

NEORHUSFLAVANONE, A NEW BIFLAVANONE FROM WAX-TREE

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Neorhusflavanone was identified as 4',4'',5,5'',7,7''-hexahydroxy-8,8''-biflavanone, i.e. 8,8''-binaringenin, by i.r., u.v., n.m.r., and mass spectroscopic comparison with the synthetic compound, and conversion into cupressuflavone derivatives using NBS as dehydrogenating agent.

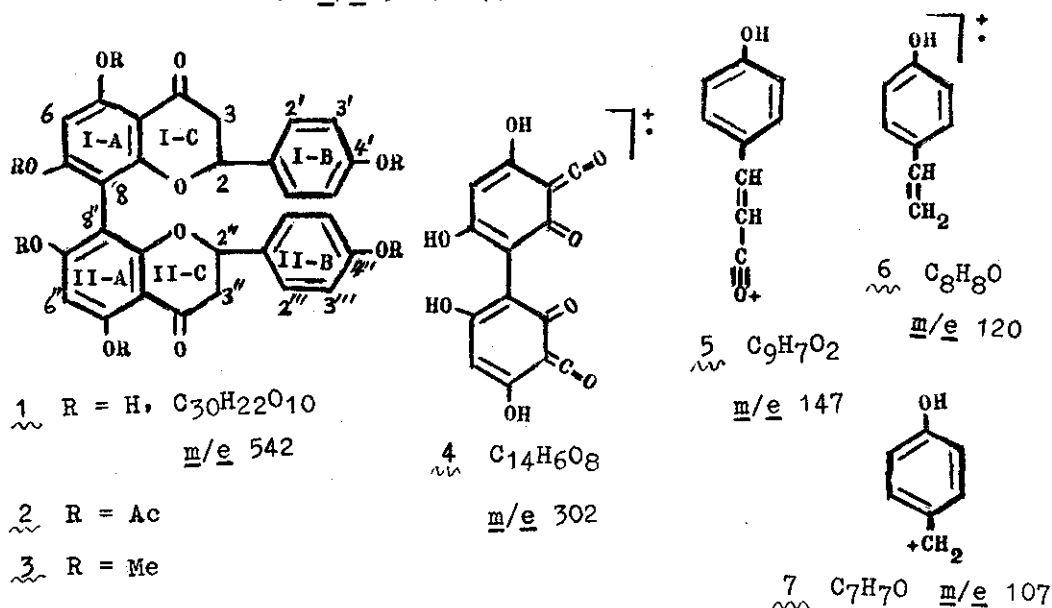
Previously we have reported the isolation of seven optically active biflavanoids, rhusflavanone,² succedaneaflavanone,³ agathisflavone,⁴ robustaflavone,⁵ amentoflavone,⁶ rhusflavone,⁷ and hinokiflavone⁶ from the seed-kernel of wax-tree, Rhus succedanea L. (Anacardiaceae).

Continuous investigation of the minor constituents in the rhusflavanone-containing fraction C_I² led to the isolation of a new biflavanone, named neorhusflavanone (1) as a minor constituent.

The fraction C_I was rechromatographed on polyamide, eluting with MeOH-H₂O (3:2) to yield successively fractions of neorhusflavanone, rhusflavone, and succedaneaflavanone.

Neorhusflavanone formed pale yellow microcrystals, m.p. 274-280° from EtOAc [α]_D²⁸ -357° (c 0.2 in MeOH). The i.r. spectrum showed a broad OH absorption at 3400 cm⁻¹, a chelated flavanone CO band

at 1625 cm^{-1} , aromatic ring absorptions at 1605 and 1520 cm^{-1} , and 1,4-disubstituted benzene ring absorption at 820 cm^{-1} . The u.v. spectrum in MeOH was very similar to that of rhusflavanone and succedaneaflavanone, showing three maxima at 322 (sh. $\log \epsilon$ 4.24), 296 (4.42) and 275 (sh. 4.37) nm, which on addition of NaOAc or AlCl_3 underwent the characteristic bathochromic shift of 5,7,4'-trihydroxyflavanone. Neorhusflavanone showed the molecular ion peak at m/e 542, and the fragmentation pattern was very similar to that of rhusflavanone and succedaneaflavanone as follows: m/e 302, 147, 120, and 107.



The n.m.r. spectrum showed the presence of six hydroxy protons, ten aromatic protons, and six chromanone ring protons of two flavanone units. (Table 1)

Acetylation of 1 gave a hexaacetate (2), m.p. $106-110^\circ$. Methylation of 1 afforded a hexamethyl ether (3), m.p. $246-248^\circ$,

M^+ m/e 626. The i.r. spectra of 2 and 3 showed CO band of 5-O-substituted flavanone at 1692 and 1680 cm^{-1} respectively. The n.m.r. spectra (Table 1) of 2 and 3 showed six acetoxy groups and six methoxy groups respectively, ten aromatic protons and six chromanone ring protons, indicating that 1 is composed of two naringenin units joined by an interflavanoyl C-C linkage between rings I-A and II-A, namely 8,8"-, 6,6"- or 6,8"-binaringenin.

As 6,6"- and 6,8"-linked binaringenin were the known compounds, i.e. succedaneaflavanone and rhusflavanone respectively, the new compound neorhusflavanone must be 8,8"-linked binaringenin.

Confirmation of the 8,8"-linked structure for 1 was provided by the dehydrogenation of its hexaacetate (2) and hexamethyl ether (3) in CCl_4 with NBS¹⁰ which afforded 8,8"-linked cupressuflavone hexaacetate and hexamethyl ether respectively in good yield. The cupressuflavone hexaacetate obtained was further hydrolyzed with NaHCO_3 to give cupressuflavone.

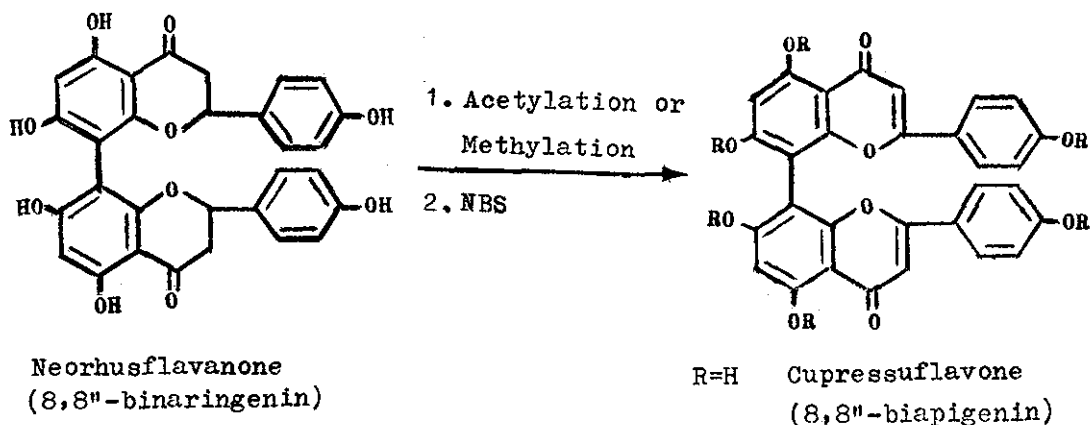


Table 1. NMR spectra (δ ppm) of neorhusflavanone (1) and its hexaacetate (2) and hexamethyl ether (3)

Position	1 (DMSO- d_6)	2 (CDCl $_3$)	3 (CDCl $_3$)
3,3"	2.67-3.23 (4H) <u>m</u>	2.60-3.05 (4H) <u>m</u>	2.58-2.99 (4H) <u>m</u>
2,2"	4.80-5.05 (2H) <u>m</u>	4.88-5.03 (2H) <u>m</u>	5.0-5.38 (2H) <u>m</u>
6,6"	5.94 (2H) <u>s</u>	6.73 (2H) <u>s</u>	6.13 (2H) <u>s</u>
3',5',3'',5''	6.67 (4H) <u>d</u>		6.75-7.09 (8H) <u>m</u>
2',6',2'',6''	7.0-7.24 (4H) <u>m</u>	7.07 (8H) <u>bs</u>	
5,5"	11.31 (2H, 2xOH) <u>s</u>	2.38 (6H, 2xOAc) <u>s</u>	3.90 (6H, 2xOMe) <u>s</u>
7,7"	9.13 (2H, 2xOH) <u>bs</u>		
4,4"	8.40 (2H, 2xOH) <u>bs</u>	2.23 (6H, 2xOAc) <u>s</u> 2.05 (6H, 2xOAc) <u>s</u>	3.77 (6H, 2xOMe) <u>s</u> 3.73 (6H, 2xOMe) <u>s</u>

Further confirmation of the structure was made by a comparison with the synthetic compound starting from biphenyl in two steps.¹¹ The t.l.c., i.r., and mass spectra of the synthetic 8,8"-binaringenin hexamethyl ether was identical with that of neorhusflavanone hexamethyl ether, except minor differences in melting points and n.m.r. spectra: the signal of H-6 at δ 6.13 in natural product (m.p. 246-248°) was splitted into equal intensity doublets at δ 6.12 and 6.18 in the synthetic compound (m.p. 284-286°) owing to the racemic and diastereomeric properties.

Thus it has definitely established that neorhusflavanone is 8,8"-binaringenin.

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