

# Prenylated flavonoids and other constituents from the twigs of *Dorstenia angusticornis* (Moraceae)<sup>☆</sup>

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## 1. Subject and source

*Dorstenia* (Moraceae) is a mainly tropical genus of some 170 species (Mabberley, 1987). There are 23 species in Cameroon where a decoction of the leaves is administered for the treatment of cough, headache and stomach pain (Bouquet, 1969). The genus is made up largely of herbaceous perennials with succulent and non-succulent scrambling rhizomes (Berg et al., 1989).

The twigs of *Dorstenia angusticornis* were collected in February 2002 from Kumba South West Province of Cameroon. Voucher specimen (No 28165/sfcam) is deposited at the National Herbarium Yaounde, Cameroon.

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## 2. Previous work

A previous work on *D. angusticornis* described the isolation and characterization of lupeol, stipulin, gancaonin Q, paratocarpins C and F, angusticornins A and B together with  $\beta$ -sitosterol and its  $\beta$ -D-glucopyranoside (Ngadjui et al., 2005).

## 3. Present study

The air-dried and powdered twigs of *D. angusticornis* (1 kg) were successively soaked in  $\text{CH}_2\text{Cl}_2$ :MeOH (1:1) mixture and MeOH for 24 and 2 h, respectively, at room temperature. These two extracts were combined on the basis of TLC results and the solvents removed under reduced pressure to give a dark green residue (55 g); part of this residue (50 g) was subjected to vacuum liquid chromatography (VLC) on silica gel (60, 180 g) and eluted with petrol 40–60/ethyl acetate mixtures, EtOAc and EtOAc:MeOH mixtures to give 35 fractions of 200 ml each. Fractions were monitored by TLC and  $^1\text{H}$  NMR and similar fractions were combined. Fractions 1–5 (3 g), eluted with petrol–EtOAc (9:1) examined on TLC with the same solvent system contained mainly mixtures of hydrocarbons and phytosterols. Recrystallisation of these fractions yielded  $\beta$ -sitosterol (35 mg) and lupeol (25 mg) (Tane et al., 1995). Fractions 6–12 (6 g), obtained with 25% petrol–EtOAc crystallized in the same solvent to give gancaonin Q (50 mg) (Fukai et al., 1991). Combined fractions 13–26 (20 g) eluted with 70% petrol–EtOAc were passed through a Sephadex LH-20 column and eluted with  $\text{CHCl}_3$ :MeOH (2:1) mixture. The post-chlorophyll fractions were combined and subjected successively to silica gel CC and prepTLC to give: stipulin (20 mg) (Abegaz et al., 1998), angusticornins A (2, 10 mg) and B (12 mg) (Ngadjui et al., 2005), angusticornin C (1, 6 mg), paratocarpin C (3, 15 mg) and paratocarpin F (4, 21 mg) (Hano et al., 1995a,b). Fractions 27–31 (3.5 g) and 32–35 (1.5 g) eluted with EtOAc and 10% EtOAc–MeOH, respectively, yielded precipitates which were recrystallized to give  $\beta$ -sitosterol-3-O-D-glucopyranoside (80 mg).

The HREIMS of compound **1** showed the molecular ion peak at  $m/z$  406.1812, consistent with the molecular formula  $\text{C}_{25}\text{H}_{26}\text{O}_5$ . Its  $^1\text{H}$  NMR spectrum displayed a highly deshielded signal of a chelated hydroxyl group at  $\delta$  13.93, chalcone *trans*-vinyl proton resonances constituting an AB system at  $\delta$  7.83 and 7.45; two aryl proton signals which appeared as doublets at  $\delta$  7.74 and 6.44 ( $J = 8.9$  Hz) were assigned to the *ortho* oriented H-6' and H-5', respectively. An ABX-system: a doublet at  $\delta$  6.82, an *ortho*- and *meta*-coupled double doublet at  $\delta$  7.44 and a *meta*-coupled signal at  $\delta$  7.30 observed in the  $^1\text{H}$  NMR spectrum of **1** led to the deduction that the protons responsible for these signals could only be located in ring B. The  $^1\text{H}$  NMR spectrum of **1** also indicated two prenyl units; one as hydroxydimethyldihydropyrano and another as dimethylpyrano moiety (Table 1). From the foregoing data two structures can be proposed for this compound: one with the hydroxydimethyldihydropyrano moiety in ring A and the other prenyl unit in ring B (**1**) or the alternative with the dimethylpyrano group in ring A and the other prenyl unit in ring B. The methylene proton signals (H-4'') at  $\delta$  2.80 and 3.00 of the

hydroxydimethyldihydropyrano group indicated long range correlations (HMBC, Table 1) with C-2' (165.3), C-3' (108.8) and C-4' (160.2); also the up field aryl proton signal at  $\delta$  6.44 (H-5',  $\delta_C$  108.9 from HMQC, Table 1) showed long range interactions to three quaternary carbon signals at  $\delta$  116.4 (C-1'), 108.8 (C-3') and 160.2 (C-4'). Therefore, the structure of angusticornin C (**1**) was established as 6''',6''-dimethylpyrano[2''',3''':3,4]-6''',6''-dimethyldihydropyrano[2'',3'':3',4']-2',5''-dihydroxychalcone. Similarities observed in the multiplicities and chemical shifts of the benzylic methylene and oxymethine proton signals (at 4'' and 5'' of **1**, respectively) to the corresponding signals in the  $^1\text{H}$  NMR spectra of compounds 2–4 (Ngadjui et al., 2005), and the occurrence of paratocarpins C (**3**) and F (**4**) with angusticornin A (**2**) in the same plant confirm the proposed structure for compound **1**. Yellow oil:  $[\alpha]_D^{25} - 43^\circ$  ( $\text{CHCl}_3$ ;  $c$  0.12); UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm (log  $\epsilon$ ): 202 (4.53), 265 (4.34), 290 (4.23), 377 (3.98); IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3463 (OH), 3418 (OH), 1636 (C=O), 1559;  $^1\text{H}$  NMR spectral data (600 MHz,  $\text{CDCl}_3$ , Table 1);  $^{13}\text{C}$ , HMQC and HMBC: Table 1; APCIMS  $m/z$  (rel. Int.): 407[M + H] $^+$  (100), 389 (16), 335 (15), 221 (10), 213 (25); HREIMS  $m/z$  406.1812 (calc. for  $\text{C}_{25}\text{H}_{26}\text{O}_5$ , 406.1821).

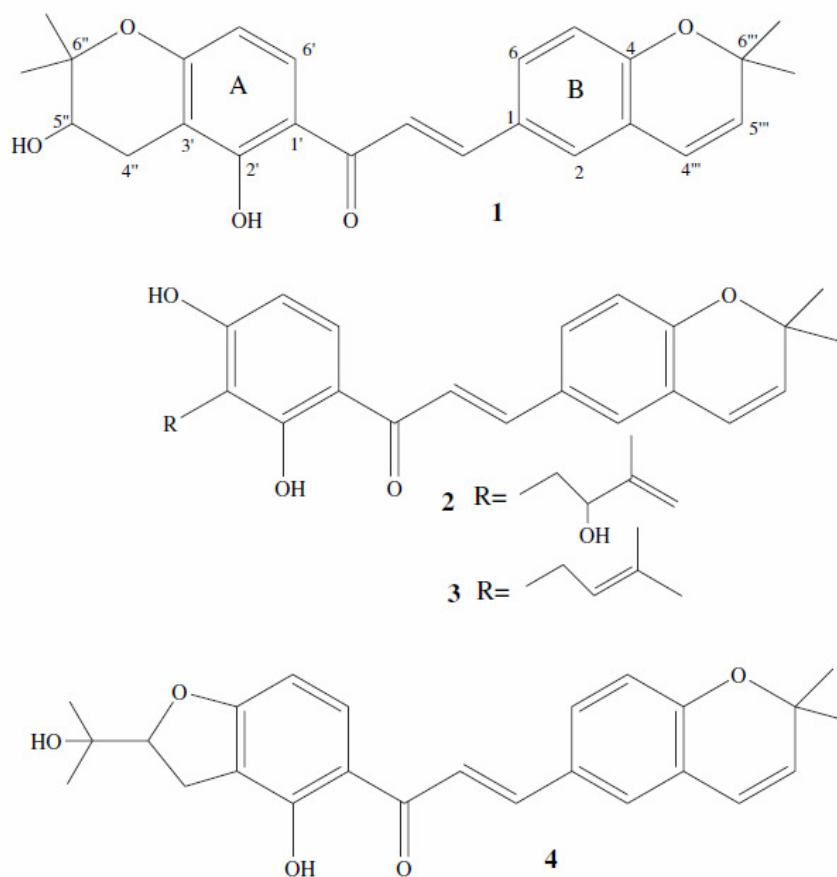


Table 1  
 $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectral data, HMQC and important HMBC  $^2\text{J}$ ,  $^3\text{J}$ -correlated carbons of angusticornin C (I) in  $\text{CDCl}_3$

C/H	$\delta_{\text{H}}$	$\delta_{\text{C}}$	HMQC	HMBC $^2\text{J}$ and $^3\text{J}$ -correlated carbons $^1\text{H} \rightarrow ^{13}\text{C}$
1		127.8 (s)		
2	7.30 (d, 1.9)	130.0 (d)	130.0	C- $\beta$ , C-1, C-4, C-4 $'''$
3		122.1 (s)		
4		158.2 (s)		
5	6.82 (d, 8.4)	117.3 (d)	117.3	C-4, C-1, C-3
6	7.44 (dd, 1.9, 8.4)	129.6 (d)	129.6	C- $\beta$ , C-4
$\alpha$	7.45 (d, 15.3)	118.0 (d)	118.0	C- $\beta$ , C-1
$\beta$	7.83 (d, 15.3)	144.1 (d)	144.1	C- $\beta'$
$\beta'$	—	192.4 (s)		
1'	—	116.4 (s)		
2'	—	165.3 (s)		
3'	—	108.8 (s)		
4'	—	160.2 (s)		
5'	6.44 (d, 8.9)	108.9 (d)	108.9	C-1', C-3', C-4'
6'	7.74 (d, 8.9)	131.0 (d)	131.0	C-2', C-4'
4''a	3.00 (dd, 5.1, 17.3)	26.4 (t)	26.4	C-2', C-3', C-4', C-6''
4''b	2.80 (dd, 5.3, 17.3)	26.4 (t)	26.4	C-2', C-3', C-4', C-6''
5''	3.90 (t, 5.2)	68.7 (d)	68.7	C-4'', C-6''
6''	—	77.8 (s)		
4'''	6.37 (d, 9.8)	122.3 (d)	122.3	C-4, C-6'''
5'''	5.69 (d, 8.9)	131.4 (d)	131.4	C-3
6'''	—	78.0 (s)		
6''-Me	1.42 (s),	25.0 (q)	25.0	C-6''
6''-Me	1.38 (s)	20.6 (q)	20.6	C-6''
6'''-Me	1.48 (s)	28.6 (q)	28.6	C-6'''
2'-OH	13.93 (s)	—		

Multiplicities and coupling constant in Hz are given in parentheses.

#### 4. Chemotaxonomic significance

Prenylated coumarins and flavonoids have previously been isolated (Ngadjui and Abegaz, 2003) from various *Dorstenia* species. Angusticornin C (I) is a new derivative reported for the first time; stipulin, paratocarpins C and F, angusticornins A and B were also obtained. These are expectable compounds in that they occur commonly in other species of the genus. It is interesting to note that all the flavonoids so far reported from this genus appear to be only from African *Dorstenia* species; but more data would have to be obtained to confirm, if indeed this is truly so and if this observation has any chemotaxonomic significance.

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