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TERPENOIDS FROM *CALOCEDRUS FORMOSANA*

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Key Word Index—*Calocedrus formosana*; Cupressaceae; wood; 1-oxohinokiol; naphthaldehyde sesquiterpene; naphthoate sesquiterpene; 3,4-dihydro analogues; hinokiol; shonanol.

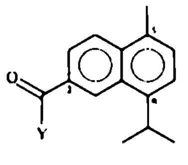
Abstract—A novel diterpene, 1-oxohinokiol was isolated from the acetone extract of the wood of *C. formosana*. Four novel sesquiterpenes, 5-methyl-8-isopropyl-2-naphthalenecarboxaldehyde, methyl 5-methyl-8-isopropyl-2-naphthalenecarboxylate and their 3,4-dihydro analogues were also isolated. The structural assignments were based on the spectroscopic analysis and confirmed by chemical correlation.

INTRODUCTION

Calocedrus formosana, a member of the Cupressaceae, is an economically important tree indigenous to Taiwan [1]. In a recent study of the constituents of the wood, we found a lignan dihydroanhydride, namely (+)-calocedrin [2]. We report now some novel terpenoid constituents isolated from the wood.

RESULTS AND DISCUSSION

The acetone extract of the wood of *C. formosana* was subjected to chromatography on silica gel. The terpenoidal components **1**–**7** were isolated by elution with gradients of hexane–ethyl acetate. Compound **1**, M^+ at m/z 212, showed an IR absorption at 1685 cm^{-1} attributable to a conjugated carbonyl group. The ^1H NMR spectrum of **1** exhibited the resonances of an aromatic methyl group (δ2.70, *s*), an aldehyde group (δ10.20, *s*), an isopropyl group and five aromatic protons. Compound **1** was recognized as the sesquiterpene 5-methyl-8-isopropyl-2-naphthalenecarboxaldehyde; this is the first report of its occurrence in nature although a synthetic sample has been reported [3]. Compound **2**, M^+ at m/z 214, also showed the IR absorption (1665 cm^{-1}) of a conjugated carbonyl group. The ^1H NMR spectrum revealed characteristic resonances of an aromatic methyl (δ2.28, *s*), an isopropyl group, an olefinic proton (δ7.64, *s*), an aldehyde proton (δ9.70, *s*) and two *ortho*-aromatic protons. Compound **2** was readily transformed into compound **1** by oxidation with chloranil in refluxing benzene. Thus, the structure of compound **2** was confirmed to be the 3,4-dihydro analogue of **1**. Compound **3**, M^+ at m/z 242, was recognized as a methyl ester of an aromatic acid as evidenced by the IR absorption at 1720 cm^{-1} and the characteristic resonance of a methyl group at δ3.99 (*s*) in the ^1H NMR spectrum. The structure of **3** was revealed to be closely related to that of **1** by comparison of their ^1H NMR spectra. Reduction of ester **3** ($LiAlH_4$, Et_2O, 0°) gave an alcohol product, which was then oxidized by manganese dioxide (hexane, 25°) to afford compound **1**. The novel natural sesquiterpene **3** was thus determined to be methyl 5-methyl-8-isopropyl-2-naphthalene carboxylate. Compound **4**, M^+ at m/z 244, was also a methyl ester as revealed by the IR absorption at 1710 cm^{-1} and the resonance of a methyl group at δ3.83 (*s*). By comparison of the ^1H NMR spectrum of **4** with those of **2** and **3**, the structure of **4** was inferred to be the 3,4-dihydro analogue of **3**. Compound **4** was oxidized to **3** by chloranil, and thus the structural assignment was confirmed.



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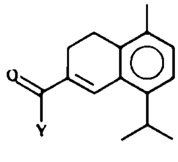
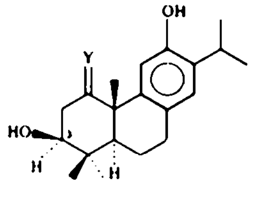
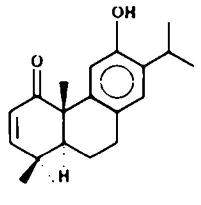
3 Y = OCH_3



2 Y = H
4 Y = OCH_3



5 Y = H,H
7 Y = O



6

Compound **5**, M^+ at m/z 302, and compound **6**, M^+ at m/z 298, were identified as (+)-hinokiol [4] and (+)-shonanol [5], respectively, by the evidence of the optical rotations and their spectroscopic properties. Compound **7**, M^+ at m/z 316, $[\alpha]_D^{25}$ + 130° (*c* 0.68, acetone), was isolated as colourless crystals, mp 228–229°. The IR spectrum of **7** exhibited absorptions at 1710 and 3540 cm^{-1} attributable to the carbonyl and hydroxyl groups. The ^1H NMR spectrum of **7** revealed five methyl groups appearing at δ1.10 (*s*), 1.13 (*s*), 1.20 (*d*, J = 7 Hz), 1.23 (*d*, J = 7 Hz) and 1.55 (*s*). The signals at δ6.83 (*s*) and 6.97 (*s*) were attributable to the resonances of two *para*-aromatic protons. Based on the above data, compound **7** was inferred to have the abietane-type structure related to those of hinokiol and shonanol. Treatment of 7 with a catalytic amount of *p*-toluenesulphonic acid in refluxing benzene yielded a dehydration product (77%), which was identified as (+)-shonanol by comparison of the physical and spectroscopic properties (mp, [α], TLC, IR, MS and ^{1}H NMR). Therefore, compound 7 was determined to be (+)-1-oxohinokiol with a C-3 hydroxyl group at the *β*-position. The corresponding resonance of the axial proton occurred at δ 3.70 (*dd*, J = 10, 5 Hz).

EXPERIMENTAL

Plant material. *Calocedrus formosana* (Florin) Florin was collected in the campus of the National Taiwan University. The skinned and air-dried wood (600 g) from branches 6–8 cm in diam. was selected for study. After extraction × 3 with Me_2CO, the combined extracts were concd *in vacuo* to give 20 g of residue. Components were separated by CC on silica gel (230 g) and elution with hexane–EtOAc gradients.

5-Methyl-8-isopropyl-2-naphthalenecarboxaldehyde (1). R_f 0.42 (EtOAc–hexane, 2:98). UV $\lambda_{\max}^{\mathrm{CHCl_3}}$ nm (ε): 251 (16 580), 294 (6470), 301 (5490), 350 (2890), 357 (2970). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 2715, 1685. MS *m/z* (rel. int.): 212 $[M]^+$ (54), 197 (100), 154 (21). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.43 (6H, *d*, J = 6.8 Hz), 2.70 (3H, *s*), 3.84 (1H, *septet*, J = 6.8 Hz), 7.42 (1H, *d*, J = 7.2 Hz, H-7), 7.46 (1H, *d*, J = 7.2 Hz, H-6), 7.98 (1H, *dd*, J = 8.8, 1.2 Hz, H-3), 8.13 (1H, *d*, J = 8.8 Hz, H-4), 8.66 (1H, *d*, J = 1.2 Hz, H-1), 10.20 (1H, *s*, CHO).

3,4-Dihydro-5-methyl-8-isopropyl-2-naphthalenecarboxaldehyde (2). R_f 0.41 (EtOAc–hexane 2:98). UV $\lambda_{\max}^{\mathrm{CHCl_3}}$ nm (ε): 241 (6270), 311 (12 990). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 2720, 1665, 1620. MS *m/z* (rel. int.): 214 $[M]^+$ (65), 199 (100), 171 (50), 143 (65), 128 (35). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.28 (6H, *d*, J = 7 Hz), 2.28 (3H, *s*), 2.52 (2H, *dd*, J = 8, 8 Hz, H-3), 2.79 (2H, *dd*, J = 8, 8 Hz, H-4), 3.36 (1H, *septet*, J = 7 Hz), 7.12 (1H, *d*, J = 8 Hz, H-7), 7.18 (1H, *d*, J = 8 Hz, H-6), 7.64 (1H, *s*, H-1), 9.70 (1H, *s*, CHO).

Methyl 5-methyl-8-isopropyl-2-naphthalenecarboxylate (3). R_f 0.45 (EtOAc–hexane, 2:98). UV $\lambda_{\max}^{\mathrm{CHCl_3}}$ nm (ε): 248 (13 810), 292 (4240), 302 (3600), 330 (1840), 342 (2010). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 1720. MS *m/z* (rel. int.): 242 $[M]^+$ (60), 227 (100), 211 (7), 195 (5), 183 (3), 168 (26), 153 (16). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.40 (6H, *d*, J = 6.7 Hz), 2.68 (3H, *s*), 3.83 (1H, *septet*, J = 6.7 Hz), 3.99 (3H, *s*, CO_2CH_3), 7.37 (1H, *d*, J = 7.5 Hz, H-7), 7.40 (1H, *d*, J = 7.5 Hz, H-6), 8.05 (1H, *d*, J = 8.7 Hz, H-4), 8.09 (1H, *dd*, J = 8.7, 1.7 Hz, H-3), 8.93 (1H, *d*, J = 1.7 Hz, H-1).

Methyl 3,4-dihydro-5-methyl-8-isopropyl-2-naphthalenecarboxylate (4). R_f 0.42 (EtOAc–hexane, 2:98). UV $\lambda_{\max}^{\mathrm{CHCl_3}}$ nm (ε): 240 (6330), 301 (11 460). IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 1710, 1630. MS *m/z* (rel. int.): 244 $[M]^+$ (93), 229 (100), 213 (23), 212 (28), 201 (15), 197 (43), 185 (15), 169 (48), 154 (28), 143 (40). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (6H, *d*, J = 7 Hz), 2.26 (3H, *s*), 2.55 (2H, *dd*, J = 8, 8 Hz, H-3), 2.78 (2H, *dd*, J = 8, 8 Hz, H-4), 3.34 (1H, *septet*, J = 7 Hz), 3.83 (3H, *s*, CO_2CH_3), 7.08 (1H, *d*, J = 8 Hz, H-7), 7.12 (1H, *d*, J = 8 Hz, H-6), 7.91 (1H, *s*, H-1).

(+)-1-Oxohinokiol (7). Colourless crystals, mp 228–229°, $[\alpha]_D^{25}$ +130° (*c* 0.68; Me_2CO). R_f 0.27 (hexane–Me_2CO, 7:3). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 203 (16 190), 281 (2900). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3540, 3300, 1710. MS *m/z* (rel. int.): 316 $[M]^+$ (100), 301 (43), 243 (93). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.10 (3H, *s*), 1.13 (3H, *s*), 1.20 (3H, *d*, J = 7 Hz), 1.23 (3H, *d*, J = 7 Hz), 1.55 (3H, *s*), 3.18 (1H, *m*), 3.70 (1H, *dd*, J = 10, 5 Hz, H-3), 6.83 (1H, *s*), 6.97 (1H, *s*).

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