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GYNOCARDIN IN *CERATIOSICYOS LAEVIS* (ACHARIACEAE)

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Key Word Index—*Ceratiosicyos laevis*; Achariaceae; cyanogenic glucoside; gynocardin; 4-cyclopentene-1α,2β,3α-triol; chemotaxonomy.

Abstract—The cyclopentenoid cyanogenic glucoside gynocardin and 4-cyclopentene-1α,2β,3α-triol have been isolated from foliage of *Ceratiosicyos laevis* (Achariaceae). The systematic significance of the cyanogenic glycosides in Violales is briefly discussed.

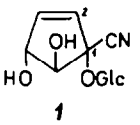
INTRODUCTION

The small South African family Achariaceae comprises three monotypic genera *Acharia*, *Ceratiosicyos* and *Guthriea*. It has been allied with Passifloraceae and Cucurbitaceae [1, 2] and, in most modern taxonomic systems, all three families are included in the order Violales. A few families within Violales elaborate a unique type of cyanogenic glucosides with a cyclopentenoid moiety, namely Flacourtiaceae, Passifloraceae [3], Turneraceae [4], Malesherbiaceae [5] and Caricaceae [6].

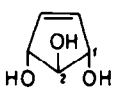
Recently, the three genera of Achariaceae have been reported to be cyanogenic [1], and hence it was of taxonomic interest to establish the type of cyanogen(s) present within this family. For this purpose Dr. van Wyk supplied us with material of *Ceratiosicyos laevis*, and we report the results.

RESULTS AND DISCUSSION

Two cyclopentenoid compounds were obtained from an extract of dry leaves and stems of *Ceratiosicyos laevis* (Thunb.) A. Meeuse, both purified and characterized as esters. The first compound was the cyanogenic glucoside gynocardin (**1**), as indicated by the ^{1}H and ^{13}C NMR spectra [7–9]. Acetylation provided the crystalline hexaacetate, which confirmed the identity of **1**. The ^{1}H NMR spectrum of the second compound showed a singlet at δ5.87, a doublet at 4.48 and a triplet at 3.98, integrating for 2, 2 and 1 proton(s), respectively, suggesting that the compound was a symmetrical cyclopentenetriol. The ^{13}C NMR spectrum corroborated this notion. Furthermore, the low field chemical shifts of the two latter signals suggested that the hydroxy groups were all-*trans* positioned as in 4-cyclopentene-1α,2β,3α-triol (**2**). Benzoylation of **2** gave the crystalline tribenzoate which, by comparison with an authentic sample, proved the identity of **2**.



1



2

The cyclopentenetriol **2** is a new natural product. A similar compound, 3-hydroxy-4-cyclopentenone, has been isolated from *Passiflora perfoliata*, but this plant presumably contains the corresponding α-hydroxynitrile, which, by degradation during work-up may give rise to the cyclopentenone [8]. Most likely, **2** is not a precursor of gynocardin since it has been shown recently that a similar glucoside, deidaclin, biosynthetically derives from cyclopentenyl-glycine in *Turnera ulmifolia* [10]. The occurrence of cyclopentenoid cyanogenic glucosides is apparently restricted to certain families within Violales and thus seems to be a good taxonomic marker. The present result adds further evidence for placing Achariaceae in the Violales and, in addition, increases the taxonomic value of the cyclopentenoid cyanogens.

EXPERIMENTAL

Mps are corrected. Prep. TLC was performed on silica gel and the bands detected by heating with a hot wire. The plant material was collected by Dr. A. E. van Wyk at Kowyns Pass near Graskop in the Eastern Transvaal. The voucher specimen (A. E. van Wyk 6933) is deposited in the H.G.W.J. Schweickerdt Herbarium (PRU), Dept. of Botany, University of Pretoria. Dry foliage of *C. laevis* (30 g) was homogenized in 80% EtOH (300 ml) and left overnight. The extract was evaporated to dryness and the residue partitioned in Et_2O–H_2O. The aq. phase was passed through alumina (neutral, 80 g) which was washed with H_2O (250 ml) and the combined eluates were taken to dryness. The residue was redissolved in H_2O–MeOH and evaporated onto silica gel (30 g) followed by elution with Me_2CO–MeOH (9:1; 500 ml). Evaporation gave a colourless syrup (220 mg) and an ^{1}H NMR spectrum at this point showed signals corresponding to gynocardin at δ6.0–6.4, and in addition a singlet at 5.9. Prep. TLC using $CHCl_3$–MeOH (3:1) as the eluent gave two bands of which the slowest moving (58 mg) consisted of impure gynocardin (**1**), solely characterized by NMR; ^{1}H NMR (500 MHz, D_2O = 4.75 ppm): δ6.22 (*dd*, *J* = 6.5 and 1.5 Hz, H-2), 6.07 (*dd*, *J* = 6 and 1 Hz, H-3), 4.87 (*d*, *J* = 8 Hz, H-1'), 4.68 (*dt*, H-4), 4.33 (*d*, *J* = 5.5 Hz, H-5), 3.97 (*dd*, *J* = 2.5 and 12 Hz, H-6'), 3.72 (*dd*, *J* = 7 and 12 Hz, H-6') 3.57 (*m*, H-5'), 3.56 (*t*, *J* = 10 Hz, H-3'), 3.42 (*t*, *J* = 10 Hz, H-4'), 3.38 (*dd*, *J* = 8 and 10 Hz, H-2'); ^{13}C NMR (125.7 MHz, D_2O): δ140.1 (C-2), 127.6 (C-3), 115.9 (CN), 99.4 (C-1'), 86.6 (C-5), 77.8 (C-4), 76.2 (C-5'), 75.5 (C-3') 72.9 (C-2'), 69.8

(C-4'), 60.9 (C-6'); in agreement with the data reported [7, 8]. Acetylation (Ac_2O–pyridine) provided the hexaacetate (50 mg), mp 119–120° (EtOH); $[\alpha]_D^{20} + 37°$ (*c* 0.5; $CHCl_3$), lit. [7] 119–120°; $[\alpha]_D^{25} + 40°$ (*c* 1.7; $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ6.24 (*dd*, J = 2.2 and 5.9 Hz, H-2), 6.03 (*br d*, J = 5.9 Hz, H-3) 5.71 (*d*, J = 2.3 Hz, H-5), 5.60 (*m*, H-4), 5.25 (*t*, J = 9.5 Hz, H-3'), 5.06 (*t*, J = 9.7 Hz, H-4'), 5.03 (*dd*, J = 8.0 and 9.3 Hz, H-2') 4.96 (*d*, J = 8.0 Hz, H-1'), 4.18 (*m*, 6'-CH_2), 3.83 (*m*, H-5'), 2.21, 2.08, 2.06, 2.03 and 2.00 (3:6:3:3:3, 6 × OAc). The faster moving band (62 mg) contained impure 4-cyclopentene-1α,2β,3α-triol (**2**). ^1H NMR (500 MHz, D_2O): δ5.87 (*s*, 2H, H-4 and H-5), 4.48 (*d*, J = 5.0 Hz, H-1 and H-3), 3.98 (*t*, J = 5.0 Hz, H-2), consistent with that reported [11]. ^{13}C NMR (125.7 MHz, D_2O): δ134.6 (C-4 and C-5), 89.0 (C-2), 80.4 (C-1 and C-3). Benzoylation provided the tribenzoate; crystallized from EtOH, mp (and mmp) 98–99° (lit. [12] 98°).

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