

## Convenient Synthesis of Two Mango Allergens

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**Abstract:** The mango allergens, 5[2'(Z)-heptadecenyl]resorcinol (**10**) and 5[12'(Z)-heptadecenyl]resorcinol (**20**) have been synthesized by simple routes using easily accessible starting materials.

**Keywords:** Mango allergens, synthesis, phenolics.

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### Introduction

It is by now established [1] that several long chain phenolic compounds act as natural allergens imparting resistant properties to plants. Amongst the various sources of the allergens, the cashew nut shell as well as the Japanese and Chinese lacs are well known for producing the phenolic compounds like cardols [2] and urushiols [3]. Sometimes back, we have isolated [4] a non-volatile allergen, 5[2'(Z)-heptadecenyl]resorcinol (**10**) from the mango latex. Subsequently, another isomeric resorcinol viz. 5[12'(Z)-heptadecenyl]resorcinol (**20**) was isolated by Cojocarú *et al.* [5] from raw mango fruit peel. They have demonstrated that these phenolic compounds also act as preservatives in the necrotic organs of the plants against microbial infection. Considering that occupational allergenic contact dermatitis is a growing problem in the green house industry, the study of mango allergen seems interesting. With this aim, we have developed a novel synthesis of the above compounds in sufficient quantities to study their allergen and other biological activities. The synthesis (Scheme 1) is brief and conveniently produces the target compounds from easily accessible starting materials.

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## Results and Discussion

### Synthesis of 5[2'(Z)-heptadecenyl]resorcinol (10)

Commercially available 1-tetradecanol (**1**) was converted to the bromide **2** via a standard route and reacted with monosodium acetylide [6] to furnish the alkyne **3**. For the required aromatic moiety, 3,5-dihydroxybenzoic acid (**4**) was converted to the ester **5** by esterification followed by methylation. Its LAH reduction to the alcohol **6** followed by chlorination gave compound **7**. Alkylation [7] of the alkyne **3** with the chloride **7** was accomplished using *n*-BuLi as the base in the presence of CuI to furnish **8**. Its *cis*-selective partial hydrogenation afforded the dimethyl ether **9** which was demethylated with BBr<sub>3</sub> to furnish the target allergen **10**.

### Synthesis of 5[12'(Z)-heptadecenyl]resorcinol (20)

This was synthesized by two methods. In the first route, 1,10-decanediol (**11**) was monobrominated [8] to the bromohydrin **12** which on pyranylation gave compound **13**. Alkylation of 1-hexyne with **13** followed by acid catalyzed depyranylation afforded the alcohol **15**. Its *cis*-selective partial hydrogenation over P-2 Ni [9] produced the alkenol **16** which was brominated with Ph<sub>3</sub>P.Br<sub>2</sub> [10] to furnish **17**. This was then converted to the corresponding Grignard reagent and reacted with 3,5-dimethoxybenzaldehyde yielding compound **18**. Its mesylation and subsequent reduction with LAH gave **19**.

In an alternative approach, 10-undecenol (**21**) was brominated to give **22**. As above, the Grignard reagent prepared from **22** was reacted with 3,5-dimethoxybenzaldehyde to furnish the alcohol **23** which on mesylation and LAH reduction afforded the alkene **24**. This on *anti*-Markonikov hydration with NaBH<sub>4</sub>-TiCl<sub>4</sub> [11] followed by pyridinium chlorochromate (PCC) [12] oxidation gave the aldehyde **26**. Its *Z*-selective Wittig olefination with *n*-pentyltriphenylphosphonium bromide in the presence of dimethyl ion as the base led to **19**. As done for **10**, demethylation of **19** with BBr<sub>3</sub> afforded the title compound **20**. The spectral and microanalytical data of both the synthetic samples were in good agreement with those reported [4,5] in literature.

## Experimental

### General

All the boiling points are uncorrected. The IR spectra were scanned with a Perkin-Elmer spectrophotometer model 837. The PMR spectra were recorded in CDCl<sub>3</sub> with a Varian A-60 (60 MHz) instrument. The GLC analyses were carried out using Shimadzu GC-7A chromatograph using a 3% OV-17 column and a N<sub>2</sub> flow rate 40 mL/min. Anhydrous reactions were carried out under Ar using freshly dried solvents. The organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.

*1-Bromotetradecane (2)*

A mixture of the alcohol **1** (21.4 g, 0.1 mol), 48% HBr (50 mL) and H<sub>2</sub>SO<sub>4</sub> (5 mL) was heated for 8 h at 130 °C, brought to room temperature, diluted with water and extracted with ether. The ether layer was washed several times with half-saturated brine, dried, concentrated and distilled under reduced pressure to give pure **2**. yield: 23.5 g (85%); bp: 118-120 °C/2 mm; IR: 2950, 2880, 1475, 1265 cm<sup>-1</sup>; PMR: δ 0.9 (dist. t, 3H), 1.27 (br. s, 24H), 3.4 (t, *J* = 6 Hz, 2H).

*1-Hexadecyne (3)*

A solution of sodium acetylide (0.13 mol) in NH<sub>3</sub> (100 mL) was prepared as described [13] in literature. Ammonia was slowly removed and the bromide **2** (13.85 g, 0.05 mol) in DMF (30 mL) was added to it in 0.5 h. The mixture was heated at 70 °C for 4 h, brought to room temperature and treated with aqueous saturated NH<sub>4</sub>Cl solution. It was diluted with water, extracted with ether, the ether layer washed with water and brine and dried. Removal of solvent followed by distillation of the residue gave pure **3**. yield: 7.0 g (65%); bp: 103 °C/1 mm, (lit. [14] bp: 115 °C/5 mm); IR: 3320, 2860, 2120 cm<sup>-1</sup>; PMR: δ 0.87 (dist. t, 3H), 1.3 (br. s, 24H), 1.9-2.18 (m, 3H).

*Methyl 3,5-Dimethoxybenzoate (5)*

A mixture of the acid **4** (15.4 g, 0.1 mol) and BF<sub>3</sub>.Et<sub>2</sub>O (2.0 mL) in MeOH (100 mL) was refluxed for 12 h. Most of the solvent was removed in vacuo, water added to the residue which was extracted with ether. The ether layer was washed aqueous 10% NaHCO<sub>3</sub>, water and brine and dried. Removal of solvent followed by crystallization gave the ester of **4**. yield: 13.5 g (80%); mp: 165 °C; IR: 3380, 1700, 1610 cm<sup>-1</sup>; PMR: δ 3.86 (s, 3H), 6.6-7.2 (m, 3H), 12.9 (br. s, D<sub>2</sub>O exchangeable, 2H).

A mixture of the above ester (8.4 g, 0.05 mol), dimethyl sulphate (14.2 mL, 0.15 mol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (27.6 g 0.2 mol) in acetone (100 mL) was refluxed for 16 h. After bringing to room temperature, the reaction mixture was filtered, concentrated and worked-up as above. Removal of solvent followed by crystallization (MeOH-H<sub>2</sub>O) gave **5**. yield: 8.4 g (86%); mp: 43 °C, (lit. [15] mp: 42 °C); UV: 252 (log e 3.76), 306 (log e 3.46) nm; IR: 3050, 1750, 1580, 1210 cm<sup>-1</sup>; PMR: δ 3.83 (s, 6H), 3.93 (s, 3H), 6.62-7.12 (m, 3H); MS (m/z): 196 (M<sup>+</sup>), 165, 138, 122, 104, 92, 79.

*3,5-Dimethoxybenzyl alcohol (6)*

To a stirred suspension of LAH (3.8 g, 0.1 mol) in ether (50 mL) was added a solution of **5** (7.84 g, 0.04 mol) in ether (30 mL). The reaction mixture was refluxed for 3 h, brought to room temperature and the excess LAH decomposed with aqueous saturated Na<sub>2</sub>SO<sub>4</sub>. The supernatant ether layer was decanted, the solid residue extracted with ether and the combined organic extract concentrated to give

pure **6**. yield: 5.95 g (87%); mp: 48 °C, (lit. [15] mp: 48 °C); UV: 280 (log e 3.28) nm; IR: 3350, 2950, 1580, 830 cm<sup>-1</sup>; PMR: δ 2.26 (s, D<sub>2</sub>O exchangeable, 1H), 3.8 (s, 6H), 4.63 (s, 2H), 6.3-6.7 (m, 3H).

#### *3,5-Dimethoxybenzyl chloride (7)*

To a cooled (0 °C) and stirred solution of **6** (5.88 g, 0.035 mol) and pyridine (0.4 mL) in ether (100 mL) was added SOCl<sub>2</sub> (8.0 g) in ether (50 mL) in portions. The mixture was stirred for 2.5 h at room temperature. It was extracted with ice cold water, the ether layer separated and evaporated in vacuo and the residue recrystallized from petroleum ether to get **7** as fine shining needles. yield: 4.95g (76%); mp: 66 °C; IR: 3050, 2950, 1580, 820 cm<sup>-1</sup>; PMR: δ 3.83 (s, 6H), 4.5 (s, 2H), 6.3-6.7 (m, 3H).

#### *5-(2'-Heptadecynyl)-resorcinol dimethylether (8)*

To a cooled (-78 °C) and stirred mixture of **3** (5.5 g, 0.025 mol) in THF (100 mL) was added *n*-BuLi (15 mL, 0.024 mol, 1.6 M in hexane). After stirring for 0.5 h, CuI (1.9 g, 0.01 mol) was added followed by the chloride **7** (3.72 g, 0.02 mol) in THF (25 mL). The the mixture was slowly brought to room temperature and stirred for 5 h. It was poured in cold water, the organic layer separated and the aqueous layer extracted with ether. The combined organic extract was washed with water and brine and dried. Removal of solvent followed by distillation gave pure **8**. yield: 3.05 g (41%); bp: 155-160 °C/0.2 mm; IR: 2995, 1600, 1210, 825, 680 cm<sup>-1</sup>; PMR: δ 0.9 (dist. t, 3H), 1.3 (br. s, 24H), 2.2 (t, *J* = 6 Hz, 2H), 2.83 (s, 2H), 3.8 (s, 6H), 6.35 (m, 3H). Anal Calcd. for C<sub>25</sub>H<sub>40</sub>O<sub>2</sub>: %C 80.59, %H 10.82; Found: %C 80.45, %H 10.60.

#### *5-(2'(Z)-Heptadecenyl)-resorcinol dimethylether (9)*

A mixture of **8** (1.86 g, 5.0 mmol) and triethylamine (TEA) (0.2 mL) and 5% Pd-CaCO<sub>3</sub> (50 mg) in THF (20 mL) was shaken under a slight positive pressure of H<sub>2</sub>. After the required uptake of H<sub>2</sub>, the reaction mixture was diluted with ether (20 mL) and passed through a short pad of silica gel. The eluent was washed with dil. 2N HCl, water and brine and dried. Removal of solvent afforded pure **9**. yield: 1.54 g (83%); bp: 155-160 °C/0.1 mm; IR: 3010, 2995, 1600, 1210, 835, 690 cm<sup>-1</sup>; PMR: δ 0.9 (dist. t, 3H), 1.32 (br. s, 24H), 1.9-2.1 (m, 2H), 2.56 (d, *J* = 6 Hz, 2H), 3.8 (s, 6H), 5.4-5.5 (m, 2H), 6.33 (s, 3H); MS (m/z): 374 (M<sup>+</sup>), 191, 183, 168, 151, 137, 136, 121, 57, 43. Anal Calcd. for C<sub>25</sub>H<sub>42</sub>O<sub>2</sub>: %C 80.16, %H 11.30; Found: %C 79.95, %H 11.15.

#### *5-(2'(Z)-Heptadecenyl)-resorcinol (10)*

To a cooled (-78 °C) and stirred solution of **9** (0.374 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was injected BBr<sub>3</sub> (3.0 mmol). After stirring for 6 h at the same temperature and 12 h at room temperature, the

reaction was quenched with aqueous saturated  $\text{NH}_4\text{Cl}$  solution, the organic layer separated washed with water and brine and dried. Removal of solvent followed by preparative TLC of the crude product (5% MeOH/ $\text{CHCl}_3$ , as the developing solvent, silica gel) furnished pure **10** [4]. yield: 0.245 g (71%); IR: 3440, 3010, 3000, 1600, 840, 680  $\text{cm}^{-1}$ ; PMR:  $\delta$  0.88 (dist. t, 3H), 1.3 (br. s, 24H), 1.9-2.1 (m, 2H), 2.54 (d,  $J = 6$  Hz, 2H), 5.3-5.5 (m, 2H), 6.24 (br. s,  $\text{D}_2\text{O}$  exchangeable, 2H), 6.4-6.55 (m, 3H).

#### *1-Tetrahydropyranyloxy-10-bromodecane (13)*

A mixture of the diol **11** (8.7 g, 0.05 mol) and 48% HBr (20 mL) in heptane (50 mL) was refluxed for 4 h. The organic layer was separated, a fresh lot of heptane (50 mL) added and refluxing continued for another 4 h. The process was repeated four times, the organic extracts were combined and washed successively with aqueous 5%  $\text{NaHCO}_3$ , water and brine and dried. Solvent removal followed by column chromatography of the residue (silica gel, 0-15% EtOAc/hexane) afforded **12**. yield: 8.3 g (70%); bp: 125-127  $^\circ\text{C}/3$  mm, (lit. [16] bp: 166-169  $^\circ\text{C}/10$  mm); IR: 3340, 1450, 1250, 1050  $\text{cm}^{-1}$ ; PMR:  $\delta$  1.33 (br. s, 16H), 1.65 (s,  $\text{D}_2\text{O}$  exchangeable, 1H), 3.45 (t,  $J = 6$  Hz, 2H), 3.62 (t,  $J = 6$  Hz, 2H).

A solution of **12** (7.1 g, 0.03 mol) and 3,4-dihydropyran (DHP) (2.9 g, 0.04 mol) and pyridinium *para*-toluenesulphonate (PPTS) (0.5 g) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was stirred at room temperature for 4 h. The reaction mixture was washed with aqueous 10%  $\text{NaHCO}_3$ , water and brine. After drying and solvent removal, the residue was column chromatographed (silica gel, 0-10% ether/hexane) to give pure **13**. yield: 7.8 g (81%); IR: 2920, 1460, 910, 870  $\text{cm}^{-1}$ ; PMR:  $\delta$  1.33 (br. s, 16H), 1.6-1.8 (m, 6H), 3.28-3.65 (m, 6H), 4.6 (br. s, 1H).

#### *Hexadec-11-yn-1-ol (15)*

To a stirred suspension of  $\text{NaNH}_2$  [prepared from Na (3.00g, 0.013 mol)] in  $\text{NH}_3$  (100 mL) was added 1-hexyne (14.7 mL, 0.13 mol) in THF (50 mL). The mixture was stirred for 2 h, most of the  $\text{NH}_3$  was evaporated and the content resuspended in THF (70 mL). To this was added **13** (32.0 g, 0.1 mol) in THF (30 mL) at  $-78$   $^\circ\text{C}$ . The mixture was stirred for 5 h at the same temperature, treated with aqueous saturated  $\text{NH}_4\text{Cl}$  and the organic layer separated. The aqueous portion was extracted with ether, the combined organic extract washed with water and brine and dried. Removal of solvent gave **14** which was taken in MeOH (100 mL) and refluxed for 3 h in the presence of *para*-toluenesulphonic acid (PTS) (0.5 g). Most of the solvent was removed in vacuo, water added to it and the mixture extracted with ether. The ether layer was washed with aqueous 5%  $\text{NaHCO}_3$ , water and brine and dried. Removal of solvent followed by distillation gave **15**. yield: 14.6 g (61%); bp: 138  $^\circ\text{C}/2$  mm; IR: 3360, 1480, 1070  $\text{cm}^{-1}$ ; PMR:  $\delta$  0.88 (dist. t, 3H), 1.32 (br. s, 20H), 1.53 (s,  $\text{D}_2\text{O}$  exchangeable, 1H), 2.1-2.3 (m, 4H), 3.66 (t,  $J = 6$  Hz, 2H).

*(11Z)-Hexadec-11-en-1-ol (16)*

To a stirred solution of Ni(OAc)<sub>2</sub> (1.24 g, 5.0 mmol) in EtOH (50 mL) was added NaBH<sub>4</sub> (0.285 g, 7.5 mmol). Within 5 min, a black suspension of P-2 Ni formed and the evolution of H<sub>2</sub> ceased. Ethylenediamine (EDA) (0.9 g) was added to it followed by **15** (11.9 g, 0.05 mol) and the mixture shaken in an atmosphere of H<sub>2</sub>. After the required uptake of H<sub>2</sub>, the mixture was diluted with ether and the supernatant passed through a pad of silica gel. The eluent was concentrated and the residue distilled to get pure **16**. yield: 9.71 g (81%); bp: 145 °C/1.5 mm; IR: 3390, 3010, 1470, 1065 cm<sup>-1</sup>; PMR: δ 0.9 (dist. t, 3H), 1.29 (br. s, 20H), 1.8 (s, D<sub>2</sub>O exchangeable, 1H), 2.0-2.3 (m, 4H), 3.68 (t, *J* = 6 Hz, 2H), 5.4-5.5 (m, 2H).

*(11Z)-1-Bromohexadec-11-ene (17)*

To a cooled (0 °C) and stirred solution of Ph<sub>3</sub>P (9.5 g, 0.04 mol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added bromine (7.5 mL, 0.04 mol, 5.5 M in CCl<sub>4</sub>). After stirring for 15 min, the cooling bath was removed and a mixture of **16** (7.2 g, 0.03 mol) and pyridine (3 mL) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) introduced into the mixture. After stirring for 2 h, the mixture was concentrated, the residue extracted with hexane and the supernatant decanted. The hexane layer was passed through a pad (50 mm) of neutral alumina and concentrated in vacuo to afford pure **17**. yield: 6.3g (69%); bp: 128 °C/0.5 mm; IR: 2995, 1470, 1250 cm<sup>-1</sup>; PMR: δ 0.9 (dist. t, 3H), 1.3 (br. s, 20H), 1.7-2.3 (m, 4H), 3.48 (t, *J* = 6 Hz, 2H), 5.3-5.5 (m, 2H).

*1-(3',5'-Dimethoxyphenyl)-heptadec-12-en-1-ol (18)*

To a cooled (0 °C) and stirred solution of the Grignard reagent [prepared from **17** (6.0 g, 0.02 mol) and Mg (0.528 g, 0.022 mol) in THF (60 mL)] was added 3,4-dimethoxybenzaldehyde (3.32 g, 0.02 mol) in THF (20 mL). After stirring for 4 h, the reaction was quenched with aqueous saturated NH<sub>4</sub>Cl solution, the organic portion separated and the aqueous layer extracted with ether. The combined organic extract was washed with water and brine and dried. Removal of solvent followed by column chromatography of the residue (silica gel, 0-15% EtOAc/hexane) gave **18**. yield: 4.1g (52%); bp: 145-147 °C/0.05 mm; IR: 3420, 3010, 1610, 1170, 1075 cm<sup>-1</sup>; PMR: δ 0.9 (dist. t, 3H), 1.29 (br. s, 22H), 1.5 (s, D<sub>2</sub>O exchangeable, 1H), 1.9-2.3 (m, 4H), 3.76 (s, 6H), 4.12 (t, *J* = 6 Hz, 1H), 5.3-5.5 (m, 2H), 6.33 (m, 3H). Anal. Calcd. for C<sub>25</sub>H<sub>42</sub>O<sub>3</sub>: %C 76.87, %H 10.84; Found: %C 77.08, %H 11.04.

*5-(12'(Z)-Heptadecenyl)-resorcinol dimethyl ether (19)*

To a cooled (0 °C) and stirred solution of **18** (3.9 g, 0.01 mol) and TEA (2.1 mL, 0.012 mol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added mesyl chloride (1.1 mL, 0.012 mol). The mixture was stirred at the same

temperature for 3 h, poured in ice-water, the organic layer separated and the aqueous portion extracted with  $\text{CHCl}_3$ . The combined organic extract was washed with water and brine, dried and concentrated in vacuo to get a residue which was used directly for the next step.

To a stirred suspension of LAH (0.76 g, 0.02 mol) in ether (50 mL) was dropwise added the above mesylate in ether (20 mL). The mixture was refluxed for 8 h, brought to room temperature and treated with aqueous saturated  $\text{Na}_2\text{SO}_4$ . The resultant mixture was filtered, the eluent concentrated and the residue purified by distillation to furnish pure **19**. yield: 1.82 g (90%); bp: 152 °C/0.02 mm; IR: 3000, 2940, 1610, 1470, 1220, 1150  $\text{cm}^{-1}$ ; PMR:  $\delta$  0.9 (dist. t, 3H), 1.27 (br. s, 22H), 1.8-2.2 (m, 4H), 2.68 (t,  $J = 6$  Hz, 2H), 3.76 (s, 6H), 5.3-5.5 (m, 2H), 6.33 (s, 3H); MS (m/z): 374 ( $\text{M}^+$ ), 304, 223, 151, 137, 136, 57. Anal. Calcd. for  $\text{C}_{25}\text{H}_{42}\text{O}_2$ : %C 80.16, %H 11.30; Found: %C 80.35, %H 11.12.

#### 5-(12'(Z)-Heptadecenyl)-resorcinol (**20**)

As described for **10**, demethylation of **19** (0.374 g, 1.0 mmol) was carried out with  $\text{BBr}_3$  (3.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL). The resultant product was purified by preparative TLC of (5% MeOH/ $\text{CHCl}_3$ ) as the developing solvent, silica gel to furnish pure **20**. yield: 0.235 g (68%); IR: 3400, 3030, 3010, 1610, 1210, 1160  $\text{cm}^{-1}$ ; PMR:  $\delta$  0.9 (dist. t, 3H), 1.30 (br. s, 22H), 1.9-2.1 (m, 4H), 2.55 (t,  $J = 6$  Hz, 2H), 5.3-5.5 (m, 2H), 6.4-6.5 (m, 3H), 8.1 (br. s,  $\text{D}_2\text{O}$  exchangeable, 2H).

#### 1-Bromo-undec-10-ene (**22**)

As described for **17**, bromination of **21** (8.5 g, 0.05 mol) was carried out with  $\text{Ph}_3\text{P}$  (13.2 g, 0.05 mol) and bromine (10.0 mL, 0.05 mol, 5.5 M in  $\text{CCl}_4$ ) and pyridine (5 mL) in  $\text{CH}_2\text{Cl}_2$  (75 mL). Usual isolation afforded pure **22**. yield: 10.0 g (85%); bp: 114-115 °C/5 mm, (lit. [17] bp: 103 °C/4 mm); IR: 3070, 1640, 1460, 990, 910  $\text{cm}^{-1}$ ; PMR:  $\delta$  1.33 (br. s, 14H), 1.9-2.2 (m, 2H), 3.56 (t,  $J = 6$  Hz, 2H), 4.8-6.3 (m, 3H).

#### 1-(3',5'-Dimethoxyphenyl)-dodec-11-en-1-ol (**23**)

To a cooled (0 °C) and stirred solution of the Grignard reagent prepared from **22** (9.32 g, 0.04 mol) and Mg (1.06 g, 0.04 mol) in THF (50 mL) was dropwise added 3,5-dimethoxybenzaldehyde (6.64 g, 0.04 mol) in THF (30 mL). Stirring was continued at the same temperature for 2 h and at room temperature for 12 h. It was quenched with aqueous saturated  $\text{NH}_4\text{Cl}$ , the organic layer separated and the aqueous portion extracted with ether. The organic extract was washed with water and brine and dried. Removal of solvent followed by distillation gave pure **23**. yield: 8.9 g (63%); bp: 133-135 °C/1.5 mm; IR: 3400, 3120, 1650, 1470, 995, 915  $\text{cm}^{-1}$ ; PMR:  $\delta$  1.33 (br. s, 16H), 1.9-2.5 (m, 2H), 2.84 (br. s,  $\text{D}_2\text{O}$  exchangeable, 1H), 3.8 (s, 6H), 4.16 (t,  $J = 6$  Hz, 1H), 4.8-6.3 (m, 3H), 6.5-7.1 (m, 3H). Anal. Calcd. for  $\text{C}_{20}\text{H}_{32}\text{O}_3$ : %C 74.96, %H 10.07; Found: %C 74.85, %H 9.90.

*1-(3',5'-Dimethoxyphenyl)-dodec-11-ene (24)*

As described for the preparation of **19**, mesylation of **23** (8.0 g, 0.025 mol) with mesyl chloride (2.2 mL, 0.025 mol) was carried out in the presence of triethyl amine (4.2 mL, 0.025 mol) in CH<sub>2</sub>Cl<sub>2</sub> (60 mL). The resultant product was directly reduced with LAH (1.9 g, 0.05 mol) in ether (75 mL). The product **24** obtained was purified by distillation. yield: 6.1 g (80%); bp: 128-130 °C/1 mm; IR: 3120, 1650, 1470, 1000, 915 cm<sup>-1</sup>; PMR: δ 1.27 (br. s, 16H), 1.9-2.3 (m, 4H), 3.8 (s, 6H), 4.8-6.3 (m, 3H), 6.5 (m, 3H). Anal Calcd. for C<sub>20</sub>H<sub>32</sub>O<sub>2</sub>: %C 78.89, %H 10.59; Found: %C 78.80, %H 10.45.

*12-(3',5'-Dimethoxyphenyl)-dodecanal (26)*

To a stirred suspension of NaBH<sub>4</sub> (2.3 g, 0.06 mol) in 1,2-dimethoxyethane (DME) (25 mL) was injected TiCl<sub>4</sub> (3.5 mL, 0.03 mol) and the mixture stirred for 1 h. To this was added the alkene **24** (6.08 g, 0.02 mol) and stirring continued for 16 h at room temperature. The excess hydride was carefully decomposed by addition of water and the mixture extracted with ether. The ether layer was washed with water and brine and dried. Removal of solvent followed by distillation gave pure **25**. yield: 5.0 g (77%); bp: 144-145 °C/0.5 mm; IR: 3350, 3010, 1610, 1580 cm<sup>-1</sup>; PMR: δ 1.27 (br. s, 20H), 2.37 (t, *J* = 6 Hz, 2H), 3.2 (s, D<sub>2</sub>O exchangeable, 1H), 3.6 (t, *J* = 6 Hz, 2H), 3.8 (s, 6H), 6.5 (s, 3H).

To a stirred solution of **25** (4.85 g, 0.015 mol) in CH<sub>2</sub>Cl<sub>2</sub> (75 mL) was added PCC (4.86 g, 0.022 mol) in one lot. After completion of the reaction (*cf.* TLC, 3 h), the mixture was diluted with ether (75 mL) and the supernatant passed through a 2'' pad of silica gel. The eluent was concentrated in vacuo to give pure **26**. yield: 3.65 g (76%); IR: 3000, 2750, 1750, 1610 cm<sup>-1</sup>; PMR: δ 1.32 (br. s, 18H), 2.3-2.7 (m, 4H), 3.8 (s, 6H), 6.33 (s, 3H), 9.85 (t, *J* = 1.5 Hz, 1H).

*(5-(12'(Z)-Heptadecenyl)-resorcinol dimethylether (19)*

To a stirred solution of dimsyl ion [0.012 mol, in DMSO (30 mL)] was added *n*-pentyltriphenylphosphonium bromide (5.0 g, 0.012 mol) in portions. After stirring for 1 h, the resulting red ylide was diluted with THF (40 mL), cooled to -20 °C and the aldehyde **26** (3.2 g, 0.01 mol) in THF (10 mL) added in dropwise manner. Stirring was continued for 1 h at the same temperature and at room temperature for 12 h. Water was added to the mixture, the organic layer separated and the aqueous portion extracted with ether. The organic extract was washed with water and brine, dried, concentrated and the residue purified as earlier to get pure **19**. Its spectral data were identical with those of the product obtained by the other route. yield: 1.8 g (48%).

## References and Notes

1. Lampe, K. F.; Fagerstrom, R. In *Plant Toxicity and Dermatitis*, Williams and Wilkins Co., Baltimore **1968**; b. Fisher, A. A. In *Contact Dermatitis*, 2nd Edition, Lea and Fabiger Pub., Philadelphia **1973**.
2. Dawson, C. R.; Wasserman, D. *J. Am. Chem. Soc.* **1948**, *70*, 3675; Symes, W. F.; Dawson, C. R. *Nature* **1953**, *171*, 841.
3. Majima, R. *Chem. Ber.* **1922**, *55B*, 172; b. Sukhtankar, S. V.; Dawson, C. R. *J. Am. Chem. Soc.* **1954**, *76*, 5070.
4. Bandopadhyay, C.; Gholap, A. S.; Mamdapur, V. R. *J. Agric. Food. Chem.* **1985**, *33*, 377.
5. Cojocar, M.; Dorby, S.; Glotter, E.; Goldman, A.; Gottlieb, H. E.; Jacoby, B.; Prusky, D. *Phytochemistry* **1986**, *25*, 1093.
6. Jenner, E. F.; Meier, K. D. *Angew. Chem.* **1959**, *71*, 245.
7. Friary, R.; Seidl, V. *J. Org. Chem.* **1986**, *51*, 3214.
8. Logemann, E.; Schill, G. *Bert dt. Chem. Ges.* **1978**, *7*, 2165.
9. Brown, C. A.; Ahuja, V. K. *J. Chem. Soc.* **1973**, 553..
10. Wiley, G. A.; Hershkowitz, R. I.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964.
11. Kano, S.; Tanaka, Y.; Hibino, S. *J. Chem. Soc. Chem. Commun.* **1980**, 415 and ref. cited therein.
12. Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.
13. Brandmsa, L. In *Preparative Acetylenic Chemistry*, Elsevier Publ. Co., Amsterdam **1971**.
14. Krafft, B. *Ber.* **1896**, *29*, 2236.
15. Ridley, D. D.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1968**, *21*, 2979.
16. Pattison, F. L. M.; Stothers, J. B.; Woolford, R. G. *J. Am. Chem. Soc.* **1956**, *78*, 2225.
17. Tomecko, C. G.; Adams, R. *J. Am. Chem. Soc.* **1927**, *49*, 522.

*Samples Availability:* Available from the authors.