presence de méthyl-3 quercetine chez *Ophioglossum vulgatum*[8], *O lusitanicum*, *O reticulatum*[1] (Ophioglossacees) et chez *Polystichum aculeatum*[1] (Aspidiacees)

EXPERIMENTALE

30 g de frondes seches d *Asplenium viride* (recoltees a la Combe d'Ire reserve des Bauges-74 France) sont hydrolysees par fractions de 3 g, par HCl 2 N pendant 40 mn au bain-marie bouillant. Les flavoroides sont extraits par Et_2O, apres evaporation spontanee du solvant le residu flavonique est dissous dans H_2O bouillante et immediatement filtre sur creuset, puis place en chambre froide. Le precipite d'aglycones flavoniques est solubilise dans un volume minimal de MeOH puis place a la partie superieure d'une colonne de polyamide (Macherey Nagel SC 6) dont l'elution est obtenue par du C_6H_6 progressivement enrichi en MeCOEt puis MeOH [9]. La CCM de polyamide (MN DC 11 solvant C_6H_6-MeCOEt-MeOH 6 1 3) des 10 fractions collectees montre la presence dans la fraction 4 d'un compose de fluorescence violette. Apres purifications par chromatographie sur papier (AcOH 60%) et sur colonne de polyamide, environ 10 mg d'un compose jaune citron sont obtenus fluorescence violette. R_f CP Whatman No 1 BAW 0.88 TBA 0.79 AcOH 15% 0.15 AcOH 60% 0.64. UV λ_{max} MeOH 256 (268), (292) 359 nm, $AlCl_3$, 275 (304) 332, 438 nm, $AlCl_3$/HCl 268 300 (367) 406 nm. NaOAc 266 (303), (322), 386 nm, NaOAc/H_3BO_3, 260, (305) 377 nm. NaOMe 272 326, 405 nm.

SM. Principaux pics situes en valeur *m e a*. 316 (100%) 301 (4) 298 (18) 287 (16) 273 (36) 203 (10) 153 (20) 137 (16), 121 (8), 108 (6), 69 (12).

RMN in $(CD_3)_2CO$ (60 MC) deplacements chimiques en ppm (echelle δ) par rapport au TMS 7.72 (*J* 2.5 Hz 1H) 7.53 (*J* 2.5 et 8.5 Hz 1H) 7.01 (*J* 8.5 Hz 1H) 6.48 (*J* 2.5 Hz 1H) 6.26 (*J* 2.5 Hz 1H) 3.86 (3H).

[8] MARKHAM K. R., MABRY T. J. et VOIRIN, B. (1969) *Phytochemistry* **8**, 469.
[9] WOLLENWEBER E. (1970) These Universite Heidelberg Allemagne.

Phytochemistry 1974 Vol 13 pp 276 to 278 Pergamon Press Printed in England

BIFLAVONYLS FROM DRUPES OF *RHUS SUCCEDANEA*

FA-CHING CHEN, YUH-MEEI LIN and CHI-MING LIANG

Chemistry Research Center National Taiwan University Taipei 107 Taiwan Republic of China

(*Received* 19 *June* 1973 *Accepted* 9 *July* 1973)

Key Word Index—*Rhus succedanea* Anacardiaceae biflavones amentoflavone, hinokiflavone.

Plant. *Rhus succedanea* L. *Source*. Fukuoka Prefecture, Japan. *Uses*. Japan wax from the fruits. *Previous work*. Fustin and fisetin from heartwoods[1] and rhoifolin from leaves.[2] Ellagic acid[3] and fatty acids.[4] from seeds. No work on biflavones has been reported on either this or sister species.*

Present work. The coarsely powdered and defatted drupes (98.4 kg) were completely exhausted with 95% EtOH (1080 l.). The EtOH extract was concentrated *in vacuo* yielding crude yellow pigments I and II which were formerly named as rhusnetin and rhusnin, each *ca* 0.26% yield.[5] Further concentration yielded crude yellow pigment III, *ca* 2% named

* *Added in proof*. After submission of this paper the isolation of two biflavanones, 8,3-binaringenin and 8,8-biliquiritigenin, from the sister species *Semecarpus anacardium* has been reported by RAO N. S. P. ROW L. R. and BROWN, R. T. (1973) *Phytochemistry* **12**, 671.

[1] OYAMADA, T. (1934) *J. Chem. Soc. Japan* **55**, 755, (1939) *Ann.* **538**, 44.
[2] HATTORI S. and MATSUDA H. (1952) *Arch. Biochem. Biophys.* **37**, 85.
[3] CHEN F. C. (1948) *Acta Chim. Taiwanica* **1**, 57 (1950) *J. Taiwan Pharm. Assoc.* **2**, 17.
[4] CHEN F. C. (1948) *Acta Chim. Taiwanica* **1**, 59 (1950) *J. Taiwan Pharm. Assoc.* **2**, 20.
[5] CHEN F. C. (1948) *Acta Chim. Taiwanica* **1**, 63.

as rhusflavanone[6] These materials were prepared by one of us (F C C) some 30 years ago[7] Recently two optically active biflavone, hinokiflavone and amentoflavone were isolated from pigments I and II respectively

Pigment I was subjected to preparative TLC on silica gel (benzene–pyridine–formic acid, 20 5 1) as developing solvent system, R_f 0 37), yielding yellow compound A, m p $>330°$, $[\alpha]_D^{25}$ $-6°$ (48 mg/1 ml pyridine), $C_{30}H_{18}O_{10}$ It gave a orange–red colour in Mg–HCl test and a brown one with alcoholic $FeCl_3$ The IR spectra possessed a broad hydroxyl absorption at 3400 cm^{-1} and carbonyl bands at 1655 and 1650 cm^{-1} The UV spectra were similar to that of apigenin, and the maxima showed bathochromic shift on addition of NaOAc or in the presence of $AlCl_3$ indicating the presence of OH in 7, 4′ and 5 (or 3) positions[8] Acetylation of compound A with pyridine–Ac_2O gave a pentaacetate (A_I), m p 260° Methylation with Me_2 SO_4 gave a pentamethylether (A_{II}), m p 265–267°, $C_{35}H_{28}O_{10}$ M^+ 608 The NMR spectra of compound A, A_I and A_{II} showed five OH groups and 13 aromatic protons in compound A and indicated that compound A was a biflavone with an ether-linkage Two of the five hydroxy protons showed as singlets at the most down-field, δ 13 4 (s) and δ 13 1(s), indicating the two chelating OH groups at 5- and 5″-positions Eight of the thirteen aromatic protons appeared as two sets of A_2B_2 pattern, δ 8 12 (*d*, *J* 9 Hz, 2H), δ 7 16 (*d*, *J* 9 Hz, 2H), and δ 8 06 (*d*, *J* 8 Hz, 2H), δ 7 06 (*d*, *J* 8 Hz, 2H) Two of them appeared as *meta*-coupled doublets (*J* 2 Hz) at δ 6 70 (1H) and δ 6 43 (1H), which were assigned to C-8 and C-6 protons respectively The remaining three aromatic protons showed as singlets at δ 6 93 (2H) and δ 6 83 (1H) which were assigned to C-3, C-3″ and C-8″ (or C-6″) protons respectively The above evidence suggested that the structure of compound A was composed of two apigenin units joined by a C–O–C linkage as 4′-O-6″ (hinokiflavone), 4′-O-8″, 7-O-6″ or 7-O-8″ The paramagnetic induced shifts of compound A due to addition of $Eu(FOD)_3$[9] showed that the linkage must be at C-6″, e g hinokiflavone, which was confirmed by comparison with authentic hinokiflavone, its pentaacetate and pentamethylether (TLC, IR, NMR)

Pigment II was recrystallized repeatedly from EtOH and MeOH to yield a yellow crystalline compound B, m p 254–257° (resolidified at 274°), $[\alpha]_D^{25}$ + 5 4° (48 mg/1 ml pyridine), $C_{30}H_{18}O_{10}$, M^+ 538 It gave an orange–red colour in Mg–HCl test, and a brown one with alcoholic $FeCl_3$ The IR absorption appeared at 3300 (hydroxyl groups), 1650 (conjugated γ-pyrone), 1600, 1575 and 1500 cm^{-1} (C_6H_6 ring), and 830 cm^{-1} (ρ-substituted) Its UV absorption maxima in MeOH were very similar to those of apigenin and they showed the characteristic bathochromic shift on addition of NaOAc or $AlCl_3$ Acetylation of compound B afforded a hexaacetate (B_I), m p 251–252°, $C_{42}H_{30}O_{16}$, M^+ 790 Methylation of compound B gave a hexamethylether (B_{II}), m p 230–231 5°, $C_{36}H_{30}O_{10}$, M^+ 622 The NMR spectra of compound B, B_I and B_{II} showed six OH groups and twelve aromatic protons in compound B, indicating that compound B was a biflavone with a C–C linkage Two of the six hydroxyl protons showed as singlets at the most down-field,

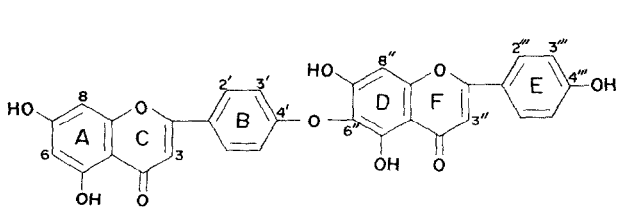
[6] CHEN, F C , LIN, Y M , *et al*, presented to the 40th Anniversary Year Meeting of the Chinese Chemical Society, Taipei 21 October 1972 Abstracts p 57

[7] This investigation was carried out at the Department of Applied Chemistry Tainan Technical College Tainan, 1940–43 We are indebted to late Professor I Sakuma, Professor I Momose, Messrs Wen Chung-san and Li An-chin for their cooperation in getting the plant material, extraction and evaporation of the pigments

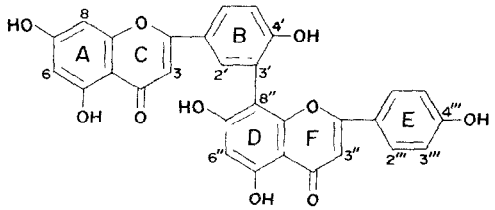
[8] JURD, L (1962) in *The Chemistry of Flavonoid Compounds* (GEISSMAN, T A , ed), p 107, Pergamon Press, Oxford

[9] OKIGAWA, M , KAWANG, N , RAHMAN, W and DHAR, M M (1972) *Tetrahedron Letters* 4125

δ 13 17 and δ 13 03, indicating the two chelating OH groups at 5 and 5″-positions Four of the 12 aromatic protons appeared as a set of A_2B_2 pattern δ 7 73 (*d*, *J* 9 Hz, 2H) and δ 6 88 (*d*, *J* 9 Hz, 2H) indicating H-2″, H-6″′ H-3″′ and H-5″′ in ring E The signals at δ 8 17 (m, 2H) and δ 7 30 (*d*, *J* 9 Hz, 1H) were assigned to H-2′ H-6′ and H-5′ in ring B The *meta* coupled doublets at δ 6 33 (*J* 2 Hz, 1H) and δ 6 62 (*J* 2 Hz 1H) were attributed to the H-6 and H-8 The three singlets at δ 6 90 (1 H), δ 6 95 (1 H) and δ 6 58 (1 H) indicating the uncoupling protons of H-3, H-3″ and H-6″ (or H-8″) These data were consistent with two flavone units with one linked to the other from C-3 of ring B to either C-8″ (*e g* amentoflavone) or C-6″ of phloroglucinol ring D The compound B was confirmed as amentoflavone by comparison with authentic amentoflavone its hexaacetate and hexamethylether (TLC, IR NMR and MS)



(A) Hinokiflavone



(B) Amentoflavone

Acknowledgements— The authors wish to express their grateful thanks to Professor N Kawano for generous gift of authentic specimens copies of NMR spectra and helpful suggestions to Professors W C Lin C H Yang T M Hseu and L C Lin for NMR UV, IR and MS, to Professor T S Shih for general technical assistance This work was supported by the National Council on Science Development as the research project CRC-6204 of Chemistry Research Center National Taiwan University

---

Phytochemistry 1974 Vol 13 pp 278 to 279 Pergamon Press Printed in England

FLAVONOL GLYCOSIDES OF *AMSONIA CILIATA*

LOWELL E URBATSCH and TOM J MABRY

The Cell Research Institute and Department of Botany, The University of Texas at Austin Austin TX 78712 U S A

(*Received* 9 *August* 1973 *Accepted* 24 *August* 1973)

Key Word Index— *Amsonia ciliata* Apocynaceae, flavonoids, tamarixetin glycosides

Seven flavonoid glycosides (no aglycones) were detected in *Amsonia ciliata* Walt including two new natural products, tamarixetin 3-*O*-arabinoside (**1**) and tamarixetin 3-*O*-galactoside (**2**) The five previously known constituents are isorhamnetin 3-*O*-galactoside (**3**), kaempferol 3-*O*-arabinoside (**4**) kaempferol 3-*O*-galactoside (**5**), quercetin 3-*O*-arabinoside (**6**), and quercetin 3-*O*-galactoside (**7**)

Since acid hydrolysis of **1** gave quercetin 4′-methyl ether (co-chromatography with an authentic sample by PC and TLC and UV spectra) and arabinose (GLC of the trimethylsilylated sugar), the only questions remaining concerned the position and the nature of attachment and the number of arabinose units attached to the aglycone skeleton