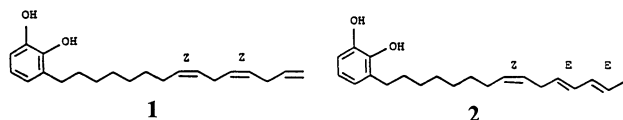


Synthesis of Urushiols with Pentadecatrienyl Side Chain, Two Constituents of the Sap of a Lac Tree, *Rhus Vernicifera*

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Synopsis. Two phenolic lipids, 3-[(8*Z*,11*Z*)-8,11,14- and 3-[(8*Z*,11*E*,13*E*)-8,11,13-pentadecatrienyl]catechol, which are the major constituents of the sap from a Japanese or Chinese lac tree, *Rhus vernicifera*, have been synthesized via the Wittig reaction of ylides derived from 3,6- and 3,5-heptadienylphosphonium salts with 3-(8-oxooctyl)catechol diacetate.

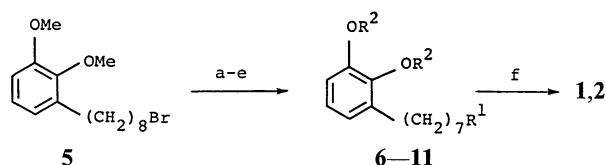
The fluid sap exuded from several kinds of Japanese or Chinese lac trees, *Rhus vernicifera*, dries into a tough and brilliant film and has been used as a naturally occurring coating material for thousands of years in the Orient.¹⁾ It is a latex composed of urushiols (60%), water (30%), plant gum (7%), water-insoluble glycoproteins (2%), and copper glycoproteins (ca. 0.1%).^{2–5)} The structures of urushiols have been determined to be catechols substituted at position 3 of the aromatic ring with a C₁₅-alkyl or alkenyl side chain.⁵⁾ The urushiols with an unsaturated side chain, **1** and **2**, are important contributors to the industrially useful polymerization properties of these natural products.^{1,6)} The presence of **1** in *poison ivy* and the sap from Japanese lacquer was reported by Dawson et al.⁷⁾ and Hashimoto et al.⁸⁾ In a previous paper we reported the synthesis of 3-[(8*Z*,11*Z*)-8,11,14- and (8*Z*,11*E*,13*E*)-8,11,13-pentadecatrienyl]veratrole by a Wittig reaction between 3-(8-oxooctyl)veratrole and the ylide derived from [(*Z*)-3,6- (**3**) and [(3*E*,5*E*)-3,5-heptadienyl]triphenylphosphonium iodide (**4**).⁹⁾ In this paper we describe an efficient synthesis of **1** and **2**.



Results and Discussion

Protection of hydroxyl groups of catechol as methyl ethers is now widely used and the protected form is very stable under various basic conditions.⁹⁾ However, deprotection cannot be carried out in acid-sensitive molecules such as urushiols having a pentadecatrienyl side chain.¹⁰⁾ Acetylation is also not exempted from some of these disadvantages. Urushiol was synthesized by a stepwise procedure based on repeated protection and deprotection of the hydroxyl group of catechol in good yields.¹¹⁾

The synthetic pathways to compounds **1** and **2** are illustrated in Scheme. For the synthesis of 3-(8-oxooctyl)catechol diacetate (**9**), veratrole was subjected to alkylation¹²⁾ with 1,8-dibromooctane (84%), demethylation¹³⁾ with boron tribromide (92%), and acetylation with acetic anhydride (76%) to give the bromide **7**. This was converted to the iodide **8** (88%) and oxidized with DMSO–NaHCO₃ to afford **9** (71%).



- 6** R¹ = CH₂Br, R² = H
7 R¹ = CH₂Br, R² = Ac
8 R¹ = CH₂I, R² = Ac
9 R¹ = CHO, R² = Ac
10 R¹ = CH=CHCH₂CH=CHCH₂CH=CH₂, R² = Ac
11 R¹ = CH=CHCH₂CH=CHCH=CHCH₃, R² = Ac

Scheme. Reagents: a, BBr₃, CH₂Cl₂; b, Ac₂O, C₅H₅N; c, NaI, Me₂CO; d, DMSO, NaHCO₃; e, BuLi, C₆H₆, **3** or **4**; f, LiAlH₄: *t*-BuOH=3:1, THF.

First, the Wittig reaction between **9** and the ylide derived from **3** gave 8,11,14-pentadecatrienyl compounds (45%). The main product **10** was isolated by HPLC. In the infrared spectrum of **10**, intense absorption bands of a monosubstituted olefin were observed at 910 and 990 cm⁻¹, without the characteristic *trans*-double bond absorption at 970 cm⁻¹. The stereochemistry of **10** was confirmed by a 270 MHz ¹H NMR spectrum with extensive decoupling experiments. Furthermore, the stereochemistry of the olefin formed by the Wittig reaction was determined to be *cis* from the diagnostic shift of the allylic methylene carbon (δ=27.2 C₂H₂C=C), which is to appear at δ=33–35 if the bond was *trans*.^{14,15)} The ¹³C NMR spectrum also demonstrated the 8-*cis*-configuration exhibiting the 8- and 9-olefinic carbon atoms at δ=130.4 and 126.9. The 10- and 13-carbon atoms of **10** occurred at δ=25.6 and 31.5 in the ¹³C NMR spectrum. These values are typical of such a long-chain dienyl and trienyl compounds.^{16–18)} Although these reaction conditions were known to result in a *cis*-stereoselective Wittig olefination,¹⁸⁾ the crude product contained 8% of (8*E*)-isomer, as demonstrated by GLC and HPLC.

3-[(8*Z*,11*E*,13*E*)-8,11,13-Pentadecatrienyl]catechol diacetate **11** was synthesized in a similar way from **9** and **4** in 40% yield. The resulting product **11** had an infrared absorption band at 985 cm⁻¹ due to disubstituted *trans,trans*-conjugated double bonds. The (8*Z*,11*E*,13*E*)-olefinic configuration was confirmed by ¹H–¹H, ¹H–¹³C COSY and a J-resolved NMR experiment. The (8*E*)-isomer could not be detected in this reaction product.

When **10** was treated with LiAlH₄ in tetrahydrofuran (THF) at room temperature, partial hydrogenation of the double bonds took place. The protecting groups of **10** were removed by treatment with LiAlH₄–*t*-butyl alcohol (1:3) in THF at –50 °C to give urushiol **1** (61%). The structure of the synthetic **1** was identified

by comparison of IR, ^1H NMR and EI-MS spectra with those of the reported data.⁵⁾

3-[(8*Z*,11*E*,13*E*)-8,11,13-Pentadecatrienyl]catechol (**2**) was synthesized from **11** in the same reductive procedure. The structure was identified by comparing the IR and ^1H NMR spectra with the reported data.⁵⁾

In conclusion, we have succeeded in the synthesis of urushiols **1** and **2** via the Wittig reaction of ylides derived from the heptadienylphosphonium salts **3** and **4** with di-*O*-acetyl-protected aldehyde **9**, respectively. This synthetic method may be applicable to the preparation of such long-chain polyene-substituted phenols as other urushiol analogues and cardanols.⁶⁾

Experimental

All ^1H NMR spectra were taken in chloroform-*d* or carbon tetrachloride with tetramethylsilane as internal standard on a Varian EM 390 spectrometer (90 MHz) and JEOL GSX 270 spectrometer (270 MHz). All ^{13}C NMR spectra were recorded on a JEOL GSX 270 spectrometer operated at 67.9 MHz. Low resolution mass spectra were taken on a JEOL DX-300 mass spectrometer. The spectra were run at 70 eV or with an emission current of 100 μA . High-performance liquid chromatograph (HPLC) was performed on a Gilson liquid chromatography with GPC (TSK gel, G1000H₈ 60 $\times$ 2.2 cm $\times$ 2, eluent: chloroform, flow rate, 4.0 ml min⁻¹ and silica gel (Develosil 10 mm $\times$ 25 cm, 5 μm , eluent: hexane-ethyl acetate=96:4, flow rate, 1.5 ml min⁻¹).

(3*Z*)-3,6-Heptadienyltriphenylphosphonium Iodide (**3**). To a solution of (*Z*)-7-iodo-1,4-heptadiene (4.0 g, 18 mmol), triphenylphosphine (7.08 g, 27 mmol) in 50 ml of acetonitrile was added under stirring for 24 h at 90°C. After 18 h the solution was filtered. The solid was washed with THF, and dried to give **3**,⁹⁾ 7.67 g (88%).

3-(8-Bromooctyl)veratrol (**5**). Butyllithium 66.2 ml (1.5 M in hexane, 99.3 mmol, 1 M=1 mol dm⁻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 NH₄Cl solution was added to the mixture at room temperature. The mixture was poured into a saturated NH₄Cl solution and extracted with ethyl acetate. The ethyl acetate solution was washed with brine, dried (K₂CO₃), and concentrated in vacuo to give 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 then with benzene to give **12**,⁹⁾ 27.5 g (84% yield).

3-(8-Bromooctyl)catechol (**6**). To a stirred solution of boron tribromide (25.0 g, 99.6 mmol) in 50 ml of dichloromethane was added dropwise a solution of **5** (23.1 g, 70.2 mmol) in 150 ml of dichloromethane 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 dichloromethane layer was treated with brine, dried (MgSO₄), and concentrated in vacuo. The residual oil was chromatographed (benzene-ethyl acetate=1:1 as eluent) to give **6** 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; ^1H NMR (90 MHz, CCl₄) δ =1.1–2.0 (m, 12H, CH₂), 2.53 (t, J =7 Hz, 2H, CH₂Ar), 3.33 (t, J =7 Hz, 2H, CH₂Br), 5.22 (br. s, 2H, OH, D₂O 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-Bromooctyl)catechol Diacetate (**7**). A solution of **6**

(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 (K₂CO₃) and concentrated in vacuo. The residue was chromatographed to afford **7** (16.3 g, 76%) as an oil. R_f =0.37 (benzene-ethyl acetate=9:1); IR (neat) 1780, 1600, 1500, 1220 cm⁻¹; ^1H NMR (90 MHz, 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), 3.33 (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-Iodooctyl)catechol Diacetate (**8**). After a mixture of **7** (5.26 g, 13.7 mmol) and NaI (3.07 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 **8** (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 (90 MHz, 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-Oxoocetyl)catechol Diacetate (**9**). A mixture of **8** (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. Then the mixture was 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 **9** as a colorless oil (9.7 g, 71% yield). R_f =0.33 (benzene-ethyl acetate=9:1); IR (neat) 2720, 1780, 1730, 1600, 1500, 1220 cm⁻¹; ^1H NMR (90 MHz, 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 =7 Hz, 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). Found: C, 67.31; H, 7.58%. Calcd for C₁₈H₂₄O₅: C, 67.48; H, 7.55%.

3-[(8*Z*,11*Z*)-8,11,14-Pentadecatrienyl]catechol Diacetate (**10**). To a suspension of **3** (2.31 g, 4.8 mmol) in 80 ml of dry benzene was added butyllithium (3.3 ml, 1.5 M in hexane, 4.8 mmol) at 20°C under nitrogen and the resulting reddish solution was stirred for 1 h. The upper layer of the phosphorane solution was taken up by a syringe and added to a stirred solution of **9** (1.02 g, 3.18 mmol) in 10 ml of dry benzene over 0.5 h at 25°C. Stirring was continued for 3 h at 25°C. The mixture was poured into a saturated aqueous ammonium chloride solution, extracted with benzene, and dried over MgSO₄. The solvent was distilled under reduced pressure and the residue was extracted with hexane. Concentration of the hexane solution under reduced pressure gave a crude product. The crude product was chromatographed over silica gel with benzene-ethyl acetate (9:1) as eluent and GPC with chloroform as eluent. The residue was purified by HPLC to give **10** (0.524 g, 42%) as an oil. R_f =0.48 (benzene-ethyl acetate=9:1); IR (neat) 3020, 2920, 1770, 1600, 1465, 1370, 1260, 1205, 1160, 1010, 995, 910, 780, 720 cm⁻¹; ^1H NMR (270 MHz, CDCl₃) δ =1.13–1.75 (m, 10H, 2,3,4,5,6-CH₂), 2.03 (m, 2H, 7-CH₂), 2.27 (s, 3H, CH₃COO), 2.31 (s, 3H, CH₃COO), 2.50 (t, J =7 Hz, 2H, CH₂Ar), 2.82 (m, 4H, C=CCH₂C=CCH₂C=C), 4.80–5.09 (m, 2H, 15-C=CH, $J_{\text{cis-14,15}}$ =10.0, $J_{\text{gem-15,15}}$ =1.7, $J_{\text{trans-14,15}}$ =17.0, $J_{\text{13,15}}$ =1.6 Hz), 5.27 (m, 4H, 8,9,11,12-C=CH), 5.74–5.89 (m, 1H, 14-C=CH, $J_{\text{trans-14,15}}$ =17.0, $J_{\text{cis-14,15}}$ =10.0, $J_{\text{13,14}}$ =6.1 Hz), 6.78–7.25 (m, 3H, ArH), ^{13}C NMR (CDCl₃) δ =20.3 (CH₃CO), 20.9 (CH₃CO), 25.6 (C-10), 27.2 (C-7), 31.5

(C-13), 114.6 (C-15), 120.8 (ArC-6), 126.2 (ArC-4), 126.9 (C-9), 127.2 (ArC-5), 127.8 (C-11), 129.4 (C-12), 130.4 (C-8), 136.6 (ArC-3), 136.8 (C-14), 140.5 (ArC-2), 142.4 (ArC-1), 168.2 (C=O), 168.3 (C=O); EI-MS m/z (rel intensity, %) 398 (M^+ , 5), 355 (12), 136 (27), 124 (26), 123 (100); Found: C, 75.21; H, 8.55%. Calcd for $C_{25}H_{34}O_4$: C, 75.34; H, 8.60%. The spectral data of (8*E*)-isomer are as follows: IR (neat) 3020, 2920, 1770, 1600, 1465, 1370, 1260, 1205, 1160, 1010, 995, 970, 910, 780, 720 cm^{-1} ; EI-MS m/z (rel intensity, %) 398 (M^+ , 4), 355 (11), 136 (20), 123 (100).

3-[(8*Z*,11*E*,13*E*)-8,11,13-Pentadecatrienyl]catechol Diacetate (11). Compound **9** and **4** were allowed to react in a similar manner to that described in the preparation of **10** to give **11** as an oil (40%). $R_f=0.43$ (benzene-ethyl acetate=9:1); IR (neat) 3015, 2926, 1770, 1615, 1591, 1469, 1370, 1258, 1210, 1170, 1213, 1013, 985, 909, 789, 725 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) $\delta=1.33$ (m, 6H, 3,4,5- CH_2), 1.57 (m, 4H, 2,6- CH_2), 1.73 (d, $J=7$ Hz, 3H, $CH_3C=C$), 2.03 (m, 2H, 7- CH_2), 2.29 (s, 3H, CH_3COO), 2.33 (s, 3H, CH_3COO), 2.51 (t, $J=8$ Hz, 2H, CH_2Ar), 2.82 (m, 2H, $C=CCH_2C=C$), 5.31–5.45 (m, 2H, 8,9- $C=CH$), 5.45–5.66 (m, 2H, 11,14- $C=CH$), 5.90–6.10 (m, 2H, 12,13- $C=CH$), 7.03 (m, 1H, ArH), 7.09–7.21 (m, 2H, Ar). The accurate chemical shifts and coupling constants were determined by the decoupling experiments: 8-CH: 5.43, 9-CH: 5.37, 11-CH: 5.51, 12,13-CH: 6.01, 14-CH: 5.58; $J_{7,8}=6.2$, $J_{8,9}=11.0$, $J_{11,12}=J_{13,14}=14.4$, $J_{10,11}=J_{14,15}=6.5$ Hz. ^{13}C NMR ($CDCl_3$) $\delta=18.0$ (C-15), 20.3 (CH_3CO), 20.9 (CH_3CO), 27.1 (C-7), 29.1, 29.2, 29.4, 29.5, 29.7 (C-2-6), 30.0 (C-1), 30.2 (C-10), 120.8 (ArC-6), 126.2 (ArC-4), 126.3 (C-9), 127.1 (C-8), 127.2 (ArC-5), 129.8 (C-14), 129.4 (C-12), 130.8 (C-11), 131.5 (C-13), 136.6 (ArC-3), 140.5 (ArC-2), 142.4 (ArC-1), 168.2 (C=O), 168.3 (C=O); EI-MS m/z (rel intensity, %) 398 (M^+ , 57), 355 (55), 313 (24), 285 (10), 135 (45), 124 (56), 123 (100); Found: C, 75.38; H, 8.49%. Calcd for $C_{25}H_{34}O_4$: C, 75.34; H, 8.60%.

3-[(8*Z*,11*Z*)-8,11,14-Pentadecatrienyl]catechol (1). To a solution of $LiAlH_4$ (68 mg, 1.8 mmol) in 5 ml of dry THF was added *tert*-butyl alcohol (400 mg, 5.4 mmol) in dry THF (5 ml) at 0°C and the mixture was stirred for 10 min. To the resulting mixture, a solution of **10** (78 mg, 0.2 mmol) in 5 ml of dry THF was added at –50°C, and the mixture was stirred for 50 min. 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 ethyl acetate. 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) and by HPLC (silica gel Si 60, 5 μm , 10 mm $\times$ 25 cm eluting with hexane-ethyl acetate=94:6, 1.5 ml min $^{-1}$) to give **1** (39 mg, 61%) as an oil. $R_f=0.34$ (benzene-ethyl acetate=9:1); IR (neat) 3450, 3030, 2920, 1600, 1500, 1475, 1360, 1275, 990, 910, 720 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) $\delta=1.13$ –1.75 (m, 10H, 2,3,4,5,6- CH_2), 2.03 (m, 2H, 7- CH_2), 2.55 (t, $J=7$ Hz, 2H, CH_2Ar), 2.82 (m, 4H, $C=CCH_2C=CCH_2C=C$), 4.80–5.09 (m, 2H, 15- $C=CH$, $J_{cis-14,15}=10.0$, $J_{gem-15,15}=1.7$, $J_{cis-14,15}=17.0$, $J_{13,15}=1.6$ Hz), 5.1–5.3 (m, 2H, OH, D_2O exchangeable), 5.27–5.49 (m, 4H, 8,9,11,12- $C=CH$), 5.74–5.89 (m, 1H, 14- $C=CH$, $J_{trans-14,15}=17.0$ Hz), 6.60 (s, 3H, ArH); EI-MS m/z (rel intensity, %) 314 (M^+ , 5), 179 (25), 136 (21), 124 (27), 123 (100). Retention time of **1** on GLC (10.40 min; OV-1, 0.32 mm $\times$ 25 m, programmed from 200 to 280°C at 5°C min $^{-1}$).

3-[(8*Z*,11*E*,13*E*)-8,11,13-Pentadecatrienyl]catechol (2). This was prepared from **11** and $LiAlH_4$ -*t*-BuOH in THF in a similar manner to that described in the preparation of **1**. 2: Yield; 65% oil; $R_f=0.39$ (benzene-ethyl acetate=9:1); IR (neat) 3480, 3030, 2940, 2860, 1625, 1600, 1475, 1375, 1270, 1230, 1178, 985, 825, 770, 730 cm^{-1} ; 1H NMR (270 MHz,

$CDCl_3$) $\delta=1.31$ (m, 8H, 3,4,5,6- CH_2), 1.57 (m, 2H, 2- CH_2), 2.03 (m, 2H, 7- CH_2), 2.59 (t, $J=8$ Hz, 2H, CH_2Ar), 2.81 (m, 2H, $C=CCH_2C=C$), 5.31–5.45 (m, 3H, 8,9- CH_2), 5.45–5.66 (m, 2H, 11,14- $C=CH$), 5.7 (br. s, 2H, OH, D_2O exchangeable), 5.92–6.09 (m, 2H, 12,13- $C=CH$), 6.69 (s, 3H, ArH); The accurate chemical shifts and coupling constants were determined by decoupling experiments: 8-CH: 5.43, 9-CH: 5.37, 11-CH: 5.53, 12, 13-CH: 6.02, 14-CH: 5.58; $J_{8,9}=10.4$, $J_{9,10}=J_{7,8}=6.5$, $J_{10,11}=J_{14,15}=7.0$, $J_{13,14}=J_{11,12}=14.4$ Hz; ^{13}C NMR ($CDCl_3$) $\delta=19.0$ (C-15), 27.1 (C-7), 29.1, 29.2, 29.4, 29.5, 29.6 (C-2-6), 29.8 (C-1), 30.3 (C-10), 112.0 (ArC-6), 120.0 (ArC-4), 122.0 (ArC-5), 127.0 (C-9), 127.2 (C-8), 129.4 (C-14), 129.9 (C-12), 130.4 (C-11), 130.7 (C-13), 131.5 (ArC-3), 142.0 (ArC-2), 143.1 (ArC-1); EI-MS m/z (rel intensity, %) 314 (M^+ , 9), 179 (5), 136 (11), 124 (27), 113 (100). Compound **2** was identified by comparison of the retention times on GLC (10.25 min; OV-1, 0.32 mm $\times$ 25 m, programmed from 200°C to 280°C at 5°C min $^{-1}$) and HPLC (11.35 min; silica gel, 10 mm $\times$ 25 cm, 5 μm , hexane-ethyl acetate=96:4, 1.5 ml min $^{-1}$) with those of the natural sample and by GC-MS analysis.

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