

1,2-Aryl Migration in the Biosynthesis of Rotenone and Amorphin

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THE co-occurrence of the rotenoid dolineone (I) with the isoflavanone (II),¹ and of toxicarol with "toxicarol isoflavone,"² suggest that rotenoid and isoflavanone biosynthesis have basic similarities.^{3,4}

Experimental evidence, however, is lacking. Characteristic of isoflavanone biogenesis [*e.g.* formononetin (III, R=OMe, R'=H, R''=OH) or biochanin A (III, R=OMe, R'=R''=OH)] is the

¹ L. Crombie and D. A. Whiting, *J. Chem. Soc.*, 1962, 1569.

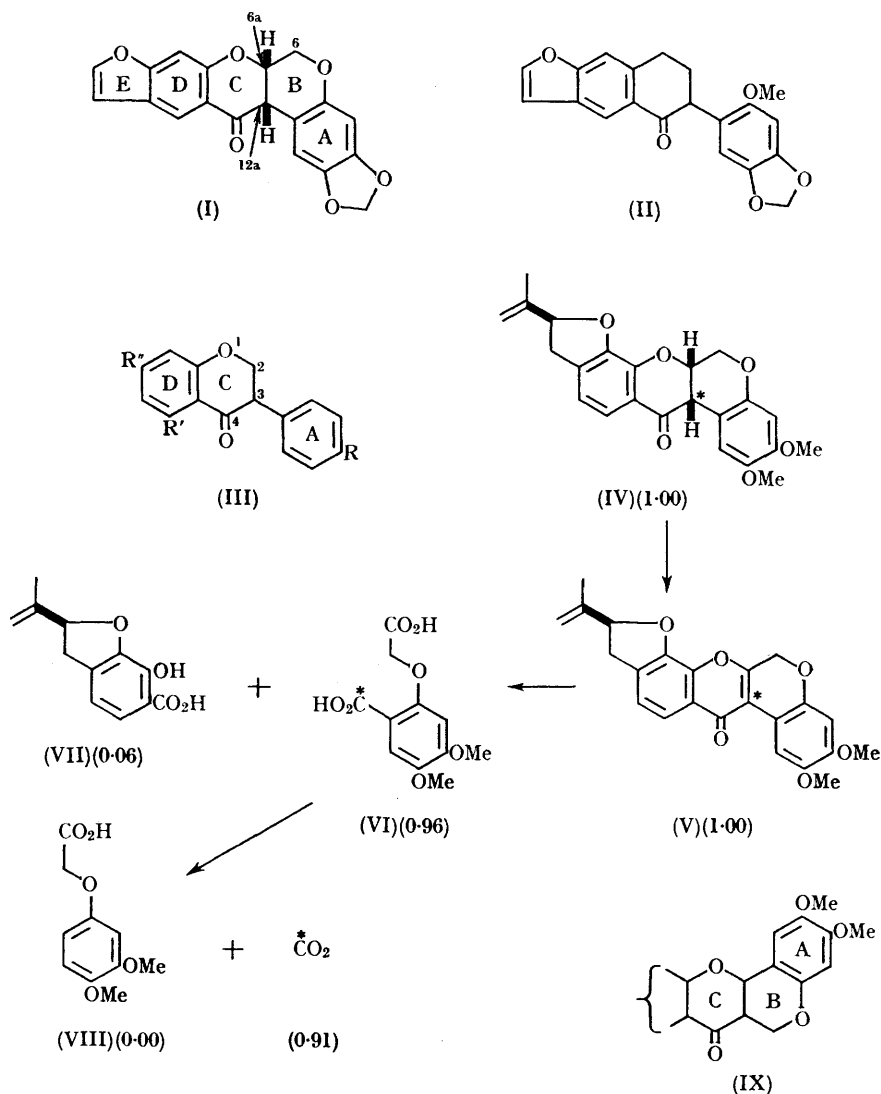
² S. H. Harper, *J. Chem. Soc.*, 1942, 595; S. H. Harper and W. G. E. Underwood, *J. Chem. Soc.*, in the press.

³ H. Grisebach and W. D. Ollis, *Experientia*, 1961, 17, 4.

⁴ L. Crombie, *Fortschr. Chem. org. Naturstoffe*, 1963, 21, 275.

derivation of ring A (but not ring D) by the phenylalanine-cinnamic acid pathway.⁵ During the biosynthesis of (III), a 1,2-migration of aryl ring A from C-2 to C-3 occurs.⁵ The experiments

isolated from the roots (4×10^{-2} % incorporation). Degradations are shown in the scheme: the asterisks refer to the labelling position and the values in brackets to the proportion of the activity



below support a corresponding $6a \rightarrow 12a$ migration of the aryl residue A in rotenoid biosynthesis.

[2-¹⁴C]Phenylalanine was fed to six one-year old *Derris elliptica* plants and the rotenone was

in the compound, referred to rotenone as 1-00. The rotenone was converted into 6a,12a-dehydrorotenone and degraded by alkaline hydrogen peroxide into rissic acid (VI) and tubaic acid

⁵ H. Grisebach, "Recent Developments in the Chemistry of Natural Phenolic Compounds," Ed. W. D. Ollis, London, Pergamon, 1961, 59.

(VII). The rissic acid was decarboxylated to give the acid (VIII) and carbon dioxide. Most of the radioactivity of the original rotenone (minimum 0.91) was carried by the latter which originates from C-12a in (IV). Aryl migration from C-6a to C-12a may happen before ring B is closed or in a precursor such as (IX).³ The

source of the "extra" C-6 present in rotenoids⁴ is also under investigation.

Similar feeding experiments on germinating seeds of *Amorpha fruticosa* demonstrate that analogous biosynthetic considerations apply to the glycosidic rotenoid amorphin.⁶

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⁶ L. Crombie and R. Peace, *Proc. Chem. Soc.*, 1963, 246; J. Claisse, L. Crombie and R. Peace, *J. Chem. Soc.*, in the press.