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RHUSFLAVANONE - A NEW BIFLAVANONE FROM RHUS SUCCEDANEA

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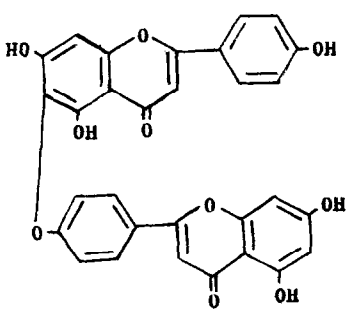
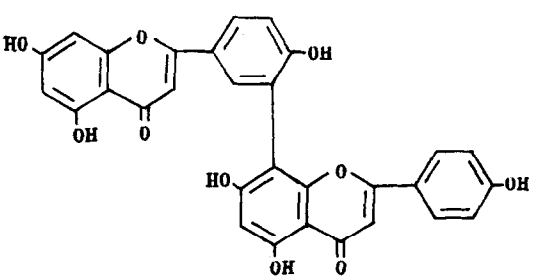
Two optically active biflavone, hinokiflavone (I) and amentoflavone (II) have been isolated from the ethanol extract of defatted drupes of Rhus succedanea L.(Anacardiaceae),[1] which grows in the southern part of China and Japan. Further concentration of the extract yielded crude yellow pigment (ca. 2% yield) which was subjected to column chromatography on silica gel eluting with benzene-EtOAc giving three fractions C_I, C_{II} and C_{III}. The fraction C_I was chromatographed on polyamide (nylon 66) eluting with 70% CH_3OH yielding colorless small needles, m.p. 204-206°, $C_{30}H_{22}O_{10}$, M^+ m/e 542, named rhusflavanone (III).[2] It gave a purple colour in Mg-HCl test and a violet-blue one with alcoholic $FeCl_3$. The i.r. spectrum showed a broad hydroxyl absorption band at 3400 cm^{-1} and carbonyl band at 1630 cm^{-1}. The u.v. spectrum in CH_3OH was very similar to that of naringenin, showing four maxima in region of 336 (3.80), 294 (4.49), 223 (4.65) and 208 (4.68) nm, underwent a bathochromic shift on addition of sodium acetate or $AlCl_3$ indicating the presence of OH groups in 7 and 5 positions. [$\lambda_{max}^{MeOH-NaOAc}$ (log ε) 320 (4.36), 300 (4.36), 271 (4.42), 257 (4.38) nm; $\lambda_{max}^{MeOH-AlCl_3}$ (log ε) 384 (3.88), 315 (4.63), 256 (4.25), 224 (4.76) nm.]

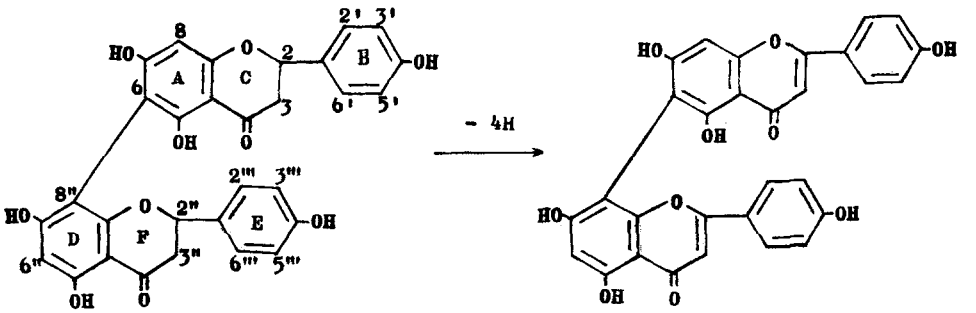


(I) Hinokiflavone



(II) Amentoflavone

The n.m.r. spectrum of rhusflavanone showed the presence of six OH and ten aromatic protons, indicating that rhusflavanone was a biflavanone with C-C linkage. The doublets centered at δ5.48 (dd, J=12 Hz, 4 Hz, 2H) were attributed to H-2 in ring C and H-2" in ring F coupled with the four protons of H-3 and H-3" at δ3.23 ~ 2.80 (m, 4H) by double resonance techniques. The value of coupling constant indicated the equatorial configuration of ring B and E.[3] The singlets at the down-field, δ12.57 and 12.43 were assigned to the two chelating OH groups at 5 and 5"-positions. Eight of the ten aromatic protons appeared as two sets of A_2B_2 pattern, δ7.41 (d, J=9 Hz, 2H) and 6.88 (d, J=9 Hz, 2H), 7.26 (d, J=8 Hz, 2H) and 6.79 (d, J=8 Hz, 2H) due to H-2', H-6', H-3' and H-5' in ring B and H-2"', H-6"', H-3"' and H-5"' in ring E, respectively. The signals at δ6.12 (s, 1H) and 6.07 (s, 1H) were assigned to the protons of H-8 and H-6". As the n.m.r. spectrum is clearly indicative of the unsymmetrical nature of linking between the two naringenin units, the possibility of 8-8" and 6-6" linkages must be ruled out. Rhusflavanone should, therefore, be assigned the structure of 6-8" binaringenin (III).



(III) Rhusflavanone (IV) Agathisflavone

Acetylation of rhusflavanone with pyridine-acetic anhydride gave a hexaacetate as colorless needles, m.p. 130-131°. The i.r. spectrum of the acetate showed absorption at 1688 cm^{-1} (flavanone carbonyl) and at 1770 cm^{-1} (the acetoxy carbonyl groups), and it was transparent around 1650 cm^{-1} indicating no chalcone formation, although isomerisations of flavanone to chalcone during acetylation of flavanones with acetic anhydride-sodium acetate are well known.[4] The signals due to acetoxy protons integrated for 18 protons appeared as singlets (3H) at δ2.40, 2.32, 2.28, 2.15, 2.10 and 2.02. The heterocyclic protons in ring C and F appeared as multiplets at δ5.45-5.35 (2H) and 3.05-2.85 (4H) corresponding to H-2, H-2" and H-3, H-3" of the two flavanone units respectively. Eight of the ten aromatic protons appeared as two sets of A_2B_2 pattern, δ7.55 (d, J=9 Hz, 2H),

7.17 (d, J=9 Hz, 2H), 7.44 (d, J=8 Hz, 2H), 7.14 (d, J=8 Hz, 2H) indicating H-2', H-6', H-3' and H-5' in ring B and H-2"', H-6"', H-3"' and H-5"' in ring E. The signals at δ6.91 (s, 1H) and 6.71 (s, 1H) were assigned to the protons of H-8 and H-6".

The structure of III was further supported by the interpretation of the mass spectra (Schema 1). The fragmentation can be explained on the basis of this structure for rhusflavanone. Finally an unequivocal evidence in support this structure was provided by the dehydrogenation of rhusflavanone with iodine and potassium acetate in acetic acid[5] yielding a biflavone (IV), m.p. >300°, which was methylated to give a methylether m.p. 159-161°, found to be identical with an authentic speciment of hexa-O-methylagathisflavone[6] (TLC, IR and NMR). This is the first report of isolation of new 6,8"-binaringenin in the family- Anacardiaceae.

Studies on the fractions C_{II} and C_{III} are in progress.

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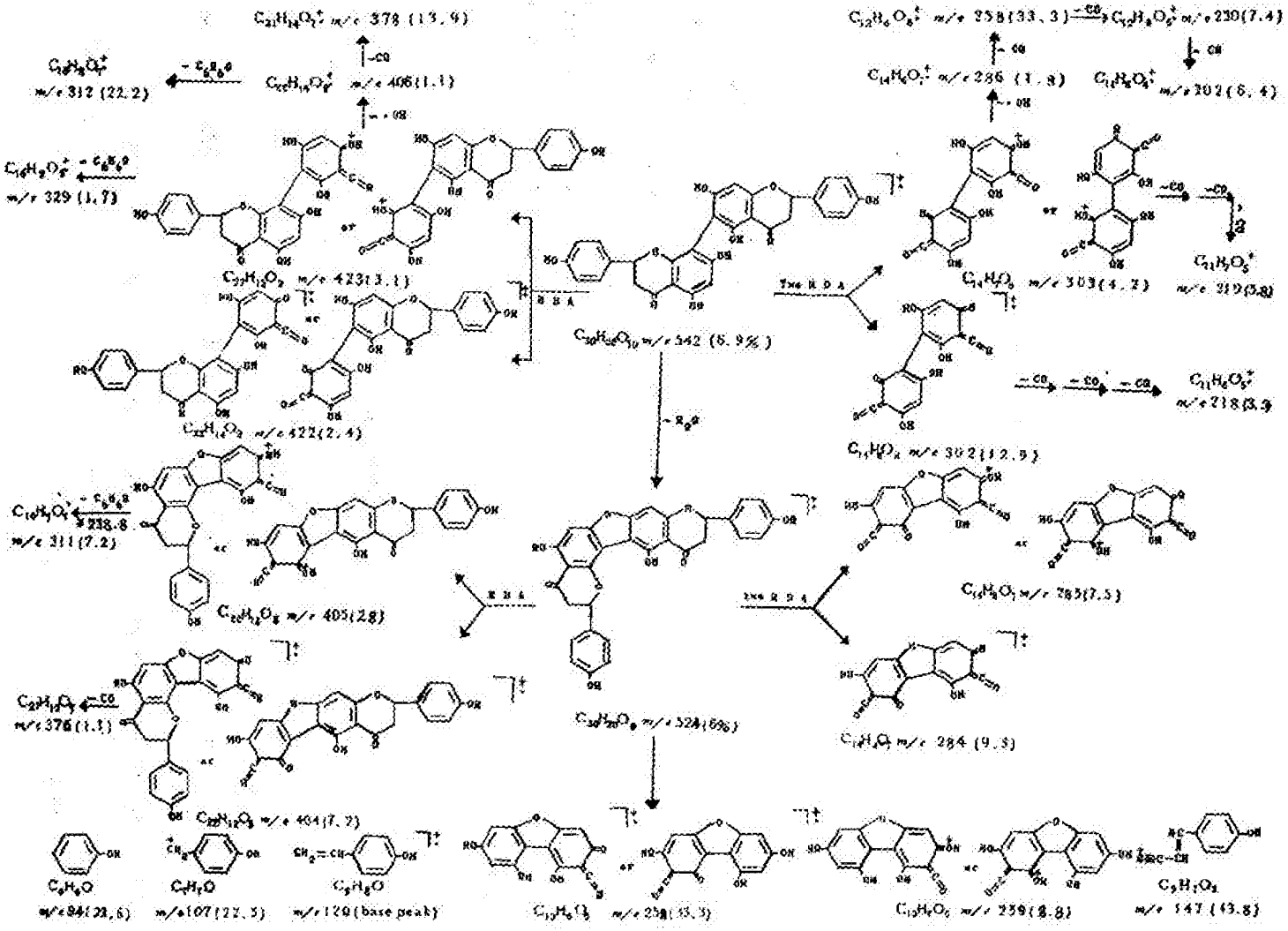

SCHEME 1 Mass spectral fragmentation of 8methylflavanone