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TERPENOID AND OTHER CONSTITUENTS OF *HERNANDIA VOYRONI* AND *ANTHOCLEISTA AMPLEXICAULIS**

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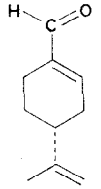
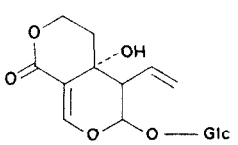
Key Word Index—*Hernandia voyroni*, Hernandiaceae; *Anthocleista amplexicaulis*; Loganiaceae; terpenoids; (+)-perillaldehyde; swertiamarin; (+)-bornesitol

Plant sources. H. voyroni Jum. (Hernandiaceae), *A. amplexicaulis* (Loganiaceae). R. Pernet[1] has identified perillaldehyde as a constituent of the oil obtained from *H. peltata* Meissn. He also investigated extracts obtained from *H. voyroni*, whose alkaloid contents he estimated to be 0·5%, and in addition isolated 2·9% of an oil with camphor-like smell. We have further examined this oil and we have isolated (+)-perillaldehyde (**1**) from this species. Derivatives of **1** (oxime, semicarbazone) were prepared and compared with authenitic samples.

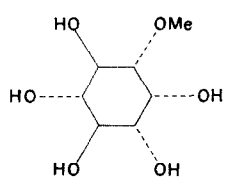
Swertiamarin (**2**) and (+)-bornesitol (**3**) were isolated from *A. amplexicaulis*, tetraacetyl- and dihydrotetraacetyl-**2** were prepared, spectroscopically investigated and compared with authentic specimens. **2** has previously been isolated from *A. procera*.[2] **3** was transformed into its pentaacetyl derivative and the constitution of this product was elucidated by NMR spectroscopy. **3** has been previously found in *Sarcocephalus diderichii* (Rubiaceae).[3]



(1)



(2)



(3)

* Part 4 in the series "Plants from Madagascar"; for part 1, see SCHLITTLER, E. and WEBER, N. (1972) *Lloydia* **35**, 181. Part 2, see SCHITTLER, E. and WEBER, N. (1972) *Helv. Chim. Acta* **55**, 2061. Part 3, see WEBER, N. (1973) *Chem. Ber.* **106**, 3769.

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EXPERIMENTAL

M.ps are uncorrected. NMR spectra were recorded with TMS as an internal standard. UV in MeOH. IR in KBr-pellets. Optical rotation on a Perkin–Elmer-141 polarimeter. TLC were performed on neutral alumina type T (Merck), solvent CH_2Cl_2–MeOH (10:1). Column chromatography on alumina (Woelm, neutral). Bark and branches of *H. voyroni* were collected in November 1967 in Morondava/Madagascar, leaves of *A. amplexicaulis* in October 1967 in Perinet/Madagascar.

Extraction of H. voyroni. 100 g of stem bark and branches were extracted and worked up according to Schlittler *et al.*[4] Ethereal oils were separated by steam distillation and extracted from the aq. phase with Et_2O. The ether residue yielded 0·3 g of crude oil which was purified by vacuum distillation. The main fraction (110–120°/12 mm) contained **1** and after redistillation a colourless oil with a camphor-like smell was obtained: UV λ_{max} 228 (log 4·2), 307 (1·7) nm; IR (film) ν_{max} 2815 and 2723 (aldehyde), 1687 (α,β-unsat. aldehyde), 1645 (C=C) cm^{-1} *oxime*: m.p. 100–101° (MeOH), $[\alpha]_D$ + 147° (*c* 0·86; Et_2O). compared (UV, IR, m.m.p.) with an authentic sample.

Semicarbazone. m.p. 195–197° (MeOH).

Extraction of A. amplexicaulis. 190 g ground leaves were defatted with petrol. and extracted with $CHCl_3$ and EtOAc (5% H_2O) according to Taylor-Smith.[5]

(a) *Chloroform extract*. Evaporation of the $CHCl_3$ extract left 6 g dark green residue which was chromatographed over 130 g alumina. The development of the chromatogram was followed up by TLC. Elution with acetone gave a dark green fraction (2·2 g, discarded); further elution with Me_2CO–H_2O (10:1) and Me_2CO–H_2O (1:1) afforded two fractions (1·8 and 1·0 g) which were pooled, dissolved in 10 ml MeOH and ppt. with 100 ml Et_2O. The ppt. thus formed was dissolved in little MeOH, taken on an alumina column and eluted with MeOH–H_2O (10:1). After evaporation of the solvent 1·0 g of a yellowish foam of **2** was obtained: $[\alpha]_D$ − 105° (*c* 0·97; MeOH).

Swertiamarin tetraacetate was obtained by acetylation of **2** (Ac_2O–pyridine at r.t. overnight), m.p. 194° (MeOH), $[\alpha]_D$ − 116° (*c* 1·06; $CHCl_3$), compared (UV, IR, NMR) with authentic material (Found: C, 53·12; H, 5·44. $C_{24}H_{30}O_{14}$ requires: C, 53·13; H, 5·57%).

Dihydroswertiamarin tetraacetate was obtained by catalytic hydrogenation of **2** tetraacetate, m.p. 190° (MeOH), $[\alpha]_D$ − 108° (*c* 2·59; $CHCl_3$); UV, IR and NMR spectra were identical with published data[2,6] (Found: C, 52·84; H, 5·88. $C_{24}H_{32}O_{14}$ requires: C, 52·93; H, 5·93%).

Gentiopicroside tetraacetate was obtained by dehydration of **2** tetraacetate with Ac_2O–$KHSO_4$, m.p. 139–140° (MeOH), $[\alpha]_D$ − 180° (*c* 0·86; $CHCl_3$); UV and IR spectra were identical with the ones published.[2,6]

(b) *Ethyl acetate extract*. Evaporation of the EtOAc extract left 14 g of a crude brown residue which was chromatographed according to Koch *et al.*[2] over 130 g alumina. First fraction (Me_2CO): 5·5 g, discarded; second fraction (Me_2CO–H_2O, 10:1) afforded 2·2 g (**2**), after acetylation (Ac_2O–pyridine) gave 0·3 g of **2** tetraacetate; third fraction (Me_2CO–H_2O, 1:1) left 2·0 g (**3**), after acetylation (Ac_2O–pyridine) 0·48 g of (+)-bornesitol pentaacetate were obtained, m.p. 145–146° (after softening above 140°) (MeOH), $[\alpha]_D$ + 10° (*c* 2·88; acetone), UV no absorption above 210 nm; MW 404 (*ms*), (Found: C, 50·21; H, 5·93; OCH_3, 7·65. $C_{16}H_{21}O_{10}(Me)_1$ requires: C, 50·35; H, 5·91; Me, 7·63%). ^{1}H-NMR: (a) 60 MHz, $CDCl_3$, δ 2·02 (3 MeC=O), 2·06 (MeC=O), 2·19 (1 MeC=O), 3·36 (1 MeO), 3·53 (*d*, 1H), 4·85–5·85 (*m*, 4H) ppm (b) 100 MHz, $CDCl_3$ + C_6D_6 Eu(DPM)$_3$ shift spectrum δ 2·59, 2·65, 3·00, 3·52 and 3·81 (5 MeC=O) ppm (c) 270 MHz, $CDCl_3$, Fourier Transform spectrum δ 4·95 (1H, J_{a-a}10·0; J_{a-e}2·8), 5·10 (1H, J_{a-a}9·7), 5·35 (1H, J_{a-a}10·0), 5·46 (1H, $J_{a\ a}$10·3), 5·72 (1H, J_{a-e}2·75) ppm.

(+)-*Bornesitol* was obtained by hydrolysis of **2** pentaacetate with NH_3–EtOH, m.p. 201–203°, $[\alpha]_D$ + 29° (*c* 3·80; H_2O).

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[4] vide Comm. **2**.

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