 (ArC-3), 131.2 (C-8), 132.4 (C-11), 142.0 (ArC-2), 143.1 (ArC-1); EI-MS m/z (rel intensity, %) 314 (M^+ , 42), 179 (10), 163 (18), 136 (25), 123 (100), 79 (54).

3 Results and Discussion

3-(8-Oxo-1-octyl)catechol Diacetate (8). For the synthesis of 8, veratrole was subjected to alkylation¹⁶⁾ with 1,8-dibromooctane (84%), demethylation¹⁷⁾ with boron tribromide (92%), and acetylation with acetic anhydride (76%) to give the bromide 6. This was converted to the iodide 7 (88%) and oxidized with DMSO- $NaHCO_3$ to afford 8 (71%).

(3*E*,5*Z*)-3,5-Heptadienyltriphenylphosphonium Iodide (18). At the first step of the synthesis of 18, the hydroxyl group in 3-butyn-1-ol was subjected to protection with tetrahydropyran (THP) to give 9 (89%). The Grignard reaction between paraformaldehyde and the Grignard reagent derived from 9 and $EtMgBr$ gave 10 (90%). Trans-hydrogenation of 10 by lithium aluminium hydride gave 11 (62%). The oxidation of 11 with 12 gave 13 (71%). The Wittig reaction between 13 and the ylide derived from ethyltriphenylphosphonium bromide gave 14 (cis-trans isomer:trans-trans isomer=7:3, 80%). The elimination of the THP group from 14 gave 15 (cis-trans isomer : trans-trans isomer=7:3, 80%). These were brominated using carbon tetrabromide and triphenylphosphine to give 16 (cis-trans isomer : trans-trans isomer=7:3, 89%). These were converted to the iodide to give 17 (cis-trans isomer : trans-trans isomer=7:3, 67%). Phosphonium salt 18 (cis-trans isomer : trans-trans isomer=7:3) were derived from the reaction between the iodide 17 and triphenylphosphine (90%).

3-[(8*Z*,11*E*,13*Z*)-8,11,13-Pentadecatrienyl]catechol (1). The Wittig reaction between 8 and the ylide derived from the phosphonium salt 18 (cis-trans isomer : trans-trans isomer=7:3) gave 8,11,13-pentadecatrienyl compounds (50%). The main product 19 was isolated from the (8*E*)- and (13*E*)-isomers by HPLC. The isolated product 19 had infrared absorption bands at 947 and 988 cm^{-1} due to disubstituted trans-, cis- conjugated double bonds. The (8*Z*, 11*E*, 13*Z*)-olefinic configuration was confirmed by 1H - 1H COSY and J-resolved NMR experiment.

The protection groups of 19 were removed by treatment with $LiAlH_4$ -t-butylalcohol (1:3) in dry tetrahydrofuran (THF) at -50°C to give 1 (90%). The structure of the synthetic 1 was identified by infrared (IR) spectroscopy, 1H NMR, ^{13}C NMR and MS.

Fig. 1 TIC of Chinese Urushiol

- 1 ; 3-[(8Z,11E)-8,11,14-pentadecatrienyl]catechol (3)
 2 ; 3-(pentadecamonoenyl)catechol and 3-(pentadecadienyl)catechol
 3 ; 3-(pentadecanyl)catechol
 4 ; 3-[(8Z,11E,13E)-8,11,13-pentadecatrienyl]catechol (2)
 5 ; 3-[(8Z,11E,13Z)-8,11,13-pentadecatrienyl]catechol (1)

Analysis of saps of different origins. The saps of *Rhus vernicifera* from Xi'an in China, Iwate in Japan obtained at June and September, Woonchun and Wonju in Korea were analysed using GPC and GC/MS. The total ion chromatogram (TIC) of the sap from Xi'an in China is shown in Fig. 1. Three peaks 1, 4 and 5 with $[M]^+=314$ were seen at retention times of 17.06 min, 18.94 min and 19.08 min. They were identified as triene urushiols by the mass spectra. The triene urushiol is actually a composite of at least three compounds. These are undoubtedly *cis*- and *trans*-isomers of the triene side chains, but also of some structural isomers with three double bonds. The structural identification was carried out by the comparison of the retention times with 8Z, 11E, 13Z-triene urushiol (1) which is synthesized in this study, 8Z, 11E, 13E-triene urushiol (2) and 8Z, 11Z, 14-triene urushiol (3) which had been previously synthesized. As the result, they were identified as 3, 2 and 1, respectively. The peak 2 was identified as the monoene (MW 318) and diene (MW 316) urushiols. The peak 3 was identified as saturated urushiol (MW 320).

The olefinic urushiols are the important constituents for a high degree of polymerization of urushiol by the action of *Rhus* laccase in the film-making process or the drying process from the sap of the lacquer. All the saps with good performance as a lacquer coating materi-

Table 2 Quantitative analysis of saps of different origin

Peak NO.	TIC R.T. min	MS m/z (M+)	Urushiol (season)	China Xi'an	Japan Iwate (June	Korea Woonchun Wonju (September)		
1	17.06	314	8Z, 11Z, 14-triene	18.1	21.4	6.5	9.8	24.4
2	17.30	318, 316	mono and diene	22.4	22.3	21.1	18.6	22.8
3	18.00	320	saturated	2.9	2.8	3.6	3.1	2.5
4	18.94	314	8Z, 11E, 13E-triene	20.5	—	—	—	—
5	19.08	314	8Z, 11E, 13Z-triene	31.7	49.0	63.3	61.9	43.7
			others	4.4	4.5	5.5	6.6	6.6

al had a high content of the triene urushiol. Hence, the quantitative analysis of the triene urushiol is one of the best way to judge the performance of the saps. The result of the quantitative analysis of urushiol is given in **Table 2**. The composition of the urushiol varies depending on the growing conditions of the *Rhus vernicifera* tree and on the seasons when the sap is obtained. The most abundant constituent in general is triene urushiol and the next most abundant are the mono and diene urushiols. The presence of the total trienes were contained 68.1%–71.7%. These all saps must have good performance because of a high content of the triene.

4 Conclusion

3-[(8Z,11E,13Z)-8,11,13-pentadecatrienyl]catechol (1) was synthesized in good yields via the Wittig reaction of ylides derived from (3E, 5Z)-3,5-heptadienyltriphenylphosphonium iodide (18) with 3-(8-oxo-1-octyl)catechol diacetate (8) and, by a stepwise procedure of repeated protection and deprotection of the hydroxyl group of catechol.

Furthermore, the saps of *Rhus vernicifera* of different origins were analysed comparing with 1 as reference. As the result, it is revealed that the content of the triene urushiol varies depending on the growing conditions of the *Rhus vernicifera* tree and on the seasons when the sap is obtained. Therefore, considering these factors is efficient to obtain the sap with the best performance.

Acknowledgments

We are grateful to Professor Jung Oh Hyun of Seoul National University for providing the Korean urushi saps, and to Mr. Li Zhang of the Xi'an Institute of Lacquer, China for providing the Chinese urushi sap. We thank Mr. Jun Onodera and Mr. Tetsuo Higuchi for helpful discussions of Application and Reserch Center, Analytical Instruments Division, JEOL Ltd.

(Received : Aug. 25, 1997 ; Accepted : Nov. 21, 1997)

References

- 1) Y. Abe, "Shitsugeinyuumon", Kougeishuppan, Tokyo, 1987, p. 25.
- 2) J. Kumanotani, "Polymer Application of Renewable Resource Materials", ed. by C.E. Carraher, L.H. Sperling, Plenum Press, New York (1983), p. 225–248.
- 3) J. Kumanotani, K. Inoue, M. Achiwa, L.W. Chen, *Polym. Sci. Technol.*, **33**, 163 (1986).
- 4) R. Majima, *Ber. Dtsch. Chem. Ges. B*, **55**, 172 (1922).
- 5) S.V. Sunthanker, C.R. Dawson, *J. Am. Chem. Soc.*, **76**, 5070 (1954).
- 6) Y. Du, R. Oshima, J. Kumanotani, *J. Chromatogr.*, **284**, 463 (1984).
- 7) Y. Yamauchi, R. Oshima, J. Kumanotani, *J. Chromatogr.*, **243**, 71 (1982).
- 8) J. Bartus, W.J. Simonsick, C. Garner, T. Nishiura, T. Kitayama, K. Hatada, O. Vogel, *Polym. J.*, **26**, 27 (1994).
- 9) W.F. Symes, C.R. Dawson, *J. Am. Chem. Soc.*, **76**, 2959 (1954).
- 10) O. Hashimoto, K. Minami, *Mokuzai Gakkaishi*, **25**, 789 (1979).
- 11) J.H.P. Tyman, *Chem. Soc. Rev.*, **8**, 499 (1979).
- 12) T. Miyakoshi, H. Kobuchi, *Nippon Kagaku Kaishi*, **11**, 1271 (1990).
- 13) T. Miyakoshi, T. Saito, Y. Du, *J. Jpn. oil Chem. Soc.*, **39**, 56 (1990).
- 14) T. Miyakoshi, N. Niimura, H. Kobuchi, "56th National Meeting of the Chemical Society of Japan", Tokyo, April 1988, Abstr., 3XIB36.
- 15) T. Miyakoshi, H. Kobuchi, *J. Jpn. oil Chem. Soc.*, **40**, 210 (1991).
- 16) H. Halim, H.D. Locksley, J.J. Memon, *J. Chem. Soc. Perkin Trans. 1*, 2331 (1980).
- 17) J.H.P. Tyman, *Chem. Ind.*, 1974 526

[報文] 水溶液中における準安定な油微粒子の生成と成長 —光散乱法, 伝導度プローブ法による検討—

加茂川恵司^{*1,*2}・酒井 俊郎^{*3}・桃澤 信幸^{*2,*3}・島崎 益男^{*3}

榎村 眞一^{*4}・酒井 秀樹^{*2,*3}・阿部 正彦^{*2,*3}

*1 文部省初等中等教育局 (〒100-0013 東京都千代田区霞ヶ関)

*2 東京理科大学界面科学研究所 (〒162-0825 東京都新宿区神楽坂 1-3)

*3 東京理科大学理工学部 (〒278-0022 千葉県野田市山崎 2641)

*4 エム・テック株式会社 (〒547-0002 大阪市平野区加美東 3-3-8)

ベンゼンなどの油性物質を水中に滴下して超音波または機械的分散処理を行うことにより, 界面活性剤を含まない準安定油滴分散溶液を調製した。種々の油滴濃度, 超音波照射時間, 分散方法で調製した油滴の大きさの経時変化を, 動的散乱および伝導度測定により調べた。その結果, 油滴のサイズは 10^{-1} , 10^{-2} , 10^{-3} nm オーダーにそれぞれピークを有する 3 つの離散的な分布を与えることがわかった。油滴サイズの分布の中心は処理後 10~50 分の間に増大したが, 3 個のピークを与える粒子径の値は変化しなかった。これらの結果から, 界面活性剤を含まない系においても, マイクロエマルジョン-エマルジョンサイズの微小な油滴が過渡的に調製できることが示唆された。

(連絡者: 阿部正彦) Vol. 47, No. 2, 159 (1998)

[報文] 3-[(8 Z, 11 E, 13 Z)-8, 11, 13-pentadecatrienyl] catechol の合成および *Rhus vernicifera* 漆樹液中のトリエンウルシオール成分の分析

新村 典康・神谷 幸男・佐藤 崇弘・片野 一郎・宮腰 哲雄

明治大学理工学部工業化学科 (〒214-8571 川崎市多摩区東三田 1-1-1)

ウルシオールの主成分である 3-[(8 Z, 11 E, 13 Z)-8, 11, 13-pentadecatrienyl] catechol の合成について検討した。(3 E, 5 Z)-3, 5-heptadienyl-triphenylphosphonium iodide から得られた ylide と 3-(8-oxo-1-octyl) catechol diacetate との Wittig 反応および, カテコール水酸基の段階的な保護, 脱保護により目的化合物を高収率で合成することができた。更に, 合成トリエンウルシオールを標品として, 産地や収穫時期の異なる漆樹液中のトリエンウルシオール成分の定量分析を行った。塗料としての品質が高い漆樹液には多量のトリエンウルシオールが含まれている。従って, トリエンウルシオール成分の定量分析は, 漆樹液を評価する良い手法である。本研究によって, トリエンウルシオール成分の含有量は産地や収穫時期によって異なることが判明した。

(連絡者: 新村典康) Vol. 47, No. 2, 171 (1998)