Pergamon

Tetrahedron Letters 42 (2001) 2985–2986

TETRAHEDRON
LETTERS

A novel 7(6→2)abeoabietane-type diterpene, obtusanal, from the Heartwood of *Chamaecyparis obtusa* var. *formosana*

Yueh-Hsiung Kuo* and Chia-Hsien Chen

Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

Received 27 October 2000; revised 10 January 2001; accepted 9 February 2001

Abstract—A novel 7(6→2)abeoabietane-type diterpene, obtusanal (**1**), together with a known 12-hydroxy-6,7-secoabieta-8,11,13-triene-6,7-dial (**2**) isolated from the heartwood of *Chamaecyparis obtusa* var. *formosana*, were elucidated on the basis of 2D-NMR data. The biosynthesis of **1** was proposed deriving from 12-hydroxy-3-oxo-6,7-secoabieta-8,11,13-triene-6,7-dial (**6**) via aldol condensation. © 2001 Elsevier Science Ltd. All rights reserved.

The *Chamaecyparis obtusa* var. *formosana* (Taiwan hinoki; Cupressaceae) can live for over a thousand years. It is a huge tree indigenous to Taiwan and grows at 1300–2800 m above sea level. It is decay and white-ant resistant and has thus been classified as a species with excellent durability. Its timber is yellowish-red with a distinguished purple–pink streak. In a previous paper,[1] we reported one novel diterpene and three new abietane-type diterpenes from the wood of this tree. Further detailed reinvestigation of the wood has yielded a novel 7(6→2)abeoabietane diterpene, obtusanal (**1**), and a known 12-hydroxy-6,7-secoabieta-8,11,13-triene-6,7-dial (**2**).[2] The structures of this novel diterpene were elucidated based on the following spectral evidence.

Obtusanal (**1**) suggested the presence of phenolic acetyl, acetoxyl, aldehyde, cyclohexanone and phenyl groups ascribing to its IR absorption bands at 1757, 1734, 1725, 1706, 1610 and 1514 cm^{-1}, respectively. A ^1H NMR spectrum indicated the presence of two singlet methyl groups [δ 0.44 (H-18), 1.01 (H-19)], an isopropyl group attached on the phenyl [δ 1.16, 1.17 (each 3H, d, $J=6.9$ Hz, H-16, H-17), 2.96 (1H, sep, $J=6.9$ Hz)], two acetyl groups [δ 2.12, 2.32], an aldehyde group [δ 9.76 (d, $J=6.9$ Hz)], three methine protons [δ 2.48 (dd, $J=6.9$, 1.9 Hz, H-5), 3.39 (dd, $J=7.4$, 4.7 Hz, H-2) and 6.15 (d, $J=7.4$ Hz, H-7)], two methylene protons [δ 2.09 (1H, dd, $J=14.3$, 1.9 Hz, H-1_α), 2.53 (1H, dd, $J=14.3$, 4.7 Hz, H-1_β)] and two singlet *para*-phenyl protons [δ 6.96 (H-11) and 7.13 (H-14)]. The lower field signal at δ 6.15 was assigned as a benzylic proton attached to an acetoxyl group. The MS of **1** had an exact mass of m/z 414.2050 indicating the molecular formula $C_{24}H_{30}O_6$. Removal of two acetyl units from the formula $C_{24}H_{30}O_6$ of **1** would afford a parent diterpene with two methyl groups, one isopropylphenol moiety and an aldehyde group. Compound **1** has an index of hydrogen deficiency (IHD) of 10 on account of its molecular formula. As well as four carbonyl groups and one phenyl group, compound **1** has two rings. Based on the above physical data, the skeleton of **1** is similar to that of **2**, except an aldehyde group linked to phenyl in **2** is converted to an acetoxyl, and a benzylic carbon connecting to ring A. The COSY spectrum exhibited the following results: H-5/H-6; H-2/H-1_β, -7; H-1_α/H-1_β, -5. The carbonyl absorption at 1706 cm^{-1} and H-5 having W-form coupling ($J=1.9$ Hz) with H-1_α confirmed it has the same moiety as cyclohexanone. The ^{13}C NMR data[3] exhibited four methyl groups, four substituted phenyl including one oxygenated and two acetyl signals. Two methyl groups (δ 1.01 and 0.44) and a methine proton (δ 3.39) showed HMBC correlation to the ketone group indicating that they were near to this ketone. In addition to the following HMBC correlation, H-5/C-9; H-20/C-9; H-7/C-8, -9; H-1/C-3, -9, could describe the gross structure as **1**. As to its relative stereochemistry, it can be demonstrated by NOESY technique (H-6/H-1_β, H-5/H-18, -19, CH_3COO-C-7/H-1α, -2, H-7/H-14, H-17/H-14 showing NOESY correlation). H_3-18 appeared at highfield (δ 0.44) due to its α-axial orientation which was shielded by an aromatic group. The structure of **1** is a novel 7(6→2)abeoabietane skeleton. The proposed retrobiotransform of **1** is shown in Fig. 1. The precursor of **1** is diol **3** derived from 12-hydroxy-3-oxo-6,7-

---

Keywords: *Chamaecyparis obtusa* var. *formosana*; 7(6→2)abeoabietane-type diterpene; obtusanal.

* Corresponding author.

0040-4039/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(01)00249-0

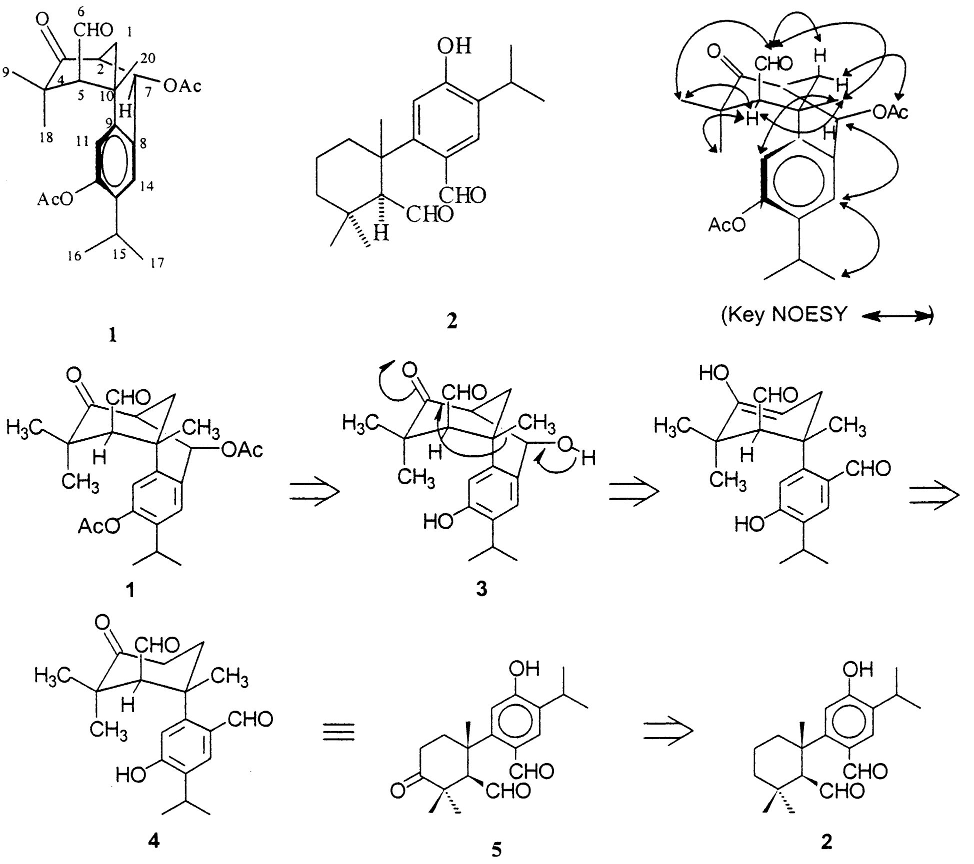

Figure 1. Retrobiotransformation of **1**.

secoabieta-8,11,13-triene-6,7-dial (**5**) via aldol condensation. Compound **5** is a biooxidative product from **2**. Compound **1** was assumed to have the (5*S*)-configuration analogous to those abietanes found in the plants of the Cupressaceae[2,4] and Taxodiaceae families.[5] The CD spectrum of **1** showed a negative cotton effect at 330 nm ($\theta = -30400$). C_7 and C_{18} disubstituents each canceled the effect, therefore the aldehyde group must lie in the upper right (–). (5*S*)-Configuration can be concluded.

Acknowledgements

This research was supported by the National Science Council of the Republic of China.

References

1. (a) Kuo, Y. H.; Chen, C. H.; Huang, S. L. *Chem. Pharm. Bull.* **1998**, *46*, 181 and references cited therein; (b) Kuo, Y. H.; Chen, C. H.; Huang, S. L. *J. Nat. Prod.* **1998**, *61*, 829.
2. Fang, J. M.; Jan, S. T.; Cheng, Y. S. *J. Chem. Res. (S)* **1986**, 350.
3. Physical data for two compounds: Compound **1**: liquid; $[\alpha]_D$ +5.5 (*c* 0.3, $CHCl_3$); HR-EIMS *m*/*z* 414.2050 (calcd 414.2042 for $C_{24}H_{30}O_6$); EIMS *m*/*z* (%): 414 (M^+, 12), 242 (25), 200 (100), 185 (23), 159 (28). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.1 (C-1), 46.5 (C-2), 212.5 (C-3), 44.1 (C-4), 69.6 (C-5), 202.5 (C-6), 71.9 (C-7), 131.9 (C-8), 143.4 (C-9), 35.4 (C-10), 119.7 (C-11), 148.5 (C-12), 140.1 (C-13), 125.4 (C-14), 27.5 (C-15), 22.8 (C-16), 22.8 (C-17), 25.7 (C-18), 29.7 (C-19), 27.2 (C-20), 21.2 and 170.8 (CH_3COOC-7), 20.9 and 169.4 (CH_3COOC-12). Compound **2**: mp 191–192°C; $[\alpha]_D$ +20.0 (*c* 1.2, $CHCl_3$); EIMS *m*/*z* (%): 316 (M, 45), 301 (40), 287 (52), 273 (32), 231 (35), 217 (35), 203 (100);CD (MeOH) $[\theta]_{330}$-30400, $[\theta]_{292}$+22080.
4. (a) Fang, J. M.; Shan, C. M.; Cheng, Y. S. *J. Chin. Chem. Soc.* **1986**, *33*, 245; (b) Fang, J. M.; Lai, L. J.; Cheng, Y. S. *J. Chin. Chem. Soc.* **1986**, *33*, 265.
5. Lin, W. H.; Fang, J. M.; Chang, Y. S. *Phytochemistry* **1995**, *40*, 871.