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APODANTHEROSIDE, AN IRIDOID GLUCOSIDE FROM *FERETIA APODANTHERA*

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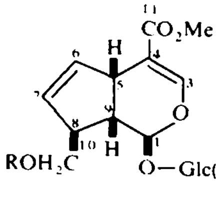
Key Word Index– *Feretia apodanthera*; Rubiaceae; iridoid glucoside; apodantheroside.

INTRODUCTION

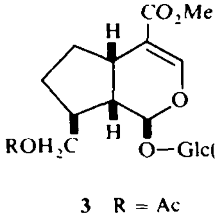
Previous investigations on *Feretia apodanthera* Del. (Rubiaceae) have described the isolation and the identification of eight iridoid glucosides: feretoside, gardenoside, geniposide, desacetyl asperulosidic acid, 11-methyl ixoside, apodanthoside and 10-ethyl apodanthoside [1-3]. Only the first three occur in the flowers [3]. This paper deals with a new iridoid also isolated from the flowers.

RESULTS AND DISCUSSION

Flowers of *Feretia apodanthera* were collected near Ouagadougou (Haute-Volta). A voucher sample has been deposited at the Laboratoire de Pharmacognosie, Faculté de Pharmacie, Paris. Column chromatography of the floral extract affords some fractions containing crude geniposide which gives only one spot upon TLC. Acetylation of the residue yields two acetylated iridoid glucosides which can be fractionated by column chromatography on silica gel: geniposide pentaacetate (yield: 0.03%) and apodantheroside pentaacetate (**2**) (yield: 0.02%) which is the new compound. Its structure can be deduced from spectroscopic analysis and is proved by chemical correlation.



1 R = H
2 R = Ac



3 R = Ac

Apodantheroside pentaacetate (**2**) was obtained as colourless needles (mp 126°) from Et_2O hexane. It shows UV absorption [λ_{max} nm (logε): 233 (4.01)] which is characteristic of an iridoid chromophore, as is the IR spectrum (ν cm^{-1}: 1770, 1750, 1655, 1620). Except for a peak at m/e 331 corresponding to the tetraacetylglucopyranose moiety, the mass spectrum exhibits a molecular ion peak ($M^+ = 598$) and a fragment ion at m/e 268 attributable to the aglycone moiety. The ^1H NMR spectrum (270 MHz, $CDCl_3$, TMS) shows: between 1.95 and 2.05 ppm five singlets of three protons each assignable to five acetyl groups; at 2.55 ppm the C-9 proton as a triplet ($J_{9-8} = J_{9-5} = 9$ Hz); at 3.0 and 3.7 ppm two signals of one proton each corresponding to C-8 proton ($J_{8-9} = 9$, $J_{8-7} = 1.5$ Hz) and to C-5 proton ($J_{5-9} = 9$, $J_{5-6} = 2.5$ Hz); at 3.75 ppm the singlet (3 protons) of a carbomethoxyl group; at 4.2 and 4.3 ppm two AB systems ($J = 12$ Hz) arising from the CH_2 groups (C-6′ and C-10) of the two acetylated primary alcohol functions; at 5.9 and 6.3 ppm. The two signals of the olefinic protons in C-7 ($J_{7-6} = 6$, $J_{7-8} = 1.5$ Hz) and in C-6 ($J_{6-7} = 6$, $J_{6-5} = 2.5$ Hz); and at 6.15 and 7.35 ppm the two singlets of C-1 and C-3 protons. Furthermore, the structure of β-D-glucose is confirmed by measurement of shifts and coupling constants of the signals arising from the glucosidic moiety [4].

These data suggest structure **2** for apodantheroside pentaacetate. A chemical correlation confirms this structure and establishes the stereochemistry. Catalytic hydrogenation (Pd–C) of **2** affords 6,7-dihydroapodantheroside pentaacetate (**3**) (yield: 80%). **3** is obtained as colourless needles (mp 140°) from Et_2O-hexane. UV [λ_{max} nm (logε): 234 (4.01)]: ^1H NMR (270 MHz, $CDCl_3$, TMS): δ ppm 1.4 and 1.8 (4 H, 2*m*, H-6 and H-7), 1.95–2.05 (5 × 3 H, 5*s*, 5 × OCOMe), 2.2 (1 H, *m*, H-9), 2.80 (1 H, *m*, H-5), 3.70 (3 H, *s*, COOMe), 4.0 (2 H, *dd*, H-10), 4.2 (2 H, AB system, H-6′), 5.2 (1 H, *d*, H_1, $J_{1-9} = 4$ Hz), 7.4 (1 H, *s*, H-3). According to these physical and spectroscopic data, **3** is identified as the 8α-H epimer of the 7,8-dihydrogeniposide pentaacetate, the mp (140–141°) of which is very different from that of the 8β-H compound (mp 121–122°) [5]. The structure **2** can thus be assigned to apodantheroside pentaacetate.

The genuine iridoid glucoside occurs as a mixture with geniposide (which differs in that the double bond is 7,8 instead of 6,7). From the identical polarities of the two compounds, it is clear that apodantheroside (**1**) does not contain any acetyl substitution. This iridoid glucoside, which has not been encountered before in nature, is described here for the first time. It exhibits the same configuration at C-8 as loganin and could be derived from the latter by simple biosynthetic processes.

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