Five New Diterpenoids from the Wood of *Cunninghamia konishii*

Yen-Cheng Li[†] and Yueh-Hsiung Kuo*[,†,‡]

Department of Chemistry, National Taiwan University, and National Research Institute of Chinese Medicine, Taipei, Taiwan, Republic of China

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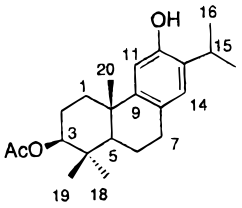
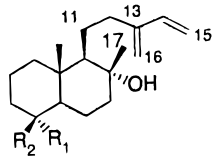
Five new diterpenes, 3β-acetoxyabieta-8,11,13-trien-12-ol (**1**), 8α-hydroxy-13(16),14-labdadien-19-al (**2**), 16-hydroxy-19-oxomanoyl oxide (**3**), 15-nor-14-oxo-8(17),12-labdadiene-18-ol (**4**), and 15,16-bisnor-13-oxo-8(17),11-labdadien-18-ol (**5**), were isolated from the wood of *Cunninghamia konishii*. Their structures were elucidated by 2D NMR spectroscopy and by chemical methods.

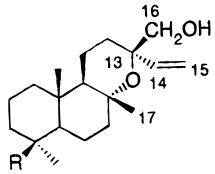
Only two species of *Cunninghamia* (Taxodiaceae) grow in Taiwan. *Cunninghamia konishii* Hayata is a coniferous tree, distributed in the northern and central parts of Taiwan at altitudes of 1300−2700 m. The wood of this tree is one of the best building materials available in Taiwan. In previous investigations on the chemical composition, the essential oils of the wood[1,2] and the milled bark[3] were reported. We now describe the compounds obtained from the wood. The methanol extract of the wood of *C. konishii* was concentrated to give a residue that was suspended in water and partitioned with *n*-hexane, ethyl acetate, and *n*-BuOH, successively. Repeated chromatography of the ethyl acetate extract over silica gel and by HPLC yielded five new compounds (**1**−**5**).



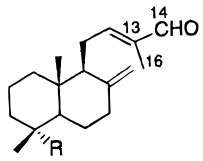
1 R = Ac
6 R = H



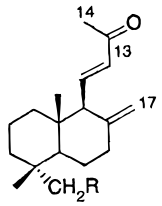
2 R_1=CH_3, R_2=CHO
7 R_1=CHO, R_2=CH_3 (*ent*-)



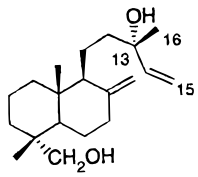
3 R = CHO
8 R = CH_2OH (*ent*-)



4 R = CH_2OH
10 R = COOMe (*ent*-)



5 R = OH
11 R = H



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Results and Discussion

Compound **1** showed a molecular formula $C_{22}H_{32}O_3$ by high-resolution mass spectrometry. Absorptions in the IR spectrum were attributable to a hydroxyl (3413 cm^{-1}), an ester carbonyl (1737 cm^{-1}), and a benzene ring (1615 and 1495 cm^{-1}). Observed ^1H NMR signals were attributable to a phenyl group (δ 6.81 and 6.58), a phenolic proton (δ 5.03, disappeared upon addition of D_2O), an acetoxy group (δ 2.05), an isopropyl group [δ 3.09 (1H, sept), 1.21 and 1.20 (3H each, d)], and three singlet methyl groups (δ 1.18, 0.94, and 0.92). A typical H_β-1 signal of a dehydroabietane diterpene was observed at δ 2.17 (1H, ddd, J = 13.2, 3.3, 3.3 Hz).[4,5] Comparison of the ^1H and ^{13}C NMR (Table 1) spectral data **1** and hinokiol (**6**)[6] permitted the assignment of **1** as a hinokiol derivative with an extra acetyl group at C-3. The proton resonating at δ 4.51 (dd, J = 11.1, 4.9 Hz) was attributable to H-3 with an α-axial orientation and was geminal to the acetoxyl group. Compound **1** was hydrolyzed with 0.5 N sodium hydroxide to afford a product that was identical to **6** by comparison with an authentic sample. On the basis of additional confirmation by DEPT and 2D NMR, the structure of **1** was elucidated as 3β-acetoxyabieta-8,11,13-trien-12-ol.

The new labdadiene-type derivative, compound **2**, was found to have a molecular formula of $C_{20}H_{32}O_2$, and its UV spectrum showed a maximum at 224 nm due to the presence of a conjugated diene. The IR spectrum showed hydroxyl (3433 cm^{-1}) and carbonyl (1716 cm^{-1}) absorption bands. Its ^1H NMR spectrum contained a singlet at δ 9.72 (1H, formyl group situated at a quaternary carbon) as well as an A_2B_2X system [δ 6.33 (1H, dd, J = 17.6, 10.8 Hz, H-14), 5.27 (1H, d, J = 17.6 Hz, H_a-15), 5.03 (1H, d, J = 10.8 Hz, H_b-15), and 4.99 (2H, brs, H-16)], which was similar to that shown by 6-deoxyandalusal (**7**).[7] Comparison of the chemical shift of the three methyl singlets of **2** and **7** [δ 1.16 (H_3-17), 1.01 (H_3-18), 0.65 (H_3-20) for **2**; δ 1.08 (H_3-17), 0.97 (H_3-19), 0.83 (H_3-20) for **7**] showed H_3-20 in **2** to be shielded, an effect attributable to the presence of an axial formyl group at C-19. The relative stereochemistry was elucidated by the NOESY method; the formyl group exhibited a NOE correlation with H_3-20, and H_3-20 showed

* To whom correspondence should be addressed. Tel.: 886-2-23690152-119. Fax: 886-2-23636359.
† Department of Chemistry, National Taiwan University.
‡ National Research Institute of Chinese Medicine.

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Table 1. ^{13}C NMR Spectral Data of Compounds **1**−**5** (75 MHz, in $CDCl_3$)

position	1	2	3	4	5
1	36.5	39.1	38.3	38.8	40.3
2	18.9	18.3	18.3	18.6	18.3
3	80.7	34.3	34.3	35.3	35.4
4	37.2	48.3	48.3	38.0	39.1
5	49.8	56.5	56.7	48.3	47.3
6	24.4	20.2	19.8	23.9	22.9
7	29.9	44.5	43.5	37.6	36.3
8	126.8	73.8	75.0	148.0	148.3
9	147.4	60.4	51.5	56.5	60.7
10	37.9	39.4	37.6	39.4	38.0
11	110.9	24.6	14.7	24.4	146.4
12	150.9	34.9	26.8	156.3	133.6
13	131.8	147.2	76.7	138.9	198.1
14	126.6	138.7	143.8	195.2	27.3
15	26.8	113.5	114.2		
16	22.7[a]	115.8	68.6	9.4	
17	22.5[a]	24.0	25.7	107.8	108.7
18	28.2	24.2	24.1	71.9	71.8
19	16.5	205.4	205.4	17.6	17.8
20	24.9	14.2	13.9	14.9	15.6
OAc	21.3				
	171.1				

[a] Interchangeable.

an NOE correlation with H_3-17. This evidence indicated that the formyl group and the two methyl groups at δ 0.65 (H_3-17) and 1.16 (H_3-20) were all in the axial orientation. The additional proof for this structure **2** was obtained by using HMBC and HMQC techniques. Hence, compound **2** was assigned as 8α-hydroxy-13(16),14-labdadien-19-al.

The most polar compound, **3**, obtained in this study exhibited a molecular formula of $C_{20}H_{32}O_3$ on the basis of HRMS. Its IR spectrum indicated hydroxyl (3432 cm^{-1}), carbonyl (1718 cm^{-1}), and monosubstituted double bond (3071, 1634, 992, and 908 cm^{-1}) functional groups. The ^1H and ^{13}C NMR spectra showed that **3** contained an aldehyde (δ 9.72), three singlet methyl groups, a hydroxymethylene group [δ_H 3.28 (2H, s), δ_C 68.6], and a vinylic ABX system [δ 5.79 (dd, J = 17.2, 10.8 Hz), 5.24 (dd, J = 17.2, 1.6 Hz), and 5.11 (dd, J = 10.8, 1.6 Hz)], similar to jabugodiol (**8**),[8] except that one of the two hydroxymethylene groups in **8** was replaced by a formyl group in **3**. The presence of the C-9 signal at δ 51.5 (the corresponding signal occurred at 52.8 for **8**) also indicated that **3** is a manoyl oxide derivative.[8] Comparison of the two methyl singlets of **3** (δ 1.00, 0.66) and **2** (δ 1.01, 0.65) indicated that the hydroxymethylene group [δ_H 3.28 (2H, s)] in **3** was not situated at C-4β or C-10, and its most probable location should be either C-8 or C-13. The similar chemical shifts of C-8 and C-13 of **3** and **8** [δ 75.0 and 76.7 for **3**; δ 75.5 and 76.3 for **8**] indicated that the hydroxymethylene group [δ_H 3.28 (2H, s, H_2-16)] was situated at C-13 (H_2-16 of **8** is also equivalent at δ 3.30). Thus, the formyl group of **3** was placed at C-4β because of the observation of the H_3-20 methyl signal resonating at a higher field (δ 0.66). Regarding the stereochemistry of **3**, pronounced NOESY correlations between the formyl proton (H-19) and H_3-20, H_3-20 and H_3-17, and H_3-17 and H_2-16 illustrated that the protons of H-19, H_3-20, H_3-17, and H_2-16 were all in the axial orientation. Reduction of **3** with sodium borohydride in methanol afforded a product that was identical to (+)-**8** by comparing ^1H and ^{13}C NMR spectral data. Analysis of all of the evidence above confirmed the structure of **3** as 16-hydroxy-19-oxomanoyl oxide.

High-resolution EIMS of **4** demonstrated a molecular formula $C_{19}H_{30}O_2$, and the IR spectrum showed a conjugated carbonyl group (ν_{max} 1692 cm^{-1}). The existence of 19 carbons with 29 directly attached protons was confirmed from ^{13}C/DEPT NMR experiments and indicated an exocyclic double bond [δ 107.8 (t), 148.0 (s)] in addition to a conjugated aldehyde [δ 195.2 (d), 138.9 (s), 156.3 (d)]. The chemical shifts (C-1 to C-10, C-19 and C-20) in the ^{13}C NMR spectrum of **4** showed similarities to those of 13-epitorreferol (**9**).[9] Therefore, the labdane skeleton and the relative stereochemistry around the rigid decalin ring system could be established. The ^1H NMR spectrum of **4** indicated the appearance of three methyl groups (δ 0.76, 0.78, and 1.77), a hydroxymethylene group [δ 3.10 and 3.14 (1H each, d)], three olefin protons [δ 4.37, 4.83 (1H each, brs), and 6.41 (1H, br t)], and one formyl proton (δ 9.32, s). All of these data were similar to those of the model compound 15-nor-14-oxo-8(17),12-labdadien-18-oate (**10**)[10] except for the occurrence of a hydroxymethylene group instead of a carboxylate group. The formyl proton (H-14) and H-12 were shown to be *syn* on the basis of an NOE correlation between them, and the hydroxymethylene group was assigned in the equatorial position because of the lack of any NOE correlation between the hydroxymethylene protons and H_3-20. Therefore, the structure of **4** was proposed as 15-nor-14-oxo-8(17),12-labdadien-18-ol.

Compound **5**, $[\alpha]^{27}_D$ +8.5°, was analyzed as $C_{18}H_{28}O_2$ by HRMS. Its ^{13}C NMR spectrum showed signals for 18 carbons. The UV absorption at 225 nm and the IR absorption bands at 3420 (OH), 1667 (C=O), and 887 (>C=CH_2) cm^{-1} suggested the presence of a hydroxyl group, an enone system, and exocyclic double-bond functionalities in the molecule. The presence of the second functionality was further indicated by its ^1H NMR signals at δ 2.25 (3H, s), 6.05 (1H, d, J = 16.0 Hz), and 6.84 (1H, dd, J = 16.0, 10.3 Hz), being assigned to a *trans*-α,β-unsaturated methyl ketone group. The third functionality was indicated by its ^{13}C NMR signals at δ 148.3 (s) and 108.7 (t), which were attributable to a 1,1-disubstituted olefin. In addition, the ^1H NMR spectrum of **5** also showed signals for two tertiary methyl groups at δ 0.77 and 0.91 (3H each, s) and two terminal methylene protons at δ 4.40 and 4.78 (1H each, brs), and an AB system [δ 3.10 and 3.41 (1H each, d)] was derived from a hydroxymethylene group. The ^1H and ^{13}C NMR signals of **5** and 15,16-dinor-8(17),11-labdadien-13-one (**11**) were compared,[11] and the structure of compound **5** could be deduced as the 18-hydroxy derivative of **11**. The olefinic proton δ 6.84 (H-11) gave an NOE correlation with an acetyl methyl at δ 2.25 (H_3-14) indicating a *cis* relationship between H-11 and H_3-14. The methyl group at δ 0.91 (H_3-20) correlated to a signal at δ 0.77 (H_3-19) but not to the hydroxymethylene group. This result also confirmed that the hydroxyl group has located at C-18. The H_2-18 and H-5 signals as well as the H-5 and H-9 showed NOE correlations consistent with the structure proposed. Therefore, the structure of **5** was assigned as 15,16-bisnor-13-oxo-8(7),11-labdadien-18-ol.

Experimental Section

General Experimental Procedures. Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer. 2D NMR spectra were run on a Varian Unity 400 spectrometer. EIMS, FABMS, UV, and specific rotations were taken on a JEOL JMS-HX110 mass spectrometer, a Hitachi S-3200 spectrometer, and a JASCO DIP-180 digital polarimeter, respectively. Extracts were chromatographed on silica gel (Merck 3374, 70−230 mesh) and purified with a semi-preparative normal-phase HPLC column (250 × 10 mm, 7 μm, LiChrosorb Si 60).

Plant Material. The wood of *C. konishii* Hayata was collected at Luantashan, Nantau Hsien, Taiwan, in December 1996 and was identified by Prof. Shao-Shun Ying, Department of Forestry, National Taiwan University. A voucher specimen (013492) has been deposited at the Herbarium of the Department of Botany, National Taiwan University, Taipei, Taiwan.

Extraction and Isolation. The wood of *C. konishii* was crushed into pieces to give 6.5 kg (air-dried) of raw material, which was extracted with MeOH (60 L) three times (7 days each time) at room temperature. The combined extracts were evaporated *in vacuo* to give a black residue (60.2 g) that was suspended in water (500 mL) and partitioned into *n*-hexane (500 mL × 3), EtOAc (500 mL × 4), and *n*-BuOH (500 mL × 3), successively. The EtOAc fraction (15.6 g) was chromatographed by silica gel column chromatography (using hexane−EtOAc and EtOAc−MeOH mixtures as solvent systems). Elution with hexane−EtOAc (7:3) gave **4**, and hexane−EtOAc (3:2) gave **1**, while compounds **2**, **3**, and **5** were eluted with hexane−EtOAc (1:1). Further purification by HPLC gave **1** (2.3 mg), **2** (2.5 mg), **3** (2.5 mg), **4** (2.7 mg), and **5** (3.6 mg) using hexane−EtOAc−CH_2Cl_2−*i*-PrOH (10:1:5:0.2), hexane−EtOAc−CH_2Cl_2−*i*-PrOH (6:1:4:0.2), hexane−EtOAc−CH_2Cl_2−*i*-PrOH (3:1:3:0.2), hexane−EtOAc−CH_2Cl_2−*i*-PrOH (10:1:2:0.2), and acetone−CH_2Cl_2−*i*-PrOH (1:6:0.2), respectively.

3β-Acetoxyabieta-8,11,13-trien-12-ol (1): pale yellow oil; $[\alpha]^{25}_D$ +62.9° (*c* 0.21, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 205 (4.36), 225 (sh, 3.88), 282 (3.42) nm; IR (dry film) ν_{max} 3413 (OH), 1737 (C=O, ester), 1615, 1495 (benzene ring), 1363, 1234, 1028 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.81 (1H, s, H-14), 6.58 (1H, s, H-11), 5.03 (1H, brs, OH), 4.51 (1H, dd, J = 11.1, 4.9 Hz, H-3), 3.09 (1H, sept, J = 6.8 Hz, H-15), 2.83 (1H, ddd, J = 12.6, 4.0, 1.5 Hz, H$_\beta$-7), 2.75 (1H, ddd, J = 12.6, 11.3, 3.5 Hz, H$_\alpha$-7), 2.17 (1H, ddd, J = 13.2, 3.3, 3.3 Hz, H$_\beta$-1), 2.05 (3H, s, OAc), 1.60 (1H, ddd, J = 13.2, 11.0, 3.0 Hz, H$_\alpha$-1), 1.36 (1H, dd, J = 12.0, 2.1 Hz, H-5), 1.21, 1.20 (3H each, d, J = 6.8 Hz, H-16 and H-17), 1.18 (3H, s, H-20), 0.94 (3H, s, H-19), 0.92 (3H, s, H-18); ^{13}C NMR, see Table 1; EIMS (70 eV) *m/z* 344 [M$^+$] (100), 329 (12), 285 (39), 283 (27), 269 (22), 213 (20); HREIMS *m/z* 344.2354 (calcd for $C_{22}H_{32}O_3$, 344.2353).

8α-Hydroxy-13(16),14-labdadien-19-al (2): pale yellow oil; $[\alpha]^{27}_D$ +9.5° (*c* 0.23, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 224 (4.35) nm; IR (dry film) ν_{max} 3433 (OH), 3085 (C−H, vinyl), 1716 (C=O, aldehyde), 1643, 1593 (C=C−C=C), 1462, 1386, 1081, 990, 903, 893 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.72 (1H, s, H-19), 6.33 (1H, dd, J = 17.6, 10.8 Hz, H-14), 5.27 (1H, d, J = 17.6 Hz, H$_a$-15), 5.03 (1H, d, J = 10.8 Hz, H$_b$-15), 4.99 (2H, brs, H-16), 1.27 (1H, dd, J = 10.4, 3.2 Hz, H-5), 1.16 (3H, s, H-17), 1.01 (3H, s, H-18), 0.65 (3H, s, H-20); ^{13}C NMR, see Table 1; EIMS (70 eV) *m/z* 304 [M$^+$] (11), 289 (27), 275 (89), 257 (100), 243 (16), 236 (8), 227 (13); HREIMS *m/z* 304.2386 (calcd for $C_{20}H_{32}O_2$, 304.2404).

16-Hydroxy-19-oxomanoyl oxide (3): pale yellow oil; $[\alpha]^{27}_D$ +19.5° (*c* 0.19, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 284 (1.26) nm; IR (dry film) ν_{max} 3432 (OH), 3071 (C−H, vinyl), 1718 (C=O, aldehyde), 1634 (C=C), 1453, 1376, 1073, 992, 908 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.72 (1H, s, H-19), 5.79 (1H, dd, J = 17.2, 10.8 Hz, H-14), 5.24 (1H, dd, J = 17.2, 1.6 Hz, H$_a$-15), 5.11 (1H, dd, J = 10.8, 1.6 Hz, H$_b$-15), 3.28 (2H, s, H-16), 1.27 (3H, s, H-17), 1.00 (3H, s, H-18), 0.66 (3H, s, H-20); ^{13}C NMR, see Table 1; EIMS (70 eV) *m/z* 320 [M$^+$] (1), 305 [M$^+$-CH_3] (73), 287 (100), 277 (8), 275 (5), 269 (6), 265 (8), 259 (22), 154 (90), 136 (92); HREIMS *m/z* 320.2344 (calcd for $C_{20}H_{32}O_3$, 320.2353).

15-Nor-14-oxo-8(17),12-labdadien-18-ol (4): amorphous; $[\alpha]^{27}_D$ +23.8° (*c* 0.25, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 232 (4.08) nm; IR (dry film) ν_{max} 3439 (OH), 3072 (C−H, vinyl), 1692 (C=O, conjugated), 1641 (C=C), 1441, 1383, 1034, 990, 893 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.32 (1H, s, H-14), 6.41 (1H, t, J = 7.6 Hz, H-12), 4.83 (1H, brs, H$_a$-17), 4.37 (1H, brs, H$_b$-17), 3.41 (1H, d, J = 10.9 Hz, H$_a$-18), 3.10 (1H, d, J = 10.9 Hz, H$_b$-18), 1.77 (3H, s, H-16), 1.50 (1H, dd, J = 10.8, 4.0 Hz, H-5), 0.78 (1H, s, H-20), 0.76 (3H, s, H-19); ^{13}C NMR, see Table 1; EIMS (70 eV) *m/z* 290 [M$^+$] (83), 279 (24), 276 (22), 259 (100), 232 (85), 217 (14); HREIMS *m/z* 290.2242 (calcd for $C_{19}H_{30}O_2$, 290.2247).

15,16-Bisnor-13-oxo-8(17),11(*E*)-labdadien-18-ol (5): pale yellow oil; $[\alpha]^{27}_D$ +8.5° (*c* 0.33, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 225 (4.10), 279 (3.31) nm; IR (dry film) ν_{max} 3420 (OH), 3078 (C−H, vinyl), 1667 (C=O, conjugated), 1641 (C=C), 1383, 1254, 1041, 887 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.84 (1H, dd, J = 16.0, 10.3 Hz, H-11), 6.05 (1H, d, J = 16.0 Hz, H-12), 4.78 (1H, brs, H$_a$-17), 4.40 (1H, brs, H$_b$-17), 3.41 (1H, d, J = 10.9 Hz, H$_a$-18), 3.10 (1H, d, J = 10.9 Hz, H$_b$-18), 2.51 (1H, d, J = 10.3 Hz, H-9), 2.25 (3H, s, H-14), 1.47 (1H, dd, J = 10.1, 3.8 Hz, H-5), 0.91 (3H, s, H-20), 0.77 (3H, s, H-19); ^{13}C NMR, see Table 1; EIMS (70 eV) *m/z* 276 [M$^+$] (100), 245 (67), 207 (15), 154 (80), 136 (76), 107 (37), 91 (29); HREIMS *m/z* 276.2101 (calcd for $C_{18}H_{28}O_2$, 276.2089).

Saponification of 1 with NaOH in MeOH. Compound **1** (2 mg) in MeOH (1 mL) was stirred at room temperature with 0.5 N NaOH/MeOH (0.5 mL) under Ar for 5 h. The reaction mixture was poured into water (10 mL) and then acidified with 3 N HCl to pH 3. The solution was extracted with ether (20 mL × 3). The organic layer was concentrated under reduced pressure to give a residue. The residue was purified by silica gel chromatography to afford hinokiol (**6**) [1 mg, EtOAc−hexane (4:6)].

Reduction of 3 with $NaBH_4$. Excess $NaBH_4$ (10 mg) was added in small portions into a solution of **3** (2.2 mg) in MeOH (2.5 mL), and the reaction mixture was allowed to stand for 30 min. The mixture solvent (15 mL each of EtOAc and *n*-hexane) was added to the

reaction mixture and washed with H_2O (10 mL × 3). Evaporation of the organic layer under reduced pressure gave a residue that was chromatographed on silica gel to produce jabugodiol (**8**) [1.5 mg, EtOAc−hexane (4:6)].

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