Three Pyranonaphthazarin Pigments from *Gnomonia erythrostoma*

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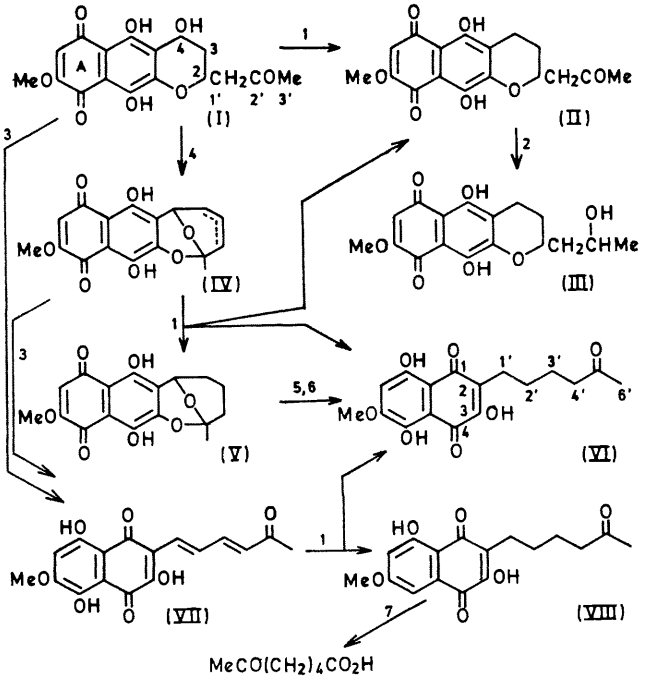
Summary Three pigments produced by *Gnomonia erythrostoma* have been shown to be 2-acetonyl-4-hydroxy-8-methoxydihydropyrano[3,2-*g*]naphthazarin (I), its 4-deoxy-derivative (II), and 2-(2′-hydroxy-n-propyl)-8-methoxydihydropyrano[3,2-*g*]naphthazarin (III) or the corresponding 7-methoxy-isomers.

WHEN grown in deep culture *Gnomonia erythrostoma* produced a deep red broth from which an antibacterial mixture of pigments was extracted. Chromatography of the mixture gave mainly erythrostominone (I), $C_{17}H_{16}O_8$,† m.p. 184—186°, $[\alpha]_D^{25}$ + 231°, with a smaller amount of deoxyerythrostominone (II), $C_{17}H_{16}O_7$, and a trace of deoxyerythrostominol (III), $C_{17}H_{18}O_7$. The u.v. spectrum of erythrostominone [λ_{max} nm (ϵ) 231·5 (34,900), 280 (7760), 315 (7940), 480sh (7330), 509 (8560), and 546 (5300)] suggested that it contained a naphthazarin nucleus,[1] and in agreement, addition of sodium hydrosulphite solution to the pigment immediately gave a colourless solution from which the quinone was regenerated on oxidation. The i.r. and n.m.r. spectra (see Table) of erythrostominone supported structure (I), thus the former indicated the presence of unbonded hydroxy- and keto-groups, whilst the n.m.r. spectrum contained, in addition to the tabulated peaks, resonances at τ 6·16 (OMe) and −2·6 and −3·19 (singlets, *peri*-OH's). Furthermore, irradiation of the proton at τ 5·32 reduced the lines centred at τ 7·1 to an AB system (J 16 Hz) and simplified the multiplet at τ 8·25. The methoxy-group is placed at C-8 on biogenetic considerations, whilst the chemical shift of the 7-proton (τ 3·73) shows[2] that the principal tautomer in chloroform solution has a quinonoidal ring A. The half-band width[3] (*ca.* 5 Hz)



SCHEME. 1. H_2/Pd–C/HOAc. 2. $NaBH_4$. 3. EtOH–1N-HCl, under reflux. 4. *p*-Me·C_6H_4·SO_3H–benzene, under reflux. 5. HOAc, under reflux. 6. H_2/Pd–C/EtOAc. 7. RuO_2–$NaIO_4$ (see ref. 4).

† All compounds gave satisfactory analyses and/or accurate masses.

of the proton at C-4 in erythrostominone indicates that the 4-hydroxy-group is pseudo-axial.

The presence of the benzylic hydroxy-group at C-4 in erythrostominone was confirmed by hydrogenation which gave *inter alia* deoxyerythrostominone (II). The latter no longer showed an unbonded hydroxy-group in the i.r. whilst its n.m.r. spectrum (see Table) was similar to that of erythrostominone except that the resonance at τ 5·15 was replaced by a multiplet at τ 7·4 (Ar·CH_2·).

Reduction of deoxyerythrostominone with sodium borohydride confirmed the presence of a methyl ketone by yielding *inter alia* deoxyerythrostominol (III) (see Table).

τ Values of protons measured at 100 *MHz in* $CDCl_3$ (J *and* $W_{\frac{1}{2}}$ *in Hz*)

Compound	2-H	3-H	4-H	7-H	1′-H	2′-H	3′-H	ν_{max} ($CHBr_3$) cm.$^{-1}$
(I)	5·32m	8·25m	5·15m $W_{\frac{1}{2}}$ *ca.*5	3·73s	7·1, 8 lines	—	7·77s	3580, 1720, 1604
(II)[a]	5·47m	8·3m	7·4m	3·72s	7·1, 8 lines	—	7·74s	1713, 1601
(III)	5·59m	8·12m	7·37m	3·65s	8·12m	5·82m	8·72d *J* 6·5	3580 (unbonded OH), 1603

Compound	5-H	7-H	1′-H	2′-H	3′-H	4′-H	6′-H	
(IV)	—	3·64s	4·75m	[b]	[b]	[b]	8·25s	1604
(V)[a]	—	3·64s	4·75m		8·15m		8·35s	1603
(VI)	—	3·47s	7·46m		8·39m	7·46m	7·87s	3410, 1710, 1627
(VII)[c]								3250, 1655, 1632, 1612
(VIII)[e]	2·96d *J* 2·5	3·47d *J* 2·5	7·54m		8·48m	7·54m	7·84s	3390, 1710, 1655, 1612

[a] 60 MHz. [b] 4·32m and 3·91m (vinylic protons) and 7·5m (allylic-CH_2-). [c] Insoluble. [d] Nujol mull. [e] In $(CD_3)_2SO$–$CDCl_3$.

The structure of the non-aromatic portion of the pigments was firmly established by the reaction sequence in the Scheme. Both the 6-oxo-heptanoic acid and its semicarbazone were identical with authentic specimens.[5]

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