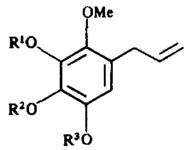
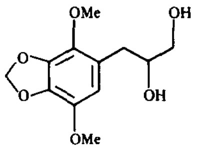


1a R^1——R^2 = CH_2, R^3 = Me
1b R^1 = Me, R^2 = R^3 = CH_2
1c R^1 = R^3 = Me, R^2 = H



2

Transformation of **1c** *in* **2**. A soln of OsO_4 (100 mg) in C_5H_5N (1 ml) was added to a soln. of **1c** (90 mg) in C_5H_5N (0.5 ml). After stirring (3 hr, room temp.) a soln of $NaHSO_3$ (120 mg) in C_5H_5N (3 ml) and H_2O (2 ml) was added and the mixture stirred for 30 min before addition of 10% HCl (3 ml). Stirring continued for 30 min and the mixture then extracted with $CHCl_3$. The organic layer was washed, dried and evapd. The residue was purified (TLC, Si gel) to give **2**.

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4,4′-DIHYDROXYCHALCONE FROM THE HEARTWOOD OF *CHAMAECYPARIS OBTUSA*

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Key Word Index—*Chamaecyparis obtusa*; Cupressaceae; heartwood; phenolic extractives; 4,4′-dihydroxychalcone.

Abstract—A new chalcone, 4,4′-dihydroxychalcone was isolated from the heartwood of *Chamaecyparis obtusa*. The structure was elucidated by direct comparison with a synthetic sample.

INTRODUCTION

Japanese cypress (*Chamaecyparis obtusa* Endl.), is highly valued for its pink heartwood. The phenolic extractives responsible for this colour are hinokinin, hinokiresinol, hinokione and hinokiol [1–7]. The present authors while reinvestigated the basis of this colour found, in addition to four known compounds (Sawaranin, cryptoresinol, 3-methoxyhinokiresinol and isocryptoresinol) [8–10], one new substance which is now described in this note.

RESULTS AND DISCUSSION

The phenolic part of ethyl acetate-soluble fraction from the methanolic extract of the heartwood of *C. obtusa* was acetylated, and this eventually provided the acetate (**1b**) of the new compound, in a yield of 0.001% based on dried heartwood powder.

Upon preliminary TLC analysis of the original ethyl acetate fraction, compound **1a** appeared as a yellow spot which was positive to 2,4-dinitrophenylhydrazine and diazotized sulphanilic acid reagents. The CI- and EIMS spectra on the eluate (**1a**) indicated a M^+ of 240 and the UV spectra suggested it to be a chalcone [12]. It was confirmed from mass spectrometry that the molecular formula of **1b** was $C_{15}H_{10}O_3\,(Ac)_2$. The chemical shifts of two acetoxyl groups in the ^{1}H NMR spectrum suggested that they had originated as phenolic groups. Two pairs of A_2B_2 system signals revealed the presence of two 1,4-disubstituted phenyl nuclei. The remaining signal of the AB system was due to *trans*-ethylenic protons adjacent to electrophilic groups. The presence of a carbonyl group was confirmed by the chemical shift of the signal in the ^{13}C NMR spectrum and absorption band in the IR spectrum. The structure of **1b** as 4,4′-diacetoxychalcone was finally confirmed by the direct comparison with a synthetic sample prepared from the condensation of *p*-hydroxyacetophenone and *p*-hydroxybenzaldehyde, followed by acetylation. **1a** also gave a dimethyl ether **1c**. The presence of **1a** in fresh Hinoki heartwood was confirmed by co-HPLC with the synthetic sample. This is the first report of 4,4′-dihydroxychalcone in nature.

EXPERIMENTAL

Plant materials. Heartwoods of *Chamaecyparis obtusa* were collected at the Experimental Forest of Gifu University, Hagiwara, Gifu Pref (April, 1986).

Isolation. The heartwood powder of *C. obtusa* was extracted with MeOH and the concd extract fractionated with *n*-hexane, Et_2O and EtOAc successively. The EtOAc-soluble fraction was further fractionated with 5% NaOH aq. soln. The phenolic part was acetylated with Ac_2O in pyridine. The acetylated materials applied to silica gel column ($CHCl_3$ as eluent), followed by further purification on fractional recrystallization. In addition to known compounds, 4,4′-diacetoxychalcone (**1b**) was isolated and purified.

4,4′-*Diacetoxychalcone* (**1b**). Needles (Et_2O and Me_2CO), mp 125–126 (126 [13]) TLC R_f value (C_6H_6–EtOAc–AcOH, 40:10:1): 0.61. ^{1}H NMR δ(ppm) ($CDCl_3$): 2.30 (3H, *s*, aro-OAc), 2.32 (3H, *s*, aro-OAc), 7.40 (4H, *dd* (A_2B_2 system), $J = 8.4$ Hz, aro-$H_{2,3,5,6}$), 7.62 [2H, *dd* (AB system), $J = 15.7$ Hz, —CH=CH–(trans)], 7.64 (4H, *dd* (A_2B_2 system), $J = 8.8$ Hz, aro–$H_{2',3',5',6'}$). ^{13}C NMR (ppm) ($CDCl_3$): 21.0, 21.1 (2 CO$\underline{\text{Me}}$), 121.8 ($C_{3',5'}$), 121.9, 122.0, 122.2 ($C_{3,5'}$ C_α), 129.5 ($C_{2,6}$), 129.9, 130.0 ($C_{2',6'}$), 132.4 (C_1), 135.6 ($C_{1'}$), 143.8 (C_β), 152.3 ($C_{4'}$), 154.1 ($C_{4'}$), 168.8, 169.0 (2–$\underline{\text{C}}$OMe), 188.9 (–ϕ–CO–). IR ν_{max}^{KBr} (cm^{-1}): 1755 (CO), 1670 (CO). EIMS m/z (%): 324 (M^+) (10), 282 [$M - 42^+$] (61), 240 [$M - 42 \times 2^+$] (100), 239 (29), 223 (13), 222 (15), 212 (10), 211 (12), 165 (8), 146 (21), 145 (17), 121 (21), 119 (8). UV λ_{max} (MeOH) (nm): 228, 315.

Synthesis of 4,4′-*dihydroxychalcone* (**1a**). 4,4′-Dihydroxychalcone (**1a**) was obtained by condensing *p*-hydroxyacetophenone and *p*-hydroxybenzaldehyde in the presence of aq. KOH.

4,4′-*Dihydroxychalcone* (**1a**). Yellow needles (aq. MeOH), mp. 207–208° (200°[13]). TLC (C_6H_6–EtOAc–AcOH, 40:20:1): 0.62. HPLC (Unisil Q, EtOAc–*n*-$C_6H_8 = 2:1$; UV monitor 350 nm) (min): 7.5. UV λ_{max}^{MeOH} (nm): 234, 350 (23 700); $\lambda_{max}^{MeOH+NaOMe}$ (nm): 248, 350 (sh), 413; $\lambda_{max}^{MeOH+NaOAc}$ (nm): 240 (sh), 354; $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ (nm): 350. EIMS *m/z* (%): 240 (M^+) (100), 239 (42), 223 (14), 212 $[M - CO]^+$ (12), 211 (13), 165 (10), 147 ($O^+\equiv$C–C=C–ϕ–OH) (29), 146 (28), 121 [HO–ϕ–CO]$^+$ (38), 119 [HC=CH–ϕ–OH]$^+$ (15), 118 (10), 94 (12), 93–HO–ϕ]$^+$ (17), 91 (16). CIMS (*iso*–C_4H_{10}) *m/z*: 242 (52), 241 $[M+H]^+$ (100), 240 $[M]^+$ (18), 121 (28). ^{1}H NMR δ(ppm) (Me_2CO): 7.24 [4H, *dd* (A_2B_2 system), $J = 8.4$ Hz, aro – $H_{2,3,5,6}$], 7.46 [4H, *dd* (A_2B_2 system), $J = 8.8$ Hz, aro – $H_{2',3',5',6'}$), 7.70 [2H, *dd* (AB system), $J = 15.8$ Hz, – CH = CH – (*trans*)]. 4,4′-Diacetoxychalcone (**1b**) was prepared from synthetic **1a** by the Ac_2O–pyridine method.

4,4′-*Dimethoxychalcone* (**1c**). 4,4′-Dimethoxychalcone (**1c**) was prepared with the treatment of CH_2N_2–Et_2O. Pale yellow needles (MeOH), mp 102–103. ^{1}H NMR δ(ppm) ($CDCl_3$): 3.72 (3H, *s*, aro-OMe), 3.76 (3H, *s*, aro-OMe), 7.22 (4H, *dd* (A_2B_2 system), $J = 8.4$ Hz, aro-$H_{2,3,5,6}$), 7.34 [2H, *dd* (AB system), $J = 15.8$ Hz, –CH=CH–(*trans*)], 7.45 (4H, *dd* (A_2B_2 system), $J = 8.8$ Hz, aro-$H_{2',3',5',6'}$). EIMS *m/z* (%): 268 $[M]^+$ (100), 267 (32), 254 $[M - 14]^+$ (10), 253 (40), 240 $[M - 28]^+$ (10), 237 (23), 225 (26), 165 (10), 161 (22), 160 (21), 135 (37), 123 (21), 120 (10), 108 (18), 107 (15).

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