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Gynocardin and cyclopentenylglycine in *Rawsonia lucida*☆

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1. Subject and source

Rawsonia lucida Harw. & Sond. is the type species of *Rawsonia*, a small genus of Flacourtiaceae represented in tropical Africa. Leaves of the plant were collected in April 1997 in Kakamega Forest in Western Kenya. Voucher specimen (DFHJJ1) was deposited in Herbarium C (Botanical Museum, University of Copenhagen, Copenhagen).

☆Part 18 in the series "Natural Cyclopentanoid Cyanohydrin Glycosides". For Part 17 see Andersen et al., 1998.

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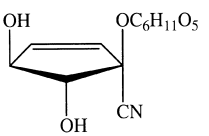
2. Previous work

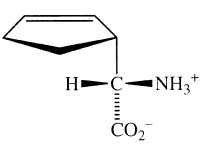
R. lucida was reported as strongly cyanogenic in an extensive survey of Flacourtiaceae by Spencer and Seigler (1985), and later by Burrows et al. (1992). However, the exact nature of the cyanogenic glycoside present was not elucidated. Apart from these studies, no phytochemical investigations of the genus *Rawsonia* have yet been reported.

3. Present study

Dried leaves of *R. lucida* liberated 5.6 μmol HCN/g, as determined according to Nahrstedt (1977). The material (300 g) was extracted with boiling MeOH and fractionated on silica gel using a step gradient of MeOH in AcOEt, the fractions being monitored for cyanogenesis using picrate sandwich assay (Brimer et al., 1983). Final purification of the cyanogenic fractions was achieved by MPLC (Orpegen HD Sil RP-18, 4% aqueous MeOH), to give a total of 0.22 g of gynocardin (**1**). The identity was confirmed by comparison of 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra of the isolated glycoside and its hexaacetate (prepared by overnight treatment with Ac_2O/pyridine) with those of authentic (**1**) and its hexaacetate (Jaroszewski and Olafsdottir, 1987) and with literature data (Hübel et al., 1981; Jensen and Nielsen, 1986).



1



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In a parallel experiment, 30 g of the plant material was extracted twice, each time by overnight stirring with 300 ml H_2O. The combined extracts were freeze-dried and the residue subjected to ion exchange on Dowex-50 W (H^+), from which the total amino acids were eluted with 2 M aqueous ammonia. The amino acid fraction was chromatographed on silica gel using *t*-BuOH/2-butanone/acetone/MeOH/H_2O/conc. NH_3 40:20:20:1:14:15, using synthetic cyclopentenylglycine (Olafsdottir et al., 1992; Dennis et al., 1955) as a reference. Appropriate fractions were pooled, freeze-dried, dissolved in D_2O, and subjected to ^{1}H NMR analysis (400 MHz) at pH 6.7. The ^{1}H NMR spectrum of the isolate showed characteristic resonances of the olefinic protons (δ 5.66 and 6.03) of (2S,1′R)-2-(2′-cyclopentenyl)glycine (**2**) (cf. Katagiri et al., 1997; Cramer et al., 1980), further identified by spiking with synthetic cyclopentenylglycine (mixture of both diastereoisomers). The amount of (**2**) isolated was approx. 0.2 mg, as estimated from the ^{1}H NMR spectra by the standard addition method.

4. Chemotaxonomic significance

In addition to *Rawsonia lucida* investigated in this work, the verified examples of the occurrence of gynocardin in Flacourtiaceae include *Gynocardia odorata* (Kim et al., 1970), *Pangium edule* (De Jong, 1909), *Carpotroche brasiliensis* (Spencer et al., 1982) and *Kiggelaria africana* (Jaroszewski and Olafsdottir, 1987). Moreover, a cyclopentanoid amide with the same oxygenation pattern as gynocardin was isolated from *Lindackeria dentata* (Gibbons et al., 1998). Cyclopentenylglycine, the possible biosynthetic precursor of gynocardin (Olafsdottir et al., 1992), has so far been isolated only from *Hydnocarpus anthelmintica* and *Caloncoba echinata* (Cramer et al., 1980).

The Flacourtiaceae consists of two distinct groups (cf. Bernhard and Endress, 1999), a notoriously cyanogenic group consisting of Oncobeae s. l. and Pangieae, and the non-cyanogenic group including mainly Casearieae, Flacourtieae, Homalieae and Scolopieae. Paropsieae, which appears to be only sporadically cyanogenic (Spencer and Seigler, 1985), links to the Passifloraceae. The previously identified sources of gynocardin all belong to Oncobeae–Pangieae. *Rawsonia* has been either placed together with *Streptothamnus* and *Berberidopsis* in Berberidopsideae (Hutchinson, 1967), included in Oncobeae (Gilg, 1925), or placed in Erythrospermeae (Lemke, 1988). While *Streptothamnus–Berberidopsis* clearly constitutes a separate group (Lemke, 1988; Bernhard and Endress, 1999), also from the point of view of the cyanogenic constituents that are present (Jaroszewski et al., 1988), *R. lucida* is the first member of the Erythrospermeae sensu Lemke in which a cyanogenic constituent has been identified. The presence of gynocardin suggests a close relationship of *Rawsonia* with Pangieae and Oncobeae s. str.

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