Synthesis of Urushiol Components and Analysis of Urushi Sap from *Rhus vernicifera*

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Abstract : An efficient method for synthesizing unsaturated urushiol components in urushi sap, was established, Wittig reaction of ylides derived from alkyl- and alkenyltriphenylphosphonium iodides, as side chain parts of urushiol, with 3-(8-oxo-1-octyl)catechol diacetate or 3-(10-oxo-1-decyl)catechol diacetate, as aromatic part of urushiol.

Quantitative analysis of urushiol components in the urushi sap was done using GC for comparison with synthesized urushiol components as reference. In this manner, we proved the structures of most urushiol components and established percentage compositions of urushiols in the sap of *Rhus vernicifera* of Japan, Korea and China. (approximately 95%), by quantitative analysis of urushiol derived from *Rhus vernicifera*, the most abundant constituent was triene urushiol (approximately 71%) and the next abundant were mono (14–16%) and diene (5–8%) urushiol. Content was found to depend on growth conditions of the *Rhus vernicifera* tree and on the particular season for obtaining sap.

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Key words : urushi, urushiol, lacquer, synthesis of urushiol

1 Introduction

Sap from *Rhus vernicifera* (Japanese, Chinese and Korean lacquer trees) has been used as a surface coating material for several thousand years in Asian countries, because it dries into a tough and brilliant film (1,2). The sap is obtained by tapping lacquer trees in the same way that natural rubber is harvested from rubber trees. The main constituents of the sap are latex composed of urushiol (55–70%), water (20–25%), plant gum (6.5–10%), water-insoluble glycoprotein (1.4–2.8%) and laccase enzyme (0.1–1%) (3–5).

Urushiols, major components of the sap, are compounds of 3-substituted catechols with saturated and unsaturated side chains. The composition of the olefinic side chain of urushiol components has been investigated using gel permeation chromatography (GPC), high performance liquid chromatography (HPLC) and nuclear magnetic resonance (NMR) spectroscopy. Structures and constituents of urushiol from Japanese lacquer are

shown in Fig. 1 by Kumanotani *et al.* (6–8), but in their results, some parts which did not agree with ours. In a previous paper, we reported the synthesis of trienylurushiols, i.e., 3-[(8Z,11E,13Z)-8,11,13-pentadecatrienyl]catechol, 3-[(8Z,11E,13E)-8,11,13-pentadecatrienyl]catechol and 3-[(8Z,11E)-8,11,14-pentadecatrienyl]catechol which are major urushiol components (9,10), and the analysis of sap from *Rhus vernicifera* using gas chromatography (GC) (10).

Although urushiol components 1, 3, 5 and 6 in Fig. 2 were synthesized by H. Halim, M. V. Sargent and H. J. Bestmann *et al.* (11–13), in this study the novel synthetic route of mono-enyl and dienylurushiols 1~6, shorter than their routes, was established by adapting ozonolysis method in the synthesis of aromatic part. Additionally, the urushi sap from *Rhus vernicifera* was analyzed using DB-17 (methylphenyl(50%)silicone) as separation column for GC and GC/MS, then many urushiol components were detected in comparison with DB-1 (methylsilicone) previously used. The performance of oily components is discussed in terms of content of the olefinic urushiol monomer components in comparison with the standard urushiols, synthesized in this work.

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	C15	%
	R=	4.5
		15.0
		1.5
		4.4
		6.5
		55.4
		1.7
		7.4
	C17	
		1.5
		1.8

Fig.1 Structure and Constituents of Urushiol from *Rhus vernicifera* (Japanese lacquer tree).

2 Results and Discussion

2.1 Synthesis of Urushiol Components

Urushiol components shown in Fig. 2, were synthesized via Wittig reaction from an ylide derived from a phosphonium salt as the side chain with 3-(8-oxo-1-octyl)catechol diacetate or 3-(10-oxo-1-decyl)catechol diacetate as the aromatic part, followed by removal of acetate groups, as previously reported (8,9).

We previously reported that synthesis of 3-(8-Oxo-1-

-octyl)catechol diacetate **9** was synthesized by a step-wise procedure based on repeated protection and deprotection of the hydroxyl group of catechol using veratrol as starting material. In this study compound **9** was synthesized by ozonolysis of the double bond of the natural urushiol side chain, because almost all urushiol components from *Rhus vernicifera* have double bond in the 8-position of the side chain.

Hydroxyl groups of urushiol components, isolated by silica gel openchromatography, were protected by acetic anhydride to give O-diacetyl urushiol **8**. The double bond of O-diacetyl urushiol **8** was ozonated. The ozonide was reduced to give 3-(8-oxo-1-octyl)catechol diacetate **9** (scheme 1). Compound **9**, synthesized by ozonolysis of natural urushiol, was identified as 3-(8-oxo-1-octyl) catechol diacetate by comparing ^1H and ^{13}C NMR spectra of compound **9** from ozonolysis and the previously reported method. 3-(10-Oxo-1-decyl) catechol diacetate **12** was synthesized using natural laccol components of main components of Vietnamese lacquer lipid, having double bond in the 10-position of the side chain, by this method, too.

Six alkyl- and alkenyltriphenylphosphonium iodides as side chain were synthesized from various alcohols and carboxylic acid (scheme 2). Compounds **13** and **14** were synthesized by well known method (14,15). Phosphonium salt **18** was synthesized by reducing (*E*)-3-heptenic acid **15** with LiAlH_4 , and iodination of hydroxyl group of compound **16** and reaction compound **17** with triphenylphosphine. Compound **21** was synthesized by iodination of hydroxyl group of **19**, and reaction **20** with triphenylphosphine. Phosphonium salt **28** was synthesized from 3-butyne-1-ol **22** as starting material.

Monoenyl urushiol components

Dienyl urushiol components

Fig.2 Stereostructures of Synthesized Urushiol Components.

Scheme 1 Synthesis of 3-(8-oxo-1-octyl)catechol Diacetate and 3-(8-oxo-1-decyl)catechol Diacetate.

Scheme 2 Synthesis of Alkyl- and Alkenyltriphenylphosphonium Iodides.

After hydroxyl group of **22** was protected by DHP, compound **24** was prepared by Grignard reaction of **23** with *n*-dipropyl sulfate. Compound **24** was reduced in *Z*-form with palladium catalyst to give compound **25**. THP group of compound **25** was deprotected by *p*-TsOH-MeOH, followed by iodination of the hydroxyl group to give compound **27**. Phosphonium salt **28** was prepared by reacting **27** with triphenylphosphine.

Compounds **1** and **4**~**6** were produced by *cis* selective Wittig reaction of ylides derived from alkyl- and alkenyl phosphonium iodides **14**, **18**, **21**, and **28** with aromatic parts **9** and removal of acetate groups. Compound **2** and **3** were synthesized by *cis* selective Wittig reaction of ylides derived from alkyl- and alkenyl phosphonium iodides **13** and **14** with aromatic parts **12** and removal of acetate groups. Condition of *cis* selective Wittig reaction

was two methods of free salt-reaction type (10) and low temperature-reaction type (at -78°C in THF) (13). Both Wittig reaction makes a *Z* double bond at high rate. The resultant olefin from the Wittig reaction was confirmed as the *Z*-form at more than 80% by GC and NMR spectral analysis.

2.2 Analysis of the Saps of *Rhus vernicifera* Lacquer Trees

Saps of *Rhus vernicifera* from Japanese (Iwate), Korean (Wonju), and Chinese (Xi'an) lacquer were analyzed. Each native sap was mixed with acetone (sap: acetone = 1:3 (v/v)). The resulting mixture was filtered. The filtrate was evaporated to give a crude urushiol preparation as residue. 200 mg residue were dissolved in 2 mL chloroform and the solution was applied onto a GPC column (TSK-gel G1000H6 $\times$ 2,60 cm $\times$ 21.5 mm I.D.; TOSOH). The column was eluted with chloroform to separate monomeric components from crude urushiol. Monomeric fractions were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). A previous paper reported the analysis of sap from the *Rhus vernicifera* lacquer tree using GC and GC/MS with DB-1 (methylsilicone 100%) as a separation column (10), but the results were not acceptable because of overlapping peaks in the chromatogram. We thus used DB-17 (methylphenyl (50%)silicone) as a separation column for GC and GC/MS analysis. The resultant chromatogram of the monomeric fraction from Chinese lacquer tree had no overlapping peak as shown in Fig. 3. As results, new components, peaks 7~9, 14 and 15, could be detected in gas chromatogram. The peaks in the chromatogram were identified as saturated ($[\text{M}]^+ = 320$), monoene ($[\text{M}]^+ = 318$), diene ($[\text{M}]^+ = 316$), triene ($[\text{M}]^+ = 314$) urushiol components, monoene ($[\text{M}]^+ = 346$), and diene ($[\text{M}]^+ = 344$) laccol components, by mass spectra. The laccol components have C-17 side chains.

The unsaturated urushiols have one, two and three double bond in the side chains, double bonds may have the *E* or *Z* configuration. Structural identification was carried out by comparison of retention times with urushiol components 1~6 synthesized, and (8*Z*, 11*E*, 13*Z*)-, (8*Z*, 11*E*, 13*E*)- and (8*Z*, 11*Z*, 14)- triene urushiol and saturated urushiol, previously synthesized. Urushiol components of *Rhus vernicifera* of Japan, Korea and China were identified as shown in Table 1. Structures and compositions of approximately 95% urushiol components were clear in this study. By quantitative analysis of urushiol derived from *Rhus vernicifera*, the most

Fig.3 Gas Chromatogram of Urushiol Components from Chinese Lacquer Tree.

abundant constituent was triene urushiol (approximately 71%) and the next abundant were mono (14~16%) and diene (5~8%) urushiol. Olefinic urushiols are important constituents for high degree of polymerization of urushiol by action of *Rhus* laccase in film-drying. All the saps gave good film performance because of high content of triene urushiols.

3 Conclusion

Alkenylurushiol components 1~6 were synthesized via the Wittig reaction of ylides derived from the corresponding alkyl- and alkenyltriphenylphosphonium iodides with corresponding aromatic parts using ozonolysis of natural lipid component from lacquer sap.

The saps of *Rhus vernicifera* were analyzed by comparison with urushiols 1~6 synthesized in this study and with saturated and three triene urushiols, previously synthesized. The structures of most urushiol components were determined and we established the percentage composition (approximately 95% total) of the urushiols in the sap of *Rhus vernicifera* of Japan, Korea and China.

4 Experimental

4.1 GPC, GC, and GC/MS Conditions

GPC was carried out on a LC-908 (JAI co., Ltd.) equipped with a refractive index detector and ultraviolet

Table 1 Analysis of Urushiol with GC and GC/MS, and Structure of Urushiols.

peak	m/z	Japan(Iwate)		China(Xian)		Korea(Wonju)		Structure of side chain R	
		Retention time (min.)	Area (%)	Retention time (min.)	Area (%)	Retention time (min.)	Area (%)		
1	320	10.39	2.5	10.33	2.7	10.34	3.1		
2	318	10.81	16.4	10.74	14.4	10.75	14.3		
3	318	11.08	0.8	11.02	0.5	11.02	1.2	Pentadecenylcatechol	
4	316	11.59	2.4	11.53	4.7	11.54	2.8		
5	316	11.74	3.0	11.66	3.2	11.67	2.3		
6	314	12.14	20.7	12.07	17.9	12.09	9.4		
7	316	12.4	12.32	12.32	1.6	12.34	1.4	Pentadecadienylcatechol	
8	316	12.8	1.8	12.73	0.2	12.76	0.6	Pentadecadienylcatechol	
9	318	14.31	0.4	14.23	0.1	14.24	0.6	Pentadecenylcatechol	
10	314	15.01	3.1	14.92	20.2	14.95	5.5		
11	314	15.56	46.8	15.47	32.9	15.53	56.3		
12	346	17.53	0.2	17.43	0.4	17.49	0.2		
13	344	18.22	0.3	18.13	0.1	18.16	0.5		
14	314	—	—	19.93	0.2	19.9	0.2	Pentadecatrienylcatechol	
15	314	20.78	1.2	20.65	0.5	20.73	1.6	Pentadecatrienylcatechol	

detector (254 nm) and GPC column (TSK-gel G1000 H6×2, 60 cm×21.5 mm I.D.; TOSOH). Flow rate was 3.5 mL/min with chloroform as eluent.

GC was conducted with a SHIMADZU GC-17A instrument equipped with a flame-ionization detector. GC/MS was carried out using an HP6890 (Hewlett-Packard, Ltd.) instrument and mass spectrometer in the EI-mode (70 eV). A DB-17 column (J&W Scientific) was used: DB-17 (methylphenyl(50%)silicone), 30 m×0.25 mm I.D., thickness of liquid phase film (df)=0.25 mm. The carrier gas was helium and samples were injected in the split mode (splitting ratio 50:1). GC and GC/MS were carried out at constant temperature of 250°C for 30 min.

4.2 Synthesis of Urushiol Components

All ¹H NMR spectra were taken in chloroform-d with tetramethylsilane as internal standard on a JNM-GSX 270 or JNM-GSX 400 spectrometer (JEOL Ltd.). All ¹³C NMR spectra were recorded on a JNM-GSX 270 or JNM-GSX 400 spectrometer (JEOL Ltd.) operated at 67.9 MHz and 100 MHz, respectively.

Compounds 18, 21, 23, 26 and 28 were synthesized in

similar method as described in our previous paper (16). Compounds 30~34 were synthesized in similar method as described by M. V. Sargent *et al.* (13).

3-Alkenylcatechol diacetate 8

Compound 8 (73.3%) was derived from natural urushiol, extract from Chinese lacquer sap, by known procedure (10). R_f=0.35-0.50 (hexane-ethyl acetate=4:1); ¹H-NMR (270 MHz, CDCl₃/TMS) δ(ppm)=2.27 (s, 3H, -OAc), 2.31 (s, 3H, -OAc), 2.51 (t, 2H, J=7.0 Hz, -CH₂-Ph), 7.02-7.27 (m, 3H, Ph); ¹³C-NMR (67.9 MHz, CDCl₃/TMS) δ(ppm)=168.2, 169.2 (C-15, 17)

3-(8-Oxo-1-octyl)catechol diacetate 9

Ozone was passed into a solution of compound 8 (7.00 g, 19.3-19.7 mmol) and dry methylene chloride (105 mL) at r.t. and was stirred until T.L.C spots of compound 8 vanished. Dimethyl sulfide (3.80 g, 58.5 mmol) was added to the reaction mixture and stirred for 12 h. The mixture was washed with water and the organic layer was dried (Na₂SO₄) and concentrated *in vacuo*. The residue was isolated using silica gel (hexane-ethyl

acetate=4:1) to give 3-(8-oxo-1-octyl)catechol diacetate **9** (3.95g, 62.6%). Compound **9** was identified by comparison with standard product previously synthesized (**10**).

3-Alkenylcatechol diacetate **11**

3-Alkenylcatechol diacetate **11** (61.0% yield) was prepared from natural laccol components **10** by known procedure (**10**). Rf=0.35-0.45 (hexane-ethyl acetate=4:1); ¹H-NMR (270 MHz, CDCl₃/TMS) δ(ppm)=2.26(s, 3H, -OAc), 2.31(s, 3H, -OAc), 2.51(t, 2H, J=7.0 Hz, -CH₂-Ph), 7.01-7.18(m, 3H, Ph); ¹³C-NMR (67.9MHz, CDCl₃/TMS) δ(ppm)=168.2, 169.2(C-17,19)

3-(8-Oxo-1-octyl)catechol diacetate **12**

Compound **12** (64.0% yield) was prepared from compound **11** in a similar to compound **9**. Rf=0.20 (hexane-ethyl acetate=4:1); ¹H-NMR (270 MHz, CDCl₃/TMS) δ(ppm)=1.29(m, 10H, -CH₂-×5), 1.60(m, 4H, -CH₂-C-Ph, -CH₂-C-CHO), 2.27(s, 3H, -OAc), 2.31(s, 3H, -OAc), 2.41(t, J=7.4Hz, 2H, -CH₂-CHO), 2.51(t, J=7.4Hz, 2H, -CH₂-Ph), 7.01-7.26(m, 3H, Ph), 9.75(s, 1H, -CHO); ¹³C-NMR (67.9 MHz, CDCl₃/TMS) δ(ppm)=20.3, 20.7[C-18, 20], 22.0-30.0[C-7-14], 43.6[C-13], 120.7[C-3], 126.0[C-1], 127.0[C-2], 136.4[C-6], 140.4[C-5], 168.0, 168.1[C-17,19], 202.6[C-16]

(E)-3-Heptene-1-ol **16**

Compound **15** (6.00 g, 46.8 mmol) in 10.0 mL dry THF was added dropwise to a stirred solution of LAH (2.66 g, 70.2 mmol) and dry THF (10 mL). The mixture was stirred at 70°C for 5h. Excess LAH in the reaction mixture was treated with methanol and the mixture was poured into a solution of ice water and 1N -HCl. The solution was decanted with ethyl ether and the organic layer was dried with Na₂SO₄. The organic solvent was removed under reduced pressure (20°C/80 mmHg) to give the crude product. The crude product was chromatographed over silica gel (hexane-ethyl acetate=4:1) to give **16** (3.92g, 73.3%). Rf=0.35(hexane-ethyl acetate=4:1); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm)=0.87-0.92 [t, J=7.42, 6.92Hz, 3H, -CH₃], 1.32-1.47[(sextet, J=6.92, 7.42Hz, 2H, -C=C-C-CH₂-), (s, 1H, -OH)], 1.96-2.05[quartet, J=6.43, 6.92, 8.91Hz, 2H, -C=C-CH₂-], 2.23-2.30[quartet, J=6.93, 2H, -CH₂-C-O-], 3.59-3.65[t, J=5.44, 5.94 Hz, 2H, -CH₂-O-], 5.33-5.61[m, 2H, -CH=CH-]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm)=13.5[C-

7], 22.5 [C-6], 34.7[C-5], 35.9[C-2], 62.0[C-1], 125.2[C-3], 133.0[C-4]

(E)-1-Iodo-3-heptene **17**

Compound **16** (2.40 g, 21.0 mmol) was added to a solution of triphenylphosphine (8.26 g, 31.5 mmol), I₂ (6.93 g, 27.3 mmol), imidazole (4.29 g, 63.0 mmol) and benzene (135 mL), and stirred at r.t. for 30 min. The benzene layer was isolated from the viscous yellow product, which was washed with ethyl ether. The ethyl ether wash was added to the benzene layer. The organic solvent was concentrated *in vacuo*. The cold hexane was added to the residue to remove the triphenylphosphine oxide byproduct. The hexane solution was filtered and concentrated *in vacuo* again to give the residue. The residue was chromatographed over silica gel (hexane) to give **17** (3.17 g, 67.3%). Rf=0.53(hexane); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm)=0.87-0.92 [t, J=7.42Hz, 3H, -CH₃], 1.32-1.46[sextet, J=6.92, 7.42 Hz, 2H, -C=C-C-CH₂-], 1.94-2.01 [quartet, J=6.93, 7.41Hz, 2H, -C=C-CH₂-], 2.50-2.58[qua, J=6.93Hz, 2H, -CH₂-C-O-], 3.12-3.17[t, J=7.42, 2H, -CH₂-O-], 5.26-5.61[m, 2H, -CH=CH-]; ¹³C-NMR (68 MHz, CDCl₃/TMS) δ(ppm)=6.2[C-1], 13.6[C-7], 22.4[C-6], 34.5[C-5], 36.8[C-2], 128.4[C-3], 133.4 [C-4]

(E) - 3 - Heptenyltriphenylphosphonium iodide **18** (78.8% yield); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm)=0.79-0.85[t, J=6.93, 7.42Hz, 3H, -CH₃], 1.20-1.33[sextet, J=7.42, 6.93Hz, 2H, -C=C-C-CH₂-], 1.83-1.96[quartet, J=6.43, 6.92, 7.42Hz, 2H, -C=C-CH₂-], 2.36-2.49[m, 2H, -CH₂-C-P], 3.67-3.78[m, 2 H, -CH₂-P], 5.39-5.60[m, 2H, -CH=CH-], 7.70-7.99 [m, 15H, Ph₃]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm)=13.6[C-7], 22.1[C-6], 22.9, 23.7[d,C-1], 25.5, 25.7[d,C-2], 34.2[C-5], 128.2[C-3], 133.8[C-4], 117.3-135.1[Ph₃]

(Z)-Iodo-3-nonene **20**

Compound **20** (85.3%) was prepared from compound **19** as described for compound **17**. Rf=0.53 (hexane); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm)=0.87-0.92 [t, J=6.43, 6.92Hz, 3H, -CH₃], 1.22-1.39 [m, 6H, -CH₂-×3], 1.98-2.05[quartet, J=6.43, 6.93 Hz, 2H, -C=C-CH₂-], 2.59-2.67[quartet, J=6.92, 7.42Hz, 2H, -CH₂-C-P], 3.11-3.16[t, J=7.42Hz, 2H, -CH₂-P], 5.26-5.59[m, 2H, -CH=CH-]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm)=5.5[C-1], 14.0[C-9], 22.5[C-6], 27.4, 29.2[C-2,5], 31.4,31.5[C-7, 8],

127.7, 132.7[C-3, 4]

(*Z*)-3-Nonenyltriphenylphosphonium iodide **21** (88.4%); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm) = 0.81–0.86 [t, J = 6.43, 7.42Hz, 3H, -CH₃], 1.10–1.29 [m, 6H, -CH₂- × 3], 1.74–1.90 [quartet, J = 6.43, 7.41, 2H, -C=C-CH₂-], 2.38–2.51 [m, 2H, -CH₂-C-P], 3.65–3.73 [m, 2H, -CH₂-P], 5.36–5.61 [m, 2H, -CH=CH-], 7.70–7.87 [m, 15H, Ph₃]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm) = 13.9[C-9], 20.2[C-2], 22.3[C-8], 23.0, 23.7[d, C-1], 27.1[C-5], 28.3, 31.3[C-6, 7], 132.8[C-3], 132.8[C-4], 117.2–135.2[Ph₃]

2-(3-Butynyloxy)tetrahydro-2H-pyran **23**

Compound **23** was derived from compound **22** in a similar manner as described in our previous paper (16). Compound **23** was identified by comparison with standard product previously synthesized (16).

2-(3-Heptynyloxy)tetrahydro-2H-pyran **24**

A solution of ethyl bromide (14.1 g, 129 mmol) in dry THF (10.0 mL) was added using a funnel to magnesium (3.15 g, 129 mmol) with stirring at r.t. under dry nitrogen. After the magnesium had reacted, a solution of compound **23** (10.0 g, 64.8 mmol) in dry THF (10 mL) was dropped into the mixture at r.t. The reaction mixture was stirred at 40°C for 1hr. A solution of di-*n*-propyl sulfate (28.3 g, 155 mmol) in THF (25 mL) and HMPA (20 mL) was added to the reaction mixture at r.t, which was stirred at 70°C for 12hr. Sufficient HCl aq (3N) was added to the reaction mixture for hydrolysis. The mixture was extracted with diethyl ether. The organic layer was dried with Na₂SO₄ and the organic solvent was removed *in vacuo* to give the residue. The residue was isolated over silica gel (hexane:ethyl acetate = 95:5) to give 2-(3-heptynyloxy)tetrahydro-2H-pyran **24** (6.97g, 54.8%). Rf = 0.50 (hexane-ethyl acetate = 95:5); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm) = 0.94–0.99 [t, J = 7.17Hz, 3H, -CH₃], 1.46–1.76 [m, 8H, CH₂ × 3 in pyran, -C≡C-C-CH₂-], 2.09–2.20 [m, 2H, -C≡C-CH₂-], 2.44–2.49 [m, 2H, -C≡C-CH₂-], 3.28–3.59 [m, 2H, -O-CH₂- in pyran], 3.72–3.92 [m, 2H, -O-CH₂-], 4.60–4.65 [s, 1H, -O-CH-O-]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm) = 13.6[C-12], 19.2[C-3], 20.3[C-10], 20.9[C-7], 22.7[C-11], 25.3[C-2], 30.4[C-4], 62.2[C-6], 65.6[C-1], 69.3[C-9], 81.2[C-8], 98.8[C-5]

(*Z*)-2-(3-Heptynyloxy)tetrahydro-2H-pyran **25**

Compound **24** (5.88 g, 30.0 mmol) was added to a

solution of Pd catalyst (Pd(5%)-CaCO₃-PbO(3%), 0.67 g) in MeOH (60.0mL). The reaction flask was connected to a hydrogen tank and alternately evacuated and filled with hydrogen. The mixture was stirred until hydrogen ceased to be absorbed. The mixture was filtered to remove Pd catalyst. The liquid was concentrated *in vacuo*, and the residue, chromatographed over silica gel with hexane-ethyl acetate (95:5) to give compound **25** (4.61g, 77.5%). Rf = 0.67 (hexane-ethyl acetate = 95:5); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm) = 0.88–0.93 [t, J = 7.42Hz, 3H, -CH₃], 1.26–1.48 [quartet, J = 6.92, 7.42Hz, 2H, -C=C-C-CH₂-], 1.50–1.90 [m, 6H, -CH₂- × 3], 2.00–2.10 [quartet, J = 6.43, 7.92Hz, 2H, -C=C-CH₂-], 2.32–2.39 [qua, J = 6.43, 6.92Hz, 2H, -C=C-CH₂-], 3.42–3.75 [m, 2H, -O-CH₂- in pyran], 3.50–3.90 [m, 2H, -O-CH₂-], 4.61 [t, 1H, -O-CH-O-], 5.35–5.50 [m, 2H, -CH=CH-]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm) = 13.7[C-12], 19.2[C-3], 22.7[C-11], 25.3[C-2], 27.9[C-10], 29.3[C-7], 30.4[C-4], 62.1[C-6], 67.0[C-1], 98.6[C-5], 125.0[C-9], 131.6[C-8]

(*Z*)-3-Heptene-1-ol **26**

Compound **26** (91.4% yield) was derived from compound **25** by the modified procedure (16). Rf = 0.38 (hexane-ethyl acetate = 4:1); ¹H-NMR (270 MHz, CDCl₃/TMS) δ(ppm) = 0.88–0.94 [t, J = 7.42Hz, 3H, -CH₃], 1.32–1.45 [(m, J = 7.42Hz, 2H, -C=C-C-CH₂-), (s, 1H, -OH)], 2.01–2.09 [quartet, J = 6.43, 6.93, 7.42 Hz, 2H, -C=C-CH₂-], 2.30–2.37 [quartet, J = 6.43, 7.42 Hz, 2H, -C=C-CH₂-], 3.62–3.67 [t, J = 6.43Hz, 2H, -CH₂-O-], 5.33–5.61 [m, 2H, -CH=CH-]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm) = 13.8[C-7], 22.8[C-6], 29.1[C-5], 30.7[C-2], 62.1[C-1], 125.2[C-4], 133.0[C-3]

(*Z*)-1-Iodo-3-heptene **27**

Compound **27** (64.6% yield) was prepared from compound **26** in a similar manner as described in compound **17**. Rf = 0.70 (hexane); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm) = 0.86–0.91 [t, J = 6.92, 7.42Hz, 3H, -CH₃], 1.37–1.46 [m, J = 6.92, 7.42Hz, 2H, -C=C-CH₂-], 1.97–2.05 [quartet, J = 6.93, 2H, C=C-CH₂], 2.60–2.67 [quartet, J = 6.92, 7.42Hz, 2H, -C=C-CH₂-], 3.10–3.15 [t, J = 7.42Hz, 2H, -CH₂-P], 5.26–5.58 [m, 2H, -CH=CH-]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm) = 5.7[C-1], 13.8[C-7], 22.8[C-6], 29.1[C-5], 30.7[C-2], 125.8[C-4], 133.0[C-3]

(*Z*)-3-Heptenyltriphenylphosphonium iodide **28**

(81.3% yield); $^1\text{H-NMR}$ (270MHz, CDCl_3/TMS) δ (ppm) = 0.76–0.84 [t, $J=7.42\text{Hz}$, 3H, $-\text{CH}_3$], 1.20–1.33 [m, $J=7.42$, 6.92Hz, 2H, $-\text{C}=\text{C}-\text{CH}_2-$], 1.73–1.90 [quartet, $J=7.42\text{Hz}$, 2H, $-\text{C}=\text{C}-\text{CH}_2-$], 2.39–2.50 [m, 2H, $-\text{C}=\text{C}-\text{CH}_2-$], 3.63–3.72 [m, 2H, $-\text{CH}_2-\text{P}$], 5.35–5.63 [m, 2H, $-\text{CH}=\text{CH}-$], 7.71–7.87 [m, 15H, P-PPh_3]; $^{13}\text{C-NMR}$ (68MHz, CDCl_3/TMS) δ (ppm) = 13.6 [C-7], 19.7, 19.8 [d, C-2], 21.8 [C-6], 22.6, 23.3 [d, C-1], 28.7 [C-5], 127.8 [C-3], 132.0 [C-4], 117.2–135.2 [Ph₃]

(Z)-O-Diacetyl-3-(8-pentadecenyl)catechol 29

Compound **29** (45.7% yield) was synthesized from compound **9** and **14** in a similar manner as described in our previous paper (10). $R_f=0.50$ (hexane-ethyl acetate = 4:1); $^1\text{H-NMR}$ (270 MHz, CDCl_3/TMS) δ (ppm) = 0.86–0.90 [t, 3H, $-\text{CH}_3$], 1.30 [m, 14H, $-\text{CH}_2-\times 7$], 1.58 [m, 2H, $\text{Ph}-\text{CH}_2-$], 2.02 [m, 4H, $-\text{C}=\text{C}-\text{CH}_2-\times 2$], 2.35, 2.36 [s, 6H, $-\text{COCH}_3 \times 2$], 2.62 [t, 2H, $\text{Ph}-\text{CH}_2-$], 3.53 [m, 2H, $-\text{CH}=\text{CH}-$], 6.90–7.19 [m, 3H, Ph]; $^{13}\text{C-NMR}$ (68MHz, CDCl_3/TMS) δ (ppm) = 13.7 [C-21], 19.9, 20.3 [C-22, 24], 22.3, 28.5–31.4 [C-8–12, 17–19], 26.8, 32.2 [C-13, 16], 30.1 [C-7], 129.9, 130.1 [C-14, 15], 120.4 [C-3], 125.8 [C-1], 126.9 [C-2], 136.3 [C-6], 140.1 [C-5], 142.0 [C-4], 167.8, 167.9 [C-22, 24]

(Z)-O-Diacetyl-3-(10-pentadecenyl)catechol 30 (33.0% yield); $R_f=0.40$ (hexane-ethyl acetate = 4:1); $^1\text{H-NMR}$ (270MHz, CDCl_3/TMS) δ (ppm) = 0.88–0.89 [t, $J=3.40$, 3H, $-\text{CH}_3$], 1.27–1.34 [m, 16H, $-\text{CH}_2-\times 8$], 1.52–1.60 [m, 2H, $-\text{CH}_2-$], 1.99–2.01 [m, 4H, $-\text{C}=\text{C}-\text{CH}_2-\times 2$], 2.31, 2.33 [s, 6H, $-\text{COCH}_3 \times 2$], 2.56–2.64 [m, 7.91Hz, 2H, $\text{Ph}-\text{CH}_2-$], 5.31–5.39 [m, 2H, $-\text{CH}=\text{CH}-$], 6.74–7.00 [m, 3H, Ph]; $^{13}\text{C-NMR}$ (68MHz, CDCl_3/TMS) δ (ppm) = 14.0 [C-21], 20.6, 21.0 [C-23, 25], 26.9, 27.2 [C-15, 18], 29.3–29.5 [C-8–14, 19, 20], 29.9 [C-7], 120.1 [C-3], 126.5 [C-1], 127.3 [C-2], 129.8, 129.9 [C-16, 17], 135.9 [C-6], 138.3 [C-5], 141.9 [C-4], 169.6, 169.7 [C-22, 24]

(Z)-O-Diacetyl-3-(10-heptadecenyl)catechol 31 (23.0% yield); $R_f=0.40$ (hexane-ethyl acetate = 4:1); $^1\text{H-NMR}$ (270MHz, CDCl_3/TMS) δ (ppm) = 0.85–0.90 [t, $J=6.43$, 6.92Hz, 3H, $-\text{CH}_3$], 1.15–1.30 [m, 20H, $-\text{CH}_2-\times 10$], 1.54–1.58 [m, 2H, $-\text{CH}_2-$], 1.98–2.02 [m, 4H, $-\text{C}=\text{C}-\text{CH}_2-\times 2$], 2.25, 2.30 [s, 6H, $-\text{COCH}_3 \times 2$], 2.48–2.53 [t, $J=7.42$, 7.91Hz, 2H, $\text{Ph}-\text{CH}_2-$], 5.33–5.38 [m, 2H, $-\text{CH}=\text{CH}-$], 6.91–7.20 [m, 3H, Ph]; $^{13}\text{C-NMR}$ (68 MHz, CDCl_3/TMS) δ (ppm) = 14.1 [C-1],

20.5, 20.6 [C-25, 27], 22.6–29.7 [C-9–12, 17–22], 27.1 [C-13, 16], 29.9 [C-8], 30.0 [C-7], 120.7 [C-3], 125.8 [C-1], 127.2 [C-2], 129.9, 131.5 [C-14, 15], 136.6 [C-6], 140.4 [C-5], 142.2 [C-4], 168.3, 168.5 [C-22, 24]

O-Diacetyl-3-[(8Z, 11E)-8,11-pentadecenyl]catechol 32 (30.0% yield); $R_f=0.50$ (hexane-ethyl acetate = 4:1); $^1\text{H-NMR}$ (270MHz, CDCl_3/TMS) δ (ppm) = 0.85–0.91 [t, $J=7.42$, 6.92Hz, 3H, $-\text{CH}_3$], 1.17–1.41 [m, 10H, $-\text{CH}_2-\times 5$], 1.53–1.58 [t, $J=6.93$, 7.42Hz, 2H, $\text{Ph}-\text{CH}_2-$], 1.80–2.04 [m, 4H, $-\text{C}=\text{C}-\text{CH}_2-\times 2$], 2.28, 2.31 [s, 6H, $-\text{COCH}_3 \times 2$], 2.48–2.54 [t, $J=7.42$, 7.91Hz, 2H, $\text{Ph}-\text{CH}_2-$], 2.70–2.74 [t, $J=5.44$, 4.95Hz, 2H, $-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$], 5.33–5.43 [m, 4H, $-\text{CH}=\text{CH}-\times 2$], 7.01–7.18 [m, 3H, Ph]; $^{13}\text{C-NMR}$ (68MHz, CDCl_3/TMS) δ (ppm) = 13.7 [C-21], 20.3, 20.7 [C-23, 25], 22.6, 29.1, 29.3, 29.4, 29.6, 29.8 [C-8–12, 20], 27.1 [C-13], 30.1 [C-7], 30.4 [C-16], 34.6 [C-19], 120.8 [C-3], 126.2 [C-1], 127.2 [C-2], 136.7 [C-6], 140.5 [C-5], 142.4 [C-4], 127.8, 128.5, 130.3, 130.6 [C-14, 15, 17, 18], 168.2, 168.4 [C-22, 24]

O-Diacetyl-3-[(8Z, 11Z)-8,11-heptadecenyl]catechol 33 (30.0% yield); $R_f=0.43$ (hexane-ethyl acetate = 4:1); $^1\text{H-NMR}$ (270MHz, CDCl_3/TMS) δ (ppm) = 0.86–0.91 [t, $J=6.43$, 6.93Hz, 3H, $-\text{CH}_3$], 1.25–1.35 [m, 12H, $-\text{CH}_2-\times 6$], 1.40–1.56 [m, 4H, $-\text{CH}_2-\times 2$], 2.01–2.08 [quartet, $J=6.43$, 4H, $-\text{C}=\text{C}-\text{CH}_2-\times 2$], 2.28, 2.31 [s, 6H, $-\text{COCH}_3 \times 2$], 2.48–2.53 [t, $J=7.42$, 7.91Hz, 2H, $\text{Ph}-\text{CH}_2-$], 2.75–2.79 [t, $J=5.44$, 5.93Hz, 2H, $-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$], 5.30–5.40 [m, 4H, $-\text{CH}=\text{CH}-\times 2$], 7.01–7.18 [m, 3H, Ph]; $^{13}\text{C-NMR}$ (68MHz, CDCl_3/TMS) δ (ppm) = 14.1 [C-23], 20.3, 20.7 [C-25, 27], 25.6 [C-16], 27.2 [C-13, 19], 29.8 [C-7, 8], 22.6, 29.2, 29.3, 29.3, 29.4, 29.6, 30.1 [C-9–12, 20–22], 127.9, 128.0, 130.1, 130.2 [C-14, 15, 17, 18], 120.8 [C-3], 126.2 [C-1], 127.2 [C-2], 136.7 [C-6], 140.5 [C-5], 142.4 [C-4], 168.4, 169.0 [C-24, 26]

O-Diacetyl-3-[(8Z, 11Z)-8,11-pentadecenyl]catechol 34 (55.8% yield); $R_f=0.48$ (hexane-ethyl acetate = 4:1); $^1\text{H-NMR}$ (270MHz, CDCl_3/TMS) δ (ppm) = 0.85–1.00 [t, $J=7.42\text{Hz}$, 3H, $-\text{CH}_3$], 1.22–1.45 [m, 10H, $-\text{CH}_2-\times 5$], 1.56 [m, 2H, $-\text{CH}_2-$], 2.00–2.07 [m, 4H, $-\text{C}=\text{C}-\text{CH}_2-\times 2$], 2.27–2.31 [s, 6H, $-\text{COCH}_3 \times 2$], 2.48–2.56 [t, $J=7.91\text{Hz}$, 2H, $\text{Ph}-\text{CH}_2-$], 2.75–2.79 [t, $J=5.44\text{Hz}$, 2H, $-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$], 5.32–5.43 [m, 4H, $-\text{CH}=\text{CH}-\times 2$], 6.98–7.18 [m, 3H, Ph]; $^{13}\text{C-NMR}$ (68 MHz, CDCl_3/TMS) δ (ppm) = 13.8 [C-21], 20.3, 20.7 [C-23, 25], 25.6 [C-16], 27.2 [C-13], 29.2 [C-19], 29.3

[C-8], 30.0[C-7], 22.8, 27.1, 29.4, 29.6, 29.8[C-9-12, 20], 127.9, 128.1, 129.9, 130.1[C-14, 15, 17, 18], 120.8[C-3], 126.1[C-1], 127.2[C-2], 136.7[C-6], 140.5[C-5], 142.4[C-4], 168.2, 168.4[C-22, 24]

(Z)-3-(8-Pentadecenyl)catechol 1

2N-Sodium methoxide (1.60 mL, 3.20 mmol) was added to a solution of **29** and methanol (41.0 mL) at 25 °C and stirred for 1 hr. Cation exchange resin was added to the solution until it became neutral. The solution was filtered to remove the resin and concentrated *in vacuo* to give the residue. The residue was chromatographed using silica gel (hexane-ethyl acetate=4:1) to give urushiol 1 (0.36 g, 61.5%). Compound **1** was identified by comparison with standard product previously reported (11).

Compounds **2~6** were synthesized in a similar manner as described in compound **1**.

(Z)-3-(10-Pentadecenyl)catechol 2 (43.5% yield); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm) = 0.86-0.91[t, J=6.7Hz, 3H, -CH₃], 1.31-1.39[m, 16H, -CH₂-×8], 1.54-1.62[m, 2H, Ph-C-CH₂-], 1.98-2.02[m, 4H, -C=C-CH₂-×2], 2.55-2.61[t, J=7.9Hz, 2H, Ph-CH₂-], 5.29-5.41[m, 2H, -CH=CH-], 5.60[s, 2H, -OH×2], 6.71[s, 3H, Ph]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm) = 13.9[C-21], 22.3-31.9[C-7-14, 19-20], 27.2[C-15], 31.9[C-18], 112.9[C-3], 120.1[C-1], 122.1[C-2], 129.4[C-6], 129.8[C-16, 17], 141.8[C-5], 142.9[C-4]

(Z)-3-(10-Heptadecenyl)catechol 3 (69.5% yield). Compound **3** was identified by comparison with standard product previously reported (13).

3-[(8Z, 11E)-8,11-Pentadecenyl]catechol 4 (55.0% yield); R_f=0.44 (hexane-ethyl acetate=4:1); ¹H-NMR (400MHz, CDCl₃/TMS) δ(ppm) = 0.86-0.90[t, J=7.33Hz, 3H, -CH₃], 1.24-1.43[m, 10H, -CH₂-×5], 1.58-1.66[m, 2H, Ph-C-CH₂-], 1.92-2.01[m, 4H, -C=C-CH₂-×2], 2.58-2.61[t, J=7.78Hz, 2H, Ph-CH₂-], 2.70-2.74[t, J=5.34Hz, 2H, -C=C-CH₂-C=C-], 5.16[s, 2H, -OH], 5.32-5.49[m, 4H, -CH=CH-×2], 6.71[s, 3H, Ph]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm) = 13.7[C-21], 22.9, 29.2, 29.4, 29.5, 29.6, 29.8[C-8-12, 20], 29.2[C-13], 29.8[C-7], 30.4[C-16], 34.6[C-19], 112.9[C-3], 120.1[C-1], 122.1[C-2], 129.3[C-6], 141.8[C-5], 142.9[C-4], 127.8, 128.5, 130.4, 130.6[C-14, 15, 17, 18]

3-[(8Z, 11Z)-8,11-Heptadecenyl]catechol 5 (60.0% yield). Compound **5** was identified by comparison with standard product previously reported (13).

3-[(8Z, 11Z)-8,11-Pentadecenyl]catechol 6 (50.0% yield); R_f=0.35 (hexane-ethyl acetate=4:1); ¹H-NMR (270MHz, CDCl₃/TMS) δ(ppm) = 0.88-0.94[t, J=7.42Hz, 3H, -CH₃], 1.33-1.42[m, 10H, -CH₂-×5], 1.56-1.66[m, 2H, Ph-C-CH₂-], 2.00-2.07[quartet, J=6.60Hz, 4H, -C=C-CH₂-×2], 2.57-2.63[t, J=7.92Hz, 2H, Ph-CH₂-], 2.76-2.80[t, J=5.44Hz, 2H, -C=C-CH₂-C=C-], 4.99, 5.10[s, 2H, -OH×2], 5.30-5.43[m, 4H, -CH=CH-×2], 6.71[s, 3H, Ph]; ¹³C-NMR (68MHz, CDCl₃/TMS) δ(ppm) = 13.8[C-21], 25.6[C-16], 27.2[C-13], 29.2[C-19], 29.3[C-8], 29.7[C-7], 22.8, 29.4-29.6[C-9-12, 20], 112.9[C-3], 120.1[C-1], 122.1[C-2], 129.3[C-6], 141.8[C-5], 143.0[C-4], 127.9, 128.1, 129.9, 130.1[C-14, 15, 17, 18]

References

1. Abe, Y. (1987) *Shitugeinyuemon*, Kougei Press Ltd., Tokyo, pp. 25-44.
2. Kumanotani, J. (1983) *Polymer Application of Renewable Resource Materials*, ed. by Carraher, C. E. & Sperling L. H., Plenum Press, New York, pp. 225-248.
3. Kumanotani, J., Inoue, K., Achiba, M. & Chen, L. W. (1986) *Polym. Sci. Technol.*, **33**, 163-176.
4. Majima, R. (1922) *Ber. Dtsch. Chem. Ges. B*, **55**, 172-191.
5. Sunthanker, S. V. & Dawson, C. R. (1954) *J. Am. Chem. Soc.*, **76**, 5070-5074.
6. Yamauchi, Y., Oshima, R. & Kumanotani, J. (1982) *J. Chromatogr.*, **243**, 71-84.
7. Du, Y., Oshima, R. & Kumanotani, J. (1984) *J. Chromatogr.*, **284**, 463-473.
8. Du, Y., Oshima, R., Iwatsuki, H. & Kumanotani, J. (1984) *J. Chromatogr.*, **295**, 179-186.
9. Miyakoshi, T., Kobuchi, H., Niimura, N. & Yoshihiro, Y. (1991) *Bull. Chem. Soc. Jpn.*, **64**, 2560-2562.
10. Niimura, N., Kamiya, Y., Sato, T., Katano, I. & Miyakoshi, T. (1998) *J. Jpn Oil Chem. Soc. (J. Oleo Sci.)*, **47**, 37-44.
11. Halim, H., Locksley, H. D. & Memon, J. J. (1980) *J. Chem. Soc. Perkin I*, 2331-2337.
12. Bestmann, H. J. & Hessenauer, N. (1990) *SYNLETT*, 555-556.
13. Sargent, M. V. & Wangchareontrakul, S. (1989) *J. Chem. Soc. Perkin Trans. I*, 431-439.
14. Dejarlais, W. J. & Emken, E. A. (1976) *Lipids*, **11**, 594-598.

15. Cohen, N., Banner, B. L., Lopresti, R. J., Wong, F., Rosenberger, M., Liu, Y. Y., Thorn, E. & Liebman, A. (1983) *J. Am. Chem. Soc.*, **105**, 3661–3672.
  16. Miyakoshi, T. & Kobuchi, H. (1991) *J. Jpn. Oil. Chem. Soc. (J. Oleo Sci.)*, **40**, 210–215.
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