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SORBIFOLIN 6-GALACTOSIDE FROM *GARCINIA ANDAMANICA*

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Key Word Index—*Garcinia andamanica*; Guttifereae; sorbifolin 6-galactoside; scutellarein 7-diglucoside.

Abstract—A new flavone glycoside, sorbifolin 6-galactoside, has been isolated from the leaves of *Garcinia andamanica* along with the known scutellarein 7-diglucoside. Their structures were established using spectroscopic and chemical evidence.

INTRODUCTION

Garcinia, a genus consisting of 180 species, 30 of which are found in India, possesses many medicinal properties [1]. Since no work seems to have been done on the flavonoid constituents of *Garcinia andamanica* King, the present work was undertaken.

RESULTS AND DISCUSSION

Compound **1** on hydrolysis with 10% HCl gave an aglycone, sorbifolin (**2**) mp 290–292°, which showed λ_{max} at 253, 308 nm. A yellow colour with Wilson's boric acid reagent [3] and maxima at 269 and 333 nm in the UV spectrum indicated it to be a flavone glycoside. It gave a brownish green colour with $FeCl_3$ and displayed strong IR bands at 3400 cm^{-1} (OH) and 1700 cm^{-1} (C=O). The absence of shifts with sodium acetate and sodium acetate/boric acid ruled out the possibility of a free hydroxyl group at the 7-position and an *O*-dihydroxyl system, respectively. A free 5-hydroxyl was evidenced by a bathochromic shift of 15 nm with $AlCl_3$.

The ^{1}H NMR of the acetate, mp 111–112°, showed a sharp singlet at δ6.78, indicating the presence of a C-3 proton of the γ-pyrone nucleus. One aromatic methoxyl group was observed through a singlet at δ3.99. The remaining singlet at δ6.48 was assigned to an aromatic proton shielded by two *ortho* and one *para* oxygens and was found to arise from the C-8 proton of 5,6,7-trioxygenated flavone. The ^{1}H NMR showed two aromatic acetoxyls at δ2.46 (3H) and δ2.27 (3H) and four alcoholic acetoxyls at δ1.99 (9H, *s*, 3 × OAc), δ1.73 (3H, *s*, OAc) indicating the presence of glucose or galactose. The aromatic region also contains multiplets of four other protons which were assigned to hydrogens of ring B and since the doublets at δ7.78 (J = 9 Hz) and δ7.15 (J = 9 Hz) correspond to an A_2B_2 pattern, they were assigned to 2′,6′ and 3′,5′ protons, respectively. The position of the sugar was confirmed by hydrolysis of the methylated glycoside. The partial methyl ether thus obtained was characterized by mp, mmp with an authentic sample [4] (mp 221°) as 6-hydroxy 4′,5,7-trimethoxy flavone. The formation of this methyl ether proved the attachment of the sugar residue at the 6-position. The quantitative estimation of sugar by the Somogyis copper micro method showed the presence of 1 mole of sugar per mole of aglycone [5]. The identity of the sugar was confirmed as galactose by co-paper chromatography with an authentic sample.

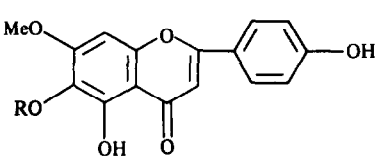
Scutellarein 7-diglucoside was identified by mp, mmp, co-chromatography and comparison of UV and ^{1}H NMR spectra with an authentic sample [6].

EXPERIMENTAL

Mps were uncorr. ^{1}H NMR spectra were recorded on a Varian A-60D instrument using TMS as internal standard and chemical shifts are reported on a δ (ppm) scale. Chromatography was performed using silica gel (BDH).

Isolation procedures. Air dried leaves of *G. andamanica* (procured from Andamans) were refluxed with MeOH. The methanolic concentrate was successively treated with petrol (60–80°), C_6H_6 and $CHCl_3$. The brown residue was further purified by CC over silica gel. Elution with EtOAc afforded a mixture of two compounds which was subjected to prep. TLC (silica gel) to give sorbifolin 6-galactoside (**1**), mp > 300° (d) along with scutellarein 7-diglucoside.

Acetylation of **1**. **1** (35 mg) was treated with Ac_2O (3 ml) and dry pyridine (1.5 ml) at 100° for 3 hr. Work-up in the usual way afforded a hexaacetate derivative (25 mg) as colourless needles, mp 111–112°. ^{1}H NMR ($CDCl_3$) δ6.48 (1H, *s*, H-8); 6.78 (1H, *s*, H-3); 7.15 (2H, *d*, J = 9 Hz, H-3′, 5′); 7.78 (2H, *d*, J = 9 Hz, H-2′, 6′); 3.99 (3H, *s*, OMe-7); 2.46, 2.27 (3H each, *s*, OAc-4′,5); 1.99 (9H, *s*, 3 × OAc); 1.73 (3H, *s*, OAc).



1 R = Galactose
2 R = H

Hydrolysis of **1**. Hydrolysis in 10% HCl at 100° for 2 hr yielded sorbifolin (**2**) mp 290–292°; UV λ_{max}^{MeOH} nm: 253, 308, $AlCl_3$ 263, 323 nm; NaOAc 254, 309 nm. Acetate (Ac_2O–pyridine 24 hr) colourless needles, mp 226–228°. Calc. for $C_{22}H_{18}O_9$; C 61.95, H 4.26. Found; C 62.03, H 4.30%. Methylation of **1** gave a methyl ether (dimethyl sulphate, Me_2CO and K_2CO_3, 24 hr) colourless needles, mp 187–189°. Calc. for $C_{19}H_{18}O_6$; C 66.66, H 5.26. Found; C 66.61, H 5.23%.

Identification of sugar. The sugar fraction from acid hydrolysis of **1** was neutralized in vacuum over NaOH and chromatographed on Whatman No. 1 paper using *n*-BuOH–HOAc–H_2O (4:1:5) and *n*-BuOH–EtOH–H_2O (12:3.3:5.7). Aniline hydrogen phthalate was used as a spraying reagent. Galactose was identified by comparison with an authentic sample.

Scutellarein 7-diglucoside was found identical in all respects to an authentic sample [6].

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FLAVONOID DISTRIBUTION IN *ARNICA* SUBGENUS *CHAMISSONIS*

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Key Word Index—*Arnica*; subgenus *Chamissonis*; Compositae; flavonoids; chemotaxonomy.

Abstract—Twenty-eight flavonoid aglycones have been identified from *Arnica chamissonis*, *A. longifolia*, *A. amplexicaulis*, *A. mollis*, and *A. parryi* of the subgenus *Chamissonis* of the genus *Arnica*. The flavonoid pattern was largely homogeneous. Only *A. mollis* is an exception by the occurrence of 7-methylation.

INTRODUCTION

The genus *Arnica* L. is divided by Maguire [1] into five subgenera and consists of *ca* 32 species, most of which are confined to western North America. As part of a chemosystematic study of *Arnica* we now report on the flavone aglycones in the flowers of five of the seven species of the subgenus *Chamissonis* Maguire. Up to now little was known about the flavonoids of *Arnica* [2–11]. Only subgenus *Austromontana* has been recently intensively examined [12].

RESULTS AND DISCUSSION

Twenty-eight different compounds were isolated and identified by UV, MS and ^{1}H NMR including flavones, flavonols, flavanones and their methyl ethers, some of them with 6-methylation.

Section *Euchamissonis* consists of only one species, *Arnica chamissonis*, which is one of the most widely distributed species of the genus. Maguire differentiates three subspecies: *genuina*, *foliosa* and *incana* [1]. According to the presently accepted nomenclature of Hultén subsp. *incana* is now a variety of *A. foliosa* (see Table 1) [13] and according to Maguire subsp. *chamissonis* represents the stock of subgenus *Chamissonis* [1].

Our chemical examination showed that the flavonoid pattern in section *Euchamissonis* is relatively homogeneous (see Table 1). Besides the ubiquitous compounds **1–4** and the frequently found **5–9**, 11 6-methoxyflavones and -flavonols (**11–21**), which are typical for plants of the Compositae [14] were isolated. However, quercetin 3′,4′-dimethyl ether (**10**) and 6-methoxykaempferol 4′-methyl ether (**17**) are recorded for the first time in the Compositae and patuletin 4′-methyl ether (**20**) for the second time in nature [15]. Patuletin 3′,4′-dimethyl ether (**21**) is a new natural product [11].

Compared with *A. chamissonis* the number of flavonoids in *A. longifolia*, the sole species of section *Eulongifolia*, is reduced and compounds with 4′-methy-