

Citronellol and Citronellyl Esters from the Paracloacal Glands of the Broad-Snouted Caiman, *Caiman latirostris* (Crocodylia, Reptilia)

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The secretions of the paracloacal glands of an adult male broad-snouted caiman (*Caiman latirostris*) were analyzed by GC/MS. 3,7-Dimethyl-6-octen-1-ol (citronellol) and four citronellyl esters, with acid moieties ranging from two to five carbons, were identified. Squalene, β -farnesene, and straight-chain esters also were observed.

Introduction

An analysis of the paracloacal gland secretions of crocodilians yielded the first reptilian skin compound for which a detailed chemical structure was proposed. Fester and Bertuzzi (1934) isolated from the pooled glandular exudates of two caimans from Brazil, *Caiman crocodilus* and *C. latirostris*, an alcohol with a rose-like odor that they named “yacarol”. This compound initially was identified as 2,6-dimethyl-2-hepten-7-ol. A subsequent analysis by Fester *et al.* (1937) comparing the melting points and other physical properties of the glandular component with those of known compounds, however, indicated 3,7-dimethyl-6-octen-1-ol (citronellol, Fig. 1). We report here the results of an analysis by GC/MS confirming citronellol in the paracloacal gland secretions of the

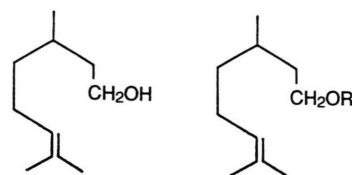


Fig. 1. The structural formulae of citronellol (left) and citronellyl esters (right), where R denotes acid moieties of 2, 3, 4, and 5 carbons.

broad-snouted caiman (*C. latirostris*), a species restricted to southern regions of South America in Argentina, Bolivia, Brazil, Paraguay, and Uruguay. In addition, we document several citronellyl esters in the exudates of this species.

Material and Method

Paracloacal gland secretions were obtained from an adult male *C. latirostris* (total length = 1.3 m) maintained at the St. Augustine Alligator Farm, FL. Each gland was manually palpated and compressed to force glandular secretions into the mouth of a glass vial placed near the gland duct openings. Several milliliters of CH_2Cl_2 were added to the vial before it was sealed with a Teflon-lined cap and placed on dry ice. The vial was kept frozen (-10°C) until analysis.

Lipids in the secretions were fractionated by thin-layer chromatography (TLC) and subsequently analyzed by GC/MS. Glass TLC plates coated with a 0.75-mm layer of silica gel were developed in 3% ethyl acetate in hexane. TLC bands were visualized by spraying plates with a solution of Rhodamine B and dichlorofluorescein. Bands were scraped from plates, extracted with diethyl ether, and analyzed by GC/MS.

GC/MS analyses were performed on a Hewlett-Packard (Palo Alto, CA) 5890 gas chromatograph equipped with a 30-m x 0.25-mm DB-1 fused silica column (J & W Scientific, Folsom, CA) and interfaced with a Hewlett-Packard 5970 Mass Selective Detector. The carrier gas was chromatography grade helium at a head pressure of 105 kPa. All spectra were obtained at an ionizing voltage of 70 eV.

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Results and Discussion

A TLC band with an R_f of 0.89 yielded squalene (m/z (rel. int.) values: 410 (1), 137 (10), 81 (60), 69 (100), and 41 (30)) and a sesquiterpene, with a molecular ion at m/z 204 (m/z (rel. int.) values: 204 (3), 161 (9), 133 (18), 93 (50), 69 (85), and 41 (100)). The ion of the sesquiterpene at m/z 69 is characteristic of open-chain terpenoids; this and other fragment ions in the mass spectrum of this compound are consistent with β -farnesene.

A broad TLC band ca. 4 cm wide with an R_f of 0.70 yielded the following citronellyl esters: citronellyl acetate (m/z (rel. int.) values: 138 (16), 123 (32), 69 (53), 61 (5), 43 (100), and 41 (90)); citronellyl propanoate (m/z (rel. int.) values: 138 (20), 123 (32), 75 (5), 69 (63), 43 (13), and 41 (100)); citronellyl butanoate (m/z (rel. int.) values: 138 (15), 123 (43), 89 (5), 69 (64), 43 (64), and 41 (100)); and citronellyl pentanoate (or a methyl butanoate) (m/z (rel. int.) values: 138 (12), 123 (47), 103 (3), 69 (60), 43 (11), and 41 (100)) (Fig. 1). Other esters identified in this band are tetradecyl propanoate (m/z (rel. int.) values: 241 (3), 196 (3), 168 (3), 111 (15), 75 (67), 57 (100), and 43 (48)); hexadecyl propanoate (m/z (rel. int.) values: 269 (5), 224 (3), 196 (3), 111 (20), 97 (39), 75 (68), 57 (100), 43 (48), and 41 (40); and hexadecenyl propanoate (m/z (rel. int.) values: 296 (1), 222 (15), 138 (8), 110 (30), 82 (84), 75 (15), 69 (80), and 57 (100)); the double-bond position of the latter compound is unknown. Two compounds co-eluting on GC were identified as tetradecyl dodecanoate (m/z (rel. int.) values: 396 (15), 201 (64), 183 (10), 125 (10), 83 (40), 57 (80), and 43 (100)) and dodecyl tetradecanoate (m/z (rel. int.) values: 396 (15), 229 (54), 168 (23)); ions at m/z 229 and m/z 168 are definitive for dodecyl tetradecanoate.

A TLC band with an R_f of 0.15 yielded two compounds, cholesterol (m/z (rel. int.) values: 386 (100), 368 (57), 353 (51), 326 (16), 301 (78), 275 (65), 213 (46), 145 (41), 107 (43), and 43 (84)) and citronellol (m/z (rel. int.) values: 156 (5), 138 (6), 123 (16), 95 (30), 81 (38), 69 (66), and 41 (100)). These results support the claim of Fester *et al.* (1937) on the presence of the latter compound in *C. latirostris*. Because Fester and colleagues saponified the glandular secretions of caimans prior to analysis, however, it has been unclear whether the alcohol they obtained was esterified in its native state. Our results demonstrate both free and esterified citronellol in the paracloacal gland secretions of *C. latirostris*.

Citronellol also has been identified by GC/MS in the paracloacal glands of dwarf (*Paleosuchus palpebrosus*) and smooth-fronted caimans (*P. trigonatus*), and citronellyl acetate has been observed in *P. palpebrosus* (Shafagati *et al.*, 1989). Our study and others of the paracloacal gland lipids of caimans provide the only demonstrations of citronellol and its esters in vertebrates. Interestingly, analyses of the paracloacal gland products of two other alligatorids, the American (*Alligator mississippiensis*) (Weldon *et al.*, 1988; Ibrahim *et al.*, 1998) and the Chinese alligators (*A. sinensis*) (Dunn *et al.*, 1993), have failed to indicate these compounds.

Acknowledgements

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