

Investigation of *Croton caudatus* Geisel – Isolation of Stigmastan-3,6-dione,5 α

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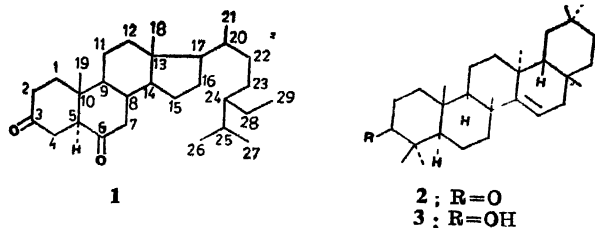
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CROTON caudatus Geisel (Fam.: Euphorbiaceae; collected in Darjeeling) is a medium-sized plant growing profusely in the Eastern Himalayan range at an altitude of about 6000 ft. The leaves are odorous and find extensive application in relieving pain from sprains¹. Among the local people of Darjeeling, this plant is popular for its use in the treatment of stomach disorders. Its extracts have been found to possess some insecticidal and insect-repelling properties. Previous examination of the plant led to the isolation of three triterpenoids, viz. taraxerone, taraxerol and taraxeryl acetate besides sitosterol and two rearranged labdane type norditerpene, viz. teucvidin and croto-caudin from this plant². The present reinvestigation on the stem-bark of this plant led to the isolation of a compound belonging to a rare class of nortriterpenoids, viz. stigmastan-3,6-dione,5 α (1) in addition to taraxerone, taraxerol, sitosterol and an unidentified compound (5% methanolic chloroform, M^+ 412), m.p. 205°.



The concentrated petrol (b.p. 60–80°) extract of the dried and powdered stem-bark of *Croton caudatus* when chromatographed over silica gel yielded taraxerone (2), C₃₀H₄₈O (M^+ 424), m.p. 238°; ν_{\max} (KBr) 1 700 cm⁻¹; m/z 424 (M^+), 409 (M^+ -CH₃), and taraxerol (3), C₃₀H₅₀O (M^+ 426), m.p. 278°; ν_{\max} (KBr) 3 480 cm⁻¹; m/z 426 (M^+), 411 (M^+ -CH₃), 393 (M^+ -CH₃-H₂O) in the petrol-benzene (1 : 1) eluates, and sitosterol, m.p. 137° in the benzene eluates. These three compounds were identified by direct comparison (m.p., m.m.p., co-tlc in several systems, superimposable ir and ¹H nmr spectra) with the authentic samples.

Repeated fractional crystallisation of the solid, obtained from the benzene eluate in later fractions afforded a white crystalline solid, m.p. 195°; ν_{\max} (KBr) 1 710 cm⁻¹, which gave a pale green coloration with the Liebermann-Bürchardt reagent, showing its steroidal/terpenoidal nature and no colour with TNM for a double bond. The 70 eV high-resolution mass spectra showed a molecular

ion peak at m/z 428.366211 (diff. 0.7629 amu from calculated) corresponding to molecular formula C₂₉H₄₈O₂. Its fragmentation pattern suggested that it had the stigmastane skeleton, with the sequential loss of methylene groups from the molecular ion followed by peaks at m/z 287 (M^+ -C₁₀H₂₁) and 245 (M^+ -C₁₀H₂₁-42)³ suggesting the possible identity of the compound with stigmastan-3,6-dione,5 α (1) which has been supported by a detailed 200 MHz ¹H nmr analysis of compound 1 whose assignments are given here: 200 MHz ¹H nmr δ (CDCl₃) 0.70 (3H, s, C₁₈ protons), 0.85–0.95 (9H, m, C₂₆, C₂₇ and C₂₉ protons), 0.93 (3H, d, J 6.4 Hz, C₂₁ protons), 0.97 (3H, s, C₁₉ protons), 1.26 (16H, brs, C₁, C₁₁, C₁₂, C₁₅, C₁₆, C₂₂, C₂₃ and C₂₈ protons), 1.48–2.12 (7H, m, C₈, C₉, C₁₄, C₁₇, C₂₀, C₂₄ and C₂₅ protons), 2.07–2.37 (5H, m, C₂, C₄ and C₅ protons), 2.57 (2H, C₇ protons-AB system).

Stigmastan-3,6-dione,5 α was first isolated by Hayashi *et al.*⁴ from *Metasequoia glyptostroboides* Hu et Cheng, and subsequently from other sources, viz. *Macranga tanarius*⁵, *Aristolochia* species⁷ and *Boehmeria platyphylla*⁸. This rare compound has been isolated for the first time from the genus *Croton*.

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Potentiometric and Visual Determination of Potassium using Periodate as Reagent

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THE literature survey reveals that the titrimetric methods for the determination of potassium suffer from many disadvantages like using costly