Dinklagins A, B and C: three prenylated flavonoids and other constituents from the twigs of *Dorstenia dinklagei*

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Abstract

Three prenylated flavonoids, dinklagins A, B and C identified, respectively, as (−)-6-(3,3-dimethylallyl)-7-hydroxy-6‴, 6‴-dimethylchromeno-(4′,3′,2‴,3‴)-flavanone, (+)-5,4′,5″ξ-trihydroxy-6″,6″-dimethylchromano-(7,6,2″,3″)-flavone and (+)6-(2ξ-hydroxy-3-methyl-3-butenyl)-5,7,4′-trihydroxyflavone were isolated from the twigs of *Dorstenia dinklagei* together with the known 6-prenylapigenin, 4-hydroxylonchocarpin, stipulin and 5,4′-dihydroxy-6″,6″-dimethylchromano-(7,6,2″,3″)-flavone. Their structures were determined on the basis of spectral data and by comparison with data reported in the literature and with authentic specimens for known compounds. © 2002 Published by Elsevier Science Ltd.

Keywords: *Dorstenia dinklagei*; Moraceae; Twigs; Isolation; Prenylated chalcones; Dinklagins A, B and C

1. Introduction

The genus *Dorstenia* (Moraceae) consists of about 170 undergrowth mostly tropical species (Mabberley, 1987; Barthlott, 1998). Medicinal preparations containing the leaves of these plants have been used in folk medicine for many applications such as for cough, headache and stomach pain (Bouquet, 1969). The chemistry of this genus has been reviewed recently (Abegaz et al., 2000) and is now recognized as a rich source of prenylated and geranylated coumarins (Franke et al., 2001) and flavonoids (Abegaz et al., 1998, 2000; Ngadjui et al., 1998a,b, 1999a,b,c, 2000). These reports indicate that the African *Dorstenia* species produce a variety of mono-, di-, triprenylated and even geranylated chalcones, flavanones, and flavones with further modification in the prenyl and geranyl sustituent groups, while species originating from Central and South America, did not yield any prenylated flavonoids. As part of our work on isolation and identification of chemical constituents of African *Dorstenia* species (Abegaz et al., 1998, 2000; Ngadjui et al., 1998a,b, 1999a,b,c, 2000), we have now studied the combined dichloromethane/methanol (1:1) and methanol extract of the twigs of *Dorstenia dinklagei* Engler. This plant has so far, not been subjected to any chemical or pharmacological investigations. In this paper we report the isolation and structural characterization of three new prenylated flavonoids for which the names dinklagins A (**1**), B (**2**) and C (**3**) are proposed as well as the known 6-prenylapigenin (Abegaz et al., 1998), 5,4′-dihydroxy-6″,6″-dimethylchromano-(7,6,2″,3″)- flavone and stipulin (Abegaz et al., 1998), 4-hydroxylonchocarpin (Dagne et al., 1989). The structures of these secondary metabolites were established using spectroscopic methods and by comparison of measured spectra with published information and in some cases by direct comparison with authentic specimens.

2. Results and discussion

Repeated column chromatography and preparative TLC of the dichloromethane/methanol extract of the twigs of *D. dinklagei* yielded the novel compounds **1**–**3** and other known compounds.

Compound **1** was obtained as white plates from hexane-ethyl acetate. The molecular formula $C_{25}H_{26}O_4$ was deduced from HREIMS data. The red color produced

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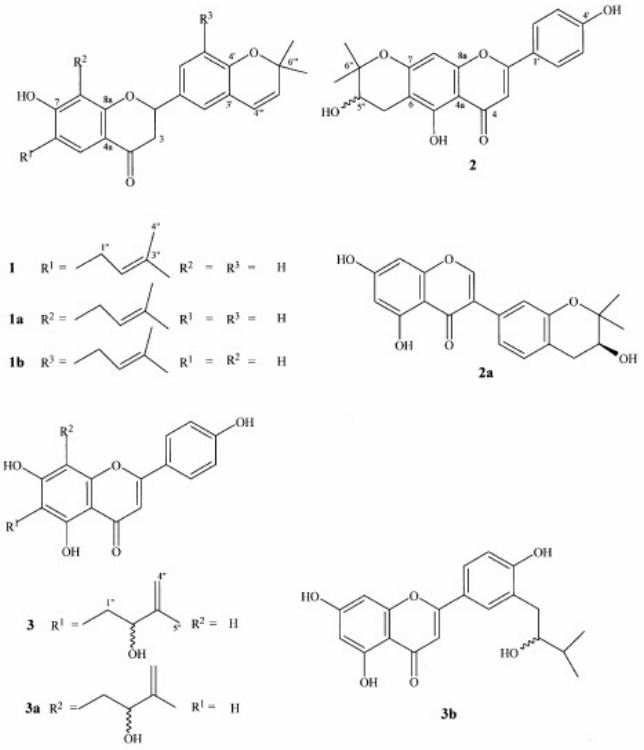

on reaction of **1** with magnesium-hydrochloric acid together with the UV spectra data employing shift reagents (Experimental) suggested that **1** was a 7-or 4′-hydroxyflavanone (Mabry et al., 1970; Agrawal, 1989). The flavanone nature of **1** was confirmed from NMR spectra which showed signals for an sp^3 oxymethine, a carbonyl group and a methylene at δ_C 80.1 (*d*), 191.6 (*s*), and 44.5 (*t*), respectively, and an ABX system [δ_H 2.78 (*dd*, J=2.8, 16.9 Hz), 3.00 (*dd*, J=13.3, 16.8 Hz) and 5.35 (*dd*, 2.8, 13.4 Hz), typically assignable to two H-3 and H-2 protons of a flavanone. The up-field chemical shift of the carbonyl resonance (δ_C 191.6) suggests the absence of the hydroxyl group in position 5. This was supported by the ^{1}H NMR of **1** (not the carbonyl) in $CDCl_3$, which did not show any downfield proton signal above 10 ppm. This ^{1}H NMR also displayed eight aryl/vinyl proton signals, two of which were assigned to the pyran ring (see later); one of the proton signals was consistent with a prenyl group (vide infra) and two appeared as singlets at δ 7.71 and 6.45 ppm. The value of the chemical shift of the former proton signal suggests that it should be *peri* to a carbonyl group; this is consistent with H-5. The remaining three proton signals, which formed an ABD system, [δ 7.20 (*dd*, J=2.1, 8.3 Hz), 7.09 (*d*, J=2.1 Hz) and 6.82 (*d*, J=8.3 Hz)] were located in ring B. Signals that could be assigned to a 2, 2-dimethylpyrano group were as follows: two doublets of one proton each at δ 5.67 and 6.35 J=9.9 Hz and a six-proton singlet at δ 1.46 for the *gem* dimethyl group. The prenyl and the 2,2-dimethyl pyran groups cannot be located on the same ring. Two possibilities were considered; one with the pyran in ring B and the prenyl group at C-6 (**1**) or an alternative structure with the pyran in ring A and the prenyl group at C-3′. This issue was settled by HMBC data which indicated a cross peak for the methylene carbon of the prenyl group (δ_C 29.4), and the downfield proton signal at δ 7.71 assigned to H-5. Thus the prenyl group, which is characterized by ^{1}H NMR chemical shift values: [3.34 (*d*, J=7.1 Hz methylene), 5.30 (*t*, J=7.1 Hz, olefinic proton) and 1.79 (6H, two olefinic methyls)] is without doubt located at C-6. From the foregoing spectroscopic data compound **1** was characterized as (−)-6-(3,3-dimethylallyl)-7-hydroxy-6″,6″-dimethylchromeno-(4′,3′, 2″,3″)-flavanone, for which the name dinklagin A is proposed. NMR spectral data of dinklagin A (**1**) and its important HMBC correlations are shown in Table 1. Euchrenone a_5 (**1a**) and abyssinone III (**1b**) isomers of **1**

Table 1
NMR assignments and important HMBC correlation data of compound **1** in $CDCl_3$. Chemical shifts are given in ppm; multiplicities and coupling constants J (parentheses) in Hz

C/H	δ_C	δ_H	^2J and ^3J correlated carbons
2	80.1 *s*	5.35 *dd* (2.8, 13.4)	—
3a	44.5 *t*	3.00 *dd* (13.3, 16.8)	191.6, 131.3
3b	44.5 *t*	2.78 *dd* (2.8, 16.9)	191.6, 115.2
4	191.6 *s*	—	—
4a	115.2 *s*	—	—
5	128.8 *d*	7.71 *s*	191.6, 162.6, 162.1, 29.4
6	122.2 *s*	—	—
7	162.1 *s*	—	—
8	104.1 *d*	6.45 *s*	162.6, 162.1, 115.2
8a	162.6 *s*	—	—
1′	131.3 *s*	—	—
2′	124.8 *d*	7.09 *d* (2.1)	127.6, 122.4
3′	121.8 *s*	—	—
4′	153.8 *s*	—	—
5′	116.9 *d*	6.82 *d* (8.3)	153.8, 131.3, 121.8
6′	127.6 *d*	7.20 *dd* (2.1, 8.3)	—
1″	29.4 *t*	3.34 *d* (7.1)	—
2″	121.6 *d*	5.30 *brt* (7.1)	—
3″	136.0 *s*	—	—
4″	18.3 *q*	1.79 *s*	136.0, 121.6, 26.2, 18.3
5″	26.2 *q*	1.79 *s*	136.0, 121.6, 26.2, 18.3
4‴	122.4 *d*	6.35 *d* (9.9)	153.8, 124.8, 121.8
5‴	131.7 *d*	5.67 *d* (9.8)	121.8, 28.5
6‴	77.6 *s*	—	—
6‴(Me)$_2$	28.5 *q*	1.46 *s*	131.7, 122.4, 77.6, 28.5
7-OH	—	6.02 *brs*	162.1, 122.2

were isolated, respectively, from *Euchresta formosana* (Mizuno et al., 1989) and *Erythrina abyssinica* (Kamat et al., 1981). The UV spectral data using shift reagents (Experimental) and the ^{13}C NMR signals at δ 182.7 for **2** and 182.8 for **3** indicated that **2** and **3** were 5-hydroxyflavones (Mabry et al., 1970; Agrawal, 1989). Compound **2**, isolated as a powder, showed IR absorption bands due to hydroxyl (3475, 3418 cm^{-1}) and carbonyl (1647 cm^{-1}) groups. Its molecular formula was deduced to be $C_{20}H_{18}O_6$ on the basis of NMR and HREIMS spectral measurements. Its ^1H NMR showed two singlets of one proton each at δ 6.48 and 6.65 assignable to H-3 and H-6 or H-8.The characteristic NMR signals (Experimental) of **2** revealed the presence of a *p*-disubstituted benzene ring [two double-doublets of two protons each at δ_H 7.95 and 7.03, J=1.9 and 8.8 Hz, δ_C 128.7 (*d*), and 116 (*d*)] and one hydroxydimethyldihydropyran group. Thus an oxymethine, a methylene and *gem*-dimethyl signals at δ_C 68.4 (*d*), 20.7 (*t*) and 25.5, 25.3 (both *q*), respectively, and an ABX system [δ_H 2.62 (*dd*, J=7.3, 17.0 Hz), 2.96 (*dd*, J=5.2, 17.0 Hz) and 3.88 (*brt*, J=6.5 Hz) assignable to two benzylic protons attached to an sp^3 carbon] were observed. Two possibilities were considered regarding the orientation of this pyran group located in ring A: one with a linear pyran (**2**) or an alternative structure with an angular pyran group. This question is related to the designation of whether the singlet signal at δ 6.48 is appropriate for H-6 or H-8. The other singlet signal at 6.65 was undoubtedly assigned to H-3 on account of the HMBC correlations observed between it and the carbonyl signal at δ_C 182.7 and C-1′ signal at 122.9. The chemical shift of δ_C 94.9, which was correlated by HMQC experiments to this Ar-CH signal (δ_H 6.48), is consistent with its location at C-8 and not C-6 (Agrawal, 1989). Thus the pyran group is deduced to have a linear arrangement. From the foregoing data the structure of compound **2** was determined as (+)-5,4′,5″ξ-trihydroxy-6″,6″-dimethylchromano-(7,6,2″,3″)-flavone for which the name dinklagin B is proposed. This structure is supported by both ^{13}C NMR spectrum and CIMS. The CIMS showed a fragment ion at m/z 283 diagnostic for the hydroxydimethyldihydropyran degradation (Drewes, 1973); another important ion at m/z 337 due to the loss of a molecule of water was also observed. The ^{13}C NMR signals (Experimental) were fully assigned using DEPT spectra and by comparison of measured values with those reported for ficuisoflavone (**2a**) isolated from the bark of *Ficus microcarpa* (Li and Kuo, 1997; Agrawal, 1989).

Compound **3** was assigned $C_{20}H_{18}O_6$ as molecular formula from HREIMS measurements. Its IR spectrum showed absorptions bands for hydroxyl (3422 cm^{-1}) and conjugated carbonyl (1648 cm^{-1}) groups. The ^1H NMR of **3** (Experimental) displayed signals for two sets of *ortho* and *meta* coupled protons at δ 7.84 and 6.93 (2H each J=1.0, 8.8 Hz) characteristic of a *p*-disubstituted benzene ring as in **2**. Two sharp singlets at δ 6.57 and 6.48 were also observed. The presence of 2-hydroxy-3-methyl-3-butenyl group in **3** was deduced from its NMR spectra which displayed signals for an sp^3 oxymethine [δ_C 75.5 (*d*)], a terminal methylene [δ_H 4.73 (*s*), 4.81 (*s*), δ_C 110.0 (*t*)] an sp^2 quaternary carbon (δ 147.7), a vinyl methyl [δ_C 16.8 (*q*), δ_H 1.85 (*s*)] and an ABX system [δ_H 2.89 (*dd*, J=7.3, 13.6 Hz), 3.02 (*dd*, J=5.8, 13.6 Hz) and 4.41 (*t*, J=6.5 Hz)]. This hydroxymethylbutenyl group located in ring A can be substituted either in position 6 (**3**) or in position 8. It was unambiguously fixed at C-6 because of the chemical shift of the carbon doublet at δ 95.8 characteristic of unsubstituted C-8 5-hydroxyflavone (Agrawal, 1989). The location of this group was readily established from HMBC studies where the two proton signals of the C-1″ showed correlations with the two oxygenated sp^2 carbon signals at C-5 and C-7. Dinklagin C (**3**) was then characterized as (+)6-(2″ξ-hydroxy-3-methyl-3-butenyl)-5, 7, 4′-trihydroxyflavone. The ^{13}C NMR signals (Experimental) were fully assigned using DEPT, HMQC and HMBC spectra and by comparison of measured values with those reported for ephedroidin (**3a**) and (**3b**) isolated, respectively, from *Genista ephedroides* (Pistelli et al., 1998) and *Vancouveria hexandra* (Iinuma et al., 1993). Important HMBC correlations of **3** are displayed in Table 2.

Table 2
Important HMQC and HMBC correlations observed for compound **3**. ^1J (from HMQC) and ^2J-, ^3J-gradient from HMBC correlations of **3**

δ_H	Position	^1J-correlated carbon	^2J-, ^3J-correlated carbons
7.84	2′, 6′	128.3	164.9 (C-2), 161.7 (C-4′), 128.3 (C-2′, C-6′)
6.93	3′, 5′	116.0	161.7 (C-4′), 122.3 (C-1′), 116.0 (C-3′, C-5′)
6.57	3	102.7	182.8 (C-4), 164.9 (C-2), 122.3 (C-1′), 103.8 (C-4a)
6.48	8	93.8	164.4 (C-7), 156.7 (C-8a), 109.7 (C-6), 103.8 (C-4a)
4.81	4″a	110.0	75.5 (C-2″), 16.8 (C-5″)
4.73	4″b	110.0	75.5 (C-2″), 16.8 (C-5″)
4.41	2″	75.5	147.7 (C-3″), 28.7 (C-1″)
3.02	1″a	28.7	164.4 (C-7), 159.6 (C-5), 147.7 (C-3″), 109.7 (C-6), 75.5 (C-2″)
2.89	1″b	28.7	164.4 (C-7), 159.6 (C-5), 147.7 (C-3″), 109.7 (C-6), 75.5 (C-2″)
1.85	5″	16.8	147.7 (C-3″), 110.0 (C-4″), 75.5 (C-2″)

The NMR spectra of 6-prenylapigenin displayed signals for chelated carbonyl δ 182.8, two protons as singlet each at δ 6.49 and 6.59 and one prenyl group characterized by ^{13}C NMR chemical shift values of 16.8 *q*, 21.2 *t*, 24.8 *q*, 122.3 *d* and 131.0 *s*. This compound was found to be identical with 6-prenylapigenin isolated from *Dorstenia kameruniana* (Abegaz et al., 1998). Interestingly this compound and dinklagin B (**2**) had the same R_f on TLC. After multiple developments on preparative TLC, we were able to separate them. The two compounds on analytical TLC plate sprayed with 10% sulphuric acid and heated, showed two different colors: **2** is green meanwhile 6-prenylapigenin is yellow. Stipulin and 5,4′-dihydroxy-6″,6″-dimethylchromano-(7,6,2″,3″)-flavone were identified by comparison of recorded spectra with those reported for the same compounds recently isolated from *D. kameruniana* (Abegaz et al., 1998). Likewise, 4-hydroxylonchocarpin was identified by comparison of acquired spectroscopic data with those reported for the same compound by Dagne et al. (1989).

The results of this work and our earlier investigation on the genus *Dorstenia* (Abegaz et al., 1998, 2000; Ngadjui et al., 1998a,b, 1999a,b,c, 2000) showed that African *Dorstenia* species are rich sources of mono-, di-, triprenylated and geranylated chalcones, flavanones and flavones of considerable complexity in the modification of the prenyl and geranyl substituent groups. Noteworthy is the absence of any coumarins in this plant meanwhile all *Dorstenia* species are assumed to contain furanocoumarins (Franke et al., 2001). 6-Prenyl-apigenin was shown in our previous study (Abegaz et al., 1998) to be extremely toxic to HL-60 promyelocytic leukemia cells, with 50% kill observed on day two at 50 μM concentration.

3. Experimental

3.1. General

Mps uncorr.; UV: MeOH solution; IR: KBr disk; CI and HREIMS: direct inlet; ^{1}H and ^{13}C NMR ($CDCl_3$, Acetone-d_6 and CD_3OD) 300 and 75 MHz, respectively, with the residual solvent peaks as internal references. COSY, HMQC and HMBC experiments were performed with gradient enhancements.

3.2. Plant material

The twigs of *D. dinklagei* were collected at Eseka, Cameroon. Mr. P. Mizili of the National Herbarium in Yaounde identified the plant. Voucher specimen (HNC30019) is deposited at the National Herbarium, Yaounde, Cameroon.

3.3. Extraction, isolation and characterization

The sun-dried and powdered twigs of *D. dinklagei* (1 kg) were soaked in a mixture of CH_2Cl_2/MeOH (1:1) and pure MeOH for 24 and 3 h, respectively, at the room temp. A greenish dark residue (45 g) was obtained after concentration of the combined organic extract under red. pres. Part (40 g) of this residue was subjected to CC on silica gel and eluted with hexane followed by hexane–EtOAc gradient. 4-Hydroxylonchocarpin (80 mg), 5,4′-dihydroxy-6″,6″-dimethylchromano-(7,6,2″,3″)-flavone (10 mg), dinklagin A (**1**, 15 mg), stipulin (20 mg) and 6-prenylapigenin (25 mg) were obtained from 10%, 12.5%, 15%, 20% and 25% EtOAc in hexane, respectively. Repeated CC and PTLC on frs eluted with 30% yielded: dinklagin B (**2**, 10 mg), dinklagin C (**3**, 15 mg) and 6-prenylapigenin (10 mg). Known compounds were identified from spectroscopic and physical data and published information and/or comparison with authentic specimens. New derivatives were characterized as follows:

3.4. (−)-6-(3,3-Dimethylallyl)-7-hydroxy-6‴,6‴-dimethylchromeno-(4′,3′,2‴,3‴)-flavanone, dinklagin A (*1*)

White crystals in hexane–EtOAc, mp 197–198 °C. $[\alpha]_D^{25}$ −31.9° (MeOH; *c* 0.016). UV λ_{max}^{MeOH} nm (log ε): 209 (4.13), 274 (3.87), 316 (3.67); $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): no change; $\lambda_{max}^{MeOH+NaOAc}$ nm log (ε): 213 (4.66), 273 (sh,

3.82), 322 (3.82), 336 (3.80). IR ν_{max}^{KBr} cm^{-1}: 3415 (OH), 1645 (C=O), 1625, 1163, 1100, 1050. ^1H NMR spectral data (300 MHz, $CDCl_3$) and ^{13}C NMR spectral data (75 MHz, $CDCl_3$) Table 1. CIMS (iso-butane, probe), 200 eV, *m/z* (rel. int.): 391 $[M+H]^+$ (100), 336 $[(M+H)-C_4H_7]^+$ (10), 335 (18), 299 (5), 289 (5), 205 (6) 187 (10), 164 (40). HREIMS: found 390.1833; calc. for $C_{25}H_{26}O_4$ 390.1831.

3.5. (+)-5,4′,5″ξ-Trihydroxy-6″,6″-dimethylchromano-(7,6,2″,3″)-flavone, dinklagin B (2)

Yellowish powder in hexane–EtOAc, mp 265–268 °C. $[\alpha]_D^{25}$ +48° (MeOH; *c* 0.011). UV λ_{max}^{MeOH} nm (log ε): 215 (4.47), 271 (4.24), 301 (*sh*, 4.14), 334 (4.31); $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): 216 (4.43), 282 (4.20), 306 (4.21), 358 (4.32); $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): no change; $\lambda_{max}^{MeOH+NaOAc}$ nm log (ε): 212 (4.96), 271 (4.23), 300 (*sh*, 4.03), 386 (4.28); $\lambda_{max}^{MeOH+NaOMe}$ nm log (ε): 214 (4.97), 271 (4.39), 301 (*sh*, 4.23), 388 (4.48). IR ν_{max}^{KBr} cm^{-1}: 3475 (OH), 3418 (OH), 1647 (C=O), 1475, 1377, 1252, 1146. ^1H NMR spectral data (300 MHz, acetone-d_6): δ 1.34 (3H, *s*, C6″-CH_3), 1.41 (3H, *s*, C6″-CH_3), 2.62 (1H, *dd*, *J*=7.3, 17.0 Hz, H-4″a), 2.96 (1H, *dd*, *J*=5.2, 17.0 Hz, H-4″b), 3.88 (1H, *brt*, *J*=6.5 Hz, H-5″), 4.40 (1H, *brs*, 4′-OH), 6.48 (1H, *s*, H-8), 6.65 (1H, *s*, H-3), 7.03 (2H, *dd*, *J*=1.9, 8.7 Hz, H-3′, H-5′), 7.95 (2H, *dd*, *J*=1.9, 8.8 Hz, H-2′, H-6′) and 13.36 (1H, *s*, 5-OH). ^{13}C NMR spectral data (75 MHz, acetone-d_6): δ 20.7 (*t*, C-4″), 25.3 (*q*, C6″-$\underline{C}H_3$), 25.5 (*q*, C6″-$\underline{C}H_3$), 68.4 (*d*, C-5″), 79.2 (*s*, C-6″), 94.9 (*d*, C-8), 103.3 (*d*, C-3), 104.4 (*s*, C-4a), 104.5 (*s*, C-6), 116.4 (*d*, C-3′, C-5′), 122.9 (*s*, C-1′), 128.8 (*d*, C-2′, C-6′), 156.0 (*s*, C-8a), 159.8 (*s*, C-5), 159.9 (*s*, C-4′), 161.2 (*s*, C-7), 164.6 (*s*, C-2), 182.7 (*s*, C-4). CIMS (*iso*-butane, probe), 200 eV, *m/z* (rel. int.): 355 $[M+H]^+$ (100), 337 $[(M+H)-H_2O]^+$ (99), 319 (8), 295 (10), 283 $[(M+H)-(CH_3)_2CHCHO]^+$ (32), 237 (5). HREIMS: found 354.1107; calc for $C_{20}H_{18}O_6$ 354.1103.

3.6. (+)6-(2ξ-Hydroxy-3-methyl-3-butenyl)-5, 7, 4′-trihydroxyflavone, dinklagin C (3)

Yellow powder from hexane–EtOAc; mp 236–238 °C. $[\alpha]_D^{25}$ +13.5° (MeOH, *c* 0.020). UV λ_{max}^{MeOH} nm log (ε): 217 (4.66), 274 (4.45), 335 (4.49); $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε) 221 (4.61), 287 (*sh*, 4.40), 304 (4.43), 358 (4.53); $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): no change; $\lambda_{max}^{MeOH+NaOAc}$ nm log (ε): 206 (4.81), 276 (4.55), 299 (4.35), 380 (4.45); $\lambda_{max}^{MeOH+NaOMe}$ nm log (ε): 214 (4.81), 278 (4.48), 327 (4.34), 393 (4.64). IR ν_{max}^{KBr} cm^{-1}: 3422 (OH), 1645 (C=O), 1626, 1448, 1357, 1248, 1182, 1101. ^1H NMR spectral data (300 MHz, CD_3OD): δ 1.85 (3H, *s*, H-5″), 2.89 (1H, *dd*, *J*=7.3, 13.6 Hz, H-1″a), 3.02 (1H, *dd*, *J*=5.8, 13.6 Hz, H-1″b), 4.41 (1H, *t*, *J*=6.5 Hz, H-2″), 4.73 (1H, *brs*, H-4″a), 4.81 (1H, *brs*, H-4″b), 6.48 (1H, *s*, H-8), 6.57 (1H, *s*, H-3), 6.93 (2H, *dd*, *J*=1.0, 8.8 Hz, H-3′, H-5′), 7.84 (2H, *dd*, *J*=1.0, 8.8 Hz, H-2′, H-6′). ^{13}C NMR spectral data (75 MHz, CD_3OD): δ 16.8 (*q*, C-5″), 28.7 (*t*, C-1″), 75.5 (*d*, C-2″), 93.8 (*d*, C-8), 102.7 (*d*, C-3), 103.8 (*s*, C-4a), 109.7 (*s*, C-6), 110.0 (*t*, C-4″), 116.0 (*d*, C-3′, C-5′), 122.3 (*s*, C-1′), 128.3 (*d*, C-2′, C-6′), 147.7 (*s*, C-3″), 156.7 (*s*, C-8a), 159.6 (*s*, C-5), 161.7 (*s*, C-4′), 164.4 (*s*, C-7), 164.9 (*s*, C-2) and 182.8 (*s*, C-4). CIMS (*iso*-butane, probe), 200 eV, *m/z* (rel. int.): 355 $[M+H]^+$ (100), 337 $[(M+H)-H_2O]^+$ (80), 319 (10), 309 (7), 295 (8), 283 (10), 237 (8). HREIMS: found 354.1106; calc. for $C_{20}H_{18}O_6$ 354.1103.

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References

Abegaz, B.M., Ngadjui, B.T., Dongo, E., Tamboue, H., 1998. Prenylated chalcones and flavonoids from the leaves of *Dorstenia kameruniana*. Phytochemistry 49, 1147–1150.

Abegaz, B.M., Ngadjui, B.T., Dongo, E., Bezabih, M.-T., 2000. Chemistry of the genus *Dorstenia*. Current Organic Chemistry 4, 1079–1090.

Agrawal, P.K., 1989. Carbon-13 NMR of Flavonoids. Elsevier, Amsterdam.

Barthlott, W., 1998. The Royal Horticultural Society. DuMont's große Pflanzen-Enzyklopädie A.–Z. DuMont Buchverlag, Köln.

Bouquet, A., 1969. Feticheurs et Medicine Traditionelle de Congo Brazzaville. Memoire ORSTOM 36, 295.

Dagne, E., Bekele, A., Waterman, P.G., 1989. The flavonoids of *Millettia ferruginea* subsp. *darasana* in Ethiopia. Phytochemistry 28, 1897–1900.

Drewes, S., 1973. Chroman and related compounds. In: Budzikiewicz (Ed.), Progress in Mass Spectrometry, Vol 2. Verlag Chemie, pp. 3–18.

Franke, K., Porzel, A., Masaoud, M., Adam, G., Schmidt, J., 2001. Furanocoumarins from *Dorstenia gigas*. Phytochemistry 56, 611–621.

Iinuma, M., Kanie, Y., Tanaka, T., Mizuno, M., Lang, F.A., 1993. Five phenolic compounds from the underground parts of *Vancouveria hexandra*. Heterocycles 35, 407–413.

Kamat, V.S., Chuo, F.Y., Kubo, I., Nakanishi, K., 1981. Antimicrobial agents from an East African medicinal plant, *Erytrhina abyssinica*. Heterocycles 15, 1163–1170.

Li, Y.-C., Kuo, Y.-H., 1997. Two new isoflavones from the bark of *Ficus microcarpa*. Journal of Natural Products 60, 292–293.

Mabberley, D.J., 1987. The Plant Book. Cambridge University Press, New York, p. 192.

Mabry, T., Markham, K.R., Thomas, M.B., 1970. The Systematic Identification of Flavonoids. Springer Verlag, New York.

Mizuno, M., Tamura, K.-I., Tanaka, T., Iinuma, M., 1989. Six flavonoids from the roots of *Euchresta formosana*. Phytochemistry 28, 2811–2812.

Ngadjui, B.T., Dongo, E., Happi, E.N., Bezabih, M.-T., Abegaz, B.M., 1998a. Prenylated flavones and phenyl propanoids from the roots of *Dorstenia psilurus*. Phytochemistry 48, 733–737.

Ngadjui, B.T., Abegaz, B.M., Dongo, E., Tamboue, H., Fogue, K., 1998b. Geranylated and prenylated flavonoids from the twigs of *Dorstenia mannii*. Phytochemistry 48, 349–354.

Ngadjui, B.T., Dongo, E., Tamboue, H., Fogue, K., Abegaz, B.M., 1999a. Prenylated flavanones from the twigs of *Dorstenia mannii*. Phytochemistry 50, 1401–1406.

Ngadjui, B.T., Kapche, G.W.F., Tamboue, H., Abegaz, B.M., Connolly, J.D., 1999b. Prenylated flavonoids and dihydro-4-phenylcoumarin from *Dorstenia poinsettifolia*. Phytochemistry 51, 119–123.

Ngadjui, B.T., Tabopda, T., Dongo, E., Kapche, G.W.F., Sandor, P., Abegaz, B.M., 1999c. Dorsilurins C, D and E, three prenylated flavonoids from the roots of *Dorstenia psilurus*. Phytochemistry 52, 731–735.

Ngadjui, B.T., Kouam, S.F., Dongo, E., Kapche, G.W.F., Abegaz, B.M., 2000. Prenylated flavonoids from the aerial parts of *Dorstenia mannii*. Phytochemistry 55, 915–919.

Pistilli, L., Bertoli, A., Giachi, I., Manunta, A., 1998. Flavonoids from *Genista ephedroides*. Journal of Natural Products 61, 1404–1406.