

STRUCTURES OF DROSOPTERINS

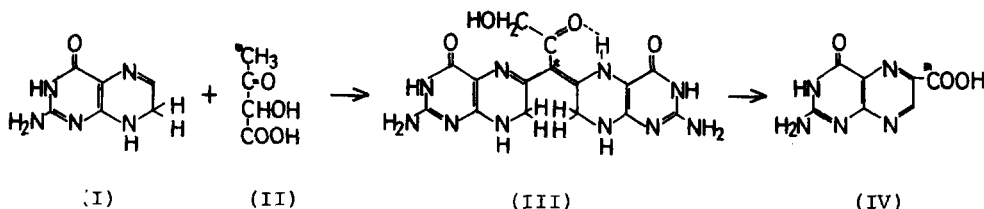
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The molecular formulae and the syntheses of drosopterin and isodrosopterin (*Drosophila* pigments) have been reported.¹⁻³⁾ Recently, Schlobach and Pfleiderer have proposed the structure III for drosopterins (atropisomers).⁴⁻⁸⁾ A new evidence which supports this formulation was that the terminal methyl carbon atom of 2-hydroxy-3-ketobutyric acid-4-¹⁴C (II) was incorporated into the α -carbon atom in the side chain of drosopterins.⁷⁾ We carried out this experiment as described by Schlobach and Pfleiderer.



Ethyl 2-hydroxy-3-ketobutyrate-4-¹⁴C (5 g)⁹⁾ prepared from ethyl 3-ketobutyrate-4-¹⁴C (1.56 mCi/M; 10 g) was hydrolyzed by treatment with 0.2 N sodium hydroxide (325 ml) under nitrogen for 1 hr. 1 M Sodium biphosphate (12.5 ml) and a solution of 7,8-dihydropterin (Na salt) (I) (1 g) in water (100 ml) were added. The mixture was kept standing for 24 hrs at 30⁰C. The resulting drosopterins were purified on a Florisil column (developers: water and 20% aqueous acetone containing ammonia (1% in total)), a cellulose column (developer: water) and a DEAE-cellulose column (developer: 0.04 M ammonium acetate), yield, 57 mg. The drosopterins (14 mg) were treated with 0.15 N sodium hydroxide (2 ml) for 40 min at 90-95⁰C and then oxidized with

potassium permanganate (100 mg). The oxidation product (6-carboxypterin, IV) was purified by chromatography using a DEAE-cellulose column (developer: 0.004 N hydrochloric acid) and a cellulose column (developer: 2-propanol, 1% ammonia (2:1)), yield, 1.12 mg (17%). Acetic acid was determined for drosopterins (Kuhn - Roth), found, 15.2% (calcd., 13.8%). The specific radioactivities of drosopterins, 6-carboxypterin (IV) and acetic acid were determined by using a Beckmann LS-250 liquid scintillation counter and Bray's scintillator¹⁰).

Specific Radioactivity:	Drosopterins	1,711 cpm/ μ M,
6-Carboxypterin	169 cpm/ μ M, ¹¹	Acetic acid 1,862 cpm/ μ M

The above evidence definitely shows that the terminal methyl carbon of ethyl 2-hydroxy-3-ketobutyrate-4-¹⁴C is not incorporated in the α -carbon atom of the side chain of drosopterins.

Furthermore, d, l-sepiapterin and 6-acetyl-7,8-dihydropterin were synthesized by the reaction of 3-hydroxy-2-oxobutyric acid I in the presence of zinc chloride. 6-Acetyl-7,8-dihydropterin, a new pteridine found in D. melanogaster sepi, was synthesized in a better yield by the reaction of II and I under similar conditions.¹² Thus, we conclude that drosopterins are produced by the addition reaction of the carbanion formed by decarboxylation of II to the 6 position of I.

Further work on the structures of drosopterins is in progress.

References and Note

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