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SYNTHESIS OF HEXA-O-METHYL-6,8"-BINARINGENIN^{+}

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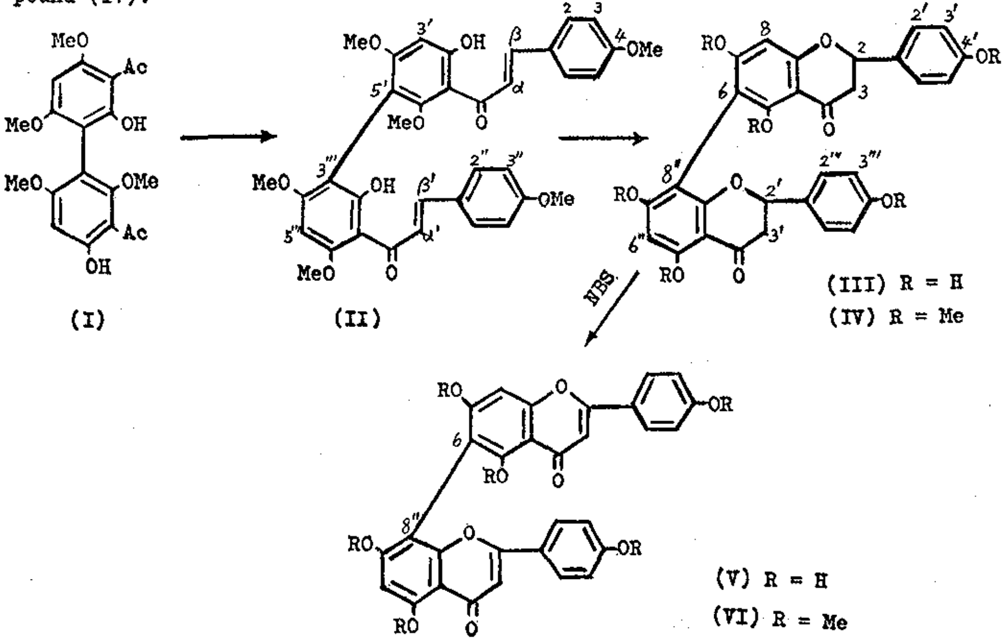
A two-step synthesis of the title compound starting from 3,3'-diacetyl-2,4'-dihydroxy-2',4,6,6'-tetramethoxybiphenyl has been accomplished and the proposed structure of 6,8"-binaringenin for rhusflavanone is confirmed.

The structure of a new biflavanone, rhusflavanone, isolated from the seed-kernel of wax-tree, *Rhus succedanea* (Anacardiaceae) was established previously as 6,8"-linked binaringenin on the basis of spectral and chemical evidence.[1,2] Further collaborative proof for the correctness of the structure (III) for rhusflavanone is now provided by an unambiguous synthesis of the title compound (IV).



3,3'-Diacetyl-2,4'-dihydroxy-2',4,6,6'-tetramethoxybiphenyl (I) was chosen as the starting material, which was procured according to the procedure reported by Kawano *et al*.[3]

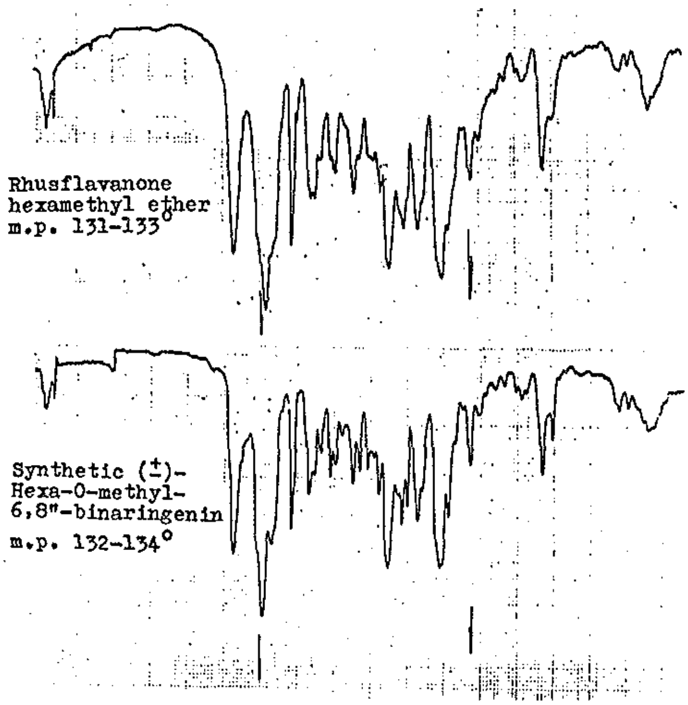
Condensation of I with two moles of *p*-anisaldehyde in the presence of alkali gave bichalcone (II) in 37% yield, m.p. 206-208°, $C_{36}H_{34}O_{10}$, M^{+} *m/e* 626; i.r. (KBr): ~2500 (OH), 1630 (chalcone CO), 1603, 1560, 1520, 1470 (arom.), 835 (1,4-disub.) cm^{-1}; n.m.r. ($CDCl_3$-TMS): two hydroxyl protons at δ 14.03 (s, 1H, OH-2') and 14.42 (*s*, 1H, OH-2"'); six methoxyl groups at δ 3.60 (s, 3H), 3.83 (*s*, 3H), 3.88 (*s*, 3H), 3.90 (*s*, 6H), and 4.11 (*s*, 3H); two aromatic protons at δ 6.25 (*s*, 1H, H-5"') and 6.50 (*s*, 1H, H-3'); eight aromatic protons at 3,3",5,5" and 2,2", 6,6" appeared at δ 7.00 (*d*, *J* 9 Hz, 2H), 7.05 (*d*, *J* 9 Hz, 2H), and 7.68 (*d*, *J* 9 Hz, 4H); four protons at δ 7.93 (s, 2H) and 7.97 (*s*, 2H) indicating the H-α, α', β, β' of the two chalcone units.

Acidic cyclization of II by refluxing with alcoholic H_3PO_4 for 8 days, followed by treatment of preparative t.l.c. (SiO_2, benzene: EtOAc = 1:1, R_f 0.33, blue fluorescence band) gave colorless needles (IV), m.p. 132-134°, for which the spectroscopic data supported the biflavanone structure of IV: i.r. (KBr), 1680 cm^{-1} (flavanone CO): n.m.r. ($CDCl_3$-TMS): δ 5.35~5.62 (*m*, 2H) and 2.83~3.12 (*m*, 4H) indicating the six protons at 2, 2", 3, and 3" positions of the two heterocyclic rings of the two flavanone units; eight aromatic protons at 2',6', 2"',6"', 3',5' and 3"',5"' appeared as doublets (*J* 9 Hz, each 2H) at δ 7.48, 7.24, 7.02 and 6.91; six methoxyl groups at 5, 4 (or 4"'), 7,7" and 5" appeared as singlets at δ 3.65, 3.68 (each 1.5H), 3.72, 3.78 (each 1.5H), 3.82 (3H), 3.85 (6H), and 4.05 (3H); 8 and 6" protons appeared as singlets at δ 6.40, 6.47 (each 0.5H) and 6.30 (1H) respectively. In addition, the n.m.r. spectrum indicated a biflavanone structure (IV), dehydrogenation of which with NBS gave the corresponding hexa-*O*-methyl-biapigenin (VI), m.p. 258-260° (lit., 262-265°,[3] 242°[5]). Thus the chemical and spectroscopic evidences were entirely consistent with biflavanone structure for IV.

The natural rhusflavanone hexamethyl ether, m.p. 131-133°, was identical with the above synthetic compound IV in all respects (m.p., mixed m.p., mass spectra, and t.l.c.) except a just slight difference in i.r. and n.m.r. spectra: the signals of H-8, MeO-5 and 4' (or 4"') at δ 6.47, 3.65 and 3.78 in natural rhusflavanone hexamethyl ether were split into equal intensity doublets in synthetic compound, owing to the racemic and diastereomeric properies.

Thus it has definitely established that rhusflavanone is 6,8"-binaringenin (III).

Satisfactory analytical data were obtained for all the above compounds.



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[+] Paper presented to the 10th IUPAC Symposium on the Chemistry of Natural Products, E-41, Dunedin, New Zealand, August 23, 1976.

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