Pigments of *Gnomonia erythrostoma*. Part I. The Structures of Erythrostominone, Deoxyerythrostominone, and Deoxyerythrostominol

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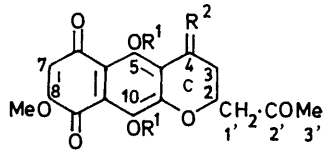
Three antibacterial pigments have been isolated from deep cultures of *Gnomonia erythrostoma*. By a combination of spectroscopic investigation and chemical degradation erythrostominone has been shown to be 2-acetonyl-3,4-dihydro-4,5,10-trihydroxy-8-methoxy-2*H*-naphtho[2,3-*b*]pyran-6,9-quinone (1); deoxyerythrostominone is its 4-deoxy-derivative (2), and deoxyerythrostominol is 3,4-dihydro-5,10-dihydroxy-2-(2-hydroxypropyl)-8-methoxy-2*H*-naphtho[2,3-*b*]pyran-6,9-quinone (21).

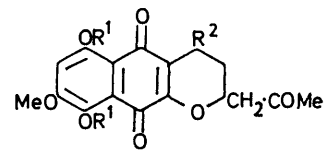
When *Gnomonia erythrostoma* is grown in aerated stirred culture it produces a deep red broth from which a mixture of antibacterial pigments can be extracted. The isolation of three pigments, named erythrostominone, deoxyerythrostominone, and deoxyerythrostominol, has been reported, and a brief account of the determination of their structures has been given.[1]

Erythrostominone, the main constituent of the mixture, was shown to have the formula $C_{17}H_{16}O_8$ by high resolution mass spectrometry. Its u.v. spectrum [$\lambda_{max.}$ 231·5, 280, 315, 480sh, 509, and 546 nm (ε 34,900, 7760, 7940, 7330, 8560, and 5300)] suggested that it contained a 5,8-dihydroxy-1,4-naphthoquinone (naphthazarin) nucleus,[2] and, in agreement, addition of sodium hydrogen sulphite solution to the pigment in ethanol immediately gave a colourless solution from which the quinone was regenerated on aerial oxidation. The i.r. spectrum of erythrostominone (in bromoform) showed a strong broad carbonyl band at 1604 cm^{-1}, indicating a quinone in which both carbonyl groups were strongly hydrogen bonded,[3] together with unbonded hydroxy- and keto-groups ($\nu_{max.}$ 3580 and 1720 cm^{-1}). Since *peri*-hydroxy-groups do not usually show OH stretching bands in the i.r.,[4] erythrostominone presumably possesses three hydroxy-groups. Its n.m.r. spectrum (see Table 1) showed singlets assigned to chelated hydroxy-protons,[5,6] a singlet at τ 3·73 attributed to a proton in a hydroxy- or methoxy-substituted quinonoid ring rather than an aromatic proton,[6] and a resonance due to a methoxy-group; it was concluded that erythrostominone contained a disubstituted methoxynaphthazarin nucleus. The structure of ring C depicted in formula (1) was strongly supported by the resonances due to the aliphatic part of the molecule (see Table 1). In confirmation, irradiation at the frequency of the proton at τ 5·32 reduced the eight lines centred at τ 7·1 to an AB system (*J* 16 Hz) and simplified the multiplet at τ 8·25. Thus, spectroscopic data are in agreement with structure (1) or its 7-methoxy-isomer for erythrostominone, but do not exclude other structures. The work described below rigorously establishes the validity of structure (1).

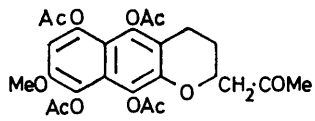
The presence of the benzylic hydroxy-group at C-4 in erythrostominone was confirmed by catalytic hydrogenation in acetic acid. When the uptake of hydrogen was stopped at 2 mol. equiv., the main product was a deoxy-compound, $C_{17}H_{16}O_7$, identical with the deoxyerythrostominone isolated from the fermentation. Erythrostominone was recovered from solution in glacial acetic acid, indicating that its conversion into the deoxy-compound is a hydrogenolysis and not an acid-catalysed dehydration followed by hydrogenation. The deoxy-compound had a u.v. spectrum almost identical with that of erythrostominone, but its i.r. spectrum no longer showed a signal for an unbonded hydroxy-group. Its n.m.r. spectrum (see Table 1) was similar to that of erythrostominone except that the signal at τ 5·15 in the latter was replaced by a resonance at τ 7·4. Hence, the deoxy-compound was assigned structure (2).



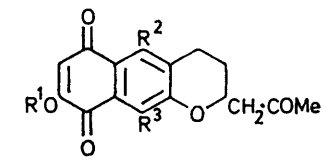
	R^1	R^2
(1)	H	H,OH
(2)	H	H_2
(3)	H	O
(4)	H	H,O·CH_2·SMe
(5)	Ac	H,OAc
(6)	Ac	H_2



	R^1	R^2
(7)	Ac	OAc
(8)	H	OH
(9)	Ac	H



(10)



	R^1	R^2	R^3
(11)	H	OH	OH
(12)	Me	OH	H
(13)	Me	H	OH
(14)	Me	OAc	H
(15)	Me	H	OAc

Further evidence for the presence of the benzylic hydroxy-group was provided by oxidation of erythrostominone. Although a number of oxidising agents gave intractable gums, acetic anhydride–dimethyl sulphoxide afforded a low yield of the ketone (3) together with a gum

[1] B. E. Cross, M. N. Edinberry, and W. B. Turner, *Chem. Comm.*, 1970, 209.
[2] R. H. Thomson, 'Naturally Occurring Quinones,' 2nd edn., Academic Press, London, 1971, p. 49.
[3] Ref. 2, p. 67.
[4] H. Bloom, L. H. Briggs, and B. Cleverley, *J. Chem. Soc.*, 1959, 178.
[5] Ref. 2, p. 73.
[6] R. E. Moore and P. J. Scheuer, *J. Org. Chem.*, 1966, **31**, 3272.

believed to be the methylthiomethoxy-derivative (4). The former showed no hydroxy-absorption in the i.r., but had a carbonyl band at 1690 cm^{-1} which was assigned to an aryl ketone system; in agreement its u.v. absorption extended to longer wavelength than that of erythrostominone.

Acetylation of erythrostominone gave a product shown by its n.m.r. spectrum to be a mixture of the two isomeric triacetates (5) and (7) in the ratio of *ca.* 2 : 1. The spectrum showed a peak due to the acetate of an alcohol (τ 7·99) and singlets due to two aryl acetates (τ 7·67 and 7·66), but more significantly it contained two signals (τ 6·25 and 6·18) attributable to methoxy-groups which together only integrated for a total of three protons. Furthermore there were singlets at 4·11 and 3·19 with a combined integral corresponding to one proton. It is well known that naphthazarins can exist as an equilibrium mixture involving four tautomers [7] corresponding to structures (1) and (8) and the related 1,5-naphthoquinones. Since the latter are normally regarded [7] as making only a small contribution to the equilibrium they are not considered here. Consequently the singlets at τ 4·11 and 3·19 in the mixture of triacetates can be assigned to the 7-proton in structures (5) and (7), respectively. The i.r. spectrum of the mixture of triacetates showed bands due to alkyl (1735 cm^{-1}) and aryl acetates (1777 and 1765 cm^{-1}); the carbonyl bands of the quinone now absorbed at 1679 and 1640 cm^{-1}, reflecting the loss of hydrogen bonding as a result of acetylation of the *peri*-hydroxy-groups. Similarly, acetylation of deoxyerythrostominone gave a mixture, shown by spectroscopic evidence to consist of the diacetates (6) and (9). The formation of these mixtures of acetates confirms the presence of the naphthazarin nucleus in both erythrostominone and deoxyerythrostominone.

Reductive acetylation of erythrostominone gave a leuco-tetra-acetate, in which the benzylic hydroxy-group was shown to have been lost: the same leuco-compound was obtained by reductive acetylation of the mixture of deoxyerythrostominone diacetates (6) and (9). Structure (10) for the leuco-derivative was confirmed by spectroscopic evidence. Thus its i.r. and n.m.r. spectra showed that all the acetates were derived from phenolic hydroxy-groups ($\nu_{max.}$ 1765 cm^{-1}; τ 7·7, 7·65, 7·63, and 7·61) and its u.v. spectrum was consistent with that of a substituted naphthalene.[8] Reductive acetylation of deoxyerythrostominone was more complex; in addition to the expected leuco-tetra-acetate (10), a considerable amount of a diacetate, $C_{20}H_{22}O_8$, was formed. The latter showed no methoxy-peak in its n.m.r. spectrum, but contained a hydroxy-group (τ −2·99), and on acetylation it gave a triacetate, $C_{22}H_{24}O_9$; the structures of these two compounds are unknown. Demethylation of deoxyerythrostominone with hydrobromic acid in acetic acid gave the trihydroxy-quinone which was shown by its n.m.r. spectrum (see Table 1) to exist predominately as the tautomer (11) in solution in dimethyl sulphoxide–chloroform.

TABLE 1

^1H N.m.r. data (τ values; solutions in $CDCl_3$; J and $W_{\frac{1}{2}}$ in Hz)

Compound	2-H	3-H	4-H	7-H	8-OMe	1′-H	2′-H	3′-H	Other signals
(1) *	5·32(m)	8·25(m)	5·15(m, $W_{\frac{1}{2}}$ *ca.* 5)	3·73(s)	6·16(s)	7·1 (8 lines)		7·77(s)	−2·6(s) and −3·19(s) (*peri*-OH's)
(2) *	5·47(m, $W_{\frac{1}{2}}$ *ca.* 15)	8·3(m)	7·4(m)	3·72(s)	6·15(s)	7·1 (8 lines)		7·74(s)	−2·56(s) and −3·09(s) (*peri*-OH's)
(11) *†	5·44(m)	8·3(m)	7·41(m)	3·61(s)		7·1 (8 lines)		7·76(s)	
(18)	5·52(m)	8·3(m)	7·22(m)	3·21(d, J 2·5)	6·07(s)	7·22(m)		7·73(s)	2·49(d, J 2·5, 9-H)
(14) or (15)	5·46(m)	8·28(m)	7·23(m)	4·03(s)	6·13(s)	7·23(m)		7·71(s)	7·53(s, ArOAc); 2·52(s, 5- and/or 10-H)
(21)	5·59(m)	8·12(m)	7·37(m)	3·65(s)	6·06(s)	8·12(m)	5·82(m)	8·72(d, J 6·5)	
(22) or (23)	5·59(m)	8·14(m)	7·36(m)	4·03(s)	6·12(s)	8·14(m)	5·88(m)	8·72(d, J 6·5)	2·95(s, 5- and/or 10-H); −2·65(s, phenolic OH)

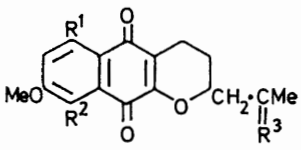
* 100 MHz. † In $(CD_3)_2SO$–$CDCl_3$.

Prolonged hydrogenation of erythrostominone in glacial acetic acid over palladised charcoal led to the uptake of *ca.* 4 mol. equiv. of hydrogen and gave an orange product which contained very little deoxyerythrostominone (*cf.* before). Hydrogenation of the latter under similar conditions gave the same orange product, which had the formula $C_{17}H_{16}O_6$, so that deoxyerythrostominone appeared to have lost an oxygen atom by hydrogenolysis to give a monohydroxy-quinone. Because of the tautomerism of the naphthazarin nucleus, four monohydroxy-quinone structures are possible, *viz.* (12), (13), (16), and (17), if (unexpectedly) a *peri*-hydroxy-group has been lost. The i.r. spectrum of the product showed $\nu_{max.}$ ($CHBr_3$) 1714 (C=O of ketone), 1679 (C=O of unbonded quinone), and 1631 and 1605 cm^{-1} (C=O of hydrogen bonded quinone and C=C). Its n.m.r. spectrum contained singlets at τ −2·32 and −2·61 which could be attributed to *peri*-hydroxy-groups, but the integral of the two signals was only equivalent to one proton; there were also four low-field signals which integrated for a total of two protons, so that the product must be a mixture. Doublets at τ 3·5 and 2·95 (J 2·5 Hz) were assigned to the *meta*-coupled protons at position 7 and 9 respectively in structure (16) (the proton at C-9 is deshielded by the 5,10-quinone carbonyl group).[6]

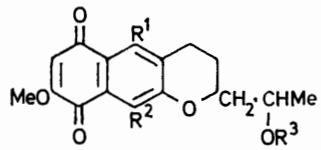
[7] Ref. 2, p. 75.

[8] A. I. Scott, 'Interpretation of the Ultraviolet Spectra of Natural Products,' Pergamon, London, 1964, p. 126.

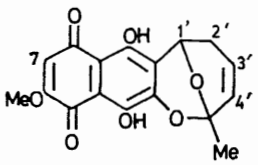
A singlet at τ 4·12 was attributed to the 7-proton in either quinone (12) or quinone (13), and similarly the other singlet at τ 3·03 was assigned to the 10-proton in structure (12) or to the 5-proton in quinone (13). The quinones (12) and (13) cannot be distinguished by their n.m.r. spectra, so that either or both may be present.



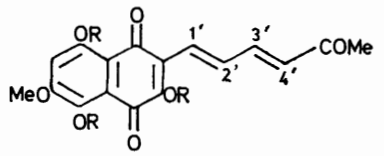
	R^1	R^2	R^3
(16)	OH	H	O
(17)	H	OH	O
(18)	OAc	H	O
(19)	OH	H	H,OH
(20)	OAc	OAc	H,OAc



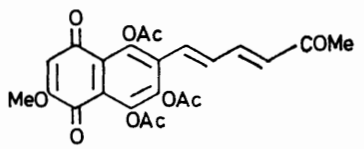
	R^1	R^2	R^3
(21)	OH	OH	H
(22)	OH	H	H
(23)	H	OH	H
(24)	OAc	OAc	Ac



(25)
(26) $\Delta^{2'}$-isomer



	R
(27)	H
(28)	Ac



(29)

Since no signals attributable to *ortho*-coupled protons could be seen in the n.m.r. spectrum the isomer (17) was assumed to be absent.

Acetylation of the mixture of monohydroxy-quinones followed by careful preparative layer chromatography afforded two products. One of them was clearly shown by analytical and spectroscopic data (see Table 1) to be the monoacetate (18). The other product, also a monoacetate with a sharp m.p., had an n.m.r. spectrum (see Table 1) indicating that it had either structure (14) or (15) or was a mixture of the two.

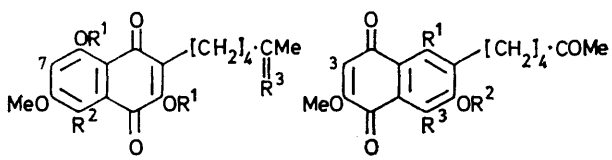
The presence of the methyl ketone grouping in erythrostominone and deoxyerythrostominone was established by reduction with sodium borohydride. It is known [9] that the reduction of hydroxy-naphthoquinones with sodium borohydride can be complicated, and the product from erythrostominone was not characterised. However in its n.m.r. spectrum, the resonance at τ 7·77 assigned to the acetyl group in erythrostominone, was replaced by a doublet at τ 8·75 (*J* 6·5 Hz), and an additional multiplet appeared at τ 5·8 (2′-C*H*·OH), thus supporting the structure of the side-chain. Complete confirmation of this conclusion was provided by the reduction of deoxyerythrostominone with sodium borohydride. Two main products were obtained, one of these, shown to be the alcohol (21) by its n.m.r. spectrum (see Table 1) and by the fact that its u.v. spectrum closely resembled that of erythrostominone, proved to be identical with deoxyerythrostominol, thus establishing the structure of the latter. On acetylation it gave a mixture of the isomeric triacetates (20) and (24) in which, as expected, the 2′-proton signal had moved downfield to τ 4·76. The other reduction product, $C_{17}H_{18}O_6$, was shown by its orange colour and u.v. spectrum to have lost a hydroxy-group. Its n.m.r. spectrum (see Table 1), which indicated that it was a monohydroxy-quinone with structure (22) or (23) or that it was a mixture of the two, also contained weak doublets at τ 3·45 and 2·9 (*J* 2·5 Hz) assigned to the aromatic protons in the quinone (19) believed to be present as an impurity.

The structure of ring C of erythrostominone was finally established by examination of the products obtained by treatment of the pigment with various acidic reagents. When erythrostominone was heated under reflux in benzene in the presence of toluene-*p*-sulphonic acid, and with azeotropic removal of water, an unstable red compound, $C_{17}H_{14}O_7$, was formed. The same product was obtained when erythrostominone was dissolved in cold concentrated sulphuric acid. The u.v. spectrum of this compound was almost identical with that of erythrostominone, showing that the methoxynaphthazarin nucleus remained intact. However its i.r. spectrum, unlike that of erythrostominone, showed no absorptions due to either a hydroxy- or a keto-group. Meaningful n.m.r. spectra of the compound could not be obtained because pure samples decomposed in solution with precipitation of an insoluble product while the spectrum was being determined. However signals (see Table 2) could be seen due to two *peri*-hydroxy-groups, a methoxy group, a quinonoid proton, two olefinic protons, an ArC*H*·O group, an allylic methylene group, and a methyl group [τ 8·25(s)] which was no longer part of a methyl ketone system. Either structure (25) or its isomer (26) is consistent with these results; these structures are discussed in detail later. The compound decomposed slowly in neutral solution but more rapidly under acidic conditions or on heating. In all cases the sparingly soluble product was an isomer, more readily obtained by heating erythrostominone under reflux with ethanol–N-hydrochloric acid, which has been assigned the dienone structure (27) on the basis of spectroscopic data and the reactions described later. The u.v. spectrum of the dienone (27) [$\lambda_{max.}$ ($CHCl_3$) 243, 306sh, 320sh, 328, 486, 526sh, and 570sh nm (ε 16,400, 36,000, 42,800, 45,100, 15,900, 12,700, and 6370)] showed much more intense absorption, which had shifted to longer wavelength than that of erythrostominone; its i.r. spectrum (Nujol) showed a conjugated ketone absorption at 1655 cm^{-1}, hydrogen-bonded quinone carbonyl absorption at 1612 cm^{-1}, and a band at 3250 cm^{-1} indicating a hydroxy-group in addition to the *peri*-hydroxy-groups. The presence of the third hydroxy-group in the dienone was confirmed by acetylation, which gave a triacetate whose

[9] R. E. Moore, H. Singh, C. W. J. Chang, and P. J. Scheuer, *J. Org. Chem.*, 1966, **31**, 3638.

n.m.r. spectrum showed it to be the expected mixture of the two isomers (28) and (29).

Hydrogenation of the dienone (27) gave two major and two minor products. One of the former was red, had the formula $C_{17}H_{18}O_7$, and its spectroscopic properties showed that it had structure (30). Its i.r. spectrum showed bands at 3410 (OH), 1710 (C=O of ketone), and 1627 cm^{-1} (hydrogen-bonded C=O of quinone), and its n.m.r. spectrum revealed the presence of a methyl ketone system (τ 7·87) and showed two four-proton multiplets at τ 8·39 and 7·46 assigned to the 2′-H_2 and 3′-H_2 and to the 1′-H_2 and 4′-H_2 groupings, respectively; its u.v. spectrum was very similar to that of erythrostominone. Acetylation yielded a gum, shown by its n.m.r. spectrum (see Table 2) to be a mixture of the isomeric triacetates (31) and (37); the same mixture of triacetates was obtained by hydrogenation of the mixture of acetates (28) and (29). Reductive acetylation of this mixture of triacetates gave the colourless penta-acetate (40), whose u.v. spectrum was as expected for a substituted naphthalene.[8]



	R^1	R^2	R^3
(30)	H	OH	O
(31)	Ac	OAc	O
(32)	H	H	O
(33)	Me	H	O
(34)	Ac	H	O
(35)	H	H	H,OH
(36)	Ac	H	H,OAc

	R^1	R^2	R^3
(37)	OAc	Ac	OAc
(38)	OH	H	H
(39)	H	H	OH

The second main product from the hydrogenation of the dienone (27) was an orange compound, shown by its formula of $C_{17}H_{18}O_6$ to have lost one oxygen atom, and by the formation of a boroacetate complex [10] with boroanoic acid in 42% yield. The latter was identified by comparison of the keto-acid and its semicarbazone with authentic specimens.[13] Structure (32) was finally verified by total synthesis [14] of its dimethyl ether (33).

The elucidation of the structures of the dienone (27), and of its hydrogenation products (30) and (32), determined the carbon skeleton of the non-aromatic portion of erythrostominone and the other two pigments, and showed that the naphthazarin nucleus carried an oxygen substituent α to the side-chain. This evidence, taken in conjunction with the spectroscopic data for the three pigments, and the other degradations already described, completely established the structures of erythrostominone, deoxyerythrostominone, and deoxyerythrostominol as (1), (2), and (21), respectively. The half-band width [15] (*ca.* 5 Hz) of the n.m.r. signal due to the proton at C-4 in erythrostominone indicates that the 4-hydroxy-group is pseudo-axial; the absolute stereochemistry of the pigments is under investigation.

One of the minor products from the hydrogenation of the dienone (27) (see before) was orange and had the formula $C_{17}H_{18}O_6$, *i.e.* hydrogenolysis of a hydroxy-group

TABLE 2

^{1}H N.m.r. data (τ values; solutions in $CDCl_3$; J in Hz)

Compound	5-H	7-H	1′-H	2′-H	3′-H	4′-H	6′-H	Other signals
(25) and/or (26) * [a]		3·64(s)	4·75(m)	†	†	†	8·25(s)	6·11(s, OMe); −2·61(s) and −3·08(s) (*peri*-OH's)
(31) and (37)		3·14(s) 4·03(s) [c]	7·52(m)	8·51(m)	8·51(m)	7·52(m)	7·9(s)	6·11(s) and 6·19(s, OMe); 7·63(s), 7·61(s), 7·58(s), and 7·56(s) (total 9H, 3 × ArOAc)
(32) *‡ [a]	2·96(d, J 2·5)	3·47(d, J 2·5)	7·54(m)	8·48(m)	8·48(m)	7·54(m)	7·84(s)	6·21(s, OMe)
(35) ‡	2·89(d, J 2·5)	3·39(d, J 2·5)	7·46(m)	8·55(m)	8·55(m)	8·55(m)	8·87(d, J 6·5)	6·32(m, 5′-H); 6·11(s, OMe)
(42) [b]		3·64(s)	4·75(m)		8·15(m)		8·35(s)	6·06(s, OMe)
(43) [a]		3·42(s)	3·02(m)	3·28(m)	7·43(m)	7·43(m)	7·82(s)	6·04(s, OMe)

* 100 MHz. † 4·32(m) And 3·91(m) (vinylic protons) and *ca.* 7·5(m, allylic $-CH_2-$). ‡ In $(CD_3)_2SO$–$CDCl_3$.

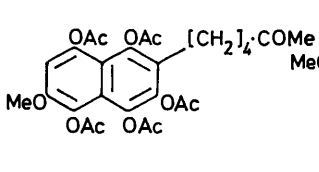
[a] For numbering see formulae. [b] Numbering as in formula (25). [c] 3-H in compound (37).

[10] A. K. Macbeth and F. L. Winzor, *J. Chem. Soc.*, 1935, 334.
[11] J. E. Davies, F. E. King, and J. C. Roberts, *J. Chem. Soc.*, 1955, 2782.
[12] J. A. Caputa and R. Fuchs, *Tetrahedron Letters*, 1967, 4729; D. M. Piatak, G. Herbst, J. Wicha, and E. Caspi, *J. Org. Chem.*, 1969, **34**, 116.
[13] N. Polgar and R. Robinson, *J. Chem. Soc.*, 1954, 389; E. E. Blaise and A. Koehler, *Bull. Soc. chim. France*, 1910, **7**, 215.
[14] B. E. Cross and L. J. Zammitt, unpublished work.
[15] N. S. Bhacca and D. H. Williams, 'Applications of N.m.r. Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, p. 77.

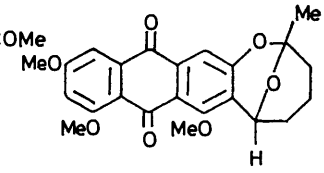
had occurred. Its n.m.r. spectrum contained one-proton singlets at τ 4·01 and 2·81 assigned to the quinonoid and aromatic protons, respectively, in structure (38) or (39). Both the compound and its diacetate had sharp m.p.s and there was no evidence to suggest that they were mixtures; however it was not possible on the evidence available to distinguish between the two structures.

The second minor product from the hydrogenation of the dienone (27) was identified by its n.m.r. spectrum (see Table 2), which showed a resonance due to the 5′-C*H*·OH group at τ 6·32, as the quinone (35), *i.e.* it was derived from one of the major products of the hydrogenation, *viz.* (32), by reduction of the keto-group in the side-chain. Its structure was confirmed by the n.m.r. spectrum of its triacetate (36), which showed an aliphatic acetate signal at τ 7·98 and a downfield shift of the 5′-H signal to τ 5·22.

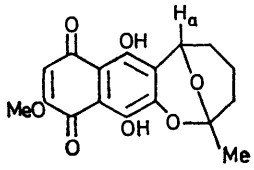
The evidence for the structure of the rearrangement product (25) or (26) (see before) of erythrostominone can now be considered. Hydrogenation of the rearrangement product in glacial acetic acid afforded deoxyerythrostominone, the trihydroxy-quinone (30), previously obtained by hydrogenation of the dienone (27), and a red product isomeric with deoxyerythrostominone. However hydrogenation in neutral ethyl acetate gave only the red product. The u.v. spectrum of the latter showed that it contained the methoxynaphthazarin nucleus of erythrostominone; its i.r. spectrum revealed



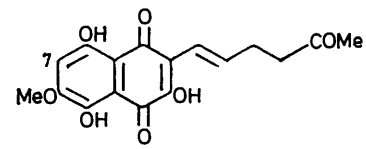
(40)



(41)



(42)

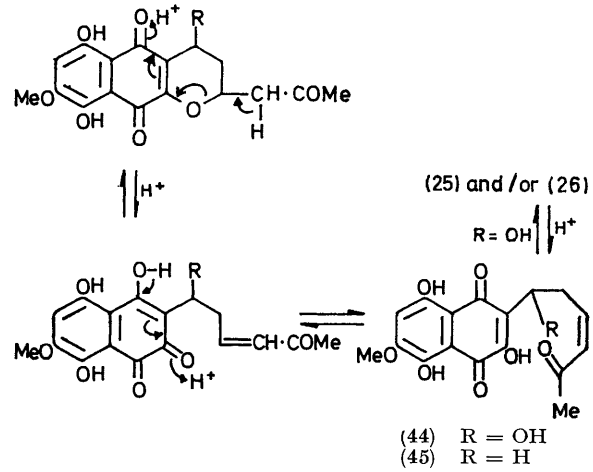


(43)

the absence of hydroxy- and keto-group absorptions. The n.m.r. spectrum (see Table 2) suggested that it had the cyclic acetal structure (42); in particular the signals due to the methyl group and to H_a closely resemble those due to the cyclic acetal portion of averufin tri-*O*-methyl ether [16] (41) [τ 8·45 (Me) and 4·55 (H)].

When the cyclic acetal (42) was boiled in glacial acetic acid it gave an isomeric red compound, whose i.r. spectrum revealed that both a hydroxy- and a keto-group ($\nu_{max.}$ 3340 and 1703 cm^{-1}) had been formed, *i.e.* the cyclic acetal had been hydrolysed. The n.m.r. spectrum of the product (see Table 2) confirmed the presence of a methyl ketone system and revealed signals attributed to two olefinic protons, showing that dehydration had occurred. Hence the hydrolysis product was assigned structure (43), and this was confirmed when hydrogenation afforded the trihydroxy-quinone (30) in good yield. These results establish the structure of the cyclic acetal (42), from which it follows that the unstable acid-catalysed rearrangement product of erythrostominone is an unsaturated cyclic acetal which has structure (25) or (26). A double-resonance experiment, made in an attempt to distinguish between these two structures, was difficult to interpret because decomposition of the unsaturated cyclic acetal (see before) during the determination of the spectrum led to line broadening. Irradiation at the frequency of the benzylic proton at τ 4·75 not only simplified the allylic methylene resonance at τ 7·5, as expected for structure (25), but also changed the olefinic proton signals, suggesting that it might have structure (26). These results are inconclusive and it is possible that the cyclic acetal is a mixture of the two double-bond isomers.

The formation of the unsaturated cyclic acetal (25) can be explained by a mechanism such as that shown in the Scheme, which is based on one of the tautomers of



SCHEME

erythrostominone; the isomer (26) is presumed to arise by acid-catalysed migration of the double bond in the acetal (25). In support of this mechanism, treatment of deoxyerythrostominone with boiling ethanol–N-hydrochloric acid led to extensive racemisation, presumably *via* opening of the pyran ring as shown in the Scheme. Since deoxyerythrostominone lacks the 4-hydroxy-group of erythrostominone, the ring-opened form (45) cannot yield a cyclic acetal and on ring-closure regenerates the original pigment. The instability of the cyclic acetal (25) and/or (26) presumably arises because in the open-chain intermediate (44) dehydration of the benzylic hydroxy-group occurs readily, leading to the dienone (27). The results of hydrogenating the unsaturated cyclic acetal (see before) may be rationalised if the acetal is in equilibrium with the open-chain form (44) in acetic acid solution but not in neutral ethyl acetate.

[16] P. Roffey, M. V. Sargent, and J. A. Knight, *J. Chem. Soc.* (*C*), 1967, 2328.

Treatment of erythrostominone with ethanol–0·1N-sodium hydroxide at room temperature afforded the dienone (27) as the main product, together with a small amount of a compound $C_{17}H_{14}O_7$ of unknown structure. The formation of the former is presumably initiated by hydrolysis of the vinylogous ester system in erythrostominone. The reactions of the *G. erythrostoma* pigments with alkali are under investigation.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were measured for solutions in ethanol with a Unicam SP 800 spectrometer, and optical rotations were determined with a Perkin-Elmer 141 Polarimeter with acetone as solvent. I.r. spectra were obtained for Nujol mulls with a Unicam SP 200 spectrometer and for solutions in bromoform with a Perkin-Elmer 125 spectrometer. Unless otherwise stated, n.m.r. spectra were recorded for solutions in deuteriochloroform with a Varian A60 spectrometer (tetramethylsilane as internal standard). Mass spectra were obtained using an A.E.I. MS 902 instrument.

Kieselgel G (Merck) was used for both t.l.c. and preparative layer chromatography (p.l.c.). Silica gel (Whatman Chromedia SG 31) was used for column chromatography. Light petroleum refers to the fraction of b.p. 60—80°. Ethyl acetate extracts were dried over anhydrous sodium sulphate.

Isolation of the Pigments.—Gnomonia erythrostoma (ex CBS) was grown at 18—20° under stirred aerated conditions on a medium containing Dextrose (2·5%), Bactotryptone (0·25%), potassium dihydrogen phosphate (0·1%), magnesium sulphate heptahydrate (0·05%), and minor elements concentrate [17] (0·1%). After 262 h the broth was filtered and the filtrate (57 l) was adjusted to pH 2 with concentrated hydrochloric acid and extracted with chloroform (2 × 6 l). Evaporation of the chloroform gave a dark red semi-solid (36 g) which was chromatographed on silica gel (70 × 6 cm). Fractions (1 l) were collected (eluant in parentheses).

Fractions 1—7 (chloroform) contained an orange gum (0·28 g) which was shown (t.l.c.) to be a mixture of several components and was not investigated further.

Fractions 8—14 (chloroform) afforded a solid which crystallised from acetone–light petroleum as red rods (2·87 g) of *deoxyerythrostominone* (2), m.p. 148—150°, $[\alpha]_D^{25}$ +277° (*c* 0·1) (Found: 61·35; H, 4·95%; *m/e* 332·0885. $C_{17}H_{16}O_7$ requires C, 61·4; H, 4·85%; *M*, 332·0896), $\nu_{max.}$ ($CHBr_3$) 1713 (C=O) and 1601br (H-bonded C=O of quinone and C=C) cm^{-1}; $\lambda_{max.}$ 234, 275, 317, 477sh, 505, and 542 nm (ε 30,900, 6740, 7640, 6900, 8200, and 5400).

Fractions 18—28 [chloroform–ethyl acetate (1 : 1) and ethyl acetate] gave a solid which crystallised from acetone–light petroleum as red needles (15·82 g) of *erythrostominone* (1), m.p. 184—186°, $[\alpha]_D^{25}$ +231° (*c* 0·1) (Found: C, 58·7; H, 4·7; OMe, 8·6%; *m/e* 348·0831. $C_{17}H_{16}O_8$ requires C, 58·6; H, 4·6; OMe 8·9%; *M*, 348·0845).

Fractions 16 and 17 [chloroform–ethyl acetate (1 : 1)] contained a dark red mixture of gum and crystals which was rechromatographed on Kieselgel G (12 × 4 cm). Elution with chloroform–methanol–formic acid (97 : 1 : 2) separated three red bands. The first band gave deoxyerythrostominone (148 mg). The second band afforded a gum (60 mg) which slowly crystallised. Recrystallisation from acetone–light petroleum gave *deoxyerythrostominol* (21) as red needles (32 mg), m.p. 139—141°, $[\alpha]_D^{25}$ +271° (*c* 0·1) (Found: C, 60·8; H, 5·5%; *m/e* 334·1040. $C_{17}H_{18}O_7$ requires C, 61·1; H, 5·4%; *M*, 334·1052), $\nu_{max.}$ 3580 and 1603br cm^{-1}; $\lambda_{max.}$ 234, 275, 317, 475sh, 505, and 541 nm (ε 29,000, 7020, 7690, 6940, 8360, and 5350).

Further elution gave erythrostominone (122 mg).

Reduction of Erythrostominone with Sodium Hydrogen Sulphite.—An aqueous solution of sodium hydrogen sulphite was added to a solution of erythrostominone (10 mg) in ethanol (5 ml). The red colour was immediately discharged, giving a colourless solution, but when a stream of air was bubbled through the solution the red colour of the quinone was regenerated. Extraction with ethyl acetate then gave a high recovery of erythrostominone.

Hydrogenation of Erythrostominone.—(a) *Until* ca. 3 *mol. equiv. of hydrogen were absorbed.* Erythrostominone (525 mg) in glacial acetic acid (50 ml) was hydrogenated over 10% palladium–charcoal (205 mg) for 5·5 h. There was a rapid uptake of *ca.* 2 mol. equiv. of hydrogen in the first 0·5 h, and then slow uptake of hydrogen over the next 5 h to give a total uptake of 3·14 mol. equiv. On admission of air the colour of the solution changed from pale yellow to dark orange. Filtration, followed by evaporation *in vacuo*, gave a gum which was chromatographed on Kieselgel G (14 × 4 cm). Chloroform–formic acid (49 : 1) eluted a solid which crystallised from ethanol to give orange needles (195 mg), m.p. 142—148°, of a mixture of the isomeric *monohydroxyquinones* (16) and [(12) and/or (13)] which could not be separated by further chromatography or crystallisation (Found: C, 64·3; H, 5·1%; *m/e* 316·0938. Calc. for $C_{17}H_{16}O_6$: C, 64·55; H, 5·1%; *M*, 316·0947), $\lambda_{max.}$ 218·5, 264, 310, and 439 nm (ε 24,100, 18,100, 9380, and 3850); τ 8·3 (2H, m, 3-H_2), 7·82 (3H, s, MeCO), 7·23 (4H, m, 4-H_2 and 1′-H_2), 6·21 (3H, s, 8-OMe), 5·56 (1H, m, 2-H), 4·12 (s, quinonoid H), 3·03 (s, aromatic H), and 3·5 and 2·95 (doublets, *J* 2·5 Hz, aromatic H) (total of 2H between τ 4·12 and 2·95), and −2·32 and −2·61 (total 1H, singlets, phenolic OH's).

Further elution of the column with chloroform–formic acid (49 : 1) gave material which crystallised from acetone–light petroleum as red rods (73 mg), m.p. 148—150°, identical (i.r. spectrum) with deoxyerythrostominone (2).

(b) *Until* 2 *mol. equiv. of hydrogen were absorbed.* Hydrogenation of erythrostominone (105 mg) in glacial acetic acid (45 ml) over 10% palladium–charcoal (40 mg) led to the uptake of 2·1 mol. equiv. of hydrogen in 25 min. Chromatography of the product as in (a) gave the mixture of monohydroxyquinones (10 mg) obtained in (a), followed by material (65 mg) which crystallised from acetone–light petroleum in red rods (37 mg) identical (i.r. spectrum) with deoxyerythrostominone.

(c) *Until uptake ceased.* In one experiment hydrogenation was allowed to continue for 27 h; the uptake of hydrogen was *ca.* 4 mol. equiv. In this case little deoxyerythrostominone was detected in the product and the mixture of monohydroxyquinones was isolated in high yield.

Hydrogenation of Deoxyerythrostominone.—Deoxyerythrostominone (258 mg) in glacial acetic acid (45 ml) was hydrogenated over 10% palladised charcoal (100 mg) for 9 h. One mol. equiv. of hydrogen was absorbed in the first 0·5 h, and then further uptake of hydrogen (1·2 mol.

[17] P. W. Brian, P. J. Curtis, and H. G. Hemming, *Trans. Brit. Mycol. Soc.*, 1946, **29**, 173.

equiv.) continued slowly throughout the reaction time. Recovery and chromatography of the product, as before, gave the mixture of monohydroxyquinones (see before) (47 mg) and starting material (182 mg).

Acetylation of the Monohydroxy-quinone Mixture (16) *and* [(12) *and/or* (13)].—The mixture (65 mg) was treated with pyridine (5 ml) and acetic anhydride (3 ml) at room temperature for 37 h. Recovery gave a gum which was purified by p.l.c. Development (×3) with benzene–methanol (97 : 3) separated two bands, material from which was recovered in acetone. That from the first band crystallised from acetone–light petroleum as yellow plates (14 mg), of 2-*acetonyl*-6-*acetoxy*-3,4-*dihydro*-8-*methoxy*-2H-*naphtho*[2,3-b]-*pyran*-5,10-*quinone* (18), m.p. 160—161° (Found: C, 63·5; H, 4·85%; *m/e* 358·1052. $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·1%; *M*, 358·1052), $\nu_{max.}$ 1764 (aryl acetate), 1710 (C=O of ketone), 1678 and 1642 (C=O of quinone), and 1605 and 1575sh (C=C) cm^{-1}; $\lambda_{max.}$ 263·5, 296, 341, and 384sh nm (ε 9980, 3670, and 1620); n.m.r. spectrum see Table 1 and τ 7·57 (3H, s, ArO·CO*Me*).

Material from the second band crystallised from acetone–light petroleum to give the quinone monoacetate (14) and/or (15) as yellow needles (22 mg), m.p. 194—196° (Found: C, 63·7; H, 5·35%; *m/e* 358·1052), $\nu_{max.}$ 1765 (aryl acetate), 1715, 1685, and 1645 (C=O of quinone), and 1620, 1597, and 1570 (C=C) cm^{-1}; $\lambda_{max.}$ 269, 294, 340, and 380sh nm (ε 27,400, 13,300, 2900, and 2000).

Oxidation of Erythrostominone with Acetic Anhydride–Dimethyl Sulphoxide.—Erythrostominone (175 mg) was treated with dimethyl sulphoxide (2 ml) and acetic anhydride (1 ml) at room temperature for 19 h. The solution was poured into water; the product was recovered in ethyl acetate and was chromatographed on Kieselgel G (14 × 4 cm). Elution with chloroform–methanol–formic acid (47 : 2 : 1) gave a red gum (102 mg), believed to be the methylthiomethoxy-derivative (4). Further elution afforded a solid which was repeatedly crystallised from chloroform–light petroleum to give 2-*acetonyl*-3,4-*dihydro*-5,10-*dihydroxy*-8-*methoxy*-4-*oxo*-2H-*naphtho*[2,3-b]*pyran*-6,9-*quinone* (3), as dark red needles (8 mg), m.p. 207—209° (Found: C, 59·1; H, 4·2%; *m/e* 346·0692. $C_{17}H_{14}O_8$ requires C, 59·0; H, 4·1%; *M*, 346·0689), $\nu_{max.}$ 1718 (C=O of ketone), 1690 (C=O of aryl ketone), 1614 (H-bonded C=O of quinone), and 1590 and 1570 (C=C) cm^{-1}; $\lambda_{max.}$ 226, 248, 311, 480sh, 513, 455sh, and 564sh nm (ε 22,800, 24,900, 15,050, 8170, 9270, 7200, and 3900).

Attempted oxidation of erythrostominone with Jones reagent, with chromium trioxide in pyridine, or with manganese dioxide gave intractable gums.

Acetylation of Erythrostominone.—Erythrostominone (115 mg) was treated with pyridine (4 ml) and acetic anhydride (3 ml) at room temperature for 17 h and the solution was then diluted with iced water. Recovery of the product in ethyl acetate gave a solid which was chromatographed on Kieselgel G (13 × 2·4 cm). Elution with chloroform–formic acid (49 : 1) gave a solid (67 mg) which crystallised from ethanol as yellow prisms, m.p. 163—165°, of a mixture of the two isomeric erythrostominone triacetates (5) and (7) which could not be separated by further chromatography or crystallisation (Found: C, 58·0; H, 4·6%; *m/e* 474·1159. Calc. for $C_{23}H_{22}O_{11}$: C, 58·2; H, 4·7%; *M*, 474·1162), $\nu_{max.}$ 1777sh and 1765 (aryl acetates), 1735 (alkyl acetate), 1715 (C=O of ketone), 1679 and 1640 (C=O of quinone), and 1594 (C=C) cm^{-1}; $\lambda_{max.}$ 263, 291·5, 350, and 380sh nm (ε 24,000, 10,000, 3780, and 2200); τ (100 MHz), 8·28 (2H, m, 3-H_2), 7·99 (3H, s, RO·COMe), 7·82 (3H, s, MeCO), 7·67 (3H, s, ArO·COMe), 7·66 (3H, s, ArO·COMe), 7·14 (2H, m, 1′-H_2), 6·18 and 6·25 (total 3H, singlets, OMe), 5·41 (1H, m, 2-H), 4·1 (1H, m, C*H*·OAc), and 4·11 and 3·19 (total 1H, singlets, quinonoid H and aromatic H, respectively) [the ratio of (5) to (7) was *ca.* 2 : 1].

Acetylation of Deoxyerythrostominone.—Deoxyerythrostominone (321 mg) was treated with pyridine (10 ml) and acetic anhydride (10 ml) at room temperature for 120 h. Isolation of the product in the usual way gave a gum which was chromatographed on Kieselgel G (10 × 4 cm). Elution with chloroform–methanol–formic acid (48 : 1 : 1) followed by crystallisation from ethanol or acetone–light petroleum gave yellow needles (205 mg), m.p. 192—195°, of a mixture of two isomeric deoxyerythrostominone diacetates (6) and (9) which could not be separated by further chromatography or crystallisation (Found: C, 60·5; H, 5·05%; *m/e* 416·1103. Calc. for $C_{21}H_{20}O_9$: C, 60·6; H, 4·8%; *M*, 416·1107), $\nu_{max.}$ (CHBr), 1768 (aryl acetates), 1714 (C=O of ketone), 1679, 1642sh, and 1630 (C=O of quinone), and 1590 and 1567 (C=C) cm^{-1}; $\lambda_{max.}$ 263, 293, 350, and 380sh nm (ε 23,150, 9370, 3630, and 2420); τ 8·3 (2H, m, 3-H_2), 7·76 (3H, s, MeCO), 7·6 (3H, s, ArO·COMe), 7·57 (3H, s, ArO·COMe), 7·16 (4H, m, 4-H_2 and 1′-H_2), 6·17 and 6·08 (total 3H, singlets, OMe), 5·51 (1H, m, 2-H), and 4·06 and 3·13 (total 1H, singlets, quinonoid and aromatic H, respectively).

Reductive Acetylation of Erythrostominone.—A large excess of activated zinc dust was added at intervals to a solution of erythrostominone (300 mg) and anhydrous sodium acetate (600 mg) in acetic anhydride (15 ml). The suspension was stirred at room temperature for 70 h, poured into iced water, and acidified with dilute hydrochloric acid. Recovery of the organic material in ethyl acetate gave a gum which was chromatographed on Kieselgel G (12 × 4 cm). Elution with chloroform–methanol–formic acid (97 : 1 : 2) separated three main bands.

The first band yielded a pale yellow glass (143 mg), shown (t.l.c. and n.m.r.) to be a mixture of at least two components, which could not be purified by further chromatography.

Material from the second band (96 mg) was rechromatographed on Kieselgel G (12 × 2·4 cm). Elution with chloroform–methanol–formic acid (97 : 1 : 2) afforded a solid which crystallised from acetone–light petroleum as prisms (32 mg), m.p. 196—197°, identical (i.r. spectrum) with deoxyerythrostominone leucotetra-acetate (10) (see later).

The third band (53 mg) was shown (n.m.r. spectrum) to contain incompletely acetylated material.

Reductive Acetylation of Deoxyerythrostominone.—A large excess of activated zinc dust was added at intervals to deoxyerythrostominone (200 mg) and anhydrous sodium acetate (300 mg) in acetic anhydride (6 ml) and the suspension was stirred at room temperature for 45 h. Recovery of the product, as in the preceding experiment, gave a gum which was chromatographed on Kieselgel G (12 × 4 cm). Elution with chloroform–methanol–formic acid (95 : 3 : 2) separated two main bands.

Material from the first band was rechromatographed on Kieselgel G (12 × 2·4 cm). Elution with chloroform–methanol–formic acid (97 : 1 : 2) gave a solid which crystallised from acetone–light petroleum as needles (27 mg) of a demethyl-leuco-diacetate, m.p. 145—147° (Found: C, 61·35; H, 5·3. Calc. for $C_{20}H_{22}O_8$: C, 61·5; H, 5·7%), $\nu_{max.}$ ($CHBr_3$) 1765 (aryl acetate), 1730 (alkyl acetate),

1715sh (C=O of ketone), and 1622 cm^{-1}; $\lambda_{max.}$ 224·5, 233sh, 240sh, 285, and 329 nm (ε 22,000, 13,600, 11,400, 15,700, and 7090); τ 8·23 (2H, m), 7·98 (3H, s, RO·COMe), 7·85 (4H, m), 7·8 (3H, s, MeCO), 7·77 (3H, s, ArO·COMe), 7·28 (4H, m), 5·43 (1H, m), 3·72br (1H, s), and −2·99 (1H, s).

Its triacetate crystallised from acetone–light petroleum as needles, m.p. 185—186·5° (Found: C, 61·0; H, 5·4%; *m/e* 432·1414. Calc. for $C_{22}H_{24}O_9$: C, 61·1; H, 5·6%; *M*, 432·1420), $\nu_{max.}$ ($CHBr_3$) 1765 (aryl acetate), 1730 (alkyl acetate), 1715sh (C=O of ketone), 1680, 1604, and 1575 cm^{-1}; $\lambda_{max.}$ 228 and 277 nm (ε 17,650 and 14,500); τ 8·38 (2H, m), 7·97 (3H, s, RO·COMe), 7·85 (4H, m), 7·8 (3H, s, MeCO), 7·75 (3H, s, ArO·COMe), 7·6 (3H, s, ArO·COMe), 7·31 (4H, m), 5·42 (1H, m), and 3·69br (1H, s).

Material from the second band was rechromatographed on Kieselgel G (14 × 4 cm). Elution with chloroform–methanol–formic acid (97 : 1 : 2) gave a solid which crystallised from acetone–light petroleum as prisms (43 mg), m.p. 196—197°, of *deoxyerythrostominone leucotetra-acetate* (10) (Found: C, 59·8; H, 5·45%; *m/e* 502·1483. $C_{25}H_{26}O_{11}$ requires C, 59·8; H, 5·2%; *M*, 502·1475), $\nu_{max.}$ 1765 (aryl acetates), 1712 (C=O of ketone), 1640 and 1580w cm^{-1}; $\lambda_{max.}$ 248, 284sh, 291sh, 313, and 338sh nm (ε 80,900, 4980, 5560, 6680, and 3900); τ 8·29 (2H, m, 3-H_2), 7·8 (3H, s, MeCO), 7·7, 7·65, 7·63, and 7·61 (12H, singlets, 4 aryl acetates), 7·27 (4H, m, 4-H_2 and 1′-H_2), 6·15 (3H, s, OMe), 5·44 (1H, m, 2-H), and 3·17 (1H, s, 7-H).

Reductive Acetylation of Deoxyerythrostominone Diacetates (6) *and* (9).—Treatment of the mixture of isomeric deoxyerythrostominone diacetates, as in the previous experiment, gave deoxyerythrostominone leucotetra-acetate identified by t.l.c. and i.r. and n.m.r. spectra.

Demethylation of Deoxyerythrostominone.—Deoxyerythrostominone (100 mg) was refluxed with glacial acetic acid (15 ml) and 47% hydrobromic acid (3 ml) for 1 h. The solution was cooled and diluted with water, and the product was recovered in ethyl acetate and was chromatographed on Kieselgel G (10 × 2·4 cm). Elution with chloroform–methanol–formic acid (95 : 3 : 2) afforded a solid which crystallised from acetone–light petroleum as reddish-mauve plates (22 mg) of *2-acetonyl-3,4-dihydro-5,8,10-trihydroxy-2H-naphtho*[2,3-b]*pyran-6,9-quinone* (11), m.p. 186—188° (Found: C, 60·6; H, 4·5%; *m/e* 318·0732. $C_{16}H_{14}O_7$ requires C, 60·4; H, 4·4%; *M*, 318·0739), $\nu_{max.}$ 3330 (OH), 1715 (C=O of ketone), and 1695 and 1610br (H-bonded C=O of quinone and C=C) cm^{-1}; $\lambda_{max.}$ 233, 271, 323, 484sh, 514, and 550 nm (ε 27,600, 13,900, 7830, 6200, 7100, and 4990).

Reduction of Erythrostominone with Sodium Borohydride.—Erythrostominone (150 mg) in methanol (90 ml) was added to a stirred solution of sodium borohydride (180 mg) in methanol (90 ml). The red colour of the solution changed to yellow within 3 min and then darkened slowly to orange-red. After 15 min the solution was diluted with water, acidified with dilute hydrochloric acid, and evaporated *in vacuo*. Recovery in ethyl acetate gave a gum which was chromatographed on Kieselgel G (13 × 4 cm). Chloroform–methanol–formic acid (93 : 5 : 2) eluted a number of minor bands and then a broad red band. The latter gave a gummy solid (37 mg) which resisted attempts at crystallisation and was probably a slightly impure sample of 3,4-dihydro-4,5,10-trihydroxy-2-(2-hydroxypropyl)-8-methoxy-2*H*-naphtho[2,3-*b*]pyran-6,9-quinone, τ (pyridine) 8·75 (3H, d, *J* 6·5 Hz, 3′-H_3), 8·06 (4H, m, 3-H_2 and 1′-H_2), 6·22 (3H, s, 8-OMe), 5·8 (1H, m, 2′-H), and 5·3 (2H, m, 2-H and 4-H).

Reduction of Deoxyerythrostominone with Sodium Borohydride.—Deoxyerythrostominone (150 mg) in methanol (110 ml) was added to a stirred solution of sodium borohydride (180 mg) in methanol (80 ml) at room temperature. After 15 min the product was recovered as in the preceding experiment and was chromatographed on Kieselgel G (16 × 4 cm). Elution with chloroform–methanol–formic acid (95 : 3 : 2) separated two bands.

The first band gave a gum which was purified by p.l.c. Development with chloroform–methanol–formic acid (95 : 3 : 2) gave a yellow band, material from which was recovered in acetone and crystallised from acetone–light petroleum to give the alcohol (22) and/or (23) [containing (n.m.r. spectrum) *ca.* 20% of the isomer (19)] as orange plates (12 mg.), m.p. 137—141° (Found: *m/e* 318·1100. Calc. for $C_{17}H_{18}O_6$: *M*, 318·1103), $\nu_{max.}$ 3450 (OH), 1682 (C=O of quinone), 1630 (H-bonded C=O of quinone), and 1592 (C=C) cm^{-1}; $\lambda_{max.}$ 221, 266, 306, and 432 nm (ε 30,000, 19,400, 8890, and 4120).

Material from the second band from the column was rechromatographed on Kieselgel G (14 × 2·4 cm). A red solid was eluted with chloroform–methanol–formic acid (95 : 3 : 2) and was purified by p.l.c. Repeated development (×6) with chloroform–formic acid (49 : 1) separated the main red band from a trace of a yellow band. Material from the former was recovered in chloroform–formic acid (49 : 1) and crystallised from acetone–light petroleum in red needles (6 mg), m.p. 138—141°, identical (t.l.c. and i.r. spectrum) with deoxyerythrostominol (21).

Acetylation of Deoxyerythrostominol.—Deoxyerythrostominol (15 mg) was treated with pyridine (4 ml) and acetic anhydride (3 ml) at room temperature for 18 h. Recovery in the usual manner afforded a gum which was purified by p.l.c. Development with chloroform-formic acid (49 : 1) and recovery in acetone gave a mixture of the isomeric deoxyerythrostominol triacetates (20) and (24) as a yellow glass (17 mg) (Found: *m/e* 460·1378. Calc. for $C_{23}H_{24}O_{10}$: *M*, 460·1369), $\nu_{max.}$ 1772 (aryl acetate), 1733 (alkyl acetate), 1681 and 1634 (C=O of quinone), and 1592 and 1572 (C=C) cm^{-1}; $\lambda_{max.}$ 263, 293, 350, and 380sh nm (ε 21,500, 8625, 3210, and 2110); τ 8·69 (3H, d, *J* 6·5 Hz, 3′-H_3), 8·23 (4H, m, 3-H_2 and 1′-H_2), 7·96 (3H, s, RO·COMe), 7·57 (6H, s, 2 × ArO·COMe), 7·3 (2H, m, 4-H_2), 6·18 and 6·1 (total 3H, singlets, OMe), 5·76 (1H, m, 2-H), 4·76 (1H, m, 2′-H), 4·08 and 3·16 (total 1H, singlets, quinonoid H and aromatic H, respectively).

Reactions of Erythrostominone in Acid Solutions.—(a) *In acetic acid.* Erythrostominone (10 mg) in glacial acetic acid was left at room temperature for 2·5 h; it was recovered on evaporation at 90° *in vacuo*.

(b) *Toluene-*p*-sulphonic acid in benzene.* Erythrostominone (500 mg) in dry benzene (180 ml) was refluxed for 3 h with toluene-*p*-sulphonic acid (15 mg), using a Dean and Stark apparatus for the removal of water. The recovered product was chromatographed on Kieselgel G (12 × 4 cm). Elution with chloroform–methanol–formic acid (48 : 1 : 1) followed by crystallisation from acetone–light petroleum gave the unsaturated cyclic acetal (25) and/or (26) as red rods (188 mg), m.p. 235—240° (Found: C, 61·75; H, 4·2%; *m/e* 330·0743. Calc. for $C_{17}H_{14}O_7$: C, 61·8; H, 4·3%; *M*, 330·0740), $\nu_{max.}$ ($CHBr_3$) 1604br (H-bonded C=O of quinone and C=C) cm^{-1}; $\lambda_{max.}$ 231, 278·5, 317, 476sh, 508, and 545 nm (ε 29,700, 7750, 9000, 7430, 8300, and 5370).

(c) *Concentrated sulphuric acid.* Erythrostominone (22 mg) in concentrated sulphuric acid (10 ml) was left at 0° for

15 min. The reddish purple solution was poured into iced water; the produced was recovered in ethyl acetate and was chromatographed on Kieselgel G (10 × 2·4 cm). Elution with chloroform–methanol–formic acid (95 : 3 : 2) gave a band which afforded red crystals (10 mg) identical (t.l.c. and i.r. spectrum) with the cyclic acetal (25) and/or (26).

(d) *Ethanolic hydrochloric acid.* Erythrostominone (500 mg) in ethanol (250 ml) was refluxed with N-hydrochloric acid (250 ml) for 3 h and left overnight at 0°. The precipitate was filtered off, washed with cold ethanol, and crystallised from glacial acetic acid to give 3,5,8-*trihydroxy*-6-*methoxy*-2-(5-*oxohexa*-1,3-*dienyl*)-1,4-*naphthoquinone* (27) as red needles (360 mg), m.p. 238—242° (Found: C, 61·7; H, 4·35%; *m/e* 330·0736. $C_{17}H_{14}O_7$ requires C, 61·8; H, 4·3%; *M*, 330·0740).

Stability of the Cyclic Acetal (25) *and/or* (26).—(a) *In neutral solution.* A solution of the acetal in chloroform was left for 24 h. T.l.c. then showed that the dienone (27) had been formed.

(b) *On heating.* The acetal was heated at 145—150° for 30 min. It lost its crystalline form and the product had m.p. 235—240° [the m.p. of the dienone (27) is 238—242°]. T.l.c. indicated complete conversion into the dienone (27).

(c) *In acid solution.* The acetal (14 mg) in ethanol (20 ml) and N-hydrochloric acid (20 ml) was left for 48 h (after about 10 min a solid began to precipitate). The precipitate (10 mg), which was collected and washed with ethanol, had m.p. 235—240° and was identical with the dienone (27) (t.l.c. and i.r. spectrum).

Acetylation of the Dienone (27).—The dienone (80 mg) was treated with pyridine (6 ml) and acetic anhydride (4 ml) at room temperature for 1 h. The product was recovered in the usual manner and was chromatographed on Kieselgel G (10 × 2·4 cm). Elution with chloroform–methanol–formic acid (95 : 3 : 2) followed by crystallisation from acetone–light petroleum gave orange rods (42 mg), m.p. 208—211°, of a mixture (ratio *ca.* 4 : 1) of 3,5,8-triacetoxy-6-methoxy-2-(5-oxohexa-1,3-dienyl)-1,4-naphthoquinone (28) and 5,7,8-triacetoxy-2-methoxy-6-(5-oxohexa-1,3-dienyl)-1,4-naphthoquinone (29) (Found: 60·3; H, 4·3%; *m/e* 456·1056. Calc. for $C_{23}H_{20}O_{10}$: C, 60·5; H, 4·4%; *M*, 456·1056), $\nu_{max.}$ 1778 and 1763 (aryl acetates), 1669vs (C=O of conjugated ketone and quinone), and 1628w and 1583 (C=C) cm^{-1}; $\lambda_{max.}$ 279sh, 304, and 374 nm (ε 28,100, 33,100, and 13,700); τ (90 MHz) 7·7 (3H, s, MeCO), 7·62 (6H, s, 2 ArO·COMe), 7·58 (3H, s, ArO·COMe), 6·17 and 6·1 (total 3H, singlets, OMe), 4·0 and 3·11 (total 1H, singlets, quinonoid H and aromatic H, respectively), and *ca.* 3·0, *ca.* 3·5, and *ca.* 3·8 (total 4H, multiplets, olefinic protons).

The dienone was recovered from pyridine solution under the conditions used for this acetylation.

Hydrogenation of the Dienone (27).—The dienone (478 mg) and 10% palladium–charcoal (270 mg), in glacial acetic acid (330 ml), were hydrogenated for 5 min at *ca.* 60° (uptake *ca.* 4 mol. equiv.). Filtration and evaporation *in vacuo* gave a gum which was chromatographed on Kieselgel G (14 × 4 cm). Elution with chloroform–formic acid (49 : 1) (10 ml fractions) gave (fractions 1—15) a gum which was discarded.

Fractions 16—18 afforded a solid which crystallised from acetone-light petroleum to give 3,8-*dihydroxy*-6-*methoxy*-2-(5-*oxohexyl*)-1,4-*naphthoquinone* (32) as orange needles (115 mg), m.p. 165—168° (Found: C, 64·05; H, 5·75%; *m/e* 318·1090. $C_{17}H_{18}O_6$ requires C, 64·1; H, 5·7%; *M*, 318·1103), $\lambda_{max.}$ 263, 311, 384, and 436 nm (ε 21,800, 11,400, 3620, and 3070).

Its *diacetate* (34) crystallised from acetone–light petroleum as yellow needles, m.p. 113—114° (Found: C, 62·6; H, 5·6%; *m/e* 402·1331. $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%; *M*, 402·1315), $\nu_{max.}$ ($CHBr_3$) 1772, 1710, 1673, 1654, 1599, and 1567w cm^{-1}; $\lambda_{max.}$ 266, 281sh, 342, and 380 nm (ε 17,600, 10,800, 2080, and 1910); τ 8·45 (4H, m, 2′-H_2 and 3′-H_2), 7·88 (3H, s, MeCO), 7·62 (3H, s, ArO·COMe), 7·57 (3H, s, ArO·COMe), 7·5 (4H, m, 1′-H_2 and 4′-H_2), 6·07 (3H, s, 6-OMe), 3·16 (1H, d, *J* 2·5 Hz, 7-H), and 2·48 (1H, d, *J* 2·5 Hz, 5-H).

The quinone gave a yellow solution in acetic anhydride which turned a reddish mauve colour on treatment with boric acid–acetic anhydride solution.

Fractions 21—26 gave a solid which crystallised from acetone–light petroleum as red plates (79 mg), of 3,5,8-*trihydroxy*-6-*methoxy*-2-(5-*oxohexyl*)-1,4-*naphthoquinone* (30), m.p. 162—164° (Found: C, 61·05; H, 5·5%; *m/e* 334·1049. $C_{17}H_{18}O_7$ requires C, 61·1; H, 5·4%; *M*, 334·1053), $\lambda_{max.}$ 233, 270, 318, 450sh, 480sh, 510, and 548 nm (ε 23,200, 7170, 7230, 3910, 5570, 6510, and 4320); τ (100 MHz) 8·39 (4H, m, 2′-H_2 and 3′-H_2), 7·87 (3H, m, MeCO), 7·46 (4H, m, 1′-H_2 and 4′-H_2), 6·05 (3H, s, 6-OMe), and 3·47 (1H, s, 7-H).

Acetylation in the usual way gave an isomeric mixture (ratio *ca.* 1·2 : 1) of 3,5,8-triacetoxy-6-methoxy-2-(5-oxohexyl)-1,4-naphthoquinone (31) and 5,7,8-triacetoxy-2-methoxy-6-(5-oxohexyl)-1,4-naphthoquinone (37) as a yellow gum (Found: *m/e* 460·1371. Calc. for $C_{23}H_{24}O_{10}$: *M*, 460·1369), $\nu_{max.}$ ($CHBr_3$) 1772, 1763, 1703, 1673, 1653sh, 1645, 1621, and 1583 cm^{-1}; $\lambda_{max.}$ 254, 266, 282sh, and 348 nm (ε 14,400, 13,300, 11,500, and 2980).

Fractions 29—34 were purified by p.l.c. Development (×2) with chloroform–methanol–formic acid (97 : 1 : 2) separated an orange-yellow band which was recovered in acetone. Crystallisation from acetone–light petroleum gave 3,8-*dihydroxy*-6-*methoxy*-2-(5-*hydroxyhexyl*)-1,4-*naphthoquinone* (35) as orange needles (26 mg), m.p. 149—151° (Found: C, 63·85; H, 6·5%; *m/e* 320·12605. $C_{17}H_{20}O_6$ requires C, 63·7; H, 6·3%; *M*, 320·1260), $\nu_{max.}$ 3580 and 3230 (OH), 1672 and 1655 (C=O of quinone), and 1610br (H-bonded C=O of quinone and C=C) cm^{-1}; $\lambda_{max.}$ 263, 313, 380, and 436 nm (ε 21,300, 11,500, 3730, and 2740).

Its *triacetate* (36), purified by p.l.c., was a yellow gum (Found: *m/e* 446·1586. $C_{23}H_{26}O_9$ requires *M*, 446·1577), $\nu_{max.}$ (film) 1775, 1732, 1681, 1660, 1604, and 1572 cm^{-1}; $\lambda_{max.}$ 266, 280sh, 342, and 380 nm (ε 21,900, 13,200, 2130, and 1930); τ 8·81 (3H, d, *J* 6·5 Hz, 6′-H_3), 8·54 (6H, m, 2′-H_2, 3′-H_2, and 4′-H_2), 7·98 (3H, s, RO·COMe), 7·62 (3H, s, ArO·COMe), 7·56 (3H, s, ArO·COMe), 7·42 (2H, m, 1′-H_2), 6·07 (3H, s, 6-OMe), 5·22 (1H, m, 5′-H), 3·16 (1H, d, *J* 2·5 Hz, 7-H), and 2·47 (1H, d, *J* 2·5 Hz, 5-H).

Fractions 44—50 gave a solid which was purified by p.l.c. Development (×2) with chloroform–methanol–formic acid (95 : 3 : 2) separated an orange-yellow band, material from which was recovered in acetone. Crystallisation from acetone–light petroleum gave 5,7-dihydroxy-2-methoxy-6-(5-oxohexyl)-1,4-naphthoquinone (38) or 7,8-dihydroxy-2-methoxy-6-(5-oxohexyl)-1,4-naphthoquinone (39) as orange-yellow needles (30 mg), m.p. 175—177° (Found: C, 64·1; H, 5·8%; *m/e* 318·1103. Calc. for $C_{17}H_{18}O_6$: C, 64·1; H, 5·7%; *M*, 318·1103), $\nu_{max.}$ 3200 (OH), 1688 (H-bonded C=O of ketone and free C=O of quinone), 1635 and 1597br (H-bonded C=O of quinone and C=C) cm^{-1}; $\lambda_{max.}$ 221, 267, 304,

and 427 nm (ε 31,500, 19,550, 10,300, and 4520); τ [$(CD_3)_2$-SO–$CDCl_3$] 8·4 (4H, m, 2′-H_2 and 3′-H_2), 7·88 (3H, s, MeCO), 7·44 (4H, m, 1′-H_2 and 4′-H_2), 6·12 (3H, s, 2-OMe), 4·01 (1H, s, 3-H), and 2·81 (1H, s, 8-H).

Its diacetate crystallised from acetone–light petroleum as pale yellow needles, m.p. 197—199° (Found: C, 62·5; H, 5·3%; *m/e* 402·1320. Calc. for $C_{21}H_{22}O_8$: C, 62·7; H, 5·5%; *M*, 402·1315), $\nu_{max.}$ 1762, 1708, 1688, 1652, 1622, and 1595 cm^{-1}; $\lambda_{max.}$ 254, 286, and 342 nm (ε 20,000, 13,250, and 3260); τ 8·4 (4H, m, 2′-H_2 and 3′-H_2), 7·89 (3H, s, MeCO), 7·62 (3H, s, ArO·COMe), 7·53 (3H, s, ArO·COMe), 7·45 (4H, m, 1′-H_2 and 4′-H_2), 6·15 (3H, s, 2-OMe), 4·01 (1H, s, 3-H), and 2·23 (1H, s, 8-H).

When the dienone (27) was hydrogenated for 3 min under similar conditions, the uptake of hydrogen was *ca.* 3 mol. equiv. and the yield of the quinone (30) was increased at the expense of the other three products.

Reductive Acetylation of the Triacetoxy-quinone Mixture (31) *and* (37).—The mixture (55 mg), acetic anhydride (6 ml), anhydrous sodium acetate (110 mg), and a large excess of activated zinc dust were stirred at room temperature for 22 h. The product was recovered in the usual manner and purified by p.l.c. Development (×2) with chloroform–methanol–formic acid (97 : 1 : 2) separated a band which showed a dark blue fluorescence in u.v. light. Recovery of material from this band in acetone followed by crystallisation from acetone–light petroleum gave 1,3,4,5,8-*penta-acetoxy*-6-*methoxy*-2-(5-*oxohexyl*)*naphthalene* (40) as prisms (42 mg), m.p. 190—191° (Found: C, 59·25; H, 5·6%; *m/e* 546·1737. $C_{27}H_{30}O_{12}$ requires C, 59·3; H, 5·5%; *M*, 546·1737), $\nu_{max.}$ 1767 (aryl acetates), 1714 (C=O of ketone), 1638sh, and 1622 cm^{-1}; $\lambda_{max.}$ 240, 269sh, 283sh, 294, 307, 331, and 345 nm (ε 92,600, 3000, 5600, 7700, 7300, 3260, and 3800); τ 8·46 (4H, m, 2′-H_2 and 3′-H_2), 7·9 (3H, s, MeCO), 7·65 (9H, s, 3 × ArO·COMe), 7·63 (3H, s, ArO·COMe), 7·6 (3H, s, ArO·COMe), 7·57 (4H, m, 1′-H_2 and 4′-H_2), 6·13 (3H, s, 6-OMe), and 3·02 (1H, s, 7-H).

Hydrogenation of the Triacetoxy-quinone Mixture (28) *and* (29).—The mixture (120 mg), in glacial acetic acid (45 ml), was hydrogenated over 10% palladium–charcoal (70 mg) until the uptake of hydrogen had ceased (0·5 h; uptake 3·9 mol. equiv.). Recovery in the usual way gave a gum which was chromatographed on Kieselgel G (11 × 2·4 cm). Chloroform–methanol–formic acid (97 : 1 : 2) eluted a gum which was purified by p.l.c. Development (×3) with chloroform–formic acid (49 : 1) separated a yellow band, material from which was recovered in acetone as a yellow gum (48 mg), identical (t.l.c. and i.r. and n.m.r. spectra) with the mixture of quinones (31) and (37) prepared before.

Reductive Acetylation of 3,8-*Dihydroxy*-6-*methoxy*-2-(5-*oxohexyl*)-1,4-*naphthoquinone* (32).—The quinone (42 mg) in acetic anhydride (6 ml) was stirred at room temperature for 19 h with anhydrous sodium acetate (100 mg) and a large excess of activated zinc dust. The product, recovered in the usual way, was purified by p.l.c. Development with chloroform–methanol–formic acid (97 : 1 : 2) and recovery of material from the main band, which showed a dark bluish mauve fluorescence in u.v. light, afforded 1,3,4,8-*tetra-acetoxy*-6-*methoxy*-2-(5-*oxohexyl*)*naphthalene* as a glass (40 mg) (Found: *m/e* 488·1687. $C_{25}H_{28}O_{10}$ requires *M*, 488·1682), $\nu_{max.}$ 1760 (aryl acetates), 1707 (C=O of ketone), 1641, 1621, and 1582 cm^{-1}; $\lambda_{max.}$ 238, 264sh, 275, 284, 294, 323, and 337 nm (ε 76,650, 3520, 4870, 5640, 4760, 1950, and 2480); τ 8·44 (4H, m, 2′-H_2 and 3′-H_2), 7·91 (3H, s, MeCO), 7·64 (6H, s, 2 × ArO·COMe), 7·59 (6H, s, 2 × ArO·COMe), 7·55 (4H, m, 1′-H_2 and 4′-H_2), 6·14 (3H, s, 6-OMe), 3·17 (1H, d, *J* 2·5 Hz, 7-H), and 3·04 (1H, d, *J* 2·5 Hz, 5-H).

Methylation of 3,8-*Dihydroxy*-6-*methoxy*-2-(5-*oxohexyl*)-1,4-*naphthoquinone* (32).—The quinone (35 mg), in chloroform (5 ml), was stirred at room temperature for 88 h with freshly prepared dry silver oxide (100 mg) and methyl iodide (0·5 ml). Further quantities of silver oxide (100 mg) and methyl iodide (0·5 ml) were added after 1, 18, and 22 h. The inorganic material was removed by filtration, the filtrate was evaporated *in vacuo*, and the product was purified by p.l.c. Development (×2) with chloroform–formic acid (49 : 1) separated a yellow band, material from which was recovered in acetone and was crystallised from acetone–light petroleum to give 3,6,8-*trimethoxy*-2-(5-*oxohexyl*)-1,4-*naphthoquinone* (33) as yellow needles (12 mg), m.p. 128—129·5° (Found: C, 65·75; H, 6·35%; *m/e* 346·1427. $C_{19}H_{22}O_6$ requires C, 65·9; H, 6·4%; *M*, 346·1416), $\nu_{max.}$ 1708 (C=O of ketone), 1664 and 1645 (C=O of quinone), 1628, 1600, and 1566 cm^{-1}; $\lambda_{max.}$ 218, 265, 298, 376sh, and 410 nm (ε 19,300, 15,300, 10,700, 2690, and 2720); τ 8·45 (4H, m, 2′-H_2 and 3′-H_2), 7·87 (3H, s, MeCO), 7·49 (4H, m, 1′-H_2 and 4′-H_2), 6·05 (3H, s, OMe), 6·04 (3H, s, OMe), 5·96 (3H, s, 3-OMe), 3·29 (1H, d, *J* 2·5 Hz, 7-H), and 2·77 (1H, d, *J* 2·5 Hz, 5-H).

Oxidation of 3,8-*Dihydroxy*-6-*methoxy*-2-(5-*oxohexyl*)-1,4-*naphthoquinone* (32) *with Ruthenium Tetroxide*.—The quinone (100 mg) in acetone (12 ml) was added at room temperature to a stirred solution of ruthenium tetroxide prepared *in situ* by the addition of sodium periodate (300 mg) in water (2 ml) to ruthenium dioxide (40 mg) in acetone (5 ml). Stirring was continued and a solution of sodium periodate (1·15 g) in acetone–water (1 : 1; 12 ml) was added, in portions, over 4 h. After a further 1 h at room temperature, propan-2-ol (3 ml) was added and the mixture was diluted with acetone (30 ml). The precipitated solid was removed by filtration, the acetone was evaporated *in vacuo*, and the product was recovered in ethyl acetate and purified by p.l.c. Development with chloroform–methanol–formic acid (93 : 5 : 2) separated a broad band, material from which was recovered in acetone as an orange gum (60 mg), shown by t.l.c. to be a mixture of three components, which suggested that the oxidation had not gone to completion.

The gum, in acetone (10 ml), was added to a stirred mixture of ruthenium dioxide (30 mg) in acetone (4 ml) and sodium periodate (225 mg) in water (1·5 ml). Stirring was continued at room temperature for 3·25 h while a solution of sodium periodate (400 mg) in acetone–water (1 : 1; 5 ml) was added in portions. Recovery, as before, gave a gum which was purified by p.l.c. Development with chloroform–methanol–formic acid (93 : 5 : 2) and recovery of material from the main band in acetone afforded a pale yellow oil (21 mg), identical (t.l.c., i.r. and n.m.r. spectra) with authentic 6-oxoheptanoic acid.[13]

Its semicarbazone crystallised from ethanol as prisms, m.p. 143—145°, identical (m.p., mixed m.p., and i.r. spectrum) with authentic 6-oxoheptanoic acid semicarbazone.[13]

Hydrogenation of the Cyclic Acetal (25) *and/or* (26).—(a) *In acid-free ethyl acetate.* The acetal (110 mg), in ethyl acetate (50 ml; previously washed with sodium hydrogen carbonate solution), was hydrogenated over 10% palladium–charcoal (55 mg) for 5 min (uptake *ca.* 2 mol. equiv.). Filtration and recovery followed by crystallisation from acetone–light petroleum gave 2,6-*epoxy*-3,4,5,6-*tetrahydro*-7,12-*dihydroxy*-10-*methoxy*-2-*methyl*-2H-*naphth*[2,3-b]*oxocin*-

8,11-*quinone* (42) as crimson needles (85 mg), m.p. 148—150° (Found: C, 61·2; H, 4·85%; *m/e* 332·0881. $C_{17}H_{16}O_7$ requires C, 61·4; H, 4·85%; *M*, 332·0896), $\nu_{max.}$ ($CHBr_3$) 1603br cm^{-1}; $\lambda_{max.}$ 231, 275, 317, 480sh, 511, and 549 nm (ε 27,200, 8900, 8160, 6820, 8000, and 5250).

(b) *In glacial acetic acid.* The acetal (200 mg), in glacial acetic acid (75 ml), was hydrogenated over 10% palladium–charcoal (110 mg) for 5 min (uptake *ca.* 2 mol. equiv.). Recovery as in (a) gave a gum which was chromatographed on Kieselgel G (10 × 4 cm). The column was eluted with chloroform–formic acid (49 : 1) and 10 ml fractions were collected. Fractions 9—11 contained a gum (5 mg) which was discarded.

Fractions 12—15 yielded material which crystallised from acetone–light petroleum as crimson needles (41 mg), m.p. 148—150°, identical (t.l.c. and i.r. spectrum) with the cyclic acetal (42).

Fractions 17 and 18 were rechromatographed on Kieselgel G (8 × 2·4 cm). Elution with chloroform–methanol–formic acid (95 : 3 : 2) separated two main bands. The first band afforded a solid which crystallised from acetone–light petroleum as red rods (37 mg) of (±)-deoxyerythrostominone, m.p. 170—172°, $[\alpha]_D$ +39° (*c* 0·04) *, identical (t.l.c., i.r. and n.m.r. spectra) with (+)-deoxyerythrostominone (2).

The second band gave a solid (31 mg) which crystallised from acetone–light petroleum as red plates of 3,5,8-trihydroxy-6-methoxy-2-(5-oxohexyl)-1,4-naphthoquinone (30), identified by its i.r. spectrum.

Treatment of the Cyclic Acetal (42) *with Boiling Acetic Acid.*—The acetal (30 mg) was refluxed in glacial acetic acid for 3·5 h, the solution was evaporated *in vacuo*, and the residue was purified by p.l.c. Development with chloroform–methanol–formic acid (95 : 3 : 2) gave a reddish mauve band, material from which was recovered with chloroform–formic acid (49 : 1) and was crystallised from acetone–light petroleum to give red needles (11 mg), m.p. 161—163°, of 3,5,8-*trihydroxy*-6-*methoxy*-2-(5-*oxohex*-1-*enyl*)-1,4-*naphthoquinone* (43) (Found: *m/e* 332·0889. $C_{17}H_{16}O_7$ requires *M*, 332·0896), $\nu_{max.}$ 3340, 1703, and 1590br cm^{-1}; $\lambda_{max.}$ 223, 266, 330, 474, 490sh, 512, and 552 nm (ε 17,200, 24,300, 6920, 8450, 7450, 6920, and 3810).

Hydrogenation of 3,5,8-*Trihydroxy*-6-*methoxy*-2-(5-*oxohex*-1-*enyl*)-1,4-*naphthoquinone* (43).—The quinone (18 mg), in ethyl acetate (30 ml), was hydrogenated over 10% palladium–charcoal (10 mg) for 5 min (uptake *ca.* 2 mol. equiv.). Recovery in the usual way followed by crystallisation from acetone–light petroleum gave red plates (10 mg), m.p. 162—164°, identical (t.l.c. and i.r. spectrum) with the 2-(5-oxohexyl)naphthoquinone (30) prepared before.

Racemisation of Deoxyerythrostominone (with L. J. Zammitt).—The quinone (50 mg) in ethanol (50 ml) was refluxed with N-hydrochloric acid (50 ml) for 6 h and then left overnight. The solution was diluted with water and concentrated *in vacuo*. Recovery in ethyl acetate followed by crystallisation from acetone–light petroleum gave (±)-deoxyerythrostominone as red rods, m.p. 170—172°, $[\alpha]_D$ +40° (*c* 0·05),* identical (i.r. spectrum) with (+)-deoxyerythrostominone.

Reaction of Erythrostominone with Base.—Erythrostominone (296 mg) in ethanol (90 ml) and 0·1N-sodium hydroxide solution (90 ml) was set aside at room temperature for 41 h. The purple solution was diluted with water, most of the ethanol was removed *in vacuo*, and the aqueous residue was acidified with dilute hydrochloric acid. The product was recovered in ethyl acetate and was chromatographed on Kieselgel G (10 × 2·8 cm). Elution with chloroform–methanol–formic acid (95 : 3 : 2) separated three main bands.

The first band was rechromatographed on silica gel (14 × 1·8 cm). Elution with chloroform afforded a compound which crystallised from acetone–light petroleum as red needles (10 mg), m.p. 128—130° (Found: *m/e* 330·0740. Calc. for $C_{17}H_{14}O_7$: *M*, 330·0740), $\nu_{max.}$ ($CHBr_3$) 1605br cm^{-1}; $\lambda_{max.}$ 231·5, 275, 318, 480sh, 509 and 546 nm (ε 28,100, 7000, 7280, 6370, and 7430). The second band gave a red crystalline solid (197 mg) identified (i.r. spectrum) as erythrostominone. The third band gave a red solid (48 mg) identical (i.r. spectrum) with the dienone (27).

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* The rotation is believed [14] to be due to the presence of a small amount of a highly optically active impurity.