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TERPENOIDS FROM *TRIPTERYGIUM WILFORDII*

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Key Word Index—*Tripterygium wilfordii*; Celastraceae; root barks; triterpene; diterpene; wilforic acid; triptobenzene.

Abstract—The methanol extract of the dried root barks of *Tripterygium wilfordii* afforded three novel D:A friedooleanan and 24-norfriedoolean triterpenoids: 2,3-dihydroxy-24-nor-D:A-friedooleana-1,3,5(10)-triene-29-oic, 2β-hydroxy-3-oxo-24-nor-D:A-friedooleana-4-ene-29-oic acid and 2α-hydroxy-3-oxo-D:A-friedooleana-29-oic acid named wilforic acid A, B and C, and two novel abietane diterpenoids: 11-hydroxy-14-methoxy-18(4→3)-*abeo*-abieta-3,8,11,13-tetraene-18-oic acid and 14,19β-dihydroxy-18(4→3)-*abeo*-abieta-3,8,11,13-tetraene-18,19-olide named triptobenzene H and I. Their structures were established on the basis of spectroscopic studies.

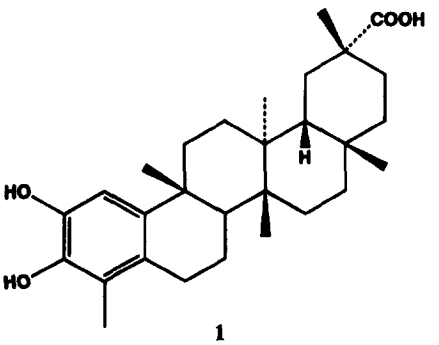
INTRODUCTION

Tripterygium wilfordii Hook fil. has been used as an anticancer drug and an insecticide by the Chinese for hundreds of years [1, 2]. Recently, this plant has been used to treat rheumatoid arthritis and spondylitis in some Chinese clinics [3]. The therapeutic effectiveness of *T. wilfordii* in a variety of autoimmune diseases, including rheumatoid arthritis, has been suggested by a number of studies in China during the past 20 years [4, 5]. Recently anti-AIDS agents and an anti-HIV principle were isolated from this plant [6], and the terpenoid constituents of this plant were also reported [7, 8]. In the course of our search for bioactive metabolites from plants [9], we have been interested in this plant. In our previous paper, we reported the isolation of diterpene quinoids and triterpenes which are interleukin-1 inhibitors from *T. wilfordii* Hook fil. var. *regelii* Makino [10, 11]. In a continuation of our studies on the chemical components of genus of *Tripterygium*, we isolated three novel triterpenes, 2,3-dihydroxy-24-nor-D:A-friedoolean-1,3,5(10)-triene-29-oic acid (**1**), 2βhydroxy-3-oxo-24-nor-D:A-friedoolean-4-ene-29-oic acid (**2**) and 2α-hydroxy-3-oxo-D:A-friedooleanan-29-oic acid (**3**) and novel diterpenoids, 11-hydroxy-14-methoxy-19(4→3)-*abeo*-abieta-3,8,11,13-tetraene-18-oic acid (**4**) and 14,19β-dihydroxy-18(4→3)-*abeo*-abieta-3,8,11,13-tetraene-18,19-olide (**5**), which we have named wilforic acid A, B, C, triptobenzene H and I, respectively, along with known compounds **6**–**17**. This paper deals with the structural investigations of these novel triterpenes and diterpenes.

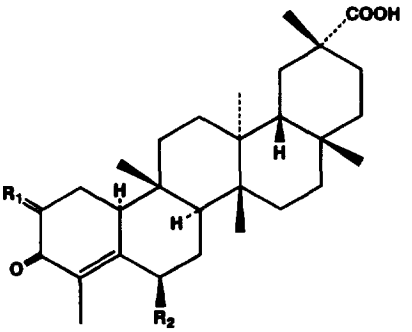
RESULTS AND DISCUSSION

A methanol extract of root barks of *T. wilfordii* afforded three triterpenes; 24-nor-D:A-friedooleanane triterpenes [wilforic acid A (**1**), B (**2**)] and D:A-friedooleanane triterpene [wilforic acid C (**3**)] and two novel abietane type diterpenes [triptobenzene H (**4**), I (**5**)] and known compounds **6**–**17**.

Wilforic acid A (**1**) showed a hydroxy absorption band at 3402 cm^{-1} and carbonyl band at 1702 cm^{-1} in the IR spectrum. The UV spectrum of **1** showed the presence of an aromatic ring at 249 and 286 nm. The ^1H NMR spectrum revealed the presence of six methyls [δ 1.01, 1.16, 1.19, 1.29, 1.44 and 2.39 (3H, *s*)], and one methine [δ 7.07 (1H, *s*)] attached to an aromatic ring. The ^{13}C NMR spectrum of **1** showed one carbonyl carbon signal at δ 181.3, benzene ring carbon signals at δ 109.4 (*d*), 122.9 (*s*), 125.1 (*s*), 142.7 (*s*), 142.8 (*s*), 144.5 (*s*), six methyl carbon signals, nine methylene carbon signals, two methine carbon signals and five quaternary carbon signals. The mass spectrum of **1** showed the peak due to $[M]^+$ at *m/z* 454. These facts agreed with the molecular formula of **1** as $C_{29}H_{42}O_4$, which was supported by the high resolution mass spectral data. Many types of triterpene were isolated from Celastraceae plants [12], compound **1** was assumed to 24-nor-D:A-friedooleanane type triterpene from the carbon number (C_{29}) and the presence of six methyls and one carboxylic acid. The ^{13}C NMR spectral data of **1** was similar to those of regeol A (**18**) [11] in carbon number from C-1 to C-14 and C-25, and regeol B (**19**) [11] in carbon number from

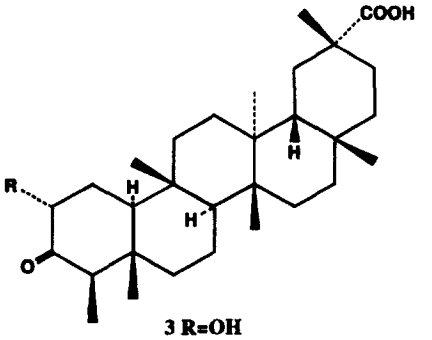


1

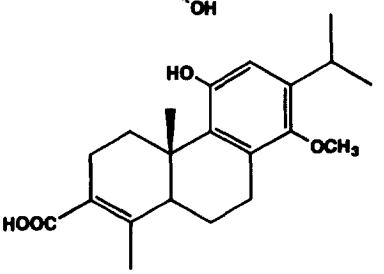


2 R_1=  R_2=H

19 R_1=  R_2=OH



3 R=OH
20 R=H



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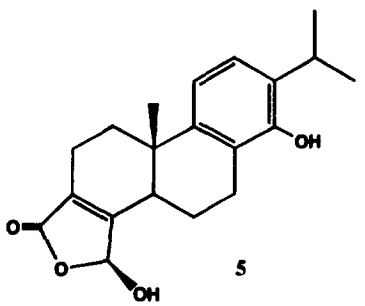

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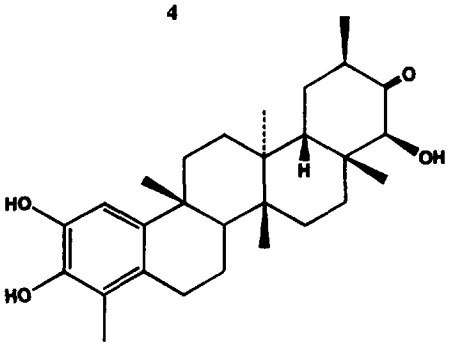

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C-11 to C-23 and from C-26 to C-30 (Table 1). This suggested that the A- and B-rings of **1** are the same as in regeol A (**17**), and the C-, D- and E-rings of **1** are the same as in regeol B (**19**). To confirm this structure of **1**, we measured 2D NMR spectra. From the ^{13}C-^{1}H COSY and ^{13}C-^{1}H long range correlation spectra of **1**, the C-, D- and E-rings were confirmed to be the same as in regeol B. In the ^{13}C-^{1}H long range correlation spectrum concerning the A- and B-ring systems, the proton signal at δ 7.07 (1-H) showed long range correlation with the carbon signals at δ 144.5 (C-2), 142.8 (C-3) and 125.1 (C-5); the proton signal at δ 2.39 (23-H_3) with the carbon signals at δ 122.9 (C-4), 125.1 (C-5); the proton signal at δ 2.78 (6-H) with the carbon signals at δ 45.0 (C-8) and 125.1 (C-5); and the proton signal at δ 1.29 (25-H_3) with the carbon signals at δ 45.0 (C-8), 37.1 (C-9), 142.7 (C-10) and 34.6 (C-11). These facts clearly indicated that the A-ring was a benzene ring and the two hydroxy groups were at C-2 and C-3. Thus the structure of wilforic acid A should be formulated as **1**. There are many 24-nor-D:A-friedoleanane type triterpenes [10], but the isolation of wilforic acid which has a benzene ring in the ring A is the second example.

Wilforic acid B (**2**) revealed in the ^{1}H NMR spectrum the presence of six methyls [δ 0.76, 0.91, 1.01, 1.09, 1.26, 1.82 (each 3H, *s*)] and one methine [δ 3.96 (1H, *dd*, J = 14.2, 6.4 Hz)] attached to a hydroxy group. The ^{13}C NMR spectrum of **2** showed α,β-unsaturated carbonyl carbon signal at δ 200.1, a carboxylic acid carbon signal at δ 184.7, double bond carbon signals at δ 127.6 and 159.6, six methyl, 10 methylene, three methine and five quaternary carbon signals. The ^{13}C NMR spectrum data of **2** was very similar to that of regeol B (**19**) [11] (Table 1) except for the signals due to C-6, C-7, C-9 and C-10. The HR mass spectrum of **2** showed the peak due to $[M]^+$ at m/z 456.3240, which agreed with a molecular formula of **2** as $C_{29}H_{44}O_4$. From these facts, the structure of **2** was deduced to be a dehydroxy form of regeol B. From the ^{13}C-^{1}H long range correlation spectrum of **2**, the C-, D- and E-rings were confirmed to be the

Table 1. ^{13}C NMR data for compounds **1–3**, regeol A (**18**), B (**19**) and maytenoic acid (**20**)

C	1	2	3	18	19	20
1	109.4	28.6	30.8	108.3	29.5	22.3
2	142.8	71.6	74.1	141.4	70.1	41.5
3	144.5	200.1	213.3	139.8	201.0	213.2
4	122.9	127.6	52.7	122.5	128.0	58.3
5	125.1	159.6	43.1	126.3	158.7	42.1
6	28.8	31.0	41.3	28.0	75.6	41.4
7	19.1	21.0	18.5	18.3	34.4	18.3
8	45.0	48.6	50.9	43.3	47.5	50.8
9	37.1	37.8	37.2	36.7	40.4	37.5
10	142.7	52.5	52.6	143.8	49.6	59.8
11	34.6	33.1	35.4	34.2	33.7	35.4
12	29.5	29.1	30.5	30.0	30.1	30.3
13	39.4	38.8	39.5	40.0	39.6	39.2
14	39.6	39.5	39.7	39.3	40.7	39.3
15	30.7	29.3	29.8	27.9	29.5	29.6
16	37.4	36.4	37.8	29.6	36.5	36.2
17	30.5	30.1	30.4	44.9	30.5	30.2
18	44.7	44.3	44.8	45.4	44.7	44.3
19	31.1	29.5	30.8	31.7	31.0	29.5
20	40.6	40.4	40.7	41.3	39.7	40.4
21	30.4	30.4	29.7	214.3	30.5	29.4
22	36.7	36.1	36.7	77.6	37.4	36.7
23	12.2	11.2	6.8	11.5	12.6	6.8
24	—	—	14.2	—	—	14.7
25	27.8	16.7	18.0	28.2	17.3	18.1
26	17.8	16.2	18.5	15.3	16.6	18.4
27	16.5	17.7	16.1	19.2	17.5	16.4
28	32.1	30.2	32.1	25.2	32.1	31.9
29	181.3	184.7	181.2	—	181.0	183.5
30	32.1	31.7	32.1	14.8	32.3	31.5

same as those of wilforic acid A. In the ^{13}C-^1H long range correlation spectrum, the methyl signal at δ 0.91 (26-H_3) was correlated with the carbon signals at δ 48.6 (C-8), 39.5 (C-14) and 29.3 (C-15), the methyl proton signal at δ 0.76 (25-H_3) with the carbon signals at δ 37.8 (C-9), 52.5 (C-10) and 33.1 (C-11), the methyl proton signal at δ 1.82 (23-H_3) with the carbon signals at δ 200.1 (C-3), 127.6 (C-4) and 159.6 (C-5). From these results, the assignments of carbon signals from C-3 to C-10 were confirmed as shown in Table 1. From the HOHAHA spectrum of **2**, the proton signal at δ 3.96 was correlated with the proton signals at δ 1.52 (1-H) and 2.30 (10-H), which showed the position of the hydroxy group to be on C-2. The relative stereochemistry at C-2 was determined to be β-hydroxy. In the NOESY spectrum, the proton signal at δ 2.30 (10-H) was correlated with the proton signals at δ 3.96 (2-H) and 1.63 (8-H). The coupling constants (J = 14.2 and 6.4 Hz) of 2-H showed the presence of an axial proton at C-2. The structure of wilforic acid B (**2**) was determined to be shown.

Wilforic acid C (**3**) was assigned the molecular formula $C_{30}H_{48}O_4$ (HRMS). The ^1H NMR spectrum revealed the presence of seven methyls [δ 0.73, 0.84, 0.88, 1.14, 1.22, 1.44 (each 3H, *s*) and 0.98 (3H, *d*, J = 6.7 Hz)] and one methine [δ 4.39 (1H, *br t*)]. The ^{13}C NMR spectrum of **3** showed a carbonyl carbon signal at δ 213.3, one carboxylic acid carbon signal at δ 181.2, one methine carbon attached to an oxygen function signal at δ 74.1, and seven methyl, 10 methylene, five methine and eight quaternary carbon signals (Table 1). The ^{13}C NMR spectrum of **3** was very similar to that of maytenoic acid (**20**) [13] except for the signals at δ 30.8 (*t*), 52.6 (*d*), 52.7 (*d*) and 74.1 (*d*) in compound **3**. From the comparison of spectral data and molecular formula of both compounds (**3** and **20**), the structure of **3** was concluded to have a hydroxymethine in place of the methylene found in maytenoic acid (**20**). To confirm the position and configuration of the hydroxy group and the assignment of the NMR data, we measured the 2D NMR spectra. From the ^1H-^1H COSY spectrum of **3**, the presence of partial structures –CH(OH)–CH_2–CH,< >CH–CH_3 were suggested. In the ^{13}C-^1H long range correlation spectrum, the proton signal at δ 4.39 (2-H) was correlated with the carbon signals at δ 213.3 (C-3), 52.7 (C-4) and 52.6 (C-10), the proton signal at δ 0.98 (23-H_3) with the carbon signals at 213.3 (C-3), 52.7 (C-4) and 43.1 (C-5), the proton signal at δ 2.13 (1-H) with the carbon signals at δ 74.1 (C-2), 213.3 (C-3) and 52.6 (C-10). These facts clearly indicated that a hydroxy group was at C-2 in compound **3**. The relative stereochemistry was determined using the NOESY spectrum. The proton signal at δ 2.26 (10-Hα) was correlated with the proton signals at δ 2.13 (1-Hα) and 3.21 (4-Hα), the proton signal at δ 1.83 (1-Hβ) with the proton signals at δ 0.84 (25-H_3), 4.39 (2-Hβ) and 0.73 (24-H_3). The coupling constants of the proton signal at δ 4.39 (2-Hβ) were very small (J = *ca* 2 Hz). From these facts the relative stereochemistry of **3** was determined as 2α-hydroxy-3-keto-4β-methyl in the ring A. Thus, the structure of wilforic acid C was formulated as shown.

Triptobenzene H (**4**) [14], $C_{21}H_{28}O_4$ showed a hydroxy band at 3400 cm^{-1} and a carboxylic acid band at 1680 cm^{-1} in the IR spectrum. The UV spectrum showed the presence of an aromatic ring. The ^1H NMR spectrum of **4** revealed the presence of an isopropyl group [δ 1.17, 1.19 (each 3H, *d*, J = 6.8 Hz), 3.25 (1H, *sept.*, J = 6.8 Hz)], three methyls [δ 1.18, 2.18, 3.69 (each 3H, *s*)], and one methine [δ 6.40 (1H, *s*)] attached to a double bond. The ^{13}C NMR spectrum of **4** showed one carbonyl carbon signal at δ 174.2, four double bond signals including a benzene ring, five methyl carbon signals, four methylene carbon signals, two methine carbon signals and one quaternary carbon signal. From these facts, the structure of **4** was deduced to have an abietane skeletone the same as triptobenzene A–G [15]. The ^{13}C NMR spectral data of **4** were similar to those of triptoquinone A [10] in the rings A- and B-. The partial structures of –CH_2–CH_2, >CH–CH_2–CH_2–, –$CH(CH_3)_2$ were confirmed from the ^1H-^1H COSY spectrum. From the ^{13}C-^1H long range correlation spectrum, the assignment of ^1H and ^{13}C NMR data was confirmed. In the NOESY

spectrum the proton signal at δ 3.69 ($-OCH_3$) was correlated with the proton signal at δ 3.25 (isopropyl-H). This fact clearly indicated that the position of the methoxy group is on C-14. Thus the structure of triptobenzene H was formulated as **4**. This compound was the same as hypoglic acid isolated from *T. wilfordii* [16].

Triptobenzene I (**5**), $C_{20}H_{24}O_4$ showed hydroxy absorption and α,β-unsaturated lactone absorption in the IR spectrum. The ^1H NMR spectrum of **5** showed the presence of an isopropyl group, one methyl [δ 1.01 (3H, *s*)], one methine [δ 6.09 (1H, *br s*)] attached to hydroxy group, and two methines [δ 6.92, 7.06 (each 1H, *d*, J = 7.8 Hz)] attached to a double bond. The ^{13}C NMR spectrum of **5** showed one carbonyl carbon signal at δ 171.2, four double bond signals at δ 116.3 (*d*), 120.8 (*s*), 123.5 (*d*), 129.0 (*s*), 131.4 (*s*), 144.0 (*s*), 151.0 (*s*) and 161.6 (*s*), and four methylene carbon signals, three methine carbon signals at δ 27.2, 40.2 and 97.2, and one quaternary carbon signal. From these facts, it was concluded that compound **5** also had an abietane skeletone. The ^{13}C NMR spectra data of **5** were very similar to those of triptophenolide [17] except for the methine carbon signal at δ 97.2 in compound **5** and the methylene carbon signal at δ 70.4 in troptophenolide. From this fact the structure of compound **5** was estimated to be 19-hydroxy-triptophenolide. The partial structures of $-CH_2CH_2-$, $>CHCH_2CH_2-$, $-CH{=}CH-$ and $-CH(CH_3)_2$ were elucidated from the ^1H-^1H COSY spectrum. In the ^{13}C-^1H long range correlation spectrum, the assignment of ^1H and ^{13}C NMR spectral data was elucidated (see Experimental). The relative stereochemistry of **5** was elucidated from the NOESY spectrum. The methine proton signal at δ 2.71 (5-Hα) was correlated with the proton signals at δ 6.09 (19-Hα), 1.67 (1-Hα) and 2.32 (6-Hα); the methyl proton signal at δ 1.01 (20-H_3) with the proton signals at δ 1.89 (6-Hβ) and 2.38 (2-Hβ); and the proton signal at δ 2.32 (6-Hα) with the proton signal at δ 6.09 (19-Hα). From these facts the orientation of the 19-hydroxy group was assigned to be β. Thus the structure of triptobenzene I was formulated as shown.

The following known triterpenoids were identified: celastrol (**6**) [18], regelin (**7**) [19], maytenoic acid (**20**) [13], tripterigic acid methylester (**9**) [20] and diterpenoides—triptoquinone A (**10**), B (**11**) [10], neotriphenolide (**12**) [21], quinone 21 (**13**) [8], triptobenzene A (**14**) [15], triptonolide (**15**) [22], triptenin B (**16**) [23] and triptophenolide (**17**).

EXPERIMENTAL

^1H NMR: 400 MHz with TMS as int. standard, ^{13}C NMR: 100 MHz, chromatography column: silica gel (Merck) and Sephadex LH 20 (Pharmacia), HPLC: GPC (Shodex packed column, GS-310).

Plant material. The root outer bark of *Tripterygium wilfordii* Hook fil. was purchased from Kunming, Yunnan Province in China.

Extraction and isolation. The root outer bark (19.4 kg) of *T. wilfordii* was crushed and extracted 3 × with MeOH (50 l each) at 60° for 6 hr. The MeOH extracts were concd *in vacuo* to give a residue (850 g), which was partitioned between EtOAc and H_2O. The EtOAc layer was concd to give a residue (411 g), which was chromatographed on a silica gel column. The column was eluted with solvent of increasing polarity [hexane–EtOAc (3:1, 3:2, 1:1, 1:2, 1:4), EtOAc, EtOAc–MeOH (19:1, 9:1, 4:1) and MeOH] to give 15 frs (frs 1–15). Fr. 7 (21.8 g) on CC over silica gel ($CHCl_3$–MeOH, 21:1) gave 4 frs (7.1–7.4), fr. 7.4 (2.6 g) on CC over Sephadex LH-20 (MeOH) gave 4 frs (7.4.1–7.4.4), Fr. 7.4.4 (0.58 g) on CC over silica gel (CH_2Cl_2–MeOH, 99:1) yielded **1** (263 mg), fr. 7.4.2 (1.3 g) on CC over silica gel (CH_2–MeOH, 99:1) yielded **4** (26 mg). Fr. 9 (5.5 g) on CC over silica gel ($CHCl_3$–MeOH, 19:1) gave 9 frs (9.1–9.9), fr. 9.4 (935 mg) on CC over Toyopearl HW40 ($CHCl_3$–MeOH, 2:1) gave 6 frs (9.4.1–9.4.6), fr. 9.4.3 (258 mg) on CC over silica gel (Et_2–hexane, 5:1) gave 3 frs (9.4.3.1–9.4.3.3), fr. 9.4.3.1 (109 mg) by using prep. TLC (Et_2O) yielded **2** (11 mg), and fr. 9.4.3.2 (78 mg) by using HPLC (GPC, MeOH) yielded **9** (9 mg). Fr. 9.9 (654 mg) on CC over Sephadex LH20 (MeOH) and HPLC (GPC, MeOH) yielded **3** (30 mg), fr. 9.8 (663 mg) on CC over Toyopearl HW40 ($CHCl_3$–MeOH, 2:1) and HPLC (GPC, $CHCl_3$) yielded **5** (5 mg). Fr. 7.2 (12.3 g) on CC over Sephadex LH20 (MeOH) gave **6** (2.2 g) and 4 frs (7.2.1–7.2.4), fr. 7.2.2 (2.2 g) on CC over silica gel (CH_2–Cl_2–Me_2CO, 97:3 and hexane–EtOAc 7:3) yielded **7** (171 mg) and **11** (17 mg), fr. 7.2.3 (2.7 g) on CC over silica gel ($CHCl_3$–MeOH, 49:1) gave 12 frs (7.2.3.1–7.2.3.12), fr. 7.2.3.8 (810 mg) on CC over silica gel ($CHCl_3$–MeOH, 99:1 and Et_2O–hexane, 7:3) yielded **8** (30 mg), fr. 7.2.3.12 (398 mg) on CC over silica gel (CH_2–MeOH, 99:1) yielded **10** (40 mg), fr. 7.2.3.7 (223 mg) on CC over silica gel (hexane–acetone, 2:1) yielded **12** (23 mg), fr. 7.2.3.1 (60 mg) on CC over silica gel (CH_2Cl_2–Me_2O, 99:1) yielded **13** (37 mg), fr. 7.2.3.5 (152 mg) by using HPLC (GPC, $CHCl_3$) and on CC over silica gel (hexane–EtOAc, 3:2) yielded **17** (19 mg). Fr. 7.2.4 (1.4 g) on CC over silica gel ($CHCl_3$–MeOH, 49:1) gave 2 frs (7.2.4.1–7.2.4.2), fr. 7.2.4.1 (83 mg) by using HPLC (GPC, $CHCl_3$) and prep. TLC ($CHCl_3$–MeOH, 9:1) yielded **15** (4 mg), fr. 7.2.4.2 on CC over Sephadex LH20 (MeOH) and silica gel ($CHCl_3$–MeOH, 19:1) yielded **16** (17 mg). Fr. 9.4.4 (178 mg) on CC over silica gel (hexane–EtOAc, 1:1) yielded **14** (115 mg).

Wilforic acid (**1**). Amorphous powder, $[\alpha]_D^{25}$ −22.0° ($CHCl_3$ *c* 2.3), IR ν_{max}^{KBr} cm^{-1}: 3402, 2938, 1702, 1619, 1460, 1382, 1307, 1215, 1020, 829. UV λ_{max}^{MeOH} nm (ε): 249 (3.7), 286 (3.70). ^1H NMR: δ (C_5D_5N): 1.01 (3H, *s*, 27-H_3), 1.16 (3H, *s*, 28-H_3), 1.19 (3H, *s*, 26-H_3), 1.29 (3H, *s*, 25-H_3), 1.44 (3H, *s*, 29-H_3), 1.77 (1H, *dd*, J = 13.2, 3.9 Hz, 11-H), 1.98 (1H, *br d*, J = 13.2 Hz, 11-H), 2.31 (1H, *ddd*, J = 14.2, 14.2, 4.4 Hz, 16-H), 2.39 (3H, *s*, 23-H_3), 2.52 (1H, *br d*, J = 14.2 Hz, 21-H), 2.59 (1H, *m*, 6-H), 2.66 (1H, *d*, J = 14.7 Hz, 19-

H), 2.78 (1H, *dd*, J = 17.1, 5.9 Hz, 6-H), 7.07 (1H, *s*, 1-H). ^{13}C NMR (C_5D_5N): see Table 1. EI-MS *m/z* (rel. int.): 454 $[M]^+$ (100), 439 $[M\text{-}CH_3]^+$ (15), 235 (28), 203 (65), 189 (40), 177 (28). HR-MS *m/z* 454.3083 $[M]^+$ $C_{29}H_{42}O_4$ required 454.3083.

Wilforic acid B (**2**). Amorphous powder, IR ν_{max}^{KBr} cm^{-1}: 3400, 2926, 1698, 1463, 1138, 757, 666. ^{1}H NMR: δ ($CDCl_3$): 0.76 (3H, *s*, 25-H_3), 0.91 (3H, *s*, 26-H_3), 1.01 (3H, *s*, 27-H_3), 1.09 (3H, *s*, 28-H_3), 1.26 (3H, *s*, 30-H_3), 1.82 (3H, *s*, 23-H_3), 1.50 (1H, *m*, 7-H), 1.52 (1H, *m*, 1-H), 1.63 (1H, *m*, 8-H), 1.78 (1H, *m*, 7-H), 1.98 (1H, *m*, 6-H), 2.05 (1H, *m*, 16-H), 2.30 (1H, *m*, H-10), 2.90 (1H, *dd*, J = 16.6, 3.9 Hz, 6-H), 3.96 (1H, *dd*, J = 14.2, 6.4 Hz, 2-H). ^{13}C NMR ($CDCl_3$): see Table 1. EI-MS *m/z* (rel. int.): 456 $[M]^+$ (100), 358 (65), 316 (41), 235 (57), 140 (58), 121 (37). HR-MS *m/z* 456.3240 $[M]^+$ $C_{29}H_{44}O_4$ required 456.3239.

Wilforic acid C (**3**). Amorphous powder, $[\alpha]_D^{25}$ −27.3° ($CHCl_3$ *c* 1.1), IR ν_{max}^{KBr} cm^{-1}: 3450, 2943, 1708, 1460, 1391, 1213, 1138, 1052, 998, 883, 738. ^{1}H NMR: δ (C_5D_5N): 0.73 (3H, *s*, 24-H_3), 0.84 (3H, *s*, 25-H_3), 0.88 (3H, *s*, 27-H_3), 0.98 (3H, *d*, J = 6.7 Hz, 23-H_3), 1.14 (3H, *s*, 30-H_3), 1.22 (3H, *s*, 26-H_3), 1.44 (3H, *s*, 28-H_3), 1.83 (1H, *ddd*, J = 14.1, 13.8, 3.1 Hz, 1-H), 2.13 (1H, *br d*, J = 14.1 Hz, 1-H), 2.26 (1H, *br d*, J = 13.8 Hz, 10-H), 2.53 (1H, *dd*, J = 13.8, 3.8 Hz, 22-H), 2.53 (1H, *d*, J = 14.7 Hz, 21-H), 2.67 (1H, *d*, J = 15.1 Hz, 12-H), 3.22 (1H, *q*, J = 6.7 Hz, 4-H), 4.39 (1H, *br t*, J = 2.0 Hz, 2-H). ^{13}C NMR (C_5D_5N): see Table 1. EI-MS *m/z* (rel. int.): 472 $[M]^+$ (18), 454 (31), 426 (26), 411 (21), 289 (29), 155 (62), 109 (100), 95 (73), 81 (57). HR-MS *m/z* 472.3553 $[M]^+$ $C_{30}H_{48}O_4$ required 472.3572.

Triptobenzene H (**4**). Amorphous powder, $[\alpha]_D^{25}$ +171.0° ($CHCl_3$ *c* 1.0), IR ν_{max}^{KBr} cm^{-1}: 3400, 2960, 1680, 1620, 1410, 1260, 1220, 1030, 800, 760. UV λ_{max}^{MeOH} nm (log ε): 223 (3.98), 280 (3.34), 287 (3.34). ^{1}H NMR: δ ($CDCl_3$): 1.17, 1.19 (each 3H, *d*, J = 6.8 Hz, 16, 17-H_3), 1.18 (3H, *s*, 20-H_3), 1.59 (1H, *m*, 6-H), 1.64 (1H, *m*, 1-H), 2.18 (3H, *br s*, 19-H_3), 2.21 (1H, *dd*, J = 19.2, 6.4 Hz, 6-H), 2.38 (1H, *br d*, J = 12.4 Hz, 5-H), 2.41 (1H, *m*, 2-H), 2.63 (1H, *m*, 2-H), 2.68 (1H, *m*, 7-H), 3.03 (1H, *ddd*, J = 13.2, 7.6, 3.6 Hz, 1-H), 3.10 (1H, *dd*, J = 16.3, 3.2 Hz, 7-H), 3.25 (1H, *sept*, J = 6.8 Hz, 15-H), 3.69 (3H, *s*, OCH_3), 6.40 (1H, *s*, 12-H). ^{13}C NMR ($CDCl_3$): 18.6 (*q*, C-20), 18.7 (*q*, C-19), 19.9 (*t*, C-6), 23.8, 23.9 (each *q*, C-16, 17), 24.8 (*t*, C-2), 26.1 (*d*, C-15), 26.3 (*t*, C-7), 32.6 (*t*, C-1), 37.3 (*s*, C-10), 48.9 (*d*, C-5), 60.7 (*q*, OCH_3), 111.8 (*d*, C-12), 124.3 (*s*, C-3), 131.0 (*s*, C-8), 131.1 (*s*, C-9), 139.3 (*s*, C-13), 148.8 (*s*, C-14), 150.8 (*s*, C-4), 150.9 (*s*, C-11), 174.2 (*s*, C-18). EI-MS *m/z* (rel. int.): 344 $[M]^+$ (100), 454 (31), 329 (41), 311 (60), 283 (21), 245 (30), 241 (19), 205 (15), 91 (17), 43 (25). HR-MS *m/z* 344.1963 $[M]^+$ $C_{21}H_{28}O_4$ required 344.1988.

Triptobenzene I (**5**). Amorphous powder, IR ν_{max}^{KBr} cm^{-1}: 3430, 2690, 1747, 1491, 1421, 1182, 1068, 949, 897, 811, 757. UV λ_{max}^{MeOH} nm (log ε): 223 (3.98), 270 (3.46). ^{1}H NMR: δ ($CDCl_3$): 1.01 (3H, *s*, 20-H_3), 1.24, 1.25 (each 3H, *d*, J = 6.8 Hz, 16, 17-H_3), 1.67 (1H, *m*, 1-H), 1.89 (1H, *m*, 6-H), 2.32 (1H, *m*, 6-H), 2.38 (1H, *m*, 2-H), 2.48 (1H, *m*, 1-H), 2.51 (1H, *m*, 2-H), 2.71 (1H, *br d*, J = 15.1 Hz, 5-H), 2.87 (1H, *m*, 7-H), 3.12 (1H, *sept*, J = 6.8 Hz, 15-H), 6.09 (1H, *s*, 19-H), 6.92 (1H, *d*, J = 7.8 Hz, 11-H), 7.06 (1H, *d* J = 7.8 Hz, 12-H). ^{13}C NMR ($CDCl_3$): 18.3 (*t*, C-6), 19.8 (*t*, C-2), 22.5 (*t*, C-7), 22.8 (*q*, C-20), 22.7, 22.8 (each *q*, C-16, 17), 27.2 (*d*, C-15), 32.5 (*t*, C-1), 36.3 (*s*, C-10), 40.2 (*d*, C-5), 97.2 (*d*, C-19), 116.3 (*d*, C-11), 120.8 (*s*, C-8), 123.5 (*d*, C-12). 129.0 (*s*, C-3), 131.4 (*s*, C-13), 144.0 (*s*, C-9), 151.0 (*s*, C-14), 161.6 (*s*, C-4), 171.2 (*s*, C-18). EI-MS *m/z* (rel. int.): 328 $[M]^+$ (92), 313 (100), 253 (15). HR-MS *m/z* 328.1675 $[M]^+$ $C_{20}H_{24}O_4$ required 328.1651.

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