New Long-Chain Esters and Adenine Analogs from the Leaves of Formosan *Bridelia balansae*

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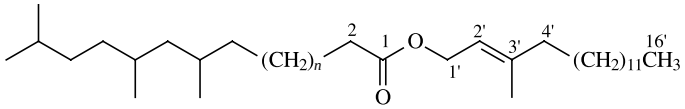
Six new compounds, including the two long-chain esters balansenate I (= 6,8,11-trimethyldodecanoic acid (2*E*)-3-methylhexadec-2-enyl ester; **1**) and balansenate II (= 10,12,15-trimethylhexadedecanoic acid (2*E*)-3-methylhexadec-2-enyl ester; **2**), the eburicane-like triterpenoid bridelone (= hexadecahydro-4,4,10,13,14-pentamethyl-17-(5-methyl-1,4-dimethylenehexyl)-3*H*-cyclopenta[*a*]phenanthren-3-one; **3**), the 'deimino-xanthine', bridelonine (= 5-(3-methylbut-2-enyl)pyrrolo[3,4-*d*]imidazole-4,6(1*H*,5*H*)-dione; **6**), and the two adenine analogs 9-(3-methylbut-2-enyl)adenine (**7**) and 1-(3-methylbut-2-enyl)adenine (**8**), besides three known compounds, *i.e.*, N^6-(3-methylbut-2-enyl)adenine (**4**), 3-(3-methylbut-2-enyl)adenine (**5**), and adenine (**9**), were isolated from the leaves of Formosan *Bridelia balansae*. The novel skeleton of **6** consists of a fused pyrrolidine-2,5-dione and imidazole moiety. The already known adenines **7** and **8** were isolated for the first time from a plant. The structures of the isolated compounds were elucidated by spectroscopic analyses.

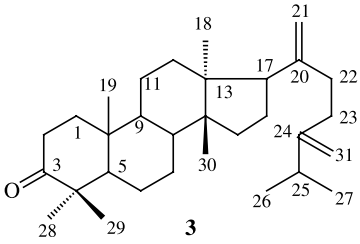
Introduction. – *Bridelia balansae* TUTCH (Euphorbiaceae) is a small tree distributed in Indo-China, southern China, the Ryukyus, and Taiwan [1]. Its leaves are used as an antitussive to treat bronchitis in China [2]. The chemical constituents of *Bridelia* genus plants have been previously reported to contain triterpenoids, flavonoids, benzenoids, tannins, green pigments, *etc.* [3–12]. Nevertheless, phytochemical studies of this species have never been conducted. Our investigation of the leaves of Formosan *B. balansae* led to the isolation of compounds **1**–**5** from the $CHCl_3$-soluble part and of compounds **6**–**9** from the BuOH-soluble part. Compounds **1**–**3** and **6** were new compounds from a natural source. Adenines **7** [13][14] and **8** [15], which were synthesized before, were isolated for the first time from a plant. Adenine **4** had been previously obtained from a genus *Castanea* [16] plant and the pathogen *Pseudomonas* [17]. We describe the isolation and structural elucidation of these compounds.

Results and Discussion. – Balansenate I (**1**) and II (**2**) were obtained as colorless oils with laevorotatory optical activity. The molecular formula of **1** was determined as $C_{32}H_{62}O_2$ and of **2** as $C_{36}H_{70}O_2$ by the EI-MS and HR-EI-MS, respectively. The structure of **1** was elucidated to be 6,8,11-trimethyldodecanoic acid (2*E*)-3-methylhexadec-2-enyl ester, and **2** was determined as 10,12,15-trimethylhexadecanoic acid (2*E*)-3-methylhexadec-2-enyl ester, as corroborated by the MS, IR, and ^{1}H- and ^{13}C-NMR spectra and the DEPT, COSY, HETCOR, HMBC, and NOESY (*Fig.*) experiments.

The IR spectra of **1** and **2** shows the ester absorption near 1730 cm^{-1} [18]. The MS of **1** and **2** exhibit the same fragments at *m/z* 296, 278, and 123 suggesting the presence of the 3-methylhexadec-2-enyl ester moiety.



1, $n = 2$
2, $n = 6$



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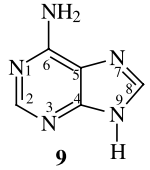

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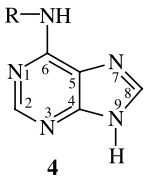

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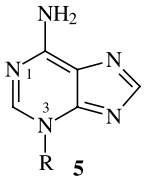

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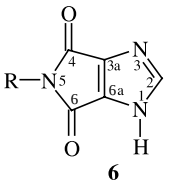

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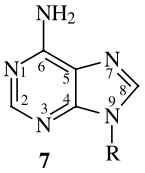

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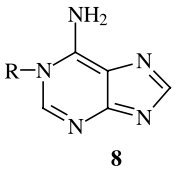

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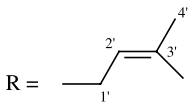

The fragment at *m/z* 296 ($[CH_3(CH_2)_{12}C(CH_3)=CHCH_2OC(OH)=CH_2]^+$) is probably due to a C(2)–C(3) bond cleavage induced by a *McLafferty* rearrangement of the ester group dehydration yields then the fragment at *m/z* 278 ($[(CH_2)_{13}C(CH_3)=CHCH_2OC=CH_2]^+$), and the base peak is at *m/z* 123 ($[(CH_2)_2C(CH_3)=CHCH_2OC=CH_2-1]^+$). The NOE correlations $CH_2(1')$/Me–C(3′) and H–C(2′)/$CH_2(4')$ confirm the (*E*)-configuration of C(2′)=C(3′) in **1** and **2**. The ^{1}H-NMR features of **1** are similar to those of **2**, except that **2** has four more CH_2 units, as also confirmed by the MS. Furthermore, the ^{13}C-NMR spectra of both **1** and **2** show the signals of C(1′) and C(1) at δ 61.2 and 173.9, respectively, and of the olefinic C(2′)=C(3′) at δ 118.1 and 142.5, respectively.

The ^{1}H-NMR signal of **1** at δ 2.00 (br. *t*, $J = 7.2$ Hz), shifted downfield by the neighboring C(2′)=C(3′) bond, is assigned to $H_2(4')$. The signals at δ 5.33 (*tq*, $J = 7.2$, 1.2 Hz), 4.58 (*d*, $J = 7.2$ Hz), and 1.69 (*d*, $J = 1.2$ Hz) are assigned to H–C(2′), $CH_2(1')$, and Me–C(3′), respectively. The ^{1}H-NMR spectrum of **2** also shows similar signals at δ 2.00, 5.34, 4.59, and 1.69 due to $CH_2(4')$, H–C(2′), $CH_2(1')$, and Me–C(3′), respectively.

Bridelone (**3**) was obtained as colorless prisms with dextrorotatory optical activity. Its molecular formula was established as $C_{31}H_{50}O$ by the EI-MS (M^+ at *m/z* 438) and HR-EI-MS. From the spectral evidence, the structure of **3** was elucidated to be

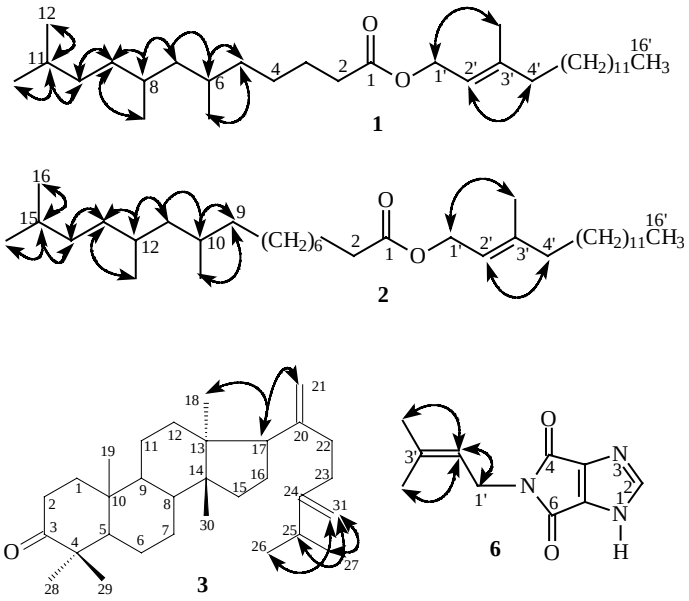

Figure. *NOESY Correlations of* **1**–**3** *and* **6**

hexadecahydro-4,4,10,13,14-pentamethyl-17-(5-methyl-1,4-dimethylenehexyl)-3*H*-cyclopenta[*a*]phenanthren-3-one (lanostane numbering), which was further confirmed by the DEPT, COSY, HETCOR, HMBC, and NOESY (*Fig.*) experiments.

The IR spectrum of **3** shows the carbonyl absorption at 1704 cm^{-1}. Analysis of the ^1H- and ^{13}C-NMR spectra allows to deduce the presence of an eburicane-like skeleton, but with 31 C-atoms, including a C(3)=O group (δ 218.0) and two sets of terminal CH_2=C groups (δ 107.5 (C(21)), 155.9 (C(20)), 106.2 (C(31)) and 152.7 (C(24))). The NMR profiles of **3** also resemble to those of 24-methylenecycloartan-3-one [19], except that **3** has two additional geminal protons at δ 4.70 and 4.73 (each *d*, $J = 1.2$ Hz) due to the terminal CH_2(21)=C group. The Me(19) group of **3** is derived from the cycloartane skeleton by the rupture of the cyclopropane ring in the latter. Moreover, the downfield position of the signal of H–C(25) at δ 2.13 (*m*) is due to the anisotropic effect of the terminal C(24)=C(31) bond. The ^1H-NMR spectrum exhibits five Me *s* at δ 0.89, 0.95, 1.02, 1.04, and 1.09 due to Me(18), Me(19), Me(29), Me(28), and Me(30), besides two equivalent Me signals at δ 1.05 (*d*, $J =$ 6.8 Hz, 6 H) due to Me(26) and Me(27), respectively.

The molecular formula of bridelonine (**6**) was established as $C_{10}H_{11}O_2N_3$ by the EI-MS (M^+ at *m/z* 205) and HR-EI-MS. From the analysis of the spectral evidence, the structure of **6** was determined to be 5-(3-methylbut-2-enyl)-1-pyrrolo[3,4-*d*]imidazole-4,6-(1*H*,5*H*)-dione, which was further confirmed by COSY and NOESY (*Fig.*) experiments. The novel structure **6** resembles that of 1-methylxanthine (= 3,7-dihydro-1-methyl-1*H*-purine-2,6-dione) [20], except that, in **6**, the pyrrolidine ring replaces the pyrimidine ring of xanthine.

In the UV spectrum of **6**, the λ_{max} at 274 nm indicates the presence of an aromatic moiety. The IR spectrum shows the NH absorption at 3437 cm^{-1} and N–C=O at 1680 cm^{-1}. The analysis of the ^1H- and ^{13}C-NMR spectra suggest that **6** has a novel skeleton consisting of a fused pyrrolidine-2,5-dione and imidazole moiety. The ^1H-NMR spectrum of **6** shows the signals of the 3-methylbut-2-enyl group at δ 1.91 and 1.80 (2 *s*) due to Me(4′)

and Me(3′), at δ 5.18 (*d*, $J = 7.2$ Hz) due to CH_2(1′), and at δ 5.61 (br. *t*, $J = 7.2$ Hz) due to the olefinic H–C(2′). The aromatic H–C(2) at δ 8.46 (*s*) is downfield-shifted by the deshielding effect of the 3-methylbut-2-enyl group at N(5). The amino signal at δ 9.30 (br. *s*, D_2O exchangeable) is assigned to H–N(1).

The adenines **7** and **8** are positional isomers with the 3-methylbut-2-enyl substituent at different positions of the adenine skeleton. Their molecular formulae were established as $C_{10}H_{13}N_5$ by the EI-MS (M^+ at *m/z* 203) and HR-EI-MS. By comparison of their spectroscopic data with literature data of corresponding synthesized compounds [13–15], **7** and **8** were identified as 9-(3-methylbut-2-enyl)adenine and 1-(3-methylbut-2-enyl)adenine, respectively. Both of them were isolated for the first time from plant material.

Adenines **7** and **8** show the same MS fragments at *m/z* 203, 188, 135, and 108. The UV spectrum with λ_{max} at 274 nm indicates the presence of the adenine skeleton. The IR spectrum shows the NH absorption around 3400 cm^{-1}. The ^{1}H-NMR signals of H–C(8) and H–C(2) of **8** are shifted downfield as compared to those of **7** since the 3-methylbut-2-enyl group at N(1) of **8** exerts a more-important deshielding effect than that at N(9) of **7**.

Among the isolated adenines **4**, **5** [21][22][23], **7**, and **8** are isomeric analogs of the (also isolated) parent adenine (**9**) [24] with the 3-methylbut-2-enyl group at different positions. The novel 'deimino-xanthine' **6** was probably formed from adenine analogs.

Experimental Part

General. Column chromatography (CC): silica gel *60* (*Merck* 70–230 mesh, 230–400 mesh, ASTM) and *Sephadex* (*LH-20*). TLC: silica gel *60* F_{254} precoated plates (*Merck*). M.p.: *Yanaco* micro-melting-point apparatus; uncorrected. Optical rotations: *Jasco DIP-370* polarimeter; in $CHCl_3$. UV Spectra: *Jasco UV-240* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer 2000-FT-IR* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H-, ^{13}C- and 2D-NMR: *Varian Unity-Plus-400* spectrometer; δ in ppm, *J* in Hz. EI-MS: *VG-Biotech Quattro-5022* spectrometer; *m/z* (rel. %). HR-EI-MS: *Jeol JMX-HX-110* mass spectrometer.

Plant Material. Leaves of *B. balansae* were collected at Pingtung Hsien, Taiwan, in August 1995. A voucher sample was deposited in the Herbarium of the School of Pharmacy, College of Pharmacy, Kaohsiung Medical University, Kaohsiung, Taiwan, R.O.C.

Extraction and Isolation. Air-dried leaves (6.22 kg) were extracted with MeOH, and the extract was concentrated *in vacuo* to leave a brownish fluid. The MeOH extract was partitioned into $CHCl_3$-soluble (A; 320 g), BuOH-soluble (B; 80 g), and H_2O-soluble parts (C; 300 g). A 100-g sample of the $CHCl_3$-soluble part *A* was submitted to CC (silica gel, $CHCl_3$/MeOH step gradients): *Fr. A1–A20*. Repeated purification of *Fr. A1* ($CHCl_3$; 2.3 g) by CC (silica gel, hexane/CH_2Cl_2) yielded **1** (20 mg). *Fr. A2* ($CHCl_3$; 0.66 g) was subjected to CC (silica gel, hexane/CH_2Cl_2): *Fr. A2.1–A2.12*. *Fr. A2*.1 (hexane/CH_2Cl_2 40:1; 50 mg) was subjected to CC (silica gel, hexane/AcOEt): *Fr. A2.1.1–A.2.1.10*. *Fr. A2.3* (hexane/AcOEt 40:1; 35 mg) was purified by prep. TLC (hexane/AcOEt 30:1): **2** (25.6 mg). Repeated purification of *Fr. A3* ($CHCl_3$; 1.42 g) by CC (silica gel, hexane/AcOEt) gave **3** (15.2 mg). *Fr. A13* ($CHCl_3$/MeOH 10:1; 3.56 g) was subjected to CC (silica gel, $CHCl_3$/MeOH): *Fr. A13.1–A13.40*. *Fr. A13.9* ($CHCl_3$/MeOH 5:1; 5 mg) was purified by prep. TLC ($CHCl_3$/MeOH 5:1): **4** (0.7 mg). *Fr. A13.26* ($CHCl_3$/MeOH 10:1; 2 g) was subjected to CC (silica gel, $CHCl_3$/MeOH): *Fr. A13.26.1–A13.26.20*. *Fr. A13.26.9* ($CHCl_3$/MeOH 10:1; 1.5 g) was subjected to CC (silica gel, $CHCl_3$/MeOH): *Fr. A13.26.9.1–A13.26.9.20*. *Fr. A13.26.9.9* ($CHCl_3$/MeOH 10:1; 5 mg) was purified with prep. TLC ($CHCl_3$/MeOH 10:1): **5** (0.7 mg).

Fr. B. (80 g) was submitted to CC (silica gel, $CHCl_3$/MeOH 9:1, step gradients): *Fr. B1–B20*. *Fr. B.3* ($CHCl_3$/MeOH 9:1; 5.66 g) was subjected to CC (*Sephadex LH-20*, MeOH/H_2O): *Fr. B3.1–B3.30*. *Fr. B3.2* (MeOH; 32 mg) was purified by reversed-phase prep. TLC (MeOH/H_2O 40:1): **6** (1.5 mg), **7** (1.2 mg), and **8** (0.5 mg). *Fr. B4* ($CHCl_3$/MeOH 10:1; 0.8 g) was subjected to CC (*Sephadex LH-20*, MeOH/H_2O): *Fr. B4.1–B4.25*. *Fr. B4.12* (MeOH; 7 mg) was purified by prep. TLC ($CHCl_3$/MeOH 10:1): **9** (1.2 mg).

*6,8,11-Trimethyldodecanoic Acid (2*E*)-3-Methylhexadec-2-enyl Ester* (= *Balansenate I*; **1**). Colorless oil. $[\alpha]_D^{25} = -14.5$ ($c = 0.24$, $CHCl_3$). IR (neat): 1728 (C=O). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.84 (*d*, $J = 6.8$, Me−(8)); 0.86 (*t*, $J = 6.8$, Me(16′)); 0.86 (*d*, $J = 6.8$, Me−C(11), Me(12)); 0.88 (*d*, $J = 6.4$, Me−C(6)); 1.06 (*m*, CH_2(10)); 1.14 (*m*, CH_2(5)); 1.21 (*m*, CH_2(4)); 1.25 (*m*, 20 H, CH_2(5′) to CH_2(14′)); 1.28 (*m*, CH_2(3)); 1.38 (*m*, H−C(6), H−C(8)); 1.42 (*m*, CH_2(9)); 1.52 (*m*, H−C(11)); 1.61 (br. *t*, $J = 7.2$, CH_2(7)); 1.69 (*d*, $J = 1.2$, Me−C(3′)); 2.00 (br. *t*, $J = 7.2$, CH_2(4′)); 2.29 (*t*, $J = 7.2$, CH_2(2)); 4.58 (*d*, $J = 7.2$, CH_2(1′)); 5.33 (*tq*, $J = 7.2$, 1.2, H−C(2′)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 14.1 (*Me*−C(8)), 16.3 (*Me*−C(3′)), 19.7 (*Me*−C(11), Me(12)); 22.6 (C(5)); 22.7 (*Me*−C(6)); 24.8 (C(3)); 25.0 (C(7)); 28.0 (C(11)); 24.5, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 37.2, 37.3 (C(5′) to C(14′)); 31.9 (C(4)); 32.7 (C(6)); 32.8 (C(8)); 34.4 (C(2)); 36.6 (C(10)); 37.4 (C(9)); 39.4 (C(15′)); 39.8 (C(4′)); 61.2 (C(1′)); 118.2 (C(2′)); 142.5 (C(3′)); 173.9 (C(1)). EI-MS: 478 (0.2, M^+), 296 (6, $[CH_3(CH_2)_{12}C(CH_3)=CHCH_2OC(OH)=CH_2]^+$), 278 (26, $[(CH_2)_{13}C(CH_3)=CHCH_2OC=CH_2]^+$), 123 (100, $[(CH_2)_2C(CH_3)=CHCH_2OC=CH_2-1]^+$). HR-EI-MS: 478.47474 ($C_{32}H_{62}O_2^+$; calc. 478.47498).

*10,12,15-Trimethylhexadecanoic Acid (2*E*)-3-Methylhexadec-2-enyl Ester* (= *Balansenate II*; **2**). Colorless oil. $[\alpha]_D^{25} = -16.5$ ($c = 0.28$, $CHCl_3$). IR (neat): 1738 (C=O). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.85 (*d*, $J = 6.8$, Me−C(12)); 0.86 (*t*, $J = 6.8$, Me(16′)); 0.86 (*d*, $J = 6.8$, Me−C(15), Me(16)); 0.89 (*d*, $J = 6.4$, Me−C(10)); 1.04 (*m*, CH_2(9)); 1.06 (*m*, CH_2(14)); 1.14 (*m*, CH_2(15′)); 1.21 (*m*, CH_2(4)), 1.25 (*m*, 20 H, CH_2(5′) to CH_2(14′)); 1.28 (*m*, CH_2(5)); 1.38 (*m*, H−C(10), H−C(12)); 1.42 (*m*, CH_2(13)); 1.53 (*m*, H−C(15)); 1.61 (br. *t*, $J = 7.2$, CH_2(11)); 1.69 (*d*, $J = 1.2$, Me−C(3′)); 2.00 (br. *t*, $J = 6.8$, CH_2(4′)); 2.29 (*t*, $J = 7.2$, CH_2(2)); 4.59 (*d*, $J = 7.2$, CH_2(1′)); 5.34 (*tq*, $J = 7.2$, 1.2, H−C(2′)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 14.1 (*Me*−C(12)); 16.3 (*Me*−C(3′)); 19.7 (*Me*−C(15), Me(16)); 22.6 (Me(16′)); 22.7 (C(5)); 22.7 (*Me*−(10)); 24.8 (C(3)); 25.0 (C(11)); 28.0 (C(15)); 24.5, 29.1, 29.2, 29.31, 29.34, 29.4, 29.51, 29.58, 29.6, 29.7 (2C), 29.8, 37.2, 37.3 (C(5′) to C(14′)); 31.9 (C(4)); 32.7 (C(10)); 32.8 (C(12)); 34.4 (C(2)); 36.6 (C(14)); 37.4 (C(9)); 39.4 (C(15′)); 39.8 (C(4′)); 61.2 (C(1′)); 118.1 (C(2′)); 142.6 (C(3′)); 173.9 (C(1)). EI-MS: 534 (0.01, M^+), 296 (0.4, $[CH_3(CH_2)_{12}C(CH_3)=CHCH_2OC(OH)=CH_2]^+$), 278 (50, $[(CH_2)_{13}C(CH_3)=CHCH_2OC=CH_2]^+$), 123 (100, $[(CH_2)_2C(CH_3)=CHCH_2OC=CH_2-1]^+$). HR-EI-MS: 534.5380 ($C_{36}H_{70}O_2^+$; calc. 534.5376).

*Hexahydro-4,4,10,13,14-pentamethyl-17-(5-methyl-1,4-dimethylenehexyl)-3*H*-cyclopenta[*a*]phenanthren-3-one* (= *Bridelone*; **3**). Colorless prisms. M.p. 69–71°. $[\alpha]_D^{25} = +163.9$ ($c = 0.16$, $CHCl_3$). IR (KBr): 1704 (C=O). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.89 (*s*, Me(18)); 0.95 (*s*, Me(19)); 1.02 (*s*, Me(29)); 1.04 (*s*, Me(28)); 1.05 (*d*, $J =$ 6.8, Me(26), Me(27)); 1.09 (*s*, Me(30)); 1.36 (*m*, H−C(5)); 1.40 (*m*, H−C(8)); 1.70 (*m*, H−C(17)); 2.13 (*m*, H−C(25)); 2.22 (*m*, H−C(9)); 4.70 (*d*, $J = 1.2$, H_a−C(21)); 4.73 (*d*, $J = 1.2$, H_b−C(21)); 4.73 (*d*, $J = 1.2$, H_a−C(31)); 4.76 (*d*, $J = 1.2$, H_b−C(31)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 15.3 (C(18)); 15.8 (C(19)); 16.0 (C(28)); 20.9 (C(29)); 21.0 (C(30)); 26.7 (C(26)); 26.7 (C(27)); 33.9 (C(25)); 36.9 (C(10)); 39.9 (C(2)); 40.3 (C(14)); 45.5 (C(17)); 47.4 (C(13)); 47.6 (C(8)); 49.4 (C(4)); 50.3 (C(5)); 55.3 (C(9)); 106.2 (C(31)); 107.5 (C(21)); 152.7 (C(24)); 155.9 (C(20)); 218.0 (C(3)). EI-MS: 438 (2.98, M^+), 313 (10.64), 245 (11.02), 205 (46.12). HR-EI-MS: 438.3856 ($C_{31}H_{50}O^+$; calc. 438.3862).

*5-(3-Methylbut-2-enyl)pyrrolo[3,4-*d*]imidazole-4,6(1*H*,5*H*)-dione* (= *Bridelonine*; **6**). Colorless sands. M.p. >300°. UV (MeOH): 274 (4.04), 209 (4.13). IR (KBr): 3437 (NH), 1680 (N−C=O), 1624 (arom. ring). ^{1}H-NMR ($(CD_3)_2CO$, 400 MHz): 1.80 (*s*, Me−C(3′)); 1.91 (*s*, Me(4′)); 5.18 (*d*, $J = 7.2$, CH_2(1′)); 5.61 (br. *t*, $J =$ 7.2, H−C(2′)); 8.46 (*s*, H−C(2)); 9.30 (br. *s*, D_2O exchangeable, H−N(1)). ^{13}C-NMR ($(CD_3)_2CO$, 100 MHz): 19.1 (*Me*−C(5′)); 26.6 (C(4′)); 50.1 (C(1′)); 117.7 (C(2′)); 144.13 (C(2)); 144.13 (C(3′)); 149.5 (C(3a),C(6a)); 159.20 (C(4),C(6)). EI-MS: 205 (34.1, M^+), 204 (51.6), 138 (61.6), 137 (100), 136 (89.6), 109 (55.4), 69 (92.9). HR-EI-MS: 205.0860 ($C_{10}H_{11}O_2N_3^+$; calc. 205.0855).

9-(3-Methylbut-2-enyl)adenine (**7**). Colorless prisms. M.p. 188–189°. UV (MeOH): 274 (2.8), 212 (4.1). IR (KBr): 3434 (NH), 1621 (purine ring). ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.83 (*d*, $J = 1.6$, Me(4′)); 1.85 (*d*, $J = 1.6$, Me−C(3′)); 5.00 (br. *d*, $J = 7.2$, CH_2(1′)); 5.50 (br. *tq*, $J = 7.2$, 1.6, H−C(2′)); 8.04 (*s*, H−C(8)); 8.07 (*s*, H−C(2)). EI-MS: 203 (32, M^+), 188 (86), 135 (100), 108 (90). HR-EI-MS: 203.1174 ($C_{10}H_{13}N_5^+$; calc. 203.1171)

1-(3-Methylbut-2-enyl)adenine (**8**). Colorless prisms. M.p. >300°; UV (MeOH): 274 (4.04), 209 (4.13). IR (KBr): 3393 (NH), 1648 (purine ring). ^{1}H-NMR (CD_3OD, 400 MHz): 1.81 (*s*, Me−C(3′)); 1.91 (*s*, Me(4′)); 5.09 (*d*, $J = 7.2$, CH_2(1′)); 5.50 (br. *t*, $J = 7.4$, H−C(2′)); 8.49 (*s*, H−C(8)); 8.60 (*s*, H−C(2)). EI-MS: 203 (28, M^+), 188 (73), 135 (100), 108 (78). HR-EI-MS: 203.1172 ($C_{10}H_{13}N_5^+$; calc. 203.1171).

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