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

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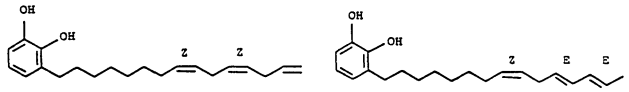
Synopsis. Two phenolic lipids, 3-[(8*Z*,11*Z*)-8,11,14- and 3-[(8*Z*,11*E*,13*E*)-8,11,13-pentadecatrienyl]catechol, which are the major constituents of the sap from a Japanese or Chinese lac tree, *Rhus vernicifera*, have been synthesized via the Wittig reaction of ylides derived from 3,6- and 3,5-heptadienylphosphonium 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 C_{15}-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 laquer 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**.

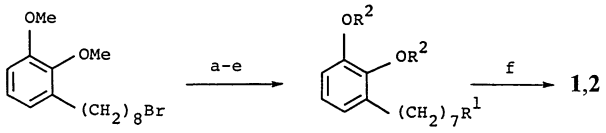


1 **2**

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 alkylation[12] with 1,8-dibromooctane (84%), demethylation[13] 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–$NaHCO_3$ to afford **9** (71%).



5 **6—11**

6 $R^1=CH_2Br$, $R^2=H$
7 $R^1=CH_2Br$, $R^2=Ac$
8 $R^1=CH_2I$, $R^2=Ac$
9 $R^1=CHO$, $R^2=Ac$
10 $R^1=CH{=}CHCH_2CH{=}CHCH_2CH{=}CH_2$, $R^2=Ac$
11 $R^1=CH{=}CHCH_2CH{=}CHCH{=}CHCH_3$, $R^2=Ac$

Scheme. Reagents: a, BBr_3, CH_2Cl_2; b, Ac_2O, C_5H_5N; c, NaI, Me_2CO; d, DMSO, $NaHCO_3$; e, BuLi, C_6H_6, **3** or **4**; f, $LiAlH_4$: *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. Furtheremore, 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 $\underline{C}H_2C{=}C$), which is to appear at δ=33—35 if the bond was *trans*.[14,15] The ^{13}C 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 ^{13}C 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–^{13}C COSY and a J-resolved NMR experiment. The (8*E*)-isomer could not be detected in this reaction product.

When **10** was treated with $LiAlH_4$ in tetrahydrofuran (THF) at room temperature, partial hydrogenation of the double bonds took place. The protecting groups of **10** were removed by treatment with $LiAlH_4$–*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, ^{1}H 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 ^{1}H 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 ^{1}H 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, G1000H$_8$ 60×2.2 cm×2, eluent: chloroform, flow rate, 4.0 ml min^{-1} and silica gel (Develosil 10 mm×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 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 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 ($MgSO_4$), 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}; ^{1}H NMR (90 MHz, CCl_4) δ=1.1—2.0 (m, 12H, CH_2), 2.53 (t, *J*=7 Hz, 2H, CH_2Ar), 3.33 (t, *J*=7 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-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 (K_2CO_3) 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}; ^{1}H NMR (90 MHz, CCl_4) δ=1.1—2.0 (m, 12H, CH_2), 2.27 (s, 3H, CH_3CO), 2.31 (s, 3H, CH_3CO), 2.51 (t, *J*=7 Hz, 2H, CH_2Ar), 3.33 (t, *J*=7 Hz, 2H, CH_2Br), 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 $Na_2S_2O_3$, dried over $MgSO_4$, 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}; ^{1}H NMR (90 MHz, CCl_4) δ=1.1—2.0 (m, 12H, CH_2), 2.27 (s, 3H, CH_3CO), 2.31 (s, 3H, CH_3CO), 2.51 (t, *J*=7 Hz, 2H, CH_2Ar), 3.05 (t, *J*=7 Hz, 2H, CH_2I), 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-Oxooctyl)catechol Diacetate (9). A mixture of **8** (18.5 g, 42.8 mmol), 200 ml of DMSO, $NaHCO_3$ (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 $MgSO_4$, filtered, and evaporated. Column chromatography (gradient elution, benzene–ethyl acetate= 9 : 1—3 : 1) gave **9** as a colorless oil (9.7g, 71% yield). R_f=0.33 (benzen–ethyl acetate=9 : 1); IR (neat) 2720, 1780, 1730, 1600, 1500, 1220 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ=1.1—1.8 (m, 10H, CH_2), 2.27 (s, 3H, CH_3CO), 2.31 (s, 3H, CH_3CO), 2.35 (t, *J*=7 Hz, 2H, CH_2CO), 2.50 (t. *J*=7 Hz, 2H, CH_2Ar), 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 $C_{18}H_{24}O_5$: 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 $MgSO_4$. 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}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.13—1.75 (m, 10H, 2,3,4,5,6-CH_2), 2.03 (m, 2H, 7-CH_2), 2.27 (s, 3H, CH_3COO), 2.31 (s, 3H, CH_3COO), 2.50 (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, $J_{cis\text{-}14,15}$=10.0, $J_{gem\text{-}15,15}$=1.7, $J_{trans\text{-}14,15}$ =17.0, $J_{13,15}$=1.6 Hz), 5.27 (m, 4H, 8,9,11,12-C=CH), 5.74—5.89 (m, 1H, 14-C=CH, $J_{trans\text{-}14,15}$=17.0, $J_{cis\text{-}14,15}$=10.0, $J_{13,14}$=6.1 Hz), 6.78—7.25 (m, 3H, ArH), ^{13}C NMR ($CDCl_3$) δ=20.3 (CH_3CO), 20.9 (CH_3CO), 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, $CDCl_3$) δ=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 ($CDCl_3$) δ=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×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, $CDCl_3$) δ=1.13—1.75 (m, 10H, 2,3,4,5,6-CH_2), 2.03 (m, 2H, 7-CH_2), 2.55 (t, *J*= 7Hz, 2H, CH_2Ar), 2.82 (m, 4H, C=CCH_2C=CCH_2C=C), 4.80—5.09 (m, 2H, 15-C=CH, $J_{cis\text{-}14,15}$=10.0, $J_{gem\text{-}15,15}$=1.7, $J_{cis\text{-}14,15}$=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, $J_{trans\text{-}14,15}$ =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×25 m, programed 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, $CDCl_3$) δ=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 ($CDCl_3$) δ=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×25 m, programed from 200 °C to 280 °C at 5 °C min^{-1}) and HPLC (11.35 min; silica gel, 10 mm×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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