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Components of *Cipadessa baccifera*

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Abstract

Four compounds were isolated from dry seeds of *Cipadessa baccifera* (Roth) Miq. along with the known 2β,3β,4β-trihydroxypregnan-16-one, febrifugin, and khaysin T. Their structures were elucidated on the basis of spectral analysis to be cipadesin, 17α,20*R*-dihydroxypregnan-3,16-dione, 1,4-epoxy-16-hydroxyheneicos-1,3,12,14,18-pentaene and 1,4-epoxy-16-hydroxyheneicos-1,3,12,14-tetraene.

Keywords: *Cipadessa baccifera*; Meliaceae; Tetranortriterpenoids; Sterols; Heneicosene derivatives; Cipadesin; 17α,20*R*-Dihydroxypregnan-3,16-dione; 1,4-Epoxy-16-hydroxyheneicos-1,3,12,14,18-pentaene; 1,4-Epoxy-16-hydroxyheneicos-1,3,12,14-tetraene

1. Introduction

Cipadessa baccifera (Roth) Miq., used to treat dysentery, skin itch, malaria and burns (Jiangsu New Medical College, 1977), is widely distributed in the southwest of China, especially in Guangxi Zhuang Autonomous Region (Hou, 1982). From this genus, flavonoid glucosides (Liang et al., 1991), flavonoids (Liang et al., 1994) and three diterpenoids (Rojatkar and Nagasampagi, 1994; Rojatkar et al., 1994) were isolated previously. However, plants belonging to the family Meliaceae are generally reported to contain triterpenoids and tetranortriterpenoids as chemotaxononic markers. In seeking tetranortriterpenoids from Meliaceae, we examined the ethanolic extract obtained from the dry seeds of *Cipadessa baccifera*. Seven compounds, including three tetranortriterpenoids (**1**–**3**), two sterols (**4**, **5**), and two new heneicosenes (**6**, **7**), were obtained.

2. Results and discussion

The ethanolic extract of *C. baccifera* was partitioned using H_2O and $CHCl_3$. The $CHCl_3$ fraction was subjected to CC on silica gel, resulting in the isolation of seven compounds. Compounds **2**, **3** and **5** were identified as febrifugin (Rao et al., 1978), khaysin T (Kadota et al., 1990), and 2β,3β,4β-trihydroxypregnan-16-one (Ketwaru et al., 1993), respectively, by comparison with published data. The structures of the new compounds cipadesin (**1**), 17α,20*R*-dihydroxypregnan-3,16-dione (**4**) 1,4-epoxy-16-hydroxyheneicos-1,3,12,14,18-pentaene (**6**), and 1,4-epoxy-16-hydroxyheneicos-1,3,12,14-tetraene (**7**) were established on the basis of spectroscopic evidence.

The HR–EIMS spectrum of **1** showed a molecular formula of $C_{32}H_{48}O_8$, which was confirmed by analysis of ^{13}C NMR and DEPT spectra. Its IR spectrum revealed absorptions for a carbonyl group at 1728 cm^{-1} and a double bond at 1652 cm^{-1}. The ^1H NMR spectrum indicated the presence of four tertiary methyl groups (δ_H 0.79, 0.83, 1.11 and 1.15), one methoxy group (δ_H 3.72), three downfield signals attributed to a β-substituted furanyl ring (δ_H 7.79, 7.42 and 6.47), two protons attached to a carbon adjacent to an oxygen atom [δ_H 5.69 (*s*), 4.81 (*d*, J = 8.9 Hz)], a doublet methyl (δ 1.14, J = 6.2 Hz), and a triplet methyl group (δ 0.92, J = 7.4 Hz). Under EIMS conditions, the fragment ion peak at m/z 452 was attributed to the loss of 102 AMU (C_4H_9COOH) from the molecular ion peak. Besides the C_4H_9COO– and–OCH_3 substituent groups, compound **1** contained 26 carbons and was assumed to be a tetranortriterpenoid. In the HMBC spectrum, δ_H 5.69 (*s*, H-17) showed cross peaks to δ_C 169.2 (*s*, C-16), 120.8 (*s*, C-20) and 21.8 (*q*, C-18), respectively, which suggested the presence of δ-lactone as D-ring. Furthermore, cross signals from the methyl proton resonance at δ_H 1.15 (*s*, 3H) to a ketonic carbonyl

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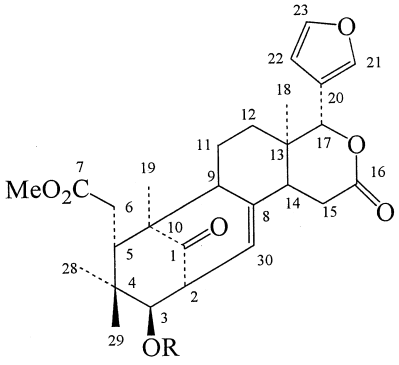

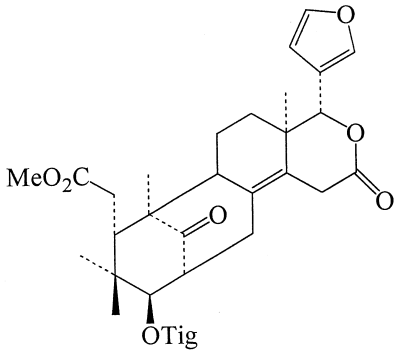

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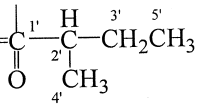

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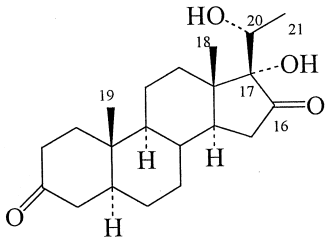

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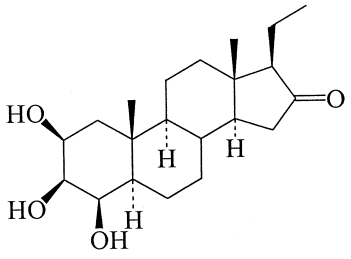

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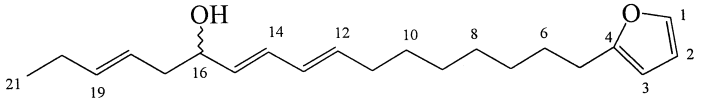

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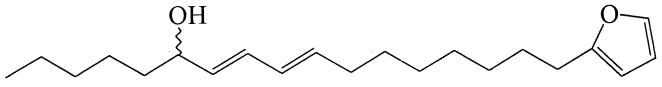

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carbon (δ_C 216.9), and an olefinic proton δ_H 5.38 (*dd*, $J=6.8$, 2.4 Hz) to the latter placed an olefinic linkage between C-8 and C-30, and the ketone group at C-1. The above data suggested that compound **1** was a swietenolide-related limonoid (Mikolajczak et al., 1988; Kadota et al., 1990; Govindachari et al., 1999).

The ^1H and ^{13}C NMR spectral data of compound **1** were very similar to those of methyl 3β-isobutyryloxy-1-oxomelia-8(30)-enate (Mikolajczak et al., 1988), with the exception of signals for a substituent group. The molecular weight of **1** was fourteen amu greater than that of methyl-3β-isobutyryloxy-1-oxomelia-8(30)-enate, which suggested C_4H_9COO- as substituent group at C-3 in compound **1** in place of the C_3H_7COO- in methyl-3β-isobutyryloxy-oxomeliac-8(30)-enate. Two methyl proton signals δ_H 1.14 (3H, *d*, $J=6.2$ Hz) and δ_H

0.92 (3H, *t*, $J=7.4$ Hz), were attributed to the ester group from the HMBC spectrum, which located a 2-methyl-butyryloxyl ester at C-3. The 2-methyl-butyryl-oxy group also took a β orientation as determined by the large coupling constant of H-3 ($J=8.9$ Hz) (Rao et al., 1978; Mikolajczak et al., 1988). Thus compound **1** was elucidated to be methyl-3β2-methyl-butyryloxy)-1-oxomeliac-8(30)-enate, named cipadesin.

Compound **4** showed an EIMS molecular ion peak at m/z 348 in accordance with the formula $C_{21}H_{32}O_4$, which was confirmed by analysis of its ^{13}C NMR and DEPT spectra. The ^{13}C and ^{1}H NMR spectra of **4** showed the signals for two tertiary methyl groups (δ_H 1.00, 0.76), a secondary methyl (δ_H 1.11), an oxymethine (δ_C 67.9), two characteristics quaternary carbons (δ_C 35.7 and 44.0), one hydroxytertiary carbon (δ_C 81.0) and two ketonic carbonyl groups (δ_C 211.2, 221.7). The above data suggested compound **4** was a 5α-pregnan-dione substituted with hydroxyls (Gong, 1986). In the ^{1}H NMR spectrum of **4**, the presence of resonances at δ_H 4.10 (1H, *dq*, 1.6, 6.4) and 1.11 (3H, *d*, 6.4) indicated that two hydroxy groups were attached to C-17 and C-20. This was confirmed by nalysis of the HMBC spectrum, which showed long range coupling for δ_H 1.11 (3H, *d*, 6.4, H-21) to δ_C 67.9 (C-20), and δ_H 0.76 (3H, *s*, H-18) to δ_C 81.0 (*s*, C-17). The correlation between δ_H 4.10 (1H, *dq*, 1.6, 6.4, H-20) and 1.11 (3H, *d*, 6.4, H-21) in ^{1}H–^{1}H COSY spectrum also supported the above assumption. In the ROESY spectrum, NOE interactions between δ_H 0.76 (3H, *s*, H-18) with H-20, and H-18 with H-21 placed 17-OH at α position. In addition, NOE interactions between δ_H 4.00 (20-OH) with 3.39 (17-OH), and H-15β with H-21 suggested a 20*R* configuration.

The chemical shift values of two ketonic carbonyl groups (δ_C 221.7 and 211.2) suggested the downfield resonance was part of a five-membered ring (D-ring) while the other belonged to a six-membered ring (Gong, 1986). The observation of cross signals between δ_H 2.36, 1.82 (each 1H, H-15) to δ_C 221.7, and 4.10 (H-20) to the latter in the HMBC spectrum indicated placement of the ketone group at C-16. C-3 was also determined to be the upfield ketone by the HMBC spectrum, which showed cross peaks between δ_H 2.36 (2H, *m*, H-2) to δ_C 211.2, and δ_H 2.25 (2H, *m*, H-4) to the latter.

According to the above spectral evidence, **4** was elucidated as 17α,20*R*-dihydroxy-pregnan-3,16-dione. The structure was further supported by a strong fragment ion peak at *m/z* 304 resulting from McLafferty rearrangement of the side-chain caused by the C-16 ketone group and H-21 under EIMS conditions. The McLafferty rearrangement made the loss of 44 very easy to explain, resulting in the strong peak at *m/z* 304 (Zhao and Sun, 1992).

Compound **6** possessed the molecular formula $C_{21}H_{32}O_2$, as indicated by its positive ion HR–FABMS, ^{13}C and DEPT NMR spectra. It showed a conjugated double bond absorption in the IR and UV spectra. The ^{13}C and ^{1}H NMR spectra of **6** revealed the presence of one primary methyl group [δ_C 14.1, δ_H 0.96 (*t*, $J=7.6$

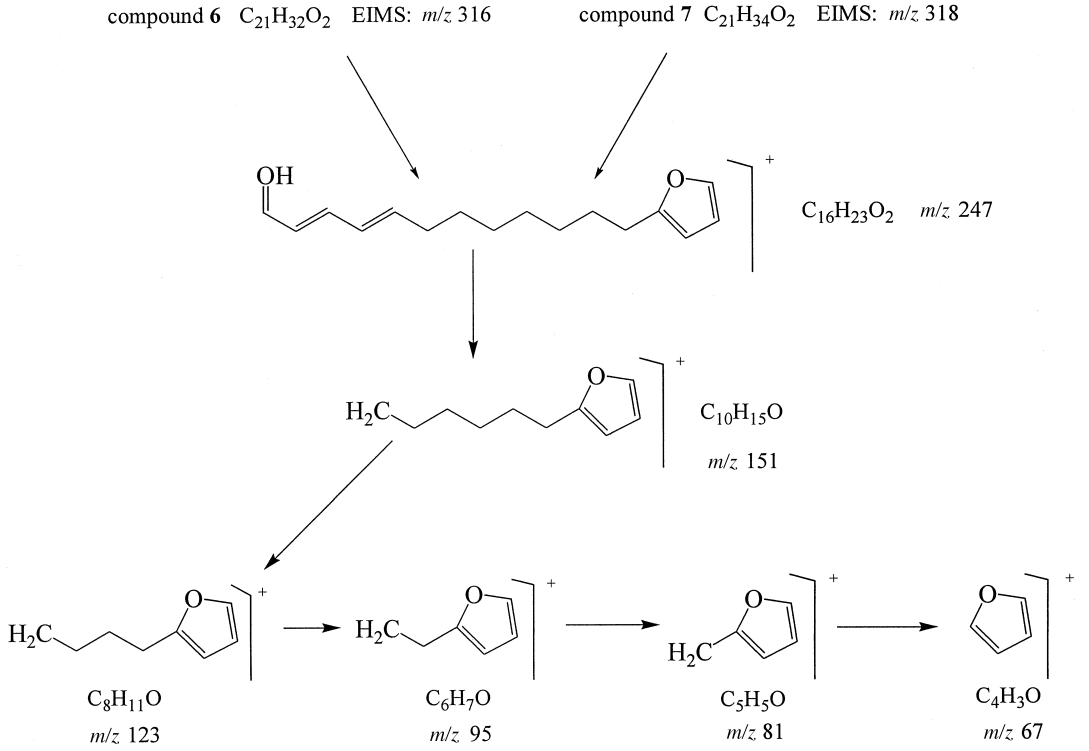

Fig. 1. Main EIMS cleavage fragments of compounds **6** and **7**.

Hz)], nine methylene groups (δ_C 35.2, 29.5, 29.1, 29.0, 27.9, 27.9, 27.8, 27.8, 20.7), an oxymethine (δ_C 72.1), 10 olefinic carbons (δ_C 156.5, 140.5, 135.1, 134.9, 132.9, 127.6, 125.8, 123.7, 109.9, 104.5), and nine corresponding olefinic protons. The olefinic linkages explained five degrees of unsaturation, while the extra degree of unsaturation required by the molecular formula ($C_{21}H_{32}O_2$) indicated the presence of one ring. So compound **6** was proposed to be a heneicos-pentaene with a ring and a secondary hydroxyl.

The signals at δ_C 104.5 (*d*), 109.9 (*d*), 140.5 (*d*) and 156.5 (*s*) and the corresponding protons at δ_H 7.28 (*dd*, $J=1.8$, 0.8 Hz), 6.26 (*q*, $J=1.8$ Hz) and 5.96 (*q*, $J=0.8$ Hz), indicated the presence of an α-substituted furan ring in **6**. This assumption was confirmed by analysis of the HMBC spectrum, in which δ_H 7.28 (*d*, $J=1.8$, 0.8 Hz, H-1), 6.26 (*q*, $J=1.8$ Hz, H-2), 5.96 (*q*, $J=0.8$ Hz, H-3), and 2.60 (2H, *t*, $J=7.6$ Hz, H-5) showed cross signals to δ_C 156.5 (*s*, C-4). The correlation between H-1 and H-2, H-2 and H-3 in $^1H-^1H$ COSY further supported this assumption. The EIMS spectrum of **6** showed a strong fragment ion peak at *m*/*z* 247, indicating the loss of a C_5H_9– fragment from the molecular ion peak and the formation of a stable fragment ion (Fig. 1), which suggested the presence of a $CH_3CH_2CH{=}CHCH_2$– moiety. In the HMBC spectrum of **6**, cross signals between δ_H 2.32 (2H, *m*, H-17) to δ_C 123.7 (C-18), and δ_H 0.96 (3H, *t*, $J=7.5$ Hz, H-21) to δ_C 134.9 (C-19) confirmed this assumption. The HMBC spectrum also showed cross peaks between H-17 and δ_C 72.1 (C-16), δ_H 5.68 (*dd*, $J=15.2$, 6.5 Hz, H-15) and δ_C 72.1 (C-16), δ_H 6.50 (*dd*, J = 15.2, 10.5 Hz, H-14) and δ_C 135.1 (C-15), δ_H 5.96 (*dd*, $J=15.2$, 8.8 Hz, H-13) to the latter, and between δ_H 2.16 (*m*, *H*-11) and δ_C 127.6 (C-13), which placed the remaining two olefinic linkages between C-14 and C-15, C-12 and C-13, and positioned the hydroxyl group at C-16. The large coupling constants (ca. 15.2 Hz) between H-13 and H-12, C-14 and H-15, H-18 and H-19 indicated that the three olefinic bonds were of the E-type. Thus, compound **6** was elucidated as (*Z*,*Z*,*E*,*E*,*E*)-1,4-epoxy-16-hydroxyheneicos-1,3,12,14,18- pentaene.

Compound **7** gave the molecular formula $C_{21}H_{34}O_2$ in its HR–EIMS. Comparing the ^{13}C NMR spectrum of compound **7** with that of **6** showed that two olefinic carbons present in **6** were replaced by two methylenes in **7**. The above data was consistent with the evidence that **7** possessed two hydrogens more than **6**. Furthermore, comparing the chemical shift values of two compounds suggested that compound **7** was an 18,19-dihydro derivative of **6**. This inference was confirmed by the presence of a strong fragment ion peak at *m*/*z* 247.1688 (calcd for $C_{16}H_{23}O_2$, 247.1698) in its HR–EIMS spectrum, which revealed the loss of a C_5H_{11}– fragment from the molecular ion and formation of the same fragment ion peak as seen for **6** (Fig. 1). This assumption was also supported by the results of an HMBC experiment. Accordingly, compound **7** was determined as (*Z*,*Z*,*E*,*E*)-1,4-epoxy-16-hydroxyheneicos-1,3,12,14-tetraene. Signals for compounds **1**, **4**, **6** and **7** were assigned on the basis of $^1H-^1H$ COSY, HMBC and HMQC data.tpb 1pc

3. Experimental

3.1. General

Mps. were obtained on a Sichuan Micromelting apparatus and are uncorrected. UV spectra were measured with a Shimadzu double-beam 210A spectrophotometer in MeOH. IR spectra were obtained on a Bio-Rad FTS-135 infra-red spectrophotometer. ^1H NMR, ^{13}C NMR and 2D NMR spectra were recorded on a Bruker AM-400 MHz and a DRX-500 NMR spectrometer with TMS as internal standard. MS data were recorded on a VG Autospec-3000 spectrometer, 70eV for EIMS and HR–EIMS and using *m*-nitrobenzyl alcohol as the matrix for FAB and HR–FABMS

3.2. Plant material

The seeds of *C. baccifera* were collected from Xishuangbanna, Yunnan Province, PR China in December, 1996. The plant was identified by Professor G.-D. Tao, Xishuangbanna Botany Garden, Academia Sinica. A voucher specimen (no. 39538) was deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia Sinica, Kunming, PR China.

3.3. Extraction and isolation

The air-dried and powdered seeds (4.0 kg) of *C. baccifera* were extracted with EtOH (10 l×3) under reflux for 3 h each time. The solvent was removed in vacuo, and the residue was partitioned using H_2O and $CHCl_3$. The $CHCl_3$ fraction was concentrated in vacuo to afford 62 g of residue, which was subjected to CC on silica gel, eluted with petroleum ether–Me_2CO (9:1–1:1). The fractions were collected and combined by monitoring with analytic TLC. Fractions 2–10 were repeatedly chromatographed over silica gel with various eluent systems, and purified on a reverse-phase C_{18} silica gel column using CH_3OH–H_2O (8:2–6:4) as eluent to yield **1** (16 mg), **2** (2.31 g), **3** (24 mg), **4** (25 mg), **5** (14 mg), **6** (1.04 g) and **7** (680 mg).

3.4. Cipadesin (*1*)

$C_{32}H_{42}O_8$, colorless needles (MeOH); mp 112–114°C $[\alpha]_D^{26}$: −145.4 ($CHCl_3$; *c* 0.17); IR (KBr) ν_{max} cm^{-1}: 2973, 1937, 1728, 1652, 1596, 1504, 1437, 1461, 1383, 1296, 1220, 1195, 1148, 1025, 938, 900, 875; EIMS *m*/*z*:

554 $[M]^+$ (98), 470 (12), 452 (14), 437 (17), 416 (24), 379 (5), 363 (16), 315 (13), 253 (16), 219 (10), 187 (10), 175 (32), 157 (16), 141 (23), 121 (31), 109 (18), 95 (71), 69 (46), 55 (100); HR–EIMS *m/z*: 554.2280 (calcd for $C_{32}H_{42}O_8$, 554.2280); ^{1}H NMR spectral data (500 MHz, $CDCl_3$): δ 7.79 (1H, *s*, H-21), 7.42 (1H, *s*, H-23), 6.46 (1H, *d*, *J* = 1.6 Hz, H-22), 5.69 (1H, *s*, H-17), 5.38 (1H, *dd*, *J* = 6.8, 2.4 Hz, H-30), 4.81 (*d*, *J* = 8.9 Hz, H-3), 3.72 (3H, *s*, OCH_3), 3.49 (1H, *dd*, *J* = 8.9, 7.4 Hz, H-2), 3.42 (1H, *dd*, *J* = 8.1, 3.5 Hz, H-5), 2.88 (1H, *dd*, *J* = 18.8, 6.6 Hz, H-15a), 2.82 (1H, *d*, *J* = 18.8 Hz, H-15b), 2.45 (1H, *m*, H-2′), 2.37 (2H, *d*, *J* = 8.8 Hz, H-6), 2.18 (2H, brs, H-9), 2.08, 1.68 (each 1H, *m*, H-11), 1.65, 1.35 (each 1H, *m*, H-12), 1.15 (3H, *s*, H-19), 1.14 (3H, *d*, *J* = 6.2 Hz, H-4′), 1.10 (3H, *s*, H-18), 0.92 (3H, *t*, *J* = 7.4 Hz, H-5′), 0.83 (3H, *s*, H-28), 0.79 (3H, H-29); ^{13}C NMR spectral data (100 MHz, $CDCl_3$): δ 216.9 (s, C-1), 176.2 (s, C-1′), 174.0 (*s*, C-7), 169.2 (*s*, C-16), 142.9 (*d*, C-23), 142.0 (*d*,C-21), 138.4 (*s*, C-8), 122.9 (*d*, C-30), 120.8 (*s*, C-20), 109.8 (*d*, C-22), 77.0 (*d*, C-17, C-3), 56.8 (*d*, C-9), 52.1 (*q*, OCH_3), 50.0 (*s*, C-10), 48.9 (*d*, C-2), 45.3 (*d*, C-14), 41.5 (*d*, C-5), 40.8 (*d*, C-2′), 38.6 (*s*, C-4), 37.0 (*s*, C-13), 34.5 (*t*, C-15), 33.0 (*t*, C-6), 29.8 (*t*, C-12), 26.5 (*t*, C-3′), 22.5 (*q*, C-28), 21.8 (*q*, C-18), 20.7 (*t*, C-11), 20.7 (*q*, C-29), 16.3 (*q*, C-5′), 15.7 (*q*, C-19), 11.4 (*q*, C-4′).

3.5. 17α,20R-Dihydroxypregnan-3,16-dione (**4**)

$C_{21}H_{32}O_4$, colorless needles (Me_2CO); $[\alpha]_D^{26}$: −106.3 ($CHCl_3$; c 0.31); IR (KBr) ν_{max} cm^{-1}: 3464, 2939, 2869, 1707, 1435, 1418, 1292, 1250, 1234, 1127, 1079, 100, 978, 887; EIMS *m/z*: 348 $[M]^+$ (20), 330 (20), 314 (18), 304 (95), 289 (100), 230 (40), 217 (25), 149 (50), 135 (20), 121 (28), 105 (36), 95 (38), 81 (48), 67 (48), 55 (94); HR–FABMS *m/z*: 347.2176 $[M-1]^-$ (calcd for $C_{21}H_{31}O_4$, 347.2222); ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 4.10 (1H, *dq*, *J* = 1.6, 6.4 Hz, H-20), 4.00 (1H, *brs*, 20-OH), 3.39 (1H, s, 17-OH), 2.36 (1H, *dd*, *J* = 14.5, 7.6 Hz, H-15β), 1.82 (1H, *dd*, *J* = 6.2, 12.5 Hz, H-15α), 2.35 (2H, *m*, H-2), 2.25 (2H, *m*, H-4), 2.10 (1H, *m*, H-14), 2.00 (2H, *m*, H-1), 1.9, 1.59 (each 1H, *m*, H-12), 1.7, 1.4 (each 1H, *m* C-11), 1.52 (2H, *m*, H-8), 1.50 (2H, *m*, H-5), 1.31 (2H, *m*, H-6), 1.55, 1.00 (each 1H, *m*, H-7), 1.11 (1H, *d*, *J* = 6.4 Hz, H-21), 1.00 (3H, *s*, H-19), 0.76 (3H, *s*, H-18); ^{13}C NMR spectral data (100 MHz, $CDCl_3$): δ 221.7 (*s*, C-16), 211.2 (*s*, C-3), 81.0 (*s*, C-17), 67.9 (*d*, C-20), 53.2 (*d*, C-9), 46.4 (*d*, C-5), 45.3 (*d*, C-14), 44.5 (*t*, C-4), 44.0 (*s*, C-13), 38.1 (*t*, C-1), 38.0 (*t*, C-2), 36.9 (*t*, C-15), 35.7 (*s*, C-10), 34.1 (*d*, C-8), 31.8 (*t*, C-7), 29.7 (*t*, C-12), 28.6 (*t*, C-6), 20.2 (*t*, C-11), 16.0 (*q*, C-21), 13.6 (*q*, C-18), 11.4 (*q*, C-19).

3.6. 1,4-Epoxy-16-hydroxyheneicos-1,3,12,14,18-pentaene (**6**)

$C_{21}H_{32}O_2$, viscous oil; UV (MeOH) λ_{max} nm (log ε):230 (4.12); IR (KBr) ν_{max} cm^{-1}: 3405, 3010, 1654, 1597, 1508, 1462, 1414, 1148, 1009, 985, 951, 727; EIMS m/z:316 $[M]^+$ (20), 298 (5), 263 (5), 247 (75), 229 (5), 149 (10), 135 (13), 121 (23), 107 (26), 95 (64), 81 (100), 67 (55), 55 (71); HR–FAB–MS *m/z*: 315.2395 $[M-1]^-$ (calcd. for $C_{21}H_{31}O_2$, 315.2324); ^{1}H NMR spectral data (500 MHz, $CDCl_3$): δ 7.28 (1H, *dd*, *J* = 1.8, 0.8 Hz, H-1), 6.50 (1H, *dd*, *J* = 15.2, 10.5 Hz, H-14), 6.26 (1H, *q*, *J* = 1.8 Hz, H-2), 5.96 (1H, *q*, *J* = 0.8 Hz, H-3), 5.96 (1H, *dd*, *J* = 15.2, 8.8 Hz, H-13), 5.68 (1H, *dd*, *J* = 15.2, 6.5 Hz, H-15), 5.55 (1H, *m*, H-19), 5.44 (1H, *m*, H-12), 5.37 (1H, *m*, H-18), 4.20 (1H, *q*, *J* = 6.2 Hz, H-16), 2.60 (2H, *t*, *J* = 7.6 Hz, H-5), 2.32 (2H, *m*, H-17), 2.16 (2H, *m*, H-11), 2.06 (2H, *m*, H-20), 1.62 (2H, *m*, H-6), 1.36 (2H, *m*, H-10), 1.31 (6H, br, H-7, H-8, H-9), 0.96 (3H, *t*, *J* = 7.5 Hz, H-21); ^{13}C NMR spectral data (125 MHz, $CDCl_3$):δ 156.5 (*s*, C-4), 140.5 (*d*, C-1), 135.1 (*d*, C-15), 134.9 (*d*, C-19), 132.9 (*d*, C-12), 127.6 (*d*, C-13), 125.8 (*d*, C-14), 123.7 (*d*, C-18), 109.9 (*d*, C-2), 104.5 (*d*, C-3), 72.1 (*d*, C-16), 35.2 (*t*, C-17), 29.5 (*t*, CH_2), 29.1 (*t*, CH_2), 29.0 (*t*, C-20), 27.9 (*t*, C-5), 27.8 (*t*, C-11), 27.8 (*t*, C-6), 27.7 (*t*, CH_2), 20.7 (*t*, C-20), 14.1 (*q*, C-21).

3.7. 1,4-Epoxy-16-hydroxyheneicos-1,3,12,14-tetraene (7)

$C_{21}H_{34}O_2$, viscous oil; UV (MeOH) λ_{max} nm (log ϵ): 230 (4.16); IR (KBr) ν_{max} cm^{-1}: 3405, 3010, 1656, 1506, 1462, 1412, 1148, 1006, 985, 951; EIMS *m/z*: 318 $[M]^+$ (55), 300 (20), 275 (10), 247 (50), 229 (10), 218 (20), 204 (25), 186 (10), 175 (27), 163 (25), 151 (25), 135 (46), 121 (50), 107 (51), 95 (78), 81 (100), 67 (61); HR–EIMS *m/z*: 318.2544 (calcd for $C_{21}H_{34}O_2$, 318.2558); ^{1}H NMR spectral data (400 MHz, CD_3OD): δ 7.29 (1H, *d*, *J* = 1.4 Hz, H-1), 6.48 (1H, *dd*, *J* = 15.2, 6.8 Hz, H-14), 6.24 (1H, *q*, *J* = 2.0 Hz, H-2), 5.96 (1H, *s*, H-3), 5.96 (1H, *dd*, *J* = 15.2, 6.6 Hz, H-13), 5.61 (1H, *dd*, *J* = 15.2, 6.8 Hz, H-15), 5.38 (1H, *dt*, *J* = 14.6, 7.6 Hz, H-12), 4.06 (1H, *q*, *J* = 6.4 Hz, H-16), 2.59 (2H, *t*, *J* = 7.4 Hz, H-4), 2.16 (2H, *dt*, *J* = 7.6, 6.8 Hz, H-11), 1.61 (2H, *m*, H-6), 1.53-1.25 (16H, H-7, H-8, H-9, H-10, H-17, H-18, H-19, H-20), 0.89 (3H, *t*, *J* = 6.7 Hz, H-21); ^{13}C NMR spectral data(100 MHz, CD_3OD): δ 157.5 (*s*, C-4), 141.8 (*d*, C-1), 137.3 (*d*, C-15), 132.9 (*d*, C-12), 129.4 (*d*, C-13), 126.5 (*d*, C-14), 110.9 (*d*, C-2), 105.6 (*d*, C-3), 73.3 (*d*, C-16), 38.4 (*d*, C-17), 32.9, 30.7, 30.2, 30.1, 30.1, 29.6, 29.2, 28.6, 26.2, 23.6 (*t*, CH_2), 14.4 (*q*, C-21).

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