[Chem. Pharm. Bull. 18(5) 916—918 (1970)]

UDC 581.19 : 582.734.04 : 547.814.5.02.05 : 547.972.2.02

Studies on Unutilized Resource. IV.[1] Flavonoids in the Leaves of *Sorbaria stellipila* Schneid (Rosaceae)

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(Received November 29, 1969)

The fresh leaves of *Sorbaria stellipila* Schneid (*S. sorbifolia* A. Br. *var. stellipila* Maxim.) was extracted with methanol and the methanolic extract was extracted with ethyl acetate. The ethyl acetate extract afforded sorbarin (scutellarein-7-monorhamnoside) and a new flavonoide (I) as yellow needles, mp 290—292°. I corresponded to the molecular formula of $C_{16}H_{12}O_6$.

Complete ethyl ether of I was identified as 7-methoxy-,5,6,4′-triethoxyflavone by direct comparison with the authentic sample, which was produced from sorbarin.

Consequently, I was determined as scutellarein-7-methyl ether (5,6,4′-trihydroxy-7-methoxyflavone), and named sorbifolin.

In the previous paper,[3] sorbarin (scutellarein-7-monorhamnoside) was isolated from the fresh leaves of *Sorbaria stellipila* Schneid (=*S. sorbifolia* A. Br. *var. stellipila* Maxim.). Besides sorbarin, a new flavonoide, which would be named sorbifolin here after, has now been isolated from the same plant source, and the present paper deals with the result of experiments carried out on the elucidation of its chemical structure.

The fresh leaves were extracted with methanol and the methanolic extract was extracted with ether. The insoluble part was further extracted with ethyl acetate and the latter extract afforded sorbifolin (I) as yellow needles, mp 290—292°. I colored greenish brown to ferric chloride solution, exhibited a positive reduction test for flavonoids and negative gossypetin reaction test.[4] Paper partition chromatography (P.P.C.) of I gave *Rf* values of 0.7 (butanol–acetic acid–water=4:1:2), 0.64 (60% acetic acid) and 0.265 (30% acetic acid). I corresponded to the molecular formula of $C_{16}H_{12}O_6$.

In order to determine the position of hydroxyl groups, alkaline fusion of I was carried out and *p*-hydroxybenzoic acid, mp 210°, was obtained as phenol carboxylic acid, but phenol portion was not obtained. This suggests that the phenol is a polymerizable polyhydroxyphenol.

Demethylation of I with hydriodic acid gave a product as yellow needles, mp over 350°, corresponding to the molecular formula of $C_{15}H_{10}O_6$.

The demethylated product formed a tetraacetate colorless needles, mp 239°, which was identified as scutellarein tetraacetate by direct comparison with an authentic sample.

Acetylation of I afforded colorless needles, mp 226—228° (II), negative to ferric chloride and corresponding to the molecular formula of $C_{22}H_{18}O_9$.

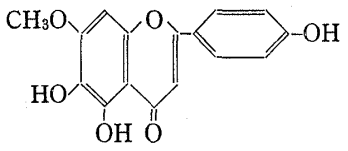
The nuclear magnetic resonance (NMR) spectrum[5] of II taken in deuterochloroform showed a pair of 2H doublets (J=9 cps) centered at 7.90 and 7.28 ppm, assignable to the proton located at the 2′,6′ and 3′,5′-position, and two 1H singlets at 6.96 and 6.58 ppm assig-

1) Part III: M. Arisawa, Y. Ishiwari, T. Nakaoki, S. Sekino and T. Takakuwa, *Shoyakugaku Zasshi*, in press.
2) Location: *Umezawa-cho, 2-9-1, Toyama.*
3) M. Arisawa and T. Nakaoki, *Yakugaku Zasshi*, **89**, 705 (1969).
4) A.G. Perkin, *J. Chem. Soc.*, **103**, 650 (1913).
5) Tetramethylsilan as an internal standard.

nable to the proton located at 8 and 3-position on aromatic ring, respectively. 3H singlet at 3.95 ppm was attributed to one methoxyl group, and 3H singlet at 2.42 and 6H singlet at 2.35 ppm were attributed to three acetoxyl groups. These facts indicated that I is scutellarein monomethyl ether.

Oxidation of I with hydrogen peroxide afforded *p*-hydroxybenzoic acid. The incomplete methyl ether of I by diazomethane afforded scutellarein-6,7,4′-trimethyl ether. II showed melting point depression on admixture with hispidulin (scutellarein-6-methyl ether) acetate, mp 169—171°.[6]

In agreement with these facts, ultraviolet spectrophotometry of I showed the presence of a free hydroxyl group at 5 and 4′-position, and its absence at 7-position in its molecule.



sorbifolin

Finally, sorbifolin triethyl ether was identified as 7-methoxy-5,6,4′-triethoxyflavone (IV) by direct comparison with the authentic specimen which was produced from sorbarin (scutellarein-7-monorhamnoside). It follows, therefore, that I has the structure of 5,6,4′-trihydroxy-7-methoxyflavone, *i.e.*, scutellarein-7-methyl ether.

Experimental[7]

Isolation of Sorbarin and Sorbifolin——The fresh leaves were refluxed twice with MeOH, the residue was successively extracted with ether and EtOAc. EtOAc extract was treated with MeOH. Sorbarin crystallized as pale yellow needles. The filtrate of sorbarin was treated with activate charcoal and then concentrated. Sorbifolin crystallized as yellow needles.

Properties of Sorbarin——Pale yellow needles, mp>300°, greenish brown to $FeCl_3$. Mg+HCl: orange, Zn+HCl: orange. The dilute acid hydrolyzate, reduce the Fehling solution. P.P.C. *Rf* :0.59 (4:1:2 sorbarin 0.59), 0.67 (60% AcOH sorbarin 0.67), 0.41 (30% AcOH sorbarin 0.41). UV λ_{max}^{EtOH} mμ (log ε): 288 (4.17), 340 (4.31). Its IR spectrum was found to be superimposable with that of authentic sorbarin. Acetylation of sorbarin with Ac_2O and H_2SO_4 in the usual manner gave its acetate as colorless needles, mp 156—158°, underpressed on admixture with the authentic sample.

Properties of Sorbifolin (I)——Yellow needles, mp 290—292°, greenish brown to $FeCl_3$. Mg+HCl: orange yellow, $Ba(OH)_2$: green. P.P.C. *Rf*: 0.70 (4:1:2), 0.64 (60% AcOH), 0.625 (30% AcOH). UV λ_{max}^{EtOH} mμ (log ε): 253 (4.23), 308 (3.94). UV $\lambda_{max}^{EtOH\text{-}AlCl_3}$ mμ: 263, 323. UV $\lambda_{max}^{EtOH\text{-}AcONa}$ mμ: 254, 309. UV $\lambda_{max}^{EtOH\text{-}AcONa}$ mμ: 257, 310. *Anal.* Calcd. for $C_{16}H_{12}O_6$: C, 63.98; H, 4.03. Found: C, 64.10; H, 4.11.

Alkaline fusion of I furnished *p*-hydroxybenzoic acid as the only detectable fusion product. Oxidation of I with hydrogen peroxide afforded the same acid.

Acetylation of I with Ac_2O and H_2SO_4 in the usual manner gave its acetate as colorless needles, mp 226—228°, no color to $FeCl_3$. NMR (10% solution in $CDCl_3$): 7.90 (2H, doublet, J=9.0 cps., >C–H×2), 7.28 (2H, doublet, J=9.0 cps., >C–H×2), 6.96 (1H, singlet, >C–H), 6.58 (1H, singlet, >C–H), 3.95 (3H, singlet, OCH_3), 2.42 (3H, singlet, $O\cdot CO\cdot CH_3$), 2.35 (6H, singlet, $O\cdot CO\cdot CH_3\times 2$). *Anal.* Calcd. for $C_{22}H_{18}O_9$: C, 61.95; H, 4.26. Found: C, 62.03; H, 4.30.

Demethylation of I——A mixture of 200 mg of I, 4 ml of HI (d=1.7) and 2 drops of phenol was refluxed for 8 hr on oil bath. The reaction mixture was added into H_2O and treated with $NaHSO_4$. Dark yellow solid was separated from the mixture. Recrystallized from MeOH. Yellow needles, mp>350°, greenish brown to $FeCl_3$. P.P.C. *Rf*: 0.74 (4:1:2 scutellarein 0.74), 0.52 (60% AcOH scutellarein 0.52). UV λ_{max}^{EtOH} mμ: 288, 340. *Anal.* Calcd. for $C_{15}H_{10}O_6$: C, 62.92; H, 3.52. Found: C, 63.05; H, 3.63.

Its IR spectrum was found to be superimposable with that of authentic scutellarein. Acetylation of demethylated product with Ac_2O and H_2SO_4 in the usual manner gave its acetate as colorless needles, mp 239°, underpressed on admixture with an authentic sample. Its IR spectrum was found to be hardly distinguishable from that of the authentic specimen.

Methylation of I——To a solution of I (100 mg) in MeOH (200 ml), an ether solution of CH_2N_2, prepared from 5 g of nitrosomethylurea, was added. After standing at room temp. for 24 hr, the solvent was removed and the residue was treated MeOH. Pale yellow needles that separated were collected, recrystallized from MeOH to almost colorless needles, mp 187—189°, which gave greenish brown with $FeCl_3$. *Anal.* Calcd. for $C_{18}H_{16}O_6$: C, 65.83; H, 4.92. Found: C, 65.88; H, 5.01. Its IR spectrum was found to be superimposable

6) M. Aritomi, *Chem. Pharm. Bull.* (Tokyo), **15**, 432 (1967).
7) All melting points were uncorrected.

with that authentic scutellarein-6,7,4′-trimethyl ether, underpressed on admixture with the authentic sample.

Ethylation of I——A mixture of sorbifolin (20 mg) in acetone (5 ml) refluxed for 24 hr with K_2CO_3 (1 g) and diethyl sulfate (0.4 ml), and poured into ice-water. The precipitate was chromatographed over silica-gel. Recrystallized from MeOH to colorless needles, mp 136—138°, which gave no color to $FeCl_3$, yielding 15 mg. *Anal.* Calcd. for $C_{22}H_{24}O_6$: C, 68.72; H, 6.30. Found: C, 68.85; H, 6.28. Its IR spectrum was found to be superimposable with that of the authentic sample, which was produced from sorbarin, and underpressed on admixture with the authentic sample which was produced from sorbarin.

7-Hydroxy-5,6,4′-triethoxyflavone (III)——A suspension of sorbarin (500 mg) in acetone (150 ml) was refluxed for 48 hr with K_2CO_3 (7 g) and diethyl sulfate (2 ml), and poured into ice-water. The precipitate was collected, washed with H_2O and dried. A solution of the precipitate in 5% H_2SO_4 was refluxed for 2 hr. The aglycone that separated was collected, washed with H_2O and recrystallized from MeOH. Colorless needles, mp 185—187°, which gave no color to $FeCl_3$ yielding 320 mg. *Anal.* Calcd. for $C_{21}H_{22}O_6$: C, 67.79; H, 6.78. Found: C, 67.88; H, 6.91.

7-Methoxy-5,6,4′-triethoxyflavone (IV)——To a solution of III (100 mg) in MeOH (100 ml), an ether solution of CH_2N_2, prepared from 5 g of nitrosomethylurea, was added. After standing at room temp. for 24 hr, the solvent was removed and the residue was treated MeOH. Colorless crystals that separated were collected, recrystallized from MeOH. Colorless needles, mp 138—139°, yielding 100 mg. *Anal.* Calcd. for $C_{22}H_{24}O_6$: C, 68.72; H, 6.30. Found: C, 68.75; H, 6.32. Its IR spectrum was found to be superimposable with that of authentic sorbifolin triethyl ether, and underpressed on admixture with authentic sorbifolin triethyl ether.

Acknowledgement The authors wish to express their heartiest thank to Prof. N. Morita, Dr. M. Shimizu, Faculty of Pharmacy, University of Toyama, for their kind advice and encouragements, and to Dr. M. Aritomi, Faculty of Education, Kumamoto University for his kind gift of the sample of hispidulin acetate. The authors wish to thank President K. Shioi, Kokando Co., Ltd., for his kind conveniences and supports. Thanks are also due to Faculty of Pharmacy, University of Toyama for the NMR spectra and elemental analyses.