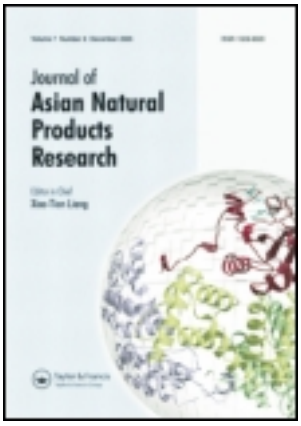

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Dorstenpictanone: a new bicyclic polyprenylated compound from *Dorstenia picta*

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One new bicyclic polyprenylated compound, dorstenpictanone (**1**), was isolated from *Dorstenia picta.* The structure of the new compound was elucidated by detailed spectroscopic analysis such as ^{1}H NMR, ^{13}C NMR, COSY, HMQC, HMBC, and HREIMS. The relative configuration of dorstenpictanone (**1**) was distinguished by comparative analysis of the NMR spectral data with known analogues together with the ROESY experiment.

Keywords: bicyclic polyprenylated; *Dorstenia picta*; Moraceae; natural product

1. Introduction

The plants from the genus *Dorstenia* Bur. (Moraceae) are largely made up of undergrowth and herbaceous perennials with succulent and scrambling rhizomes [1]. This genus *Dorstenia* comprises about 170 species of which *Dorstenia poinsettifolia*, *Dorstenia psilurus*, *Dorstenia dinklagei*, and *Dorstenia picta* are found in Cameroon [1]. Medicinal preparations containing the leaves and twigs of these plants of genus *Dorstenia* have been used for many applications such as anti-snakebite, anti-infection, and anti-rheumatic remedies in the medicinal plant therapy in Africa, Central America, and South America [2]. The extract of *D. psilurus* showed anti-hypertensive effects on hypertensive rats [3]. The leaves of *D. poinsettifolia* Engl. and *Dorstenia barteri* (Bureau) are used for the treatment of yaws and infected wounds [4]. Extracts and/or compounds from other species showed anti-inflammatory, analgesic, anti-oxidant, and cytotoxic activities [2]. The chemistry of genus *Dorstenia* has been reviewed [2] and is recognized as a rich source of prenylated and geranylated natural products [2]. In the course of phytochemical studies of medicinal plants from Africa [5–10], we investigated *D. picta* and obtained a new bicyclic polyprenylated compound, dorstenpictanone (**1**). Here, we describe the isolation and structural elucidation of dorstenpictanone (**1**).

2. Results and discussion

D. picta was extracted with MeOH. The crude extract was fractionated on a silica gel column and it yielded a pure new compound **1**. The structure was elucidated by careful spectroscopic analysis (Figure 1).

Dorstenpictanone (**1**) was obtained as an amorphous powder. The IR spectrum exhibited absorption at 3400 cm^{-1} for

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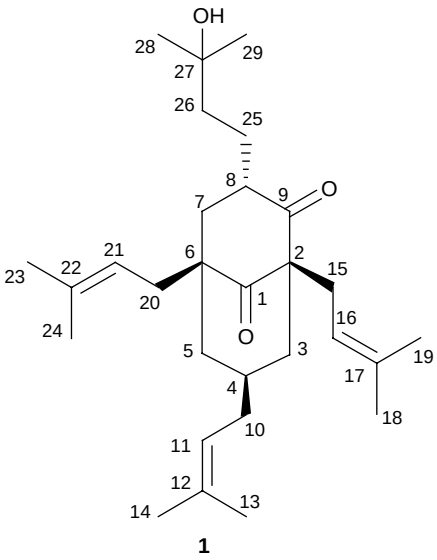

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Figure 1. Chemical structure of dorstenpictanone (**1**).

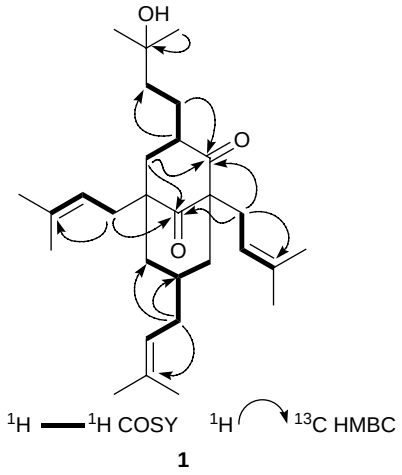

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Figure 2. Key COSY and HMBC correlations for dorstenpictanone (**1**).

hydroxyl group. A $[M]^+$ peak at *m/z* 442.3440 in the HREIMS, along with the analysis of ^{1}H NMR, ^{13}C NMR, and DEPT spectra, showed a molecular formula of $C_{29}H_{46}O_3$, indicating seven degrees of unsaturation.

The ^{1}H NMR spectrum of **1** (see 'Experimental' section) showed the characteristic resonances of three prenyl groups [δ 1.60 (3H, s), 1.62 (3H, s), and 1.65 (3H, s); 1.71 (3H, s), 1.73 (3H, s), and 1.80 (3H, s); 3.35 (1H, br d, $J = 7.2$ Hz, H-15a), 2.95 (1H, dd, $J = 18.5$, 3.2 Hz, H-15b), 3.15 (1H, br d, $J = 7.2$ Hz, H-20a), 2.78 (1H, dd, $J = 18.5$, 3.2 Hz, H-20b), 2.58 (1H, m, H-10a), and 2.38 (1H, m, H-10b); and 5.15 (1H, m, H-16), 5.07 (1H, m, H-21), and 5.00 (1H, m, H-11)]. The ^{13}C NMR spectrum of compound **1** showed signals for five methines including three downfiled methine signals [δ 124.1 (C-21), 122.5 (C-11), and 121.6 (C-16)] for three prenyl groups, eight methylenes, and eight quaternary carbons. Besides 15 signals for three prenyl groups, ^{13}C NMR spectrum showed signals for three methylene and four quaternary carbons including signals for two nonconjugated carbonyl groups at δ 208.2 and 207.9 and two methine signals. In addition, the key HMBC correlations (Figure 2) of H-4 with C-3, C-5, C-6, and C-2, H-5 with C-1, C-4, C-6, and C-20, H-8 with C-9, C-7, and C-6, and H-7 with C-1, C-6, and C-9 verified the core bicyclo[3.3.1]nonane-1,9-dione system [11,12]. HREIMS required the compound to be bicyclic, considering the subtraction of five double bond equivalents for two carbonyl groups and three prenyl double bonds.

The NMR spectra of **1** also showed signal for C_5 unit, and this conclusion was confirmed by ^{1}H–^{1}H COSY and HMBC correlations of fragments C-25 to C-29 (Figure 2). The HMBC correlations of H-25 with C-7, C-8, and C-9 confirmed the attachment of C_5 unit to C-8 of the bicyclic nonane core system.

Similarly, HMBC correlations of H-10 with C-3, C-4, C-6, and C-5, H-15 with C-1, C-2, and C-9, and H-20 with C-1, C-6, and C-7 verified the positions of three prenyl groups at C-4, C-2, and C-6 of the core bicyclo[3.3.1]nonane-1,9-dione system, respectively.

The configuration of **1** was determined by the ROESY experiment conjugated with

the comparative analysis of the NMR spectral data with its analogues. According to the literature, when H-4 is in α-orientation, the chemical shift of C-4 is always between 41 and 44 ppm, and the difference of H_α-5 and H_β-5 is also always between 0.3 and 1.2 ppm, regardless of NMR solvent or nature of the C-4 substituent [12–15]. On the other hand, the difference in chemical shifts of the H_α-5 and H_β-5 is 0.0–0.2 ppm and the chemical shift of C-4 is δ 45–49 ppm, if H-4 is in β-orientation [12,14,15]. In compound **1**, the fact that the chemical shifts of C-4 is 42.4 ppm, and the difference of H_α-5 and H_β-5 ($\Delta\delta$ ca. 0.45 ppm) indicated that H-4 was in α-orientation. The ROESY correlations (Figure 3) of H_2-10/H_β-5, H_β-5/H_2-20, H_2-20/H_β-8, H_2-10/H_β-3, and H_β-3/H_2-16 showed that all these protons lie on the same face of the molecule.

In addition, ROESY correlations of H_α-5/H-4 and H-4/H_α-3 showed that all these protons lie on the other face of the molecule. The above ROESY peaks indicated that **1** had the same relative configuration at C-2, C-3, and C-6 as furohyperforin and uralodin B [12]. Hence, the structure of **1** was elucidated and named as dorstenpictanone (**1**).

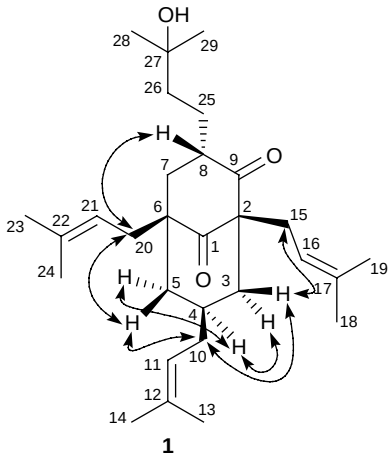

Figure 3. Key ROESY correlations for dorstenpictanone (**1**).

3. Experimental

3.1 General experimental procedures

IR spectra were recorded from Nicolet-510P spectrophotometer; ν_{max} in cm^{-1}. The ^1H NMR spectra were recorded on Bruker AMX-500 instruments using TMS as an internal reference. The chemical shifts are reported in ppm (δ), whereas the coupling constants (J) in Hertz. The ^{13}C NMR spectra were recorded at 125 MHz on the same instrument. EIMS and HREIMS were carried out using MAT 8200 and Micromass LCT mass spectrometers, in m/z.

Column chromatography (CC) was carried out using silica gel (70–230 and 230–400 mesh; E-Merck, Darmstadt, Germany) and Sephadex LH-20 (Amersham Biosciences AB, Uppsala, Sweden). Aluminum sheets precoated with silica gel 60 F 254 (0.2 mm thick; E-Merck) were used for TLC to check the purity of the compounds and were visualized under UV light (254 and 366 nm) followed by ceric sulfate as the spray reagent.

3.2 Plant material

The roots of *D. picta* were collected from Nkolbibanda, Cameroon, during March 2003, and identified by Dr Louis Zapfack (plant taxonomist). A voucher specimen (No. 57063 HNC) has been deposited at the National Herbarium Yaoundem Cameroon.

3.3 Extraction and isolation

The air-dried leaves and twigs (5 kg) of *D. picta* were exhaustively extracted with MeOH at room temperature. The extract was evaporated to dryness yielding 580 g of residue. The whole extract was extracted with *n*-hexane, $CHCl_3$, EtOAc, and *n*-butanol. The *n*-hexane and EtOAc extracts were combined (80 g) and the combined

extract was subjected to CC (silica gel, *n*-hexane, *n*-hexane–EtOAc, and EtOAc, in order of increasing polarity) yielding 13 fractions. Fraction F_7 (1.1 g) was eluted with a mixture of *n*-hexane–EtOAc (1.5:8.5) yielding dorstenpictanone (**1**) (6.0 mg).

3.3.1 Dorstenpictanone (1)

White solid. IR (KBr) ν_{max}: 3400, 2963, and 1600 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 0.82 (3H, s, Me-28), 1.06 (3H, s, Me-29), 1.45 (2H, m, H-26), 1.55 (2H, m, H-25), 1.58 (1H, m, H_α-5), 1.60 (3H, s, Me-13), 1.62 (3H, s, Me-14), 1.63 (1H, m, H-7a), 1.65 (3H, s, Me-24), 1.70 (1H, m, H-3a), 1.71 (3H, s, Me-23), 1.73 (3H, s, Me-19), 1.80 (3H, s, Me-18), 1.85 (1H, m, H-7b), 1.99 (1H, m, H-4), 2.03 (1H, m, H_β-5), 2.22 (1H, m, H-3b), 2.35 (1H, m, H-8), 2.38 (1H, m, H-10b), 2.58 (1H, m, H-10a), 2.95 (1H, dd, $J = 14.5$, 7.2 Hz, H-15b), 2.78 (1H, dd, $J = 14.5$, 7.2 Hz, H-20b), 3.15 (1H, br dd, $J = 14.5$, 3.2 Hz, H-20a), 3.35 (1H, br d, $J = 7.2$ Hz, H-15a), 5.15 (1H, m, H-16), 5.07 (1H, m, H-21), and 5.00 (1H, m, H-11). ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.2 (C-1), 207.9 (C-9), 134.8 (C-22), 131.8 (C-12), 130.9 (C-17), 124.1 (C-21), 122.5 (C-11), 121.6 (C-16), 73.1 (C-27), 68.9 (C-2), 56.1 (C-6), 42.4 (C-4), 40.7 (C-3), 38.9 (C-8), 39.8 (C-5), 31.9 (C-7), 30.8 (C-20), 30.5 (C-29), 28.3 (C-15), 26.6 (C-10), 26.3 (C-25), 26.1 (C-14), 25.7 (C-18), 24.7 (C-26), 22.1 (C-13), 21.9 (C-28), 20.1 (C-23), 17.9 (C-19), and 16.1 (C-24). EIMS: *m/z* (%) 474.3 (17) $[M]^+$. HREIMS: *m/z* 442.3447 $[M]^+$ (calcd for $C_{29}H_{46}O_3$, 442.3440).

References

[1] B. Vouffo, K. Krohn, S.F. Kouam, H. Hussain, E. Dongo, K. Meier, and B. Schulz, *Biochem. Syst. Ecol.* **36**, 655 (2008).

[2] B.M. Abegaz, B.T. Ngadjui, E. Dongo, and M.T. Bezabih, *Curr. Org. Chem.* **4**, 1079 (2000).

[3] T. Dimo, A. Rakotonirina, P.V. Tan, E. Dongo, A.B. Dongo, P. Kamtchouing, B.M. Abegaz, G. Cros, and B.T. Ngadjui, *Phytomedicine* **8**, 101 (2001).

[4] D.W. Thomas, J.M. Thomas, W.A. Bromely, and F.T. Mbenkum, *Korup Ethnobotany Survey* (W.W.F. Survey, 1989), p. A31.

[5] D. Tazooa, K. Krohn, H. Hussain, S.F. Kouam, and E. Dongoa, *Z. Naturforsch.* **62B**, 1208 (2007).

[6] K.Z. Antoine, H. Hussain, E. Dongo, S.F. Kouam, B. Schulz, and K. Krohn, *J. Asian Nat. Prod. Res.* **12**, 629 (2010).

[7] K.O. Eyong, K. Krohn, H. Hussain, G.N. Folefoc, A.E. Nkengfack, B. Schulz, and Q. Hu, *Chem. Pharm. Bull.* **53**, 616 (2005).

[8] M.Y. Bouberte, K. Krohn, H. Hussain, E. Dongo, B. Schulz, and Q. Hu, *Nat. Prod. Lett.* **20**, 842 (2006).

[9] M.Y. Bouberte, K. Krohn, H. Hussain, E. Dongo, B. Schulz, and Q. Hu, *Z. Naturforsch.* **61B**, 78 (2006).

[10] R.S. Miemanang, K. Krohn, H. Hussain, and E. Dongo, *Z. Naturforsch.* **61B**, 1123 (2006).

[11] J.-Y. Lee, R.K. Duke, V.H. Tran, J.M. Hook, and C.C. Duke, *Phytochemistry* **67**, 2550 (2006).

[12] X.Q. Chen, Y. Li, X. Cheng, K. Wang, J. He, Z.H. Pan, M.M. Li, L.Y. Peng, G. Xu, and Q.S. Zhao, *Chem. Biodiv.* **7**, 196 (2010).

[13] R. Ciochina and R.B. Grossman, *Chem. Rev.* **106**, 3963 (2006).

[14] J.S.A.R. Teixeira and F.G. Cruz, *Tetrahedron Lett.* **46**, 2813 (2005).

[15] R.B. Grossman and H. Jacobs, *Tetrahedron Lett.* **41**, 5165 (2000).