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4′-Deoxy iridoid glycosides from *Centranthus longiflorus*

Ayşe Kuruüzüm-Uz[a,*], Zuhal Güvenalp[b], L. Ömür Demirezer[a], Isabelle Bergère[c], Karsten Ströch[c], Axel Zeeck[c]

[a]*Hacettepe University, Faculty of Pharmacy, Department of Pharmacognosy, TR-06100 Ankara, Turkey*
[b]*Atatürk University, Faculty of Pharmacy, Department of Pharmacognosy, Erzurum, Turkey*
[c]*Georg-August University, Institute of Organic Chemistry, D-37077 Göttingen, Germany*

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Abstract

The new iridoid glycosides, 4′-deoxykanokoside A and 4′-deoxykanokoside C, were isolated from the methanolic root extract of *Centranthus longiflorus* ssp. *longiflorus*. They were accompanied by the three known iridoid glycosides, kanokoside A, kanokoside C and valerosidatum, and two known phenylpropanoid glycosides, coniferin and isoconiferinoside. The structures were elucidated mainly by spectroscopic methods. The presence of 4-deoxy glucose as a part of plant glycosides is rather unusual. Cytotoxic effects of the isolated compounds were also investigated.

Keywords: *Centranthus longiflorus*; Valerianaceae; Deoxyglycosides; Iridoids; Phenylpropanoids

1. Introduction

Centranthus longiflorus Stev. ssp. *longiflorus* (Valerianaceae) is used in folk medicine for sedative and antispasmodic purposes (Baytop, 1984). In a previous paper, we described the isolation and characterization of a new iridolactone (longiflorone) together with a valepotriate (valtrate hydrine B8), two known iridoid glycosides (patrinoside and kanokoside A), oleanolic acid, sitosterol and quercetin 3-*O*-rutinoside from the methanolic extract of the aerial parts of *C. longiflorus* ssp. *longiflorus* (Demirezer et al., 1999). The iridoids containing aqueous extract of this plant (100 mg/kg) showed sedative, anticonvulsant and antidepressant effects, similar to the effect of diazepam (5 mg/kg) on mice and rats (Büyükokuroglu et al., 2002). We now turned to the methanolic extract of the roots of this plant and report the isolation and structure elucidation of two new unusual deoxy iridoid glycosides named 4′-deoxykanokoside A (**1**) and 4′-deoxykanokoside C (**2**), besides other known glycosides from this plant. In addition cytotoxic effects of the isolated compounds were investigated.

2. Results and discussion

The methanolic extract of the roots of *C. longiflorus* ssp. *longiflorus* was suspended in H_2O and fractionated into $CHCl_3$. Repeated column chromatography of the aqueous layer resulted in five iridoid glycosides (**1**–**5**) and two phenylpropanoid glycosides (**6**–**7**). The 1D-(^{1}H, ^{13}C, APT) and 2D-NMR (COSY, HSQC, HMBC, NOESY) spectroscopic data and MS values of **3**–**7** were in excellent agreement with those reported for kanokoside A (**3**), kanokoside C (**4**) (Endo and Taguchi, 1977; Nishiya et al., 1992), valerosidatum (**5**) (Thies, 1970; Inouye et al., 1974; Boros and Stermitz, 1991; Tomassini et al., 1995), coniferin (**6**) and isoconiferinoside (**7**) (Sugiyama et al., 1993; Della Greca et al., 1998).

The iridoids **1**–**5** are hygroscopic amorphous powders. From 350 g dried roots the following amounts of the glycosides were isolated: 48 mg (**1**), 15 mg (**2**), 169 mg (**3**), 70 mg (**4**), 38 mg (**5**), 27 mg (**6**), 35 mg (**7**). As evident from ^{1}H and ^{13}C NMR data and in accordance with Valeriana type iridoid glycosides, they contain a β-glucopyranosyl unit attached at C-11 and an isovaleryl group at C-1.

Compound **1** was assigned the molecular formula $C_{21}H_{32}O_{11}$ on the basis of the ESI-MS spectrum at m/z 483 $[M+Na]^+$ and with the aid of the ^{13}C NMR. In

* Corresponding author. Tel.: +90-312-305-10-89; fax: +90-312-311-47-77.
E-mail address: ayseuz@hacettepe.edu.tr (A. Kuruüzüm-Uz).

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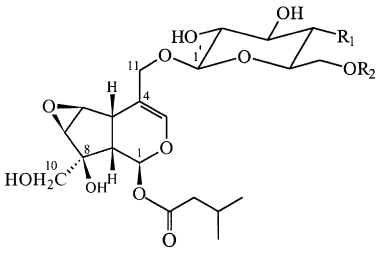
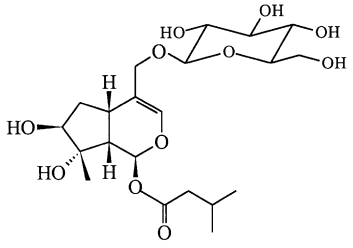


1 R_1,R_2= H
2 R_1=H, R_2= Glu
3 R_1=OH, R_2= H
4 R_1=OH, R_2= Glu



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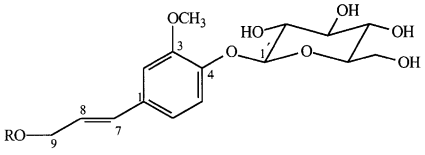

6 R= H
7 R= Glu

comparison with kanokoside A (**3**) (Endo and Taguchi, 1977; Nishiya et al., 1992) most ^{1}H and ^{13}C NMR spectral data of **1** (Table 1) were identical (iridoid skeleton and isovaleryl group) except of four signals in the sugar unit (positions 3′, 4′, 5′ and 6′). The most significant difference was the lack of one methine group (δ_H 3.27 in **3**) and instead of a methylene group appearing at δ_H 1.35/1.91 (2H, ABXY-system, $J_{A,B}$ = 12.5 Hz) which represents a deoxygenated carbon atom of the sugar moiety. However, in comparison with the ^{13}C NMR spectrum of **3** (Nishiya et al., 1992), specifically the resonances of C-3′ ($\delta_C \cong +6$ ppm), C-4′ ($\delta_C \cong +35$ ppm), and C-5′ ($\delta_C \cong +4$ ppm) were shifted upfield and C-6′ ($\Delta\delta_C \cong -3$ ppm) downfield indicating the absence of a hydroxy group at C-4′ position (Junior, 1984; Sheppard et al., 2000). The comparison with the ^{13}C values of 4-deoxy-β-D-glucose supports this assumption [Bock and Pedersen, 1983; measured in D_2O: δ_C = 97.1 (C-1), 76.9 (C-2), 71.3 (C-3), 35.1 (C-4), 73.2 (C-5), 64.5 (C-6)]. Consequently, together with the HSQC and HMBC correlations, the compound was established as 4′-deoxykanokoside A (**1**).

Compound **2** was assigned the molecular formula $C_{27}H_{42}O_{16}$ by ESI-MS at *m/z* 645 $[M+Na]^+$ and with the aid of the ^{13}C NMR. Because of the relationship to

Table 1
^{1}H and ^{13}C NMR spectral data for compounds **1, 3** and desglucoserrulatoside (CD_3OD)

Atom Numbers	**1**		**3**		Desgluco-serrulatoside
1	6.39 (1H, br. *s*)	90.5	6.39 (1H, br. *s*)	90.6	93.1
3	6.40 (1H, br. *s*)	142.5	6.41 (1H, *d*, *J* = 2.0 Hz)	142.6	141.0
4	–	109.3	–	109.2	115.9
5	3.07 (1H, *dd*, *J* = 8.5,1.5 Hz)	35.4	3.07 (1H, *d*, = 8.5/1.5 Hz)	35.4	38.4
6	4.03 (1H, *d*, *J* = 2.5 Hz)	59.7	4.03 (1H, *d*, *J* = 2.5 Hz)	59.7	38.2
7	3.35 (1H, *d*, *J* = 2.5 Hz)	60.1	3.35 (1H, *d*, *J* = 2.5 Hz)	60.2	129.4
8	–	80.1	–	80.1	144.2
9	2.01 (1H, *d*, *J* = 8.5 Hz)	43.4	2.01 (1H, *d*, *J* = 7.5 Hz)	43.4	47.2
10	3.68 (2H, *d*, *J* = 4.0 Hz)	67.0	3.68 (2H, *d*, *J* = 4.0 Hz)	67.0	61.1
11	4.22 (1H, *d*, *J* = 11.5 Hz)	69.5	4.24 (1H, *d*, *J* = 11.5 Hz)	69.5	69.3
	4.33 (1H, *d*, *J* = 11.5 Hz)		4.34 (1H, *d*, *J* = 11.5 Hz)		
Sugar					
1′	4.32 (1H, *d*, *J* = 8.0 Hz)	102.5	4.39 (1H, *d*, *J* = 8.0 Hz)	102.1	98.6
2′	3.10 (1H, *dd*, *J* = 9.0, 8.0 Hz)	76.9	3.20 (1H, *dd*, *J* = 9.0, 8.0 Hz)	75.1	70.8
3′	3.60 (1H, *m*)	72.3	3.36 (1H, *m*)	78.2	69.4
4′	1.35 (1H, *dt*, *J* = 12.5, 11.0 Hz)	36.5	3.27 (1H, *m*)	71.8	30.6
	1.91 (1H, *ddd*, *J* = 12.5, 5.5, 2.0 Hz)				
5′	3.53 (1H, *m*)	73.9	3.27 (1H, *m*)	78.0	73.1
6′	3.56 (2H, br. *s*)	65.6	3.65 (1H, *m*)		
			3.88 (1H, *dd*, J = 11.5, 1.5 Hz)	62.9	66.0
Isovaleryl					
1″	–	173.0	–	173.0	173.1
2″	2.16 (1H, *d*, *J* = 1.5 Hz)	44.1	2.16 (1H, *d*, *J* = 1.5 Hz)	44.1	44.2
	2.18 (1H, *d*, *J* = 2.0 Hz)		2.18 (1H, *d*, *J* = 2.0 Hz)		
3″	2.03 (1H, *m*)	26.8	2.03 (1H, *m*)	26.8	26.7
4″	0.93 (3H, *d*, *J* = 7.0 Hz)	22.6	0.94 (3H, *d*, *J* = 7.0 Hz)	22.6	22.6
5″	0.93 (3H, *d*, *J* = 7.0 Hz)	22.6	0.94 (3H, *d*, *J* = 7.0 Hz)	22.6	22.6

Table 2
^{1}H and ^{13}C NMR spectral data for compounds **2, 4** and serrulatoside (CD_3OD)

Atom Numbers	**2**		**4**		Serrulatoside
1	6.39 (1H, br. *s*)	90.6	6.39 (1H, br. *s*)	90.5	93.2
3	6.43 (1H, *d*, *J* = 2.0 Hz)	142.7	6.44 (1H, *d*, *J* = 2.0 Hz)	142.8	141.1
4	–	109.2	–	109.1	115.8
5	3.07 (1H, *dd*, *J* = 8.5, 1.5 Hz)	35.5	3.07 (1H, *dd*, *J* = 8.5, 1.5 Hz)	35.4	38.3
6	4.05 (1H, *d*, *J* = 2.5 Hz)	59.7	4.05 (1H, *d*, *J* = 2.5 Hz)	59.7	38.4
7	3.35 (1H, *d*, *J* = 2.5 Hz)	60.2	3.35 (1H, *d*, *J* = 2.5 Hz)	60.2	129.4
8	–	80.1	–	80.1	144.2
9	2.01 (1H, *d*, *J* = 7.5 Hz)	43.4	2.01 (1H, *d*, *J* = 7.5 Hz)	43.3	47.1
10	3.68 (2H, *d*, *J* = 4.0 Hz)	67.0	3.68 (2H, *d*, *J* = 4.0 Hz)	67.0	61.1
11	4.22 (1H, *d*, *J* = 11.5 Hz)	69.6	4.24 (1H, *dd*, *J* = 11.5, 6.0 Hz)	69.6	69.5
	4.33 (1H, *d*, *J* = 11.5 Hz)		4.33 (1H, *d*, *J* = 11.5 Hz)		
Sugars					
1′	4.34 (1H, *d*, *J* = 8.0 Hz)	102.5	4.40 (1H, *d*, *J* = 8.0 Hz)	102.0	98.7
2′	3.11 (1H, *dd*, *J* = 9.0, 7.5 Hz)	76.9	3.21 (1H, *dd*, *J* = 9.0, 8.0 Hz)	75.0	70.7
3′	3.59 (1H, *m*)	72.2	3.35 (1H, *m*)	78.0	69.3
4′	1.38 (1H, *d*t, *J* = 12.5, 11.5 Hz)	36.7	3.28 (1H, *m*)	71.6	30.9
	1.94 (1H, *ddd*, *J* = 12.5, 5.5, 1.5 Hz)				
5′	3.75 (1H, *m*)	72.8	3.47 (1H, *ddd*, *J* = 9.5, 6.0, 2.0 Hz)	77.0	72.1
6′	3.68 (1H, *m*)	72.6	3.77 (1H, *dd*, *J* = 12.0, 6.0 Hz)	70.1	72.9
	3.82 (1H, *m*)		4.15 (1H, *dd*, *J* = 12.0, 2.0 Hz)		
1″	4.37 (1H, *d*, *J* = 8.0 Hz)	104.9	4.39 (1H, *d*, *J* = 8.0 Hz)	105.0	104.8
2″	3.19 (1H, *dd*, *J* = 9.0, 7.5 Hz)	75.1	3.21 (1H, *dd*, *J* = 9.0, 8.0 Hz)	75.1	75.1
3″	3.34 (1H, *m*)	78.1	3.35 (1H, *m*)	78.0	78.0
4″	3.27 (1H, *m*)	71.6	3.28 (1H, *m*)	71.7	71.7
5″	3.27 (1H, *m*)	78.0	3.28 (1H, *m*)	78.0	78.1
6″	3.66 (1H, *dd*, *J* = 12.0, 5.5 Hz)	62.8	3.66 (1H, *m*)	62.7	62.8
	3.86 (1H, *dd*, *J* = 12.0, 1.5 Hz)		3.86 (1H, *dd*, *J* = 12.0, 2.0 Hz)		
Isovaleryl					
1‴	–	173.0	–	173.0	173.1
2‴	2.16 (1H, *d*, *J* = 1.0 Hz)	44.1	2.16 (1H, *d*, *J* = 1.0 Hz)	44.1	44.1
	2.18 (1H, *d*, *J* = 1.5 Hz)		2.18(1H, *d*, *J* = 1.5 Hz)		
3‴	2.03 (1H, *m*)	26.8	2.03 (1H, *m*)	26.8	26.7
4‴	0.94 (3H, *d*, *J* = 7.5 Hz)	22.6	0.94 (3H, *d*, *J* = 6.5 Hz)	22.6	22.6
5‴	0.94 (3H, *d*, *J* = 7.5 Hz)	22.6	0.94 (3H, *d*, *J* = 6.5 Hz)	22.6	22.6

kanokoside C ($\Delta m/z = 16$, lacking one hydroxy group) its spectral data were compared with those of kanokoside C (**4**) (Nishiya et al., 1992) and **1**. The ^{1}H NMR showed the expected protons for the iridoid skeleton and the isovaleryl group.

The coupling constants of the anomeric protons at δ_H 4.34 and 4.37 (each 1H, *d*, *J* = 8.0 Hz) are consistent with the β-configuration for both sugar residues. The remaining protons, in comparison to 4′-deoxykanokoside A and kanokoside C, on the basis of 1D and 2D NMR experiments led to the conclusion that the sugar moiety was 4′-deoxygentiobioside (Tables 1 and 2). A HMBC experiment showed correlations between 1′-H and C-11 as well as C-6′ and 1″-H which proved the 4′-deoxygentiobioside. Thus, this compound was established to be 4′-deoxykanokoside C (**2**).

The stereochemical assignments in the kanokosides were confirmed by NOESY experiments.

On the base of the ^{1}H NMR, ^{13}C NMR and mass spectral data given in previous studies, compound **5** was identified as valerosidatum. Because of the different stereochemistry at C-8 of **5** compared with compounds **1**–**4**, which is unusual for compounds isolated from the same plant, we performed selective NOE experiments for 1-H, 7-H, 9-H and 10-H_3 to prove our assumption. Irradiations revealed correlations from 10-H_3 to 1-H, 7-H and 9-H, from 9-H to 1-H, 5-H and 10-H_3, from 7-H to 6-H_2 and 10-H_3 and from 1-H to 9-H and 10-H_3. Together with the coupling constants $J_{1,9} = 4.0$ Hz and $J_{6,7} = 3.5$ Hz, which are important for the conformation of the iridoid skeleton, and by comparison with ^{13}C NMR values of 2′,3′-diacetylvalerosidatum (Tomassini et al., 1997) and 8-*epi*-valerosidatum (Junior, 1983) we could confirm the stereochemistry of **5**. The isolation of valerosidatum together with patrinoside and kanokosides A–D from valerian roots has already been reported (Endo and Taguchi, 1977).

4′-Deoxykanokoside A (**1**) and 4′-deoxykanokoside C (**2**) are rare natural glycosides which are characterized by the lack of one hydroxy group in the glucose moiety.

A similar iridoid (serrulatoside) has been isolated from *Penstemon serrulatus* (Scrophulariaceae) (Junior, 1984).

In Valerianaceae phenylpropanoids are found as relatively minor constituents. While the flavonoids in both aglycone and glycosidic forms exist, the other types of phenylpropanoids do not exist as the glycosidic forms in Valerianaceae (Houghton, 1997). Coniferin (**6**) and isoconiferinoside (**7**) have now been found for the first time in Valerianaceae.

The compounds **1**–**7** were tested in accordance to NCI-directives (Grever et al., 1992) against three different cancer cell lines (HM02, HepG2 and MCF7). They all showed a weak cytostatic/cytotoxic activity (GI_{50} = 1–9 μg/ml).

3. Experimental

3.1. General

IR spectra: FT-IR spectrometer Perkin-Elmer 1600. UV spectra: Varian Cary 3E. Optical rotation: Perkin-Elmer 343 spectrometer. ESI-MS: Finnigan LC-Q. ^{1}H NMR, ^{13}C NMR, APT, ^{1}H-^{1}H COSY, HSQC, HMBC and NOESY spectra: Varian Inova-500, Varian U 300, Bruker AMX 300. Chemical shifts are expressed in δ values, relative to TMS, solvents were used as internal references.

3.2. Plant material

Plant material was collected from Erzurum — spir, in Eastern Anatolia in July, 2000 (1960 m) and identified by Dr. Yusuf Kaya (Department of Biology, Faculty of Science and Literature, Atatürk University, Erzurum, Turkey). A voucher specimen (no: HUEF 96022) has been deposited in the herbarium of Hacettepe University, Faculty of Pharmacy, Ankara, Turkey.

3.3. Extraction and isolation

Dried and powdered roots of *C. longiflorus* ssp. *longiflorus* (350 g) were extracted with methanol (2×3.5 l) at 40–60 °C. The methanolic extracts were combined and concentrated (80 g). The residue was suspended in H_2O and partitioned with $CHCl_3$. The aqueous layer (47 g) was subjected to a column of Sephadex LH-20 eluting with MeOH. Iridoid fractions were chromatographed on a silica gel column using $CHCl_3$–MeOH (9:1–1:1) to yield six main fractions. All fractions were applied to repeated silica gel, Sephadex LH-20 and RP-18 column chromatography to yield compound **1** (48 mg), compound **2** (15 mg), compound **3** (169 mg), compound **4** (70 mg), compound **5** (38 mg), compound **6** (27.5 mg) and compound **7** (35 mg).

3.4. 4′-Deoxykanokoside A (*1*)

Amorphous; $[\alpha]_D^{20} = -122^\circ$ ($c = 0.1$, MeOH). IR ν_{max} (KBr): 3409, 2958, 2929, 2873, 1734, 1675, 1631 cm^{-1}. ^{1}H NMR (500 MHz; CD_3OD) and ^{13}C NMR (125.6 MHz; CD_3OD): see Table 1. ESI-MS: *m/z* 483 $[M + Na]^+$, $C_{21}H_{32}O_{11}$.

3.5. 4′-Deoxykanokoside C (*2*)

Amorphous; $[\alpha]_D^{20} = -107^\circ$ ($c = 0.1$, MeOH). IR ν_{max} (KBr): 3405, 2956, 2929, 2873, 1735, 1671, 1650, 1635 cm^{-1}. ^{1}H NMR (500 MHz; CD_3OD) and ^{13}C NMR (125.6 MHz; CD_3OD): see Table 2. ESI-MS: *m/z* 645 $[M + Na]^+$, $C_{27}H_{42}O_{16}$.

3.6. Kanokoside A (*3*)

Amorphous; $[\alpha]_D^{20} = -137^\circ$ ($c = 0.1$, MeOH). IR ν_{max} (KBr): 3408, 2958, 2873, 1738, 1673, 1634 cm^{-1}. ^{1}H NMR (500 MHz; CD_3OD) and ^{13}C NMR (75.5 MHz; CD_3OD): see Table 1. ESI-MS: *m/z* 499 $[M + Na]^+$, $C_{21}H_{32}O_{12}$.

3.7. Kanokoside C (*4*)

Amorphous; $[\alpha]_D^{20} = -123^\circ$ ($c = 0.1$, MeOH). IR ν_{max} (KBr): 3421, 2959, 2929, 2875, 1738, 1675, 1635, 1461, 1415, 1372 cm^{-1}. ^{1}H NMR (500 MHz; CD_3OD) and ^{13}C NMR (75.5 MHz; CD_3OD): see Table 2. ESI-MS *m/z* 661 $[M + Na]^+$, $C_{27}H_{42}O_{17}$.

3.8. Valerosidatum (*5*)

Amorphous; $[\alpha]_D^{20} = -60^\circ$ ($c = 0.1$, MeOH). IR ν_{max} (KBr): 3402, 2964, 2929, 2869, 1737, 1667, 1635, 1606, 1559, 1541 cm^{-1}. ESI-MS: *m/z* 485 $[M + Na]^+$, $C_{21}H_{34}O_{11}$.

3.9. Coniferin (*6*)

Amorphous; $[\alpha]_D^{20} = -55^\circ$ ($c = 0.1$, MeOH). UV (MeOH): λ_{max} (log ϵ) = 257 (4.13) nm. IR ν_{max} (KBr): 3422, 2924, 1650, 1635, 1622, 1514 cm^{-1}. ESI-MS: *m/z* 365 $[M + Na]^+$, $C_{16}H_{22}O_8$.

3.10. Isoconiferinoside (*7*)

Amorphous; $[\alpha]_D^{20} = -61^\circ$ ($c = 0.1$, MeOH). UV (MeOH): λ_{max} (log ϵ) = 258 (4.19) nm. IR ν_{max} (KBr): 3417, 2923, 1650, 1636, 1512 cm^{-1}. ESI-MS: *m/z* 528 $[M + Na]^+$, $C_{22}H_{32}O_{13}$.

3.11. Assay for cytotoxic activity

Cytotoxic effect of the pure compounds were tested against the three cancer cell lines [HM02 (stomach

carcinoma), HepG2 (liver carcinoma) and MCF7 (mamma carcinoma)] according to NCI-directives (Grever et al., 1992).

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