SHORT COMMUNICATIONS

The Structure of a New Flavone, "Arthraxin"

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We have isolated from *Arthraxon hispidus* Makino, commonly called "Kobunagusa," a new flavonoid (I, mp 336°C, empirical formula $C_{21}H_{16}O_9$), which we wish to call "arthraxin." Kobunagusa has been used as a source of natural dyestuff for "Kihachijo," which is a traditionally well-known brilliant yellow silk cloth produced on Hachijo island. The only report on a chemical study of the dyestuff has been made by Hayashi *et al.*,[1] and they did not succeed in obtaining a pure substance because of the difficulty of purification.

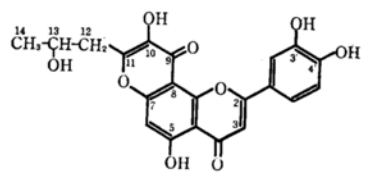
Compound I has neither methoxyl nor methylenedioxy groups, and it forms a penta methyl ether (II), $C_{21}H_{11}O_4(OCH_3)_5$ and a penta acetate (III), $C_{21}H_{11}O_4(OCOCH_3)_5$. The ultraviolet absorption spectrum of I in ethanol showed characteristic absorption bands at 256, and 340 mμ and a pronounced inflection at 273 mμ. The λ_{max} of the band at 256 mμ did not shift with the addition of anhydrous sodium acetate. This fact indicated the absence of the hydroxyl group or the presence of the protected hydroxyl group at C^7.[2] The infrared absorption spectrum of I demonstrated the presence of the $>$CO of γ-pyrone by the band at 1645 cm^{-1} and the absence of a furan ring or a lactone grouping in the molecule. On fusion with caustic potash, I yielded protocatechuic acid and pholoroglucinol.

The NMR spectrum of I in deuterated DMSO indicated the presence of 1H at C^6 (τ 3.70, s), C^3 (τ 3.35, s),[3] C$^{5'}$ (τ 3.10—3.20,m), C$^{2'}$, and C^6 (τ 2.60—2.75, m).[4] The spectrum also suggested the presence of the CH_3–CH(OH)–CH_2– grouping by the signals at τ 8.50 (d, 3H of –CH_3), τ 7.20—7.40 (m, 2H of –CH_2–), and τ 5.30 (m, 1H of –CH–). The NMR spectrum of II in $CDCl_3$ showed the presence of five OCH_3 groups by the signals at τ 6.50 (s, 3H), τ 6.15 (s, 3H), τ 6.10 (s, 3H), τ 6.05 (s, 3H), and τ 5.95 (s, 3H).[5] The mass spectra further showed the presence of five OH groups in I by the difference in the molecular weights of II (482) and I (412).[6]

On the basis of these results, it can be considered that I is a luteolin derivative with a $C_6H_8O_4$ residue attached at C^7 and C^8. As three OH groups are present in the benzene rings, the remaining two OH groups must be present in this $C_6H_8O_4$ residue. The mass spectrum of I gave the fragments of *m/e* 397 and 379, which were interpreted by the general pattern of fragmentation:

$$\underset{(412)}{R\text{–}CH_2\text{–}\underset{OH}{CH}\text{–}CH_3} \xrightarrow{-CH_3} \underset{(397)}{[R\text{–}CH_2\text{–}\underset{OH}{CH}]^+} \xrightarrow{-H_2O} \underset{(379)}{[R\text{–}CH{=}CH]^+}$$

From these data and the fragmentations of the mass spectra of I and II, the following structure was deduced to be the most probable one for arthraxin.



The structure of flavone, in which a side-chain, CH_3–CH(OH)–CH_2– or a γ-pyrone ring is attached to the benzene ring, has not yet been established.

1) K. Hayashi and T. Inoue, *Acta Phytochimica*, **15**, 53 (1949).

2) L. Jurd and R. M. Horowitz, *J. Org. Chem.*, **22**, 1618 (1957).

3) J. Massicot and Jean-Pierre Marthe, *Bull. Soc. Chim. France*, **1962**, 1962; J. Massicot, Jean-Pierre Marthe and S. Heitz, *ibid.*, **1963**, 2712.

4) T. J. Batterham and R. J. Highet, *Australian J. Chem.*, **17**, 428 (1964); A. C. Waiss, Jr., R. E. Lundin and D. J. Stern, *Tetrahedron Letters*, **1964**, 513.

5) R. H. Bible, Jr., "Guide to the NMR Empirical Method," Plenum Press, New York (1967), pp. 106,158; R. I. Reed, *J. Chem. Soc*, **1963**, 5949.