# Eleven New Triterpenes from *Eurycorymbus cavaleriei*

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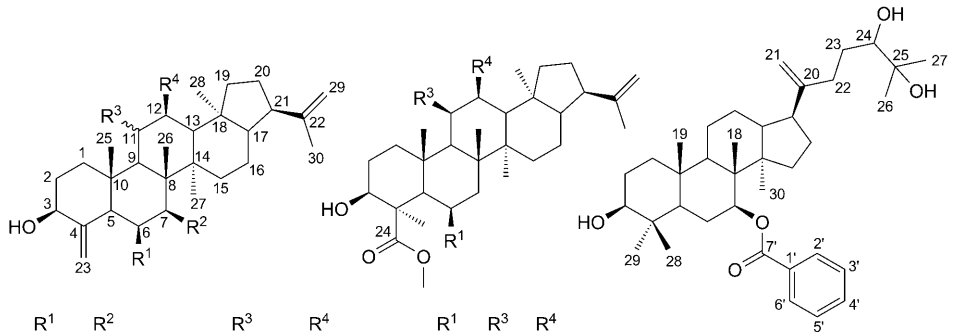
Eleven new triterpenes, cavalerols A – K (**1** – **11**, resp.), ten of which were derivatives of hopane and one was derivative of dammarane, were isolated from the twigs of *Eurycorymbus cavaleriei*. Their structures were elucidated by spectroscopic methods including 2D-NMR analysis. Cavalerol D (**4**) and cavalerol F (**6**), cavalerol B (**2**), and cavalerol G (**7**) were two pairs of isomers, and silver ion was introduced for their differentiation by multi-stage tandem mass spectrometry. And nine compounds, except **5** and **10**, were tested for quinone reductase (QR) induction activities *in vitro*, and results showed that compounds **2**, **4**, and **7** exhibited moderate induction activities with CD values of 8.62, 9.13, and 2.56 μg/ml, respectively, and compounds **6** and **8** showed cytotoxicity against hepa 1c1c7 cell line with $IC_{50}$ values of no more than 1 μg/ml.

**1. Introduction.** – *Eurycorymbus cavaleriei* (H. LÉV.) REHDER et HAND.-MAZZ. is an endemic tree species in P. R. China and the only species in this genus [1]. Previous research revealed chemical constituents from the petroleum ether fraction [2][3]. Here, we report the isolation and structure elucidation of eleven new triterpenes, cavalerols A – K (**1** – **11**, resp.; for structures, see *Fig. 1*), including 21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$,7$\beta$,11$\alpha$-tetrol (**1**), 11$\alpha$-(acetyloxy)-7$\beta$-(benzoyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$-diol (**2**), 11$\alpha$-(acetyloxy)-7$\beta$-(caproyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$-diol (**3**), 7$\beta$-(benzoyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$,11$\alpha$-triol (**4**), 6$\beta$-(acetyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,12$\beta$-diol (**5**), 7$\beta$-(benzoyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$,11$\beta$-triol (**6**), 6$\beta$-(acetyloxy)-7$\beta$-(benzoyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,11$\beta$-diol (**7**), 6$\beta$-(acetyloxy)-12$\beta$-(benzoyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-dien-3$\beta$-ol (**8**), methyl 3$\beta$,12$\beta$-dihydroxy-21$\alpha H$-hop-22(29)-en-24-oate (**9**), methyl 6$\beta$-(acetyloxy)-3$\beta$,11$\beta$-dihydroxy-21$\alpha H$-hop-22(29)-en-24-oate (**10**), 7$\beta$-(benzoyloxy)dammar-20(21)-ene-3$\beta$,24$\xi$,25-triol (**11**). Cavalerols A – H (**1** – **8**, resp.) possessed the norhopene skeleton which was reported in [4]. Compounds **1** – **4**, **6** – **9**, and **11** were evaluated for their induction ability of NAD(P)H : quinone reductase (QR).

Cavalerol B (**2**) and cavalerol D (**4**), cavalerol F (**6**) and cavalerol G (**7**) were each two pairs of isomers that are difficult to differentiate. Since the silver complexation will



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| **1** | OH | OH | $\alpha$-OH | H |
| **2** | OH | BzO | $\alpha$-AcO | H |
| **3** | OH | $Me(CH_2)_4COO$ | $\alpha$-AcO | H |
| **4** | OH | BzO | $\alpha$-OH | H |
| **5** | AcO | H | H | OH |
| **6** | OH | BzO | $\beta$-OH | H |
| **7** | AcO | BzO | $\beta$-OH | H |
| **8** | AcO | H | H | BzO |

| | $R^1$ | $R^3$ | $R^4$ |
|---|---|---|---|
| **9** | H | H | OH |
| **10** | AcO | OH | H |

**11**

Fig. 1. *Structures of cavalerols* A – K (**1** – **11**, resp.)

help to enhance the ionization efficiencies of the compounds [5][6], the silver ion was introduced into **2**, **4**, **6**, and **7**, leading to great improvement of the $MS^n$ spectra. The *quasi*-molecular ions became more obvious, and the ions in $MS^n$ were much more stabilized and easy to identify. The silver complexes exhibited significant differences in the $MS^n$ spectra, enabling differentiation of corresponding compounds.

**2. Results and Discussion.** – 2.1. *Structure Elucidation.* Compound **1** was obtained as white amorphous powder (MeOH). The HR-ESI-MS displayed a *quasi*-molecular-ion peak at *m*/*z* 463.2536 $[M - H_2O + Na]^+$, consistent with the formula of $C_{29}H_{44}NaO_3$. The $^1$H-NMR spectrum (*Table 1*) of **1** showed the signals of four CH–O H-atoms ($\delta$(H) 3.49, 3.68, 3.87, 3.95), one isopropenyl ($\delta$(H) 1.63, 4.66, 4.66), one terminal vinyl ($\delta$(H) 5.35, 5.09), and five Me groups ($\delta$(H) 0.66, 0.95, 1.03, 1.23, 1.63). The $^{13}$C-NMR spectrum (*Table 2*) displayed 29 signals, which were ascribed four CH–O groups ($\delta$(C) 71.0, 71.7, 73.6, 68.7), isopropenyl C-atoms ($\delta$(C) 19.4, 109.9, 147.7), terminal vinyl C-atoms ($\delta$(C) 104.5, 149.1), and the five Me C-atoms ($\delta$(C) 14.9, 17.3, 15.8, 12.2, 19.4). The DEPT spectra also indicated the presence of six quaternary C-atoms, seven secondary C-atoms, and nine tertiary C-atoms. As indicated above, the 1D-NMR data were compared with those of the hopene derivative reported as 21$\alpha$*H*-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$-diol and showed several similarities [4] except for the two O-bearing C-atoms ($\delta$(C) 71.0 (C(7)), 68.7(C(11))). In the $^1$H,$^1$H-COSY spectrum, correlations between the $\delta$(H) 1.56 (H–C(5)), and 3.87 (H–C(6)), H–C(7)), 3.95 (H–C(11)), and 1.34 (H–C(9)) were detected, and the HMQC spectrum of **1** revealed correlations between H–C(11) ($\delta$(H) 3.95) and C(11) ($\delta$(C) 68.7), and H–C(7) ($\delta$(H) 3.49) and C(7) ($\delta$(C) 71.0), so the OH groups were at C(7) and C(11), repectively, which was also confirmed by the HMBC spectrum of **1** (*Fig. 2*,*a*).

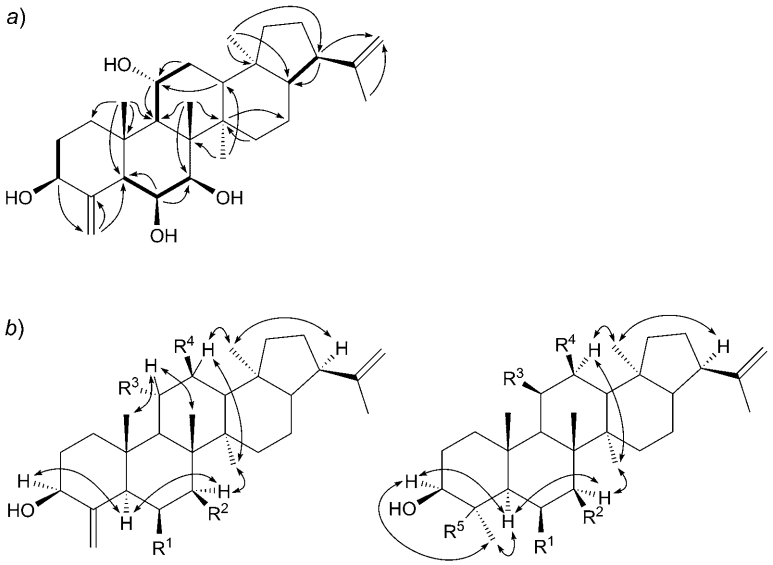



Fig. 2. a) *Key* $^1H,^1H$*-COSY* (—) *and HMBC* (H → C) *correlations of compound* **1**. b) *Key NOESY data* (H ↔ H) *of compounds* **1**–**11**.

NOESY experiments of compound **1** (*Fig. 2*, *b*) established the configurations of the OH groups at C(3), C(6), C(7) as $\beta$ through correlations displayed between $H_\alpha$–C(3), and $H_\alpha$–C(7) and $H_\alpha$–C(5); and $H_\alpha$–C(7) and Me(27). The configuration of the HO–C(11) was confirmed to be $\alpha$ by the correlation between $H_\beta$–C(11), and Me(25) and Me(26). Thus, the structure of compound **1** was established as 21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$,7$\beta$,11$\alpha$-tetrol.

Compound **2** showed $^1$H- and $^{13}$C-NMR spectral features very similar (*Tables 1* and *2*) to those of compound **1**. In the $^{13}$C-NMR spectra, the signals at $\delta$(C) 165.4 (C(1′)), 130.1 (C(2′)), 129.7 (C(3′)), 128.7 (C(4′)), 133.4 (C(5′)), 128.7 (C(6′)), 129.7 (C(7′)), C=O signal ($\delta$(C) 170.0), and Me signal ($\delta$(C) 22.1) strongly indicated the presence of BzO and AcO groups. In the HMBC spectrum, it was observed that H–C(7) signal ($\delta$(H) 5.30 (*d*, $J$ = 4.0, H–C(7))) correlated with that of C(1′) ($\delta$(C) 165.4 (C(1′))), indicating that the BzO group was located at C(7), and H–C(11) signal ($\delta$(H) 5.48) and Me ($\delta$(H) 2.06) correlated with the CO signal ($\delta$(C) 170.0), indicating that AcO was located at C(11). So, the compound **2** was elucidated as 11$\alpha$-(acetyloxy)-7$\beta$-(benzoyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$-diol. The positions of the BzO groups of compounds **4**, **6**, **7**, **8**, and **11**, as well as those of the AcO groups of compounds **3**, **5**, **7**, **8**, and **10** were determined in the same way.

Compound **3** was obtained as yellow amorphous powder (MeOH), the $^1$H- and $^{13}$C-NMR data were similar to those of **2** except signals corresponding to Bz groups. After assignment of the core C-atoms, there were still signals of one Me ($\delta$(C) 13.9; $\delta$(H) 0.90 (*t*, $J$ = 7.0)), one CO ($\delta$(C) 172.8), and four $CH_2$ groups ($\delta$(C) 35.0, $\delta$(H) 2.33–2.36 (*m*); $\delta$(C) 24.3, $\delta$(H) 1.30–1.33 (*m*); $\delta$(C) 31.3, $\delta$(H) 1.63–1.66 (*m*); $\delta$(C) 22.3, $\delta$(H) 1.30–1.34 (*m*)). These data were ascribed to the caproyl (= hexanoyl) group [7], which was confirmed by the HMBCs (*Fig. 3*, *a*). The HMBC showed correlation of

Table 1. *$^1$H-NMR Data of Compounds* **1**–**6**

| | **1**[a]) | **2**[b]) | **3**[b]) | **4**[b]) | **5**[b]) | **6**[b]) |
|---|---|---|---|---|---|---|
| $CH_2$(1) | 0.97–0.99, 2.81–2.84 (2*m*) | 1.27–1.29, 2.28–2.30 (2*m*) | 1.24–1.26, 2.25–2.28 (2*m*) | 1.43–1.45, 1.83–1.86 (2*m*) | 1.15–1.17, 1.87–1.89 (2*m*) | 1.17–1.19, 2.85–2.88 (2*m*) |
| $CH_2$(2) | 1.27–1.29, 1.61–1.64 (2*m*) | 1.44–1.46, 1.91–1.94 (2*m*) | 1.42–1.44, 1.93–1.95 (2*m*) | 1.50–1.52, 1.96–1.98 (2*m*) | 1.47–1.49, 2.05–2.07 (2*m*) | 1.47–1.50, 1.88–1.91 (2*m*) |
| H–C(3) | 3.68 (*dd*, *J* = 11.5, 5.0) | 3.97 (*dd*, *J* = 11.5, 5.0) | 3.95 (*dd*, *J* = 11.5, 5.0) | 3.97 (overlap) | 3.98 (overlap) | 3.96 (*dd*, *J* = 11.5, 5.0) |
| H–C(5) | 1.56 (*s*) | 1.83 (*s*) | 1.76 (*s*) | 1.78 (*s*) | 1.77 (*s*) | 1.82 (*s*) |
| H–C(6) | 3.87 (*dd*, *J* = 2.0, 1.0) | 4.37 (*dd*, *J* = 2.0, 1.0) | 4.23 (*dd*, *J* = 2.0, 1.0) | 4.45 (*dd*, *J* = 3.0, 1.5)) | 5.33–5.35 (*m*) | 4.37 (*dd*, *J* = 2.0, 1.0) |
| H–C(7) or $CH_2$(7) | 3.49 (*d*, *J* = 4.0) | 5.30 (*d*, *J* = 4.0) | 5.05 (*d*, *J* = 4.0)) | 5.27 (*d*, *J* = 4.0) | 1.73, 1.65 (overlap) | 5.28 (*d*, *J* = 4.0) |
| H–C(9) | 1.34 (*s*) | 1.97 (*s*) | 1.88 (*s*) | 1.63 (*s*) | 1.57 (*s*) | 1.67 (*s*) |
| H–C(11) or $CH_2$(11) | 3.94–3.96 (*m*) | 5.47–5.49 (*m*) | 5.43–5.46 (*m*) | 3.97–4.00 (*m*) | 1.50–1.52, 1.98–2.01 (2*m*) | 4.28–4.31 (*m*) |
| $CH_2$(12) or H–C(12) | 1.49–1.51, 1.57–1.59 (2*m*) | 1.56–1.59, 1.81–1.83 (2*m*) | 1.30–1.32, 1.83–1.86 (2*m*) | 1.62–1.64, 2.08–2.10 (2*m*) | 4.00–4.03 (*m*) | 1.61–1.64, 1.80–1.83 (2*m*) |
| H–C(13) | 1.58–1.60 (*m*) | 1.69–1.71 (*m*) | 1.63–1.65 (*m*) | 1.50–1.53 (*m*) | 1.55 (*d*, *J* = 1.0) | 1.65 (overlap) |
| $CH_2$(15) | 1.35–1.38, 1.66–1.69 (2*m*) | 1.04–1.07, 1.46–1.49 (2*m*) | 0.98–1.44 (*m*) | 1.02–1.04, 1.55–1.58 (2*m*) | 1.19–1.21, 1.35–1.38 (2*m*) | 1.03–1.05, 1.46–1.49 (2*m*) |
| $CH_2$(16) | 1.11–1.13, 1.28–1.31 (2*m*) | 1.08–1.10, 1.20–1.22 (2*m*) | 1.18–1.20, 1.36–1.38 (2*m*) | 1.12–1.14, 1.20–1.22 (2*m*) | 1.18–1.20, 1.42–1.45 (2*m*) | 1.09–1.11, 1.20–1.22 (2*m*) |
| H–C(17) | 0.95–0.97 (*m*) | 0.97–0.99 (*m*) | 1.00–1.02 (*m*) | 0.98–1.00 (*m*) | 1.00–1.03 (*m*) | 0.98–1.00 (*m*) |
| $CH_2$(19) | 1.05–1.07, 1.43–1.46 (2*m*) | 1.10–1.12, 1.48–1.50 (2*m*) | 1.11–1.13, 1.47–1.50 (2*m*) | 1.34–1.36, 1.87–1.89 (2*m*) | 1.35–1.38, 1.82–1.85 (2*m*) | 1.07–1.10, 1.52–1.55 (2*m*) |
| $CH_2$(20) | 1.36–1.39, 1.80–1.82 (2*m*) | 1.44–1.46, 1.81–1.83 (2*m*) | 1.46–1.49, 1.83–1.86 (2*m*) | 1.40–1.44, 1.80–1.82 (2*m*) | 1.48–1.51, 1.87–1.90 (2*m*) | 1.45–1.48, 1.85–1.87 (2*m*) |
| H–C(21) | 2.19–2.21 (*m*) | 2.18–2.20 (*m*) | 2.23–2.25 (*m*) | 2.13–2.15 (*m*) | 1.19–2.20 (*m*) | 2.19–2.21 (*m*) |
| $CH_2$(23) | 5.35, 5.09 (2*s*) | 5.39, 5.22 (2*s*) | 5.42, 5.23 (2*s*) | 5.35, 5.22 (2*s*) | 5.17, 4.68 (2*s*) | 5.38, 5.22 (2*s*) |
| Me(25) | 1.03 (*s*) | 1.12 (*s*) | 1.08 (*s*) | 1.08 (*s*) | 1.03 (*s*) | 1.26 (*s*) |
| Me(26) | 1.23 (*s*) | 1.72 (*s*) | 1.53 (*s*) | 1.66 (*s*) | 1.25 (*s*) | 1.66 (*s*) |
| Me(27) | 0.95 (*s*) | 1.12 (*s*) | 1.06 (*s*) | 1.08 (*s*) | 0,93 (*s*) | 1.09 (*s*) |
| Me(28) | 0.66 (*s*) | 0.68 (*s*) | 0.68 (*s*) | 0.82 (*s*) | 0.85 (*s*) | 0.68 (*s*) |

*Table 1* (cont.)

| | **1**[a]) | **2**[b]) | **3**[b]) | **4**[b]) | **5**[b]) | **6**[b]) |
|---|---|---|---|---|---|---|
| $CH_2$(29) | 4.66, 4.66 (2*d*, *J* = 6.0) | 4.62, 4.62 (2*d*, *J* = 14.5) | 4.69, 4.69 (2*d*, *J* = 13.5) | 4.64, 4.64 (2*d*, *J* = 14.0) | 4.70, 4.70 (2*d*, *J* = 13.0) | 4.63,4.63 (2*d*, *J* = 13.0) |
| Me(30) | 1.63 (*s*) | 1.63 (*s*) | 1.68 (*s*) | 1.63 (*s*) | 1.66 (*s*) | 1.63 (*s*) |
| $R^1$ or $R^3$ = AcO | | 2.06 (*s*) | 2.04 (*s*) | | 2.06 (*s*) | |
| $R^2$ = BzO or hexanoyl | | | | | | |
| H–C(2′) or $CH_2$(2′) | | 8.03 (*d*, *J* = 7.5) | 2.33–2.36 (*m*) | 8.05 (*d*, *J* = 7.5) | | 8.03 (*d*, *J* = 7.5) |
| H–C(3′) or $CH_2$(3′) | | 7.47 (*t*, *J* = 7.5) | 1.30–1.33 (*m*) | 7.48 (*t*, *J* = 7.5) | | 7.47 (*t*, *J* = 7.5) |
| H–C(4′) or $CH_2$(4′) | | 7.60 (*t*, *J* = 7.5) | 1.63–1.66 (*m*) | 7.60 (*t*, *J* = 7.5) | | 7.59 (*t*, *J* = 7.5) |
| H–C(5′) or $CH_2$(5′) | | 7.47 (*t*, *J* = 7.5) | 1.30–1.34 (*m*) | 7.48 (*t*, *J* = 7.5) | | 7.47 (*t*, *J* = 7.5) |
| H–C(6′) or Me(6′) | | 8.03 (*d*, *J* = 7.5) | 0.90 (*t*, *J* = 7.0) | 8.05 (*d*, *J* = 7.5) | | 8.03 (*d*, *J* = 7.5) |

[a]) Recorded in ($D_6$)DMSO at 500 MHz. [b]) Recorded in $CDCl_3$ at 500 MHz.

Table 2. *$^{13}$C-NMR Data for Compounds* **1**–**11**

| Position | **1**[a]) | **2**[b]) | **3**[b]) | **4**[b]) | **5**[b]) | **6**[b]) | **7**[a]) | **8**[b]) | **9**[b]) | **10**[a]) | **11**[b]) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 41.8 | 42.1 | 42.0 | 40.2 | 40.1 | 42.2 | 39.2 | 40.1 | 38.2 | 39.8 | 38.8 |
| 2 | 32.8 | 32.7 | 32.7 | 32.2 | 32.4 | 32.7 | 31.7 | 32.0 | 27.6 | 27.0 | 27.2 |
| 3 | 71.7 | 72.9 | 72.8 | 73.0 | 73.0 | 73.0 | 70.9 | 73.0 | 75.5 | 74.5 | 78.5 |
| 4 | 149.1 | 149.1 | 149.1 | 148.6 | 149.2 | 149.4 | 149.2 | 149.1 | 53.9 | 53.7 | 38.7 |
| 5 | 50.4 | 50.0 | 50.0 | 50.3 | 50.8 | 50.3 | 47.6 | 50.7 | 51.0 | 51.0 | 52.9 |
| 6 | 73.6 | 71.3 | 71.4 | 71.4 | 71. | 71.5 | 70.8 | 71.8 | 21.3 | 72.1 | 24.6 |
| 7 | 71.0 | 75.0 | 74.2 | 75.3 | 35.5 | 75.4 | 72.7 | 35.4 | 32.7 | 36.1 | 77.7 |
| 8 | 43.1 | 48.5 | 48.0 | 38.2 | 40.8 | 48.3 | 45.7 | 40.8 | 41.6 | 39.6 | 45.1 |
| 9 | 53.2 | 51.3 | 51.1 | 47.5 | 47.2 | 54.0 | 46.3 | 46.8 | 49.1 | 48.7 | 50.6 |
| 10 | 40.1 | 39.5 | 39.3 | 46.3 | 38.5 | 39.7 | 38.0 | 38.6 | 36.5 | 35.8 | 37.0 |
| 11 | 68.7 | 72.7 | 72.6 | 69.7 | 70.1 | 70.3 | 67.4 | 28.3 | 32.1 | 67.6 | 24.8 |
| 12 | 36.0 | 31.4 | 31.3 | 31.8 | 32.1 | 36.5 | 31.7 | 72.9 | 70.1 | 31.9 | 27.2 |
| 13 | 46.3 | 46.2 | 46.1 | 53.8 | 53.8 | 46.7 | 53.2 | 50.7 | 53.9 | 53.0 | 45.7 |
| 14 | 48.1 | 43.9 | 43.7 | 43.1 | 43.9 | 43.9 | 45.1 | 44.1 | 43.4 | 42.9 | 48.7 |
| 15 | 35.9 | 34.8 | 34.7 | 35.4 | 33.1 | 34.8 | 35.1 | 33.0 | 33.3 | 32.8 | 33.8 |
| 16 | 21.1 | 21.3 | 21.2 | 20.9 | 20.5 | 21.3 | 20.9 | 20.5 | 20.5 | 20.3 | 21.1 |
| 17 | 53.3 | 53.6 | 53.4 | 53.5 | 53.9 | 53.5 | 53.1 | 53.8 | 54.7 | 53.4 | 46.6 |
| 18 | 43.7 | 44.0 | 43.9 | 45.6 | 43.2 | 43.8 | 43.0 | 43.0 | 43.2 | 43.0 | 11.2 |
| 19 | 39.7 | 40.0 | 39.9 | 43.3 | 43.0 | 40.1 | 42.8 | 42.9 | 43.0 | 42.7 | 16.2 |
| 20 | 26.7 | 27.0 | 27.0 | 27.3 | 27.6 | 27.0 | 26.7 | 27.5 | 26.6 | 26.7 | 152.3 |
| 21 | 47.4 | 47.8 | 47.8 | 46.6 | 46.5 | 47.8 | 46.3 | 46.8 | 46.6 | 46.3 | 107.7 |
| 22 | 147.7 | 147.7 | 147.7 | 147.7 | 147.7 | 147.7 | 147.4 | 147.7 | 147.9 | 147.6 | 31.2 |
| 23 | 104.5 | 106.0 | 105.9 | 105.6 | 104.4 | 105.6 | 103.7 | 104.5 | 10.6 | 11.7 | 30.0 |
| 24 | | | | | | | | | 178.1 | 176.9 | 78.2 |
| 25 | 15.8 | 16.3 | 16.2 | 15.8 | 15.6 | 16.1 | 15.6 | 15.6 | 16.2 | 17.3 | 73.1 |
| 26 | 12.2 | 13.4 | 13.2 | 12.8 | 17.4 | 13.3 | 12.3 | 17.3 | 17.6 | 16.6 | 23.2 |
| 27 | 17.3 | 17.8 | 17.8 | 18.5 | 17.7 | 17.8 | 18.3 | 17.7 | 16.7 | 17.2 | 26.5 |
| 28 | 14.9 | 14.9 | 14.8 | 15.1 | 15.2 | 14.9 | 14.7 | 15.2 | 15.2 | 15.0 | 15.5 |
| 29 | 109.9 | 109.8 | 109.7 | 110.1 | 110.1 | 109.7 | 110.1 | 110.1 | 110.0 | 110.1 | 28.0 |
| 30 | 19.4 | 19.6 | 19.6 | 19.4 | 19.3 | 19.6 | 19.2 | 19.3 | 19.4 | 19.1 | 15.7 |
| $R^1$ or $R^3$ = AcO | | 170.0 | 169.9 | | 170.5 | | 169.9 | 170.5 | | 169.4 | |
| | | 22.1 | 22.0 | | 21.7 | | 20.9 | 21.7 | | 21.4 | |
| $R^2$ or $R^4$ = BzO or hexanoyl | | | | | | | | | | | |
| 1′ | | 130.1 | 172.8 | 130.1 | | 130.2 | 130.0 | 165.9 | | | 130.9 |
| 2′ | | 129.7 | 35.0 | 129.6 | | 129.6 | 129.0 | 130.8 | | | 129.5 |
| 3′ | | 128.7 | 24.3 | 128.7 | | 128.6 | 128.8 | 129.8 | | | 128.3 |
| 4′ | | 133.4 | 31.3 | 133.4 | | 133.3 | 133.2 | 128.4 | | | 132.7 |
| 5′ | | 128.7 | 22.3 | 128.7 | | 128.6 | 128.8 | 132.8 | | | 128.3 |
| 6′ | | 129.7 | 13.9 | 129.6 | | 129.6 | 129.0 | 128.4 | | | 129.5 |
| 7′ | | 165.4 | | 165.4 | | 165.5 | 164.6 | 129.8 | | | 165.7 |
| *Me*O–C(24) | | | | | | | | | 51.7 | 52.1 | |

[a]) Recorded in ($D_6$)DMSO at 125 MHz. [b]) Recorded in $CDCl_3$ at 125 MHz.

the H–C(7) signal ($\delta$(H) 5.05 (*d*, $J = 4.0$)) with the signal of C(1′) ($\delta$(C) 172.8), suggesting that the caproyloxy group was located at C(7). Thus, the structure of compound **3** was determined as 11$\alpha$-(acetyloxy)-7$\beta$-(caproyloxy)-21$\alpha H$-24-norhopa-4(23),22(29)-diene-3$\beta$,6$\beta$-diol.

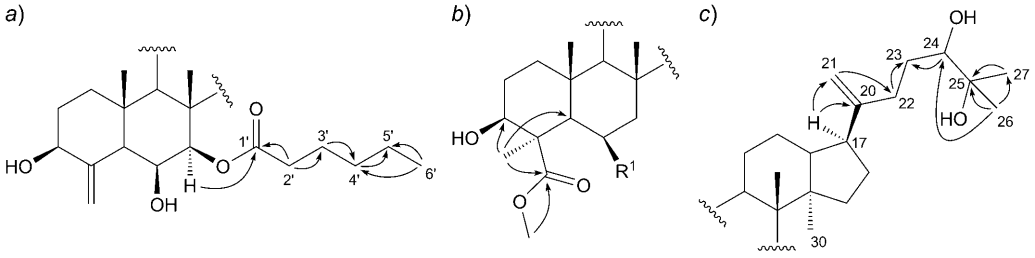



Fig. 3. a) *HMBCs* (H → C) *of substituent* ($R^2$) *of compound* **3**. b) *Significant HMBCs* (H → C) *of compounds* **9** *and* **10**. c) *Significant HMBCs of compound* **11**.

The compounds **9** and **10** were both obtained as white amorphous powder (MeOH). $^1$H- and $^{13}$C-NMR data (*Tables 3* and *2*, resp.) showed a signal for an additional CH−O group and a high-field Me signal compared with those of 2$\beta$-hydroxy-21$\beta H$-hop-22(29)-ene-24-oic acid [8]. In the HMBC spectrum of compound **9**, the H−C(3) signal ($\delta$(H) 3.98 (*m*)) correlated with the signals of Me(23) ($\delta$(C) 178.1, 10.6), indicating the presence of HO−C(3) instead of HO−C(2) as reported. The high-field Me signal at $\delta$(H) 3.71 (MeO) correlated with those of C(4) ($\delta$(C) 178.1, 53.9), suggesting that the MeOCO group was located at C(4) (*Fig. 3*,*b*), as determined also for compound **10**. On the basis of the $^1$H,$^1$H-COSY correlations between the signals at $\delta$(H) 3.98 (*m*, H−C(12)) and 1.02 (*s*, H−C(13)), the OH group of compound **9** was located at C(12). For compound **10**, the HO−C(11) of was confirmed through the correlation between the signals at $\delta$(H) 3.70 (*m*, H−C(11)) and 1.38 (*m*, H−C(13)) in the $^1$H,$^1$H-COSY spectrum, and the AcO group was located at C(6) according to the correlation between the signals at $\delta$(H) 4.70 (*m*, H−C(6)) and $\delta$(C) 169.4 (C(1′)) in the HMBC spectrum. Thus, compound **9** was established as methyl 3$\beta$,12$\beta$-dihydroxy-21$\alpha H$-hop-22(29)-en-24-oate and compound **10** as methyl 3$\beta$,11$\beta$-dihydroxy-6$\beta$-acetyloxy-21$\alpha H$-hop-22(29)-en-24-oate.

Compound **11** was obtained as yellow amorphous powder (MeOH), and its $^1$H- and $^{13}$C-NMR spectra were similar to those of (24*S*)-dammar-20-ene-3$\beta$,24,25-triol [9], the only difference in $^{13}$C-NMR being signals at $\delta$(C) 165.7 (C(1′)), 130.9 (C(2′)), 129.5 (C(3′)), and signals corresponding to C(7′) ($\delta$(C) 129.5, $\delta$(H) 8.03 (*d*, $J = 7.5$)), C(4′) ($\delta$(C) 128.3) and C(6′) ($\delta$(C) 128.3, $\delta$(H) (7.47 (*t*, $J = 7.5$)), and C(5′) ($\delta$(C) 132.7, $\delta$(H) (7.59 (*t*, $J = 7.5$)), which strongly indicated the presence of a BzO group. The location of the BzO group at C(7) was supported by the correlation between the signals of H−C(7) and C(1′) in the HMBC spectrum (*Fig. 3*,*c*). The correlation between $H_\alpha$−C(17) and Me(30) displayed in NOESY experiment confirmed the configuration of H−C(17) as $\alpha$. Thus, the structure of compound **11** was elucidated as 7$\beta$-(benzoyloxy)dammar-20(21)-ene-3$\beta$,24$\xi$,25-triol.

The orientations of the substituents of compounds **2**, **3**, and **4** were all the same as the compound **1**. For the compounds **6** and **7**, the configuration of H−C(11) was revealed as $\alpha$, since no correlations were observed between the H−C(11), and Me(25) and Me(26). For the compounds **5**, **8**, **9**, and **10**, the configuration of H−C(12) were determined as $\alpha$ on the basis of the significant correlations between H−C(12), and

Table 3. *$^1$H-NMR Data of Compounds* **7**–**11**

| | **7**[a]) | **8**[b]) | **9**[b]) | **10**[a]) | **11**[b]) |
|---|---|---|---|---|---|
| $CH_2$(1) | 1.79–1.81, 2.50–2.53 (2*m*) | 1.19–1.21, 1.79–1.82 (2*m*) | 1.06–1.08, 1.73–1.76 (2*m*) | 1.06–1.09, 1.60–1.62 (2*m*) | 0.96–0.98, 1.71–1.73 (2*m*) |
| $CH_2$(2) | 1.78–1.81, 1.90–1.93 (2*m*) | 1.46–1.48, 1.96–1.98 (2*m*) | 1.46–1.48, 1.85–1.88 (2*m*) | 1.31–1.33, 1.70–1.74 (2*m*) | 1.64–1.66, 1.83–1.86 (2*m*) |
| H–C(3) | 3.82 (*dd*, *J* = 11.0, 5.0) | 3.98 (*dd*, *J* = 11.0, 5.0) | 3.98 (overlap) | 3.74 (overlap) | 3.25 (*dd*, *J* = 11.5, 4.5) |
| H–C(5) | 2.20 (*s*) | 1.78 (*s*) | 1.45 (*s*) | 1.48 (*s*) | 0.94 (*s*) |
| H–C(6) or $CH_2$(6) | 5.55 (*dd*, *J* = 2.0, 1.0) | 5.35–5.38 (*m*) | 1.01–1.03, 1.55–1.58 (2*m*) | 4.68–4.71 (*m*) | 1.65–1.68, 1.87–1.91 (2*m*) |
| H–C(7) or $CH_2$(7) | 5.24 (*d*, *J* = 4.0) | 1.77, 1.69 (overlap) | 1.21–1.23, 1.40–1.43 (2*m*) | 1.49, 1.41 (*d*, *J* = 4.0) | 5.30 (*dd*, *J* = 11.0, 4.5) |
| H–C(9) | 1.67 (*s*) | 1.67 (*s*) | 1.40 (overlap) | 1.38 (*d*, *J* = 1.0) | 1.36 (*s*) |
| H–C(11) or $CH_2$(11) | 3.70–3.74 (*m*) | 1.46–1.48, 1.95–1.98 (2*m*) | 1.32–1.35, 1.86–1.89 (2*m*) | 3.68–3.71 (*m*) | 1.04–1.06, 1.57–1.60 (2*m*) |
| $CH_2$(12) or H–C(12) | 1.74–1.79 (*m*) | 5.52–5.55 (*m*) | 3.96–3.99 (*m*) | 1.36–1.38, 1.73–1.76 (2*m*) | 1.64–1.66, 1.82–1.86 (2*m*) |
| H–C(13) | 1.42 (overlap) | 2.01 (*d*, *J* = 1.0) | 1.02 (*s*) | 1.35–1.38 (*m*) | 1.63–1.66 (*m*) |
| $CH_2$(15) | 0.80–0.82, 1.45–1.48 (2*m*) | 1.22–1.25, 1.41–1.44 (2*m*) | 1.16–1.19, 1.33–1.36 (2*m*) | 1.02–1.05, 1.25–1.29 (2*m*) | 0.97–0.99, 1.75–1.78 (2*m*) |
| $CH_2$(16) | 1.02–1.07 (*m*) | 1.18–1.20, 1.42–1.45 (2*m*) | 1.16–1.18, 1.39–1.43 (2*m*) | 1.23–1.27 (*m*) | 1.34–1.36, 1.57–1.60 (2*m*) |
| H–C(17) | 0.86–0.89 (*m*) | 1.06–1.08 (*m*) | 1.36–1.40 (*m*) | 0.90–0.92 (*m*) | 2.11–2.13 (*m*) |
| Me(18) | | | | | 1.25 (*s*) |
| $CH_2$(19) or Me(19) | 1.36–1.38, 1.87–1.90 (2*m*) | 1.40–1.42, 1.49–1.51 (2*m*) | 1.30–1.33, 1.82–1.85 (2*m*) | 1.20–1.24, 1.85–1.88 (2*m*) | 0.88–0.91, 0.92–0.95 (2*m*) |
| $CH_2$(20) | 1.30–1.32, 1.69–1.72 (2*m*) | 1.40–1.42, 1.69–1.72 (2*m*) | 1.60–1.62, 1.68–1.71 (2*m*) | 1.52–1.55 (*m*) | |
| H–C(21) or $CH_2$(21) | 2.04–2.07 (*m*) | 2.13–2.16 (*m*) | 2.19–2.21 (*m*) | 2.11–2.14 (*m*) | 1.98–2.00, 2.22–2.25 (2*m*) |
| $CH_2$(22) | | | | | 1.42–1.44, 1.58–1.61 (2*m*) |
| $CH_2$(23) or Me(23) | 5.07, 4.36 (*s*) | 5.17, 4.67 (*s*) | 1.12 (*s*) | 1.17 (*s*) | |
| H–C(24) | | | | | 3.37 (*d*, *J* = 10.5) |
| Me(25) | 0.97 (*s*) | 1.00 (*s*) | 0.87 (*s*) | 1.13 (*s*) | |
| Me(26) | 1.51 (*s*) | 1.34 (*s*) | 0.99 (*s*) | 1.08 (*s*) | 1.15 (*s*) |
| Me(27) | 1.00 (*s*) | 1.04 (*s*) | 0.96 (*s*) | 0.85 (*s*) | 1.20 (*s*) |
| Me(28) | 0.72 (*s*) | 0.78 (*s*) | 0.84 (*s*) | 0.75 (*s*) | 0.77 (*s*) |
| $CH_2$(29) or Me(29) | 4.58, 4.58 (*d*, *J* = 14.0) | 4.69, 4.69 (*d*, *J* = 13.0) | 4.71, 4.71 (*d*, *J* = 16.0) | 4.65, 4.66 (*s*) | 1.01 (*s*) |
| Me(30) | 1.56 (*s*) | 1.66 (*s*) | 1.67 (*s*) | 1.60 (*s*) | 0.94 (*s*) |
| AcO–C(6) | 1.96 (*s*) | 2.07 (*s*) | | 1.99 (*s*) | |
| $R^2$ or $R^4$ = BzO | | | | | |
| H–C(2′,6′) | 7.87 (*d*, *J* = 7.5) | 8.07 (*d*, *J* = 7.5) | | | 8.01 (*d*, *J* = 7.5) |
| H–C(3′,5′) | 7.45 (*t*, *J* = 7.5) | 7.45 (*t*, *J* = 7.5) | | | 7.45 (*t*, *J* = 7.5) |
| H–C(4′) | 7.63 (*t*, *J* = 7.5) | 7.56 (*t*, *J* = 7.5) | | | 7.55 (*t*, *J* = 7.5) |
| MeO–C(24) | | | 3.71 (*s*) | 3.55 (*s*) | |

[a]) Recorded in ($D_6$)DMSO at 500 MHz. [b]) Recorded in $CDCl_3$ at 500 MHz.

Me(27) and Me(28). The configuration of Me(23) at C(4) of **9** and **10** was determined as $\alpha$ through the correlations between $H_\alpha$–C(3), $H_\alpha$–C(5), and Me(23) (*Fig. 3*,*b*).

The murine hepatoma cell line Hepa 1c1c7 was employed to test the induction of NAD(P)H:quinone reductase (QR). Activity is expressed by the concentration to double (*CD*) QR activity over basal levels, and toxicity is expressed as the concentration to kill 50% of the cells ($IC_{50}$). Nine compounds except **5** and **10** were tested for QR induction activities *in vitro*, and the results revealed that compounds **2**, **4**, and **7** exhibited moderate induction activities with *CD* values of 8.62, 9.13, and 2.56 μg/ml, respectively. On the other hand, we found that compounds **6** and **8** exhibited strong cytotoxicity against hepa 1c1c7 cell line with $IC_{50}$ values of no more than 1 μg/ml.

2.2. *Isomer Differentiation.* Compounds **4** and **6** were isomers with the same molecular weight, and they were different only in the configuration of HO–C(11), as shown in *Fig. 4*,*a*. It was not easy to obtain the *quasi*-molecular ions, and there were no differences in MS fragmentation pathways of **4** and **6**; however their silver complexes made a differentiation possible. In the mass spectra of **4** and **6**, the dominant ion were peaks at *m*/*z* 671 ($[M+{}^{109}Ag]^+$; *Fig. 4*,*b*), and their $MS^2$ and $MS^3$ were similar with dominant ion peaks at *m*/*z* 549 ($[M+{}^{109}Ag-C_7H_6O_2]^+$) and 531 ($[M+{}^{109}Ag-C_7H_6O_2-H_2O^+$). The mass difference between the ions at *m*/*z* 671 and 549 is 122 Da, due to the loss of one benzoyloxy group. The ion corresponding to *m*/*z* 531 was derived from the loss of one molecule of $H_2O$ from the ion with the peak at *m*/*z* 549. When subjecting the ion at *m*/*z* 531 to $MS^4$, silver complex of compound **4** yielded the fragment-ion peak at *m*/*z* 377 ($[M-C_7H_6O_2-H_2O-H_2O-C_2H_3]^+$), with the 50% abundance of the peak at *m*/*z* 513 ($[M+{}^{109}Ag-C_7H_6O_2-H_2O-H_2O]^+$); however, silver complex of compound **6** led to the peaks at *m*/*z* 513 and 501 ($[M+{}^{109}Ag-C_7H_6O_2-H_2O-CH_2O]^+$), with only 10% abundance of the peak at *m*/*z* 377. These two fragmentation pathways had distinct differences and were sufficient to distinguish the two isomers, as shown in *Fig. 4*. We could hypothesize that the conformation of silver complexes of these two compounds were related with the configuration of HO–C(11).

Compounds **2** and **7** were another pair of isomers. Compound **2** was substituted with a benzoyloxy group at C(7) and an AcO group at C(11), while compound **7** was substituted with an AcO group at C(6) and a benzoyloxy group at C(7), and the configuration at C(11) was different. It was assumed that $MS^n$ spectra of silver complexes of compounds **2** and **7** would be different from each other. The mass spectra of silver complexes of both presented the peaks at *m*/*z* 713 ($[M+{}^{109}Ag]^+$), and this peak was selected for $MS^2$ analysis. In the $MS^2$ spectra, both of them revealed the predominant ion peaks at *m*/*z* 531 ($[M+{}^{109}Ag-C_7H_6O_2-C_2H_4O_2^+$) due to the loss of BzOH and AcOH. However, the ion corresponding to the peak at *m*/*z* 591 ($[M+{}^{109}Ag-C_7H_6O_2]^+$) observed in the $MS^2$ (*m*/*z* 713) spectrum of compound **2** has 50% abundance, and the ion ascribed to the peak at *m*/*z* 377 ($[M+{}^{109}Ag-C_7H_6O_2-C_2H_4O_2-H_2O-C_2H_3]^+$) observed in the $MS^3$ (*m*/*z* 531) spectrum of compound **2** has 28% abundance, differing from those in the $MS^2$ and $MS^3$ spectra of compound **7**. The ion corresponding to the peak at *m*/*z* 513, which was dominant in the $MS^3$ spectra of ions with peaks at *m*/*z* 653, 591, 531, was subjected to $MS^4$, and both of compounds **2** and **7** gave the ion peak at *m*/*z* 495. In the $MS^5$ spectrum of the ion with the peak at *m*/*z* 495 ($[M+{}^{109}Ag-C_7H_6O_2-C_2H_4O_2-H_2O-H_2O]^+$), silver ion was much easier to

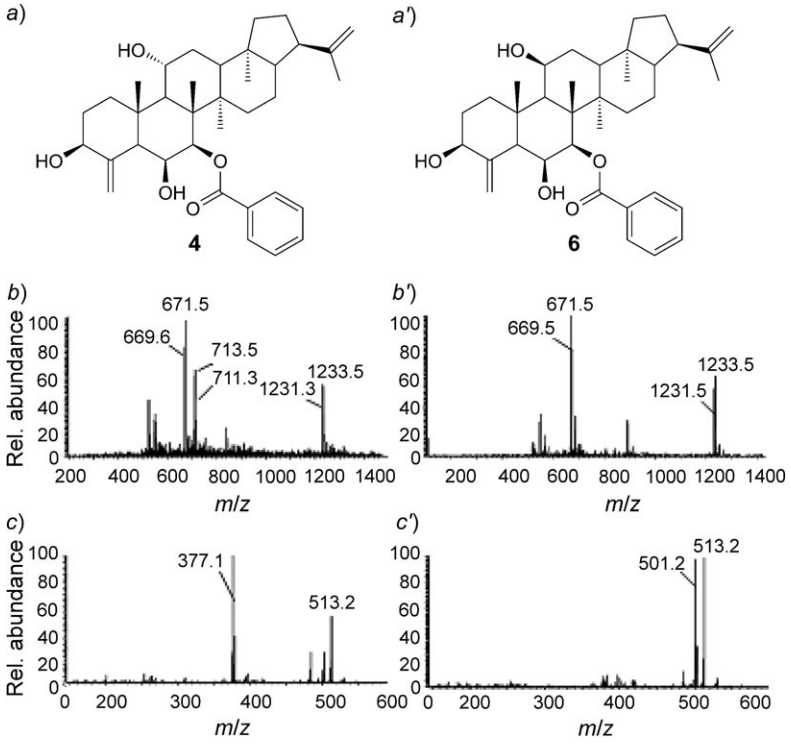



Fig. 4. *ESI-MS*$^n$ *Spectra of silver/triterpenoid* 1:1 (*v*/*v*) *complexes of compounds* **4** *and* **6**. *a*) Structure of **4**; *a'*) structure of **6**; *b*) full-scan MS of silver complex of **4**; *b'*) full-scan MS of silver complex of **6**; *c*) $MS^4$ of ion at *m*/*z* 531 of **4**; *c'*) $MS^4$ of ion at *m*/*z* 531 of **6**.

break away from the complex of compound **7** than from **2** to give the ion peak at *m*/*z* 386 ($[M - C_7H_6O_2 - C_2H_4O_2 - H_2O - H_2O]^+$). These two distinct differences in their dissociation patterns, which were supposed to be related with the silver ion complexing with O–C(6) or O–C(11), were sufficient to differentiate compound **2** from compound **7** (*Fig. 5*).

## Experimental Part

*General.* Column chromatography (CC): medium-pressure liquid chromatography (MPLC) *Büchi B-688* system; column-layer chromatography: silica gel ($SiO_2$; *Qingdao Puke Parting Materials Co.*). Prep. HPLC: *Agilent 1200* system with a photodiode array detector using a *ZORBAX-C*$_{18}$ column (7 μm, *ODS*, 250 × 21.2 mm). Optical rotations: *JASCO P-1010* polarimeter. IR Spectra: *JASCO FTIR4100*. 1D- and 2D- (HSQC, HMBC, COSY, NOESY) NMR spectra: *Bruker 500* MHz *Ultra-Shield Plus* spectrometer. ESI-MS: *LCQ DECA* system (*Thermofinnigan*) equipped with a hot ESI source (HESI; electrospray voltage: 3.0 kV, sheath gas: $N_2$, vaporizer temp.: 50°, capillary temp.: 250°, collision gas: Ar, collision pressure: 1.5 mTorr).

*Plant Material.* See [3].

*Extraction and Isolation.* The air-dried pieces of the twigs (15.0 kg) were extracted with 95% EtOH (3 × 45 l) to give a crude extract, which was dissolved in the distilled $H_2O$ to give a suspension, and the

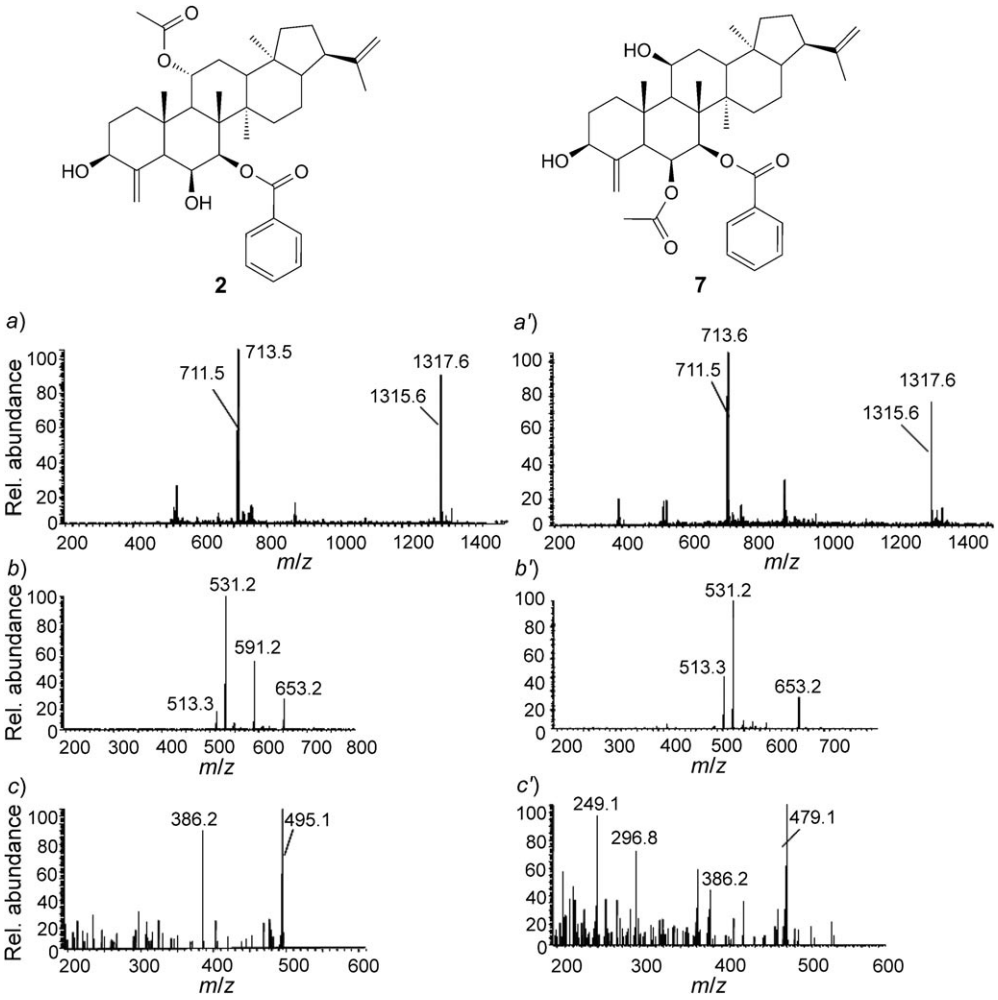



Fig. 5. *ESI-MS*$^n$ *Spectra of silver/triterpenoid 1 : 1* (*v*/*v*) *complexes of compounds* **2** *and* **7**. *a*) Full-scan MS of silver complex of **2**; *a′*) full-scan MS of silver complex of **7**; *b*) MS$^2$ of ion at *m*/*z* 713 of **2**; *b′*) MS$^2$ of ion at *m*/*z* 713 of **7**; *c*) MS$^5$ of ion at *m*/*z* 495 of **2**; *c′*) MS$^5$ of ion at *m*/*z* 495 of **7**.

suspension was extracted with petroleum ether (PE; 3 × 1 l), $CH_2Cl_2$ (4 × 1 l), AcOEt (4 × 1.5 l), and BuOH (3 × 1 l), successively. The $CH_2Cl_2$ fraction (50 g) was subjected to chromatography ($SiO_2$; PE/AcOEt 8 : 1, 5 : 1, 3 : 1, 2 : 1 (*v*/*v*)), to afford a complex mixture, which, following RP-HPLC with MeCN/$H_2O$, led to the isolation of cavalerols A – K (**1** – **11**, resp.): gradient 50 : 50 – 100 : 0 in 50 min, 8 ml/min: **1** (6.5 mg; $t_R$ 25 min) and **2** (5.7 mg; $t_R$ 44 min); gradient 50 : 50 – 90 : 10 in 40 min, 8 ml/min: **3** (8.5 mg; $t_R$ 40 min); gradient 70 : 30 – 100 : 0 in 20 min, 10 ml/min: **4** (12.3 mg; $t_R$ 16 min) and **5** (3.1 mg; $t_R$ 25 min); gradient 85 : 15 – 90 : 10 in 25 min, 10 ml/min: **6** (10.1 mg; $t_R$ 25.5 min), **7** (7.3 mg; $t_R$ 27 min), and **8** (8.2 mg; $t_R$ 22.5 min); gradient 20 : 80 – 88 : 12 in 40 min, 10 ml/min, and reaching 100 : 0 in 1 min: **9** (6.9 mg; $t_R$ 53.5 min) and **10** (5.4 mg; $t_R$ 57.5 min); and 100 : 0, 10 ml/min: **11** (8.7 mg; $t_R$ 17 min).

*Cavalerol A* (=(*3*R,*5a*R,*5b*R,*6*R,*7*S,*9*S,*11a*R,*12*R,*13b*S)*-Icosahydro-5a,5b,11a,13b-tetramethyl-8-methylidene-3-(prop-1-en-2-yl)-1*H*-cyclopenta[*a*]chrysene-6,7,9,12-tetrol*; **1**). White amorphous powder

(MeOH). $[\alpha]_D = +70.6$ ($c = 0.5$, MeOH). IR (MeOH): 3373, 2942, 2832, 1450, 1390. $^1$H- and $^{13}$C-NMR: see *Table 1* and *2*, resp. HR-ESI-MS: 463.2536 ($[M - H_2O + Na]^+$, $C_{29}H_{44}NaO_3^+$; calc. 463.3188).

*Cavalerol B* (=(*3*R,*5a*R,*5b*R,*6*R,*7*S,*9*S,*11a*S,*12*R,*13b*S)*-12-(Acetyloxy)icosahydro-7,9-dihydroxy-5a,5b,11a,13b-tetramethyl-8-methylidene-3-(prop-1-en-2-yl)-1*H*-cyclopenta[*a*]chrysen-6-yl Benzoate*; **2**). White amorphous powder (MeOH). $[\alpha]_D = +20.7$ ($c = 1.1$, MeOH). IR (MeOH): 3444, 2946, 2832, 1643, 1450, 1390. $^1$H- and $^{13}$C-NMR: see *Table 1* and *2*, resp. HR-ESI-MS: 627.3703 ($[M + Na]^+$, $C_{38}H_{52}NaO_6^+$; calc. 627.3662).

*Cavalerol C* (=(*3*R,*5a*R,*5b*R,*6*R,*7*S,*9*S,*11a*S,*12*R,*13b*S)*-12-(Acetyloxy)icosahydro-7,9-dihydroxy-5a,5b,11a,13b-tetramethyl-8-methylidene-3-(prop-1-en-2-yl)-1*H*-cyclopenta[*a*]chrysen-6-yl Hexanoate*; **3**). Yellow amorphous powder (MeOH). $[\alpha]_D = +10.7$ ($c = 0.5$, MeOH). IR (MeOH): 3400, 3392, 2831, 1454, 1410. $^1$H- and $^{13}$C-NMR: see *Table 1* and *2*, resp. HR-ESI-MS: 621.4129 ($[M + Na]^+$, $C_{37}H_{58}NaO_6^+$; calc. 621.4131).

*Cavalerol D* (=(*3*R,*5a*R,*5b*R,*6*R,*7*S,*9*S,*11a*R,*12*R,*13b*S)*-Icosahydro-7,9,12-trihydroxy-5a,5b,11a,13b-tetramethyl-8-methylidene-3-(prop-1-en-2-yl)-1*H*-cyclopenta[*a*]chrysen-6-yl Benzoate*; **4**). White amorphous powder (MeOH). $[\alpha]_D = +56.7$ ($c = 0.7$, MeOH). IR (MeOH): 3420, 3385, 2942, 2831, 1450, 1410. $^1$H- and $^{13}$C-NMR: see *Table 1* and *2*, resp. HR-ESI-MS: 585.3561 ($[M + Na]^+$, $C_{36}H_{50}NaO_5^+$; calc. 585.3556).

*Cavalerol E* (=(*3*R,*5a*R,*5b*R,*7*R,*9*S,*11a*R,*13*R,*13b*S)*-Icosahydro-9,13-dihydroxy-5a,5b,11a,13b-tetramethyl-8-methylidene-3-(prop-1-en-2-yl)-1*H*-cyclopenta[*a*]chrysen-7-yl Acetate*; **5**). White amorphous powder (MeOH). $[\alpha]_D = +4.3$ ($c = 0.5$, MeOH). IR (MeOH): 3430, 2942, 2832, 1450, 1410. $^1$H- and $^{13}$C-NMR: see *Table 1* and *2*, resp. HR-ESI-MS: 489.2849 ($[M - H_2O + Na]^+$; $C_{31}H_{46}NaO_3^+$; calc. 489.3345).

*Cavalerol F* (=(*3*R,*5a*R,*5b*R,*6*R,*7*S,*9*S,*11a*R,*12*S,*13b*S)*-Icosahydro-7,9,12-trihydroxy-5a,5b,11a,13b-tetramethyl-8-methylidene-3-(prop-1-en-2-yl)-1*H*-cyclopenta[*a*]chrysen-6-yl Benzoate*; **6**). White amorphous powder (MeOH). $[\alpha]_D = +25.6$ ($c = 2.00$, MeOH). IR (MeOH): 3355, 2945, 2832, 1450, 1410. $^1$H- and $^{13}$C-NMR: see *Table 1* and *2*, resp. HR-ESI-MS: 585.3549 ($[M + Na]^+$, $C_{36}H_{50}NaO_5^+$; calc. 585.3556).

*Cavalerol G* (=(*3*R,*5a*R,*5b*R,*6*R,*7*S,*9*S,*11a*R,*12*S,*13b*S)*-7-(Acetyloxy)icosahydro-9,12-dihydroxy-5a,5b,11a,13b-tetramethyl-8-methylidene-3-(prop-1-en-2-yl)-1*H*-cyclopenta[*a*]chrysen-6-yl Benzoate*; **7**). Yellow amorphous powder (MeOH). $[\alpha]_D = +17.9$ ($c = 0.70$, MeOH). IR (MeOH): 3400, 2945, 2832, 1650, 1450, 1410. $^1$H- and $^{13}$C-NMR: see *Table 3* and *2*, resp. HR-ESI-MS: 587.5499 ($[M - H_2O + H]^+$, $C_{38}H_{51}O_5^+$; calc. 587.3736).

*Cavalerol H* (=(*3*R,*5a*R,*5b*R,*7*R,*9*S,*11a*R,*13*R,*13b*S)*-7-(Acetyloxy)-9-hydroxy-5a,5b,11a,13b-tetramethyl-8-methylidene-3-(prop-1-en-2-yl)icosahydro-1*H*-cyclopenta[*a*]chrysen-13-yl benzoate*; **8**). Yellow amorphous powder (MeOH). $[\alpha]_D = +16.0$ ($c = 0.5$, MeOH). IR (MeOH): 3400, 2947, 2832, 1645, 1450, 1410. $^1$H- and $^{13}$C-NMR: see *Table 3* and *2*, resp. HR-ESI-MS: 611.3713 ($[M + Na]^+$, $C_{38}H_{52}NaO_5^+$; calc. 611.3712).

*Cavalerol I* (=*Methyl (3β,12β,17ξ,21β)-3,12-Dihydroxyhop-22(29)-en-24-oate*; **9**). White amorphous powder (MeOH). $[\alpha]_D = +82.7$ ($c = 0.8$, MeOH). IR (MeOH): 3418, 2947, 2832, 1644, 1450, 1410. $^1$H- and $^{13}$C-NMR: see *Table 3* and *2*, resp. HR-ESI-MS: 509.3625 ($[M + Na]^+$, $C_{31}H_{50}NaO_4^+$; calc. 509.3607).

*Cavalerol J* (=*Methyl (3β,6β,11β,17ξ,21β)-6-(Acetyloxy)-3,11-dihydroxyhop-22(29)-en-24-oate*; **10**). White amorphous powder (MeOH). $[\alpha]_D = -7.1$ ($c = 2.0$, MeOH). IR (MeOH): 3452, 2947, 2832, 1663, 1450. $^1$H- and $^{13}$C-NMR: see *Table 3* and *2*, resp. HR-ESI-MS: 518.3255 ($[M - H_2O - MeO + Na]^+$, $C_{32}H_{47}NaO_4^+$; calc. 518.3372).

*Cavalerol K* (=*(3β,7β)-3,24,25-Trihydroxydammar-20-en-7-yl Benzoate*; **11**). Yellow amorphous powder (MeOH). $[\alpha]_D = +13.46$ ($c = 1.3$, MeOH). IR (MeOH): 3355, 2945, 2832, 1644, 1451, 1410. $^1$H- and $^{13}$C-NMR: see *Table 3* and *2*, resp. HR-ESI-MS: 603.4045 ($[M + Na]^+$, $C_{37}H_{56}NaO_5^+$; calc. 603.4025).

*Cell Culture, Crystal Violet Assay for Determining Cell Viability, and NQO1 Induction Assay.* See [3] and [10].

*Preparation of Triterpene Solns. and Silver Complexes.* All the stock solns. of triterpenes ($1 \times 10^{-3}$ M) and silver nitrate ($5 \times 10^{-3}$ M), as well as the working soln. of silver/triterpene 1:1 (*v*/*v*) complexes were prepared in HPLC-grade MeOH.

*$MS^n$ Analysis of the Triterpenes and Silver Complexes.* See [5].

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