# Diterpenoid and Phenolic Compounds from *Juncus effusus* L.

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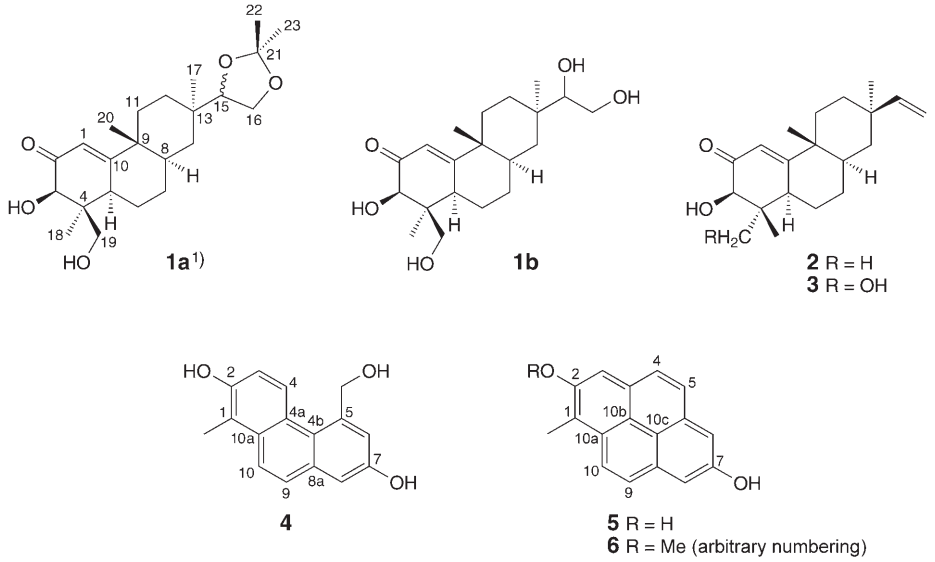
A novel diterpene, named effusenone A (**1a**), which is the first reported rosane-type diterpene from a *Juncaceae* plant, and three novel phenolic compounds, 5-(hydroxymethyl)-1-methylphenanthrene-2,7-diol (**4**), 1-methylpyrene-2,7-diol (**5**), and 7-methoxy-8-methylpyren-2-ol (**6**) were isolated from the stem of *Juncus effusus* L. by normal-phase and reversed-phase silica gel column chromatography. Their structures were identified by spectroscopic methods, especially 2D-NMR techniques.

**Introduction.** – *Juncus effusus* L. is a plant belonging to the *Juncaceae* family, which ranges from the tropical and subtropical zones to the frigid zone and is often found in wetlands and coastal marshes [1]. There are 77 species, 1 subspecies, and 10 mutations among the *Juncaceae* plants in China [2]. The chemical constituents of three *Juncaceae* plants, *i.e.*, of *J. effusus* L., *J. roemrianus*, and *J. acutus*, have been extensively studied. Many phenanthrenoids [3], cycloartane triterpenes [4], and benzocoumarins [5] were isolated from those plants, and phenanthrenoids were major bioactive compounds which showed cytotoxic, antimicrobial and antialgal activities [3]. Recently, it was found that dehydroeffusol (= 5-ethenyl-1-methylphenanthrene-2,7-diol) isolated from *J. effusus* L. displayed photosensitizing activity against some microbes and photosensitized DNA-binding activity, and it represented a novel type of photosensitizers from plants [6]. Those interesting activities have prompted us to reinvestigate the constituents of *J. effusus* L. As a result, a novel diterpene, named effusenone A (**1a**), which is the first reported rosane-type diterpene from a *Juncaceae* plant, and three novel phenolic compounds, 5-(hydroxymethyl)-1-methylphenanthrene-2,7-diol (**4**), 1-methylpyrene-2,7-diol (**5**), and 7-methoxy-8-methylpyren-2-ol (**6**) were isolated from the medullae of *Juncus effusus* L. by normal-phase and reversed-phase silica gel column chromatography. Their structures were identified by spectroscopic methods, especially 2D-NMR techniques. This paper deals with the structural investigation of those natural products.

**Results and Discussion.** – Compound **1a** was obtained as a yellow oil. The molecular formula was determined to be $C_{23}H_{36}O_5$ by HR-EI-MS with indicated 6 degrees of unsaturation. The $^1$H- and $^{13}$C-NMR data (*Table 1*) suggested that **1a** was a rosane (= (4a*R*,4b*R*,7*R*,8a*R*,10a*R*)-7-ethyltetradecahydro-1,1,4b,7-tetramethylphenanthrene) diterpenoid having a 1,2-dihydroxyethyl side chain [7]. $^1$H,$^1$H-COSY, HMBC (*Table 1*




and *Fig. 1*) and ROESY experiments and comparison with known compounds established the structure of **1a** as (3$\beta$)-3,19-dihydroxy-15,16-(isopropylidenedioxy)-ros-1(10)-en-2-one.

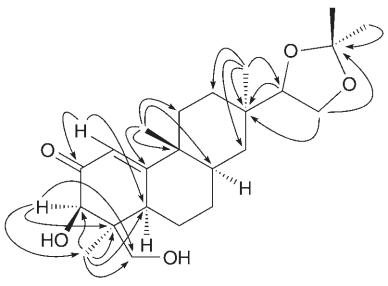


Fig. 1. *Significant HMBC correlations of compound* **1**

The $^1$H-NMR spectrum of **1a** showed one olefinic proton at $\delta$ 6.12 (*s*), three tertiary Me *s* ($\delta$ 0.87, 1.04, and 1.34), and one oxymethine proton at $\delta$ 4.12 (br. *s*). Two one-proton signals at $\delta$ 3.52 (*d*, $J$ = 11.2 Hz) and 3.64 (*d*, $J$ = 11.2 Hz) and the $^{13}$C-NMR signal at $\delta$ 63.3 (*t*) indicated the presence of an oxymethylene moiety. The *ABX* system at $\delta$(H) 3.78 (*t*, $J$ = 7.2 Hz), 3.72 (*t*, $J$ = 7.0 Hz), and 3.92 (*t*, $J$ = 6.0 Hz) and the $\delta$(C) 64.6 (*t*) and 84.2 (*d*) were consistent with a $-$CH(O)$-$CH$_2$(O) fragment in compound **1a**, which was confirmed by the $^1$H,$^1$H-COSY correlations $\delta$ 3.78 (*t*, $J$ = 7.2 Hz), $\delta$ 3.72 (*t*, $J$ = 7.0 Hz), and 3.92 (*t*, $J$ = 6.0 Hz), and $\delta$ 3.72/$\delta$ 3.92. The $^1$H-NMR spectrum further showed two Me signals at $\delta$ 1.35 and 1.42, and the $^{13}$C-NMR three signals at $\delta$ 108.7 (*s*), 25.0 (*q*), and 26.1 (*q*), indicating that **1a** contained an isopropylidene moiety. Besides the three C-signals of the isopropylidene moiety, the $^{13}$C-NMR and DEPT spectra displayed the presence of seven CH$_2$ groups, two of which were

[1)] Trivial atom numbering; for systematic names, see *Exper. Part*.

Table 1. *$^1$H-NMR, $^{13}$C-NMR, and HMBC Data ($CDCl_3$) of Compound* **1**. $\delta$ in ppm, $J$ in Hz.

| | $\delta$(H) | $\delta$(C) | HMBC (H → C) |
|---|---|---|---|
| H–C(1) | 6.12 (*s*) | 119.8 (*d*) | C(2), C(3), C(5), C(9) |
| C(2) | – | 199.1 (*s*) | |
| H–C(3) | 4.12 (*s*) | 80.4 (*d*) | C(4), C(18), C(19) |
| C(4) | – | 46.8 (*s*) | |
| H–C(5) | 2.69 (br. *d*, $J$ = 13.5) | 44.0 (*d*) | |
| $CH_2$(6) | 0.92–0.95 (*m*) | 17.8 (*t*) | |
| $CH_2$(7) | 1.22–1.28 (*m*) | 29.7 (*t*) | |
| H–C(8) | 1.72–1.74 (*m*) | 30.2 (*d*) | |
| C(9) | – | 39.2 (*s*) | |
| C(10) | – | 177.1 (*s*) | |
| $CH_2$(11) | 1.69–1.79 (*m*) | 33.7 (*t*) | |
| $CH_2$(12) | 0.99–1.04 (*m*) | 36.5 (*t*) | |
| C(13) | – | 35.4 (*s*) | |
| C(14) | 1.35–1.40 (*m*) | 28.1 (*t*) | |
| H–C(15) | 3.78 (*t*, $J$ = 7.2) | 84.2 (*d*) | C(13) |
| $CH_2$(16) | 3.72 (*t*, $J$ = 7.0), 3.92 (*t*, $J$ = 6.0) | 64.6 (*t*) | C(13), C(15), C(21) |
| Me(17) | 0.87 (*s*) | 18.7 (*q*) | C(12), C(13), C(14), C(15) |
| Me(18) | 1.34 (*s*) | 20.5 (*q*) | C(3), C(4), C(5), C(19) |
| $CH_2$(19) | 3.64 (*d*, $J$ = 11.2), 3.52 (*d*, $J$ = 11.2) | 63.3 (*t*) | C(4), C(5) |
| Me(20) | 1.04 (*s*) | 19.1 (*q*) | C(8), C(9), C(10), C(11) |
| C(21) | – | 108.7 (*s*) | |
| Me(22) | 1.35 (*s*) | 25.0 (*q*) | C(21) |
| Me(23) | 1.42 (*s*) | 26.1 (*q*) | C(21) |

oxymethylene groups, four CH groups, two of which were oxygenated, three quaternary C-atoms, three Me groups, and an $\alpha,\beta$-unsaturated carbonyl group ($\delta$ 119.8 (*d*), 177.1 (*s*), 199.1 (*s*)). The isopropylidene moiety at the rosane skeleton was located at C(15) and C(16)[1]), as suggested by the HMBC correlations (*Fig. 1*) of the Me groups at $\delta$(H) 1.35 and 1.42, and of the $OCH_2$ group at $\delta$(H) 3.72 (*t*, $J$ = 7.0 Hz) and 3.92 (*t*, $J$ = 6.0 Hz) with the quaternary C-atom at $\delta$(C) 108.7 (*s*). The position of the OH group in compound **1a** was determined to be C(3) by the HMBC correlation $\delta$(H) 4.12/$\delta$(C) 46.8 (C(4)), 20.5 (C(19) or C(18)), and 63.3 (C(19) or C(18)). Comparison of the signals of C(1), C(2), C(3), C(4), C(5), and C(10) with those of the known compound 18-hydroxyhugorosenone (**3**), isolated from *Hugonia casteneifolia* [8], revealed similar $\delta$(C), except for the chemical shifts of C(3) and C(5). This suggested that ring A of **1a** should be the same as that of **3**, except for the location of the hydroxymethyl group. In the diterpenes **2** [8] and **3** bearing a 3$\beta$-hydroxy and a 3$\beta$,18-dihydroxy moiety, respectively, the chemical shift of C(3) of the latter was shielded by *ca.* 5 ppm. The $\delta$(C) of C(3) in **1a** and **2** was almost the same, *i.e.*, the $\delta$(C) of C(3) of **1a** was only slightly affected by the hydroxymethyl group. Thus, the second OH group of **1a** should be located at C(19) [9]. The assumption was further supported by the NOEs Me(18) ($\delta$ 1.34 (*s*)), H–C(5) ($\delta$ 2.69 (br. *d*, $J$ = 13.5 Hz)) and H–C(3) (4.12 (*s*)) in the ROESY plot. The relative configuration of **1a** was deduced from the ROESY data. The presence of NOE cross-peaks H–C(8)/H–C(5) and Me(17), and Me(20)/H–C(15) clearly established that Me(17), Me(20), and H–C(8) were $\alpha$-, $\beta$-, and $\alpha$-positioned, respectively. However, the relative configuration at C(15) was not determined from the ROESY data.

The presence of an isopropylidene acetal in naturally occurring metabolites is very rare, and this functionality of **1a** was shown to arise from the acetone used for the extract separation by chromatography on silica gel. Indeed, TLC analysis of the crude extract revealed the absence of compound **1a**. Thus, the structure of the natural-

product precursor of **1a** in the plant must be (3$\beta$)-3,15,16,19-tetrahydroxyros-1(10)-en-2-one (**1b**).

Previous phytochemical investigations of three species of the *Junaceae* genus yielded phenanthrenoids and cycloartane triterpenes. This is the first report of a rosane-type diterpene in the genus. Rosanes are unusual diterpenoids for the *Junaceae*. Rosanes arise by migration of the Me–C(10) group of pimaranes to C(9) and occur in both enantiomeric series predominantly in high plants [10]. The absolute configuration of **1a** was not determined.

Compound **4** was obtained as a yellow amorphous powder. The EI-MS of **4** had an apparent molecular-ion peak at *m/z* 254; the molecular formula was determined to be $C_{16}H_{14}O_3$ by HR-EI-MS. The $^1$H- and $^{13}$C-NMR (*Table 2*) and HMBC data (*Table 2* and *Fig. 2*) suggested that **4** was 5-(hydroxymethyl)-1-methylphenanthrene-2,7-diol. Further confirmation of the structure was provided by the 2D-NMR data.

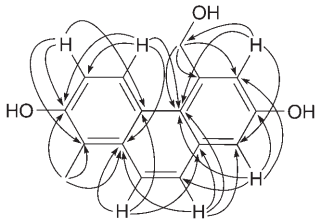



Fig. 2. *Significant HMBC correlations of compound* **4**

Table 2. *$^1$H-NMR, $^{13}$C-NMR, and HMBC Data ($CDCl_3$) of Compound* **4**. $\delta$ in ppm, *J* in Hz.

| | $\delta$(H) | $\delta$(C) | HMBC (H → C) |
|---|---|---|---|
| C(1) | – | 117.2 (*s*) | |
| C(2) | – | 152.2 (*s*) | |
| H–C(3) | 7.24 (*d*, *J* = 9.0) | 115.5 (*d*) | C(1), C(2), C(4a) |
| H–C(4) | 8.56 (*d*, *J* = 9.0) | 126.4 (*d*) | C(2), C(3), C(4b), C(10a) |
| C(4a) | – | 125.0 (*s*) | |
| C(4b) | – | 124.5 (*s*) | |
| C(5) | – | 140.2 (*s*) | |
| H–C(6) | 7.48 (*d*, *J* = 2.4) | 119.4 (*d*) | C(4b), C(8), $CH_2$–C(5) |
| C(7) | – | 154.4 (*s*) | |
| H–C(8) | 7.23 (*d*, *J* = 2.4) | 111.4 (*d*) | C(4b), C(6), C(7), C(9) |
| C(8a) | – | 133.9 (*s*) | |
| H–C(9) | 7.64 (*d*, *J* = 9.0) | 127.4 (*d*) | C(4b), C(8), C(8a), C(10a), |
| CH(10) | 7.88 (*d*, *J* = 9.0) | 122.9 (*d*) | C(1), C(4a), C(8a), C(10a), |
| C(10a) | – | 132.8 (*s*) | |
| Me–C(1) | 2.57 (*s*) | 10.7 (*q*) | C(1), C(2), C(10a) |
| $CH_2$–C(5) | 5.18 (*s*) | 65.2 (*t*) | C(4b), C(5), C(6) |

The $^1$H-NMR spectrum of **4** exhibited the signal for an aromatic Me group at $\delta$ 2.57 (*s*), six aromatic protons, including four *ortho*-coupled protons at $\delta$ 7.24 and 8.56, and $\delta$ 7.64 and 7.88, and two *meta*-coupled protons at $\delta$ 7.23 and 7.48, and one oxygenated $CH_2$ group at $\delta$ 5.18 (*s*). The $^{13}$C-NMR of **4** showed 16 C-atoms: six aromatic CH groups, eight quaternary aromatic C-atoms including two

oxygentaed ones, one Me group, and an oxygenated $CH_2$ group. The NMR data of **4** closely resembled that of dehydroeffusol (= 5-ethenyl-1-methylphenanthrene-2,7-diol) isolated from the same plant [11]. However, the signals of three olefinic protons and two olefinic C-atoms in the NMR spectra of dehydroeffusol were absent in those of **4**, and the signals of a $CH_2$ group attached to an OH group ($\delta$ 65.2 (*t*), $\delta$ 5.18 (*s*, 2 H)) were present in those of **4**, indicating that the $CH_2$=CH−C(5) of dehydroeffusol was replaced by $HOCH_2$−C(5). In the HMBC plot (*cf. Fig. 2*), the correlations $CH_2$−C(5)/C(6), C(4b), and C(5), and H−C(6)/C(8), C(4b), and $CH_2$−C(5), clearly indicated the presence of a $CH_2OH$ group at C(5) of **4**.

Compound **5**, obtained as a yellow amorphous powder, had a molecular formula $C_{17}H_{12}O_2$ as revealed by the HR-EI-MS (*m*/*z* 248.0834 ($C_{17}H_{12}O_2^+$)). Its $^1$H- and $^{13}$C-NMR (*Table 3*) and HMBC data (*Fig. 3*) and comparison with those at 1,6-dimethylpyrene-2,7-diol [12], isolated from *Juncus acutus*, established the structure of **5** as 1-methylpyrene-2,7-diol.

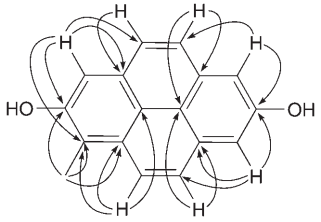



Fig. 3. *Significant HMBC correlations of compound* **5**

Table 3. *$^1$H- and $^{13}$C-NMR Data* ((D$_6$)acetone) *of Compounds* **5** *and* **6**. $\delta$ in ppm, *J* in Hz.

| | **5** | | **6**[a]) | |
|---|---|---|---|---|
| | $\delta$(H) | $\delta$(C) | $\delta$(H) | $\delta$(C) |
| C(1) | – | 119.3 (*s*) | – | 121.0 (*s*) |
| C(2) | – | 152.8 (*s*) | – | 155.3 (*s*) |
| H−C(3) | 7.73 (*s*) | 112.0 (*d*) | 7.86 (*s*) | 107.6 (*d*) |
| C(3a) | – | 120.0 (*s*) | – | 120.3 (*s*) |
| H−C(4) | 7.88 (*s*) | 127.3 (*d*) | 8.03 (*d*, *J* = 8.7) | 127.7 (*d*) |
| H−C(5) | 7.88 (*s*) | 126.3 (*d*) | 7.93 (*d*, *J* = 8.7) | 126.3 (*d*) |
| C(5a) | – | 132.2 (*s*) | – | 132.4 (*s*) |
| H−C(6) | 7.65 (*d*, *J* = 2.4) | 111.6 (*d*) | 7.68 (*s*) | 111.9 (*d*) |
| C(7) | – | 155.0 (*s*) | – | 155.2 (*s*) |
| H−C(8) | 7.64 (*d*, *J* = 2.4) | 111.6 (*d*) | 7.68 (*s*) | 111.9 (*d*) |
| C(8a) | – | 119.9 (*s*) | – | 119.6 (*s*) |
| H−C(9) | 7.99 (*d*, *J* = 9.3) | 127.0 (*d*) | 8.00 (*d*, *J* = 8.7) | 127.3 (*d*) |
| H−C(10) | 8.21 (*d*, *J* = 9.3) | 124.1 (*d*) | 8.21 (*d*, *J* = 8.7) | 124.1 (*d*) |
| C(10a) | – | 129.5 (*s*) | – | 129.5 (*s*) |
| C(10b) | – | 131.6 (*s*) | – | 131.8 (*s*) |
| C(10c) | – | 129.9 (*s*) | – | 129.6 (*s*) |
| Me−C(1) | 2.77 (*s*) | 10.8 (*q*) | 2.77 (*s*) | 10.8 (*q*) |
| MeO | – | – | 4.11 (*s*) | 55.8 (*q*) |

[a]) For convenience, the atom numbering of **5** and **6** is identical; for systematic names, see *Exper. Part.*

The $^1$H-NMR spectrum of **5** revealed the presence of one Me group at $\delta$ 2.77 (*s*), two *ortho*-coupled protons at $\delta$ 8.21 and 7.99, two *meta*-coupled protons at $\delta$ 7.65 and 7.64, and three *s* protons at $\delta$ 7.88 (*s*, 2 H) and 7.73 (*s*, 1 H). The $^{13}$C-NMR spectrum of **5** showed 17 C-signals, including 7 CH groups at $\delta$ 112.0, 111.6, 111.6, 127.0, 124.1, 126.3, and 127.3, 9 quaternary C-atoms (including two oxygenated ones at $\delta$ 155.0 and 152.8), and one Me group at $\delta$ 10.8. The NMR data of **5** were very similar to those of 1,6-dimethylpyrene-2,7-diol [12], except for the following observations. In the $^1$H-NMR spectrum of **5**, the two Me groups at $\delta$ 2.76 (*s*, 6 H) and the aromatic proton at $\delta$ 7.67 (*s*, 1 H) of 1,6-dimethylpyrene-2,7-diol were replaced by the signal of one Me group at $\delta$ 2.77 (*s*, 3 H) and two *meta*-coupled protons at $\delta$ 7.65 and 7.64. The $^{13}$C-NMR spectrum of 1,6-dimethylpyrene-2,7-diol had one more quaternary and Me C-signal compared with those of **5**. All these data suggested that the Me group at C(6) of 1,6-dimethylpyrene-2,7-diol was absent in compound **5**. The HMBC plot (*cf. Fig. 3*) showed the cross-peaks H–C(6)/C(5) and C(7), and H–C(8)/C(7), C(8a), and C(9). The Me–C(6) of 1,6-dimethylpyrene-2,7-diol being absent in **5**, **5** had only a partially symmetric structure involving C(2) to C(7). Therefore, H–C(4) and H–C(5) were magnetically equivalent giving rise to a *s* at $\delta$ 7.88 (*s*, 2 H) in the $^1$H-NMR spectrum. In the HSQC plot, the protons at 7.88 (*s*, 2 H) were correlated with 126.3 (C(4)) and 127.3 (C(5)).

Compound **6** was obtained as a yellow amorphous powder. Its $^{13}$C-NMR spectra were similar to those of **5**, suggesting similar basic C-skeletons. The structure of **6** was deduced from its $^1$H- and $^{13}$C-NMR (*Table 3*) and NOESY data as 7-methoxy-8-methylpyren-2-ol.

The $^1$H-NMR spectrum of **6** was also similar to that of **5**, except for four *ortho*-coupled protons at $\delta$ 8.21 and 8.00, and $\delta$ 8.03 and 7.93 and one MeO group at $\delta$ 4.11 in the case of **6**, and two *ortho*-coupled protons at $\delta$ 8.21 and 7.99 and two *s* protons at $\delta$ 7.88 (*s*, 2 H) in the case of **5**. This suggested that one of the OH groups of **5** was replaced by an MeO group in **6**. In the NOESY plot, a cross-peak between H–C(3) and the MeO group was observed (atom numbering as for **5**, see *Table 3*).

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## Experiment Part

*General.* Column chromatography (CC) and TLC: silica gel *60 H* pre-coated silica gel *GF254* plates, resp., from *Qingdao Haiyang Chemical Group Co.*, China; $C_{18}$ reversed-phase silica gel from YMC *Co., Ltd.*, Japan. Optical rotation: *Jasco-DIP-181* polarimeter. $^1$H- and $^{13}$C-NMR Spectra: *Bruker AM-400* instrument; $\delta$ in ppm rel. to $SiMe_4$ as internal standard (=0 ppm), *J* in Hz. MS: *Varian MAT-711* spectrometer; in *m/z* (rel. %)

*Plant Material.* The stems of *Juncus effusus* L. were purchased from the *Wuhan Red Cross Pharmaceutical Company*, China. The plant material was identified by Prof. *Ding-rong Wan*, College of Life Sciences, South Central University for Nationalities, Wuhan, China. The voucher specimen was deposited in the herbarium of the College of Life Sciences, South Central University for Nationalities.

*Extraction and Isolation.* The dried stems (10 kg) of *Juncus effusus* L. were powdered and extracted with 95% EtOH. The EtOH extract (166 g) was extracted successively with petroleum ether, AcOEt, and BuOH. The AcOEt extract (55 g) was subjected to CC (silica gel, petroleum ether/acetone 9:1, 8:2, 7:3, 1:1, 3:7, and 0:1): *Fractions 1–75*. The combined *Fr. 15–20* (670 mg) were repeatedly subjected to CC (silica gel and octadecylsilane (ODS)): **5** (1 mg). The combined *Fr. 31–34* (1.95 g) were repeatedly subjected to CC (silica gel and ODS): **6** (1.9 mg). The combined *Fr. 39–62* (15.05 g) were repeatedly subjected to CC (silica gel and ODS): **1a** (6.1 mg) and **4** (7.2 mg).

*Effusenone A* (=*(3β)-3,19-Dihydroxy-15,16-(isopropylidenedioxy)ros-1(10)-en-2-one* =rel-*(1*R*,2*S*,4b*S*,7*S*,8a*S*,10a*S*)-7-(2,2-Dimethyl-1,3-dioxolan-4-yl)-1,4b,5,6,7,8,8a,9,10,10a-decahydro-2-hy-*

*droxy-1-(hydroxymethyl)-1,4b,7-trimethylphenanthren-3(2*H*)one*; **1a**): Yellow oil. $[\alpha]_D = -32.3$ ($c = 0.3$, $CHCl_3$). $^1$H- and $^{13}$C-NMR: *Table 1*. EI-MS: 392 (6, $M^+$), 377 (21), 360 (19), 287 (19), 137 (19), 121 (11), 101 (100). HR-EI-MS: 392.2564 ($C_{23}H_{36}O_5^+$; calc. 392.2563).

*5-(Hydroxymethyl)-1-methylphenanthrene-2,7-diol* (**4**): Yellow amorphous powder. $^1$H- and $^{13}$C-NMR: *Table 2*. EI-MS: 254 (100, $M^+$), 237 (11), 221 (18), 165 (11). HR-EI-MS: 254.0945 ($C_{16}H_{14}O_3^+$; calc. 254.0943).

*1-Methylpyrene-2,7-diol* (**5**): Yellow amorphous powder. $^1$H- and $^{13}$C-NMR: *Table 3*. EI-MS: 248 (9, $M^+$), 219 (58), 189 (100), 99 (39), 87 (56), 62 (64), 59 (99). HR-EI-MS: 248.0834 ($C_{17}H_{12}O_2^+$; calc. 248.0837).

*7-Methoxy-8-methylpyren-2-ol* (**6**): Yellow amorphous powder. $^1$H- and $^{13}$C-NMR: *Table 3*. EI-MS: 262 (22, $M^+$), 231 (22), 189 (12), 167 (22), 149 (89), 108 (24), 81 (54), 69 (100). HR-EI-MS: 262.0981 ($C_{18}H_{14}O_2^+$; calc. 262.0994).

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