A New Class of Sesterterpenoids from the Secretion of *Ceroplastes rubens* (Coccidae)

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Five novel sesterterpenoids (1)—(5) from the secretion of the scale insect *Ceroplastes rubens* Maskell have been isolated and characterized to be the first representatives of series having the tricyclo[8.4.1.0]pentadecane and tetracyclo[9.4.0.0.0]pentadecane skeletons.

We report the isolation[1,2] and structure of five novel sesterterpenoids from the secretion of the scale insect *C. rubens:* cerorubenic acid-I (**1**), cerorubenic acid-II (**2**), cerorubenic acid-III (**3**), cerorubenol-I (**4**), and cerorubenol-II (**5**). The sesterterpenoids (**1**)—(**5**) are the first representatives of series having the tricyclo[8.4.1.0]pentadecane and tetracyclo-[9.4.0.0.0]pentadecane skeletons. These compounds have been shown to act,[3] in part, as kairomones, responsible for the ovipositional behaviour of the parasitic wasp *Anicetus beneficus* (Encrytidae) towards *C. rubens.*[4]

C. rubens was collected in Osaka Prefecture (1979) and Kyushu District (1981—1982), where they were found as deep red hemispheres about 3 mm in diameter on citrus trees. Compounds (**1**)—(**5**) were isolated by $CHCl_3$ extraction of the insect bodies, filtration, concentration, addition of acetone, removal of acetone insoluble material, KOH extraction, neutralization, methylation, SiO_2 chromatography, and successive $AgNO_3$–SiO_2 flash chromatography of the neutral–acidic fractions.

Cerorubenic acid-I (**1**), an oil, was isolated as its oily methyl ester $C_{26}H_{38}O_2$ (*m/z* 382.2487, M^+, calc. 382.2869); $[\alpha]_D^{24}$ $-67.8°$ (*c*, 0.54, $CHCl_3$); ν_{max} (neat) 1716 cm^{-1} (conjugated ester). Its mass spectrum indicated loss of the side chain (*m/z* 227, $M^+ - C_9H_{15}O_2$). The n.m.r. data shown in (A) and (B) were consistent with structure (**1**), assignments being based on heteronuclear decoupling, lanthanide induced shifts, and comparison within this series. The upfield shift (δ 20.9 p.p.m., t) of the bridging C-24[†] can be explained by the shielding effect of the 10-ene system. Extensive $\{^1H-^1H\}$ difference decoupling

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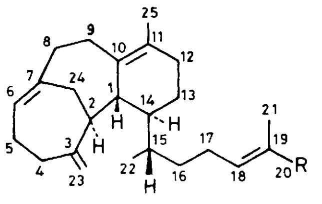
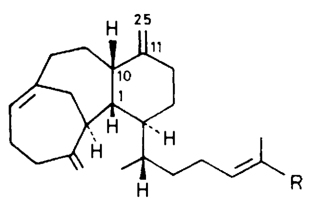
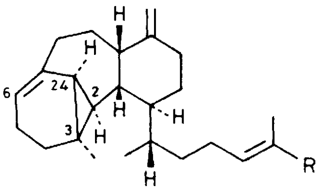
[†] The numbering system is based on that of the presumed biogenetic precursor geranylfarnesyl cation.





R = CO_2H, cerorubenic acid-I (**1**) R = CO_2H, cerorubenic acid-II (**2**)

R = CH_2OH, cerorubenol-I (**4**) R = CH_2OH, cerorubenol-II (**5**)



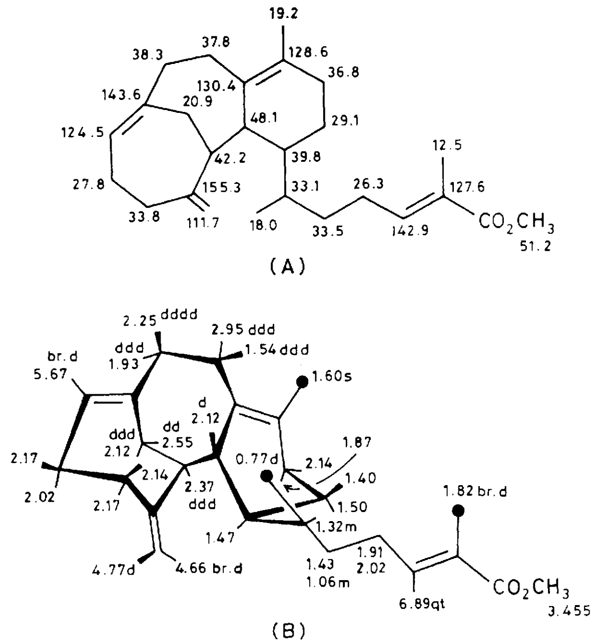
R = CO_2H, cerorubenic acid-III (**3**)

and 2-dimensional J correlation allowed all protons to be assigned and many of the J values to be determined. The relative configurations were established by nuclear Overhauser enhancement (n.O.e.) difference spectra and J values.‡

The acid (**1**) was slowly oxidized in the air to give epoxycerorubenic acid, 6,7-α-epoxy-(**1**), $C_{26}H_{38}O_3$ (m/z 398.2837, M^+, calc. 398.2863). The replacement of the olefinic peaks at δ 143.6 (s, C-7) and 124.5 p.p.m. (d, C-6) by peaks at δ 60.7 (d) and 61.2 p.p.m. (s) in the ^{13}C n.m.r. spectrum, together with the lack of an OH group (i.r.) indicated the presence of an epoxide. The 6-H n.m.r. signal (δ 2.66, t, J 7 Hz) indicated that the epoxide had the α-stereochemistry. This facile oxidation probably reflects the inherent strain in the [8.4.1.0] tricyclic ring system.

Cerorubenic acid-II (**2**) was isolated as its methyl ester, oil, $C_{26}H_{38}O_2$ (m/z 382.2832, M^+, calc. 382.2869); $[\alpha]_D^{21}$ −83.8° (c, 0.73, $CHCl_3$), ν_{max} 1712 cm^{-1} (conjugated ester). The ^{13}C n.m.r. spectrum indicated that the 10-ene observed in (**1**) had been replaced by an exocyclic 11,25-ene in (**2**). The β-configuration of 10-H, *i.e.*, a *cis*-ring junction, was established by the 4% n.O.e. at 1-H upon irradiation of 10-H (δ 2.60). Treatment of (**2**) with p-$MeC_6H_4SO_3H$–MeOH at 40—50 °C, for 2 h yielded (**1**).

Cerorubenic acid-III (**3**) was also isolated as its methyl ester, an oil, $C_{26}H_{38}O_2$ (m/z 382.2875, M^+, calc. 382.2869); $[\alpha]_D^{24}$ −60° (c, 0.001, $CHCl_3$) with ν_{max} 1715 cm^{-1} (conjugated ester). Its mass spectrum was similar to those of (**1**) and (**2**), except for intensity differences. The presence of six olefinic carbon atoms (^{13}C n.m.r.) indicated that (**3**) was tetracyclic. The upfield shifts of peaks at δ 24.9 (d, C-2) and 20.7 p.p.m. (s, C-3) suggested a cyclopropyl moiety. In comparison with (**2**), one exocyclic double bond has been lost and a new Me group has appeared; the cyclopropyl ring should thus involve either C-3 or C-11. In the ^1H n.m.r. spectrum, the presence of two upfield coupled protons, δ 0.75 (t, J 9 Hz, 2-H) and 0.95 (d, J 9 Hz, 24-H), also supported the presence of a cyclopropyl system. Finally, 2-dimensional J correlation, difference decoupling, and comparisons of J values with those of (**1**) and (**2**) established the structure of (**3**). A small allylic long-range coupling (<1 Hz) between 6-H and 24-H could be detected using 2-dimensional J correlation but was not observed by difference decoupling.



(A)

(B)

N.m.r. assignments (C_6D_6; δ values) of cerorubenic acid-I methyl ester (A), ^{13}C; (B), ^1H. Black circles denote methyl groups. Coupling constants (J/Hz): 1-H 9; 2-H 1, 6, 9; 8-H 6, 13, 13; 8′-H 1, 2, 6, 13; 9-H 6, 13, 13; 9′-H 2, 6, 13; 15-H 2.5, 7, 8; 18-H 1.5, 8.5; 21-H 1.5; 22-H 7; 24-H 2, 6, 13; 24′-H 1, 13.

Cerorubenols-I (**4**) and II (**5**), $C_{25}H_{38}O$ (m/z 354.2930 and 354.2910, M^+, calc. 354.2921) were also both oils, $[\alpha]_D^{24}$ −45.0° (c, 0.52, $CHCl_3$), and −98.7° (c, 0.39, $CHCl_3$) respectively; ν_{max} 3350 cm^{-1} (OH). Their mass spectra showed peaks due to the loss of the side chain. Their ^{13}C n.m.r. spectra indicated that (**4**) and (**5**) were closely related to (**1**) and (**2**), respectively. $LiAlH_4$ reduction of the methyl esters of (**1**) and (**2**) yielded alcohols identical in all respects with (**4**) and (**5**).

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‡ ^1H N.m.r. data were obtained on a Nicolet NT-360 spectrometer with a 1280/293B data system. When 2-H (δ 2.37) was irradiated, a 3.7% n.O.e. was observed with 23-H (δ 4.66), but no n.O.e. was observed with 1-H. This, along with the observed $J_{1,2}$ 9 Hz coupling indicated that 1-H and 2-H were *trans*. The lack of coupling between 1-H and 14-H, corresponding to a dihedral angle of 80—100°, suggested their *trans* relationship. The configuration at C-15 was established noting the 3.7% n.O.e. observed between 22-H (methyl) and 1-H, *and* the small (2.5 Hz) coupling detected between 14-H and 15-H corresponding to a dihedral angle of 60—115°. To confirm the position of the tetra-substituted double bond, 9-H (δ 2.95) was irradiated, when a 3.6% n.O.e. was observed at 25-H (methyl).