

Isolation of cantharidin from *Cyaneolytta sapphirina*

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The isolation of cantharidin from *Cyaneolytta sapphirina* Makl. (*Coleoptera Meloidae*) is reported.

Cyaneolytta sapphirina Makl. (*Coleoptera, Meloidae*) a species of blistering beetle is known in the Sudan under the common name of Fassaya. Attracted by light, it appears mostly by night during the rainy season of August and September in Khartoum province. For present purposes the beetles were collected in August from Gabel-El Awlia, Khartoum province.

Isolation methods

100 beetles killed by exposure (2 h) to ether, initially weighed 10 g. They were dried at 32° (R.H. 50%), then brought to constant weight in a vacuum dessicator over anhydrous CaCl₂ (48 h): the beetles then weighed 3.5 g.

Free cantharidin

Dried beetles (10 g) in the form of a coarse powder were extracted (18 h) with acetone in a soxhlet apparatus. Removal of acetone gave a dark brown residue (1.6 g), which was dissolved in benzene on a silica gel column (Merck) (0.05-0.2 mm). The column was eluted successively with 200 ml each of benzene, benzene-ether (95:5, v/v), ether, chloroform, acetone and methanol. The residues from the above fractions weighed 0.13, 0.10, 0.5, 0.06, 0.3 and 0.4 g respectively.

The presence of free cantharidin in each fraction was detected by thin-layer chromatography on silica gel G (Merck), developed by acetone-benzene (1:4, v/v) using cantharidin (BDH) as a reference. The plates were sprayed with 50% H₂SO₄ and heated to 150° in an oven: cantharidin (*R_F*, 0.7) was observed in the benzene-ether eluate and was purified by washing with a small volume of light petroleum-ethanol (19:1) when a microcrystalline powder (3.5 mg) (0.035%) m.p. (214-216°) was obtained; sublimation gave colourless needles m.p. 217-218°.

Combined cantharidin

Dried beetles (10 g) in the form of coarse powder were treated (48 h at 35°) with shaking in benzene-light petroleum (2:1) (100 ml) containing 2 ml of concentrated HCl. After filtration and evaporation this gave a brown viscous residue (0.5 g) containing large prismatic crystals. The crystals were separated by washing with a mixture of light petroleum-ethanol (19:1) and filtered. The impure crystalline residue (130 mg) in benzene was chromatographed as above when colourless prismatic crystals (100 mg; 1%) resulted. Sublimation at 120° and 1 mm Hg yielded pure

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cantharidin m.p. 217–218° (found; C, 61.4; H, 6.17; calc for $C_{10}H_{12}O_4$; C, 61.2; H, 6.17%; this material gave a molecular ion at m/e 196). The infrared spectrum was identical with that of an authentic specimen, as were the nmr and mass spectra. Mixed m.p. with an authentic specimen gave no depression.

DISCUSSION

Although cantharidin has been isolated from different species of the genera *Cantharis* (=Lytta) (Porfirio, 1931), *Mylabris* (Iyer & Guha, 1931) and *Epicauta* (Walter & Cole, 1967), this is the first report of the presence of cantharidin in the genus *Cyaneolytta*.

In *Cyaneolytta sapphirina*, the amount of free cantharidin is small, most being in a combined form which yields only to hydrolysis with hydrochloric acid. The total amount estimated by the method of the U.S.P. XI (1936) is 3% matching the case of *Epicauta gorhami* (Shimato, Nizuno & Bato, 1953). From other sources concentrations of about 1% are more normally found (Walter & Cole, 1967).

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