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SHORT REPORTS

TETRAPHYLLINS A AND B, DEIDACLIN AND EPITETRAPHYLLIN B FROM *TETRAPATHAEA TETRANDRA* (PASSIFLORACEAE)

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Key Word Index—*Tetrapathaea tetrandra*; Passifloraceae; konia; New Zealand passion fruit; tetraphyllin A; tetraphyllin B; deidaclin; epitetraphyllin B; cyanogenic glycosides.

Abstract—Tetraphyllin A, deidaclin, tetraphyllin B and epitetraphyllin B have been isolated from the vegetative parts of *Tetrapathaea tetrandra* (Passifloraceae), a liana which is native to New Zealand. The fruits of this plant have previously been shown to contain tetraphyllins A and B. This is the first report of the isolation of four cyclopentenoid cyanogenic compounds from a single plant.

INTRODUCTION

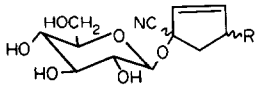
Tetrapathaea tetrandra Cheeseman, commonly known as konia or New Zealand passion fruit, is monotypic and endemic to New Zealand. This woody liana (diameter up to 20 cm and length up to 15 m) produces a bright orange colored fruit which is regarded as inedible [1–4]. This genus is distinct from others in the Passifloraceae in that it has dioecious habit and tetramerous floral morphology [1–3].

The plant has not been studied extensively, but the seed oil has been examined [5]. This oil was previously used by the Maoris for annointing the body and for treating chronic sores and chapped nipples [6], and has been used commercially as a machine oil [7]. The entire plant contains alkaloids [8]. Further, the presence of two cyanogenic glucosides, tetraphyllins A and B, have been reported from the fruits of this plant [9]. Tetraphyllin B may be identical to barterin, previously reported from *Barteria fistulosa*, another passifloraceous plant [10]. Tetraphyllin A has not been reported from other sources, but tetraphyllin B is now known to occur in several other plants [10–12, 15, 19–20].

RESULTS AND DISCUSSION

Because Russell and Reay [9] had previously reported the presence of tetraphyllins A and B in the fruits of *Tetrapathaea tetrandra* in a ratio of *ca* 1:7, we attempted to reisolate the cyanogens from vegetative material of the same plant in order to obtain standard materials.

In addition to tetraphyllins A and B, we found epitetraphyllin B [11, 12] and deidaclin [10, 13, 14] (Fig. 1). The ^{1}H NMR spectra of the TMSO derivatives showed the presence of all four cyanogens. Upon separation, spectra were obtained for both the tetraphyllin A and tetraphyllin B epimeric pairs. If epitetraphyllin B and deidaclin were present in the fruits as well as the vegetative material that we investigated, they would not have been detected for two reasons. First, the quantities were such that the 60 MHz NMR would not have found them. Second, determination of spectra of cyclopentenoid cyanogens in deuterium labelled water or of cyclopentenoid cyanogens in deuterochloroform does not reveal the presence of epimers. We have found that TMS ether derivatization or unique solvent systems must be employed [15]. Thus, the presence of small amounts of these last two cyanogens in the materials of Russell and Reay cannot be excluded. This is the first reported isolation of four cyclopentenoid cyanogens from a single plant.



Tetraphyllin A, deidaclin, R = H
Tetraphyllin B, epitetraphyllin B, R = OH

Fig. 1.

Although we cannot absolutely rule out epimerization in this instance, we have been able to isolate single compounds without evidence of epimerization from other plants and do not see changes on repetitive work-up of authentic materials. Pure compounds did not epimerize when worked-up with the same procedures used to isolate the mixture from *Tetrapathaea tetrandra*.

EXPERIMENTAL

Isolation and purification of the glycoside mixture. Leaves and stems of *Tetrapathaea tetrandra* (416 g) were blended with MeOH and the mixture added to cold 80% MeOH. The resulting material was filtered and the residue washed with 80% MeOH (60 ml). The resulting soln was concd under vacuum to yield a brown syrup (100 ml), which was extracted with $CHCl_3$, and the aq. phase placed on a column of cellulose (Whatman CF1, CF11 and microcrystalline cellulose, Applied Science, 1:1:1). Fractions

were eluted with MeCOEt–Me_2CO–H_2O (15:5:3). A few drops of each fraction were transferred to a vial buffered to pH 6.8 and a few drops of enzyme preparation added (see below). HCN, released as a result of enzymatic hydrolysis, was detected with Feigl–Anger paper [16, 17]. The cyanogenic material (fractions 40–70) was concd to 50 ml and rechromatographed as before on a cellulose column (1:1:0.5), with Me_2CO–H_2O (5:1) as eluant. The cyanogenic fractions were combined, concd to 5 ml and chromatographed on paper (Whatman 3MM, 22 × 57 cm) with *iso*–PrOH–*n*-BuOH–H_2O (6:3:1). The cyanogenic compounds were detected by cutting a 1 cm strip from the center of the chromatogram and testing cm^2 sections from this strip. The cyanogenic band (R_f 0.45) was eluted with H_2O, concd and rechromatographed (PC) with MeCOEt–Me_2CO–H_2O (15:5:3). At this point two cyanogenic bands were observed: band 1 (tetraphyllin B and epitetraphyllin B, R_f 0.5, 206 mg) and band 2 (tetraphyllin A and deidaclin, R_f 0.85, 186 mg). Tetraphyllin B and epitetraphyllin B occurred in a ratio of *ca* 20:1, and tetraphyllin A and deidaclin in a ratio of *ca* 12:1. Overall yield of cyanogens was *ca* 0.094%.

Enzyme preparation. Leaves of *Turnera ulmifolia* (100 g) were ground in a blender with Me_2CO (500 ml). The suspension was then filtered and rinsed with Me_2CO (250 ml). The solid material retained in the filter was dried and resuspended in Pi buffer (pH 6.8, 500 ml), stirred in an ice bath for 1 hr and then filtered. The filtrate was dialysed against pH 6.8 buffer for 12 hr. The product was concd under vacuum to a final vol. of 500 ml and its hydrolytic activity confirmed by testing standard materials using the Feigl–Anger method.

Spectral determination. NMR spectra were measured on a Nicolet NT360 spectrometer as their TMS derivatives in $CDCl_3$. These derivatives were prepared as previously described [18].

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