

THE STRUCTURES OF NEW FLAVONE DI-C-GLYCOSIDES FROM *APOMETZGERIA PUBESCENS*

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Abstract—The structures of seven flavone C-glycosides from *Apometzgeria pubescens* were determined with the aid of ^{13}C NMR spectroscopy. They were all found to have glucose and/or arabinose in the 6- and 8-positions.

In an earlier paper [1] we reported the isolation of nine new flavone di-C-glycosides **2–6** and **8–11** from *A. pubescens*, but the structures of most were only partially elucidated. In this paper the structures of compounds **4**, **6**, **8** and **9** are defined with the aid of ^{13}C NMR spectroscopy and the structures of **2**, **3** and **5** are proposed by analogy.

Compound **4** was previously assigned the structure of a tricetin 6-C-arabinoside-6-C-hexoside and the ^{13}C NMR spectral data confirm this. The pattern of sugar carbon signals is equivalent to C-arabinosyl/glucosyl (pyranose form) but not to C-arabinosyl/galactosyl [2, 3]. Doubled glucose C-5 and C-6 signals (82.6, 82.3; 61.7, 61.1) indicate the presence of two slightly different glucoses, probably representing the isomers, tricetin 6-C-arabinoside-8-C-glucoside and tricetin 6-C-glucoside-8-C-arabinoside [2]. Thus **4** is tricetin 6-C-arabinopyranoside-8-C-glucopyranoside whereas **6**, the impurity in **4** [1], is tricetin 6-C-glucopyranoside-8-C-arabinopyranoside.

Compound **8** was preliminarily assigned the structure apigenin 6-C-arabinoside-8-C-pentoside and the proposed oxygenation and substitution patterns are now confirmed by the ^{13}C NMR data. Further, it was found to co-chromatograph with apigenin 6,8-di-C-arabinopyranoside from *Hymenophyllum leptopodium* [4] and the pattern of sugar carbon signals matches that expected for a 6,8-di-C-arabinoside with arabinose in the pyranose form [2]. Thus **8** is apigenin 6,8-di-C-arabinopyranoside.

Compound **9** was previously assigned the structure 3',4'-dimethyltricetin (apometzgerin) 6-C-arabinoside-8-C-pentoside. In the ^{13}C NMR spectrum there are two OMe signals, one at 56.3 ppm and the second at 60.3 ppm. The latter is displaced due to the presence of two *ortho* substituents, thus confirming the proposed methylation pattern in the aglycone. The sugar signals are the same as for **8** and the arabinose is therefore again in the pyranose form. Thus **9** is apometzgerin 6,8-di-C-arabinopyranoside.

Several further structures are assignable on the basis of the chromatographic identities of certain permethyl ether derivatives. Thus compound **5** which was previously defined as a tricetin 6,8-di-C-hexoside can now be assigned the 6,8-di-C-glucopyranoside structure since its PM-ether is chromatographically identical with that of **1** under

conditions which distinguish di-C-galactosides and di-C-glucosides [3]. Similarly, **2** is defined as tricetin 6-C-arabinopyranoside-8-C-glucopyranoside and **3** as tricetin 6,8-di-C-arabinopyranoside on the basis of the chromatographic identities of their PM-ethers with those of **4** and **9** respectively.

The structure elucidation of compound **11** is described in another paper [5] in which it is shown to be identical with apigenin 6-C-arabinopyranoside-8-C-(2-O-ferulyl)-glucopyranoside from *Metzgeria conjugata*.

Table 1 summarizes the structures now assigned to flavonoids isolated from *A. pubescens*.

EXPERIMENTAL

For plant material and extraction see ref. [1].

Co-chromatographic procedures. (a) Apigenin 6,8-di-C-arabinoside: PC (TBA, 15% HOAc) and Si gel TLC (EtOAc–C₃H₅N–H₂O–MeOH, 16:4:2:1), (b) Permethyl ether derivatives: Si gel TLC (EtOAc; CHCl₃–EtOAc–Me₂CO, 5:1:4 and 5:4:1).

^{13}C NMR spectra (in ppm from TMS, DMSO-*d*₆). Aliphatic carbon signals only were recorded and their assignments are based on previous work by Österdahl [2] and Besson *et al.* [3]. Assignments are in parentheses and refer to glucose (G) or arabinose (A) carbons.

Table 1. Flavone glycosides of *Apometzgeria pubescens*

Compound	Flavonoid
1	Tricetin 6,8-di-C-glucopyranoside [1]
2	Tricetin 6-C-arabinopyranoside-8-C-glucopyranoside
3	Tricetin 6,8-di-C-arabinopyranoside
4	Tricetin 6-C-arabinopyranoside-8-C-glucopyranoside
5	Tricetin 6,8-di-C-glucopyranoside
6	Tricetin-6-C-glucopyranoside-8-C-arabinopyranoside
7	Isoschaftoside [1]
8	Apigenin 6,8-di-C-arabinopyranoside
9	Apometzgerin 6,8-di-C-arabinopyranoside
10	Apometzgerin 6-C-hexoside-8-C-pentoside [1]
11	Apigenin 6-C-arabinopyranoside-8-C-(2-O-ferulyl)-glucopyranoside [5]

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Compound 4. 82.3/82.6 (G-5), 79.3 (G-3), 73.3–75 (G-1, 2 × A), 71.2 (G-2, A), 70.5 (G-4), 69.9 (A), 68.8 (A), 61.1/61.7 (G-6), 57.4/56.5 (OMe) ppm.

Compound 8. 75.1 (2 × A), 74.5 (2 × A), 70.6–71.3 (2 × A), 69.2 (4 × A) ppm.

Compound 9. 74.3–75.3 (4 × A), 70.6/70.8 (2 × A), 69.1 (4 × A), 60.3 (4'-OMe), 56.3 (3'-OMe) ppm.

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AN OCTAMETHOXYFLAVONE FROM *POGOSTEMON PURPURASCENS**

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Key Word Index *Pogostemon purpurascens*; Labiatae; purpurascenin; 3,5,6,7,8,2',4',5'-octamethoxyflavone.

Abstract—3,5,6,7,8,2',4',5'-Octamethoxyflavone has been isolated from the whole plant of *Pogostemon purpurascens*.

Pogostemon purpurascens (Labiatae) is a herb found growing in the Deccan Peninsula [1]. Fresh leaves of this plant are used to clean wounds and the root extract is reportedly used as antidote to scorpion and snake bites [2]. Here we report the isolation and characterization of a new flavone, purpurascenin (1), from the acetone extract of the whole plant collected from the Bhimashanker area of Maharashtra. This is the first report of an octamethoxyflavone from the Labiatae. Exoticin [3] (3,5,6,7,8,3',4',5'-octamethoxyflavone, the dimethyl ether of digicitrin [4]) is the only other octamethoxyflavone isolated so far from natural sources.

The UV and ^1H NMR spectra of 1 indicated it to be a flavonoid. The ^1H NMR spectrum displayed five sharp singlets between 3.8 and 4.08 ppm comprising eight methoxyls and two singlets (1H each) at 6.66 and 6.88 ppm. There was no indication of any hydroxyl in the spectrum. In the mass spectrum, the peak at m/z 241 ($\text{C}_{11}\text{H}_{13}\text{O}_6$) indicated that all four positions in ring A were substituted by methoxyls. The fragment at m/z 419 corresponding to the loss of acetyl radical from the molecular ion clearly showed the presence of methoxyl at C_3 [5]. It was obvious that the two free positions were in ring B; this was also supported by fragments at m/z 195

($\text{C}_{10}\text{H}_{11}\text{O}_4$) and 192 ($\text{C}_{11}\text{H}_{12}\text{O}_3$). As the ring B protons exhibited two sharp singlets, these could either be at C3', C6' or C4', C6'. The decision in favour of the former was made by degradation. On treatment with alkali, purpurascenin gave an acidic and a neutral product. The acidic fraction yielded a crystalline compound, mp 143–144°, identified as asaronic acid [6] (2,4,5-trimethoxybenzoic acid, mp, mmp). The neutral fraction, after chromatographic purification, was a gum whose spectral properties were in accord to its being formulated as 2-hydroxy-3,4,5,6, ω -pentamethoxyacetophenone. On the basis of the above data, the structure of purpurascenin can be assigned as 3,5,6,7,8,2',4',5'-octamethoxyflavone (1).

EXPERIMENTAL

The reported mps are uncorr. TMS was used as internal standard in the ^1H NMR spectra.

The whole plant, *Pogostemon purpurascens* (roots, stem, leaves and flowers) was dried in the shade and powdered material (1 kg) was extracted with Me_2CO (4l. × 3). Solvent from the filtered extract was removed at 40°/40 mm to give a dark viscous mass (30 g, 3%). This (19 g) was chromatographed over Si gel (1 kg). The C_6H_6 – Me_2CO (9:1) eluate yielded pale greenish yellow solid. 1, purpurascenin (2.4 g; 17.9%), mp 132–133°. An analytical sample was prepared by passing the solid through a

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