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II. TWO NEW FLAVONES FROM TEPHROSIA POLYSTACHYOIDES BAK.F.*

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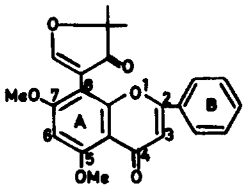
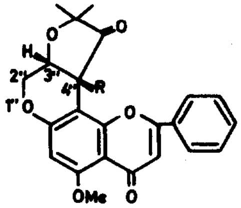
Tachrosin, a novel flavone isolated from Tephrosia polystachyoides Bak.f. has been shown to have structure (1).[1] We now report the structures of two minor components, stachyoidin (2) and tephrodin (3), also isolated from T. polystachyoides Bak.f.

(1)





(2) R=H

(3) R=OCOCH$_3$

(4) R=D

Accurate mass determination on the M$^+$-ion of stachyoidin indicates a molecular formula of $C_{23}H_{20}O_6$, while elementary analysis gives a molecular formula of $C_{23}H_{20}O_6 \cdot CH_3OH$, m.p. 113-114° (from methanol-petroleum ether 40-60°), $[\alpha]_D^{24}$ - 330.0° (c = 1.00, CH_3OH). Stachyoidin gives a positive Shinoda test[2] for a flavone and shows a band at 1645 cm^{-1} in the IR spectrum (KBr) characteristic of a flavone.[3] A band at 1770 cm^{-1} is assigned to a 3-furanone group.[1] The UV spectrum (CH_3OH) exhibits absorption at 218, 268 and 308 (shoulder) nm (log ϵ 4.52, 4.55 and 4.23 respectively), suggesting a 5,7 di-oxygenated flavone.[1]

The NMR spectrum** of stachyoidin reveals the presence of one mole of methanol, as is evident from the singlets at τ 6.56 (3H) and τ 8.13 (1H, D_2O exchangeable). The C-3 proton appears as a singlet at τ 3.34, indicative of a flavone.[4] The unsubstituted nature of the B-ring is revealed by multiplets at ca. τ 2.04 (2H) and ca. τ 2.54 (3H). A singlet at τ 6.11 (3H) is assigned to the aromatic methoxyl group. The chemical shift of the methoxyl group shows a characteristic solvent dependence upon change of solvent from $CDCl_3$ to benzene-d_6, the singlet now appearing at τ 6.68. This pronounced upfield shift shows that the methoxyl group has an ortho-proton and thus proves stachyoidin to be substituted at C-8.[5]

The proton at C-6 appears as a singlet at τ 3.62. The high field singlets at τ 8.63 (3H) and τ 8.79 (3H) are assigned to two C-methyl groups.

The benzylic proton at C-4" appears as a doublet at τ 5.74 (J_1 = 7.5 Hz) due to coupling with the methine proton at C-3". The two methylene protons appear as a pair of doublets

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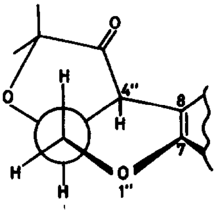
* For part I see ref. 1.

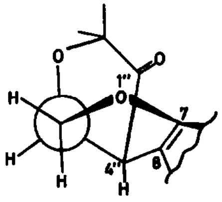
** NMR spectra were recorded on a Varian HA-100 instrument with TMS as internal standard (τ = 10.00) in $CDCl_3$.

at τ 5.62 (1H, J_2 = 12.0 Hz) and τ 5.91 (1H, J_2 = 12.0 Hz). Both these doublets exhibit further splitting as a result of the coupling of the methylene protons with the methine proton at C-3" (J_3 = 3.1 Hz and J_4 = 2.0 Hz respectively). The methine proton at C-3" appears as a pair of double doublets at τ 5.15 (J_1 = 7.5 Hz, J_3 = 3.1 Hz and J_4 = 2.0 Hz).

From the coupling constant for the protons at C-3" and C-4" (J_1 = 7.5 Hz) a cis ring-fusion is assumed. Following this assumption there are two possible conformations for stachyoidin *viz*. (5) and (6).



(5)



(6)

From the observed values for the coupling constants between the methylene protons and the methine proton at C-3" (J_3 = 3.1 Hz, J_4 = 2.0 Hz) and by application of the Karplus equation, it follows that (6) is the preferred conformation of stachyoidin.

The relationship between the protons is further proven by exchanging the methine proton at C-4" with deuterium[6] (4, R = D), resulting in the disappearance of the doublet at τ 5.74 and the collapse of the pair of double doublets at τ 5.15 to a double doublet (J_3 = 3.1 Hz, J_4 = 2.0 Hz).

Acetoxylation of stachyoidin with lead-IV-acetate in glacial acetic acid gives a compound, $C_{25}H_{22}O_8$, m.p. 236-237° (from benzene-petroleum ether 40-60°), $[\alpha]_D^{24}$ - 22.5° (c = 0.98, CH_3OH), identical with tephrodin (3).

The NMR spectrum of tephrodin (3) shows a singlet at τ 7.94 (3H) which is assigned to the acetate group. The rest of the spectrum is similar to that of compound (4).

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