The Structures of Two Novel Neolignans, Asatone and Isoasatone

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Isolation and structures of two novel neolignans, asatone (**1**) and isoasatone (**2**), are described. The structure of the latter, established by means of an X-ray crystallographic analysis of its dihydroxy derivative, is in full agreement with its chemical and spectral data. From a biogenetic point of view, furthermore, thermal and photochemical reactions of these neolignans and their derivatives were carried out. In particular, asatone was photochemically converted into isoasatone.

The chemical constituents of many species of *Asarum* genus, *Aristolochiaceae*, have been investigated by many authors.[1] Particularly, chemotaxonomic studies on species of *Asarum*, *Asiasarum* and *Heterotropa* have been extensively carried out by Saiki and his co-workers.[2] In most cases, however, chemical constituents have been examined in steam-distillates of the fresh or air-dried whole herb of the plant.

The decoction of the stems and rhizomes of *Asarum taitonense* Hayata (Taiton Kanaoi in Japanese)[3] is used in Taiwan as a remedy for neuralgia by the local people.[4] In the course of our searching for physiologically active substances of this plant, we isolated two neoligans, named "asatone" and "isoasatone". In this paper, we wish to describe the isolation and structures of these neolignans. From a biogenetic point of view, thermal and photochemical reactions of these neolignans are also presented.

Isolation of Asatone (1) and Isoasatone (2). A sample of the dried and pulverized material of the whole herb of *Asarum taitonense* Hayata was directly refluxed with large amounts of hexane for 3 h, and then filtered. The filtrates were concentrated under reduced pressure to give a greenish yellow solid, which was chromatographed on silica gel and eluted with hexane–EtOAc (8: 1) to afford asatone (**1**), mp 101—102 °C, in *ca.* 0.2% yield. On the other hand, the residue was further extracted with $CHCl_3$ (under reflux, 3 h). The extracts were also chromatographed on silica gel, and eluted with hexane–EtOAc (8: 1) to give rise to white crystals of isoasatone (**2**), mp 156.5—158 °C, in *ca.* 0.001% yield. Asatone and isoasatone both have the same molecular formula ($C_{24}H_{32}O_8$). Furthermore, it should be noted that the mass spectra of these two neolignans are quite similar to each other [*m/e* 448 (M^+), 416, 384, 348, and 224]. However, the other spectral data are pretty different, as shown in Table 1.

The Structure of Asatone. As described above, asatone (**1**), a major component of *Asarum taitonense* Hayata, has a molecular formula [$C_{24}H_{32}O_8$ (*m/e* 448 (M^+))]. As cited in Table 1, the NMR methyl singlets at δ 3.0—3.6 ppm and IR absorption bands at 1740 and 1720 cm^{-1} indicate that asatone has six MeO and two CO groups, all of which are in different environment to one another. The presence of two allyl groups in **1** is based on its NMR spectrum [δ4.90—5.28, 5.50—6.20, 2.60—2.95, and 2.15 ppm] coupled with catalytic hydrogenation of **1**, which has been carried out over 10% Pd–C in EtOAc to afford tetrahydroasatone (**3**), mp 128—129 °C: $C_{24}H_{36}O_8$ [*m/e* 452 (M^+)]. The NMR spectrum of **3** has methyl triplet at δ 0.87 (6H, J=6.5 Hz) ppm and multiplets at δ 1.10—1.80 and 1.85—2.15 ppm corresponding to four methylene groups instead of multiplets at δ 4.90—5.28 and 5.50—6.20 ppm in **1**. Furthermore, it should be noted that at least one of the two allyl groups in **1** must be attached to an asymmetric quaternary carbon atom: irradiation at δ 5.85 ppm in **1** caused the quartet at δ 2.15 ppm to collapse to doublet, the large coupling constant (J=14.5 Hz) of which should be regarded as a J-value between geminal protons.

Asatone (**1**) has two CO groups, whose properties can be elucidated by $NaBH_4$ reduction, as follows. When treated with $NaBH_4$ in EtOH (room temp., 1.5 h), **1** afforded a mixture of three reduction products [hydroxyasatone-A (**4**): mp 127—128 °C, $C_{24}H_{34}O_8$,

TABLE 1. SPECTRAL DATA OF ASATONE (**1**) AND ISOASATONE (**2**)

	Asatone (**1**)	Isoasatone (**2**)
ν_{max}(KBr)	1740, 1720, and 1635 cm^{-1}	1735 and 1640 cm^{-1}
λ_{max}(MeOH)	278 and 229 nm (ε 5660) and 5100, respectively)	221 nm (ε 2010)
δ($CDCl_3$)	2.15(1H, dd, J=7.5 and 14.5 Hz), 2.60—2.95(3H, m), 2.88(2H, br.s), 3.05(3H, s), 3.31 (3H, s) 3.38(3H, s), 3.42(3H, s), 3.47(3H, s), 3.60(3H, s), 4.90—5.28(4H, m), 5.39(1H, s), 5.55(1H, q, J=1.9 Hz) and 5.50—6.20(2H, m) ppm	2.56(2H, dd, J=8.6 and 14.3 Hz), 2.80(2H, s), 2.85(2H, dd, J=7.5 and 14.3 Hz), 3.00 (2H, s), 3.25(6H, s), 3.27(6H, s), 3.38(6H, s), 5.00(2H, br.d, J=15 Hz), 5.03(2H, br.d, J=11.5 Hz) and 5.35—5.80(2H, m) ppm

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λ_{max} 218 nm (ε, 4500), ν_{max} 3500 cm^{-1} and δ 3.93 (1H, s) ppm; hydroxyasatone-B (**5**): mp 108—109 °C, $C_{24}H_{34}O_8$, λ_{max} 277 nm (ε, 4400), ν_{max} 3510 cm^{-1} and δ 3.92 (1H, s) ppm; dihydroxyasatone (**6**): mp 156—158 °C, $C_{24}H_{36}O_8$, ν_{max} 3550 and 3425 cm^{-1} (no CO band) and δ 3.80 (2H, br. s)]. In particular, each NMR spectrum of **4** and **5** has the sharp singlet corresponding to one proton attached to the carbon atom bearing the resulting OH group, indicating that the α- and α'-positions of each CO group in **1** must be fully substituted. Furthermore, the comparison of the spectral data between **1** and **4** indicates that asatone (**1**) has an α,β-unsaturated carbonyl system [A] in which only one olefinic proton is located at the β-position, since the NMR singlet at δ 5.39 (1H, s) ppm in **1** is shifted to δ 4.60 ppm in **4**. On the other hand, the α,β-unsaturated carbonyl system [A] is present in the isomer (**5**) and the resulting OH group must be derived from the isolated CO group in **1**. In the case of the third compound (**6**), which is further hydrogenated on 10% Pd–C to the corresponding tetrahydro-compound (**7**) (mp 151—152 °C, $C_{24}H_{40}O_8$), two CO groups are completely reduced to OH groups.

The partial structure [A] is further extended to [B], as follows. Catalytic hydrogenation of **1** in MeOH was carried out over 10% Pd–C (room temp., overnight) to afforded a mixture of **3** and hexahydroasatone (**8**) in *ca.* 70 and 10% yields, respectively. The UV and IR spectra of **8** [mp 133—134 °C; $C_{24}H_{38}O_8$: ν_{max} 1750 and 1745 cm^{-1}] indicate that conjugate double bond in [A] has been hydrogenated. Furthermore, the NMR spectrum of **8** has two new signals at δ 2.31 (2H, d, J= 5.5 Hz) and 3.63 (1H, t, J=5.5 Hz) ppm. Irradiation at δ 2.31 ppm caused the triplet at δ 3.63 ppm to collapse to singlet. This finding strongly supports the presence of the partial structure [B] in **1**.

Further information on the structure of asatone (**1**) was obtained by zinc reduction of **1** as well as of **3**.

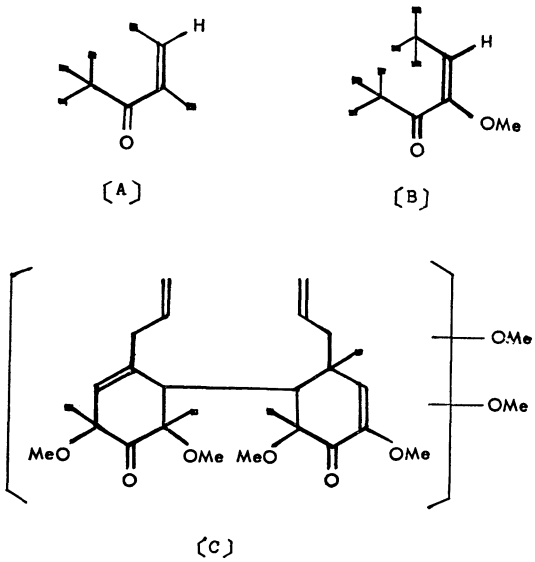


Fig. 1.

When treated with activated zinc powder in AcOH (under reflux, 6 h), tetrahydroasatone (**3**) was readily converted into 2,6-dimethoxy-4-propylphenol (**9**) and a biphenyl-type compound (**10**) in 57 (as 2eq.) and 23% yields, respectively. Further treatment of **9** with Ac_2O–pyridine gave the corresponding acetate (**11**), mp 88—88.5 °C (lit, 87 °C)[5]; $C_{13}H_{18}O_4$ [*m/e* 238 (M^+)]; ν_{max} 1765 cm^{-1}: λ_{max} 275 and 227 nm (ε, 790 and 6140, respectively). In connection with the formation of 9, the symmetric structure (**10**) of the biphenyl-type compound can be deduced on the basis of its spectral and chemical properties: $C_{22}H_{30}O_6$ [*m/e* 390 (M^+)]; ν_{max} 3460, 1610, 1585, and 1495 cm^{-1}; δ 0.81 (6H, t, J=7.0 Hz), 1.15—1.80 (4H, m), 2.22 (4H, td, J=7.0 and 1.5 Hz), 3.60 (6H, s), 3.95 (6H, s) and 6.60 (2H, br. s) ppm. Acetylation of **10** afforded in quantitative yield the corresponding diacetate (**12**), mp 117—118 °C;

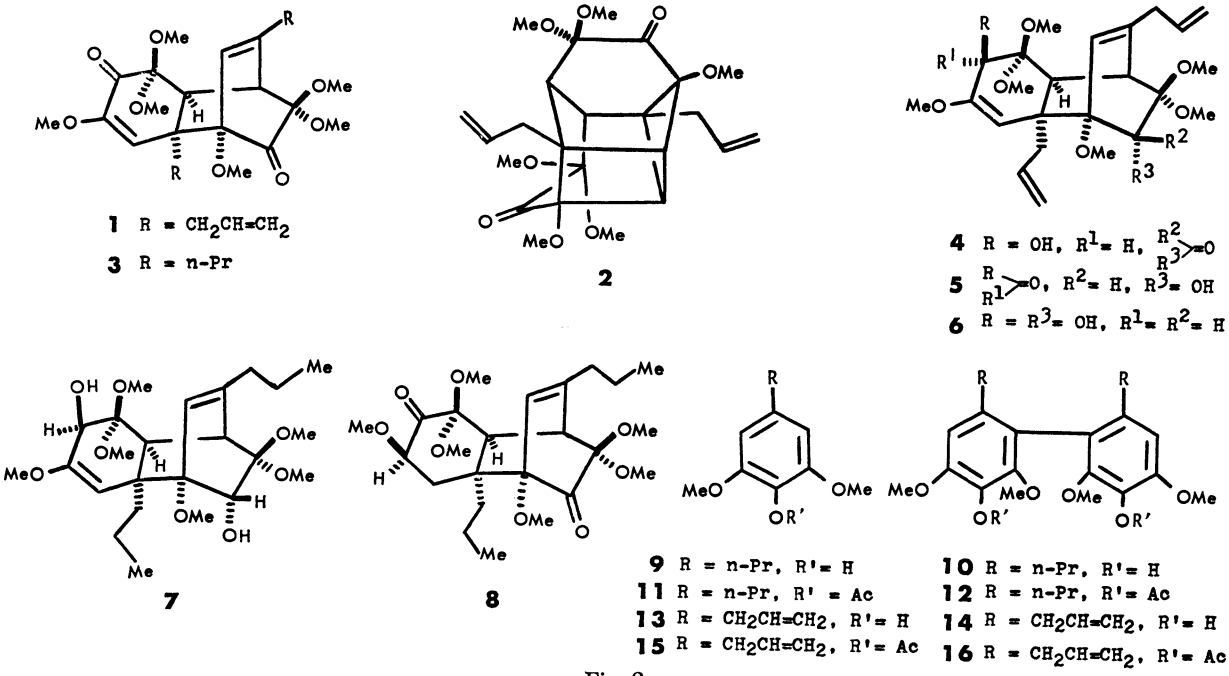


Fig. 2.

$C_{26}H_{34}O_8$: ν_{max} 1770 cm^{-1}; λ_{max} 279 and 232 nm (ε, 2470 and 13750, respectively). These two acetates (**11** and **12**) were also obtained directly from **3** in 51 (as 2 eq.) and 24% yields, respectively, on zinc reduction using Ac_2O (under reflux, 7 h) instead of AcOH. Under essentially the same condition, zinc reduction of asatone (**1**) in AcOH afforded a mixture of 2,6-dimethoxy-4-allylphenol (**13**) and a biphenyl-type compound (**14**) in 37 (as 2 eq.) and 19% yields, respectively. Acetylation of the former followed by catalytic hydrogenation (10% Pd–C in EtOAc) gave rise to **11** *via* 2,6-dimethoxy-4-allylphenyl acetate (**15**). Acetylation of **14** also afforded the corresponding diacetate (**16**), mp 125—125.5 °C; $C_{26}H_{30}O_8$ [*m/e* 470 (M^+)]; ν_{max} 1775 cm^{-1}. Clearly, two allyl groups are present in **16** [δ 3.10 (4H, d, J=6.7 Hz), 4.75—5.10 (4H, m) and 5.45—6.10 (2H, m) ppm]. The formation of these aromatic compounds in high yields strongly suggests that the carbon skeleton of asatone (**1**) consists of two C_6–C_3 units and **1** may have a partial structure [C]. Finally the structure of asatone (**1**) including its stereochemistry was elucidated on the basis of the photochemical reaction of asatone leading to the formation of isoasatone (**2**) in 64% yield,[6] whose structure had been unambiguously established by means of an X-ray crystallographic analysis of dihydroxyisoasatone (**17**),[7] as described later.

On the basis of the structure (**1**) thus obtained, the spectral data of asatone will be discussed below. As seen in Table 1, the UV absorption band [λ_{max} 278 nm (ε, 5100)] of **1** is observed at longer wavelength than calculated one. This is probably due to some effects of α',α'-dimethoxyl groups as well as of the isolated and tri-substituted double bond. Furthermore, the NMR broad singlet at δ 2.88 ppm in **1** (δ 2.84 ppm in **3**) is not due to one methylene group[8], but assignable to two methine protons which have the same chemical shift although these two protons are in different environment to each other. In fact, the ^{13}C NMR spectrum of asatone is in good agreement with the structure (**1**), and a tentative assignment of each signal is as follows: δ ($CDCl_3$) 39.0 (t), 41.3 (t), 116.9 (t), 118.2 (t), 133.4 (d), and 135.2 (d) [2×(CH_2=CH–CH_2)]; 43.9 (d) and 44.5 (d) [2×(>CH–)]; 49.8 (s) (>C<); 50.1—50.2[9], 54.8 (q) and 55.5 (q) (6×OMe); 92.1 (s) [>C(OMe)–]; 93.2 (s) and 98.7 (s) [2×(>C(OMe)$_2$)]; 116.6 (d) and 144.9 (s) (–HC=C<); 121.7 (d) 150.2 (s) and 188.7 (s) [(MeO)C=CH–C=O]; 201.4 (s) ppm (C=O).

The Structure of Isoasatone. Isoasatone (**2**) has been isolated, as a minor component, together with asatone (**1**) and has the same molecular formula ($C_{24}H_{32}O_8$) as that of the latter.

From a structural point of view, asatone and isoasatone both are quite similar to each other, as follows. They have two allyl and two CO groups in addition to six MeO groups. In fact, on catalytic hydrogenation with 10% Pd–C in EtOAc two allyl groups were reduced, giving the corresponding tetrahydro-compound (**18**), mp 161—162 °C; $C_{24}H_{36}O_8$; δ 0.90 (6H, t, J=5.5 Hz) and 1.70—2.30 (8H, complex) ppm. Furthermore, isoasatone was treated with $LiAlH_4$ in THF to give dihydroxyisoasatone (**17**), mp 153—154 °C; $C_{24}H_{36}O_8$; ν_{max} 3500 and 3430 cm^{-1} (no CO band); no UV absorption maximum; δ 3.71 (2H, s) ppm. Finally, this diol as colorless needles was subjected to an X-ray crystallographic analysis,[7] which proved it to have the complex structure (**17**), which is in good agreement with the physical data of dihydroxyisoasatone. Therefore, the

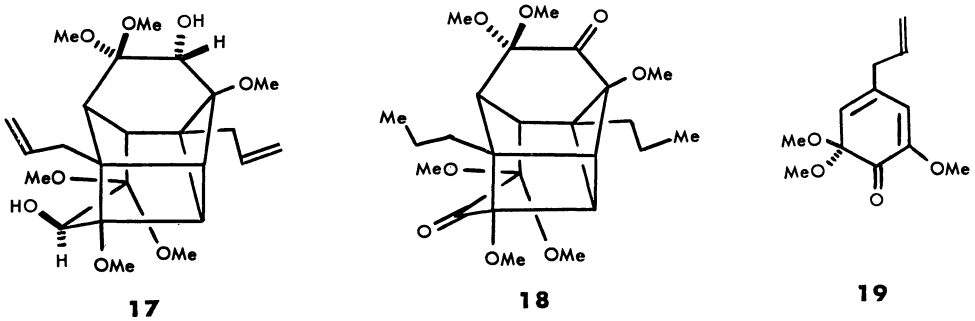
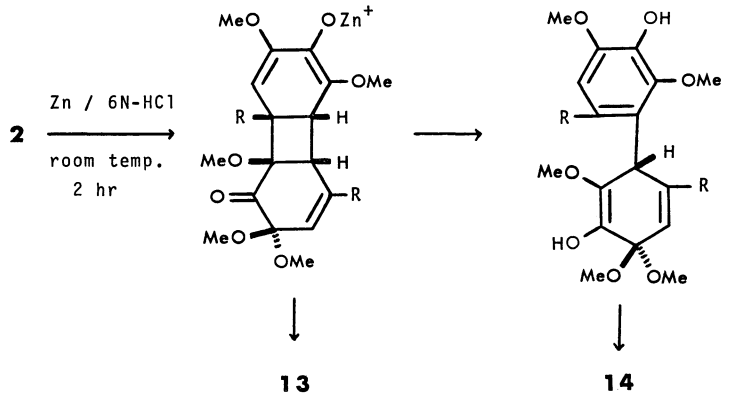


Fig. 3.



Scheme 1. Zinc reduction of isoasatone (**2**).

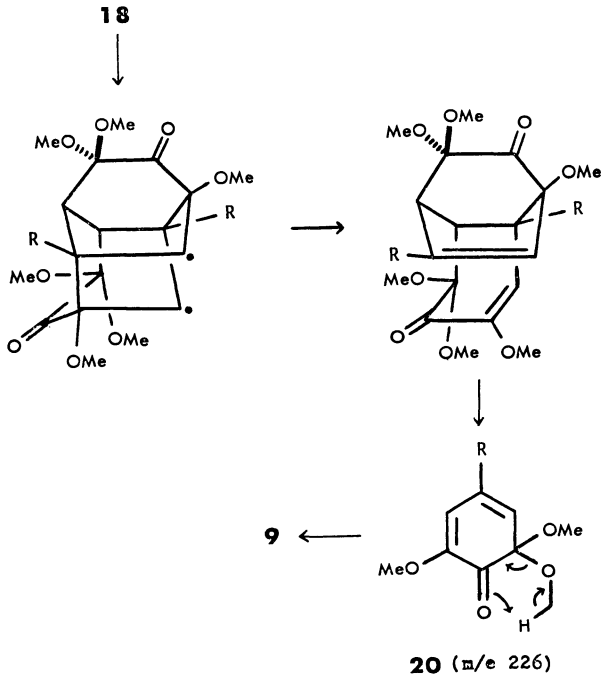
structure of isoasatone should be represented by **2**, in which the UV absorption maximum at 221 nm may be due to the conjugative overlap of the cyclobutane ring with the CO group, the α- and α′-positions of which are fully substituted with MeO groups.

As seen in the case of asatone (**1**), interestingly, zinc reduction of isoasatone (**2**) in 6 M·HCl–MeOH also gave a mixture of two phenolic compounds (**13** and **14**) in 46 (as 2 eq.) and 12% yields, respectively. On the basis of the structure (**2**), the formation process of these compounds is shown in Scheme **1**.

Biogenesis of Asatone and Isoasatone. Asatone (**1**) and isoasatone (**2**) both are optically inactive, and regarded as racemic compounds ($[\alpha]_D^{20}=\pm 0°$). From a biogenetic point of view, the carbon skeleton of these two neolignans consists of two C_6-C_3 units. Probably, 2,6-dimethoxy-4-allylphenol (**13**) is enzymatically oxidized to an optically inactive dienone (**19**), two molecules of which further react to each other to yield asatone (**1**). Further photochemical [π2+π2]cycloaddition of 1 may take place, leading to the formation of isoasatone (**2**) which has a bicyclo[2.2.0]hexane system.

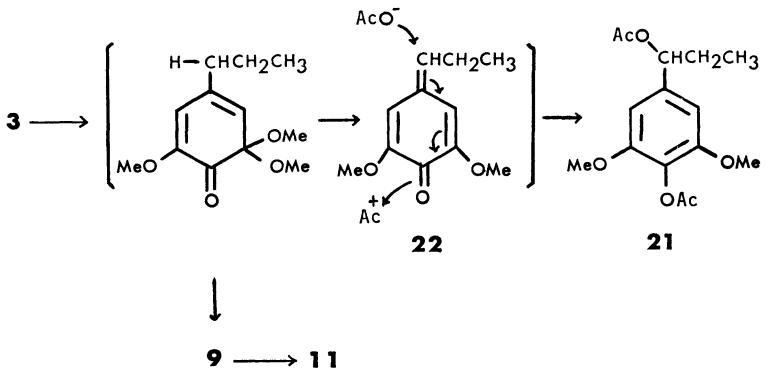
Thermal and Photochemical Reactions of Asatone, Isoasatone and Related Compounds. In connection with the biogenesis of these two neolignans, thermal and photochemical reactions of these compounds were carried out, as follows.

The mass spectra of asatone (**1**) and its derivatives indicate that each base peak is observed at the position corresponding to half of the molecular weight [**1**, 224 ($C_{12}H_{16}O_4$); **3**, 226 ($C_{12}H_{18}O_4$); **4**, 226 ($C_{12}H_{18}O_4$); **5**, 226 ($C_{12}H_{18}O_4$); **6**, 226 ($C_{12}H_{18}O_4$); **7**, 228 ($C_{12}H_{20}O_4$)]. Clearly, the retro-Diels-Alder reaction in each compound must take place regardless of the presence of CO group, giving rise to the corresponding cyclohexadiene or dienone, to which the base peak is assignable. The mass spectra of isoasatone (**2**) and its derivatives are also found to be quite similar to that of asatone (**1**) [2, 224 ($C_{12}H_{16}O_4$); **17**, 226 ($C_{12}H_{18}O_4$); **18**, 226 ($C_{12}H_{18}O_4$)]. In the case of the isoasatone series, a highly strained bicyclo[2.2.0]hexane system of each compound is thermally decomposed in a stepwise manner and then further subjected to the retro-Diels-Alder reaction to give the corresponding cyclohexadiene or dienone, as shown in Scheme 2 (**18**→**20**). When heated in a sealed tube at 290—300 °C for 30 min, tetrahydroisoasatone (**18**) afforded 2,6-dimethoxy-4-propylphenol (**9**) in *ca.* 55% yield. As shown in Scheme 2, the thermal reaction of

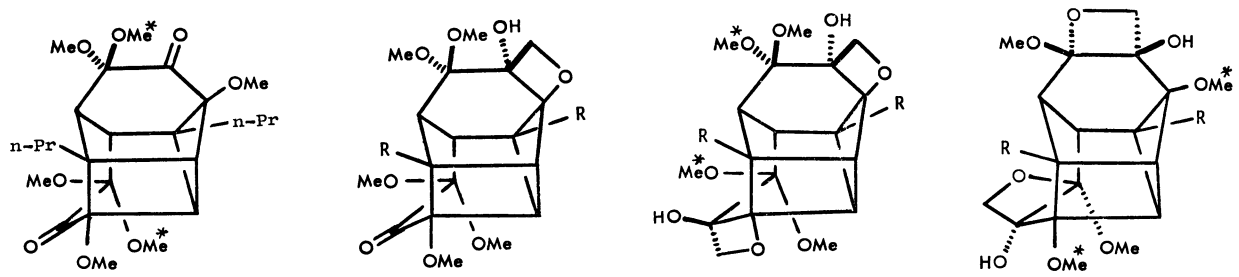


Scheme 2. Thermal reaction of tetrahydroisoasatone (**18**).

18 takes place in the same manner as that of the fragmentation reaction on electron impact, leading to the formation of the corresponding dienone (**20**), which must be further decomposed to **9**. In Scheme 2, it seems to be that the biradical formation process at the initial step requires more vigorous condition as compared with the others. In fact, tetrahydroisoasatone (**18**) is quite stable to acetic anhydride even under reflux conditions. On the other hand, when heated in acetic anhydride under reflux, tetrahydroasatone (**3**) afforded a mixture of 2,6-dimethoxy-4-propylphenyl acetate (**11**) and a diacetate (**21**), 14 and 49 (as 2 eq.) % yields, respectively. The structure of the latter was based on its spectral data: $C_{15}H_{20}O_6$ [m/e 296 (M^+)]; ν_{max} 1770 and 1740 cm^{-1}: λ_{max} 276 and 226 nm (ε, 970 and 9600, respectively); δ 0.90 (3H, t, J=7.5 Hz), 1.87 (2H, quintet, J=7.5 Hz), 2.08 (3H, s), 2.30 (3H, s), 3.78 (6H, s), 5.61 (1H, t, 7.5 Hz) and 6.58 (2H, s) ppm. In particular, the presence of a CH_3CH_2–CH(OAc)–grouping is confirmed by the NMR and IR spectra (δ 0.90, 1.87, 2.08 and 5.61 ppm; ν_{max} 1740 cm^{-1}). The formation process of these two acetates is shown in Scheme 3. It



Scheme 3. The formation process of **11** and **21**.



18a **23** **24a** **24b**

Fig. 4.

is noted that a methylene quinone (**22**) is regared as a plausible intermediate, from which the diacetate (**21**) can be produced.

From the above experiments, it is clear that the dienone (**19**) is the possible precursor for these neolignans.

Asatone (**1**) and isoasatone (**2**) both co-occur in the plant, and the former can be regarded as a plausible precursor of **2**. Thus, chemical correlation between them was successfully carried out by photochemical reaction of asatone, as follows.

When irradiated in hexane using 0.02% aq. K_2CrO_4 solution as a filter at 10 °C, asatone (**1**) was converted into isoasatone (**2**) in 64% yield. In the case of tetrahydroasatone (**3**), the corresponding tetrahydro-compound (**18**) was also obtained in 60% yield. On irradiation of **3** using pyrex filter, two oxetanes (**23** and **24a**) were produced in 47 and 20% yields, respectively, in addition to tetrahydroisoasatone (**18**) (*ca.* 30% yield). Clearly, the dihydroxyoxetane (**24a**) must be produced from **18** *via* the monohydroxyoxetane (**23**). In fact, these two compounds (**18** and **23**) were each subjected to further photochemical reaction to give **24a** in almost quantitative yields. The structures of these oxetanes are discussed below.

The monohydroxyoxetane is a colorless viscous liquid with a molecular formula ($C_{24}H_{36}O_8$), whose IR spectrum indicates the presence of each one OH and CO group (ν_{max} 3550 and 1730 cm^{-1}). This oxetane has five MeO groups (see Table 2) and a methylene group which constitutes a part of the oxetane ring [δ 4.33 (1H, d, J=5.5 Hz) and 4.67 (1H, d, J=5.5 Hz) ppm]. In the case of the dihydroxyoxetane (**24a**, mp 167—168 °C; $C_{24}H_{36}O_8$), which has four MeO groups and no CO group, two oxetane rings must be present [δ 4.11 (2H, d, J=5.0 Hz) and 4.49 (2H, d, J=5.0 Hz) ppm]. Furthermore, it should be noted that only half of the total protons are observed in the NMR spectrum of the dihydroxyoxetane. In connection with tetrahydroisoasatone (**18**), finally, the structure of dihydroxyoxetane (**24a**) was elucidated by measurements of intramolecular nuclear Overhauser effects (NOE), which were focused on the signals corresponding to MeO groups and methine protons (see Table 2).

In the NMR spectrum of **18**, low-intensity irradiation at δ 3.31 ppm caused **12** and 10% enhancements in the integrated intensities of two methine signals at δ 2.82 and 2.90 ppm, respectively. On the other hand, on irradiation at δ 3.22 ppm, any enhancement was not

Table 2. The NMR spectra of **18**, **23**, and **24**

Tetrahydro-isoasatone (**18**)	Monohydroxy-oxetane (**23**)	Dihydroxy-oxetane (**24a**)
2.82 (2H, s)	2.6—2.8 (3H, complex)	2.62(2H, s)
2.90(2H, s)	3.00(4H, s)[a]	2.65(2H, s)
3.22(6H, s)	3.23(3H, s)	2.97(6H, s)
3.31(12H, s)	3.32(3H, s)	3.31(6H, s)
	3.33(3H, s)	
	3.35(3H, s)	

a) One of the four methine protons is included.

detected in the signal intensities of the methine protons (δ 2.82 and 2.90 ppm). From the molecular model of **18**, it is clear that the methyl singlet at δ 3.22 ppm is assigned to one of the two α,α-dimethoxyl groups, that is marked by "asterisk" in **18a**. In the case of the dihydroxyoxetane, only low-intensity irradiation at δ 3.31 ppm caused 12% enhancement in the integrated intensity of the methine singlet at δ 2.62 ppm, and any interaction between the MeO group (δ 2.97 ppm) and two methine protons (δ 2.62 and 2.65 ppm) was not detected. From these data, the structure of the dihydroxyoxetane can be represented by **24a** or **24b**. However, the former is more favorable than **24b**, because the methyl singlet at δ 3.31 ppm is reasonably assigned to the MeO group marked by "asterisk" in **24a**. In the case of **24b**, the signal at δ 3.31 ppm must be assigned to the MeO group marked by "asterisk", although the NMR signal due to the remaining MeO group is expected to be observed in a lower magnetic field that that of the asterisked one, since this MeO group and the newly formed OH group on the oxetane ring both are in a *cis*-configuration to each other. The structure of the monohydroxyoxetane is represented by **23** on the basis of the structure of the dihydroxyoxetane (**24a**), which has been already derived from the former.

Experimental

All mps were uncorrected. The IR and UV spectra were recorded on a JASCO Model IR-S and on a Perkin-Elmer 202 spectrophotometer, respectively. The NMR spectra were (100 MHz) taken on a JEOL JNM-C60H (60 MHz) or JNM-PS 100 using $CDCl_3$ as solvent, unless otherwise stated. Only prominent peaks are cited. Chemical shifts are given in ppm from TMS as an internal standard. Coupling constants are given in Hz (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet). The mass spectra were obtained on

a Hitachi RMU-6D mass spectrometer operating with an ionization energy (70 eV). Preparative TLC were carried out on Kieselgel PF_{254} (E. Merk A.G., Germany).

Isolation of Asatone and Isoasatone. A sample of the dried and pulverized material of the whole herb (9 kg), which was collected at Chia-I, Taiwan, was extracted with large amounts of hexane (40 l) by refluxing for 3 h. The hot mixtures were filtered from the undissolved residue which was extracted with the same solvent (40 l, each time) for twice. The combined filtrates were concentrated under reduced press. to give a greenish yellow crude crystalline solid (32 g) besides a dark green jelly (140 g) after filtration. The resulting crystalline solid was treated with column chromatography using silica gel (Kieselgel, E. Merk A. G. Germany) (2 kg), and eluted with hexane–EtOAc (8: 1). From the eluates, after recrystallized from hexane, white crystals of asatone (17.6 g) were isolated: mp 101—102 °C; *m/e* 448 (M^+) and 224 (Found: C, 64.01; H, 7.26%. Calcd for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19%).

The undissolved residue from hexane extractions was then extracted with $CHCl_3$ successively by refluxing for three times in the same way as hexane extractions. The combined $CHCl_3$ extracts were concentrated under reduced press. to give a dark green jelly (100 g). The resultant jelly was chromatographed on silica gel (Kieselgel, E. Merk A. G., Germany) (7 kg), and eluted with hexane–EtOAc (8: 1). From the eluates, after recrystallized from hexane, white crystals of isoasatone (120 mg) were isolated; mp 156.5—158 °C; *m/e* 448 (M^+) and 224 (Found: C, 64.55; H, 7.07%. Calcd for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19%).

*Catalytic Hydrogenation of Asatone (**1**).* Catalytic hydrogenation of asatone (90 mg) in EtOAc (2.5 ml) was carried out over 10% Pd–C (10 mg) at room temp. overnight. After filtration of the catalyst, the solvent was evaporated under reduced press. to give a white crystalline solid, which was recrystallized from hexane to give white crystals of tetrahydroasatone (**3**) (85 mg), mp 128—129 °C; ν_{max} (Nujol) 1745, 1720, and 1635 cm^{-1}; λ_{max} (MeOH) 278 and 229 nm (ε, 5100 and 3940, respectively); δ 0.87 (6H, t, J=6.5 Hz), 1.10—1.80 and 1.85—2.15 (8H, m), 2.80 (2H, br.s), 3.05 (3H, s), 3.30 (3H, s), 3.37 (3H, s), 3.41 (3H, s), 3.46 (3H, s), 3.60 (3H, s), 5.41 (1H, s), and 5.51 (1H, q, J=1.5 Hz) ppm; *m/e* 452 (M^+), 420, 388, 356, 345, 226, and 211 (Found: *m/e* 452.2425. Calcd for $C_{24}H_{36}O_8$: *m/e* 452.2410. Found: *m/e* 226.1236. Calcd for $C_{12}H_{18}O_4$: *m/e* 226.1205).

*$NaBH_4$ Reduction of Asatone (**1**).* To a solution of of asatone (400 mg) in EtOH (3 ml) was carefully added $NaBH_4$ (40 mg), with stirring. The mixture was further stirred at room temp. for 1.5 h, and then decomposed with ice water. After addition of 1M·HCl aq. solution (*ca.* 0.5 ml), the aqueous solution was extracted with ether. The ethereal solution was washed with sat. NaCl aq. solution, and then dried over Na_2SO_4. Removal of the solvent afforded an oily substance, which was purified by preparative TLC using a mixed solvent [hexane–EtOAc (2: 1)] to give three crystalline compounds, namely, hydroxyasatone-A (**4**) (66 mg), hydroxyasatone-B (**5**) (108 mg) and dihydroxyasatone (**6**) (20 mg), respectively, after crystallized from hexane. The physical data of these three reduction products are described below.

Hydroxyasatone-A: Mp 127—128 °C; ν_{max} (Nujol) 3500, 3085, 1745, 1685, 1660, and 1640 cm^{-1}; λ_{max} (MeOH) 235 sh. and 218 nm (ε, 2640 and 4500, respectively); δ 3.93 (1H, s), 4.60 (1H, s), and 5.75 (1H, q, J=1.5 Hz) ppm; *m/e* 450 (M^+), 422, 418, 386, 381, 349, 345, 316, 307, and 226 (Found: *m/e* 450.2232. Calcd for $C_{24}H_{34}O_8$: *m/e* 450.2253. Found: *m/e* 226.1207. Calcd for $C_{12}H_{18}O_4$: *m/e* 226.1205).

Hydroxyasatone-B: Mp 108—109 °C; ν_{max} (Nujol) 3510, 3050, 1715, 1660, and 1635 cm^{-1}; $\lambda_{хеш}$ (MeOH) 277 and 213 nm (ε, 4390 and 2510, respectively); δ 3.92 (1H, s), 5.50 (1H, q, J=1.5 Hz), and 5.60 (1H, s) ppm; *m/e* 450 (M^+), 422, 418, 386, 381, and 226 (Found: *m/e* 450.2232. Calcd for $C_{24}H_{34}O_8$: *m/e* 450.2253. Found: *m/e* 226.1197. Calcd for $C_{12}H_{18}O_4$: 226.1205).

Dihydroxyasatone: Mp 156—158 °C; ν_{max} (Nujol) 3550, 3425, 3060, 1685, 1665, and 1635 cm^{-1}; λ_{max} (MeOH) 222 nm (ε, 2590); δ 3.80 (2H, br.s), 4.78 (1H, s) and 5.72 (1H, q, J=1.5 Hz) ppm; *m/e* 452 (M^+ for $C_{24}H_{36}O_8$), 434, 420, 389, 379, and 226. High resolution mass spectrum of this compound has not been measured, but its structure can be supported by its physical data coupled with the next experiment.

*Catalytic Hydrogenation of Dihydroxyasatone (**6**).* Catalytic hydrogenation of **6** (15 mg) in EtOAc (3 ml) was carried out over 10% Pd–C (5 mg) at room temp. for 4 h. After filtration of the catalyst, the solvent was removed under reduced press. to give white crystals of dihydroxytetrahydroasatone (**7**) (15 mg), mp 151—152 °C (from hexane); ν_{max} (Nujol) 3500 and 1675 cm^{-1}; λ_{max} (MeOH) 217 nm (ε, 2400); δ 3.77 (2H, br.s), 4.80 (1H, s) and 5.71 (1H, q, J=1.5 Hz) ppm; *m/e* 456 (M^+) and 228 (Found: C, 63.11; H, 8.83%. Calcd for $C_{24}H_{40}O_8$: C, 63.13; H, 8.83%).

*Reduction of Tetrahydroasatone (**3**) with $LiAlH_4$.* To a solution of **3** (100 mg) in THF (1.5 ml) was added $LiAlH_4$ (20 mg) with stirring at 0 °C, and then the reaction temperature was elevated to room temp. The reaction mixture was further stirred at room temp. for 6 h, and then poured into ice-water and extracted with EtOAc. The extracts were washed successively with water and with sat. NaCl aq. solution, and then dried over $MgSO_4$. The solvent was removed under reduced press. to give almost colorless crystals of **7** (98 mg) (mp and IR spectrum).

*Formation of Hexahydroasatone (**8**).* Catalytic hydrogenation of asatone (200 mg) in MeOH (2 ml) was carried out over 10% Pd–C (40 mg) at room temp. for 12 h. After filtration of the catalyst, the solvent was removed under reduced press. to leave an almost colorless oil, which was separated by preparative TLC using hexane–EtOAc (3: 1) to afford two fractions. The upper fraction afforded white crystals of hexahydroasatone (20 mg), mp 133—134 °C (from hexane); ν_{max} (Nujol) 1750, 1745, and 1635 cm^{-1}; λ_{max} (MeOH) 221 nm (ε, 2812); δ 0.82 (3H, t, J=7.0 Hz), 0.90 (3H, t, J=7.0 Hz), 1.15—1.84 (6H, m), 1.95 (2H, t, J=7.0 Hz), 2.31 (2H, d, J=5.5 Hz)*, 2.78 (2H, s), 3.14 (3H, s), 3.28 (3H, s), 3.35 (6H, s), 3.43 (3H, s), 3.50 (3H, s), 3.63 (1H, t, J=5.5 Hz)*, and 5.85 (1H, q, J=1.9 Hz) ppm; *m/e* 426 (M^+−28), 395, 379, and 363 (Found: C, 63.22; H, 8.65%. Calcd for $C_{24}H_{38}O_8$: C, 63.41; H, 8.43%).

From the lower fraction, tetrahydroasatone (**3**) (144 mg) was isolated (mp and IR spectrum).

*Zinc Reduction of Tetrahydroasatone (**3**) to Hexahydroasatone (**8**).* A mixture of **3** (20 mg) and activated zinc powder (200 mg) in AcOH (2.5 ml) was stirred at room temp. for 14 h, and then poured into a lot of water, and extracted with EtOAc. The extracts were washed with water several times, and then dried over $MgSO_4$. Removal of the solvent under reduced press. afforded a brown oil (15 mg), from which hexahydroasatone (9 mg) was separated by preparative TLC using a mixed solvent [hexane–EtOAc (1: 2)] (mp and IR spectrum).

*Formation of Two Phenolic Compounds (**9** and **10**).* A mixture of tetrahydroasatone (100 mg) and zinc powder (450 mg) in AcOH (1.5 ml) was refluxed, with stirring, for

* Irradiation at δ 2.31 ppm caused the triplet at δ3.63 ppm to collapse to singlet. In the case of irradiation at δ 3.63 ppm, the doublet at δ 2.31 ppm was changed to singlet.

4.5 h. The cooled reaction mixture was poured into a lot of water, and then extracted with EtOAc. The extracts were washed with a lot of water several times, and then dried over $MgSO_4$. Removal of the solvent left a brown residue (83.6 mg), the preparative TLC of which was carried out using a mixed solvent [hexane–EtOAc (3: 1)] to afford two fractions. The upper fraction gave a colorless liquid of 2,6-dimethoxy-4-propylphenol (**9**) (49 mg); ν_{max} (Film) 3520, 1610, and 1515 cm^{-1}; δ 0.93 (3H, t, J=6.8 Hz), 1.20—1.85 (2H, m), 2.53 (2H, t, J=7.5 Hz), 3.86 (6H, s), 5.35 (1H, br.s, OH), and 6.37 (2H, s) ppm; *m/e* 196 (M^+ for $C_{11}H_{16}O_3$) and 168. This liquid was characterized as the corresponding acetate.

From the lower fraction, a colorless viscous liquid (**10**) (20 mg) was isolated; ν_{max} (Film) 3460, 1610, 1585, and 1495 cm^{-1}; δ 0.81 (6H, t, J=7.0 Hz), 1.15—1.80 (4H, m), 2.22 (4H, td, J=7.0 and 1.5 Hz), 3.60 (6H, s), 3.95 (6H, s) and 6.60 (2H, br.s) ppm; *m/e* 390 (M^+ for $C_{22}H_{30}O_6$), 329, 315, 301, 297, 287, 167, and 153. This oil was also acetylated with Ac_2O–pyridine.

*Acetylation of 2,6-Dimethoxy-4-propylphenol (**9**).* A solution of **9** (15 mg) in Ac_2O–pyridine (1: 1, 1 ml) was stirred at room temp. overnight, and then concentrated under reduced press. on a water-bath (*ca.* 80 °C) to leave white crystals of the acetate (**11**) in quantitative yield, mp 88.0—88.5 °C (from EtOH) (lit, 87 °C)[5]; ν_{max} (Nujol) 1765, 1600, 1510 sh, and 1505 cm^{-1}; λ_{max} (MeOH) 275 and 227 nm (ε, 790 and 6140, respectively); δ 0.95 (3H, t, J=7.5 Hz), 1.57 (2H, sextet, J=7.5 Hz), 2.32 (3H, s), 2.55 (2H, t, J=7.5 Hz), 3.80 (6H, s), and 6.42 (2H, s) ppm; *m/e* 238 (M^+) (Found: C, 65.05; H, 7.62%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%).

*Acetylation of the Biphenyl-type Compound (**10**).* A solution of **10** (19 mg) in Ac_2O–pyridine (1: 1, 1.5 ml) was stirred at room temp. overnight, and then worked up as usual to give pale yellow crystals of the diacetate (**12**) (20 mg), mp 117—118 °C (from EtOH); ν_{max} (Nujol) 1770, 1600, and 1585 cm^{-1}; λ_{max} (MeOH) 279 and 232 nm (ε, 2470 and 13750, respectively); δ 0.84 (6H, t, J=7.0 Hz), 1.10—1.80 (4H, m) 2.10—2.45 (4H, m), 2.31 (6H, s), 3.53 (6H, s), 3.87 (6H, s), and 6.67 (2H, s) ppm; *m/e* 474 (M^+) and 431 (Found: C, 65.38; H, 7.18%. Calcd for $C_{26}H_{34}O_8$: C, 65.80; H, 7.22%).

Zinc Reduction of Asatone in AcOH. A mixture of asatone (125 mg) and zinc powder (1 g) in AcOH (2.0 ml) was heated under reflux overnight with stirring, and then worked up as usual to give a brown oil, from which two aromatic compounds were separated by preparative TLC using a mixed solvent [hexane–EtOAc (3: 1)]. The upper fraction gave a colorless liquid of 2,6-dimethoxy-4-allylphenol (**13**) (38 mg); ν_{max} (Film) 3510, 3080, 1635, 1615, and 1513 cm^{-1}; δ 3.30 (2H, d, J=6.0 Hz), 3.82 (6H, s), 4.80—5.25 (2H, m), 5.39 (1H, br.s, OH), 5.55—6.25 (1H, m) and 6.40 (2H, s) ppm; *m/e* 194 (M^+ for $C_{11}H_{14}O_3$) and 166. This liquid was further used for the next experiment.

From the lower fraction, a colorless viscous liquid of the biphenyl-type compound (**14**) (21 mg) was isolated; ν_{max} (Film) 3460, 1640, 1613, 1585, and 1495 cm^{-1}; δ 3.00 (4H, d, J=6.0 Hz), 3.61 (6H, s), 3.90 (6H, s), 4.70—5.15 (4H, m), 5.52 (2H, br., OH), 5.45—6.20 (2H, m), and 6.60 (2H, s) ppm; *m/e* 386 (M^+ for $C_{22}H_{26}O_6$). This viscous liquid was characterized as the corresponding diacetate (**16**).

*Conversion of **13** to 2,6-Dimethoxy-4-propylphenyl Acetate (**11**).* A solution of **13** (30 mg) in Ac_2O–pyridine (1: 1, 1.5 ml) was allowed to stand at room temp. overnight, and then concentrated under reduced press. to afford a pale yellow oil of the corresponding acetate (**15**) (31 mg); ν_{max} (Film) 1775, 1640, 1608, and 1510 cm^{-1}; *m/e* 236 (M^+ for $C_{13}H_{16}O_4$), 194, 179, and 167.

Catalytic hydrogenation of the acetate (15 mg) in EtOAc (1.5 ml) was carried out over 10% Pd–C (3 mg) at room temp. overnight. After filtration of the catalyst, the solvent was removed under reduced press. to give white crystals of **11** (14 mg) (mp and IR spectrum).

*Acetylation of the Biphenyl-type Compound (**14**).* A solution of **14** (15 mg) in Ac_2O–pyridine (1: 1, 1 ml) was stirred at room temp. overnight, and then worked up as usual to give a crystalline solid (13 mg). Recrystallization from EtOH afforded white crystals of the diacetate (**16**), mp 125—125.5 °C; ν_{max} (Nujol) 1775, 1600, and 1585 cm^{-1}; λ_{max} (MeOH) 277 and 227 nm (ε, 2160 and 17750, respectively); δ 2.36 (6H, s), 3.10 (4H, d, J=6.7 Hz), 3.58 (6H, s), 3.90 (6H, s) 4.75—5.10 (4H, m), 5.45—6.10 (2H, m) and 6.70 (2H, s) ppm; *m/e* 470 (M^+) (Found: C, 66.32; H, 6.44%. Calcd for $C_{26}H_{30}O_8$: C, 66.37; H, 6.43%).

*Conversion of **16** to **12**.* Catalytic hydrogenation of the diacetate (**16**) (10 mg) in EtOAc (1.5 ml) was carried out over 10% Pd–C (2 mg) at room temp. for 5 h, and then worked up as usual to give almost colorless crystals in quantitative yield. Recrystallization from EtOH gave the corresponding tetrahydro-compound (**12**) (mp, TLC and IR spectrum).

*Zinc Reduction of Tetrahydroasatone (**3**) in Acetic Anhydride.* A mixture of **3** (100 mg) and activated zinc powder (500 mg) in Ac_2O (2 ml) was heated under reflux for 7 h with stirring. After cooling, the reaction mixture was poured into water, and then extracted with large amounts of EtOAc. The extracts were washed well water and with sat. NaCl aq. solution successively, and then dried over $MgSO_4$. Removal of the solvent gave a brown oil, which was separated by preparative TLC using a mixed solvent [hexane–EtOAc (3: 1)] to give two fractions. The upper fraction afforded a pale yellow liquid, which was crystallized from EtOH to give slightly pale yellow crystals of **11** (54 mg) (mp and IR spectrum).

From the lower part, a pale yellow oil (25 mg) was separated and crystallized from EtOH to give the diacetate of the biphenyl-type compound (**12**) (mp and IR spectrum).

*Reduction of Isoasatone (**2**) with $LiAlH_4$.* To a solution of **2** (135 mg) in THF (3 ml) was added excess amounts of $LiAlH_4$ (135 mg) with stirring, and then the reaction mixture was further stirred at room temp. for 3 h. After decomposition of the remaining reagent with EtOH, the reaction mixture was diluted with water, and then extracted with EtOAc. The extract was washed with sat. NaCl aq. solution, and then dried over Na_2SO_4. Removal of the solvent afforded a crystalline solid (140 mg), which was recrystallized from hexane–ether to give white crystals of dihydroxyisoasatone (**17**), mp 153—154 °C; ν_{max} (Nujol) 3500, 3420, 3060, 1635, and 908 cm^{-1}; δ 2.39 (2H, br. dd, J=14.3 and 8.5 Hz), 2.41 (2H, s), 2.49 (2H, s), 2.55 (2H, br. dd, J=14.3 and 7.5 Hz), 3.24 (6H, s), 3.30 (6H, s), 3.35 (6H, s), 3.71 (2H, s), 5.01 (2H, br. d, J=11 Hz), 5.03 (2H, br.d, J=15 Hz), and 5.7—6.2 (2H, m) ppm; *m/e* 452 (M^+), 437, 421, 411, 403, and 226 (Found: C, 63.57; H, 8.20%. Calcd for $C_{24}H_{36}O_8$: C, 63.70; H, 8.02%).

*Catalytic Hydrogenation of Isoasatone (**2**).* Catalytic hydrogenation of **2** (15 mg) in EtOAc (2 ml) was carried out over 10% Pd–C (5 mg) at room temp. overnight. After filtration of the catalyst, the solvent was evaporated under reduced press. to give white crystals (15 mg), which were recrystallized from hexane to give white crystals of tetrahydroisoasatone (**18**), mp 161—162 °C; ν_{max} (Nujol) 1735 cm^{-1}; λ_{max} (MeOH) 222 nm (ε, 2070); δ 0.90 (6H, br.t, J=7.0 Hz), 1.7—2.3 (8H, complex), 2.82 (2H, s), 2.90 (2H, s), 3.22 (6H, s), and 3.31 (12H, s) ppm; *m/e* 452 (M^+), 437, 420, 389, and 226 (Found: C, 63.35; H, 8.00%. Calcd for $C_{24}H_{36}O_8$: C, 63.70; H, 8.02%).

*Zinc Reduction of Isoasatone (**2**).* Excess amounts of zinc powder (500 mg) were added to a solution of isoasatone (80

mg) in MeOH (5 ml) containing concd HCl (1.5 ml) with stirring. The reaction mixture was stirred vigorously at room temp. for 2 h, and then poured into large amounts of water and extracted with EtOAc. The extract was washed with sat. NaCl aq. solution, and then dried over Na_2SO_4. Removal of the solvent left a brown oil (65 mg), which was subjected to preparative TLC using a mixed solvent [EtOAc–hexane (1:2)]. From the upper fraction, 2,6-dimethoxy-4-allylphenol (**13**) (32 mg) was obtained (TLC and IR spectrum). The biphenyl-type compound (**14**) (8.2 mg) was also obtained from the lower fraction (TLC and IR spectrum).

Thermal Reaction of Tetrahydroisoasatone (18). Tetrahydroisoasatone (38 mg) in a sealed tube was heated at 290—300 °C for 30 min, and then extracted with EtOAc. Removal of the solvent gave a brown viscous liquid, whose analytical TLC showed eight spots. Preparative TLC of this liquid was carried out in hexane–EtOAc (2:1), and a colorless liquid (9 mg) was obtained from the less polar fraction corresponding to that of 2,6-dimethoxy-4-propylphenol (**9**) (TLC and IR spectrum).

Thermal Reaction of Isoasatone (2). Isoasatone (10 mg) in a sealed tube was heated at 280—290 °C for 20 min, and then dissolved in a small amount of $CHCl_3$, and then directly separated by preparative TLC using hexane–EtOAc (2:1) to give a colorless liquid (2 mg), which was isolated from the less polar fraction corresponding to that of 2,6-dimethoxy-4-allylphenol (**14**) (TLC and IR spectrum).

Reaction of Tetrahydroasatone (3) with Acetic Anhydride. A solution of **3** (240 mg) in Ac_2O (2.5 ml) was heated under reflux for 10 h, and then concentrated under reduced press. to give a brown residue, which was purified by preparative TLC using a mixed solvent [hexane–EtOAc (3:1)] to give pale yellow crystals (35 mg) from the upper fraction. Recrystallization from EtOH afforded 2,6-dimethoxy-4-propylphenyl acetate (**11**) in a pure state (mp and IR spectrum).

From the lower part, slightly brown liquid (155 mg)** was isolated. This liquid was further purified by preparative GLC to give a colorless liquid (**21**) [retention time: 2.8 min. (10% OV-17 (ϕ 0.25 inch × 3 m); at 230 °C; Carrier gas: Nitrogen (100 ml/min); Inlet pressure, 25.5 psi)]; ν_{max} (Film) 1770, 1740, 1608, 1510, 1235, and 1200 cm^{-1}; λ_{max} (MeOH) 276 and 226 nm (ε, 970 and 9600, respectively); δ 0.90 (3H, t, J=7.5 Hz), 1.87 (2H, quintet, J=7.5 Hz), 2.08 (3H, s), 2.30 (3H, s), 3.78 (6H, s), 5.61 (1H, t, J=7.5 Hz), and 6.58 (2H, s) ppm; *m/e* 296 (M^+), 254, 183, and 149 (Found: C, 61.10; H, 6.47%. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80%).

Reaction of Asatone (1) with Acetic Anhydride. A solution of **1** (104 mg) in Ac_2O (1.5 ml) was heated under reflux overnight. Removal of the excess Ac_2O under reduced press. afforded a brown oil, whose analytical TLC showed many spots. Preparative TLC using hexane–EtOAc (3:1) afforded only small amounts of 2,6-dimethoxy-4-allylphenyl acetate (**15**) (5.3 mg) (GLC, TLC, and IR spectrum).

Photochemical Conversion of Asatone (1) to Isoasatone (2). A solution of **1** (70 mg) in hexane (8 ml) was irradiated at 10 °C for 54 h, using 0.02% K_2CrO_4 aq. solution as a filter [Apparatus: Eiko-Sha PIH-100, high pressure Hg lamp (100W)]. The reaction solution was then evaporated under reduced press. to leave an almost colorless oil, which was purified by preparative TLC using hexane–EtOAc (3:1). From the less polar fraction corresponding to that of isoasatone, white crystals (44.8 mg) were isolated after recrystallized from hexane (mp and IR spectrum).

Photochemical Conversion of Tetrahydroasatone (3) to Tetrahydroisoasatone (18). Under essentially the same condition as that of asatone (**1**), a solution of **3** (65 mg) in hexane (8 ml) was irradiated. After removal of the solvent, a colorless oil was purified by preparative TLC using a mixed solvent [hexane–EtOAc (4:1)]. From the less polar fraction corresponding to that of tetrahydroisoasatone, white crystals (39 mg) were obtained after recrystallized from hexane (mp and IR spectrum).

Photochemical Reaction of Tetrahydroasatone (3) Using Pyrex Filter. A solution of **3** (45 mg) in hexane (4 ml) was irradiated at 10 °C for 8 hr, and then the solvent was removed under reduced press. to leave a colorless viscous liquid which was chromatographed on alumina (Nakarai Chem. Co. Ltd., 200 mesh) (1 g) and eluted with hexane–benzene (10:1) to give white crystals of tetrahydroisoasatone (**18**) (13.5 mg) (mp, TLC and IR spectrum). Further elution with hexane–benzene (5:1) afforded a colorless viscous liquid of the monohydroxyoxetane (**23**) (21 mg), ν_{max} ($CHCl_3$) 3550 and 1730 cm^{-1}; δ 0.88 (3H, t, J=6.0 Hz), 0.92 (3H, t, J=6.5 Hz), 1.4—2.1 (8H, complex), 2.6—2.8 (3H, complex), 3.00 (4H, s), 3.23 (3H, s), 3.32 (3H, s), 3.33 (3H, s), 3.35 (3H, s), 3.92 (1H, s, OH), 4.33 (1H, d, J=5.5 Hz), and 4.67 (1H, d, J=5.5 Hz) ppm; *m/e* 452 (M^+), 420, 405, and 226 (Found: *m/e* 452.24050. Calcd for $C_{24}H_{36}O_8$: *m/e* 452.24100). Further elution only with benzene gave white crystals of dihydroxyoxetane (**24a**) (9 mg), mp 167—168 °C (from hexane); ν_{max} (Nujol) 3500 sh. and 3450 cm^{-1}; δ (CCl_4) 0.90 (6H, t, J=6.5 Hz), 1.2—1.9 (8H, complex), 2.62 (2H, s), 2.65 (2H, s), 2.97 (6H, s), 3.31 (6H, s), 4.11 (2H, d, J=5.0 Hz), and 4.49 (2H, d, J=5.0 Hz) ppm; *m/e* 452 (M^+), 420, 404, and 226 (Found: *m/e* 452.24356. Calcd for $C_{24}H_{36}O_8$: *m/e* 452.24100).

The Formation of the Dihydroxyoxetane from Tetrahydroisoasatone (18). Tetrahydroisoasatone (10 mg) in a thin Pyrex NMR tube was dissolved in hexane (*ca.* 2 ml), and then irradiated at room temp. for 8 h [the NMR spectrum of the reaction solution indicated that **18** was completely converted into the oxetane (**24a**)]. Removal of the solvent gave white crystals of the dihydroxyoxetane in quantitative yield (mp and IR spectrum).

Photochemical Conversion of the Monohydroxyoxetane (23) to the Dihydroxyoxetane. Under essentially the same condition as described above, a solution of **23** (10 mg) in hexane (*ca.* 2 ml) was irradiated, and then concentrated under reduced press. to give white crystals of the dihydroxyoxetane in quantitative yield (mp and IR spectrum).

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** The purity of this liquid is more than 95%.

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