A STUDY OF THE CONSTITUENTS OF THE HEARTWOOD OF *TSUGA CHINENSIS PRITZ. VAR. FORMOSANA* (HAY.)

JIM-MIN FANG (方俊民), KUO-MIN WEI (魏國銘) AND YU-SHIA CHENG* (鄭玉瑕)

Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.

Key Word Index—*Tsuga chinensis Pritz. var. formosana* (Hay.); pinaceae; epimanool; lignans; methoxyphenolics; cedrusin; α-conidendrin; tsugacetal; resinols; isolariciresinol; secoisolariciresinol; matairesinol; hydroxymatairesinol; oxomatairesinol.

By means of spectroscopic analysis, X-ray crystallography and chemical correlation the heartwood of Taiwan hemlock was found to contain compounds of sterols, carboxylic acids, 13-epimanool, *o*-methoxyphenolics, coniferaldehyde, benzofuranoid neolignan, α-conidendrin, tsugacetal, isolariciresinol, secoisolariciresinol, matairesinol, hydroxymatairesinol and oxomatairesinol. Among them (+)-tsugacetal is a novel lignan acetal having an α-conidendrin related structure with the acetal methoxy group at the β-position.

Tsuga chinensis Pritz. var. formosana (Hay.) Li et Keng, known as Taiwan hemlock, is one of the major trees indigenous to the high mountain areas of Taiwan. The heartwood of the plant is frequently used in architecture and in the paper industry. Some studies of the chemical constitution of the Tsuga genus have been reported.[1] However, a previous study of the Taiwan hemlock[1d] only found a few compounds. We have resumed the chemical analysis of the heartwood of *Tsuga chinensis*, and found the constitution to be quite different from that of other species.

By means of solvent extraction and column chromatography, eighteen compounds were isolated from the methanolic extract of the heartwood of *Tsuga chinensis Pritz. var. formosana* (Hay.). Compounds **1-2** were identified as β-sitosterol and campesterol (71:29) by comparison with authentic samples on a GC (OV 17 column). Compounds **3-5** were isolated in the form of a mixture and recognized as carboxylic acids from their absorptions at 3400-2500 cm^{-1} in the IR spectrum. Acids **3**, **4** and **5** were determined to be *ei*-, *do*- and *tetra*-consanoic acids according to their parent peaks at *m/z* 312, 340 and 368 in the mass spectra.

Compound **6**, having a parent peak at *m/z* 292, is suggested to be a diterpenoid alcohol for it showed a fragment of *m/z* 274 due to the elimination of a water molecule. In the ^1H NMR spectrum, alcohol **6** revealed resonances of five olefinic protons and four methyl groups. The exocyclic methylene protons showed at δ 4.53 (br, *s*) and 4.83 (br, *s*). The ABX type olefinic protons appeared at δ 5.05 (*dd*, J=10.5, 1.5 *Hz*), 5.20 (*dd*, J=18, 1.5 *Hz*) and 5.95 (*dd*, J=18, 10.5 *Hz*). The four methyl groups appeared as singlets at δ 0.67, 0.80, 0.87 and 1.27, respectively. The most upfield singlet was assigned to Me-10, while the most downfield singlet was assigned to Me-13 geminal to the hydroxyl group. The structure of **6** was thus inferred to be 13-epimanool, $[\alpha]_D^{25}$ +51.3° (c 1.13 in chloroform, lit.[2] +51°).

Compounds **7-10** were found to be phenolics as revealed by absorptions at 3600 (br, OH) and 1600 (aromatic) cm^{-1} in

the IR spectra. Phenol **7**, displaying a methoxy group at δ 3.68 (*s*) in the ^{1}H NMR spectrum, was determined to be *o*-methoxyphenol[3] by comparison with the authentic sample. Phenol **8**, M^+ *m/z* 178, contained characteristic resonances of methoxy (δ 3.93), aldehyde (δ 9.67) and olefinic protons (δ 6.56, 7.38) in the ^{1}H NMR spectrum. The *trans* configuration was apparent by the large coupling constant (16 *Hz*) between the two olefinic protons. Phenol **8** was then identified as coniferaldehyde,[4] mp 82-84° (lit.[4] 84°). Compounds **9** and **10**, isolated in a mixture form, were recognized as esters of dihydroconiferyl alcohol by evidence of the spectroscopic analyses. The IR absorption at 1735 cm^{-1} was attributable to the ester functionality, and the ^{1}H NMR signal at δ 3.85 (*s*) was attributed to the methoxy group. Saponification (NaOH, *aq* MeOH) of **9** and **10** resulted in products of *tetra*- and *hexa*-cosanoic acids. Thus, phenols **9** and **10** were determined to be 3-(4-hydroxy-3-methoxyphenyl)-propyl *tetra*- and *hexa*-cosanates.

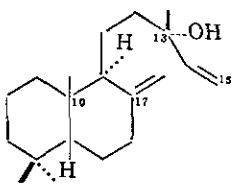
Acetylation of compound **11** (Ac_2O, pyr) yielded a tetraacetate derivative **11a**, *m/z* 514. In the ^{1}H NMR spectrum, two aliphatic acetates appeared at δ 2.04 (*s*) and 2.07 (*s*), while two aromatic acetates appeared at δ 2.29 (6H, *s*). The structure of **11a** was inferred to be a benzofuranoid lignan, cedrusin tetraacetate,[5] for it showed the resonance of a oxymethine proton (H-2) at δ 5.57 (*d*, J=6 *Hz*) in the ^{1}H NMR spectrum. The stereochemistry of C_2 and C_3 was tentatively assigned to the more stable *trans* configuration, which was partially supported by the relatively downfield chemical shift of H-3 (δ 3.6-3.9, *m*) presumably due to the deshielding effect of the adjacent aryl group. Removal of acetyl groups recovered the original cedrusin **11** as verified by a comparison of TLC's.

By comparison with the authentic sample, compound **12** was identified to be α-conidendrin, a abundant lignan lactone commonly found in the plants of Tsuga genus.[1] Compound **13**, $[\alpha]_D^{25}$ +68.3°, had the structure related to α-conidendrin as revealed by analysis of the ^{1}H NMR spectra. Besides two aromatic methoxy groups at δ 3.78 and 3.84, lignan **13** showed an additional methoxy group at δ 3.38 (*s*). The resonance at δ 4.99 (*d*, J=4.5 *Hz*) was attributable to the acetal moiety. From its ^{13}C NMR spectrum, the structure of novel lignan acetal **13**, namely (+)-tsugacetal,[6] was assigned and finally confirmed by a single-crystal X-ray analysis.[7]

Compound **14** was transformed into the tetraacetate derivative **14a**. The ^{1}H NMR of **14a** revealed two aliphatic acetates (δ 2.04, 6H), two aromatic acetates (δ 2.20, 2.28) and two aromatic methoxy groups (δ 3.76, 3.80). Thus, **14** was assigned as isolariciresinol,[8] which was identified with the reduction product of α-conidendrin ($LiAlH_4$, THF). Acetylation of compound **15** resulted in a teteraacetate derivative **15a** (*m/z* 530). Although **15a** had a similar ^{1}H NMR spectrum to that of the resinol acetate **14a**, compound **15a** displayed only fourteen signals in the ^{13}C NMR spectrum. Thus, **15a** was determined to be tetraacetate of secoisolariciresinol[8] to account for the molecular symmetry. The stereochemistry at C_8 and $C_{8'}$ was tentatively assigned by analogy to that of isolariciresinol.

The IR spectrum of compound **16** showed the absorptions of lactone (1750 cm^{-1}) and hydroxyl (3600-3100 cm^{-1}) groups. The ^{1}H NMR spectrum of **16** revealed it was a resinol lactone containing two methoxy groups at δ 3.79 (6H, *s*). Since **16** had a molecular weight (*m/z* 358) two units higher than that of α-conidendrin, compound **16** was determined to be matairesinol.[1b,9] Compound **17** was a resinol lactone as inferred by the analysis of IR and ^{1}H NMR spectra. The mass spectrum of **17** revealed the parent peak at *m/z* 374, and a fragment at *m/z* 356 due to elimination of water. Thus, **17** was determined to be hydroxymatairesinol[1b,10] and to contain an aliphatic hydroxyl group

at $C_{7'}$. The structure was supported by cyclization of **17** (*aq* HOAc, HCl cat.) to α-conidendrin, albeit the stereochemistry at $C_{7'}$ has not yet been clearly deteamined. Compoud **18** had absorptions of two carbonyl groups at 1760 and 1660 cm^{-1}, representing the lactone and ketone functionalities, respectively. The ^1H NMR of **18** showed six aromatic protons, of which two (H-2′ and H-6′) were apparently deshielded to lower fields (δ 7.10 and 7.30) by the keto group. Structure **18** was assigned to oxomatairesinol and identified with the oxidation product of hydroxymatairesinol **17** (PCC, acetone).



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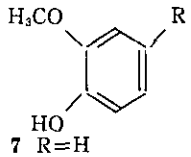
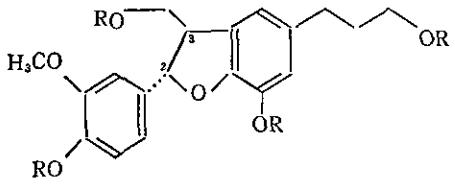
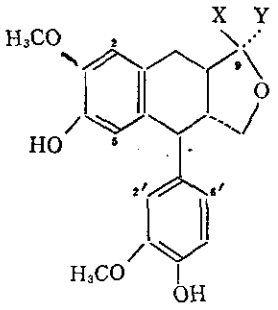


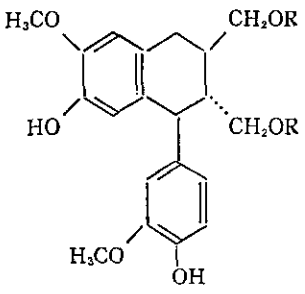
7 R=H
8 R=CH=CHCHO
9 R=$(CH_2)_3O_2C(CH_2)_{22}CH_3$
10 R=$(CH_2)_3O_2C(CH_2)_{24}CH_3$



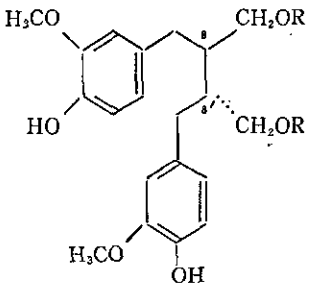
11 R=H
11a R=Ac



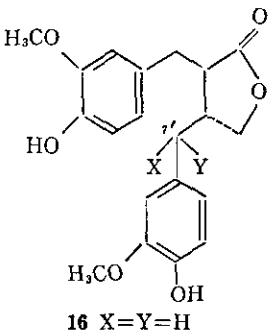
12 X, Y=O
13 X=OCH_3, Y=H



14 R=H
14a R=Ac



15 R=H
15a R=Ac



16 X=Y=H
17 X=OH, Y=H
18 X, Y=O

EXPERIMENTAL SECTION

General

Melting points were obtained on Yanagimoto Micromelting Point Apparatus, and are uncorrected. Infrared spectra were taken as film of KBr or neat oil on the Jasco Infrared spectrophotometer Model IRA-1. ^1H NMR spectra were recorded on the Varian EM-390 or Jeol JNM-FX-100 spetrometers using TMS as internal standard. ^{13}C NMR spectra were recorded on the Jeol JNM-FX-100 spec-

trometer using $CDCl_3$ *as internal standard.* Mass spectra were recorded on the Jeol JMS-300 Mass spectrometer operating at an ionizing voltage of 70 *eV*. Specific rotations were obtained on the Jasco *Dip-180 Digital Polarimeter. Gas chroma*tography was carried out on the Hewlett Packard 5710 A Gas Chromatograph. The silica gels used for column and thin layer chromatographies were purchased from the Merck Co.

Plant material:

The wood of *Tsuga chinensis Pritz. var. formosana* (Hay.) was collected in May 1981 *in the high mountain areas (2-3 km) of* Nan-Tou County, Taiwan (南投縣望鄉). The heartwood of the plant was sliced, air dried (870 *g*), and exhaustively extracted with methanol.

Method:

The methanolic extract of the heartwood was consecutively partitioned with hexane and ethyl acetate. The hexane soluble portion was *concentrated in vacuo* to give 20.9 *g* of oil. The combined ethyl acetate extract was concentrated and taken up with chloroform. The chloroform soluble portion resulted in 130 *g* of oil after removal of solvent. *The oils from* the hexane and chloroform soluble portions were individually subjected to column chromatography (SiO_2) and eluted exhaustively with gradients of hexane, ethyl acetate and methanol. From the hexane portion, six compounds of β-sitosterol **1** (287 *mg*), campesterol **2** (116 *mg*), 13-epimanool **6** (50 *mg*); *o*-methoxyphenols **7** (252 *mg*), ester **9** (70 *mg*), and ester **10** (10 *mg*) were isolated. From the chloroform portion, twelve compounds of carboxylic acids **3-5** (65 *mg*); coniferaldehyde **8** (20 *mg*), lignan **11** (30 *mg*), α-conidendrin **12** (4.7 *g*), tsugacetal **13** (320 *mg*), and resinols **14** (170 *mg*), **15** (100 *mg*), **16** (1 *g*), **17** (1.8 *g*) and **18** (35 *mg*) were isolated.

13-Epimanool 6:

Colorless oil, $[\alpha]_D^{25}$ +51.3° (c 1.13, chloroform, lit.[2] +51°). IR (neat) 3440 (OH), 3080 (=CH), 1643 (C=C), 992, 916 ($CH=CH_2$), 886 ($-RC=CH_2$) cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.67 (3H, *s*, Me-10), 0.80 (3H, *s*, Me-4), 0.87 (3H, *s*, Me-4), 1.27 (3H, *s*, Me-13), 4.53 (1H, br, *s*, H-17), 4.83 (1H, br, *s*, H-17), 5.05 (1H, *dd*, J=10.5, 1.5 *Hz*, H-15), 5.20 (1H, *dd*, J=18, 1.5 *Hz*, H-15), 5.95 (1H, *dd*, J=18, 10.5 *Hz*, H-14). MS *m/z* (rel. intensity) 290 (1, M^+), 272 (14), 257 (40), 137 (100), 71 (36).

Coniferaldehyde 8:

Pale yellow crystals, mp 82-84° (from EtOH; lit.[4] 84°). IR (neat) 3400, 1650, 1580 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.93 (3H, *s*, OCH_3), 6.56 (1H, *dd*, J=16, 7.5 *Hz*, H-2), 6.95 (1H, *d*, J=8 *Hz*, H-5'), 7.00 (1H, br, *s*, H-2'), 7.12 (1H, *dd*, J=8, 1.5 *Hz*, H-6'), 7.38 (1H, *d*, J=16 *Hz*, H-3), 9.67 (1H, *d*, J=7.5 *Hz*, CHO). MS *m/z* (rel. intensity) 178 (56, M^+), 137 (19), 28 (100).

Cedrusin 11:

Treatment of a pyridine solution of **11** with acetic anhydride overnight afforded the tetraacetate derivative **11a.** IR (neat) 1765 (acetate), 1738 (aromatic acetate), 1605, 1490 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.80-2.10 (2H, *m*), 2.04 (3H, *s*, CH_3CO_2), 2.07 (3H, *s*, CH_3CO_2), 2.29 (6H, *s*, two aromtic acetates), 2.67 (2H, *t*, J=7.5 *Hz*, $ArCH_2$), 3.60-3.90 (1H, *m*, H-3), 3.82 (3H, *s*, OCH_3), 4.10 (2H, *t*, J=6 *Hz*, CH_2CH_2OAc), 4.35 (2H, *m*, CH_2OAc), 5.57 (1H, *d*, J=6 *Hz*, H-2), 6.76-7.12 (5H, *m*, aromatic H). MS *m/z* (rel. intensity) 514 (8, M^+), 492 (10), 454 (18), 412 (42), 370 (100). Removal of acetyl groups revealed the original lignan **11** as verified by a comparison of thin layer chromatographs.

Tsugacetal 13:

Colorless crystals, mp 188-190° (from EtOH). $[\alpha]_D^{25}$ +68.3° (c 0.93 in acetone). *IR (KBr) 3400, 1600, 1580, 1500 cm*$^{-1}$. UV (EtOH, λ_{max}) 212 (ε 1.5×10^4), 283 (ε 6.9×10^3) *nm*. ^1H NMR ($CDCl_3$) δ 1.85-3.11 (4H, *m*; H-7, H-8, H-8'), 3.38 (3H, *s*, C_9-OCH_3), 3.45-3.98 (3H, *m*; H-7', H-9'), 3.78 (3H, *s*, $ArOCH_3$), 3.84 (3H, *s*, $ArOCH_3$), 4.99 (1H, *d*, J=4.5 *Hz*, H-9), 5.51 (1H, *s*, ArOH), 5.65 (1H, *s*, ArOH), 6.34 (1H, *s*, H-5), 6.55 (1H,

s, H-2), 6.58 (1H, *dd*, J=7.8, 1.5 *Hz*, H-6'), 6.67 (1H, *d*, J=1.5 *Hz*, H-2'), 6.81 (1H, *d*, J=7.8 *Hz*, H-5'). ^{13}C NMR ($CDCl_3$, *ppm*) 29.2 (C-7), 46.0 (C-8, C-8'), 50.9 (C-7'), 54.9 (acetal OCH_3), 55.9 (ArOCH_3), 72.3 (C-9'), 105.0 (C-9), 110.4 (C-2), 111.1 (C-2'), 114.2 (C-5'), 115.0 (C-5), 121.5 (C-6'), 127.9 (C-1), 132.6 (C-1'), 136.2 (C-6), 143.5 (C-4), 144.3 (C-4'), 145.0 (C-3), 146.4 (C-3'). MS *m/z* (rel. intensity) 372 (36, M^+), 341 (14), 340 (100), 310 (27), 216 (27), 137 (22). *Anal. Calc.* for $C_{21}H_{24}O_6$ requires C, 67.77; H, 6.45. *Found*: C, 67.79; H, 6.55.

Acetylation of tsugacetal **13** (Ac_2O, pyr) afforded crystalline diacetate, mp 87-88°. $[\alpha]_D^{25}$ +30.9° (c 1.0 in acetone). IR (KBr) 1750 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.19 (3H, *s*, O_2CCH_3), 2.27 (3H, *s*, O_2CCH_3), 2.27-3.17 (4H, *m*, H-7, H-8, H-8'), 3.37 (3H, *s*, acetal OCH_3), 3.42-3.99 (3H, *m*, H-7', H-9'), 3.75 (3H, *s*, OCH_3), 3.82 (3H, *s*, OCH_3), 4.98 (1H, *d*, J=4.5 *Hz*, H-9), 6.46 (1H, *s*, H-5), 6.65 (1H, *s*, H-2'), 6.69 (1H, *d*, J=8 *Hz*, H-6'), 6.74 (1H, *s*, H-2), 6.95 (1H, *d*, J=8 *Hz*, H-5'). ^{13}C NMR ($CDCl_3$, *ppm*) 20.6 ($\underline{C}H_3CO_2$), 29.5 (C-7), 45.7 (C-8), 46.1 (C-8'), 50.8 (C-7'), 54.8 (acetal OCH_3), 55.8 (ArOCH_3), 71.9 (C-9'), 104.6 (C-9), 111.9 (C-2), 112.7 (C-2'), 120.6 (C-6'), 122.6 (C-5'), 123.3 (C-5), 131.4 (C-6), 135.2 (C-1), 137.6 (C-4), 138.4 (C-1'), 142.8 (C-4'), 149.2 (C-3), 151.1 (C-3'), 168.6 ($CH_3\underline{C}O_2$).

Isolariciresinol 14:

Tetraacetate of **14** was crystallized from methanol, and recrystallized from ethyl acetate/hexane=1:3, mp 162-164° (lit.[8] 163-164°), $[\alpha]_D^{25}$ −3.5° (c 1.08 in acetone, lit.[8] −3.5°). IR (KBr) 1740 (acetate), 1610, 1600, 1500 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.04 (6H, *s*, two CH_3CO_2), 2.20 (3H, *s*, ArO_2CCH_3), 2.28 (2H, *m*, H-8, H-8'), 2.88 (2H, *d*, J=7.5 *Hz*, H-7), 3.76 (3H, *s*, OCH_3), 3.80 (3H, *s*, OCH_3), 3.80-4.24 (5H, *m*, H-9, H-7', H-9'), 6.44 (1H, *s*, H-5), 6.70 (3H, *m*, H-2, H-2', H-6'), 6.98 (1H, *d*, J=8 *Hz*, H-5'). MS *m/z* (rel. intensity) 528 (6, M^+), 486 (12), 468 (21), 426 (39), 384 (24), 366 (40). Removal of acetyl groups revealed the original isolariciresinol **14** as verified by a comparison of thin layer chomatographs.

Secoisolariciresinol 15:

Tetraacetate derivative of **15** was prepared and purified by column chromatography. $[\alpha]_D^{25}$ −10.3° (c 1.31 in acetone, lit.[9] −8°). IR (neat) 1760, 1740 cm^{-1}. MS *m/z* (rel. intensity) 530 (4, M^+), 488 (38), 446 (26), 386 (11), 137 (100). ^{1}H NMR ($CDCl_3$) δ 2.05 (6H, *s*, two CH_3CO_2), 2.17 (2H, *m*, H-8, H-8'), 2.29 (6H, *s*, two CH_3CO_2), 2.67 (4H, *d*, J=7.5 *Hz*, H-7, H-7'), 3.74 (6H, *s*, two OCH_3), 4.10 (2H, *dd*, J=11.5 *Hz*), 4.18 (2H, *dd*, J=11.5 *Hz*), 6.59 (2H, *dd*, J=8, 1.5 *Hz*, H-6, H-6'), 6.65 (2H, br, *s*, H-2, H-2'), 6.71 (2H, *d*, J=8 *Hz*, H-5, H-5'). ^{13}C NMR ($CDCl_3$, *ppm*) 20.8 ($CH_3\underline{C}O_2$), 21.0 ($CH_3\underline{C}O_2$), 35.2 (C-7, C-7'), 39.6 (C-8, C-8'), 55.8 (OCH_3), 64.3 (C-9, C-9'), 113.0, 121.0, 122.7, 138.2, 138.5, 151.0, 169.0 ($CH_3\underline{C}O_2$), 171.0 ($CH_3\underline{C}O_2$). Removal of the acetyl groups recovered the original secoisolariciresinol **15**, mp 112-114°.

Matairesinol 16

Matairesinol was crystallized from ethanol/water=2:1, and recrystallized from chloroform or 30% acetic acid, mp 117-119° (lit.[9] 119°), $[\alpha]_D^{25}$ −42.8° (c 0.53 in acetone, lit.[9] −45°). IR (KBr) 3600-3100, 1750 (lactone), 1600, 1510 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.50 (4H, br, *s*, H-7', H-8, H-8'), 2.90 (2H, br, *s*, H-7), 3.79 (6H, *s*, two OCH_3), 3.80-4.30 (2H, *m*, two H-9'), 5.70 (2H, *s*, two OH), 6.36-6.90 (6H, *m*, aromatic H). MS *m/z* (rel. intensity) 358 (31, M^+), 221 (5), 194 (4), 137 (100). Diacetate of **16**, ^{1}H NMR ($CDCl_3$) δ 2.28 (6H, *s*, two CH_3CO_2), 2.50-3.25 (6H, *m*, H-7, H-7', H-8, H-8'), 3.74 (6H, *s*, two OCH_3), 3.80-4.30 (2H, *m*, H-9'), 6.50-7.00 (6H, *m*, aromatic H).

Hydroxymatairesinol 17:

$[\alpha]_D^5$ −6.9° (c 4.15 in acetone, lit.[10] −12°). IR (neat) 3600-3100 (OH), 1750 (lactone), 1610, 1515 cm^{-1}. ^{1}H NMR (CD_3OD) δ 2.40-3.00 (4H, *m*, H-7, H-8, H-8'), 3.75 (3H, *s*, OCH_3), 3.79 (3H, *s*, OCH_3), 4.07 (1H, *m*, H-9'), 4.30 (1H, *m*, H-9'), 4.63 (1H, *d*, J=6 *Hz*, H-7'), 6.40-6.82 (6H, *m*, aromatic H). MS

m/z (rel. intensity) 374 (31, M^+), 356 (8), 153 (100), 137 (68). A solution of **17** in 30% acetic acid was added a few drops of concentrated hydrochloric acid and allowed to stay for 3 days. The resulting solids, mp 255-256°, were identified as α-conidendrin by comparison with the authentic sample.

Oxomatairesinol 18

A crystallization sample from $CHCl_3$/EtOH=19:1, mp 72-74°. IR (KBr) 3600-3100, 1760 (lactone), 1660 (ArC=O), 1590, 1515 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.95 (2H, *m*, H-7), 3.47 (1H, *m*, H-8), 3.68 (3H, *s*, OCH_3), 3.86 (3H, *s*, OCH_3), 3.80-4.40 (3H, *m*, H-8′, H-9′), 5.54 (1H, *a*, OH), 6.27 (1H, *s*, OH), 6.52 (1H, *dd*, J=8, 2 *Hz*, H-6), 6.58 (1H, br, *s*, H-2), 6.64 (1H, *d*, J=8 *Hz*, H-5), 6.79 (1H, *d*, J=8 *Hz*, H-5′), 7.10 (1H, *dd*, J=8, 2 *Hz*, H-6′), 7.30 (1H, *d*, J=2 *Hz*, H-2′). MS *m/z* (rel. intensity) 372 (32, M^+), 221 (12), 194 (100), 151 (53), 137 (46). Oxidation of hydroxymatairesinol **17** with pyridinium chlorochromate in acetone for 1 day gave **18**. Diacetate of **18**, ^1H NMR ($CDCl_3$) δ 2.27 (3H, *s*, CH_3CO_2), 2.32 (3H, *s*, CH_3CO_2), 3.06 (2H, *d*, J=6 *Hz*, H-7), 3.58 (1H, *m*, H-8), 3.68 (3H, *s*, OCH_3), 3.87 (3H, *s*, OCH_3), 4.00-4.50 (3H, *m*, H-8′, H-9′), 6.62 (1H, *dd*, J=8, 2 *Hz*, H-6), 6.73 (1H, br, *s*, H-2), 6.92 (1H, *d*, J=8 *Hz*, H-5), 7.11 (1H, *d*, J=8 *Hz*, H-5′), 7.22 (1H, *dd*, J=8, 2 *Hz*, H-6′), 7.48 (1H, *d*, J=2 *Hz*, H-2′).

Acknowledgement: The authors thank the National Science Council for financial support.

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(7) The Authors are grateful to Professor Y. Wang and Miss M.C. Cheng for the Single-Crystal X-ray Analysis of (+)-Tsugacetal.

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(*Received December 3, 1984*)