

ON THE QUESTION OF THE STRUCTURES OF GB1, GB1a AND GB2, A NEW GROUP OF
BISFLAVONOIDS. REMARKS ON THE PUBLICATION BY A. PELTER

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In his paper on the structure of bisflavonoids from the heartwood of Garcinia buchananii, Pelter (1) has discussed the possibility that an 1,2-aryl shift could be involved in the dimerisation of naringenin. He cites a number of chemical analogies for such a rearrangement, but has apparently overlooked the fact that we have proved that such an aryl shift does actually occur in plants during the biosynthesis of 5,7-dihydroxy-4'-methoxyisoflavone (biochanin A) from (-)2S-naringenin(2) and that flavanonols are not intermediates in this rearrangement(3).

In the light of our results, the structures Ba-c proposed by Pelter could be biogenetically derived from the following reaction sequence: oxidative rearrangement of naringenin, resulting in the formation of a transient carbonium ion at C-2 which could subsequently undergo nucleophilic attack by the phloroglucinol moiety of a second naringenin molecule.

It should also be mentioned that a decision between structures I and II should be possible by a tracer experiment with phenylalanine-2-¹⁴C. In the case of structure I, the p-hydroxybenzoic acid obtained by degradation should have no radioactivity, whereas in the case of structure II, about 50 % of the ¹⁴C should be located in the carboxyl group of this acid (4). It might of course be difficult to carry out such an experiment with heartwood constituents.

References

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4. H. Grisebach and N. Doerr, Z. Naturforschg. 15b, 284 (1960).