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Phytochemical Constituents of *Artemisia japonica* ssp. *littoricola*

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The phytochemical study of the aerial parts of *Artemisia japonica* ssp. *littoricola* (Asteraceae) led to the isolation of two acetylenic compounds, (3*R*)-dehydrofalcarinol (**2**) and (3*R*)-dehydrofalcarindiol (**6**), two sesquiterpenes, 1β, 6α-dihydroxy-4(15)-eudesmene (**5**) and oplodiol (**8**), and four phenolic compounds, eugenol (**1**), vanillin (**3**), 3'-methoxy-4'-hydroxy-*trans*-cinnamaldehyde (**4**) and *p*-hydroxyacetophenone (**7**). Their structures were determined by chemical and spectroscopic methods.

Key words: *Artemisia japonica* ssp. *littoricola*, Asteraceae, Acetylene, Sesquiterpene, Phenolic compound

INTRODUCTION

Artemisia japonica ssp. *littoricola* (Asteraceae) is distributed at Ul-Rung- island in Korea (Lee, 1996; Satake *et al.*, 1991). *Artemisia japonica* has been used as a traditional medicine to treat fever and eczema (Kim, 1998). Literature survey of *Artemisia japonica* ssp. *littoricola* revealed that no phytochemical and pharmacological studies have been performed. *Artemisia japonica* ssp. *littoricola* was investigated as part of a systematic study into Korean Asteraceae medicinal plants. The chromatographic separation of the CH_2Cl_2 extract of this plant led to the isolation of two acetylenes (**2** and **6**), two sesquiterpenes (**5** and **8**) and four phenolic compounds (**1**, **3**, **4** and **7**). This paper describes the isolation and structural characterization of these compounds.

MATERIALS AND METHODS

General

Mps: uncorr. NMR: in $CDCl_3$, Bruker AMX 500 and Varian UNITY INOVA 500. IR: in CCl_4, Nicolet model 205 FT-IR spectrophotometer. MS: VG70-VSEQ mass spectrometer. Column chromatography: Silica gel 60 (Merck, 70~230 mesh and 230~400 mesh), Lichroprep. RP-18 (Merck) and Sephadex LH-20. TLC: Merck precoated Si gel F_{254} plates and RP-18 F_{254s} plates. LPLC: Merck Lichroprep Lobar®-A Si 60 (240 × 10 mm)

Plant materials

Artemisia japonica ssp. *littoricola* was collected in Ul-Rung island, KyungSang-Do, Korea in July 1999. A voucher specimen (SKK-99-001) was deposited at the College of Pharmacy, SungKyunKwan University.

Extraction and isolation

The aerial parts of *Artemisia japonica* ssp. *littoricola* (5 kg) were chopped and dried then extracted with CH_2Cl_2 three times at room temp. The resulting CH_2Cl_2 extract (80 g) was chromatographed on silica gel column using a gradient solvent system of hexane:EtOAc(10:1~1:2) and EtOAc:MeOH (1:0~10:1) to give nine subfractions (C1~C9). Subfraction C2 (20 g) was further separated by silica gel column eluting with hexane:EtOAc (5:1) to give five subfractions (C21~C25). Subfraction C22 (9.4 g) was rechromatographed over silica gel eluted with CH_2Cl_2 to give three subfractions (C221~C223). The second subfraction was further purified with the Sephadex LH-20 (CH_2Cl_2:MeOH=1:1) and silica gel Lobar®-A column (CH_2Cl_2) to yield **1** (10 mg). Subfraction C23 (9.5 g) was rechromatographed over silica gel eluted with CH_2Cl_2 give three subfractions (C231~C233) and the second subfraction further purified with silica gel Lobar®-A column (CH_2Cl_2) to yield **2** (100 mg). Subfraction C6 (4.3 g) was chromatographed with silica gel column ($CHCl_3$:MeOH=20:1) to give five subfractions (C61~C65). Subfraction C62 (1.0 g) was rechromatographed with Sephadex LH-20 (CH_2Cl_2:MeOH=1:1) and RP-18 Lobar®-A column (70% MeOH) to afford **3** (7 mg)

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and **4** (4 mg). Subfraction C63 (0.8 g) was chromatographed with Sephadex LH-20 (CH_2Cl_2:MeOH=1:1) to give three subfractions (C631~C633). Subfraction C632 (140mg) was further purified by RP-18 Lobar®-A column chromatography (70% MeOH) to yield **5** (16 mg). Subfraction C-64 (0.3 g) was chromatographed with the Sephadex LH-20 (CH_2Cl_2:MeOH=1:1) to give four subfractions (C641~C-644). Subfraction C642 (45 mg) was purified with silica gel Lobar®-A column (hexane:EtOAc =2:1) to afford **6** (8 mg). Subfraction C644 (60mg) was further purified with silica gel Lobar®-A column (hexane: EtOAc = 4:1) and recrystallization (hexane:EtOAc = 4:1) to give **7** (10 mg). C7 fraction (6.5 g) was divided into five subfractions (C71~C-75) by SiO_2 column chromatography ($CHCl_3$:MeOH = 20:1). The subfraction C74 (500 mg) was chromatographed with the Sephadex LH-20 column using CH_2Cl_2:MeOH(1:1) to give two subfractions (C741 and C742). Subfraction C741 (120 mg) was purified using RP-18 Lobar®-A column chromatography (60% acetonitrile) to afford **8** (5 mg).

Eugenol (1): colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.29 (2H, br.d, *J*=6.7 Hz, H-1′), 3.85 (3H, s, OCH_3), 5.02 (1H, dm, *J*=10.1 Hz, H-3′$_{cis}$), 5.04 (1H, dm, *J*=16.8 Hz, H-3′$_{trans}$), 5.92(2H, ddt, *J*=16.8, 10.1, 6.7 Hz, H-2′), 6.66 (2H, m, H-5, H-6), 6.82 (1H, d, *J*=8.2 Hz, H-2); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 40.61 (C-1′), 56.54 (OCH_3), 111.75 (C-5), 114.91(C-3′), 116.24 (C-2), 121.85 (C-6), 132.62 (C-2′), 138.51 (C-1), 144.56 (C-4), 147.10 (C-3)

Dehydrofalcarinol (2): colorless oil; $[\alpha]_D^{25}$ -26.3°(c. 1.8, $CHCl_3$); UV ν_{max}^{EtOH} nm (log ε) : 286 (3.15), 270 (3.23), 256 (3.21), 242 (3.25), 211 (3.78); IR λ_{max}^{neat} cm^{-1}: 3373, 2927, 2855, 2253, 1643, 1412, 1280, 1117; ^{1}H-NMR (500 MHz, $CDCl_3$) :1.24~1.37 (6H, m, H-12~H-14), 1.88 (1H, br.s, 3-OH), 1.98~2.03 (4H, m, H-11, H-15), 3.00 (2H, br.d, *J*=7.0 Hz, H-8), 4.89 (1H, br.d, J≈7.5, H-3, overlab with H-17$_{trans}$), 4.91 (1H, dd, *J*=10.1, 1.8 Hz, H-17$_{trans}$), 4.97 (1H, dd, *J*=17.1, 1.8 Hz, H-17$_{cis}$), 5.21 (1H, d, *J*=10.1 Hz, H-1$_{trans}$), 5.35 (1H, br.dd, *J*=10.8, 7.0 Hz, H-9), 5.44 (1H, d, *J*=17.4 Hz, H-1$_{cis}$), 5.49 (1H, dt, *J*=10.8, 7.4 Hz, H-10), 5.78 (1H ddt, *J*=17.1, 10.1, 6.7 Hz, H-16), 5.91 (1H, ddd, *J*=17.4, 10.1, 5.5 Hz, H-2); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 18.39 (C-8), 27.84 (C-11), 29.40 (C-12), 29.45 (C-13), 29.77 (C-14), 34.44 (C-15), 64.16 (C-3), 64.79 (C-6), 71.93 (C-5), 75.00 (C-4), 80.86 (C-7), 115.01 (C-17), 117.74 (C-1), 122.80 (C-9), 133.66 (C-10), 136.84 (C-2), 139.75 (C-16)

Vanillin (3): yellow needle; mp 80°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.95 (3H, s, OCH_3), 6.20 (1H, s, OH), 7.06 (1H, d, *J*=8.4Hz, H-5), 7.44 (2H, m, H-2, H-6), 9.85 (1H, s, aldehyde H); ^{13}C-NMR (125 MHz, $CDCl_3$) : δ 56.17 (OCH_3), 108.85 (C-5), 114.41 (C-2), 127.50 (C-6), 130.00 (C-1), 147.18 (C-4), 151.70 (C-3), 190.83 (aldehyde C)

3′-Methoxy-4′-hydroxy-*trans*-cinnamaldehyde (4): yellow powder; mp 67°C; IR ν_{max} (Nujol) cm^{-1}: 3400, 1660, 1580, 1250; UV λ_{max} ($CHCl_3$) nm : 333, 302 (sh); EIMS m/z (rel. int): 178 (M^+,100), 161 (35), 147 (60), 135 (68), 107 (44), 84 (35), 77 (34); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.97 (3H, s, OCH_3), 6.03 (1H, s, OH), 6.61 (1H, dd, *J*=15.9, 7.7Hz, H-2), 6.98 (1H, d, *J*=8.2Hz, H-5′), 7.08 (1H, d, *J*=1.9Hz, H-2′), 7.13 (1H, dd, *J*=8.2, 1.9Hz, H-6′), 7.41 (1H, d, *J*=15.9Hz, H-3), 9.65 (1H, d, *J*=7.7Hz, H-1); ^{13}C-NMR (125MHz, $CDCl_3$) δ: 56.05 (OCH_3), 109.53 (C-5′), 114.98 (C-2′), 124.07 (C-6′), 126.51 (C-2), 126.73 (C-1′), 147.00 (C-4′), 148.98 (C-3′), 153.01 (C-3), 193.56 (C-1)

1β, 6α-Dihydroxy-4(15)-eudesmene (5): colorless gum, ^{1}H-NMR (500MHz, $CDCl_3$) δ : 0.70 (3H, s, H-14), 0.88 (3H, d, *J*=7.0Hz, H-12), 0.96 (3H, d, *J*=7.0Hz, H-13), 1.75 (1H, br.d, *J*=9.0 Hz, H-5α), 2.10 (1H, m, H-3), 2.73 (1H, m, *J*=7.0, 3.0 Hz, H-11), 3.44 (1H, dd, *J*=12.0, 5.0 Hz, H-1α), 3.70 (1H, t, *J*=9.0 Hz,, H-6β), 4.76 (1H, br.s, H-15a), 5.04 (1H, br.s, H-15b), ^{13}C-NMR (125MHz, $CDCl_3$) δ : 11.58 (C-14), 16.24 (C-13), 18.27 (C-8), 21.0 (C-12), 26.07 (C-11), 31.96 (C-2), 35.16 (C-3), 36.33 (C-9), 41.70 (C-10), 49.40 (C-7), 55.95 (C-5), 67.03 (C-6), 79.06 (C-1), 107.78 (C-15), 146.25 (C-4)

(3*R*)-Heptadeca-1,9(*Z*),16-trien-4,6-diyn-3,8-diol (6): colorless oil; $[\alpha]_D^{25}$ -104.0° (c. 0.02, $CHCl_3$); UV ν_{max}^{EtOH} nm (log ε) : 286 (3.12), 270 (3.21), 255 (3.19), 241 (3.22), 205 (4.10); IR λ_{max}^{neat} cm^{-1} : 3450, 2920, 2852, 2252, 1564, 1464, 1415, 1258, 1120; ^{1}H-NMR (500 MHz, $CDCl_3$) δ:1.33~1.36 and 1.37~1.44 (6H, m), 2.06 (2H, q like, *J*= ca. 6.9 Hz, H-16), 2.13 (2H, q like, *J*=ca. 7.5 Hz, H-11), 4.95 (2H, m, H-3, H-17$_{trans}$), 5.02 (1H, dq, *J*=17.2, 1.7 Hz, H-17$_{cis}$), 5.22 (1H, d, *J*=8.1 Hz, H-8), 5.28 (1H, d, *J*=10.2 Hz, H-1$_{trans}$), 5.49 (1H, dd, *J*=17.1, 0.9 Hz, H-1$_{cis}$), 5.54 (1H, dd, *J*=10.8, 8.1 Hz, H-9), 5.63 (1H, dt, *J*=10.8, 7.4 Hz, H-10), 5.83 (1H ddt, *J*=17.2, 10.3, 6.7 Hz, H-16), 5.96 (1H, ddd, *J*=17.1, 10.1, 5.4 Hz, H-2); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 28.34 (C-11), 29.35 (C-12), 29.39 (C-13), 29.78 (C-14), 34.39 (C-15), 59.30 (C-8), 64.21 (C-3), 69.42 (C-6), 70.98 (C-5), 78.94 (C-4), 80.49 (C-7), 115.06 (C-17), 118.10 (C-1), 128.42 (C-9), 135.27 (C-10), 136.44 (C-2), 139.70 (C-16)

***p*-Hydroxyacetophenone (7)**: colorless oil; ^{1}H-NMR (500MHz, $CDCl_3$): δ 2.59 (3H, s, H-2), 6.95 (2H, d, *J*= 8.5 Hz, H-3′, H-5′), 7.67 (1H, br.s, OH), 7.92 (2H, d, *J*= 8.5 Hz, H-2′, H-6′); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 27.01 (C-2), 116.28 (C-2″, C-6′), 130.23 (C-3′, C-5′), 131,95 (C-1′), 162.15 (C-4′), 199.39 (C-1)

Oplodiol (8): colorless powder, mp 96°C, $[\alpha]_D^{20}$ -6.0° (EtOH, c.0.1), ^{1}H-NMR (500MHz, $CDCl_3$) : δ 0.97 (3H, s, H-14), 1.04 (3H, d, *J*=6.9 Hz, H-12*), 1.05 (3H, d, *J*=6.9 Hz, H-13*), 1.19 (3H, s, H-15), 1.32 (1H, dd, *J*=11.7, 5.5 Hz, H-5), 1.53~1.64 (2H, m, H-3), 1.76 (1H, dt, *J*=13.8, 3.4 Hz, H-2), 1.85~1.90 (2H, m, H-2, H-9), 2.00-2.13 (3H, m, H_2-6, H-9), 2.22 (1H, sept., *J*=6.8Hz,

H-11), 3.31 (1H, dd, J=11.9, 3.9 Hz, H-1), 5.34 (1H, br.d, J=4.5 Hz, H-8) [* exchangeble], ^{13}C-NMR (125 MHz, $CDCl_3$) : δ 11.68 (C-14), 21.20 (C-13), 21.75 (C-12), 23.06 (C-6), 26.77 (C-2), 29.84 (C-15), 34.97 (C-11), 37.68 (C-10), 39.48 (C-3), 40.72 (C-9), 46.49 (C-5), 70.95 (C-4), 79.90 (C-1), 116.08 (C-8), 141.94 (C-7)

RESULTS AND DISCUSSION

Compound **1** was obtained as a colorless oil. The ^{1}H-NMR spectrum showed the typical pattern of 1-alkyl-3-methoxyl-4-hydroxyphenol (Fuzzati *et al.*, 1995; Kostova *et al.*, 1995). In addition, the ^{1}H-NMR spectrum indicated three olefinic protons [δ 5.02 (1H, dm, J=10.1 Hz), 5.04 (1H, dm, J=16.8 Hz) and 5.92(2H, ddt, J=16.8, 10.1, 6.7 Hz)] and a methylene proton signal [δ 3.29 (2 H, br.d, J=6.7 Hz)]. The ^{13}C-NMR spectrum showed 9 carbon signals, which were composed of 1-alkyl-3-methoxyl-4-phenol (δ 56.54, 111.75, 116.24, 121.85, 138.51, 144.56, 147.10), a terminal double bond (δ 114.91 and 132.62) and a methylene carbon adjacent to the double bond (δ 40.61). Based on the above evidences and a comparison of the data with the literature (Mulkens *et al.*, 1988), the structure of **1** was concluded to be eugenol.

Compound **2** was obtained as a colorless oil and its molecular formula was determined to be $C_{17}H_{22}O$ by EIMS (m/z 242, M^+). Its IR spectrum displayed absorption band at 2253 cm^{-1}, indicating the presence of alkyne groups. The ^{1}H-NMR spectrum indicated two terminal double bonds [δ 5.21 (1H, d, J=10.1 Hz), 5.44 (1H, d, J=17.4 Hz, H-1), 5.91 (1H, ddd, J=17.4, 10.1, 5.5 Hz), 4.91 (1H, d, J=10.1, 1.8 Hz), 4.97 (1H, dd, J=17.1, 1.8 Hz) and 5.78 (1H, ddt, J=17.1, 10.1, 6.7 Hz)], a *cis* double bond [δ 5.35 (1H, br.dd, J=10.8, 7.0 Hz) and 5.49 (1H, dt, J=10.8, 7.4 Hz)] and an oxygenated proton [δ 4.89 (1H, m)]. The ^{13}C-NMR spectrum indicated the presence of two triple bonds (δ 64.79, 71.93, 75.00 and 80.86), three double bonds (115.01, 117.74, 122.80, 133.66, 136.84 and 139.75) and an oxygenated carbon (δ 64.16). Analysis of the ^{1}H-^{1}H-COSY spectrum allowed the assignments of all the ^{1}H-NMR signals. Based on the evidence above and a comparison with the literature (Bernart *et al.*, 1996), the structure of **2** was determined to be dehydrofalcarinol. The NMR data of **2** was in good agreement with the C_1-C_2-C_3-C_4-C_5-C_6 moiety in (3*R*)-pentadeca-1,9(*Z*),14-trien-4,6-diyn-3,8-diol (Pandey *et al.*, 1984). The optical rotation value in (3*S*)-falcarinol was + 29° while in the 3*R*-form it was negative (Bernart *et al.*, 1996; Bernart *et al.*, 1994; Shim *et al.*, 1985). Based on these data, the structure of **2** was proposed as (3*R*)-dehydrofalcarinol ($[\alpha]_D^{25}$ 26.3°).

Compound **3** was obtained as a yellow powder and showed a molecular ion peak at m/z 152. In the ^{1}H- and ^{13}C-NMR spectra, the signals were similar to those of compound **4**, except for singlet aldehyde proton signal

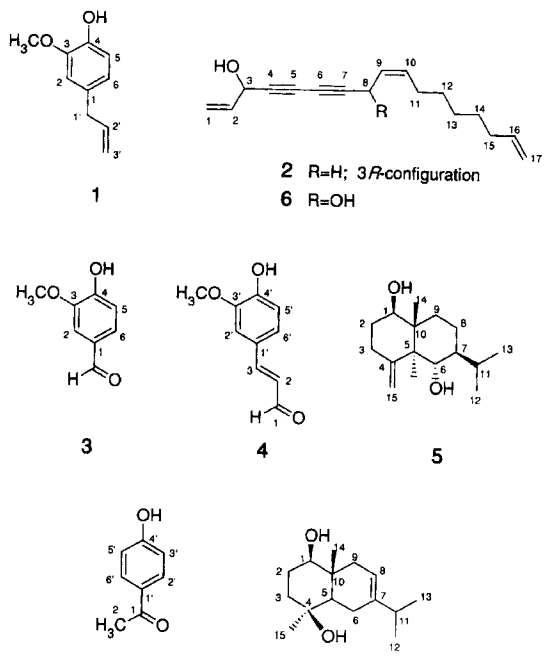

Fig. 1. Structures of compounds **1-8**

and a disappearing *trans* double bond. Thus, **3** is suggested to be vanillin. The structure was further confirmed by a comparison with authentic vanillin.

Compound **4** was obtained as a yellow powder. EIMS and DEPT data established the molecular formula of $C_{10}H_{10}O_3$. The IR spectrum showed hydroxy (3400 cm^{-1}) and carbonyl group (1660cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra indicated the presence of an aromatic ring, a *trans* double bond [δ 6.61 (dd, J=15.9, 7.7 Hz) and δ 7.41(d, J=15.9 Hz)], an aldehyde group [δ 9.65 (d, J= 7.7 Hz) in ^{1}H-NMR spectrum and δ 193.59 in ^{13}C-NMR spectrum] and a methoxy group (δ 3.97 in ^{1}H-NMR spectrum). On the basis of the spectral data and a comparison with the data reported previously (Herath *et al.*, 1998), the structure of **4** was determined as 3'-methoxy-4'-hydroxy-*trans*-cinnamaldehyde.

Compound **5** was obtained as colorless gum. The ^{1}H-NMR spectrum showed two secondary methyl groups at δ 0.88 (3H, d, J=7.0Hz) and 0.96 (3H, d, J=7.0Hz), a quaternary methyl group at δ 0.70 (3H, s), two carbinol protons at 3.44 (1H, dd, J=12.0, 5.0 Hz) and 3.70 (1H, t, J=9.0 Hz), and an exomethylene group at δ 4.76 (1H, br.s, H-15a) and 5.04 (1H, br.s, H-15b). The ^{13}C-NMR spectrum demonstrated the presence of 15 carbon signals that contained two olefinic carbon signals at δ 107.78 and 146.25, and two carbinol carbon signal at δ 67.03 and 79.06. This suggested that **5** was a eudesmane sesquiterpene with two secondary alcohol groups, an exomethylene and an isopropyl group. Thus, the structure of compound **5** was determined to be 1β, 6α-dihydroxy-4(15)-eudesmene. The NMR spectral and physical data of compound **5** were in good agreement with the

literature (Gutierrez *et al.*, 1988).

Compound **6** was obtained as a colorless oil. Both the ^{1}H- and ^{13}C-NMR spectra were very similar to those of **2** except for the presence of additional hydroxy group. The major differences were signal at δ 5.22 (1H, d, *J*=8.1 Hz) in the ^{1}H-NMR spectrum and δ 59.30 in the ^{13}C-NMR spectrum of **6**. Analysis of the ^{1}H-^{1}H-COSY of **6** allowed for the assignments of the C_1-C_2-C_3 and C_8-C_9-C_{10} linkages, indicating the location of a hydroxy group and double bond.

Based on the above evidences and a comparison with the literatures (Pandey *et al.*, 1984; Bernart *et al.*, 1996), the structure of **6** was determined to be heptadeca-1, 9(*Z*),16-trien-4,6-diyn-3,8-diol (dehydrofalcarindiol). The stereochemistry at C-3 was determined to be 3*R* by a comparison of the ^{1}H- and ^{13}C-NMR spectral data of (3*R*)-pentadeca-1,9(*Z*),14-trien-4,6-diyn-3,8-diol (Pandey *et al.*, 1984) and compound **2**. The C-3 position in falcarindiol made a smaller contribution to the optical activity than C-8 (Bernart *et al.*, 1996). The optical rotation value in (3*S*, 8*S*)-dehydrofalcarindiol was + 260°, while in **6** it was 104°. This indicated that the stereochemistry at C-8 in **6** was the *R*-form. Although the structure of **6** being (3*R*, 8*R*)-dehydrofalcarindiol is proposed, the unambiguous determination of the stereochemistry at C-8 needs to be further investigated.

Compound **7** was obtained as a colorless oil and the ^{1}H-NMR spectrum was very similar to that of **3**. The major difference was the absence of the methoxy group in **7**. Thus, the structure of **7** was inferred to be *p*-hydroxyacetophenone, which was further confirmed by a comparison with authentic *p*-hydroxyacetophenone (Hoque, 1984).

Compound **8** was obtained as a colorless powder. The ^{1}H-NMR spectrum showed two secondary methyl groups at δ 1.04 (3H, d, *J*=6.9 Hz) and 1.05 (3H, d, *J*=6.9 Hz), two quaternary methyl groups at δ 0.97 (3H, s) and 1.19 (3H, s), a carbinol protons at δ 3.31 (1H, dd, *J*=11.9, 3.9 Hz), and an olefinic proton at δ 5.34 (1H, br.d, *J*=4.5 Hz). The ^{13}C-NMR spectrum indicated the presence of 15 carbon signals that contained two olefinic carbons at δ 116.08 and 141.94, and two oxygenated carbons at δ 70.95 and 79.90. The spectral data suggested that **8** was a eudesmane sesquiterpene with a secondary alcohol, a tertiary alcohol, a double bond and a isopropyl group. Based on the available chemical structures of the sesquiterpene (Sung *et al.*, 1992; Feliciano *et al.*, 1989) and the NMR spectral data, the structure of compound **8** was determined to be oplodiol. The NMR spectral and physical data of compound **8** were in good agreement with the literature (Jung *et al.*, 1997).

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