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Terpenoids from *Tripterigyum hypoglaucum*

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Abstract

Six terpenoids have been isolated from the root bark of *Tripterygium hypoglaucum*, along with 14 known compounds. The structures of the terpenoids were elucidated as 3,11,14-oxo-abieta-8,12-diene, 3β-hydroxy-12,14-dimethoxyabieta-8,11,13-triene, 3β-hydroxy-11α-ethoxyurs-12-ene, 3β-hydroxy-11α-methoxyurs-12-ene, 3β-hydroxy-11α-methoxyolean-12-ene-28-oic acid, and 1β-benzoyl-8α-cinnamoyl-4α,5α-dihydroxydihydroagarofuran.

Keywords: *Tripterygium hypoglaucum*; Celastraceae; Root bark; Triterpenoids

1. Introduction

Species of the Celastraceae have been the subject of continued and growing interest, due to the range of biological activities exhibited (Tu, 1991; Brunihg & Wagner, 1978), with some having been used in folk medicine (Shizuri, Wada, Sugiura, Yamada & Hirata, 1973) or as stimulants (Geutahun & Krikorian, 1973) from ancient times. In the last 30 years, many triterpenes, diterpenes and sesquiterpenes have been isolated. We have studied the constituents of the Celastraceae and described the isolation and structure determination of wilforic acid, triptogelin and triptofordines from *Tripterygium wilfordii* var. *regelii* (Takaishi, Tamai, Nakano, Murakami & Tomimatsu, 1991; Takaishi et al., 1992; Ujita, Takaishi, Tokuda, Nishino, Iwashima & Fujita, 1993; Shishido et al., 1994). Recently, antitumor and immunosuppressive activities associated with celastrol were reported (Takaishi et al., 1997a, 1997b).

In continuation to our previous studies in this area, we examined the active principles of *Tripterygium hypoglaucum* and reported the presence of 14 terpenoids (Duan, Kawazoe, Bando, Kido & Takaishi, 1997; Duan, Kawazoe & Takaishi, 1997; Duan & Takaishi, 1998). In the present study, we report six new terpenoids, trivially named triptoquinone H (3,11,14-oxo-abieta-8,12-diene) (**1**), triptobenzene L (3β-hydroxy-12,14-dimethoxyabieta-8,11,13-triene) (**2**), triptohypol D (3β-hydroxy-11α-ethoxyurs-12-ene) (**3**), triptohypol E (3β-hydroxy-11α-methoxyurs-12-ene) (**4**), triptohypol F (3β-hydroxy-11α-methoxyolean-12-ene-28-oic acid) (**5**) and 1β-benzoyl-8α-cinnamoyl-4α,5α-dihydroxydihydroagarofuran (**6**), as well as 14 known compounds.

2. Results and discussion

Repeated column chromatography of the ethyl acetate soluble fraction from the methanol extract of the root bark of *Tripterygium hypoglaucum* (Levi.) Hutch yielded six new terpenoids (**1**–**6**) and 14 known compounds (**7**–**20**).

Triptoquinone H (**1**) was assigned the molecular formula $C_{20}H_{26}O_3$ by HR-MS, and the IR spectrum showed a ketone absorption band (1708 cm^{-1}). The ^{1}H-NMR spectrum revealed the presence of an isopropyl group [δ_H 1.11 (6H, *d*, J = 7.0 Hz) and 3.01 (1H, *sept*., J = 7.0 Hz)], one methine proton attached to

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the double bond [δ_H 6.37 (1H, *s*)] and three methyls [δ_H 1.20, 1.30, 1.54 (3H, *s*)]. The ^{13}C-NMR spectrum contained resonances corresponding to three carbonyl carbons at δ_C 217.0, 187.6 and 187.7, two double bonds at δ_C 131.9, 142.8, 148.2 and 153.2, and five methyl, four methylene, two methine and two quaternary carbon signals. **1** was thus assumed to be a diterpene possessing a *p*-benzoquinone ring. Some quinone-type diterpenes were previously isolated from *Triptergium wilfordii*, and the ^{13}C-NMR spectrum of **1** was very similar to that of triptoquinone B (Shishido et al., 1994), except for the presence of one methyl in **1** and one methylene attached to an oxygen function in triptoquinone B (Table 1). In the ^{13}C–^{1}H long-range correlation spectrum, the proton resonance at δ_H 1.76 (H-5) was correlated with carbon signals at δ_C 20.2 (C-20), 21.1 (C-18), 21.1 (C-19) and 217.0 (C-3), the proton resonance at δ_H 1.30 (H_3-20) with carbon signals at δ_C 34.7 (C-1), 37.5 (C-10), 50.9 (C-5) and 148.2 (C-9), and the proton resonance at δ_H 1.54 (H_3-18) with the carbon signals at δ_C 47.0 (C-4) and 217.0 (C-3). These facts indicated that the position of the ketone group was at C-3. Thus, the structure was formulated as **1** (Fig. 1).

Triptobenzene L (**2**) was assigned the molecular formula $C_{22}H_{34}O_3$ by HR-MS. The IR spectrum showed a hydroxy group absorption band (3423 cm^{-1}), and its UV absorption spectrum revealed the presence of an aromatic group (222 and 281 nm). The ^{1}H-NMR spectrum displayed resonances corresponding to an isopropyl group [δ_H 1.30, 1.33 (each 3H, *d*, J = 7.1 Hz) and 3.41 (1H, *sept*., J = 7.1 Hz)], three methyl groups [δ_H 0.90, 1.09 and 1.21 (each 3H, *s*)], one methine [δ_H 6.56 (1H, *s*)] attached to the double bond, one methine [δ_H 3.32 (1H, *dd*, J = 4.9, 11.1 Hz)] attached to an oxygen function and two methoxy groups. The ^{13}C-NMR spectrum of **2** revealed the presence of five methyl carbons, four methylene carbons, one methine attached to an oxygen function, two methine carbons, seven quaternary carbons and two methoxy groups. Compound **2** was thus deduced to be an abietane-type diterpene, similar to triptobenzenes A-H (Takaishi et al., 1997a, 1997b; Duan et al., 1997) from the same plant source. To confirm the structure of **2**, we analyzed the ^{1}H–^{13}C COSY and NOESY spectra. The proton resonance at δ_H 3.32 (H-3) was correlated with carbon signals at δ_C 21.2 (C-18), 25.2 (C-19) and 28.1 (C-2), the proton resonances at δ_H 0.90 (H_3-19) and 1.09 (H_3-18) were correlated with carbon resonances at δ_C 78.8 (C-3), the proton resonance at δ_H 3.41 (H-15) was correlated with carbon resonance at δ_C 155.8 (C-12) and 157.8 (C-14), and the methoxy groups [δ_H 3.68 and 3.78] with the carbon resonances at δ_C 155.8 (C-12) and 157.8 (C-14), respectively. Thus, the C-3 assignment of the hydroxy group and C-12 and C-14 assignments of the methoxy groups were confirmed. Furthermore, the proton signal at δ_H 6.56 (H-11) was correlated with the methoxy group (δ_H 3.68) and δ_H 1.21 (H_3-20) in the NOESY spectrum; this fact further supported the C-12 and C-14 assignment of the methoxy groups. From the coupling constant of H·3 [δ_H 3.32 (*dd*, J = 4.9, 11.1] and the NOESY correlation between the proton signals at δ_H 3.32 (H-3) and 1.30 (H-5), the relative configuration of the hydroxy group at C-3 was β. Therefore, triptobenzene L was formulated as **2** (Fig. 1).

Triptohypol D (**3**) was obtained as an amorphous solid and its spectrum showed a hydroxy absorption band (3404 cm^{-1}). The ^{1}H-NMR spectrum of **3** revealed the presence of eight methyl groups [δ_H 0.81 (6H, *s*), 0.88 (3H, *d*, J = 6.0 Hz), 0.91 (3H, *d*, J = 6.0 Hz), 1.01, 1.04, 1.07, 1.16 (each 3H, *s*)], one methine proton [δ_H 5.33 (1H, *d*, J = 2.6 Hz)] attached to the double bond, two methine protons [δ_H 3.24 (1H, *d*, J = 9.3, 16.3 Hz), 3.87 (1H, *dd*, J = 2.7, 8.9 Hz)] attached to oxygen functions and one ethoxy group [δ_H 1.14 (3H, *t*, J = 7.5 Hz), 3.37, 3.60 (each 1H, *t*, J = 7.5 Hz)]. The ^{13}C-NMR spectrum data of **3** revealed the presence of eight methyl carbons, eight methylene carbons, two methine carbons attached to an oxygen function, six methine carbons, two double bond carbons, five quaternary carbons and one ethoxy group. This evidence agreed with a molecular formula $C_{32}H_{54}O_2$, which was supported by the HR mass spec-

Table 1
^{13}C-NMR chemical shifts for compounds **1**, **2** and **6**[a]

Carbon	1	2	Triptoquinone B	6
1	34.7	37.2	34.3	73.0
2	33.9	28.1	34.1	37.3
3	217.0	78.8	220.0	23.7
4	47.0	39.0	50.4	73.2
5	50.8	49.8	51.6	79.9
6	18.6	18.6	17.8	50.4
7	25.5	25.0	25.4	83.7
8	142.8	121.0	142.4	73.3
9	148.2	148.4	147.8	50.6
10	37.5	37.9	37.0	91.6
11	187.6	103.8	187.2	20.3
12	131.9	155.8	131.7	23.9
13	153.2	126.6	153.2	84.6
14	187.7	157.8	187.4	26.7
15	26.3	28.3	26.3	30.4
16	21.3	15.5	21.3	
17	21.2	24.9	21.2	
18	21.1	25.5	22.3	
19	21.1	21.2	65.4	
20	20.2	21.2	20.9	

[a] Solvents: **1**, **2** and **6**: $CDCl_3$, TMS as int. standard; **6**: [1-OCO-Bz: 165.9, 128.2, 129.3, 128.4, 132.9; 8-OCO-Cin: 165.8, 145.2, 119.9, 134.5, 128.4, 128.8, 130.3].

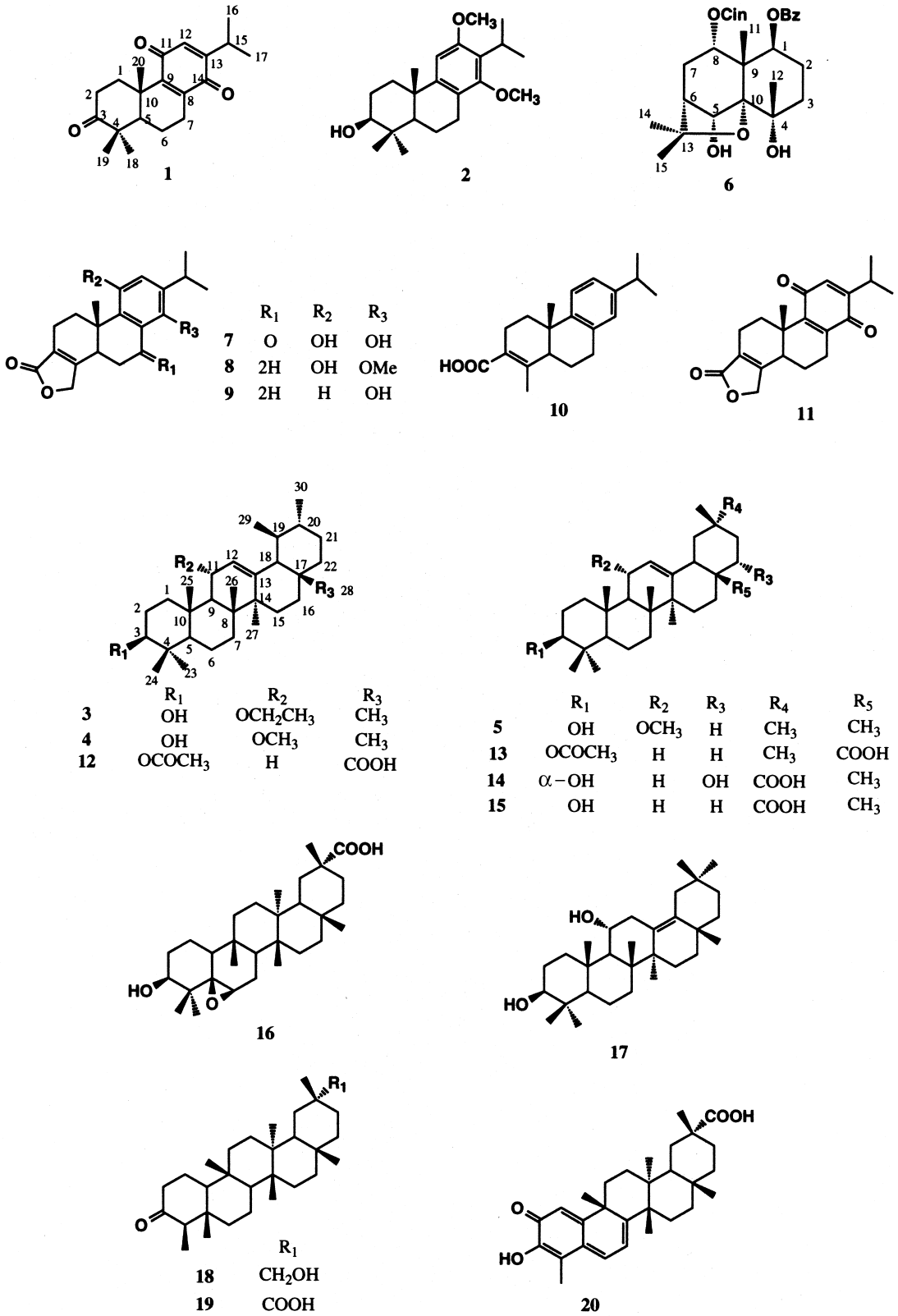

Fig. 1. Triterpenoids from *Tripterygium hypoglaucum*.

tral data. Many types of triterpens have been isolated from Celastraceae plants; compound **3** was assumed to be an ursan-type triterpene from the carbon number (C_{30}) and the presence of eight methyls including two secondary methyl groups. On comparison of the ^{13}C-NMR spectral data with those of 3β-acetoxy-urs-12-ene-28-oic acid (**12**) (Table 2), the chemical shifts of these two compounds were found similar, except for the signals due to C-11, C-16, C-20, C-28 and C-29. In the HMBC spectrum, the proton resonance at δ_H 3.24 (H-3) showed long-range correlations with the carbon resonances at δ_C 15.7 (C-24) and 28.3 (C-23), and the proton resonance at δ_H 3.87 (H-11) with the carbon resonances at δ_C 38.3 (C-10), 52.7 (C-9), 62.6 (ethoxy group), 124.9 (C-12) and 143.1 (C-13). From these facts, the hydroxy and ethoxy groups were assigned to C-3 and C-11, respectively. Furthermore, the proton resonance at δ_H 3.24 (H-3) was correlated with the proton resonance at δ_H 0.78 (H-5α) and the proton resonance at δ_H 1.07 (H_3-25) with that at δ_H 0.81 (H_3-24) and 3.87 (H-11) in the NOESY spectrum. These facts clearly showed that the relative configurations of the hydroxy and the ethoxy groups were C-3β and 11α, respectively. Therefore, the structure of **3** was determined as shown (Fig. 1).

Table 2
^{13}C-NMR spectral data for compounds **3**–**5**, **12** and **15**[a]

Carbon	3	4	5	12	15
1	39.9	39.9	39.6	38.1	38.9
2	27.7	26.9	33.3	23.5	27.0
3	78.9	78.9	78.9	80.9	79.0
4	39.1	39.1	39.1	37.7	38.8
5	55.8	55.3	55.3	55.3	55.4
6	18.5	18.4	18.5	18.2	18.5
7	33.5	33.5	33.4	32.6	32.8
8	43.0	42.9	41.9	39.3	40.0
9	52.7	52.6	51.9	47.6	47.8
10	36.3	38.2	38.3	37.0	37.1
11	75.4	76.8	76.1	22.9	23.7
12	124.9	124.1	121.7	122.6	122.9
13	143.1	143.6	149.7	143.6	144.3
14	42.1	41.5	43.2	41.6	41.8
15	26.9	27.6	26.4	27.7	26.1
16	28.1	28.1	26.9	23.	26.9
17	33.7	33.7	32.4	46.6	32.5
18	58.6	58.6	47.1	41.3	46.2
19	39.6	39.4	46.7	45.8	40.6
20	39.7	39.6	31.2	30.6	42.5
21	31.3	31.2	34.8	33.8	2.2
22	41.5	42.1	37.1	32.3	36.1
23	28.3	28.3	28.3	28.1	28.1
24	15.7	15.7	15.7	15.6	15.6
25	17.2	17.1	17.0	16.3	15.7
26	18.3	18.3	18.3	16.8	16.9
27	22.7	22.6	25.3	26.0	26.0
28	28.8	28.8	28.6	181.0	28.3
29	17.4	17.5	33.4	33.1	182.2
30	21.5	21.5	23.8	23.6	19.4
11-OEt	62.6				
	16.1				
11-OMe		52.6	53.9		
3-OAc				171.2	
				21.50	

[a] Solvents: **3**–**5**, **12** and **15**: $CDCl_3$, TMS as int. standard.

Triptohypol E (**4**) was assigned the molecular formula $C_{31}H_{44}O_2$. Its ^{13}C-NMR spectral data were very similar to those of **3** except for one methoxy group signal (δ_C 52.6) in the case of **4** and one ethoxy group signal in **3**. It was assumed that the ethoxy group in **3** was replaced by a methoxy group in **4**. In the HMBC spectrum, the proton signal at δ_H 3.79 (H-11) was correlated with the carbon signals at δ_C 38.2 (C-10), 54.7 (methoxy group), 124.1 (C-12) and 143.6 (C-13). From this fact, the methoxy group was attributed to C-11, and was assigned C-11α configuration due to the correlation between proton signals at δ_H 3.79 (H-11) and 1.07 (H_3-25) in the NOESY spectrum.

Triptohypol F (**5**) was assigned the molecular formula $C_{31}H_{52}O_2$. The ^{1}H-NMR spectrum revealed the presence of eight methyls [δ_H 0.82, 0.84, 0.89, 0.90, 1.01, 1.01, 1.05, 1.22 (each 3H, *s*)], one methine attached to an oxygen function [δ_H 3.84 (1H, *dd*, J = 3.4, 8.9 Hz)] and one olefinic proton [δ_H 5.35 (1H, *d*, J = 3.4 Hz)]. The ^{13}C-NMR spectrum of **5** showed the presence of one double bond, two methine carbons attached to an oxygen function, three methine carbons, nine methylene carbons, eight methyl carbons, six quaternary carbons and one methoxy group. From these facts, the carbon number and the presence of eight tertiary methyls, **5** was assumed to be an oleanane-type triterpene. The ^{13}C-NMR spectrum data were similar to those of **15** (Table 2) except for one methine attached to an oxygen function and a methyl (C-30) instead of a carboxyl group (C-30). In the HMBC spectrum, the proton resonance at δ_H 3.24 (H-3) showed correlation with carbon resonances δ_C 28.3 (C-24) and the proton resonance at δ_H 3.84 (H-11) with carbon resonances at δ_C 38.3 (C-10), 53.9 (methoxy group) and 149.7 (C-13). This clearly indicated that the hydroxy and the methoxy groups were attached to C-3 and C-11, respectively. In the NOESY spectrum, the proton resonance at δ_H 3.24 (H-3) was correlated with the proton resonance at δ_H 0.78 (H-5α), and the proton resonance at δ_H 1.05 (H_3-25) with that at δ_H 0.82 (H_3-24) and 3.84 (H-11). These facts clearly showed that the orientations of the hydroxy and methoxy groups were C-3β and 11α, respectively.

1β-Benzoyl-8α-cinnamoyl-4α,5α-dihydroxydihydroagarofuran (**6**), an amorphous powder, showed a hydroxy absorption band at 3436 and carbonyl absorption bands at 1719 and 1708 cm^{-1} in the IR spectrum, and the UV spectrum showed the presence of an aromatic moiety (223 nm). It contained two ben-

zoyl rings [δ_H 7.25–7.30 (2H, *m*), 7.36–7.47 (6H, *m*), 7.75 (2H, *d*, *J* = 7.2 Hz)], two olefinic protons [δ_H 6.19, 7.27 (each 1H, *d*, *J* = 16.0 Hz)], three methine protons [δ_H 4.48, 4.88, 5.65] attached to the oxygen function, and four methyls [δ_H 1.49, 1.53, 1.59 and 1.64 (each 3H, *s*)]. The ^{13}C-NMR spectrum of **6** indicated the presence of four methyls, three methylene carbons, three methine carbons attached to an oxygen function, one methine, four quaternary carbons, one benzoyl group and one cinnamoyl group. These data agreed with the molecular formula of **6** as $C_{31}H_{35}O_7$, which was supported by the HR mass spectral data. It was concluded that **6** was a sesquiterpene derived from dihydroagarofuran polyol esters found in the Celastraceae, having one benzoyl and one cinnamoyl group. In the HMBC spectrum, the proton resonance at δ_H 4.88 (H-8) was correlated with the carbon signal at δ_C 165.8 (carbonyl carbon of cinnamoyl group) and the proton resonance at δ_H 5.65 (H-1) with carbon signals at δ_C 50.6 (C-9) and 165.9 (carbonyl carbon of benzoyl group). This clearly indicated that the benzoyl and the cinnamoyl groups were attached to C-1 and C-8, respectively. In the NOESY spectrum, the proton resonance at δ_H 1.49 (H_3-11) was correlated with proton signals at δ_H 1.64 (H_3-12), 4.48 (H-5) and 4.88 (H-8), the proton resonance at δ_H 1.64 (H_3-12) with proton signals at δ_H 2.27 (H-2β) and 1.49 (H_3-11), and the proton resonance at δ_H 2.07 (H-2α) with the proton signal at δ_H 5.65 (H-1). These facts clearly showed that the relative stereochemistry of **6** was that of 1β-benzoyl-4α,5α-dihydroxy-8α-cinnamoyl-dihydroagarofuran.

The known compounds **7**–**20** were identified from spectral data comparisons to be triptobenzene K (**7**) (Duan et al., 1997), neotriptophenolide (**8**) and hypolide (**9**) (Deng, Zhou, Song & Hu, 1982), triptobenzene D (**10**) (Takaishi et al., 1997a, 1997b), quinone 21 (**11**) (Morota, Qin, Takagi, Xu, Maruno & Yang, 1995). 3β-acetoxy-urs-12-ene-28-oic acid (**12**) (Cambie, Rutledge & Wellington, 1997), oleanoic acid 3-*O*-acetate (**13**) (Hirayama, Udagawa & Shimada, 1997), triptocallic acid D (**14**) and triptocallic acid C (**16**) (Nakano, Oose & Takaishi, 1997), 3-epikatonic acid (**15**) (Coxon & Wells, 1980), hypodiol (**17**) (Duan et al., 1997), 29-hydroxyfriedelan-3-one (**18**) (Mariano, Miguel & Cristina, 1988), polpunonic acid (**19**) (Itokawa, Shirota, Ikuta, Morita, Takeya & Iitaka, 1991), and celastrol (**20**) (Morota et al., 1995).

3. Experimental

NMR spectra were recorded on a Bruker ARX-400 instrument, ^{1}H-NMR: 400 MHz with TMS as int. standard, ^{13}C-NMR: 100 MHz. MS were obtained on a JEOL JMSO-300 instrument. Chromatography utilized: silica gel, Sephadex LH-20 and Toyopearl HW-40 (TOSOH). HPLC: GPC (Shodex packed column, GS-310, MeOH; Shodex H-2001, 2002, $CHCl_3$), silica gel (YMC-Pack SIL-06 SH-043-5-06, 250 × 20 mm).

3.1. Isolation of compounds 1–20

The root bark of *Tripterigyum hypoglaucum* (Levl.) Hutch was purchased in 1995 from Kunming in Yunnan Province, China, and identified by Prof. Dr. Dao-Feng Cheng (Shanghai Medical University, China). A voucher specimen is deposited in the Faculty of Pharmaceutical Sciences, University of Tokushima, Japan.

The root bark (15.3 kg) was crushed and extracted (3 × 50 l) with MeOH at 60°C for 6 h. The MeOH extracts were concentrated in vacuo to give a residue (860 g), which was partitioned between EtOAc and H_2O. The EtOAc layer was concentrated to give a residue (314 g), which was subjected to silica gel chromatography (1.6 kg, 90 × 850 mm, 500 ml each fraction). The column was eluted with solvents 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 22 frs. (fr. 1–22). Fr. 8 (9.6 g) was chromatographed on silica gel (800 g) with $CHCl_3$–MeOH (98:2, 95:5, 9:1, 8:2) and MeOH, to give 8 frs. (fr. 8.1–8.8). Fr. 8.2 (2.19 g) was subjected to Sephadex LH chromatography with MeOH to give 4 frs. (fr. 8.2.1–8.2.4). Fr. 8.2.2 (863 mg) was subjected to chromatography on a medium pressure silica column, eluting with $CHCl_3$–hexane (95:5) and $CHCl_3$–MeOH (97:3, 9:1) to give 7 frs. (fr. 8.2.2.1–8.2.2.7). Fr. 8.2.2.2 (133 mg) was subjected to HPLC (GPC, $CHCl_3$) and HPLC (hexane:EtOAc, 2:1) to give **3** (5.8 mg), **6** (5.8 mg), **11** (4.7 mg) and **18** (7.1 mg) and five other frs. (fr. 8.2.2.2.1, 8.2.2.2.3–8.2.2.2.5, 8.2.2.2.7). Fr. 8.2.2.2.1 (20.6 mg) on HPLC (GPC, MeOH) yielded **12** (4.1 mg). Fr. 8.2.2.3 on HPLC (GPC, MeOH) and HPLC (hexane:EtOAc, 2:1) yielded **13** (4.2 mg). Fr. 8.2.2.5 (427 mg) on HPLC (GPC, MeOH) gave 9 frs. (fr. 8.2.2.5.1–8.2.2.5.9); fr. 8.2.2.5.8 (43 mg) on HPLC (hexane:EtOAc, 2:1) yielded **10** (5.2 mg) and **19** (39.6 mg); fr. 8.2.2.5.4 (82.5 mg) was separated by HPLC ($CHCl_3$:MeOH, 98:2) to yield **14** (4.7 mg). Fr. 8.2.3 (282.9 mg) on HPLC (GPC, $CHCl_3$) gave 7 frs. (fr. 8.2.3.1–8.2.3.7) which contained **20** (162.8 mg); fr. 8.2.3.3 (15.1 mg) on prep. TLC ($CHCl_3$:acetone, 8:2) yielded **7** (7.0 mg); fr. 8.2.3.2 (81.6 mg) on prep. TLC (ether:hexane, 9:1) yielded **8** (8.6 mg) and **9** (7.3 mg). Fr. 8.3 (3.17 g) was subjected to Sephadex LH-20 chromatography using MeOH as eluent; the eluent was then reapplied to a medium pressure silica column, eluting with $CHCl_3$–hexane (95:5) and $CHCl_3$–MeOH (97:3, 9:1) to give 9 frs. (fr. 8.3.1–8.3.9); fr. 8.3.6 (175.7 mg) on HPLC (GPC, MeOH) yielded **17** (11.5 mg) and fr. 8.3.6.2., which was further separated by HPLC

(hexane:EtOAc, 3:2) to give **15** (15.3 mg) and **16** (8.4 mg). Fr. 6 (7.87 g) was chromatographed on a medium pressure silica column, eluting with $CHCl_3$ to give 11 frs. (fr. 6.1–6.11). Fr. 6.3 (455.1 mg) on Toyopearl HW-40 ($CHCl_3$:MeOH, 2:1) and HPLC (hexane: EtOAc, 3:1) gave **1** (4.8 mg) and **2** (5.1 mg); fr. 6.7 (134.9 mg) on HPLC (GPC, $CHCl_3$) and HPLC (hexane:EtOAc, 3:1) gave **4** (15.1 mg) and **5** (6.3 mg).

3.2. 3,11,14-Oxo-abieta-8,12-diene (Triptoquinone H) (*1*)

Yellow oil, $[\alpha]_D^{25}$ + 102.3° (MeOH, *c* 0.7); IR ν_{max}^{KBr} cm^{-1}: 3423, 2962, 2360, 1708, 1651, 1459, 1233, 1112; UV λ_{max}^{MeOH} nm (log ε): 258 (3.98). ^{1}H-NMR spectral data ($CDCl_3$): see Table 3; ^{13}C-NMR spectral data ($CDCl_3$): see Table 1; EIMS *m/z* (rel. int.): 314 (60), 271 (30), 257 (30), 243 (45), 229 (59), 216 (51), 187 (31), 175 (28), 161 (27), 145 (32), 128 (43), 115 (38), 91 (51), 83 (45), 55 (54), 41 (100); HR-EIMS: *m/z* 314.1885, $[M]^+$ $C_{20}H_{26}O_3$, required 314.1882.

3.3. 3β-Hydroxy-12,14-dimethoxyabieta-8,11,13-triene (Triptobenzene L) (*2*)

Amorphous powder, $[\alpha]_D^{25}$ + 43.7° (MeOH, *c* 0.6); IR ν_{max}^{KBr} cm^{-1}: 3498, 3423, 3369, 2945, 2873, 2359, 2344, 1604, 1571, 1458, 1119, 1061, 1032; UV λ_{max}^{MeOH} nm (log ε): 281 (3.18), 223 (3.87); ^{1}H-NMR spectral data ($CDCl_3$): see Table 3; ^{13}C-NMR spectral data ($CDCl_3$): see Table 1; EIMS *m/z* (rel. int.): 346 (118), 331 (100), 246 (51), 231 (76), 43 (51); HR-EIMS: *m/z* 346.2494, $[M]^+$ $C_{22}H_{34}O_3$, required 346.2508.

3.4. 3β-Hydroxy-11α-ethoxyurs-12-ene (Triptohypol D) (*3*)

Amorphous powder, $[\alpha]_D^{25}$ + 14.8° (MeOH, *c* 0.3); IR ν_{max}^{KBr} cm^{-1}: 3856, 3590, 3570, 3547, 3404, 2927, 2363, 2344, 1736, 1719, 1687, 1639, 1459, 1389, 1077, 670; UV λ_{max}^{MeOH} nm (log ε): 273 (3.94); ^{1}H-NMR spectral data ($CDCl_3$): 0.81 (6H, *s*, H_3-23, H_3-28), 0.88 (3H, *d*, *J* = 6.0 Hz, H_3-29), 0.91 (3H, *d*, *J* = 6.0 Hz,

Table 3
^{1}H-NMR chemical shifts for compound **1**, **2** and **6**[a]

Proton	**1**	**2**[b]	**6**
1-H	2.57 (*m*)	1.57 (*td*, 2.2, 12.8)	5.65 (*dd*, 4.3, 12.0)
		2.27 (*dt*, 3.3, 12.8)	
2-H	1.67 (*m*)	1.78 (*m*)	2.07 (*m*)
	2.86 (*m*)	1.82 (*m*)	2.27 (*ddd*, 3.4, 6.9, 16.2)
3-H	–	3.32 (*dd*, 4.9, 11.1)	1.74 (*dt*, 3.4, 13.1)
			1.99 (*ddd*, 4.0, 11.0, 11.0)
4-H	–		–
5-H	1.76 (*m*)	1.30 (*m*)	4.48 (*d*, 5.4)
6-H	1.52 (*m*)	1.68 (*m*)	2.21 (*t*, 2.8)
	1.84 (m)	1.93 (*m*)	
7-H	2.31 (*m*)	2.65 (*m*)	2.13 (*m*)
	2.81 (*m*)	2.97 (*m*)	
8-H	–	–	4.88 (*d*, 6.9)
9-H	–	–	–
10-H	–	–	–
11-H	–	6.56 (*s*)	1.49 (3H, *s*)
12-H	6.37 (*s*)	–	1.64 (3H, *s*)
13-H	–	–	–
14-H	–	–	1.53 (3H, *s*)
15-H	3.01 (*sept*., 7.0)	3.41 (*sept*., 7.1)	1.59 (3H, *s*)
16-H	1.11 (3H, *d*, 7.0)	1.33 (3H, *d*, 7.1)	
17-H	1.11 (3H, *d*, 7.0)	1.30 (3H, *d*, 7.1)	
18-H	1.54 (3H, *s*)	1.09 (3H, *s*)	
19-H	1.20 (3H, *s*)	0.90 (3H, *s*)	
20-H	1.30 (3H, *s*)	1.21 (3H, *s*)	
12-OMe		3.68 (3H, *s*)	
14-OMe		3.78 (3H, *s*)	

[a] Solvents: **1**, **2** and **6**: $CDCl_3$, TMS as int. standard. **6**: [1-Bz: 7.75 (2H, *d*, 7.2), 7.36–7.47 (3H, m)], 8-Cin: 6.19 (*d*, 16.0), 7.27 (*d*, 16.0), 7.25–7.30 (2H, *m*), 7.36–7.47 (3H, *m*)].

[b] The signal of 3-hydroxy was not observed, but may be overlapped by other signals.

H_3-30), 1.01 (3H, *s*, H_3-24), 1.04 (3H, *s*, H_3-26), 1.07 (3H, *s*, H_3-25), 1.16 (3H, *s*, H_3-27), 1.14 (3H, *t*, J = 7.5 Hz), 3.24 (1H, *dd*, J = 9.3, 16.3 Hz, H-3), 3.37 (1H, *t*, J = 7.5 Hz), 3.60 (1H, *t*, J = 7.5 Hz), 3.87 (1H, *dd*, J = 2.7, 8.9 Hz, H-11), 5.33 (1H, *d*, J = 2.7 Hz, H-12); ^{13}C-NMR spectral data ($CDCl_3$): see Table 2; EIMS *m/z* (rel. int.): 470 $[M]^+$ (100), 424 (72), 262 (92), 191 (31), 119 (58), 95 (73), 81 (55), 69 (65), 55 (59); HR-EIMS: *m/z* 470.4091, $[M]^+$ $C_{32}H_{54}O_2$, required 470.4124.

3.5. 3β-Hydroxy-11α-methoxyurs-12-ene (Triptohypol E) (**4**)

Amorphous powder, $[\alpha]_D^{25}$ − 3.6° (MeOH, *c* 1.0); IR ν_{max}^{KBr} cm^{-1}: 3935, 3688, 3660, 3544, 3469, 3402, 2980, 2945, 1457, 1386, 1050, 753, 669; ^{1}H-NMR spectral data ($CDCl_3$): 0.81 (3H, *s*, H_3-24), 0.81 (3H, *s*, H_3-28), 0.88 (3H, *d*, J = 5.9 Hz, H_3-29), 0.93 (3H, *s*, H_3-30), 1.01 (3H, *s*, H_3-23), 1.04 (3H, *s*, H_3-26), 1.07 (3H, *s*, H_3-25), 1.15 (3H, *s*, H_3-27), 0.91 (1H, *m*, H-20), 1.28, 1.40 (each 1H, *m*, H-21), 1.29, 1.43 (each 1H, *m*, H-22), 1.32 (1H, *m*, H-7), 1.41, 1.56 (each 1H, *m*, H-6), 1.47 (1H, *dd*, J = 2.8, 9.2 Hz, H-21), 1.51 (1H, *d*, J = 3.4 Hz, H-7), 1.61 (1H, *m*, H-15), 1.63 (1H, *d*, J = 3.5 Hz, H-15), 1.67 (1H, *d*, J = 8.9 Hz, H-9), 1.75 (1H, *dt*, J = 5.0, 13.7 Hz, H-2), 1.94 (1H, *dt*, J = 3.4, 13.7 Hz, H-1), 2.03 (1H, *dt*, J = 4.7, 13.5 Hz, H-16), 3.23 (1H, *dd*, J = 6.6, 9.7 Hz, H-3), 3.79 (1H, *dd*, J = 3.0, 8.9 Hz, H-11), 5.36 (1H, *d*, J = 3.0 Hz, H-12); ^{13}C-NMR spectral data ($CDCl_3$): see Table 2; EIMS *m/z* (rel. int.): 456 (100), 424 (65), 248 (94), 119 (44), 95 (52), 81 (42), 69 (54), 55 (59), 43 (55), 41 (45); HR-EIMS: *m/z* 456.3964, $[M]^+$ $C_{31}H_{52}O_2$, required 456.3967.

3.6. 3β-Hydroxy-11α-methoxyolean-12-ene-28-oic acid (Triptohypol F) (**5**)

Amorphous powder, $[\alpha]_D^{25}$ + 15.1° (MeOH, *c* 0.6); IR ν_{max}^{KBr} cm^{-1}: 3855, 3424, 2921, 2856, 2360, 1654, 1541, 1466, 1387, 1085, 1050, 594, 437; ^{1}H-NMR spectral data ($CDCl_3$): 0.82 (3H, *s*, H_3-24), 0.84 (3H, *s*, H_3-28), 0.89 (3H, *s*, H_3-29), 0.90 (3H, *s*, H_3-30), 1.01 (3H, *s*, H_3-26), 1.01 (3H, *s*, H_3-23), 1.05 (3H, *s*, H_3-25), 1.22 (3H, *s*, H_3-27), 3.24 (3H, *s*, methoxy group), 0.78 (1H, *m*, H-5), 1.51 (1H, *m*, H-9), 1.67 (1H, *m*, H-19), 1.92 (1H, *dt*, J = 3.4, 13.9 Hz, H-1), 1.99 (1H, *m*, H-18), 2.02 (1H, *m*, H-15), 3.24 (1H, *m*, H-3), 3.84 (1H, *dd*, J = 3.4, 8.9 Hz, H-11), 5.35 (1H, *d*, J = 3.4 Hz, H-12); ^{13}C-NMR spectral data ($CDCl_3$): see Table 2; EIMS *m/z* (rel. int.): 456 (56), 424 (40), 248 (100), 85 (50), 83 (79), 69 (51), 57 (51), 55 (51), 43 (68), 41 (50); HR-EIMS: *m/z* 456.3965, $[M]^+$ $C_{31}H_{52}O_2$, required 456.3967.

3.7. 1β-Benzoyl-8α-cinnamoyl-4α,5α-dihydroxydihydroagarofuran (**6**)

Amorphous powder, $[\alpha]_D^{25}$ + 141.5° (MeOH, *c* 0.5); IR ν_{max}^{KBr} cm^{-1}: 3856, 3436, 2364, 1719, 1708, 1639, 1562, 1460, 1024, 714, 597; UV λ_{max}^{MeOH} nm (log ε): 280 (4.20), 223 (4.23), 219 (4.22); ^{1}H-NMR spectral data ($CDCl_3$): see Table 3; ^{13}C-NMR spectral data ($CDCl_3$): see Table 1; EIMS *m/z* (rel. int.): 520 $[M]^+$ (33), 487 (21), 398 (23), 372 (26), 357 (55), 300 (39), 250 (44), 232 (19), 181 (53), 131 (150), 105 (149), 77 (81), 55 (31), 43 (100); HR-EIMS: *m/z* 520.2457, $[M]^+$ $C_{31}H_{35}O_7$, required 520.2461.

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