

CIS-TRANS ISOMERISM OF A NEW α -HYDROXYCHALCONE FROM
BERCHEMIA ZEYHERI SOND. (RED IVORY)

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Initial proof of the occurrence of an α -hydroxychalcone in Nature was provided recently through the isolation in these laboratories of derivatives of $\alpha,2',3,4,4'$ -pentahydroxychalcone, prominent amongst the heartwood flavonoids of Trachylobium verrucosum (Leguminosae)¹. Indication of a wider distribution of this biogenetically significant class of compounds is presently provided by the characterization, as methyl ethers, of both cis- and trans-isomers of $\alpha,2',4,4',6'$ -pentahydroxychalcone from the red wood of Berchemia zeyheri (Rhamnaceae).

On two-dimensional chromatograms the presence of the latter α -hydroxy-chalcone (I, II, III; R=H) is masked by its concurrence with a high concentration of the 2-hydroxy-2-benzylcoumaranone analogue, maesopsin (IV; R=H)^{2,3}. Methylation of this fraction with diazomethane or with dimethyl sulphate-K₂CO₃ in dry acetone provides the full methyl ethers of the predominant trans- (II; R=Me, m.p. 132°) and also cis-isomers (III; R=Me, m.p. 161°) of the enolic form of the chalcone, in addition to maesopsin tetramethyl ether (IV; R=Me). The isomeric chalcones show marked differences in their mobility on kieselgel [t.l.c. - R_F 0.43, 0.31 resp. in benzene-ethyl acetate (8:2 v/v)], and in their ultra-violet [$\lambda_{\max}^{\text{CHCl}_3}$ 327.5, 242 nm (log ϵ 4.31, 4.10), and 300 (shoulder \sim 340), 243 nm (log ϵ 3.95, 4.09) resp.], infra-red [however, both exhibit $\nu_{\max}^{\text{CHCl}_3}$ 1660 cm⁻¹ (C=O)] and n.m.r. spectra (Table).

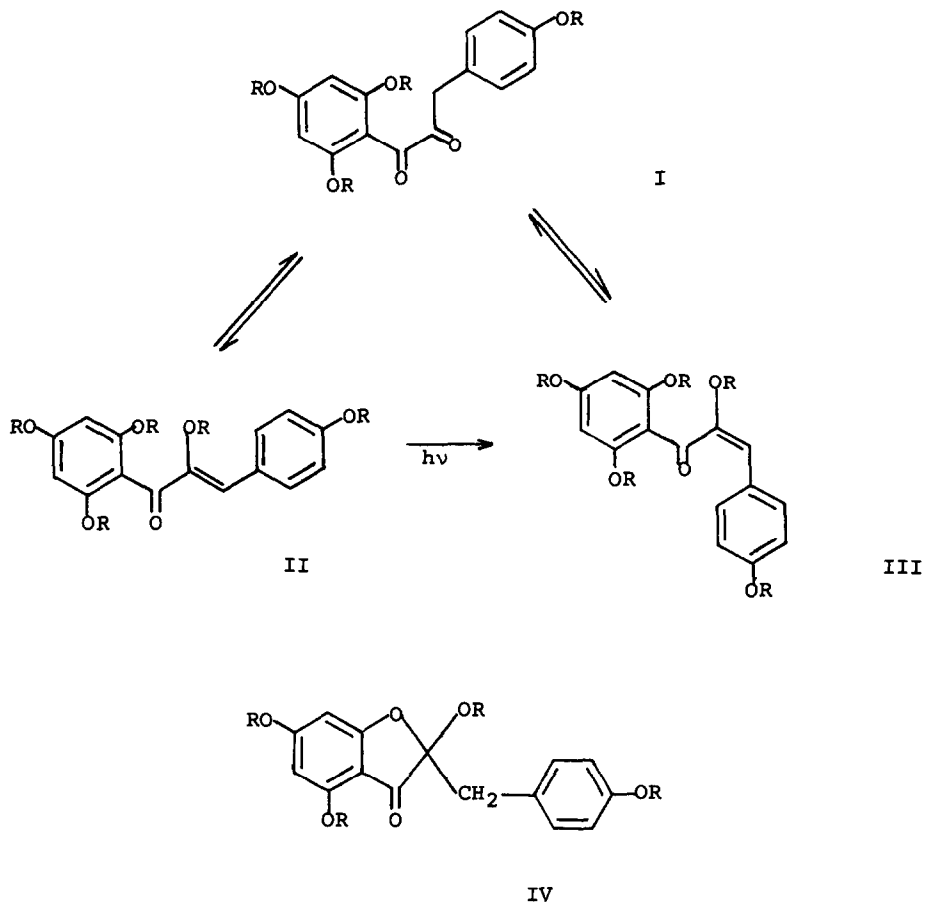


Table. N.m.r. spectra of trans- and cis- $\alpha,2',4,4',6'$ -pentamethoxychalcones.

	τ -values				
	2-H + 6-H	3-H + 5-H	β -H	3'-H + 5'-H	OCH_3
<u>trans</u>	2.25 (d)	3.13 (d)	3.44 (s)	3.82 (s)	6.16 (6H) (s) 6.20 (3H) (s) 6.26 (6H) (s)
<u>cis</u>	2.85 (d)	3.33 (d)	3.93 (s)	4.05 (s)	6.25 (12H) (s) 6.30 (3H) (s)

(d = doublets, $J \sim 8.5$ Hz, s = singlets)

Proof of structure was provided by synthesis of trans- $\alpha,2',4,4',6'$ -penta-methoxychalcone (II; R=Me) from $\omega,2,4,6$ -tetramethoxyacetophenone and anisaldehyde with KOH in ethanol-water, followed by its isomerization to the cis-form (III; R=Me) by photolysis at 350 nm in methanol for 5 hr. N.m.r. spectra of the synthetic and natural compounds were identical and mixed melting-points of the appropriate synthetic and natural pairs showed no depression. The light-induced trans \longrightarrow cis isomerization reaction confirms their stereochemistry⁴, while the spatial orientation of the isomers is probably that illustrated (II, III)⁵.

The unsubstituted condition of the α -hydroxychalcone was established (n.m.r. spectrometry) by isolation of its penta-acetate, following acetylation of the appropriate fraction. Its high mobility in aqueous medium on paper chromatograms (as opposed to the non-migration of all planar flavonoids⁶) and its colourless nature suggest that the keto-form of the free phenol (I; R=H) predominates, existing in equilibrium with the two enolic forms (II, III; R=H). On this premise, their exclusively enolic form and the phenomenon of cis-trans isomerism amongst derivatives of α -hydroxychalcones are to be anticipated. An earlier claim of cis-trans isomerism relating to a natural chalcone of the 'conventional' type (okanin, 2',3',4,4'-tetrahydroxychalcone)⁷ is open to serious doubt⁸.

The new group of α -hydroxychalcones provide the possibility of a biosynthetic path leading directly from phenylpyruvic acid to those 3-hydroxyflavonoids (or their equivalent) which constitute the bulk of heartwood flavonoids. By comparison, 'conventional' chalcones, the accepted key intermediates require successive reductive (to cinnamic acids) and oxidative steps (3-hydroxylation of the flavanone) to achieve similar conversion. Isomerization of the keto-form (I; R=H) of the α -hydroxychalcone in B. zeyheri, for example, leads logically to the 2-hydroxy-2-benzylcoumaranone (IV; R=H, maepsin), whereas its biosynthesis from 'conventional' chalcones cannot be rationalized.

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