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玫瑰花的化学成分研究(Ⅱ)

刘红燕,张永清*

山东中医药大学,济南 250355

摘　要:从玫瑰花中分离了5个化合物,通过波谱法和理化性质分别鉴定为原儿茶酸(**1**)(protoatechuic acid)、山柰酚(**2**)(Kaempferol)、草质素-8-甲醚(**3**)(Herbacetin-8-methylether)、异槲皮苷(**4**)(Tristin)、紫云英苷(**5**)(Astragalin)。其中,化合物**3**为首次从蔷薇属植物中分离得到。

关键词:玫瑰花;化学成分;分离;纯化

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Chemical Constituents from Rose Flowers(Ⅱ)

LIU Hong-Yan, ZHANG Yong-Qing*

Shandong University of Traditional Chinese Medicine, Jinan 250355, China

Abstract: Five constituents were isolated and purified from rose flowers. On the basis of spectral data and physiochemical properties, the structures of these compounds were elucidated as protoatechuic acid (**1**), kaempferol (**2**), herbacetin-8-methylether (**3**), tristin (**4**), astragalin (**5**).

Key words: rose flowers; chemical constituents; isolation; purification

Introduction

Rose flower, popularly used in the traditional Chinese medicine for female genital diseases and blood stagnation[1], is claimed to possess various biologically activity including antibacterial, antioxidant, anti-inflammatory, etc[1]. In our previous studies[2], seven active compounds were isolated from this plant. As a part of an ongoing research program for biologically active ingredients, this paper describes the isolation and structural determination of five compounds of phenolic acid and flavonoids.

Materials and Methods

Apparatus and reagents

Melting points were determined on an X-4 micro-melting point apparatus and are uncorrected. NMR spectra were recorded on Bruker AM-500 with TMS as reference. Silica gel used for column chromatography (CC) was supplied by Qingdao Marine Chemical Factory, Qingdao, China. Sephadex LH-20 was purchased from Pharmacia Biotech Company. Reagents are all analytical purity.

Plant material

The flowers of *R. rugosa* L. were collected from Pingyin, Shandong province, China and authenticated by Prof PENG Yan-li. A voucher specimen has been deposited in the herbarium of Shandong university of TCM (SDCM).

Preparation of extracts

Approximately, 7.5 kg of crude materials were extracted twice with 75% ethanol at room temperature. The filtered solvent was evaporated off by rotary evaporator to yield 1.2 kg of crude extract, which was suspended in H_2O and then partitioned with petroleum ether, $CHCl_3$, EtOAc and n-BuOH, sequentially. The EtOAc part (160 g), n-BuOH extracts (140 g) were chromatographed over Si gel column (Merck 200-300 mesh) eluted with CH_2Cl_2-MeOH mixtures of increasing polarity to get Frs. 4-6, respectively. Compound **1** (20 mg) and compound **2** (22 mg) were purified by Sephadex LH-20 with $CHCl_3$- MeOH, silica gel chromatography and then preparative TLC from Frs. 1-3, respec-

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* Corresponding author E-mail: zyq622003@126.com

tively. Frs. 4-6 were subjected to polyamide column chromatography, Si gel column (Merck 200-300 mesh) and Sephadex LH-20 to get compound **3**, compound **4** and compound **5**, correspondingly.

Result and Discussion

Compound 1 white needle crystal (MeOH) with a melting point of 205 ℃. This compound reacted positively to Ferric trichloride -potassium ferricyanide and bromocresol green reagents. ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm6.9 (H, d, J = 8.3 Hz, H-5), 7.47 (H, dd, J = 8.4 Hz, H-6), 7.53 (H, d, J = 2.0 Hz, H-2). Compared with literature data[3,4], it can be identified as protocatechuic acid.

Compound 2 yellow powder (MeOH) with the melting point of 278-281 ℃. It responded positively to HCI-Mg Reaction and negtively to Molish test. ^{1}H NMR (DMSO, 500 Hz) δppm: 12.48 (br, s, H-5), 8.06 (2H, d, J = 8.4 Hz, H-2′. H-6′), 6.92 (2H, d, J = 8.4 Hz, H-3′, H-5′), 6.44 (H, d, J = 1.9 Hz, H-8), 6.19 (H, d, J = 1.9 Hz, H-6). Compared with literature data[5,6], it should be kaempferol.

Compound 3 yellow needle crystal (MeOH) with the melting point of 269-271 ℃. It responded positively to HCI-Mg Reaction and negtively to Molish test. ^{1}H NMR (DMSO-d_6, 500 MHz) δppm: 3.82 (3H, s, OMe-8, 6.26 (H, s, H-6), 6.96 (2H, dd, J = 3.5, 11 Hz, H-3′, 5′), 8.07 (2H, dd, J = 3.5, 11 Hz, H-2′, 6′). Compared with literature data [7], it should be herbacetin-8-methylether.

Compound 4 yellow powder (MeOH) with the melting point of 225-227 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δppm: 12.64 (br, s, 1H-5), 7.58 (2H, d, J = 9 Hz, H-2′. H-6′), 6.84 (H, d, J = 9 Hz, H-5′), 6.4 (H, s, H-8), 6.2 (H, s, H-6), 5.47 (H, d, J = 7.2 Hz, glcH-1); ^{13}C NMR (150 MHz, DMSO-d_6) δppm: 156.7 (C-2), 133.8 (C-3), 177.9 (C-4), 161.7 (C-5), 99.1 (C-6), 164.5 (C-7), 93.9 (C-8), 156.6 (C-9), 104.4 (C-10), 121.6 (C-1′), 115.6 (C-2′), 145.2 (C-3′), 148.9 (C-4′), 116.6 (C-5′), 122.0 (C-6′), Glc: 101.3 (C-1″), 74.5 (C-2″), 76.9 (C-3″), 70.4 (C-4″), 78.0 (C-5″), 61.4 (C-6″). Compared with literature data [8], it should be tristin.

Compound 5 yellowish powder, with the melting point of 223-225 ℃. It responded positively to HCI-Mg Reaction and Molish test. ^{1}H NMR (600 MHz, DMSO-d_6) δppm: 8.0 (2H, d, J = 8.4 Hz, H-2′H-6′), 6.9 (2H, d, J = 8.4 Hz, H-3′. H-5′), 6.4 (H, s, J = 1.8 Hz, H-8), 6.17 (H, s, J = 1.8 Hz, H-6), 5.4 (H, J = 7.8 Hz, glc-1H); ^{13}C NMR (150 MHz, DMSO-d_6) δppm: 156.1 (C-2), 133.1 (C-3), 177.5 (C-4), 161.2 (C-5), 98.9 (C-6), 165.0 (C-7), 95.1 (C-8), 156.4 (C-9), 103.6 (C-10), 120.9 (C-1′), 130.8 (C-2′), 115.1 (C-3′), 159.9 (C-4′), 115.1 (C-5′), 130.8 (C-6′); Glc: 100.9 (C-1″), 74.2 (C-2″), 76.4 (C-3″), 69.9 (C-4″), 77.5 (C-5″), 60.9 (C-6″). Compared with literature data [9], it should be astragalin.

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