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PHENOLIC DITERPENES FROM *TRIPTERYGIUM WILFORDII* VAR. *REGELII*

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Key Word Index—*Tripterygium wilfordii*; Celastraceae; stems; bark; diterpene; triptobenzene.

Abstract—Seven new phenolic abietane type diterpenoids: 14, 19-dihydroxy-3-oxo-abieta-8, 11, 13-triene; 3, 14-dihydroxy-abieta-8, 11, 13-triene; 14, 19-dihydroxy-3, 7-dioxo-abieta-8, 11, 13-triene; 18(4 → 3)-*abeo*-abieta-3,8,11,13-tetraene-18-oic acid; 18(4 → 3)-*abeo*-14, 15-dihydroxy-abieta-3, 8, 11, 13-tetraene-18,19-olide; 18(4 → 3)-*abeo*-abieta-14,16-dihydroxy-abieta-3,8,11,13-tetraene-18,19-olide; 18(4 → 3)-*abeo*-abieta-14, 17-dihydroxy-abieta-3,8,11,13-tetraene-18,19-olide named triptobenzene A, B, C, D, E, F and G have been isolated from *Tripterygium wilfordii* var. *regelii*. Their structures have been established on the basis of spectroscopic evidence. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In a continuation of our work on terpenoids from *Tripterygium wilfordii* var. *regelii* Makino of the Celastraceae family [1–5], we have now studied the diterpenoids present in this species. Related diterpenoids of *T. wilfordii* were reported by several groups [5–19]. The structure elucidation of seven new phenolic abietane-type diterpenoids, triptobenzene A (**1**), B (**2**), C (**3**), D(**4**), E (**5**), F (**6**) and G (**7**) from the stems and bark of *T. wilfordii* var. *regelii* is the subject of this paper.

RESULTS AND DISCUSSION

Repeated column chromatography of the ethyl acetate-soluble fraction from the methanol extracts of stems and bark of *T. wilfordii* var. *regelii* yielded triptobenzene A (**1**), B (**2**), C (**3**), D (**4**), E (**5**), F (**6**) and G (**7**).

The first diterpene triptobenzene A (**1**) had a molecular formula $C_{20}H_{28}O_3$ ($[M]^+$ at m/z 316) and its IR spectrum showed ketone (1700 cm^{-1}) and hydroxy group absorptions. The UV spectrum of **1** showed the presence of an aromatic moiety with maxima at 220, 272 and 280 nm. The ^1H NMR spectrum of **1** revealed the presence of an isopropyl group [δ 1.23, 1.25 (each 3H, *d*, $J = 6.8$ Hz), 3.12 (1H, *sept*, $J = 6.8$ Hz)], two methyl groups [δ 1.28, 1.34 (each 3H, *s*)], a methylene group [δ 3.54, 4.08 (each 1H, *d*, $J = 11.2$ Hz)] bearing the hydroxy group, and a 1,2,3,4-four substituted aromatic benzene ring [δ 6.80, 7.40 (each 1H, *d*, $J = 8.3$ Hz)]. The ^{13}C NMR spectrum of **1** showed one carbonyl signal at δ 219.9, four methyl carbons, four methylene carbon signals, one methylene carbon attached to an oxygen function signal at δ 65.5, four-substituted benzene carbon signals and two quaternary carbon signals. These functional groups accounted for five of seven degrees of unsaturation which was apparent from the molecular formula. This suggested that **1** had three rings one of which was a benzene ring.

From the ^1H-^1H COSY spectrum of **1**, the presence of partial structures, $-CH_2-CH_2-$, $-CH_2-CH_2CH<$ and $-CH{=}CH-$, and the attachment of the isopropyl group to the benzene ring were suggested. From these data, it was concluded that compound **1** contained the abietane skeleton. In the ^{13}C-^1H long range correlation spectrum, the proton signal at δ 2.10 (H-5) showed long range correlation with the carbon signals at δ 18.9 (C-6), 51.0 (C-4), 65.2 (C-19) and 21.9 (C-18), the proton signal at δ 3.54 (H-19) with the carbon signals at δ 219.9 and 51.0, and the proton signal at δ 4.08 with the carbon signals at δ 219.9. These facts showed the presence of ketone and hydroxy methylene moities at C-3 and C-4, respectively. The proton signal at δ 6.80 showed long range correlation with the carbon signals at δ 120.7 and 130.5, the proton signal at δ

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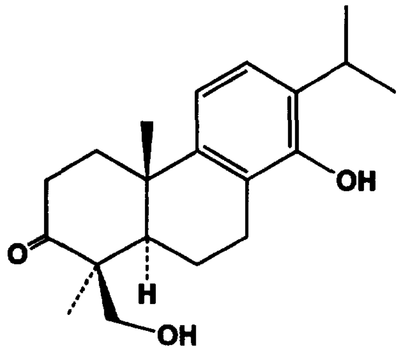

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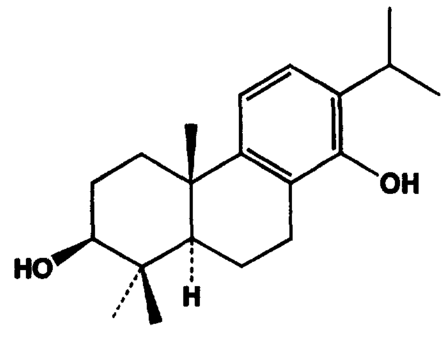

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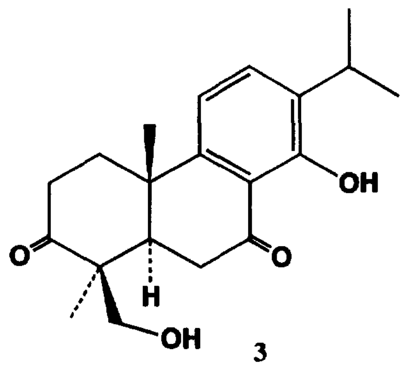

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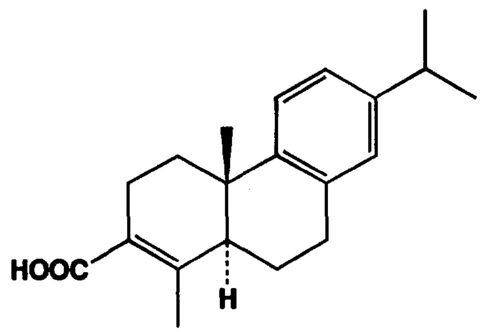

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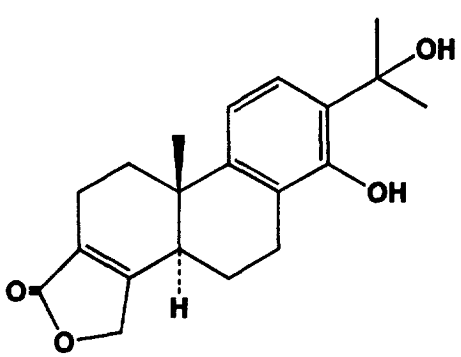

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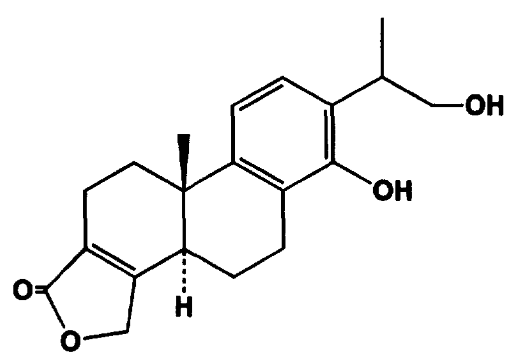

6,7

7.40 with the carbon signals at δ 145.4 and 150.0, and the proton signal at δ 3.12 with the carbon signal at δ 130.5. These facts clearly indicated the substituent pattern of the benzene ring. In the NOESY spectrum of **1**, the proton signals at δ 3.54 and 4.08 (each H-19) showed correlation with the proton signal at δ 1.28 (H-20). Thus, the configuration of the hydroxy methylene at C-4 was confirmed to be β. The assignment of the ^{1}H and ^{13}C NMR spectral data of **1** were made on the basis of the 2D NMR spectra (Table 1). There are many reports of the isolation of abietane-type diterpenoids [5–14], but the present paper describes the first isolation of compound **1** from a natural source.

Triptobenzene B (**2**), $C_{20}H_{30}O_2$ ($[M]^+$ at *m/z* 302), showed a hydroxy band at 3436 cm^{-1} and an aromatic ring band in its IR spectrum. The UV spectrum showed the presence of an aromatic ring. The ^{1}H NMR spectrum showed signal of a 1,2,3,4-tetra-substituted aromatic ring [δ 6.84, 7.01 (each 1H, *d*, J = 8.3 Hz), a hydrogen geminal to a secondary hydroxy group [δ 3.29 (1H, *dd*, J = 10.8, 5.1 Hz)], and isopropyl group [δ 1.24 (3H $\times$ 2, *d*, J = 6.8 Hz), 3.13 (1H, *sept*, J = 6.8 Hz)] and three methyls [δ 0.97, 1.07, 1.20 (each 3H, *s*)]. The structural similarity between triptobenzene A (**1**) and B (**2**) was indicated by the similarity of the ^{13}C NMR spectra of both compounds, except for C-2, 3, 4, 18 and 19 (Table 1). It was concluded that **2** was based on the same skeleton as **1**. From the ^{1}H-^{1}H COSY spectrum of **2**, the presence of

Table 1. ^{13}C NMR spectral data for compounds **1**–**7**

C	1	2	3	4	5	6	7
1	37.2	37.1	35.9	33.3	32.9	32.6	32.6
2	34.9	28.0	35.3	24.5	19.7	18.2	18.3
3	219.9	78.7	214.8	124.0	125.0	125.0	125.1
4	51.0	38.9	52.0	149.7	163.2	163.4	163.2
5	50.7	49.2	49.6	47.1	41.0	40.9	41.2
6	18.9	18.2	36.3	29.6	18.2	19.8	19.9
7	24.7	24.7	204.4	20.5	22.5	22.9	23.0
8	120.7	120.7	114.2	134.9	123.3	123.1	123.2
9	145.4	148.3	151.5	146.2	145.9	144.9	145.1
10	36.7	37.3	37.3	35.7	36.3	36.3	36.4
11	117.4	116.5	114.0	124.2	114.8	115.8	115.8
12	123.5	123.4	133.6	123.9	122.6	124.9	125.1
13	130.5	130.2	135.4	146.2	127.8	128.0	127.9
14	150.0	150.2	160.9	127.0	153.6	153.1	153.2
15	26.7	26.9	26.1	33.6	76.1	36.9	37.2
16	22.4	22.5	22.1	24.1	30.3	69.9	15.7
17	22.6	22.8	22.3	24.1	30.4	15.5	69.9
18	21.9	15.3	21.5	174.9	174.3	174.5	174.5
19	65.5	28.2	65.5	18.8	70.6	70.7	70.6
20	25.2	24.9	23.4	22.7	22.3	22.3	22.4

Measurements performed in $CDCl_3$ at 100 MHz.

partial structures, $-CH_2CH_2CH<$ and $-CH_2CH_2CH-O-$ were suggested. Thus, the structure of tritobenzene B was formulated as **2**.

Triptobenzene C (**3**), $C_{20}H_{26}O_4$ ($[M]^+$ at *m/z* 330), showed hydroxy, aromatic and ketone (1708 and 1626 cm^{-1}) bands in the IR spectrum. The ^1H NMR spectrum revealed the presence of an isopropyl group [δ 1.21, 1.23 (each 3H, *d*, $J = 6.8$ Hz), 3.34 (1H, *sept*, $J = 6.8$ Hz)], two methyls [δ 1.23, 1.39 (each 3H, *s*)], one methylene [δ 3.72, 3.97 (each 1H, *ABq*, $J = 11.2$ Hz)] attached to a hydroxy group, and 1,2,3,4-tetra-substituted aromatic protons [δ 6.78, 7.39 (each 1H, *d*, $J = 7.8$ Hz)]. The ^{13}C NMR spectrum showed two carbonyl carbon signals at δ 204.4 and 214.8 (Table 1). From the ^{13}C-^1H long range correlation spectrum, the proton signals at δ 1.21 and 1.23 (H-16 and 17) showed long range correlation with the carbon signals at δ 26.1 and 135.4, the proton signal at δ 7.39 with the carbon signals at δ 151.5 and 160.9, and the proton signal at δ 6.78 with the carbon signals at δ 114.2 and 135.4. These facts indicated the substituent pattern on the benzene ring. The proton signal at δ 1.39 (H-20) showed long range correlation with the carbon signals at δ 35.9, 49.6 and 151.5, and the proton signal at δ 1.23 (H-18) with the carbon signals at δ 49.6, 52.0, 65.5 and 214.8. These facts indicated the assignment of C-10, 5, 4, 3, and 2 (Table 1). The proton signal at δ 2.76 (H-6) showed long range correlation with the carbon signals at δ 37.3 and 204.4, and the proton signal at δ 2.80 (H-2) with the carbon signal at δ 37.3. These facts clearly indicated the presence of carbonyl carbon at C-3 and C-7. The relative configuration of **3** was determined by NOE experiments. Irradiation of the proton signal at δ 1.39 (H-20) enhanced the proton signal intensity at δ 3.97 (H-19) and irradiation of the proton signal at δ 2.47 (H-5) enhanced the proton signal intensity at δ 1.23 (H-18). Thus, the structure of triptobenzene C was formulated as **3**.

Triptobenzene D (**4**), $C_{20}H_{26}O_2$, showed the presence of a carboxylic acid group [IR: 1675 cm^{-1}; ^{13}C NMR: δ 174.9], a trisubstituted benzene ring [UV: 217, 268, 276 nm; ^1H NMR: δ 7.02, 7.24 (each 1H, *d*, $J = 8.3$ Hz), ^{13}C NMR: δ 123.9 (*d*), 124.2 (*d*), 127.0 (*d*), 134.9 (*s*), 146.2 $\times$ 2 (*s*)], an isopropyl group [^1H NMR: δ 1.24 (3H $\times$ 2, *d*, $J = 6.8$ Hz), 2.85 (1H, *sept*, $J = 6.8$ Hz)], and one double bond [^{13}C NMR: δ 124.0 (*s*), 149.7 (*s*)]. Comparison of the ^{13}C NMR spectrum of compound **3** and triptoquinone A [3] showed similar chemical shifts for C-1, 2, 3, 4, 5, 18 and 19 (Table 1). Also the ^{13}C NMR spectrum data of **3** and 3-oxo-abieta-8,11,13-triene [20] showed similar chemical shifts of ring C and the isopropyl group. From these facts the structure of triptobenzene D was formulated as **4**. The 2D NMR spectra of **4** supported this formula.

Triptobenzene E (**5**), $C_{20}H_{24}O_4$, was found to have a tetra-substituted benzene ring [UV: 220, 274, 283 nm; ^1H NMR: δ 6.85, 6.96 (each 1H, *ABq*, $J = 8.3$ Hz), ^{13}C NMR: δ 114.8 (*d*), 122.6 (*d*), 123.3 (*s*), 127.8 (*s*), 145.9 (*s*), 153.6 (*s*)], an α,β-unsaturated-γ-lactone group [IR: 1730 cm^{-1}; ^1H NMR; δ 4.77, 4.83 (each 1H, *ABq*, $J = 17.1$ Hz); ^{13}C NMR: δ 70.6 (*d*), 125.0 (*s*), 163.2 (*s*), 174.3 (*s*)], three methyls [^1H NMR: δ 1.03, 1.68, 1.69 (each 3H, *s*)] and a quaternary carbon [^{13}C NMR: δ 76.1 (*s*)] attached to the oxygen function. From the ^1H-^1H COSY spectrum, the presence of partial structures, $-CH_2CH_2-$ and $>CH-CH_2-$ were suggested. In the ^{13}C-^1H long range correlation spectrum, the proton signal at δ 1.03 (H-20) was correlated with the carbon signals at δ 32.9 (C-1), 36.3 (C-10), 145.9 (C-9) and 41.0 (C-5), the proton signal at δ 6.96 (H-12) with the carbon signals at δ 153.6 and 145.9, the proton signal at δ 6.85 (H-11) with the carbon signals at δ 145.9 and 127.8, and the proton signals at δ 1.68 and 1.69 (H-16, 17) with the carbon signals at δ 76.1 (C-15) and 127.8 (C-13). These facts indicated that the structure of triptobenzene E should be formulated as **5**. Compound **5** is related to the known compound triptophenolide [11], from which it differs by an extra hydroxy which is located on C-15.

Triptobenzene F (**6**), $C_{20}H_{24}O_4$, showed absorption at 3437 (OH) and 1737 cm^{-1} (α,β-unsaturated-γ-lactone) in its IR spectrum. The ^1H NMR spectrum indicated the presence of two methyls and two methylenes attached to oxygen functions [δ 3.74 (1H, *dd*, $J = 9.3$, 9.3), 4.00 (1H, *dd*, $J = 9.3$, 2.9 Hz), 4.77, 4.82 (each 1H, *ABq*, $J = 17.0$ Hz). The ^{13}C NMR spectrum of **6** was very similar to that of **5**, except for signals at δ 76.1 (**5**; $>CH-OH$), 30.3 (**5**; $-CH_3$), 36.9 (**6**; $-CH_3$), 69.9 (**6**; CH_2OH) and 15.5 (**6**; $-CH_3$). These facts suggested that in the structure of **6**, the hydroxy methylene and methine groups replaced the methyl (C-16 or 17) and methine attached to a hydroxy group (C-15) found in **5**.

To confirm this structure and assignments of the ^1H and ^{13}C NMR spectra, we measured the 2D NMR spectra. From the ^1H-^1H COSY spectrum of **6**, the presence of partial structures, $-CH_2CH_2-$, $>CHCH_2CH_2-$, $-CH(CH_3)CH_2OH$ were suggested. In the ^{13}C-^1H long range correlation spectrum, the proton signal at δ 6.92 (H-11) showed long range correlation with the carbon signals at δ 123.1 (C-8), 128.0 (C-13), the proton signal at δ 6.98 (H-12) with the carbon signals at δ 144.9 (C-9), 153.1 (C-14), and the proton signal at δ 1.33 (H-16 or 17) with the carbon signals at δ 36.9 (C-15), 128.0 (C-13). Thus, the structure of triptobenzene F was formulated as **6**.

Triptobenzene G (**7**), $C_{20}H_{24}O_4$, showed almost the same spectral data (IR, ^1H NMR, ^{13}C NMR, MS) as compound **6**. Both compounds **6** and **7** could be separated only by recycle HPLC (GPC column). The only differences in the ^1H NMR spectra were the chemical shifts of the methyl (H-16 or 17) and methylene attached to hydroxy groups. From these facts, the structure of triptobenzene G was formulated as the C-15 epimer of compound **6**. The absolute configuration of both compounds was not determined.

EXPERIMENTAL

^1H NMR; 270 and 400 MHz with TMS as int. stand; ^{13}C NMR: 100.2 MHz; CC: silica gel 60 (Merck), Sephadex LH-20 (Pharmacia) and Toyo Pearl HW-40 (TOSOH); HPLC GPC: H-2002 (Shodex), ODS: D-ODS-5 (YMC).

Isolation of triptobenzene A (**1**), *B* (**2**), *C* (**3**), *D* (**4**), *E* (**5**), *F* (**6**) *and G* (**7**)

(i) The extraction and subsequent fractionation (by silica gel CC) of the extract from dry stalks (108 kg) of *T. wilfordii* Hook fil. var. *regelii* is described in previous paper [4]. Frs 4.5 and 4.6 (19.96 g) were subjected to CC using Sephadex LH-20 with MeOH to give 5 frs (4.5.1–4.5.5). Fr. 4.5.4 (3.4 g) was chromatographed on Toyo Pearl HW40 with $CHCl_3$–MeOH (1:1) and silica gel with hexane–EtOAc (2:1) to give 0.040 g of **1** and 0.022 g of **5**. Fr. 4.4.6 (3.5 g) was chromatographed on silica gel with $CHCl_3$–MeOH (9:1), and silica gel with $CHCl_3$–MeOH (99:1) to give 0.030 g of **4**.

(ii) The extraction and subsequent fractionation of the extract from the dry stalks (12.0 kg) of *T. wilfordii* Hook fil. var. *regelii* is described elsewhere [4]. Fr. 10.4 (1.24 g) was chromatographed on a silica gel column with $CHCl_3$–MeOH (49:1), HPLC [ODS, MeOH–H_2O (9:1)], and silica gel column with hexane–EtOAc (1:1) to give 0.034 g of **2** and 0.024 g of **4**.

(iii) The dry bark (3.8 kg) of *T. wilfordii* Hook fil. var. *regelii* was collected in August 1991 on Mt. Turugi (Tokushima Prefecture, Japan) and extracted with MeOH (20 l) at 60°. The MeOH extracts were concd *in vacuo* to give a residue, which was partitioned between EtOAc and H_2O. The EtOAc layer was concd to give a residue (409 g), which was added to CH_2Cl_2 and sepd to CH_2Cl_2-soluble fr. and residue. The CH_2Cl_2-soluble fr. was concd *in vacuo* to give a residue (255 g), which was chromatographed on a silica gel column. The column was eluted with solvents of increasing polarity (CH_2Cl_2–MeOH) to give 17 frs (frs 1–7). Fr. 14 (167 g) was chromatographed on a silica gel column with CH_2Cl_2–MeOH to give 12 frs (14.1–14.12). Fr. 14.6 (11.6 g) was chromatographed on a silica gel with hexane–Et_2O (1:1 to 1:2) to give 12 frs (14.6.1–14.6.12). Fr. 14.6.7 (0.98 g) was chromatographed on Sephadex LH-20 with MeOH to give 9 frs (14.6.7.1–14.6.7.9). Fr. 14.6.7.8 (126 mg) was sepd by HPLC (GPC) with $CHCl_3$ to give **6** (17 mg) and **7** (6 mg).

Triptobenzene A (**1**). Amorphous powder, $[\alpha]_D^{25}$ +89.3° ($CHCl_3$ *c* 1.1). IR ν_{max}^{KBr} cm^{-1}: 3410, 1700, 1490, 1460, 1420, 1220, 1040, 760; UV λ_{max}^{MeOH} nm (ε): 220 (8200), 272 (1800), 280 (1710); ^1H NMR: δ ($CDCl_3$): 1.23, 1.25 (each 3H, *d*, $J = 6.8$ Hz, H-16, 17), 1.28 (3H, *s*, H-20), 1.34 (3H, *s*, H-18), 1.70 (1H, *dddd*, $J = 13.2$, 12.7, 12.7, 6.4 Hz, H_{ax}-6), 1.98 (1H, *m*, H_{eq}-7), 2.01 (1H, *dd*, $J = 18.1$, 8.8, Hz, H_{eq}-1), 2.10 (1H, *dd*, $J = 13.2$, 4.4 Hz, H-5), 2.48 (1H, *ddd*, $J = 18.1$, 7.8, 4.4 Hz, H_{ax}-1), 2.57 (1H, *m*, H_{ax}-70), 2.63 (1H, *dd*, $J = 15.1$, 7.8 Hz, H-2), 2.69 (1H, *ddd*, $J = 15.1$, 8.8, 4.4 Hz, H-2), 2.92 (1H, *dd*, $J = 16.6$, 6.4 Hz, H-7), 3.12 (1H, *sept*, $J = 6.8$ Hz, H-15), 3.54, 4.08 (each 1H, *d*, $J = 11.2$ Hz, H-19), 6.80 (1H, *d*, $J = 8.3$ Hz, H-11) and 7.40 (1H, *d*, $J = 8.3$ Hz, H-12); EI-MS *m/z* (rel. int.): 316 $[M]^+$ (100), 301 $[M-Me]^+$ (60), 271(90), 241(42), 201(42), 199(51), 43(58); HR-MS *m/z* 316.2006 $[M]^+$ $C_{20}H_{28}O_3$ required 316.2039.

Triptobenzene B (**2**). Amorphous powder, $[\alpha]_D^{25}$ $+18.3°$ (MeOH; *c* 1.2). IR ν_{max}^{Kbr} cm^{-1}: 3436, 1620, 1424, 1348, 1255, 1094, 1035, 813; UV λ_{max}^{MeOH} nm (ε): 270 (3000). ^{1}H NMR: δ ($CDCl_3$): 0.97 (3H, *s*, H-19), 1.07 (3H, *s*, H-18), 1.20 (3H, *s*, H-20), 1.22, 1.24 (each 3H, *d*, $J = 6.8$ Hz, H-16, 17), 2.85 (1H, *dd*, $J = 16.6$, 6.3 H, H-7), 3.13 (1H, *sept*, $J = 6.8$ Hz, H-15), 3.29 (1H, *dd*, $J = 10.8$, 5.1 Hz), 6.84 (1H, *d*, $J = 8.3$ Hz, H-11), 7.01 (1H, *d*, $J = 8.3$ Hz, H-12); EI-MS *m/z* (rel. int.): 302 $[M]^+$ (77), 287 $[M-Me]^+$ (39), 269(100), 227(41), 201(43), 199(52), 43(63); HR-MS *m/z* 302.2079 $[M]^+$ $C_{20}H_{30}O_2$ required 302.2073.

Triptobenzene C (**3**). Amorphous powder, $[\alpha]_D^{25}$ $-7.4°$ ($CHCl_3$, *c* 0.54). IR ν_{max}^{Kbr} cm^{-1}: 3429, 1708, 1626, 1428, 1353, 1251, 1161, 1115, 1049, 753; UV λ_{max}^{MeOH} nm (ε): 270 (9000). ^{1}H NMR: δ ($CDCl_3$): 1.21, 1.23 (each 3H, *d*, $J = 6.8$ Hz, H-16, 17), 1.23 (3H, *s*, H-18), 1.39 (3H, *s*, H-20), 3.34 (1H, *sept*, $J = 6.8$ Hz, H-15), 3.72, 3.97 (each 1H, *ABq*, $J = 11.2$ Hz, H-19), 6.78 (1H, *d*, $J = 7.8$ Hz, H-11), 7.39 (1H, *d*, $J = 7.8$ Hz, H-12). EI-MS *m/z* (rel. int.): 330 $[M]^+$ (90), 315 $[M-Me]^+$ (100), 285(49), 213(29), 75(72); HR-MS *m/z* 330.1839 $[M]^+$ $C_{20}H_{26}O_4$ required 330.1831.

Triptobenzene D (**4**). Needles, mp 174–177°, $[\alpha]_D^{25}$ $+48.1°$ ($CHCl_3$, *c* 1.0). IR ν_{max}^{KBr} cm^{-1}: 3400, 2960, 1675, 1620, 1500, 1445, 1370, 1270, 820; UV λ_{max}^{MeOH} nm (ε): 217 (15000), 268 (1000), 276 (800). ^{1}H NMR: δ ($CDCl_3$): 1.05, (each 3H, *s*, H-20), 1.24 (3H × 2, *d*, $J = 6.8$ Hz, H-16, 17), 1.60–1.77 (2H, *m*), 2.13 (3H, *s*, H-19), 2.28 (1H, *m*), 2.33–2.41 (2H, *m*), 2.45–2.65 (2H, *m*), 2.85 (1H, *sept*, $J = 6.8$ Hz, H-15), 2.90–3.04 (2H, *m*), 6.96 (1H, *s*, H-14), 7.02, 7.24 (each 1H, *d*, $J = 8.3$ Hz, H-11, 12); EI-MS *m/z* (rel. int.): 298 $[M]^+$ (67), 283 $[M-Me]^+$ (78), 265(19), 237(27), 199(100), 195(47), 143(29), 43(32); HR-MS *m/z* 298.1202 $[M]^+$ $C_{20}H_{26}O_2$ required 298.1926.

Triptobenzene E (**5**). Amorphous powder, IR ν_{max}^{Kbr} cm^{-1}: 3350, 1729, 1671, 1570, 1400, 1380, 1267, 1077, 1033, 755; UV λ_{max}^{MeOH} nm (ε): 220 (12000), 274 (1200), 283 (900). ^{1}H NMR: δ ($CDCl_3$): 1.03 (3H, *s*, H-20), 1.68, 1.69 (each 3H, *s*, H-16, 17), 1.88 (1H, *m*, H-2), 1.98 (1H, *ddd*, $J = 13.2$, 8.8, 3.6 Hz, H-2), 2.39 (1H, *ddd*, $J = 13.2$, 6.8, 3.9 Hz, H-6), 2.50 (1H, *dd*, $J = 13.2$, 5.7 Hz, H-6), 2.69 (1H, *br d*, $J = 13.2$ Hz, H-5), 2.84 (1H, *ddd*, $J = 18.6$, 10.7, 8.8 Hz, H-7), 2.98 (1H, *dd*, $J = 18.6$, 7.3 Hz, H-7) 4.77, 4.83 (each 1H, *ABq*, $J = 17.1$ Hz, H-19), 6.85 (1H, *d*, $J = 8.3$ Hz, H-11), 6.96 (1H, *d*, $J = 8.3$); EI-MS *m/z* (rel. int.): 328 $[M]^+$ (55), 310 $[M-H_2O]^+$ (100), 295$[M-H_2O-CH_3]^+$(70), 185(12), 147(18), 115(10); HR-MS *m/z* 328.1629 $C_{20}H_{24}O_4$ required 328.1675.

Triptobenzene F (**6**). Amorphous powder, $[\alpha]_D^{25}$ $+39.0°$ ($CHCl_3$ *c* 0.23). IR ν_{max}^{KBr} cm^{-1}: 3410, 1737, 1673, 1563, 1396, 1348, 1269, 1080, 1020, 809, 756, 648; UV λ_{max}^{MeOH} nm (ε): 273 (1800), 282 (1700); ^{1}H NMR: δ ($CDCl_3$): 1.04 (3H, *s*, H-20), 1.33 (3H, *d*, $J = 7.3$ Hz, H-17), 3.74 (1H, *dd*, $J = 9.3$, 9.3 Hz, H-16), 4.00 (1H, *dd*, $J = 9.3$, 2.9 Hz, H-16), 4.77, 4.82 (each 1H, *ABq*, $J = 17.0$ Hz, H-19), 6.92 (1H, *ABq*, $J = 8.1$ Hz, H-11), 6.98 (1H, *ABq*, $J = 8.1$ Hz, H-12); EI-MS *m/z* (rel. int.): 328 $[M]^+$, (17), 298(23), 297$[M-CH_2OH]^+$(100), 147 (7); HR-MS *m/z* 328.1683 $C_{20}H_{24}O_4$ required 328.1675.

Triptobenzene G (**7**). Amorphous powder, $[\alpha]_D^{25}$ $+31.7°$ ($CHCl_3$ *c* 0.25). IR ν_{max}^{KBr} cm^{-1}: 3422, 1734, 1673, 1563, 1393, 1348, 1270, 1081, 1017, 809, 755, 627; UV λ_{max}^{MeOH} nm (ε): 274 (1900), 278 (1900); ^{1}H NMR: δ ($CDCl_3$): 1.04 (3H, *s*, H-20), 1.33 (3H, *d*, $J = 7.2$ Hz, H-16), 3.76 (1H, *dd*, $J = 9.3$, 9.3 Hz, H-16), 4.01 (1H, *dd*, $J = 9.3$, 2.9 Hz, H-17), 4.76, 4.83 (each 1H, *ABq*, $J = 17.0$ Hz, H-19), 6.92 (1H, *ABq*, $J = 8.2$ Hz, H-11), 6.98 (1H, *ABq*, $J = 8.2$ Hz, H-12); EI-MS *m/z* (rel. int.): 328 $[M]^+$, (31), 298(23), 297$[M-CH_2OH]^+$(100), 147(12); HR-MS *m/z* 328.1679 $C_{20}H_{24}O_4$ required 328.1675.

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