Flavonoids of *Polygonum sieboldi* and *P. filiforme*

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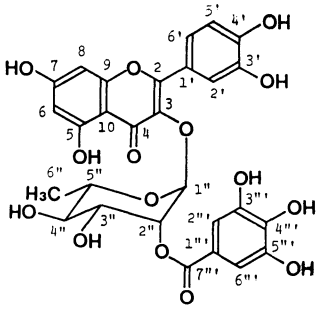
(Received May 25, 1981)

Synopsis. Five flavonoids containing a new flavonol glycoside were isolated from *Polygonum sieboldi* and *P. filiforme*. The structure of the new compound was determined as quercetin 3-rhamnoside 2″-gallate by chemical and spectroscopic data.

Many flavonoids have been isolated from *Polygonum* species (*Polygonaceae*), and we previously reported the identification of five flavonoids from *P. nodosum* Pers.[1,2] Further investigation of this species has led to the isolation of several flavonoids containing a new compound. Two known compounds, quercetin (**1**) and quercetin 3-rhamnoside (**2**), were isolated from *P. sieboldi* Maxim. (Akino-unagitsukami in Japanese) and four known compounds, **1**, **2**, myricetin 3-rhamnoside (**3**), and quercetin 3-glucoside 2″-gallate (**4**), and a new flavonoid glycoside (**5**) were isolated from *P. filiforme* Thunb. (Mizuhiki in Japanese). The ^{13}C NMR spectrum of **5** and the ^{1}H NMR spectrum of the TMSi ether of **5** (**6**) were almost identical with that of **4** with the exception of the sugar part, which was assignable as L-rhamnose from these spectra.[3,4] The fragment ions of **5** by MS spectrum are assignable as quercetin (*m/z* 302), gallic acid (170), and galloyl group (153). The UV spectrum of **5** shows also the presence of a substituted hydroxyl group at C-3 of flavonol by bathochromic shifts in addition of both NaOAc and $AlCl_3$–HCl.[2,4] The compound obtained by the hydrolysis of **5** with aqueous ammonia was identical with **2** by TLC. From the ^{13}C shift values ($\Delta\delta$) of C-2, C-3, and C-4 of rhamnose of **5** having *ca.* −3.0, +1.0, and −2.0, respectively,[3] and the downfield shift of H-2 (δ 5.56) of rhamnose of **6** by ^{1}H NMR spectrum, the galloyl group may be attached to C-2 of rhamnose. Accordingly, compound **5** has the structure of quercetin 3-α-L-rhamnopyranoside 2″-gallate. The similar compound, myricetin 3-α-L-rhamnopyranoside 2″-gallate[5] had been isolated some years ago.



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Experimental

Isolation of Flavonoids. By the previous reported procedure,[2] compounds **1** and **2** from *P. Sieboldi* Maxim., and compounds **1**, **2**, **3**, **4**, and **5** from *P. filiforme* Thunb. Compounds **1**, **2**, **3**, and **4** were identified as quercetin, quercetin 3-rhamnoside, myricetin 3-rhamnoside, and quercetin 3-glucoside 2″-gallate, respectively, by comparison with the TLC and the IR spectra of authentic samples and thier acetates.

Isolation of Quercetin 3-Rhamnoside 2″-Gallate (5). Compound **5**, yellowish plates from MeOH–H_2O, mp 207—208.5 °C; $[\alpha]_D^{25}$ −1.8 (*c*=0.9, MeOH); Found: C, 50.92; H, 3.94%. Calcd for $C_{28}H_{24}O_{15}\cdot 3H_2O$: C, 51.38; H, 4.62%; MS (20 eV) *m/z* 302, 170, and 153; UV (EtOH): λ_{max} 257 (sh), 267 (ε 27900), and 351 nm (ε 16400), (+$AlCl_3$): 276, 303 (sh), and 432 nm, (+$AlCl_3$+HCl): 271, 355, and 400 nm (sh), (+NaOAc): 273 and 359 nm; IR (Nujol): ν_{max} 3250, 1710, 1655, 1605, and 1205 cm^{-1}; ^{13}C NMR (25 MHz, DMSO-d_6): δ 17.7 (C-6″), 68.6 (C-3″), 70.8 (C-5″), 71.8 (C-2″ and 4″), 93.8 (C-8), 98.5 (C-1″), 98.9 (C-6), 104.1 (C-10), 109.0 (C-2‴ and 6‴), 115.7 (C-2′ and 5′), 119.3 (C-1‴), 120.6 (C-1′), 121.2 (C-6′), 133.4 (C-3), 138.6 (C-4‴), 145.3 (C-3′), 145.5 (C-3‴ and 5‴), 148.6 (C-4′), 156.5 (C-2), 157.3 (C-9), 161.3 (C-5), 164.3 (C-7‴), 165.0 (C-7), and 177.5 (C-4).

TMSi Ether of 5 (6). ^{1}H NMR (100 MHz, $CDCl_3$): δ 0.99 (3H, d, *J*=6 Hz, H-6″), 3.4 (1H, m, H-5″), 3.57 (1H, t, *J*=8 Hz, H-4″), 4.02 (1H, dd, *J*=8 and 2 Hz, H-3″), 5.56 (1H, t, *J*=2 Hz, H-2″), 5.66 (1H, d, *J*=2 Hz, H-1″), 6.26 (1H, d, *J*=2 Hz, H-6), 6.37 (1H, d, *J*=2 Hz, H-8), 6.97 (1H, d, 8 Hz, H-5′), 7.23 (2H, s, H-2‴ and 6‴), 7.37 (1H, d, *J*=2 Hz, H-2′), and 7.51 (1H, dd, *J*=8 and 2 Hz, H-6′).

Alkaline Hydrolysis of 5. To **5** (7 mg) were added 0.1 mol dm^{-3} aqueous ammonia (0.8 ml) and MeOH (1 ml) and the mixture allowed to stand for one day at room temperature. From the TLC of the reacting solution, the product was identified as quercetin 3-rhamnoside (**2**) [on silica gel plate; solvent, EtOAc–MeCOEt–HCO_2H–H_2O, 5 : 2 : 0.1 : 1].

We are grateful to Mr. Kozo Shibata, Osaka City University, for the measurement of ^{1}H and ^{13}C NMR.

References

1) T. Isobe, T. Fukushige, and Y. Noda, *Chem. Lett.*, **1979**, 27.
2) T. Isobe, N. Ito, and Y. Noda, *Phytochemistry*, **19**, 1877 (1980).
3) K. R. Markham, B. Ternai, R. Stanley, H. Geiger, and T. J. Mabry, *Tetrahedron*, **34**, 1389 (1978).
4) T. J. Mabry, K. R. Markham, and M. B. Thomas, "The Systematic Identification of the Flavonoids," Springer, New York (1970).
5) G. G. Zapesochnaya and G. P. Shnyakiana, *Khim. Prir. Soedin.*, **1975**, 720.