

A NEW BIFLAVONYL AC₃ FROM ARAUCARIA CUNNINGHAMII

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The fact that Araucariaceae, the only family of the order Coniferales, which escaped investigation for biflavonyls, attracted our attention. The naturally occurring biflavonyls are found to be derived from apigenin units, mostly as biphenyl and a few as biphenyl ether types. Recently biflavonyls with reduced flavonoid units such as flavans,^{1,2,3} flavanones and flavanone-flavanonol⁴ have also been reported. Pelter⁵ has proposed alternative biflavonyl structures with flavanone-isoflavanone and flavanonol-isoflavanone units.

A survey of the literature (naturally occurring biflavonyls) revealed that cupressuflavone^{6,7} is the sole example of a biflavonyl derived from apigenin with 8-8" interflavonyl linkage. We now report the isolation and structure determination of a new member of this series.

Four biflavonyls both with heterogenous and homogenous chromophores have been isolated from the dried leaves of Araucaria cunninghamii (Araucariaceae) by extraction with acetone. The phenolic extractives AC₁, AC₂, AC₃ and AC₄ were separated by the treatment of chloroform solution with sodium bicarbonate and sodium hydroxide solution. The four components were obtained as single entities by preparative thin-layer chromatography. One of the components AC₃, which was available in workable quantities has been characterized as 5,5"-dihydroxy-7,7',4',4"'-trimethoxy biflavone (I).

The elemental analysis and the molecular weight 594 (mass) were in accord with the formula $C_{34}H_{26}O_{10}$. The infrared spectrum showed carbonyl absorption at 1655 cm^{-1} , characteristic of 5-hydroxyflavones (chelated carbonyl)^{8,9}. The green colouration with ferric chloride further supported the presence of 5-hydroxyl group.

Comparison of the ultraviolet spectrum (Table I) of AC_3 with those of apigenin, acacetin and genkwanin suggested strongly that AC_3 was a derivative of 5,7,4'-trihydroxy flavone.

TABLE I

Ultraviolet Absorption Data of AC_3 , Apigenin and its Derivatives.

$$\lambda_{\max}^{m\mu}(\epsilon)$$

No.	Ethanol	
	Band I	Band II
1. AC_3	272 (34,000)	327 (33,000)
2. Apigenin	269 (18,800)	340 (20,800)
3. Acacetin	269 (20,300)	330 (20,800)
4. Genkwanin	269 (17,000)	337 (19,600)

Further the very similar positions of λ_{\max} but almost double the value of molecular extinction coefficient of AC_3 were suggestive of the compound containing two 5,7,4'-trioxygenated flavone units.

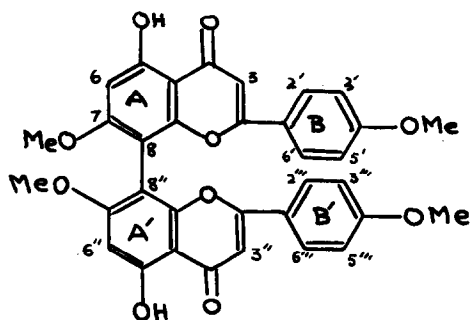
The results of examination of n.m.r. spectrum are given below (Table II).

TABLE II
Chemical Shifts of Protons in AC_3 Fraction.

Signal (δ ppm)	Number of protons	J (cps)	Assignment
7.42 (d)	4	9	2',6' and 2'', 6'' protons (ortho coupling)
6.81 (d)	4	9	3',5' and 3'', 5'' protons (ortho coupling)
6.60 (s)	4	-	3,3" and 6,6" protons
3.8	12	-	Four OMe groups.

d = doublet; s = singlet

The doublet at 7.42 ppm (4-H) is attributed to 2',6' and 2'', 6'' positions showing an ortho coupling ($J=9$ cps) with protons at 6.81 ppm (4-H) assigned to 3',5' and 3'', 5'' positions. A singlet at 3.8 ppm (12-H) is assigned to 4-OCH₃ groups. The absence of meta spin-spin splitting in the region 6.60 ppm (4-H) suggests the presence of either 6 or 8 protons of A rings. AC_3 can not have structure involving 6-8" interflavonyl linkage because of singlet at 6.60 ppm. As the signals for 8-protons generally appear at slightly downfield^{7,10} to 6.60 ppm (region of 6 and 3-protons), AC_3 may therefore be assigned structure of 8,8"-biapigeniyl type (1).



(1)

The study of the effect of base upon the ultraviolet spectra of AC₃ further supported the structure (1). The effect of base upon the spectrum of hydroxyflavones is already known¹¹. With a model hydroxyflavone (5-Hydroxy,7,4'-dimethoxy apigenin), band I shifts from 271 to 292 m μ with moderate increase in intensity, while band II at 325 m μ appears as an inflexion with very low intensity. The spectral changes shown by AC₃, band I (272-287 m μ) with moderate increase in intensity, band II (327 m μ inflexion) with very low intensity, are in full agreement with the above type thereby confirming 5-hydroxy,7,4'-dimethoxy flavone pattern. The spectral information may also be used in supporting the 8-8" linkage already arrived at by n.m.r. studies. The spectral changes in N/500 sodium ethoxide, exhibit features characteristic of ionized AC₃. This observation provides a definite support for 8-8" linkage between two 5-hydroxy-7,4'-dimethoxy flavone units.

Work is in progress and the details will appear shortly.

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