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BUFADIENOLIDES FROM *URGINEA MARITIMA* FROM EGYPT*†

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Key Word Index—*Urginea maritima* agg.; Hyacynthaceae; squill; cardiac glycosides; bufadienolides.

Abstract—Forty-one bufadienolides were isolated from the bulbs of *Urginea maritima* agg. from Egypt; 26 of them are new natural compounds. Structure elucidation was performed by comparison with authentic substances or by means of ^{1}H, ^{13}C NMR and FAB mass spectroscopy. Sixteen of the glycosides derive from nine structurally new aglycones: 16β-hydroxy-scillarenin, 16β-*O*-acetyl-scillarenin, 12β-hydroxy-5α-4,5-dihydro-scillirosidin, 16β-hydroxy-5α-4,5-dihydro-scillirosidin, 16β-*O*-acetyl-5α-4,5-dihydro-scillirosidin, 12β-hydroxy-scillirubrosidin, 16β-*O*-acetyl-scillirubrosidin, 9-hydroxy-scilliphaeosidine and 12β-hydroxy-desacetyl-scillirosidine.

INTRODUCTION

According to morphological, caryological [2] and chemical investigations [3] *Urginea maritima* (L.) Baker is an aggregate of at least six species. In the eastern Mediterranean area *Urginea aphylla* (Forskal.) Speta is described [2]. Its bufadienolide complex has been investigated in detail [4]. In examinations of the changes in the bufadienolide composition during a vegetation period [5] the cardiac glycoside complex of samples from Egypt differed completely from that of samples from Greece and Turkey. The bulbs from Egypt are coloured greenish-white and much larger than those from Greece and Turkey. They contained a great number of unknown substances besides proscillaridin A, scillaren A, scilliroside and scillirosidine, which have been described in Egyptian squill [6]. Therefore, the bufadienolide complex from samples from Egypt was investigated.

RESULTS AND DISCUSSION

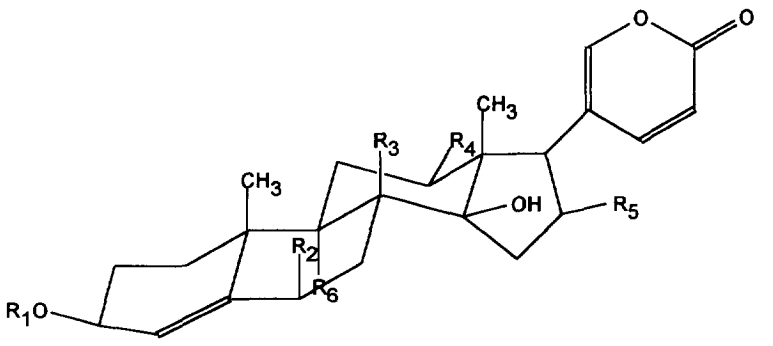
From a chloroform- and a chloroform–ethanol-extract from lyophilized bulbs of *Urginea maritima* agg. from Egypt, 41 bufadienolides were isolated by repeated column chromatography and droplet counter current chromatography. Along with 15 known substances (**1–3**, **7–14**, **32**, **35**, **40**, **41**) and 10 new glycosides of scillarenin (**4**), scillirubrosidin (**5**, **6**) and 5α-4,5-dihydro-scillirosidin (**27–31**, **33**, **34**), 16 new compounds (**15–26**, **36–39**) were obtained deriving from nine structurally new genins.

The structures of the aglycones and sugars were determined on the basis of ^{1}H and ^{13}C NMR and FAB mass spectral studies. The identity and linkage of the sugar components were additionally characterized by GC mass spectrometric analysis of the trimethylsilylesters of the resulting monosaccharides after methylation and acid hydrolysis of the substances [7]. The known bufadienolides were identified by comparison with authentic samples by means of TLC and HPLC.

The FAB mass spectrum of **15** showed a molecular weight of 592. The fragmentation pattern $(MH)^{-} - 162 - 18 - 18 - 18$ pointed to the presence of a hexose and three hydroxyl units. In the ^{1}H NMR spectrum the coupling constant of the anomeric proton doublet (J = 8 Hz) proved the β-glycosidic linkage of the sugar moiety to the aglycone. The chemical shifts of the 18- and 19-methyl protons (δ 0.82 and 1.40) were comparable to 12β-hydroxyscilliroside [4]. The signals in the ^{13}C NMR spectrum were also in good agreement with this substance except those of C-4, C-5 and C-6. Compound **15** was unambiguously identified as 6-desacetyl-12β-hydroxyscillirosid by the upfield location of C-4 (δ 126.7) and C-6 (δ 75.5), as well as the downfield shift of C-5 (δ 146.7) in accordance with the absence of signals of an acetyl moiety. The sugar was identified by GC/MS analysis as β-D-glucose. Compound **15** cannot be a decomposition product as the bulbs were lyophilized immediately after collection. The fragmentation pattern of **16** in the FAB mass spectrum indicated the presence of a desoxyhexose and of two additional hydroxyl groups in the aglycone

*Part 8 in the series "Bufadienolides from Squill". For part 7 see ref. [1].

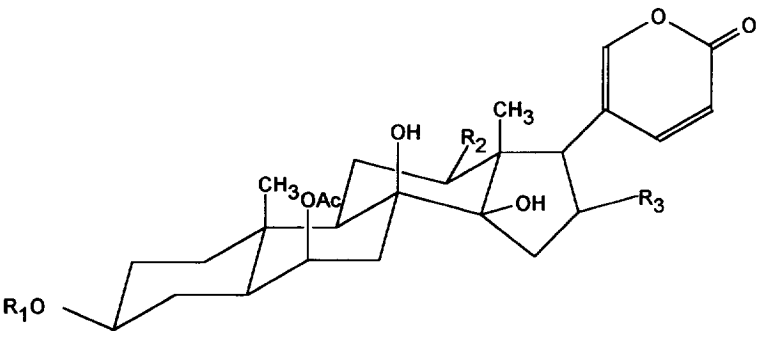
†Dedicated to Prof. Dr Wichtl on the occasion of his 70th birthday.



	R_1	R_2	R_3	R_4	R_5	R_6
1 proscillaridin (820)	rha	H	H	H	H	H
2 scillaren A (30)	rha-glu	H	H	H	H	H
3 glucoscillaren A (700)	rha-glu-glu	H	H	H	H	H
4 scillarenin-3-O-ß-D-glucosido-1"→ 4'-ß-D-glucoside (15)	glu-glu	H	H	H	H	H
5 scillirubrosidin-3-O-ß-D-glucosido-1"→ 4'-ß-D-glucoside (10)	glu-glu	H	OH	H	H	H
6 scillirubrosidin-3-O-ß-D-rhamnosido-1"→ 4'-ß-D-glucosido-1"'→ 4"-ß-D-glucoside (10)	rha-glu-glu	H	OH	H	H	H
7 scilliphaeoside (320)	rha	H	H	OH	H	H
8 scilliphaeosidin-3-O-ß-D-glucoside (40)	glu	H	H	OH	H	H
9 glucoscilliphaeoside (40)	rha-glu	H	H	OH	H	H
10 6-desacetyl-scilliroside (25)	glu	OH	OH	H	H	H
11 scilliroside (330)	glu	OAc	OH	H	H	H
12 glucoscilliroside (20)	glu-glu	OAc	OH	H	H	H
13 12ß-hydroxy-scillirosidin (10)	H	OAc	OH	OH	H	H
14 12ß-hydroxy-scilliroside (440)	glu	OAc	OH	OH	H	H
15 6-desacetyl-12ß-hydroxy-scilliroside (10)	glu	OH	OH	OH	H	H
16 12ß-hydroxy-scillirubrosidin-3-O-α-L-rhamnoside (10)	rha	H	OH	OH	H	H
17 16ß-hydroxy-proscillaridin A (10)	rha	H	H	H	OH	H
18 16ß-hydroxy-scillarenin-3-O-ß-D-glucoside (15)	glu	H	H	H	OH	H
19 16ß-hydroxy-glucoscillaren A (25)	rha-glu-glu	H	H	H	OH	H
20 16ß-O-acetyl-proscillaridin A (220)	rha	H	H	H	OAc	H
21 16ß-O-acetyl-scillarenin-3-O-ß-D-glucoside (270)	glu	H	H	H	OAc	H
22 16ß-O-acetyl-scillarenin-3-O-ß-D glucosido-1" → 4'- glucoside (40)	glu-glu	H	H	H	OAc	H
23 16ß-O-acetyl-glucoscillaren A (155)	rha-glu-glu	H	H	H	OAc	H
24 16ß-O-acetyl-scillarenin-3-O-α-L-glucomethylosido-1" → 4'-ß-D-glucosido-1"' → 4"-ß-D-glucoside (10)	glum-glu-glu	H	H	H	OAc	H
25 16ß-O-acetyl-scillirubroside (100)	glu	H	OH	H	OAc	H
26 9-hydroxy-scilliphaeoside (30)	rha	H	H	OH	H	OH

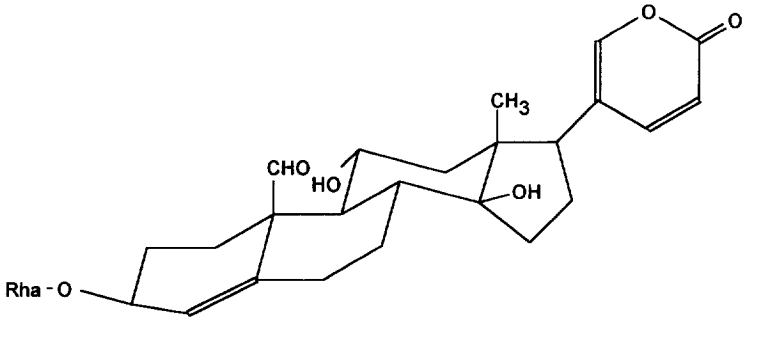
The values in parentheses show the yield (mg/1700g bulbs) of each compound isolated.

ac	acetyl
glu	glucose
glum	glucomethylose
rha	rhamnose
thev	thevetose

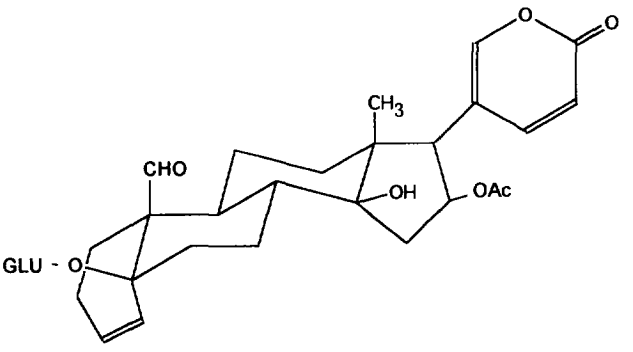


	R_1	R_2	R_3
27 5α-4,5-dihydro-scillirosidin-3-O-α-L-glucomethyloside (60)	glum	H	H
28 5α-4,5-dihydro-scillirosidin-3-O-α-L-thevetoside (250)	thev	H	H
29 5α-4,5-dihydro-scillirosidin-3-O-ß-D-glucoside (50)	glu	H	H
30 5α-4,5-dihydro-scillirosidin-3-O-α-L-rhamnosido-4'-ß-D-glucoside (80)	rha-glu	H	H
31 5α-4,5-dihydro-scillirosidin-3-O-α-L-glucomethylosido-4'-ß-D-glucoside (10)	glum-glu	H	H
32 5α-4,5-dihydro-scillirosidin-3-O-α-L-thevetosido-4'-ß-D-glucoside (580)	thev-glu	H	H
33 5α-4,5-dihydro-scillirosidin-3-O-α-L-glucomethylosido-1'' → 4'-ß-D-glucosido-1''' → 4'''-ß-D-glucoside (25)	glum-glu-glu	H	H
34 5α-4,5-dihydro-scillirosidin-3-O-α-L-rhamnosido-1'' → 4'-ß-D-glucosido-1''' → 4'''-ß-D-glucoside (150)	rha-glu-glu	H	H
35 5α-4,5-dihydro-scillirosidin-3-O-α-L-thevetosido-1'' → 4'-ß-D-glucosido-1''' → 4'''-ß-D-glucoside (120)	thev-glu-glu	H	H
36 5α-4,5-dihydro-12ß-hydroxy-scillirosidin-3-O-α-L-thevetoside (25)	thev	OH	H
37 5α-4,5-dihydro-12ß-hydroxy-scillirosidin-3-O-α-L-thevetosido-4'-ß-D-glucoside (170)	thev-glu	OH	H
38 5α-4,5-dihydro-16ß-hydroxy-scillirosidin-3-O-α-L-thevetoside (8)	thev	H	OH
39 5α-4,5-dihydro-16ß-O-acetyl-scillirosidin-3-O-α-L-thevetosido-4'-ß-D-glucoside (15)	thev-glu	H	OAc

compared to scillarenin. In the ^{1}H NMR spectrum the signals of the methyl protons of C-18 and C-19 showed a downfield shift to δ 0.84 and δ 1.22. The characteristic ^{13}C NMR resonances of C-11, C-12, C-13 and C-18 [8] proved the presence of a 12β-hydroxy moiety. The second hydroxyl group was assigned to the 8β-position due to a quaternary carbon signal at δ 77 and the downfield shift of 10 ppm for C-7 in comparison to scillarenin glycosides [8]. The sugar was determined by its ^{13}C NMR chemical shifts, CG mass spectrometric analysis and by enzymatic hydrolysis with naringinase (α-rhamnosidase) [9] as α-L-rhamnose. Thus, compound **16** was identified as 12β-hydroxyscillirubrosidin-3-*O*-α-L-rhamnoside.



40 11α-hydroxy-scilliglaucosidin-3-O-α-L-rhamnoside (40)



41 scillicyanoside (150)

Compounds **17–19** are glycosides of the same aglycone. The FAB mass spectra suggested **17** and **18** to be monosides and **19** to be a trioside. The genin differed from scillarenin by an additional hydroxyl group. Its location and orientation was assigned to C-16β, due to the downfield shift of H-18 ($\Delta = 0.07$ ppm) [10] and since H-17 was observed as a doublet at *ca* δ 2.70 in the ^{1}H NMR spectra. The coupling constant of 8 Hz proved the *cis*-configuration of the protons at C-16 and C-17 [11]. From the resonances of C-15, C-16, C-17 and C-20 in the ^{13}C-NMR spectra this substitution pattern was confirmed [8] and the aglycone of **17–19** identified as 16β-hydroxy-scillarenin. Based on the NMR data the structures were characterized as 3-*O*-α-L-rhamnoside (**17**), 3-*O*-β-D-glucoside (**18**) and 3-*O*-α-L-rhamnoside-1″→4′-β-D-glucosido-1‴→4″-β-D-glucoside (**19**). The sugar sequence of **19** was determined by methylation, acid hydrolysis and GC-MS of the trimethylsilylesters of the resulting monosaccharides [7].

From the spectral data for the compounds **20–24** the same genin was identified. The FAB mass spectra afforded for the aglycone a molecular weight of 442, the loss of 60 a.m.u. pointed to the attachment of an acetoxyl group. The fragmentation pattern proved **20** and **21** to be monosides containing a deoxyhexose and a hexose, respectively, **22** to be a bioside with two hexoses and **23** and **24** to be triosides each linked with a deoxyhexose and two hexoses. The resonances of the methyl protons at C-18 (δ 0.82) and C-19 (δ 1.08) in the ^{1}H NMR spectra were in good accordance with those of **17–19**. A signal at δ 1.87 arose from the protons of an acetyl moiety. The upfield shift of this signal due to the deshielding of the lactone ring pointed to the β-linkage of this substituent in position C-16. The chemical shifts in the ^{13}C NMR spectra presented good similarities to those of **17–19** except C-12, C-14, C-15, C-17 and C-20 which showed an upfield shift of 1–2 ppm and C-16, shifted downfield *ca* 2 ppm. Based on these data the genin of **20–24** was proved to be 16β-*O*-acetyl-scillarenin. By the methods described above the sugar chains were identified as 3-*O*-α-L-rhamnose (**20**), 3-*O*-β-D-glucose (**21**), 3-*O*-β-D-glucosido-1″→4′-β-D-glucose (**22**), 3-*O*-α-L-rhamnosido-1″→4′-β-D-glucosido-1‴→4″-β-D-glucose (**23**) and 3-*O*-α-L-6′-deoxyglucosido-1″→4′-glucosido-1‴→4″-glucose (**24**).

The FAB mass spectrum of **25** exhibited the $[MH]^+$ ion at *m/z* 621. Signals at *m/z* 459 $[MH - 162]^+$, *m/z* 441 $[MH - 162 - 18]^+$ and *m/z* 381 $[MH - 162 - 18 - 60]^+$ corresponded to the consecutive loss of a hexosyl, a hydroxyl and an acetoxyl unit. The latter was clearly identified by the characteristic ^{1}H NMR resonance at δ 1.90. Due to the upfield shift of 0.10 ppm and the doublet at δ 2.92 of the 17α-H this group had to be localized in position C-16β. The coupling constant of 8 Hz of the doublet of the anomeric proton at δ 4.48 revealed the β-linkage of the sugar, which was identified as glucose by its ^{13}C NMR shifts and by GC characterization after hydrolysis of the glycoside. The signals at δ 20.9 and 171.2 in the ^{13}C NMR spectrum, as well as the shifts of C-17 and C-20, confirmed the 16β-acetoxy moiety. The position of the hydroxyl group was deduced from the additional signal of a quaternary C-atom at δ 76.4, the absence of C-8 at about δ 42 and the upfield shift of C-11 of 3 ppm. These data allowed the identification of **25** as 16β-*O*-acetyl-scillirubroside.

Compound **26** was established as 9-hydroxy-scilliphaeoside mainly by two-dimensional NMR techniques. For the structure elucidation of the first natural occurring 9-hydroxy bufadienolide refer to literature [12].

The FAB mass spectra for **36** and **37** showed the $[MH]^+$ ions at *m/z* 637 and 799, respectively. The fragmentation pattern indicated **36** to be a monoside containing a deoxy-*O*-methylhexose and **37** to be a bioside containing a deoxy-*O*-methylhexose and a hexose. The loss of 60 a.m.u. and three 18 a.m.u. from the aglycone pointed to the presence of an acetoxyl and three hydroxyl groups.

Due to the absence of signals between δ 5 and 6 in the ^{1}H NMR spectrum the existence of a double bond in ring A could be excluded. The ^{13}C NMR chemical shift of C-19 (δ 15.3) showed the *trans*-configuration of rings A and B [10]. The other ^{13}C NMR data of the genin were in good agreement with 5α-4,5-dihydro-scillirosidin [10], except C-11, C-12, C-13, C-17 and

C-18. The ^{13}C NMR resonances of these carbon atoms [8], as well as the shifts of the C-18 and C-19 protons in the ^{1}H NMR spectrum [13], proved the attachment of a hydroxyl group at position C-12β. By the ^{1}H NMR- and ^{13}C NMR data and the results of GC mass spectrometrical analysis the sugar components were identified unambiguously as α-L-thevetose (**36**) and α-L-thevetosido-1″→4′-β-D-glucose (**37**), thus identifying **36** as 5α-4,5-dihydro-12β-hydroxy-scillirosidin-3-*O*-α-L-thevetoside and **37** as 5α-4,5-dihydro-12β-hydroxy-scillirosidin-3-*O*-α-L-thevetosido-1″→4′-β-D-glucoside.

The FAB mass spectrum of **38** showed the same molecular weight for the glycoside and for the aglycone as for compound **36**. The attachment of a hydroxyl moiety in position C-16β was proved by the doublet at δ 2.70 (17α-H) and its coupling constant of 10 Hz in the ^{1}H NMR spectrum [11], as well as by the chemical shifts of C-15, C-16, C-17 and C-20 in the ^{13}C NMR spectrum [8]. The chemical shifts of the other carbon atoms corresponded largely to those of **27** and confirmed the identification of **38** as 5α-4,5-dihydro-16β-hydroxy-scillirosidin-3-*O*-α-L-thevetoside.

The fragmentation pattern in the FAB mass spectrum suggested **39** to contain a hexose, an *O*-methyldeoxy-hexose, two acetoxyl and two hydroxyl units. The acetoxyl groups were clearly identified by the characteristic ^{1}H NMR resonances at δ 1.89 and 2.09, the latter assignable to C-6. The upfield shift of the other signal in accordance with the coupling constant of the doublet at δ 2.90 (17α-H) pointed to the location of this group at position C-16β [11]. The ^{13}C NMR data of the genin were in good agreement with those of **38**, the shift of C-15, C-16 and C-20 and additional signals at δ 21.3 and δ 171.8 confirmed the 16β-*O*-acetyl substitution. As signals arising from the sugar moiety were identical with those of **37**, compound **39** was determined as 5α-4,5-dihydro-16β-acetoxy-scillirosidin-3-*O*-α-L-thevetosido-1″,4′-D-glucoside.

Besides these new substances 10 glycosides of known genins were isolated for the first time and identified by the spectroscopic methods and the GC-MS analysis described above as scillarenin-3-*O*-β-D-glucosido-1″→4′-β-D-glucoside (**4**), scillirubrosidine-3-*O*-β-D-glucosido-1″→4′-β-D-glucoside (**5**), scillirubrosidine-3-*O*-α-L-rhamnosido-1″→4′-β-D-glucosido-1‴→4″-β-D-glucoside (**6**) and the 3-*O*-α-L-glucomethyloside (**27**), 3-*O*-α-L-thevetoside (**28**), 3-*O*-β-D-glucoside (**29**), 3-*O*-α-L-rhamnosido-1″→4′-β-D-glucoside (**30**), 3-*O*-α-L-glucomethylosido-1″→4′-β-glucoside (**31**), 3-*O*-α-L-glucomethylosido-1″→4′-β-glucosido-1‴→4″-β-D-glucoside (**33**) and 3-*O*-α-L-rhamnosido-1″→4′-β-D-glucosido-1‴→4″-β-D-glucoside (**34**) of 5α-4,5-dihydro-scillirosidin.

Thus, along with the 15 known bufadienolides, the sample from Egypt shows the most complex bufadienolide pattern of all species from the *Urginea maritima* agg. [1, 3, 4, 14, 15, 16]. The main components are proscillaridin A, glucoscillaren A, 5α-4,5-dihydro-scillirosidin-3-*O*-α-L-thevetosido-1″→4′-β-D-glucoside, 12β-hydroxy-scilliroside, scilliroside and scilliphaeoside. Almost 60% of the cardiac glycoside complex consist of glycosides of scillarenin and 5α-4,5-dihydro-scillirosidin. The high content of 12β-hydroxylated and 16β-hydroxylated or acetoxylated bufadienolides is remarkable.

EXPERIMENTAL

Plant material. Bulbs of the *Urginea maritima* agg. were collected around El Arish (Egypt), cut and lyophilized (fr. wt 5950 g, dry wt 1700 g). The material was identified by Doz. Franz Speta, OÖ Landesmuseum, Linz, Austria) and a voucher specimen is on deposit at his private herbarium in Linz.

General. TLC: silica gel 60 F_{254} precoated plates (Merck) or RP-2 F_{254} precoated plates (Merck), system 1: $CHCl_3$–MeOH–H_2O (70:22:3.5); system 2: EtOAc–MeOH–H_2O (81:11:8); system 3: MeCOEt–toluene–H_2O–MeOH–HOAc (40:5:3:2.5:1) [17]; system 4: $CHCl_3$–MeOH–H_2O (65:30:6); system 5: MeOH–H_2O (1:1) when using RP-2 plates. Detection: after 15 min at 103–105° the plate was sprayed with 50% ethanolic H_2SO_4 [18]. CC: silica gel 60 (Merck, 0.063–0.200 mm), silica gel 60 silanized for CC (Merck). DCCC: DCC-A Tokyo Rikakikai; 300 columns, 40 × 0.2 cm, system 6: $CHCl_3$–MeOH–H_2O (5:10:6), upper phase as mobile; HPLC: according to ref. [19]; enzymatic hydrolysis: according to ref. [9]; GLC-MS identification of monosaccharide units: according to ref. [7], interfacetemp. 170°, temp. gradient: 110°–250°/1° min^{-1}. FAB-MS (positive-ion-mode = PIFAB-MS and negative ion mode = NIFAB-MS): Varian Mat 311 A; FAB–canon: Ion Tech Ltd., acceleration voltage = 2.2 kV, E (neutral): 6.0 keV, Xenon, T = 40°, $p < 10^{-5}$ Torr, T_{inlet}: RT; matrix: glycerol. NMR: Bruker AM-400 spectrometer with Aspect-3000 computer; ^{1}H NMR: SF = 400.13 MHz; ^{13}C NMR: SF = 100.6 MHz, internal standard: TMS; solvents: $CDCl_3$–CD_3OD 1:1.

Extraction. Dried bulbs (1700 g) (bufadienolide context approx. 1%) were extracted as already described [16], yielding 19 g $CHCl_3$–EtOH extract and 6 g $CHCl_3$ extract.

The less polar bufadienolide concentrate (bufadienolide content *ca* 66%) was submitted to CC on silica gel with EtOAc, water saturated–MeOH mixtures of increasing polarity from 95:5 to 90:10. The main bufadienolide each of fr. 9, 10, 12, 14, 15, 16, 17, 18, 19, 22, 25, 26 and 27 was isolated by CC on silica gel with $CHCl_3$–MeOH–H_2O mixtures of different polarity. The final purification of the substances was performed by CC on silica gel by using EtOAc, water saturated–MeOH as mobile phase and led to the isolation of **1**, **7**, **11**, **13**, **17**, **20**, **21**, **27**, **28**, **32**, **36**, **38** and **39**.

The crude glycoside mixture of higher polarity (bufadienolide content *ca* 46%) was fractionated by CC on silica gel using $CHCl_3$–MeOH–H_2O (900:35:2) to (50:50:10) as mobile phase. The resulting frs were

Table 1. ^{13}C NMR chemical shifts in $CDCl_3$–CD_3OD (1:1); in ppm, δ-values, TMS as internal standard

C-atom	4	5	6	15	16	17	18	19	20	21	22	23	25	27	28	29	30	31	33	34	36	37	38	39
1	36.0	35.8	35.6	38.4	35.9	36.0	36.2	36.2	36.0	35.9	35.9	36.0	35.2	37.7	37.8	37.7	37.6	37.7	38.2	37.9	37.8	37.9	37.5	37.5
2	27.5	27.3	27.1	27.3	27.2	27.5	27.8	27.7	27.5	27.5	27.4	27.5	27.3	29.2	29.2	29.1	28.9	29.1	29.3	29.2[a]	29.2[a]	29.1	29.3	29.2
3	76.4	76.8	73.9	75.9	74.6	74.4	75.6	75.2[b]	74.4	74.6	74.6	75.0	74.3	76.6	76.3	74.9	74.8	76.0	75.2	75.2	76.0	75.1	74.4	74.4
4	121.0	121.2	120.9	126.7	121.3	121.1	121.5	121.2	121.1	121.1	121.2	121.3	121.4	31.3	31.3	31.5	31.2	31.2	31.8	31.5	31.4	31.2	31.3	31.3
5	147.9	148.5	148.3	146.7	148.1	147.8	147.9	148.0	147.8	147.6	147.4	147.7	148.0	46.5	46.6	46.5	46.4	46.5	46.6	46.5	47.5	46.6	46.5	46.5
6	32.7	28.7	28.6	75.5	28.7	32.9	32.9	33.1	32.9	32.6	32.5	32.8	28.5	77.3	77.4	78.2	76.6	77.2	77.6	76.7	77.2	77.2	77.4	77.4
7	29.2[a]	38.4	38.2	38.9	38.2	29.5	29.6	29.7	29.0	28.8	28.5	29.0	38.3	41.6	41.6	41.5	41.4	41.5	41.7	41.7	40.0	40.0	42.6	42.6
8	42.7	76.6	76.5	77.6	76.1	42.3	42.6	42.6	42.7	42.8	42.5	42.7	76.4	77.2	77.2	77.4	77.4	77.4	77.6	77.4	76.8	76.8	77.3	77.3
9	50.8	52.3[a]	52.2[a]	48.8	49.3	50.6	50.9	50.8	50.6	50.5	50.5	50.6	51.7	52.4	52.5	52.4	52.3	52.4	52.6	52.5	47.9	48.2	50.7	50.7
10	37.0	37.3	37.1	37.0	37.2	38.0	38.2	38.2	38.0	37.9	37.8	38.0	37.2	36.5	36.5	36.4	36.3	36.5	37.1	36.6	36.3	36.4	36.5	36.5
11	21.7	18.7	18.6	26.6	30.2[a]	21.4	21.7	21.8	21.6	21.4	21.3	21.6	18.3	18.8	18.9	18.8	18.7	18.8	18.9	18.9	27.1	27.3	18.7	18.2
12	41.1	41.8	41.7	77.2	77.0	41.8	41.9	41.9	40.7	40.6	40.5	40.7	41.1	40.2	40.2	40.1	40.0	40.2	37.9	40.2	76.6	76.7	40.9	40.9
13	48.9	49.1	49.5	55.8	55.7	49.9	49.6	49.0	50.1	49.7	49.9	50.1	50.6	49.9	49.9	49.9	49.8	50.0	50.0	49.1	55.9	56.0	50.9	50.9
14	85.1	85.8	85.6	85.4	86.1	85.4	85.5	85.5	84.1	83.9	83.8	84.1	84.7	85.7	85.8	85.7	85.5	85.7	85.9	85.9	86.0	86.1	84.9	84.9
15	32.7	34.7	34.6	34.0	34.9	42.2	42.4	42.5	40.7	40.6	40.5	40.7	42.5	34.6	34.6	34.5	34.4	34.5	35.0	34.7	34.6	34.7	42.2	40.2
16	29.1[a]	29.8	29.6	29.7	29.8[a]	73.5	73.4	73.3	75.4	76.3	76.3	74.8[b]	76.6	29.6	29.6	29.8	29.5	29.6	29.7	29.7[a]	29.5[a]	29.6	73.2	75.2
17	51.5	52.1[a]	51.9[a]	47.3	47.6	58.7	58.9	58.9	57.6	57.5	57.4	57.6	58.1	51.1	51.2	51.1	51.0	51.1	51.3	51.2	46.6	47.6	58.7	58.3
18	16.9	19.4	19.3	12.4	12.6	16.9	17.0	17.1	16.9	16.7	16.6	16.8	19.2	19.5	19.5	19.5	19.4	19.5	19.5	19.5	12.6	12.7	19.0	18.5
19	19.1	20.6	20.6	22.9	20.8	19.3	19.3	19.4	19.3	19.1	18.9	19.3	20.6	15.3	15.3	15.5	15.3	15.3	15.3	15.3	15.3	15.3	16.0	15.3
20	124.2	124.6	124.3	124.1	124.4	119.8	119.6	119.7	118.6	118.3	118.4	118.6	118.6	125.0	124.5	124.4	124.2	124.4	124.6	124.6	124.1	124.3	119.8	118.7
21	149.2	148.7	148.4	149.9	148.8	151.4	151.7	150.6	151.4	151.0	151.7	151.3	152.0	148.6	149.5	149.4	148.3	148.5	149.6	148.7	148.5	150.2	151.4	151.3
22	148.5	149.7	148.4	148.6	148.8	151.4	151.7	151.8	151.8	151.0	151.1	151.3	151.1	148.6	148.6	148.5	148.3	148.5	148.7	149.3	148.5	148.7	151.4	151.3
23	115.1	115.3	115.2	115.0	115.1	113.0	113.0	113.0	113.0	113.0	112.7	112.9	112.9	115.2	115.3	115.2	115.2	115.2	115.3	115.3	115.0	115.1	113.0	112.9
24	164.1	164.4	164.5	164.2	164.4	165.0	164.5	164.5	163.9	163.6	163.6	163.9	163.8	164.3	164.3	164.3	164.1	164.2	164.4	164.4	164.8	164.2	165.0	164.9
1′	102.4	102.6	99.8	102.3	100.2	100.0	102.8	100.2	100.0	102.5	102.4	99.9	102.7	97.6	97.7	101.5	98.4	97.3	97.6	98.9	97.5	97.6	97.5	97.7
2′	73.8	74.1	71.6	74.2	71.9	71.8	74.5	71.9	71.8	74.2	73.8	71.8	74.4	72.9	72.9	74.3	70.8	70.8	72.7	71.9	72.7	73.4	72.7	73.6
3′	75.4	75.7	71.7	76.6	72.0	71.8	77.1	72.0	71.9	76.6	75.4	71.7	76.8	74.3	84.5	76.8	70.0	74.7	74.3	71.8	84.3	84.4	84.4	84.6
4′	80.5	80.6	83.9	70.9	73.6	73.3	71.6	83.9	73.5	70.9	80.4	83.9	71.0	74.9	74.9	70.9	82.9	85.2	86.3	83.9	74.6	81.9	74.6	81.9
5′	75.6	75.8	67.6	76.8	69.2	69.1	77.5	68.0	69.1	77.2	75.6	67.8	77.3	68.2	68.4	77.3	68.6	67.9	67.0	67.9	68.3	67.2	68.3	67.4
6′	61.7	61.9	17.7	62.3	17.7	17.7	62.5	17.9	17.7	62.3	61.6	17.8	62.4	17.8	17.8	62.3	17.8	17.8	17.8	17.8	17.7	17.8	17.7	17.9
1″	103.8	104.0	103.9					104.2			103.8	104.0					104.7	104.7	104.2	104.2		104.2		104.3
2″	73.8	74.1	74.6[b]					74.3[c]			73.8	74.1					74.4	74.7	74.3	74.2[b]		74.4		74.8
3″	77.0	77.4	75.6					75.9[b]			77.0	75.7[a]					76.2	77.2	76.0	75.9		77.1		77.1
4″	70.4	70.6	80.6					80.7			70.4	80.6					71.8	71.4	80.6	80.7		71.2		71.3
5″	77.1	77.2	75.7					75.9[b]			77.1	75.8[a]					76.6	77.2	76.0	76.0		77.3		77.3
6″	61.7	61.9	61.8					62.0[a]			61.6	61.9					61.5	62.2	62.1	62.0[c]		62.6		62.6
1‴			105.1					105.2				105.1							105.2	105.2				
2‴			74.9[b]					74.7[c]				74.5[b]							75.0	74.3[b]				
3‴			77.2					77.5				77.3							77.4	77.5				
4‴			70.5					70.8				70.6							70.8	70.8				
5‴			77.0					77.3				77.1							77.4	77.3				
6‴			61.8					61.9[a]				61.9							62.1	61.9[c]				
CH_3CO									21.0	21.0	20.7	21.0	20.9	21.3	21.4	21.3	21.4	21.3	21.3	21.3	21.3	21.3	21.0	21.3/20.9
$\overline{CH_3CO}$									171.4	171.2	171.2	171.4	171.2	171.6	171.6	171.6	171.5	171.5	171.7	171.9	171.4	171.6	171.3	171.8/171.5
OCH_3															61.0						60.9	61.1	61.0	61.2

[a–d] Signal assignments in each column may be reversed.

purified by CC over silica gel, silanized silica gel and DCCC, yielding **2–12**, **14–16**, **18**, **19**, **21–26**, **29–35**, **37**, **40** and **41**.

The known substances **1–3**, **7–14**, **32**, **35**, **40**, **41** were identified by chromatography with authentic samples. For R_f values and retention times refer to ref. [1].

Scillarenin-3-O-*β*-D-*glucosido*-1″→4′-D-*glucoside* (**4**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 707 $[M-H]^-$, 545 $[M-H-162]^-$, 383 $[M-H-162-162]^-$, 383 $[M-H-162-162-18]^-$; PIFAB-MS: *m/z* 709 $[MH]^+$, 547 $[MH-162]^+$, 529 $[MH-162-18]^+$, 385 $[MH-162-162]^+$, 367 $[MH-162-162-18]^+$, 349 $[MH-162-162-18-18]^+$. ^{1}H NMR: *δ* 0.75 (*s*, 3H, H_3-18), 1.07 (*s*, 3H, H_3-19), 4.44 (*d*, *J* = 8 Hz, 1H, H-1′), 4.56 (*d*, *J* = 8 Hz, 1H, H-1″), 5.45 (*s*, 1H, H-4), 6.30 (*d*, *J* = 10 Hz, 1H, H-23), 7.35 (*d*, *J* = 2 Hz, 1H, H-21), 8.00 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

Scillirubrosidin-3-O-*β*-D-*glucosido*-1″→4′-*β*-D-*glucoside* (**5**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 723 $[M-H]^-$, 399 $(M-H-162-162)^-$, PIFAB-MS: *m/z* 725 $[MH]^+$, 401 $[MH-162-162]^+$, 383 $(MH-162-162-18)^+$. ^{1}H NMR: *δ* 0.88 (*s*, 3H, H_3-18), 1.20 (*s*, 3H, H_3-19), 4.46 (*d*, *J* = 8 Hz, 1H, H-1′), 4.58 (*d*, *J* = 8 Hz, 1H, H-1″), 5.48 (*s*, 1H, H-4), 6.32 (*d*, *J* = 10 Hz, 1H, H-23), 7.32 (*d*, *J* = 2 Hz, 1H, H-21), 8.00 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

Scillirubrosidin-3-O-*α*-L-*rhamnosido*-1″→4′-*β*-D-*glucosido*-1‴→4″-*β*-D-*glucoside* (**6**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 869 $[M-H]^-$, 707 $[M-H-162]^-$, 545 $[M-H-162-162]^-$, 399 $[M-H-162-162-146]^-$. PIFAB-MS; *m/z* 401 $[GH]^+$, 383 $[GH-18]^+$. ^{1}H NMR: *δ* 0.88 (*s*, 3H, H_3-18), 1.20 (*s*, 3H, H_3-19), 1.35 (*d*, *J* = 6 Hz, 3H, H_3-6′), 4.38 (*d*, *J* = 8 Hz, 1H, H-1″), 4.52 (*d*, *J* = 8 Hz, 1H, H-1‴), 4.90 (*d*, *J* = 2 Hz, 1H, H-1′), 5.35 (*s*, 1H, H-4), 6.32 (*d*, *J* = 10 Hz, 1H, H-23), 7.29 (*d*, *J* = 2 Hz, 1H, H-21), 7.95 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

6-*Desacetyl*-12*β*-*hydroxy*-*scillirosidin*-3-O-*β*-D-*glucoside* = 6-*desacetyl*-12*β*-*hydroxy*-*scilliroside* (**15**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 593 $[M-H]^-$, 431 $[M-H-162]^-$, 413 $(M-H-162-18]^-$, 395 $[M-H-162-18-18]^-$, 377 $[M-H-162-18-18-18]^-$. PIFAB-MS: *m/z* 595 $[MH]^+$, 433 $[MH-162]^+$, 415 $[MH-162-18]^+$. ^{1}H NMR: *δ* 0.82 (*s*, 3H, H_3-18), 1.40 (*s*, 3H, H_3-19), 4.46 (*d*, *J* = 8 Hz, 1H, H-1′), 5.71 (*s*, 1H, H-4), 6.31 (*d*, *J* = 10 Hz, 1H, H-23), 7.43 (*d*, *J* = 2 Hz, 1H, H-21), 7.94 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

12*β*-*Hydroxy*-*scillirubrosidin*-3-O-*α*-L-*rhamnoside* (**16**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 561 $[M-H]^-$, 415 $[M-H-146]^-$, 397 $[M-H-146-18]^-$. PIFAB-MS: *m/z* 563 $[MH]^+$, 399 $[MH-146-18]^+$. ^{1}H NMR: *δ* 0.84 (*s*, 3H, H_3-18), 1.22 (*s*, 3H, H_3-19), 1.30 (*d*, *J* = 6 Hz, 3H, H_3-6′), 4.88 (*d*, *J* = 2 Hz, 1H, H-1′), 5.35 (*s*, 1H, H-4), 6.28 (*d*, *J* = 10 Hz, 1H, H-23), 7.39 (*d*, *J* = 2 Hz, 1H, H-21), 7.92 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

16*β*-*Hydroxy*-*scillarenin*-3-O-*α*-L-*rhamnoside* = 16*β*-*hydroxy*-*proscillaridin A* (**17**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 545 $[M-H]^-$, 399 $(M-H-146]^-$, 381 $[M-H-146-18]^-$. PIFAB-MS: *m/z* 547 $[MH]^+$, 401 $[MH-146-18]^+$, 383 $[MH-146-18]^+$, 365 $[MH-146-18-18]^+$, 347 $[MH-146-18-18-18]^+$. ^{1}H NMR: *δ* 0.84 (*s*, 3H, H_3-18), 1.04 (*s*, 3H, H_3-19), 1.28 (*d*, *J* = 6 Hz, 3H, H_3-6′), 2.67 (*d*, *J* = 8 Hz, 1H, H-17), 4.90 (*d*, *J* = 2 Hz, 1H, H-1′), 5.33 (*s*, 1H, H-4), 6.25 (*d*, *J* = 10 Hz, 1H, H-23), 7.34 (*d*, *J* = 2 Hz, 1H, H-21), 7.92 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

16*β*-*Hydroxy*-*scillarenin*-3-O-*β*-D-*glucoside* (**18**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 561 $[M-H]^-$; PIFAB-MS: *m/z* 563 $[MH]^+$, 401 $[MH-162]^+$, 383 $[MH-162-18]^+$. ^{1}H NMR: *δ* 0.84 (*s*, 3H, H_3-18), 1.06 (*s*, 3H, H_3-19), 2.69 (*d*, *J* = 8 Hz, 1H, H-17), 4.40 (*d*, *J* = 8 Hz, 1H, H-1′), 5.44 (*s*, 1H, H-4), 6.24 (*d*, *J* = 10 Hz, 1H, H-23), 7.33 (*d*, *J* = 2 Hz, 1H, H-21), 7.93 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

16*β*-*Hydroxy*-*scillarenin*-3-O-*α*-L-*rhamnosido*-1″→4′-*β*-D-*glucosido*-1‴→4″-*β*-D-*glucoside* = 16*β*-*hydroxy*-*glucoscillaren A* (**19**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 869 $[M-H]^-$, 707 $[M-H-162]^-$, 545 $[M-H-162-162]^-$, 381 $[M-H-162-162-146-18]^-$. PIFAB-MS: *m/z* 871 $[MH]^+$, 547 $[MH-162-162]^+$, 383 $[MH-162-162-146-18]^+$. ^{1}H NMR: *δ* 0.84 (*s*, 3H, H_3-18), 1.06 (*s*, 3H, H_3-19), 1.36 (*d*, *J* = 6 Hz, 3H, H_3-6′), 2.72 (*d*, *J* = 8 Hz, 1H, H-17), 4.42 (*d*, *J* = 8 Hz, 1H, H-1″), 4.60 (*d*, *J* = 8 Hz, 1H, H-1‴), 4.90 (*d*, *J* = 2 Hz, 1H, H-1′), 5.36 (*s*, 1H, H-4), 6.26 (*d*, *J* = 10 Hz, 1H, H-23), 7.36 (*d*, *J* = 2 Hz, 1H, H-21), 7.96 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

16*β*-O-*Acetyl*-*scillarenin*-3-O-*α*-L-*rhamnoside* = 16*β*-O-*acetyl*-*proscillaridin A* (**20**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 587 $[M-H]^-$, 545 $[M-H-42]^-$, 441 $[M-H-146]^-$, 399 $[M-H-146-42]^-$, 381 $[M-H-146-42-18]^-$. PIFAB-MS: *m/z* 589 $[MH]^+$, 443 $[MH-146]^+$, 383 $[MH-146-60]^+$, 365 $[MH-146-60-18]^+$. ^{1}H NMR: *δ* 0.82 (*s*, 3H, H_3-18), 1.08 (*s*, 3H, H_3-19), 1.29 (*d*, *J* = 6 Hz, 3H, H_3-6′), 1.87 (*s*, 3H, $\overline{CH_3}$–CO at C-16), 2.90 (*d*, *J* = 10 Hz, 1H, H-17), 4.90 (*d*, *J* = 2 Hz, 1H, H-1′), 5.34 (*s*, 1H, H-4), 5.49 (*dd*, 1H, H-16), 6.22 (*d*, *J* = 10 Hz, 1H, H-23), 7.33 (*d*, *J* = 2 Hz, 1H, H-21), 8.22 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

16*β*-O-*Acetyl*-*scillarenin*-3-O-*β*-D-*glucoside* (**21**). Amorphous; FAB-MS; NIFAB-MS: *m/z* 603 $[M-H]^-$, 561 $[M-H-42]^-$. PIFAB-MS: *m/z* 605 $[MH]^+$, 443 $[MH-162]^+$, 383 $[MH-162-60]^+$. ^{1}H NMR: *δ* 0.82 (*s*, 3H, H_3-18), 1.06 (*s*, 3H, H_3-19), 1.87 (*s*, 3H, $\overline{CH_3}$–CO at C-16), 2.90 (*d*, *J* = 10 Hz, 1H, H-17), 4.45 (*d*, *J* = 8 Hz, 1H, H-1′), 5.46 (*s*, 1H, H-4), 6.22 (*d*, *J* = 10 Hz, 1H, H-23), 7.35 (*d*, *J* = 2 Hz, 1H,

H-21), 8.22 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

16β-O-*Acetyl-scillarenin*-3-O-β-D-*glucosido*-1″→4′-β-D-*glucoside* (**22**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 765 $[M-H]^-$, 723 $[M-H-42]^-$, 603 $[M-H-162]^-$, 561 $[M-H-162-42]^-$, 441 $[M-H-162-162]^-$, 399 $[M-H-162-162-42]^-$, 381 $[M-H-162-162-42-18]^-$, 363 $[M-H-162-162-42-18-18]^-$. PIFAB-MS: *m/z* 767 $[MH]^+$, 605 $[MH-162]^+$, 443 $[MH-162-162]^+$, 407 $[MH-162-162-18-18]^+$, 383 $[M-H-162-162-18-42]^+$. ^{1}H NMR: δ 0.82 (*s*, 3H, H_3-18), 1.07 (*s*, 3H, H_3-19), 1.89 (*s*, 3H, CH_3–CO at C-16), 2.92 (*d*, *J* = 10 Hz, 1H, H-17), 4.44 (*d*, *J* = 8 Hz, 1H, H-1′] 4.60 (*d*, *J* = 8 Hz, 1H, H-1″), 5.47 (*s*, 1H, H-4), 6.23 (*d*, *J* = 10 Hz, 1H, H-23), 7.33 (*d*, *J* = 2 Hz, 1H, H-21), 8.24 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

16β-O-*Acetyl-scillarenin*-3-O-α-L-*rhamnosido*-1″→4′-β-D-*glucosido*-1‴→4″-β-D-*glucoside* = 16β-O-*acetyl-glucoscillaren A* (**23**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 911 $[M-H]^-$, 749 $[M-H-162]^-$, 587 $[M-H-162-162]^-$, 545 $[M-H-162-162-42]^-$, 441 $[M-H-162-162]^-$, 399 $[M-H-162-162-42-146]^-$, 381 $[M-H-162-162-42-146-18]^-$, 363 $[M-H-162-162-42-18-18]^-$. PIFAB-MS: *m/z* 913 $[MH]^+$, 443 $[MH-162-162-146]^+$, 425 $[MH-162-162-146-18]^+$, 383 $[M-H-162-162-146-18-42]^+$. ^{1}H NMR: δ 0.82 (*s*, 3H, H_3-18), 1.07 (*s*, 3H, H_3-19), 1.36 (*d*, *J* = 6 Hz, 3H, H_3-6′), 1.89 (*s*, 3H, CH_3–CO at C-16), 2.92 (*d*, *J* = 10 Hz, 1H, H-17), 4.42 (*d*, *J* = 8 Hz, 1H, H-1″), 4.58 (*d*, *J* = 8 Hz, 1H, H-1‴), 4.90 (*d*, *J* = 2 Hz, 1H, H-1′), 5.34 (*s*, 1H, H-4), 6.23 (*d*, *J* = 10 Hz, 1H, H-23), 7.33 (*d*, *J* = 2 Hz, 1H, H-21), 8.24 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

16β-O-*Acetyl-scillarenin*-3-O-α-L-*glucomethylosido*-1″→4′-β-D-*glucosido*-1‴→4″-β-D-glucoside (**24**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 911 $[M-H]^-$, 869 $[M-H-42]^-$, 707 $[M-H-162-42]^-$, 399 $[M-H-162-162-42-146]^-$. PIFAB-MS: *m/z* 913 $[MH]^+$. ^{1}H NMR: δ 0.84 (*s*, 3H, H_3-18), 1.08 (*s*, 3H, H_3-19), 1.34 (*d*, *J* = 6 Hz, 3H, H_3-6′), 1.88 (*s*, 3H, CH_3–CO at C-16), 2.92 (*d*, *J* = 10 Hz, 1H, H-17), 4.44 (*d*, *J* = 8 Hz, 1H, H-1″), 4.60 (*d*, *J* = 8 Hz, 1H, H-1‴), 4.88 (*d*, *J* = 2 Hz, 1H, H-1′), 5.38 (*s*, 1H, H-4), 6.23 (*d*, *J* = 10 Hz, 1H, H-23), 7.36 (*d*, *J* = 2 Hz, 1H, H-21), 8.24 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22.

16β-O-*Acetyl-scillirubroside* (**25**). Amorphous; FAB-MS: NIFAB-MS: *m/z* 619 $[M-H]^-$, 577 $[M-H-42]^-$, 559 $[M-H-42-18]^-$, 457 $[M-H-162]^-$, 415 $[M-H-162-42]^-$. PIFAB-MS: *m/z* 621 $[MH]^+$, 459 $[MH-162]^+$, 441 $[MH-162-18]^+$, 381 $[MH-162-18-60]^+$, 363 $[MH-162-18-60-18]^+$. ^{1}H NMR: δ 0.96 (*s*, 3H, H_3-18), 1.22 (*s*, 3H, H_3-19), 1.90 (*s*, 3H, CH_3–CO at C-16), 2.92 (*d*, *J* = 10 Hz, 1H, H-17), 4.48 (*d*, *J* = 8 Hz, 1H, H-1′), 5.52 (*s*, 1H, H-4), 6.38 (*d*, *J* = 10 Hz, 1H, H-23), 7.40 (*d*, *J* = 2 Hz, 1H, H-21), 8.28 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22); ^{13}C NMR: see Table 1.

5α-4,5-*Dihydroscillirosidin*-3-O-α-L-*glucomethyloside* (**27**). FAB-MS: NIFAB-MS: *m/z* 605 $[M-H]^-$, 563 $[M-H-42]^-$, 417 $[M-H-146-42]^-$. PIFAB-MS: 607 $[MH]^+$, 547 $[MH-60]^+$, 461 $[MH-146]^-$, 401 $[MH-146-60]^+$, 383 $[MH-146-60-18]^+$, 365 $[MH-146-60-18-18]^+$. ^{1}H NMR: δ 0.87 (*s*, 3H, H_3-18), 1.21 (*s*, 3H, H_3-19), 1.26 (*d*, *J* = 6 Hz, 3H, H_3-6′), 2.09 (*s*, 3H, CH_3–CO at C-6), 4.92 (*d*, *J* = 2 Hz, 1H, H-1′), 6.30 (*d*, *J* = 10 Hz, 1H, H-23), 7.29 (*d*, *J* = 2 Hz, 1H, H-21), 7.97 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22]. ^{13}C NMR: see Table 1.

5α-4,5-*Dihydroscillirosidin*-3-O-α-L-thevetoside (**28**). FAB-MS: NIFAB-MS: *m/z* 619 $[M-H]^-$, 577 $[M-H-42]^-$, 459 $[M-H-160]^-$, 441 $[M-H-160-18]^-$, 417 $[M-H-160-42]^-$. PIFAB-MS: *m/z* 621 $[MH]^+$, 461 $[MH-160]^+$, 443 $[MH-160-18]^+$, 401 $[MH-160-60]^+$, 383 $(MH-160-60-18]^+$, 365 $[MH-160-60-18-18]^+$. ^{1}H NMR: δ 0.89 (*s*, 3H, H_3-18), 1.22 (*s*, 3H, H_3-19), 1.25 (*d*, *J* = 6 Hz, 3H, H_3-6′), 2.09 (*s*, 3H, CH_3–CO at C-6), 3.67 (*s*, 3H, CH_3–O at C-3′), 4.90 (*d*, *J* = 2 Hz, 1H, H-1′), 6.31 (*d*, *J* = 10 Hz, 1H, H-23), 7.32 (*d*, *J* = 2 Hz, 1H, H-21), 7.92 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22). ^{13}C NMR: see Table 1.

5α-4,5-*Dihydroscillirosidin*-3-O-β-D-*glucoside* (**29**). FAB-MS: NIFAB-MS: *m/z* 621 $[M-H]^-$, 579 $[M-H-42]^-$, 459 $[M-H-162]^-$, 417 $[M-H-162-42]^-$. PIFAB-MS: *m/z* 623 $[MH]^+$, 461 $[MH-162]^+$, 443 $[MH-162-18]^+$, 401 $[MH-162-60]^+$, 383 $[MH-162-60-18]^+$, 362 $[MH-160-60-18-18]^+$. ^{1}H NMR: δ 0.87 (*s*, 3H, H_3-18), 1.22 (*s*, 3H, H_3-19), 2.06 (*s*, 3H, CH_3–CO at C-6), 4.41 (*d*, *J* = 8 Hz, 1H, H-1′), 6.28 (*d*, *J* = 10 Hz, 1H, H-23), 7.28 (*d*, *J* = 2 Hz, 1H, H-21), 7.97 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22]. ^{13}C NMR: see Table 1.

5α-4,5-*Dihydroscillirosidin*-3-O-α-L-*rhamnosido*-1″→4′-β-D-*glucoside* (**30**). FAB-MS: NIFAB-MS: *m/z* 767 $[M-H]^-$, 725 $[M-H-42]^-$, 605 $[M-H-162]^-$, 563 $[M-H-162-42]^-$, 417 $[M-H-162-146-42]^-$, 399 $[M-H-162-42-146-18]^-$. PIFAB-MS: *m/z* 769 $[MH]^+$, 607 = $[MH-162]^+$, 461 $[MH-162-146]^+$, 443 $[MH-162-146-18]^+$, 383 $(MH-162-146-60-18]^+$, 365 $[MH-162-146-60-18-18]^+$. ^{1}H NMR: δ 0.86 (*s*, 3H, H_3-18), 1.20 (*s*, 3H, H_3-19), 1.30 (*d*, *J* = 6 Hz, 3H, H_3-6′), 2.09 (*s*, 3H, CH_3–CO at C-6), 4.49 (*d*, *J* = 8 Hz, 1H, H-1″), 4.88 (*d*, *J* = 2 Hz, 1H, H-1′), 6.31 (*d*, *J* = 10 Hz, 1H, H-23), 7.32 (*d*, *J* = 2 Hz, 1H, H-21), 7.97 (*dd*, $J_{21,22}$ = 2 Hz, $J_{22,23}$ = 10 Hz, 1H, H-22]. ^{13}C NMR: see Table 1.

5α-4,5-*Dihydroscillirosidin*-3-O-α-L-*glucomethylosido*-1″→4′-β-D-*glucoside* (**31**). FAB-MS: NIFAB-MS: *m/z* 767 $[M-H]^-$, 725 $[M-H-42]^-$, 605 $[M-H-162]^-$, 563 $[M-H-162-42]^-$, 545 $[M-H-162-42-18]^-$, 459 $[M-H-162-146]^-$, 417 $[M-H-162-146-42]^-$, 399 $[M-H-162-42-146-18]^-$. PIFAB-MS: *m/z* 769

$[MH]^+$, 607 $[MH - 162]^+$, 461 $[MH - 162 - 146]^+$. ^1H NMR: δ 0.87 (*s*, 3H, H_3-18), 1.21 (*s*, 3H, H_3-19), 1.27 (*d*, $J = 6$ Hz, 3H, H_3-6'), 2.06 (*s*, 3H, CH_3–CO at C-6), 4.46 (*d*, $J = 8$ Hz, 1H, H-1''), 4.97 (*d*, $J = 2$ Hz, 1H, H-1'), 6.28 (*d*, $J = 10$ Hz, 1H, H-23), 7.30 (*d*, $J = 2$ Hz, 1H, H-21), 7.95 (*dd*, $J_{21,22} = 2$ Hz, $J_{22,23} = 10$ Hz, 1H, H-22). ^{13}C NMR: see Table 1.

5α - 4,5 - *Dihydroscillirosidin* - 3 - O - α - L - *glucomethylosido*-1''→4'-β-D-*glucoside*-1'''→4''-β-D-*glucoside* (**33**). FAB-MS: NIFAB-MS: *m/z* 929 $[M - H]^-$, 869 $[M - H - 60]^-$, 767 $[M - H - 162]^-$, 725 $[M - H - 162 - 42]^-$, 707 $[M - H - 162 - 60]^-$, 605 $[M - H - 162 - 162]^-$, 563 $[M - H - 162 - 162 - 42]$, 459 $[M - H - 162 - 162 - 146]^-$. PIFAB-MS: *m/z* 931 $[MH]^+$, 607 = $[MH - 162 - 162]^+$, 461 $[MH - 162 - 162 - 146]^+$. ^1H NMR: δ 0.87 (*s*, 3H, H_3-18), 1.21 (*s*, 3H, H_3-19), 1.32 (*d*, $J = 6$ Hz, 3H, H_3-6'], 2.08 (*s*, 3H, CH_3–CO at C-6), 4.43 (*d*, $J = 8$ Hz, 1H, H-1''), 4.60 (*d*, $J = 8$ Hz, 1H, H-1'''), 4.92 (*d*, $J = 2$ Hz, 1H, H-1'), 6.32 (*d*, $J = 10$ Hz, 1H, H-23), 7.30 (*d*, $J = 2$ Hz, 1H, H-21), 8.00 (*dd*, $J_{21,22} = 2$ Hz, $J_{22,23} = 10$ Hz, 1H, H-22). ^{13}C NMR: see Table 1.

5α-4,5-*Dihydroscillirosidin*-3-O-α-L-*rhamnosido*-1''→4'-β-D-*glucosido*-1'''→4''-β-D-*glucoside* (**34**). FAB-MS: NIFAB-MS: *m/z* 929 $[M - H]^-$, 869 $[M - H - 60]^-$, 767 $[M - H - 162]^-$, 725 $[M - H - 162 - 42]^-$, 707 $[M - H - 162 - 60]^-$, 605 $[M - H - 162 - 162]$, 459 $(M - H - 162 - 162 - 146]^-$, 417 $[M - H - 162 - 162 - 42 - 146]^-$. PIFAB-MS: *m/z* 931 $[MH]^+$, 769 $[MH - 162]^+$, 607 $[MH - 162 - 162]^+$, 461 $[MH - 162 - 162 - 146]^+$, 443 $[MH - 162 - 162 - 146 - 18]^+$, 401 $[MH - 162 - 162 - 146 - 60]^+$. ^1H NMR: δ 0.88 (*s*, 3H, H_3-18), 1.21 (*s*, 3H, H_3-19), 1.34 (*d*, $J = 6$ Hz, 3H, H_3-6'], 2.09 (*s*, 3H, CH_3–CO at C-6), 4.43 (*d*, $J = 8$ Hz, 1H, H-1''), 4.59 (*d*, $J = 8$ Hz, 1H, H-1''') 4.87 (*d*, $J = 2$ Hz, 1H, H-1'), 6.32 (*d*, $J = 10$ Hz, 1H, H-23), 7.32 (*d*, $J = 2$ Hz, 1H, H-21), 8.00 (*dd*, $J_{21,22} = 2$ Hz, $J_{22,23} = 10$ Hz, 1H, H-22). ^{13}C NMR: see Table 1.

5α - 4,5 - *Dihydro* - 12β - *scillirosidin* - 3 - O - α - L - *thevetoside* (**36**). FAB-MS: NIFAB-MS: *m/z* 635 $[M - H]^-$, 593 $[M - H - 42]^-$, 475 $[M - H - 160]^-$, 433 $[M - H - 160 - 42]^-$, 415 $[M - H - 160 - 42 - 18]^-$. PIFAB-MS: *m/z* 637 $[MH]^+$, 577 $[MH - 60]^+$, 477 $[MH - 160]^+$, 417 $[MH - 160 - 60]^+$, 399 $[MH - 160 - 60 - 18]^+$. ^1H NMR: δ 0.81 (*s*, 3H, H_3-18), 1.24 (*s*, 3H, H_3-19), 1.26 (*d*, $J = 6$ Hz, 3H, H_3-6'), 2.09 (*s*, 3H, CH_3–CO at C-6), 3.67 (*s*, 1H, CH_3–O at C-3'), 4.89 (*d*, $J = 2$ Hz, 1H, H-1'), 6.30 (*d*, $J = 10$ Hz, 1H, H-23), 7.40 (*d*, $J = 2$ Hz, 1H, H-21), 7.93 (*dd*, $J_{21,22} = 2$ Hz, $J_{22,23} = 10$ Hz, 1H, H-22]. ^{13}C NMR: see Table 1.

5α-4,5-*Dihydro*-12β-*hydroxy*-*scillirosidin*-3-O-α-L-*thevetosido*-1''→4'-β-D-*glucoside* (**37**). FAB-MS: NIFAB-MS: *m/z* 797 $[M - H]^-$, 593 $[M - H - 162 - 42]^-$, 475 $[M - H - 162 - 160]^-$, 433 $[M - H - 160 - 162 - 42]^-$, 415 $[M - H - 160 - 162 - 42 - 18]^-$, 379 $[M - H - 160 - 162 - 42 - 18 - 18 - 18]^-$. PIFAB-MS: *m/z* 799 $[MH]^+$, 637 $[MH - 162]^+$, 477 $[MH - 162 - 160]^+$, 417 $[MH - 162 - 160 - 60]^+$, 399 $[MH - 162 - 160 - 60 - 18]^+$. ^1H NMR: δ 0.81 (*s*, 3H, H_3-18), 1.24 (*s*, 3H, H_3-19), 1.30 (*d*, $J = 6$ Hz, 3H, H_3-6'), 2.10 (*s*, 3H, CH_3–CO at C-6), 3.73 (*s*, 1H, CH_3–O at C-3'), 4.58 (*d*, $J = 8$ Hz, H-1''), 4.89 (*d*, $J = 2$ Hz, 1H, H-1'), 6.34 (*d*, $J = 10$ Hz, 1H, H-23), 7.46 (*d*, $J = 2$ Hz, 1H, H-21), 7.98 (*dd*, $J_{21,22} = 2$ Hz, $J_{22,23} = 10$ Hz, 1H, H-22). ^{13}C NMR: see Table 1.

5α-4,5-*Dihydro*-16β-*hydroxy*-*scillirosidin*-3-O-α-L-*thevetoside* (**38**). FAB-MS: NIFAB-MS: *m/z* 635 $[M - H]^-$, 475 $[M - H - 160]^-$. PIFAB-MS: *m/z* 637 $[MH]^+$, 477 $[MH - 160]^+$. ^1H NMR: δ 0.93 (*s*, 3H, H_3-18), 1.20 (*s*, 3H, H_3-19), 1.24 (*d*, $J = 6$ Hz, 3H, H_3-6'), 2.08 (*s*, 3H, CH_3–CO at C-6), 2.70 (*d*, $J = 10$ Hz, 1H, H-17), 3.67 (*s*, 1H, CH_3–O at C-3'), 4.92 (*d*, $J = 2$ Hz, 1H, H-1'), 5.16 (*s*, 1H, H-6), 6.30 (*d*, $J = 10$ Hz, 1H, H-23), 7.30 (*d*, $J = 2$ Hz, 1H, H-21), 7.95 (*dd*, $J_{21,22} = 2$ Hz, $J_{22,23} = 10$ Hz, 1H, H-22). ^{13}C NMR: see Table 1.

5α-4,5-*Dihydro*-16β-O-*acetyl*-*scillirosidin*-3-O-α-L-*thevetosido*-1'',4'-β-D-*glucoside* (**39**). FAB-MS: NIFAB-MS: *m/z* 839 $[M - H]^-$, 677 $[M - H - 162]^-$, 635 $[M - H - 162 - 42]^-$, 593 $[M - H - 162 - 42 - 42]^-$, PIFAB-MS: *m/z* 841 $[MH]^+$, 679 $[MH - 162]^+$, 519 $[MH - 162 - 160]^+$, 459 $[MH - 162 - 160 - 60]^-$, 459 $[MH - 162 - 160 - 42 - 18]^+$, 441 $[MH - 162 - 160 - 42 - 18 - 18]^+$. ^1H NMR: δ 0.93 (*s*, 3H, H_3-18), 1.20 (*s*, 3H, H_3-19), 1.29 (*d*, $J = 6$ Hz, 3H, H_3-6'), 1.89 (*s*, 3H, CH_3–CO at C-16), 2.09 (*s*, 3H, CH_3–CO at C-6), 2.90 (*d*, $J = 9$ Hz, 1H, H-17), 3.68 (*s*, 1H, CH_3–O at C-3'), 4.56 (*d*, $J = 8$ Hz, H-1''), 4.87 (*d*, $J = 2$ Hz, 1H, H-1'), 5.13 (*s*, 1H, H-6), 6.24 (*d*, $J = 10$ Hz, 1H, H-23), 7.33 (*d*, $J = 2$ Hz, 1H, H-21), 8.22 (*dd*, $J_{21,22} = 2$ Hz, $J_{22,23} = 10$ Hz, 1H, H-22). ^{13}C NMR: see Table 1.

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