Rhusflavanone, a New Biflavanone from the Seeds of Wax-tree [1]

By **Fa-ching Chen** * and **Yuh-meei Lin**, Chemistry Research Center, National Taiwan University, Taipei, Taiwan (Formosa) 107, Republic of China

Rhusflavanone (1), a new biflavanone from the seed-kernels of wax-tree, *Rhus succedanea* L. (Anacardiaceae), has been identified as 4',4''', 5,5'', 7,7''-hexahydroxy-6,8''-biflavanone (6,8''-binaringenin) by i.r., u.v., n.m.r., and mass spectroscopy and by conversion into agathisflavone derivatives.

THE drupes of wax-tree, *Rhus succedanea* L. (Anacardiaceae), are of great economic importance in that they yield Japan wax. Earlier work on this species has shown the presence of fustin and fisetin in the wood,[2] rhoifolin in leaves,[3] Japanic acid in the wax,[4] and ellagic acid,[5] fatty acids,[6] and flavanoids [7] in the seed-kernels. In recent reviews [8-12] about forty different biflavanoids have been enumerated, and some of them are optically active.[13-23] This prompted us to reinvestigate the flavanoids of the seed-kernels of wax-tree studied by one of us (F. C. C.) *ca.* 35 years ago.[7] Encouragingly, seven optically active biflavanoids, three of which are new, were isolated; *i.e.* concentration of the ethanol extract of the seed-kernels yielded successively fractions of ellagic acid, pigment A (hinokiflavone [24] and robustaflavone [25]) and pigment B (amentoflavone [24]). Further concentration gave a crude yellow pigment C which, subjected to silica column chromatography, afforded fractions C_I (rhusflavanone [1] and succedaneaflavanone [26]), C_{II} (rhusflavone [27]), and C_{III} (agathisflavone [28]). We now report the elucidation of the structure of rhusflavanone (1).

Fraction C_I, rechromatographed on polyamide, yielded needles, m.p. 204—206°, $C_{30}H_{22}O_{10},1.5H_2O$, M^+ 542. It gave a purple colour in the magnesium–hydrochloric acid test and a violet-blue one with ethanolic iron(III) chloride. The i.r. spectrum showed broad OH absorption at 3 400 cm^{-1} and a chelated flavanone CO band at 1 630 cm^{-1}. The u.v. spectrum showed four maxima which on addition of sodium acetate or aluminium chloride underwent a bathochromic shift characteristic of the 5,7-dihydroxyflavanone system.[29]

The n.m.r. spectrum showed the presence of six hydroxy-protons, ten aromatic protons, and six chromanone ring protons, indicating that the molecule is composed of two flavanone units joined by a C–C linkage.

Acetylation gave a hexa-acetate (2), the i.r. spectrum of which showed absorptions at 1 770 (acetoxy CO) and 1 688 (5-oxygenated flavanone CO), but no absorption around 1 650 cm^{-1}, indicating no chalcone formation, although isomerizations of flavanones to chalcones during acetylation are reported.[22]

The n.m.r. spectrum of the hexa-acetate showed six acetoxy-groups. Eight of the ten aromatic protons appeared as two A_2B_2 patterns, indicating the presence of two 1,4-disubstituted benzene rings. The signals of four protons of rhusflavanone (1) at δ 6.88 and 6.79 (H-3', -5', -3''', and -5''') were shifted 0.29 and 0.35 p.p.m. to lower field (δ 7.17 and 7.14) by acetylation, indicating the presence of OH groups at the 4'- and 4'''-positions. The remaining two aromatic protons resonated as singlets at δ 6.12 and 6.07, assigned to H-8 and H-6'', respectively. These data suggested that rhusflavanone was composed of two naringenin units joined by an interflavanonyl C–C linkage between rings IA and IIA. The n.m.r. spectra of (1) and (2) clearly indicated the unsymmetrical nature of the linkage, suggesting the 6,8''-binaringenin structure for (1).

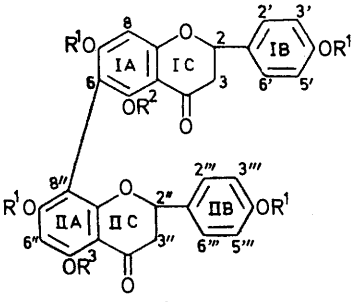
Methylation of (1) afforded a tetramethyl ether (3), a pentamethyl ether (4), and a small quantity of a

[1] Preliminary communication, Y. M. Lin and F. C. Chen, *Tetrahedron Letters*, 1973, 4747.
[2] T. Oyamada, *J. Chem. Soc. Japan*, 1934, **55**, 755, 785; *Annalen*, 1939, **538**, 44.
[3] S. Hattori and H. Matsuda, *Arch. Biochem. Biophys.*, 1952, **37**, 85.
[4] S. Shihina, *J. Soc. Chem. Ind. Japan*, 1940, **43**, 414.
[5] F. C. Chen, *Acta Chimica Taiwanica*, 1948, **1**, 57; *J. Taiwan Pharm. Assoc.*, 1950, **2**, 17.
[6] F. C. Chen, *Acta Chimica Taiwanica*, 1948, **1**, 59; *J. Taiwan Pharm. Assoc.*, 1950, **2**, 20.
[7] F. C. Chen, *Acta Chimica Taiwanica*, 1948, **1**, 63.
[8] H. D. Locksley *Progr. Chem. Org. Natural Products*, 1973, **30**, 207.
[9] K. Nakazawa, *Gifu Yakka Daigaku Kiyo*, 1962, No. 12.
[10] N. Kawano in Chemistry of Natural and Synthetic Colouring Matters and Related Fields, eds. T. S. Gore, B. S. Joshi, S. V. Sunthankar, and B. D. Tilak, Academic Press, New York and London, 1962, p. 177.
[11] W. Baker and W. D. Ollis in ' Recent Developments in the Chemistry of Natural Phenolic Compounds,' ed. W. D. Ollis, Pergamon, Oxford, 1961, p. 152.
[12] F. C. Chen, *Formosan Sci.*, 1972, **26**, 100.
[13] M. Ilyas, J. N. Usmani, S. P. Bhatnagar, M. Ilyas, W. Rahman, and A. Pelter, *Tetrahedron Letters*, 1968, 5515.
[14] A. Pelter, R. Warren, M. Ilyas, J. N. Usmani, S. P. Bhatnagar, R. H. Rizvi, M. Ilyas, and W. Rahman, *Experientia*, 1969, **25**, 350.
[15] A. Pelter, R. Warren, J. N. Usmani, R. H. Rizvi, M. Ilyas, and W. Rahman, *Experientia*, 1969, **25**, 351.
[16] K. K. Chexal, B. K. Handa, W. Rahman, and N. Kawano, *Chem. and Ind.*, 1970, 28.
[17] A. Pelter, R. Warren, J. N. Usmani, B. K. Handa, and W. Rahman, ' Abstracts of the 2nd Indo-Soviet Symposium on Natural Products Including Pharmacology,' New Delhi, 1970, Feb. 2—6.
[18] N. U. Khan, M. Ilyas, W. Rahman, M. Okigawa, and N. Kawano, *Tetrahedron Letters*, 1970, 2941.
[19] M. Konoshima, Y. Ikeshiro, S. Miyahara, and K. Y. Yen, *Tetrahedron Letters*, 1970, 4205.
[20] A. Pelter, R. Warren, N. Hamecd, M. Ilyas, and W. Rahman, *J. Indian Chem. Soc.*, 1971, **48**, 204.
[21] A. Pelter, R. Warren, B. K. Handa, K. K. Chexal, and W. Rahman, *Indian J. Chem.*, 1971, **9**, 98.
[22] A. Pelter, R. Warren, K. K. Chexal, B. K. Handa, and W. Rahman, *Tetrahedron*, 1971, **27**, 1625.
[23] J. C. Hung, M.S. Thesis, National Taiwan University, 1974; F. C. Chen, Y. M. Lin, and J. C. Hung, *Phytochemistry*, 1975, **14**, 300, 818.
[24] F. C. Chen, Y. M. Lin, and C. M. Liang, *Phytochemistry*, 1974, **13**, 276.
[25] Y. M. Lin and F. C. Chen, *Phytochemistry*, 1974, **13**, 1617.
[26] F. C. Chen and Y. M. Lin, *Phytochemistry*, 1975, **14**, 1644.
[27] F. C. Chen, Y. M. Lin, and J. C. Wu, *Phytochemistry*, 1974, **13**, 1571.
[28] Y. M. Lin and F. C. Chen, *Phytochemistry*, 1974, **13**, 657.
[29] T. J. Mabry, K. R. Markham, and M. B. Thomas, ' The Systematic Identification of Flavonoids,' Springer, New York, 1970, pp. 48—55.

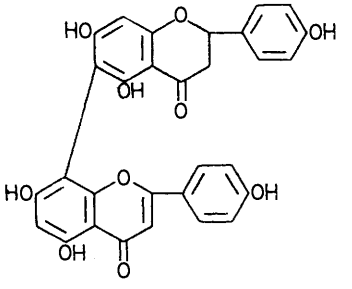
hexamethyl ether (6). Acetylation of (4) afforded a monoacetate (5). The mass spectra of (1) and its methyl ethers [(3), (4), and (6)] showed appropriate fragments formed by one and two retro-Diels–Alder cleavages of the molecular ions, indicating that the interflavanonyl linkage must be between rings IA and IIA.[1]

The n.m.r. spectrum of the hexa-acetate (2) showed signals due to the 5- and 5″-OH at δ 12.35 and 12.52, the pentamethyl ether (4) showed signals at δ 12.30 (5-OH) and 4.02 (5″-OMe), and the penta-*O*-methyl monoacetate (5) showed signals at δ 2.20 (5-OAc) and 4.01 (5″-OMe); the signals of the 5- and 5″-OMe in the hexamethyl ether (6) appeared at δ 3.65 and 4.05, respectively. The higher field signal (δ 3.65) of the 5-OMe protons in (6) can be explained on the basis of the influence of the CO group in ring Ic and of ring IIA; similar effects can be seen in the signals of 6′-OMe in hexa-acetate (9) and the hexamethyl ether (10) of agathisflavone, respectively, in almost quantitative yields. Studies on the synthesis of 6,8″-binaringenin (1) are in progress.

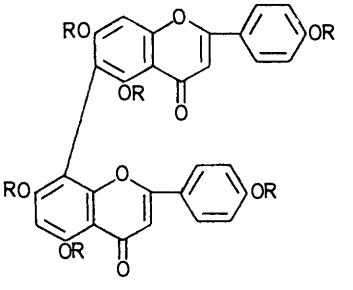
A number of papers report the conversion of biflavanones into biflavones or flavanonylflavones by iodine–potassium (or sodium) acetate in acetic acid [22,31-33] or in ethanol.[19,34] In our preliminary communication [1] we reported that dehydrogenation of (1) with iodine–potassium acetate [35] yielded a mixture of agathisflavone (6,8″-linked) (17%) and cupressuflavone (8,8″-linked) (5%), but by the *N*-bromosuccinimide (2) and (6) afforded only agathisflavone derivatives, (9) and (10), respectively, without formation of any cupressuflavone derivatives. Since isomerization of a 6,6″- to a 6,8″- and then to an 8,8″-linkage proceeds easily on dehydrogenation by the former method, the *N*-bromosuccinimide method is more reliable.[36]



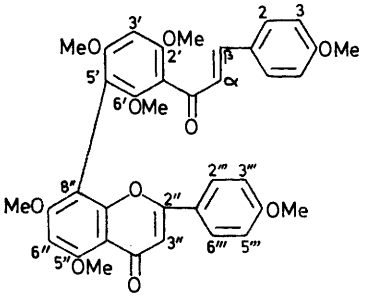
(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^2 = R^3 = Ac$
(3) $R^1 = Me$, $R^2 = R^3 = H$
(4) $R^1 = R^3 = Me$, $R^2 = H$
(5) $R^1 = R^3 = Me$, $R^2 = Ac$
(6) $R^1 = R^2 = R^3 = Me$



(7)



(8) R = H
(9) R = Ac
(10) R = Me



(11)

rhusflavone heptamethyl ether (11) [27] and the 5-OMe in agathisflavone hexamethyl ether (10).[15] In general, signals of 5-acetoxy-protons in flavanones or flavones appear at δ *ca.* 2.40;[30] however that of the 5-acetoxy protons of (6) appeared at considerably higher field (δ 2.20), indicating the effect of the 6-substituent. The above results support structure (1) for rhusflavanone.

Unequivocal confirmation of this structure was provided by dehydrogenation of compounds (2) and (6) in carbon tetrachloride with *N*-bromosuccinimide–potassium acetate under irradiation, which afforded the

The present investigation has revealed that the seed of wax-tree are rich in biflavonyls of various types, but no partial or full methyl ethers nor cupressuflavone were detected. The expected monoflavanoids were not detected.

EXPERIMENTAL

M.p.s were determined with a Gallenkamp or a Yanagimoto apparatus; the specific rotations were recorded with

[30] C. A. Henrick and P. R. Jefferies, *Austral. J. Chem.*, 1964, **17**, 934.
[31] G. A. Herbin, B. Jackson, H. D. Locksley, F. Scheinmann, and W. A. Wolstenholme, *Phytochemistry*, 1970, **9**, 221.
[32] Y. Ikeshiro and M. Konoshima, *Tetrahedron Letters*, 1972, 4383.
[33] B. Jackson, H. D. Locksley, F. Scheimann, and W. A. Wolstenholme, *J. Chem. Soc.* (*C*), 1971, 3791.
[34] T. Tominaga, *Yakugaku Zasshi*, 1956, **76**, 1385.
[35] V. B. Mahesh and T. R. Seshardi, *J. Sci. Ind. Res., India*, 1955, 14B, 608.
[36] Y. M. Lin and F. C. Chen, *Chemistry* (*Chin. Chem. Soc.*), 1974, No. 3, p. 67.

a Rex photoelectric polarimeter NEP-2; u.v., i.r., and n.m.r. spectra were recorded with a Cary-14 spectrophotometer, a JASCO IR-G spectrophotometer, and a Varian T-60 instrument, respectively. Mass spectra were obtained with a Hitachi RMS-4 spectrometer.

Extraction of Biflavanoids.—The fruits of wax-tree, obtained from Fukuoka, Japan, in 1940, were treated as described earlier.[7] The coarsely powdered and defatted drupes (98.4 kg) were exhaustively extracted with 95% ethanol (1 081 l). The extract was concentrated *in vacuo* to yield pigments A [*ca.* 0.25%: (−)-hinokiflavone [24] and (−)-robustaflavone [25] (each 0.06%)] and B [*ca.* 0.25%: (+)-amentoflavone [24] (0.08%)]. Further concentration yielded crude yellow pigment C (*ca.* 2%), of which the ethyl acetate-soluble part (38 g from 40 g of crude pigment C) was subjected to column chromatography on silica (400 g). Elution with benzene–ethyl acetate (1 : 1) yielded fractions C_I [4 g: (−)-rhusflavanone (1) (0.17%) and (−)-succedaneaflavanone [26] (0.01%)], C_{II} [0.8 g: (−)-rhusflavone (7) [27] (0.03%)], and C_{III} [1 g: (+)-agathisflavone (8) [28] (0.03%)].

Isolation of Rhusflavanone (4′,4‴,5,5″,7,7″-*Hexahydroxy*-6,8″-*biflavanone*) (1).—Fraction C_I showed one spot on t.l.c. (silica; C_6H_6–C_5H_5N–HCO_2H) but two spots on descending paper chromatography (15% HOAc). The fraction (4 g) was rechromatographed on polyamide [nylon 66 (100 g); MeOH–H_2O (7 : 3)] yielding *micro-needles* (1) (2.2 g), m.p. 204—206° (from 90% EtOH) $[\alpha]_D^{20}$ −29° (*c* 1.8 in MeOH), M^+ 542 (Found: C, 63.1; H, 4.05. $C_{30}H_{22}O_{10}.1.5H_2O$ requires C, 63.3; H, 4.45%), $\nu_{max.}$ (KBr) 3 400 (OH), 1 630 (conj. CO), 1 610, 1 520, and 1 490 cm^{-1} (arom.), $\lambda_{max.}$ (MeOH) 336 (log ε 3.80), 294 (4.49), 223 (4.65), and 208 nm (4.68), $\lambda_{max.}$ (NaOAc–MeOH) 320 (log ε 4.36), 300 (4.36), 271 (4.42), and 257 nm (4.38), $\lambda_{max.}$ ($AlCl_3$–MeOH) 384 (log ε 3.88), 315 (4.63), 256 (4.25), and 224 nm (4.76); δ [$(CD_3)_2SO$] 7.41 (2 H, d, *J* 9 Hz, H-2′ and -6′), 7.26 (2 H, d, *J* 8 Hz, H-2‴ and -6‴), 6.88 (2 H, d, *J* 9 Hz, H-3′ and -5′), 6.79 (2 H, d, *J* 8 Hz, H-3‴ and -5‴), 6.12 (1 H, s, H-8), 6.07 (1 H, s, H-6″), 5.48 (2 H, dd, *J* 12 and 4 Hz, H-2 and -2″), 3.23—2.80 (4 H, m, H-3 and -3″), 12.57 (1 H, s, HO-5″), 12.43 (1 H, s, HO-5), 10.65br (2 H, s, HO-7 and -7″), and 9.70br (2 H, HO-4′ and -4‴); *m/e* 542 (6.9%, M^+), 524 (6, $M^+ - H_2O$), 423 (3.1), 422 (2.4), 405 (28), 404 (7.2), 378 (13.9), 303 (4.2) 302 (12.9), 285 (7.5), 284 (9.3), 259 (8.8), 258 (33.3), 147 (43.8), 120 (100), 107 (22.5), and 94 (23.6). Further elution with methanol yielded succedaneaflavanone,[26] m.p. 318—322° (decomp.).

Rhusflavanone Hexa-acetate (2).—Acetylation of rhusflavanone (1) (100 mg) with acetic anhydride–pyridine (each 1 ml) at room temperature for 20 h gave *micro-needles* (2) (110 mg), m.p. 130—131° (from MeOH), M^+ 794 (Found: C, 63.2; H, 4.6. $C_{42}H_{34}O_{16}$ requires C, 63.45; H, 4.3%), $\nu_{max.}$ (KBr) 1 770 (acetoxy CO), 1 688 (flavanone CO), 1 603, 1 560, 1 510, and 1 490 cm^{-1} (arom.); δ ($CDCl_3$) 7.55 (2 H, d, *J* 9 Hz, H-2′ and -6′), 7.44 (2 H, d, *J* 9 Hz, H-2‴ and -6‴), 7.17 (2 H, d, *J* 9 Hz, H-3′ and -5′), 7.14 (2 H, d, *J* 9 Hz, H-3‴ and -5‴), 6.91 (1 H, s, H-8), 6.71 (1 H, s, H-6″), 5.45—5.35 (2 H, m, H-2 and -2″), 3.06—2.85 (4 H, m, H-3 and -3″), 2.15 (3 H, s, AcO-5), 2.40 (3 H, s, AcO-5″), 2.10 (3 H, s, AcO-7), 2.02 (3 H, s, AcO-7″), 2.32 (3 H, s, AcO-4), and 2.28 (3 H, s, AcO-4‴); *m/e* 794 (2.4%, M^+), 752 (14, $M^+ - CH_2O_2$), 710 (60.0, 752 − CH_2O_2), 668 (36.0, 710 − CH_2O_2), 626 (43.0, 668 − CH_2O_2), 584 (12.0, 626 − CH_2O_2), 542 (4.0, 584 − CH_2O_2), 524 (2.0), 492 (6.0), 465 (20), 464 (11), 448 (32), 447 (31), 423 (10), 422 (20), 405 (12.0), 404 (5.0), 303 (41.0), 302 (9.0), 286 (60.0), 285 (55.0), 284 (18.0), 259 (6.4), 258 (6.0), 148 (92.0), 121 (54.0), 120 (24.0), and 44 (100).

Methylation of Rhusflavanone (1).—A mixture of (1) (500 mg), dimethyl sulphate (3 ml), and potassium carbonate (4 g) in dry acetone (100 ml) was refluxed for 24 h. The product was chromatographed over a silica column (30 g); elution with C_6H_6–EtOAc (3 : 2) yielded the ethers (3) (80 mg), (4) (50 mg), and (6) (10 mg). The *tetramethyl ether* (3) formed needles, m.p. 172—175° (from $CHCl_3$–MeOH), M^+ 598 (Found: C, 68.05; H, 5.25. $C_{34}H_{30}O_{10}$ requires C, 68.2; H, 5.05%), $\nu_{max.}$ (KBr) 3 450 (OH), 2 980, 2 930, 2 830 (OMe), 1 635 (5-OH-flavanone CO), 1 610, 1 587, 1 573, and 1 515 cm^{-1} (arom.); δ ($CDCl_3$) 7.49 (2 H, d, *J* 9 Hz, H-2′ and -6′), 7.33 (2 H, d, *J* 9 Hz, H-2‴ and -6‴), 7.07 (2 H, d, *J* 9 Hz, H-3′ and -5′), 6.99 (2 H, d, *J* 9 Hz, H-3‴ and -5‴), 6.32 (1 H, s), 6.22 (1 H, s), 5.63—5.33 (2 H, m), 3.17—2.87 (4 H, m), 12.35 (1 H, s, HO-5), 12.52 (1 H, s, HO-5″), 3.88 (3 H, s), 3.83 (3 H, s), 3.80 (3 H, s), and 3.76 (3 H, s); *m/e* 598 (28.1%, M^+), 570 (8.1), 569 (7.0), 568 (8.1), 465 (7.0), 464 (15.1), 463 (10.8), 462 (16.2), 461 (6.5), 460 (7.0), 436 (8.1), 434 (9.7), 433 (10.8), 432 (8.1), 330 (39.0), 302 (8.1), 300 (11.8), 299 (21.6), 135 (18.9), 134 (26.0), 121 (100), and 120 (5.4). The *pentamethyl ether* (4) formed needles, m.p. 226—228° (from $CHCl_3$–MeOH), M^+ 612 (Found: C, 68.4; H, 5.4. $C_{35}H_{32}O_{10}$ requires C, 68.6; H, 5.25%), $\nu_{max.}$ (KBr) 2 500 (OH), 1 682 (5-O-subst. flavanone CO), 1 640 (5-OH-flavanone CO), 1 618, 1 600, 1 580, 1 520, and 1 485 cm^{-1} (arom.); δ ($CDCl_3$) 7.48 (2 H, d, *J* 9 Hz, H-2′ and -6′), 7.28 (2 H, d, *J* 9 Hz, H-2‴ and -6‴), 7.06 (2 H, d, *J* 9 Hz, H-3′ and -5′), 6.92 (2 H, d, *J* 9 Hz, H-3‴ and -5‴), 6.32 (1 H, s), 6.22 (1 H, s), 5.63—5.33 (2 H, m, H-2 and -2″), 3.18—2.87 (4 H, m, H-3 and -3″), 12.30 (1 H, s, HO-5), 4.02 (3 H, s, CH_3O-5″), 3.87 (3 H, s), 3.82 (3 H, s), 3.78 (3 H, s), and 3.75 (3 H, s); *m/e* 612 (100%, M^+), 598 (3.9), 582 (8.6), 479 (17.8), 478 (41.0), 449 (20.4), 448 (28.4), 447 (17.2), 446 (55.9), 345 (21.6), 344 (58.5), 316 (6.7), 314 (10.1), 313 (41.9), 312 (4.7), 299 (6.9), 298 (8.9), 286 (6.0), 161 (87.0), 134 (50.0), and 121 (75.0). The *monoacetate* (5) (30 mg), formed from (4) (60 mg) in Ac_2O (1.5 ml) and concentrated H_2SO_4 (2 drops) at room temperature (10 min), had m.p. 145—148° (resolidifying at 190° and melting again at 205°) (from n-C_6H_{14}–MeOH) (Found: C, 67.65; H, 5.35. $C_{37}H_{34}O_{11}$ requires C, 67.9; H, 5.25), $\nu_{max.}$ (KBr) 1 770 (acetoxy CO) and 1 685 cm^{-1} (5-O-subst. CO). The *hexamethyl ether* (6) formed needles, m.p. 131—133°, M^+ 626 (Found: C, 68.85; H, 5.6. $C_{36}H_{34}O_{10}$ requires C, 69.0; H, 5.45%), $\nu_{max.}$ (KBr) 1 680 (5-O-subst. flavanone CO), 1 590, 1 520, and 1 505 cm^{-1} (arom.); δ ($CDCl_3$) 7.48 (2 H, d, *J* 9 Hz, H-2′ and -6′), 7.26 (2 H, d, *J* 9 Hz, H-2‴ and -6‴), 7.02 (2 H, d, *J* 9 Hz, H-3′ and -5′), 6.91 (2 H, d, *J* 9 Hz, H-3‴ and -5‴), 6.47 (1 H, s, H-8), 6.30 (1 H, s, H-6″), 5.62—5.35 (2 H, m, H-2 and -2″), 3.12—2.83 (4 H, m, H-3 and -3″), 3.65 (3 H, s, CH_3O-5), 4.05 (3 H, s, CH_2O-5″), 3.85 (6 H, s), 3.82 (3 H, s), and 3.78 (3 H, s); *m/e* 626 (2.2%, M^+), 612 (2.2), 596 (100), 595 (26.0), 461 (34.4), 460 (94.6), 359 (4.3), 327 (8.6), 314 (4.3), 313 (13.0), 312 (8.6), 300 (4.3), 299 (4.3), 297 (17.2), 286 (4.3), 285 (8.3), 230 (21.5), 161 (39.0), 147 (8.6), 134 (13.0), 133 (26.0), and 121 (34.4).

Dehydrogenation of Rhusflavanone (1).—A mixture of (1) (460 mg), iodine (0.5 g), and potassium acetate (1 g) in acetic acid (30 ml) was refluxed for 7 h, cooled, and poured into water (30 ml). The precipitate was extracted with

ethyl acetate. Removal of the solvent and washing with benzene to remove iodine, yielded a solid which was subjected to silica column chromatography, giving two products as yellow crystals [80 mg, 20 mg], each m.p. >300°, identical with authentic samples of agathisflavone (8) and cupressuflavone, respectively (i.r., t.l.c., and n.m.r.). Methylation of the product (8) (60 mg), with dimethyl sulphate (1.5 ml), and potassium carbonate (2 g) in dry acetone (50 ml) (reflux 30 h) afforded the hexamethyl ether (10) (15 mg), m.p. 159—160° (from $CHCl_3$–MeOH), identical with authentic agathisflavone hexamethyl ether (mixed m.p., i.r., t.l.c., and n.m.r.).

Dehydrogenation of Rhusflavanone Hexa-acetate (2).—A mixture of (2) (50 mg), *N*-bromosuccinimide (13 mg), and benzoyl peroxide (3 mg) in carbon tetrachloride (30 ml) was refluxed under irradiation for 2 min. Potassium acetate (100 mg) was added and the mixture was refluxed for 5 min. After removal of carbon tetrachloride *in vacuo*, addition of water gave a precipitate (9) (35 mg), m.p. 149—151°, identical with authentic agathisflavone hexa-acetate (mixed m.p., t.l.c., i.r., and n.m.r.).

Dehydrogenation of Rhusflavanone Hexamethyl Ether (6).—A mixture of (6) (5 mg), *N*-bromosuccinimide (3 mg), benzoyl peroxide (1 mg), and potassium acetate (50 mg) in carbon tetrachloride (10 ml) was treated as above, yielding crystals (10) (3 mg), m.p. 158—160°, identical with authentic agathisflavone hexamethyl ether (mixed m.p., t.l.c., and i.r.).

We thank Professor M. Yasue, Nagoya City University, for elemental analyses; Professor N. Kawano, Nagasaki University, for a gift of authentic specimens, copies of i.r. and n.m.r. spectra, and helpful suggestions; and Professors W. C. Lin and C. H. Yang and the faculty members for n.m.r., u.v., i.r., and mass spectral measurements. This work was supported by the National Science Council as the research project of the Chemistry Research Center, National Taiwan University.

[5/1137 *Received*, 10*th June*, 1975]