The Stereochemistry of Biflavanols from Black Wattle Bark: Leucorobinetinidin-(+)-catechin and Leucorobinetinidin-(+)-gallocatechin

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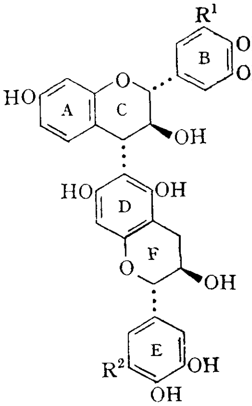
COMPONENTS F, B, and D have been isolated from the bark extract of black wattle (*Acacia mearnsii*).[1] Their individual treatment with propan-2-ol : 3N-HCl under pressure (for anthocyanidins) and with ethanol : 3N-HCl (for catechins) gave, amongst other unidentified degradation products, fisetinidin chloride and (+)-catechin from F, robinetinidin chloride and (+)-catechin from B, and robinetinidin chloride and (+)-gallocatechin from D.

The components were amorphous, and methylation with diazomethane gave amorphous methyl ethers after repeated purification by preparative thin-layer chromatography. Each methyl ether gave an amorphous diacetate {F: $C_{41}H_{44}O_{13}$, m.p. 87—97°, $[\alpha]_D^{20}$ $-124°$ (acetone), $M = 744$ by mass spectrometry; B: $C_{42}H_{46}O_{14}$, m.p. 120—124°, $[\alpha]_D^{19}$ $-71·9°$, $M = 774$; and D: $C_{43}H_{48}O_{15}$, m.p. 140°, $[\alpha]_D^{19}$ $-65·7°$, $M = 804$}. The nuclear magnetic resonance spectra of the individual diacetates at 100 Mc./sec. showed one benzenoid proton as a sharp singlet (τ 3·89 p.p.m.). From integral curves, the total of benzenoid protons (F, 10; B, 9 and D, 8) indicated the absence of one of these from the constituent flavanoid units.

The details of the nuclear magnetic resonance spectra of their acetates (nona-acetate of F, $C_{48}H_{44}O_{20}$, m.p. 115°; deca-acetate of B, $C_{50}H_{46}O_{22}$, m.p. 178—185°, and undeca-acetate of D, $C_{52}H_{48}O_{24}$, m.p. 148°) confirmed their analyses. The heterocyclic protons were in each instance characterized by the upfield position of a doublet τ 5·57 p.p.m. ($J_{2,3} = 10·0$ c./sec.), a three-proton multiplet (τ 4·94 $\sim$ 5·21 p.p.m.) which showed fine structure including a superimposed doublet (τ 5·21 p.p.m., $J_{3,4}$ 9·8 c./sec.) and a triplet downfield at τ 4·29 p.p.m. ($J_{2,3} + J_{3,4} = 19·8$ c./sec.). These doublets and the triplet are spin-coupled, and are all attributable to the C-ring. Remaining protons (F-ring) appear to be a 2-proton (τ 5·12 p.p.m., $J_{2,3} \sim 9·0$ c./sec.), a collapsed multiplet (*ca.* 4·97 p.p.m.), and two methylene protons ($\tau = 6·96 \sim 7·33$ p.p.m.), as expected from 2,3-*trans*-flavan-3-ols.

The clearly-defined upfield uncoupled benzenoid proton (singlet, $\tau = 3·89$ p.p.m.) in the methyl ether diacetates shows that the linkages in F and B (and also possibly in D) are, as expected,[2] from C-4 of the C-ring to the 6- or 8- position of the phloroglucinol D-ring as in (I) and (II) respectively. Choice between these alternatives is not possible without prior knowledge of the chemical shifts of similar protons in 6- and 8-substituted flavans.

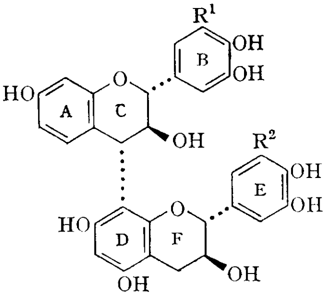


(I)

The linkage from C-4 of the leucoanthocyanidin to the phloroglucinol (D-ring) nucleus of the catechin moiety was confirmed in all three components by mass spectrometry of their methyl ether diacetates. Significant peaks in each spectrum could, as before,[3] be rationalized by invoking a reverse Diels–Alder reaction (fission) of the F-ring. Links to catechol or pyrogallol E-rings could be excluded on this basis.

The large coupling constants ($J_{2,3} = 10·0$ c./sec., $J_{3,4} = 9·5$ c./sec.) of the C-ring heterocyclic protons are consistent with a 2,3-*trans*-3,4-*trans*- and 2(*eq*),-3(*eq*),4(*eq*)-arrangement of substituents on the leucoanthocyanidin portion of the molecule. Each wattle constituent, therefore, has a 2,3-*trans*-3,4-*trans*-(leucoanthocyanidin) and 2,3-*trans*-(catechin) relative configuration. An appropriate mixture of either (+)-leucofisetinidin or (+)-leucorobinetinidin (both 2*R*, 3*S*, 4*R*) with (+)-catechin or (+)-gallocatechin (both 2*R*, 3*S*) when warmed with 0·4N-HCl (*cf.* ref. 4) forms, amongst other products, compounds which show identity with F, B, and D in colour reactions and R_F-values on two-dimensional paper chromatograms. Accordingly, the absolute configurations of F ($R^1 = R^2 = H$), B ($R^1 = OH$, $R^2 = H$) and D ($R^1 = R^2 = OH$) are most likely those indicated in (I) or (II).

The biflavanols, F, B, and D, constitute a new class in which members of the "resorcinol series" of flavanoid compounds are *C*-linked with those of the "phloroglucinol series" (*cf.* refs. 3—6).



(II)

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