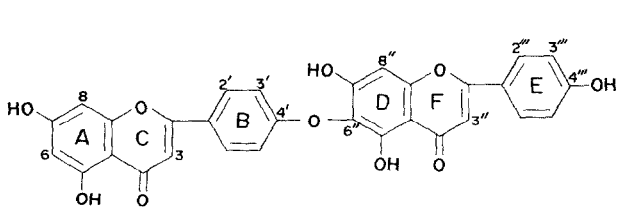
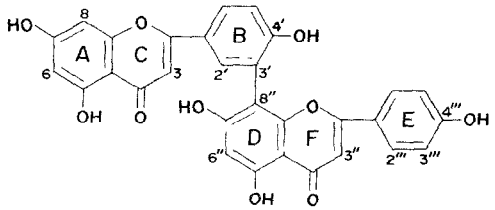
δ 13 17 and δ 13 03, indicating the two chelating OH groups at 5 and 5″-positions Four of the 12 aromatic protons appeared as a set of A_2B_2 pattern δ 7 73 (*d*, *J* 9 Hz, 2H) and δ 6 88 (*d*, *J* 9 Hz, 2H) indicating H-2″, H-6″′ H-3″′ and H-5″′ in ring E The signals at δ 8 17 (m, 2H) and δ 7 30 (*d*, *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

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FLAVONOL GLYCOSIDES OF *AMSONIA CILIATA*

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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

The presence of the methyl ether group at C_4, the arabinose at C_3, and hydroxyl groups C_5, C_7, and C'_3 in **1** was established by a standard set of six UV spectra, an NMR spectrum of the trimethylsilylated derivative and color tests The natural product was purple when viewed as a spot on a PC in UV light with NH_3 vapors, the aglycone obtained upon acid hydrolysis appeared yellow when viewed in UV light in accord with the former having a 3-*O*-sugar substituent

The presence of a C_5-hydroxyl and a C_3 substituent in **1** was further indicated by a bathochromic shift of 46 nm for Band I in the presence of $AlCl_3$–HCl relative to the methanol UV spectrum In the presence of NaOMe, Band **1** for the natural product exhibited a bathochromic shift of only 22 nm with a decrease in intensity in accord with a 3,4′-substituted quercetin derivative and the Band 2 bathochromic shift of 17 nm in the presence of NaOAc supported the presence of an unsubstituted hydroxyl group at C_7 [1]

The NMR spectrum of the trimethysilyl ether of **1** exhibited signals typical for a quercetin 3-*O*-arabinoside 4′-methyl ether a three-proton singlet at 3 86 for one methoxyl group, a doublet at 5 64 (*J* 8 5 Hz) for H-1 sugar proton, a series of signals for the other sugar protons between 3 54 and 3 42, aromatic proton signals at 7 91 (*J* 9, 2 5) and 7 40 (*J* 2 5) for H-6′ and H-2′, respectively, a doublet at 6 85 (*J* 9 0) for H-5′ and doublets at 6 50 (*J* 2 5) and 6 17 (*J* 2 5) for H-8 and H-6, three signals, 0 31, 0 25 and 0 21 for the trimethylsilyl ethers at the 3′, 5 and 7 positions *

For **2** the color reactions and UV spectra for the second new natural product, and its aglycone were virtually identical with those observed for **1** Thus, since the R_f for **2** indicated a monoglycoside and since acid hydrolysis gave quercetin 4′-*O*-methyl ether and galactose, the natural product must be quercetin 3-*O*-galactoside 4′-methyl ether

EXPERIMENTAL

A voucher specimen (Urbatsch 984) is deposited in the University of Texas Herbarium (TEX) Air dried leaves, 150 g (collected from U S A Oklahoma Pushmataha Co 5 7 mi N of the intersection of Hwys 1 4 and 3 near Antlers) of *Amsonia ciliata* were extracted from several plants at room temp 2 × with $CHCl_3$ and 2 × with 85% aq MeOH, each extraction was for 12 hr The $CHCl_3$ extracts contained no flavonoids and were discarded The crude syrup of the aq MeOH extract was chromatographed over a polyamide column (5 × 40 cm) Elution began with $CHCl_3$–MeOH (3 2), followed by increasing amounts of MeOH Five bands (shown by UV) were collected Band 1 contained compounds **1** and **2** which were separated by PC (Whatman 3 mm) using 15% aq AcOH, Band 2 contained compound **3**, band 3 contained compounds **4** and **5** which were also separated by PC, and Bands 4 and 5 contained compounds **6** and **7**, respectively

Sugar identification utilized a stainless steel column 8′ by 1/8″ (in dia) packed with 80–100 mesh 3% SE30 on chromosorb G installed in a Perkin-Elmer 900 gas chromatograph having a flow rate of 25 ml of He/min (as measured at the detector end of the column) and an isothermal oven temp of 170°

All other procedures were those outlined in Mabry *et al* [1]

Compound **1** UV λ_{max} (MeOH) 257, 269 sh, 353 nm, λ_{max} (NaOMe) 275, 375 nm, λ_{max} ($AlCl_3$) 267, 275 sh, 299 sh, 358, 400, λ_{max} ($AlCl_3$–HCl) 267, 275 sh, 300, 357, 399, λ_{max} (NaOAc) 274, 369, λ_{max} (NaOAc–H_3BO_3) 258, 268 sh, 355

Acknowledgements—This work was supported by the Robert A Welch Foundation (Grant F-130) and The National Science Foundation (Grant GB-29576X)

* Values are given in ppm (δ scale) relative to TMS as internal standard

[1] MABRY, T J MARKHAM, K R and THOMAS, M B (1970) *The Systematic Identification of Flavonoids*, Springer, Heidelberg