Biosynthesis of Anthraquinone Pigments in *Dermocybe*

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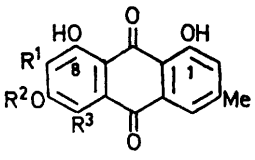
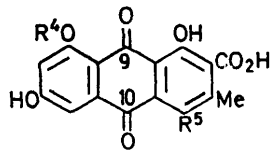
Summary The pathways of anthraquinone biosynthesis in *Dermocybe sanguinea* and *D. semisanguinea* have been investigated; labelled endocrocin is not incorporated into emodin and related anthraquinones.

THE structure of emodin (I) suggests that it may be biosynthesized from endocrocin (IV) by decarboxylation. To test this possibility experimentally, we fed the ammonium



(I) $R^1 = R^2 = R^3 = H$
(II) $R^1 = OH, R^2 = Me, R^3 = H$
(III) $R^1 = R^3 = OH, R^2 = Me$



(IV) $R^4 = R^5 = H$
(V) $R^4 = Me, R^5 = H$
(VI) $R^4 = Me, R^5 = OH$

salt of (IV), ^{14}C-labelled at C-9 and the carboxy-group,[1] to young sporophores of *Dermocybe sanguinea* (Bull. ex Fr.) Wünsche. This mushroom has recently been shown to contain (I), (IV), and several other anthraquinone pigments.[2] After 3 days, the mushrooms (135 g) were collected and worked-up as described previously, without the use of ion-exchange resin, however. The anthraquinone carboxylic acids (IV)—(VI) were separated by chromatography on acetylated polyamide and purified by preparative t.l.c. and paper chromatography (Table 1).

TABLE 1

Incorporation of [C-9 *and* CO_2H-^{14}C] *endocrocin into anthraquinones of* D. sanguinea (*Amount fed*: 16 μM, 0·32 μCi).

Pigment		Amount isolated μM	Amount isolated μCi[a]	Incorporation (%)
Emodin	(I)	785	0[b]	0
Dermoglaucin	(II)	92	0	0
Dermocybin	(III)	182	0	0
Endocrocin	(IV)	57	0·085	26·5 recovered
Dermolutein	(V)	41	0·006	1·9
Dermorubin	(VI)	177	0·03	9·4

[a] Determined by combustion analysis. [b] 210 μM sample.

The results indicate that (IV) is the precursor of the anthraquinone carboxylic acids (V) and (VI). It is not incorporated, however, into the neutral pigments (I)—(III). This casts strong doubt on the possible role of (IV) as a precursor of (I) and related pigments in *Dermocybe*.

That (I) is the precursor of (II) and (III) was shown by a separate experiment. [2,4-$^3H_2$]Emodin-6-mono-β-D-glucoside was administered to the caps of young *D. semisanguinea* (Fr.), a species closely related to *D. sanguinea*. The labelled compound was prepared by treating (I) with

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tritiated 0·7N-KOH (24 h; 110°) followed by heating with 0·7N-KOH (3h; 110°)‡ and conversion into the glucoside.[3] After 2 days, the mushrooms (40 g) were harvested and worked-up as before (Table 2).

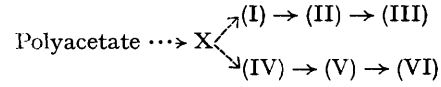
TABLE 2

Incorporation of [2,4-$^3H_2$]*emodin-6-mono-β-D-glucoside into anthraquinones of* D. semisanguinea (*Amount fed*: 7·4 μM, 7·85 μCi)

Pigment	Amount isolated μM	μCi[a]	Incorporation (%)
(I)	22·5	1·86	23·7 recovered
(II)	57	2·06	26·3
(III)	38	0·06	0·8
(IV), (V), (VI) ..	40	0	0

[a] Determined by combustion analysis,

The results are in accord with the sequence in the Scheme for anthraquinone biosynthesis in *Dermocybe*. It is likely



that both series have a common precursor X, which may be endocrocin-9-anthrone[1] or even a compound in which the ring carrying the carboxy-group is not yet aromatic.

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‡ Heating of (I) with KOT for 24 h affords [2,4,5,7-$^3H_4$]-(I), which 're-exchanges' the 5- and 7-T with H on subsequent treatment with KOH. We have shown that the aromatic protons of (I) exchanged with D (0·7N-KOD; 100°) in the order: 7-H (complete within 15 min), 5-H (*ca.* 60 min), 2-H (*ca.* 12 h), 4-H (*ca.* 24 h) (Diplomarbeit W. Lösel, TH München 1966).

[1] W. Steglich and W. Reininger, *Chem. Comm.*, 1970, 178.
[2] W. Steglich, W. Lösel, and V. Austel, *Chem. Ber.*, 1969, **102**, 4104.
[3] L. Hörhammer, L. Farkas, H. Wagner, and E. Müller, *Chem. Ber.*, 1964, **97**, 1662.