

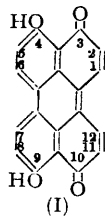
Colouring Matters of the Aphididae. Part XII. Addition Reactions of Erythroaphin-sl and its Conversion into Erythroaphin-fb.*

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Diamino-, dihydroxy-, dipiperidino-, bicyclohexylamino-, and hydroxy-piperidino-derivatives prepared from erythroaphin-*sl* are all identical with the corresponding derivatives from erythroaphin-*fb*. As they regenerate erythroaphin-*fb* after reduction with zinc and acetic acid, chemical methods are thus available for converting erythroaphin-*sl* into its *fb*-isomer. On the other hand, monohydroxy- and dibromo-erythroaphin-*sl* are distinct from the analogous compounds in the *fb*-series although both dibromoerythroaphins give one and the same dibromo-dipiperidinoerythroaphin on treatment with piperidine.

In Part VII of this series (Brown, Johnson, MacDonald, Quayle, and Todd, *J.*, 1952, 4928) it was reported that erythroaphin-*fb*, one of the aphin pigments derived from *Aphis fabae* (Part II, *J.*, 1950, 477), readily reacted with ammonia, amines, and halogens, yielding the diamino-, *NN*-disubstituted diamino-, and dihalogeno-erythroaphins-*fb*, and with alkaline oxidising agents, giving dihydroxyerythroaphin-*fb*. This behaviour is consistent with the suggestion elaborated in earlier papers that the 4 : 9-dihydroxyperylene-3 : 10-quinone nucleus (I) is an integral part of the erythroaphin molecule and that it represents the sole chromophoric system of the latter. The aphins derived from *Tuberolachnus salignus* (Part III, *J.*, 1950, 485) are very similar to, but nevertheless distinct from, those from *A. fabae*. Thus not only is erythroaphin-*sl* isomeric with erythroaphin-*fb*, but the ultra-violet and visible spectra of both compounds are identical; only in their infra-red spectra do they show differences. Since it is evident that



erythroaphin-*sl* must have the same chromophoric system as the *fb*-isomer it was decided to examine the reaction of the former with amines and halogens in the hope that it might throw further light on the relationship between the two series.

As expected, the reactions of erythroaphin-*sl* closely paralleled those of erythroaphin-*fb* but the surprising observation was made that the dihydroxy-, diamino-, dipiperidino-, and bicyclohexylamino-derivatives obtained were identical with those obtained from erythroaphin-*fb* (infra-red spectra); on reduction with zinc and acid they all yielded erythroaphin-*fb*. In this way it was possible to convert erythroaphin-*sl* into erythroaphin-*fb* and it is clear that conversion of the *sl*- into the *fb*- series occurs during production of the above disubstituted compounds.

On the other hand dibromoerythroaphin-*sl* was distinct from dibromoerythroaphin-*fb* and yielded erythroaphin-*sl* on reduction. Both these dibromo-derivatives, however, reacted with piperidine to produce one and the same dibromo-dipiperidinoerythroaphin

* Part XI, *J.*, 1954, 2378.

which we assign to the *fb*-series since it yielded, with zinc and acid, erythroaphin-*fb*; a similar merging of the two series is produced by reaction with ammonia and other amines. There is good evidence for the view that all four substituents in diamino-dibromoerythroaphin-*fb* are located in the aromatic portion of the molecule. The introduction of the amino-groups must involve, in the first instance, addition to an activated double bond and on the basis of hydrogenation evidence (Parts II and III, *loc. cit.*) there are no non-aromatic double bonds in erythroaphin. Again, if bromination had occurred in the non-aromatic portion of the molecule, then the aliphatic bromine substituents would hardly be expected to survive the action of an excess of hot aqueous ammonia or amines. Attempts to halogenate the various diaminoerythroaphins or to dehalogenate the diamino-dibromoerythroaphins have not led to any clearly defined products.

In an effort to define more precisely the factors which bring about the isomerisation of the *sl*- to the *fb*-series, monohydroxyerythroaphin-*sl* was prepared by Thiele acetylation of the aphin followed by hydrolysis and re-oxidation; the product was distinct from monohydroxyerythroaphin-*fb* and had a different infra-red absorption spectrum. Both of these monohydroxy-compounds, however, with piperidine gave the same hydroxy-piperidinoerythroaphin, which from its behaviour on reduction is assigned to the *fb*-series. Simple reduction of erythroaphin-*sl* either with sodium dithionite or with zinc and aqueous sodium hydroxide, followed by reoxidation of the dihydro-compound either in alkaline solution or in acid suspension, failed to effect isomerisation, erythroaphin-*sl* being regenerated. Likewise none of the *fb*-isomer could be detected in the product obtained by acidifying an aqueous solution of the sodium salt of erythroaphin-*sl* after it had been kept at 0° for one hour (at higher temperatures hydroxylation of the molecule occurs very readily). No reaction products of either erythroaphin with hydrazoic acid, hydrogen cyanide, benzenesulphonic acid, hydrogen chloride, or hydrogen bromide have been characterised; either no reaction occurred or secondary reactions prevented isolation of the initial product.

The easy conversion of erythroaphin-*sl* into erythroaphin-*fb* by the various routes described in this paper, together with the remarkable similarity in physical and chemical properties of the two pigments strongly suggests that they are stereoisomeric substances. The isomerism, moreover, probably involves the configuration at one or more asymmetric centres in the non-aromatic portion of the erythroaphin molecule; both compounds are optically active and have widely different rotations. Detailed discussion of the optical activity of the pigments and their derivatives as well as of the precise nature of the changes involved in *sl* → *fb* conversions is deferred to a later paper (Part XIV, in the press) since it is necessary first to derive from the results of degradative studies the general structure of the erythroaphin molecule.

EXPERIMENTAL

Diaminoerythroaphin-fb.—A solution of erythroaphin-*sl* (500 mg.) in purified dioxan (200 c.c.) containing quinol (2 g.) and nitrobenzene (10 c.c.) was kept at 70° and aqueous ammonia (*d* 0.880; 25 c.c.) was added. The progress of the reaction was followed by partitioning small samples of the reaction mixture between chloroform and 10% hydrochloric acid. After 50 min. the solution was cooled and poured into light petroleum (b. p. 40–60°; 750 c.c.). The product was purified in the same manner as diaminoerythroaphin-*fb* (Part VII, *loc. cit.*) by partition between chloroform and 10% hydrochloric acid. The final chloroform extract was shaken overnight with saturated sodium hydrogen carbonate solution, and the precipitate, largely consisting of impurities, was separated and washed with a little chloroform. The chloroform solutions were concentrated and the volume maintained by addition of hot methanol; diaminoerythroaphin-*fb* (159 mg.) then separated as reddish-brown plates. For analysis it was recrystallised from the same solvents and dried at 40°/5 × 10⁻³ mm. (Found: C, 64.2; H, 4.2; N, 5.0. Calc. for C₃₀H₂₄O₈N₂.H₂O: C, 64.5; H, 4.7; N, 5.0%). Light absorption in CHCl₃ containing 5% of Et₂O: max. at 595, 567, 525, 487, 454, 429, 335, 322, and 255 mμ (log ε 3.77, 4.23, 4.05, 3.76, 4.54, 4.41, 3.63, 3.61, and 4.55 respectively). The infra-red spectrum, determined on a mull in Nujol, showed maxima at 697, 721, 762, 775, 833, 855, 921, 980, 997, 1017, 1053, 1064, 1081, 1163, 1202, 1239, 1289, 1577, 1629, and 3333 cm.⁻¹.

Dihydroxyerythroaphin-fb.—(i) From diaminoerythroaphin-*fb*. Diaminoerythroaphin-*fb*

(48.4 mg.; prepared from erythroaphin-*sl*) was treated with nitrous acid by the method described in Part VII (*loc. cit.*). The product (29 mg.) was separated, washed with ether and ethanol, and recrystallised from acetone as long red needles (Found, on a sample dried at $20^{\circ}/10^{-3}$ mm.: C, 66.2; H, 4.2. Calc. for $C_{30}H_{22}O_{10}$: C, 66.4; H, 4.1%). Light absorption in $CHCl_3$: max. at 599, 572, 530, 494, 453, 428, 335, 322, and 252 $m\mu$ ($\log \epsilon$ 3.76, 4.22, 4.05, 3.73, 4.62, 4.46, 3.66, 3.62, and 4.59 respectively). The infra-red spectrum of a mull in Nujol showed maxima at 700, 713, 737, 772, 834, 842, 870, 935, 946, 974, 1015, 1053, 1064, 1071, 1087, 1093, 1115, 1148, 1170, 1205, 1225, 1250, 1297, 1429, 1481, 1515, 1550, 1580, 1631, and 3333 cm^{-1} .

(ii) *From erythroaphin-sl.* A solution of erythroaphin-*sl* (1.0 g.) and powdered potassium permanganate (2.0 g.) in pyridine (150 c.c.) containing a few drops of water was heated on a boiling water-bath for 2 hr. The precipitated manganese dioxide was separated and washed with hot pyridine, and the combined pyridine solutions were poured on ice (500 g.) and concentrated hydrochloric acid (200 c.c.). The red precipitate was extracted with chloroform (4×100 c.c.), and the chloroform extracts were washed with water and shaken thoroughly with *N*-sodium carbonate to extract the acidic product. The green aqueous layer was quickly washed with fresh chloroform and acidified with 3*N*-hydrochloric acid. The red precipitate was again extracted with chloroform, and the extract washed, dried, evaporated to small bulk (10 c.c.), and cooled to 0° . Dihydroxyerythroaphin-*fb* then separated as small deep-red needles (Found, in material dried at $100^{\circ}/0.1$ mm. for 6 hr.: C, 66.5, 66.4; H, 4.2, 4.0%). The ultra-violet and infra-red spectra of the product were identical with those recorded for the sample obtained by the preceding method.

Erythroaphin-fb from Diaminoerythroaphin-fb (cf. Part VII, *loc. cit.*).—Diaminoerythroaphin-*fb* (159 mg.; obtained from erythroaphin-*sl*) was reduced with zinc and acetic acid by the method described previously. After crystallisation from chloroform-ethanol, erythroaphin-*fb* (19 mg.) was obtained (Found: C, 70.5; H, 4.8. Calc. for $C_{30}H_{22}O_8$: C, 70.6; H, 4.4%). The ultra-violet and infra-red spectra agreed with those of authentic erythroaphin-*fb* (Parts II and V, *loc. cit.*).

Dipiperidinoerythroaphin-fb.—Erythroaphin-*sl* (110 mg.) was dissolved in freshly distilled piperidine (15 c.c.), and the dark green solution kept at room temperature for 3 hr.; a certain amount of crystalline product separated, and an examination (hand-spectroscope) of a chloroform extract of the acidified product (0.1 c.c.) showed that unchanged erythroaphin was no longer present. The main portion of the product was poured into 10% hydrochloric acid (ice), and the red precipitate extracted into chloroform (50 c.c., then 3×20 c.c.). The chloroform extract was washed with water and then 30% hydrochloric acid (3×30 c.c.) which removed very little of the coloured product from the chloroform. The pigment was extracted from the chloroform with 75% hydrochloric acid (5×30 c.c.), and the combined acid extracts were diluted with water (100 c.c.) and again extracted with chloroform (6×30 c.c.). The chloroform was then washed with water, then sodium hydrogen carbonate solution, and dried, and the solvent was removed. The reddish-brown residue was dissolved in pyridine (9 c.c.) and filtered, and warm aqueous methanol (15 c.c. of 80%) was added; the product crystallised as dark red plates (110 mg.) which were washed with methanol and dried. After two further crystallisations from pyridine-methanol the product (75 mg.) was dried for analysis at $90^{\circ}/10^{-4}$ mm. for 5 hr. (Found: C, 71.0; H, 6.2; N, 4.3. Calc. for $C_{40}H_{40}O_8N_2$: C, 71.0; H, 6.0; N, 4.1%). The infra-red spectrum, which was identical with the product obtained from erythroaphin-*fb*, was determined on a Nujol mull and showed maxima at 738, 773, 817, 830, 846, 852, 862, 918, 934, 966, 995, 1020, 1042, 1073, 1096, 1117, 1149, 1183, 1198, 1261, 1280, 1307, 1570, 1600, and 1631 cm^{-1} . Light absorption in $CHCl_3$: max. at 609, 575, 532, 445—448, 348, and 344 $m\mu$ ($\log \epsilon$ 3.89, 4.24, 4.10, 4.28, 3.78, and 3.78 respectively) with an inflection at 328—336 $m\mu$ ($\log \epsilon$ 3.70).

Biscyclohexylaminoerythroaphin-fb.—Erythroaphin-*sl* (100 mg.) was dissolved in freshly distilled cyclohexylamine (15 c.c.) and kept for $3\frac{1}{2}$ hr. The mixture was treated as in the foregoing experiment except that the extraction into hydrochloric acid was omitted. The solvent was removed from the final chloroform extract, the residue dissolved in pyridine (5 c.c.) and filtered, and crystallisation initiated by the addition of warm methanol (8 c.c.) containing 20% of 3*N*-hydrochloric acid. The product (90 mg.) which formed reddish-brown crystals was washed with methanol and then hot water and recrystallised from pyridine-methanolic hydrochloric acid as before. The dark red plates (70 mg.) were washed with hot water and dried at $90^{\circ}/10^{-3}$ mm. for 9 hr. (Found: N, 5.1, 5.1. $C_{42}H_{44}O_8N_2 \cdot C_5H_5N$ requires N, 5.4%). The compound was further dried at $115^{\circ}/10^{-4}$ mm. for 12 hr. (Found: N, 4.1. Calc. for

$C_{42}H_{44}O_8N_2$: N, 4.0%). Light absorption in chloroform: max. at 602, 572, 530, 462, and 253—254 $m\mu$ ($\log \epsilon$ 3.88, 4.15, 4.04, 4.31, and 4.61 respectively), with an inflection at 332—334 $m\mu$ ($\log \epsilon$ 3.93). The infra-red spectrum, which was identical with the product obtained from erythroaphin-*fb*, showed maxima (Nujol mull) at 1631, 1587, 1302, 1287, 1255, 1178, 1117, 1075, 1043, 990, 913, 889, 870, 857, and 825 cm^{-1} .

*Erythroaphin-*fb* from Biscyclohexylaminoerythroaphin-*fb** (cf. Part VII, *loc. cit.*).—Reduction of biscyclohexylaminoerythroaphin-*fb* (90 mg.; prepared from erythroaphin-*sl*) with zinc and acetic acid by the method already described gave erythroaphin-*fb* (22 mg.), the infra-red spectrum of which was identical with that of an authentic specimen.

*Dibromoerythroaphin-*sl**.—Erythroaphin-*sl* (281 mg.) was suspended in glacial acetic acid (20 c.c.), and bromine (0.5 c.c.) added. The suspension was shaken for 1 hr. and then poured into water (200 c.c.). The bromo-compound which was precipitated was separated on the centrifuge, washed, dried (353 mg.), and crystallised twice from chloroform-ethanol as dark red plates (191 mg.). For analysis it was dried for 6 hr. at 75°/0.1 mm. (Found: C, 53.5; H, 3.0. $C_{30}H_{20}O_8Br_2$ requires C, 53.9; H, 3.0%). Light absorption in $CHCl_3$: max. at 566, 525, 454—456, 345, and 264 $m\mu$ ($\log \epsilon$ 4.35, 4.21, 4.51, 3.70, and 4.70 respectively), with inflections at 472—476 and 330—340 $m\mu$ ($\log \epsilon$ 4.45 and 3.66). The infra-red spectrum of a mull in Nujol showed maxima at 667, 771, 809, 824, 838, 851, 866, 917, 962, 977, 1001, 1047, 1081, 1117, 1136, 1163, 1198, 1241, 1304, 1344, and 1626 cm^{-1} . The infra-red spectrum of dibromoerythroaphin-*fb* (Part VII, *loc. cit.*) also determined as a mull in Nujol showed maxima at 666, 755, 806, 829, 847, 870, 904, 935, 957, 1000, 1049, 1076, 1105, 1156, 1199, 1232, 1258, 1307, 1567, and 1626 cm^{-1} ; light absorption in chloroform: max. at 566, 525, 476, 452, 347, and 264 $m\mu$ ($\log \epsilon$ 4.29, 4.15, 4.38, 4.43, 3.64, and 4.63 respectively), with inflections at 342—344 and 334—336 $m\mu$ ($\log \epsilon$ 3.64 and 3.63).

*Erythroaphin-*sl* from Dibromoerythroaphin-*sl**.—The dibromo-compound (180 mg.) was suspended in glacial acetic acid (200 c.c.), and zinc dust (40 g.) added. The mixture was heated on the water-bath for 15 min., the excess of zinc separated, and the filtrate cooled and diluted with water. The pigment was extracted into chloroform, and the chloroform shaken with sodium hydrogen carbonate solution. Further purification was effected by transferring the pigment from the chloroform into 72% sulphuric acid and then back into chloroform by diluting the sulphuric acid to 64% (Part III, *loc. cit.*). The chloroform was washed with sodium hydrogen carbonate solution and then water, dried, and concentrated. Hot ethanol was added to induce crystallisation and the product (40 mg.) was recrystallised from chloroform-ethanol (Found, in material dried at 100°/0.1 mm. for 4 hr.: C, 70.6; H, 4.5%). The infra-red spectrum (Nujol mull) was identical with that of authentic erythroaphin-*sl* (Part V, *loc. cit.*).

*Dibromodipiperidinoerythroaphin-*fb**.—(i) *From dibromoerythroaphin-*sl**. A solution of dibromoerythroaphin-*sl* (87 mg.) in pyridine (20 c.c.) and piperidine (2 c.c.) was kept overnight at room temperature and then poured into ice-cooled 10% hydrochloric acid. The solution was extracted into chloroform, and the chloroform solution washed with water and then shaken with 10N-hydrochloric acid (5 × 25 c.c.). The combined acid extracts were diluted with water (70 c.c.) and the pigment was extracted back into chloroform (6 × 25 c.c.). The combined chloroform extracts were washed with water, dried, and concentrated and crystallisation was induced by the addition of hot ethanol. The product (54 mg.) which formed dark red oblong crystals was recrystallised from chloroform-ethanol and for analysis was dried for 6 hr. at 70°/0.1 mm. (Found: C, 56.5, 56.4; H, 4.7, 4.3; N, 3.3. $C_{40}H_{38}O_8N_2Br_2 \cdot H_2O$ requires C, 56.4; H, 4.7; N, 3.3; Br, 18.7%). The water of crystallisation was not removed after drying at 110°/0.1 mm. overnight (Found: C, 56.8; H, 4.3%). Light absorption in $CHCl_3$: max. at 577—578, 534—535, 495, 351, and 265—266 $m\mu$ ($\log \epsilon$ 4.34, 4.28, 4.32, 3.67, and 4.57 respectively), with an inflection at 334—337 $m\mu$ ($\log \epsilon$ 3.68). The infra-red spectrum determined on a mull in Nujol showed maxima at 665, 680, 767, 786, 808, 847, 917, 950, 1024, 1036, 1078, 1111, 1171, 1183, 1212, 1244, 1277, 1567, and 1629 cm^{-1} .

(ii) *From dibromoerythroaphin-*fb**. The foregoing experiment was repeated with dibromoerythroaphin-*fb* (115 mg.). The product (91 mg.) was dried at 100°/0.1 mm. for 6 hr. for analysis (Found: C, 56.5; H, 4.4; N, 3.3; Br, 18.6%). The infra-red curve (determined on a mull in Nujol) was identical with that of the product of the previous experiment.

*Erythroaphin-*fb* from Dibromodipiperidinoerythroaphin-*fb**.—The dibromo-compound (167 mg.) was debrominated and the product purified by the method used for dibromoerythroaphin-*sl*. The erythroaphin-*fb* (28 mg.) crystallised from chloroform-ethanol as before (Found, on a sample dried at 80°/0.1 mm.: C, 70.4; H, 4.6%). The infra-red spectrum (Nujol mull) was identical with that of authentic erythroaphin-*fb* (Part V, *loc. cit.*).

Diaminodibromoerythroaphin-fb.—A solution of dibromoerythroaphin-*fb* (105 mg.) in dioxan (60 c.c.) containing water (5 c.c.) and quinol (300 mg.) was kept at 70° under reflux for 1½ hr. while a stream of ammonia and another of air were bubbled through it. The mixture was cooled, diluted with water, and washed with light petroleum (b. p. 40–60°; 2 × 200 c.c.). The aqueous layer was acidified with hydrochloric acid (50 c.c. of 10%) and filtered and the filtrate partially neutralised with 10% sodium hydroxide solution (35 c.c.). The pigment was then extracted into chloroform (50 c.c., then 3 × 25 c.c.) and purified by extraction into 10% hydrochloric acid (6 × 25 c.c.) and then back again into chloroform (2 × 50 c.c.) after partial neutralisation with 10% sodium hydroxide solution (100 c.c.). The chloroform solution was washed and dried and the solvent removed. The residue was crystallised twice from a mixture of pyridine (10 c.c.), methanol (7 c.c.), and 10% hydrochloric acid (3 c.c.). *Diaminodibromoerythroaphin-fb* was thus obtained in black plates with a green lustre (Found, on a sample dried for 6 hr. at 90°/0.1 mm.: C, 54.8; H, 3.9; N, 5.1; Br, 20.7. C₃₀H₂₂O₈N₂Br₂C₅H₅N requires C, 54.1; H, 3.5; N, 5.4; Br, 20.6%). Light absorption in chloroform: max. at 570, 527, 480, 347, 333, and 264 mμ (log ε 4.23, 4.14, 4.45, 3.74, 3.71, and 4.63 respectively). The infra-red spectrum, determined on a mull in Nujol, showed maxima at 666, 703, 744, 762, 787, 802, 826, 858, 893, 935, 948, 1000, 1029, 1053, 1068, 1083, 1103, 1183, 1235, 1282, 1307, 1575, and 1631 cm.⁻¹.

Hydroxyerythroaphin-sl.—Erythroaphin-*sl* (500 mg.) was added to cold acetic anhydride (100 c.c.) containing perchloric acid (10 drops of 60%) and the mixture stirred at 0° for 6½ hr. The intermediate dihydro-hydroxyerythroaphin-*sl* penta-acetate was extracted and hydrolysed as described for the *fb*-isomer (Part VII, *loc. cit.*), *hydroxyerythroaphin-sl* (220 mg.) being obtained as slender red needles after crystallisation from chloroform-ethanol or from acetone (Found, on material dried at 110°/0.7 mm. for 24 hr.: C, 68.1; H, 4.5. C₃₀H₂₂O₉ requires C, 68.4; H, 4.2%). The light absorption of a solution in chloroform was identical with that of the *fb*-isomer, as were the general chemical properties. The infra-red spectrum of a mull in Nujol showed maxima at 721, 741, 766, 827, 840, 887, 942, 947, 1001, 1070, 1079, 1093, 1166, 1209, 1250, 1292, 1477, 1511, 1587, 1631, and 3226 cm.⁻¹, *i.e.*, was identical with that of hydroxyerythroaphin-*fb* (Part VII, *loc. cit.*) except for the absence of the band at 867 cm.⁻¹. (The band at 787 cm.⁻¹ previously reported in the infra-red spectrum of hydroxyerythroaphin-*fb* is now known to be due to an impurity and it should therefore be deleted from the figures there quoted.)

Monohydroxymonopiperidinoerythroaphin-fb.—(i) *From hydroxyerythroaphin-sl*. Hydroxyerythroaphin-*sl* (100 mg.) was dissolved in a mixture of pyridine (5 c.c.) and piperidine (5 c.c.) and kept at room temperature for 24 hr. The resulting deep green solution was added to 3*N*-hydrochloric acid at 0°, the cherry-red product extracted with chloroform, the extract washed with water and dried, and the solvent removed. The residue was crystallised repeatedly from chloroform-methanol, giving *monohydroxymonopiperidinoerythroaphin-fb* as deep red plates (Found, on a sample dried at 100°/2 × 10⁻⁴ mm. for 24 hr.: N, 2.2. C₃₅H₃₁O₉N requires N, 2.3%). Light absorption in CHCl₃: max. at 564, 529, 448, and 336 mμ (log ε 4.14, 4.05, 4.33, and 3.83 respectively). The infra-red spectrum of a mull in Nujol showed maxima at 722, 749, 850, 926, 985, 1067, 1111, 1144, 1175, 1203, 1577, 1629, and 3289 cm.⁻¹.

(ii) *From hydroxyerythroaphin-fb*. By a similar process hydroxyerythroaphin-*fb* (97 mg.) yielded monohydroxymonopiperidinoerythroaphin (40 mg.), the infra-red spectrum of which was identical with that of the product from the previous experiment.

Erythroaphin-fb from Monohydroxymonopiperidinoerythroaphin-fb.—By reduction with zinc and acetic acid by the method used for dibromodipiperidinoerythroaphin-*fb* (above), monohydroxymonopiperidinoerythroaphin-*fb* (74 mg.) yielded erythroaphin-*fb* (15 mg.) as red needles from chloroform-ethanol. For analysis, the product was dried at 120°/10⁻³ mm. for 8 hr. (Found: C, 70.6; H, 4.4%). The infra-red spectrum, determined on a Nujol mull, was identical with that of authentic erythroaphin-*fb*.

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