**FULL PAPER**

# Phenylethanoid Glycosides from the Roots of *Digitalis ciliata* Trautv.

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Three new phenylethanoid glycosides, named digicilisides A – C (**1** – **3**, resp.), have been isolated from the roots of *Digitalis ciliata*, along with five known phenylethanoid glycosides. The structures of **1** – **3** were identified as 2-(4-hydroxy-3-methoxyphenyl)ethyl β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)]-4-*O*-[(*E*)-feruloyl]-β-D-glucopyranoside (**1**), 2-(3,4-dihydroxyphenyl)ethyl α-L-arabinopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→3)]-[α-L-rhamnopyranosyl-(1→6)]-4-*O*-[(*E*)-feruloyl]-β-D-glucopyranoside (**2**), and 2-(3,4-dihydroxyphenyl)ethyl β-D-glucopyranosyl-(1→3)-{6-*O*-[(*E*)-feruloyl]-β-D-glucopyranosyl-(1→6)}-4-*O*-[(*E*)-caffeoyl]-β-D-glucopyranoside (**3**).

**Keywords:** *Digitalis ciliata*, Phenylethanoid glycosides, Digicilisides A – C.

## Introduction

*Digitalis ciliata* Trautv. (Plantaginaceae) is a strictly endemic plant native to the Caucasus area, and is commonly used to treat congestive heart failure [1][2]. Previous studies on *Digitalis ciliata* revealed the presence of cardiac glycosides, steroidal and triterpene saponins, pregnane glycosides, anthraquinones, and flavonoids [2 – 7]. The presence of phenylethanoid glycosides has never been reported before, whereas some members of the genus *Digitalis* have already been investigated in this respect [8 – 16]. As a continuation of our work on the roots of *D. ciliata*, we further investigated its secondary metabolites, primarily focusing on the possible occurrence of phenylethanoid glycosides. The present article deals with the isolation and the structure elucidation of three new phenylethanoid glycosides, **1** – **3** (*Fig. 1*), as well as five known glycosides obtained from the underground parts of the plant.

## Results and Discussion

The roots of *D. ciliata* (500 g) were extracted with 80% MeOH once at room temperature and twice at 60 °C. The obtained extract was partitioned between AcOEt, BuOH, and $H_2O$. A part of the BuOH extract was passed through a porous-polymer polystyrene resin (*Diaion HP-20*) column, and the fraction eluting with 50% MeOH was subjected to silica gel column chromatography (CC) to afford three new phenylethanoid glycosides, **1** – **3**, in addition to five known compounds. The known glycosides were identified as purpureaside B [8], 3′′′′-*O*-methylmaxoside [13], purpureaside E [14], maxoside [16], and chionoside F [17], by comparison of their spectroscopic data with literature values.

Compound **1** was obtained as yellow amorphous powder, possessing the elemental composition $C_{37}H_{50}O_{20}$ as concluded from the $[M + H]^+$ ion peak at *m/z* 815.3541 in the HR-TOF-MS. The $^1$H-NMR spectrum of **1** showed the signals of two *ABX* systems at δ 7.23 – 6.70, two (*E*)-olefinic H-atoms as an *AB* system at δ 7.66 and 6.43 (*d*, *J* = 16.0 Hz), a benzylic $CH_2$ group at δ 2.83 (*t*, *J* = 7.5 Hz), and two nonequivalent H-atoms of a $CH_2$–O group at δ 4.00 – 3.75 (*m*), as well as two MeO signal at δ 3.90 and δ 3.82, which were typical for a (*E*)-feruloyl moiety and a (3,4-dihydroxyphenyl)ethyl moiety linked *via* the O-atom to C(1′), respectively. Moreover, the $^1$H-NMR spectrum displayed three anomeric-H-atom resonances at δ 4.63 (*d*, *J* = 1.5 Hz, H–C(1′′′)), 4.53 (*d*, *J* = 8.0 Hz, H–C(1′′)), and 4.41 (*d*, *J* = 7.8 Hz, H–C(1′)), indicating a triglycosidic structure, which was confirmed by the corresponding anomeric C-atom resonances at δ 101.8, 105.4, and 103.8 in the $^{13}$C-NMR spectrum typical for α-L-rhamnopyranosyl and two β-D-glucopyranosyl moieties. The location of the MeO groups at C(3′′′′) and at C(3) of the acyl and aglycone units were deduced from the downfield shift (*ca.* 0.1 ppm) of the (*E*)-olefinic H-atoms [18] and the cross-peak δ 3.90 (MeO–C(3′′′′))/δ 148.9 C(3′′′′) and δ 3.82 (MeO–C(3))/δ 147.0 C(3) in the HMBC spectrum. On the basis of $^1$H- and $^{13}$C-NMR spectroscopic data (*Tables 1* and *2*), the structure of **1** was identified as 2-(4-hydroxy-3-methoxyphenyl)ethyl β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)]-4-*O*-[(*E*)-feruloyl]-β-D-glucopyranoside, a novel natural product named digiciliside A.

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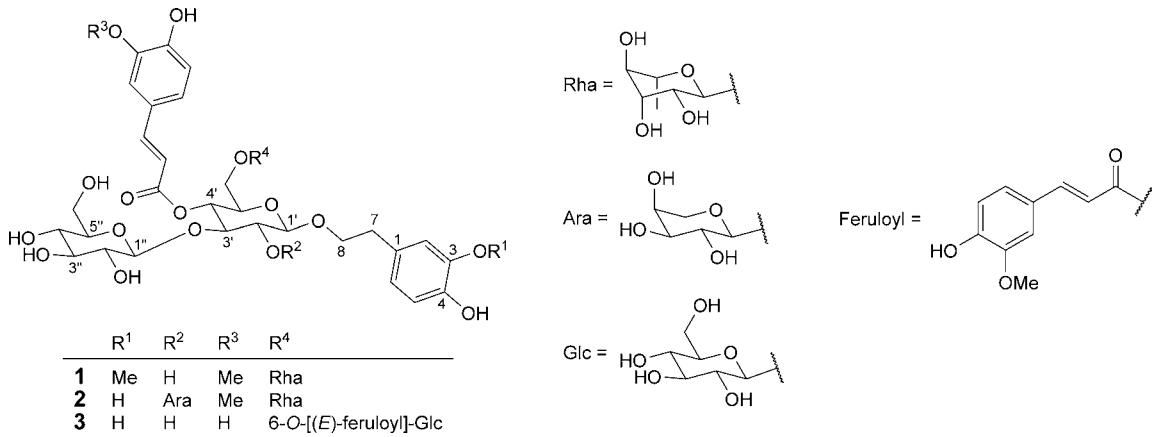


Fig. 1. Chemical structures of **1** – **3**

Compound **2** was obtained as yellow amorphous powder, and its molecular formula, $C_{41}H_{56}O_{24}$, was deduced by a prominent $[M + H]^+$ ion peak at *m/z* 933.3261 in the HR-TOF-MS. The $^1$H-NMR spectrum of **2** showed the proton signals due to a 1,3,4-trisubstituted benzene ring at $\delta$ 7.21 (*d*, *J* = 2.0 Hz, H–C(2‴‴)), 7.10 (*dd*, *J* = 8.0, 2.0 Hz, H–C(6‴‴)), and 6.80 (*d*, *J* = 8.0 Hz, H–C(5‴‴)), and a (*E*)-disubstituted C=C bond at $\delta$ 7.67 (*d*, *J* = 16.0 Hz, H–C(7‴‴)) and 6.42 (*d*, *J* = 16.0 Hz, H–C(8‴‴)), suggesting the presence of a feruloyl moiety. The $^1$H-NMR signals at $\delta$ 6.69 (*d*, *J* = 1.8 Hz, H–C(2)), 6.67 (*d*, *J* = 8.0 Hz, H–C(5)), and 6.57 (*dd*, *J* = 8.0, 1,8 Hz, H–C(6)) confirmed the presence of a 1,3,4-trisubstituted benzene ring, as well as two $CH_2$ protons at $\delta$ 4.00 – 3.72 (*m*, $CH_2$(8)) and 2.78 (*t*, *J* = 7.3 $CH_2$(7)) indicated a 3,4-dihydroxyphenylethyl moiety. Furthermore, the $^1$H-NMR spectrum displayed signals for four anomeric H-atoms at $\delta$ 4.65 (*d*, *J* = 7.9 Hz, H–C(1″)), 4.64 (*d*, *J* = 1.5 Hz, H–C(1‴)), 4.54 (*d*, *J* = 7.2 Hz, H–C(1⁗)), and 4.51 (*d*, *J* = 8.0 Hz, H–C(1′)), as well as one Me group at $\delta$ 1.21 (*d*, *J* = 6.5 Hz, Me(6‴)). The $^{13}$C-NMR spectrum of **2** revealed the presence of 41 carbon signals, including signals typical for 3,4-dihydroxyphenylethyl, feruloyl, two $\beta$-D-glucopyranosyl units, as well as $\alpha$-L-rhamnopyranosyl and $\alpha$-L-arabinopyranosyl moieties. Interpretation of the $^1$H,$^1$H-COSY, HSQC, and HMBC spectra of **2** led to the unambiguous assignment of all H- and C-atom resonances (*Tables 1* and *2*). In the HMBC spectrum, correlations between $\delta$ 4.51 (H–C(1′))/$\delta$ 72.2 C(8) and $\delta$ 4.99 (H–C(4′))/$\delta$ 167.5 C(9⁗) were observed, indicating that the 3,4-dihydroxyphenylethyl and feruloyl moieties were attached to C(1′) and C(4′) of central glucose, respectively. In addition, correlations between $\delta$ 4.65 (H–C(1″))/$\delta$ 81.1 C(3′), $\delta$ 4.64 (H–C(1‴))/$\delta$ 67.2 C(6′), and $\delta$ 4.54 (H–C(1⁗))/$\delta$ 82.3 C(2′) were observed, which led to assignment of the sugar sequence and linkage positions. Therefore, the structure of **2** was established as 2-(3,4-dihydroxyphenyl)ethyl $\alpha$-L-arabinopyranosyl-(1→2)-[$\beta$-D-glucopyranosyl-(1→3)]-[$\alpha$-L-rhamnopyranosyl-(1→6)]-4-*O*-[(*E*)-feruloyl]-$\beta$-D-glucopyranoside, for which the name digiciliside B is proposed.

Compound **3** was obtained as yellow amorphous powder. Its molecular formula was determined to be $C_{45}H_{54}O_{24}$ by the $[M + H]^+$ ion peak at *m/z* 979.2348 in the HR-TOF-MS. The $^1$H-NMR spectrum of **3** exhibited the resonances for a (*E*)-caffeoyl group (three aromatic H-atoms as an *ABX* system at $\delta$ 7.04 (*d*, *J* = 2.1 Hz), 6.92 (*dd*, *J* = 8.1 and 2.1 Hz), and 6.77 (*d*, *J* = 8.1 Hz), two (*E*)-olefinic H-atoms as an *AB* system at $\delta$ 7.56 and 6.28 (*d*, *J* = 15.8 Hz), and a 2-(3,4-dihydroxyphenyl)ethoxy moiety (three aromatic H-atoms as an *ABX* system at $\delta$ 6.68 (*d*, *J* = 1.8 Hz), 6.67 (*d*, *J* = 8.0 Hz), and 6.56 (*dd*, *J* = 8.0 and 1.8 Hz). Furthermore, signals typical for a benzylic $CH_2$ group at $\delta$ 2.80 (*t*, *J* = 7.3 Hz) and two nonequivalent H-atoms of a $CH_2$–O group at $\delta$ 4.01 – 3.70 (*m*) were observed. The presence of three anomeric H- and C-atoms ($\delta$ 4.41 (*d*, *J* = 7.8 Hz) and $\delta$ 103.6; $\delta$ 4.39 (*d*, *J* = 8.0 Hz) and $\delta$ 105.5; $\delta$ 4.34 (*d*, *J* = 7.9 Hz) and $\delta$ 104.7) was typical for three $\beta$-linked glucopyranosyl units. The NMR data of **3** were found to be similar to those of maxoside [16], except for the additional (*E*)-feruloyl signals in **3** (three aromatic H-atoms as an *ABX* system at $\delta$ 7.19 (*d*, *J* = 2.0 Hz), 7.08 (*dd*, *J* = 8.0 and 2.0 Hz), and 6.82 (*d*, *J* = 8.0 Hz), two (*E*)-olefinic H-atoms as an *AB* system at $\delta$ 7.64 and 6.39 (*d*, *J* = 16.0 Hz), and a MeO group at $\delta$ 3.87 (*s*)). The downfield shifts for the $CH_2$(6‴) ($\delta$ 4.52 and 4.32) and C(6‴) signals ($\delta$ 64.8) and the upfield shift for the C(5‴) signal ($\delta$ 77.5) confirmed that the esterification site for the (*E*)-feruloyl unit was at HO–C(6‴), which was further supported by the three-bond correlation of $CH_2$(6‴) to the C(9⁗) group at $\delta$ 168.4 of the feruloyl unit in the HMBC spectrum (*Fig. 2*). Consequently, compound **3** was established as 2-(3,4-dihydroxyphenyl)-ethyl $\beta$-D-glucopyranosyl-(1→3)-{6-*O*-[(*E*)-feruloyl]-$\beta$-D-glucopyranosyl-(1→6)}-4-*O*-[(*E*)-caffeoyl]-$\beta$-D-glucopyranoside, a new compound which was named digiciliside C.

 

Table 1. $^1$H-NMR data (600 MHz, in $CD_3OD$) of **1** – **3**. $\delta$ in ppm, $J$ in Hz.

| Position | **1** | **2** | **3** |
|---|---|---|---|
| *Aglycone* | | | |
| 2 | 6.73 (*d*, *J* = 2.0) | 6.69 (*d*, *J* = 1.8) | 6.68 (*d*, *J* = 1.8) |
| 5 | 6.83 (*d*, *J* = 8.0) | 6.67 (*d*, *J* = 8.0) | 6.67 (*d*, *J* = 8.0) |
| 6 | 6.70 (*dd*, *J* = 8.0, 2.0) | 6.57 (*dd*, *J* = 8.0, 1.8) | 6.56 (*dd*, *J* = 8.0, 1.8) |
| 7 | 2.83 (*t*, *J* = 7.5) | 2.78 (*t*, *J* = 7.3) | 2.80 (*t*, *J* = 7.3) |
| 8 | 4.00 – 3.75 (*m*) | 4.00 – 3.72 (*m*) | 4.01 – 3.70 (*m*) |
| 3-MeO | 3.82 (*s*) | | |
| *Central β-*D*-Glc* | | | |
| 1′ | 4.41 (*d*, *J* = 7.8) | 4.51 (*d*, *J* = 8.0) | 4.41 (*d*, *J* = 7.8) |
| 2′ | 3.48 (*dd*, *J* = 9.3, 7.8) | 3.70 (*dd*, *J* = 9.4, 8.0) | 3.47 (*dd*, *J* = 9.4, 7.8) |
| 3′ | 3.94 (*t*, *J* = 9.3) | 4.10 (*t*, *J* = 9.4) | 3.88 (*t*, *J* = 9.4) |
| 4′ | 4.99 (*t*, *J* = 9.3) | 4.99 (*t*, *J* = 9.4) | 4.87 (*t*, *J* = 9.4) |
| 5′ | 3.70 (*m*) | 3.71 (*m*) | 3.83 (*m*) |
| 6′ | 3.76[a]) | 3.77[a]) | 3.83[a]) |
| | 3.49[a]) | 3.50[a]) | 3.71[a]) |
| *3′-O-β-*D*-Glc* | | | |
| 1″ | 4.53 (*d*, *J* = 8.0) | 4.65 (*d*, *J* = 7.9) | 4.39 (*d*, *J* = 8.0) |
| 2″ | 3.14 (*dd*, *J* = 9.4, 7.9) | 3.10 (*dd*, *J* = 9.3, 7.9) | 3.12 (*dd*, *J* = 9.4, 7.9) |
| 3″ | 3.32 (*t*, *J* = 9.3) | 3.29 (*t*, *J* = 9.3) | 3.27 (*t*, *J* = 9.3) |
| 4″ | 3.22 (*t*, *J* = 9.3) | 3.02 (*t*, *J* = 9.4) | 3.03 (*t*, *J* = 9.4) |
| 5″ | 3.17 (*m*) | 3.23 (*ddd*, 9.4, 6.5, 2.5) | 3.21 (*m*) |
| 6″ | 3.68 (*dd*, *J* = 12.0, 2.5), | 3.79 (*dd*, *J* = 11.8, 2.5), | 3.61 (*dd*, *J* = 12.0, 2.5), |
| | 3.49 (*dd*, *J* = 12.0, 5.5) | 3.44 (*dd*, *J* = 12.0, 6.4) | 3.47 (*dd*, *J* = 12.0, 5.5) |
| *6′-O-Sugar* | α-L-Rha | α-L-Rha | *β*-D-Glc |
| 1‴ | 4.63 (*d*, *J* = 1.5) | 4.64 (*d*, *J* = 1.5) | 4.34 (*d*, *J* = 7.9) |
| 2‴ | 3.84 (*m*) | 3.84 (*m*) | 3.23 (*dd*, *J* = 9.4, 7.9) |
| 3‴ | 3.63 (*m*) | 3.65 (*m*) | 3.33 (*t*, *J* = 9.4) |
| 4‴ | 3.34 (*t*, *J* = 9.5) | 3.34 (*t*, *J* = 9.5) | 3.50 (*t*, *J* = 9.4) |
| 5‴ | 3.60 (*m*) | 3.61 (*m*) | 3.36 (*m*) |
| 6‴ | 1.21 (*d*, *J* = 6.5) | 1.21 (*d*, *J* = 6.5) | 4.52 (*dd*, *J* = 11.8, 2.5), |
| | | | 4.32 (*dd*, *J* = 11.8, 5.2) |
| *2′-O-α-*L*-Ara* | | | |
| 1⁗ | | 4.54 (*d*, *J* = 7.2) | |
| 2⁗ | | 3.57 (*obscured*) | |
| 3⁗ | | 3.49 (*dd*, *J* = 9.0, 3.4) | |
| 4⁗ | | 3.73 (*m*) | |
| 5⁗ | | 3.77 (br. *d*, *J* = 12.0), | |
| | | 3.20 (*dd*, *J* = 12.5, 1.0) | |
| *4′-O-(E)-Feruloyl or -caffeoyl*[b]) | | | |
| 2⁗[c])/2‴′ | 7.23 (*d*, *J* = 2.0) | 7.21 (*d*, *J* = 2.0) | 7.04 (*d*, *J* = 2.1) |
| 5⁗[c])/5‴′ | 6.81 (*d*, *J* = 8.0) | 6.80 (*d*, *J* = 8.0) | 6.77 (*d*, *J* = 8.1) |
| 6⁗[c])/6‴′ | 7.10 (*dd*, *J* = 8.0, 2.0) | 7.10 (*dd*, *J* = 8.0, 2.0) | 6.92 (*dd*, *J* = 8.1, 2.1) |
| 7⁗[c])/7‴′ | 7.66 (*d*, *J* = 16.0) | 7.67 (*d*, *J* = 16.0) | 7.56 (*d*, *J* = 15.8) |
| 8⁗[c])/8‴′ | 6.43 (*d*, *J* = 16.0) | 6.42 (*d*, *J* = 16.0) | 6.28 (*d*, *J* = 15.8) |
| 3⁗-MeO[d])/3‴′-MeO | 3.90 (*s*) | 3.89 (*s*) | |
| *6‴-O-(E)-Feruloyl* | | | |
| 2‴′ | | | 7.19 (*d*, *J* = 2.0) |
| 5‴′ | | | 6.82 (*d*, *J* = 8.0) |
| 6‴′ | | | 7.08 (*dd*, *J* = 8.0, 2.0) |
| 7‴′ | | | 7.64 (*d*, *J* = 16.0) |
| 8‴′ | | | 6.39 (*d*, *J* = 16.0) |
| 3‴′-MeO | | | 3.87 (*s*) |

[a]) Overlapped with other signals. [b]) Ferulic acid, (2*E*)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid; caffeic acid, (2*E*)-3-(3,4-dihydroxyphenyl)prop-2-enoic acid. [c]) For **1** and **3**. [d]) For **1**.

Several phenylethanoid glycosides have been reported from the genus *Digitalis* up to now, but not for *Digitalis ciliata*. For the first time, their occurrence could be confirmed in this species, which therefore can be considered as an interesting source of unusual phenylethanoid glycosides esterified with two aromatic acids, compounds that are rare for the entire genus.

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Table 2. $^{13}$C-NMR data (600 MHz, in $CD_3OD$) of **1** – **3**. $\delta$ in ppm.

| Position | **1** | **2** | **3** |
|---|---|---|---|
| *Aglycone* | | | |
| 1 | 132.2 | 131.3 | 131.2 |
| 2 | 116.7 | 116.8 | 117.0 |
| 3 | 147.0 | 144.5 | 144.5 |
| 4 | 146.8 | 146.0 | 146.1 |
| 5 | 112.5 | 116.0 | 116.0 |
| 6 | 120.8 | 121.0 | 120.9 |
| 7 | 36.5 | 36.4 | 36.4 |
| 8 | 71.9 | 72.2 | 72.2 |
| 3-MeO | 56.2 | | |
| *Central β-D-Glc* | | | |
| 1′ | 103.8 | 103.2 | 103.6 |
| 2′ | 74.6 | 82.3 | 74.8 |
| 3′ | 83.7 | 81.1 | 84.3 |
| 4′ | 70.3 | 70.2 | 71.0 |
| 5′ | 74.2 | 74.1 | 74.4 |
| 6′ | 67.1 | 67.2 | 69.8 |
| *3′-O-β-D-Glc* | | | |
| 1″ | 105.4 | 104.1 | 105.5 |
| 2″ | 75.6 | 75.2 | 75.7 |
| 3″ | 77.3 | 77.7 | 77.4 |
| 4″ | 70.9 | 71.7 | 70.9 |
| 5″ | 77.7 | 77.8 | 77.5 |
| 6″ | 62.0 | 63.0 | 62.2 |
| *6′-O-Sugar* | α-L-Rha | α-L-Rha | β-D-Glc |
| 1‴ | 101.8 | 101.8 | 104.7 |
| 2‴ | 71.7 | 71.8 | 74.9 |
| 3‴ | 71.9 | 72.1 | 71.4 |
| 4‴ | 73.7 | 73.7 | 75.2 |
| 5‴ | 69.5 | 69.6 | 77.5 |
| 6‴ | 17.8 | 17.8 | 64.8 |
| *2′-O-α-L-Ara* | | | |
| 1⁗ | | 105.1 | |
| 2⁗ | | 72.9 | |
| 3⁗ | | 74.8 | |
| 4⁗ | | 69.5 | |
| 5⁗ | | 67.0 | |
| *4′-O-(E)-Feruloyl or -caffeoyl*[a]) | | | |
| 1⁗[b])/1′′′′′ | 127.3 | 127.3 | 127.4 |
| 2⁗[b])/2′′′′′ | 111.3 | 111.5 | 115.0 |
| 3⁗[b])/3′′′′′ | 148.9 | 149.1 | 146.7 |
| 4⁗[b])/4′′′′′ | 150.1 | 150.2 | 149.6 |
| 5⁗[b])/5′′′′′ | 116.1 | 116.1 | 116.1 |
| 6⁗[b])/6′′′′′ | 124.0 | 124.0 | 122.7 |
| 7⁗[b])/7′′′′′ | 147.0 | 147.1 | 147.2 |
| 8⁗[b])/8′′′′′ | 115.3 | 115.3 | 114.7 |
| 9⁗[b])/9′′′′′ | 167.7 | 167.5 | 168.7 |
| 3⁗-MeO[c])/3′′′′′-MeO | 56.2 | 56.3 | |
| *6‴-O-(E)-Feruloyl* | | | |
| 1′′′′′ | | | 127.6 |
| 2′′′′′ | | | 111.6 |
| 3′′′′′ | | | 149.4 |
| 4′′′′′ | | | 150.7 |
| 5′′′′′ | | | 116.2 |
| 6′′′′′ | | | 124.0 |
| 7′′′′′ | | | 146.9 |
| 8′′′′′ | | | 115.0 |
| 9′′′′′ | | | 168.4 |
| 3′′′′′-MeO | | | *56.4* |

[a]) See *Table 1* for ferulic and caffeic acid. [b]) For **1** and **3**. [c]) For **1**.

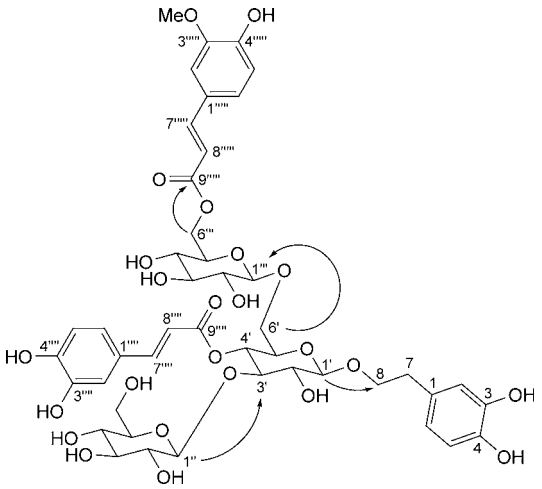


Fig. 2. Key HMBC correlations of **3**

## Experimental Part

### General

Thin layer chromatography (TLC): silica gel *60F$_{254}$* plates ($SiO_2$; *Merck*, Darmstadt, Germany), which were developed in the solvent system $CHCl_3$/MeOH/$H_2O$ 26:14:3. Column chromatography (CC): *Diaion HP-20* (*Sigma–Aldrich*) and $SiO_2$ (0.040 – 0.063 mm; *Merck*). All solvents for extraction and chromatographic separation were of anal. grade and purchased from *Merck*. Optical rotations: *Perkin-Elmer 192* polarimeter. UV Spectra: *JASCO V-550* UV/VIS spectrophotometer; $\lambda_{max}$ (log $\varepsilon$) in nm. IR Spectra: *PerkinElmer 1600* spectrometer; KBr; $\tilde{\nu}$ in $cm^{-1}$. $^1$H- and $^{13}$C-NMR spectra: *Avance II 600 MHz* spectrometer (600 and 150 MHz, resp.; *Bruker BioSpin GmbH*, Rheinstetten, Germany) equipped with a *Bruker TXI* probehead; in $CD_3OD$ (99.95%; *Euriso-Top*); at 300 K; $\delta$ in ppm rel. to $Me_4Si$ as internal standard, *J* in Hz. Standard pulse sequences and phase cycling were used for DQF-COSY, HSQC, and HMBC spectra. The NMR data were processed using *MestRe-C* UXNMR software (Santiago de Compostela, Spain). HR-ESI-TOF-MS (pos.): *microOTOF-QII* mass spectrometer (*Bruker*); in *m*/*z*. Exact mass calibration was performed on daily bases with the ESI-L low concentration tuning mix from *Agilent* (Santa Clara, CA, USA).

### Plant Material

The roots of *Digitalis ciliata* were collected in September 2012 in the northwest of Georgia (Svaneti region). Samples of *D. ciliata* were identified by Dr. *Jemal Aneli*, Department of Pharmacobotany, Institute of Pharmacochemistry, Tbilisi, Georgia, and a respective herbarium specimen (No. 118) was deposited at this department.

### Extraction and Isolation

A quantity of 500 g of powdered underground parts of *Digitalis ciliata* was extracted by shaking with 80%

 

MeOH (2.5 l) for 1 h once at r.t. and twice at 60 °C. The collected extracts were dried under reduced pressure (70 g), and the concentrate was partitioned between AcOEt (4 g), BuOH (50 g), and $H_2O$ (16 g). Part of the BuOH extract (10 g) was subjected to *Diaion HP-20* column chromatography (50 × 4 cm) and eluted with a gradient system of $H_2O$/MeOH 10:0 to 0:10 to yield four fractions (500 ml each), 30% MeOH (0.64 g), 50% MeOH (5.2 g), 80% MeOH (3.3 g), and 100% MeOH (0.3 g). Part of the 50% MeOH fraction (2.5 g) was then separated by CC ($SiO_2$; 100 g, 500 × 25 mm), eluted with $CHCl_3$/MeOH/$H_2O$ 26:14:3, to afford eight individual phenylethanoid glycosides, digiciliside A (**1**; 15 mg), digiciliside B (**2**; 34 mg), digiciliside C (**3**; 9 mg), maxoside (40 mg), 3′′′′-*O*-methylmaxoside (8 mg), purpureaside E (5 mg), purpureaside B (32 mg), and chionoside F (11 mg).

**Digiciliside A** (= **2-(4-Hydroxy-3-methoxyphenyl)ethyl *β*-D-Glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)]-4-*O*-[(*E*)-feruloyl]-*β*-D-glucopyranoside**; **1**). Yellow amorphous powder. $[\alpha]_D^{22} = -22.3$ ($c = 0.50$, MeOH). UV (MeOH): 219 (4.21), 288 (3.56), 328 (4.02). IR: 3400, 2922, 1700, 1630, 1593, 1515, 1155, 1062. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*. HR-ESI-TOF-MS: 815.3541 ($[M + H]^+$, $C_{37}H_{51}O_{20}^+$; calc. 815.2968).

**Digiciliside B** (= **2-(3,4-Dihydroxyphenyl)ethyl α-L-Arabinopyranosyl-(1→2)-[*β*-D-glucopyranosyl-(1→3)]-[α-L-rhamnopyranosyl-(1→6)]-4-*O*-[(*E*)-feruloyl]-*β*-D-glucopyranoside**; **2**). Yellow amorphous powder. $[\alpha]_D^{22} = -17.5$ ($c = 0.50$, MeOH). UV (MeOH): 204 (4.55), 220 (4.28), 292 (4.10), 329 (4.20). IR: 3402, 2920, 1695, 1627, 1590, 1515, 1155, 1065. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*. HR-TOF-MS: 933.3261 ($[M + H]^+$, $C_{41}H_{57}O_{24}^+$; calc. 933.3234).

**Digiciliside C** (= **2-(3,4-Dihydroxyphenyl)ethyl *β*-D-Glucopyranosyl-(1→3)-{6-*O*-[(*E*)-feruloyl]-*β*-D-glucopyranosyl-(1→6)}-4-*O*-[(*E*)-caffeoyl]-*β*-D-glucopyranoside**; **3**). Yellow amorphous powder. $[\alpha]_D^{22} = -35.2$ ($c = 0.50$, MeOH). UV (MeOH): 245 (sh, 3.95), 288 (4.00), 313 (4.10). IR: 3400, 2919, 1696, 1631, 1604, 1515, 1449, 1155, 1060. $^1$H- and $^{13}$C-NMR: *Tables 1* and *2*. HR-TOF-MS: 979.2348 ($[M + H]^+$, $C_{45}H_{55}O_{24}^+$; calc. 979.3078).

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