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STYRENES FROM *DORSTENIA BARNIMIANA*

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Key Word Index—*Dorstenia barnimiana*, Moraceae, styrenes, benzofurans, bergaptene

Abstract—Three new styrenes have been isolated from *Dorstenia barnimiana* (Moraceae) and were assigned the structures 6-methoxy-5-vinylbenzofuran, 4,6-dimethoxy-5-vinylbenzofuran and 2,4-dimethoxystyrene

INTRODUCTION

Dorstenia barnimiana is a seasonal African plant whose roots are used in folk medicine for skin diseases. In the literature only one paper [1] about the genus has described the isolation of steroids. This paper deals with the structure elucidation of three new styrenes isolated from the acetone extract of roots of the plant.

RESULTS AND DISCUSSION

Silica gel chromatography of the acetone extract of *Dorstenia barnimiana* afforded the three new compounds 1–3 together with bergaptene, glutinol [2] and β-amyrin acetate. Hydrogen and carbon counts from the NMR spectra and M^+ at *m/z* 174 in the mass spectrum indicated a molecular formula $C_{11}H_{10}O_2$ for compound **1**. The ^1H NMR spectrum showed the signals of a methoxy group, a vinylic side chain, two isolated aromatic protons and two furan protons. Cumulatively these data account for a benzofuran skeleton, which was also supported by the ^{13}C NMR spectrum, whose signals were in agreement with the literature [3]. The position of the substituents was established on consideration of the inter-ring coupling between the H-3 furan proton and the upfield aromatic proton (H-7) [4]. Compound **1** was thus assigned the structure of 6-methoxy-5-vinylbenzofuran.

Compound **3**, $C_{12}H_{12}O_3$ (M^+ at *m/z* 204), displayed a very similar ^1H NMR spectrum, only the signal of the H-4 proton of **1** being replaced by that of a second methoxy group. As a confirmation in the ^{13}C NMR spectrum of **3**, only one of the methoxyl signals appeared at 60 ppm [5]. The comparison between the ^{13}C NMR spectra of **1** and **3** evidenced the downfield shift of the signal of C-4 and the upfield shifts of the resonances of C-3a, C-5 and C-7, as required for the introduction of the 4-methoxy group. Therefore compound **3** was assigned the structure of 4,6-dimethoxy-5-vinylbenzofuran.

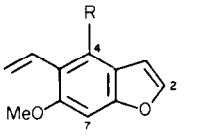
The ^1H NMR spectrum of compound **2**, $C_{10}H_{12}O_2$ (M^+ at *m/z* 164), showed the signals for two methoxyls, a vinylic side chain and three aromatic protons *ortho–ortho–meta* coupled. The substitution pattern of the aromatic ring was established when **2** was oxidized with IO_4^- / MnO_4^- to yield 2,4-dimethoxybenzaldehyde and its corresponding acid. Consequently compound **2** is 2,4-dimethoxystyrene.

Notably, metabolites **1** and **3** are the first examples of natural styrenes which contain a furan mojety. Compounds **1**, **2** and **3** have been tested against the following microorganisms *Staphylococcus aureus*, *S. epidermidis*, *Streptococcus faecalis*, *Escherichia coli*, *Enterobacter cloacae*, *Klebsiella oxytoca*, *Proteus mirabilis*, *Pseudomonas aeruginosa*, *Acinetobacter* and *Candida albicans*, but they did not show any significant inhibitory activity.

EXPERIMENTAL

Plant material Roots of *Dorstenia barnimiana* Schweinf. were collected in Ethiopia and a voucher sample (DB-86) is deposited at the Herbarium of Centro Chimica dei Recettori (Roma).

Extraction and fractionation Powdered air-dried roots (290 g) were extracted exhaustively with cold Me_2CO. Evapn of the Me_2CO gave a residue (26 g), which was dissolved in MeOH–H_2O (9:1) and extracted several times with hexane. The pooled hexane extracts (21.5 g) were chromatographed on a silica gel column eluting with hexane–EtOAc mixtures, to give several fractions, only two of which were further processed. The former on silica gel CC and prep. TLC (CH_2Cl_2–hexane, 9:1) afforded **1** (14 mg), **2** (195 mg), **3** (265 mg), β-amyrin acetate (80 mg) and lupeyl acetate (traces). From the latter fraction mainly bergaptene (60 mg) and glutinol (25 mg) were obtained. The known compounds were identified by the spectral data and comparison (co-TLC, mmp) with authentic samples.



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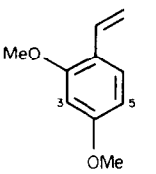

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6-Methoxy-5-vinylbenzofuran (1) Oil, $C_{11}H_{10}O_3$ UV λ_{max}^{MeOH} nm (log ε) 246 (4 10), 311 (3 61), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1625, 1610, 1580, 1430, 1300, 1210, 1150, 1090, ^1H NMR ($CDCl_3$) δ 7 50 (1H, *d*, $J = 2$ Hz, H-2), 6 60 (1H, br *d*, $J = 2$ Hz, H-3), 7 69 (1H, *s*, H-4), 7.00 (1H, *br* s, H-7), 7 40–6 90 (1H, *m*, A part of AX_2, H_α), 5 83–5 13 (2H, *m*, X_2 part of AX_2, H_β), 3 86 (3H, *s*, OMe), ^{13}C NMR ($CDCl_3$) δ 155 7, 155 6 (C-6, C-7a), 144 2 (C-2), 132 3 (C-8), 123 8, 120 5 (C-3a, C-5), 118 3 (C-4), 113 5 (C-9), 106 4 (C-3), 94 5 (C-7), 55 9 (OMe), MS m/z (rel int.) 174 $[M]^+$ (100), 159 (31), 131 (37)

2,4-Dimethoxystyrene (**2**) Oil, $C_{10}H_{12}O_2$ UV λ_{max}^{MeOH} nm (log ε) 261 (4 00), 303 (3 64), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1620, 1600, 1500, 1410, 1260, 1150, 1120, ^1H NMR ($CDCl_3$) δ 7 36 (1H, *d*, $J = 8$ Hz, H-6), 7 26-6 70 (1H, *m*, A part of AX_2, H_α), 6 46(1H, *dd*, $J = 8$ Hz + 2 Hz, H-5), 6 40(1H, *d*, $J = 2$ Hz, H-3), 5 73-5 00 (2H, *m*, X_2 part of AX_2, H_β), 3 76 (6H, *s*, 2xOMe), ^{13}C NMR ($CDCl_3$) δ 160 6(C-4), 157 9(C-2), 131 3 (C-7), 127 3 (C-6), 112 2 (C-8), 104 8 (C-5), 98 4 (C-3), 55 5 (OMe), 55 4 (OMe), MS m/z (rel int) 164 $[M]^+$ (100), 149 (53)

Oxidation of **2** Compound **2** (110mg) in Me_2CO (3 ml) was added dropwise to a stirred soln of $NaIO_4$ (1 2 g) and $KMnO_4$ (47 mg) in H_2O (4 ml)–Me_2CO (8 ml). The mixture was stirred for 20 hr at room temp Evapn of the Me_2CO and extraction with $CHCl_3$ gave a residue which on silica gel yielded 2,4-dimethoxybenzaldehyde (24 mg) and 2, 4-dimethoxybenzoic acid (20 mg), identified by comparison with authentic samples

4,6-Dimethoxy-5-vinylbenzofuran (**3**) Oil, $C_{12}H_{12}O_3$ UV λ_{max}^{MeOH} nm (log ε) 244 (4 54), 306 (3 47), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1620, 1600, 1580, 1530, 1400, 1350, 1300, 1140, 1100, ^1H NMR ($CDCl_3$) δ 7 43 (1H, *d*, $J = 2$ Hz, H-2), 6 80 (1H, *br d*, $J = 2$ Hz, H-3), 6 76 (1H, *br* s, H-7), 7 23-6 70 (1H, *m*, A part of AX_2, H_α), 6 03–5 10 (2H, *m*, X_2 part of AX_2, H_β), 4 00 3 86 (3H each, 2 × s, 2 × OMe), ^{13}C NMR ($CDCl_3$) δ 157 1, 156 (C-7a, C-5), 151 9 (C-4), 142 7 (C-2), 127 7 (C-8), 117 5 (C-9), 113 8, 112 4 (C-5, C-3a), 104 6 (C-3), 90 0 (C-7), 60 0 (4-OMe), 55 9 (6-OMe), MS *m/z* (rel int.) 204 $[M]^+$ (100), 189 (68), 161 (44).

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PELARGONIDIN 3-(6″-SUCCINYL GLUCOSIDE)-5-GLUCOSIDE FROM PINK *CENTAUREA CYANUS* FLOWERS

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Key Word Index—*Centaurea cyanus*, Compositae, pink flowers, acylated anthocyanin, succinic acid

Abstract—A new anthocyanin acylated with succinic acid has been isolated from pink flowers of *Centaurea cyanus* It has been identified as pelargonidin 3-(6″-succinylglucoside)-5-glucoside

While continuing our investigation of malonated and other acylated anthocyanins in plants of the Compositae [1], we found a new pigment in the pink flowers of a cultivated form of the corn poppy *Centaurea cyanus* L The mutation from the usual blue colour to pink is probably controlled by a single gene [2] The blue flowers were originally thought to contain cyanidin 3,5-diglucoside, but more recent work has shown that the pigment is cyanidin 3-(6″-succinylglucoside)-5-glucoside, this was the first anthocyanin to be found in association with succinic acid [3, 4] The same succinyl derivative was subsequently reported in six other *Centaurea* species [5] but a malonated cyanidin 3-glucoside was found to occur in leaves of *C cyanus* and in cell cultures of the same plant [6]

The new pigment of the pink flowers is a pelargonidin