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## Anodic Oxidation of 4-Allyl-2,6-dimethoxyphenol and Related Compounds: Syntheses of Asatone and Related Neolignans

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4-Allyl-2,6-dimethoxyphenol and related compounds have been subjected to anodic oxidation to afford a number of oxidation products including asatone-type neolignans, heterotropanone-type compounds and arylpropanoids. Furthermore, the formation processes of these oxidation products are shown to involve both radical and cationic reactions which are dependent upon the applied potentials, solvent media and substituents on the aromatic ring.

**Keywords**—allylphenol; neolignan; electrochemical oxidation; Diels–Alder reaction; biomimetic synthesis

Recently, a number of novel neolignans have been isolated from two different kinds of plant, *Asarum teitonense* HAYATA and *Heterotropa takaoi* MAEKAWA.<sup>1)</sup> Among them, asatone (**1**) and related neolignans are of great interest as physiologically active substances.<sup>2)</sup> From a biogenetic point of view, as described in the previous paper,<sup>1)</sup> asatone (**1**) must be produced by Diels–Alder reaction of 4-allyl-2,6,6-trimethoxy-2,4-cyclohexadien-1-one (**2**), which is derived from 4-allyl-2,6-dimethoxyphenol (**3**) on phenol-oxidative methoxylation, as shown in Chart 1. Thus, we have carried out anodic oxidation of allylphenols in methanol and obtained asatone-type neolignans, heterotropanone-type compounds and arylpropanoids. In addition, many new types of neolignan have also been synthesized, although they have not yet been found in nature. Furthermore, we discuss the formation processes of these oxidation

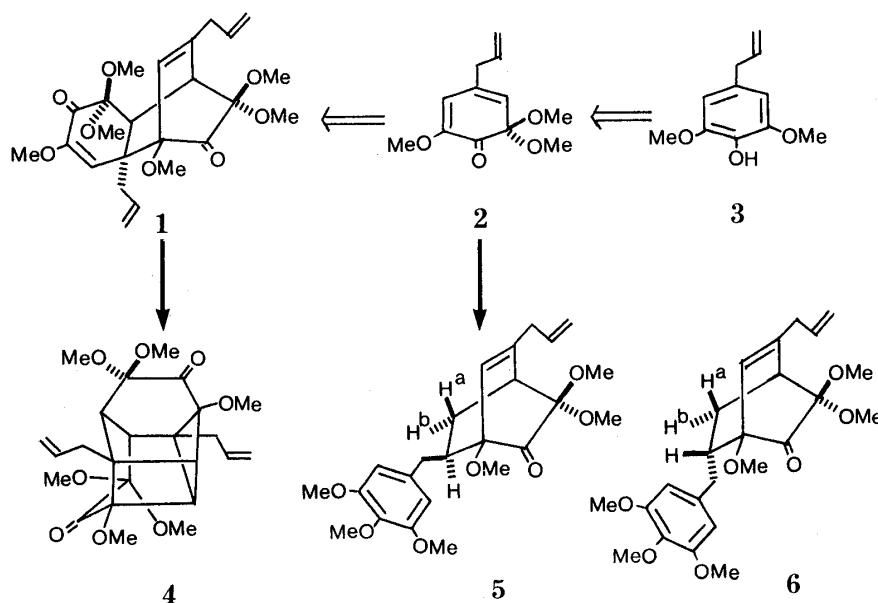


Chart 1. Biogenesis of Asatone (**1**) and Related Neolignans

products on the basis of voltammetric and coulometric experiments.

### Results and Discussion

Anodic oxidation of 4-allyl-2,6-dimethoxyphenol (**3**) in methanol containing  $\text{LiClO}_4$  as a supporting electrolyte was carried out at a constant current ( $0.31 \text{ mA/cm}^2$ ), using a glassy carbon beaker as an anode and the tip of a platinum wire as a cathode, without separation. During the electrolysis, the anode potential was recorded to be lower than  $+660 \text{ mV vs. SCE}$ , and the reaction was quenched at  $2.0 \text{ F/mol}$ . The reaction mixture was carefully separated by column chromatography (Develosil ODS-10) to afford asatone (**1**) and 4-allyl-2,6,6-trimethoxy-2,4-cyclohexadien-1-one (**2**)<sup>3</sup> in 4.2 and 32% yields, respectively. This dienone (**2**), obtained as a colorless oil, was quite unstable and was quantitatively converted into asatone (**1**) when allowed to stand at room temperature. Accordingly, asatone (**1**) was synthesized from 4-allyl-2,6-dimethoxyphenol (**3**) in 36% total yield; this result represents formal

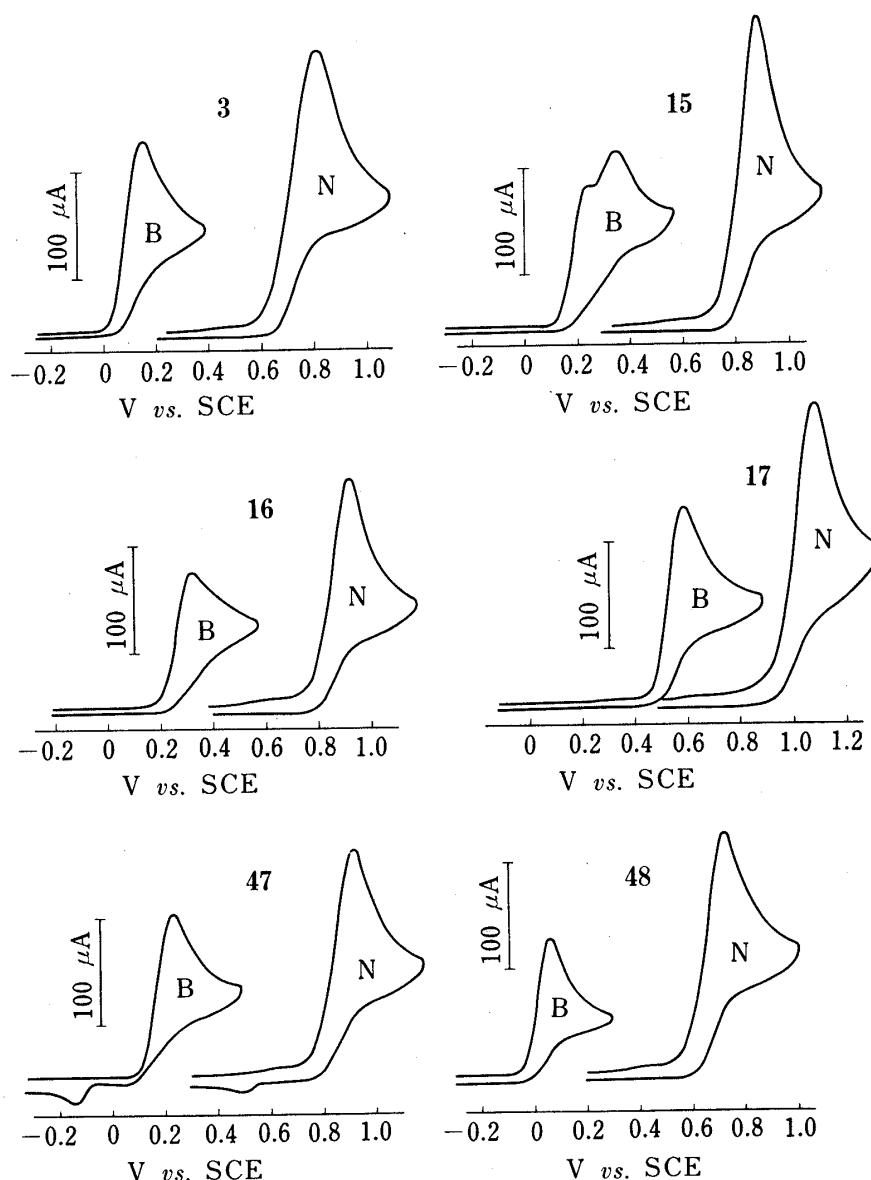


Fig. 1. Cyclic Voltammograms of Six Phenols (**3**, **15**, **16**, **17**, **47** and **48**)

Phenols,  $2.0 \text{ mmol} \cdot \text{l}^{-1}$ ; supporter  $\text{LiClO}_4$ ,  $0.2 \text{ mol} \cdot \text{l}^{-1}$ ; solvent, MeOH; WE, glassy carbon ( $0.26 \text{ cm}^2$ ); sweep rate,  $50 \text{ mV} \cdot \text{s}^{-1}$  (B = basic, N = neutral).

syntheses of isoasatone (4),<sup>1)</sup> heterotropanone (5) and isoheterotropanone (6),<sup>4)</sup> as shown in Chart 1. As expected from the cyclic voltammogram of 3 (see Fig. 1), in addition, several  $-2e$  oxidation products (7, 8, 9, 10 and 11) were also obtained in 28, 20, *ca.* 1, *ca.* 1 and 4.4% yields, respectively. After electrolysis, on the other hand, the methanolic solution was concentrated slowly at 50 °C, and then subjected to column chromatography (Develosil ODS-10) to afford a heterotropanone-type dimer (9), an isoheterotropanone-type dimer (10), an arylpropanoid (11) and allyl 2,4,6-trimethoxyphenyl ether (12) in 27, 4.4, 4.9 and 27% yields, respectively. The newly formed ether (12) must be produced from 4-allyl-2,4,6-trimethoxy-2,5-cyclohexadien-1-one (7) by retro-Claisen rearrangement. In fact, when heated in methanol under reflux, the dienone (7) was readily converted into 12 in high yield. Furthermore, it

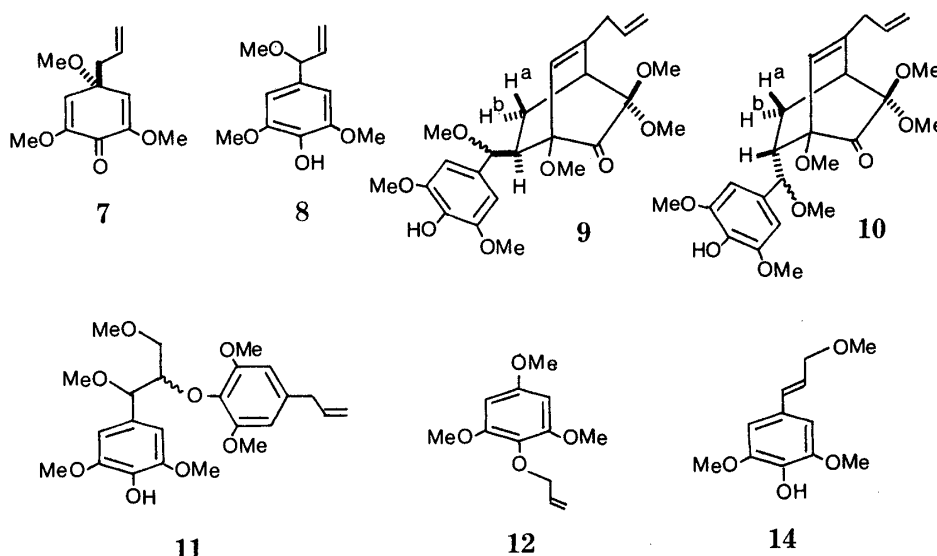


Chart 2

should be noted that the heterotropanone-type dimer (9) is selectively obtained by Diels–Alder reaction of 2 with 8 or an extended quinonemethide (13). The structures of these two dimers (9 and 10), both of which have the same molecular formula,  $C_{24}H_{32}O_8$ , and the same remarkable fragment ion at  $m/e$  223 formed by retro-Diels–Alder reaction on electron impact, were elucidated by comparing their  $^{13}C$  and  $^1H$  nuclear magnetic resonance ( $^{13}C$  and  $^1H$  NMR) spectra with each other as well as with those of two naturally occurring neolignans (5 and 6). As can be seen in Table I, the  $^{13}C$  NMR spectral data for 9 and 10 are quite similar to each other, indicating that these two oxidation products are stereoisomers. In addition, they show  $^{13}C$  NMR signals corresponding to those of both heterotropanone (5) and isoheterotropanone (6) except for the signals due to the different benzyl groups. Furthermore, of the two oxidation products (9 and 10), the former has the same stereostructure as heterotropanone (5), while both 6 and 10 also have the same stereochemistry, as judged from their  $^1H$  NMR signals assignable to  $H^a$  and  $H^b$  (see Table II).

The structure of the arylpropanoid (11) with the molecular formula  $C_{24}H_{32}O_8$  was also based on its spectral data, as follows. In addition to the four singlets due to methoxyl groups attached to the two aromatic rings [ $\delta$  3.71 (6H, s) and 3.82 (6H, s)], the two methyl singlets at  $\delta$  3.28 and 3.30 are due to the two newly formed methoxyl groups, one of which must be located at the benzylic position [ $m/e$  197 and  $\delta$  4.41 (1H, d,  $J=5.5$  Hz)]. As can be seen in the structure (11), the remaining one seems to be attached to the end of the side chain, as judged from the  $^1H$  NMR signals assignable to the  $MeO-CH^aH^b-CH^c(OAr)-$  grouping [ $\delta$  3.52 ( $H^a$ ), 3.7–3.8 ( $H^b$ ) and 4.32 ( $H^c$ )].

The formation process of these oxidation products (1, 7, 8, 9, 10 and 11) is shown in Chart 3, indicating that 4-allyl-2,6,6-trimethoxy-2,4-cyclohexadien-1-one (2) is an impor-

TABLE I.  $^{13}\text{C}$  NMR Spectral Data for Heterotropanone and Related Compounds

	5 <sup>1)</sup>	6 <sup>1)</sup>	9	10
$\text{>C=O}$	201.7	201.0	200.5	201.5 (s)
$-\text{CH}_2-\text{CH}=\text{CH}_2$	39.5	39.6	39.3	39.5 (t)
	117.2	117.3	117.2	117.2 (t)
	133.9	133.7	133.9	133.7 (d)
$-\text{CH}=\text{C}$	118.8	120.2	118.5	118.8 (d)
	144.8	146.2	142.9	142.6 (s)
$-\overset{ }{\text{C}}(\text{OMe})-$	86.1	86.5	85.2	85.4 (s)
$-\overset{ }{\text{C}}(\text{OMe})_2$	94.2	94.7	93.9	94.1 (s)
$\text{MeO}-$	49.2	49.0	49.6	49.5 (q)
	50.7	50.7	50.4	50.5 (q)
	53.7	52.9	53.8	54.2 (q)
	56.0	56.0	56.3	56.4 (2 $\times$ q)
	60.0	60.6	56.5	56.9 (q)
$-\overset{ }{\text{CH}}-$	39.7	41.4	41.1	41.5 (d)
	41.2	41.7	43.1	45.4 (d)
$-\text{CH}_2-$	27.1	26.2	22.5	22.1 (t)
	37.4	36.2		(t)
$-\overset{ }{\text{CH}}-\text{OMe}$			82.4	79.8 (d)
	106.1	105.8	105.5	103.0 (2 $\times$ d)
	135.0 (2 $\times$ s)	136.1 (2 $\times$ s)	129.9 (s)	132.8 (s)
	152.8 (2 $\times$ s)	152.8 (2 $\times$ s)	134.3 (s)	134.7 (s)
			146.7 (2 $\times$ s)	147.1 (2 $\times$ s)

TABLE II.  $^1\text{H}$  NMR Spectral Data for Heterotropanone and Related Compounds

	5 <sup>1)</sup>	6 <sup>1)</sup>	9	10
$\text{H}^{\text{a}}$	1.13	1.52	1.46	1.62
	(1H, ddd, $J=3, 5, 14\text{ Hz}$ )	(1H, ddd, $J=3, 10, 14\text{ Hz}$ )	(1H, ddd, $J=3, 6, 13\text{ Hz}$ )	(1H, dd, $J=3, 10\text{ Hz}$ )
$\text{H}^{\text{b}}$	1.92	1.69	1.99	1.62
	(1H, ddd, $J=3, 9, 14\text{ Hz}$ )	(1H, ddd, $J=3, 5, 14\text{ Hz}$ )	(1H, ddd, $J=3, 10, 13\text{ Hz}$ )	(1H, dd, $J=3, 8\text{ Hz}$ )

tant intermediate, from which asatone (**1**), hetero- and isoheterotropanone-type compounds (**9** and **10**) are derived.

As shown in Fig. 1, the cyclic voltammogram of 4-allyl-2,6-dimethoxyphenol (**3**) in basic media shows a single anodic peak. Therefore, the radical species produced from the phenolate anion is expected to be readily oxidized to the corresponding cation in the second step.

When electrolyzed in basic media at a constant current (0.50 mA/cm<sup>2</sup>), **3** was mainly converted into three compounds (**8**, **11** and **14**) in 10, 25 and 35% yields, respectively, when the reaction was quenched at 1.5 F/mol. In this case, the potential of the working electrode was lower than 58 mV vs. SCE. In particular, it should be noted that one of the benzylic protons of this cation is selectively removed by methoxy or hydroxy anion to afford an extended quinonemethide (**13**), from which these three compounds (**8**, **11**, **14**) are produced, as demonstrated in Chart 4. We also carried out anodic oxidation of 4-allylphenols with different substituents (**15**, **16** and **17**) to synthesize a number of asatone-type neolignans, although they

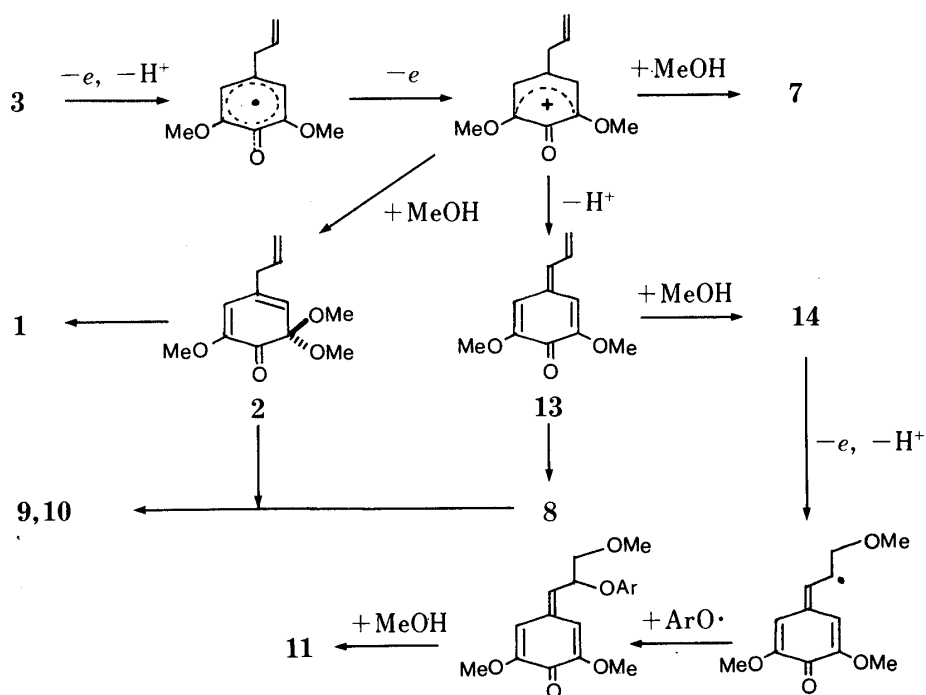


Chart 3. Anodic Oxidation of 4-Allyl-2,6-dimethoxyphenol (3) in Methanol

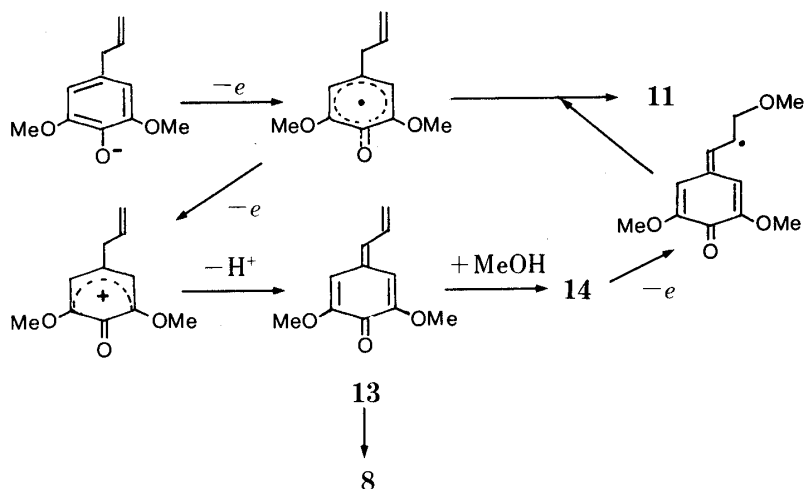


Chart 4. Anodic Oxidation of 4-Allyl-2,6-dimethoxyphenol (3) in Basic Media

have not yet been found in nature.

A solution of eugenol (15) in methanol containing  $\text{LiClO}_4$  as a supporting electrolyte was electrolyzed at a constant current ( $0.56 \text{ mA/cm}^2$ )<sup>5</sup> and the reaction was quenched at  $2.0 \text{ F/mol}$  to afford six oxidation products (18, 19, 20, 21, 22 and 23) in 2.6, 58, 17.1, 1.2, 3.7 and 3.1% yields, respectively; their structures were also determined on the basis of their spectral data. As seen in the case of 4-allyl-2,6,6-trimethoxy-2,4-cyclohexadien-1-one (2), 4-allyl-6,6-dimethoxy-2,4-cyclohexadien-1-one (19) as a main product was also unstable and was quantitatively converted into demethoxyasatone (20) in the same manner as that of 2, when allowed to stand at room temperature.<sup>6</sup> In this case, another possible structure (24) was considered for this dimer, but could be ruled out on the basis of the following chemical evidence: on irradiation at room temperature, demethoxyasatone (20) in hexane was readily converted into the corresponding demethoxyisoasatone (25) in 60% yield, and the  $^1\text{H}$  NMR spectrum of 25 exhibits only half of the total proton signals, indicating that demethoxyisoasatone has a symmetric character, as seen in the case of isoasatone (4).

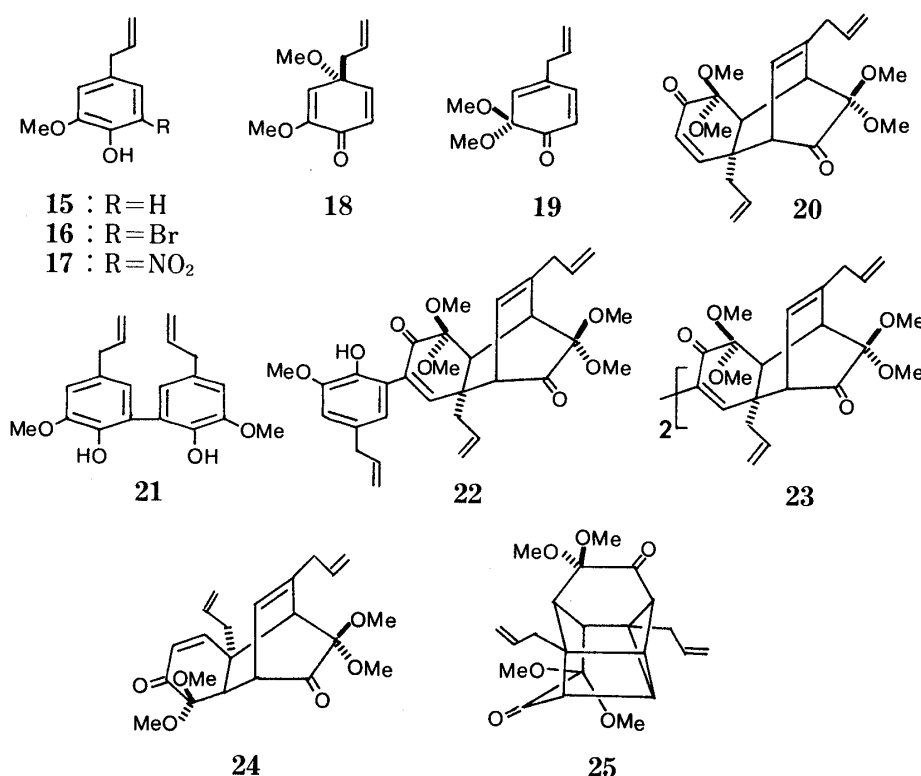


Chart 5

Of the remaining minor components, the last two oxidation products (**22** and **23**) are structurally more complex as compared with demethoxyasatone (**20**). The structure of the former (**22**) was unambiguously elucidated by analysis of its <sup>1</sup>H NMR and high resolution mass spectra (MS) [C<sub>32</sub>H<sub>38</sub>O<sub>8</sub> (*m/e* 550.2505)]; in addition to the signals of dehydrodieugenol (**21**), its <sup>1</sup>H NMR spectrum has signals corresponding to those of demethoxyasatone (**20**) except for the  $\alpha$ -substituted cyclohexanone moiety [ $\delta$  6.36 (1H, s) in **22**;  $\delta$  5.93 (1H, d, *J* = 10 Hz) and 6.27 (1H, d, *J* = 10 Hz) in **20**]. The dimeric compound (**23**) has the molecular formula C<sub>44</sub>H<sub>54</sub>O<sub>12</sub> [*m/e* 774.3602 (M<sup>+</sup>)] and has a symmetric structure which consists of two  $\alpha$ -substituted demethoxyasatone moieties [ $\delta$  6.03 (2H, s) in **23**], as can be seen in the case of **22**, on the basis of the <sup>1</sup>H NMR spectrum showing only half of the total proton signals.

As shown in Fig. 1, the cyclic voltammogram of eugenol (**15**) in neutral media showed the corresponding 2 electron oxidation, the peak current of which involves  $-2e$  oxidation, suggesting that the oxidation potential at the initial step is nearly equal to or higher than that in the following oxidation step leading to the formation of the corresponding cation, from which the dienones (**18** and **19**) must be derived (see Chart 6). On the other hand, dehydrodieugenol (**21**) as a minor product is derived from the radical species formed at the initial step. On further oxidation, dehydrodieugenol (**21**) is converted into the corresponding 2,4-cyclohexadien-1-ones (**26** and **27**), from which the dimers (**22** and **23**) must be produced, respectively, on Diels–Alder reaction with 4-allyl-6,6-dimethoxy-2,4-cyclohexadien-1-one (**19**).

Furthermore, anodic oxidation of **15** in methanol containing 1 N NaOH was carried out at a constant current (1.5 mA/cm<sup>2</sup>) and the reaction was quenched at 1.0 F/mol to afford dehydrodieugenol (**21**) in almost quantitative yield, *via* the radical species of **15**. As expected from the cyclic voltammogram of **15**, in this case, the applied potential was +200–220 mV vs. SCE, and no  $-2e$  oxidation product, considered to be derived from the cationic species, could be detected.

When electrolysis was carried out in methanol containing LiClO<sub>4</sub> as a supporting

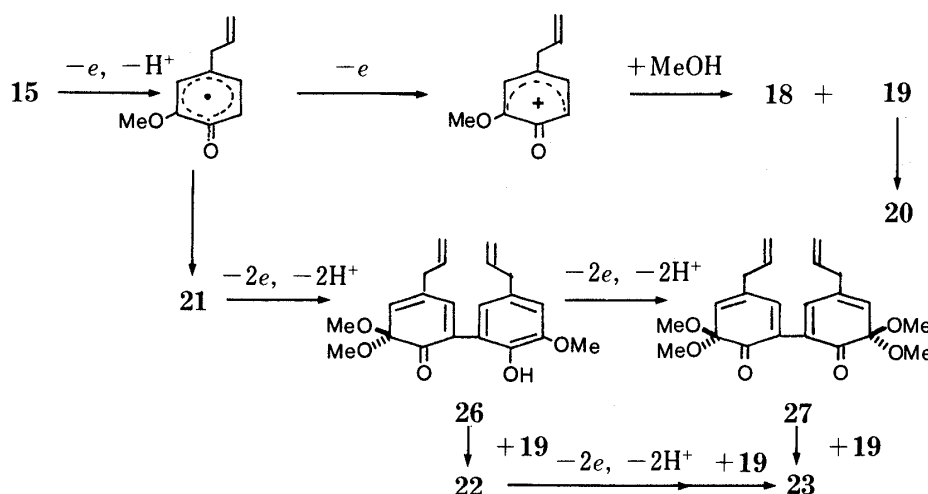


Chart 6. Anodic Oxidation of Eugenol (15)

electrolyte at a constant current ( $0.38 \text{ mA/cm}^2$ )<sup>7)</sup> and the reaction was quenched at  $2.0 \text{ F/mol}$ , 4-allyl-2-bromo-6-methoxyphenol (**16**) was converted into an asatone-type dimer (**28**) in 14% yield, in addition to **29** and **30** (**29**, 20% yield; **30**, 13% yield), whose structures were deduced from careful comparison of their  $^1\text{H}$  NMR spectra with those of **1**, **7** and **14**. All of them are regarded as  $-2e$  oxidation products and must be derived from the cationic species of **16**, as seen in its cyclic voltammogram (see Fig. 1).

Anodic oxidation of **16** in basic media was also carried out at a constant current ( $0.31 \text{ mA/cm}^2$ ;  $1.2 \text{ F/mol}$ )<sup>8)</sup> to afford four oxidation products (**30**, **31**, **32** and **33**) in 5.5, 23, 45 and 11% yields, respectively. The tentative structures of the two arylpropanoids (**32** and **33**) are based on their  $^1\text{H}$  NMR spectra [ $\delta$  4.05 (2H, d,  $J=5 \text{ Hz}$ ), 4.51 (1H, d,  $J=4 \text{ Hz}$ ) and 4.9 (1H, m) in **32**;  $\delta$  3.4—3.9 (2H, overlapped with MeO signals), 4.36 (1H, d,  $J=6 \text{ Hz}$ ) and 4.61 (1H, m) in **33**]. Clearly, all of the oxidation products (**30**, **31**, **32** and **33**) must be derived from an extended quinonemethide (**34**) which should be easily formed by deprotonation at the benzylic position of the cationic species of **16**. In a series of 4-allylphenols with different substituents, 4-allyl-2-methoxy-6-nitrophenol (**17**) with an electron-attracting group requires a higher oxidation potential as compared with the others (**3**, **15** and **16**), and different results may be obtained in the case of **17**.

Anodic oxidation of the nitrophenol (**17**) in methanol containing  $\text{LiClO}_4$  as a supporting electrolyte was carried out at a constant current ( $0.19 \text{ mA/cm}^2$ ;  $+1050$ — $1170 \text{ mV vs. SCE}$ ) and the reaction was quenched at  $2.0 \text{ F/mol}$  to afford four oxidation products (**35**, **36**, **37** and **38**) in 38, 4.7, 5.5 and 8.2% yields, respectively; their structures were based on their spectral data. The structure and formation process of 4-allyl-2,5-dimethoxy-6-nitrophenol (**35**) will be discussed later. The two arylpropanoids (**37** and **38**), having a common fragment ion at  $m/e$  212 in their MS, are stereoisomers, whose stereochemistry is based on their  $^1\text{H}$  NMR spectra [ $\delta$  4.43 (1H, d,  $J=6 \text{ Hz}$ ) and  $\delta$  4.61 (1H, m) in **37**;  $\delta$  4.62 (1H, d,  $J=8 \text{ Hz}$ ) and 4.25 (1H, m) in **38**].<sup>9)</sup> In the case of acidic media [ $\text{MeOH-AcOH}$  (16:1)],<sup>10)</sup> the same products as described above were obtained in addition to 4-allyl-2,4,5-trimethoxy-6-nitro-2,5-cyclohexadien-1-one (**39**) (**35**, **36**, a mixture of **37** and **38**, and **39** in 14.2, 5.7, 9.7 and 16.4% yields, respectively). Presumably, the last one is produced from **35** on further  $-2e$  oxidation. On the other hand, when electrolyzed at a constant current ( $0.42 \text{ mA/cm}^2$ ;  $1.9 \text{ F/mol}$ ) in basic media,<sup>11)</sup> the nitrophenol (**17**) was converted into seven oxidation products (**35**, **40**, **41**, a mixture of **37** and **38**, **42** and **43**) in 6.9, 12.3, 4.4, 8.8, 22 and 22% yields, respectively. The stereochemistry of the two trimers (**42** and **43**), having a remarkable fragment peak at  $m/e$  212 in their MS, is also based on their  $^1\text{H}$  NMR spectra [ $\delta$  4.19 (1H, dd,  $J=6, 10 \text{ Hz}$ ), 4.33 (1H, dd,  $J=5, 10 \text{ Hz}$ ), 4.55

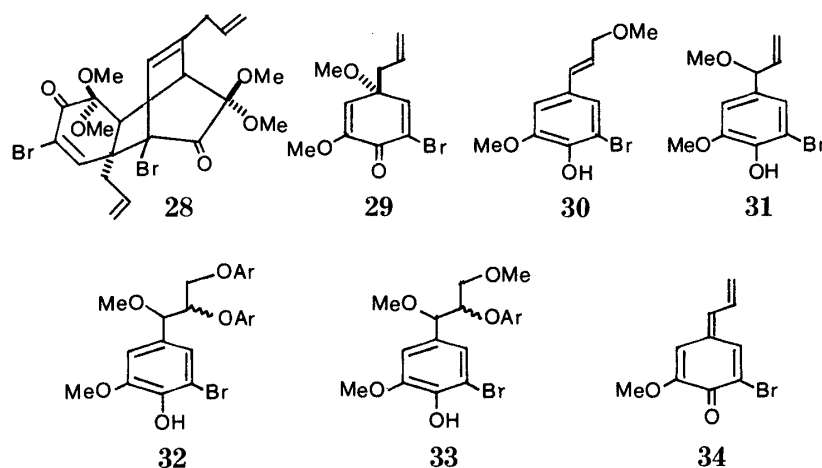


Chart 7

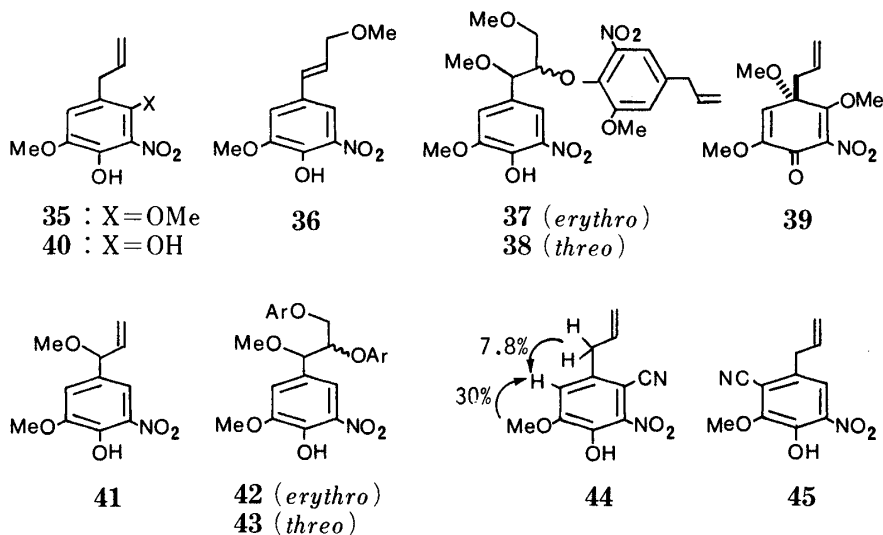


Chart 8

(1H, d,  $J=5$  Hz) and 5.0—5.3 (1H, overlapped with other signals) in **42**;  $\delta$  4.16 (1H, dd,  $J=4, 10$  Hz), 4.29 (1H, dd,  $J=4, 10$  Hz), 4.57 (1H, d,  $J=6$  Hz) and 4.77 (1H, m) in **43**]. Finally, anodic oxidation of **17** in methanol containing NaCN was carried out at a constant current (0.13 mA/cm<sup>2</sup>; +500—650 mV vs. SCE) to afford a cyano compound (**44**) in 50% yield,<sup>12)</sup> in addition to small amounts of **35** and **40**. Of two possible structures (**44** and **45**), the former was compatible with the results of nuclear Overhauser effect (NOE) experiments, as shown in **44**. Accordingly, both the methoxy and hydroxy compounds (**35** and **40**) seem to adopt the same orientation as that of **44**. The formation process of these compounds (**35**, **40** and **44**) is shown in Chart 9, in which the initially formed 2,5-cyclohexadien-1-one (**46**) is selectively attacked by a given nucleophile at the  $\beta$ -position of the double bond conjugated to both nitro and carbonyl groups, followed by aromatization to afford each 5-substituted phenol (**35**, **40** and **44**). Furthermore, the methoxy compound (**35**) with an additional electron-donating group is further oxidized to **39**, while the cyano compound (**44**) with an electron-attracting group is quite stable under these oxidation conditions.

We further carried out anodic oxidation of two 2-allylphenols (**47** and **48**) in methanol using LiClO<sub>4</sub> as a supporting electrolyte. On electrolysis at a controlled potential (+850 mV vs. SCE; 2.5 F/mol), as expected from its cyclic voltammogram (see Fig. 1), 2-allyl-6-methoxyphenol (**47**) was mainly converted into the desired asatone-type dimer (**49**) in 41% yield, in addition to small amounts of two oxidation products (**50** and **51** in 4.6 and 10%



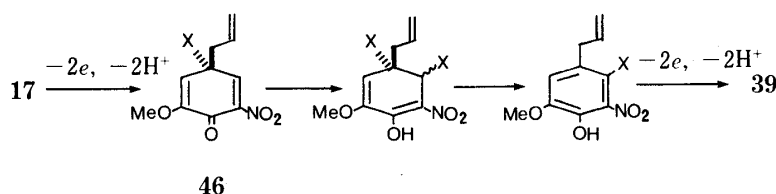


Chart 9

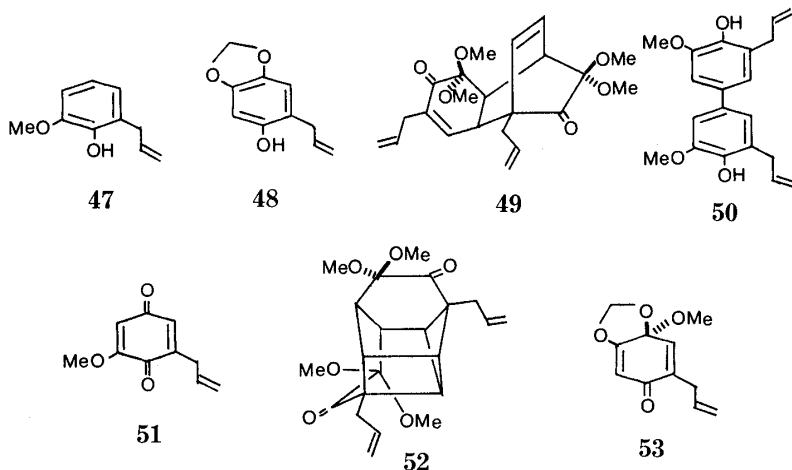


Chart 10

yields, respectively), the structures of which were elucidated from their spectral data. The structure of the asatone-type dimer (**49**) was confirmed by photochemical reaction of **49**, which was carried out in hexane using a Pyrex filter, to afford an isoasatone-type compound (**52**) in 75% yield, having a symmetric structure as judged from its  $^1\text{H}$  NMR spectrum.

2-Allyl-4,5-methylenedioxyphenol (**48**) was also electrolyzed at a constant current ( $0.63\text{ mA/cm}^2$ )<sup>13</sup> to afford in almost quantitative yield the known dienone (**53**), from which some interesting neolignans were synthesized by Büchi *et al.*<sup>14</sup>

In the present study, a number of new types of neolignans have been synthesized, including asatone, heterotropenone and related neolignans,<sup>2)</sup> despite the fact that extensive studies have already been made on anodic oxidation of many phenolic compounds.<sup>15)</sup>

### 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.  $^1\text{H}$  and  $^{13}\text{C}$  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 at an ionization energy of 70 eV. High resolution MS were also taken on a Hitachi M-80 mass spectrometer operating at an ionization energy of 70 eV.

Preparative high performance liquid chromatography (HPLC) was carried out on a main glass column ( $20\text{ mm}\phi \times 500\text{ mm}$ ) equipped with a precolumn [ $15\text{ mm}\phi \times 150\text{ mm}$ ; Unisil  $\text{C}_{18}$  ( $15\text{--}40\text{ }\mu\text{m}$ ) 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.

**Instruments Used for Electrode Reactions**—A PARCO model 173 instrument (Princeton Applied Research Co., Ltd.) was used as a potentio/galvanostat. A PARCO model 175 universal programmer was also used as a function generator. Cyclic voltammograms at rapid sweep rate were observed on a digital storage oscilloscope, model DS-334 (NF Circuit Design Block Co., Ltd.), and recorded on a Technicorder type 3077 (Yokogawa Electric Works Ltd.). On anodic oxidation, a 200 ml glassy carbon beaker (Tokai Carbon GC-20) and a platinum electrode ( $1.0\text{ mm}\phi \times 10\text{ mm}$ ) were used as an anode and an auxiliary electrode, respectively, without separation. The quantity of electricity was

measured with a PARCO model 179 digital coulometer and/or a detonating gas coulometer.

**Anodic Oxidation of 4-Allyl-2,6-dimethoxyphenol (3) in Methanol**—A solution of **3** (388 mg) in MeOH (200 ml) containing LiClO<sub>4</sub> (4.3 g) was electrolyzed at a constant current (50 mA; 0.31 mA/cm<sup>2</sup>; +620–660 mV vs. SCE) and the reaction was quenched at 2.0 F/mol. The reaction solution was adsorbed on a precolumn connected to a main column (Develosil ODS-10) and then eluted with 0.01 M AcONH<sub>4</sub> in MeOH–H<sub>2</sub>O (60:40) (flow rate: 10 ml/min). Each fraction was carefully concentrated under reduced pressure, and then extracted with AcOEt. Each AcOEt extract was concentrated under reduced pressure to afford, in this order, 4-allyl-2,4,6-trimethoxy-2,5-cyclohexadien-1-one (**7**) (110 mg), a trimethoxyphenol (**8**) (82 mg), 4-allyl-2,6,6-trimethoxy-2,4-cyclohexadien-1-one (**2**) (130 mg) and a mixture of two heterotropone-type neolignans (**9** and **10**) (9.8 mg; relative ratio, 1:1). Further elution with MeOH afforded an oil (56 mg), which was separated by preparative thin-layer chromatography (TLC) [Kieselgel PF<sub>254</sub>; hexane–AcOEt (2:3)] to give asatone (**1**) (17 mg) and an arylpropanoid (**11**) (18 mg).

**7** as a Colorless Oil: IR (film): 1690, 1660, 1625 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.51 (2H, d, *J* = 7 Hz), 3.17 (3H, s), 3.69 (6H, s), 5.05 (1H, br d, *J* = 16 Hz), 5.09 (1H, br d, *J* = 11 Hz), 5.59 (2H, s), 5.56–5.88 (1H, m); *Anal.* Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>: *m/e* 224.1048. Found: *m/e* 224.1070.

**8** as a Colorless Oil: IR (film): 3400 br, 1620, 1520 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.31 (3H, s), 3.89 (6H, s), 4.54 (1H, d, *J* = 6 Hz), 5.18 (1H, br d, *J* = 10 Hz), 5.25 (1H, br d, *J* = 17 Hz), 5.55 (1H, s, OH), 5.94 (1H, ddd, *J* = 6, 10, 17 Hz), 6.58 (2H, s). *Anal.* Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>: *m/e* 224.1048. Found: *m/e* 224.1049.

**2** as a Colorless Oil: IR (film) 1695, 1665, 1640, 1600 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.85 (2H, d, *J* = 6 Hz), 3.21 (6H, s), 3.56 (3H, s), 5.01 (1H, br d, *J* = 11 Hz), 5.04 (1H, br d, *J* = 15 Hz), 5.48 (2H, br s), 5.5–5.9 (1H, m). MS *m/e*: 224 (M<sup>+</sup> for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>), 193, 181, 165. The high resolution mass spectrum of this dienone has not yet been measured, but its structure is supported by the above spectral data. When allowed to stand at room temperature overnight, this oil was completely converted into asatone (**1**).

**9** as a Colorless Oil: IR (film): 3425, 1740 br, 1615, 1520 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.46 (1H, ddd, *J* = 3, 6, 13 Hz), 1.99 (1H, ddd, *J* = 3, 10, 13 Hz), 2.51–2.94 (4H, complex), 3.21 (3H, s), 3.29 (6H, s), 3.62 (3H, s), 3.88 (6H, s), 4.48 (1H, d, *J* = 5 Hz), 4.87 (1H, br d, *J* = 16 Hz), 4.92 (1H, br d, *J* = 10 Hz), 5.15 (1H, br s), 5.26 (1H, tdd, *J* = 6, 10, 16 Hz), 5.50 (1H, s, OH), 6.50 (2H, s). MS *m/e*: 448 (M<sup>+</sup>), 223, 197. *Anal.* Calcd for C<sub>24</sub>H<sub>32</sub>O<sub>8</sub>: *m/e* 448.2094. Found: *m/e* 448.2095.

**10** as a Colorless Oil: IR (film): 3425, 1740, 1610, 1515 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.62 (1H, dd, *J* = 3, 8 Hz), 1.62 (1H, dd, *J* = 3, 10 Hz), 2.22 (1H, ddd, *J* = 2, 8, 10 Hz), 2.82 (1H, dt, *J* = 2, 3 Hz), 2.98 (2H, br d, *J* = 6 Hz), 3.22 (3H, s), 3.23 (3H, s), 3.32 (3H, s), 3.63 (3H, s), 3.87 (6H, s), 4.53 (1H, d, *J* = 2 Hz), 5.16 (1H, br d, *J* = 10 Hz), 5.21 (1H, br d, *J* = 17 Hz), 5.49 (1H, s, OH), 5.83 (1H, br s), 5.85 (1H, tdd, *J* = 6, 10, 17 Hz), 6.43 (2H, s). MS *m/e*: 448 (M<sup>+</sup>), 223, 197. *Anal.* Calcd for C<sub>24</sub>H<sub>32</sub>O<sub>8</sub>: *m/e* 448.2094. Found: *m/e* 448.2088.

**11**: mp 100–101 °C (from hexane). IR (KBr): 3350 br, 1615, 1590, 1520, 1500 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.28 (3H, s), 3.30 (3H, s), 3.2–3.3 (2H, overlapped with two MeO signals), 3.52 (1H, dd, *J* = 3, 11 Hz), 3.71 (6H, s), 3.82 (6H, s), 3.7–3.8 (1H, overlapped with two MeO signals), 4.32 (1H, m), 4.41 (1H, d, *J* = 5.5 Hz), 4.99 (1H, br d, *J* = 10 Hz), 5.01 (1H, br d, *J* = 17 Hz), 5.44 (1H, s, OH), 5.88 (1H, m), 6.28 (2H, s), 6.53 (2H, s). *Anal.* Calcd for C<sub>24</sub>H<sub>32</sub>O<sub>8</sub>: *m/e* 448.2094. Found: *m/e* 448.2114.

Under the same conditions as described above, anodic oxidation of 4-allyl-2,6-dimethoxyphenol (**3**) (388 mg) was carried out at a constant current (50 mA; 0.31 mA/cm<sup>2</sup>). The reaction solution was concentrated at 50 °C, and then adsorbed on a precolumn connected to a main column (Develosil ODS-10) and eluted with 0.01 M AcONH<sub>4</sub> in MeOH–H<sub>2</sub>O (60:40). Each fraction was carefully concentrated under reduced pressure, and then extracted with AcOEt. Each AcOEt extract was concentrated under reduced pressure to afford allyl 2,4,6-trimethoxyphenyl ether (**12**) (113 mg), **9** (112 mg), **10** (18 mg) and arylpropanoid (**11**) (20 mg).

**12** as a Colorless Oil: IR (film): 1590, 1500 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.73 (3H, s), 3.79 (6H, s), 4.37 (2H, dd, *J* = 2, 6 Hz), 5.14–5.28 (2H, complex), 5.88–6.38 (1H, m), 6.13 (2H, s). MS *m/e*: 224 (M<sup>+</sup> for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>), 183.

**Anodic Oxidation of 4-Allyl-2,6-dimethoxyphenol (3) in Basic Media**—A solution of **3** (388 mg) in MeOH (200 ml) containing 1 N NaOMe (10 ml) and LiClO<sub>4</sub> (4.3 g) was electrolyzed at a constant current (80 mA; 0.5 mA/cm<sup>2</sup>; +25–58 mV vs. SCE) and the reaction was quenched at 1.5 F/mol. After neutralization with 1 N HClO<sub>4</sub>, the reaction solution was directly adsorbed on a precolumn and separated on a main column (Develosil ODS-10) using 0.01 M AcONH<sub>4</sub> in MeOH–H<sub>2</sub>O (60:40) (flow rate: 10 ml/min). Each fraction was concentrated under reduced pressure and extracted with AcOEt. Each AcOEt extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure to afford, in this order, **8** (36 mg), **14** (122 mg) and **11** (83 mg).

**14** as a Colorless Oil: IR (film): 3400 br, 1600, 1510 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.38 (3H, s), 3.84 (6H, s), 4.05 (2H, d, *J* = 6 Hz), 5.95 (1H, s, OH), 6.10 (1H, dt, *J* = 16, 6 Hz), 6.50 (1H, d, *J* = 16 Hz), 6.59 (2H, s). *Anal.* Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>: *m/e* 224.1048. Found: *m/e* 224.1051.

**Anodic Oxidation of Eugenol (15) in Methanol**—A solution of **15** (328 mg) in MeOH (200 ml) containing LiClO<sub>4</sub> (4.3 g) was electrolyzed at a constant current (90 mA; 0.56 mA/cm<sup>2</sup>; +730–780 mV vs. SCE) and the reaction was quenched at 2.0 F/mol. As usual, the reaction solution was directly adsorbed on a precolumn and separated on a main column (Unisil C<sub>18</sub> 27–40 μm) using MeOH–H<sub>2</sub>O (60:40) (flow rate: 15 ml/min). Each fraction was successively concentrated under reduced pressure, extracted with AcOEt, and then evaporated under reduced

pressure to afford **18** (8 mg), **19** (180 mg), demethoxyasatone (**20**) (53 mg), the starting material (66 mg), dehydrodieugenol (**21**)<sup>16</sup> (3 mg) and a mixture of **22** and **23** (24 mg), in that order. The mixture was further separated by preparative TLC [Kieselgel PF<sub>254</sub>; benzene-AcOEt (10:1)] to afford **22** (10.8 mg) and **23** (9.6 mg).

**18**: mp 56—56.5 °C (from hexane). IR (film): 1680, 1650, 1620 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.49 (2H, br d, *J* = 7 Hz), 3.19 (3H, s), 3.67 (3H, s), 5.04 (1H, br d, *J* = 18 Hz), 5.07 (1H, br d, *J* = 10 Hz), 5.53 (1H, d, *J* = 3 Hz), 5.70 (1H, m), 6.30 (1H, d, *J* = 10 Hz), 6.68 (1H, dd, *J* = 3, 10 Hz). Anal. Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>: *m/e* 194.0942. Found: *m/e* 194.0964.

**19** as an Almost Colorless Oil: IR (film): 1690, 1660, 1640 sh cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.98 (2H, br d, *J* = 8 Hz), 3.35 (6H, s), 5.11 (1H, br d, *J* = 17 Hz), 5.16 (1H, br d, *J* = 10 Hz), 5.79 (1H, m), 5.96 (1H, d, *J* = 10 Hz), 6.09 (1H, br s), 6.72 (1H, dd, *J* = 2, 10 Hz). MS *m/e*: 194 (M<sup>+</sup> for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>). Elemental analysis of this dienone (**19**) has not yet been carried out, but its structure is supported by the above spectral data coupled with the following chemical evidence: when allowed to stand at room temperature overnight, this dienone was spontaneously converted into demethoxyasatone (**20**) in quantitative yield.

**20**: mp 77—78 °C (from hexane). IR (KBr): 1735, 1710, 1640 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.32 (1H, dd, *J* = 7, 15 Hz), 2.58 (1H, dd, *J* = 8, 15 Hz), 2.70—2.95 (4H, complex), 3.05 (4H, s, one of the methine proton is included), 3.30 (3H, s), 3.38 (3H, s), 3.40 (3H, s), 4.87—5.20 (4H, complex), 5.42 (1H, br d, *J* = 6 Hz), 5.50—6.12 (2H, complex), 5.93 (1H, d, *J* = 10 Hz), 6.27 (1H, d, *J* = 10 Hz). Anal. Calcd for C<sub>22</sub>H<sub>28</sub>O<sub>6</sub>: *m/e* 388.1884. Found: *m/e* 388.1841.

**22**: mp 55—57 °C (from hexane). IR (KBr): 3450, 1735, 1705, 1640, 1595, 1490 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.37 (1H, dd, *J* = 7, 14.5 Hz), 2.67 (1H, dd, *J* = 8, 14.5 Hz), 2.75—2.90 (4H, complex), 3.10 (1H, d, *J* = 6 Hz), 3.16 (3H, s), 3.29 (2H, br d, *J* = 7 Hz), 3.32 (3H, s), 3.43 (6H, s), 3.84 (3H, s), 4.90—5.25 (6H, complex), 5.54 (1H, d, *J* = 6 Hz), 5.64—6.18 (3H, complex), 6.36 (1H, s), 6.40 (1H, d, *J* = 2 Hz), 6.64 (1H, s, OH), 6.65 (1H, d, *J* = 2 Hz). Anal. Calcd for C<sub>32</sub>H<sub>38</sub>O<sub>8</sub>: *m/e* 550.2564. Found: *m/e* 550.2505.

**23**: mp 174—175 °C (from hexane). IR (KBr): 1735, 1705, 1640 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.29 (2H, dd, *J* = 7, 15 Hz), 2.64 (2H, dd, *J* = 8, 15 Hz), 2.62—2.90 (8H, complex), 3.04 (2H, d, *J* = 6.5 Hz), 3.29 (12H, br s), 3.36 (6H, s), 3.40 (6H, s), 4.86—5.23 (8H, complex), 5.34 (2H, br d, *J* = 6.5 Hz), 5.45—6.00 (4H, complex), 6.03 (2H, s). Anal. Calcd for C<sub>44</sub>H<sub>54</sub>O<sub>12</sub>: *m/e* 774.3612. Found: *m/e* 774.3602.

**Anodic Oxidation of Eugenol (15) in Basic Media**—A solution of **15** (82 mg) in MeOH (40 ml) containing 1 N NaOH (2.5 ml) and LiClO<sub>4</sub> (1.6 g) was electrolyzed at a constant current (21 mA; 1.5 mA/cm<sup>2</sup>; +200—220 mV vs. SCE) and the reaction was quenched at 1.0 F/mol. After neutralization with HClO<sub>4</sub>, the reaction solution was treated according to the same procedure as described above to afford dehydrodieugenol (**21**)<sup>16</sup> in quantitative yield.

**Photochemical Conversion of Demethoxyasatone (20) into Demethoxyisoasatone (25)**—A solution of **20** (60 mg) in hexane (10 ml), in a Pyrex tube, was irradiated at room temperature overnight, and then concentrated under reduced pressure. The oily residue was purified by preparative TLC (Kieselgel PF<sub>254</sub>) using hexane-AcOEt (3:2) to afford **25** (36 mg): mp 133—134 °C (from hexane). IR (KBr): 1730, 1645 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.35 (2H, dd, *J* = 6, 14 Hz), 2.74 (2H, dd, *J* = 8, 14 Hz), 2.81 (2H, s), 2.86 (4H, s), \*3.27 (6H, s), 3.34 (6H, s), 5.06 (2H, br d, *J* = 17 Hz), 5.11 (2H, br d, *J* = 10 Hz), 5.69 (2H, m). Anal. Calcd for C<sub>22</sub>H<sub>28</sub>O<sub>6</sub>: *m/e* 388.1884. Found: *m/e* 388.1894.

\* <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ: 2.40 (2H, d, *J* = 5 Hz), 2.73 (2H, d, *J* = 5 Hz).

**Anodic Oxidation of 4-Allyl-2-bromo-6-methoxyphenol (16)<sup>17</sup> in Methanol**—A solution of **16** (486 mg) in MeOH (200 ml) containing LiClO<sub>4</sub> (4.3 g) was electrolyzed at a constant current (60 mA; 0.38 mA/cm<sup>2</sup>; +820—860 mV vs. SCE) and the reaction was quenched at 2.0 F/mol. The reaction solution was concentrated under reduced pressure and then extracted with ether. The ethereal extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a crude oil (366 mg), which was separated by preparative TLC [Kieselgel PF<sub>254</sub>; hexane-AcOEt (3:1)] to afford the starting bromophenol (102 mg), **28** (60 mg), **29** (87 mg) and **30** (55 mg).

**28**: mp 111—113 °C (from hexane). IR (KBr): 1745, 1720, 1640, 1605 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.22 (1H, dd, *J* = 7, 14 Hz), 2.7—3.2 (5H, complex), 3.06 (3H, s), 3.30 (3H, s), 3.39 (6H, s), 5.0—5.3 (4H, complex), 5.5—6.1 (1H, m), 5.54 (1H, q, *J* = 2 Hz), 6.93 (1H, s). Anal. Calcd for C<sub>22</sub>H<sub>26</sub><sup>81</sup>Br<sub>2</sub>O<sub>6</sub>: *m/e* 548.0054. Found: *m/e* 548.0036.

**29** as a Colorless Oil: IR (film): 1680, 1640, 1600 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.50 (2H, d, *J* = 6 Hz), 3.21 (3H, s), 3.68 (3H, s), 4.9—5.2 (2H, m), 5.5—6.0 (1H, m), 5.62 (1H, d, *J* = 2 Hz), 7.16 (1H, d, *J* = 2 Hz). MS *m/e*: 274 (M<sup>+</sup> for C<sub>11</sub>H<sub>13</sub><sup>81</sup>BrO<sub>3</sub>) and 272 (M<sup>+</sup> for C<sub>11</sub>H<sub>13</sub><sup>79</sup>BrO<sub>3</sub>).

**30** as a Colorless Oil: IR (film): 3350 br, 1600, 1570 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.38 (3H, s), 3.90 (3H, s), 4.07 (2H, d, *J* = 6 Hz), 6.06 (1H, s, OH), 6.15 (1H, dt, *J* = 16, 6 Hz), 6.51 (1H, d, *J* = 16 Hz), 6.87 (1H, d, *J* = 2 Hz), 7.13 (1H, d, *J* = 2 Hz). Anal. Calcd for C<sub>11</sub>H<sub>13</sub><sup>79</sup>BrO<sub>3</sub>: *m/e* 272.0047. Found: *m/e* 272.0027.

**Anodic Oxidation of 4-Allyl-2-bromo-6-methoxyphenol (16) in Basic Media**—A solution of **16** (486 mg) in MeOH (90 ml) and 1 N NaOH (10 ml) containing LiClO<sub>4</sub> (4.3 g) was electrolyzed at a constant current (50 mA; 0.31 mA/cm<sup>2</sup>; +223—340 mV vs. SCE) and the reaction was quenched at 1.2 F/mol. The reaction solution was concentrated under reduced pressure to leave a residue, which was extracted with AcOEt. The AcOEt extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to afford an oil (470 mg), which was separated by preparative TLC [Kieselgel PF<sub>254</sub>; hexane-AcOEt (4:1)] to give **31** (112 mg), **30** (27 mg), **32** (204 mg) and **33** (55 mg) in addition to the starting material (49 mg).

**31** as a Colorless Oil: IR (film): 3500 br, 1640, 1600, 1585 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.31 (3H, s), 3.88 (3H, s),

4.51 (1H, br d,  $J=7$  Hz), 5.1—5.4 (2H, m), 5.8—6.1 (1H, m), 6.00 (1H, s, OH), 6.80 (1H, d,  $J=2$  Hz), 7.04 (1H, d,  $J=2$  Hz). MS  $m/e$ : 274 ( $M^+$  for  $C_{11}H_{13}^{81}BrO_3$ ), 272 ( $M^+$  for  $C_{11}H_{13}^{79}BrO_3$ ).

**32** as a Colorless Oil: IR (film): 3500 br, 1635, 1590, 1560  $cm^{-1}$ .  $^1H$  NMR ( $CCl_4$ )  $\delta$ : 3.19 (4H, d,  $J=6$  Hz), 3.28 (3H, s), 3.64 (3H, s), 3.73 (3H, s), 3.83 (3H, s), 4.05 (2H, d,  $J=5$  Hz), 4.51 (1H, d,  $J=4$  Hz), 4.9—5.2 (5H, m), 5.6—6.1 (2H, m), 5.76 (1H, brs, OH), 6.47 (2H, m), 6.78 (2H, m), 6.93 (1H, brs), 7.08 (1H, brs). Anal. Calcd for  $C_{31}H_{33}^{79}Br_3O_7$ :  $m/e$  753.9774. Found:  $m/e$  753.9726.

**33** as a Colorless Oil: IR (film): 3450 br, 1640, 1590, 1560  $cm^{-1}$ .  $^1H$  NMR ( $CCl_4$ )  $\delta$ : 3.1—3.4 (2H, overlapped with two MeO signals), 3.23 (3H, s), 3.31 (3H, s), 3.4—3.9 (2H, overlapped with two MeO signals), 3.75 (3H, s), 3.85 (3H, s), 4.36 (1H, d,  $J=6$  Hz), 4.61 (1H, m), 5.07 (1H, br d,  $J=16$  Hz), 5.09 (1H, br d,  $J=12$  Hz), 5.6—6.1 (1H, m), 5.91 (1H, brs, OH), 6.52 (1H, d,  $J=2$  Hz), 6.85 (1H, d,  $J=2$  Hz), 6.87 (1H, d,  $J=2$  Hz), 7.09 (1H, d,  $J=2$  Hz). Anal. Calcd for  $C_{22}H_{26}^{81}Br^{79}BrO_6$ :  $m/e$  546.0075. Found:  $m/e$  546.0088.

**Anodic Oxidation of 4-Allyl-2-methoxy-6-nitrophenol (17)<sup>18</sup> in Methanol**—A solution of **17** (418 mg) in MeOH (200 ml) containing  $LiClO_4$  (4.3 g) was electrolyzed at a constant current (30 mA; 0.19 mA/ $cm^2$ ; +1050—1170 mV vs. SCE) and the reaction was quenched at 2.0 F/mol. After removal of the solvent, the residue was separated by preparative HPLC (Unisil  $C_{18}$ ; 22 mm  $\phi$   $\times$  300 mm) using MeOH– $H_2O$  (70:30). Each fraction was successively concentrated under reduced pressure, extracted with AcOEt, and then concentrated under reduced pressure to afford, in order of elution, **35** (138 mg), **36** (17 mg), the starting material (100 mg) and a mixture of two arylpropanoids (60 mg). This mixture was further separated by preparative TLC (Kieselgel PF<sub>254</sub>) using benzene–AcOEt (5:1) to afford **37** (20 mg) and **38** (30 mg).

**35**: mp 61—62 °C (from hexane). IR (KBr): 3430 br, 1640, 1600, 1540  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.36 (2H, br d,  $J=6$  Hz), 3.79 (3H, s), 3.87 (3H, s), 5.06 (1H, br d,  $J=16$  Hz), 5.09 (1H, br d,  $J=10$  Hz), 5.70—6.14 (1H, m), 6.81 (1H, s), 7.50 (1H, brs, OH). Anal. Calcd for  $C_{11}H_{13}NO_5$ :  $m/e$  239.0792. Found:  $m/e$  239.0785.

**36**: mp 55—58 °C (from hexane). IR (KBr): 3250, 1620, 1600, 1540  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.40 (3H, s), 3.94 (3H, s), 4.07 (2H, d,  $J=5$  Hz), 6.21 (1H, dt,  $J=17, 5$  Hz), 6.54 (1H, br d,  $J=17$  Hz), 7.17 (1H, d,  $J=2$  Hz), 7.63 (1H, d,  $J=2$  Hz). Anal. Calcd for  $C_{11}H_{13}NO_5$ :  $m/e$  239.0792. Found:  $m/e$  239.0789.

**37** as a Pale Yellow Powder: IR (KBr): 3400 br, 1610, 1520  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.1—3.5 (2H, overlapped with two MeO signals), 3.16 (3H, s), 3.30 (3H, s), 3.5—4.0 (2H, overlapped with two MeO signals), 3.79 (3H, s), 3.96 (3H, s), 4.43 (1H, d,  $J=6$  Hz), 4.61 (1H, m), 5.04 (1H, br d,  $J=16$  Hz), 5.08 (1H, br d,  $J=10$  Hz), 5.6—6.1 (1H, m), 6.75 (1H, d,  $J=2$  Hz), 6.99 (1H, d,  $J=2$  Hz), 7.21 (1H, d,  $J=2$  Hz), 7.61 (1H, d,  $J=2$  Hz). MS  $m/e$ : 478 ( $M^+$ ), 212. Anal. Calcd for  $C_{22}H_{26}N_2O_{10}$ :  $m/e$  478.1586. Found:  $m/e$  478.1598.

**38** as a Pale Yellow Powder: IR (KBr): 3400 br, 1610, 1520  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 2.9—3.4 (2H, overlapped with two MeO signals), 3.14 (3H, s), 3.22 (3H, s), 3.6—4.0 (2H, overlapped with two MeO signals), 3.82 (3H, s), 3.92 (3H, s), 4.25 (1H, m), 4.62 (1H, d,  $J=8$  Hz), 5.12 (1H, br d,  $J=16$  Hz), 5.15 (1H, br d,  $J=10$  Hz), 5.6—6.2 (1H, m), 6.85 (1H, d,  $J=2$  Hz), 7.14 (1H, d,  $J=2$  Hz), 7.16 (1H, d,  $J=2$  Hz), 7.64 (1H, d,  $J=2$  Hz). MS  $m/e$ : 478 ( $M^+$ ), 212. Anal. Calcd for  $C_{22}H_{26}N_2O_{10}$ :  $m/e$  478.1586. Found:  $m/e$  478.1573.

**Anodic Oxidation of 4-Allyl-2-methoxy-6-nitrophenol (17) in Acidic Media**—A solution of **17** (418 mg) in MeOH (200 ml) containing AcOH (12 g) and  $LiClO_4$  (4.3 g) was electrolyzed at a constant current (30 mA; 0.19 mA/ $cm^2$ ; ca. +1160 mV vs. SCE) and the reaction was quenched at 2.0 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 concentrated under reduced pressure to leave an oil, which was separated on a Lobar column (LiChroprep RP-8, 40—63  $\mu m$ ; 25 mm  $\phi$   $\times$  310 mm) using MeOH– $H_2O$  (65:35). Each fraction was successively concentrated under reduced pressure, extracted with AcOEt, and then separated by preparative TLC (Kieselgel PF<sub>254</sub>) using benzene–AcOEt (5:1) to afford **39** (65 mg), **35** (50 mg), **36** (20 mg), the starting material (110 mg) and a mixture of **37** and **38** (34 mg), in order of elution.

**39**: mp 137.5—138 °C (from ether). IR (KBr): 1680 1620, 1530  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 2.66 (2H, br d,  $J=8$  Hz), 3.18 (3H, s), 3.68 (3H, s), 4.06 (3H, s), 5.08 (1H, br d,  $J=18$  Hz), 5.12 (1H, br d,  $J=8$  Hz), 5.36 (1H, s), 5.30—5.80 (1H, m). Anal. Calcd for  $C_{12}H_{15}NO_6$ :  $m/e$  269.0899. Found:  $m/e$  296.0909.

**Anodic Oxidation of 4-Allyl-2-methoxy-6-nitrophenol (17) in Basic Media**—A solution of **17** (418 mg) in MeOH (200 ml) containing 5 N NaOH (0.6 ml) and  $LiClO_4$  (4.3 g) was electrolyzed at a constant current (50 mA; 0.42 mA/ $cm^2$ ; +500—600 mV vs. SCE) and the reaction was quenched at 1.9 F/mol. The reaction solution was neutralized with 1 N  $HClO_4$ , concentrated under reduced pressure, and then extracted with AcOEt. The AcOEt extract was concentrated under reduced pressure to leave an oil, which was dissolved in 0.02 N HCl in MeOH– $H_2O$  (90:10) (20 ml) and subjected to preparative HPLC [HP-255, 22 mm  $\phi$   $\times$  300 mm; 0.02 N HCl in MeOH– $H_2O$  (90:10)]. Each fraction was concentrated under reduced pressure, extracted with AcOEt and then separated by preparative TLC (Kieselgel PF<sub>254</sub>) using benzene–AcOEt (9:1) to afford, in order of elution, **35** (30 mg), **40** (50 mg), **41** (19 mg), the starting material (40 mg), a mixture of **37** and **38** (38 mg) and a mixture of two trimers (**42** and **43**) (170 mg) whose relative ratio was 1:1. This mixture of the trimers was separated by preparative TLC (Kieselgel PF<sub>254</sub>;  $CHCl_3$ ) to afford **42** and **43** in the pure state.

**40**: mp 38—39 °C (from hexane). IR (KBr): 3400 br, 1610, 1540  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.37 (2H, br d,  $J=6$  Hz), 3.88 (3H, s), 5.08 (1H, br d,  $J=16$  Hz), 5.11 (1H, br d,  $J=10$  Hz), 5.7—6.2 (1H, m), 7.09 (1H, s), 10.37 (1H, s,

OH), 10.52 (1H, br s, OH). *Anal.* Calcd for  $C_{10}H_{11}NO_5$ :  $m/e$  225.0635. Found:  $m/e$  225.0628.

**41** as a Pale Yellow Powder: IR (KBr): 3300 br, 1620, 1540  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.32 (3H, s), 3.92 (3H, s), 4.56 (1H, d,  $J=6$  Hz), 5.26 (1H, br d,  $J=12$  Hz), 5.30 (1H, br d,  $J=18$  Hz), 5.6–6.1 (1H, m), 7.11 (1H, d,  $J=2$  Hz), 7.62 (1H, d,  $J=2$  Hz), 10.74 (1H, s, OH). *Anal.* Calcd for  $C_{11}H_{13}NO_5$ :  $m/e$  239.0792. Found:  $m/e$  239.0772.

**42** as a Pale Yellow Powder: IR (KBr): 3400 br, 1630, 1610, 1520  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.31 (3H, s), 3.34 (4H, d,  $J=6$  Hz), 3.74 (3H, s), 3.86 (3H, s), 3.99 (3H, s), 4.19 (1H, dd,  $J=6, 10$  Hz), 4.33 (1H, dd,  $J=5, 10$  Hz), 4.55 (1H, d,  $J=5$  Hz), 5.0–5.3 (1H, overlapped with other signals), 5.10 (2H, d,  $J=16$  Hz), 5.12 (2H, d,  $J=10$  Hz), 5.88 (2H, m), 6.85 (2H, br s), 7.05 (1H, d,  $J=2$  Hz), 7.07 (1H, d,  $J=2$  Hz), 7.37 (1H, d,  $J=2$  Hz), 7.75 (1H, d,  $J=2$  Hz), 10.69 (1H, s, OH). MS  $m/e$ : 655 ( $M^+$  for  $C_{31}H_{33}N_3O_{13}$ ), 212.

**43** as a Pale Yellow Powder: IR (KBr): 3400 br, 1630, 1610, 1520  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.22 (3H, s), 3.32 (4H, d,  $J=6$  Hz), 3.74 (3H, s), 3.78 (3H, s), 3.92 (3H, s), 4.16 (1H, dd,  $J=4, 10$  Hz), 4.29 (1H, dd,  $J=4, 10$  Hz), 4.57 (1H, d,  $J=6$  Hz), 4.77 (1H, m), 5.07 (2H, dd,  $J=2, 16$  Hz), 5.10 (2H, dd,  $J=2, 10$  Hz), 5.87 (2H, m), 6.78 (2H, br s), 7.01 (1H, d,  $J=2$  Hz), 7.08 (1H, d,  $J=2$  Hz), 7.20 (1H, overlapped with the solvent signal), 7.63 (1H, d,  $J=2$  Hz), 10.72 (1H, s, OH). MS  $m/e$ : 655 ( $M^+$  for  $C_{31}H_{33}N_3O_{13}$ ), 212.

**Anodic Oxidation of 4-Allyl-2-methoxy-6-nitrophenol (17) in the Presence of NaCN**—A solution of **17** (418 mg) in MeOH (200 ml) containing NaCN (196 mg) and  $LiClO_4$  (4.3 g) was electrolyzed at a constant current (20 mA; 0.13 mA/ $cm^2$ ; +500–650 mV vs. SCE) and the reaction was quenched at 1.1 F/mol. The reaction solution was concentrated under reduced pressure and partitioned between AcOEt and  $H_2O$ , after neutralization with dil.  $HClO_4$ . The AcOEt extract was concentrated under reduced pressure to leave an oil (440 mg), which was dissolved in MeOH (6 ml) and separated by preparative HPLC (HP-255, 22 mm  $\phi$   $\times$  300 mm) using MeOH– $H_2O$  (90:10) to afford **44** (107 mg), **35** (6 mg), **40** (6 mg) and the starting material (226 mg), in order of elution.

**44**: mp 117–118  $^{\circ}C$  (from hexane). IR (KBr): 3380 br, 2210  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.68 (2H, br d,  $J=6$  Hz), 4.07 (3H, s), 5.19 (1H, br d,  $J=16$  Hz), 5.22 (1H, br d,  $J=10$  Hz), 5.7–6.2 (1H, m), 6.99 (1H, s), 8.32 (1H, br s, OH). *Anal.* Calcd for  $C_{11}H_{10}N_2O_4$ :  $m/e$  234.0639. Found:  $m/e$  234.0623.

**Anodic Oxidation of 2-Allyl-6-methoxyphenol (47) in MeOH**—A solution of **47** (328 mg) in MeOH (200 ml) containing  $LiClO_4$  (4.3 g) was electrolyzed at a controlled potential (+800 mV vs. SCE; 150–5 mA) and the reaction was quenched at 2.5 F/mol. The reaction solution was concentrated under reduced pressure, and then extracted with ether. Removal of the solvent gave an oil (440 mg) which was separated by preparative TLC [Kieselgel PF<sub>254</sub>; benzene–AcOEt (5:1)] to afford **49** (160 mg), **50** (15 mg) and **51** (35 mg).

**49**: mp 123–125  $^{\circ}C$  (from hexane). IR (KBr): 1725, 1690, 1640  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 2.20–2.78 (2H, m), 3.02 (3H, s), 3.19 (3H, s), 3.36 (3H, s), 3.43 (3H, s), 2.8–3.4 (5H, overlapped with MeO signals), 4.93–5.26 (4H, complex), 5.52 (1H, br d,  $J=8$  Hz), 5.56–6.02 (2H, m), 6.18 (1H, m), 6.25 (1H, m). *Anal.* Calcd for  $C_{22}H_{28}O_6$ :  $m/e$  388.1884. Found:  $m/e$  388.1936.

**50**: mp 101.5–102.5  $^{\circ}C$  (from hexane). IR (KBr): 3400 br, 1635, 1600  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.46 (4H, br d,  $J=7$  Hz), 3.94 (6H, s), 4.98–5.26 (4H, m), 5.67 (2H, br s, OH), 5.84–6.28 (2H, m), 6.88 (4H, s). *Anal.* Calcd for  $C_{20}H_{22}O_4$ :  $m/e$  326.1516. Found:  $m/e$  326.1490.

**51**: mp 62–65  $^{\circ}C$  (from hexane). IR (KBr): 1675, 1640, 1625, 1590  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.18 (2H, br d,  $J=7$  Hz), 3.81 (3H, s), 5.02–5.28 (2H, m), 5.60–6.02 (1H, m), 5.87 (1H, br s), 6.49 (1H, br s). MS  $m/e$ : 178 ( $M^+$  for  $C_{10}H_{10}O_3$ ).

**Photochemical Conversion of Asatone-Type Compound (49) into Isoasatone-Type Compound (52)**—A solution of **49** (20 mg) in hexane (20 ml), in a Pyrex tube, was irradiated at room temperature for 1 h. Removal of the solvent afforded an oil, which was directly purified by preparative TLC [Kieselgel PF<sub>254</sub>; benzene–AcOEt (5:1)] to afford **52** (15 mg): mp 83–85  $^{\circ}C$  (from hexane). IR (KBr): 1720, 1640  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 2.2–3.1 (10H, complex), 3.22 (6H, s), 3.36 (6H, s), 5.08 (2H, br d,  $J=15$  Hz), 5.10 (2H, br d,  $J=11.5$  Hz), 5.82 (2H, ddt,  $J=11.5, 15, 7$  Hz). *Anal.* Calcd for  $C_{22}H_{28}O_6$ :  $m/e$  388.1884. Found:  $m/e$  388.1870.

**Anodic Oxidation of 2-Allyl-4,5-methylenedioxyphenol (48) in Methanol**—A solution of **48** (356 mg) in MeOH (200 mg) containing  $LiClO_4$  (4.3 g) was electrolyzed at a constant current (100 mA; 0.63 mA/ $cm^2$ ; +750–850 mV vs. SCE) and the reaction was quenched at 2.0 F/mol. The reaction solution was directly subjected to preparative HPLC [Unisil C<sub>18</sub> (4.0 mm  $\phi$   $\times$  300 mm); MeOH– $H_2O$  (50:50)] to afford only the known dienone (**53**)<sup>14</sup> in almost quantitative yield.

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#### References and Notes

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