# Stereochemistry of a Natural 4,6-Linked (+)-Bileucofisetinidin

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"LEUCOFISETINIDIN 3", a homogeneous tannin fraction (by paper chromatography) from the heartwood of black wattle (*Acacia mearnsii*),[1] is resolved into three components by paper ionophoresis in borate buffer.[2,3] Following methylation of the fraction with diazomethane, the mixture was separated by preparative thin-layer chromatography. The most prominent crystalline component, $C_{36}H_{38}O_{11}$, m.p. 167°, $[\alpha]_D^{20}$ + 63·7° (*c*, 0·8 in ethanol), was a hexa-*O*-methyl derivative.

The hexamethyl ether gave an amorphous triacetate, $C_{42}H_{44}O_{14}$, m.p. 115°, $[\alpha]_D^{20}$ + 89·8° (*c*, 0·5 in ethanol), $M$ = 772 by mass spectrometry. The complex nuclear magnetic resonance spectrum of the triacetoxy-hexa-*O*-methyl derivative at 100 Mc./sec. confirmed the presence of three acetyl ($\tau$ 8·20, 8·22, and 8·24 p.p.m.) and six methoxyl groups [$\tau$ 6·17, 6·19 (two methoxyls each) and 6·27, 6·32 p.p.m. (one methoxyl each)]. Such grouping of methoxyl proton resonances (*cf.* diastereoisomeric 3,4-diacetoxy-7,3′,4′-trimethoxyflavans[4]) and the presence of six heterocyclic protons was consistent with the presence of two flavan units each based on resorcinol and catechol nuclei (*cf.* degradative evidence[1]). The presence of three acetoxy-groups and a total of eleven benzenoid protons representing a loss of one of the latter, indicated a link from the heterocyclic system of one flavan unit to the benzenoid system of the other.

Application of spin-decoupling methods showed the presence of two ABX heterocyclic proton systems with allocations as in the Figure. The multiplet centred at $\tau$ 4·50 p.p.m. consists of the overlap of two C-3 proton quartets, while the remaining heterocyclic protons are represented by doublets attributable to spin-coupled protons at C-4 and C-2. The downfield position of one heterocyclic proton at C-4 (F-ring) ($\tau$ = 3·84 p.p.m.) is attributable to the simultaneous presence of an acetoxy-group at this carbon as in 2,3-*trans*-3,4-*trans*-flavan-3,4-diols (3·78 p.p.m.),[4] (+)-peltogynol (3·75 p.p.m.),[5] and (+)-mopanol (3·76 p.p.m.).[5]

Those benzenoid proton resonances which are located upfield ($\tau$ = 3·24—3·68) show a single clear ABX system (Figure) attributable to the 5-, 6-, and 8- positions on the A-ring ($J_{5,8}$, 8·5; $J_{6,8}$, 2·5 c./sec.). Superimposed upon these are two singlets ($\tau$ = 3·42, 3·61 p.p.m.), which are assigned

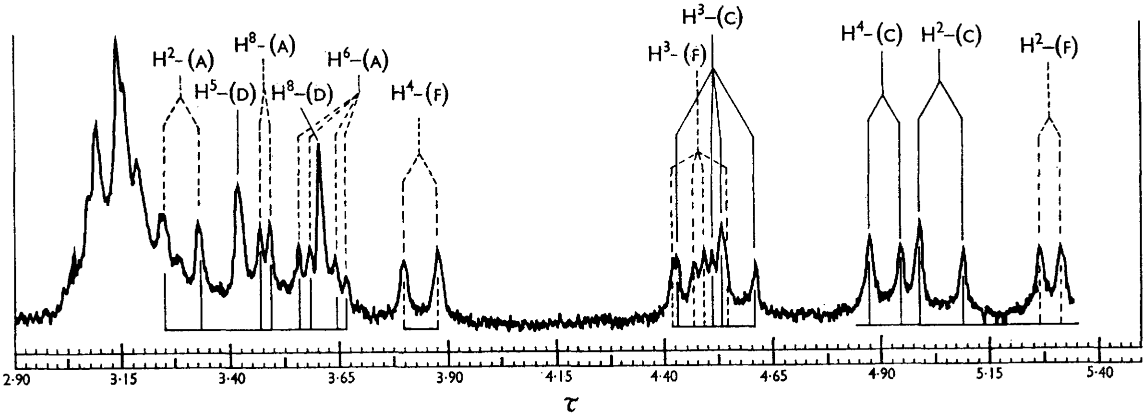


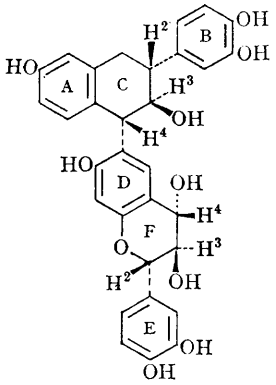
FIGURE. *Benzenoid and heterocyclic proton resonances of (+)-bileucofisetinidin.*

to *para*-coupled protons ($J < 1$ c./sec.) at the 5- and 8-positions respectively on the D-ring, the downfield proton being broadened by long-range coupling with a benzylic proton. The above indicates a link to the 6-position on a resorcinol nucleus rather than to the 6′-position on a catechol nucleus. The two identical and superimposed ABC systems originating from the catechol B- and E-rings occur downfield as in most flavanoids and overlap in one broad, partly resolved signal ($\tau$ = 3·00—3·24 p.p.m.).

The mass spectrum of the triacetoxy-hexa-*O*-methyl derivative, molecular ion peak at 772, may be rationalized by invoking a reverse Diels–Alder reaction of the F-ring. The significant fragments at $m/e$ 519 ($M-253$), 490 ($M-282$), 447 ($M-325$), and 431 ($M-341$), may be accommodated only on the basis of a linkage to a resorcinol nucleus, the alternative linkage to a catechol nucleus being excluded.

The tannin represents the first of a new group of 4,6-linked 5-deoxybiflavans in which both units belong to the leuco- or pro-anthocyanidin group, and also the first instance where the mode of link in a biflavan is established unambiguously. Similar links in biflavans have been suggested,[6–8] and were initially proposed by Freudenberg.[9]

The large spin–spin coupling constants of the heterocyclic protons (C-ring: $J_{2,3}$, 10·3; $J_{3,4}$, 7·3 c./sec., and F-ring: $J_{2,3}$, 5·1; $J_{3,4}$, 8·0 c./sec.) indicate that the tannin has a 2,3-*trans*-3,4-*trans*-arrangement of substituents for each flavan unit (*cf.* $J$ for four possible geometrical arrangements of leucofisetinidins[4]), for which a 2*R*, 3*S*, 4*R*–2*R*, 3*S*, 4*R* (I) configuration is inferred from its association with (+)-mollisacacidin (2*R*, 3*S*, 4*R*).[10]



(I)

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