Erythrina Alkaloids. Part 6.[1] Isolation and Characterisation of Alkaloids from *Erythrina berteroana* Seeds and Leaves: Formation of Oxoerythroidines

Amrik S. Chawla,† Anthony H. Jackson,* and Peter Ludgate
Department of Chemistry, University College, Cardiff CF1 1XL

The major alkaloids present in *E. berteroana* seeds and leaves are α- and β-erythroidines (1) and (3). Smaller amounts of erysodine (5a), erysovine (5b), erysopine (5c), erysoline (5d), and erysonine (5e) were also detected. Preparative h.p.l.c. studies also revealed the presence of new alkaloids 8-oxo-α-erythroidine (2) in the extract of the seeds, and of 8-oxo-β-erythroidine (4) in the extract of the leaves. Both compounds could also be obtained by direct oxidation of the corresponding erythroidines. These new 8-oxo-erythroidines were fully characterised by a combination of spectroscopic methods, and by comparisons with the spectra of the parent erythroidines.

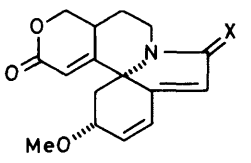
During the last few years a series of studies of the alkaloid content of the seeds of some 70 different species of the *Erythrina* genus have been undertaken both in our laboratory,[1-5] and in that of Rinehart at Illinois.[6,7] The main aims of this work so far have been to screen the seeds for alkaloids using gas chromatography/mass spectrometry (g.c./m.s.) as the primary analytical tool, and hence to facilitate chemotaxonomic studies. We now report our detailed studies on the leaves and seeds of *E. berteroana* which have led to the characterisation of two new alkaloids 8-oxo-α- and 8-oxo-β-erythroidines.

The first studies of the alkaloids in *E. berteroana* seeds were described by Folkers and Koniuszy [8] who isolated erysovine (5b). Subsequently Boekelheide and his co-workers [9] characterised the two major alkaloids as α- and β-erythroidines, and assigned their structures as (1) and (3), respectively. Radioactive α- and β-erythroidines were also isolated from *E. berteroana* plants in the course of biosynthetic studies.[10] More recently Rinehart's group studied the alkaloid composition of the seeds by g.c./m.s. and reported the presence of erysodine (5a) and erysovine (5b), and small amounts of erysopine (5c), erysoline (5d), and erysonine (5e), in addition to α- and β-erythroidines (1) and (3).[6] We have also studied the alkaloid content of two samples of seeds and a sample of leaves (kindly provided by Dr. B. A. Krukoff) and our results are very similar to those reported by Rinehart.

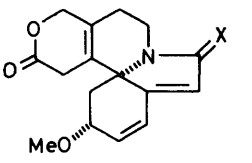
As in all our earlier studies of *Erythrina* alkaloids we carried out preliminary separations into three fractions: (a) a hexane-soluble fraction; (b) a methanol-soluble 'free' alkaloid fraction; and (c) a 'liberated' alkaloid fraction (obtained by hydrolysis of alkaloids occurring as glycosides). After trimethylsilylation each fraction was subjected to gas chromatography and subsequently to combined gas chromatography/mass spectrometry in order to characterise as many of the alkaloids present as possible. The field desorption mass spectra of the crude alkaloid mixtures were also used to characterise the products.

The gas chromatogram of the derivatised 'free' alkaloids obtained from *E. berteroana* seeds showed that α- and β-erythroidines (1) and (3) constituted more than 90% of the alkaloids, erysodine (5a) and erysovine (5b) accounting for most of the remainder. In the case of the leaves the α- and β-erythroidine fractions amounted to more than 95% of the 'free' alkaloids, the β-erythroidine (3) being present in greatest amount; of the three minor peaks observed the molecular ion of one corresponded to an oxo-derivative of β-erythroidine. The much smaller 'liberated' alkaloid fraction from the seeds contained a wider range of alkaloids but the major components were erysodine and erysovine. Traces of erysopine (5c), erysoline (5d), and erysonine (5e) were also observed, as well as β- but not α-erythroidine; a number of other minor peaks in the gas chromatogram could not be identified but the mass spectra of two of these corresponded to 11-hydroxy-derivatives of erysotine (6a) [or erysosalvine (6b)] and erythratidine (6c). There was so little material in the extract from the 'liberated' fraction from the leaves that no positive evidence for the presence of alkaloids could be obtained. In all these preliminary studies the individual alkaloids were characterised by comparisons of their electron impact mass spectra (obtained during the course of g.c./m.s. runs) with those of authentic materials.

Dienoid alkaloids all show characteristic fragmentation [7]



(1) X = H_2
(2) X = O



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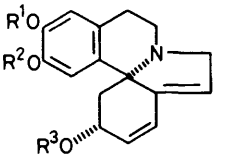
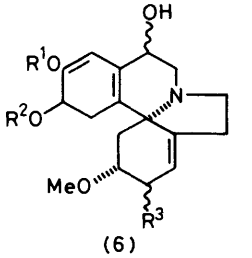


(5)

a; R^1 = H, R^2 = R^3 = Me
b; R^1 = R^3 = Me, R^2 = H
c; R^1 = R^2 = H, R^3 = Me
d; R^1 = Me, R^2 = R^3 = H
e; R^1 = R^3 = H, R^2 = Me



(6)

a; R^1 = H, R^2 = Me, R^3 = H,OH
b; R^1 = Me, R^2 = H, R^3 = H,OH
c; R^1 = R^2 = Me, R^3 = α-OH,β-H

† On leave from Department of Pharmaceutical Sciences, Panjab University, Chandigarh 160014 (India).

Table. ^{1}H N.m.r. spectral data of α- and β-erythroidines and their 8-oxo-derivatives (δ values; solution in $CDCl_3$)

	1-H	2-H	3-H	4-H*a*	4-H*e*	7-H	8-H	10-H*a*	10-H*e*	11-H*a*	11-H*e*	12-H	14-H	17-H*a*	17-H*e*	OCH_3
α-Erythroidine (1)	5.88 (d)	6.38 (dd)	3.76 (m)	1.69 (q)	2.57 (qt)	5.75 (br s)	3.60 (s)	2.83 (m)	2.83 (m)	1.75 (q)	2.93 (dt)	3.25 (m)	5.75 (s)	4.03 (q)	4.42 (q)	3.35
8-Oxo-α-erythroidine (2)	6.25 (d)	6.74 (dd)	3.75 (m)	1.62 (q)	2.78 (q)	6.02 (s)	—	3.11 (m)	4.35 (dq)	1.45 (dq)	1.93 (m)	3.03 (m)	5.83 (d)	3.97 (q)	4.46 (q)	3.41
β-Erythroidine (3)	5.90 (d)	6.44 (dd)	4.11 (m)	1.79 (q)	2.55 (q)	5.71 (s)	3.63 (d) 3.50 (q)	3.17 (q)	3.22 (q)	1.68 (m)	2.35 (m)	—	3.07 (*e*) (d) 2.98 (*a*) (d)	4.57 (d)	4.77 (d)	3.38
8-Oxo-β-erythroidine (4)	6.25 (d)	6.77 (dd)	4.08 (m)	1.72 (q)	2.82 (q)	5.96 (s)	—	3.22 (dq)	4.34 (dq)	2.02 (br dd)	2.40 (m)	—	3.10 (*a*,*e*) (d)	4.59 (d)	4.73 (d)	3.42

Coupling constants (Hz)

	1,2	2,3	3*a*,4*a*	3*a*,4*e*	4*a*,4*e*	7, {8α / 8β}	8α,8β	10*a*,10*e*	10*a*,11*a*	10*a*,11*e*	10*e*,11*a*	10*e*,11*e*	11*a*,11*e*	11*a*,12	11*e*,12	14,12	14*a*,14*e*	17*e*,17*a*	17*a*,12	17*e*,12
(1)	10.0	2.5	10.5	5.5	12.0	—	0	14.0	0	4.0	4.0	0	8.0	0	14.5	0	—	11.5	9.0	5.5
(2)	10.0	2.0	10.0	6.0	12.0	—	—	14.0	15.0	4.0	5.0	2.0	14.0	12.0	0	2.0	—	12.0	10.0	6.0
(3)	11.0	2.0	13.0	7.0	9.0	3.5	14.0	13.0	0.5	13.0	6.0	6.0	16.0	—	—	—	18.0	14.0	—	—
(4)	12.0	2.5	12.0	6.0	10.0	—	—	14.0	6.0	8.0	2.0	8.0	15.0	—	—	—	—	16.0	—	—

corresponding to cleavages of methyl and methoxy from the 3-methoxy-group (*i.e.*, M^+, $M^+ - 15$, and $M^+ - 31$ ions); the tentative identifications of the 11-hydroxy alkaloids were based on their typical alkenoid spectra together with additional ions corresponding to cleavages of the derivatised 11-hydroxy-group (losses of 89, 90, and 91 mass units, *i.e.* TMSO, TMSOH, and TMSOH + H).

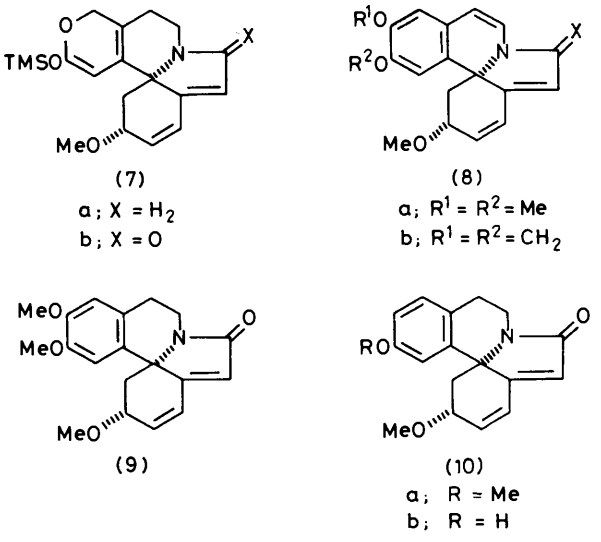
Following these preliminary studies analytical h.p.l.c. investigations were begun, and once a suitable system and column packing material had been evaluated, the method was further developed into a small-scale isolation process. The following alkaloids were detected in *E. berteroana* seeds and then isolated semi-preparatively: 8-oxo-α-erythroidine (2), α-erythroidine (1), β-erythroidine (3), erysodine (5a), and erysovine (5b). With the exception of the 8-oxo-α-erythroidine, these alkaloids were characterised by comparisons with authentic materials (*e.g.* l.c. and g.c. chromatographic retention times, mass spectra, n.m.r. spectra and m.p.s as appropriate). Semi-preparative isolation of alkaloids from *E. berteroana* leaves afforded 8-oxo-β-erythroidine (4), and α- and β-erythroidines. There was insufficient material in the 'liberated' alkaloid fractions from either seeds or leaves to justify preparative l.c. studies.

The isolation of two new alkaloids 8-oxo-α- and 8-oxo-β-erythroidines in the course of this work prompted us to make a complete study of their spectroscopic characteristics, and to compare these with those of the parent compounds. Their formulation as 8-oxo-derivatives followed initially from mass spectral data, later confirmed by high-resolution experiments and subsequently by u.v., i.r., and ^1H and ^{13}C n.m.r. spectroscopy; the salient features are itemised in the experimental section and in the Table. The electron impact mass spectra were very similar to those of the parent alkaloids, simply being shifted 14 units to higher mass. The additional ^{13}C lactam carbonyl resonances at 163.3 and 168.3 p.p.m. in the α- and β-series, respectively were particularly useful diagnostic features, as well as the absence of the 8-methylene proton resonances seen in the ^1H spectra of the parent compounds. Details of the ^{13}C n.m.r. spectral data of these compounds along with other *Erythrina* alkaloids will be published elsewhere.[11] The position of the carbonyl group was also consistent with the u.v. spectra and the i.r. spectra showed additional carbonyl absorption compared with the parent compounds.

Full confirmation of the structural assignments for the new alkaloids was achieved by highfield ^1H n.m.r. spectroscopy (at 360 and 400 MHz) together with decoupling experiments, and comparisons with the spectra of α- and β-erythroidines (Table). All four alkaloids showed the typical pattern of peaks in the lowfield regions of the spectrum associated with the dienoid system, and also the characteristic aliphatic methoxy-resonances.

The spectra of the α-erythroidine and its 8-oxo-analogue also exhibited additional vinylic proton resonances due to the proton at position-14, and the 17-proton resonances were both at lower field in the β-erythroidine (3) and 8-oxo-β-erythroidine (4) spectra, than those of the α-series (as expected because of the deshielding effect of the 12,13-double bond in the β-series).

A number of other features in the proton n.m.r. spectra are also worthy of comment. The 11-H*a* resonance in the spectrum of 8-oxo-α-erythroidine is at the highest field (δ 1.45) of all the proton signals in all four spectra, and similarly the 11-H*e* resonance of the same compound is also at highfield (δ 1.93) and 1 p.p.m. higher than that of the same resonance in α-erythroidine. These results are attributed to the different degrees of twisting of the structures caused by the positions of the double bond in the α- and β-series and the presence or absence of the 8-oxo-group. The geminal coupling of the 11-protons in α-erythroidine is also notably lower than those of the other three compounds, and indeed this spectrum was the most troublesome to assign because the 10-H resonances overlapped to give a very complex multiplet which could not be decoupled satisfactorily whilst the 12-H and 11-H resonances were deceptively simple. Thus all the coupling constants had to be determined from the other resonances. The lowfield shifts (δ 4.35 and 4.34, respectively) of the 10-H*e* observed in the spectra of both the 8-oxo-α-and β-erythroidines are attributed to the deshielding effects of the 8-oxo-group which may well be in the same plane as the 10-H*e* bond as indicated by molecular models. Earlier n.m.r. studies of *Erythrina* alkaloids have concerned mainly the aromatic alkenoid and dienoid series,[12] and this is the first detailed description of the highfield ^1H spectra of the lactonic alkaloids. However, since this work was completed the 60 MHz ^1H spectra of α- and β-erythroidines isolated from *E. americana* flowers have been described.[13]



The circular dichroism curves of both the isomers of 8-oxo-erythroidine show that these alkaloids have identical configurations to those of the parent erythroidines.

It is not certain how much of the oxoerythroidines are present in the seeds, or leaves, because we have observed that solutions of α-erythroidine in chloroform slowly oxidise in air over a few days to give appreciable amounts of the 8-oxo-derivative. The β-erythroidine in contrast is rather more stable, and is much slower to undergo aerial oxidation to the oxo-derivative. Only the 8-oxo-β-alkaloid was detected [as its $SiMe_3$ derivative (7b)] by gas chromatography, as the 8-oxo-α-alkaloid proved to be too polar to be eluted under the standard conditions used; this is consistent with the behaviour of the parent compounds, the (derivatised) β-erythroidine (7a) having a much shorter retention time than the (underivatised) α-erythroidine. It may well be that the reason for the relatively smaller yield of α-erythroidine compared with the β-isomer may be due to preferential oxidation of the former. (We have checked by gas chromatography of purified samples that the derivatisation process, or the extraction process, does not cause isomerisation.)

The isolation of 8-oxo-alkaloids has earlier been reported in the dienoid series. Ito and his co-workers isolated erythrabine (8a) and erysotramidine (9) from *E. arborescens*.[14,15] Later, a similar alkaloid crystamidine (8b) was isolated from *E. cristagalli*.[16] Two other 8-oxo compounds coccoline (10a) and coccolinine (10b) have been isolated from *Cocculus laurifolius*.[1]

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise stated, i.r. spectra were recorded in chloroform, and u.v. and c.d. spectra in ethanol. The n.m.r. spectra were determined in $CDCl_3$ on Bruker 360 MHz and 400 MHz instruments using tetramethylsilane as an internal standard.

The EI low and high resolution mass spectra were obtained with a Varian CH5D mass spectrometer at 3 kV and 70 eV. F.D. mass spectra were determined with the same instrument using a tungsten emitter wire coated with carbon needles with wire currents at 12—15 mA.

Gas chromatography of the derivatised ($SiMe_3$) alkaloids was carried out with a Varian 2740 gas chromatograph equipped with a flame ionisation detector using a glass column (180 cm × 5 mm int. diam.) packed with 3% OV-17 on Gas Chrom *Q* 100–120 mesh. The oven temperature was programmed from 225 to 275 °C at 2 °C min the carrier gas was nitrogen at a flow rate of 30 ml/min, and the injector and detector were both set at 280 °C. The retention times (in min) of the various alkaloids detected in the present studies are as follows: trimethylsilyl-β-erythroidine 6.8; trimethylsilyl-8-oxo-β-erythroidine, 14.9; trimethylsilylerysonine, 15.1; trimethylsilylerysoline, 15.6; trimethylsilylerysopine, 16.1; trimethylsilylerysodine, 16.4; trimethylsilylerysovine, 17.4; α-erythroidine, 17.5; trimethylsilyl-11-hydroxyerysotine, or 11-hydroxyerysosalvine, 18.9; trimethylsilyl-11-hydroxyerythratidine, 20.3. The g.c.-m.s. characteristics of the trimethylsilyl (TMS) derivatives were determined with a Varian CH5D mass spectrometer coupled with a Varian 1740 gas chromatograph *via* a two-stage Watson-Beimann separator. The temperature of the ion source was 220 °C and the accelerating and ionizing potentials were 3 kV and 70 eV, respectively. The spectra were recorded electrically using a Varian 620i data system, and after subtraction of background peaks, were normalized and plotted on a Statos 21 fast printer.

The h.p.l.c. analysis was carried out with a Waters Associates Chromatography pump (M-6000) and Cecil variable wavelength UV detector set at 280 nm using stainless-steel columns [analytical 10 or 15 cm × 4.5 mm; semi-preparative (10μ) 30 cm × 6.5 mm] packed with 5μ Partisil and 10μ Partisil, respectively.

Source of Plant Material.—The leaves and seeds used in these studies were supplied by Dr. B. A. Krukoff and they are backed by herbarium material deposited at the New York Botanical Garden and other herbaria; *E. berteroana* Urban leaves, B. A. Krukoff 1980/12; Guatemala *E. berteroana* Urban seeds, Tim Folsom 3661, 3662, 3663, 3664, Panama 1978.

Extraction of E. berteroana *Leaves.*—The air-dried powdered leaves (140 g) were extracted with methanol in a Soxhlet unit for 90 h. The solvent was distilled off and the residue dissolved in 2% (w/v) sulphuric acid. The acid solution was washed with chloroform (2 × 100 ml), basified ($NaHCO_3$), and extracted with chloroform (3 × 100 ml). The chloroform extracts were washed with water, dried (Na_2SO_4) and evaporated under reduced pressure to yield the ' free ' alkaloidal residue (0.29 g).

The remaining aqueous solution was adjusted to pH 2 by addition of dilute sulphuric acid, heated to 60—70 °C for 7 h, cooled, made basic again, and extracted with chloroform (3 × 100 ml). This extract was worked up in the same way as described above to give the ' liberated ' alkaloids (0.1 g). The two alkaloid fractions were processed separately to identify and isolate their components. A similar extraction of a second batch of leaves (480 g) gave similar ' free ' (0.95 g) and ' liberated ' (0.35 g) alkaloidal fractions.

Extraction of E. berteroana *Seeds.*—The powdered seeds (200 g) were extracted with methanol in a Soxhlet unit for 72 h. The methanolic extract, on following the same method as described above, yielded ' free ' (0.1 g) and ' liberated ' (0.085 g) alkaloid fractions.

G.c./M.s. Analysis.—The crude alkaloid mixture (2—3 mg) was derivatized as a trimethylsilyl (TMS) derivative by treatment for 30 min with *N,O*-bis(trimethylsilyl)acetamide (25 μl) in acetonitrile (25 μl). This was subjected to gas chromatography, and subsequently to combined gas chromatography/mass spectrometry, which revealed the presence of β-erythroidine (3), 8-oxo-β-erythroidine (4), and α-erythroidine (1) in the ' free ' fraction from leaves whereas the similar fraction obtained from the seeds showed the presence of α- and β-erythroidines, erysodine (5a), and erysovine (5b). The ' liberated ' fraction obtained from the seeds indicated the occurrence of erysodine (5a) and erysovine (5b) as the major components, and erysopine (5c), erysoline (5d), and erysonine (5e) as the minor components. Trace amounts of β-erythroidine (3), and the 11-hydroxy-derivatives of erysotine (6a) [or erysosalvine (6b)] and erythratidine (6c) were also observed. Nothing conclusive could be deduced from the mass spectra of the ' liberated ' fraction obtained from the leaves. The field desorption mass spectra of the ' free ' fraction from leaves, and ' free ' and ' liberated ' fractions from seeds confirmed the presence of the components characterised by g.c./m.s. analysis.

The mass spectral data of the various alkaloids characterised by g.c./m.s. are given below. Except for α-erythroidine the *m/z* values of all other alkaloids correspond to the TMS derivatives.

β-Erythroidine (3): *m/z* 345 (M^+, 40%), 330 ($M^+ - CH_3$, 17), 314 ($M^+ - OCH_3$, 40), 224 (65), 196 (75), 130 (100), and 73 (64).

8-Oxo-β-erythroidine (4): *m/z* 359 (M^+, 10) 344 ($M^+ - CH_3$, 16), 242 (62), 227 (78), and 73 (100).

α-Erythroidine (1): *m/z* 273 (M^+, 55), 258 ($M^+ - CH_3$, 23), 242 ($M^+ - OCH_3$, 100), 240 (30), 214 (16), 196 (18), 182 (26), 170 (23), and 130 (34).

Erysodine (5a): *m/z* 371 (M^+, 53), 356 ($M^+ - CH_3$, 49), 340 ($M^+ - OCH_3$, 100), 337 (15), 313 (10), 310 (10), 287 (10), and 73 (26).

Erysovine (5b): *m/z* 371 (M^+, 58), 356 ($M^+ - CH_3$, 59), 340 ($M^+ - OCH_3$, 100), 338 (14), 313 (8), 310 (18), and 73 (28).

Erysopine (5c): *m/z* 429 (M^+, 62), 414 ($M^+ - CH_3$, 24), 398 ($M^+ - OCH_3$, 100), 340 (12), and 73 (45).

Erysonine (5d): *m/z* 429 (M^+, 100), 340 (58), 338 (38), 326 (12), 313 (24), 308 (10), and 73 (58).

Erysoline (5e): 429 (M^+, 100), 414 ($M^+ - CH_3$, 16), 398 ($M^+ - OCH_3$, 3), 340 (51), 338 (42), 326 (12), 313 (21), 308 (12), 287 (10), and 73 (60).

11-Hydroxyerysotine (6a) or *11-hydroxyerysosalvine* (6b): *m/z* 549 (M^+, 7), 460 (20), 458 (100), 403 (41), and 73 (95).

11-Hydroxyerythratidine (6c): *m/z* 491 (M^+, 10), 476 (2), 401 (30), 400 (100), 385 (30), 370 (20), 356 (12), 345 (11), 307 (10), 197 (40), and 73 (80).

H.p.l.c. Analysis.—The ' free ' fraction obtained from leaves, and the ' free ' and ' liberated ' fractions obtained from seeds were subjected to analytical, and subsequently to semi-preparative h.p.l.c. using the columns indicated above with chloroform–ethanol (96 : 4, v : v) containing concentrated ammonia solution (0.1%) as eluant. The ' free ' fraction from

the seeds afforded fractions identified as 8-oxo-α-erythroidine (2), α-erythroidine (1), β-erythroidine (3), erysodine (5a), and erysovine (5a), and the corresponding fraction from the leaves yielded 8-oxo-β-erythroidine (4), α-erythroidine (1) and β-erythroidine (3). The ' liberated ' fraction from the seeds gave only erysodine (5a) and erysovine (5b). The retention times (in minutes) of these alkaloids using the analytical column with a solvent flow-rate of 1 ml/min were as follows: 8-oxo-α-erythrodine, 8.5; 8-oxo-β-erythroidine, 12.1; α-erythroidine, 15.4; β-erythroidine, 16.3; erysodine and erysovine, 18.5. The identities of all these compounds were confirmed by spectroscopic means (n.m.r. and m.s.) and by comparisons with authentic materials as appropriate.

Spectroscopic and analytical data is listed below for each of the compounds isolated by preparative h.p.l.c.

α-Erythroidine (1). This was obtained as a glass, $\nu_{max.}$ 1 720 cm^{-1} (lactonic carbonyl group); $\lambda_{max.}$ 227 nm (log ε 4.18); n.m.r. (see Table); *m/z* 273 (M^+, 72%), 258 ($M^+ - CH_3$, 34), and 242 ($M^+ - OCH_3$, 100); $\Delta\varepsilon_{243} = -33.5$ dm^2 mol^{-1}, $\Delta\varepsilon_{270} = 0$, and $\Delta\varepsilon_{283} = 12.2$ dm^2 mol^{-1}.

8-*Oxo-α-erythroidine* (2). This crystallised from acetone, and had m.p. 183 °C, $[\alpha]_D$ + 137.9° (*c*, 0.116 in EtOH); $\nu_{max.}$ 1 700 cm^{-1} (lactonic CO) and 1 745 cm^{-1} (five-membered lactam CO); $\lambda_{max.}$ 222 (log ε 4.19) and 253 nm (log ε 4.16); n.m.r. (see Table); *m/z* 287 (M^+, 100%), 272 ($M^+ - CH_3$, 17), and 256 ($M^+ - OCH_3$, 47) [Found: M^+, 287.1166 (HRMS). $C_{16}H_{17}NO_4$ requires M^+, 287.1157], $\Delta\varepsilon_{233} = -109$ dm^2 mol^{-1}, $\Delta\varepsilon_{265} = 0$, and $\Delta\varepsilon_{277} = 58.7$ dm^2 mol^{-1}.

β-*Erythroidine* (3). This was obtained as glass, $\nu_{max.}$ 1 720 cm^{-1} (lactonic carbonyl group); $\lambda_{max.}$ 230 nm (log ε 3.97); n.m.r. (see Table); *m/z* 273 (M^+, 63%), 258 ($M^+ - CH_3$, 32), and 242 ($M^+ - OCH_3$, 100). The base in absolute ethanol on treatment with sodium iodide and acetic acid formed a crystalline hydriodide and recrystallised from absolute ethanol, m.p. 124—125 °C (decomp.) (Found: C, 47.9; H, 4.9; I, 31.75; N, 3.4. $C_{16}H_{20}INO_3$ requires C, 47.90; H, 5.03; I, 31.63; N, 3.49%), $\Delta\varepsilon_{253} = -19.6$ dm^2 mol^{-1}, $\Delta\varepsilon_{272} = 0$, and $\Delta\varepsilon_{285} = 10.2$ dm^2 mol^{-1}.

8-*Oxo-β-erythroidine* (4). This was obtained as a glass, $[\alpha]_D$ +32° (*c*, 0.156 in EtOH), $\nu_{max.}$ 1 700 cm^{-1} (lactonic CO) and 1 750 cm^{-1} (five-membered lactam CO), $\lambda_{max.}$ 254 nm (log ε 3.83); n.m.r. (see Table), *m/z* 287 (M^+, 100%), 272 ($M^+ - CH_3$, 27), and 256 ($M^+ - OCH_3$, 46) [Found: M^+, 287.1146 (HRMS), $C_{16}H_{17}NO_4$ requires M^+, 287.1157], $\Delta\varepsilon_{237} = -23.0$ dm^2 mol^{-1}, $\Delta\varepsilon_{261} = 0$, and $\Delta\varepsilon_{277} = 11.5$ dm^2 mol^{-1}.

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