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PHENOLIC GLYCOSIDES FROM *ADONIS ALEPPICA*

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Key Word Index—*Adonis aleppica*; Ranunculaceae; flavonoid glycosides; phenolic glycosides; phenylpropanoids; NMR; structure elucidation.

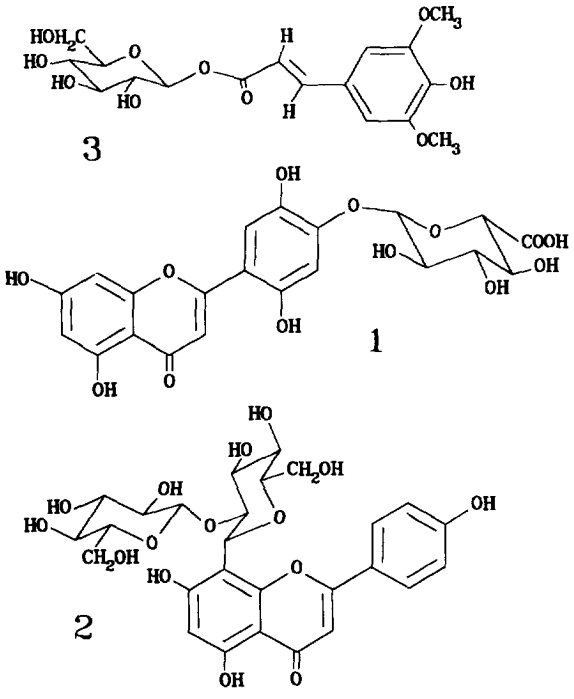
Abstract—Isoetin-4′-*O*-β-glucuronide, a new derivative of the rare 2′,4′,5′-trihydroxyflavone isoetin, has been isolated from *Adonis aleppica*, along with the known vitexin-2″-*O*-β-rhamnoside. These structures were established by means of DCI-NH_3-mass spectral and NMR methods including full establishment of the CH-spin systems for both compounds. Furthermore, structural evidence is given for the presence of sinapoylglucose representing the first phenylpropanoid glycoside isolated from a member of the genus *Adonis*.

INTRODUCTION

The botanical classification of annual *Adonis* species (= sectio *Adonis*) is still full of contradictions. Recently, the form of the fruits has been pointed out as the main distinctive mark, although there are certain difficulties in its determination depending on the degree of ripeness [1]. From the phytochemical point of view, plants of the genus *Adonis* are well known for the occurrence of cardiac glycosides [2–4]. Only a few cardenolide studies have dealt with the isolation of phenolic constituents [5–7]. We have now developed an effective isolation procedure on the basis of vacuum liquid (VLC), column (CC), droplet counter current (DCCC) and middle pressure liquid chromatography (MPLC) allowing the isolation of both flavonoids, as well as cardenolide glycosides from the same extract [3]. This method has been successfully applied to *Adonis aleppica* Boiss., an annual endemic herb of the Mesopotamian region [1]. In previous communications, *A. aleppica* was shown to produce a large number of cardenolides, especially long-chained oligoglycosides (= alepposides) [2] and sulphates [8], as well as the aliphatic alcohol glucoside aleppotrioloside [9].

RESULTS AND DISCUSSION

From the polar fractions of the total plant extract of *A. aleppica* the two major flavonoid glycosides **1** and **2**, as well as the phenylpropanoid glycoside **3** were isolated. Their structures have been elucidated by means of UV, DCI-NH_3-mass spectra (DCI-MS), 1D and 2D ^{1}H NMR, ^{1}H BB and gated-decoupling ^{13}C NMR, as well as ^{13}C–^{1}H HETCOR experiments and were determined as isoetin 4′-*O*-β-glucuronide (**1**), vitexin 2″-*O*-β-rhamnoside (**2**) and 1′-sinapoylglucose (**3**).



The molecular formula of **1** was deduced as $C_{21}H_{18}O_{13}$ from ^{13}C NMR and neg. DCI-MS (*m/z* 302 $[M(agl)]^-$, 478 $[M]^-$) proposing the presence of a hexuronic acid moiety ($\rightarrow -176$ amu) linked to a flavone skeleton. A special feature of **1** is the 2′ (*para*)-hydroxylation of the B-ring causing a marked irradiation of H-3 and resulting in the pure singlet absorptions for

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Table 1. One and 2D ^1H and ^{13}C NMR data of isoetine-4′-*O*-glucuronide (**1**) [200/50 MHz, DMSO-d_6, δ in ppm, J in Hz]

Pos.	δ_H (Mult., J)	Corr	δ_C (APT)	$^1J_{C,H}$	$^nJ_{C,H}$ ($n \geq 2$)
2	—		161.6 (C)	—	$^2J_{C2,H3'} = 5.3$, $^3J_{C2,H6'} = 1.6$
3	7.05 (*s*)	↔	104.9 (CH)	160.3	$\Delta\nu = 4$
4	—		182.1 (C)	—	$^2J_{C4,H3} < 1$
5	13.00 (*s*)		161.4 (C)	—	$^2J_{C5,H6} = 3.5$
6	6.17 (*d*, 2.2)	↔	98.9 (CH)	162.1	$^2J_{C6,H8} = 3.8$
7	—		164.4 (C)	—	$^2J_{C7,H6} = {}^2J_{C7,H8} = 3.1$
8	6.43 (*d*, 1.8)	↔	94.0 (CH)	165.4	$^3J_{C8,H6} = 4.4$
9	—		157.6 (C)	—	$^2J_{C9,H8} = 4.2$
10	—		103.9 (C)	—	$^3J_{C10,H8} = 5.3$ $^3J_{C10,H6} = 4.4$, $^3J_{C10,H3} = 4.4$
1′	—		110.7 (C)	—	$^3J_{C12,H3'} = 6.2$ $^3J_{C12,H3} \approx {}^2J_{C1',H6'} \approx 0$
2′	—		151.2 (C)	—	$^3J_{C2',H6'} = 9.6$, $^2J_{C2,H3'} = 3.8$
3′	6.77 (*s*)	↔	108.2 (CH)	171.4	$\Delta\nu = 5$
4′	—		148.9 (C)	—	$^3J_{C4',H6'} = 8.9$ $^3J_{C4',H1'} = 3.6$, $^2J_{C4',H3'} = 3.6$
5′	—		139.9 (C)	—	$^3J_{C5',H3'} = 7.3$, $^2J_{C5',H6'} = 4.4$
6′	7.33 (*s*)	↔	114.2 (CH)	160.2	$\Delta\nu = 5$
1″	4.90 (*br d*, 7.0)	↔	101.3 (CH)	163.8	$\Delta\nu = 10$
2″	3.41 (*dd*, 6/5)	↔	73.2 (CH)	145.0	$^3J_{C2'',H4''} = 3.4$
3″	3.37_3 (*t*, 5)	↔	75.5 (CH)	172.8	$\Delta\nu = 14$
4″	3.36_5 (*t*, 6)	↔	71.8 (CH)	144.7	$\Delta\nu = 9$
5″	3.83 (*d*, 8.5)	↔	75.9 (CH)	145.9	$\Delta\nu = 8$
6″	—		170.6 (C)	—	$^3J_{C6'',H4''} = 3.2$, $^2J_{C6'',H5''} = 1$

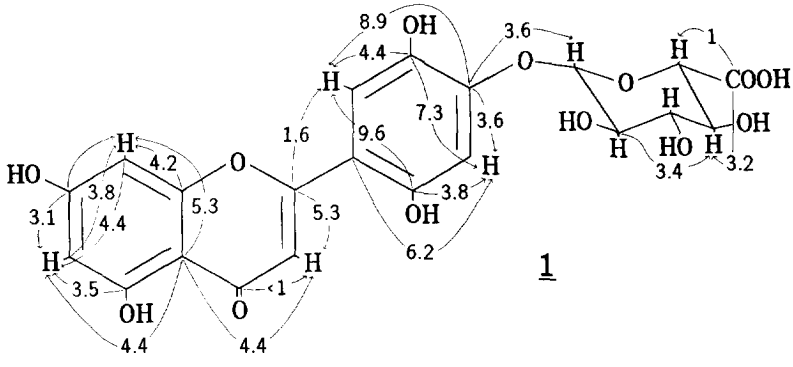

Fig. 1. Heteronuclear long-range coupling constants and pathways of isoetin-4′-*O*-glucuronide (**1**) derived from 2D LR-CH and 1D gated-decoupling experiments (values given in Hz).

the B-ring protons H-3′ and H-6′ (Table 1). NMR measurements included the determination of ^1J and long-range ^{13}C–^1H-correlations (Table 1, Fig. 1) and confirmed all assignments. In case of the H-3/H-3′ [10] they should be revised as far as C-3/C-3′ can be clearly distinguished from their long-range coupling behaviour. In this context, another remarkable detail is the large size of the geminal coupling constant ^2J (C-2, H-3) typically occurring in unsaturated γ-pyrones [11]. 4′-*O*-Linkage of the glucuronic acid moiety is apparent from the heteronuclear splitting of the C-4′ signal of the gated-decoupling ^{13}C NMR (Table 1), from the ^1H glycosylation effect affecting H-3′ (+ 0.20 ppm) and from UV shift measurements. Addition of NaOMe gives rise to a very large bathochromic shift (113 nm) due to a free 2′-OH group; there is also degradation of the spectrum because of the hydroquinone partial structure. In the NaOAc and $AlCl_3$ spectra bathochromic effects of free 3′,4′ (*ortho*)-dihydroxy groups are lacking. Finally, the relatively low maximum absorbance of band I in methanol correlated with a non-planar conformation of the A/C and B-rings. This finding is consistent with the result of torsion-forcing calculations of **1** as shown in the molecule plot in Fig. 2.

Flavonoid **2** according to DCI-MS and ^{13}C NMR data is a flavone *C*-diglycoside bearing two hexoses. In analogy to **1**, interpretation of comprehensive NMR experiments (^1H, ^1H–^1H COSY, ^1H BB and GD ^{13}C, ^{13}C–^1H HETCOR) led to the structure of vitexin 2″-*O*-β-

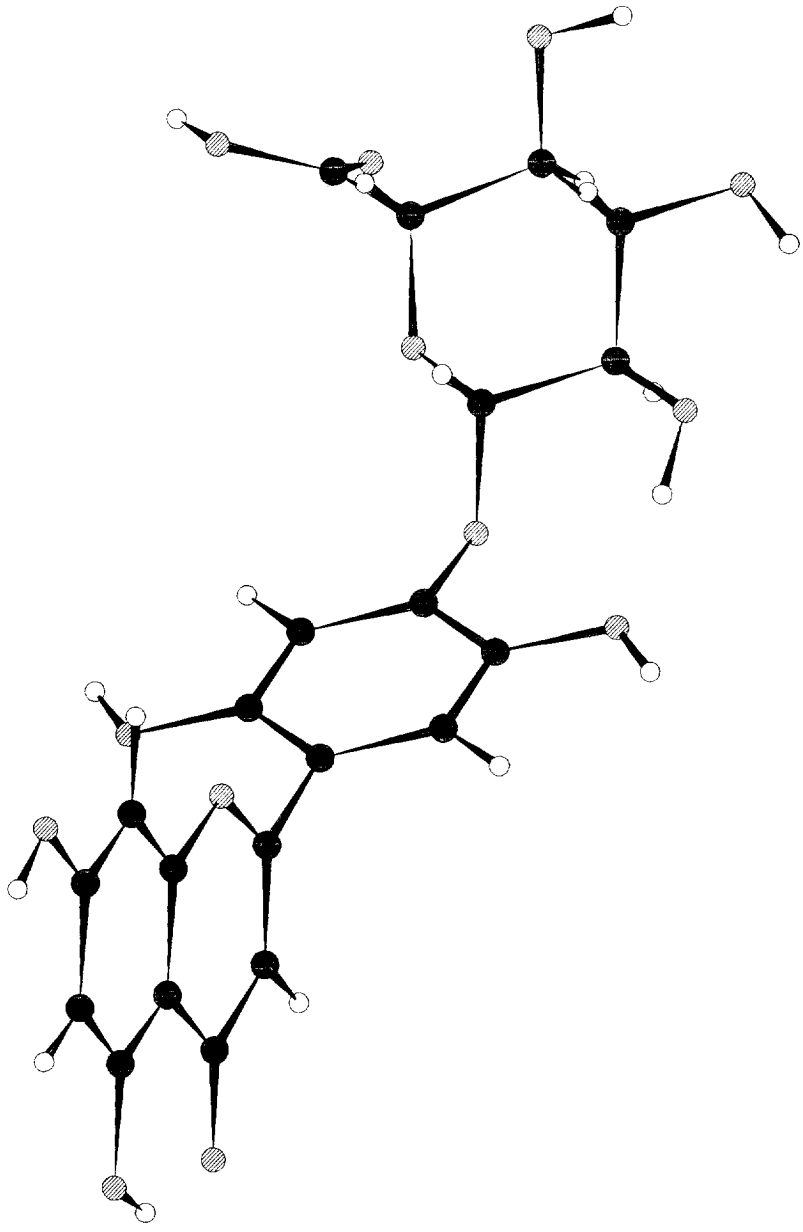

Fig. 2. Molecular conformation of isoetin-4′-*O*-glucuronide (**1**) resulting from torsion-forcing calculations with DISCOVER.

glucoside (Table 2). Signals of the two β-glucose moieties were completely assigned from ^1H–^1H COSY and ^{13}C–^1H HETCOR maps, the latter proving the *C*-glycosidic junction by shift value (71.6 ppm) and $^1J_{CH}$ value of C-1″ (142.6 Hz). Absolute evidence for C–C linkage in position 8 is obtained from the vicinal coupling C-9↔H-1″ (5.9 Hz) representing the only heteronuclear correlation for C-9. A significant downfield shift of the H-2″ signal in addition to ^{13}C glycosidation effects for C-2″/3″ (α/β) indicate a 1‴→2″ sugar linkage. As far as all assignments have been verified by a ^{13}C–^1H HETCOR experiment, revision of the ^{13}C NMR data in ref. [12] concerning C-2″/C-5″ of vitexin-2″-*O*-rhamnoside seems appropriate.

The symmetrical 4′-monohydroxy substitution of ring B gives rise to a symmetrical CH coupling behaviour: C-4′ itself produces a triplet of triplets due to equal ^2J and ^3J couplings, and the ^1J couplings of all CH carbons are identical (161 Hz). Following the vicinal coupling of 4 Hz between C-2 and H-2′/6′, the dihedral angle between ring B and A/C is different to **1** indicating a more planar conformation (φ *ca* 45°). Distinction of C-2 and C-7 signals was achieved by their different coupling pattern with only small ^2Js for C-7. Finally, it can be stated that

Table 2. One and 2D ^1H and ^{13}C NMR data of vitexin-2″-*O*-glucoside (**2**) [200/50 MHz, DMSO-d_6, δ in ppm, J in Hz]

Pos.	δ_H (Muly., J)	Corr	δ_C (APT)	$^1J_{C,H}$	$^nJ_{C,H}$ ($n \geq 2$)
2	—		163.7 (C)	—	$^2J_{C2,H3} = 5.5$ $^3J_{C2,H2'} = {}^3J_{C2,H6'} = 4.1$
3	7.05 (*s*)	↔	104.9 (CH)	167.4	$\Delta\nu = 6$
4	—		181.9 (C)	—	$^2J_{C4,H3} < 1$
5	13.15 (*s*)		160.6 (C)	—	$^2J_{C5,H6} = {}^2J_{C2,H5} = 3.6$
6	6.17 (*s*)	↔	98.4 (CH)	160.3	$^3J_{C6,H5} = 5.3$
7	—		163.5 (C)	—	$^2J_{C7,H6} \approx {}^3J_{C7,H1''} \approx 2$
8			103.7 (C)	—	*
9	—		156.3 (C)	—	$^2J_{C9,H1''} = 5.9$
10	—		103.6 (C)	—	*
1′	—		121.7 (C)	—	$^3J_{C1',H3'} = {}^3J_{C1',H5'} = 7.7$ $^2J_{C1',H2} < {}^2J_{C1',H6'} = 2.1$ $^2J_{C1,H3} \approx 0$
2′	8.00 (*dd*, 9/1)	↔	128.9 (CH)	161.3	$^3J_{C2',H6'} = 6.7$, $^2J_{C2',H3'} < 1$
3′	6.90 (*dd*, 9/1))	↔	115.9 (CH)	161.2	$^3J_{C3',H5'} = 4.4$ $^3J_{C3',H4'} < 1$, $^2J_{C3',H2'} < 1$
4′	—		161.2 (C)	—	$^2J_{C4',H3'} = {}^2J_{C4,H5'} = 2.0$ $^3J_{C4',H2'} = {}^3J_{C4',H6'} = 9.2$
5′	6.90 (*dd*, 9/1)	↔	115.9 (C)	161.2	$^3J_{C5',H3'} = 4.4$ $^3J_{C5',H4'} < 1$, $^2J_{C5,H2'} < 1$
6′	8.00 (*dd*, 9/1)	↔	128.9 (CH)	161.3	$^3J_{C6,H2'} = 6.7$, $^2J_{C6,H5'} < 1$
1″	4.84 (*d*, 9.9)	↔	71.6 (CH)	142.6	$\Delta\nu = 14$
2″	4.90 (*t*, 9.3)	↔	81.3 (CH)	144.5	$\Delta\nu = 14$
3″	3.50 (*t*, 8.3)	↔	78.4 (CH)	141.3	$\Delta\nu = 12$
4″	3.46 (*t*, 8.9)	↔	70.2 (CH)	144.0	$\Delta\nu = 12$
5″	3.48 (*m*)	↔	81.7 (CH)	141.0	$\Delta\nu = 10$
$6''_A$	3.78 (*br d*, 11)	↔	61.0 (C)	140.5	$\Delta\nu = 9$
$6''_B$	3.56 (*dd*, 5/13)				
1‴	3.94 (*dd*, 7 5)	↔	105.2 (CH)	156.8	$\Delta\nu = 14$
2‴	2.79 (*dd*, 7/8)	↔	74.4 (CH)	142.0	$\Delta\nu = 7$
3‴	≈ 2.9	↔	76.3 (CH)	140.2	$\Delta\nu = 17$
4‴	2.96	↔	69.5 (CH)	143.7	$\Delta\nu = 11$
5‴	2.84	↔	76.0 (CH)	136.9	$\Delta\nu = 8$
$6''_A$	3.13 (*br d*, 13)	↔	60.4 (C)	141.3	$\Delta\nu = 7$
$6''_B$	2.97				

*Not determined because of signal overlap.

wherever partial structures of **1** and **2** are comparable, analogous ^{13}C signal multiplicities were registered (e.g. signals of C-2, C-5, C-6 and C-1′/H-3 coupling).

Compound **3**, according to UV spectral properties (see Experimental), was found to be a phenolic compound. The positive mode DCI-MS showed the signal of a quasimolecular ion at m/z 404 (in accord with $C_{17}H_{22}O_{10}$) and a sequential ion at m/z 242 indicating the loss of one hexose unit. The glycosidic nature of **3** was also gleaned from the ^1H NMR (Table 3). The doublet at δ5.57 (J = 7.0 Hz) due to an anomeric proton and the AB-type signals assignable to two hydroxymethylene protons suggested the presence of β-glucose (glc). Within the olefinic/aromatic region two signals of *trans* olefinic protons (δ6.53 and 7.72, J = 15.9 Hz) and a singlet absorption of two aromatic protons (δ7.01) were assigned. Taking into account the singlet absorption integrating for six protons at δ3.86, the aglycone moiety of **3** should consist of a cinnamic acid skeleton bearing a symmetrical 3,5-dimethoxy-4-hydroxy substitution. Further evidence for the identification of a sinapoyl and a glc moiety came from the ^{13}C NMR (Table 3) showing good agreement with published data.

As usually found in olefinic phenylpropanoids, both ^1H and ^{13}C NMR of **3** show a second set of weaker signals due to isomerization of the α/β double bond ($\Delta_{\alpha/\beta}$). Thus, the acylglycosidic linkage in **3** cannot only be proved by the shift values of C-1′ (δ95.6 in **3**, *ca* 104.3 ppm in acetalglycosides) and C-2′ (δ74.0 in **3**, otherwise *ca* 75.6 ppm). It is also evident from the occurrence of a second signal due to the anomeric proton of the *cis* olefinic glycoside indicating the close neighborhood of the anomeric proton and $\Delta_{\alpha/\beta}$. Finally, the structure of 1′-*O*-[*E*/*Z*]-sinapoyl-β-glucose for **3** is in full concordance with the long-range CH couplings ($^{2/3}J$, Table 3) observed in a gated-decoupling ^{13}C NMR. Analysis of the '*ddd*' signal of the carbonyl carbon leads to ^3J (H-1′) = 3.0 Hz providing the ester linkage, while ^3J(H-β) = 6.7 Hz and ^2J (H-α) = 3.2 Hz are indicating Δ_{trans} configuration (14.6 and < 1 Hz in the *cis* isomer, respectively) [11]. Due to magnetic equivalence of H-2 and H-6 (symmetrical substitution pattern) the signal of C-4 ap-

Table 3. ^1H and ^{13}C NMR data of sinapoylglucose (**3**, *trans*-isomer) in comparison with the sinapic acid moiety (Sin) of methylleucosceptosid A and glucose (Glc) in the monoterpene esterglucoside digipenstrosid [25] (200/50 MHz, DMSO-d_6–CD_3OD (1:1), δ in ppm, J in Hz)

C	δ_H, Mult., J	δ_C	$J_{C,H}$	$^2J_{C,H}$	$^3J_{C,H}$	DEPT	Sin	Glc
1		125.9	—			C	126.5	
2	7.01, *s*	107.4	159			CH	107.0	
3		149.3	—	1.8, H-2		C	149.5	
4		139.8	—		7.1, H-2/6	C	139.9	
5		149.3	—	1.8, H-6		C	149.5	
6	7.01, *s*	107.4	159			CH	107.0	
α	6.53, *d*, 15.9	115.6	165			CH	115.5	
β	6.53, *d*, 15.9	148.1	155			CH	148.2	
C=O		166.9	—	3.2, H-α	3.0, H-1′ 6.7, H-β	C	168.2	
2*OMe	3.86, *s*	57.1	145			Me	56.8	
1′	5.57, *d*, 7.0	95.6	164			CH		96.0
2′		73.9	145			CH		74.0
3′		77.9	142			CH		78.1
4′		70.9	149			CH		71.1
5′		79.0	141			CH		78.8
$6'_A$	3.79, *br d*, 12	62.1	141			CH		62.3
$6'_B$	3.60, *dd*, 5							

pears as a triplet with $^3J = 7.1$ Hz, while the coinciding absorptions of C-3/5 are doublets of quartets overlapping each other and forming a quintet.

With the isolation of sinapoylglucose (**3**) a phenylpropane glycoside has been detected in a member of the genus *Adonis* for the fist time. The structure was ascertained by detailed NMR studies, lacking so far [13]. Mono- and diesters of sinapic acid and glucose have recently been reported from *Raphanus sativus* (Brassicaceae) [14–16], while related compounds (e.g. 1′-*O*-sinapoyl-6′-*O*-gallloyl-glucose) occur in *Cynanchum hancockianum* (Asclepiadaceae) [17].

Isoetin-4′-*O*-β-glucuronide (**1**) is a new natural product representing the first 4′-*O*-glycoside belonging to the series of 2′,4′,5′-trihydroxyflavones. This unusual flavonoid glycoside supports the exceptional position of *A. aleppica* within the genus *Adonis* as already inferred from the occurrence of novel types of cardenolides, e.g. alepposides and sulphates [2, 3, 8]. Isoetin has been found in the Lycopsida (*Isoetes delilei*) [10] and glycosides are known from some Asteraceae [18, 19], but this is the first report on its occurrence in a member of the Ranunculaceae. In contrast to this, *C*-glycosylflavones e.g. vitexin (v), orientin (o), homoorientin (h) and adonivernith (a) have previously been detected in *Adonis* plants, but only in perennial species belonging to the sectio *Consiligo*: *A. amurensis* (o/h/a [20]), *A. mongolica* (o [7]), *A. sibiricus* (o/a [21]), *A. tianschanicus* (o/a [22]), *A. turkestanica* (v/o/h [23]), *A. venalis* [5, 6] and *A. wolgensis* (v [24]).

EXPERIMENTAL

Plant material. Authentic plant material of *Adonis aleppica* Boiss. (total plants, 3.5 kg dry wt) was collected in April 1990 near Urfa (Turkey) and identified by the authors. Voucher specimens are deposited at the Heinrich-Heine Universität, Düsseldorf, Germany.

Instrumentation. NMR spectra were recorded at 300 K on a Bruker AC 200 spectrometer using 5 mm tubes and solns in DMSO-d_6 (99.5% D, **1** and **2**) or DMSO-d_6–CD_3OD (1:1, **3**). The solvent shifts were used as int. standards (DMSO-d_6: δ_H 2.49 ppm, δ_C 39.5 ppm). Standard ^1H (gated-decoupling), ^{13}C, APT (Attached Proton Test), DEPT, COSY and HETCOR experiments were measured using the Brucker standard software. DCl-mass spectra were run on a Finnigan INCOS 50 system with NH_3 as reactant gas (emitter heating rate 10 mA s^{-1}, calibration with FC43). Middle pressure liquid chromatography (MPLC) prepns were carried out on self-built glass columns (20 cm × 16 mm i.d.) with a Knauer HPLC pump (Model 64), a DuPont detector and additional TLC detection. Gradient elution was performed using corresponding vessels as described in ref. [3]. Droplet counter current chromatography (DCCC) was run on a Büchi 670 apparatus. Molecular calcns were carried out using the Biosym Software Package.

Extraction and purification. Whole plants (3.5 kg, air-dried) were successively extracted with 23 l $CHCl_3$, 49 l MeOH and 24 l MeOH–H_2O (70%) with the Ultra-Turrax apparatus. The combined extracts (1145 g) were evapd *in vacuo* (40°) to give a brown gummy residue, divided into 7 portions, redissolved in H_2O and exhaustively extracted with $CHCl_3$–*iso*-PrOH (3:2) and *n*-BuOH. The $CHCl_3$–*iso*-PrOH (3:2) layers were combined, the solvent was removed *in vacuo* and the residue (162 g) filtered over XAD-2 (1 kg) in 3 portions by stepwise elution with H_2O, MeOH and Me_2CO. Vacuum liquid chromatography (VLC) of the MeOH eluates (48 g) on cellulose (Avicel^R Merck, stepwise gradient elution with petrol–EtOAc–MeOH) followed by gel filtration on

1000 g Sephadex LH-20 (MeOH) afford 3.4 g of an enriched cardenolide mixt. (fr. 1) also containing **3**. VLC on silica gel 60 (stepwise gradient elution with petrol–EtOAc–MeOH–H_2O, →fr. 1a = 1380 mg) followed by DCCC ($CHCl_3$–MeOH–*iso*-PrOH–H_2O 9:12:1:8, descending mode) led to a crude fr. (140 mg) of **3**. The latter was isolated after gel filtration on 120 g Sephadex LH-20 (MeOH) by means of MPLC on silica gel RP-18 using MeOH–H_2O gradient elution to yield 98 mg pure **3**.

The combined *n*-BuOH layers (105 g) were chromatographed on XAD-2 (1 kg) in 2 portions by stepwise elution with H_2O, MeOH–H_2O (1:1) and MeOH. VLC of the MeOH–H_2O eluates (33 g) on silica gel 60 and cellulose (Avicel^R Merck, stepwise gradient elution with EtOAc–MeOH–H_2O gradients, both) led to a fr. (33 g) containing polar cardenolide glycosides, cardenolide sulphates and flavonoid glycosides [3]. Their sepn was achieved by gel chromatography on Sephadex LH-20 followed by DCCC in descending mode where the flavonoids remained in the stationary phase. MPLC on RP-18 silica gel with MeOH–H_2O gradient elution yielded pure **1** (50 mg) and **2** (90 mg).

Isoetin-4′-O-glucuronide **1**. $C_{21}H_{18}O_{13}$, yellow solid (50 mg); UV λ_{max} nm: 264, 286(sh), 368 (MeOH); 262, 269, 337, 481 (+ NaOMe, degr.); 270, 291, 401 (+ $AlCl_3$); 270, 291 (+ $AlCl_3$–HCl); 264, 284 (sh), 369 (+ NaOAc); 254, 286, 371 (+ NaOAc–H_3BO_3); DCI-NH_3-MS neg. mode *m/z* (rel. int.): 158 [glucuronic acid $- 2H_2O]^-$, 176 [glucuronic acid $- H_2O]^-$, 302 [M(agl)]$^-$, 478 [M]$^-$; ^{1}H and ^{13}C NMR: Table 1.

Vitexin-2″-O-glucoside **2**. $C_{27}H_{30}O_{15}$, yellow solid (90 mg); UV λ_{max} nm: 270, 303(sh), 335 (MeOH); 280, 330, 395 (+ NaOMe); 277, 305, 352, 386 (+ $AlCl_3$); 279, 303, 345, 383 (+ $AlCl_3$–HCl); 278, 299, 380 (+ NaOAc); 270, 302 (sh), 342 (+ NaOAc–H_3BO_3); DCI–NH_3–MS *m/z* (rel. int.): 180 [Glc $- H_2O + NH_4]^+$, 271 [M(agl) $+ H]^+$, 325 [(Glc $-$ Glc) $- H_2O + H]^+$, 343 [(Glc $-$ Glc) $+ H]^+$, 415 [M $-$ Glc $+ H]^-$, 595 [M $+ H]^+$; ^{1}H and ^{13}C NMR: Table 2.

Sinapoylglucose (**3**). $C_{17}H_{22}O_{10}$, pale-yellow needles (98 mg); mp (uncorr.) 95°; $[\alpha]_D^{20}$ $-$ 71° (MeOH; *c* 1.00); UV λ_{max} nm: 332, 241 228 (sh), 206 (MeOH, MeOH + $AlCl_3$); 402, 270, 218 (+ NaOMe); 402, 348 (sh), 258 (sh), 224 (+ NaOAc); IR ν_{max}^{KBr} cm^{-1}: 3320 (OH), 3060 (CH_{arom}), 1710 (C = O), 1580 (arom.); DCI-NH_3-MS *m/z* (rel. int.): 404 $[MNH_4]^+$ (20), 386 $[MNH_4 - H_2O]^+$ (4), 259 [M $-$ (Glc $- H_2O$) $+ NH_4 + NH_3]^+$ (8), 242 [M $-$ (Glc $- H_2O$) $+ NH_4]^+$ (15), 198 [Glc $+ NH_4]^+$ (61), 180 [Glc $- H_2O + NH_4]^+$ (100), 162 [Glc $- 2H_2O$ $+ NH_4]^+$ (12); ^{1}H and ^{13}C NMR: Table 3.

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