[Chem. Pharm. Bull. 31(8)2834—2844(1983)]

Anodic Oxidation of Some Propenylphenols: Synthesis of Physiologically Active Neolignans

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(Received March 4, 1983)

Some propenylphenols have been subjected to anodic oxidation to afford a number of oxidation products including arylpropanoid-, asatone-, austrobailignan-, carpanone- and licarin-type neolignans. The formation process of these compounds involves both radical and cationic reactions controlled by the applied potentials, solvent media and substituents on the aromatic rings.

Keywords——propenylphenol; neolignan; electrochemical oxidation; biomimetic reaction

Structural and synthetic studies on both lignans and neolignans have been attracting increasing attention[1] because of the physiological and biological activities of these compounds (antitumor substances, plant germination inhibitors and insect antifeedants). In connection with these neolignans, we wish to describe anodic oxidation of some propenylphenols, resulting in the formation of many different types of neolignan, most of which can plausibly be produced *via* the corresponding quinonemethides as intermediates.

Results and Discussion

As seen in Fig. 1, *E*- and *Z*-isoeugenols (**1** and **2**) show similar cyclic voltammograms. The former has two anodic peaks (E_p: +730 and 990 mV *vs.* SCE) slightly lower than the corresponding ones (E_p: +800 and 990 mV *vs.* SCE) of the *Z*-isomer. Preparative anodic oxidation of *E*-isoeugenol (**1**) in methanol containing $LiClO_4$ as a supporting electrolyte was carried out at a controlled potential (+800 mV *vs.* SCE) using a platinum plate as an anode and the tip of a platinum wire as a cathode, without separation, and the reaction was quenched at 1.5 F/mol to afford several oxidation products (**3**, **4**, **5**, **6**, **7**, **8** and **9**) in 17, 6.9, 5.6, 4.8, 8.1, 9.8 and 28.5% yields, respectively. Of these oxidation products, two (**7** and **8**) were previously reported as photooxidation products of isoeugenol.[2] Although the stereochemistry of these two isomers has not yet been determined, the former (**7**), whose methyl doublet is observed at higher magnetic field than that of **8** (δ 1.08 in **7**; δ 1.32 in **8**), can be assigned as the *threo* isomer.[3] Compound **9**, which was isolated from *Myristica fragrans* HOUTT[4] as well as from *Licaria aritu* GROUND,[5] is also a known oxidation product of isoeugenol.[2,6] The structures of the remaining oxidation products were determined on the basis of their spectral data, particularly proton nuclear magnetic resonance (^{1}H NMR) and mass spectra (MS), as follows.

In the case of the two stereoisomers (**3** and **4**), the former must be the *threo* isomer, as judged from the chemical shifts of the methyl doublets (δ 0.94 in **3**; δ 1.14 in **4**).[3] The structure of the austrobailignan-type compound (**5**) is confirmed by its ^{1}H NMR spectrum, which indicates the presence of two environmentally different MeO–C<u>H</u>–C<u>H</u>(<u>Me</u>)– groupings

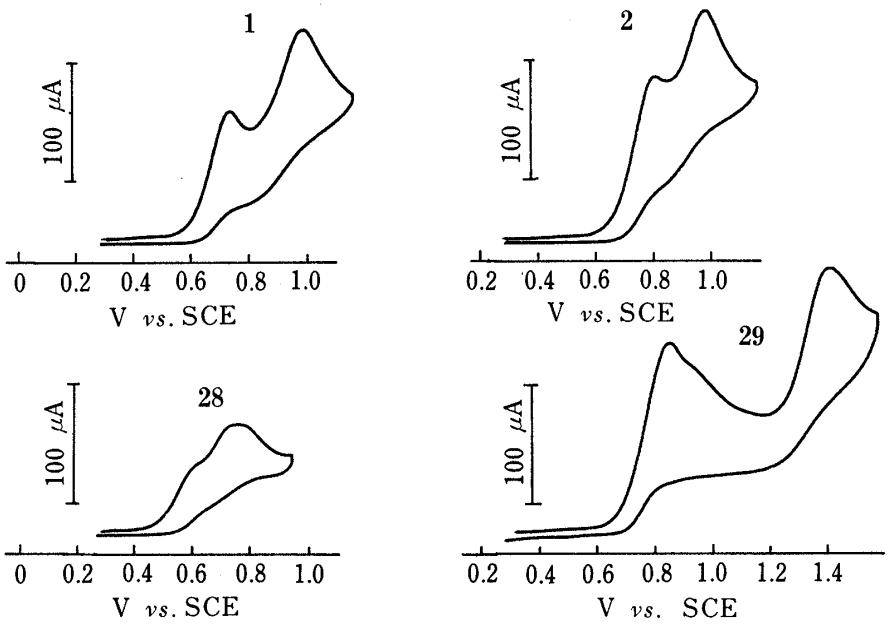


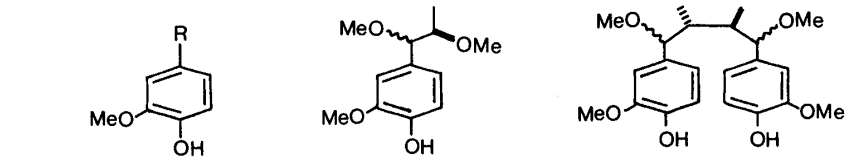
Fig. 1. Cyclic Voltammograms of 4 Phenols (**1**, **2**, **28** and **29**)

Phenols, 2.0 mmol·l^{-1}; supporter $LiClO_4$, 0.2 mol·l^{-1}; solvent, MeOH; WE, glassy carbon (0.26 cm^2); sweep rate, 50 mV·s^{-1}.

(δ 0.70, 0.79, 1.63—2.05, 2.34—2.72, 3.41 and 4.14), in addition to six aromatic protons (δ 5.71—6.80). Although the stereochemistry remains undecided, the relative configuration of the two secondary methyl groups seems to be the same as that of **6**, as discussed later. The structure of **6** was also elucidated on the basis of the ^{1}H NMR spectrum, which indicates the presence of two secondary methyl groups (δ 0.88 and 1.13), one MeO–CH–CH–CH– grouping (δ 1.5—1.9, 3.26 and 4.27), two methoxyl groups attached to aromatic rings (δ 3.58 and 3.80) and five aromatic protons (δ 6.14, 6.53, 6.64, 6.86 and 7.00). Furthermore, the stereostructure can be represented by **6**, as judged from the coupling constants of the two methine signals [δ 3.46 (1H, br d, J=8 Hz) and 4.27 (1H, br d, J=8 Hz)]. On dimerization of the two radical species of *E*-isoeugenol, these two compounds (**5** and **6**) would be produced *via* C–C bond formation at the side chain, which could take place at the initial stage leading to the formation of a plausible intermediate (**10**).[7] In this case, clearly, the radical coupling compounds (**5**—**9**) are mainly obtained as compared with the $-2e$ products (**3** and **4**). When electrolyzed at higher potential (+1400 mV *vs.* SCE) using a glassy carbon beaker as an anode and the tip of a platinum wire as a cathode,[8] *E*-isoeugenol (**1**) was converted into several oxidation products (**3**, **4**, **6**, **7** and **8**, **9**, **11** and **12**) in 30, 16.6, 1.2, 5.3, 6.5, 6.2 and 4.7% yields, respectively. The newly formed dienones (**11** and **12**), the structures of which are based on their ^{1}H NMR spectra (δ 3.26, 5.84, 6.00 and 6.74 in **11**; δ 3.26, 5.81, 5.95 and 6.72 in **12**), including to the methyl doublets (δ 1.00 in **11**; δ 1.15 in **12**), must be derived from **3** and **4**, respectively, by further oxidation.

A solution of *Z*-isoeugenol (**2**) in methanol containing $LiClO_4$ as a supporting electrolyte was electrolyzed at a controlled potential of +800 mV *vs.* SCE to afford the two arylpropanoids (**13** and **14**) and a licarin-type compound (**15**) corresponding to the radical coupling products of *E*-isoeugenol (**7**, **8** and **9**), in 16, 14, and 4.7% yields, respectively, in addition to several known compounds (**3**, **4**, **5** and **6**).

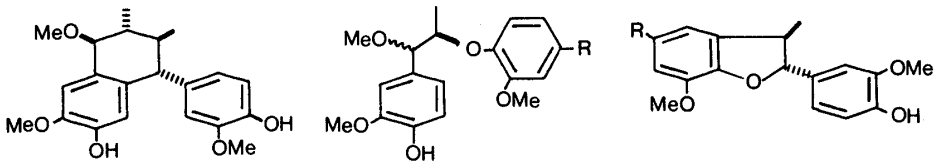
On electrolysis at a potential higher than +800 mV *vs.* SCE using a glassy carbon beaker as an anode,[9] *Z*-isoeugenol (**2**) was converted into an asatone-type dimer (**16**) in 14% yield, together with various known compounds (**3**, **4**, **6**, **11**, **12**, **13**, **14** and **15**). The structure of this new dimer (**16**) was elucidated on the basis of its ^{1}H NMR spectrum, which is quite similar to



1 : R=CH=CHMe(*E*)
2 : R=CH=CHMe(*Z*)

3 (*threo*)
4 (*erythro*)

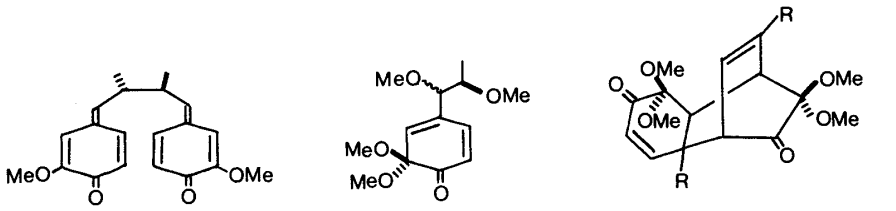
5



6

7 : R=CH=CHMe(*E*)(*threo*)
8 : R=CH=CHMe(*E*)(*erythro*)
13 : R=CH=CHMe(*Z*)(*threo*)
14 : R=CH=CHMe(*Z*)(*erythro*)

9 : R=CH=CHMe(*E*)
15 : R=CH=CHMe(*Z*)



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11 (*threo*)
12 (*erythro*)

16 : R=CH=CHMe(*Z*)
17 : R=CH_2−CH=CH_2

Chart 1

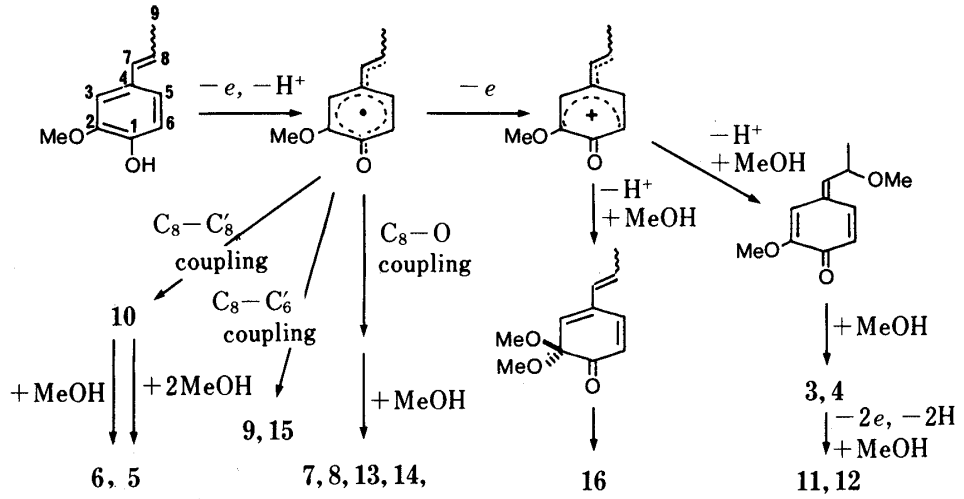
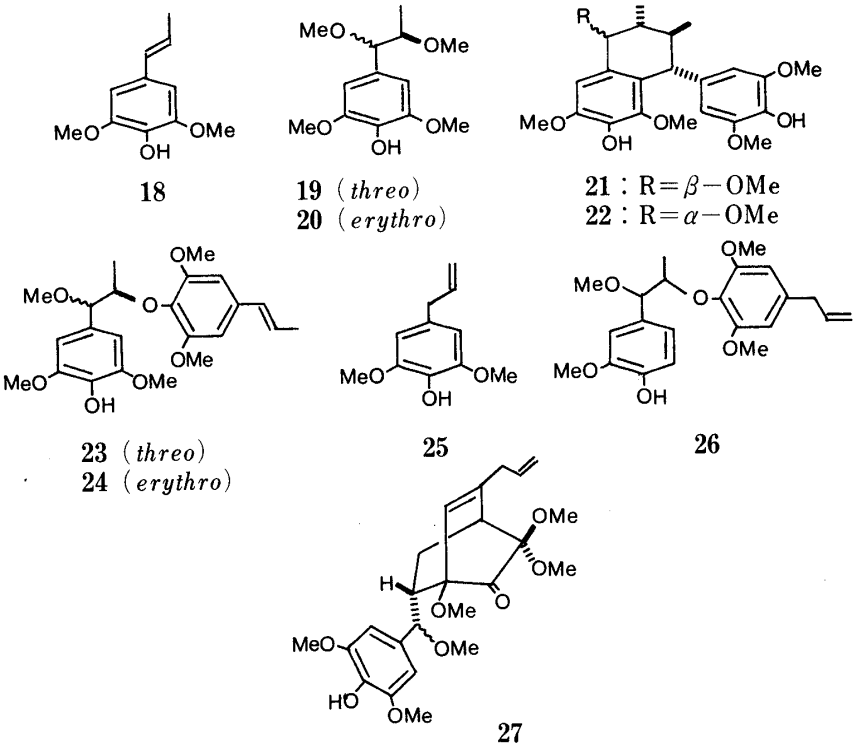


Chart 2. Anodic Oxidation of *E*- and *Z*-Isoeugenols

that of demethoxyasatone (**17**)[10] except for the side chain signals. The probable formation processes of these oxidation products are shown in Chart 2. At the present stage, however, we cannot satisfactorily explain some of the differences between *E*- and *Z*-isoeugenols.

We also carried out anodic oxidation of 2,6-dimethoxy-4-(1-propenyl)phenol (**18**),[11] using a glassy carbon beaker as an anode, as follows. A solution of **18** in methanol containing $LiClO_4$ as a supporting electrolyte was electrolyzed at a constant current (0.25 mA/cm^2; +500—690 mV *vs.* SCE; 1.0 F/mol) to give several oxidation products (**19**, **20**, **21**, **22**, **23** and **24**) in 23, 11, 4.9, 6.9, 1.7 and 6.6% yields, respectively. The structures of the products were elucidated by comparing the spectral data with those of the corresponding products derived



18 19 (*threo*) 20 (*erythro*) 21 : R=β−OMe 22 : R=α−OMe

23 (*threo*) 24 (*erythro*) 25 26

27

Chart 3

from *E*-isoeugenol. In particular, the stereostructures of **21** and **22** are based on the coupling constant of the signal due to the methine proton attached to the carbon atom bearing a methoxyl group [δ 4.16 (1H, br d, J=10 Hz) in **21**; δ 4.08 (1H, d, J=6 Hz) in **22**].

Since some substances which inhibit the growth of silkworm larvae are known to be dimeric arylpropanoids,[4] anodic oxidation of a mixture of *Z*-isoeugenol (**2**) and 4-allyl-2,6-dimethoxyphenol (**25**) was carried out at a controlled potential (+800 mV *vs.* SCE; 1.7 F/mol) to give the desired arylpropanoid (**26**) in 34% yield, in addition to various known minor components (**3**, **4**, **6**, **13**, **14** and **27**[10]) in 2.3, 4.1, 6.4, 6.1, 5.8 and 3.8% yields, respectively. The structure of the newly formed arylpropanoid (**26**) is supported by its mass and ^{1}H NMR spectra [*m/e* 221 and 167; δ 1.24 (3H, d, J=6.5 Hz) and 4.36 (1H, d, J=4 Hz)]. In particular, the doublet at δ 4.36 with a small coupling constant (J=4 Hz) indicates that this arylpropanoid adopts the *erythro* form, as can be seen from the following data: J-values in the *erythro* isomers (**4**, **8** and **14**) are 5, 5.5 and 6 Hz, respectively, while the corresponding values are slightly larger than 6 Hz in the *threo* isomers (**3**, **7** and **13**).

In connection with the 4-propenylphenols, which afford a number of dimeric compounds *via* the corresponding *p*-quinonemethides as plausible intermediates, anodic oxidation of two 2-(1-propenyl)phenols (**28** and **29**) was carried out in methanol containing $LiClO_4$ as a supporting electrolyte, using a glassy carbon beaker as an anode and the tip of a platinum wire as a cathode.

On electrolysis at a controlled potential (+600 mV *vs.* SCE; 1.0 F/mol), 3,4-methylenedioxy-6-(1-propenyl)phenol (**28**) was readily converted into three $-1e$ oxidation products (**30**, **31** and **32**) and 2-hydroxy-4,5-methylenedioxybenzaldehyde (**33**) in 47, 16, 12 and 1% yields, respectively. The spectral data for **32** are identical with those of carpanone, which has been isolated from the plant *Cinnamomum* sp., Lauraceae.[12),13)] The structures of the remaining compounds (**30** and **31**) were determined on the basis of their spectral data: the stereochemistry of **30** is confirmed by the ^{1}H NMR signals at δ 3.41 (1H, d, J=12 Hz) and 3.60 (1H, d, J=8 Hz), both of which are assignable to benzylic methine protons.

As shown in Chart 5, these three dimeric compounds (**30**, **31** and **32**) can plausibly be

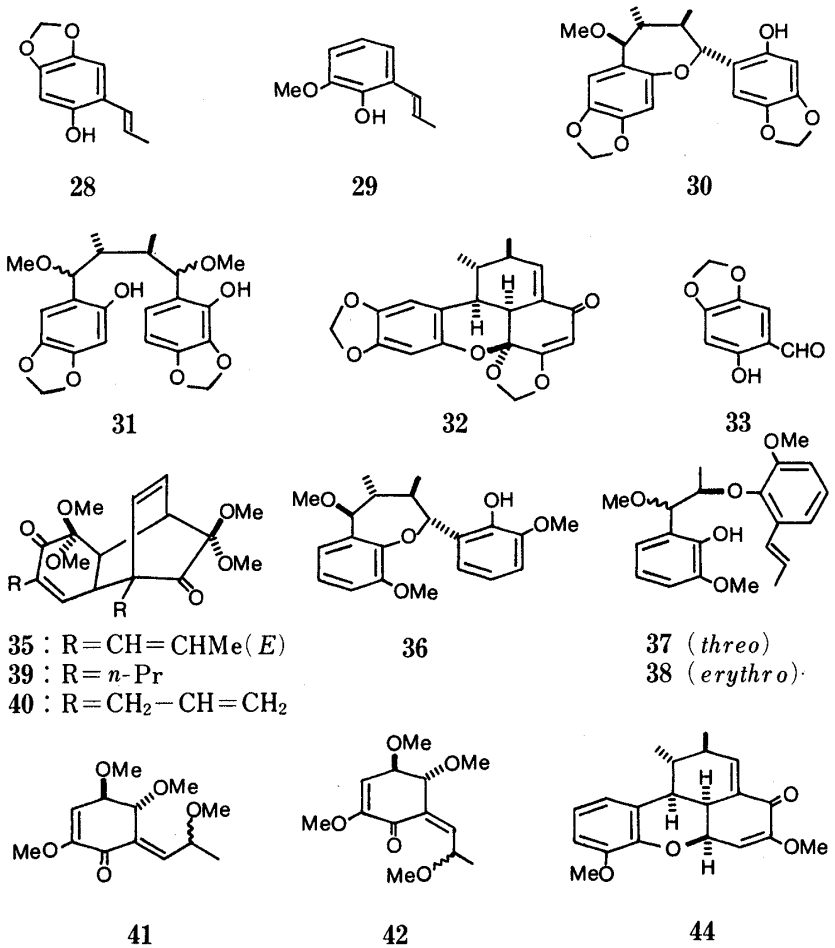


Chart 4

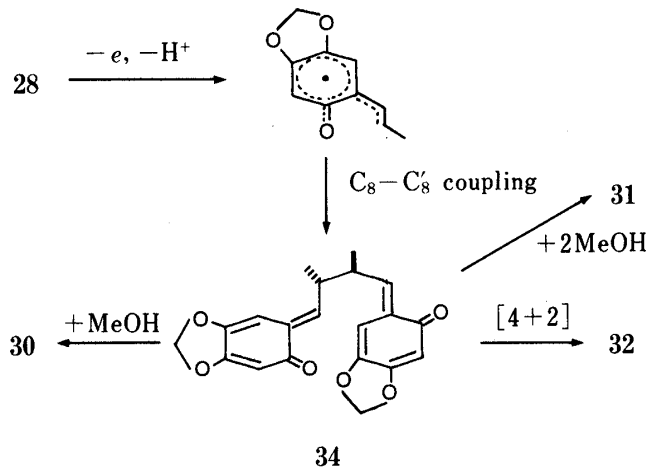


Chart 5. Anodic Oxidation of 3,4-Methylenedioxy-6-propenylphenol (**28**)

derived from the bis-*o*-quinonemethide (**34**) as a common intermediate, which can itself be formed by a C–C coupling reaction between the two radical species produced from 3,4-methylenedioxy-6-(1-propenyl)phenol (**28**) at the initial oxidation step. Finally, anodic oxidation of 2-methoxy-6-(1-propenyl)phenol (**29**) was carried out under various conditions, using a glassy carbon beaker as an anode and the tip of a platinum wire as a cathode, respectively.

When electrolyzed at a controlled potential (+900 mV *vs.* SCE; 1.2 F/mol) in methanol containing $LiClO_4$ as a supporting electrolyte, 2-methoxy-6-(1-propenyl)phenol (**29**) was

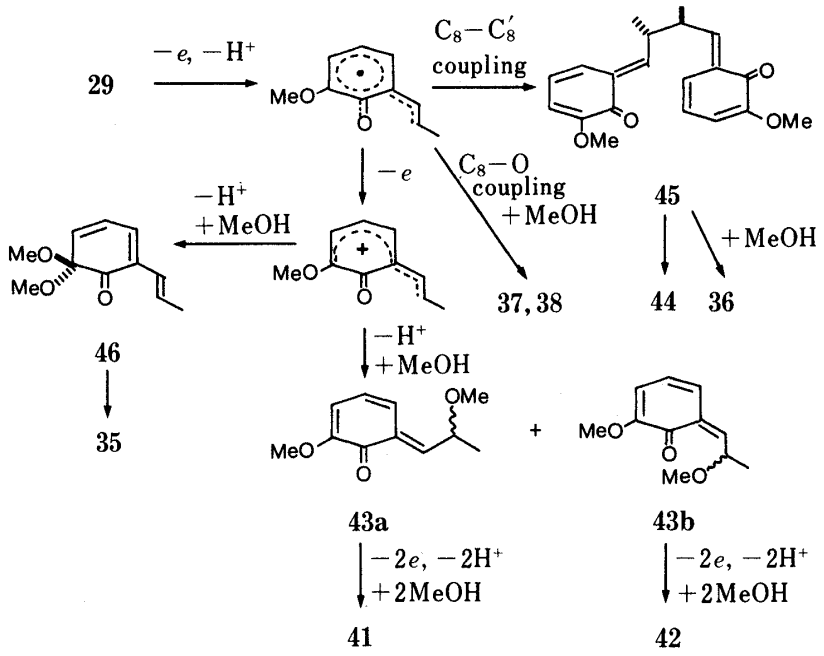


Chart 6. Anodic Oxidation of 2-Methoxy-6-propenylphenol (**29**)

converted into an asatone-type dimer (**35**) in 25% yield, in addition to three $-1e$ oxidation products (**36**, **37** and **38**) in low yields, whose structures were based on their spectral data. The stereochemistry of **35** was confirmed by the following chemical evidence: on hydrogenation over 5% Pd-C in methanol (room temp., 1 h), the dimer (**35**) with the two propenyl groups was readily converted into the corresponding tetrahydro compound (**39**), which was also obtained on hydrogenation of the known asatone-type compound (**40**) produced from 2-allyl-6-methoxyphenol on anodic oxidation.[10] Of the remaining arylpropanoids (**36**, **37** and **38**), two (**37** and **38**) are stereoisomeric; the former is regarded as a *threo* isomer, while the latter must adopt an *erythro* form, as judged from the ^{1}H NMR spectra [δ 1.02 (3H, d, $J=6$ Hz), 4.45 (1H, quintet, $J=6$ Hz) and 4.68 (1H, d, $J=6$ Hz) in **37**; δ 1.13 (3H, d, $J=6$ Hz), 4.22 (1H, m) and 4.65 (1H, d, $J=3$ Hz) in **38**]. On electrolysis at higher potential (+1600 mV *vs.* SCE; 1.9 F/mol), the asatone-type dimer (**35**) was synthesized in 45% yield, in addition to small amounts of two $-4e$ oxidation products (**41** and **42**), whose exocyclic double bond geometry is based on the ^{1}H NMR signals due to the olefinic proton (δ 6.63 in **41**; δ 5.94 in **42**). These two compounds (**41** and **42**) are presumably produced by further oxidative methoxylation at the double bond in a plausible *o*-quinonemethide intermediate (**43a** or **43b**). When the anodic oxidation was carried out exhaustively (+1600 mV *vs.* SCE; 3.1 F/mol), on addition of acetic acid, the $-4e$ oxidation products (**41** and **42**) were obtained in 6.8 and 6.6% yields, respectively, although the yield of **35** was reduced to 26%.

On the other hand, when electrolyzed in basic media (5 N NaOH–MeOH) at a constant current (0.083 mA/cm^2; +150—250 mV *vs.* SCE; 1.1 F/mol), 2-methoxy-6-(1-propenyl)-phenol (**29**) was newly converted into a carpanone-type dimer (**44**) in 16% yield, in addition to the arylpropanoids (**36**, **37** and **38**). The structure of this dimer (**44**) was confirmed by comparing its spectral data with those of carpanone (**32**).

Among the $-1e$ oxidation products (**36**, **37**, **38** and **44**), as shown in Chart 6, **36** and **44** must be derived from bis-*o*-quinonemethide (**45**), whereas **37** and **38** are considered to be C_8-O radicalcoupled dimers. The asatone-type dimer (**35**, $-2e$ oxidation product) must be produced from a trienone (**46**) *via* a cationic species.

As compared with the allylphenols,[10] clearly, the conjugated phenols, which have a propenyl group at the *ortho*- or *para*-position, are readily subject to anodic oxidation to afford

the corresponding *o*- or *p*-quinonemethides as well as bis-*o*- or *p*-quinonemethides, from which a number of naturally occurring neolignans and related compounds are derived. Further synthetic studies on physiologically active neolignans are in progress, using the highly reactive *o*- and *p*-quinonemethide species which are produced on anodic oxidation.

Experimental

All the melting points were measured on a Shimadzu or Mitamura Riken melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Hitachi 215 or Shimadzu IR-400 spectrophotometer. Ultraviolet (UV) spectra were taken on a Hitachi 214 spectrophotometer. ^1H and ^{13}C NMR spectra were taken on a JEOL JNM-PS 100 (100 MHz) or JNM-FX 100 (25.0 MHz) spectrometer. Chemical shifts are given in ppm from tetramethylsilane (TMS) as an internal standard. Coupling constants are given in Hz (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet). Mass spectra (MS) were obtained on a Hitachi M-52 mass spectrometer operating with an ionization energy of 70 eV. High resolution MS were also taken on a Hitachi M-80 mass spectrometer operating with an ionization energy of 70 eV.

Preparative high-performance liquid chromatography (HPLC) was carried out on a main glass column (20 mmϕ × 500 mm) equipped with a precolumn [15 mmϕ × 150 mm; Unisil C_{18} (15—40 μm) 26 ml] using an APUS-24 (Gasukuro Kogyo Inc.) or a KSU-45 pump (Kyowa Seimitsu Co., Ltd.) and both UV model 502 (Gasukuro Kogyo Inc.) and RI model R-403 (Waters Associates Inc.) detectors.

The instruments used for electrode reactions were described in the preceding paper. A 200 ml glassy carbon beaker was used as an anode, unless otherwise stated.

Anodic Oxidation of *E*-Isoeugenol (1) in Methanol Using a Platinum Plate as an Anode——A solution of **1** (328 mg) in MeOH (100 ml) including $LiClO_4$ (6.4 g) was electrolyzed at a controlled potential (+800 mV *vs.* SCE; 30—3 mA) using a platinum plate (45 cm^2) as an anode and the tip of a platinum wire as a cathode, without separation, and the electrolysis was quenched at 1.5 F/mol. The reaction solution was concentrated under reduced pressure below 40 °C, and roughly separated by preparative HPLC [column: 22 mmϕ × 300 mm; HP-255] using a mixed solvent of MeOH–H_2O (93 : 7) to afford three fractions, and then using methanol to give two fractions.

The first fraction obtained with the mixed solvent was concentrated under reduced pressure and then partitioned between AcOEt and water. The AcOEt extract was dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure afforded an oil, which was further separated by preparative thin-layer chromatography (TLC) [Kieselgel PF_{254}; hexane–AcOEt (1 : 1)] to give two compounds [**3** (77 mg) and **4** (31 mg)].

3 (*threo*) as a Colorless Oil: IR (film): 3350 br, 1610, 1520 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.94 (3H, d, J=6 Hz), 3.23 (3H, s), 3.38 (1H, quintet, J=6 Hz), 3.42 (3H, s), 3.83 (3H, s), 3.98 (1H, d, J=6 Hz), 5.76 (1H, br s, OH), 6.67—6.93 (3H, aromatic). MS *m/e*: 226 (M^+) and 167. High MS *m/e*: 226.1203 Calcd for $C_{12}H_{18}O_4$ (M^+). Found: 226.1201.

4 (*erythro*) as a Colorless Oil: IR (film): 3325 br, 1610, 1520 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.14 (3H, d, J=6 Hz), 3.27 (6H, s), 3.41 (1H, dq, J=5, 6 Hz), 3.90 (3H, s), 4.08 (1H, d, J=5 Hz), 5.65 (1H, s, OH), 6.19—6.95 (3H, aromatic). MS *m/e*: 226 (M^+) and 167. High MS *m/e*: 226.1203 Calcd for $C_{12}H_{18}O_4$ (M^+). Found: 226.1205.

The second fraction was concentrated under reduced pressure and then directly separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (3 : 2)] to afford the austrobailignan-type compound (**5**) as an oil (22 mg): IR (film): 3350, 1615 sh, 1605, 1515 br cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.70 (3H, d, J=7 Hz), 0.79 (3H, d, J=7 Hz), 1.63—2.05 (1H, m), 2.34—2.72 (1H, m), 3.21 (3H, s), 3.24 (3H, s), 3.41 (1H, d, J=10 Hz), 3.82 (6H, s), 4.14 (1H, d, J=8 Hz), 5.46 (2H, br s, OH), 5.71—6.80 (6H, complex). MS *m/e*: 390 (M^+) and 167. High MS *m/e*: 390.2040 Calcd for $C_{22}H_{30}O_6$ (M^+). Found: 390.2063.

The third fraction was concentrated under reduced pressure to leave a white solid (**6**) (17 mg): mp 162—163 °C (from AcOEt). IR (KBr): 3400, 1610, 1515 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.88 (3H, d, J=6 Hz), 1.13 (3H, d, J=6 Hz), 1.5—1.9 (2H, complex), 3.26 (3H, s), 3.46 (1H, br d, J=8 Hz), 3.58 (3H, s), 3.80 (3H, s), 4.27 (1H, br d, J=8 Hz), 5.53 (1H, s, OH), 5.59 (1H, s, OH), 6.14 (1H, s), 6.53 (1H, d, J=2 Hz), 6.64 (1H, dd, J=8, 2 Hz), 6.86 (1H, d, J=8 Hz), 7.00 (1H, s). MS *m/e*: 358 (M^+) and 326. High MS *m/e*: 358.1778 Calcd for $C_{21}H_{26}O_5$ (M^+). Found: 358.1768.

The first fraction eluted with MeOH was further separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to afford two arylpropanoids as almost colorless oils [**7** (*threo*), 29 mg; **8** (*erythro*), 35 mg)].[2] The spectral data of these compounds are identical with those of the known photooxidation products of *E*-isoeugenol.[2]

The remaining fraction eluted with MeOH was concentrated under reduced pressure, and then purified by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to afford a crystalline solid (**9**) (93 mg), mp 131—133 °C (from hexane), the spectral data of which are also identical with those of the known neolignan isolated from *Myristica fragrans* HOUTT as well as from *Licaria aritu* GROUND.[2,4-6]

Anodic Oxidation of *E*-Isoeugenol (1) in Methanol at Higher Potential——A solution of **1** (328 mg) in MeOH (100 ml) containing $LiClO_4$ (1.6 g) was electrolyzed at a controlled potential (+1400 mV *vs.* SCE; 160—100 mA) and the reaction was quenched at 1.7 F/mol. The reaction solution was concentrated under reduced pressure below 40 °C, and then roughly separated by preparative HPLC [column: 22 mmϕ × 300 mm; HP-255] using a mixed solvent of

MeOH–H_2O (93 : 7) to afford four fractions according to the same procedure as described above. From the first fraction, both **3** (129 mg) and **4** (71 mg) were obtained. The second fraction was separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to give the starting material (17 mg), **6** (4 mg) and two dienones [**11** (*threo*), 30 mg; **12** (*erythro*), 23 mg].

11 as a Colorless Oil: IR (film): 1685, 1660 cm^{-1}. ^1H NMR (CCl_4) δ: 1.00 (3H, d, J=6 Hz), 3.26 (6H, s), 3.28 (3H, s), 3.32 (3H, s), 3.36 (1H, quintet, J=6 Hz), 3.63 (1H, d, J=6 Hz), 5.84 (1H, d, J=10 Hz), 6.00 (1H, br d, J=2 Hz), 6.74 (1H, dd, J=10, 2 Hz). MS *m/e*: 256 (M^+), 241, 226, 197 and 167. High MS *m/e*: 256.1309 Calcd for $C_{13}H_{20}O_5$ (M^+). Found: 256.1334.

12 as a Colorless Oil: IR (film): 1685, 1660 cm^{-1}. ^1H NMR (CCl_4) δ: 1.15 (3H, d, J=6 Hz), 3.26 (6H, s), 3.28 (3H, s), 3.31 (3H, s), 3.11—3.36 (1H, m), 3.44 (1H, d, J=6 Hz), 5.81 (1H, d, J=10 Hz), 5.95 (1H, br d, J=2 Hz), 6.72 (1H, dd, J=10, 2 Hz). MS *m/e*: 256 (M^+), 197 and 167. High MS *m/e*: 256.1309 Calcd for $C_{13}H_{20}O_5$ (M^+). Found: 256.1338.

From the third fraction eluted with MeOH, a mixture of arylpropanoids (**7** and **8**) (18 mg) was also obtained, but further separation was not attempted. From the last fraction, a licarin-type neolignan (**9**) (20 mg) was obtained.

Anodic Oxidation of *Z*-Isoeugenol (2) in Methanol Using a Platinum Plate as an Anode——A solution of **2** (328 mg) in MeOH (100 ml) containing $LiClO_4$ (6.4 g) was electrolyzed at a controlled potential (+800 mV *vs.* SCE; 25—4 mA) using a platinum plate (45 cm^2) as an anode and the tip of a platinum wire as a cathode, without separation, and the electrolysis was quenched at 1.5 F/mol. The reaction solution was concentrated under reduced pressure, and then roughly separated by preparative HPLC [column: 22 mmϕ × 300 mm, HP-255; MeOH–H_2O (93 : 7)] to give five fractions. According to the same procedure as described in the case of *E*-isoeugenol, the first fraction was separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (1 : 1)] to afford **3** (32 mg) and **4** (21 mg). The second fraction was further purified by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 3)] to afford **5** (11 mg). The third fraction was also separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to give **6** (73 mg) in addition to the starting material (9 mg). Further separation of the fourth fraction by preparative TLC [Kieselgel PF_{254}: hexane–AcOEt (4 : 1)] yielded two arylpropanoids (**13**, 57 mg; **14**, 49 mg).

13 (*threo*) as a Colorless Oil: IR (film): 3500 sh, 3350 br, 1605, 1580, 1520 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.09 (3H, d, J=6 Hz), 1.90 (3H, dd, J=7, 2 Hz), 3.26 (3H, s), 3.81 (3H, s), 3.86 (3H, s), 4.27 (1H, d, J=6 Hz), 4.48 (1H, quintet, J=6 Hz), 5.64 (1H, br s, OH), 5.69 (1H, dq, J=12, 7 Hz), 6.36 (1H, dq, J=12, 2 Hz), 6.75—7.01 (6H, complex). MS *m/e*: 358 (M^+), 226, 195 and 167. High MS *m/e*: 358.1778 Calcd for $C_{21}H_{26}O_5$ (M^+). Found: 358.1745.

14 (*erythro*) as a Colorless Oil: IR (film): 3350 br, 1605, 1580, 1520 br cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.32 (3H, d, J=6 Hz), 1.88 (3H, dd, J=7, 2 Hz), 3.31 (3H, s), 3.76 (3H, s), 3.85 (3H, s), 4.28 (1H, d, J=6 Hz), 4.40 (1H, quintet, J=6 Hz), 5.63 (1H, br s, OH), 5.68 (1H, dq, J=12, 7 Hz), 6.37 (1H, dq, J=12, 2 Hz), 6.75—6.99 (6H, complex). MS *m/e*: 358 (M^+), 326, 195 and 167; High MS *m/e*: 358.1778 Calcd for $C_{21}H_{26}O_5$ (M^+). Found: 358.1745.

The remaining fraction was further purified by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to afford a licarin-type neolignan (**15**) (15 mg) as an oil: IR (film): 3400, 1615, 1600, 1520, 1500 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.39 (3H, d, J=7 Hz), 1.93 (3H, dd, J=7, 2 Hz), 3.46 (1H, dq, J=10, 7 Hz), 3.87 (6H, s), 5.11 (1H, d, J=10 Hz), 5.63 (1H, s, OH), 5.69 (1H, dq, J=11, 7 Hz), 6.39 (1H, dq, J=11, 2 Hz), 6.59—7.02 (5H, complex). MS *m/e*: 326 (M^+), 311, 202 and 149. High MS *m/e*: 326.1516 Calcd for $C_{20}H_{22}O_4$ (M^+). Found: 326.1504.

Anodic Oxidation of *Z*-Isoeugenol (2) in Methanol——A solution of **2** (656 mg) in MeOH (100 ml) containing $LiClO_4$ (4.3 g) was electrolyzed at a controlled potential (+1000 mV *vs.* SCE; 110—30 mA) and the reaction was quenched at 1.2 F/mol. The reaction solution was concentrated under reduced pressure and then roughly separated by preparative HPLC [column: 22 mmϕ × 300 mm, HP-255; MeOH–H_2O (95 : 5)] to afford five fractions.

According to the same procedure as described above, the first fraction was extracted with AcOEt and then roughly separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (1 : 1)] to afford a mixture of **3** and **4** (80 mg), which was not further separated. The second fraction was concentrated under reduced pressure, and then separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to give **11** (25 mg), **12** (11 mg) and **6** (35 mg), in addition to the starting material (273 mg).

The third fraction was also concentrated under reduced pressure to leave an asatone-type dimer (**16**) as an almost colorless solid (64 mg): mp 96—98 °C (from hexane). IR (KBr): 1735, 1710 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.73 (3H, br d, J=6 Hz), 1.78 (3H, br d, J=6.5 Hz), 3.08 (3H, s), 2.97—3.17 (3H, complex), 3.24 (3H, s), 3.37 (3H, s), 3.39 (3H, s), 5.27 (1H, dq, J=12, 1 Hz), 5.37—5.74 (4H, complex), 5.94 (1H, d, J=10 Hz), 6.48 (1H, br d, J=10 Hz). MS *m/e*: 388 (M^+) and 194. High MS *m/e*: 388.1883 Calcd for $C_{22}H_{28}O_6$ (M^+). Found: 388.1881.

According to the same procedure as described above, a mixture of the two arylpropanoids (**13** and **14**) (113 mg) was obtained from the fourth fraction, and **15** (78 mg) from the last fraction.

Anodic Oxidation of 2,6-Dimethoxy-4-(1-propenyl)phenol (18) in Methanol——A solution of **18** (388 mg) in MeOH (200 ml) containing $LiClO_4$ (4.3 g) was electrolyzed at a constant current (40 mA; 0.25 mA/cm^2; +500—690 mV *vs.* SCE) and the reaction was quenched at 1.0 F/mol. The reaction solution was concentrated on a pre-column [15 mmϕ × 150 mm, Unisil C_{18} (25—40 μm)] and then subjected to preparative HPLC [column: 20 mmϕ × 500 mm, Develosil ODS-10; 0.01 M $AcONH_4$ in MeOH–H_2O (60 : 40)] to give four fractions.

The first fraction was concentrated under reduced pressure and partitioned between AcOEt and H_2O. The

AcOEt extract was dried over anhydrous Na_2SO_4, and then filtered. The filtrate was concentrated under reduced pressure to give **19** (*threo*) as a colorless oil (67 mg): IR (film): 3400 br, 1610, 1510 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.94 (3H, d, J=6 Hz), 3.23 (3H, s), 3.39 (3H, s), 3.45 (1H, m), 3.88 (6H, s), 3.95 (1H, d, J=7 Hz), 5.62 (1H, br s, OH), 6.51 (2H, s). High MS *m/e*: 256.1310 Calcd for $C_{13}H_{20}O_5$ (M^+). Found: 256.1313.

The second fraction was separated by preparative TLC [Kieselgel PF_{254}; hexane–ether (1 : 1)] to afford **19** (48 mg) and **20** (55 mg).

20 (*erythro*) as an Oil: IR (film): 3400 br, 1610, 1510 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.17 (3H, d, J=6 Hz), 3.24 (3H, s), 3.26 (3H, s), 3.36 (1H, quintet, J=6 Hz), 3.88 (6H, s), 4.02 (1H, d, J=6 Hz), 5.59 (1H, s, OH), 6.53 (2H, s). High MS *m/e*: 256.1310 Calcd for $C_{13}H_{20}O_5$ (M^+). Found: 256.1296.

The third fraction was also separated by preparative TLC [Kieselgel PF_{254}; hexane–ether (1 : 1)] to afford **21** (20 mg) and **22** (28 mg), in addition to the starting material (10 mg).

21: mp 155—157 °C (from ether). IR (KBr): 3490, 3370 br, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.00 (3H, d, J=6 Hz), 1.09 (3H, d, J=6 Hz), 1.52 (2H, m), 3.13 (3H, s), 3.30 (3H, s), 3.54 (1H, br d, J=8 Hz), 3.80 (6H, s), 3.88 (3H, s), 4.16 (1H, br d, J=10 Hz), 5.30 (1H, s, OH), 5.32 (1H, s, OH), 6.27 (2H, s), 6.80 (1H, s). High MS *m/e*: 418.1990 Calcd for $C_{23}H_{30}O_7$ (M^+). Found: 418.2026.

22: mp 69—71 °C (from ether). IR (film): 3380 br, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.82 (3H, d, J=6 Hz), 0.98 (3H, d, J=6 Hz), 2.18 (2H, m), 3.23 (3H, s), 3.34 (3H, s), 3.6—3.8 (1H, superimposed on MeO signals), 3.78 (6H, s), 3.89 (3H, s), 4.08 (1H, d, J=6 Hz), 5.32 (1H, s, OH), 5.42 (1H, s, OH), 6.32 (2H, s), 6.64 (1H, s). High MS *m/e*: 418.1990 Calcd for $C_{23}H_{30}O_7$ (M^+). Found: 418.1962.

The remaining fraction was further separated by preparative TLC [Kieselgel PF_{254}; hexane–ether (1 : 1)] to afford two arylpropanoids [**23** (*threo*), 7 mg; **24** (*erythro*), 27 mg].

23 (*threo*) as an Almost Colorless Oil: IR (film): 3420 br, 1610, 1580 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.98 (3H, br d, J=5 Hz), 1.85 (3H, br d, J=6 Hz), 3.20 (3H, s), 3.81 (6H, s), 3.88 (6H, s), 4.08—4.44 (2H, m), 5.43 (1H, s, OH), 5.00—6.42 (2H, m), 6.50 (2H, s), 6.60 (2H, s). MS *m/e*: 418 (M^+) and 197. High MS *m/e*: 418.1990 Calcd for $C_{23}H_{30}O_7$ (M^+). Found: 418.2010.

24 (*erythro*) as a Colorless Oil: IR (film): 3420 br, 1610, 1580 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.23 (3H, d, J=7 Hz), 1.84 (3H, br d, J=6 Hz), 3.34 (3H, s), 3.77 (6H, s), 3.84 (6H, s), 4.22 (1H, m), 4.34 (1H, br d, J=3 Hz), 5.39 (1H, s, OH), 6.00—6.44 (2H, m), 6.50 (4H, s). MS *m/e*: 418 (M^+) and 197. High MS *m/e*: 418.1990 Calcd for $C_{23}H_{30}O_7$ (M^+). Found: 418.2005.

Cross-Coupling Reaction between *Z*-Isoeugenol (2) and 4-Allyl-2,6-dimethoxyphenol (25)——A solution of **2** (164 mg) and **25** (194 mg) in MeOH (100 ml) containing $LiClO_4$ (6.4 g) was electrolyzed at a controlled potential (+800 mV *vs.* SCE; 50—3 mA) and the reaction was quenched at 1.7 F/mol. The reaction solution was concentrated under reduced pressure below 40 °C, and then roughly separated by preparative HPLC [column: 22 mmϕ × 300 mm, HP-255; MeOH–H_2O (93 : 7)] to give five fractions.

The first fraction was concentrated under reduced pressure and partitioned between AcOEt and H_2O. The AcOEt extract was dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure afforded an oil (108 mg), which was separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to give **3** (10 mg) and **4** (18 mg), in addition to the starting materials (**2**, 9 mg; **25**, 5 mg). The second fraction was concentrated under reduced pressure to leave an oil (32 mg), from which **25** (27 mg) was recovered. The third fraction was also concentrated under reduced pressure to leave an amorphous powder (39 mg), which was purified by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to afford **6** as white crystals (22 mg).

The fourth fraction was concentrated under reduced pressure to give an oil (143 mg), which was separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to give a cross-coupling dimer (**26**) (117 mg) and the known isoheterotropanone-type dimer (**27**) (14 mg).

26 as a Colorless Oil: IR (film): 3400, 1640, 1595 br, 1520, 1510 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.24 (3H, d, J=6.5 Hz), 3.27—3.36 (2H, overlapped with MeO signals), 3.33 (3H, s), 3.74 (6H, s), 3.82 (3H, s), 4.14 (1H, m), 4.36 (1H, d, J=4 Hz), 5.04 (1H, br d, J=11 Hz), 5.07 (1H, br d, J=16 Hz), 5.50 (1H, br s, OH), 5.93 (1H, m), 6.34 (2H, s), 6.63—6.88 (3H, complex). MS *m/e*: 388 (M^+), 221, 195, 194 and 167. High MS *m/e*: 388.1883 Calcd for $C_{22}H_{28}O_6$ (M^+). Found: 388.1869.

After concentration of the remaining fraction, the crude residue (43 mg) was separated by preparative TLC [Kieselgel PF_{254}; hexane–AcOEt (2 : 1)] to afford two known arylpropanoids (**13**, 21 mg; **14**, 20 mg).

Anodic Oxidation of 3,4-Methylenedioxy-6-(1-propenyl)phenol (28)——A solution of **28** (356 mg) in MeOH (200 ml) containing $LiClO_4$ (4.3 g) was electrolyzed at a controlled potential (+600 mV *vs.* SCE; 50—2 mA) and the electrolysis was quenched at 1.0 F/mol. The reaction solution was concentrated under reduced pressure and then extracted with ether. The ethereal extract was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and then separated by preparative HPLC (column: 22 mmϕ × 300 mm, HP-255; MeOH) to afford four fractions. The first fraction, which was treated as usual, was purified by preparative TLC (Kieselgel PF_{254}; benzene) to afford **30** (169 mg): mp 169—172 °C (from AcOEt). IR (KBr): 3370 br, 1635, 1580 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 0.72 (3H, d, J=6 Hz), 1.10 (3H, d, J=6 Hz), 1.40—2.20 (2H, complex), 2.96 (3H, s), 3.41 (1H, d, J=12 Hz), 3.60 (1H, d, J=8 Hz), 5.02 (1H, s), 5.61 (1H, s), 5.72 (2H, s), 5.76 (2H, s), 6.18 (1H, s), 6.23 (1H, s),

8.73 (1H, s, OH). High MS *m/e*: 386.1364 Calcd for $C_{21}H_{22}O_7$ (M^+). Found: 386.1376.

The second fraction was also concentrated under reduced pressure and purified by preparative TLC (Kieselgel PF_{254}; benzene) to give **31** (63 mg): mp 87—89 °C (from benzene). IR (KBr): 3350 br, 1620 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.77 (3H, d, J=6 Hz), 0.80 (3H, d, J=6 Hz), 1.70—2.04 (1H, m), 2.40—2.88 (1H, m), 3.26 (3H, s), 3.33 (3H, s), 4.14 (2H, d, J=10 Hz), 5.75 (2H, m), 5.80 (2H, br s), 6.28 (1H, s), 6.30 (1H, s), 6.67 (1H, s), 6.72 (1H, s). High MS *m/e*: 418.1625 Calcd for $C_{22}H_{26}O_8$ (M^+). Found: 418.1570.

After concentration of the third fraction, further purification by preparative TLC (Kieselgel PF_{254}; benzene) afforded carpanone (**32**) (39 mg) (mp, IR and ^1H NMR spectra).[12,13]

The last fraction was concentrated under reduced pressure and purified by preparative TLC [Kieselgel PF_{254}; benzene–AcOEt (9 : 1)] to afford 2-hydroxy-4,5-methylenedioxybenzaldehyde (**33**) (3 mg): mp 85—87 °C (from benzene). IR (KBr): 1640, 1605 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 5.99 (2H, s), 6.45 (1H, s), 6.84 (1H, s), 9.59 (1H, s). High MS *m/e*: 166.0264 Calcd for $C_8H_6O_4$ (M^+). Found: 166.0237.

Anodic Oxidation of 2-Methoxy-6-(1-propenyl)phenol (29) in Methanol——A solution of **29** (328 mg) in MeOH (200 ml) containing $LiClO_4$ (4.3 g) was electrolyzed at a controlled potential (+900 mV *vs.* SCE; 100—10 mA) and the reaction was quenched at 1.2 F/mol. The reaction solution was concentrated under reduced pressure and roughly separated by preparative HPLC [column: 22 mmϕ × 300 mm, Unisil C_{18} (24—40 μm); MeOH–H_2O (75 : 25)] to afford three fractions. According to the same procedure as described above, the first fraction was extracted with AcOEt. The AcOEt extract was dried over anhydrous Na_2SO_4, and then filtered. The filtrate was concentrated under reduced pressure and purified by preparative TLC [Kieselgel PF_{254}; benzene–AcOEt (5 : 1)] to afford **36** (8 mg): mp 170—173 °C (from ether). IR (KBr): 3475, 1605, 1585 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.95 (3H, d, J=6 Hz), 1.01 (3H, d, J=6 Hz), 1.6—2.6 (2H, m), 3.70 (3H, s), 3.83 (3H, s), 3.84 (3H, s), 4.18 (1H, d, J=10 Hz), 4.60 (1H, d, J=9 Hz), 5.95 (1H, s, OH), 6.5—7.1 (6H, complex). High MS *m/e*: 358.1777 Calcd for $C_{21}H_{26}O_5$ (M^+). Found: 358.1775.

The second fraction was concentrated under reduced pressure, and then separated by preparative TLC [Kieselgel PF_{254}; benzene–AcOEt (5 : 1)] to give two arylpropanoids [**37** (*threo*), 5 mg; **38** (*erythro*), 5 mg].

37: mp 208—210 °C (from ether). IR (KBr): 3430 br, 1600, 1580, 1480 br cm^{-1}. ^1H NMR (CCl_4) δ: 1.02 (3H, d, J=6 Hz), 1.87 (3H, dd, J=6.5, 2 Hz), 3.21 (3H, s), 3.72 (3H, s), 3.84 (3H, s), 4.45 (1H, quintet, J=6 Hz), 4.68 (1H, d, J=6 Hz), 5.98 (1H, dq, J=15.5, 6.5 Hz), 6.14 (1H, s), 6.5—6.9 (7H, complex). High MS *m/e*: 358.1778 Calcd for $C_{21}H_{26}O_5$ (M^+). Found: 358.1767.

38: mp 204—206 °C (from ether). IR (KBr): 3530 br, 1600, 1580, 1480 cm^{-1}. ^1H NMR (CCl_4) δ: 1.13 (3H, d, J=6 Hz), 1.90 (3H, dd, J=6.5, 2 Hz), 3.29 (3H, s), 3.74 (3H, s), 3.80 (3H, s), 4.22 (1H, m), 4.65 (1H, d, J=3 Hz), 5.80 (1H, s), 6.05 (1H, dq, J=16, 6.5 Hz), 6.5—7.0 (7H, complex). High MS *m/e*: 358.1778 Calcd for $C_{21}H_{26}O_5$ (M^+). Found: 358.1785.

The last fraction was also concentrated under reduced pressure and purified by preparative TLC [Kieselgel PF_{254}, benzene–AcOEt (5 : 1)] to afford an asatone-type dimer (**35**) (95 mg): mp 128—129 °C (from hexane). IR (KBr): 1740, 1710, 1650 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.78 (3H, d, J=6.5 Hz), 1.86 (3H, d, J=6.5 Hz), 3.05 (3H, s), 3.19 (3H, s), 3.39 (3H, s), 3.44 (3H, s), 2.9—3.4 (3H, overlapped with MeO signals), 5.6—6.4 (7H, complex). High MS *m/e*: 388.1884 Calcd for $C_{22}H_{28}O_6$ (M^+). Found: 388.1888.

Catalytic Hydrogenation of 35——Catalytic hydrogenation of **35** (22 mg) in MeOH (10 ml) over 5% Pd-C (10 mg) was carried out at room temperature for 1 h. The catalyst was filtered off, and the filtrate was concentrated under reduced pressure, then purified by preparative TLC [Kieselgel PF_{254}; benzene–AcOEt (5 : 1)] to afford **39** as an amorphous powder (12 mg): IR (KBr): 1735, 1705 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.91 (3H, t, J=7 Hz), 0.98 (3H, t, J=7 Hz), 1.20—1.85 (6H, complex), 2.18 (2H, t, J=7 Hz), 3.02 (3H, s), 3.18 (3H, s), 3.00—3.25 (3H, overlapped with MeO signals), 3.36 (3H, s), 3.43 (3H, s), 5.50 (1H, br d, J=8 Hz), 6.03—6.18 (2H, complex). High MS *m/e*: 392.2197 Calcd for $C_{22}H_{32}O_6$ (M^+). Found: 392.2230.

Catalytic Hydrogenation of 40——Catalytic hydrogenation of **40** (96 mg) in MeOH (20 ml) over 5% Pd-C (20 mg) was carried out under the same conditions as described for **35** to afford the tetrahydro compound (**39**) (35 mg), whose spectral data were identical with those of the compound obtained from **35** (IR, and ^1H NMR spectra).

Anodic Oxidation of 2-Methoxy-6-(1-propenyl)phenol (29) in Methanol at Higher Potential——A solution of **29** (328 mg) in MeOH (200 ml) containing $LiClO_4$ (4.3 g) was electrolyzed at a controlled potential (+1600 mV *vs.* SCE; 400—100 mA) and the reaction was quenched at 1.9 F/mol. The reaction solution was concentrated under reduced pressure, and then roughly separated by preparative HPLC [column: 22 mmϕ × 300 mm, Develosil C_{18} (25—40 μm); MeOH–H_2O (80 : 20)] to afford three fractions. Each fraction was further separated by preparative TLC [Kieselgel PF_{254}; benzene–AcOEt (2 : 1)] to afford the starting material (10 mg), **35** (170 mg) and two dienones (**41**, 10 mg; **42**, 10 mg).

41: mp 76—78 °C (from AcOEt). IR (KBr): 1690, 1635 cm^{-1}. ^1H NMR (CCl_4) δ: 1.23 (3H, d, J=6 Hz), 3.24 (3H, s), 3.26 (3H, s), 3.33 (3H, s), 3.60 (3H, s), 3.7—4.6 (3H, complex), 5.59 (1H, d, J=6 Hz), 6.63 (1H, d, J=8 Hz). High MS *m/e*: 256.1309 Calcd for $C_{13}H_{20}O_5$ (M^+). Found: 256.1311.

42: mp 73—77 °C (from AcOEt). IR (KBr): 1680, 1630 cm^{-1}. ^1H NMR (CCl_4) δ: 1.20 (3H, d, J=6 Hz), 3.21 (3H, s), 3.38 (6H, s), 3.59 (3H, s), 3.99—4.21 (2H, m), 4.61 (1H, m), 5.56 (1H, d, J=6 Hz), 5.94 (1H, d, J=8 Hz). High MS *m/e*: 256.1309 Calcd for $C_{13}H_{20}O_5$ (M^+). Found: 256.1304.

Anodic Oxidation of 2-Methoxy-6-(1-propenyl)phenol (29) in Acidic Media——A solution of **29** (328 mg) in MeOH (200 ml) containing AcOH (12 g) and $LiClO_4$ (4.3 g) was electrolyzed at a controlled potential (+1600 mV *vs.* SCE; 100—0 mA) and the reaction was quenched at 3.1 F/mol. The reaction solution was concentrated under reduced pressure and extracted with AcOEt. The AcOEt extract was dried over anhydrous Na_2SO_4, and then filtered. The filtrate was concentrated under reduced pressure, and then separated by preparative TLC [Kieselgel PF_{254}; benzene–AcOEt (2 : 1)] to afford **35** (100 mg), **41** (35 mg) and **42** (34 mg).

Anodic Oxidation of 2-Methoxy-6-(1-propenyl)phenol (29) in Basic Media——A solution of **29** (328 mg) in MeOH (200 ml) containing 5 N NaOH (1.0 ml) and $LiClO_4$ (4.3 g) was electrolyzed at a constant current (10 mA; 0.083 mA/cm^2; +150—250 mV *vs.* SCE) and the reaction was quenched at 1.1 F/mol. The solution was concentrated under reduced pressure and extracted with AcOEt. The AcOEt extract was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and then separated by preparative TLC [Kieselgel PF_{254}; benzene–AcOEt (2 : 1)] to afford a carpanone-type dimer (**44**) (53 mg), in addition to a mixture of **36**, **37** and **38**, which were detected by analytical TLC [Kieselgel PF_{254}; hexane–ether (2 : 1)].

44: mp 181—184 °C (from AcOEt). IR (KBr): 1680, 1630, 1585 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.57 (3H, d, J=7 Hz), 1.16 (3H, d, J=7 Hz), 2.19 (1H, m), 2.54 (1H, m), 3.02—3.40 (2H, complex), 3.73 (3H, s), 3.80 (3H, s), 4.62 (1H, dd, J=6, 2 Hz), 6.17 (1H, d, J=6 Hz), 6.56—7.04 (3H, complex), 7.14 (1H, br d, J=5 Hz). High MS *m/e*: 326.1517 Calcd for $C_{20}H_{22}O_4$ (M^+). Found: 326.1519.

Acknowledgement The authors wish to thank Drs. Y. Shizuri and S. Nishiyama, Keio University, for measurements of high resolution MS.

References and Notes

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