

## Six Podocarpane-Type Trinorditerpenes from the Bark of *Taiwania cryptomerioides*

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Six podocarpane-type trinorditerpenes were isolated from the bark of *Taiwania cryptomerioides*. Their structures, 14-hydroxy-13-methoxy-8,11,13-podocarpatrien-7-one (**1**), 13-hydroxy-12-methoxy-8,11,13-podocarpatriene (**2**), 12-hydroxy-13-methoxy-8,11,13-podocarpatriene (**3**), 14-hydroxy-13-methoxy-8,11,13-podocarpatriene (**4**), 13-hydroxy-8,11,13-podocarpatriene (**5**), and 13,14-dihydroxy-8,11,13-podocarpatrien-7-one (**6**), were determined principally from spectral evidence.

**Key words** *Taiwania cryptomerioides*; Taxodiaceae; Trinorditerpene; podocarpane

*Taiwania cryptomerioides* HAYATA (Taxodiaceae) is an economically important tree species indigenous to Taiwan and *Taiwania* is one of the most decay-resistant species in the country. We have previously investigated the chemical components of its heartwood<sup>1–4</sup> and bark,<sup>5–7</sup> and found various sesquiterpenes, lignans, and abietane-type diterpenes. Kamil<sup>8</sup>) has described the bisflavones found in its leaves. Recently, many other compounds have been obtained from its leaves, including several with novel structural skeletons as described by Lin.<sup>9–12</sup> A podocarpane-type trinorditerpene 1 $\beta$ ,13,14-trihydroxy-8,11,13-podocarpatriene-7-one<sup>12</sup>) was isolated for the first time from this plant. Because many interesting novel skeletal components have been reported, we were encouraged to study the chemical constituents of its bark again. We report here six new podocarpane-type trinorditerpenes, **1**–**6**, 14-hydroxy-13-methoxy-8,11,13-podocarpatrien-7-one (**1**), 13-hydroxy-12-methoxy-8,11,13-podocarpatriene (**2**), 12-hydroxy-13-methoxy-8,11,13-podocarpatriene (**3**), 14-hydroxy-13-methoxy-8,11,13-podocarpatriene (**4**), 13-hydroxy-8,11,13-podocarpatriene (**5**), and 13,14-dihydroxy-8,11,13-podocarpatrien-7-one (**6**).

The molecular formula of compound **1** was established as C<sub>18</sub>H<sub>24</sub>O<sub>3</sub> by high resolution mass spectroscopy (HR-MS). IR absorptions were attributable to a hydroxyl group (3473 cm<sup>-1</sup>), an aromatic group (3041, 1580, 1481 cm<sup>-1</sup>), and a conjugated carbonyl (1635 cm<sup>-1</sup>). The UV absorption at  $\lambda_{\max}$  221.5 and 269.5 nm was attributable to the phenone moiety. The <sup>1</sup>H-NMR spectrum showed three singlets of methyl groups at  $\delta$  0.92, 0.97 and 1.18 (H-18, H-19, H-20) (Table 1) and two aromatic *ortho* protons occurred at  $\delta$  6.71 (d,  $J$ =8.4 Hz, H-11) and 6.98 (d,  $J$ =8.4 Hz, H-12). No isopropyl group was observed by NMR. Compound **1** is a C<sub>17</sub> podocarpane diterpene with a methoxy group [ $\delta_{\text{H}}$  3.86 (3H, s),  $\delta_{\text{C}}$  56.2]. Comparison of the <sup>13</sup>C-NMR (Table 2) data of **1** with that of the known 1 $\beta$ ,13,14-trihydroxy-8,11,13-podocarpatrien-7-one (**7**),<sup>12</sup>) suggests that **1** possesses the same skeletal structure. Three of six aromatic carbon signals appear at lower field,  $\delta$  148.5, 146.5 and 153.1, and those signals were assigned to C-9,<sup>12</sup>) C-13, and C-14, respectively. The singlet at  $\delta_{\text{C}}$  12.98 indicates a hydrogen bond between a hydroxyl (C-14) and a carbonyl (C-7) group.<sup>12, 13</sup>) A typical H $\beta$ -1 signal at  $\delta$  2.32 (br d,  $J$ =12.3 Hz) for dehydroabietane and dehydropodocarpane type derivatives<sup>12, 14–16</sup>) is present. An ABX system at  $\delta$  1.82 (1H, dd,  $J$ =4.5, 13.0 Hz), 2.59

(1H, dd,  $J$ =13.0, 18.9 Hz) and 2.69 (1H, dd,  $J$ =4.5, 18.9 Hz) was observed and was assigned to H-5 and H-6, respectively. Meanwhile, H-11 ( $\delta$  6.71) and H $\beta$ -1 ( $\delta$  2.32), and MeO-13 ( $\delta$  3.86) and H-12 ( $\delta$  6.98) show correlations in nuclear Overhauser enhancement and exchange spectroscopy (NOESY), establishing the structure of the aromatic ring. This assignment is also supported by proton-detected heteronuclear multiple-quantum coherence (HMQC) and proton detected heteronuclear multiple bond correlation (HMBC) experiments. Accordingly, **1** is 14-hydroxy-13-methoxy-8,11,13-podocarpatrien-7-one.

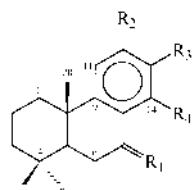
Compound **2** has the molecular formula C<sub>18</sub>H<sub>26</sub>O<sub>2</sub> on the basis of exact mass spectral data. Only two functional groups (aromatic, hydroxyl) were present in its IR spectrum. Four singlet methyl groups at  $\delta$  0.90, 0.92, 1.16, and 3.83 (–OCH<sub>3</sub>) and two singlet phenyl protons at  $\delta$  6.56 and 6.72 (Table 1) in its <sup>1</sup>H-NMR spectrum indicated that **2** is also a tricyclic dehydropodocarpane skeleton diterpenoid with substitution at both C-12 and C-13. An H $\beta$ -1 signal, indicating a dehydropodocarpane molecule, was also observed at  $\delta$  2.18 (br d,  $J$ =13.6 Hz). Three downfield <sup>13</sup>C-NMR signals at  $\delta$  141.9, 143.1 and 144.6 (Table 2) were assigned as C-9, C-13 and C-12, respectively. C-12 and C-13 are phenyl carbons bond to oxygen; the connected groups are a hydroxyl (an exchangeable br s at  $\delta$  5.40) and a methoxyl ( $\delta_{\text{H}}$  3.83;  $\delta_{\text{C}}$  55.8). The phenyl proton at  $\delta$  6.72 exhibited an NOE correlation with H $\beta$ -1 and with the methoxyl group. This evidence confirms the methoxyl group connecting at C-12. The <sup>13</sup>C-NMR and HMBC data, in addition to the above evidence, show that **2** is 13-hydroxy-12-methoxy-8,11,13-podocarpatriene. Our identification of compound **2** is the first time it has been isolated from a natural source, although it has been synthesized from abietic acid (**8**).<sup>17</sup>)

Compound **3** has a tricyclic diterpenoid skeleton similar to that of **2**, as indicated by the presence in the <sup>1</sup>H-NMR spectrum of four singlet methyl groups at  $\delta$  0.89, 0.92, 1.14 and 3.81 and the appearance of two singlet phenyl protons at  $\delta$  6.48 and 6.81. The molecular formula C<sub>18</sub>H<sub>26</sub>O<sub>2</sub>, based on HR-MS, indicated that **3** is an isomer of **2**. Comparison of the <sup>1</sup>H- and <sup>13</sup>C-NMR data (Tables 1, 2) of **3** with those of **2** indicated that the difference between **2** and **3** is in the position of the hydroxyl and methoxyl groups. The expected signal for an H $\beta$ -1 of dehydropodocarpane at  $\delta$  2.17 (1H, br d,  $J$ =13.2 Hz) is also present. NOESY data (H $\beta$ -1 correlated

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with  $\delta$  6.81, and the methoxyl group correlated with  $\delta$  6.48) indicates that the structure of **3** is 12-hydroxy-13-methoxy-8,11,13-podocarpatriene. HMBC data also supported the assigned structure.

Compound **4**, an isomer of **3**, had HR-MS and  $^{13}\text{C}$ -NMR data (Table 2) consistent with the molecular formula  $\text{C}_{18}\text{H}_{26}\text{O}_2$ . Analysis of the IR spectrum of **4** suggested it contained a hydroxyl group ( $3430\text{ cm}^{-1}$ ) and a phenyl group ( $1610, 1586, 1500\text{ cm}^{-1}$ ). It has a tricyclic diterpenoid skeleton similar to that of **3** as indicated by the presence in the  $^1\text{H}$ -NMR spectrum (Table 1) of four singlet methyl groups at  $\delta$  0.92, 0.95, 1.17, and 3.81, and two aromatic *ortho* protons at  $\delta$  6.76 (d,  $J=8.7\text{ Hz}$ , H-11) and 6.69 (d,  $J=8.7\text{ Hz}$ , H-12).



- 1  $\text{R}_1 = \text{O}$ ,  $\text{R}_2 = \text{H}$ ,  $\text{R}_3 = \text{OMe}$ ,  $\text{R}_4 = \text{OH}$   
 2  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{OMe}$ ,  $\text{R}_3 = \text{OH}$ ,  $\text{R}_4 = \text{H}$   
 3  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{OH}$ ,  $\text{R}_3 = \text{OMe}$ ,  $\text{R}_4 = \text{H}$   
 4  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{H}$ ,  $\text{R}_3 = \text{OMe}$ ,  $\text{R}_4 = \text{OH}$   
 5  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{R}_4 = \text{H}$ ,  $\text{R}_3 = \text{OH}$   
 6  $\text{R}_1 = \text{O}$ ,  $\text{R}_2 = \text{H}$ ,  $\text{R}_3 = \text{R}_4 = \text{OH}$

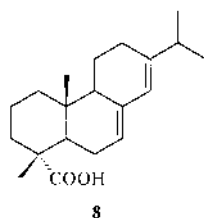
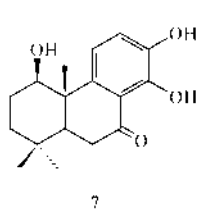


Chart 1

Comparison of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of **4** with that of **3** indicated that the difference between **4** and **3** is the position of the hydroxyl ( $\delta$  5.64, brs, exchangeable with  $\text{D}_2\text{O}$ ) and methoxyl groups. The expected signal for an  $\text{H}_{\beta-1}$  of dehydropodocarpene at  $\delta$  2.40 (1H, br d,  $J=12.8\text{ Hz}$ ) has a NOESY correlation with  $\delta$  6.76 (H-11), and the methoxyl group correlates with  $\delta$  6.69 (H-12). This evidence agrees with the structure of **4** being 14-hydroxy-13-methoxy-8,11,13-podocarpatriene. HMBC data also confirm the assigned structure.

Three singlet methyl groups and a 1,2,4-trisubstituted phenyl moiety in compound **5** are indicated by signals at  $\delta$  0.90, 0.92, 1.14 (3H each, s), 6.48 (1H, d,  $J=2.8\text{ Hz}$ ), 6.57 (1H, dd,  $J=2.8, 8.6\text{ Hz}$ ) and 7.08 (1H, d,  $J=8.6\text{ Hz}$ ) (Table 1). One hydroxyl group attached to a phenyl group was revealed by the signals at  $\delta$  4.60 (exchangeable with  $\text{D}_2\text{O}$ ) and  $\delta_{\text{C}}$  152.8 (Table 2). Analysis of the  $^1\text{H}$ -,  $^{13}\text{C}$ -, HMQC and HMBC NMR data indicated that the structure of **5** ( $\text{C}_{17}\text{H}_{24}\text{O}$ ) is 12- or 13-hydroxy-8,11,13-podocarpatriene. The phenyl proton ( $\delta$  7.08) shows an NOE correlation with  $\text{H}_{\beta-1}$  [ $\delta$  2.20 (1H, br d,  $J=13.1\text{ Hz}$ )], showing that the hydroxyl group is located at C-13. Akita<sup>17)</sup> has synthesized this compound from abietic acid (**8**).

Compound **6** has the formula  $\text{C}_{17}\text{H}_{22}\text{O}_3$ , based on HR-MS and  $^{13}\text{C}$ -NMR data (Table 2), indicating an index of hydrogen deficiency (IHD) of seven. Analysis of the IR spectrum suggested that the molecule contains a hydroxyl group ( $3363\text{ cm}^{-1}$ ), a phenyl group ( $1580, 1480\text{ cm}^{-1}$ ), and a conjugated ketone, together with a strong hydrogen bond ( $1626, 3100\text{--}2600\text{ cm}^{-1}$ ). The UV absorption at  $\lambda_{\text{max}}$  273 nm was consistent with this. Two exchangeable phenolic protons at  $\delta$  5.53 and 12.80 (Table 1) indicate that one of the hydroxyl groups is attached at C-14 with a strong hydrogen bond to the C-7 carbonyl group. Three singlet methyl groups are

Table 1.  $^1\text{H}$ -NMR Spectral Data of Compounds **1**–**6** (300 MHz in  $\text{CDCl}_3$ )

H	1	2	3	4	5	6
1	1.47 m 2.24 br d (12.3)	1.36 m 2.18 br d (13.6)	1.32 m 2.17 br d (13.2)	1.36m 2.40 br d (12.8)	1.30 m 2.20 br d (13.1)	1.48 m 2.24 br d (13.6)
2	1.52 m 1.70 m	1.60 m 1.80 m	1.58 m 1.82m	1.60m 1.82m	1.62 m 1.81 m	1.64 m 1.74 m
3	1.22 m 1.55 m	1.22 m 1.44 m	1.18 m 1.44m	1.22 m 1.46 m	1.17 m 1.45 m	1.24 m 1.52 m
5	1.82 dd (4.5, 13.0)	1.27 <sup>a)</sup>	1.28 <sup>a)</sup>	1.28 <sup>a)</sup>	1.22 <sup>a)</sup>	1.82 dd (6.4, 11.2)
6	2.59 dd (13.0, 18.9) 2.69 dd (4.5, 18.9)	1.60 m 1.80 m	1.68 m 1.72 m	1.68m 1.90m	1.64 m 1.82 m	2.64 dd (11.2, 18.8) 2.70 dd (6.4, 18.8)
7		2.80 m	2.79 m	2.64m 2.92m	2.80 m	
11	6.71d (8.4)	6.72 s	6.81 s	6.76 (8.7)	7.08 d (8.6)	6.67 d (7.8)
12	6.98d (8.4)			6.69 (8.7)	6.57 dd (2.8, 8.6)	7.01 d (7.8)
14		6.56 s	6.48 s		6.48 d (2.8)	
18	0.92 s	0.92 s	0.92 s	0.95 s	0.92 s	0.92 s
19	0.97 s	0.90 s	0.89 s	0.92 s	0.90 s	0.97 s
20	1.18 s	1.16 s	1.14 s	1.17 s	1.14 s	1.18 s
–OH	12.98 s	5.40 br s	5.36 br s	5.64 br s	4.60 br s	5.53 s, 12.80 s
–OMe	3.86 s	3.83 s	3.81 s	3.81		

a) Overlapping with other signals.

Table 2.  $^{13}\text{C}$ -NMR Spectral Data of Compounds 1–6 (75 MHz in  $\text{CDCl}_3$ )

C	1	2	3	4	5	6
1	38.0	39.2	39.0	39.1	39.0	37.9
2	18.8	19.2	19.2	19.3	19.0	18.8
3	41.3	41.7	41.7	41.7	41.7	41.2
4	33.2	33.4	33.4	33.3	33.4	33.2
5	49.2	50.6	50.6	50.0	50.5	49.5
6	36.3	19.3	19.3	19.3	19.3	36.1
7	206.5	29.9	30.2	24.1	30.4	206.7
8	115.4	128.2	126.6	122.3	136.9	115.1
9	148.5	141.9	143.1	144.3	143.0	148.2
10	37.7	37.6	37.4	37.3	37.3	37.7
11	112.8	106.9	110.5	114.8	125.6	113.6
12	117.9	144.6	144.6	108.8	112.8	120.8
13	146.1	143.1	143.3	143.2	152.8	142.7
14	153.1	114.2	110.6	142.4	114.8	149.4
18	32.5	33.3	33.3	33.3	33.3	32.5
19	21.4	21.6	21.6	21.6	21.6	21.4
20	23.6	24.7	24.7	25.0	24.9	23.6
–OCH <sub>3</sub>	56.2	55.8	55.8	55.9		

found at  $\delta$  0.92, 0.97 and 1.18. Three signals at  $\delta$  1.82 (1H, dd,  $J=6.4$ , 11.2 Hz), 2.64 (1H, dd,  $J=11.2$ , 18.8 Hz) and 2.70 (1H, dd,  $J=6.4$ , 18.8 Hz) were assigned as H-5 and H-6, respectively. Comparison of the spectral data of **6** with that of compound **1** suggested that a hydroxyl group in **6** replaces the methoxyl group in **1**. A pair of aromatic protons with *ortho* coupling at  $\delta$  6.67 (d,  $J=7.8$  Hz) and  $\delta$  7.01 (d,  $J=7.8$  Hz), as well as an NOE correlation between  $\delta$  6.67 and  $\delta$  2.24 (1H, br d,  $J=13.6$  Hz,  $H_{\beta-1}$ ), indicate that the hydroxyl groups are located at C-13 and C-14. Therefore, the structure of **6** is 13,14-dihydroxy-8,11,13-podocarpatrien-7-one. The results of HMBC and NOESY experiments confirmed the assigned structure.

## Experimental

**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.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were obtained on a Bruker AM-300 at 300 and 75 MHz in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as an internal standard. EI-MS, FAB-MS, UV, and specific rotations were recorded on a JEOL JMS-HX 300, a JEOL JMS-HX 110, a Hitachi S-3200 spectrometer, and a JASCO DIP-180 digital polarimeter, respectively. Extracts were chromatographed on silica gel (Merck 3374, 70–230 mesh).

**Plant Material** The bark of *T. cryptomerioides* was collected in Tai-Chun, Taiwan, in 1996. The plant material was identified by Mr. Muh-Tsuen Gun, formerly a technician of the Department of Botany, National Taiwan University. A voucher specimen has been deposited at the Herbarium of the Department of Botany of the National Taiwan University, Taipei, Taiwan.

**Extraction and Isolation** Air-dried bark of *T. cryptomerioides* (12 kg) was extracted three times with acetone (60 l) at room temperature (7 d per extraction). The acetone extract was evaporated *in vacuo* to leave a black residue which was suspended in  $\text{H}_2\text{O}$  (8 l), and then partitioned (3 $\times$ ) with 1 l of ethyl acetate. The EtOAc fraction (360 g) was chromatographed on silica gel using a mixture of *n*-hexane and EtOAc of increasing polarity as eluent and further purified by HPLC, eluting with  $\text{CH}_2\text{Cl}_2$ :EtOAc (50:1). Six components, 14-hydroxy-13-methoxy-8,11,13-podocarpatrien-7-one (**1**) (2.4 mg), 13-hydroxy-12-methoxy-8,11,13-podocarpatriene (**2**) (4.2 mg), 12-hydroxy-13-methoxy-8,11,13-podocarpatriene (**3**) (2.6 mg), 14-hydroxy-13-methoxy-8,11,13-podocarpatriene (**4**) (5 mg), 13-hydroxy-8,11,13-podocarpatriene (**5**) (5.3 mg), and 13,14-dihydroxy-8,11,13-podocarpatrien-7-one (**6**) (3.5 mg) were obtained in pure form.

14-Hydroxy-13-methoxy-8,11,13-podocarpatrien-7-one (**1**): Amorphous

solid;  $[\alpha]_D^{22} = -7.7^\circ$  ( $c=0.23$ ,  $\text{CHCl}_3$ ); UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm (log  $\epsilon$ ): 221 (4.04), 269 (3.84), 356 (3.39) nm; IR (film)  $\nu_{\text{max}}$  3473, 3041, 1635, 1580, 1481, 1351, 1250, 1050, 806  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR, see Table 1, and  $^{13}\text{C}$ -NMR, see Table 2; EI-MS (70 eV) (rel. int. %)  $m/z$  288 [ $\text{M}]^+$  (100), 273 (46), 255 (47), 205 (38); HR-EI-MS  $m/z$  288.1726 ( $\text{M}^+$  Calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_3$ , 288.1726).

13-Hydroxy-12-methoxy-8,11,13-podocarpatriene (**2**): Yellowish oil;  $[\alpha]_D^{18} = +17.8^\circ$  ( $c=0.40$ ,  $\text{CHCl}_3$ ); IR (film)  $\nu_{\text{max}}$  3456, 3035, 1619, 1507, 1255, 1195, 1049, 870  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR, see Table 1, and  $^{13}\text{C}$ -NMR, see Table 2; EI-MS (70 eV) (rel. int. %)  $m/z$  274 [ $\text{M}]^+$  (63), 259 (100), 201 (26), 189 (27); HR-EI-MS  $m/z$  274.1934 ( $\text{M}^+$  Calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_2$ , 274.1929).

12-Hydroxy-13-methoxy-8,11,13-podocarpatriene (**3**): Yellowish oil;  $[\alpha]_D^{15} = +19.2^\circ$  ( $c=0.22$ ,  $\text{CHCl}_3$ ); IR (dry film)  $\nu_{\text{max}}$  3395, 3039, 1621, 1593, 1503, 1275, 1175, 1029, 870  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR, see Table 1, and  $^{13}\text{C}$ -NMR, see Table 2; EI-MS (70 eV) (rel. int. %)  $m/z$  274 [ $\text{M}]^+$  (58), 259 (100), 189 (42), 177 (40), 163 (47); HR-EI-MS  $m/z$  274.1936 ( $\text{M}^+$  Calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_2$ , 274.1929).

14-Hydroxy-13-methoxy-8,11,13-podocarpatriene (**4**): Amorphous solid;  $[\alpha]_D^{15} = +20.1^\circ$  ( $c=0.40$ ,  $\text{CHCl}_3$ ); UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm (log  $\epsilon$ ): 278 (3.2); IR (film)  $\nu_{\text{max}}$  3430, 1610, 1586, 1500, 1202, 1062, 976, 804  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR, see Table 1, and  $^{13}\text{C}$ -NMR, see Table 2; EI-MS (70 eV) (rel. int. %)  $m/z$  274 [ $\text{M}]^+$  (60), 259 (100), 203 (16), 189 (27); HR-EI-MS  $m/z$  274.1941 ( $\text{M}^+$  Calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_2$ , 274.1929).

13-Hydroxy-8,11,13-podocarpatriene (**5**): Colorless needle; mp: 125–127  $^\circ\text{C}$ ;  $[\alpha]_D^{21} = +16.7^\circ$  ( $c=0.43$ ,  $\text{CHCl}_3$ ); IR (film)  $\nu_{\text{max}}$  3390, 3041, 1501, 1222, 1155, 970  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR, see Table 1, and  $^{13}\text{C}$ -NMR, see Table 2; EI-MS (70 eV) (rel. int. %)  $m/z$  244 [ $\text{M}]^+$  (26), 229 (86), 205 (46), 159 (30), 146 (100), 133 (60); HR-EI-MS  $m/z$  244.1820 ( $\text{M}^+$  Calcd for  $\text{C}_{17}\text{H}_{24}\text{O}$ , 244.1828).

13,14-Dihydroxy-8,11,13-podocarpatrien-7-one (**6**): Amorphous solid;  $[\alpha]_D^{17} = -13.9^\circ$  ( $c=0.21$ ,  $\text{CHCl}_3$ ); UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm (log  $\epsilon$ ): 211 (4.15), 227 (4.11), 273 (4.07), 360 (3.54) nm; IR (film)  $\nu_{\text{max}}$  3363, 3100–2600, 1626, 1580, 1480, 1250, 1116, 970, 830  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR, see Table 1, and  $^{13}\text{C}$ -NMR, see Table 2; EI-MS (70 eV) (rel. int. %)  $m/z$  274 [ $\text{M}]^+$  (100), 259 (66), 191 (44), 189 (39), 177 (23), 91 (22); HR-EI-MS  $m/z$  274.1559 ( $\text{M}^+$  Calcd for  $\text{C}_{17}\text{H}_{22}\text{O}_3$ , 274.1567).

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