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Short Report

Xeractinol – A New Flavanonol C-glucoside from *Paepalanthus argenteus* var. *argenteus* (Bongard) Hensold (Eriocaulaceae)

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Um novo composto, isolado a partir do extrato metanólico das folhas de *Paepalanthus argenteus* var. *argenteus* (Bongard) Hensold foi caracterizado como xeractinol, um novo diidroflavonol C-glucosilado. Sua estrutura foi elucidada com base em extensiva análise espectroscópica (RMN uni- e bidimensionais, EM, HREIMS, IV, UV). Cálculos *ab initio* de estrutura eletrônica corroboram nossa proposição para a estrutura molecular. O diidroflavonol aqui isolado pode servir como marcador taxonômico de *Paepalanthus* subg. *Xeractis*, uma vez que este flavonóide não foi encontrado em nenhum outro *taxon* de Eriocaulaceae.

New compound isolated from methanolic extract from the leaves of *Paepalanthus argenteus* var. *argenteus* (Bongard) Hensold was characterized as xeractinol, a new dihydroflavonol C-glucoside. The structure was elucidated on the basis of extensive spectroscopic analysis (1D and 2D NMR, MS, HREIMS, IR and UV). *Ab initio* electronic structure calculations support our proposal to the molecular structure. The dihydroflavonol herein isolated may serve as taxonomic marker of *Paepalanthus* subgenus *Xeractis*, because this flavonoid have not been reported in any other *taxon* of Eriocaulaceae.

Keywords: *Paepalanthus argenteus* var. *argenteus*, Eriocaulaceae, dihydroflavonol, xeractinol, *ab initio* calculations

Introduction

Eriocaulaceae is a pantropical, predominantly herbaceous monocotyledonous family, comprising around 1200 species included in 10 genera.[1] They are frequent components of the vegetation in montane shallow pools or swamps, especially on sandy ground. This family is characterized as a monophyletic *taxon* with the following synapomorphies: very small, unisexual, white flowers, in dense capitula, with only one ovule per locule, and spiraperturate pollen.[1]

Eriocaulaceae is a rich source of phenolic compounds, like naphthopyranones and glycosilated flavonóides.[2-5] We have already reported that flavonoids and naphthopyranones are of taxonomic significance to the systematic of Eriocaulaceae.[6,7] We report here the isolation and characterization of xeractinol, a new flavanonol from the leaves of *Paepalanthus argenteus* var. *argenteus* (Bongard) Hensold.

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Results and Discussion

The flavanonol C-glucoside **1** (xeractinol) was obtained directly from the fractionation of the methanolic extract of leaves of *P. argenteus* var. *argenteus* by column chromatography on Sephadex LH-20 (Pharmacia) eluted with MeOH. It gave a yellow spot on TLC under UV light. The IR spectrum exhibited bands at 3425 (OH) and at 1656 (C=O) and 1604 cm^{-1} (C=C). The UV spectra showed absorptions bands at 287 and 330 nm. The ES-MS spectrum of **1** showed a pseudo molecular ion $[M+H]^+$ at *m/z* 467, consistent with a molecular formula $C_{21}H_{22}O_{12}$. The $[(M+H)-120]^+$ ion was formed by an A-type cleavage, which is consistent with a C-6 glucoside substituent.[9] The peak at *m/z* 177 is due to the ion with formula $C_9H_{15}O_5$, resulting from the retro-Diels-Alder fragmentation of **1** in which part of the sugar moiety is bounded to the A-ring, thus evidencing that the sugar moiety is linked to this part of the molecule. The $[(M+H)-90]^+$ ion corresponds to the cleavage of the B-ring. The negative HREIMS $[M-H]^-$ at *m/z* 465.1039 suggest $C_{21}H_{22}O_{12}$ to be the molecular

formula. The ^{1}H NMR of **1** showed two doublets with *J* 11 Hz at δ 4.95 and at δ 4.46, related to the H-2 and H-3, respectively, of a 3-hydroxy substituted flavanone.[9] The singlet at δ 5.92 was assigned to H-8. The doublet at δ 6.74 (2H, *J* 2.0) is related to H-2' and H-6' (magnetically equivalent) and the doublet at δ 6.87 (*J* 2.0) is related to H-4'. The glucose moiety was confirmed in C-linkage by the presence of an anomeric proton at δ 4.48 (*J* 10.0) as well as from six other signals between δ 3.67 and δ 3.98. The ^{13}C NMR (DMSO d_6) spectrum showed 21 signals, six of which could be assigned to a β-D-glucopyranosyl moiety and fifteen other signals were similar to those of a flavanonol moiety.[8,12] Aglycone moiety 197.9 (C-4), 166.2 (C-7), 162.7 (C-5), 161.4 (C-9), 145.9 (C-3'), 145.1 (C-5'), 128.1 (C-1'), 119.5 (C-6'), 115.4 (C-4'), 115.3 (C-2'), 106.1 (C-6), 100.3 (C-10), 94.9 (C-8), 83.1 (C-2), 71.7 (C-3); sugar moiety 81.6 (C-5"), 79.2 (C-3"), 73.1 (C-1"), 70.8 (C-4"), 70.5 (C-2"), 61.7 (C-6a"). DEPT experiment allowed differentiating between C, CH and CH_2. The C-2 signal appeared at δ 83.1 and the C-3 signal at δ 71.7. According to these values, aryl and hydroxyl substituents at C-2 and C-3 are equatorially oriented (2,3-*trans*).[8] The HMQC spectrum showed all the direct correlations between C and H. The HMBC experiment showed the coupling between H-1"(δ 4.48) and C-6 (δ 106.1), C-7 (δ 166.2) and C-5 (δ 162.7). The HMBC experiment also showed correlations between the low field OH-5 signal (δ 12.41) and C-5 (δ 162.7), C-6 (δ 106.1) and C-10 (δ 100.3), confirming that the glucose moiety is bonded to C-6; between H-4' (δ 6.87) and C-3' (δ 145.5), C-5' (δ 145.1), C-2' (δ 115.3), C-6' (δ 119.5); between H-2 (δ 4.95) and C-6' (δ 119.5), C-2' (δ 115.3), C-1' (δ 128.1), C=O (δ 197.9); between H-3 (δ 4.46) and C-1' (δ 128.1), C=O (δ 197.9); between H-2' (δ 6.74) and C-1' (δ 128.1), C-4' (δ 115.4); between H-6' (δ 6.74) and C-1' (δ 128.1), C-4' (δ 115.4); between H-8 (δ 5.92) and C-6 (δ 106.1), C-9 (δ 161.4) and C-10 (δ 100.3).

Considering the two hydrogen atoms bonded to carbon 2 and 3, there are four possible isomers. The isomer seen in Figure 1 was named *trans* a. Considering this structure, the isomer *trans* b has the hydrogen atoms with changed positions relative to the plane of the ring to which they are attached; to *cis* a the hydrogen attached to carbon 3 changes position with the hydroxyl group. Considering *cis* a, in *cis* b both hydrogen change position relative to the plane of the ring. In order to know which one is the most stable isomer, we made use of quantum chemistry theory. The results (Table 1) disfavor the *cis* configurations, once the difference in total energy between the *trans* and *cis* configurations is high enough to prevent the *cis* configurations to occur. So, at least is possible to conclude that one of the *trans* configurations is the most probable structure, once the difference in total energy between *trans*-a and *trans*-b is very low. Thus, **1** was identified as (2R, 3R)-2-(3,5-dihydroxyphenyl)-6-β-D-glucopyranosyl-2,3-dihydro-3,5,7-trihydroxy-4H-1-benzopyran-4-one (xeractinol), Figure 1.

Table 1. Differences of theoretical total energy (kJ mol^{-1}), taking *trans*-a as the reference level

Isomer	*trans*-a	*trans*-b	*cis*-a	*cis*-b
TE-TE$_{trans\text{-a}}$	0.000	0.196	20.554	23.828

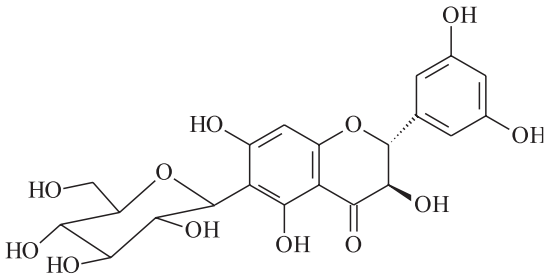

Figure 1. Xeractinol (**1**) from *Paepalanthus argenteus* var. *argenteus.*

According to previous works, *P.* subg. *Platycaulon* is characterized by naphthopyranone derivatives and 7-methoxy flavonol derivatives;[3,4] *P.* sect. *Actinocephalus* presents mainly flavonol glycosides and acylated flavonols;[2] in *P.* subg. *Xeractis* 6-methoxyflavone derivatives are major constituents as well as in *Leiothrix* and *Syngonanthus*, which also contain flavones rather than flavonols.[6,7] The dihydroflavonol herein isolated may serve as taxonomic marker of *Paepalanthus* subg. *Xeractis*, since this type of flavonoid have not been reported in any other *taxon* of Eriocaulaceae.

Experimental

Plant material

Paepalanthus argenteus var. *argenteus* was collected at Serra do Cipó, Minas Gerais, Brazil in February 1998. Dr. Nancy Hensold (Field Museum, Chicago) carried out identification of plant material. Voucher specimens were deposited at Herbarium SPF, Brazil (*P. argenteus* var. *argenteus*, SANO 920).

Extraction and isolation

The separated powdered leaves of the species were extracted with $CHCl_3$ and then with 80% MeOH

(maceration at room temp., one week each solvent). The solvents were evaporated *in vacuum* yielding black syrups. Two g of the 80% MeOH extract of *P. argenteus* var. *argenteus* were redissolved in MeOH and subjected to gel permeation column chromatography on Sephadex LH-20 (Pharmacia) eluted with MeOH affording substance **1** (140 mg). Two other compounds were isolated after purification by HPLC (Dynamax RP-18, Varian 8 μm, 30 cm × 5 cm i.d., 1 mL min^{-1}, λ 254 nm) and determined as being quercetagetin 7-methyl ether 3-*O*-neohesperidoside (32 mg) and 3,4-dihydro-10-hydroxy-7-methoxy-3-methyl-1*H*-3,4-dihydro-naphtho-[2,3c]-pyran-1-one-9-*O*-β-D-allopyranosyl (1-6)-β-D-glucopyranoside (27mg) by their spectrometric data.[3,4,8,9] NMR spectra in DMSO-d_6 were obtained using a Varian INOVA 500 spectrometer, operating at 500 MHz for ^1H and 125 MHz for ^{13}C. The DEPT (distortionless enhancement by polarization transfer) experiments were performed using a transfer pulse of 135°. Polarization transfer delays were adjusted to average CH coupling of 135 Hz. ^1H-^1H DFQ-COSY, ^1H-^{13}C HSQC, HMBC and 1D-TOCSY experiments were obtained using conventional pulse sequences. Low resolution ES-MS spectra was performed in a Fisons VG Platform spectrometer in the positive mode (100V), the samples were dissolved in MeOH and injected directly. HREIMS of **1** was performed by using a ultrOTOF$_Q$ – ESI-TOF Mass Spectrometer Bruker Daltonics (Billerica, MA, USA) instrument in the negative mode; samples were dissolved in MeOH:H_2O (80:20). IR: KBr. UV: MeOH. TLC: silica gel 60H (Merck, 10-40 μm). The flavonoids were detected with NP/PEG reagent under UV light.[10] Quantum chemistry theory calculations, including geometry optimization and electronic structure, were carried out employing *ab initio* B3LYP/6-31G(d) density functional theory methodology with the GAMESS package.[11] The calculations for all isomers were done *in vacuo*.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

Acknowledgments

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