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CORRECTED STRUCTURES OF PASSICORIACIN, EPICORIACIN AND EPITETRAPHYLLIN B AND THEIR DISTRIBUTION IN THE FLACOURTIACEAE AND PASSIFLORACEAE

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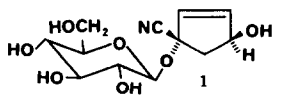
Abstract—Three cyanogenic glycosides, passicoriacin, epicoriacin and epitetraphyllin B, have had their structures reassigned as epivalkenin, taraktophyllin and volkenin respectively, based on a reinterpretation of their spectral data.

INTRODUCTION

Recently we reported the presence of tetraphyllin B, epitetraphyllin B, passicoriacin, and epipassicoriacin in vegetative material of *Passiflora coriacea* (Passifloraceae) [1] and that passicoriacin and epipassicoriacin co-occur in *Passiflora suberosa* with two epoxide-containing cyanogenic glycosides [2]. The proposed structures of passicoriacin and epipassicoriacin were based on an earlier structure of epitetraphyllin B [3] that now has been shown to be incorrect [4] and, thus, the proposed structures for passicoriacin, and epipassicoriacin must be changed.

In a subsequent paper, Jaroszewski *et al.* [5] reported cyclopentenoid cyanogenic glycosides from *Taraktogenos heterophylla* and *Hydnocarpus anthelmintica* (Flacourtiaceae). These glycosides have similar spectral properties (some spectra were measured under different conditions)



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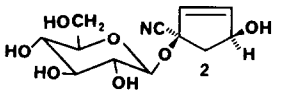

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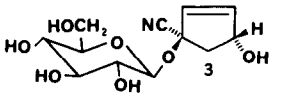

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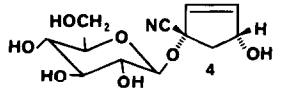

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and appear to be identical to those above [1, 2]. In particular, taraktophyllin closely matches the spectral properties of epipassicoriacin and epivolkenin corresponds to passicoriacin.

We agree that the names proposed by Jaroszewski and coworkers [4–6] (i.e. volkenin, taraktophyllin and epivolkenin) should be used in preference to epitetraphyllin B, epipassicoriacin and passicoriacin, respectively, primarily for the reasons specified. In view of these changes, the structures in our recent publication [1] should be as follows: structure **1** represents tetraphyllin B, structure **2** epivolkenin, structure **3** taraktophyllin, and structure **4** volkenin.

The assignment of chemical shifts in ref. [1] was based on analysis of mixtures of all four cyanogens and purified mixtures of taraktophyllin and epivolkenin whereas assignments in refs [4–6] and [7] are based on isolated compounds. The following changes in the spectral data in ref. [1] should be made: the chemical shift for H-5 of volkenin (formerly epitetraphyllin B) OTMS ether should be 2.37 (instead of 2.20). In the spectrum of taraktophyllin (formerly epipassicoriacin) OMS ether, the chemical shift for H-4 should be 4.82 (instead of 4.98) and that for H-1′ should be 4.60 (instead of 4.48).

As indicated by re-interpretation of the NMR spectra, the major cyanogenic constituents of *Carpotroche brasiliensis* are gynocardin and epivolkenin [6] and not gynocardin and tetraphyllin B [8]. Further re-evaluation of spectra from other flacourtiaceous plants (*Buchnerodendron lasiocalyx*, *Carpotroche longifolia*, *C. pacifica*, *Camptostylus biennis*, *C. mannii*, *Lindernackia dentata*, *L. laurina*, *L. paludosa*, and *Mavna longifolia*) indicates that they also possess gynocardin and epivolkenin and not gynocardin and tetraphyllin B as previously reported [9].

A levorotatory cyanogenic glycoside, barterin, was originally reported from *Barteria fistulosa* [10]. Tetraphyllin B and taraktophyllin are levorotatory, whereas volkenin and epivolkenin are dextrorotary [4, 5]. The reported ^{1}H NMR data [10] are similar to (but not identical with) that for volkenin [4–6] or tetraphyllin B [4–6].

We reported the presence of volkenin (epitetraphyllin B) in *Barteria fistulosa* based on ^{1}H NMR spectral data [11]. The absorptions centred at 6.20, 6.08, 5.04, 4.64, 2.73, and 2.38 ppm (trimethylsilyl ether in $CDCl_3$) are in close agreement with chemical shifts reported for volkenin [4]. The optical rotation of the compound isolated in our work was not determined. It is now clear that the compound we isolated was not the same as barterin [6].

It has been suggested that the enzymes involved in the biosynthesis of taraktophyllin and epivolkenin exhibit a different type of stereospecificity (from those of tetraphyllin B and volkenin) and that the allylic hydroxyl group at C-4 is introduced from the face *trans* to the cyano group of the cyclopentene ring as in gynocardin [6]. Although only compounds of this type appear to be encountered (to date) in the Flacourtiaceae, the presence of both series of compounds in *Passiflora coriacea* and *P. suberosa* [1, 2] and of taraktophyllin in an accession of *Adenia fruticosa* (unpublished data) (all Passifloraceae), indicates that this relationship does not extend across all families of this group.

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