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CAFFEOYL PHENYLETHANOID GLYCOSIDES IN *SANANGO RACEMOSUM* AND IN THE GESNERIACEAE

SØREN ROSENDAL JENSEN

Department of Organic Chemistry, The Technical University of Denmark, DK-2800, Lyngby, Denmark

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Key Word Index—*Sanango racemosum*; Gesneriaceae; caffeoyl phenylethanoid glycosides; sanangoside; allopyranoside; conandroside; myconoside; dihydrocaffeic acid ester.

Abstract—An investigation of *Sanango racemosum* for systematically useful glycosides has been performed. No iridoids could be detected, but reverse phase chromatography provided the caffeoyl phenylethanoid glycosides (CPGs) calceolarioside C and conandroside together with the new 2-(3,4-dihydroxyphenyl)ethyl 3-caffeoyl-β-allopyranoside which has been named sanangoside. The genus *Sanango* has previously been considered a member of Buddlejaceae, but recent work has shown that this is improbable. The presence of CPGs in *S. racemosum* combined with the lack of iridoid glucosides suggested a possible relationship with the Gesneriaceae. A survey of 20 species within this family showed that sanangoside was present in four species of subfamily Gesnerioideae and that all the investigated plants in the family contained CPGs, while no iridoids could be detected. The European genera *Ramonda* and *Haberlea* were characteristic by containing only the CPG-analogue myconoside, a dihydrocaffeoyl ester. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

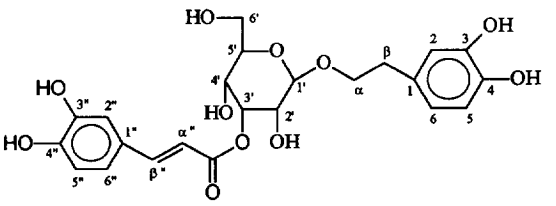
In a study of Loganiaceae (as defined by Leeuwenberg and Leenhouts [1]), a representative number of genera (19 of 29) and species from all ten tribes were investigated for iridoids and caffeoyl phenylethanoid glycosides (CPGs) such as verbascoside (**6**) by the author [2]. It was found that the tribes Buddlejeae and Retzieae which produce decarboxylated iridoids derived from 8-epideoxyloganic acid [3], consistently also contained CPGs. In conclusion, Loganiaceae is apparently polyphyletic, and this is consistent with the opinion of most contemporary taxonomists [c.f. 4].

The monotypic genus *Sanango*, a small tree from Amazonian Peru and Equador, which has traditionally been considered to belong to the tribe Buddlejeae in Loganiaceae (or in Buddlejaceae), was not at hand in the original investigation of the family. However, when it recently became available, it was the subject of a multi-disciplinary investigation [5–8], and the conclusion was that it fitted well within the Gesneriaceae. Chemotaxonomically, it was the lack of iridoids combined with the presence of CPGs, that indicated Gesneriaceae as the closest taxon. However, being mainly used as ornamentals, members of this family have not been the subject of much chemical work. It therefore seemed appropriate to do a supplementary investigation of some representatives from the family for useful chemical markers such as iridoids and CPGs.

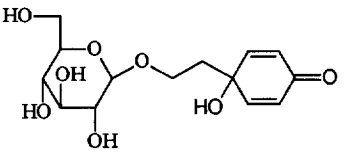
According to Wiehler [9], the Gesneriaceae comprises about 2850 species, 126 genera and 10 tribes classified into the subfamilies Gesnerioideae, Coronanthoideae and Cyrtandroideae. Previous work by Harborne [10] and by Quist and Pedersen [11] in which 46 species were investigated by chromatography and 590 species by ESR spectroscopy, respectively, showed that CPGs (i.e. verbascoside (**6**) and similar compounds) were almost universally present in the family. However, these techniques are somewhat non-specific and apparently do not discriminate between the different compounds present in the plants. Not many CPGs have actually been isolated and characterized from members of the family. Those reported comprise only conandroside (**3**), from *Conandron ramoidioides* [12], verbascoside (**6**) and calceolarioside C (**9**) from *Mitraria coccinea* [13], six compounds including chiritosides A–C (**16–18**) from *Chirita chinensis* [14] and pauciflóside (**12**) from *Lysionotus pauciflorus* [15]. Finally, an unusual compound derived from dihydrocaffeic acid, namely myconoside (**15**) has been reported from *Ramonda myconii* in a congress abstract [16], but neither experimental details nor spectral data were given and a full paper has not appeared.

RESULTS AND DISCUSSION

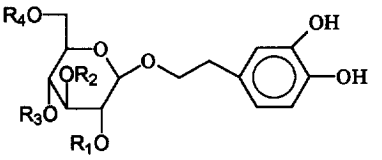
Dry leaves of *S. racemosum* were extracted with ethanol and the water solubles subjected to reverse phase chromatography. All fractions were examined by HPLC and NMR, but no iridoid glucosides could be detected. Three main fractions contained the CPGs **1**, **8**



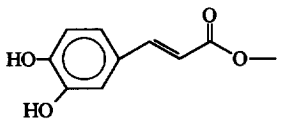
1 sanangoside

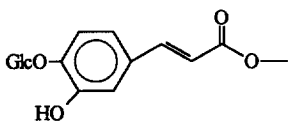


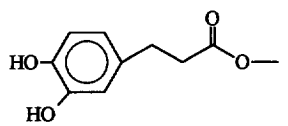
2 cornoside



Compound	R1	R2	R3	R4	name
3	H	Caff	H	H	plantainoside A
4	H	H	Caff	H	calceolarioside A
5	H	H	H	Caff	calceolarioside B
6	H	Rha	Caff	H	verbascoside
7	H	Rha	H	Caff	isoverbascoside
8	H	Xyl	Caff	H	conandroside
9	H	H	Caff	Xyl	calceolarioside C
10	H	Glc	Caff	H	plantamajoside
11	H	Api	Caff	H	calceolarioside E
12	H	Api	Caff	Api	paucifloside
13	Ac	Rha	Caff	H	2'-acetylverbascoside
14	Ac	Rha	H	Caff	tubuloside B
15	H	Api	DHC	Api	myconoside
16	H	GCaff	H	H	chiritoside A
17	H	H	GCaff	H	chiritoside B
18	H	H	H	GCaff	chiritoside C

Caff = 

GCaff = 

DHC = 

and **9**. Of these, **1** was new, while **9** was found to be identical to calceolarioside C by comparison with the published NMR data [17], and **8** appeared to be conandroside although the reported NMR data [12] are those of the nonaacetate and not of the genuine compound.

From the ^{13}C NMR spectrum of **1** (Table 1), it could at once be established that the compound contained a 3,4-dihydroxyphenylethyl moiety and a caffeoyl moiety as in **8** and **9**. However, in **1** only six additional signals were seen in the spectrum, showing the presence of only a single sugar moiety. In the ^1H NMR spectrum, the signals for the sugar protons H-1′, H-2′ and H-3′ could be assigned by decoupling experiments, with the latter seen as a triplet ($J = 3$ Hz) at δ 5.66. The low field position proved the C-3 oxygen to be the point of attachment for the caffeoyl group, and the coupling pattern indicated the sugar to be a β-allopyranosyl moiety. The ^{13}C spectrum proved this since a downfield shift for C-3 and upfield shifts for C-2 and C-4 was seen when comparing with a spectrum of patrinalloside, an iridoid β-allopyranoside [18]. This established the structure as **1**. A similar compound, plantainoside A (**3**), with β-glucopyranose as the core sugar has recently been isolated from *Plantago asiatica* [19] and it is also present in *Chirita sinensis* [14]. Except for the signals arising from the sugar moieties, the ^{13}C NMR spectra of **1** and **3** were almost coincident. The new compound was named sanangoside.

CPGs with an allopyranosyl moiety as the core sugar are rare; they have not so far been reported from sympetalous plants (i.e. Lamiales/Scrophulariales or Oleales). However, three analogues have been isolated from *Magnolia obovata*, namely magnolioside A, B and C [20, 21]. In these compounds additional sugar moieties (rhamnosyl and/or glucosyl) are attached to the core β-allopyranosyl unit.

The ^{13}C NMR spectrum of **8** (Table 1) showed 27 signals which could be assigned to (i) a dihydroxyphenylethyl, (ii) a caffeoyl, (iii) a core β-glucopyranosyl and (iv) a pentosyl moiety. Comparison with the spectrum of **9** showed the pentosyl moiety to be a β-xylopyranosyl group and the point of attachment to the core glucosyl was seen to be at the C-3 oxygen due

Table 1. ^{13}C NMR data for new (and model) compounds in methanol-d_4

Compound carbon atom		**1**	**8**	**15**	**12***
Aglucone	C-1	131.7	131.3	131.4	131.4
	C-2	117.1	117.1	117.1	117.1
	C-3	146.1	146.0	146.0	146.1
	C-4	144.6	144.5	144.6	144.6
	C-5	116.3	116.3	116.3	116.3
	C-6	121.3	121.3	121.3	121.3
	C-β	36.6	36.4	36.5	36.6
	C-α	71.9	72.1	72.2	72.4
Core sugar	C-1′	102.2	103.7	104.0	104.2
	C-2′	71.1	75.6	75.3	75.7
	C-3′	74.9	85.2	82.6	81.3
	C-4′	67.8	70.8	70.9	70.9
	C-5′	76.2	75.7	74.3	74.6
	C-6′	62.8	62.2	67.9	68.4
Acyl group	C-1″	128.0	127.7	133.5	127.8
	C-2″	115.3	115.1	116.5	115.0
	C-3″	146.7	146.7	144.6	146.9
	C-4″	149.4	149.5	146.2	149.8
	C-5″	116.6	116.6	116.5	116.5
	C-6″	122.9	123.0	120.6	123.1
	C-β″	146.9	147.2	37.3	147.7
	C-α″	115.7	115.1	31.0	115.2
	C=O″	169.2	168.4	173.9	168.2
3′-*O*-sugar	C-1‴		106.8	111.9	111.5
	C-2‴		74.8	77.9	78.2
	C-3‴		77.4	80.4	80.6
	C-4‴		70.9	75.0	75.2
	C-5‴		67.2	65.7	65.6
6′-*O*-sugar	C-1⁗			110.9	111.0
	C-2⁗			78.2	78.1
	C-3⁗			80.6	80.6
	C-4⁗			75.0	75.1
	C-5⁗			65.5	65.6

*Data from [15, 26]. Some signals were reassigned.

to the low field shift value for this carbon at δ 85.2. Therefore, **8** was conandroside.

The five species within Gesneriaceae so far reported to contain CPGs and the 21 species investigated in the present work are listed in Table 2 together with the compounds found in the plants. CPGs were present in all the species examined, consistent with the early work; and no iridoid glucosides could be detected. Seventeen different CPGs together with the glucoside cornoside (**2**) were isolated. Of the CPGs, **15**, which was isolated from *R. myconii*, *R. serbica* and *Haberlea rhodopensis* appeared to be different from the other compounds since no caffeoyl group was evident from the NMR spectra.

Thus, the ^{13}C NMR spectrum of **15** showed 32 signals, of which eight could be assigned to a dihyroxyphenylethyl moiety, six to a core glucosyl unit, acylated at the C-4 oxygen, and with auxiliary sugars attached to the C-3 and C-6 oxygens. Two low field signals at *ca* 111 ppm showed the presence of two apiofuranosyl moieties as in paucifloside (**12**). Actually, comparison (Table 1) with the spectrum of **12** showed extremely good correspondence, except for the acyl moiety, which in **15** appeared to be a dihydrocaffeoyl group. The compound must therefore be the aforementioned myconoside. Due to its significant absorption in ESR spectroscopy, Quist and Pedersen [11] also noted the presence of a derivative of the rare dihydrocaffeic acid in all the European genera *Ramonda*, *Jankaea* and *Haberlea*.

It is taxonomically interesting (and significant) that sanangoside (**1**) was found to be present in four of the fourteen species within the subfamily Gesnerioideae to which *Sanango* has been assigned [8]. The compound was not found in the other subfamilies. When **1** was present in a crude aqueous extract in sufficient amount, it could be detected in ^1H NMR by its signal at 5.6 ppm, since this region is usually free of other signals. Even in *Gesneria christii* where the content of **1** was as low as about 1% of the crude extract, this peak was clearly visible. Sanangoside has not been detected elsewhere in plants.

A surprisingly high ratio of the CPGs found in the family contained the pentoses xylose or apiose as auxiliary sugar(s), namely **8**, **9**, **11**, **12** and **15**. Such compounds are somewhat rare and their presence may

Table 2. Cornoside (**2**), sanangoside (**1**) and other caffeoyl esters found in the Gesneriaceae

		Access. no.*	Compound(s)
Subfamily Gesnerioideae			
Gloxinieae	*Koellikeria erinoides* (DC.) Mansf.	4166K/2	**1, 8**
	Sinningia cardinalis (Lehm.) H. Moore	IOK-24/95†	**6**
Episcieae	*Episcia cupreata* (Hook.) Hemsl.	P1955/5405	**1, 4, 5, 8**
	Nautilocalyx forgettii (Spraque) Spraque	P1935/5599	**6, 11**
	Nautilocalyx lychei (Hook. fil.) Sprague	P1980/5135	**6, 11, 12**
	Alloplectus cristatus (L.) Mart	S1981/0263	**11**
	Columnea querceti Oerst.	P1977/5485	**6, 7, 11**
	Codonanthe carnosa (Gardn.) Hanst.	4159B/3	**(2), 6, 7**
	Nematanthus wettsteinii (Fritsch.) H. E. Moore	S1979/0963	**2, 5, 8**
Gesnerieae	*Gesneria christii* Urban	GRF/G-1008‡	**1, 8**
	Gesneria leucomalla (Hanst.) Kunze	GRF/G-1010‡	**8**
	Gesneria onacaensis Rusby	Wiehler 93258‡	**6**
	Gesneria pedicellaris Alain	S1966/1506‡	**1, 8**
	Gesneria ventricosa Swartz	GRF/G-940‡	**8**
Subfamily Coronantheroideae			
Coronathereae	*Mitraria coccinea* Cav.	[13]	**6, 9**
Subfamily Cyrtandroideae			
Trichosporeae	*Aeschynanthus longicaulis* R. Br.	P1968/5304	**2, 6, 7**
	Aeschynanthus radicans Jack	P1967/5528	**6, 7, 13, 14**
	Aeschynanthus speciosus Hook.	P1952/5571	**6, 7, 10**
	Lysionotus pauciflorus Maxim.	[16]	**12**
Didymocarpeae	*Conandron ramoidioides* Sieb. & Zucc.	[12]	**6, 8**
	Ramonda myconi (L.) Rchb.	[15]	**15**
	Ramonda serbica Panc.	P1982/5605	**15**
	Haberlea rhodopensis Frisvald	4025/1	**15**
	Saintpaulea tongwensis B. L. Burtt	P1986/5072	**4, 8**
	Chirita sinensis Lindl.	[14]	**3, 4, 5, 16, 17, 18**
	Streptocarpus saxorum Engl.	S1970/0363	**6, 7**
Unaffiliated			
	Titanotrichum oldhamii (Hemsl.) Soler.	4166M/1	**2, 8, 11**

*Accession numbers (The Botanical Garden of Copenhagen)/literature reference.

†Voucher deposited at The Botanical Museum, Copenhagen.

‡Voucher deposited at Gesneriad Research Foundation, Sarasota, Florida, U.S.A.

be considered an advanced character since they are limited to a few of the advanced sympetalous families within Scrophulariales/Lamiales in contrast to verbascoside (**6**) with the auxiliary sugar rhamnose, which is the most widespread CPG [22 and c.f. 23]. Conversely, of the 27 investigated plant species, 19 had one or more of these present.

Iridoids have so far not been reported from Gesneriaceae and none were detected in the present work. This is despite the fact that Gesneriaceae is a true member of Lamiales (=Scrophulariales) sensu Dahlgren [24], where iridoids otherwise are present in all families [2] (although not in all genera) investigated.

In conclusion, with regard to chemical characters, *Sanango* with (i) the unique compound sanangoside (**1**), (ii) the 'advanced' CPGs **8** and **9** combined with (iii) the lack of iridoids, must be considered to fit well within Gesneriaceae.

EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were recorded in methanol-d_4, using the solvent peaks (δ 3.31 and 49.0, respectively, as standards). Reverse phase chromatography was performed on Merck Lobar C_{18}-columns size B (or C for larger amounts) eluting with water–MeOH mixtures (5:1 to 1:1) and monitoring simultaneously at 206 and 254 nm with a UV detector. Vouchers of *S. racemosum* (Neill 9458) have been deposited at DLF, MO and US.

Sanango racemosum. Dry leaves (150 g) were blended with EtOH (500 ml) and left for 4 days at room temp. After filtering, the material was extracted again for 3 days with 80% EtOH (500 ml). The combined extracts were concd (9.3 g), redissolved in water (50 ml) and extracted with ether (2 × 150 ml) to remove lipophilic material. The dark red aq. extract was taken to dryness to give a foam (6.5 g). An aliquot of this (2.3 g) was chromatographed. All frs giving a positive response by the detector were evapd and an NMR spectrum recorded, but no iridoids were found. However, when eluting with 3:2 and 1:1 a number of frs with verbascoside-like UV-absorptions were collected. These were tested by HPLC and 3 frs proved to contain only a single compound (the remaining frs were mixts representing about half of the mass). The above 3 frs were taken to dryness to give (in order of elution) compounds **1** (50 mg), **9** (30 mg) and **8** (60 mg).

Koellikeria erinoides. Fresh plant (34 g) was blended with EtOH (2 × 150 ml) and the extract taken to dryness. The residue was dissolved in H_2O (10 ml), extracted with ether and the aq. phase taken to dryness to give crude aq. extract (735 mg). Reverse phase chromatography (B-column) with H_2O–MeOH (2:1 to 1:1) as the eluent gave **1** (48 mg) and a fr. (148 mg) containing mainly **8**.

Sinningia cardinalis. Fresh plant (44 g) gave crude aq. extract (820 mg). Chromatography gave **6** (357 mg).

Episcia cupreata. Fresh plant (61 g) gave crude aq. extract (658 mg). Chromatography gave **1** (4 mg), **4** (35 mg), **8** (50 mg) and **5** (34 mg).

Nautilocalyx forgettii. Fresh plant (30 g) gave crude aq. extract (348 mg). Chromatography gave **11** (39 mg) and **6** (25 mg).

Nautilocalyx lychei. Fresh plant (51 g) gave crude aq. extract (877 mg). Chromatography gave **12** (14 mg), **11** (32 mg) and **6** (131 mg).

Alloplectus cristatus. Fresh plant (40 g) gave crude aq. extract (660 mg). Chromatography gave **11** (170 mg).

Columnea querceti. Fresh plant (71 g) gave crude aq. extract (880 mg). Chromatography gave **11** (52 mg) and **6** (180 mg) together with **7** in a mixt. with two unidentified compounds (53 mg).

Codonanthe carnosa. Fresh plant (43 g) gave crude aq. extract (595 mg). Chromatography first gave a fr. (167 mg) containing a trace of **2** as seen by ^{1}H NMR, then **6** (153 mg) and **7** (34 mg).

Nematanthus wettsteinii. Fresh plant (52 g) gave crude aq. extract (903 mg). Chromatography gave a fr. containing **2** (200 mg), then **5** (130 mg) and **8** (40 mg). Rechromatography (H_2O–MeOH 15:1) of the first fr. above gave pure **2** (67 mg).

Gesneria christii. Dry leaves (3.5 g) gave crude aq. extract (385 mg). Chromatography gave **1** (5 mg, impure) and **8** (14 mg).

Gesneria leucomalla. Dry leaves (11 g) gave crude aq. extract (300 mg). Chromatography gave **8** (10 mg).

Gesneria onacaensis. Dry leaves (7 g) gave crude aq. extract (710 mg). Chromatography gave **6** (120 mg).

Gesneria pedicellaris. Fresh plant (17 g) gave crude aq. extract (230 mg). Chromatography gave **1** (<5 mg) and **8** (10 mg).

Gesneria pedunculosa. Dry leaves (3.5 g) gave crude aq. extract (50 mg). By HPLC, **8** could be detected in trace amounts, but it was not visible by ^{1}H NMR.

Gesneria tomentosa. Dry leaves (3.4 g) gave crude aq. extract (110 mg). By HPLC, **8** could be detected in trace amounts, but it was not visible by ^{1}H NMR.

Gesneria ventricosa. Dry leaves (9 g) gave crude aq. extract (120 mg). Chromatography gave **8** (10 mg).

Aeschynanthus longicaulis. Fresh plant (23 g) gave crude aq. extract (920 mg) and **2** was detected by ^{1}H NMR but not isolated. Chromatography gave **6** (212 mg) and **7** (57 mg).

Aeschynanthus radicans. Fresh plant (37 g) gave crude aq. extract (730 mg). Chromatography gave **6** (122 mg), a 1:1 mixture of **7** and **13** (122 mg) and **14** (40 mg).

Aeschynanthus speciosus. Fresh plant (32 g) gave crude aq. extract (680 mg). Chromatography gave **10** (30 mg), **6** (93 mg) and **7** (46 mg).

Haberlea rhodopensis. Fresh plant (17 g) gave crude aq. extract (800 mg). Chromatography gave **15** (342 mg).

Ramonda myconi. Fresh plant (11 g) gave crude aq. extract (676 mg). Only **15** and sugars could be detected by ^{1}H NMR.

Ramonda serbica. Fresh plant (15 g) gave crude aq. extract (625 mg). Only **15** and sugars could be detected by ^{1}H NMR.

Saintpaulea tongwensis. Fresh plant (43 g) gave crude aq. extract (204 mg). Chromatography gave **4** (16 mg) and **8** (25 mg).

Streptocarpus saxorum. Fresh plant (43 g) gave crude aq. extract (515 mg). Chromatography gave **6** (58 mg) and **7** (13 mg).

Titanotrichum oldhamii. Fresh plant (36 g) gave crude aq. extract (1000 mg). Chromatography gave impure **2** (<10 mg), **11** (80 mg) and **8** (180 mg).

Sanangoside (**1**). Foam, $[\alpha]_D^{21}$ −55° (MeOH; *c* 0.8). ^{1}H NMR (500 MHz): δ 6.71 (*d*, J = 2 Hz, H-2), 6.68 (*d*, J = 8 Hz, H-5), 6.57 (*dd*, J = 2 and 8 Hz, H-6), 5.62 (*br t*, J = *ca*. 3 Hz, H-3′); 4.70 (*d*, J = 8 Hz, H-1′), 4.06 (*m*, H-α) 3.86 (*br d*, J = 11 Hz, H-6′), 3.67–3.77 (4H, H-α, H-3′, H-4′, H-6′), 3.54 (*dd*, J = 3 and 8 Hz, H-2′), 2.79 (*br t*, J = 7.5 Hz, β-CH_2), 7.07 (*d*, J = 2 Hz, H-2″), 6.97 (*dd*, J = 2 and 8 Hz, H-6″), 6.79 (*d*, J = 8 Hz, H-5″), 7.58 (*d*, J = 16 Hz, H-β″), 6.36 (*d*, J = 16 Hz, H-α″). ^{13}C NMR data in Table 1. (Found: C, 54.1; H, 5.9. $C_{23}H_{26}O_{11}$, 2 H_2O requires: C, 53.7; H, 5.9%.)

Conandroside (**8**). A foam; $[\alpha]_D^{21}$ −38° (MeOH; *c* 0.7). ^{1}H NMR (250 MHz, methanol-d_4; using solvent suppression technique): δ 6.75 (*br s*, H-2), 6.72 (*d*, J = 8 Hz, H-5), 6.61 (*dd*, J = 2 and 8 Hz, H-6), 4.97 (*t*, J = 9.5 Hz, Glu-H_4), 4.47 (*d*, J = 7.5 Hz, Xyl-H_1), 4.46 (*d*, J = 8 Hz, Glu-H_1), 4.07 (*m*, H-α), 3.1–3.9 (remaining carbohydrate Hs and H-α), 2.84 (*t*, J = 7.5 Hz, β-CH_2), 7.12 (*br s*, H-2″), 7.01 (*br d*, J = 8 Hz, H-6″), 6.84 (*d*, J = 8 Hz, H-5″), 7.62 (*d*, J = 16 Hz, H-β″), 6.42 (*d*, J = 16 Hz, H-α″). ^{13}C NMR data in Table 1. (Found: C, 52.0; H, 6.0. $C_{28}H_{34}O_{15}$, 2 H_2O requires: C, 52.0; H, 5.9%.)

Myconoside (**15**). A syrup; $[\alpha]_D^{21}$ −67° (MeOH; *c* 0.4). ^{1}H NMR (500 MHz methanol-d_4); δ 6.67 (4H, *m*, H-2, H-2″, H-5, H-5″), 6.56 and 6.54 (each *dd*, J = 2 and 8 Hz, H-6 and H-6″), 5.25 (*d*, J = 2.5 Hz, H-1‴″), 4.85 (*d*, J = 2.5 Hz, H-1‴), 4.80 (*t*, partly covered by HDO-signal, J = 9.5 Hz, H-4′), 4.32 (*d*, J = 8 Hz, H-1′), 3.97 and 3.70 (*ms*, 2 × H-α), 3.92 and 3.74 (*AB* syst., J = 9.5 Hz, 5‴″-CH_2), 3.87 and 3.86 (each *d*, J = 2.5 Hz, H-2‴ and H-2‴″), 3.83 and 3.69 (*AB* syst., J = 9.5 Hz, 5‴-CH_2), 3.64 (*t*, J = 9 Hz, H-3′), 3.57 and 3.52 (each 2H, *s*-like, 4‴-CH_2 and 4‴″-CH_2), 3.55 (2H, *m*, H-5′ and H-6′), 3.34 (*dd*, J = 8 and 9 Hz, H-2′), 3.30 (*dd*, J = 5.5 and 11.5 Hz, H-6′), 2.78 (4H, α-CH_2 and α″-CH_2), 2.63 (*t*-like, J = 7.5 Hz, β″-CH_2). ^{13}C NMR data in Table 1. (Found: C, 49.9; H, 6.3. $C_{33}H_{44}O_{19}$, 3 H_2O requires: C, 49.6; H, 6.3%.)

The remaining compounds were identified by their ^{1}H and/or (mainly) ^{13}C NMR spectra by comparison with published data: **2** [25]; **3**, **4**, **5**, **16**, **17** and **18** [14]; **6** and **11** [26]; **7** [27]; **9** [17]; **10** [28]; **12** [15, 26]; **13** and **14** [29].

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Note added in proof: A paper on the structure of myconoside (**15**) has appeared: Cañigueral, S., Salvia, M. J., Vila, R. and Iglesias, J. (1996) *J. Nat. Prod.* **59**, 419.

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