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AGATHISFLAVONE FROM THE DRUPES OF *RHUS SUCCEDANEA*

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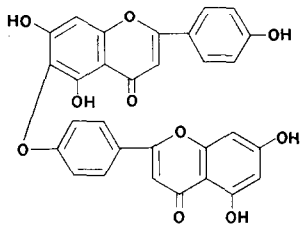
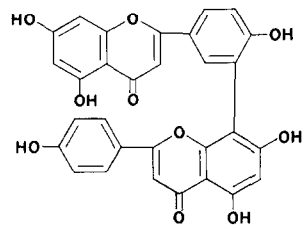
Key Word Index—*Rhus succedanea*; Anacardiaceae; biflavones; agathisflavone.

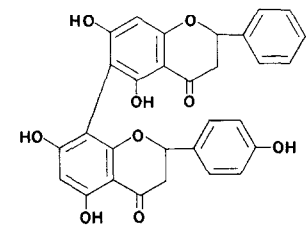
Two optically active biflavones, hinokiflavone (**1**) and amentoflavone (**2**) (each *ca* 0·25% yield) have been isolated from the ethanol extract of the drupes of *Rhus succedanea* L.[1] Further concentration of the extract yielded a mixture of yellow pigments (*ca* 2%) which was subjected to column chromatography on SiO_2 with C_6H_6–EtOAc giving three fractions C_1, C_2 and C_3. Fraction C_1 was found to be a new biflavanone, 6,8″-binaringenin, which was designated rhusflavanone (**3**).[2]



(1) Hinokiflavone



(2) Amentoflavone



(3) Rhusflavanone

In the present paper we wish to report the isolation and characterization of a considerable amount of agathisflavone (**4**) in fraction C_3. Although 7-*O*-, 4‴,7-di-*O*-,[3] and 7,7″-di-*O*-methylagathisflavone[4] have been isolated from *Agathis palmerstonii*[3] and *Araucaria bidwillii*[4] and the presence of minor amounts of the parent compound was reported recently in *A. bidwillii* and *Agathis alba*,[5,6] the isolation of large quantities of agathisflavone has not yet been accomplished.

Fraction C_3 was chromatographed on polyamide (nylon 66) and elution with MeOH yielded amentoflavone (**2**) and a bright yellow crystalline compound, m.p. > 330°, whose MW showed it to be a biflavone, $C_{30}H_{18}O_{10}$, M^+ *m/e* 538. The IR spectra possessed a broad hydroxyl absorption at 3350 cm^{-1} and carbonyl band at 1650 cm^{-1}. The UV spectra in MeOH were very similar to that of amentoflavone showing two maxima in regions of 332 (4·60) and 273 (4·60) nm, underwent a bathochromic shift on addition of NaOAc or $AlCl_3$, indicating the presence of OH groups in 7 and 5 positions. $\lambda_{max}^{NaOAc-MeOH}$ nm (log

[1] CHEN, F. C., LIN, Y. M. and LIANG, C. M. (1974) *Phytochemistry* **12**, 276.

[2] LIN, Y. M. *et al.*, presented to the 40th Anniversary Meeting of the Chinese Chemical Society (Taipei), Abstracts, p. 57, Oct., 1972. LIN, Y. M. and CHEN, F. C. (1973) *Tetrahedron Letters* 4747. Full details of this work will be published later.

[3] PELTER, A., WARREN, R., USMANI, J. N., RIZVI, R. H., ILYAS, M. and RAHMAN, W. (1969) *Experienta* **25**, 351.

[4] KHAN, N. U., ILYAS, M., RAHMAN, W., OKIGAWA, M. and KAWANO, N. (1970) *Tetrahedron Letters* 2941.

[5] KHAN, N. U., ANSARI, W. H., USAMANI, J. N., ILYAS, M. and RAHMAN, W. (1971) *Phytochemistry* **10**, 2129.

[6] KHAN, N. U., ILYAS, M., RAHMAN, W., MASHIMA, T., OKIGAWA, M. and KAWANO, N. (1972) *Tetrahedron* **28**, 5689 (1972).

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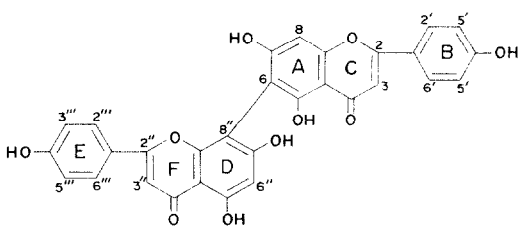
TABLE 1. NMR SPECTRA (δ ppm) OF C_3(AGATHISFLAVONE) AND ITS ACETATE AND METHYL ETHER

Compound (solvent)	Position 2′,6′	2‴,6‴	3′,5′	3‴,5‴	6″	8	3	3′	5″	5	7,7″	4	4″
Biflavone [C_3] (DMSO d_6)	8·14*d* (J 9H$_z$)	7·73*d* (*J*8)	7·10*d* (*J*9)	6·91*d* (*J*8)	6·52*s*	6·87*s*	[6·98*s*	6·90*s*]	13·42*s* (1H)	13·15*s* (1H)	[10·73*bs* (2H)	10·42*bs* (1H)	10·30*bs*] (1H)
Hexaacetate (CDCl$_3$)	8·04*d* (*J*9)	7·64*d* (*J*8·5)	7·39*d* (*J*9)	7·18*d* (*J*8·5)	7·13*s*	7·61*s*	[6·80*s*	6·70*s*]	2·47*s* (3H)	2·18*s*	1·99*s* 2·18*s*	2·27*s*	2·37*s*
Hexamethyl ether (CDCl$_3$)	7·95*d* (*J*9)	7·43*d* (*J*9)	7·07*d* (*J*9)	6·85*d* (*J*9)	6·70*s*	6·95*s*	[6·60*s*	6·57*s*]	4·10*s* (3H)	3·65*s* (3H)	3·83*s* (3H)	3·90*s* (6H)	3·78*s* (3H)

Spectra were taken on a Varian T-60 instrument using TMS as internal standard.

ϵ) 282 (4·62), 293 (sh, 4·60), 337 (4·47). $\lambda_{max}^{AlCl_3\ MeOH}$ nm (log ϵ) 280 (4·55), 302 (4·52), 350 (4·59), 387 (sh, 4·42).

The NMR spectra (Table 1) of the new compound showed six OH groups, eight protons as two sets of A_2B_2 doublets at δ 8·14, 7·10 and δ 7·73, 6·91, and four protons (singlets) at δ 6·98, 6·90, 6·87 and 6·52. The absence of *meta* coupling suggested a interflavonyl linkage between rings *A* and *D*. As the NMR spectra were clearly indicative of the unsymmetrical nature of linking between two apigenin units, the possibility of 8–8″ and 6–6″ linkages must be ruled out. Therefore the new biflavone must be assigned the structure of 6,8″-biapigenin, i.e. agathisflavone (**4**).



(**4**) Agathisflavone

This was further supported by examination of its acetate and methyl ether. Acetylation with pyridine–Ac_2O gave a colourless crystalline hexaacetate, m.p. 154–156°, its NMR spectra (Table 1) were also in accord with the structure **4**. Methylation with Me_2SO_4 afforded a colourless compound, m.p. 158–160°, which was characterized as hexa-*O*-methylagathisflavone by comparison with an authentic sample (TLC, IR and NMR).

The present investigation has revealed that the drupes of *R. succedanea* is rich in biflavonyls of various types; a biflavanone (rhusflavanone), two biflavones (amentoflavone and agathisflavone) and a biflavone ether (hinokiflavone), but no partial or full methyl ethers were detected. The constituents of the fraction C_2 are under investigation.

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