Polyhydroxyanthraquinones from the Insect *Eriococcus coriaceus*

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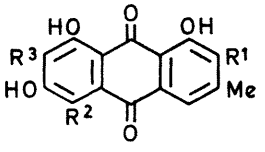
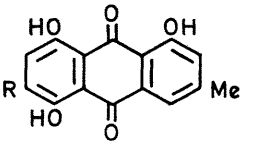
Summary A group of seven polyhydroxyanthraquinones based on emodin and 7-acetylemodin has been isolated from the coccid *Eriococcus coriaceus*.

WE have isolated a group of seven polyhydroxyanthraquinones from *Eriococcus coriaceus* Mask. (Hemiptera–Coccoidea), a scale insect parasitising *Eucalyptus* species.



(I)



(II)

Two of these pigments have been isolated previously by Chan and Crow[1] from a related species, *Eriococcus confusus*. Skeletally the group differs from the several other coccid-derived anthraquinones[2] in being based on emodin (I; $R^1 = R^2 = R^3 = H$) or the hitherto unknown 7-acetylemodin (I; $R^1 = Ac$, $R^2 = R^3 = H$). The components are C_{15} and C_{17} compounds hypothetically derivable *via* the acetate–malonate pathway. Insect-derived quinones based on a C_{17} nucleus have not previously been observed.[2,3]

The pigments occur in the living insect as glycosides, at present under investigation, and these are converted into aglycones either by autolysis or acidic hydrolysis. The aglycones were shown to consist chiefly of emodin (I; $R^1 = R^2 = R^3 = H$),[1†] ω-hydroxyemodin (I; $R^1 = R^2 = R^3 = H$, CH_2OH in place of Me),[4†] 7-acetylemodin (I; $R^1 = Ac$, $R^2 = R^3 = H$), the anthragallol (I; $R^1 = R^2 = H$, $R^3 = OH$), and the purpurins (II; R = OH),[5,6] (I; $R^1 = Ac$ $R^2 = OH$, $R^3 = H$), and (II; R = OH, CH_2OH in place of Me). All new compounds gave satisfactory analyses and high resolution mass spectra.

The presence of a *C*-acetyl group in 7-acetylemodin (I; $R^1 = Ac$, $R^2 = R^3 = H$), λ_{max} (methanol/1% acetic acid) 439 nm, was indicated by an i.r. absorption maximum at 1685 cm^{-1} and a three-proton singlet, τ (CF_3CO_2H) 7·30, the remainder of the spectrum being consistent with the structure assigned. On degradation with alkaline hypoiodite, followed by dithionite reduction to remove an introduced nuclear iodo substituent, it gave endocrocin (I;

$R^1 = CO_2H$, $R^2 = R^3 = H$).[4,6]† This establishes the structure unambiguously.

The three purpurin derivatives (II; R = OH), (I; R^1 = Ac, R^2 = OH, R^3 = H), and (II; R = OH, CH_2OH in place of Me), λ_{max} (dioxan) 493,497, and 494 nm, respectively, were identified on spectroscopic grounds. Their structures were confirmed by means of the characteristic purpurin–xanthopurpurin reduction with alkaline dithionite[7] to give emodin, 7-acetylemodin, and ω-hydroxyemodin. Compound (II; R = OH), obtained synthetically,[5] was identical with the natural material. The latter was converted into xanthorin (II; R = OMe)[5] and then reduced with alkaline dithionite to give helminthosporin (II; R = H),[4]† the expected product.[8]

The anthragallol (I; $R^1 = R^2 = H$, $R^3 = OH$) was synthesised for the first time by room-temperature oxidation of emodin with persulphate in concentrated sulphuric acid. It was obtained in 20% yield and was identical with the natural product. The scope of this novel oxidation which has been observed for other hydroxylated anthraquinones is under investigation.

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† Identical with an authentic sample.

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