Bruceines K and L from the Ripe Fruits of *Brucea javanica*

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Bruceine K (**1**), a pentacyclic C_{20}-quassinoid bearing a unique 12,20-epoxy moiety, and bruceine L (**2**), along with the ten known compounds (6*S*,7*E*)-6,9,10-trihydroxy- and (6*S*,7*E*)-6,9-dihydroxymegastigma-4,7-dien-3-one (**3** and **4**, resp.), cleomiscosins A–C, luteoline, quercetine, bruceantinol, pinoresinol, and thevetiaflavone, were isolated from the ripe fruits of *Brucea javanica*. Bruceines K (**1**) and L (**2**) were determined to be (1*β*,2*α*,11*β*,12*β*,14*ξ*,15*β*)-12,20-epoxy-1,2,11,13,14,15-hexahydroxypicras-3-en-16-one and (1*β*,2*α*,11*β*,12*β*,15*β*)-13,20-epoxy-1,2,11,12-tetrahydroxy-16-oxo-15-(senecioyloxy)-picras-3-en-21-oic acid methyl ester (senecioic acid = 3-methylbut-2-enoic acid), respectively, on the basis of NMR (^{1}H- and ^{13}C-NMR, DEPT, ^{1}H,^{1}H-COSY, NOESY, HMQC, and HMBC) and ESI-MS data. Among the known compounds, (6*S*,7*E*)-6,9,10-trihydroxy- and (6*S*,7*E*)-6,9-dihydroxymegastigma-4,7-dien-3-one (**3** and **4**, resp.), cleomiscosin C, luteoline, quercetine, and thevetiaflavone were isolated for the first time from the *Brucea* plants.

Introduction. – The dried ripe fruits of *Brucea javanica* (L.) MERR. (Simaroubaceae), known as *Bruceae Fructus* (Ya-Dan-Zi in Chinese), has been used for the treatment of dysenteric disorders, malaria, and tumors in Chinese medicine and is known to be a rich source of quassinoids [1]. In a previous study, an 80% EtOH extract displayed significant cytotoxicity in three pancreatic-cancer cell lines (PANC-1, SW1990, and CAPAN-1) with IC_{50} values ranging from 1.5 to 5 μg/ml, while it exerted minimal cytotoxic action on Hs68 cells, a line of normal foreskin fibroblasts, with an IC_{50} value larger than 100 μg/ml [2]. A bioassay-guided isolation led to the separation of bruceine K (**1**), a new pentacyclic C_{20} quassinoid bearing a unique 12,20-epoxy bridge, and bruceine L (**2**), a new naturally occurring quassinoid, from the AcOEt-soluble fraction of the ripe fruits of *Brucea javanica*. This article reports the detailed structural elucidation of compounds **1** and **2** (*Fig. 1*).

Results and Discussion. – Compound **1** was obtained as an amorphous white powder. A molecular formula $C_{20}H_{28}O_9$ was determined based on the HR-ESI-MS (*m*/*z* 435.163429 ($[M+Na]^+$)), indicating seven degrees of unsaturation. The IR spectrum displayed characteristic absorptions for OH (3411 cm^{-1}) and *δ*-lactone and ester

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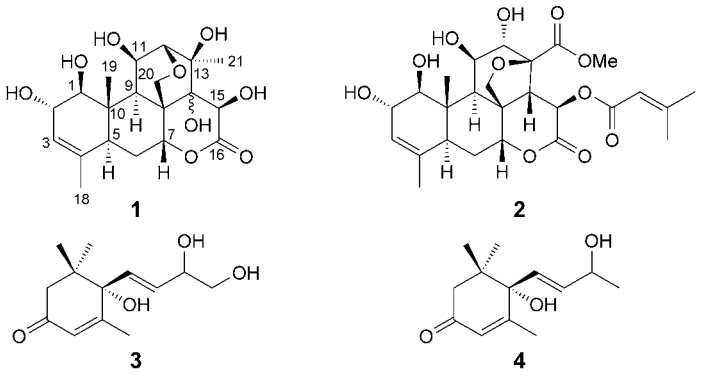

Fig. 1. *Compounds* **1**–**4** *isolated from the ripe fruits of* Brucea javanica

(1711 cm^{-1}) groups. The ^1H-, ^{13}C-, and DEPT-NMR spectra (*Table 1*) showed the presence of three Me, two CH_2 (including one O-bearing CH_2), and nine CH groups (including six O-bearing and an olefinic CH), and six quaternary C-atoms (including a C=O, four O-bearing, and one olefinic C-atom). The presence of a C=C bond and a C=O group accounted for two degrees of unsaturation. Compound **1** was proposed to be a C_{20}-quassinoid possessing five rings, and careful interpretation of the NMR data

Table 1. *^1H- and ^{13}C-NMR Data* (100 and 400 MHz, resp.; CD_3OD) *of* **1**. δ in ppm, J in Hz.

	δ(H)	δ(C)	HMBC	NOESY
H–C(1)	3.51 (*d*, *J* = 7.4)	82.8 (*d*)	C(2), C(9), C(10), C(19)	H–C(5), H–C(9), H–C(11)
H–C(2)	3.98 (*m*)	74.2 (*d*)		Me(19)
H–C(3)	5.38 (*d*, *J* = 1.3)	125.2 (*d*)	C(1), C(5), C(18)	Me(18)
C(4)		136.6 (*s*)		
H–C(5)	2.39 (*d*, *J* = 13.0)	43.8 (*d*)	C(6)	H–C(1), H–C(9)
H_α–C(6)	2.14 (*dt*, *J* = 2.9, 14.8)	28.6 (*t*)	C(7), C(8), C(10)	H_β–C(6)
H_β–C(6)	1.69 (*dd*, *J* = 2.6, 14.8)			H_α–C(6)
H–C(7)	5.05 (*t*, *J* = 2.6)	81.9 (*d*)	C(5), C(9), C(16)	H_a–C(20)
C(8)		51.0 (*s*)		
H–C(9)	2.05 (*d*, *J* = 4.2)	46.7 (*d*)	C(8), C(10), C(19), C(20)	H–C(1), H–C(5), H–C(11), H–C(15)
C(10)		45.4 (*s*)		
H–C(11)	4.57 (*d*, *J* = 5.1)	75.8 (*d*)	C(9), C(13)	H–C(9), H–C(12)
H–C(12)	3.73 (*d*, *J* = 0.7)	81.3 (*d*)	C(9), C(11), C(13), C(14), C(21)	H–C(11), Me(21)
C(13)		82.4 (*s*)		
C(14)		84.8 (*s*)		
H–C(15)	5.12 (*s*)	70.6 (*d*)	C(13), C(16)	H–C(9)
C(16)		176.3 (*s*)		
Me(18)	1.64 (*s*)	21.1 (*q*)	C(3), C(4), C(5)	H–C(3)
Me(19)	1.20 (*s*)	12.2 (*q*)	C(1), C(5), C(9), C(10)	H–C(2), H_β–C(6), H_b–C(20)
H_a–C(20)	3.80 (*dd*, *J* = 1.4, 7.3)	70.8 (*t*)	C(7), C(8), C(9)	H–C(7), H_b–C(20)
H_b–C(20)	4.60 (*d*, *J* = 7.3)		C(8), C(12), C(14)	Me(19), H_a–C(20)
Me(21)	1.40 (*s*)	18.4 (*q*)	C(12), C(14)	H–C(12)

(^{1}H-, ^{13}C-, and DEPT-NMR, ^{1}H,^{1}H-COSY, HMQC, HMBC, and NOESY) led to the establishment of its structure (*Fig. 1*). In the ^{1}H,^{1}H-COSY plot, the δ(H) 3.98 (*m*, H–C(2)) showed correlations with δ(H) 3.51 (*d*, J = 7.4 Hz, H–C(1)) and 5.38 (*d*, J = 1.3 Hz, H–C(3)), suggesting the presence of structural fragment **1a** (*Fig. 2*). The correlations of δ(H) 1.69 (*dd*, J = 2.6, 14.8 Hz, H_β–C(6)) and 2.14 (*dd*, J = 2.9, 14.8 Hz, H_α–C(6)) with δ(H) 2.39 (*d*, J = 13.0 Hz, H–C(5)) and 5.05 (*t*, J = 2.6 Hz, H–C(7)) established fragment **1b** (*Fig. 2*). The cross-peak between δ(H) 2.05 (*d*, J = 4.2 Hz, H–C(9)) and 4.57 (*d*, J = 5.1 Hz, H–C(11)) suggested a partial structure **1c** (*Fig. 2*). In the HMBC spectrum (*Table 1* and *Fig. 3*), the cross-peaks between δ(H) 1.64 (*s*, Me(18)) and δ(C) 125.2 (C(3)), 136.6 (C(4)), and 43.8 (C(5)), as well as correlations between δ(H) 1.20 (*s*, Me(19)) and δ(C) 82.8 (C(1)), 43.8 (C(5)), 46.7 (C(9)), and 45.4 (C(10)) led to the establishment of fragment **1d** (*Fig. 2*). The partial structure **1e** (*Fig. 2*) was then established based on the HMBC cross-peaks H–C(1) and Me(19)/C(9), H–C(7)/C(5) and C(9), and also H_a–C(20) (δ(H) 3.80 (*dd*, J = 4.1, 7.3 Hz)) and H_b–C(20) (δ(H) 4.60 (*d*, J = 7.3 Hz))/C(7) (δ(C) 81.9), C(8) (δ(C) 51.0), and C(9). Although no ^{1}H,^{1}H-COSY cross-peak H–C(11) (δ(H) 4.57 (*d*, J = 5.1 Hz))/H–C(12) (δ(H) 3.73 (*d*, J = 0.7 Hz)) was observed, the direct connection between C(11) (δ(C) 75.8) and C(12) (δ(C) 81.3) could be deduced from the HMBC H–C(12)/C(9) and

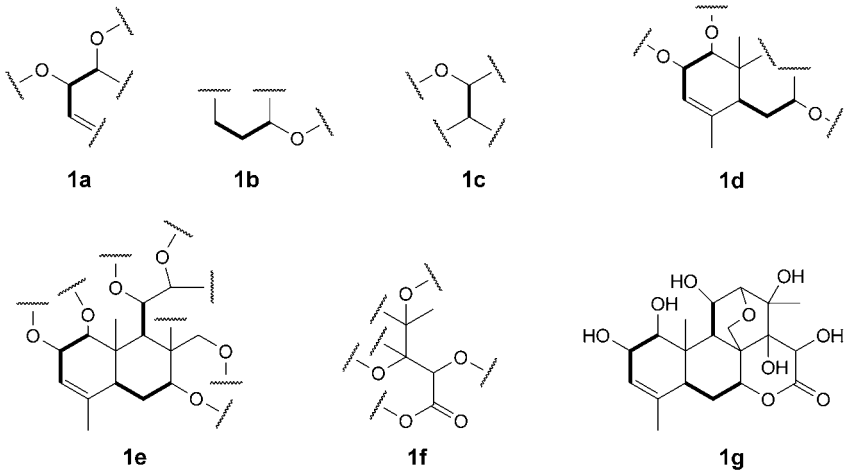

Fig. 2. *Structural fragments and key ^{1}H,^{1}H-COSY features of* **1**

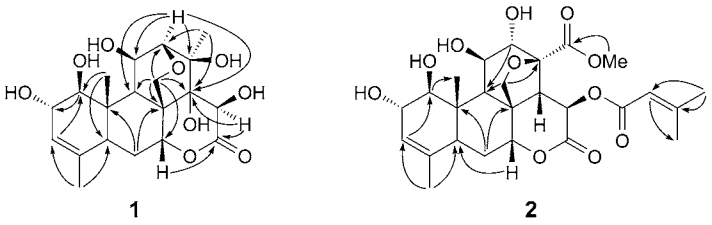

Fig. 3. *Key HMBC features of* **1** *and* **2**

C(11). For the remaining C-atoms, the partial structure **1f** was proposed based on the HMBC cross-peaks H–C(15) (δ(H) 5.12)/C(13) (δ(C) 82.4) and C(16) (δ(C) 176.3), Me(21) (δ(H) 1.40)/C(12) and C(14) (δ(C) 84.8) (*Fig. 2*), as well as on biogenetic considerations. The connection of **1e** and **1f** at C(12)–C(13), C(9)–C(14), and C(7)–O–C(16) results in two six-membered rings which could satisfy all observed correlations in the HMBC spectrum. Furthermore, the HMBC H_b–C(20)/C(12) confirmed the occurrence of an O-bridge between C(12) and C(20). Based on the above structural evidence and the molecular formula of the compound, the O-substituents at C(1), C(2), C(11), C(13), C(14), and C(15) were proposed to be OH groups. Consequently, the planar structure of **1** was proposed as shown in **1g** (*Fig. 2*), which is a pentacyclic C_{20}-quassinoid bearing a unique 12,20-epoxybridge. To the best of our knowledge, this is the first example of a quassinoid structure bearing an O-bridge between C(12) and C(20) [1][3]. Most known quassinoids have an O-bridge between C(20) and C(11) or between C(20) and C(13). To determine the relative configuration of **1**, a NOESY experiment was carried out. From a biogenetic point of view, an α-orientation of H–C(5) and H–C(9), and β-orientation of Me(19) were assumed (*Table 1* and *Fig. 4*). The NOESY correlations H–C(1)/H–C(5) and H–C(9), H–C(11)/H–C(9), H–C(11)/H–C(12), H–C(12)/Me(21), as well as H–C(15)/H–C(9) revealed an α-orientation of H–C(1), H–C(11), H–C(12), H–C(15), and Me(21). The β-orientation of H–C(2), H–C(7), and CH_2(20) was indicated by the NOESY correlations H–C(2)/Me(19), H–C(7)/H_a–C(20), and H_b–C(20)/Me(19). It is worth pointing out that the presence of H_α–C(11) and H_α–C(12) is very uncommon in quassinoids; most of them possess H_α–C(11) and H_β–C(12) structures, and a few possess H_β–C(11) and H_α–C(12) orientation [3]. Accordingly, compound **1** was determined to be (1β,2α,11β,12β,14ξ,15β)-12,20-epoxy-1,2,11,13,14,15-hexahydroxypicras-3-en-16-one, which is given the trivial name bruceine K.

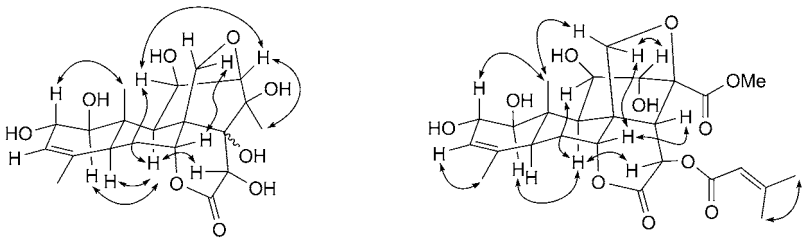

Fig. 4. *Key NOESY correlations of* **1** *and* **2**

Compound **2** was obtained as an amorphous white powder. Its molecular formula $C_{26}H_{34}O_{11}$ was determined from the HR-ESI-MS ion peak at *m*/*z* 545.198634 ([*M* + Na]$^+$), indicating ten degrees of unsaturation. The IR spectrum displayed characteristic absorptions for OH (3431 cm^{-1}) and δ-lactone and ester (1735 cm^{-1}) groups. Its ^{13}C-NMR data (*Table 2*) were very similar to those of javanicolide D, except for the resonances of the ester chain at C(15) [4]. The ^{1}H-NMR spectrum (*Table 2*) showed signals ascribable to three tertiary Me groups (δ(H) 1.24, 1.93, and 2.16), an olefinic Me

group (δ(H) 1.65), a COOMe group (δ(H) 3.71), and two olefinic H-atoms (δ(H) 5.40 and 5.66). The ^{13}C-NMR (δ(C) 20.5, 27.5, 115.5, 158.0, and 161.0) and the HMBC data (*Table 2* and *Fig. 3*) revealed the presence of a sencioyloxy (=(3-methylbut-2-enoyl)oxy) group. Based on the analysis of 1D- and 2D-NMR spectra, the structure of **2** was determined as (1β,2α,11β,12α,15β)-13,20-epoxy-1,2,11,12-tetrahydroxy-16-oxo-15-(senecioyloxy)picras-3-en-21-oic acid methyl ester, and was given the trivial name bruceine L. The configuration was confirmed by a NOESY experiment (*Fig. 4*). Its NMR data are almost identical to the reported values for a hydrolytic product of yadanzioside E [4][5]. Compound **2** is, therefore, a new naturally occurring substance, which has been obtained previously by enzymatic hydrolysis of yadanzioside E [5].

Table 2. *^{1}H- and ^{13}C-NMR Data* (100 and 400 MHz, resp.; CD_3OD) *of* **2**. δ in ppm, *J* in Hz.

	δ(H)	δ(C)	HMBC
H–C(1)	3.56 (*d*, *J* = 7.4)	82.7 (*d*)	C(2), C(19)
H–C(2)	3.98 (*m*)	74.1 (*d*)	
H–C(3)	5.4 (*d*, *J* = 1.3)	125.5 (*d*)	C(1), C(5), C(18)
C(4)		136.5 (*s*)	
H–C(5)	2.47 (*d*, *J* = 13.5)	44.1 (*d*)[a])	C(4)
H_α–C(6)	2.15[b])	29.0 (*t*)	C(8), C(10)
H_β–C(6)	1.81 (*dt*, *J* = 2.4, 14.9)		
H–C(7)	4.8[b])	85.5 (*d*)	C(5)
C(8)		47.2 (*s*)	
H–C(9)	2.09 (*d*, *J* = 4.1)	44.0 (*d*)[a])	C(1)
C(10)		45.2 (*s*)	
H–C(11)	4.72 (*d*, *J* = 4.8)	75.7 (*d*)	
H–C(12)	4.21 (br. *s*)	75.9 (*d*)	C(9), C(11), C(13)
C(13)		82.6 (*s*)	
C(14)	3.34 (br. *s*)	50.0 (*d*)	
H–C(15)	[c])	68.0 (*d*)	
C(16)		168.0 (*s*)	
Me(18)	1.65 (*s*)	21.1 (*q*)	C(3), C(4), C(5)
Me(19)	1.24 (*s*)	12.1 (*q*)	C(9), C(10)
H_a–C(20)	3.68[b])	74.7 (*t*)	C(9)
H_b–C(20)	4.76 (*d*, *J* = 7.6)		C(13)
Me(21)		170.1 (*q*)	
MeO	3.71 (*s*)	52.9 (*q*)	C(21)
C(1′)		161.0 (*s*)	
H–C(2′)	5.66 (*s*)	115.5 (*d*)	C(4′), C(5′)
C(3′)		158.0 (*s*)	
Me(4′)	1.93 (*s*)	27.5 (*q*)	C(2′), C(3′), C(5′)
Me(5′)	2.16 (*s*)	20.5 (*q*)	C(2′), C(3′), C(4′)

[a]) Assignments in the same column may be interchangeable. [b]) Multiplicity was not determined due to the overlapping of the signals. [c]) Signal not detectable, as happened to javanicolides E and F [6]. The relative configuration of H_α–C(15) was confirmed by a NOESY experiment in C_5D_5N.

In addition, ten known compounds including (6*S*,7*E*)-6,9,10-trihydroxymegastigma-4,7-dien-3-one (**3**) [7] and (6*S*,7*E*)-6,9-dihydroxymegastigma-4,7-dien-3-one (**4**) [8] (megastigmane = 2-butyl-1,1,3-trimethylcyclohexane), cleomiscosin A [9–11], cleo-

miscosin B [11][12]), cleomiscosin C [11], luteoline [13], quercetine [14], bruceantinol [15][16], pinoresinol [11][17], and thevetiaflavone [18] were identified. Among them, cleomiscosin C, luteoline, quercetine, and thevetiaflavone were isolated for the first time from the *Brucea* plants. The NMR spectroscopic data of compounds **3** and **4** were identical with those of cucumegastigmane I and vomifoliol, respectively [7][8]. The (6*S*,7*E*)-configuration of the structures was evidenced by their positive optical rotations, $[\alpha]_D^{20} = +132.95$ ($c = 0.088$, MeOH) for **3** and $[\alpha]_D^{20} = +140.10$ ($c = 0.571$, MeOH) for **4**, and by the multiplicities of H–C(7) and H–C(8) [7][8]. However, the absolute configuration of C(9) was not determined due to limited sample quantity, though in principle it could be determined by a modified *Mosher*'s method [7]. Thus, **3** and **4** were elucidated as (6*S*,7*E*)-6,9,10-trihydroxymegastigma-4,7-dien-3-one = (4*S*)-4-[(1*E*)-3,4-dihydroxybut-1-en-1-yl]-4-hydroxy-3,5,5-trimethylcyclohex-2-en-1-one and (6*S*,7*E*)-6,9-dihydroxymegastigma-4,7-dien-3-one = (4*S*)-4-hydroxy-4-[(1*E*)-3-hydroxybut-1-en-1-yl]-3,5,5-trimethylcyclohex-2-en-1-one, respectively. To the best of our knowledge, this is the first report on the isolation of megastigmanes from the *Brucea* plants.

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Experimental Part

General. Column chromatography (CC): macroporous resin *D 101*, *Diaion HP-20*, *Diaion HP-20ss*, *MCI*, *RP-18* silica gel (SiO_2; 40–63 μm), and *Sephadex LH-20*. TLC: SiO_2 *60* F_{254} and *RP-18* F_{254} plates. HPLC: *Alltima-*C_{18} semi-prep. column (250 × 10 mm, 5 μm) and *Agilent-HP-1100* system detection at 210 and 230 nm. Optical rotations: in MeOH at r.t.; *Jasco-P-1020* digital polarimeter; quartz cell with a path length of 3 mm. IR Spectra: *Jasco FT/IR-480-Plus* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker-400* FT-NMR spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI-MS and HR-ESI-MS: *ThermoFinnigan-MAT-95-XL* spectrometer; in *m*/*z*.

Plant Material. Dried ripe fruits were purchased from *Zhixin Pharmaceutical Co.*, a GMP-certified supplier of Chinese herbal medicines based in Guangzhou, China. Its identity was further authenticated as the ripe fruits of *Brucea javanica* (L.) MERR. by one of the authors (*Z.-X. L.*), and a voucher specimen (Pan-Ca. 01) was deposited with the Herbarium of the School of Chinese Medicine, The Chinese University of Hong Kong.

Extraction and Isolation. Dried ripe fruits of *Brucea javanica* (30 kg) were ground into small pieces and heated under reflux in 80% aq. EtOH for 3 × 1 h. The mixture was filtered and the filtrate concentrated to remove EtOH. The slurry residue was then suspended in hot H_2O and partitioned successively with hexane, AcOEt, and BuOH to obtain the hexane-soluble fraction (*HF*; oil, yield 9.0%), AcOEt-soluble fraction (*EAF;* yield 0.45%), and BuOH-soluble fraction (*BF*; yield 1.1%). The *EAF* was applied to CC (*D 101*, 80% aq. MeOH, then acetone). The 80% aq. MeOH eluate was then separated by CC (*Diaion HP-20*, 10% MeOH/H_2O 100% MeOH): *Frs. 1–40*. *Frs. 1–8* were then applied to CC (*Diaion HP-20ss*, 10 → 45% MeOH/H_2O): *Frs. I.1–I.30*. *Frs. I.1–I.10* were further separated by CC (*RP-18*, 5 → 20% MeOH/H_2O: twenty-five sub-fractions. The fifth and sixth sub-fractions were applied to a semi-prep. HPLC (H_2O/MeCN 88:12, 5 ml/min): **3** (9 mg). The sixteenth sub-fraction was purified by semi-prep. HPLC (25 → 30% MeCN/H_2O within 15 min, 3 ml/min): **4** (8 mg). *Frs. 20–27* were separated by CC (*Diaion HP-20)* into six fractions, and the third fraction was further separated by CC (*Sephadex LH-20*, MeOH): *Frs. II.1–II.11 Fr. II.2* was then applied to CC (*Diaion HP-20ss*, H_2O/MeOH 70:30 → 20:80): *Frs. II.2.1–II.2.25*. *Fr. II.2.4* and *Frs. II.2.7–II.2.9* yielded, **1** (30 mg) and **2** (20 mg), resp., by semi-prep. HPLC (5 → 30% MeCN/H_2O within 20 min for **1**, and 25 → 30% MeCN/H_2O within 20 min for **2** (flow 5 ml/min). Cleomiscosin A and B precipitated together from *Fr. II.4*, their

mixture was re-dissolved in DMSO and separated into cleomiscosin A (50 mg) and B (65 mg) by semi-prep. HPLC (30 → 45% MeCN/H_2O within 15 min, 3 ml/min). During the purification of cleomiscosin A and B, a peak before the former was also collected: cleomiscosin C (11 mg). Luteoline **8** (96 mg) and quercetine (57 mg) precipitated directly from the *Frs. II.8 – II.10. Frs. 33 – 39* were further separated, by CC (*Diaion HP-20,* 30% MeOH/H_2O → 100% MeOH): *Frs. III.1 – III.12. Fr. III.6* was then applied CC (*Sephadex LH-20*, MeOH) to obtain twenty fractions. The third fraction was further purified by semi-prep. HPLC (40 → 45% MeCN/H_2O in 30 min, flow 3 ml/min): bruceantinol (30 mg). Following the similar procedure, pinoresinol was purified from the fifth and sixth fractions, while thevetiaflavone (35 mg) precipitated directly from the fifth fraction.

(1β,2α,11β,12β,14ξ,15β)-12,20-Epoxy-1,2,11,13,14,15-hexahydroxypicras-3-en-16-one (= *Bruceine K*; **1**): Amorphous white powder. $[\alpha]_D^{20} = +153.90$ ($c = 1.475$, MeOH). IR: 3411, 1711, 1638, 1441, 1385, 1265, 1159, 1077, 1037. ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 1*. ESI-MS: 435 ($[M+Na]^+$). HR-ESI-MS: 435.163429 ($[M+Na]^+$, $C_{20}H_{28}O_9Na^+$; calc. 435.1626).

(1β,2α,11β,12α,15β)-13,20-Epoxy-1,2,11,12-tetrahydroxy-15-[(3-methyl-1-oxobut-2-en-1-yl)oxy]-16-oxopicras-3-en-21-oic Acid Methyl Ester (= *Bruceine L*; **2**): Amorphous white powder. $[\alpha]_D^{20} = +137.16$ ($c = 0.705$, MeOH). IR: 3431, 1735, 1648, 1440, 1382, 1232, 1142, 1051, 1037. ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 1*. ^{13}C-NMR (C_5D_5N): 82.3 (C(1)); 73.3 (C(2)); 126.4 (C(3)); 134.4 (C(4)); 43.4 (C(5)); 28.7 (C(6)); 84.4 (C(7)); 46.8 (C(8)); 43.2 (C(9)); 44.7 (C(10)), 75.7 (C(11)); 75.9 (C(12)); 82.5 (C(13)); 50.4 (C(14)); 68.4 (C(15)); 168.4 (C(16)); 20.9 (C(18)); 12.3 (C(19)); 74.1 (C(20)); 171.5 (C(21)); 52.3 (MeO); data assigned according to the reported values [4][5]. ESI-MS: 545 ($[M+Na]^+$). HR-ESI-MS: 545.198634 ($[M+Na]^+$, $C_{26}H_{34}O_{11}Na^+$; calc. 545.1993).

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