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卢旺达产迷迭香化学成分研究 I

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摘要: 为了解迷迭香(*Rosmarinus officinais* L.)中的化学成分,从其 95% 乙醇提取物中分离得到了 13 种化合物,经波谱分析,分别鉴定为(*Z*)-3-hexenyl glucoside (**1**), (*Z*)-3-hexenyl *O*-β-D-glucopyranosyl-(1″→6′)-β-D-glucopyranoside (**2**), erythritol-1-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (**3**), 2,3,4,5-tetrahydroxyhexyl-6-*O*-*trans*-caffeoyl-β-glucopyranoside (**4**), 1,2,3,4-tetrahydroxy-2-methylbutane-4-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (**5**), 咖啡酸 (**6**), 迷迭香酸 (**7**), methyl rosmarinate (**8**), methyl benzoate-4-β-glucoside (**9**), benzyl-β-D-glucopyranoside (**10**), benzyl-*O*-β-D-apiofuranosyl-(1→2)-β-D-glucopyranoside (**11**), 1,2-di-*O*-β-D-glucopranosyl-4-allylbenzene (**12**)及(+)-syringaresinol-4′-*O*-β-D-glucopyranoside (**13**)。其中,化合物 **1**~**5** 和 **8**~**13** 为首次从迷迭香属分离得到,并修正了化合物 **13** 的波谱数据。

关键词: 迷迭香; 化学成分; 酚酸
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Chemical Constituents from Rwandan Plant *Rosmarinus officinalis* L. (I)

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Abstract: In order to understand the chemical constituents of *Rosmarinus officinalis*, 13 compounds were isolated from its 95% EtOH extract. On the basis of spectral data, their structures were identified as (*Z*)-3-hexenyl glucoside (**1**), (*Z*)-3-hexenyl *O*-β-D-glucopyranosyl-(1″→6′)-β-D-glucopyranoside (**2**), erythritol-1-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (**3**), 2,3,4,5-tetrahydroxyhexyl-6-*O*-*trans*-caffeoyl-β-glucopyranoside (**4**), 1,2,3,4-tetrahydroxy-2-methylbutane-4-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (**5**), caffeic acid (**6**), rosmarinic acid (**7**), methyl rosmarinate (**8**), methyl benzoate-4-β-glucoside (**9**), benzyl-β-D-glucopyranoside (**10**), benzyl-*O*-β-D-apiofuranosyl-(1→2)-β-D-glucopyranoside (**11**), 1,2-di-*O*-β-D-glucopranosyl-4-allylbenzene (**12**) and (+)-syringaresinol-4′-*O*-β-D-glucopyranoside (**13**). Among them, compounds **1**–**5** and **8**–**13** were isolated from the *Rosmarinus* genus for the first time. For the known ones, the NMR data of compound **13** was corrected.
Key words: *Rosmarinus officinalis*; Chemical constituent; Phenolic acid

Rosmarinus officinais L. (Lamiaceae) popularly known as rosemary, is a shrub widely distributed in Europe, Asia, and Africa. And one of its elective growing areas is the Mediterranean basin where spontaneous plants are diffusely distributed. Rosemary has been traditionally used as a culinary spice, mainly to modify or improve food flavors as well as in folk medicine, being a greatly valuable medicinal herb[1].

Diterpenoids, flavonoids, triterpenoids, essential oils and phenolic acids are their main constitutents.

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The derived essential oils are mainly used in local application for their balsamic, antispasmodic and anti-inflammatory activities[2]. Among them, phenolic acids are the main antioxidant compounds present in rosemary[3].

In the course of our study on the constituents of this plant, thirteen compounds were isolated and identified from its aerial parts, and their chemical structures (Fig. 1) were elucidated based on physico-chemical properties and spectral data.

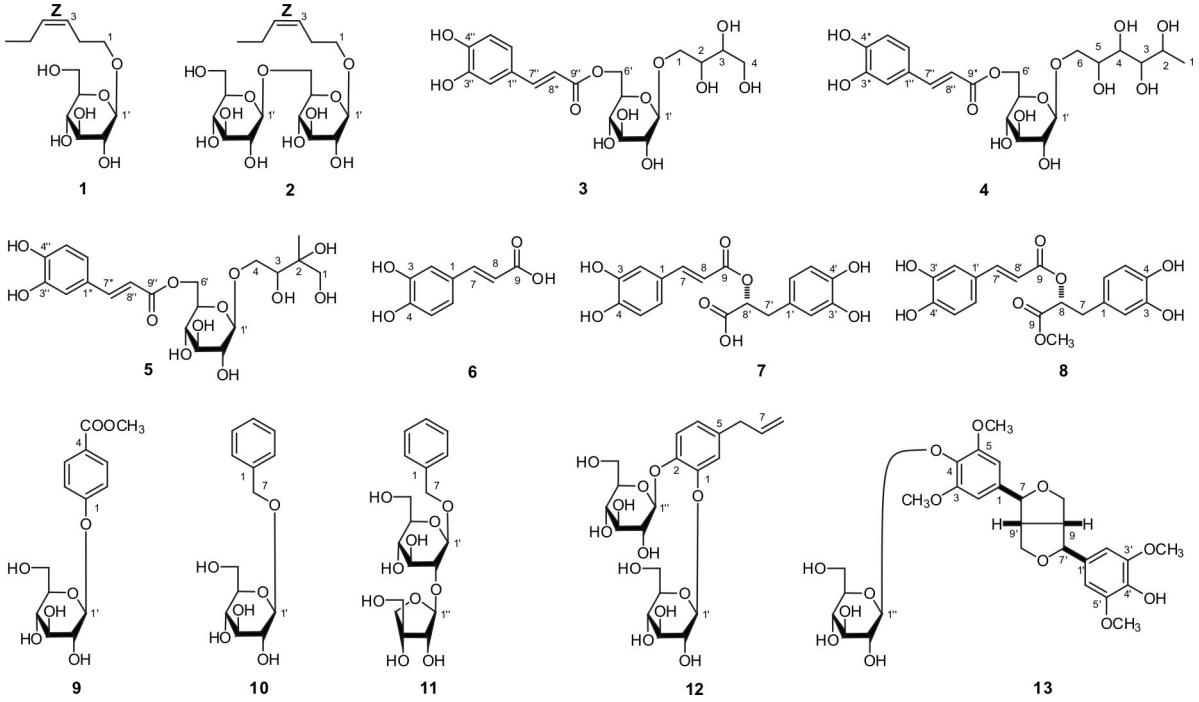

Fig. 1 Structure of compounds **1**–**13**

1 Materials and methods

1.1 Plant material

The dried aerial parts of *Rosmarinus officinais* (Lamiacea) were collected from Butarie, Rwanda and identified by Dr. LI Tian-xiang. The voucher specimen (No. 20110910) was deposited at the Academy of Traditional Chinese Medicine of Tianjin University of TCM.

1.2 General experimental procedures

Optical rotations were measured on a Rudolph Autopol® IV automatic polarimeter. IR spectra were recorded on a Varian 640-IR FT-IR spectrophotometer. UV spectra were obtained on a Varian Cary 50 UV-Vis spectrophotometer. NMR spectra were determined on a Bruker 500 MHz NMR spectrometer at 500 MHz for ^{1}H and 125 MHz for ^{13}C NMR, with TMS as an internal standard. Positive- and Negative-ion HRESI-TOF-MS were recorded on an Agilent Technologies 6520 Accurate-Mass Q-Tof LC/MS spectrometer.

Column chromatographies were performed on macroporous resin D101 (Haiguang Chemical Co., Ltd., Tianjin, China), Silica gel (48–75 μm, Qingdao Haiyang Chemical Co., Ltd., Qingdao, China), and ODS (40–63 μm, YMC Co., Ltd., Tokyo, Japan). Preparative HPLC (PHPLC) column, Cosmosil $5C_{18}$-MS-II (20 mm i.d.×250 mm, Nakalai Tesque, Inc., Tokyo, Japan) were used to purify the constituents. Pre-coated TLC plates with Silica gel GF_{254} (Tianjin Silida Technology Co., Ltd., Tianjin, China) were used to detect the purity of isolates achieved by spraying with 10% aqueous H_2SO_4-EtOH, followed by heating.

1.3 Extraction and isolation

The dried aerial parts of *R. officinalis* (2.5 kg)

were refluxed with 95% EtOH. The solvent was evaporated under reduced pressure to yield the 95% EtOH extract (455 g). Then, the extract (379 g) was partitioned in a $CHCl_3$-H_2O mixture (1∶1, V/V) to give both $CHCl_3$ (269 g) and H_2O (100 g) partitions. Then, the H_2O layer (100 g) was subjected to D101 macroporous resin column chromatography (CC) and eluted with H_2O and 95% EtOH, successively. As a result, H_2O (47 g) and 95% EtOH (45 g) eluted fractions were obtained.

The EtOH fraction (36 g) was subjected to normal phase silica gel CC [$CHCl_3$ → $CHCl_3$-MeOH (100∶3→100∶5 →100∶7, V/V) → $CHCl_3$-MeOH-H_2O (10∶3∶1 → 7∶3∶1, V/V/V) → MeOH] to yield 11 fractions (Fr. 1–Fr. 11).

Fraction 6 (0.7 g) was purified by PHPLC [CH_3CN-H_2O (17∶83, V/V)] into 8 subfractions (Fr. 6-1–Fr. 6-8). Subfraction 6-7 was identified as (*Z*)-3-hexenyl glucoside (**1**, 14.1 mg). Subfractions 6-5 (52.2 mg) and 6-8 (243.8 mg) was further purified by PHPLC to obtain caffeic acid (**6**, 16.8 mg), (+)-syringaresinol-4′-*O*-β-D-glucopyranoside (**13**, 4.1 mg). Fraction 7 (5.5 g) was subjected to ODS CC [MeOH-H_2O (20∶80→30∶70→40∶60→50∶50→60∶40→70∶30→100∶0, V/V)] to yield 9 subfractions (Fr. 7-1–Fr. 7-9). Subfraction 7-2 (616.4 mg) was purified by PHPLC to isolate both (*Z*)-3-hexenyl β-D-glucopyranoside (**1**, 8.3 mg) and rosmarinic acid (**7**, 126.1 mg). Subfraction 7-5 (1.61 g) was also purified by PHPLC to offer benzyl-β-D-glucopyranoside (**10**, 5.7 mg) and methyl benzoate-4-β-D-glucopranoside (**9**, 2.2 mg). Subfractions 7-5-14 (554.6 mg) and 7-5-15 (147.8 mg) were also combined and further purified by subjecting it to silica gel CC [$CHCl_3$→$CHCl_3$-MeOH (100∶3→100∶5→100∶7, V/V)→$CHCl_3$-MeOH-H_2O (20∶3∶1→10∶3∶1→7∶3∶1, V/V/V)→MeOH] to give 14 fractions (Fr. 7-5-14-1–Fr. 7-5-14-14). Furthermore, subfraction 7-5-14-8 (126.2 mg) was subjected to PHPLC to give methyl rosmarinate (**8**, 42.8 mg).

Fraction 9 (10.0 g) was separated by ODS CC, silica gel CC and PHPLC to offer benzyl-*O*-β-D-apiofuranosyl(1→2)-β-D-glucopyranoside (**11**, 41.4 mg). Fraction 10 (6.3 g) was subjected to PHPLC through gradient elution [MeOH-H_2O (25∶75→40∶60→60∶40→80∶20→100∶0, V/V)] to yield 35 subfractions (Fr. 10-1–Fr. 10-35). Subfractions 10-14 (73.0 mg), 10-16 (36.4 mg), 10-17 (86.8 mg), and 10-22 (127.5 mg) were purified by PHPLC respectively to give erythritol-1-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (**3**, 6.3 mg), 2,3,4,5-tetrahydroxyhexyl-6-*O*-*trans*-caffeoyl-β-glucopyranoside (**4**, 9.9 mg), 1,2,3,4-tetrahydroxy-2-methylbutane-4-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (**5**, 4.6 mg), and (*Z*)-3-hexenyl *O*-β-D-glucopyranosyl-(1″→6′)-β-D-glucopyranoside (**2**, 9.3 mg) and 1,2-di-*O*-β-D-glucopranosyl-4-allylbenzene (**12**, 36.2 mg).

1.4 Structural elucidation

(*Z*)-3-Hexenyl β-D-glucopyranoside (1) White powder. Negative-ion mode *m*/*z*: 297.1078 $[M + Cl]^-$ (calcd for $C_{12}H_{22}O_6Cl$ 297.1110). ^1H NMR (CD_3OD, 500 MHz): δ [3.56 (1H, dt, *J* = 7.0, 9.5 Hz), 3.87 (1H, m, overlapped), H_2-1], 2.39 (2H, dt, *J* = 7.0, 7.0 Hz, H_2-2), 5.38 (1H, m, H-3), 5.46 (1H, m, H-4), 2.08 (2H, m, H_2-5), 0.97 (3H, t, *J* = 7.0 Hz, H_3-6), 4.30 (1H, d, *J* = 8.0 Hz, H-1′), 3.20 (1H, dd, *J* = 8.0, 9.0 Hz, H-2′), 3.38 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 3.30 (2H, m, overlapped, H-4′ and 5′), [3.69 (1H, dd, *J* = 5.0, 12.0 Hz), 3.87 (1H, m, overlapped), H_2-6′]; ^{13}C NMR (CD_3OD, 125 MHz): δ 70.6 (C-1), 28.7 (C-2), 125.7 (C-3), 134.6 (C-4), 21.5 (C-5), 14.6 (C-6), 104.2 (C-1′), 75.0 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 77.8 (C-5′), 62.6 (C-6′). The NOE correlations between δ_H 2.08 (H_2-2) and δ_H 1.92 (H_2-5) observed in the NOESY spectrum indicated the configuration in $\triangle^{3,4}$ was Z. On the basis of above mentioned and by comparing the ^1H and ^{13}C NMR data of it with the reported data[4], the structure of **1** was identified as (*Z*)-3-hexenyl β-D-glucopyranoside.

(*Z*)-3-Hexenyl *O*-β-D-glucopyranosyl-(1″→6′)-β-D-glucopyranoside (2) White powder. Negative-ion mode *m*/*z*: 459.1623 $[M + Cl]^-$ (calcd for $C_{18}H_{32}O_{11}Cl$ 459.1639). ^1H NMR (C_5D_5N, 500 MHz): δ [3.60 (1H, dt, *J* = 7.0, 9.5 Hz), 4.11 (1H, m, overlapped), H_2-1], 2.39 (2H, dt, *J* = 7.0, 7.0 Hz, H_2-2), 5.44 (1H, m, H-3), 5.36 (1H, m, H-4), 1.92 (2H, m, H_2-5), 0.82 (3H, t, *J* =

7.0 Hz, H_3-6), 4.72 (1H, d, *J* = 7.5 Hz, H-1′), 3.91 (1H, dd, *J* = 7.5, 9.0 Hz, H-2′), 4.16 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 4.10 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 3.99 (1H, m, H-5′), [4.27 (1H, dd, *J* = 5.5, 11.0 Hz), 4.77 (1H, dd, *J* = 2.0, 11.0 Hz), H_2-6′], 5.03 (1H, d, *J* = 8.0 Hz, H-1″), 3.98 (1H, dd, *J* = 8.0, 9.0 Hz, H-2″), 4.13 (1H, dd, *J* = 9.0, 9.0 Hz, H-3″), 4.18 (1H, dd, *J* = 9.0, 9.0 Hz, H-4″), 3.86 (1H, m, H-5″), [4.31 (1H, dd, *J* = 4.5, 11.5 Hz), 4.45 (1H, br. d, ca. *J* = 12 Hz), H_2-6″]; ^{13}C NMR (C_5D_5N, 125 MHz): δ 69.4 (C-1), 28.3 (C-2), 125.6 (C-3), 133.4 (C-4), 20.8 (C-5), 14.4 (C-6), 104.5 (C-1′), 75.0 (C-2′), 78.4 (C-3′), 71.5 (C-4′), 77.2 (C-5′), 70.1 (C-6′), 105.5 (C-1″), 75.1 (C-2″), 78.4 (C-3″), 71.6 (C-4″), 78.4 (C-5″), 62.7 (C-6″). The NOE correlations between δ_H 2.39 (H_2-2) and δ_H 1.92 (H_2-5) were observed in the NOESY spectrum, which indicated that the configuration in $\triangle^{3,4}$ was Z. Finally, the compound **2** was identified as (*Z*)-3-hexenyl *O*-β-D-glucopyranosyl-(1″→6′)-β-D-glucopyranoside by comparison of the physical, ^{1}H and ^{13}C NMR data with the reported data[5].

Erythritol-1-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (3) White powder. Negative-ion mode *m*/*z*: 445.1380 $[M - H]^-$ (calcd for $C_{19}H_{25}O_{12}$ 445.1351). ^{1}H NMR (CD_3OD, 500 MHz): δ [3.67 (1H, dd, *J* = 6.5, 11.0 Hz), 4.09 (1H, dd, *J* = 2.5, 11.0 Hz), H_2-1], 3.76 (1H, ddd, *J* = 2.5, 6.5, 14.0 Hz, H-2), 3.60 (1H, ddd, *J* = 2.0, 6.0, 14.0 Hz, H-3), [3.58 (1H, dd, *J* = 6.0, 11.0 Hz), 3.74 (1H, dd, *J* = 2.0, 11.0 Hz), H_2-4], 4.35 (1H, d, *J* = 8.0 Hz, H-1′), 3.26 (1H, dd, *J* = 8.0, 9.0 Hz, H-2′), 3.40 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 3.36 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 3.55 (1H, m, H-5′), [4.30 (1H, dd, *J* = 5.5, 12.0 Hz), 4.51 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′], 7.05 (1H, d, *J* = 2.0 Hz, H-2″), 6.78 (1H, d, *J* = 8.5 Hz, H-5″), 6.95 (1H, dd, *J* = 2.0, 8.5 Hz, H-6″), 7.57 (1H, d, *J* = 16.0 Hz, H-7″), 6.29 (1H, d, *J* = 16.0 Hz, H-8″). Compound **3** was identified as erythritol-1-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside by comparison of the physical, ^{1}H and ^{13}C NMR (Table 1) data with the reported data[6].

2,3,4,5-Tetrahydroxyhexyl-6-*O*-*trans*-caffeoyl-β-glucopyranoside (4) White powder. Negative-ion mode *m*/*z*: 489.1609 $[M - H]^-$ (calcd for $C_{21}H_{29}O_{13}$ 489.1614). ^{1}H NMR (CD_3OD, 500 MHz): δ [3.73 (1H, dd, *J* = 6.5, 10.5 Hz), 4.11 (1H, dd, *J* = 2.5, 10.5 Hz), H_2-1], 3.83 (1H, ddd, *J* = 2.5, 6.5, 15.0 Hz, H-2), 3.59 (1H, m, H-3), 3.57 (1H, m, H-4), 3.86 (1H, m, H-5), 1.18 (3H, d, *J* = 6.5 Hz, H_3-6), 4.35 (1H, d, *J* = 7.5 Hz, H-1′), 3.27 (1H, dd, *J* = 7.5, 9.0 Hz, H-2′), 3.41 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 3.37 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 3.54 (1H, m, H-5′), [4.30 (1H, dd, *J* = 6.0, 12.0 Hz), 4.52 (1H, dd, *J* = 2.0, 11.0 Hz), H_2-6′], 7.05 (1H, d, *J* = 2.0 Hz, H-2″), 6.77 (1H, d, *J* = 8.0 Hz, H-5″), 6.94 (1H, dd, *J* = 2.0, 8.0 Hz, H-6″), 7.58 (1H, d, *J* = 16.0 Hz, H-7″), 6.29 (1H, d, *J* = 16.0 Hz, H-8″). Compound **4** was identified as 2,3,4,5-tetrahydroxyhexyl-6-*O*-*trans*-caffeoyl-β-glucopyranoside according to the ^{1}H, ^{13}C NMR (Table 1) and 2D-NMR experiments.

1,2,3,4-tetrahydroxy-2-methylbutane-4-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (5) White powder. Negative-ion mode *m*/*z*: 459.1509 $[M - H]^-$ (calcd for $C_{20}H_{27}O_{12}$ 459.1508). ^{1}H NMR (C_5D_5N, 500 MHz): δ [4.06 (1H, d, *J* = 11.0 Hz), 4.16 (1H, d, *J* = 11.0 Hz), H_2-1], 4.58 (1H, dd, *J* = 3.0, 8.0 Hz, H-3), [4.33 (1H, dd, *J* = 3.0, 10.5 Hz), 4.89 (1H, dd, *J* = 8.0, 10.5 Hz), H_2-4], 1.60 (3H, s, 2-CH_3), 5.03 (1H, d, *J* = 8.0 Hz, H-1′), 4.05 (1H, dd, *J* = 8.0, 8.5 Hz, H-2′), 4.20 (1H, dd, *J* = 8.5, 9.0 Hz, H-3′), 4.12 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 4.03 (1H, m, H-5′), [4.88 (1H, dd, *J* = 5.5, 12.0 Hz), 5.04 (1H, dd, *J* = 2.0, 11.0 Hz), H_2-6′], 7.53 (1H, d, *J* = 2.0 Hz, H-2″), 7.17 (1H, d, *J* = 8.0 Hz, H-5″), 7.08 (1H, dd, *J* = 2.0, 8.0 Hz, H-6″), 7.92 (1H, d, *J* = 16.0 Hz, H-7″), 6.58 (1H, d, *J* = 16.0 Hz, H-8″); ^{1}H NMR (CD_3OD, 500 MHz): δ [3.43 (1H, d, *J* = 11.0 Hz), 3.53 (1H, d, *J* = 11.0 Hz), H_2-1], 3.81 (1H, dd, *J* = 2.5, 8.5 Hz, H-3), [3.39 (1H, dd, *J* = 2.5, 10.5 Hz), 3.56 (1H, dd, *J* = 8.5, 10.5 Hz), H_2-4], 1.10 (3H, s, 2-CH_3), 4.35 (1H, d, *J* = 8.0 Hz, H-1′), 3.26 (1H, dd, *J* = 8.0, 9.0 Hz, H-2'), 3.41 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 3.37 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 3.53 (1H, m, H-5′), [4.32 (1H, dd, *J* = 6.0, 12.0 Hz), 4.51 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′], 7.05 (1H, d, *J* = 2.0 Hz, H-2″), 6.77 (1H, d, *J* = 8.0 Hz, H-5″), 6.94 (1H, d, *J* = 2.0, 8.0 Hz, H-6″), 7.58 (1H, d, *J* = 16.0 Hz, H-7″), 6.29 (1H, d, *J* = 16.0 Hz, H-8″). Compound **5** was

identified as 1,2,3,4-tetrahydroxy-2-methylbutane-4-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside by comparison of the physical, ^{1}H and ^{13}C (Table 1) NMR data with the reported data[6].

Table 1 ^{13}C NMR (125 MHz, δ) data of compounds **3**–**5**

Position	**3**[a]	**4**[a]	**5**[b]	**5**[a]		**3**[a]	**4**[a]	**5**[b]	**5**[a]
1	73.1	73.2	68.7	68.5	5′	75.6	75.5	75.5	75.5
2	72.6	71.7	74.1	74.5	6′	64.7	64.5	64.5	64.5
3	73.6	72.7	74.6	74.7	1″	127.8	127.6	126.9	127.6
4	64.7	74.7	72.9	72.4	2″	115.3	115.1	115.9	115.1
5		70.3			3″	146.9	146.8	147.6	146.8
6		19.5			4″	149.7	149.6	150.4	149.6
2-CH_3			20.7	19.6	5″	116.6	116.4	116.6	116.5
1′	105.1	104.9	105.7	104.9	6″	123.1	123.0	122.1	123.0
2′	75.2	75.1	75.3	75.2	7″	147.3	147.2	146.0	147.2
3′	77.8	77.6	78.3	77.7	8″	114.9	114.7	114.9	114.8
4′	71.7	71.6	71.4	71.6	9″	169.2	169.0	167.6	169.1

a: CD_3OD; b: C_5D_5N

Caffeic acid (6) White powder. Positive-ion mode *m*/*z*: 181.0504 $[M + H]^+$ (calcd for $C_9H_9O_4$ 181.0495). ^{1}H NMR (CD_3OD, 500 MHz): δ 7.04 (1H, br. s, H-2), 6.78 (1H, d, *J* = 8.0 Hz, H-5), 6.93 (1H, br. d, ca. *J* = 8 Hz, H-6), 7.52 (1H, d, *J* = 16.0 Hz, H-7), 6.23 (1H, d, *J* = 16.0 Hz, H-8); ^{13}C NMR (CD_3OD, 125 MHz): δ 128.0 (C-1), 115.1 (C-2), 146.8 (C-3), 149.4 (C-4), 116.5 (C-5), 122.8 (C-6), 146.7 (C-7), 116.1 (C-8), 171.6 (C-9). Compound **6** was identified as caffeic acid by comparison of the physical, ^{1}H and ^{13}C NMR data with the reported data[7].

Rosmarinic acid (7) White powder. $[\alpha]_D^{25}$ + 37.7° (*c* 0.78, in MeOH). Negative-ion mode *m*/*z*: 359.0786 $[M - H]^-$ (calcd for $C_{18}H_{15}O_8$ 359.0772). ^{1}H NMR (CD_3OD, 500 MHz): δ 6.76 (1H, d, *J* = 2.0 Hz, H-2), 6.70 (1H, d, *J* = 8.0 Hz, H-5), 6.62 (1H, dd, *J* = 2.0, 8.0 Hz, H-6), [3.00 (1H, dd, *J* = 8.5, 14.0 Hz), 3.10 (1H, both dd, *J* = 3.0, 14.0 Hz), H_2-7], 5.18 (1H, dd, *J* = 3.0, 8.5 Hz, H-8), 7.04 (1H, d, *J* = 1.5 Hz, H-2′), 6.77 (1H, d, *J* = 8.0 Hz, H-5′), 6.94 (1H, dd, *J* = 1.5, 8.0 Hz, H-6′), 7.54 (1H, d, *J* = 16.0 Hz, H-7′), 6.26 (1H, d, *J* = 16.0 Hz, H-8′); ^{13}C NMR (CD_3OD, 125 MHz): δ 129.5 (C-1), 117.6 (C-2), 146.2 (C-3), 145.2 (C-4), 116.3 (C-5), 121.8 (C-6), 38.1 (C-7), 75.3 (C-8), 173.7 (C-9), 127.7 (C-1′), 115.2 (C-2′), 146.8 (C-3′), 149.7 (C-4′), 116.5 (C-5′), 123.1 (C-6′), 147.6 (C-7′), 114.6 (C-8′), 168.6 (C-9′). Compound **7** was identified as rosmarinic acid by comparison of the physical, and ^{1}H NMR data with the reported data[8].

Methyl rosmarinate (8) White powder, $[\alpha]_D^{25}$ + 31.6° (*c* 0.93, in MeOH). Negative-ion mode *m*/*z*: 373.0919 $[M - H]^-$ (calcd for $C_{19}H_{17}O_8$ 373.0929). ^{1}H NMR (CD_3OD, 500 MHz): δ 6.72 (1H, d, *J* = 2.0 Hz, H-2), 6.70 (1H, d, *J* = 8.0 Hz, H-5), 6.57 (1H, dd, *J* = 2.0, 8.0 Hz, H-6), 3.03 (2H, m, H_2-7), 5.20 (1H, dd, *J* = 5.0, 7.5 Hz, H-8), 3.69 (3H, s, 9-OCH_3), 7.05 (1H, d, *J* = 2.0 Hz, H-2′), 6.79 (1H, d, *J* = 8.0 Hz, H-5′), 6.95 (1H, dd, *J* = 2.0, 8.0 Hz, H-6′), 7.56 (1H, d, *J* = 16.0 Hz, H-7′), 6.26 (1H, d, *J* = 16.0 Hz, H-8′); ^{13}C NMR (CD_3OD, 125 MHz): δ 128.7 (C-1), 117.5 (C-2), 146.1 (C-3), 145.3 (C-4), 116.3 (C-5), 121.8 (C-6), 37.9 (C-7), 74.6 (C-8), 172.1 (C-9), 52.6 (9-OCH_3), 127.5 (C-1′), 115.2 (C-2′), 146.7 (C-3′), 149.7 (C-4′), 116.5 (C-5′), 123.2 (C-6′), 147.9 (C-7′), 114.1 (C-8′), 168.3 (C-9′). Compound **8** was identified as methyl rosmarinate by comparison of the physical, ^{1}H and ^{13}C NMR data with the reported data[9].

Methyl benzoate-4-β-D-glucopyranoside (9) White powder. Positive-ion mode *m*/*z*: 337.0911 $[M + Na]^+$ (calcd for $C_{14}H_{18}O_8Na$ 337.0894). ^{1}H

NMR (CD_3OD, 500 MHz): δ 7.97 (2H, d, *J* = 9.0 Hz, H-2,6), 7.15 (2H, d, *J* = 9.0 Hz, H-3,5), 3.87 (3H, s, 1-$COOCH_3$), 5.01 (1H, d, *J* = 7.0 Hz, H-1′), 3.47 (2H, m, H-2′ and 3′), 3.35 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 3.48 (1H, m, H-5′), [3.71 (1H, dd, *J* = 5.5, 12.0 Hz), 3.91 (1H, dd, *J* = 2.0, 12.0 Hz), H_2-6′]; ^{13}C NMR (CD_3OD, 125 MHz): δ 125.1 (C-1), 132.5 (C-2,6), 117.3 (C-3,5), 163.0 (C-4), 168.3 (1-$COOCH_3$), 52.5 (1-$COOCH_3$), 101.7 (C-1′), 74.8 (C-2′), 78.0 (C-3′), 71.3 (C-4′), 78.3 (C-5′), 62.5 (C-6′). Compound **9** was identified as methyl benzoate-4-β-D-glucopyranoside according to the ^{1}H, ^{13}C, and 2D-NMR experiments.

Benzyl-β-D-glucopyranoside (10) White powder. Negative-ion mode *m*/*z*: 305.0768 $[M + Cl]^-$ (calcd for $C_{13}H_{18}O_6Cl$ 305.0797). ^{1}H NMR (CD_3OD, 500 MHz): δ 7.42 (2H, m, H-2,6), 7.32 (2H, m, H-3,5), 7.26 (1H, m, H-4), 4.67, 4.93 (^{1}H each, both d, *J* = 11.0 Hz, H_2-7), 4.36 (1H, d, *J* = 7.5 Hz, H-1′), 3.28 (1H, dd, *J* = 7.5, 9.0 Hz, H-2′), 3.35 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 3.31 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 3.30 (1H, m, overlapped, H-5′), [3.69 (1H, dd, *J* = 5.5, 11.5 Hz), 3.89 (1H, dd, *J* = 2.0, 11.5 Hz), H_2-6′]; ^{13}C NMR (CD_3OD, 125 MHz): δ 139.1 (C-1), 129.3 (C-2,6), 129.2 (C-3,5), 128.7 (C-4), 71.8 (C-7), 103.3 (C-1′), 75.1 (C-1′), 78.1 (C-3′), 71.7 (C-4′), 78.0 (C-5′), 62.8 (C-6′). Compound **10** was identified as benzyl-β-D-glucopyranoside by comparison of the physical, ^{1}H and ^{13}C NMR data with the reported data[10] and 2D-NMR determination.

Benzyl-*O*-β-D-apiofuranosyl(1→2)-β-D-glucopyranoside (11) White powder. Negative-ion mode *m*/*z*: 401.1456 $[M - H]^-$ (calcd for $C_{18}H_{25}O_{10}$ 401.1452). ^{1}H NMR (CD_3OD, 500 MHz): δ 7.42 (2H, m, H-2,6), 7.33 (2H, m, H-3,5), 7.26 (1H, m, H-4), 4.63, 4.91 (1H each, both d, *J* = 11.5 Hz, H_2-7), 4.42 (1H, d, *J* = 7.5 Hz, H-1′), 3.42 (1H, dd, *J* = 7.5, 9.0 Hz, H-2′), 3.48 (1H, dd, *J* = 9.0, 9.0 Hz, H-3′), 3.33 (1H, dd, *J* = 9.0, 9.0 Hz, H-4′), 3.25 (1H, m, overlapped, H-5′), [3.69 (1H, dd, *J* = 5.5, 12.0 Hz), 3.89 (1H, dd, *J* = 2.5, 12.0 Hz), H_2-6′], 5.38 (1H, d, *J* = 1.5 Hz, H-1″), 3.95 (1H, d, *J* = 1.5 Hz, H-2″), 3.64, 3.93 (1H each, both d, *J* = 9.5 Hz, H_2-4″), 3.50, 3.57 (1H each, both d, *J* = 11.5 Hz, H_2-5″); ^{13}C NMR (CD_3OD, 125 MHz): δ 138.9 (C-1), 129.30 (C-2,6), 129.26 (C-3,5), 128.7 (C-4), 71.8 (C-7), 102.1 (C-1′), 78.9 (C-2′), 78.6 (C-3′), 71.7 (C-4′), 77.8 (C-5′), 62.8 (C-6′), 110.6 (C-1″), 77.9 (C-2″), 80.6 (C-3″), 75.3 (C-4″), 66.0 (C-5″). Compound **11** was identified as benzyl-*O*-β-D-apiofuranosyl-(1→2)-β-D-glucopyranoside according to the ^{1}H, ^{13}C and 2D-NMR experiments. The NMR data of it in CD_3OD was reported, firstly. And the configurations of the glycosides were determined by comparison of the ^{1}H and ^{13}C NMR data with those of 3,4-dimethoxyphenyl-1-*O*-β-D-apiofuranosyl (1→2)-β-D-glucopyranoside[11].

1,2-Di-*O*-β-D-glucopranosyl-4-allylbenzene (12) White powder. Negative-ion mode *m*/*z*: 509.1425 $[M + Cl]^-$ (calcd for $C_{21}H_{30}O_{12}Cl$ 509.1431). ^{1}H NMR (CD_3OD, 500 MHz): δ 7.10 (1H, d, *J* = 2.0 Hz, H-2), 7.17 (1H, d, *J* = 8.5 Hz, H-5), 6.84 (1H, dd, *J* = 2.0, 8.5 Hz, H-6), 3.34 (2H, m, H_2-7), 5.94 (1H, m, H-8), 5.04 (2H, m, H_2-9), 4.84 (1H, d, *J* = 8.0 Hz, H-1′), 3.49 (2H, m, H-2′ and 2″), 3.46 (2H, m, H-3′ and 3″), 3.41 (2H, m, H-4′ and 4″), 3.35 (2H, m, H-5′ and 5″), 3.71, 3.86 (2H each, both m, H_2-6′ and 6″); ^{13}C NMR (CD_3OD, 125 MHz): δ 137.4 (C-1), 121.0 (C-2 and 5), 149.2 (C-3), 147.5 (C-4), 124.8 (C-6), 40.6 (C-7), 138.7 (C-8), 116.0 (C-9), 104.1 (C-1′), 75.1 (C-2′ and 2″), 77.7 (C-3′ and 3″), 71.3 (C-4′ and 4″), 78.2 (C-5′ and 5″), 62.4 (C-6′ and 6″), 104.3 (C-1″). Compound **12** was identified as 1,2-di-*O*-β-D-glucopranosyl-4-allylbenzene by comparison of the physical, ^{1}H and ^{13}C NMR data with the reported data[12].

(+)-Syringaresinol-4′-*O*-β-D-glucopyranoside (13) White powder. $[\alpha]_D^{25}$ −13.7° (*c* 0.19, in MeOH). Negative-ion mode *m*/*z*: 579.2057 $[M - H]^-$ (calcd for $C_{28}H_{35}O_{13}$ 579.2083). ^{1}H NMR (CD_3OD, 500 MHz): δ 6.72 (2H, s, H-2,6), 4.76 (1H, d, *J* = 4.0 Hz, H-7), 3.13 (2H, m, H-8,8′), 4.28 (2H, dd, *J* = 6.0, 9.0 Hz, H_a-9, 9′), 3.91 (2H, dd, *J* = 3.5, 9.0 Hz, H_b-9,9′), 3.86 (6H, s, 3,5-OCH_3), 6.65 (2H, s, H-2′,6′), 4.72 (1H, d, *J* = 4.5 Hz, H-7′), 3.84 (6H, s, 3′,5′-OCH_3), 4.82 (1H, d, *J* = 7.5 Hz, H-1″), 3.48 (1H, dd, *J* = 7.5, 9.0 Hz, H-2″), 3.20 (1H, m, H-3″), 3.41 (2H, m, H-3″ and 5″), 4.82 (1H, d, *J* = 7.5 Hz, H-1″), [3.67 (1H, dd, *J* = 5.0, 12.0 Hz), 3.77 (1H, dd, *J* = 2.5,

12.0 Hz), H_2-6″]; ^{13}C NMR (CD_3OD, 125 MHz): δ 135.7 (C-1), 104.9 (C-2,6), 154.4 (C-3,5), 139.6 (C-4), 87.2 (C-7), 55.7 (C-8)*, 72.9 (C-9 and 9′), 57.1 (3,5-OCH_3), 133.0 (C-1′), 104.6 (C-2′,6′), 149.4 (C-3′,5′), 136.3 (C-4′), 87.6 (C-7′), 55.5 (C-8′)*, 56.8 (3′,5′-OCH_3), 105.4 (C-1″), 75.7 (C-2″), 77.8 (C-3″), 71.3 (C-4″), 78.3 (C-5″), 62.6 (C-6″). Compound **13** was identified as (+)-syringaresinol-4′-*O*-β-D-glucopyranoside by comparison of the physical, ^{1}H and ^{13}C NMR data with the reported data[13]. And the ^{13}C NMR data of 2, 6, 2′, 6′, 1″, 7, and 7′-position [δ 105.4 (C-2,6), 104.9 (C-2′,6′), 104.6 (C-1″), 87.6 (C-7), 87.2 (C-7′) in reference] were corrected according to the 2D NMR experiments. On the other hand, the data of C-8 and C-8′ could be exchanged with each other.

2 Discussion

In the course of our studies on the constituents of this plant by using chromatographies such as D101 resin, silica gel, ODS, Sephadex LH-20 and HPLC column chromatogaraphies, 13 compounds were isolated from its aerial parts, including phenolic acids, phenylpropyl glycosides, including (*Z*)-3-hexenyl glucoside (**1**), (*Z*)-3-hexenyl *O*-β-D-glucopyranosyl-(1″→6′)-β-D-glucopyranoside (**2**), erythritol-1-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (**3**), 2,3,4,5-tetrahydroxyhexyl-6-*O*-*trans*-caffeoyl-β-glucopyranoside (**4**), 1,2,3,4-tetrahydroxy-2-methyl-butane-4-*O*-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (**5**), caffeic acid (**6**), rosmarinic acid (**7**), methyl rosmarinate (**8**), methyl benzoate-4-β-glucoside (**9**), benzyl-β-D-glucopyranoside (**10**), benzyl-*O*-β-D-apiofuranosyl-(1→2)-β-D-glucopyranoside (**11**), 1,2-di-*O*-β-D-glucopranosyl-4-allylbenzene (**12**) and (+)-syringaresinol-4′-*O*-β-D-glucopyranoside (**13**). Among them, Compounds **1**–**5**, **8**–**13** were isolated from the *Rosmarinus* genus firstly. For the known ones, the NMR data of **13** were corrected.

Nowadays, various pharmacological activities, such as hepatoprotective, antibacterial, antithrombotic, antiulcerogenic, anti-inflammatory, and antioxidant were found for *R. officinalis*. This is closely related to its containing phenolic compounds. The result will provide bases for further studies in *R. officinalis*.

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