NEORHUSFLAVANONE, A NEW BIFLAVANONE FROM WAX-TREE

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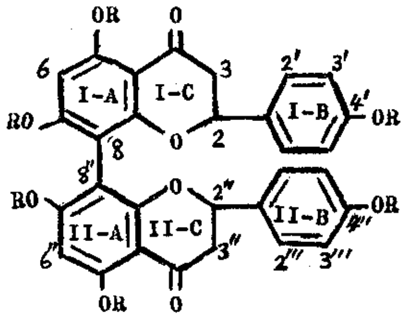
Neorhusflavanone was identified as 4',4''',5,5",7,7"-hexahydroxy-8,8"-biflavanone, i.e. 8,8"-binaringenin, by i.r., u.v., n.m.r., and mass spectroscopic comparison with the synthetic compound, and conversion into cupressuflavone derivatives using NBS as dehydrogenating agent.

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

Continuous investigation of the minor constituents in the rhusflavanone-containing fraction C_I[2] 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 $MeOH-H_2O$ (3:2) to yield succesively fractions of neorhusflavanone, rhusflavone, and succedaneaflavanone.

Neorhusflavanone formed pale yellow microcrystals, m.p. 274-280° from EtOAc $[\alpha]_D^{28}$ -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 ϵ 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.

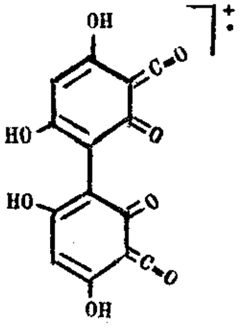


1 R = H, $C_{30}H_{22}O_{10}$

m/*e* 542

2 R = Ac

3 R = Me

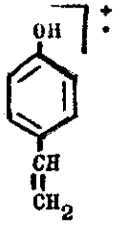


4 $C_{14}H_6O_8$

m/*e* 302

5 $C_9H_7O_2$

m/*e* 147



6 C_8H_8O

m/*e* 120

7 C_7H_7O *m*/*e* 107

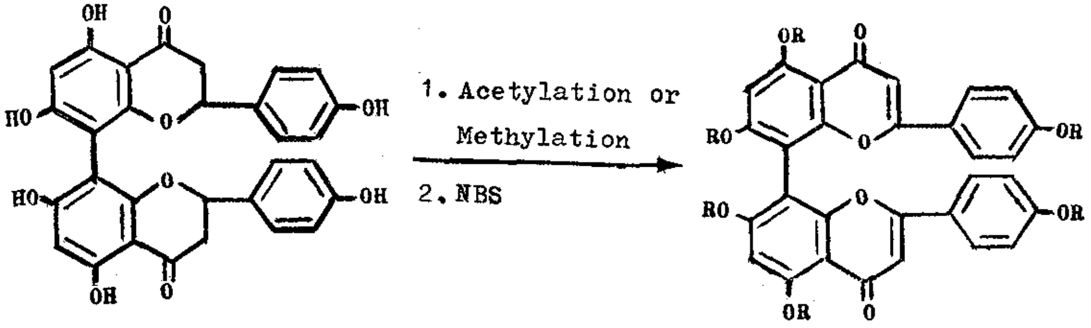
The n.m.r. spectrum showed the presence of six hydroxy protons, ten aromatic protons, and six chromanone ring protons of two flavanone units. (Table 1)

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

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 NBS[10] 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.



Neorhusflavanone
(8,8"-binaringenin)

R=H Cupressuflavone
(8,8"-biapigenin)

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) *m*	2.60-3.05 (4H) *m*	2.58-2.99 (4H) *m*
2,2"	4.80-5.05 (2H) *m*	4.88-5.03 (2H) *m*	5.0-5.38 (2H) *m*
6,6"	5.94 (2H) *s*	6.73 (2H) *s*	6.13 (2H) *s*
3',5',3"',5"'	6.67 (4H) *d*	7.07 (8H) *bs*	6.75-7.09 (8H) *m*
2',6',2"',6"'	7.0-7.24 (4H) *m*		
5,5"	11.31 (2H, 2×OH) *s*	2.38 (6H, 2×OAc) *s*	3.90 (6H, 2×OMe) *s*
7,7"	9.13 (2H, 2×OH) *bs*	2.23 (6H, 2×OAc) *s*	3.77 (6H, 2×OMe) *s*
4,4"'	8.40 (2H, 2×OH) *bs*	2.05 (6H, 2×OAc) *s*	3.73 (6H, 2×OMe) *s*

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 δ6.13 in natural product (m.p. 246-248°) was splitted into equal intensity doublets at δ6.12 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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