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CUPRESSUFLAVONE, A NEW MEMBER OF THE BIFLAVONYL GROUP

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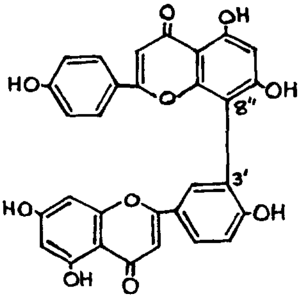
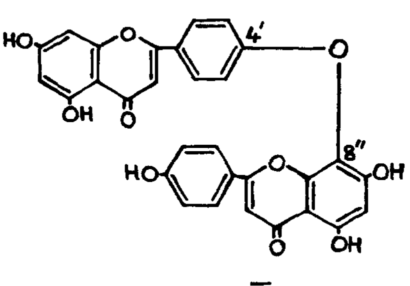
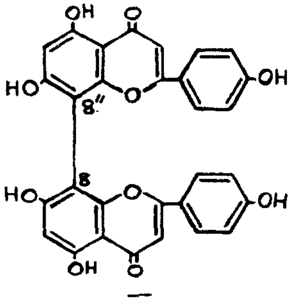
In recent years a number of natural products have been discovered which are dimers of simpler compounds. Biflavonyls are a more recent addition to this class. Eight of these compounds are known and all of them are derivatives of apigenin. Amentoflavone (3',8"-biapigeninyl) (I) is the parent substance of the major group and six others are its partial methyl ethers; these are, sotetsuflavone, bilobetin, gingketin, isogingketin, sciadopitysin and kayaflavone[1]. These have the biphenyl linkage in them. The eighth compound is hinokiflavone (II) which is a biflavonyl ether[2].



I



II



III

We wish to report the isolation from Cupressus torulosa and C. sempervirens of a new representative of the biflavonyl group in which the linkage between the two apigenin units is through the 8 and 8" positions.

Air-dried leaves were exhaustively extracted with hot acetone; waxes and chlorophyll were removed from the acetone concentrate with hot ligroin. The residue was boiled with alcohol and the greenish-yellow solid that remained undissolved was filtered. Further purification could be done by treatment with hot acetone which dissolved the impurities. Final crystallisation from pyridine-methanol gave the pigment as an yellow solid which did not melt below 360°. It was very sparingly soluble in the usual organic solvents, moderately soluble in chloroform and easily in pyridine.

Analytical data agreed with the molecular formula $C_{30}H_{18}O_{10}$; no methoxyl or C-methyl groups were present. The substance gave a hexaacetate (m.p. 251-253°), a tetramethyl ether (m.p. 259-261°), a hexamethyl ether (m.p. 295-297°) and a hexaethyl ether (m.p. 267-269°). The hexamethyl ether formed an oxime, m.p. 290-291°. These properties excluded the possibility that the pigment is any of the already known natural biflavonyls and hence has been given the name cupressuflavone. Degradation of the hexamethyl ether with absolute ethanolic alkali or alkaline hydrogen peroxide gave anisic acid as the only recognisable product.

The proton magnetic resonance spectrum of the methyl ether in deuterochloroform showed the presence of 30 protons and six methoxyl groups in the molecule and was consistent with a symmetrical dimer type of structure. Examining the literature we have come across the publication of Nakazawa[3] wherein is reported the synthesis of 8,8"-biapigeninyl hexamethyl ether (m.p. 297°)and its oxime (m.p. 294°).A direct comparison (m.m.p. and U.V. and I.R. spectra) of the cupressuflavone hexamethyl ether with synthetic 8,8"-biapigeninyl hexamethyl ether showed that they are identical. It is,therefore, concluded that cupressuflavone is the so far unknown 8,8"-biapigeninyl (III).

We convey thanks to Mr. N.S.Bhacca of the Varian Associates for the P.M.R. spectrum and are grateful to Prof. Nakazawa for a sample of synthetic 8,8"-biapigeninyl hexamethyl ether.

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2. Y. Fukui, Chem. Abs., 54, 24699 (1960).
3. K. Nakazawa, Chem. Pharm. Bull., 10, 1032 (1962).