

## MONOHYDROXYLATED CYCLOPENTENONE CYANOHYDRIN GLUCOSIDES OF FLACOURTIACEAE\*

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**Key Word Index**—*Kiggelaria africana*; *Carpotroche brasiliensis*; Flacourtiaceae; gynocardin; tetraphyllin B; taraktophyllin; volkenin; epivolkenin; cyclopentenone cyanohydrin glucosides.

**Abstract**—*Kiggelaria africana* and *Carpotroche brasiliensis* contain, besides gynocardin, 1-( $\beta$ -D-glucopyranosyloxy)-4-hydroxy-2-cyclopentene-1-carbonitriles with *cis* allylic oxygens. Earlier reports on *trans* oxygenated isomers in the Flacourtiaceae should be verified.

### INTRODUCTION

The Flacourtiaceae [2, 3] is an aggregate of loosely connected tribes [4], some of which are characterized by their cyanogenesis [5–7]. In contrast to Passifloraceae, which usually produce cyclopentenone cyanohydrin glucosides nonhydroxylated or monohydroxylated in the aglucone portion [8, 9], the dihydroxylated derivative gynocardin (1) [7, 10, 11] is typical of the Flacourtiaceae. We wish to point out that according to our present knowledge the latter family appears to be dominated by cyclopentenones having *cis* allylic oxygens, as in 1–3, whereas the majority of the cyclopentenones encountered in the Passifloraceae are *trans*-dioxxygenated, as in 4 and 5.

### RESULTS AND DISCUSSION

*Kiggelaria africana* (Flacourtiaceae–Pangieae) is a shrub or tree common in the forests of southern parts of Africa. The plant was recognized early as being cyanogenic [12], but subsequent chemical investigations have been concerned with other constituents [13–15]. We have investigated cyanohydrin glucosides of *K. africana* and found, besides the major glucoside 1, the monohydroxylated cyclopentenones *epi*-volkenin (2) and taraktophyllin (3) [1]. All of these glucosides have a *cis*-1,4-dioxxygenated 2-cyclopentene ring, epivolkenin (2) being a possible biosynthetic precursor of gynocardin (1). Similar hydroxylation of taraktophyllin (3) would give 6, the yet uncharacterized diastereomer of 1. However, in spite of careful investigation we have not been able to trace 6 in the extract of the plant.

In an investigation of *Carpotroche brasiliensis*, belonging to a related tribe Oncobeeae, Spencer *et al.* reported the presence of tetraphyllin B to give: (4), the *trans*-1,4-dioxxygenated 2-cyclopentene [17], along with gynocardin [16]. The  $^1\text{H}$ NMR spectrum ( $\text{CDCl}_3$ ) of the *per-O*-trimethylsilyl derivative of the alleged tetraphyllin B reproduced in the article shows methylene protons at  $\delta$ 2.25 and slightly above 3.00, the allylic proton at 4.83, and the olefinic protons at 6.10 and below 6.00 [16].

Although the authors claim that this spectrum is identical to that of the trimethylsilyl derivative of tetraphyllin B, Spencer and Seigler's [18, 19], as well as our own [9], data on the latter give  $\delta$ 2.23 and 2.93, 4.99, 6.21 and 6.02 ( $\text{CDCl}_3$ ). On the other hand, the corresponding signals of the trimethylsilyl derivative of epivolkenin (2),  $\delta$ 2.24 and 3.01, 4.82, 6.11 and 5.96 ( $\text{CDCl}_3$ ) [1], match perfectly those reported previously [16], and we conclude that *C. brasiliensis* produces a mixture of 1 and 2, not 1 and 4.

It appears, therefore, that in all verified cases members of the Flacourtiaceae contain cyclopentenoid glucosides with *cis* allylic oxygens. Although we do not exclude that *trans* oxygenated (such as 4 and 5) glycosides may eventually be found in the Flacourtiaceae, we cannot at present regard the remaining reports of Spencer and Seigler on the co-occurrence of gynocardin (1) and tetraphyllin B (4) in Oncobeeae [7] as conclusive. The possible taxonomic value of stereochemical differences in the oxygenation pattern of cyclopentenoid cyanohydrin glycosides has yet to be explored.

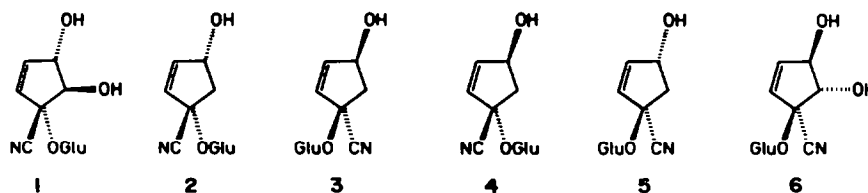
### EXPERIMENTAL

Leaves of *K. africana* L. were collected in a greenhouse of the Botanical Garden, University of Copenhagen, Copenhagen. A voucher specimen is preserved at this laboratory. The leaves were freeze-dried and the material (9.7 g) extracted and fractionated in the usual way [1, 8], using  $\text{EtOAc-Me}_2\text{CO-CH}_2\text{Cl}_2\text{-MeOH-H}_2\text{O}$  (20:15:6:5:4).

The cyanogenic (sandwich picrate assay [20]) fractions were further purified by prep. reverse-phase HPLC [ $1.6 \times 25$  cm column, Lichrosorb RP-18, 10  $\mu\text{m}$ , 5 ml/min of  $\text{H}_2\text{O-MeOH}$  (10:1), RI detection], to give ca 200 mg of crude gynocardin, which was further purified by normal-phase HPLC [ $1.6 \times 25$  cm column, Lichrosorb Si 60, 7  $\mu\text{m}$ , 4 ml/min of  $\text{EtOAc-MeOH-H}_2\text{O}$  (85:13:2), RI detection]. Yield 135 mg (1.4% dry wt) of gynocardin; mp 162–163° (corr.), lit. [10] 165–166°;  $[\alpha]_D^{22} + 82^\circ$  (*c* 0.5, MeOH), lit. [10]  $[\alpha]_D^{28} + 72.9^\circ$  (*c* 0.96,  $\text{H}_2\text{O}$ );  $^1\text{H}$ NMR spectrum ( $\text{CD}_3\text{OD}$ , 250 MHz) was identical with that of authentic gynocardin, isolated at this laboratory from *Gynocardia odorata* seeds [10].

The remaining material eluted from the reverse-phase column was fractionated further on the normal-phase column to give

\*Part 5 in the series 'Cyclopentenoid Cyanohydrin Glycosides'. For part 4 see ref. [1].



Glu =  $\beta$ -D-glucopyranosyl

9 mg of taraktophyllin and 5 mg of epivolkenin (*R*, 18.2 and 19.2 min, respectively). The HPLC *R*<sub>s</sub> and <sup>1</sup>H NMR spectra (250 MHz, CD<sub>3</sub>OD) of the samples were identical with those of our authentic materials [1]. The material was further characterized by CD spectra of the optically active 4-hydroxy-2-cyclopentenones obtained by enzymatic hydrolysis of the glucosides, as described for 4 and 5 [9].

Examination of all other fractions obtained from the HPLC columns by <sup>1</sup>H NMR (250 MHz) failed to detect any material giving a spectrum attributable to the structure 6.

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