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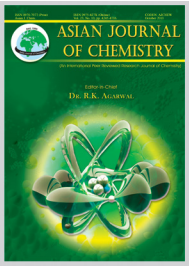

*NOTE*

# Chemical Constituents from the Fruits of *Cicuta virosa* L. var. *latisecta* Celak

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In this paper, the chemical constituents from the fruits of *Cicuta virosa* L. var *latisecta* Celak were isolated and characterized. Isolation and purification were carried out on the column chromatography of silica gel and Sephadex LH-20. Twelve compounds were isolated and identified as rel-(3S, 4S, 5S)-3-[(2R)-2-hydroxydocosanoyl-pentacosanoylaminol]-4-hydroxyl-5-[(4Z)-tetradecane-4-ene]-2, 3, 4, 5-tetra-hydrofuran (**1a-1d** mixture), quercetin (**2**), isorhamnetin (**3**), isorhamnetin-3-O-β-D-glucopyranoside (**4**), (24R)-cycloart-25-ene-3,24-diol (**5**) and (24S)-cycloart-25-ene-3,24-diol (**6**) mixture, (6H,7H)-α-spinasterone (**7**), 2,3-dihydrooenanthetol (**8**) and *n*-tricasanoic acid (**9**).

**Key Words: *Cicuta virosa* L. var *latisecta* Celak, Fruits, Chemical constituents.**

*Cicuta virosa* L. var. *latisecta* Celak (Umbelliferae) is a popular spice plant mainly distributed in Jiangsu province of China. The fruit locally named *shiluozi* in Chinese has been used as spice and a folk remedy for the treatment of dyspepsia for a long history[1]. In previous reports, we investigated its chemical components and found nine known constituents[2-5] from the aerial part of herb. The chemical study on the fruit of this plant was undertaken in our laboratory and nine compounds were isolated from the ethanolic extract of the fruit. In this paper, we report the isolation and structural elucidation of the nine compounds from the fruit of *C. virosa* L. var *latisecta* Celak. The nine compounds were *rel*-(3S, 4S, 5S)-3-[(2R)-2-hydroxydocosanoyl-pentacosanoylaminol]-4-hydroxyl-5-[(4Z)-tetradecane-4-ene]-2,3,4,5-tetra-hydrofuran (**1a-1d** mixture), quercetin (**2**), isorhamnetin (**3**), isorhamnetin-3-O-β-D- glucopyranoside (**4**), (24R)-cycloart-25-ene-3,24-diol (**5**) and (24S)-cycloart-25-ene-3,24-diol (**6**) mixture, (6H,7H)-α-spinasterone (**7**), 2,3-dihydrooenanthetol (**8**), *n*-tricasanoic acid (**9**). Compound **1a-1d** was a mixture of cerebrosides. Compounds **5** and **6** were enantiomers. All above compounds were obtained from the fruit of *C. virosa* L. var *latisecta* Celak for the first time.

$^{1}$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra were recorded with Brucher ACF-500 NMR spectrometers. Mass spectra were obtained on MS Agilent 1100 Series LC/MSD Trap Mass spectrometer (ESI-MS). All solvents used were of analytical grade. Column chromatography was performed with: macroporous resin D101(Tian-jin Hongyuan Chemical Co. Ltd., Tianjin, China), silica gel(100-200, 200-300 mesh ) and $GF_{254}$ silica gel for TLC; (Qing-dao Marine Chemical Co. Ltd., Qingdao, China), Sephadex LH-20 (Pharmacia Fine Chemical Co. Ltd.) and ODS-$C_{18}$ (Merck).

**Plant material:** The fruits of *C. virosa* L. var *latisecta* Celak (15 kg) were collected in Xinghua county of Jiangsu province, China, in July 2007 and were identified by Prof. Qian Shihui. A voucher specimen was deposited in the Jiangsu Academy of Traditional Chinese Medicine.

**Extraction and isolation:** The dried fruits of *C. virosa* L. var *latisecta* Celak (15 kg) were reflux with 80 % (v/v) ethanol three times and the alcohol was evaporated in vacuum. The residue (1700 g) was suspended in water and partitioned with petroleum ether and ethyl acetate. The ethyl acetate-soluble fraction (142 g) was subjected to silica gel column chromatography, eluted with $CHCl_3$-MeOH(100:1, 98:2, 95:5, 10:1, 8.5:1.5, 8:2,7:3, 1:1) gradiently. The fractions was subjected to repeated silica gel, Sephadex LH-20 and ODS column chromatography and further purified by recrystallization. At last compounds **1a-1d** (87 mg), **2** (115 mg), **3** (203 mg), **4** (80 mg), **5** and **6** (30 mg), **7** (70 mg), **8** (35 mg) and **9** (74 mg) were obtained.

Compounds **1a~1d** Amorphous white powder (Acetone); EI-MS m/z 678 $[Md+H]^+$, 664 $[Mc+H]^+$, 650 $[Mb+H]^+$, 635

$[Ma]^+$, 384 [Md-sphingoid moiety +3H]$^+$, 370 [Mc-sphingoid moiety +3H]$^+$, 356 [Mb-sphingoid moiety +3H]$^+$, 339 [Ma-sphingoid moiety]$^+$, 280 [sphingoid mieoty -$H_2O$ + 2H]$^+$, 262 [sphingoid mieoty-2$H_2O$ + 2H]$^+$. $^1$H NMR ($C_5D_5N$, 300 MHz) δ: 8.48 (1H, d, *J* = 7.1 Hz, NH ), 4.52 (1H, m, H-2β), 3.92 (1H, m, H-2α), 4.77 (1H, m, H-3), 4.32 (1H, m, H-4), 4.14 (1H, m, H-5), 1.72 (2H, m, H-6), 1.60 (1H, m, H-7α), 1.72 (1H, m, H-7β), 2.01 (2H, m, H-8α and 11α), 2.07 (2H, m, H-8β and 11β), 5.46 (2H, m, H-9 and 10), 4.64 (1H, dd, *J* = 7.8, 3.7 Hz, H-2'), 2.24 and 2.03 (2H, m, H-3'), 1.72 (2H, m, H-4'), 1.25 and 1.30 (54H, br.d, $CH_2$), 0.87 (6H, t, *J* = 6.7 Hz, $CH_3$). $^{13}$C NMR ($C_5D_5N$, 75 MHz) δ: 71.63 (C-2), 51.87 (C-3), 74.61 (C-4), 86.06 (C-5), 33.79 (C-6), 26.40 (C-7), 32.88 (C-8), 130.37 (C-9), 131.05 (C-10), 32.92 (C-11), 175.51 (C-1'), 72.54 (C-2'), 35.58 (C-3'), 25.86 (C-4'), 22.95-32.11 ($CH_2$), 14.28 ($CH_3$ × 2). Compound **1a-1d** was identified as a mixture of cerebrosides of rel-(3S, 4S, 5S)-3-[(2R)-2- hydroxy-docosanoyl-pentacosanoylaminol]-4-hydroxyl-5-[(4Z)-tetradecane-4-ene]-2,3,4,5-tetrahydrofuran by comparison of physical and spectral data with literature[6].

Compound **2** yellow powder (MeOH); ESI-MS m/z 300.9 $[M-H]^-$, 150.7, 178.7, $^1$H NMR (DMSO-$d_6$, 500 MHz) δ: 12.48 (-OH-5), 9.52 (br, -OH × 4), 6.41 (1H, d, *J* =1.7 Hz, H-8), 6.19 (1H, d, *J* = 1.7 Hz, H-6), 7.68 (1H, d, *J* = 1.9 Hz, H-2'), 6.89 (1H, d, *J* = 8.5 Hz, H-5'), 7.54 (1H, dd, *J* = 8.5, 1.9 Hz, H-6'). Compound **2** was identified as quercetin by comparison of physical and spectral data with literature[7].

Compound **3** yellow powder (MeOH); ESI-MS m/z 314.9 $[M-H]^-$, 399.8 $[M-H-CH_3]^-$, $^1$H NMR (DMSO-$d_6$, 500 MHz) δ: 12.51 (OH-5), 9.77 (br, OH × 3), 6.53 (1H, d, *J* = 1.7 Hz, H-8), 6.25 (1H, d, *J* = 1.7 Hz, H-6), 7.81 (1H, d, *J* = 1.6 Hz, H-2'), 6.99 (1H, d, *J* = 8.5 Hz, H-5'), 7.75 (1H, dd, *J* = 8.5, 1.6 Hz, H-6'), 3.89 (3H, s, $OCH_3$). Compound **3** was identified as isorhamnetin by comparison of physical and spectral data with literature[8].

Compound **4** yellow granular crystal (MeOH); ESI-MS m/z 477.1 $[M-H]^-$, 479.1 $[M+H]^+$, 313.9 $[M-H-Glc]^-$. $^1$H NMR (DMSO-$d_6$, 300 MHz) δ: 12.61 (s, OH-5), 10.84 (s, OH-7), 9.76 (s, OH-4'), 6.45 (1H, d, *J* = 2.0 Hz, H-8), 6.22 (1H, d, *J* = 2.0 Hz, H-6), 7.95 (1H, d, *J* = 1.9 Hz, H-2'), 6.93 (1H, d, *J* = 8.4 Hz, H-5'), 7.51 (1H, dd, *J* = 8.4, 1.9 Hz, H-6'), 3.85 (3H, s, $OCH_3$), 5.57 (1H, d, *J* = 7.2 Hz, H-glc 1''). $^{13}$C NMR (DMSO-$d_6$, 75 MHz) δ: 156.45 (C-2), 133.21 (C-3), 177.61 (C-4), 161.42 (C-5), 98.89 (C-6), 164.33 (C-7), 93.88 (C-8), 156.58 (C-9), 104.25 (C-10), 121.29 (C-1'), 113.73 (C-2'), 147.10 (C-3'), 149.60 (C-4'), 115.41 (C-5'), 122.25 (C-6'), 101.02 (C-1''), 74.53 (C-2''), 76.64 (C-3''), 70.06 (C-4''), 77.63 (C-5''), 60.84 (C-6''), 55.90 ($OCH_3$). Compound **4** was identified as isorhamnetin-3-O-β-D-glucopyranoside by comparison of physical and spectral data with literature[9].

Compound **5** and **6** white lamellae crystal ($CHCl_3$); ESI-MS m/z 443.3 $[M+H]^+$, 441.1 $[M-H]^-$. $^1$H NMR ($CDCl_3$, 500 MHz) δ: 0.56 (1H, d, *J* = 3.3 Hz, H-19β), 0.33 (1H, d, *J* = 3.7 Hz, H-19α), 0.96 (3H, s), 0.96 (3H, s), 0.89 (3H, s), 0.80 (3H, s), 0.88 (3H, d, *J* = 6.0 Hz, H-21), 1.72 (3H, s, H-27), 4.93 (1H, br, H-26), 4.83 (1H, br, H-26), 4.01 (1H, m, H-24), 3.27 (1H, m, H-3). The compounds were identified as isorhamnetin by cycloartane triterpene aglycone by the data of $^1$H NMR and were identified as mixture by the 37 C cignals of $^{13}$C NMR. $^{13}$C NMR ($CDCl_3$, 125 MHz) δ: 31.89 (C5-1), 31.95 (C6-1), 30.37 (C-2), 78.81 (C-3), 40.46 (C-4), 47.10 (C-5), 21.09 (C-6), 28.11 (C5-7), 28.06 (C6-7), 47.95 (C-8), 19.98 (C-9), 26.08 (C-10), 25.99 (C-11), 35.54 (C-12), 45.27 (C-13), 48.79 (C-14), 32.88 (C-15), 26.46 (C-16), 52.17 (C-17), 18.00 (C-18), 29.86 (C-19), 35.93 (C5-20), 35.89 (C6-20), 18.31 (C5-21), 18.30 (C6-21), 31.95 (C5-22), 31.89 (C6-22), 31.51 (C5-23), 31.66 (C6-23), 76.33 (C-24), 147.49 (C5-25), 147.77 (C6-25), 111.33 (C5-26), 110.84 (C6-26), 17.19 (C5-27), 17.58 (C6-27), 19.30 (C-28), 13.98 (C-29), 25.42 (C-30). Compound **5** and **6** were identified as (24R)-cycloart-25-ene-3,24-diol and (24S)-cycloart-25-ene-3,24-diol by comparison of physical and spectral data with literature[10].

Compound **7** white needle crystal (MeOH); ESI-MS m/z 413.4 $[M+H]^+$. $^1$H NMR ($CDCl_3$, 300 MHz) δ: 5.02 (1H, dd, H-22), 5.05 (1H, dd, H-23),0.69 (3H, s), 0.80 (3H, s), 1.02 (3H, d), 1.00 (3H, d), 0.85 (3H, d), 0.81 (3H, d). $^{13}$C NMR ($CDCl_3$, 75 MHz) δ: 38.59 (C-1), 38.19 (C-2), 212.03 (C-3), 44374 (C-4), 46.74 (C-5), 28.99 (C-6), 31.73 (C-7), 53.88 (C-8), 35.43 (C-9), 35.68 (C-10), 21.45 (C-11), 39.82 (C-12), 42.51 (C-13), 56.91 (C-14), 24.30 (C-15), 28.99 (C-16), 56.10 (C-17), 11.49 (C-18), 12.26 (C-19), 40.46 (C-20), 21.05 (C-21), 138.24 (C-22), 129.37 (C-23), 51.24 (C-24), 31.87 (C-25), 18.99 (C-26), 21.17 (C-27), 25.38 (C-28), 12.21 (C-29). Compound **7** was identified as (6H, 7H)-α-spinasterone by comparison of physical and spectral data with literature[11].

Compound **8** reddish brown oil; $^1$H NMR ($CDCl_3$, 300 MHz) δ: 3.73 (2H, t, *J* = 6.1 Hz, H-1), 1.79 (2H, tt, *J* = 6.1, 6.7 Hz, H-2), 2.46 (2H, t, *J* = 6.7 Hz, H-3), 5.48 (1H, d, *J* = 15.6 Hz, H-8), 6.66 (1H, dd, *J* = 15.6, 10.6 Hz, H-9), 6.09 (1H, dd, *J* = 15.1, 10.6 Hz, H-10), 5.84 (1H, dt, *J* = 15.1, 7.0 Hz, H-11), 2.11 (2H, dt, *J* = 7.0, 7.2 Hz, H-12), 1.38 (2H, m, H-13), 1.28 (6H, m, $CH_2$ × 3), 0.87 (3H, t, *J* = 7.0 Hz, H-17). Compound **8** was identified as **2**, 3-dihydrooenanthetol by comparison of physical and spectral data with literature[12].

Compound **9** White powder; $^1$H NMR ($CDCl_3$, 300 MHz) δ: 11.13 (1H, br), 2.46 (2H, t), 1.64 (2H, m), 0.89 (3H, t), 1.25 (38H, m). Compound **9** was identified as n-tricasanoic acid by physical and spectral data.

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