Phenylethyl Glycosides from *Digitalis lanata*

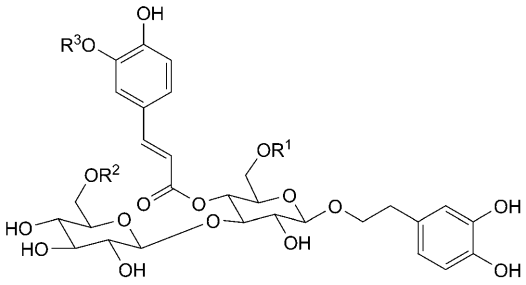
by **Hasan Kırmızıbekmez***[a]), **Engin Celep**[a]), **Milena Masullo**[b]), **Carla Bassarello**[b]), **Erdem Yeşilada**[a]), and **Sonia Piacente**[b])

[a]) Yeditepe University, Faculty of Pharmacy, Department of Pharmacognosy, TR-34755 Kayışdağı, İstanbul, Turkey
(phone: +90-216-5780000-3050; fax: +90-216-5780068; e-mail: hasankbekmez@yahoo.com)
[b]) Salerno University, Department of Pharmaceutical Sciences, Via Ponte Don Melillo, I-84084 Fisciano-Salerno

Three new phenylethyl glycosides, 3‴-*O*-methylmaxoside (=2-(3,4-dihydroxyphenyl)ethyl *O*-*β*-D-glucopyranosyl-(1→3)-*O*-[*β*-D-glucopyranosyl-(1→6)]-4-*O*-(*E*)-feruloyl-*β*-D-glucopyranoside; **1**), digilanatosides A (=2-(3,4-dihydroxyphenyl)ethyl *O*-6-*O*-(*E*)-sinapoyl-*β*-D-glucopyranosyl-(1→3)-4-*O*-(*E*)-caffeoyl-*β*-D-glucopyranoside; **2**), and digilanatoside B (=2-(3,4-dihydroxyphenyl)ethyl *O*-6-*O*-(*E*)-*p*-coumaroyl-*β*-D-glucopyranosyl-(1→3)-4-*O*-(*E*)-caffeoyl-*β*-D-glucopyranoside; **3**) were isolated from the aerial parts of *Digitalis lanata*, along with two known phenylethyl glycosides, purpureaside A and maxoside, a phenylpropanoid glucose ester, 1-*O*-(*E*)-feruloyl-*β*-glucopyranose, a benzoquinolethanoid glucoside, cornoside, a cardenolide, lanatoside C, a furostane-type steroidal saponin, purpureagitoside, and a disaccharide, sucrose. Their structures were elucidated on the basis of spectroscopic evidence (1D- and 2D-NMR, and HR-MALDI-MS).

Introduction. – *Digitalis lanata* EHRH. (formerly Scrophulariaceae, now Plantaginaceae) is a biennial or perennial plant which is native to Eastern Europe comprising Northwest of Turkey [1]. It is well known for its secondary cardiac glycoside, digoxin which is widely used for the treatment of congestive heart failure and atrial fibrillation. Previous studies on *Digitalis lanata* revealed the presence of cardiac glycosides, steroidal saponins, and pregnane glycosides [2–8]. In addition, only one compound, maxoside (=2-(3,4-dihydroxyphenyl)ethyl *O*-*β*-D-glucopyranosyl-(1→3)-*O*-[*β*-D-glucopyranosyl-(1→6)]-*β*-D-glucopyranoside 4-[(2*E*)-3-(3,4-dihydroxyphenyl)prop-2-enoate]), was reported as a phenylethyl glycoside from *D. lanata* [9], while some members of the genus have been investigated in terms of their phenylethyl glycoside contents [10–13]. As a continuation of our work on the phenylethyl glycosides from medicinal plants, we investigated the secondary metabolites of *D. lanata*, primarily focusing on its phenylethyl glycoside composition. The present article deals with the isolation and the structure elucidation of three new phenylethyl glycosides, **1**–**3**, as well as seven known metabolites obtained from the aerial parts of the title plant. Besides, the contribution of the isolated compounds to the chemotaxonomy of the genus *Digitalis* is also evaluated.

Results and Discussion. – The air-dried aerial parts of *D. lanata* were extracted with MeOH. After partition between H_2O and organic solvents, the H_2O-soluble part of the MeOH extract was submitted to multiple chromatographic steps to afford three new



	R^1	R^2	R^3
1	β-Glc	H	Me
2	H	(*E*)-sinapoyl	H
3	H	(*E*)-*p*-coumaroyl	H

phenylethyl glycosides, **1**–**3**, in addition to seven known metabolites. The known compounds were identified as purpureaside A [10], maxoside [9], 1-*O*-(*E*)-feruloyl-β-D-glucopyranose[1]) [14], cornoside [15], lanatoside C [7], purpureagitoside [3], and sucrose [16], by comparison of their spectroscopic data with literature values.

Compound **1** was obtained as a yellow amorphous powder, possessing the elemental composition $C_{36}H_{48}O_{21}$ as concluded from the $[M+H]^+$ ion peak at *m*/*z* 817.2762 in the HR-MALDI-MS. On the basis of ^{1}H- and ^{13}C-NMR spectroscopic data (*Tables 1* and *2*) secured by 2D-NMR analyses and comparison with those of maxoside [9], the structure of **1** was identified as 2-(3,4-dihydroxyphenyl)ethyl *O*-β-D-glucopyranosyl-(1→3)-*O*-[β-D-glucopyranosyl-(1→6)]-4-*O*-(*E*)-feruloyl-D-β-glucopyranoside[1]), and named 3′′′′-*O*-methylmaxoside[2]).

The ^{1}H-NMR spectrum of **1** showed the signals of two *ABX* systems at δ 7.25–6.60, two *trans*-olefinic H-atoms as an *AB* system at δ 7.67 and 6.45 (*d*, J = 15.9 Hz), a benzylic CH_2 group at δ 2.82 (*t*, J = 7.5 Hz) and two nonequivalent H-atoms of a CH_2–O group at 4.06–3.76 (*m*), as well as an MeO signal at δ 3.93 which were typical for a *trans*-feruloyl and a 2-(3,4-dihydroxyphenyl)ethoxy moiety. Moreover, the ^{1}H-NMR spectrum displayed three anomeric-H-atom resonances at δ 4.56 (*d*, J = 7.7 Hz, H–C(1′′)), 4.45 (*d*, J = 7.8 Hz, H–C(1′)), and 4.34 (*d*, J = 7.8 Hz, H–C(1′′′)), indicating a triglucosidic structure, which was confirmed by the corresponding anomeric-C-atom resonances at δ 105.4, 103.7, and 104.3 in the ^{13}C-NMR spectrum. The NMR data of **1** were almost the same as those of maxoside [9], except for the presence of signals at δ 3.93 and 56.2 arising from the MeO group in the NMR spectra of **1**. The location of the MeO group at C(3′′′′) of the acyl unit was deduced from the downfield shift (*ca.* 0.1 ppm) of the *trans*-olefinic H-atoms [17] and the cross-peak δ 3.93 (MeO–C(3′′′′))/δ 150.5 C(3′′′′) in the HMBC spectrum. Therefore, **1** contains a feruloyl unit instead of the caffeoyl moiety of maxoside.

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[1]) The D-configuration of the glucopyranose moieties is tentative.

[2]) Trivial atom numbering; for systematic names, see *Exper. Part.*

Table 1. *^{1}H-NMR Data* (CD_3OD) *of* **1**–**3**[a]). δ in ppm, J in Hz.

		1[a])	**2**[a])	**3**[a])
Aglycone:	H–C(2)	6.74 (*d*, *J* = 2.0)	6.70 (*d*, *J* = 1.8)	6.72 (*d*, *J* = 1.9)
	H–C(5)	6.70 (*d*, *J* = 8.0)	6.67 (*d*, *J* = 8.0)	6.70 (*d*, *J* = 8.0)
	H–C(6)	6.60 (*dd*, *J* = 8.0, 2.0)	6.55 (*dd*, *J* = 8.0, 1.8)	6.58 (*dd*, *J* = 8.0, 1.9)
	$CH_2(\alpha)$	3.76–4.06 (*m*)	3.70–4.01 (*m*)	3.71–4.03 (*m*)
	$CH_2(\beta)$	2.82 (*t*, *J* = 7.5)	2.78 (*t*, *J* = 7.5)	2.80 (*t*, *J* = 7.2)
Glc:	H–C(1′)	4.45 (*d*, *J* = 7.8)	4.41 (*d*, *J* = 7.9)	4.43 (*d*, *J* = 7.6)
	H–C(2′)	3.51 (*dd*, *J* = 9.3, 7.8)	3.46 (*dd*, *J* = 9.0, 7.9)	3.48 (*dd*, *J* = 8.5, 7.6)
	H–C(3′)	3.97 (*t*, *J* = 9.4)	3.87 (*t*, *J* = 9.0)	3.93 (*t*, *J* = 9.5)
	H–C(4′)	5.03 (*t*, *J* = 9.4)	4.88 (*t*, *J* = 9.0)	4.91 (*t*, *J* = 9.5)
	H–C(5′)	3.79–3.83 (*m*)	3.83–3.88 (*m*)	3.84–3.89 (*m*)
	CH_2(6′)	3.97[b]), 3.68[b])	3.64[b]), 3.49[b])	3.66[b]), 3.46[b])
Glc(1 → 3):	H–C(1″)	4.56 (*d*, *J* = 7.7)	4.33 (*d*, *J* = 8.2)	4.36 (*d*, *J* = 8.1)
	H–C(2″)	3.15 (*dd*, *J* = 9.3, 7.7)	3.24 (*dd*, *J* = 8.9, 8.2)	3.24 (*dd*, *J* = 8.7, 8.1)
	H–C(3″)	3.34 (*t*, *J* = 9.3)	3.37 (*t*, *J* = 8.9)	3.37 (*t*, *J* = 8.9)
	H–C(4″)	3.22[b])	3.34[b])	3.34[b])
	H–C(5″)	3.23[b])	3.50–3.55 (*m*)	3.50–3.55 (*m*)
	CH_2(6″)	3.85 (*dd*, *J* = 12.0, 2.1), 3.66 (*dd*, *J* = 12.0, 5.5)	4.55 (*dd*, *J* = 11.8, 1.9), 4.35 (*dd*, *J* = 11.8, 6.0)	4.54 (*dd*, *J* = 12.0, 1.8), 4.31 (*dd*, *J* = 12.0, 6.2)
Glc(1 → 6):	H–C(1‴)	4.34 (*d*, *J* = 7.8)		
	H–C(2‴)	3.21[b])		
	H–C(3‴)	3.34 (*t*, *J* = 9.3)		
	H–C(4‴)	3.28 (*t*, *J* = 9.5)		
	H–C(5‴)	3.20[b])		
	CH_2(6‴)	3.72[b]), 3.49[b])		
Feruloyl or caffeoyl[c]):	H–C(2⁗) or –C(2‴)[d])	7.25 (*d*, *J* = 1.9)	7.02 (*d*, *J* = 2.0)	7.06 (*d*, *J* = 2.0)
	H–C(5⁗) or –C(5‴)[d])	6.84 (*d*, *J* = 8.2)	6.76 (*d*, *J* = 8.1)	6.79 (*d*, *J* = 8.1)
	H–C(6⁗) or –C(6‴)[d])	7.13 (*dd*, *J* = 8.2, 1.9)	6.91 (*dd*, *J* = 8.1, 2.0)	6.94 (*dd*, *J* = 8.1, 2.0)
	H–C(α′)	6.45 (*d*, *J* = 15.9)	6.27 (*d*, *J* = 15.8)	6.30 (*d*, *J* = 15.9)
	H–C(β′)	7.67 (*d*, *J* = 15.9)	7.55 (*d*, *J* = 15.8)	7.58 (*d*, *J* = 15.9)
	MeO–C(3⁗)	3.93 (*s*)		
Sinapoyl or *p*-coumaroyl[c]):	H–C(2⁗)		6.92 (*s*)	7.47 (*d*, *J* = 8.5)
	H–C(3⁗)		–	6.83 (*d*, *J* = 8.5)
	H–C(5⁗)		–	6.83 (*d*, *J* = 8.5)
	H–C(6⁗)		6.92 (*s*)	7.47 (*d*, *J* = 8.5)
	H–C(α″)		6.43 (*d*, *J* = 15.9)	6.36 (*d*, *J* = 15.9)
	H–C(β″)		7.64 (*d*, *J* = 15.9)	7.65 (*d*, *J* = 15.9)
	MeO–C(3⁗,5⁗)		3.88 (*s*)	

[a]) Recorded at 600 MHz. [b]) Overlapped with other signals. [c]) Ferulic acid = 3-(4-hydroxy-3-methoxyphenyl)-prop-2-enoic acid; caffeic acid = 3-(3,4-dihydroxyphenyl)prop-2-enoic acid; sinapic acid = 3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoic acid; *p*-coumaric acid = 3-(4-hydroxyphenyl)prop-2-enoic acid. [d]) For compounds **2** and **3**.

Compound **2** was obtained as a yellow amorphous powder. Its molecular formula was determined to be $C_{40}H_{46}O_{20}$ by the $[M+H]^+$ ion peak at m/z 847.2655 in the HR-MALDI-MS. The NMR data (*Tables 1* and *2*) clearly established that **2** is a phenylethyl

Table 2. *^{13}C-NMR Data* (CD_3OD) *of* **1**–**3**[2]). δ in ppm.

		1[a])	**2**[a])	**3**[a])
Aglycone:	C(1)	131.3 (*s*)	131.2 (*s*)	131.2 (*s*)
	C(2)	116.9 (*d*)	116.8 (*d*)	116.9 (*d*)
	C(3)	146.0 (*s*)	145.9 (*s*)	145.9 (*s*)
	C(4)	144.5 (*s*)	144.5 (*s*)	144.4 (*s*)
	C(5)	116.3 (*d*)	115.9 (*d*)	116.0 (*d*)
	C(6)	121.1 (*d*)	121.0 (*d*)	121.0 (*d*)
	C(α)	72.1 (*t*)	72.1 (*t*)	72.2 (*t*)
	C(β)	36.4 (*t*)	36.3 (*t*)	36.4 (*t*)
Glc:	C(1′)	103.7 (*d*)	103.8 (*d*)	103.7 (*d*)
	C(2′)	74.8 (*d*)	74.9 (*d*)	75.0 (*d*)
	C(3′)	83.7 (*d*)	84.4 (*d*)	84.3 (*d*)
	C(4′)	70.5 (*d*)	71.0 (*d*)	71.0 (*d*)
	C(5′)	74.3 (*d*)	74.8 (*d*)	74.5 (*d*)
	C(6′)	69.1 (*t*)	62.0 (*t*)	62.1 (*t*)
Glc(1 → 3):	C(1″)	105.4 (*d*)	105.1 (*d*)	104.7 (*d*)
	C(2″)	75.5 (*d*)	75.0 (*d*)	74.8 (*d*)
	C(3″)	77.4 (*d*)	77.3 (*d*)	77.4 (*d*)
	C(4″)	71.0 (*d*)	71.4 (*d*)	71.3 (*d*)
	C(5″)	77.7 (*d*)	75.1 (*d*)	75.1 (*d*)
	C(6″)	62.3 (*t*)	64.2 (*t*)	64.3 (*t*)
Glc(1 → 6):	C(1‴)	104.3 (*d*)		
	C(2‴)	74.9 (*d*)		
	C(3‴)	77.5 (*d*)		
	C(4‴)	71.1 (*d*)		
	C(5‴)	77.7 (*d*)		
	C(6‴)	62.2 (*t*)		
Feruloyl or caffeoyl[b]):	C(1⁗) or C(1‴)[c])	127.6 (*s*)	127.4 (*s*)	127.5 (*s*)
	C(2⁗) or C(2‴)[c])	111.6 (*d*)	115.1 (*d*)	115.0 (*d*)
	C(3⁗) or C(3‴)[c])	150.5 (*s*)	146.7 (*s*)	146.6 (*s*)
	C(4⁗) or C(4‴)[c])	149.3 (*s*)	149.5 (*s*)	149.5 (*s*)
	C(5⁗) or C(5‴)[c])	116.5 (*d*)	116.1 (*d*)	116.2 (*d*)
	C(6⁗) or C(6‴)[c])	124.0 (*d*)	122.7 (*d*)	123.0 (*d*)
	C(α′)	115.3 (*d*)	114.7 (*d*)	114.7 (*d*)
	C(β′)	147.2 (*d*)	147.2 (*d*)	147.3 (*d*)
	C=O	168.5 (*s*)	168.2 (*s*)	168.4 (*s*)
	*Me*O–C(3⁗)	56.2 (*q*)		
Sinapoyl or *p*-coumaroyl[b]):	C(1⁗)		126.3 (*s*)	126.7 (*s*)
	C(2⁗)		106.7 (*d*)	131.2 (*d*)
	C(3⁗)		149.1 (*s*)	116.4 (*d*)
	C(4⁗)		139.3 (*s*)	161.1 (*s*)
	C(5⁗)		149.1 (*s*)	116.4 (*d*)
	C(6⁗)		106.7 (*d*)	131.2 (*d*)
	C(α″)		115.2 (*d*)	114.7 (*d*)
	C(β″)		147.2 (*d*)	146.9 (*d*)
	C=O		168.8 (*s*)	169.0 (*s*)
	*Me*O–C(3⁗,5⁗)		56.3 (*q*)	

[a]) Recorded at 150 MHz. [b]) See *Table 1* for ferulic, caffeic, sinapic, and *p*-coumaric acid. [c]) For compounds **2** and **3**.

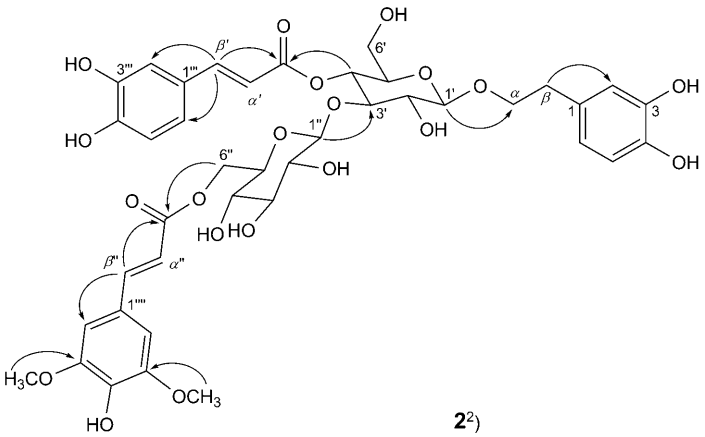
diglucoside esterified with a caffeic acid (= 3-(3,4-dihydroxyphenyl)prop-2-enoic acid) and a sinapic acid (= 3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoic acid). Based on further spectroscopic data, the structure of **2** was elucidated as 2-(3,4-dihydroxyphenyl)ethyl *O*-6-*O*-(*E*)-sinapoyl-*β*-D-glucopyranosyl-(1 → 3)-4-*O*-(*E*)-caffeoyl-*β*-D-glucopyranoside[1]), and named digilanatoside A[2]).

The ^{1}H-NMR spectrum of **2** exhibited the resonances for a *trans*-caffeoyl (three aromatic H-atoms as an *ABX* system at δ 7.02 (*d*, $J = 2.0$ Hz), 6.91 (*dd*, $J = 8.1$ and 2.0 Hz), and 6.76 (*d*, $J = 8.1$ Hz), two *trans*-olefinic H-atoms as an *AB* system at δ 7.55 and 6.27 (*d*, $J = 15.8$ Hz)), and a 2-(3,4-dihydroxyphenyl)ethoxy (three aromatic H-atoms as an *ABX* system at δ 6.70 (*d*, $J = 1.8$ Hz), 6.67 (*d*, $J = 8.0$ Hz), and 6.55 (*dd*, $J =$ 8.0 and 1.8 Hz) as well as a benzylic CH_2 group at δ 2.78 (*t*, $J = 7.5$ Hz) and two nonequivalent H-atoms of a CH_2-O group at δ 4.01–3.70 (*m*)). The NMR spectra indicated the presence of two anomeric H- and C-atoms (δ 4.41 (*d*, $J = 7.9$ Hz) and δ 103.8; δ 4.33 (*d*, $J = 8.2$ Hz) and δ 105.1) which were identified as arising from two *β*-linked glucopyranosyl units. The NMR data of **2** were found to be similar to those of purpureaside A (= 2-(3,4-dihydroxyphenyl)ethyl 3-*O*-*β*-D-glucopyranosyl-*β*-D-glucopyranoside 4-[(2*E*)-3-(3,4-dihydroxyphenyl)prop-2-enoate) [10], except for the additional *trans*-sinapoyl signals in **2** (two equivalent aromatic H-atoms at δ 6.92 (*s*), two *trans*-olefinic H-atoms as an *AB* system at δ 7.64 and 6.43 (*d*, $J = 15.9$ Hz), and two MeO groups at δ 3.88 (*s*)). The downfield shifts for the CH_2(6″) (δ 4.55 and 4.35) and C(6″) signals (δ 64.2) and the upfield shift for the C(5″) signal (δ 75.1) established that the esterification site for the *trans*-sinapoyl unit was at OH–C(6″) of the second glucose unit which was further confirmed by the three-bond correlation of CH_2(6″) to the C=O group at δ 168.8 of the sinapoyl unit in the HMBC spectrum (*Fig.*). Consequently, compound **2** was found to be a 6″-*O*-sinapoyl derivative of purpureaside A.

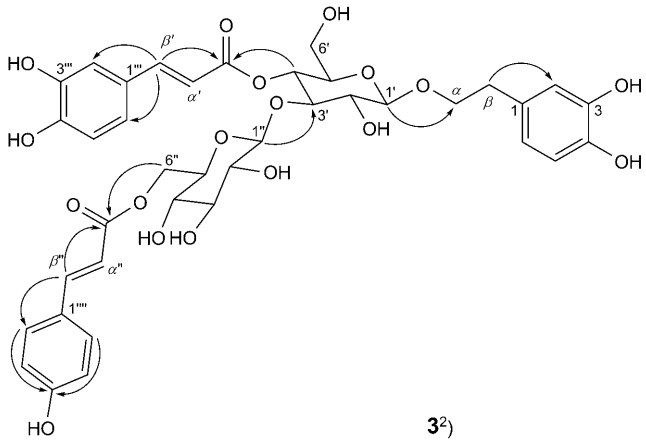
Compound **3** was obtained as a yellow amorphous powder. The molecular formula, $C_{38}H_{42}O_{18}$, was deduced by HR-MALDI-MS (*m*/*z* 787.2441 ($[M+H]^+$)). The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), COSY, HSQC, and HMBC (*Fig.*) experiments established the structure of **3** as 2-(3,4-dihydroxyphenyl)ethyl *O*-6-*O*-(*E*)-*p*-coumaroyl-*β*-D-glucopyranosyl-(1 → 3)-4-*O*-(*E*)-caffeoyl-*β*-D-glucopyranoside[1]), which was given the trivial name digilanatoside B[2]).

The ^{1}H- and ^{13}C-NMR spectrum of **3** revealed the presence of signals indicative of a *trans*-caffeoyl moiety, a 2-(3,4-dihydroxyphenyl)ethoxy group, and two anomeric CH groups, as in compound **2**. A close structural similarity of **2** and **3** was evident from a comparison of the ^{1}H- and ^{13}C-NMR signals assigned by 1D-TOCSY and 2D-NMR techniques (COSY, HSQC, and HMBC), except for the presence of a *trans*-*p*-coumaroyl unit in **3** instead of the *trans*-sinapoyl moiety in **2**. The esterification site for the *trans*-*p*-coumaroyl unit was also the same (OH–C(6″)) which was further confirmed by cross-peaks between CH_2(6″) (δ 4.54, 4.31) of the second glucose unit and the C=O group (δ 169.0) of the *trans*-*p*-coumaroyl moiety in the HMBC spectrum (*Fig.*). Thus, compound **3** was found to be a 6″-*O*-*p*-coumaroyl derivative of purpureaside A.

Several phenylethyl glycosides have been reported from the genus *Digitalis* up to now [9–13][18]. Digilanatosides A and B are the first two examples of phenylethyl glycosides obtained from the genus *Digitalis* bearing two aromatic acyl units.



2[2])



3[2])

Figure. *Significant HMBCs* (H → C) *for* **2** *and* **3**

Phenylethyl glycosides esterified with two aromatic acids are rare compounds, and similar compounds have also been obtained from few genera including *Globularia* [17][19], and *Veronica* [20]. On the other hand, cornoside which is accepted as the precursor of phenylethyl glycosides was also isolated (cornoside = 4-[2-(β-D-glucopyranosyloxy)ethyl]-4-hydroxycyclohexa-2,5-dien-1-one). Cornoside was reported to have a limited distribution and was mainly found within Lamiales [21]. Phenylethyl glycosides are suggested to be valuable taxonomic markers in Dicotyledonous plants. These types of compounds are also utilized to support the phylogenetic relationships found by the DNA sequence analysis. Thus, the genera *Digitalis*, *Globularia*, and *Veronica*, which were recently moved to the expanded Plantaginaceae [22], have a similar phenylethyl glycoside profile, particularly phenylethyl glycosides with two aromatic acyl moieties. Regarding the carbohydrate composition, which is also considered to be a taxonomic marker, sucrose (= β-D-fructofuranosyl α-D-glucopyranoside) is also reported for the first time from the genus *Digitalis*.

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Experimental Part

General. TLC: Precoated silica gel *60 F_{254}* (SiO_2; *Merck*) aluminium plates; eluents $CHCl_3$/MeOH/H_2O 80:20:1, 70:30:3, and 61:32:7, and AcOEt/MeOH/H_2O 20:2:1; visualization by spraying with 1% vanillin/H_2SO_4 soln. followed by heating at 105° for 2–3 min. Column chromatography (CC): SiO_2 *60* (0.063–0.200 mm; *Merck*, Darmstadt), polyamide (*Fluka*). Medium-pressure liquid chromatography (MPLC): *CombiFlash® Companion®* (*Teledyne Isco*), *RediSep®* columns (*LiChroprep C_{18}*, 130 and 43 g; *Teledyne Isco*). Optical rotations: *Jasco-DIP-1000* polarimeter. UV Spectra: *HP-Agilent-8453* spectrophotometer; λ_{max} in nm. IR Spectra (KBr): *Perkin-Elmer-2000* FT-IR spectrometer; in cm^{-1}. NMR Spectra: *Bruker-AMX-600* instruments (600 (^{1}H) and 150 MHz (^{13}C)) with XWIN NMR 3.6 software package; δ in ppm, J in Hz. HR-MALDI-MS: *Voyager DE* in MeOH; position mode; in m/z (rel. %).

Plant Material. Digitalis lanata EHRH. was collected from Vize, Kırklareli, Turkey, in June 2007. A voucher specimen (Akaydın 11530) has been deposited with the Herbarium of the Faculty of Education, Hacettepe University, Ankara, Turkey.

Extraction and Isolation. The air-dried and powdered aerial parts of *D. lanata* (180 g) were extracted with MeOH (2 × 800 ml) at 45° for 4 h. The combined MeOH extracts were concentrated to yield a residue (48.1 g, 26%). The extract was suspended in H_2O (75 ml) and then partitioned successively with equal volumes of hexane (3 × 75 ml) and $CHCl_3$ (3 × 75 ml). The aq. layer provided 35.2 g of an extract upon lyophilization. An aliquot of the H_2O extract (30 g) was subjected to CC (polyamide (120 g), H_2O (400 ml), then 10 → 100% MeOH/H_2O in steps of 10% of MeOH (each 250 ml)): *Frs. A–M*. *Fr. C* (4.5 g) was subjected to CC (SiO_2 (140 g), $CHCl_3$/MeOH/H_2O 95:5:1, 90:10:1, 85:15:1, 80:20:2, and 70:30:3, each 250 ml): *Frs. C1–C4*. *Fr. C3* (97 mg) was purified by CC (SiO_2 (14 g), $CHCl_3$/MeOH/H_2O 85:15:1 and 80:20:1, both 200 ml): cornoside (10 mg). *Fr. D* (939 mg) was subjected to MPLC (*LiChroprep C_{18}* (130 g), 0 → 90% MeOH/H_2O): sucrose (30 mg), and *Frs. D2–D4*. *Fr. D2* (180 mg) was applied to MPLC (*LiChroprep C_{18}* (43 g), 5 → 30% MeOH/H_2O): maxoside (59 mg). The 1-*O*-(*E*)-feruloyl-*β*-D-glucopyranose[1]) (3 mg) and *3‴′*-O-*methylmaxoside* (**1**; 7 mg) were obtained from *Fr. D3* (24 mg) by CC (SiO_2 (5 g), $CHCl_3$/MeOH/H_2O 90:10:1, 85:15:1, 80:20:2, and 70:30:3 each 50 ml). *Fr. D4* (90 mg) was further submitted to CC (SiO_2 (14 g), $CHCl_3$/MeOH/H_2O 90:10:1, 80:20:2, 70:30:3, and 61:32:7, each 100 ml): lanatoside C (4 mg) and purpureagitoside (15 mg). *Fr. I* (120 mg) was separated by MPLC (*LiChroprep C_{18}* (43 g), 15 → 90% MeOH/H_2O): purpureaside A (15 mg), and *digilanatoside A* (**2**; 9 mg). *Fr. K* (145 mg) was similarly purified by (*LiChroprep C_{18}* (43 g), 10 → 60% MeOH/H_2O): *digilanatoside B* (**3**; 9 mg).

3‴′-O-*Methylmaxoside* (=*2-(3,4-Dihydroxyphenyl)ethyl* O-*β*-D-*Glucopyranosyl-(1 → 3)*-O-*[β*-D-*glucopyranosyl-(1 → 6)]-β*-D-*glucopyranoside 4-[(2*E*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate]*[1]); **1**): Yellow amorphous powder. $[\alpha]_D^{24} = -5.6$ ($c = 0.58$, MeOH). UV (MeOH): 289 (4.23), 320 (4.32). IR (KBr): 3400, 2919, 1695, 1631, 1602, 1515, 1262, 1157, 1065. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-MALDI-MS: 817.2762 ($[M+H]^+$, $C_{36}H_{49}O_{21}^+$; calc. 817.2766).

Digilanatoside A (=*2-(3,4-Dihydroxyphenyl)ethyl 3*-O-*β*-D-*Glucopyranosyl-6*-O-*[(2*E*)-3-(4-hydroxy-3,5-dimethoxyphenyl)-1-oxoprop-2-en-1-yl]-β*-D-*glucopyranoside 4-[(2E)-3-(3,4-Dihydroxyphenyl)prop-2-enoate]*[1]); **2**): Yellow amorphous powder. $[\alpha]_D^{24} = -27.2$ ($c = 0.42$, MeOH). UV (MeOH): 245 (sh, 3.93), 288 (3.96), 313 (4.05). IR (KBr): 3400, 2922, 1696, 1631, 1604, 1516, 1449, 1374, 1283, 1159, 1071. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-MALDI-MS: 847.2655 ($[M+H]^+$, $C_{40}H_{47}O_{20}^+$; calc. 847.2661).

Digilanatoside B (=*2-(3,4-Dihydroxyphenyl)ethyl 3*-O-*β*-D-*Glucopyranosyl-6*-O-*[(2*E*)-3-(4-hydroxyphenyl)-1-oxoprop-2-en-1-yl]-β*-D-*glucopyranoside 4-[(2*E*)-3-(3,4-Dihydroxyphenyl)prop-2-enoate]*[1]); **3**): Yellow amorphous powder. $[\alpha]_D^{24} = -35.4$ ($c = 0.42$, MeOH). UV (MeOH): 245 (sh, 4.39), 291 (4.47), 313 (4.56). IR (KBr): 3400, 2920, 1695, 1629, 1604, 1516, 1446, 1273, 1169, 1073. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-MALDI-MS: 787.2441 ($[M+H]^+$, $C_{38}H_{43}O_{18}^+$; calc. 787.2449).

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