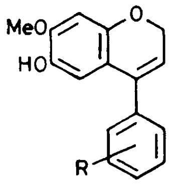
New Neoflavanoid Structural-types from *Dalbergia*

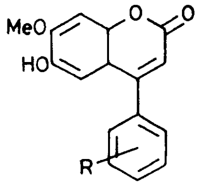
By DERVILLA M. X. DONNELLY,* THURLOCH Ó CRIODAIN, and MICHAEL O'SULLIVAN
(Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland)

Summary The isolation and structural elucidation of a series of 3-arylbenzofurans and the first binary neoflavanoid is reported.

ALTHOUGH 6-membered heterocyclic neoflavanoids [neoflavenes (**1**) and 4-arylcoumarins (**2**)] in *Dalbergia* species are well documented,[1] the only known neoflavanoids with a 5-membered heterocyclic ring are (2*S*,3*S*)-melanoxin (**3**), (2*R*,3*R*)-obtusafuran (**4**), and the recently reported isoparvifuran (**5**).[2] The dihydrofurans (**3**) and (**4**), classified with the neoflavanoids on grounds of a biogenetic proposal,[3] have a 1,2-diarylpropanoid skeleton but isoparvifuran is a 2-methyl-3-phenyl-benzofuran. This communication reports on the isolation from *D. baroni* of a series of benzofurans (**5**), (**6**), and (**7**) and on the first binary neoflavanoid which was obtained from *D. latifolia*.



(1)



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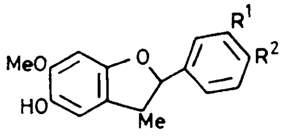
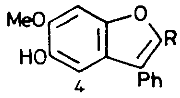


(3) R^1=OH R^2=OMe
(4) R^1= R^2= H



(5) R=Me, isoparvifuran
(6) R=CHO
(7) R=CH$_2$OH

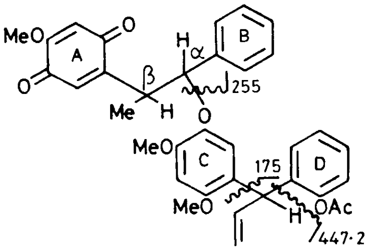
Similarities exist in the ^{1}H n.m.r. spectra of the 5-*O*-acetyl derivatives of the benzofurans (**5**), (**6**), and (**7**). These include (i) singlets (δ 7·19—7·41 and 7·01—7·18) attributable to the 4- and 7-protons, (ii) a broad singlet (δ 7·4) in each case associated with the phenyl substituent, and (iii) one methoxy (δ 3·85) and one phenolic acetate (δ 2·3) resonance in each compound. In addition the benzofuran (**6**) has a signal (δ 9·6) consistent with a formyl group and the di-*O*-acetyl derivative of (**7**) has signals (δ 2·28 and 2·10) which were assigned to a phenolic (ν 1765 cm^{-1}) and an aliphatic ester (ν 1736 cm^{-1}). The benzofuran (**5**) which has a singlet (δ 2·48) for a methyl group differed in melting point (123—

124 °C) and u.v. spectrum from the known 5-hydroxy-6-methoxy-3-methyl-2-phenylbenzofuran (161 °C),[4] but had identical spectroscopic properties and melting point to those reported for isoparvifuran.[2]

The structures (**6**) and (**7**) were confirmed by independent synthesis *via* an oxidative rearrangement of dalbergin[5] which unambiguously indicated the presence of a phenyl group at the **3**-position and an oxygenated carbon at the 2-position of the benzofuran. This series of 3-phenylbenzofurans demonstrates a possible biogenetic oxidative sequence.

The second structural-type was an optically active binary neoflavanoid isolated from *D. latifolia* Guill et Perr., for which the name dalcriodain is proposed. The spectroscopic data determined on its monoacetate derivative, m.p. 118—120 °C (n-hexane); $[\alpha]_D^{24}$ + 128° (c 4·0 $CHCl_3$); $\nu_{max}(CHCl_3)$ 1755 (ArOAc), 1670, and 1649 cm^{-1} (quinone); $C_{35}H_{34}O_8$, M^+ 582·22254, indicate that the compound possesses two structural moieties; namely a 1,1-diarylpropene [$\delta(CDCl_3)$ 4·8 (J_{BX} 17, J_{BC} 0·9, and J_{BA} 1·0 Hz), 5·2 (J_{CX} 10, J_{CA} 1·0, and J_{CB} 0·9 Hz), 6·3 (J_{XB} 17, J_{XC} 10, and J_{XA} 5·3 Hz), and 5·5 (m) ($CH_ACH_X{=}CH_BH_C$ system)] resembling latifolin [1-(2-hydroxyphenyl)-1-(5-hydroxy-2,4-dimethoxyphenyl)-prop-2-ene];[1] and a 1-phenyl-2-benzoquinonylpropane [δ_H ($CDCl_3$) 1·34 (d, J 7·0 Hz, Me), 5·86 and 6·42 (2 × s, quinone-H), 4·9—5·1 (m, H_α), and 3·5—3·7 (m, H_β); δ_C ($CDCl_3$) 13·22, 39·13, and 83·16 p.p.m.].

The structure (**8**) which is proposed for *O*-acetyldalcriodain has an interneoflavonyl alkyl–aryl ether linkage between a phenolic group of the propene moiety and the benzyl group of the substituted propane. This structure accounts for the observed rapid breakdown of the molecular ion in the mass spectrum, which by cleavage of the C_α–C_β bond in *O*-acetyldalcriodain (**8**) yields m/z 165 and 417. The latter ion then breaks at the benzyl ether to afford m/z 327 and 328, indicative of two methoxy-groups and an acetate group on one C_{15} fragment. The molecular ion also fragments at the benzyl ether, m/z 327 and 255 (base peak).



(**8**)

The coupling of the neoflavonyl units at the phenol on the more substituted ring of the 1,1-diarylpropene moiety was identified from a chemical ionisation (c.i.) mass spectrum of (**8**) in which the ions m/z 447 and 175 were present. From a study of the c.i. spectra of a series of dalbergiphenols, it was observed that fragmentation about the benzylic carbon is the primary method of breakdown.[6]

The oxygenation pattern in ring c of the binary neoflavanoid (**8**) proved to be similar to that in latifolin as hydrogenation of (**8**) with subsequent acetylation gave di-*O*-acetyldihydrolatifolin.

A scarcity of material is the limiting factor in defining the absolute stereochemistry of (**8**). Further structural work is in progress on additional bineoflavanoids found in *D. cochinchinensis*: cochins A (M^+ 522), B (M^+ 554), and C (M^+ 538).

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