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NORDITERPENES FROM THE HEARTWOOD OF *PICEA MORRISONICOLA*

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Key Word Index—*Picea morrisonicola*; Pinaceae; norditerpene; norabietane-type.

Abstract—Four norabietanes were isolated and identified from the acetone extract of the heartwood of *Picea morrisonicola*. Two of these were new compounds: 4α,15-dihydroxy-18-norabieta-8,11,13-trien-7-one and 4β,15-dihydroxy-19-norabieta-8,11,13-trien-7-one. Their structures were elucidated by spectroscopic methods. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Six species of *Picea* are grown in Taiwan. From these, several workers have described the chemical constituents of some species including *P. abies* [1–3], *P. glauca* [4] and *P. glehnii* [5]. These contain lignans, flavonoids and their glucosides, stilbenes and their glucosides, phenolics and their glucosides and diterpenoids. *P. morrisonicola* H. is a building material and the only species indigenous to Taiwan. In connection with our interests in diterpenoids [6–10] and since no chemical studies of this plant had been reported, we investigated the diterpenoid components of the heartwood of this plant. In this paper, we report on the isolation and characterization of two new norditerpenes, 4α,15-dihydroxy-18-norabieta-8,11,13-trien-7-one (**1**), 4β,15-dihydroxy-19-norabieta-8,11,13-trien-7-one (**2**) and two known norditerpenes, 4α-hydroxy-18-norabieta-8,11,13-trien-7-one (**3**) [11] and 18-norabietan-8,11,13-trien-4α-ol (**4**) [12].

RESULTS AND DISCUSSION

Compound **1** was assigned the molecular formula $C_{19}H_{26}O_3$ (HRMS): *m/z* 302.2244). It showed IR absorption bands at 3419 cm^{-1} (–OH), 1602 and 1492 cm^{-1} (aromatic ring) and 1673 cm^{-1} (conjugated ketone). The UV spectrum indicated the presence of a benzoyl group ($\lambda_{\max}^{\mathrm{MeOH}}$ 209, 252, 298 nm). The ^{1}H NMR spectrum (Table 1) revealed that **1** has a 1-hydroxyisopropyl group attached to a phenyl group, two singlet methyl groups and three 1, 2, 4-trisubstituted phenyl protons [δ 7.34 (1H, *d*, J = 8.3 Hz), 7.70 (1H, *dd*, J = 8.3, 2.2 Hz) and 8.04 (1H, *d*, J = 2.2 Hz)]. Other signals at δ 2.11 (1H, *dd*, J = 14.1, 3.6 Hz), 2.60 (1H, *dd*, J = 17.9, 14.1 Hz), 2.96 (1H, *dd*, J = 17.9, 3.6 Hz) and 2.30 (1H, *br d*, J = 12.3 Hz, a typical H$_\beta$-1 signal for dehydroabietane type derivative) [6, 7] were present. Irradiation at δ 2.11, the signals at δ 2.60 and 2.96 each collapsed to a doublet (J = 17.6 Hz). Nineteen signals were present in the ^{13}C NMR spectrum (Table 1) of **1** and these indicated that the structure was that of a nordehydroditerpene diterpene. The ^{1}H and ^{13}C NMR spectra data of **1** were very close to those of **3** [11]. The major difference was a 1-hydroxylisopropyl group [δ_H 1.56 (6H, *s*); δ_C 72.2 (C-15)] attached to a phenyl group instead of an isopropyl group. The stereochemistry of **1** was confirmed by NOESY experiments. Thus irradiation of Me-10 (at δ1.28) caused a NOE on H$_\beta$-6 (at δ2.60) and Me-4 (at δ1.19). The above evidence established that **1** was 4α,15-dihydroxy-18-norabieta-8,11,13-trien-7-one.

Compound **2** was found to have the molecular formula $C_{19}H_{26}O_3$ (HRMS). Its IR spectrum showed bands attributable to hydroxy groups (3445 cm^{-1}), a conjugated carbonyl group (1666 cm^{-1}) and a benzene ring (1608 and 1492 cm^{-1}). There were also significant absorption bands in its UV spectrum at $\lambda_{\max}$ 208, 252 and

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Table 1. ^{1}H NMR and ^{13}C NMR data for compounds **1** and **2** (300 MHz, 75 MHz in $CDCl_3$)

H	**1**	**2**	C	**1**	**2**
1α	1.65 (*m*)	1.65 (*m*)	1	37.1	37.1
1β	2.30 (*br d*, 12.3)	2.35 (*br d*, 12.3)	2	20.1	18.0
2	1.76 (*m*)	1.76 (*m*)	3	42.5	40.7
3	1.69 (*m*)	1.69 (*m*)	4	71.5	71.4
5	2.11 (*dd*, 14.1, 3.6)	1.91 (*dd*, 14.1, 3.6)	5	50.9	47.9
6α	2.96 (*dd*, 17.9, 3.6)	2.89 (*dd*, 17.9, 3.6)	6	35.0	35.3
6β	2.60 (*dd*, 17.9, 14.1)	2.80 (*dd*, 17.9, 14.1)	7	198.8	199.4
11	7.34 (*d*, 8.3)	7.34 (*d*, 8.3)	8	130.4	130.7
12	7.70 (*dd*, 8.3, 2.2)	7.70 (*dd*, 8.3, 2.2)	9	153.5	153.8
14	8.04 (*d*, 2.2)	8.04 (*d*, 2.2)	10	38.6	37.5
16	1.56 (*s*)	1.56 (*s*)	11	124.0	123.6
17	1.56 (*s*)	1.56 (*s*)	12	130.5	130.4
18		1.20 (*s*)	13	147.2	147.0
19	1.19 (*s*)		14	123.1	123.1
20	1.28 (*s*)	1.33 (*s*)	15	72.2	72.3
			16	31.6	31.6
			17	31.6	31.6
			18		30.1
			19	22.7	
			20	22.7	23.8

299 nm. Three aromatic protons in an ABX pattern at δ7.34 (1H, *d*, J = 8.3 Hz), 7.70 (1H, *dd*, J = 8.3, 2.2 Hz), 8.04 (1H, *d*, J = 2.2 Hz), indicated a dehydroabietanone having an oxo group at C-7. The signal at δ71.4 was attributable to C-4 having a hydroxyl substituent. Another ABX type of chemical shifts at δ1.91 (1H, *dd*, J = 14.1, 3.6 Hz), 2.80 (1H, *dd*, J = 17.9, 14.1 Hz) and 2.89 (1H, *dd*, J = 17.9, 3.6 Hz) due to H-5 and H_2-6. It was obvious that the large coupling constants were due to the presence of a carbonyl group. A typical signal of H_β-1 of a dehydroabietane was observed at δ2.35 (1H, *br d*, J = 12.3 Hz). Furthermore, four singlet methyl group signals at δ1.20, 1.33, 1.56 and 1.56 provided proof for the structure of norhydroabietane with a 1-hydroxyisopropyl group attached on a phenyl group. By comparison of ^{1}H and ^{13}C NMR spectral data for **1** and **2**, compound **2** was assigned as the 4-epimer of **1** i.e. Me-10 at lower field (δ 1.33 vs δ 1.28) and C-5 at higher field (δ 47.9 vs δ 50.9). This structure was fully supported by the ^{13}C NMR spectrum and additional proof for this structure was obtained using DEPT, HMQC and HMBC techniques. Its relative stereochemistry was elucidated by NOESY; Me-10 exhibited an nOe on H_β-6 and Me-4 caused nOe effect of H_α-6 and H-5 (Fig. 1). This evidence established that compound **2** was 4β,15-dihydroxy-19-norabieta-8,11,13-trien-7-one.

EXPERIMENTAL

General

M.p.: uncorr.; ^{1}H- and ^{13}C-NMR: Bruker AM-300 spectrometer; 2D-NMR: Varian Unity 400 spectrometer; EIMS, FABMS; JEOL JMS-HX 110; CC: silica gel (Merck 3374, 70–230 mesh).

Plant material

The heartwood of *Picea morrisonicola* H. was collected on Mount Taichuang, Taiwan and was verified by Professor Shao-Shun Ying, Department of Forest, National Taiwan University. A voucher specimen has been deposited at the Herbarium of the Department of Botany, National Taiwan University, Taipei, Taiwan.

Extraction and isolation

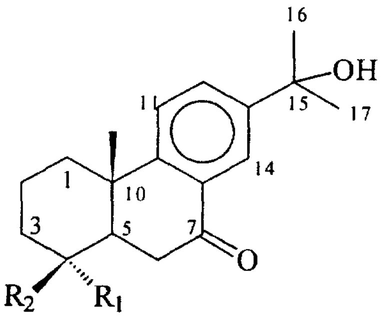
Dried heartwood of *P. morrisonicola* was crushed into small pieces to give 7.5 kg of raw material, which was extracted with Me_2CO (3 × 90 l) (7 days each time) at room temp. The combined extracts were evaporated *in vacuo* to give a black residue that was suspended with water (2 l) and then partitioned with EtOAc (2 l, ×3). The combined organic layer was purified by silica gel CC with a gradient solvent system (hexane–CH_2Cl_2–EtOAc) to give **1** (12.5 mg), **2** (5.4 mg), **3** (7.8 mg) and **4** (15.5 mg).

4α,15-*Dihydroxy*-18-*norabieta*-8,11,13-*trien*-7-*one* (**1**)

Oil, $[\alpha]_D^{25}$ +1.5° ($CHCl_3$; *c* 0.9). UV λ_{max} nm: 209, 252, 298; IR ν_{max}^{Neat} cm^{-1}: 3419 (OH), 1673 (C=O), 1602, 1492 (aromatic). ^{1}H and ^{13}C NMR: Table 1; EI-MS (70 eV) *m/z* (rel. int.): 302 [M+] (10), 287 (20), 284 (10), 266 (75), 251 (100), 209 (35), 199 (18), 128 (16), 115 (10); HRMS *m/z*: 302.2244, $C_{19}H_{26}O_3$ requires 302.2245.

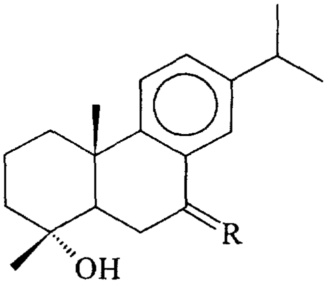
4β,15-*Dihydroxy*-19-*norabieta*-8,11,13-*trien*-7-*one* (**2**)

Oil, $[\alpha]_D^{25}$ +13.5° ($CHCl_3$; *c* 0.5); UV λ_{max} nm: 208, 252, 299; IR ν_{max}^{Neat} cm^{-1}: 3445 (OH), 1666 (C=O), 1608, 1492 (aromatic); ^{1}H and ^{13}C NMR: Table 1; EI-MS (70 eV) *m/z* (rel. int.): 302 [M+] (15), 287 (15), 284 (10), 266 (70), 251 (100), 209 (55), 199 (20), 128 (18), 115 (15); HRMS *m/z*: 302.2243, $C_{19}H_{26}O_3$ requires 302.2245.



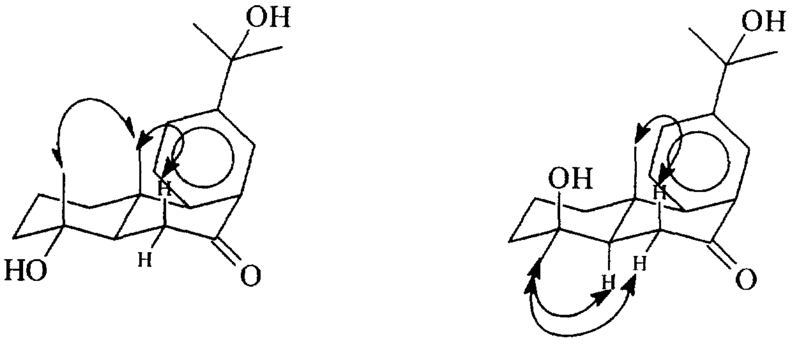
1 $R_1 = OH$, $R_2 = CH_3$

2 $R_1 = CH_3$, $R_2 = OH$



3 $R = O$

4 $R = H_2$



1 **2**

Fig. 1. NOESY data (⟵⟶).

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