# A Triterpenoid and Sesquiterpenoids from the Resinous Exudates of *Commiphora myrrha*

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A new 30(14 → 13)*abeo*-dammarane triterpenoid, myrrhasin (**1**), a new 14(10 → 1)*abeo*-eudesmane sesquiterpenoid, myrrhanolide A (**2**), and two new cadinane sesquiterpenoids, myrrhanolides B and C (**3** and **4**, resp.), as well as nine known sesquiterpenoids, **5**–**13**, were isolated from the resinous exudates of *Commiphora myrrha*. Their structures were determined on the basis of extensive MS and NMR spectroscopic analyses. The isolated compounds **1**–**6** were evaluated for their cytotoxicity against the PC3 and DU145 human prostate tumor cell lines.

**Introduction.** – *Commiphora myrrha* (NEES) ENGL. (Burseraceae), a small tree or a large shrub, is mainly distributed in the arid regions of Ethiopia, Somalia, Kenya, and India [1][2]. The resinous exudates of this plant, known as myrrh, are an important commercial and medicinal product, and used to treat blood stagnation and inflammation diseases, or to relieve swelling and pain in Traditional Chinese Medicine [2]. The crude extract of the resinous exudates of *C. myrrha* showed quenching activity against *singlet* oxygen [3], and inhibitory effects on eight human or murine cancer cell lines representing the tissues of breast, lung, pancreas, and prostate [4], repectively. Previous phytochemical investigation of *C. myrrha* led to the isolation of several sesquiterpenoids and triterpenoids [5–7].

In our continuous research on cytotoxic constituents against human prostate tumor from Traditional Chinese Medicine, we have reported the isolation of cycloartane-type triterpenoids and sesquiterpenoids from the resinous exudates of *C. opobalsamum* [8][9]. In the present report, the petroleum ether (PE) extract of the resinous exudates of *C. myrrha* was separated by repeated silica-gel column chromatography (CC) and preparative thin layer chromatography (TLC), to yield a new 30(14 → 13)*abeo*-dammarane triterpenoid, myrrhasin (**1**), a new 14(10 → 1)*abeo*-eudesmane sesquiterpenoid, myrrhanolide A (**2**), and two new cadinane sesquiterpenoids, myrrhanolides B and C (**3** and **4**, resp.), along with nine known sesquiterpenoids, **5**–**13**. Furthermore, cytotoxic activities of compounds **1**–**6** were evaluated against the PC3 and DU145 human prostate tumor cell lines.

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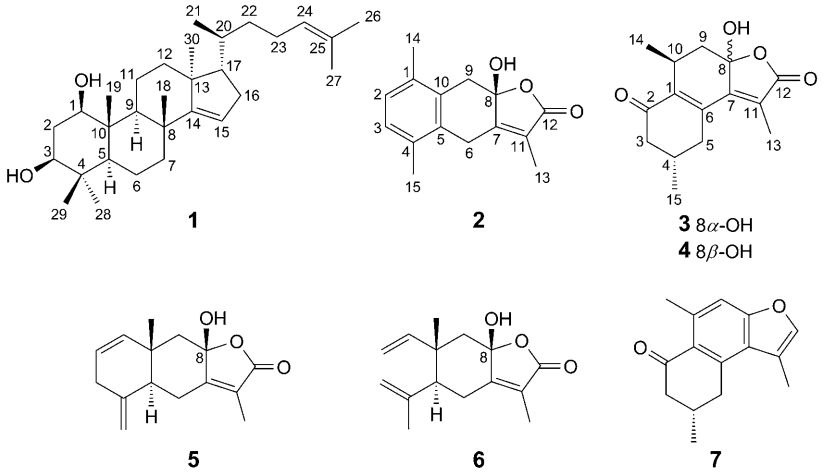


**Results and Discussion.** – Myrrhasin (**1**) was isolated as a colorless solid, which displayed a *pseudo*-molecular-ion peak at *m*/*z* 465.7 ($[M+Na]^+$) in the ESI-MS (positive-ion mode). The molecular formula was established as $C_{30}H_{50}O_2$ from the $M^+$ peak at *m*/*z* 442.3841 (calc. 442.3811) in the HR-EI-MS, indicating six degrees of unsaturation. The IR spectrum of **1** showed a OH stretching band at 3424 and C=C absorption at 1637 $cm^{-1}$. The $^1$H-NMR spectrum (*Table 1*) showed the presence of seven tertiary Me groups, a secondary Me group ($\delta$(H) 0.86 (*d*, *J* = 6.6)), two olefinic H-atoms ($\delta$(H) 5.09 and 5.29), and two CH H-atoms geminal to OH groups ($\delta$(H) 3.25 and 3.54). The $^{13}$C-NMR exhibited 30 C-atom resonances, which were classified by chemical shift and HMQC spectrum to correspond to eight Me, eight sp$^3$-$CH_2$, and six sp$^3$-CH groups (two oxygenated ones at $\delta$(C) 75.9 and 78.4), as well as to four quaternary C-atoms, and two C=C bonds, suggesting that **1** is a triterpenoid diol with two C=C bonds. The $^1$H,$^1$H-COSY spectrum led to the establishment of structural fragments as depicted with bold lines in *Fig. 1*. Connection of these fragments and the quaternary C-atoms was established by the HMBC correlations of Me(28)/C(3), C(4), and C(5); Me(18)/C(7), C(8), C(9), and C(14); Me(19)/C(1), C(5), C(9), and C(10); Me(30)/C(12), C(13), C(14), and C(17); Me(21)/C(17), C(20), and C(22); H−C(15)/C(8), C(13), and C(14); and Me(26)/C(24), C(25), and C(27) (*Fig. 1*) to give a

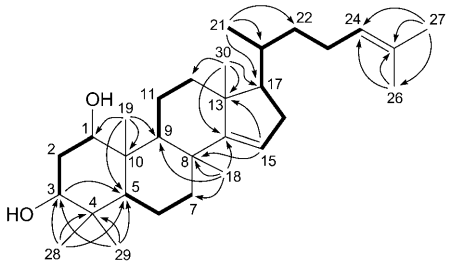

Fig. 1. *Key* $^1$*H,*$^1$*H-COSY* (—)*, and HMBC* (H → C) *data of* **1**

Table 1. *$^1$H- and $^{13}$C-NMR Data of Compound* **1**. At 600/150 MHz, resp. in $CDCl_3$; $\delta$ in ppm, $J$ in Hz.

| | $\delta$(H) | $\delta$(C) | | $\delta$(H) | $\delta$(C) |
|---|---|---|---|---|---|
| H–C(1) | 3.54 (*dd*, *J* = 4.5, 11.3) | 78.4 | $H_a$–C(16) | 1.88–2.02 (*m*) | 35.0 |
| $H_\alpha$–C(2) | 1.85–1.89 (*m*) | 37.3 | $H_b$–C(16) | 2.12–2.14 (*m*) | |
| $H_\beta$–C(2) | 1.62–1.67 (*m*) | | H–C(17) | 1.42–1.49 (*m*) | 60.1 |
| H–C(3) | 3.25 (*dd*, *J* = 4.3, 11.3) | 75.9 | Me(18) | 1.04 (*s*) | 27.9 |
| C(4) | | 38.8 | Me(19) | 0.94 (*s*) | 12.0 |
| H–C(5) | 0.69 (br. *d*, *J* = 11.5) | 53.5 | H–C(20) | 1.62–1.67 (*m*) | 33.3 |
| $H_a$–C(6) | 1.53–1.59 (*m*) | 18.4 | Me(21) | 0.86 (*d*, *J* = 6.6) | 18.5 |
| $H_b$–C(6) | 1.62–1.67 (*m*) | | $H_a$–C(22) | 1.05–1.12 (*m*) | 35.5 |
| $H_\alpha$–C(7) | 1.88–2.02 (*m*) | 41.4 | $H_b$–C(22) | 1.53–1.59 (*m*) | |
| $H_\beta$–C(7) | 1.27–1.32 (*m*) | | $H_a$–C(23) | 1.85–1.89 (*m*) | 24.9 |
| C(8) | | 38.1 | $H_b$–C(23) | 1.88–2.02 (*m*) | |
| H–C(9) | 1.62–1.67 (*m*) | 49.7 | H–C(24) | 5.09 (*t*, *J* = 6.9) | 125.0 |
| C(10) | | 43.4 | C(25) | | 131.0 |
| $H_a$–C(11) | 1.73–1.75 (*m*) | 21.0 | Me(26) | 1.60 (*s*) | 17.7 |
| $H_b$–C(11) | 1.88–2.02 (*m*) | | Me(27) | 1.68 (*s*) | 25.8 |
| H–C(12) | 1.42–1.49 (*m*) | 34.5 | Me(28) | 0.95 (*s*) | 27.8 |
| C(13) | | 46.4 | Me(29) | 0.78 (*s*) | 15.0 |
| C(14) | | 165.4 | Me(30) | 1.00 (*s*) | 18.9 |
| H–C(15) | 5.29 (*d*, *J* = 3.2) | 117.7 | | | |

30(14 → 13)*abeo*-dammarane skeleton with two OH groups at C(1) and C(3), respectively.

In the NOESY spectrum of **1**, the correlations (*Fig. 2*) of H–C(5)/H–C(1), H–C(3), $H_\alpha$–C(7), H–C(9), and Me(28); $H_\alpha$–C(2)/H–C(3); Me(30)/H–C(9), and $H_\alpha$–C(16); Me(19)/$H_\beta$–C(2), Me(29), and Me(18); and Me(21)/H–C(17) and $H_\beta$–C(16) indicated that the OH groups at C(1) and C(3), H–C(17), Me(18), Me(19), and Me(21) are $\beta$-oriented, while Me(30) is $\alpha$-oriented. Accordingly, the structure of **1** was determined to be 30(14 → 13)*abeo*-dammara-14,24-diene-1$\beta$,3$\beta$-diol.

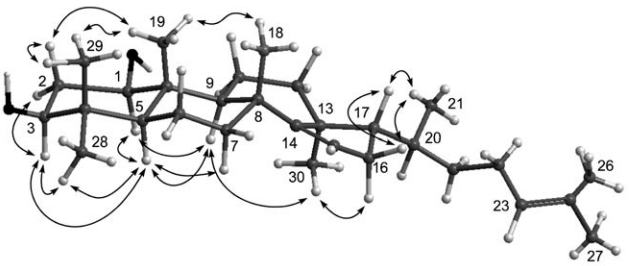


Fig. 2. *Key NOESY* (H ↔ H) *correlations of* **1**

Myrrhanolide A (**2**), isolated as a white amorphous solid, exhibited a *pseudo*-molecular-ion peak at *m*/*z* 267.4 ($[M+Na]^+$) in the ESI-MS (positive-ion mode), consistent with the molecular formula of $C_{15}H_{16}O_3$ deduced from the HR-EI-MS ($M^+$ at *m*/*z* 244.1120, calc. 244.1099). The $^{13}$C-NMR spectrum displayed signals for 15 C-atoms (*Table 2*), which were determined, with the aid of a HMQC spectrum, to belong to one

Table 2. *$^1$H- and $^{13}$C-NMR Data of Compounds* **2**–**4**. At 600/150 MHz, resp., in $CDCl_3$; $\delta$ in ppm, $J$ in Hz.

| | **2** | | **3** | | **4** | |
|---|---|---|---|---|---|---|
| | $\delta$(H) | $\delta$(C) | $\delta$(H) | $\delta$(C) | $\delta$(H) | $\delta$(C) |
| C(1) | | 134.4 | | 142.2 | | 141.8 |
| H–C(2) or C(2) | 7.03 (br. *s*) | 128.5 | | 199.5 | | 198.2 |
| $H_a$–C(3) | 7.03 (br. *s*) | 128.5 | 2.27 (*d*, $J$ = 13.9) | 47.7 | 2.31–2.37 (*m*) | 45.9 |
| or H–C(3) | | | | | | |
| $H_b$–C(3) | | | 2.52–2.57 (*m*) | | 2.52–2.57 (*m*) | |
| H–C(4) or C(4) | | 133.9 | 2.31–2.37 (*m*) | 31.5 | 2.31–2.37 (*m*) | 29.0 |
| $H_a$–C(5) or C(5) | | 130.0 | 2.52–2.57 (*m*) | 36.5 | 2.31–2.37 (*m*) | 34.7 |
| $H_b$–C(5) | | | 2.64–2.67 (*m*) | | 3.00–3.06 (*m*) | |
| $H_a$–C(6) or C(6) | 3.68 (*d*, $J$ = 19.8) | 27.0 | | 140.9 | | 140.1 |
| $H_b$–C(6) | 3.80 (*d*, $J$ = 19.8) | | | | | |
| C(7) | | 156.6 | | 153.7 | | 153.2 |
| C(8) | | 102.1 | | 101.7 | | 102.0 |
| $H_a$–C(9) | 2.90 (*d*, $J$ = 16.8) | 39.7 | 2.62 (*dd*, | 39.9 | 2.03 (*dd*, | 38.6 |
| or $H_\alpha$–C(9) | | | $J$ = 6.5, 13.6) | | $J$ = 7.1, 13.8) | |
| $H_b$–C(9) | 3.56 (*d*, $J$ = 16.8) | | 1.47 (*d*, | | 2.25 (*d*, | |
| or $H_\beta$–C(9) | | | $J$ = 9.6, 13.9) | | $J$ = 13.4) | |
| H–C(10) | | 130.0 | 3.00–3.06 (*m*) | 28.7 | 3.17–3.20 (*m*) | 28.7 |
| or C(10) | | | | | | |
| C(11) | | 122.7 | | 124.7 | | 125.4 |
| C(12) | | 171.9 | | 171.8 | | 171.8 |
| Me(13) | 1.91 (*s*) | 8.5 | 2.09 (*s*) | 10.4 | 2.13 (*s*) | 10.9 |
| Me(14) | 2.24 (*s*) | 19.9 | 1.15 (*d*, $J$ = 6.1) | 20.8 | 1.32 (*d*, $J$ = 7.2) | 20.3 |
| Me(15) | 2.30 (*s*) | 19.7 | 1.14 (*d*, $J$ = 6.6) | 21.7 | 1.12 (*d*, $J$ = 7.5) | 20.3 |

lactone CO group, three Me and two $CH_2$ groups, one oxygenated quaternary C-atom, and eight olefinic C-atoms, suggesting that **2** was a sesquiterpene lactone. The NMR data of **2** exhibited close similarity to that of tubipolide D from *Tubipora musica* [10], except for migration of Me(14) group from C(10) to C(1) and formation of a C(5)=C(10) bond in **2**. The aromatic H-atom resonances at $\delta$(H) 7.03 (2 H, br. *s*, H–C(2) and H–C(3)) and C-atom signals at $\delta$(C) 128.5 (C(2) and C(3)) revealed the presence of a 1,2,3,4-tetrasubstituted aromatic ring (ring *A*) [11], which was confirmed by the HMBC correlations of Me(14)/C(1), C(2), and C(10); Me(15)/C(3), C(4), and C(5); $CH_2$(6)/C(4), C(5), and C(10); and $CH_2$(9)/C(1), C(5), and C(10) (*Fig. 3*,*a*). The C-atom signals at $\delta$(C) 156.6 (C(7)), 102.1 (C(8)), 122.7 (C(11)), 171.9 (C(12)),

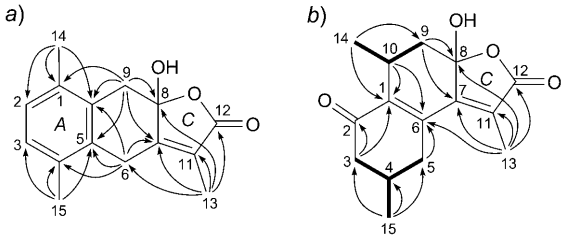


Fig. 3. *Key $^1$H,$^1$H-COSY* (—)*, and HMBC* (H → C) *correlations of* **2** (*a*)*,* **3** *and* **4** (*b*)

and 8.5 (C(13)) suggested the presence of an $\alpha,\beta$-unsaturated $\gamma$-hydroxy-$\alpha$-methyl-$\gamma$-lactone moiety (ring *C*) [10]. Additionally, HMBC correlations (*Fig. 3,a*) of $CH_2(6)$/C(7); and $CH_2(9)$/C(7) and C(8), confirmed the connection of ring *A* and ring *C* through C(6) and C(9). Therefore, the structure of **2** was established to be 14(10 → 1)*abeo*-8-hydroxy-1,3,5(10),7(11)-eudesmatetraen-12,8-olide.

Myrrhanolides B and C (**3** and **4**, resp.) were obtained as an inseparable mixture of epimers in a ratio of 3:1. Exhaustive efforts to separate this mixture were not successful, as the 8-OH groups of those two compounds readily epimerize in solution [12]. Thus, the structure elucidation was performed on the mixture.

The molecular formula for both **3** and **4** was determined to be $C_{15}H_{18}O_4$ by the HR-EI-MS ($M^+$ at 262.1216, calc. 262.1205), indicating seven degrees of unsaturation. The $^1$H- and $^{13}$C-NMR data (*Table 2*) for the **3**/**4** mixture indicated that **3** and **4** showed the presence of two secondary Me, one tertiary Me, three $CH_2$, and two CH groups, as well as one oxygenated quaternary C-atom, two C=C bonds, one ketone CO group ($\delta$(C) 198.2/199.5), and one lactone CO group ($\delta$(C) 171.8/171.8), as determined with the aid of HMQC spectra. The NMR data for the major and minor epimer were considered separately. For the major isomer myrrhanolide B (**3**), the C-atom resonances at $\delta$(C) 153.7 (C(7)), 101.7 (C(8)), 124.7 (C(11)), 171.8 (C(12)), and 10.4 (C(13)) showed the presence of an $\alpha,\beta$-unsaturated $\gamma$-hydroxy-$\alpha$-methyl-$\gamma$-lactone moiety (ring *C*) [10], which was confirmed by HMBC correlations of Me(13)/C(7), C(8), C(11), and C(12). In addition, the $^1$H,$^1$H-COSY correlations led to the establishment of two partial structures as depicted in bold lines (*Fig. 3,b*). The linkage of the two structural fragments and ring *C* was achieved by the HMBC correlations of $CH_2(9)$/C(7), C(8); H−C(10)/C(1) and C(6); $CH_2(3)$/C(1) and C(2); $CH_2(5)$/C(6); and Me(13)/C(6) (*Fig. 3,b*). Therefore, the gross structure of **3** was identified to be 8-hydroxy-2-oxo-1(6),7(11)-cadinadien-12,8-olide. The constitution of the minor isomer myrrhanolide C (**4**) was identical with that of compound **3** through analysis of the minor signals in the 1D- and 2D-NMR spectra (*Table 2*).

The relative configurations of **3** and **4** were determined by analysis of the NOESY spectrum, Chem 3D molecular modeling studies, and comparison with NMR data. The relative configuration of Me(15) was assigned to be $\alpha$, the same as the known compound myrrhone (**7**), by detailed comparison of the $^{13}$C-NMR data [5]. Me(14) was established as $\beta$-configurated for both **3** and **4** based on the coupling constants and molecular-modeling studies. The coupling constants for **3** between H−C(9) and H−C(10) ($J(9\alpha,10) = 6.5$; $J(9\beta,10) = 9.6$; *Table 2*) required a dihedral angle of *ca.* 45° between $H_\alpha$−C(9) and H−C(10), and close to 180° between $H_\beta$−C(9) and H−C(10). Similarly, a dihedral angle of *ca.* 45° between $H_\alpha$−C(9) and H−C(10), and almost 90° between $H_\beta$−C(9) and H−C(10) in **4** were needed to explain the observed coupling constants between H−C(9) and H−C(10) ($J(9\alpha,10) = 7.1$; $J(9\beta,10) < 1$; *Table 2*). In case of the $\alpha$-configuration of Me(14), these orientations bring Me(14) with 2.9 Å of the Me(15) in the molecular modeling studies, suggesting that a NOESY correlation between Me(14) and Me(15) should be observed [13][14]. In fact, no correlation of Me(14) to Me(15) was found in the NOESY spectrum, and the assumption of $\alpha$-configuration of Me(14) was incorrect. The geometric constraints dictated by the NOESY correlations and coupling constants are compatible with a Me(14) possessing the $\beta$-orientation. The Me(14) resonance in **4** was observed for the downfield shift to

$\delta$(H) 1.32, $\Delta\delta$ +0.17 ppm (*Table 2*) compared with that of **3** due to the deshielding effect of the OH group at C(8), supporting the *syn*-relationship of Me(14) and OH at C(8) in the structure of **4**, and the *anti*-relationship for **3** [15][16]. In the NOESY spectrum, correlations $H_\alpha$–C(9)/H–C(10), Me(14)/$H_\alpha$–C(9) and $H_\beta$–C(9) in **3** (*Fig. 4*,*a*) revealed the axial orientations of $H_\beta$–C(9) and H–C(10), suggesting that the OH group at C(8) in **3** was $\alpha$-oriented. However, the NOESY correlations of H–C(10)/$H_\alpha$–C(9) and $H_\beta$–C(9), and Me(14)/$H_\beta$–C(9) in **4** (*Fig. 4*,*b*) confirmed the equatorial orientations of $H_\beta$–C(9) and H–C(10), indicating the OH group at C(8) was $\beta$-oriented. Therefore, the structures of myrrhanolides B (**3**) and C (**4**) were identified to be 8$\alpha$-hydroxy-2-oxo-1(6),7(11)-cadinadien-12,8-olide and 8$\beta$-hydroxy-2-oxo-1(6),7(11)-cadinadien-12,8-olide, respectively.

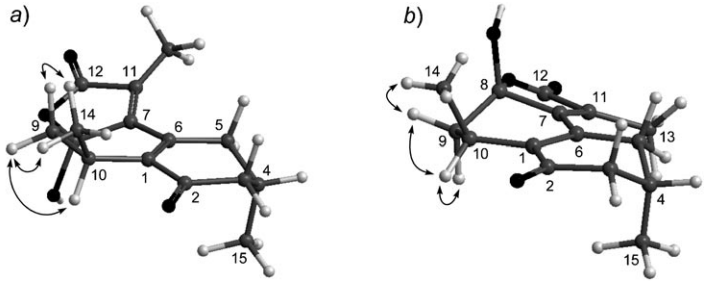


Fig. 4. *Key NOESY* (H ↔ H) *correlations of* **3** (*a*) *and* **4** (*b*)

The structures of nine known sesquiterpenoids from the resin of *C. myrrha* were identified to be hydroxylindestrenolide (**5**) [17], 8-hydroxyisogermafurenolide (**6**) [17], myrrhone (**7**) [5], curzerenone [18], (1*E*)-3-methoxy-8,12-epoxygermacra-1,7,10,11-tetraen-6-one [18], (1*E*,2*R*,4*R*)-2-methoxy-8,12-epoxygermacra-1(10),7,11-trien-6-one [19], *rel*-(1*S*,2*S*,4*R*)-epoxyfuranogermacr-10(15)-en-6-one [6], 2-methoxy-5-acetoxy-furanogermacr-1(10)-en-6-one [20], and 4$\alpha$-methoxy-6-guaien-10$\alpha$-ol [21], by comparison of their NMR and MS data with those reported in the literature.

Compounds **1**–**6** were tested for cytotoxic activity against the PC3 and DU145 human prostate tumor cell lines using the MTT assay. Only **2** and the mixture of **3** and **4** exhibited weak cytoxicity against the PC3 cell line with $IC_{50}$ values of 38.3 to 46.0 μM, respectively. All tested compounds **1**–**6** displayed no activity against the DU145 tumor cell line.

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## Experimental Part

*General.* Column chromatography (CC): silica gel ($SiO_2$; 200–300 mesh, 10–40 μm; *Qingdao Haiyang Chemical Co. Ltd.*, P. R. China). Thin-layer chromatography (TLC): silica gel $GF_{254}$ plates; visualization by heating the plates sprayed with 10% $H_2SO_4$/EtOH. Melting point (M.p.): *X-6* melting-point apparatus (*Beijing TECH Instrument Co. Ltd.*, P. R. China). Optical rotations: *Gyromat-Hp* digital automatic polarimeter. UV: *Agilent 8453E* UV/VIS Spectrometer. IR: *Nexus 470* FT Infrared spectrometer. 1D- and 2D-NMR spectra: *Bruker Avance-600* spectrometer at 600 ($^1$H) and 150

($^{13}$C) MHz. ESI-MS Spectra: *API 4000* mass spectrometer. HR-EI-MS Spectra: *Waters GCT* mass spectrometer.

*Plant Material.* The resin of *C. myrrha* was purchased in July 2005 from Affiliated Hospital of Shandong Traditional Chinese Medical University, Jinan, P. R. China. It was imported from India and identified by Prof. *Feng-Qin Zhou*, Shandong University of Traditional Chinese Medicine, P. R. China. A voucher specimen (No. 20050730CM) has been deposited with the Laboratory of Natural Products Chemistry, School of Pharmaceutical Sciences, Shandong University, P. R. China.

*Extraction and Isolation.* The resin of *C. myrrha* (2.5 kg) was ground into powder and extracted with petroleum ether (PE) in a *Soxhlet* apparatus for 48 h. The crude extract (220 g) was subjected to CC ($SiO_2$; PE/AcOEt 1:0 → 0:1) to provide eleven fractions (*Frs. A – K*). *Fr. B* (19 g) was subjected to CC ($SiO_2$; PE/AcOEt 1:0 → 4:1) to give two parts (*Frs. B1* and *B2*). Curzerenone (7 mg) was obtained from *Fr. B2* by prep. TLC (PE/AcOEt 50:1). *Fr. C* (38 g) was chromatographed over CC ($SiO_2$; PE/AcOEt 97:3 → 4:1) to afford four parts (*Frs. C1 – C4*). **7** (11 mg) was obtained from *Fr. C2* by CC ($SiO_2$; PE/AcOEt 97:3). (1*E*)-3-Methoxy-8,12-epoxygermacra-1,7,10,11-tetraen-6-one (8 mg) was isolated from *Fr. C3* by CC ($SiO_2$; PE/AcOEt 95:5) and further purified by prep. TLC (PE/$CHCl_2$/$Et_2O$, 6:4:1). *Fr. C4* was further purified by CC ($SiO_2$; PE/AcOEt, 95:5) to give (1*E*,2*R*,4*R*)-2-methoxy-8,12-epoxygermacra-1(10),7,11-trien-6-one (14 mg). *Fr. D* (16 g) was subjected to CC ($SiO_2$; PE/AcOEt 97:3) to give 2-methoxy-5-acetoxyfuranogermacr-1(10)-en-6-one (24 mg) and another three parts (*Frs. D1 – D3*). *rel*-(1*S*,2*S*)-(4*R*)-Epoxyfuranogermacr-10(15)-en-6-one (5 mg) was obtained from *Fr. D1* by prep. TLC (PE/AcOEt 2:1). *Fr. F* (10 g) was separated by CC ($SiO_2$; PE/AcOEt 9:1) to provide eight parts (*Frs. F1 – F8*). 4$\alpha$-Methoxy-6-guaien-10$\alpha$-ol was obtained from *Fr. F4* by CC ($SiO_2$; PE/$CHCl_3$/AcOEt 16:4:0.1) and purified by prep. TLC (PE/$CHCl_3$/$Me_2O$ 10:10:1). *Fr. G* (11.5 g) was subjected to CC ($SiO_2$; PE/AcOEt 91:9) to give **5** (40 mg) and three parts (*Frs. G1 – G3*). **6** (32 mg) was separated from *Fr. G2* by CC ($SiO_2$; PE/AcOEt 85:15). *Fr. G3* was subjected to CC ($SiO_2$; PE/$Me_2O$ 9:1) to give the mixture of **3** and **4** (9 mg). *Fr. H* (14 g) was chromatographed over CC ($SiO_2$; PE/$Me_2O$ 9:1) to provide two parts (*Frs. H1* and *H2*). **2** (25 mg) was isolated from *Fr. H2* by CC ($SiO_2$; PE/$CHCl_3$/$Et_2O$ 2:2:1). *Fr. J* (13 g) was separated by CC ($SiO_2$; PE/$Me_2O$ 85:15) to afford five fractions (*Frs. J1 – J5*). **1** (15 mg) was obtained from *Fr. J3* by CC ($SiO_2$; PE/$Et_2O$ 6:4).

*Myrrhasin* (=*(1β,3β,5α,13α,17α)-4,4,8-Trimethylcholesta-14,24-diene-1,3-diol*; **1**). Colorless solid (PE/$Me_2O$). $[\alpha]_D^{20} = -112.0$ ($c = 0.041$, MeOH). IR (KBr): 3424, 2969, 2933, 1740, 1637, 1466, 1449, 1375, 989. $^1$H- and $^{13}$C-NMR: *Table 1*. ESI-MS: 465.7 (100, $[M+Na]^+$), 460.8 (56, $[M+H_2O]^+$), 443.9 (26, $[M+H]^+$), 425.7 (39, $[M+H-H_2O]^+$), 407.8 (39, $[M+H-2\,H_2O]^+$), 338.6 (20), 225.6 (46). HR-EI-MS: 442.3841 ($M^+$, $C_{30}H_{50}O_2^+$; calc. 442.3811).

*Myrrhanolide A* (=*(9a*S*)-9a-Hydroxy-3,5,8-trimethyl-9,9a-dihydronaphtho[2,3-*b*]furan-2(4*H*)-one*; **2**). White, amorphous solid. $[\alpha]_D^{20} = -16.4$ ($c = 0.040$, MeOH). IR (KBr): 3424, 1749, 1731, 1701, 1419, 1140, 971. $^1$H- and $^{13}$C-NMR: *Table 2*. ESI-MS (pos.): 267.4 (42, $[M+Na]^+$), 262.4 (30, $[M+H_2O]^+$), 245.5 (100, $[M+H]^+$), 227.4 (75, $[M+H-H_2O]^+$). HR-EI-MS: 244.1120 ($M^+$, $C_{15}H_{16}O_3^+$; calc. 244.1099).

*Myrrhanolides B and C* (=*(3a*R,5S,8S*)-* and *(3a*S,5S,8S*)-3a-Hydroxy-1,5,8-trimethyl-3a,4,5,7,8,9-hexahydronaphtho[2,1-*b*]furan-2,6-dione*; **3** and **4**). White, amorphous powder. $[\alpha]_D^{20} = -13.6$ ($c = 0.040$, MeOH). IR (KBr): 3408, 3274, 2964, 2920, 1765, 1636, 1285, 999. $^1$H- and $^{13}$C-NMR: *Table 2*. ESI-MS (pos.): 263.4 (80, $[M+H]^+$), 245.4 (100, $[M+H-H_2O]^+$), 192.4 (23). HR-EI-MS: 262.1216 ($M^+$, $C_{15}H_{18}O_4^+$; calc. 262.1205).

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