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CYANOGENESIS OF *PASSIFLORA FOETIDA**

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Key Word Index—*Passiflora foetida*; Passifloraceae; chemical varieties; cyanohydrin glycosides; sulphate esters; tetraphyllin A and B; deidaclin; volkenin; linamarin; Galápagos Islands; Réunion Island

Abstract—Five cyanohydrin glycosides with a cyclopentene ring, tetraphyllin A, tetraphyllin B, tetraphyllin B sulphate, deidaclin and volkenin, were isolated from *Passiflora foetida* grown from seeds collected on the Galápagos Islands. By contrast, *P. foetida* collected on Réunion Island contained the valine-derived glycoside linamarin, along with the cyclopentanoids tetraphyllin B, volkenin and tetraphyllin B sulphate. The chemical differences between the two populations were accompanied by pronounced morphological differences. This is the first report of two populations of the same species, having different patterns of cyclopentanoid and valine-derived glycosides. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Passiflora foetida L. is a vine of South American origin which has been spread to many tropical areas in the Old World. The species is highly polymorphic and was divided by Killip into 37 varieties in addition to typical *P. foetida* [2]. We have examined material of *P. foetida* grown from seeds collected on the Galápagos Islands in the Western Pacific, and material of *P. foetida* collected on Réunion Island in the Indian Ocean. *P. foetida* from the Galápagos Islands has been considered a separate endemic variety, *P. foetida* var. *galapagensis* Killip in Wiggins and Porter 1971 [3], but was merged into *P. foetida* by Lawesson [4]. *P. foetida* is known to be strongly cyanogenic [5–10]. It has been the subject of only a few chemical investigations, and its cyanogenic compounds have never been identified [11]. The present investigation was carried out in order to compare the content of cyanohydrin glycosides in the two samples of *P. foetida* and to find out whether the two samples could be considered to be of identical taxonomical stock.

RESULTS AND DISCUSSION

Fresh material of *P. foetida* from Réunion Island and from the Galápagos Islands was shown to release the same amount of cyanide (13–14 μmol g^{-1}), as shown by use of the quantitative picrate test [12]. Extraction and fractionation of the aerial parts of both plants revealed tetraphyllin B sulphate [13] as the major cyanogenic constituent in both collections. *P. foetida* from Galápagos also contained tetraphyllin A and B, deidaclin and volkenin, and *P. foetida* from Réunion tetraphyllin B, volkenin, as well as linamarin. No linamarin could be detected in the former plant. The cyanogenic compounds were identified by ^{1}H and ^{13}C NMR spectroscopy [13–17].

The occurrence of valine-derived cyanohydrins in genera that produce cyclopentanoids has previously been reported [17–21]; sometimes both types of the glucosides are found in the same plant species [18, 20]. The present work demonstrates the occurrence of cyanogenic glycosides from the two biosynthetic pathways mentioned above in one population and the occurrence of cyanogenic glycosides from only one of these pathways in another population of the same species.

Morphological investigation of *P. foetida* from the two populations showed differences within the stipules, glands and hairs. Stipules from the sample from Réunion Island are semiannular, 5–7 mm high (5–10 mm indicated for *P. foetida* from the Mascarene Islands [22]), deeply cleft into pinnatisect, glandtipped divisions, and divisions carrying many glandtipped filaments, the glands are ovoid and 0.28 mm long in average. The stipules from the sample from the Galápagos Islands are semi-annular, 1 mm high (2–3 mm indicated by Wiggins [3]) and the margin is closely

* Part 17 in the series 'Natural Cyclopentanoid Cyanohydrin Glycosides'. For part 16 see ref. [3].

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set with filaments tipped with ovoid glands 0.56 mm long in average (0.4–0.8 mm indicated by Wiggins [3]). The petioles from both samples are hirsute, bearing glandtipped filaments like those on the stipules. The hairs on the sample from Réunion are up to 3 mm long, (2–3 mm indicated for *P. foetida* from the Mascarene Islands [22]) and the hairs on the sample from the Galápagos Islands are up to 1.2 mm long. Killip [2] indicated for *P. foetida* var. *galapagensis* hairs are on average no more than 1 mm in length.

The results of our investigation, showing both chemical and morphological differences between the samples of *P. foetida* with different geographic distribution, support Killip's recognition of material from the Galápagos Islands as a separate variety *P. foetida* var. *galapagensis* Killip.

EXPERIMENTAL

General. NMR: Bruker AMX 400. Quantitative cyanide determination was carried out by reflectometry by means of a Nycocard READER (Nycomed Pharma) [12]. HPLC: 1.6 × 25 cm column of LiChrosorb Si60 (10 μm) eluted with 4 ml min^{-1} of EtOAc–MeOH (5:3) was used to purify tetraphyllin B sulphate (R_t = 13.6 min), and a 1.6 × 25 cm column of LiChrosorb RP-18 (5 μm) eluted with 4 ml min^{-1} of H_2O–MeOH (9:1) was used to purify linamarin (R_t = 22.6 min). Tetraphyllin A, tetraphyllin B, volkenin and deidaclin was purified using the same reversed-phase system [17, 18]. Other methods and procedures were as previously described [16, 17, 23].

Plant material. The aerial parts of *P. foetida* were collected in January 1994 on Réunion Island and air-dried immediately after the collection. Another population of *P. foetida* was grown in the Botanical Garden, University of Copenhagen, from seeds collected on Galápagos, and the aerial parts were collected prior to extraction. Voucher specimens are deposited in Herbarium C.

Isolation of glycosides. Dried aerial parts of *P. foetida* (Réunion) or fresh material of *P. foetida* (Galápagos) were extracted with boiling MeOH. The extracts were chilled, filtered and evaporated *in vacuo* almost to dryness. The extracts were fractionated on silica gel in the usual way [13] and the cyanogenic compounds were purified by HPLC. The identification of compounds was accomplished by ^1H NMR and ^{13}C NMR of the glucosides in CD_3OD. The acetates of linamarin, tetraphyllin A, deidaclin, volkenin and tetraphyllin B in $CDCl_3$, obtained by overnight treatment (room temp.) with pyridine–Ac_2O, and the desulphatized tetraphyllin B sulphate accomplished with a sulphatase (Sigma Chemical Co., cat. no. S-1629) in CD_3OD, were also identified by ^1H NMR and ^{13}C NMR.

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