KAEMPFEROL AND QUERCETIN FLAVONOIDS FROM *Rosa rugosa*

Z. P. Xiao,[1,2] H. K. Wu,[1,2] T. Wu,[1,2] H. Shi,[1,2] B. Hang,[1] and H. A. Aisa[1*] UDC 547.972

The Chinese plant *Rosa rugosa* Thunb. is known to be an antioxidant and a good natural source of antioxidants [1]. Therefore, we investigated the chemical composition of flowers of *R. rugosa* Thunb. collected in Xinjiang Autonomous region (PRC).

Dry raw material (5 kg) was extracted with ethanol (70%). The alcohol extract was concentrated in vacuo and fractionated over a column packed with large-pore ion-exchange resin with elution by water and aqueous alcohol (25 and 50%). The alcohol fractions were rechromatographed over polyamide, silica gel, and Sephadex LH-20 to afford **1-9**, of which four were kaempferol flavonoids, four were quercetin flavonoids, and one was a phenylethylglycoside. The aqueous fraction was extracted with ethylacetate and chromatographed over silica gel to isolate two acidic phenolic compounds **10** and **11**.

Kaempferol (1), yellow powder (acetone), mp 278-279°C. UV spectrum (λ_{max}, MeOH, nm): 266, 322sh, 366; +$AlCl_3$: 270, 305sh, 350sh, 424; +$AlCl_3$/HCl: 270, 305sh, 347sh, 424.

PMR spectrum (400 MHz, acetone-d_6, δ, ppm, J/Hz): 8.16 (2H, d, J = 8.8, H-2′,6′), 7.03 (2H, d, J = 8.8, H-3′,5′), 6.54 (1H, d, J = 2.0, H-8), 6.27 (1H, d, J = 2.0, H-6).

^{13}C NMR spectrum (400 MHz, acetone-d_6, δ, ppm): 146.9 (C-2), 136.5 (C-3), 176.5 (C-4), 157.7 (C-5), 98.9 (C-6), 165.0 (C-7), 94.3 (C-8), 160.1 (C-9), 103.9 (C-10), 123.1 (C-1′), 130.3 (C-2′,6′), 116.1 (C-3′,5′), 161.9 (C-4′) [2].

Quercetin (2), yellow needles (acetone), mp >300°C. UV spectrum (λ_{max}, MeOH, nm): 256, 374; +$AlCl_3$: 271, 451; +$AlCl_3$/HCl: 266, 302sh, 361sh, 427.

PMR spectrum (400 MHz, acetone-d_6, δ, ppm, J/Hz): 7.81 (1H, br.s, H-2′), 7.70 (1H, d, J = 8.0, H-6′), 6.99 (1H, d, J = 8.0, H-5′), 6.53 (1H, br.s, H-8), 6.27 (1H, br.s, H-6) [2].

Juglanin (3), light yellow powder (MeOH), mp 229-230°C. UV spectrum (λ_{max}, MeOH, nm): 266, 350; +$AlCl_3$: 274, 304sh, 351sh, 399; +$AlCl_3$/HCl: 276, 302sh, 346sh, 397.

PMR spectrum (400 MHz, CD_3OD, δ, ppm, J/Hz): 7.87 (2H, d, J = 7.2, H-2′,6′), 6.84 (2H, d, J = 7.2, H-3′,5′), 6.32 (1H, d, J = 2.0, H-8), 6.12 (1H, d, J = 2.0, H-6), 5.38 (1H, br.s, H-1′), 3.37-4.23 (sugar protons).

^{13}C NMR spectrum (400 MHz, CD_3OD, δ, ppm): 158.5 (C-2), 134.9 (C-3), 179.9 (C-4), 163.1 (C-5), 99.9 (C-6), 166.0 (C-7), 94.8 (C-8), 159.5 (C-9), 105.7 (C-10), 122.8 (C-1′), 132.0 (C-2′,6′), 116.5 (C-3′,5′), 161.6 (C-4′), 109.6 (C-1″), 83.4 (C-2″), 78.6 (C-3″), 88.0 (C-4″), 62.4 (C-5″). Acid hydrolysis of **3** gave kaempferol and arabinose [3].

Avicularin (4), yellow powder (MeOH), mp 200-201°C. UV spectrum (λ_{max}, MeOH, nm): 257, 300, 356; +$AlCl_3$: 275, 335sh, 432; +$AlCl_3$/HCl: 270, 297sh, 364sh, 401.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.6 (1H, br.s, 5-OH), 7.56 (1H, dd, J = 8.4, 2.4, H-6′), 7.48 (1H, d, J = 2.4, H-2′), 6.86 (1H, d, J = 8.4, H-5′), 6.42 (1H, d, J = 2.0, H-8), 6.20 (1H, d, J = 2.0, H-6), 5.57 (1H, d, J = 1.2, H-1″), 3.25-4.15 (sugar protons).

^{13}C NMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 156.8 (C-2), 133.3 (C-3), 177.5 (C-4), 160.8 (C-5), 98.5 (C-6), 164.2 (C-7), 93.5 (C-8), 156.3 (C-9), 103.7 (C-10), 120.8 (C-1′), 115.4 (C-2′), 144.8 (C-3′), 148.2 (C-4′), 115.3 (C-5′), 121.6 (C-6′), 107.6 (C-1″), 81.8 (C-2″), 76.6 (C-3″), 85.6 (C-4″), 60.4 (C-5″). Acid hydrolysis of **4** gave quercetin and arabinose [3].

Astragalin (5), yellow needles (MeOH), mp 219-220°C. UV spectrum (λ_{max}, MeOH, nm): 266, 300sh, 351; +$AlCl_3$: 274, 304sh, 351sh, 397; +$AlCl_3$/HCl: 275, 302sh, 346sh, 396.

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1) Xinjiang Technical Institute of Physics and Chemistry, CAS, Urumqi 830011, China, tel: +08609913835679, e-mail: haji@ms.xjb.ac.cn; 2) Graduate University of the Chinese Academy of Sciences, Beijing 100049, China. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 600-601, November-December, 2006. Original article submitted September 22, 2006.

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PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.6 (1H, br.s, 5-OH), 10.9 (1H, br.s, 7-OH), 10.2 (1H, br.s, 4′-OH), 8.05 (2H, d, J = 7.2, H-2′,6′), 6.89 (2H, d, J = 7.2, H-3′,5′), 6.46 (1H, d, J = 2.0, H-8), 6.23 (1H, d, J = 2.0, H-6), 5.47 (1H, d, J = 7.6, H-1″), 3.07-3.58 (sugar protons).

^{13}C NMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 156.1 (C-2), 133.1 (C-3), 177.3 (C-4), 160.8 (C-5), 98.4 (C-6), 163.8 (C-7), 93.5 (C-8), 156.3 (C-9), 103.9 (C-10), 120.8 (C-1′), 130.8 (C-2′,6′), 115.0 (C-3′,5′), 159.7 (C-4′), 100.6 (C-1″), 74.0 (C-2″), 76.1 (C-3″), 69.6 (C-4″), 77.3 (C-5″), 60.6 (C-6″). Acid hydrolysis of **5** gave kaempferol and glucose [4].

Hyperoside (6), light yellow powder (MeOH), mp 234-236°C. UV spectrum (λ_{max}, MeOH, nm): 257, 305sh, 361; +$AlCl_3$: 275, 342sh, 434; +$AlCl_3$/HCl: 269, 300sh, 368sh, 404.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.6 (1H, s, 5-OH), 7.66 (1H, d, J = 8.4, H-6′), 7.54 (1H, br.s, H-2′), 6.82 (1H, d, J = 8.4, H-5′), 6.42 (1H, br.s, H-8), 6.21 (1H, br.s, H-6), 5.37 (1H, d, J = 7.6, H-1″), 3.26-3.64 (sugar protons).

^{13}C NMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 156.1 (C-2), 133.4 (C-3), 177.3 (C-4), 160.8 (C-5), 98.5 (C-6), 163.9 (C-7), 93.4 (C-8), 156.2 (C-9), 103.7 (C-10), 121.0 (C-1′), 115.0 (C-2′), 144.5 (C-3′), 148.1 (C-4′), 115.7 (C-5′), 121.9 (C-6′), 101.6 (C-1″), 70.9 (C-2″), 72.9 (C-3″), 67.4 (C-4″), 75.6 (C-5″), 59.9 (C-6″). Acid hydrolysis of **6** produced quercetin and galactose [2].

Kaempferol-3-*O*-(2″-*O*-*β*-D-glycopyranosyl)-*β*-D-glucopyranoside (7), yellow powder (MeOH), mp 234-235°C. UV spectrum (λ_{max}, MeOH, nm): 266, 300sh, 350; +$AlCl_3$: 275, 304sh, 350sh, 396; +$AlCl_3$/HCl: 275, 302sh, 346sh, 395.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.6 (1H, br.s, 5-OH), 8.04 (2H, d, J = 7.2, H-2′,6′), 6.91 (2H, d, J = 7.2, H-3′,5′), 6.40 (1H, d, J = 2.0, H-8), 6.16 (1H, d, J = 2.0, H-6), 5.69 (1H, d, J = 7.6, H-1″), 4.61 (1H, d, J = 8.0, H-1″), 3.04-3.67 (sugar protons).

^{13}C NMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 156.3 (C-2), 132.7 (C-3), 177.1 (C-4), 160.8 (C-5), 98.7 (C-6), 164.0 (C-7), 93.6 (C-8), 155.2 (C-9), 103.8 (C-10), 120.9 (C-1′), 130.8 (C-2′), 115.1 (C-3′), 159.6 (C-4′), 115.1 (C-5′), 130.8 (C-6′), 97.8 (C-1″), 82.1 (C-2″), 76.2 (C-3″), 69.4 (C-4″), 76.3 (C-5″), 60.5 (C-6″), 103.4 (C-1‴), 74.1 (C-2‴), 77.3 (C-3‴), 69.2 (C-4‴), 76.8 (C-5‴), 60.2 (C-6‴). Acid hydrolysis of **7** produced kaempferol and glucose [4].

Quercetin-3-*O*-(2″-*O*-*β*-D-glucopyranosyl)-*β*-D-galactopyranoside (8), yellow powder (MeOH), mp 225-226°C. UV spectrum (λ_{max}, MeOH, nm): 256, 356; +$AlCl_3$: 274, 339sh, 428; +$AlCl_3$/HCl: 270, 363sh, 399.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.7 (1H, br.s, 5-OH), 9.3 (1H, br.s, 3′-OH), 7.69 (1H, dd, J = 8.8, 2.4, H-6′), 7.61 (1H, d, J = 2.4, H-2′), 6.86 (1H, d, J = 8.8, H-5′), 6.42 (1H, d, J = 2.0, H-8), 6.21 (1H, d, J = 2.0, H-6), 5.64 (1H, d, J = 7.6, H-1″), 4.57 (1H, d, J = 7.6, H-1‴), 3.07-3.80 (sugar protons).

^{13}C NMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 155.3 (C-2), 133.0 (C-3), 177.3 (C-4), 160.8 (C-5), 98.4 (C-6), 163.8 (C-7), 93.4 (C-8), 156.1 (C-9), 103.7 (C-10), 121.0 (C-1′), 115.2 (C-2′), 144.6 (C-3′), 148.2 (C-4′), 115.7 (C-5′), 122.1 (C-6′), 98.3 (C-1″), 80.6 (C-2″), 73.1 (C-3″), 67.3 (C-4″), 75.7 (C-5″), 59.7 (C-6″), 74.1 (C-2‴), 76.6 (C-3‴), 69.2 (C-4‴), 76.2 (C-5‴), 60.4 (C-6‴). Acid hydrolysis of **8** produced quercetin and galactose [5].

Based on the PMR and ^{13}C NMR data, **9**-**11** were identified as 2-phenylethyl-*O*-*β*-D-glucopyranoside (**9**), protocatechuic acid (**10**), and gallic acid (**11**).

Thus, juglanin (**3**), avicularin (**4**), hyperoside (**6**), kaempferol-3-*O*-(2″-*O*-*β*-D-glucopyranosyl)-*β*-D-glucopyranoside (**7**), quercetin-3-*O*-(2″-*O*-*β*-D-glucopyranosyl)-*β*-D-galactopyranoside (**8**), and protocatechuic acid (**10**) were isolated for the first time from *R. rugosa* Thunb.

REFERENCES

1. S. M. Niu, S. H. Zhu, W. Li, D. Wang, C. H. Wang, and F. Liu, *Acta Sci. Nat. Univ. Nankaiensis*, **37**, 29 (2004).
2. G. Ye and C. G. Huang, *Chem. Nat. Comp.*, **42**, 232 (2006).
3. M. Olszewska and M. Wolbis, *Acta Pol. Pharm.*, **58**, 367 (2001).
4. B. H. Hu, Z. Tian, and Z. C. Lou, *Acta Bot. Sin.*, **30**, 565 (1988).
5. Y. Zheng, X. W. Li, M. Y. Gui, and Y. R. Jin, *Chin. Pharm. J.*, **41**, 176 (2006).