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SHORT COMMUNICATION

BIFLAVONYL PIGMENTS FROM *THUJA ORIENTALIS* (CUPRESSACEAE)

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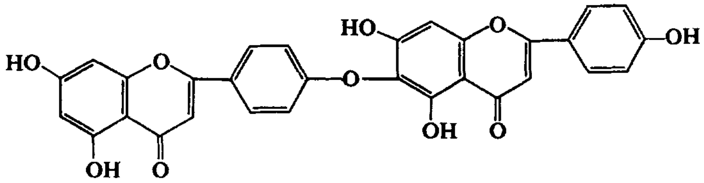
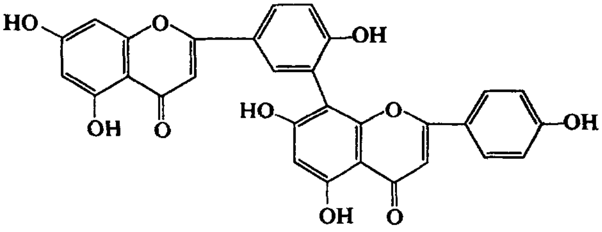
Earlier studies on *Thuja* species[1,2] revealed the presence of biflavonyl hinokiflavone (I) and its partial methyl ethers. In the present communication are reported the results of detailed studies on *Thuja orientalis* (Indian variety) for its biflavonyl pigments.



Hinokiflavone(I)

The phenolic extractives of the leaves of *T. orientalis* were separated by column chromatography on magnesium silicate followed by preparative TLC on silica gel to give two components. The first compound, m.p. 250–255° $[\alpha]_D^{30}$ +100° (pyridine–ethanol, 1 mg/ml) gave a hexaacetate, m.p. 222–225°, and a hexamethyl ether, m.p. 170–171°, mol. wt. 622 (mass) $[\alpha]_D^{30}$ −100° (pyridine–ethanol, 1 mg/ml). It was characterized as amentoflavone (II) by NMR studies using double irradiation technique. The interflavonyl linkage was established by solvent-induced shifts of methoxyl resonances.[3,4] Further support for its identity as amentoflavone (II) was provided by comparison of NMR spectra of its acetate and methyl ether with



Amentoflavone(II)

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[1] T. Swada, *J. Pharm. Soc. Japan* **78**, 1023 (1958).

[2] H. Miura and N. Kawano, *J. Pharm. Soc. Japan* **88**, 1459 (1968).

[3] A. Pelter, R. Warren, M. Ilyas, J. N. Usmani, S. P. Bhatnagar, R. H. Rizvi, M. Ilyas and W. Rahman, *Experientia* **25**, 350 (1969).

[4] M. Ilyas, J. N. Usmani, S. P. Bhatnagar, M. Ilyas, W. Rahman and A. Pelter, *Tetrahedron Letters* 5515 (1968).

those of authentic samples. The solvent-dependent methoxy shifts, i.r., u.v. and mass spectra were also identical. The differences in m.p. of the parent compound and its methyl ether and those reported in the literature appear to be due to the racemic nature of the earlier samples and the optical activity of the materials now isolated. This, therefore, constitutes the first example of the occurrence of a highly optically active amentoflavone in nature.

The second compound, m.p. 345–346°, gave an acetate, m.p. 240–241°, and a methyl ether, m.p. 268–270°. It was characterized as hinokiflavone (I) by NMR studies. The interflavonyl linkage involving C4′–O–C6″ was established by solvent-induced methoxyl resonances[5] of the pentamethyl ether.

EXPERIMENTAL

M.ps were determined on Kofler block and are corrected. NMR spectra were recorded in $CDCl_3$ using tetramethylsilane as internal reference. Magnesium silicate (Woelm) and silica gel G (E. Merck) were used for column and TLC respectively.

Dried and powdered leaves of *Thuja orientalis* (2 kg) yielded a crude mixture of biflavonyls (2·5 g). The crude mixture (1 g) separated by using preparative TLC into pure amentoflavone (240 mg) and hinikiflavone (150 mg).

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[5] A. PELTER, R. WARREN, J. N. USMANI, M. ILYAS and W. RAHMAN, *Tetrahedron Letters* 4259 (1969).