

ON THE BISFLAVONES IN THE LEAVES OF AGATHIS ALBA FOXWORTHY

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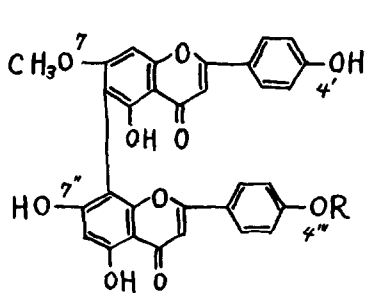
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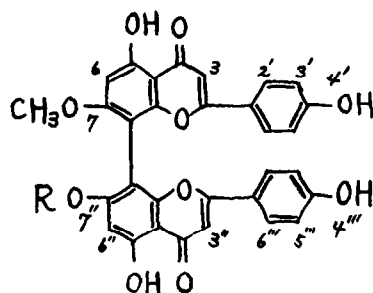
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Two bisflavones, agathisflavone-7-methyl ether (I) and agathisflavone-4'',7-dimethyl ether (II) have been reported as members of a new series of naturally occurring bisflavones isolated from *Agathis palmerstonii*.¹ We now report the isolation and characterization of four bisflavones from the leaves of *Agathis alba* Foxworthy (Araucariaceae), which is the second plant of this genus to be examined for bisflavone pigments. The four bisflavones are I, II, cupressuflavone-7-methyl ether (III) and cupressuflavone-7,7''-dimethyl ether (IV).



I R=H

II R=CH₃



III R=H

IV R=CH₃

A bisflavone mixture obtained from the leaves of this plant showed several spots by TLC suggesting the presence of two series of bisflavones (agathisflavone and cupressuflavone series). In addition to four bisflavones (the two dimethyl ethers being the major components) mentioned above, the mixture seems to be

contaminated with traces of trimethyl ethers of both the series. Solvent fractionation followed by chromatographic separation on silicic acid afforded the four bisflavones, two of which are identified as I and II by comparison of NMR spectra of their acetates with those of two bisflavones isolated from A. palmerstonii¹.

The other two components were characterized as cupressuflavone monomethyl (III) and dimethyl (IV) ethers. The monomethyl ether (III), $C_{31}H_{20}O_{10}$, m.p. 186-190°, a new compound, gave a pentaacetate, $C_{41}H_{30}O_{15}$ (mol wt., found; 762.159, calcd.; 762.158), m.p. 147-150°. The dimethyl ether (IV), $C_{32}H_{22}O_{10}$, m.p. > 300° gave a tetraacetate, $C_{40}H_{30}O_{14}$, m.p. 258-260°. The results of NMR studies of these two acetates and the authentic samples of acacetin diacetate, genkwanin diacetate and cupressuflavone hexaacetate are shown in table 1.

The monomethyl ether pentaacetate gave two sets of two singlets of 3,3" (6.51 and 6.56 ppm) and 6,6" (6.79 and 7.09 ppm) protons because of downfield shift of 7" acetoxy group and two 4H doublets 3',3"',5',5"' (7.03 ppm, J=9 cps) and 2',2"',6',6"' (7.33 ppm, J=9 cps) protons, suggesting no difference between 4' and 4" substitution groups. These data in comparison with the figures of cupressuflavone hexaacetate conclude the structure (III) for the monomethyl ether. The methoxy and acetoxy signals are also compatible with this structure.

The NMR spectrum of the dimethyl ether tetraacetate is identical with a tetraacetate of a bisflavone pigment W11, isolated from Araucaria cunninghamii and A. cookii². Although 8,8"-bisacacetin structure was proposed for this pigment, recently by a reconsideration of NMR spectra, it has been revised to 8,8"-bisgenkwanin structure (IV)^{3,4}. The NMR signals of the dimethyl ether tetraacetate shown in the table are also in accord with bisgenkwanin structure (IV). The chemical shifts of 7-methoxy protons of cupressuflavone series (3.85 or 3.86 ppm) are almost same as those of genkwanin (3.89 ppm). However, 7-acetoxy group of cupressuflavone (2.08 or 2.06 ppm) appears at higher field than that of acacetin (2.33 ppm). This may mean that 7-acetoxy protons will receive more anisotropic effects of flavone nucleus whose

Table 1. NMR signals in CDCl_3 (ppm)

Assigned position	Acacetin diacetate	Genkwanin diacetate	Cupressufla. hexaacetate	Cup. monomethyl pentaacetate	Cup. dimethyl tetraacetate
3 (3")	6.53 (H,s)	6.51 (H,s)	6.56 (2H,s)	6.51 (H,s) 6.56 (H,s)	6.55 (2H,s)
8	6.79 (H,d) J=2.5 cps	6.56 (H,d) J=2.5 cps	---	---	---
6 (6")	7.29 (H,d) J=2.5 cps	6.81 (H,d) J=2.5 cps	7.06 (2H,s)	6.79 (H,s) 7.09 (H,s)	6.79 (2H,s)
3', 5' (3", 5")	6.96 (2H,d) J=9 cps	7.19 (2H,d) J=9 cps	7.01 (4H,d) J=9 cps	7.03 (4H,d) J=9 cps	7.04 (4H,d) J=9 cps
2', 6' (2", 6")	7.78 (2H,d) J=9 cps	7.83 (2H,d) J=9 cps	7.29 (4H,d) J=9 cps	7.33 (4H,d) J=9 cps	7.34 (4H,d) J=9 cps
4' (4")	3.88 (3H,s)	2.32 (3H,s)	2.25 (6H,s)	2.27 (6H,s)	2.27 (6H,s)
7 (7")	2.33 (3H,s)	3.89 (3H,s)	2.08 (6H,s)	3.85 (3H,s) 2.06 (3H,s)	3.86 (6H,s)
5 (5")	2.43 (3H,s)	2.42 (3H,s)	2.48 (6H,s)	2.50 (6H,s)	2.51 (6H,s)

Tetramethylsilane was used as internal standard on a Hitachi H-60 instrument.

orientation is perpendicular to the other flavone nucleus than 7-methoxy group because of its longer chain.

Methylation of dimethyl ether (IV) with deuterized diazomethane⁵ afforded a tetramethyl ether, mass spectrum of which showed a peak of m/e 135, due to a side phenyl fragment, $\text{CH}\equiv\text{C}-\text{C}_6\text{H}_4-\text{OCD}_3$ (found; 135.077, calcd. for $\text{C}_9\text{H}_5\text{D}_3\text{O}$; 135.076). This observation is also compatible with the structure (IV).

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