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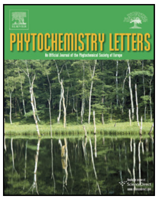

Short communication

Biflavonoids from the bark roots of *Poincianella pyramidalis* (Fabaceae)

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ABSTRACT

Poincianella pyramidalis (Fabaceae) is an endemic tree that grows in semiarid regions of Brazil. Phytochemical investigations on the bark roots of this plant led to the isolation of four new biflavonoids named (+)-5-hydroxy-7,4′-dimethoxyflavone-3α-2‴-hydroxy-4‴,4″-dimethoxydihydrochalcone (**1**), (+)-5,7-dihydroxy-4′-methoxyflavone-3α-2‴-hydroxy-4‴,4″-dimethoxydihydrochalcone (**2**), (−)-7-hydroxy-4′-methoxyflavone-3α-2‴,4‴-dihydroxy-4″-methoxydihydrochalcone (**3**), (−)-7,4′-dihydroxyflavanone-3,8-5″,6″,4″-trihydroxy-flavone (**4**), and the previously identified compound 4,2′,4′,4″,2‴,4‴-hexahydroxy-3,5‴-bichalcone (rhuschalcone VI, **5**). Their structures were determined by HR-ESI-MS and extensive analyses of NMR spectroscopic data.

1. Introduction

Fabaceae is one of the largest plant families distributed in approximately 650 genera and 18,000 species. The species within this family occur in several regions of the world, and the Fabaceae family is classified into three subfamilies: Mimosoideae, Faboideae and Caesalpinoideae (Nascimento et al., 2012). These plants often grow in semiarid regions of Brazil, such as the Caatinga forest; the Caesalpinioideae subfamily contributes approximately 100 species of 22 different genera to these regions. The local population utilizes a considerable number of these species as medicinal plants, in carpentry and as feed for cattle, goats and sheep during the dry seasons (Queiroz, 2009).

Poincianella pyramidalis (Tul.) L. P. Queiroz (Fabaceae) is a tree native to the Caatinga region, located in northeastern Brazil, and is commonly found in this region. This tree is better known as the “catingueira” or “pau-de-rato”. Previously, it was taxonomically classified as *Caesalpinia pyramidalis*. Recently, *C. pyramidalis* (Tul.), *C. pluviosa* (DC.) and *C. bracteosa* (Tul.), along with 44 other species of *Caesalpinia*, were reviewed and reclassified into the *Poincianella* genus (Lewis, 1998). The leaves and bark of *P. pyramidalis* are used in in folk medicine for the treatment of fever and stomach disorders and are also used as a diuretic. Previous studies on this species showed that the extract exhibited weak molluscicide activity (Santos et al., 2012), antimicrobial activity against *Staphylococcus aureus* (Saraiva et al., 2012), anti-inflammatory and antinociceptive (Santos et al., 2011) activities, as well as antiproliferative and antioxidant (Melo et al., 2010) activities. Terpenes, phenylpropanoids, flavonoids, and in particular, biflavonoids were isolated from the bark and leaves (Mendes et al., 2000; Bahia et al., 2005, 2010). To date, there have not been any studies investigating the root bark of this plant. As part of the phytochemical investigations on *Poincianella*, this paper describes the isolation and characterization of five biflavonoids (Fig. 1) from the root bark of *P. pyramidalis*. Four new and unusual biflavonoids with flavone–dihydrochalcone units (**1**–**3**) and flavanone–flavone units (**4**) were identified, in addition to bichalcone rhuschalcone VI (**5**) that has been previously isolated from the root bark of *Rhus pyroides* (Mdee et al., 2003) and stem bark of *Caesalpinia pluviosa* (Flores et al., 2006).

2. Results and discussion

The crude organic extract of the root bark of the plant was separated from most of the tannin material, and the resulting chloroform-soluble residue was subjected to CC to give compound **1**. Positive HR-ESI-MS presented a quasemolecular ion at *m/z* 583.1969, which was consistent a molecular formula of $C_{34}H_{30}O_9$. The presence of two singlet peaks (i.e., δ 12.23 and δ 12.68) were characteristic of a hydroxyl group at the C-5 position bonded with carbonyl groups of flavonoids, suggesting that compound **1** was a biflavonoid. The ^{13}C NMR (BB and APT) spectrum recorded 34 signals, including four methoxyl groups, two acyl carbons (δ 181.0 and 201.7) that were characteristic of flavones and dihydrochalcones, a methine carbon and a methylene carbon, suggesting a substituted dihydrochalcone structure in addition to

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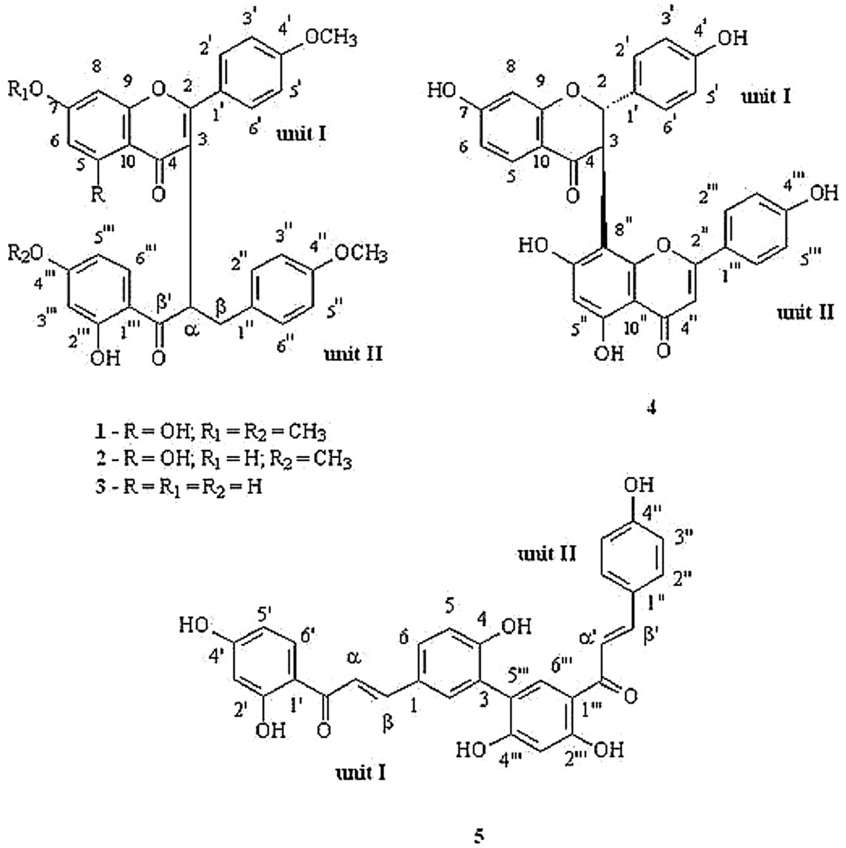

Fig. 1. Chemical structures of compounds **1**–**5**.

the other 26 Csp^2. The ^1H NMR data (Table 1) allowed for the identification of two 1,4-disubstituted aromatic groups: one AMX trisubstituted ring [δ 6.21 (*dd*, 2.4 and 9.0 Hz), 6.34 (*d*, 2.4 Hz), 7.32 (*d*, 9.0 Hz)] and one 5,6-disubstituted A-ring of a flavonoid [6.31 (1H, *d*, 1.8 Hz), 6.36 (1H, *d*, 1.8 Hz)]. The presence of a set of peaks at 4.82 (1H, *t*, 6.3 and 7.5 Hz) and a doublet of doublets at δ 3.55/3.08 (6.3, 7.5 and 13.9 Hz) were indicative of the presence of α-substituted hydrochalcone as a unit of the biflavonoid. These data were indicative of a biflavonoid composed of a flavone and hydrochalcone with two hydroxyl groups at C-5 and C-2‴ and bearing two methoxyl groups in each unit (δ 3.88, 3.82, 3.76 and 3.75). The assignment of all of the hydrogenated carbons was made possible by observing the heteronuclear correlations determined by an HMQC experiment, and the location of each substituent of the flavonoid skeleton was assigned using correlations observed in the HMBC spectrum. Thus, the correlations of the hydrogen of the methine carbon C-α (4.82) of the dihydrochalcone unit (Fig. 2) and the carbon resonances δ 35.0 (C-β), 120.2 (C-3), 131.7 (C-1″), 164.1 (C-2), 181.0 (C-4) and 201.7 (C-β′), and especially those of the two acyl carbons at C-4 and C-β′ provided conclusive evidence that the two units were bonded through C-α and C-3. On the other hand, the correlations observed for the bonded hydroxyl group at C-5 (δ 12.68) and C-6 (δ 98.2), C-10 (δ 104.9) and C-5 (δ 162.1) permitted the identification of the substitution pattern on the A-ring of the flavone unit. In the same way, the OH-bearing C-2‴ (12.23) showed correlations with δ 101.0 (C-3‴) and 165.4 (C-2‴) in the HMBC spectrum. These findings and correlations of each of the methoxyl groups with the Csp^2 of the biflavonoid permitted the assignment of all the chemical shifts and confirmed the structure of the new biflavonoid as 5-hydroxy-7,4′-dimethoxyflavone-3α-2‴-hydroxy-4‴,4″-dimethoxydihydrochalcone.

The negative HR-ESI-MS of compound **2** showed a *quasi*molecular ion *m/z* 567.1672 $[M-H]^-$, which was consistent with a molecular formula of $C_{33}H_{28}O_9$. The NMR data suggested that this compound was a biflavonoid and indicated a substitution pattern similar to that of compound **1**. However, the 1H NMR and ^{13}C APT NMR spectra indicated the presence of three methoxyl groups, and the retro Diels-Alder base peak observed in the EIMS at *m/z* 152 showed that the A-ring of the flavone unit was substituted only by hydroxyl groups. Other observed fragments (Fig. 3) contributed to assignment of the methoxyl groups in the B-ring of unit I and both the A and B-rings of unit II of this biflavonoid. The *g*HMQC spectrum of compound **2** permitted the correlation of the hydrogen atoms and their respective carbon atoms. Similar to compound **1**, the diastereotopic hydrogens of compound **2** at δ 3.07 and 3.53 were correlated with the methylene carbon C-β (δ 35.0) of unit II. These data, along with long-range correlations observed in the *g*HMBC spectra, confirmed the structure of this new biflavonoid as 5,7-dihydroxy-4′-methoxyflavone-3α-2‴-hydroxy-4‴,4″-dimethoxydihydrochalcone.

The molecular formula of **3** ($C_{32}H_{26}O_8$) was established by positive HR-ESI-MS $[M+H]^+$ at *m/z* 539.1712. The spectrometric data indicated that this compound had a similar structure to the biflavonoids that were previously described. The main difference was that there were only two methoxyl substituent groups (δ 55.3 and 55.8) in this compound. The key gHMBC correlations (Fig. 2) that permitted the identification of the A-rings of units I and II were the coupling of the C-3 of unit I and C-α of unity II and