(*RG* 4850) and the National Science Foundation (*G* 2309).

G. I. H. Hanania

Department of Chemistry,
University of Pennsylvania,
Philadelphia, U.S.A.

D. H. Irvine

Department of Chemistry,
University College,
Ibadan, Nigeria.

---

[1] Krause, R. A., and Busch, D. H., *Nature*, **181**, 1529 (1958).

[2] Whiteley, M. A., *J. Chem. Soc.*, 24 (1903).

[3] Brady, O. L., and Muers, M. M., *J. Chem. Soc.*, 1599 (1930).

[4] Brown, H. C., and Mihm, X. R., *J. Amer. Chem. Soc.*, **77**, 1723 (1955).

[5] Charles, R. G., and Freiser, H., *Anal. Chim. Acta*, **11**, 101 (1954).

[6] Leussing, D. L., and Kolthoff, I. M., *J. Amer. Chem. Soc.*, **75**, 2476 (1953).

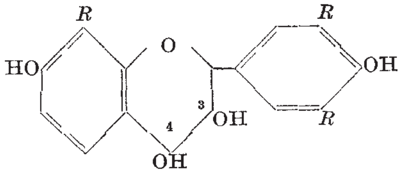
[7] Milburn, R. M., *J. Amer. Chem. Soc.*, **79**, 537 (1957).

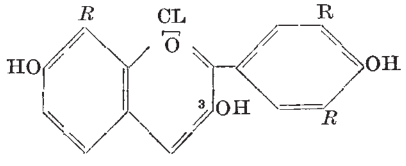
Mechanism of Formation of Anthocyanidins from Leucoanthocyani(di)ns

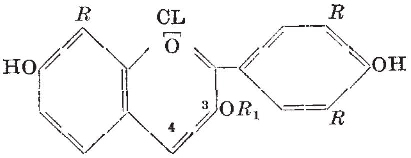
Based mainly on suggestions made earlier by Robinson and Robinson[1] for their hypothetical *leuco*anthocyanin (flavan-2.3.4-triol), the conversion of flavan-3.4-diols (I) into anthocyanidins by similar mechanism has been discussed by Bate-Smith[2], Bauer, Birch and Hillis[3] and by King and Clark-Lewis[4]. The reaction, induced by hydrochloric acid, was regarded as a dehydration of the 3.4-diol group on the heterocyclic ring (loss of hydroxyl at 4 and hydrogen at 3), followed by oxidation[2–4] or by disproportionation[3,4].

Hitherto *leuco*anthocyanins of unknown structure and also flavan-3.4-diols were conveniently treated with aqueous 2 N hydrochloric acid[5], with aqueous 3 N hydrochloric acid/propan-2-ol (1 : 5) under pressure[6] or with hydrochloric acid butan-1-ol[4,7] mixtures at 100° C. In most cases the reaction was characterized by low yields of anthocyanidins formed. Logically, if it is correctly surmised that the initial reaction constitutes a dehydration[1–4] at the diol grouping, the formation of anthocyanidins should be promoted by anhydrous conditions. This theory has now apparently found support in the observation that exclusion of moisture from the reaction mixture effects an increase in the yield of anthocyanidins formed.

For example, 7.3′.4′.5′-tetrahydroxyflavan-3.4-diol[8] is converted into anthocyanidins in approximately 37–42 per cent yield by using anyhdrous $N/30 - N/50$ hydrochloric acid in propan-2-ol in an enclosed tube under pressure. By comparison, this flavan-3.4-diol (*leuco*robinetinidin) is converted into robinetinidin only, in 3 per cent yield in 3 N hydrochloric acid and 20 per cent yield[8] with 3 N hydrochloric acid/propan-2-ol under the conditions of Pigman *et al.*[6] Under anhydrous conditions the reaction is also far more rapid, and maximum yields of anthocyanidins result in 15–20 min. compared with 40 min. under previous conditions[6]. Other flavan-3.4-diols of type I behave similarly.


(I)


(II)


(III)

R = H or OH R_1 = *iso*Propyl

Under the new anhydrous conditions two anthocyanidins of similar coloration but with different rates of migration on paper chromatograms are generated from each flavan-3.4-diol. In all instances examined the anthocyanidin of lower R_F corresponds to that (II) generated under aqueous conditions, and the anthocyanidin of higher R_F is probably the corresponding 3-*iso*propyl ether derivative III (or possibly a 4-*iso*propyl ether of a new type of anthocyanidin). Ether formation with the 3 (or possibly the 4) position of the flavan-3.4-diol occurs prior to conversion into the corresponding anthocyanidin, and is promoted by anhydrous conditions established for the reaction. In the presence of 20 per cent moisture[6] the formation of the ether (III) is almost, but not entirely, inhibited, and mainly one anthocyanidin (II) results.

Pigman *et al.*[6] in 1953 first demonstrated the presence of *leuco*anthocyanins in some commercial tanning extracts, for example, wattle (*Acacia mollissima*), quebracho (*Schinopsis* spp.) and mangrove (*Rhizophora* spp.), and the new method represents a modification of their improved conditions. The tannins present in these extracts may be converted into anthocyanidins in 5–9 per cent, 13–21 per cent (*S. quebracho-colorado*) and 16·5 per cent (*R. mucronata*) yields respectively (cf. ref. 7). Details of a study of the reaction conditions, the reaction mechanism, and implications for the chemistry of condensed tannins will be published elsewhere.

David G. Roux
M. C. Bill

Leather Industries Research Institute,
Rhodes University,
Grahamstown,
South Africa.

Sept. 30.

---

[1] Robinson, G. M., and Robinson, R., *Biochem. J.*, **27**, 206 (1933).

[2] Bate-Smith, E. C., *J. Exp. Bot.*, **4**, 1 (1953).

[3] Bauer, L., Birch, A. J., and Hillis, W. E., *Chem. and Indust.*, 443 (1954).

[4] King, F. E., and Clark-Lewis, J. W., *J. Chem. Soc.*, 3384 (1955).

[5] Bate-Smith, E. C., *Biochem. J.*, **58**, 122 (1954).

[6] Pigman, W., Anderson, E., Fischer, R., Buchanan, M. A., and Browning, B. L., *TAPPI*, **36**, 4 (1953).

[7] Hillis, W. E., and Urbach, G., *Nature*, **182**, 657 (1958).

[8] Freudenberg, K., and Roux, D. G., *Naturwiss.*, **41**, 450 (1954). Roux, D. G., and Freudenberg, K., *Liebigs Ann.*, **613**, 56 (1958).