

# Prenylated flavonoids, monoterpenoid furanocoumarins and other constituents from the twigs of *Dorstenia elliptica* (Moraceae)

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## Abstract

A monoprenylated flavan and two monoterpenoid substituted furanocoumarins were isolated from the twigs of *Dorstenia elliptica* along with 3-(3,3-dimethylallyl)-4,2',4'-trihydroxychalcone, psoralen, bergapten, *O*-[3-(2,2-dimethyl-3-oxo-2*H*-furan-5-yl)butyl]bergaptol,  $\beta$ -sitosterol and its  $\beta$ -D-glucopyranoside. The structure of the flavan was determined as 6(1,1-dimethylallyl)-7,4'-dihydroxyflavan and the monoterpenoid substituted furanocoumarins were assigned as *O*-[3-(2,2-dimethyl-3-oxo-2*H*-furan-5-yl)-3-hydroxybutyl]-bergaptol and *O*-[2-(5-hydroxy-2,6,6-trimethyl-3-oxo-2*H*-pyran-2-yl)ethyl]bergaptol, respectively, using spectroscopic analysis, especially, 2D NMR spectra.

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## 1. Introduction

The genus *Dorstenia* contains many plants that are used as anti-snakebite, anti-infection and anti-rheumatic remedies in the medicinal plant therapy of many countries in Africa, Central and South America (Bouquet, 1969; Abegaz et al., 2000). This genus is recognized as a rich source of prenylated and geranylated flavonoids and coumarins (Abegaz et al., 2000). *Dorstenia elliptica* Bureau, an undergrowth perennial plant, is used in the treatment of many diseases, especially, for eye infections (Bouquet, 1969). As part of our continuing program to study the chemical constituents of African *Dorstenia* species (Abegaz et al., 1998, 2002; Ngadjui et al., 1998a,b, 1999a,b, 2000), we have examined the extracts of the twigs of *D. elliptica*. To the best of our knowledge, no previous phytochemical or pharmacological studies have been reported on this taxon. In addition to the known 3-(3,3-dimethylallyl)-4,2',4'-trihydroxychalcone (1) (Asada et al., 1998), *O*-[3-(2,2-di-

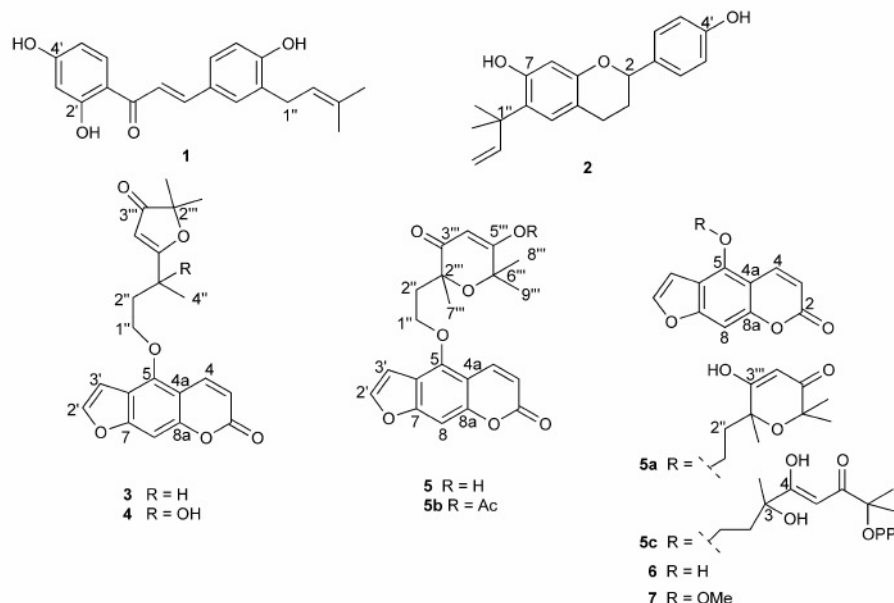
methyl-3-oxo-2*H*-furan-5-yl)butyl]bergaptol (3) (Kuster et al., 1994), psoralen (6) and bergapten (7) (Kuster et al., 1994),  $\beta$ -sitosterol and its  $\beta$ -D-glucopyranoside, we have isolated and characterized a new prenylated flavan (2) and two new monoterpenoid substituted furanocoumarins 4 and 5.

## 2. Results and discussion

The twigs of *D. elliptica* were extracted with a mixture of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (1:1) followed by 100% MeOH. The combined organic extract was evaporated under reduced pressure and subjected to vacuum liquid chromatography. Repeated column chromatography on different fractions obtained from this VLC yielded compounds 1–7 together with  $\beta$ -sitosterol and its  $\beta$ -D-glucopyranoside.

Compound (2), isolated as light yellow gum, was assigned the molecular formula C<sub>20</sub>H<sub>22</sub>O<sub>3</sub> from NMR and HREIMS spectral measurements. The 300 MHz NMR spectrum of this compound showed signals for a flavan system [an oxymethine  $\delta_{\text{H}}$  4.97, *m*, H-2,  $\delta_{\text{C}}$  85.0 (*d*), C-2; two methylenes at  $\delta$  2.87, 3.11 (H-3), 2.89, 3.16

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(H-4);  $\delta_C$  41.5 (*t*), C-3 and 34.9 (*t*), C-4]. The NMR spectra also displayed signals for a *para*-substituted phenyl ring [ $\delta_H$  7.15, 6.80, two broad doublets of two protons each  $J=8.5$  Hz]  $\delta_C$  130.9 (*d*) and 115.8 (*d*), a 1,1-dimethylallyl group {one methylene [ $\delta_H$ , 5.30, *dd*,  $J=1.0$ , 10.5 Hz, H-3''b; 5.36, *dd*,  $J=1.0$ , 17.7 Hz, H-3''a,  $\delta_C$  113.7 (*t*)], a vinyl methine [ $\delta_H$  6.18, *dd*,  $J=10.5$ , 17.7 Hz, H-2'',  $\delta_C$  148.7 (*d*)], a *gem*-dimethyl [ $\delta_H$  1.42 (6H, *s*),  $\delta_C$  27.6 (*q*)] and a quaternary carbon  $\delta_C$  40.3}. Two broad singlet signals of one proton each were also observed in the  $^1H$  NMR spectrum at  $\delta$  6.34 and 7.03, assignable to H-8 and H-5, respectively. The  $^{13}C$  NMR and DEPT spectra (Table 1) of this compound exhibited peaks for 20-carbon atoms: two methyl, three methylene, eight methine and seven quaternary carbon signals.

From the foregoing data compound **2** is identified as 6-(1,1-dimethylallyl)-7,4'-dihydroxyflavan. The proposed structure **2** was also supported by HMBC correlations (Table 1). The IR, UV and mass spectra measurements (see Section 3) were fully in agreement with this structure.

Compound **4** was assigned the molecular formula  $C_{21}H_{20}O_7$  from HREIMS ( $[M]^+$  at  $m/z$  384.1217; calc. 384.1209). The  $^1H$  NMR spectrum of this compound exhibited the presence of a furanocoumarin moiety [a broad singlet proton signal at  $\delta$  7.18 (H-8), an AB spin system [ $\delta$  6.30 (H-3) and 8.10 (H-4) (each *d*,  $J=9.8$  Hz)], and signals for the furan protons at  $\delta$  6.93 (*dd*,  $J=0.9$ , 2.3 Hz, H-3') and 7.61 (*d*,  $J=2.4$  Hz, H-2')]. It indicated also signals for two groups of methylene protons at  $\delta$  4.58 (*ddd*,  $J=6.6$ , 6.9, 12.8, H-1''), 4.51 (*ddd*,  $J=6.0$ , 6.2,

12.8 Hz, H-1''), 2.44 (*dt*,  $J=6.0$ , 13.4 Hz, H-2'') and 2.38 (*dt*,  $J=7.0$ , 13.4 Hz, H-2''), a sharp singlet signal of an olefinic proton at  $\delta$  5.75, assignable to H-4'' and three singlet signals at  $\delta$  1.64, 1.41 and 1.39, assignable to three tertiary methyl protons. The  $^1H$  NMR spectrum of **4** presented a number of similarities to that of compound **3**, a monoterpenoid furanocoumarin which was isolated from *Dorstenia brasiliensis* (Kuster et al., 1994) and was also found in other *Dorstenia* species (Terreaux et al., 1995; Tovar-Miranda et al., 1998). The most notable difference in the spectrum of this compound from that of **3** was the absence of multiplet signal for H-3'', which indicated that **4** could possess a hydroxyl group or another electron withdrawing group at C-3''. This proposal was supported by the presence of a signal for a tertiary alcohol carbon ( $\delta$  72.5, *s*) in the  $^{13}C$  NMR spectrum. This is in agreement with a tertiary methyl signal ( $\delta$  1.64, *s*) in **4** instead of a secondary methyl proton signal ( $\delta$  1.33, *d*) observed in **3**. The tertiary methyl group should be attached to an oxygenated carbon because of its downfield chemical shift. From the foregoing data compound **4** is identified as *O*-[3-(2,2-dimethyl-3-oxo-2*H*-furan-5-yl)-3-hydroxybutyl]bergaptool. The  $^{13}C$  NMR (Table 2), IR and UV (Section 3) spectra of **4** were consistent with the proposed structure. The DEPT experiments displayed nine peaks for methine and methyl carbons and two signals for methylene carbons. Its IR spectrum showed signals for a free hydroxyl, a conjugated carbonyl and a  $\delta$ -lactone vibration bands at  $\nu_{max}$  3434, 1693 and 1711  $cm^{-1}$ , respectively, and the UV spectrum displayed absorption bands

Table 1  
 $^1\text{H}$  (300 MHz),  $^{13}\text{C}$  (75 MHz) and important HMBC  $^2J$ ,  $^3J$  correlations NMR spectral data of **2** in  $\text{CDCl}_3$ . Multiplicities and coupling constant in Hz are given in parentheses

H/C	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$^2J$ , $^3J$ -correlated carbons ( $^1\text{H} \rightarrow ^{13}\text{C}$ )
2	4.97 ( <i>m</i> )	85.0 ( <i>d</i> )	130.0 (C-1'), 159.8 (C-9)
3a	2.87 ( <i>m</i> )	41.5 ( <i>t</i> )	34.9 (C-4), 85.0 (C-2), 130.0 (C-1')
3b	3.11 ( <i>m</i> )	41.5 ( <i>t</i> )	34.9 (C-4), 41.5 (C-3), 85.0 (C-2), 118.7 (C-10), 130.0 (C-1')
4a	2.89 ( <i>m</i> )	34.9 ( <i>t</i> )	41.5 (C-3), 118.7 (C-10), 122.4 (C-5), 159.8 (C-9)
4b	3.16 ( <i>m</i> )	34.9 ( <i>t</i> )	41.5 (C-3), 85.0 (C-2), 118.7 (C-10), 159.8 (C-9)
5	7.03 ( <i>brs</i> )	122.4 ( <i>d</i> )	34.9 (C-4), 40.3 (C-1''), 155.3 (C-7), 159.8 (C-9)
6	—	124.3 ( <i>s</i> )	
7	—	155.3 ( <i>s</i> )	
8	6.34 ( <i>brs</i> )	99.8 ( <i>d</i> )	118.7 (C-10), 124.3 (C-6), 155.3 (C-7), 159.8 (C-9)
9	—	159.8 ( <i>s</i> )	
10	—	118.7 ( <i>s</i> )	
1'	—	130.0 ( <i>s</i> )	
2'	7.15 ( <i>brd</i> , 8.5)	130.9 ( <i>d</i> )	115.8 (C-3', 5'), 130.9 (C-2', 6'), 154.7 (C-4')
3'	6.80 ( <i>brd</i> , 8.5)	115.8 ( <i>d</i> )	115.8 (C-3', 5'), 130.0 (C-1'), 154.7 (C-4')
4'	—	154.7 ( <i>s</i> )	
5'	6.80 ( <i>brd</i> , 8.5)	115.8 ( <i>d</i> )	115.8 (C-3', 5'), 130.0 (C-1'), 154.7 (C-4')
6'	7.15 ( <i>brd</i> , 8.5)	130.9 ( <i>d</i> )	115.8 (C-3', 5'), 130.9 (C-2', 6'), 154.7 (C-4')
1''	—	40.3 ( <i>s</i> )	
2''	6.18 ( <i>dd</i> , 10.5, 17.7)	148.7 ( <i>d</i> )	27.6 (C-4''), 5''), 40.3 (C-1''), 124.3 (C-6)
3''a	5.36 ( <i>dd</i> , 1.0, 17.7)	113.7 ( <i>t</i> )	40.3 (C-1''), 148.7 (C-2'')
3''b	5.30 ( <i>dd</i> , 1.0, 10.5)	113.7 ( <i>t</i> )	40.3 (C-1''), 148.7 (C-2'')
4'', 5''	1.42 ( <i>s</i> )	27.6 ( <i>q</i> )	27.6 (C-4''), 5''), 40.3 (C-1''), 148.7 (C-2'')
7-OH	5.85 ( <i>s</i> )		99.8 (C-8), 124.3 (C-6), 155.3 (C-7)

Table 2  
 $^1\text{H}$  (600 MHz),  $^{13}\text{C}$  (150 MHz) and important HMBC  $^2J$ ,  $^3J$  correlations NMR spectral data of **4** in  $\text{CDCl}_3$ . Multiplicities and coupling constant in Hz are given in parentheses

C/H	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$^2J$ , $^3J$ -correlated carbons ( $^1\text{H} \rightarrow ^{13}\text{C}$ )
2	—	161.5 ( <i>s</i> )	
3	6.30 ( <i>d</i> , 9.8)	113.4 ( <i>d</i> )	107.5 (C-4a), 161.5 (C-2)
4	8.10 ( <i>d</i> , 9.8)	139.4 ( <i>d</i> )	148.6 (C-5), 152.9 (C-8a), 161.5 (C-2)
4a	—	107.5 ( <i>s</i> )	
5	—	148.6 ( <i>s</i> )	
6	—	114.5 ( <i>s</i> )	
7	—	158.5 ( <i>s</i> )	
8	7.18 ( <i>brs</i> )	95.2 ( <i>d</i> )	107.5 (C-4a), 114.5 (C-6), 152.9 (C-8a), 158.5 (C-7)
8a	—	152.9 ( <i>s</i> )	
2'	7.61 ( <i>d</i> , 2.4)	145.8 ( <i>d</i> )	114.5 (C-6), 158.5 (C-7)
3'	6.93 ( <i>dd</i> , 0.9, 2.3)	105.1 ( <i>d</i> )	114.5 (C-6), 145.8 (C-2'), 158.5 (C-7)
1''a	4.58 ( <i>ddd</i> , 6.6, 6.9, 12.8)	70.0 ( <i>t</i> )	39.9 (C-2''), 70.0 (C-1''), 148.6 (C-5)
1''b	4.51 ( <i>ddd</i> , 6.0, 6.2, 12.8)	70.0 ( <i>t</i> )	39.9 (C-2''), 70.0 (C-1''), 148.6 (C-5)
2''a	2.44 ( <i>dt</i> , 6.0, 13.4)	39.9 ( <i>t</i> )	39.9 (C-2''), 72.5 (C-3''), 194.6 (C-5'')
2''b	2.38 ( <i>dt</i> , 7.0, 13.4)	39.9 ( <i>t</i> )	39.9 (C-2''), 72.5 (C-3''), 194.6 (C-5'')
3''	—	72.5 ( <i>s</i> )	
4''	1.64 ( <i>s</i> )	27.9 ( <i>q</i> )	39.9 (C-2''), 72.5 (C-3''), 194.6 (C-5'')
2''	—	90.4 ( <i>s</i> )	
3''	—	207.3 ( <i>s</i> )	
4''	5.75 ( <i>s</i> )	100.3 ( <i>d</i> )	90.4 (C-2''), 194.6 (C-5''), 207.3 (C-3'')
5''	—	194.6 ( <i>s</i> )	
6''	1.41 ( <i>s</i> )	23.2 ( <i>q</i> )	23.2 (C-6''), 23.3 (C-7''), 90.4 (C-2''), 207.3 (C-3'')
7''	1.39 ( <i>s</i> )	23.3 ( <i>q</i> )	23.2 (C-6''), 23.3 (C-7''), 90.4 (C-2''), 207.3 (C-3'')

at  $\lambda_{\text{max}}$  221, 251, 259 and 309 nm, characteristic of a linear furanocoumarin (Kuster et al., 1994).

The ion fragmentations observed in the LR and HR mass spectra of **4** were also consistent with the proposed

structure. The HREIMS showed two important ion fragments at  $m/z$  202 (bergaptol,  $\text{C}_{11}\text{H}_6\text{O}_4$ ) and 155, the latter peak resulting from the loss of  $\text{H}_2\text{O}$  and  $\text{CO}$  from the monoterpene moiety. Also the MS/MS on the

Table 3

$^1\text{H}$  (500 MHz),  $^{13}\text{C}$  (125 MHz) and important HMBC  $^2J$ ,  $^3J$  correlations NMR spectral data of **5** in  $\text{CDCl}_3$ . Multiplicities and coupling constant in Hz are given in parentheses

C/H	$\delta_{\text{H}}$ in $\text{CD}_2\text{CN}$	$\delta_{\text{H}}$ in $\text{CDCl}_3$	$\delta_{\text{C}}$ in $\text{CD}_2\text{CN}$	$^2J$ , $^3J$ -correlated carbons (H→C)
2	–	–	161.6 (s)	–
3	6.21 ( <i>d</i> , 9.8)	6.28 ( <i>d</i> , 9.8)	113.1( <i>d</i> )	107.1 (C-4a), 161.6 (C-2)
4	8.11 ( <i>d</i> , 9.8)	8.11 ( <i>d</i> , 9.8)	140.7 ( <i>d</i> )	107.1 (C-4a), 149.6 (C-5), 153.8 (C-8a), 161.6 (C-2)
4a	–	–	107.1 (s)	–
5	–	–	149.6 (s)	–
6	–	–	113.1 (s)	–
7	–	–	159.2 (s)	–
8	7.10 ( <i>brs</i> )	7.12 ( <i>brs</i> )	93.9 ( <i>d</i> )	107.1 (C-4a), 113.1 (C-6), 153.8 (C-8a), 159.2 (C-7)
8a	–	–	153.8 (s)	–
2'	7.68 ( <i>d</i> , 2.3)	7.58 ( <i>d</i> , 2.4)	146.3 ( <i>d</i> )	106.4 (C-3'), 113.1 (C-6), 159.2 (C-7)
3'	7.08 ( <i>d</i> 1.7)	6.92 ( <i>dd</i> , 0.6, 1.6)	106.4 ( <i>d</i> )	113.1 (C-6), 146.3 (C-2'), 149.6 (C-5), 159.2(C-7)
1''a	4.53 ( <i>ddd</i> , 5.3, 9.7, 14.5)	4.47 ( <i>brdd</i> , 5.2, 7.3)	68.4 ( <i>t</i> )	37.3 (C-2''), 89.8 (C-2''), 149.6 (C-5)
1''b	4.45 ( <i>ddd</i> , 4.3, 9.4, 14.5)	4.47 ( <i>brdd</i> , 5.2, 7.3)	68.4 ( <i>t</i> )	37.3 (C-2''), 89.8 (C-2''), 149.6 (C-5)
2''a	2.44 ( <i>ddd</i> , 5.4, 9.4, 14.9)	2.54 ( <i>dt</i> , 7.3, 14.7)	37.3 ( <i>t</i> )	23.0 (C-7''), 68.4 (C-1''), 89.8 (C-2'')
2''b	2.24 ( <i>dt</i> , 4.3, 14.9)	2.32 ( <i>dt</i> , 5.2, 14.7)	37.3 ( <i>t</i> )	23.0 (C-7''), 68.4 (C-1''), 89.8 (C-2'')
2'''	–	–	89.8 (s)	–
3'''	–	–	206.9 (s)	–
4'''	5.46 (s)	5.60 (s)	100.1 ( <i>d</i> )	70.7 (C-6'''), 89.8 (C-2'''), 197.8 (C-5'''), 206.9 (C-3''')
5'''	–	–	197.8 (s)	–
5'''-OH	3.48 (s)	–	–	70.7 (C-6'''), 197.8 (C-5''')
6'''	–	–	70.7 (s)	–
7'''	1.40 (s)	1.51 (s)	23.0 ( <i>q</i> )	37.3 (C-2'''), 89.8 (C-2''')
8'''	1.33 (s)	1.48 (s)	27.8 ( <i>q</i> )	27.8 (C-8''', 9'''), 70.7 (C-6'''), 197.8 (C-5''')
9'''	1.23 (s)	1.44 (s)	28.1 ( <i>q</i> )	28.1 (C-8''', 9'''), 70.7 (C-6'''), 197.8 (C-5''')

quasi-molecular ion at  $m/z$  385  $[\text{M} + \text{H}]^+$ , led to an ion at  $m/z$  367 corresponding to  $[(\text{M} + \text{H}) - 18]^+$  indicating loss of  $\text{H}_2\text{O}$  from the molecular ion. MS/MS/MS on the  $m/z$  367 ion led to a prominent peak at  $m/z$  255  $[(\text{M} + \text{H}) - 18 - 111]^+$  suggesting the cleavage of the five-membered ring from the monoterpenoid substituent. Long-range proton-carbon correlations in HMBC experiments (Table 2) were also consistent with the structure.

Compound **5** was obtained as colorless needles from hexane-ethyl acetate. The HREIMS of **5** presented a molecular ion  $[\text{M}]^+$  at  $m/z$  384.1214 consistent with the molecular formula  $\text{C}_{21}\text{H}_{20}\text{O}_7$ . The IR spectrum showed vibration bands of hydroxyl ( $3418\text{ cm}^{-1}$ ),  $\delta$ -lactone ( $1723\text{ cm}^{-1}$ ), and  $\alpha,\beta$ -unsaturated carbonyl ( $1681\text{ cm}^{-1}$ ) functionalities. Its UV spectrum showed, like **4**, absorption bands at  $\lambda_{\text{max}}$  221, 250, 258 and 310 nm which were similar to those of psoralen (**6**) and bergapten (**7**). The  $^1\text{H}$  NMR spectrum of **5** (see Table 3) suggested a structure closely related to **4**, showing signals of three tertiary methyl groups ( $\delta$  1.23, 1.33 and 1.40), a vinyl proton ( $\delta$  5.46), an oxymethylene ( $\delta$  4.53, *ddd*,  $J=5.3, 9.7, 14.5$  Hz, H-1'' and 4.45, *ddd*,  $J=4.3, 9.4, 14.5$  Hz, H-1''') a second methylene group ( $\delta$  2.44, *ddd*,  $J=5.4, 9.4, 14.9$  Hz, H-2'' and 2.24, *dt*  $J=4.3, 14.9$  Hz, H-2''') and a furanocoumarin moiety [ $(\delta$  6.21, H-3, 8.11 H-4, each *d*,  $J=9.8$  Hz), ( $\delta$  7.08, H-3', 7.68, H-2', each *d*,  $J\approx 2.0$  Hz) and  $\delta$  7.10 H-8, s]. When recorded in  $\text{CDCl}_3$  the  $^1\text{H}$  NMR spectra of **4** and **5** were virtually identical

except for small differences observed in the upfield region where the monoterpenoid moiety protons resonate, i.e. the oxymethylene proton and the three tertiary methyl group signals (compare Tables 2 and 3). It was, therefore, concluded that the monoterpenoid moiety of compound **5** has an arrangement different from the one in compound **4**. The possible arrangements consistent with the generated NMR data are the tautomeric structures **5** and **5a**. The possibility that the compound may exist as a mixture of these two tautomers was considered and acetylation was carried out in the hope of trapping the tautomers. This effort, however, resulted in the detection and subsequent isolation of only one acetylated product indicating that the compound is not a mixture but either **5** or **5a** or that the reactivity of one of the tautomers towards the acetylating reagent was many orders of magnitude higher than for the other tautomer, resulting in trapping of only the most reactive tautomer. Finally it was possible to determine the correct tautomer of this compound as **5** using extensive 2D NMR spectra. The  $^1\text{H}$  NMR spectrum of **5** in acetonitrile- $d_3$  exhibited a singlet signal at  $\delta$  3.48 exchangeable with  $\text{D}_2\text{O}$  corresponding to a hydroxyl group. This proton signal displayed cross peaks in the HMBC experiment (Table 3) with carbon signals at  $\delta$  197.8 (C-5''') and 70.7 (C-6'''). Irradiation of the hydroxyl signal at  $\delta$  3.48 in a selective gradient NOESY experiment enhanced the signals at  $\delta$  5.46 (H-4'''), 1.33 and 1.23 (H-8''' and H-9''') confirming the location of the hydroxyl

group to be on C-5<sup>''</sup>. From the above spectroscopic evidence the structure of **5** was finally established as *O*-[2-(5-hydroxy-2,6,6-trimethyl-3-oxo-2*H*-pyran-2-yl)ethyl]bergaptol. The LR and HR mass spectra of compound **5** had only one major ion corresponding to the loss of the aromatic bergaptol moiety. This ion at *m/z* 183.1022 (C<sub>10</sub>H<sub>10</sub>O<sub>5</sub>) constituted the base peak and it is significant that the corresponding ion resulting from the cleavage of the five-membered ring in **4** was not observed for **5**. We wish to speculate on the biosynthesis of these isomers (**4** and **5**) as arising from a common precursor **5c**. Ring closure of **5c** involving displacement of the –OPP group by the hydroxyl groups at C-4 and C-3 would lead to **4** and **5**, respectively.

### 3. Experimental

#### 3.1. General

Mps uncorr.; UV: MeOH solution; IR: KBr disk; Low resolution APCIMS was done using a Finnigan LCQ-Deca spectrometer. HREIMS (VG70-SEQ) at 70 eV. NMR spectra were acquired on Brüker Avance DRX 600, DRX 500 and DMX 300 instruments. <sup>1</sup>H detected <sup>1</sup>H–<sup>13</sup>C 2D (HMBC and HMQC) gradient enhanced magnitude spectra were obtained with 2 K data points, 256 time increments 24 scans per increment, and 1.5 s relaxation delay. Data were processed using the Brüker XwinNMR (Version 2.6) software. Zero filling once in the F2 and 4-fold in the F1 dimensions in combination with forward linear prediction to 4 K in the F1 dimension were performed to improve the resolution and sensitivity of the spectra. Selective gradient NOESY data were obtained using the standard Brüker BUTSELNMR program with mixing time of 500 ms. Chloroform-*d* and acetonitrile-*d*<sub>3</sub> (99.8% deuterium content) from Aldrich were used with the residual solvent peaks as internal references. CC and TLC: silica gel (70–230 mesh) and silica gel GF<sub>254</sub>.

#### 3.2. Plant material

The twigs of *Dorstenia elliptica* were collected on 19 March 2000 at Kribi, Cameroon. The plant material was identified by P. Mizili of the National Herbarium. Voucher specimen No. 44018HNC is deposited at the National Herbarium, Yaounde, Cameroon.

#### 3.3. Extraction, isolation and characterization of the constituents

The sun-dried and crushed twigs of *D. elliptica* (2.1 kg) were soaked in a mixture of CH<sub>2</sub>Cl<sub>2</sub>–MeOH (1:1) and pure MeOH for 24 and 2 h, respectively, at room temp. Concentration of the combined organic extract

gave a greenish dark extract (115 g). Part (70 g) of this residue was chromatographed on a silica gel column eluting with hexane–EtOAc mixtures, to give 40 frs of 250 ml each. Frs were monitored by TLC and <sup>1</sup>H NMR and similar frs were combined. Frs 1–6 (5 g) examined by TLC (hexane–EtOAc; 9:1) contained mainly mixtures of hydrocarbons and phytosterols. Recryst. of these combined frs yielded β-sitosterol (23 mg); Frs 7–12 (4 g) crystallized in the mixture of hexane–EtOAc to give psoralen (28 mg) and **3** (650 mg). The filtrate (3.2 g) was rechromatographed on silica gel using a mixture of hexane–EtOAc as eluent to afford psoralen (22 mg), bergapten (65 mg) and **3** (520 mg). Frs 13–30 (23 g) were passed through Sephadex LH-20 column (CHCl<sub>3</sub>–MeOH, 2:1). The post-chlorophyll frs were subjected to repeated silica gel CC and PTLC to yield **1** (24 mg) and **2** (13 mg), **4** (60 mg) and **5** (55 mg). Frs 31–40 (4.8 g) were evaporated to provide an amorphous powder which was crystallized from MeOH to give 3-*O*-β-D-glucopyranosylsitosterol (85 mg). The identity of products was established using spectroscopic and physical data and/or with comparison to authentic specimens for known compounds.

#### 3.4. 6(1, 1-Dimethylallyl)-7,4'-dihydroxyflavan (**2**)

Light yellow gum, [α]<sub>D</sub><sup>20</sup> + 3.5° (MeOH; 0.14); UV λ<sub>max</sub><sup>MeOH</sup> nm (log ε): 220 (4.89), 284 (4.25); IR ν<sub>max</sub><sup>KBr</sup> cm<sup>-1</sup>: 3420 (OH), 1620, 1590, 1530, 1455, 1120. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): Table 1; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): Table 1; EIMS *m/z* (rel. int.): 310 [M]<sup>+</sup>(100), 295 [M–Me]<sup>+</sup> (60), 175 (78), 133 (56), 107 (84), HREIMS: *m/z* 310.1548, calc. for C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>: 310.1569.

#### 3.5. *O*-[3-(2,2-dimethyl-3-oxo-2*H*-furan-5-yl)-3-hydroxybutyl]bergaptol (**4**)

Colorless needles from hexane–EtOAc, mp.168–169°, [α]<sub>D</sub><sup>20</sup> –5.0° (MeOH; 0.12); UV λ<sub>max</sub><sup>MeOH</sup> nm (log ε): 221 (4.36), 251 (4.44), 259 (4.44), 309 (4.15); IR ν<sub>max</sub><sup>KBr</sup> cm<sup>-1</sup>: 3434 (OH), 1711 (C=O), 1693 (C=O), 1621, 1581, 1452, 1352, 1169, 1105; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): Table 2; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): Table 2; CIMS *m/z* (rel. int.): 385 [M+H]<sup>+</sup> (100), 367 [M–H<sub>2</sub>O] (34), 325 (5), 281(5), 255 (10), 203 [bergaptol+H]<sup>+</sup> (15), 183 (15), 165 (7); HREIMS *m/z*, (rel. int.): 384.1217 [M]<sup>+</sup>, [C<sub>21</sub>H<sub>20</sub>O<sub>7</sub>]<sup>+</sup>, calc. 384.1209 (86), 202.0270 [C<sub>11</sub>H<sub>6</sub>O<sub>4</sub>]<sup>+</sup> (81), 183.1018 [C<sub>10</sub>H<sub>15</sub>O<sub>3</sub>]<sup>+</sup> (18), 174.0311 [C<sub>10</sub>H<sub>6</sub>O<sub>3</sub>]<sup>+</sup> (25), 165.0914 [C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>]<sup>+</sup> (11), 155.1073 [C<sub>9</sub>H<sub>15</sub>O<sub>2</sub>]<sup>+</sup> (100).

#### 3.6. 2-*O*-[2-(5-hydroxy-2,6,6-trimethyl-3-oxo-2*H*-pyran-2-yl)ethyl]bergaptol (**5**)

Colorless plates (hexane–EtOAc), mp 144–145°, [α]<sub>D</sub><sup>20</sup> –4.1° (MeOH; 0.11); UV λ<sub>max</sub><sup>MeOH</sup> nm (log ε): 221 (4.45),

250 (4.47), 258 (4.49), 310 (4.20); IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3418 (OH), 1723 (C=O), 1681 (C=O), 1623, 1577, 1454, 1345, 1135;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 500 MHz): Table 3;  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ , 125 MHz): Table 3; CIMS  $m/z$  (rel. int.): 385  $[\text{M} + \text{H}]^+$  (100), 369  $[\text{M} - \text{Me}]^+$  (10), 202  $[\text{bergapto}]^+$  (15), 183  $[\text{C}_{10}\text{H}_{15}\text{O}_3]^+$  (30), 165 (20), 154 (10), 137 (5); HREIMS  $m/z$ , (rel. int.): 384.1214  $[\text{M}]^+$ ,  $[\text{C}_{21}\text{H}_{20}\text{O}_7]^+$ , calc. 384.1209 (31), 369.0986  $[\text{C}_{20}\text{H}_{17}\text{O}_7]^+$  (7), 202.0271  $[\text{C}_{11}\text{H}_6\text{O}_4]^+$  (9), 183.1022  $[\text{C}_{10}\text{H}_{15}\text{O}_3]^+$  (100), 137.0970  $[\text{C}_9\text{H}_{13}\text{O}]^+$  (34).

### 3.7. Acetylation of **5**

**5** (15 mg) was refluxed in acetic anhydride (20 ml) at  $75^\circ$  for 3 h. The  $\text{CHCl}_3$  extract of the reaction residue was evaporated to provide an amorphous powder.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (1H, d,  $J=9.8$  Hz, H-4), 7.58 (1H, d,  $J=2.4$  Hz, H-2'), 7.14 (1H, s, H-8), 7.03 (1H, brt,  $J=1.2$  Hz, H-3'), 6.30 (1H, dd,  $J=0.9, 9.8$  Hz, H-3), 5.49 (1H, s, H-4''), 4.48 (2H, brdd, 5.2, 7.3 Hz, 2H-1\*Prime); 2.52 (1H, dt,  $J=7.3, 14.7$  Hz, H-2a), 2.31 (1H, dt,  $J=5.2, 14.7$  Hz, H-2b), 2.02 (3H, s, Ac), 1.61 (3H, s, Me-7''), 1.59, 1.48 (each 3H, s, 3H-8'', 9'').

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