

Naturally Occurring Quinones. Part XXI.¹ Anthraquinones in the Crinoids *Heterometra savignii* (J. Müller) and *Lamprometra klunzingeri* (Hartlaub)

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The pigments of *L. klunzingeri* include rhodolamprometrin (1-acetyl-2,4,5,7-tetrahydroxyanthraquinone) and the known compound rhodoptilometr in. The latter is also present in pink-and-light-yellow banded specimens of *H. savignii*.

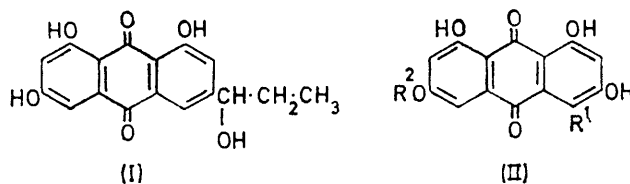
In the animal kingdom anthraquinones have a restricted distribution,² limited, so far as we know, to certain insects and crinoids (feather stars). The opportunity occurred recently to examine two species of crinoid taken from the coral reef at Elat in the Gulf of Aqaba.

Organic solvents did not extract any pigment from light and dark brown specimens of *Heterometra savignii*, and extraction with water gave a brown solution which afforded only intractable material. On the other hand, specimens with arms banded pink and light yellow imparted a bluish red colour to fresh water which could be transferred to n-butanol. Chromatography of the extract revealed a principal orange band containing material which was identified as rhodoptilometr in (I), found previously in *Ptilometra australis*.³

From magenta specimens of *Lamprometra klunzingeri* the pigment was readily extracted with water, and on chromatography it separated into two major orange and red bands. The former yielded rhodoptilometr in (I), and the latter afforded a new quinone, rhodolamprometrin, C₁₆H₁₀O₇. This compound is very similar to rhodocomatul in (II; R¹ = COPrⁿ, R² = H), which

substituent, hydrogen bonding would be expected to shift ν_{CO} below 1700 cm⁻¹.) Thus rhodolamprometrin has structure (II; R¹ = Ac, R² = H). Like the rhodocomatul ins,⁴ it appears to undergo reductive cleavage in hot alkaline dithionite, but this was not definitely established.

In the i.r. spectrum (Nujol) of rhodocomatul in 6-methyl ether (II; R¹ = COPrⁿ, R² = Me) the ketonic



Rhodolamprometrin (II; R ¹ = Ac, R ² = H)	Rhodocomatul in methyl ether (II; R ¹ = COPr ⁿ , R ² = Me)
λ_{max} (EtOH) 236, 260sh, 268, 300, 325sh, 469 nm	232, 259sh, 266, 296, 321sh, 463 nm
λ_{max} (EtOH-HO-) 248, 265sh, 325, 406, 570 nm	244, 263sh, 291sh, 323, 559 nm
τ (ArH) (CD ₃ OD) 2.96 (1H, d, J 2 Hz), 3.52 (1H, d, J 2 Hz), 3.66 (1H, s)	(CD ₃ OD-CDCl ₃) 2.75 (1H, d, J 2 Hz), 3.32 (1H, d, J 2 Hz), 3.36 (1H, s)

occurs (as its mono- and di-methyl ethers) in *Comatula* spp.,⁴ and is clearly a 1,3,6,8-tetrahydroxyanthraquinone with one more substituent. An additional peak in the n.m.r. spectrum of rhodolamprometrin at τ 7.51 (3H) and carbonyl absorption at 1700 cm⁻¹ (KBr disc) suggest that this substituent is an acetyl group, which is consistent with the molecular formula. Moreover, the three strongest peaks in the mass spectrum, which is very simple, appear at m/e 314 (*M*, 28%), 299 (*M* - CH₃, 100%), and 43 (CH₃CO, 10%) (all confirmed by accurate mass measurement). The aromatic singlet at τ 3.66 can only be attributed to a β -proton, so that the acetyl group must occupy an α -position. (If it were a β -

carbonyl band coincides with the free quinone carbonyl absorption at 1669 cm⁻¹, but in dioxan solution it is shifted to 1702 cm⁻¹. This has been ascribed⁴ to steric crowding in the C-4 region, resulting in twisting of the ketonic group out of the plane of the ring. In rhodolamprometrin the smaller acetyl side chain can evidently rotate more easily, since there is no sign of intramolecular hydrogen bonding in the solid state (ν_{CO} 1700 cm⁻¹), and in dioxan solution the ketonic band is shifted to 1729 cm⁻¹. The fact that the H-2 n.m.r. absorption is at higher field than the H-7 signal in both compounds may also be a consequence of this non-planarity, and again the effect is more marked in the C-acetyl compound.

The initial water-solubility of the two pigments might be attributed to association with other extractives, including some basic material, as the violet-red solutions evidently contained ionised hydroxyquinones [the tap water was only faintly alkaline (pH 7.65)]. Alternatively, the colour of the animals suggests that the pigments are present as salts which leach out when cells are ruptured on transfer from sea-water to fresh water. It is also possible that the pigments are present as water-soluble *O*-sulphates (as in the case of a number of other crinoid pigments⁵), and that hydrolysis occurs on acidification in the cold.

Whereas the Australian^{3,4} crinoids elaborate anthraquinones with β -C₃ and α -C₄ side chains the pigments in these Red Sea animals contain β -C₃ and α -C₂ side

¹ Part XX, E. J. C. Brew and R. H. Thomson, *J. Chem. Soc. (C)*, 1971, 2007.

² R. H. Thomson, 'Naturally Occurring Quinones,' 2nd edn., Academic Press, London, 1971.

³ V. H. Powell and M. D. Sutherland, *Austral. J. Chem.*, 1967, **20**, 541.

⁴ M. D. Sutherland and J. W. Wells, *Austral. J. Chem.*, 1967, **20**, 515.

⁵ R. A. Kent, I. R. Smith, and M. D. Sutherland, *Austral. J. Chem.*, 1970, **23**, 2325; I. R. Smith and M. D. Sutherland, *ibid.*, 1971, **24**, 1487.

chains. Acetyl side chains have been observed previously only in the bacterial bianthraquinones known as julichromes.⁶

EXPERIMENTAL

Extraction of Heterometra savignii.—Ten pink-and-light-yellow banded specimens were immersed in water overnight. The bluish red solution was acidified with 2M-hydrochloric acid (the colour changing to orange-brown), and extracted with n-butanol. The extract was evaporated *in vacuo* and the residual red material was transferred, in methanol, to silica gel plates and chromatographed in chloroform-methanol (19:1). The major orange band (14 mg) was eluted and run again in the same system to give rhodoptilometrin (3–4 mg) as an orange solid, identical (t.l.c. in three systems) with an authentic sample (Found: M , 314.0793. Calc. for $C_{17}H_{14}O_6$: M , 314.0790), ν_{\max} (KBr) 3500, 1668, and 1632 cm^{-1} , m/e 315 (12%), 314 (50), 286 (27), 285 (100), 284 (10), 270 (18), 258 (12.5), 257 (50), 256 (7), 243 (11), 241 (6), 215 (20), 187 (8.5), 143 (7.5), 137 (7.5), 121 (6.5), 115 (7), 69 (9.5), and 60 (6). The mass spectrum was virtually identical with that of an authentic sample, with the base peak at m/e 285 ($M - \text{Et}$); in the spectrum of isorhodoptilometrin [side chain $\text{CH}_2\text{CH}(\text{OH})\text{Me}$], m/e 270 ($M - \text{CH}_3\text{CHO}$) is the base peak.

Extraction of Lamprometra klunzingeri.—Two animals were immersed in water for several hours and the violet-red extract was worked up as in the foregoing experiment. The principal orange and red bands were run twice on t.l.c.

plates as before. The orange band afforded rhodoptilometrin (3–4 mg), identical with that obtained from *H. savignii*; the red band yielded *rhodolamprometrin* (2–3 mg) as a red solid (from methanol) (Found: M , 314.0414. $C_{16}H_{10}O_7$ requires M , 314.0427), ν_{\max} (KBr) 3405, 1700, 1685sh, 1634, and 1626 cm^{-1} , ν_{\max} (dioxan) 3560, 3495, 1729, 1670w, 1630, 1625, and 1609 cm^{-1} , m/e 315 (7.5%), 314 (28), 300 (25), 299 (100), 149.5 (4), 122 (7.5), 69 (7), and 43 (10). Crude pigment (*ca.* 1 mg) was reduced by heating with sodium dithionite (8 mg) in aqueous 1% sodium hydroxide (1 ml) for 15 min on a water-bath, the colour changing rapidly from violet-red to orange-yellow. After cooling, air was bubbled through the solution for 30 min. The suspension was then acidified and extracted with chloroform-ethyl acetate (1:1) to give 1,3,6,8-tetrahydroxyanthraquinone, identical (t.l.c.) with authentic material. The electronic spectrum was similar to that of tetrahydroxyanthraquinone with additional (impurity) bands in the u.v. region.

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⁶ N. Tsuji and K. Nagashima, *Tetrahedron*, 1970, **26**, 5719; 1971, **27**, 1557.