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BUFADIENOLIDES FROM ANIMAL AND PLANT SOURCES*

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Key Word Index—bufadienolide; structure elucidation; occurrence; plant and animal kingdom.

Abstract—Naturally occurring bufadienolides, which were isolated from both animal and plant sources and structurally elucidated in the period from 1967–1995, are reviewed and compiled.

INTRODUCTION

Bufadienolides are cardioactive C-24 steroids. The efficacy of these substances was already known by the ancient Egyptians who used squill, a bufadienolide-containing plant, in the treatment of heart diseases [1]. Scillaren A (**125**), one of the main glycosides from this source, was the first bufadienolide, the structure of which was elucidated unambigously in 1933 [2]. In the following years several of these steroids deriving from plants or animals were structurally elucidated [1, 3]. Since the survey of Hoch [3] due to the improvements of chromatographic and spectroscopic techniques the structures of numerous bufadienolides were established. The present review summarizes more than 250 naturally occurring substances, the structures of which were elucidated unambiguously, published from 1967–1995.

The main topics of the paper are the occurrence of bufadienolides in nature and new structures. Known compounds are only considered if they were described in a new source or when accompanying new substances in material in which they have been proved already. Additionally we give some information on the separation techniques used for the isolation of the pure compounds as well as about new methods for structure elucidation.

OCCURRENCE OF BUFADIENOLIDES IN NATURE

Bufadienolides have been proved in only few animal and plant families (see Tables 1 and 2). In the animal kingdom, these substances are most widespread in the Bufonidae: From the venom of about ten *Bufo* species bufadienolides and their esters were established [4–28]. The toad venom of different species is used for the preparation of the Asian remedies Ch'an Su and Senso [29, 30]. Investigations on the effective substances of Ch'an Su resp. Senso lead also to the isolation and characterization of numerous bufadienolides [29–40], which for a complete compilation of these substances are included in this review. In only one representative of the Colubridae bufadienolides were proved: from the nucho-dorsal glands of the snake *Rhabdophis tigrinus* several genins were isolated and structurally elucidated [41, 42]. The first bufadienolides from an arthopod source were identified in three *Photinus* species (Lampyridae) [43, 44].

In the plant kingdom cardiac glycosides seem to be restricted to angiosperms, until now bufadienolides are found in six families: Crassulaceae, Hyacinthaceae, Iridaceae, Melianthaceae, Ranunculaceae and Santalaceae. The highest number and variety of substances have been proved in Hyacinthaceae in the genera *Urginea* and *Drimia*. More than 100 different compounds—genins and glycosides—were isolated and identified from various species [45–69]. In the Ranunculaceae only *Helleborus* contains bufadienolides. In more than 15 species mainly a simple bufadienolide pattern was detected [70–79]. In the other families these compounds occur in only few species. In Tables 1 and 2 the families, genus and

* Dedicated to Prof. Dr. Gerhard Franz, University of Regensburg, on the occasion of his 60th birthday.

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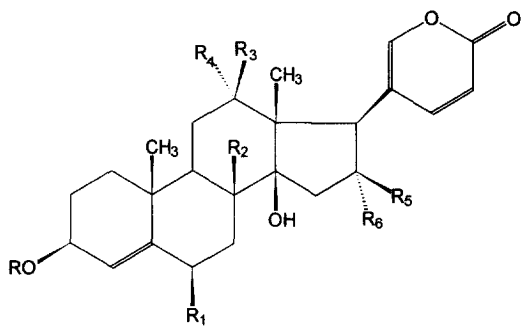


Compound	R	R_1	R_2	R_3	R_4	R_5	R_6
scillarenin (122)	-H	-H	-H	-H	-H	-H	-H
proscillaridin A (123)	-Rha	-H	-H	-H	-H	-H	-H
scillarenin-3-O-β-D-glucoside (124)	-Glc	-H	-H	-H	-H	-H	-H
scillaren A (125)	-Rha-Glc	-H	-H	-H	-H	-H	-H
scillarenin-bis-rhamnoside(126)	-Rha-Rha	-H	-H	-H	-H	-H	-H
scillarenin-3-O-α-L-(2′, 3′-diacetyl)-rhamnosido-β-D-glucoside (127)	-(2′,3′-OAc)-Rha-Glc	-H	-H	-H	-H	-H	-H
scillarenin-3-O-β-D-glucosido-β-D-glucoside (128)	-Glc-Glc	-H	-H	-H	-H	-H	-H
scillarenin-3-O-α-L-rhamnosido-3′-α-L-rhamnosido-4′-β-D-glucoside (129)	-Rha-3′-Rha-4′-Glc	-H	-H	-H	-H	-H	-H
scillarenin-3-O-α-L-rhamnosido-β-D-glucosido-3′′-β-D-glucoside (130)	-Rha-Glc-3′′-Glc	-H	-H	-H	-H	-H	-H
glucoscillaren A (131)	-Rha-Glc-Glc	-H	-H	-H	-H	-H	-H
scillarenin-3-O-α-L-rhamnosido-β-D-glucosido-6′′-β-D-glucoside (132)	-Rha-Glc-6′′-Glc	-H	-H	-H	-H	-H	-H
scillarenin-3-O-α-L-(2′, 3′-diacetoxy)-rhamnosido-β-D-glucosido-3"-β-D-glucoside (133)	-(2′,3′-OAC)-Rha-Glc-3′′-Glc	-H	-H	-H	-H	-H	-H
scillarenin-3-O-α-L-(2′, 3′-diacetoxy)-rhamnosido-β-D-glucosido-6-D-glucoside (134)	-(2′,3′-OAC)-Rha-Glc-Glc	-H	-H	-H	-H	-H	-H
scillirubrosidin (135)	-H	-H	-OH	-H	-H	-H	-H
scillirubrosidin-3-O-α -L-rhamnoside (136)	-Rha	-H	-OH	-H	-H	-H	-H
scillirubroside (137)	-Glc	-H	-OH	-H	-H	-H	-H
scillirubrosidin-3-O-β-D-glucosido-β-D-glucoside (138)	Glc-Glc-	-H	-OH	-H	-H	-H	-H
scillirubrosidin-3-O-α -L-rhamnosido-β-D-glucosido-β-D-glucoside (139)	Rha-Glc-Glc	-H	-OH	-H	-H	-H	-H
12-epi-scilliphaeoside (140)	-Rha	-H	-H	-H	-OH	-H	-H
12-epi-scilliphaeosidin-3-O-β-D-glucoside (141)	-Glc	-H	-H	-H	-OH	-H	-H
12-epi-scilliphaeosidin-3-O-α-L-birhamnoside (142)	-Rha-Rha	-H	-H	-H	-OH	-H	-H
12-epi-gluco-scilliphaeoside (143)	-Rha-Glc	-H	-H	-H	-OH	-H	-H
scilliphaeosidin (144)	-H	-H	-H	-OH	-H	-H	-H
scilliphaeoside (145)	-Rha	-H	-H	-OH	-H	-H	-H
scilliphaeosidin-3-O-β-D-glucoside (146)	-Glc	-H	-H	-OH	-H	-H	-H

glucoscilliphaeoside (147)	-Rha-Glc	-H	-H	-OH	-H	-H	-H
scilliphaeosidin-3-O-α-L-rhamnosido-β-D-glucosido-3′′-β-D-glucoside (148)	-Rha-Glc-3′′-Glc	-H	-H	-OH	-H	-H	-H
scilliphaeosidin-3-O-α-L-rhamnosido-β-D-glucosido-β-D-glucoside (149)	-Rha-Glc-Glc	-H	-H	-OH	-H	-H	-H
16-α-hydroxy-scillarenin-3-O-α-L-rhamnoside (151)	-Rha	-H	-H	-H	-H	-H	-OH
16-β-hydroxy-scillarenin-3-O-α-L-rhamnoside (152)	-Rha	-H	-H	-H	-H	-OH	-H
16-β-hydroxy-scillarenin-3-O-β-D-glucoside (153)	-Glc	-H	-H	-H	-H	-OH	-H
16-β-hydroxy-scillarenin-3-O-α-L-rhamnosido-β-D-glucosido-β-D-glucoside (154)	-Rha-Glc-Glc	-H	-H	-H	-H	-OH	-H
16-β-acetoxy-scillarenin-3-O-α-L-rhamnoside (155)	-Rha	-H	-H	-H	-H	-OAc	-H
16-β-acetoxy-scillarenin-3-O-β-D-glucoside (156)	-Glc	-H	-H	-H	-H	-OAc	-H
16-β-acetoxy-scillarenin-3-O-β-D-glucosido-β-D-glucoside (157)	-Glc-Glc	-H	-H	-H	-H	-OAc	-H
16-β-acetoxy-scillarenin, 3-O-α-L-glucomethyloside-β-D-glucosido-β-D-glucoside (158)	-Glum-Glc-Glc	-H	-H	-H	-H	-OAc	-H
16-β-acetoxy-scillarenin-3-O-α-L-rhamnosido-β-D-glucosido-β-D-glucoside (159)	Rha-Glc-Glc	-H	-H	-H	-H	-OAc	-H
6-desacetyl-scillirosidin (162)	-H	-OH	-OH	-H	-H	-H	-H
6-desacetyl-scillirosidin-3-O-α-L-rhamnoside (163)	-Rha	-OH	-OH	-H	-H	-H	-H
6-desacetyl-scilliroside (164)	-Glc	-OH	-OH	-H	-H	-H	-H
scillirosidin (165)	-H	-OAc	-OH	-H	-H	-H	-H
scilliroside (166)	-Rha	-OAc	-OH	-H	-H	-H	-H
glucosyl-scilliroside (167)	-Glc	-OAc	-OH	-H	-H	-H	-H
12-β-hydroxy-scillirubrosidin-3-O-α-L-rhamnoside (169)	-Rha	-H	-OH	-OH	-H	-H	-H
16-β-acetoxy-scillirubroside (171)	-Glc	-H	-OH	-H	-H	-OAc	-H
12-β-hydroxy-6-desacetyl-scillirosidin (174)	-H	-OH	-OH	-OH	-H	-H	-H
12-β-hydroxy-6-desacetyl-scillirosidin-3-O-β-D-glucoside (175)	-Glc	-OH	-OH	-OH	-H	-H	-H
12-β-hydroxy-scillirosidin (176)	-H	-OAc	-OH	-OH	-H	-H	-H
12-β-hydroxy-scilliroside (177)	-Glc	-OAc	-OH	-OH	-H	-H	-H

Table 1. Animal families containing bufadienolides

BUFONIDAE

Bufo americanus [4, 5], *Bufo asper* Gravenhorst [6], *Bufo bankorensis* Borbour [7], *Bufo bufo gargarizans* Cantor [8, 9], *Bufo ictericus* Spix [10], *Bufo marinus* (L.) Schneider [11–13], *Bufo melanostictus* Schneider [14–16], *Bufo viridis* Laur. [17, 18], *Bufo vulgaris formosus* Boulenger [19–28]

COLUBRIDAE

Rhabdophis tigrinus [41, 42]

LAMPYRIDAE

Photinus ignitus [43], *Photinus marginellus* [43], *Photinus pyralis* [44].

Table 2. Plant families containing bufadienolides

CRASSULACEAE
Bryophyllum pinnatum [82, 92], *Bryophyllum tubiflorum* Harv. [94, 105], *Cotyledon orbiculata* L. var. *orbiculata* [89], *Kalanchoe diagremontiana* Hamet et Perr. [83], *Kalanchoe lanceolata* (Forssk.) Pers. [106, 107], *Kalanchoe tomentosa* [101], *Tylecodon grandiflorus* (Burm. F) Toelken [90, 93], *Tylecodon wallichii* (Harv.) Toelken subsp. *wallichii* = *Cotyledon wallichi* Harv. [88]

HYACINTHACEAE
Drimia robusta Baker [45], *Urginea altissima* Baker = *Drimia altissima* (L.f.) Ker-Gawl. [46, 47], *Urginea aphylla* (Forskal) Speta [48], *Urginea burkei* Baker [49], *Urginea epigea* R. A. Dyer [50], *Urginea hesperia* Webb and Berth. [51], *Urginea indica* (Roxb.) Kunth [52–55], *Urginea maritima* (L.) Baker [56–60], *Urginea maritima* (L.) Baker s.str. [61–63], *Urginea numidica* (Jord. and Fourr.) Grey [64], *Urginea pancration* Steinh. [65, 66], *Urginea physodes* (Jacq.) Bak. [67], *Urginea rubella* Bak. [68], *Urginea sanguinea* Schinz [69]

IRIDACEAE
Homeria glauca (Woods and Evans) N.E.Br. [84, 85, 104], *Morea graminicola* [108], *Morea polystachya* [108]

MELIANTHACEAE
Bersama abyssinica Fresen. [80, 81, 86, 87, 102, 109], *Bersama absyssinica* subsp. *abyssinica* Verdc. [110], *Bersama abyssinica* subsp. *paullinioides* (Planch) Verdc. [110], *Melianthus comosus* Vahl. [100, 103, 111, 112]

RANUNCULACEAE
Helleborus abchasicus [70], *Helleborus atrorubens* Waldst. and Kit. [71–73], *Helleborus bocconei* Ten. subsp. *siculus* (Schiffner) Merxm. and Podl. [74], *Helleborus croaticus* Martinis [73], *Helleborus cyclophyllus* Boiss. [74], *Helleborus dumetorum* Waldst. and Kit. [72, 74, 75], *Helleborus dumetorum* ssp. *altrorubens* (Waldst. and Kit.) Merxm. and Podl. [74, 75], *Helleborus istriacus* (Schiffn.) Borb. [71–73], *Helleborus macranthus* Freyn. [71–73]. *Helleborus multifidus* Vis. subsp. *istriacus* (Schiffner) Merxm. and Podl. [71, 76], *Helleborus multifidus* Vis. [72–74], *Helleborus niger* L. [73, 77], *Helleborus odorus* Waldst. and Kit. [72–74, 78, 79], *Helleborus orientalis* Lam. [74], *Helleborus purpurascens* Waldst. and Kit. [74], *Helleborus viridis* L. [74, 75], *Helleborus viridis* spp. *occidentalis* Reuter (Schiffner) [74, 75]

SANTALACEAE
Thesium lineatum [113]

species in one family are listed in alphabetical order; to correspond with the references, the species are cited either with or without the author's name.

ISOLATION OF BUFADIENOLIDES FROM ANIMAL AND PLANT SOURCES

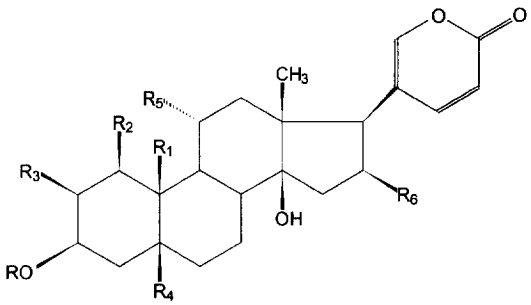
For the isolation of bufadienolides the classic methods of extraction, partition and column chromatography are followed by efficient chromatographic techniques like HPLC or DCCC for the purification of the fractions in most cases. In column chromatography silica gel and Sephadex®-LH 20 as stationary phases proved most successful, but also neutral alumina [80, 81] or dry CC on silica gel [20, 33] were employed.

Polar substances like bufotoxins from different *Bufo* species were isolated by fractionation of polar extracts on Amberlite® XAD-2 [6, 8, 16, 21–23] as well as on Amberlite® XAD-4 [11]. For the purification of bufotoxins HPLC on RP-18 phases with methanol–water [8, 26, 28] or CH_3CN–water resp. CH_3CN–$(NH_4)_2CO_3$ as mobile phase [7, 15, 16] was applied. HPLC on RP-18 phases was also employed in the isolation of bryophillin A (**207**) and bersaldegenin-3-acetate (**197**) from *Bryophyllum pinnatum* [82], of daigremontianin (**212**), daigreorigenin-acetate (**114**) and three bersaldegenin-acetates (**196–198**) from *Kalanchoe daigremontiana* [83].

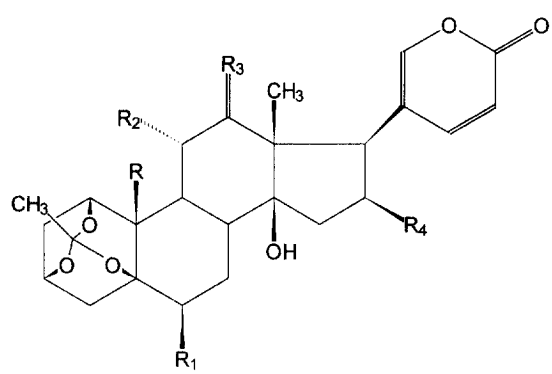
After sonification of the nucho-dorsal glands of *Rhabdophis tigrinus* with 5% CH_3CN 10 highly hydroxylated genins were isolated by HPLC on Lichrosorb RP-8 with CH_3CN–water mixtures [42]. Numerous bufadienolide glycosides were obtained from *Urginea maritima* [59, 60] and from *Urginea pancration* [65] by DCCC using chloroform–methanol–water (5:10:6) by ascent. DCCC was also used in the investigations of *Helleborus* species [77, 79], resulting in the isolation of 11α-hydroxy-desglucohellebrin (**202**) from *Helleborus odorus* using chloroform–methanol–water 2:3:2 by ascent [79].

STRUCTURE ELUCIDATION

In the structure elucidation of bufadienolides during the last two decades derivatisations, elemental analysis and partial synthesis, which were formerly chiefly used for the characterization of these compounds [4, 19, 21, 22, 32, 84–87], have been replaced by new NMR methods. Besides ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy plays a distinctive role in the assignment of stereochemistry of bufadienolides. By the application of modern pulse techniques like *J*-modulation, INEPT, DEPT and APT and especially two-dimensional methods, particularly ^{1}H, ^{1}H-correlation spectroscopy, ^{13}C,^{1}H-COSY and ^{13}C,^{1}H-long-range COSY, not only the sequence and configuration of the glycosides in the sugar moiety but also the nature of the genin present in a bufadienolide are unambiguously characterized. Nuclear



Compound	R	R_1	R_2	R_3	R_4	R_5	R_6
daigredorigenin-3-acetate (114)	-ac	$-CH_3$	-OH	-H	-OH	-H	-H
19-hydroxy-bufalin (88)	-H	$-CH_2OH$	-H	-H	-H	-H	-H
19-hydroxy-bufalin-3-O-suberoyl-L-histidine-ester (89)	-sub-hist-1	$-CH_2OH$	-H	-H	-H	-H	-H
19-hydroxy-bufalin-3-O-suberoyl-L-3-methylhistidine-ester (90)	-sub-hist-3	$-CH_2OH$	-H	-H	-H	-H	-H
hellebrigenol = 19-hydroxy-telocinobufagin (92)	-H	$-CH_2OH$	-H	-H	-OH	-H	-H
11-α,19-dihydroxy-telocinobufagin (95)	-H	$-CH_2OH$	-H	-H	-OH	-OH	-H
hellebrigenin = bufotalidine (99,185)	-H	-CHO	-H	-H	-OH	-H	-H
hellebritoxin (100)	-sub-2	-CHO	-H	-H	-OH	-H	-H
deglucohellebrin= coreliborin K (186)	-Rha	-CHO	-H	-H	-OH	-H	-H
hellebrigenin-3-O-β-D-glucoside (188)	-Glc	-CHO	-H	-H	-OH	-H	-H
physodine A (187)	-Digt	-CHO	-H	-H	-OH	-H	-H
hellebrin (189)	-Rha-Glc	-CHO	-H	-H	-OH	-H	-H
glucohellebrin (190)	-Rha-Glc-Glc	-CHO	-H	-H	-OH	-H	-H
hellebrigenin-3-O-acetate (191)	-ac	-CHO	-H	-H	-OH	-H	-H
hellebrigenin-3-β, 5-β-diacetate (192)	-ac	-CHO	-H	-H	-OAc	-H	-H
lanceotoxin B (193)	-Rha	-CHO	-H	-H	-OAc	-H	-H
thesiuside (194)	-Glc	-CHO	-H	-H	-OAc	-H	-H
lanceotoxin A (195)	2′α,3′β,4′β,5′α-hexanoyl	-CHO	-H	-H	-OAc	-H	-H
bersaldegenin-1-acetate (196)	-H	-CHO	-OAc	-H	-OH	-H	-H
bersaldegenin-3-acetate (197)	-ac	-CHO	-OH	-H	-OH	-H	-H
kalanchoside (200)	-(2′-OAc)-Thev-Rha	-CHO	-H	-OAc	-OH	-H	-H
physodine B (201)	-Glc-(2′-OAc)-Rha	-CHO	-H	-OAc	-OH	-H	-H
11-α-hydroxy-desglucohellebrin (202)	-Rha	-CHO	-H	-H	-OH	-OH	-H
16-β-hydroxy-hellebrigenin (203)	-H	-CHO	-H	-H	-OH	-H	-OH
16-β-hydroxy-hellebrigenin-3-O-β-D-glucoside (204)	-Glc	-CHO	-H	-H	-OH	-H	-OH
16-β-hydroxy-bersaldegenin-3-acetate (209)	-ac	-CHO	-OH	-H	-OH	-H	-OH



Compound	R	R_1	R_2	R_3	R_4
bersamagenin-1-β, 3-β, 5-β-orthoacetate (115)	$-CH_3$	-H	-H	-H,H	-H
16-β-hydroxy-bersamagenin-1-β, 3-β, 5-β-orthoacetate (121)	$-CH_3$	-H	-H	-H,H	-OH
melianthusigenin (182)	$-CH_2OAc$	-H	-H	-H,H	-H
bryotoxin B (183)	$-CH_2OH$	-H	-OH	=O	-H
melianthugenin = bersaldegenin-1-β, 3-β, 5-β-orthoacetate (198)	-CHO	-H	-H	-H,H	-H
6-β-O-acetyl-melianthugenin (205)	-CHO	-OAc	-H	-H,H	-H
bryophyllin A = bryotoxin C (207)	-CHO	-H	-OH	-H,H	-H
16-β-hydroxy-melianthugenin (210)	-CHO	-H	-H	-H,H	-OH
daigremontianin (212)	-CHO	-H	-OH	=O	-H

Overhauser effect (NOE) difference spectroscopy, which provides information about the relationships of protons in space, is another additional tool in the structure elucidation of cardiac glycosides. Most of the compounds isolated from *Urginea* species were identified by ^{1}H NMR spectroscopy and *J*-modulated ^{13}C-NMR spectroscopy [45, 48, 49, 51, 54, 55, 59, 60, 62–66, 69].

Two-dimensional techniques were mainly applied in the structure elucidation of bufadienolide gly-

cosides with multiple ether bridges between the genin and the carbohydrate moiety from Crassulaceae. For cotyledoside (**238**) the assignment of the ^{1}H NMR signals was performed by extensive $^{1}H,^{1}H$ homonuclear decoupling experiments, that of the ^{13}C NMR spectrum on the basis of broad band proton-decoupled and single frequency off-resonance proton-decoupled experiments. The stereochemistry of the carbohydrate moiety resulted from the measurement of NOEs [88]. ^{1}H, ^{1}H-COSY, $^{13}C,^{1}H$-COSY and $^{13}C,^{1}H$-long-range COSY were employed for the characterization of bryophyllin B (**208**) [82]. Orbicosides A–C (**259–261**) were identified in a similar way, additionally difference NOE experiments and SPI experiments to detect three bond coupling were used [89]. These techniques lead also to the structure elucidation of the tyledosides (**253–258**) [90] and of rubellin (**181**) [68].

Crystallography was used in the determination of the stereochemistry of aglycones or monoglycosides. Gamabufotalin (**30**) and arenobufagin (**72**), both isolated from Ch'an Su as hydrogen-suberate and recrystallized from methanol–ethyl acetate (1:1) were investigated by this method (38) as well as proscillaridin (**123**) crystallized from methanol [91]. The confirmation of the structures of bryophyllin A (**207**), daigremontianin (**212**) and tyledoside A (**257**), was also performed by single-crystal X-ray analysis [83, 92, 93].

In mass spectrometry especially in the determination of higher glycosides, FAB-mass spectrometry has replaced El- and FD-mass spectroscopy because of the additional information about the position of the sugars in the chain by the characteristic fragmentation pattern. Thus FAB-mass spectrometry was employed in the determination of most of the *Urginea* bufadienolide glycosides [45, 48, 49, 51, 54, 55, 59, 60, 62–66, 69]. For the structure elucidation of bryotoxin B (**183**) and C (**207**) the molecular formula assigned by El-mass spectrometry was ensured by DCI-MS [94].

GC-mass spectrometry has proved as important tool for the determination of the sugar moieties and their specific linkages in naturally occurring glycosides. Usually the alditol acetates, obtained by hydrolysis of the permethylated compounds, followed by reduction and acetylation, are analysed [95, 96]. Much more information is provided by direct trimethylsilylation without reduction of the hydrolysed products of permethylation [97]: In GC two representative peaks corresponding to both anomeric sugar configurations with a constant relation of the peak area are detected for each monosaccharide which in addition to the retention times facilitates the identification of the sugar components [98, 99]. Depending on the number and position of methyl and trimethylsilyl groups in the monosaccharide unit, characteristic fragmentation patterns are observed in the mass spectrum [97].

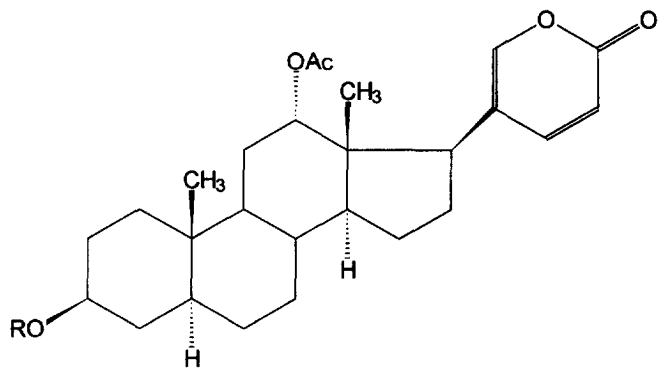
By this method and additional 2D-NOESY, scillarenin-3-*O*-α-L-rhamnosido-(3′-α-L-rhamnosyl)-4′-β-D-glucoside (**129**) and scilliglaucosidin-3-*O*-α-L-rhamnosido-(3′-α-L-rhamnosyl)-4′-β-D-glucoside (**224**) were unambiguously identified as the first cardiac glycosides with branched sugar chains [50].

STRUCTURAL VARIABILITY

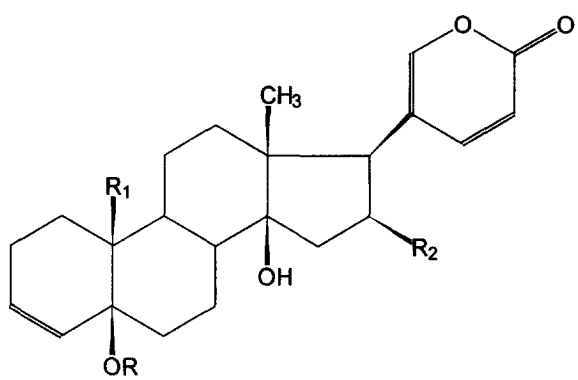
Bufadienolides are C-24 steroids, the characteristic structural feature of which is a doubly unsaturated six-membered lactone ring (α-pyrone) in position 17β. Furthermore these compounds are characterized by the *trans*-junction of rings B and C and usually the *cis*-junction of rings C and D (see Fig. 1). Physodine C (**233**) and D (**234**) from *Urginea physodes* are the first natural occurring bufadienolides with a *trans*-junction between rings C and D. Additionally these two substances do not have an oxygen function at position 14 [67]. The presence of a 14β hydroxy group or a 14,15β-epoxy group had earlier been assumed to be an integral part of the natural genins. Another group of substances without a 14β oxygen function are 14-deoxy-15,16β-epoxy-melianthugenin (**199**) and 6β-*O*-acetyl-14-deoxy-15,16β-epoxy-melianthugenin (**206**) from *Melianthus comosus* [100] and the bufa-14,20.22-trienolides abyssinin (**215**), abyssinol A (**213**), B (**184**) and C (**214**) from *Bersama abyssinica* [81] as well as 3β,5β,16β-trihydroxy-bufa-14,20,22-trienolide (**67**) from *Rhabdophis tigrinus* [42].

Besides the latter rare $\Delta^{14,15}$ compounds, bufadienolides can contain double bonds mainly at the 4(5) or more rarely at the 3(4) or 6(7) positions. From *Urginea indica* two 19-nor substances (**107**, **108**) with a 5(10) olefinic structure were isolated, which in addition are the only compounds with a 4-oxo group [55]. Bufatetraenolides known until now are helleborogenone (**267**) from different *Helleborus* species (71–74) and scillaridine (**266**) from *Urginea* species [49, 61].

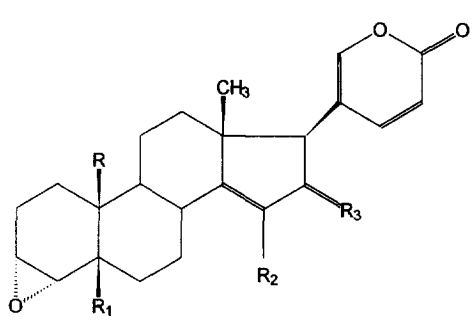
The large variety of known genins is chiefly due to the number and position of substituents. In bufadienolides hydroxy, epoxy, acetoxy, oxo and in only few compounds methoxy or formyloxy groups were proved. Common in the substitution pattern of bufadienolides is the attachment of hydroxy moieties in position 3β, 5β, 6β, 8β, 11α, 12α, 12β, 14β, 16β and 19, of acetoxy units in 3β, 5β, 6β and 16β and oxo-groups in 3, 11, 12 and 19. Rather unusual is the α-configuration of the hydroxy unit at C-3 or the attachment of these substituents in position 4β (**16**) [37], 7β (**61, 62**) [41, 42] and 15β (**37**) [37], the latter have been reported from animal sources only. From *Urginea* species the first bufadienolides with a 9-OH (**172**) [60], 11β-OH (**162**) [57], respectively, and a 16α-OH moiety (**151**) [55] were isolated. Very rarely described are 2β hydroxy or acetoxy units [44, 67, 101]. 2α-hydroxy moieties only occur in compounds which contain doubly linked carbohydrate units via 2α,3β like for example orbicusides (**259–261**) [89], cotyledoside (**238**) [88] or rubellin (**181**) [68]. A 1,3,5-



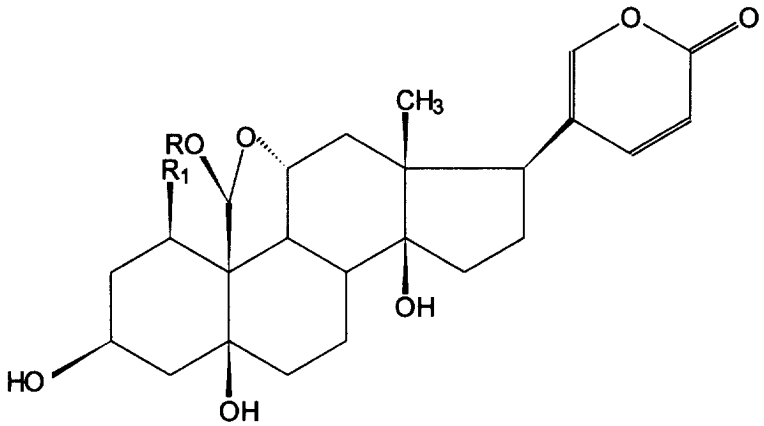
Compound	R
physodine C (**233**)	-Rha-(4→1)-Xyl
physodine D (**234**)	-(4´-OAc)-Rha-(3→1)-Glc



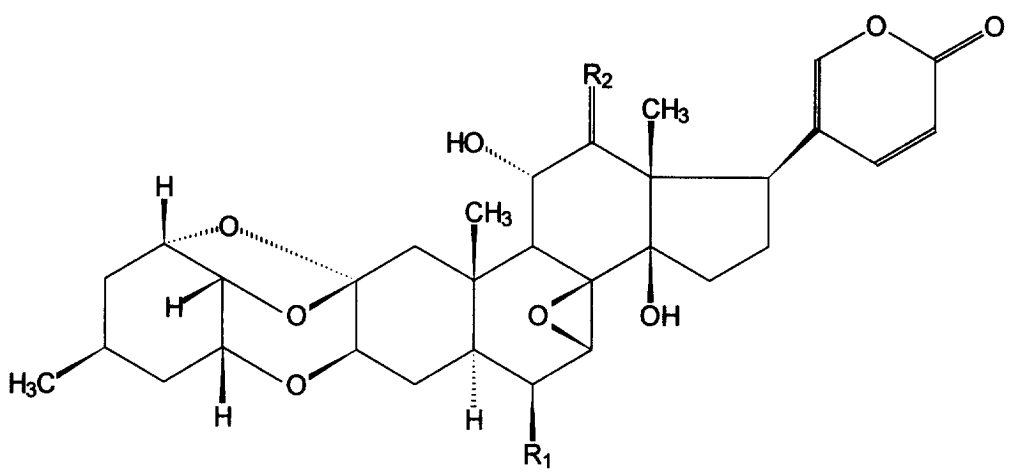
Compound	R	R_1	R_2
scilliglaucogenin (**216**)	-H	-CHO	-H
scilliglaucoside (**217**)	-Glc	-CHO	-H
bersenogenin (**218**)	-H	-CHO	-OH
scillicyanogenin (**219**)	-H	-CHO	-OAc
scillicyanoside (**220**)	-Glc	-CHO	-OAc
5-ß, 14-ß-dihydroxy-10-carboxy-5-ß, 14-ß-bufa-3, 20, 22-trienolide-5-O-ß-D-glucoside (**232**)	-Glc	-COOH	-H



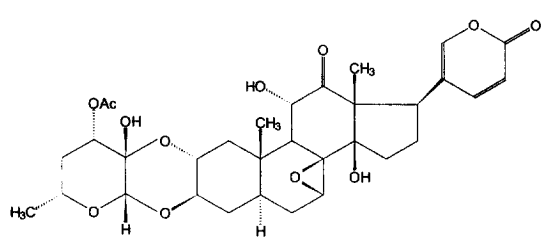
Compound	R	R_1	R_2	R_3
abyssinol B (**184**)	-CH_2OH	-OH	-OCH_3	-H,H
abyssinol A (**213**)	-CHO	-OH	-H	=O
abyssinin (**215**)	-CHO	-OAc	-OCH_3	=O



Compound	R	R_1
marinosin (**105**)	$-CH_3$	-H
bryophyllin B (**208**)	-H	-OAc



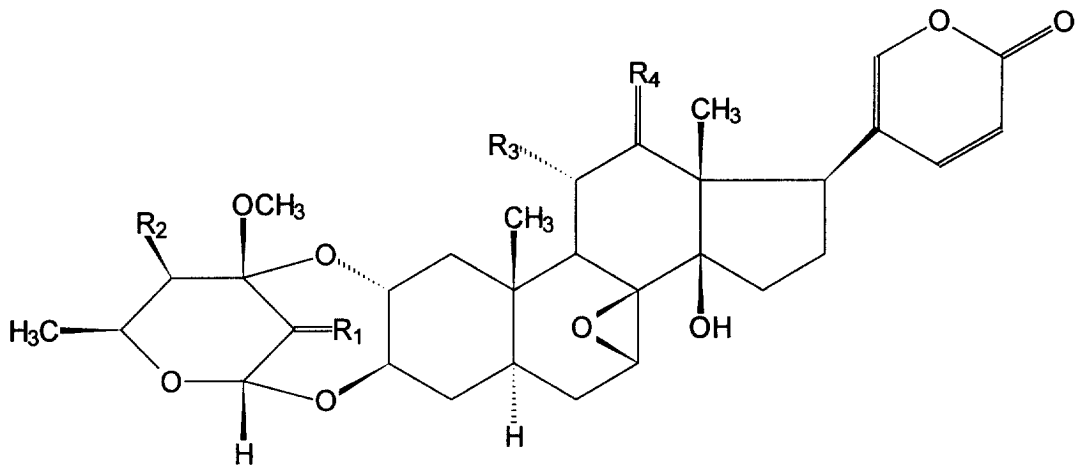
Compound	R_1	R_2
orbicuside B (**259**)	-H	-β-OH, -α-H
orbicuside A (**260**)	-H	=O
orbicuside C (**261**)	-OH	=O



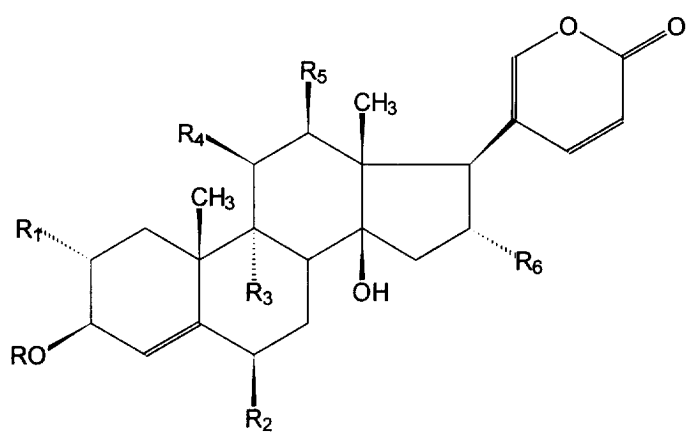
hyledoside C (**268**)

ortho-acetate group was determined in bufadienolides from *Bersama abessinica* (**115, 121, 198, 210**) [87, 102], but later on also proved in compounds from other sources [83, 94, 103] as well as 1β, 3β, 5β-hydroxylated substances [83, 103]. Physodine C and D (**233, 234**) besides their other special structural features (see above) are the first 12α acetoxy compounds [67], while only bersaldegenin-1-acetate (**196**) contains a 1β acetoxy group. In abyssinol A (**213**) and C (**214**) an oxo function appears in C-16 [81].

A 14β,15β epoxy function is common in substances from animal sources and until now not found in com-



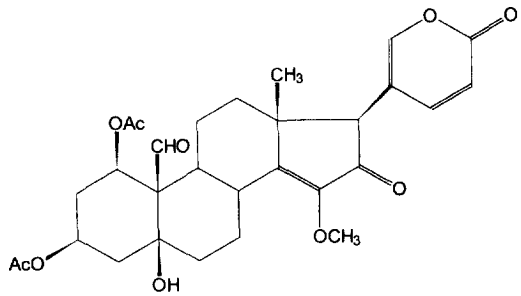
Compound	R_1	R_2	R_3	R_4
cotyledoside (**238**)	-α-OH, -β-H	-OH	-H	-H,H
tyledoside F (**253**)	-β-OH, -α-H	-H	-OH	-H,H
tyledoside B (**254**)	=O	-H	-OH	-H,H
tyledoside G (**255**)	-β-OH, -α-H	-H	-H	-β-OH, -α-H
tyledoside D (**256**)	-β-OH, -α-H	-H	-OH	=O
tyledoside A (**257**)	=O	-H	-OH	=O



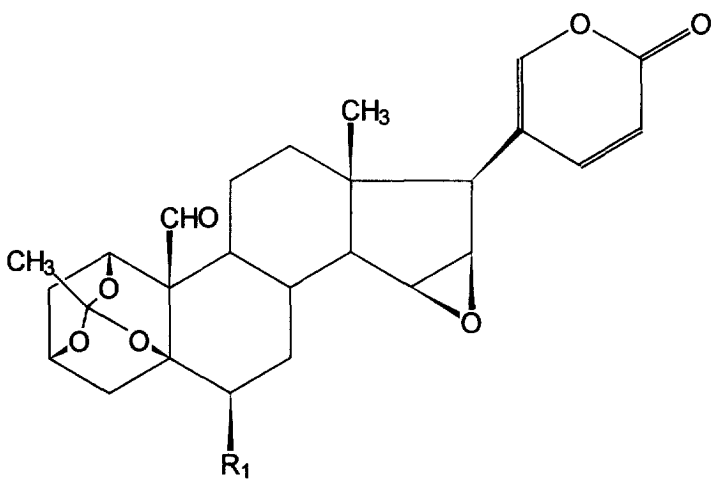
Compound	R	R_1	R_2	R_3	R_4	R_5	R_6
2-α, 3-β, 14-β, 16-α-tetrahydroxy-14-β-bufa-4, 20, 22-trienolide (**161**)	-H	-OH	-H	-H	-H	-H	-OH
6-β, 11-β-dihydroxy-scillarenin (**168**)	-H	-H	-OH	-H	-OH	-H	-H
9-hydroxy-scilliphaeoside (**172**)	-Rha	-H	-H	-OH	-H	-OH	-H

pounds from plants. In the latter such substituents very rarely are present in position 1α, 2α or 3α, 4α or 7β, 8β or 15β, 16β. Only abyssinin (**215**), abyssinol B (**184**) and C (**214**) from *Bersama abysssinica* [81] contain a methoxy moiety, 16β-formyl-oxy-bovogenin A (**264**) a formyloxy group [104].

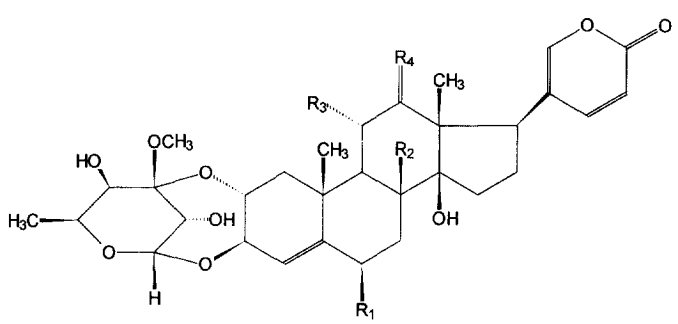
Apart from the hydroxy or oxo substitution at C-19, uncommon variations concerning this position were reported for bersaldegenin-11,19-half acetal (**208**) [82], marinosin (**105**) [13], a 19-*O*-methyl-11,19-half acetal, and 5β, 14β-dihydroxy-10-carboxy-5β, 14β-bufa-3, 20, 22-trienolide-5-*O*-β-D-glucoside (**232**) [55, 64], the first genuine bufadienolide with a 19-carboxyl function. Further numerous variations are possible concerning the substitution at the 3-hydroxy group. Animal sources besides genins usually contain bufadienolides esterified by carboxylic acids, dicarboxylic acids or sulphuric acid. The dicarboxylic acids in some cases are further conjugated to amino acids. Most frequently acetic, succinic, glutaric, adipic, pimelic



abyssinol C (**214**)



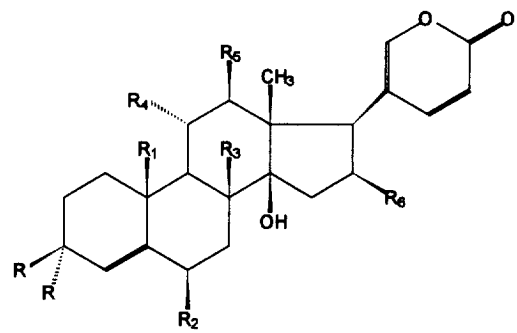
Compound	R_1
14-deoxy-15-β, 16-β-epoxy-melianthugenin (**199**)	-H
6-β-acetoxy-14-deoxy-15-β, 16-β-epoxy-melianthugenin (**206**)	-OAc



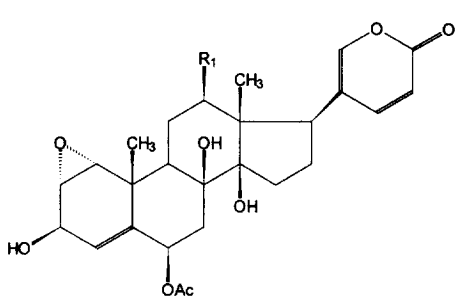
Compound	R_1	R_2	R_3	R_4
12-β,14-β-dihydroxy-2-α, 3-β-[tetrahydro-3'α, 5'β-dihydroxy-4'β-methoxy-6'-methyl-2-H-pyran-2', 4'-diylbisoxy]-bufa-4, 20, 22-trienolide (**160**)	-H	-H	-H	-β-OH,-α-H
6-β, 8-β, 12-β, 14-β-tetrahydroxy-2-α, 3-β-[tetrahydro-3', 5'-dihydroxy-4'-methoxy-6'-methyl-2H-pyran-2', 4'-diylbisoxy]-bufa-4, 20, 22-trienolide (**180**)	-OH	-OH	-H	-β-OH,-α-H
rubellin (**181**)	-OH	-OH	-OH	=O

and suberic acid are connected to the genin, the most common amino acid is arginine. In lucibufagins (**83**–**87**) also propionic and isobutyric acid were proved to be present [44]. In substances from *Bufo americanus*, glutamine occurred as an amino acid component [4, 5], while bufadienolides from *Bufo melanostictus* contain histidine, 1-methylhistidine and 3-methylhistidine [15, 16]. The bufadienolide-sulphates generally were isolated as sodium or ammonium salts.

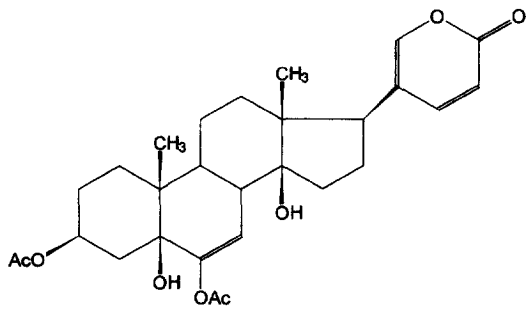
In plant sources, bufadienolides usually occur as glycosides with one to three sugars in a chain linked to the 3-hydroxy group. The first cardiac glycosides



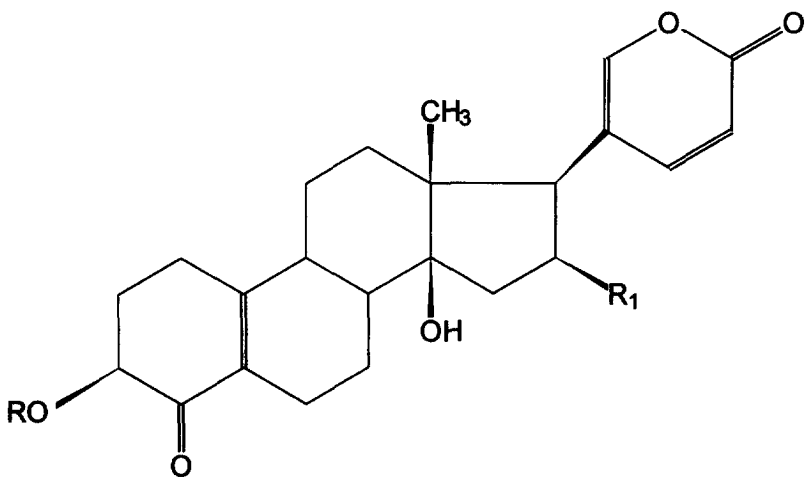
Compound	R	R_1	R_2	R_3	R_4	R_5	R_6
3-6, 10-6, 14-6-trihydroxy-19-nor-buta-4, 20, 22-trienolide-3-O-α-L-rhamnoside (168)	-6-O-Rha, -α-H	-OH	-H	-H	-H	-H	-H
3-oxo-scilliphaecidin = anhydro-scilliphaecidin (169)	=O	$-CH_3$	-H	-H	-H	-OH	-H
3-oxo-12-6-hydroxy-scillirubrosidin (170)	=O	$-CH_3$	-H	-OH	-H	-OH	-H
3-oxo-12-6-hydroxy-scillirosidin (178)	=O	$-CH_3$	-OAc	-OH	-H	-OH	-H
scilliglaucosidin (221)	-6-OH, -α-H	-CHO	-H	-H	-H	-H	-H
scilliglaucosidin-3-O-α-L-rhamnoside (222)	-6-O-Rha, -α-H	-CHO	-H	-H	-H	-H	-H
alloside (223)	-6-O-Glc, -α-H	-CHO	-H	-H	-H	-H	-H
scilliglaucosidin-3-O-α-L-rhamnosido-3´-α-L-rhamnosido-4´-6-D-glucoside (224)	6-O-Rha-3´-Rha-4´-Glc, -α-H	-CHO	-H	-H	-H	-H	-H
scilliglaucosidin-3-one (225)	=O	-CHO	-H	-H	-H	-H	-H
11-α-hydroxy-scilliglaucosidin-3-O-α-L-rhamnoside (226)	-6-O-Rha, -α-H	-CHO	-H	-H	-OH	-H	-H
12-6-hydroxy-scilliglaucosidin-3-O-6-D-glucoside (227)	-6-O-Glc, -α-H	-CHO	-H	-H	-H	-OH	-H
3-epi-benscillogenin (228)	-α-OH, -6-H	-CHO	-H	-H	-H	-H	-OH
benscillogenin (229)	-6-OH, -α-H	-CHO	-H	-H	-H	-H	-OH
scillicyanosidin (230)	-6-OH, -α-H	-CHO	-H	-H	-H	-H	-OAc
scillicyanosidin-3-O-6-D-glucoside (231)	-6-O-Glc, -α-H	-CHO	-H	-H	-H	-H	-OAc



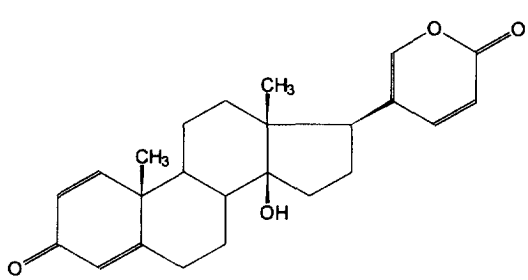
Compound	R_1
1-α, 2-α-epoxy-scillirosidin (173)	-H
1-α, 2-α-epoxy, 12-6-hydroxy-scillirosidin (179)	-OH



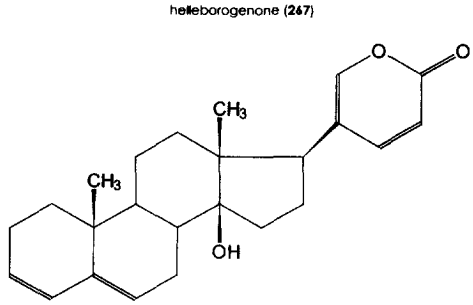
5-β, 14-β-dihydroxy-3-β,6-diacetoxy-5-β, 14-β-bufa-6, 20, 22-trienolide (**116**)



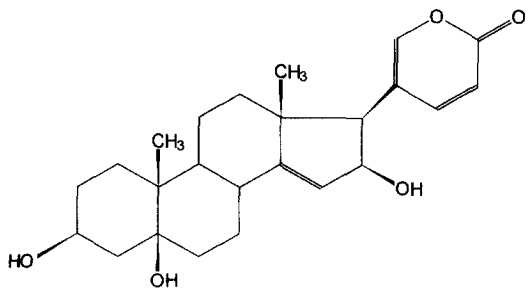
Compound	R	R_1
3-β, 14-β-dihydroxy-4-oxo-19-nor-bufa-5(10), 20, 22-trienolide-3-O-α-L-rhamnoside (**106**)	-Rha	-H
3-β, 14-β-dihydroxy-4-oxo-16-β-acetoxy-19-nor-bufa-5(10), 20, 22-trienolide (**107**)	-H	-OAc



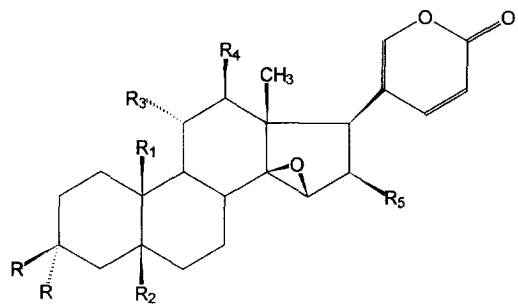
helleborogenone (**267**)



scillaridine (**266**)

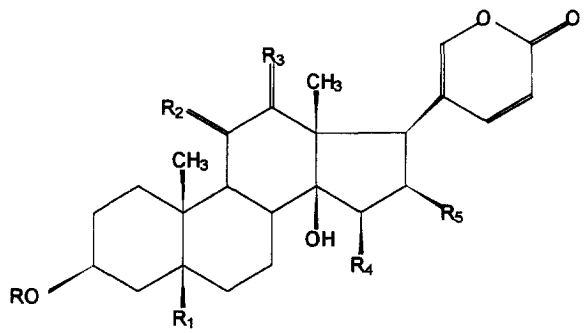


3-β, 5-β, 16-β-trihydroxy-bufa-14, 20, 22-trienolide (67)

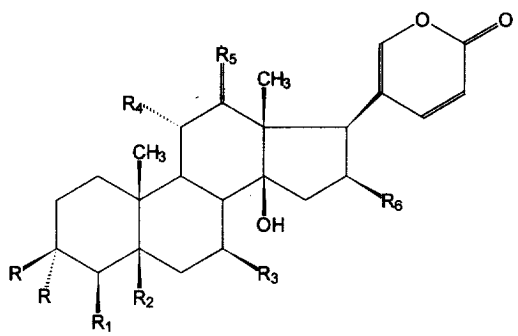


Compound	R	R_1	R_2	R_3	R_4	R_5
10-β-hydroxy-19-nor-cinobufagin (1)	-β-OH, -α-H	-OH	-H	-H	-H	-OAc
resibufogenin (9)	-β-OH, -α-H	$-CH_3$	-H	-H	-H	-H
resibufogenin-3-O-adipoylarginine-ester (10)	-β-O-adip, -α-H	$-CH_3$	-H	-H	-H	-H
resibufogenin-3-O-hemisuberate (11)	-β-O-sub-1, -α-H	$-CH_3$	-H	-H	-H	-H
resibufogenin-3-O-pimeloyl-arginine-ester (12)	-β-O-pim, -α-H	$-CH_3$	-H	-H	-H	-H
resibufogenin-3-O-succinoyl-arginine-ester (13)	-β-O-succ-2, -α-H	$-CH_3$	-H	-H	-H	-H
resibufogenin-3-O-sulfate (14)	-β-O-sul, -α-H	$-CH_3$	-H	-H	-H	-H
resibufotoxin (15)	-β-O-sub-2, -α-H	$-CH_3$	-H	-H	-H	-H
3-epi-marinobufagin-glucuronide (22)	α-O-glucuronide,-β-H	$-CH_3$	-OH	-H	-H	-H
marinobufagin (23)	-β-OH, -α-H	$-CH_3$	-OH	-H	-H	-H
marinobufagin-3-O-glutaroyl-arginine-ester (24)	-β-O-glut, -α-H	$-CH_3$	-OH	-H	-H	-H
marinobufagin-3-O-pimeloyl-arginine-ester (25)	-β-O-pim, -α-H	$-CH_3$	-OH	-H	-H	-H
marinobufagin-3-O-suberoyl-glutamine-ester (26)	-β-O-sub-glut, -α-H	$-CH_3$	-OH	-H	-H	-H
marinobufagin-3-O-succinoyl-arginine-ester (27)	-β-O-succ-2, -α-H	$-CH_3$	-OH	-H	-H	-H
marinobufagin-3-O-sulfate (28)	-β-O-sul, -α-H	$-CH_3$	-OH	-H	-H	-H
marinobufotoxin (29)	-β-O-sub-2, -α-H	$-CH_3$	-OH	-H	-H	-H
desacetyl-cinobufagin (39)	-β-OH, -α-H	$-CH_3$	-H	-H	-H	-OH
desacetyl-cinobufagin-3-O-hemisuberate (40)	-β-O-sub-1, -α-H	$-CH_3$	-H	-H	-H	-OH
desacetylcinobufagin-3-O-hemisuccinate (41)	-β-O-succ-1, -α-H	$-CH_3$	-H	-H	-H	-OH
cinobufagin (50)	-β-OH, -α-H	$-CH_3$	-H	-H	-H	-OAc
cinobufagin-3-O-adipoyl-arginine-ester (51)	-β-O-adip, -α-H	$-CH_3$	-H	-H	-H	-OAc
cinobufagin-3-O-glutaroyl-arginine-ester (52)	-β-O-glut, -α-H	$-CH_3$	-H	-H	-H	-OAc

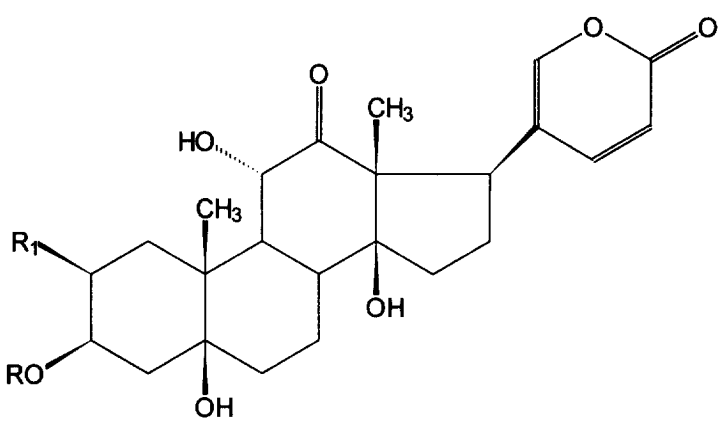
cinobufagin-3-O-hemisuberate (53)	-β-O-sub-1, -α-H	$-CH_3$	-H	-H	-H	-OAc
cinobufagin-3-O-pimeloyl-arginine-ester (54)	-β-O-pim, -α-H	$-CH_3$	-H	-H	-H	-OAc
cinobufagin-3-O-succinoyl-arginine-ester (55)	-β-O-succ-2, -α-H	$-CH_3$	-H	-H	-H	-OAc
cinobufotoxin (56)	-β-O-sub-2, -α-H	$-CH_3$	-H	-H	-H	-OAc
11α-hydroxy-marinobufagin (60)	-β-OH, -α-H	$-CH_3$	-OH	-OH	-H	-H
3-α, 5-β, 12-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide-3-O-β-D-glucuronide (63)	-α-O-glucuronide,-β-H	$-CH_3$	-OH	-H	-OH	-H
3-α, 5-β, 16-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide (65)	-α-OH,-β-H	$-CH_3$	-OH	-H	-H	-OH
3-β, 5-β, 16-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide (66)	-β-OH, -α-H	$-CH_3$	-OH	-H	-H	-OH
cinobufotalin (68)	-β-OH, -α-H	$-CH_3$	-OH	-H	-H	-OAc
cinobufotalin-3-O-hemisuberate (69)	-β-O-sub-1, -α-H	$-CH_3$	-OH	-H	-H	-OAc
cinobufotalitoxin (70)	-β-O-sub-2, -α-H	$-CH_3$	-OH	-H	-H	-OAc
12-β-hydroxy-cinobufagin (71)	-β-OH, -α-H	$-CH_3$	-H	-H	-OH	-OAc
resibufaginol (91)	-β-OH, -α-H	$-CH_2OH$	-H	-H	-H	-H
19-hydroxy-marinobufagin (93)	-β-OH, -α-H	$-CH_2OH$	-OH	-H	-H	-H
desacetyl-cinobufaginol (94)	-β-OH, -α-H	$-CH_2OH$	-H	-H	-H	-OH
11-α,19-dihydroxy-marinobufagin (96)	-β-OH, -α-H	$-CH_2OH$	-OH	-OH	-H	-H
19-hydroxy-cinobufotalin (97)	-β-OH, -α-H	$-CH_2OH$	-OH	-H	-H	-OAc
resibufagin (98)	-β-OH, -α-H	-CHO	-H	-H	-H	-H
bufotalinin(101)	-β-OH, -α-H	-CHO	-OH	-H	-H	-H
19-oxo-cinobufagin (102)	-β-OH, -α-H	-CHO	-H	-H	-H	-OAc
19-oxo-desacetyl-cinobufotalin (103)	-β-OH, -α-H	-CHO	-OH	-H	-H	-OH
19-oxo-cinobufotalin (104)	-β-OH, -α-H	-CHO	-OH	-H	-H	-OAc



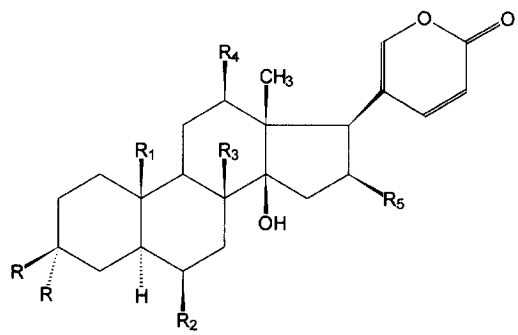
Compound	R	R_1	R_2	R_3	R_4	R_5
bufalin (2)	-H	-H	-H,H	-H,H	-H	-H
3-ß-O-acetyl-bufalin (109)	-ac	-H	-H,H	-H,H	-H	-H
bufalin-3-O-adipoyl-arginine-ester (3)	-adip	-H	-H,H	-H,H	-H	-H
bufalin-3-O-hemi-suberate (4)	-sub-1	-H	-H,H	-H,H	-H	-H
bufalin-3-O-pimeloyl-arginine-ester (5)	-pim	-H	-H,H	-H,H	-H	-H
bufalin-3-O-succinoyl-arginine-ester (6)	-succ-2	-H	-H,H	-H,H	-H	-H
bufalin-3-O-sulfate (7)	-sul	-H	-H,H	-H,H	-H	-H
bufalitoxin (8)	-sub-2	-H	-H,H	-H,H	-H	-H
telocinobufagin (17, 110)	-H	-OH	-H,H	-H,H	-H	-H
telocinobufagin-3-O-glutaroyl-arginine-ester (18)	-glut	-OH	-H,H	-H,H	-H	-H
telocinobufagin-3-O-hemisuberate (19)	-sub-1	-OH	-H,H	-H,H	-H	-H
telocinobufagin-3-O-suberoylglutamine-ester (20)	-sub-glut	-OH	-H,H	-H,H	-H	-H
telocinobufotoxin (21)	-sub-2	-OH	-H,H	-H,H	-H	-H
gamabufotalin (30)	-H	-H	-OH	-H,H	-H	-H
gamabufotalin-3-O-adipoyl-arginine-ester (31)	-adip	-H	-α-OH,H	-H,H	-H	-H
gamabufotalin-3-O-hemisuberate (32)	-sub-1	-H	-α-OH,H	-H,H	-H	-H
gamabufotalin-3-O-pimeloyl-arginine-ester (33)	-pim	-H	-α-OH,H	-H,H	-H	-H
gamabufotalin-3-O-succinoyl-arginine-ester (34)	-succ-2	-H	-α-OH,H	-H,H	-H	-H
gamabufotalin-3-O-sulfate (35)	-sul	-H	-α-OH,H	-H,H	-H	-H
gamabufotalitoxin (36)	-sub-2	-H	-α-OH,H	-H,H	-H	-H
gamabufotalin-3-O-α-L-rhamnoside (111)	-Rha	-H	-α-OH,H	-H,H	-H	-H
gamabufotalin-3-O-α-L-rhamnosido-ß-D-glucoside (112)	-Rha-Glc	-H	-α-OH,H	-H,H	-H	-H
11α-acetyl-gamabufotalin-3-O-α-L-rhamnosido-ß-D-glucoside (113)	-Rha-Glc	-H	-α-OAc,H	-H,H	-H	-H
15-ß-hydroxy-bufalin (37)	-H	-H	-H,H	-H,H	-OH	-H
desacetyl-bufotalin (38)	-H	-H	-H,H	-H,H	-H	-OH
bufotalin (42)	-H	-H	-H,H	-H,H	-H	-OAc
bufotalin-3-O-hemisuberate (43)	-sub-1	-H	-H,H	-H,H	-H	-OAc
bufotalin-3-O-suberoyl-L-histidine-ester (44)	-sub-hist-1	-H	-H,H	-H,H	-H	-OAc
bufotalin-3-O-suberoyl-L-1-methyl-histidine-ester (45)	-sub-hist-2	-H	-H,H	-H,H	-H	-OAc
bufotalin-3-O-suberoyl-L-3-methyl-histidine-ester (46)	-sub-hist-3	-H	-H,H	-H,H	-H	-OAc
bufotalin-3-O-succinoyl-arginine-ester (47)	succ-2	-H	-H,H	-H,H	-H	-OAc
bufotalin-3-O-sulfate (48)	-sul	-H	-H,H	-H,H	-H	-OAc
vulgarobufotoxin (49)	sub-2	-H	-H,H	-H,H	-H	-OAc
11α-hydroxy-telocinobufagin (59)	-H	-OH	-α-OH,H	-H,H	-H	-H
3-ß, 5-ß, 14-ß, 16-ß-tetrahydroxy-5-ß, 14-ß-bufa-20, 22-dienolide (64)	-H	-OH	-H,H	-H,H	-H	-OH
5-ß,16-ß-dihydroxy-bufalin-3-O-ß-D-glucoside (117)	-Glc	-OH	-H,H	-H,H	-H	-OH
16-ß-acetoxy-gamabufotalin-3-O-α-L-rhamnoside (118)	-Rha	-H	-α-OH,H	-H,H	-H	-OAc
arenobufagin (72)	-H	-H	-α-OH,H	=O	-H	-H
arenobufagin-3-O-hemisuberate (73)	-sub-1	-H	-α-OH,H	=O	-H	-H
arenobufagin-3-O-sulfate (74)	-sul	-H	-α-OH,H	=O	-H	-H
arenobufotoxin (75)	-sub-2	-H	-α-OH,H	=O	-H	-H
arenobufagin-3-O-α-L-rhamnosid (119)	-Rha	-H	-α-OH,H	=O	-H	-H
arenobufagin-3-O-α-L-rhamnosido-ß-D-glucoside (120)	-Rha-Glc	-H	-α-OH,H	=O	-H	-H
psi-bufarenogin (76)	-H	-H	=O	-α-OH,H	-H	-H
bufarenogin (77)	-H	-H	=O	-ß-OH,H	-H	-H
12-oxo-3-ß, 5-ß, 11-α, 14-ß-tetrahydroxy-5-ß, 14-ß-bufa-20, 22-dienolide (79)	-H	-OH	-α-OH,H	=O	-H	-H
12-oxo-3-ß-acetoxy-5-ß, 11-α, 14-ß-trihydroxy-5-ß, 14-ß-bufa-20, 22-dienolide (80)	-ac	-OH	-α-OH,H	=O	-H	-H
11-oxo-3-ß, 5-ß, 12-ß, 14-ß-tetrahydroxy-5-ß, 14-ß-bufa-20, 22-dienolide (81)	-H	-OH	=O	-ß-OH,H	-H	-H
11-oxo-3-ß-acetoxy-5-ß, 12-ß, 14-ß-trihydroxy-5-ß, 14-ß-bufa-20, 22-dienolide (82)	-ac	-OH	=O	-ß-OH,H	-H	-H



Compound	R	R_1	R_2	R_3	R_4	R_5	R_6
4-8-hydroxy-bufalin (16)	-8-OH, α-H	-OH	-H	-H	-H	-H,H	-H
bufotalon (57)	=O	-H	-H	-H	-H	-H,H	-OAc
3-α, 5-8, 11-α, 14-8-tetrahydroxy-5-8, 14-8-buta-20, 22-dienolide (58)	-α-OH, -8-H	-H	-OH	-H	-OH	-H,H	-H
3-α, 7-8, 11-α, 14-8-tetrahydroxy-5-8, 14-8-buta-20, 22-dienolide (61)	-α-OH, -8-H	-H	-H	-OH	-OH	-H,H	-H
3-8, 7-8, 11-α, 14-8-tetrahydroxy-5-8, 14-8-buta-20, 22-dienolide (62)	-8-OH, α-H	-H	-H	-OH	-OH	-H,H	-H
12-oxo-3-α, 5-8, 11-α, 14-8-tetrahydroxy-5-8, 14-8-buta-20, 22-dienolide (78)	-α-OH, -8-H	-H	-OH	-H	-OH	=O	-H



Compound	R	R_1
12-oxo-3-8-O-acetyl-2-8, 5-8, 11-α-trihydroxy-bufalin (83)	-ac	-OH
12-oxo-2-8-acetoxy-5-8, 11-α-dihydroxy-bufalin (84)	-H	-OAc
12-oxo-2-8-acetoxy-3-8-O-propionyl-5-8, 11-α-dihydroxy-bufalin (85)	-propionyl	-OAc
12-oxo-2-8-acetoxy-3-8-O-isobutyryl-5-8, 11-α-dihydroxy-bufalin (86)	-isobutyryl	-OAc
12-oxo-2-8- acetoxy-3-8-O-acetyl -5-8, 11-α-dihydroxy-bufalin (87)	-ac	-OAc



Compound	R	R_1	R_2	R_3	R_4	R_5
5-α-4, 5-dihydro-proscillaridin A (235)	-β-O-Rha, -α-H	$-CH_3$	-H	-H	-H	-H
5-α-4, 5-dihydro-glucoscillaren A (236)	-β-O-Rha-Glc-Glc, -α-H	$-CH_3$	-H	-H	-H	-H
5-α-bufalan (237)	=O	$-CH_3$	-H	-H	-H	-H
5-α-4, 5-dihydro-scillirosidin-3-O-α-L-thevetoside (239)	-β-O -Thev, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-scillirosidin-3-O-β-D-glucoside (240)	-β-O -Glc, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-scillirosidin-3-O-α-L-glucomethyloside (241)	-β-O -Glum, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-scillirosidin-3-O-α-L-rhamnosido-β-D-glucoside (242)	-β-O -Rha-Glc, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-scillirosidin-3-O-α-L-thevetosido-β-D-glucoside (243)	-β-O -Thev-Glc, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-scillirosidin-3-O-α -L-glucomethylosido-β-D-glucoside (244)	-β-O -Glum-Glc, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-scillirosidin-3-O-α-L-rhamnosido-β-D-glucosido-β-D-glucoside (245)	-β-O -Rha-Glc-Glc, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-scillirosidin-3-O-α-L-thevetosido-β-D-glucosido-β-D-glucoside (246)	-β-O -Thev-Glc-Glc, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-scillirosi-din-3-O-α-L-glucomethylosido-β-D-glucosido-β-D-glucoside (247)	-β-O -Glum-Glc-Glc, -α-H	$-CH_3$	-OAc	-OH	-H	-H
5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin (248)	-β-O H, -α-H	$-CH_3$	-OAc	-OH	-OH	-H
5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin-3-O-α-L-thevetoside (249)	-β-O -Thev, -α-H	$-CH_3$	-OAc	-OH	-OH	-H
5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin-3-O-α-L-thevetosido-β-D-glucoside (250)	-β-O -Thev-Glc, -α-H	$-CH_3$	-OAc	-OH	-OH	-H
5-α-4, 5-dihydro-16-β-hydroxy-scillirosidin-3-O-α-thevetoside (251)	-β-O -Thev, -α-H	$-CH_3$	-OAc	-OH	-H	-OH
5-α-4, 5-dihydro-16-β-acetoxy-scillirosidin-3-O-α-L-thevetosido -β-D-glucoside (252)	-β-O -Thev-Glc, -α-H	$-CH_3$	-OAc	-OH	-H	-OAc
19-oxo-5-α-4, 5-dihydro-proscillaridin A (262)	-β-O-Rha, -α-H	-CHO	-H	-H	-H	-H
16-β-hydroxy-bovogenin A (263)	-β-OH, -α-H	-CHO	-H	-H	-H	-OH
16-β-formyloxy-bovogenin A (264)	-β-OH, -α-H	-CHO	-H	-H	-H	-Oform
3-dehydro-16-β-hydroxy-bovogenin A (265)	=O	-CHO	-H	-H	-H	-OH

with a branched sugar chain were isolated from *Urginea epigea* (**129**, **224**) [50]. In $\Delta^{3,4}$ compounds, the sugars are attached to the 5β-OH. In general the monosaccharide units are connected $1 \rightarrow 4$. Hence only different linkages of the sugars are given in Table 4. In contrast with cardenolides, bufadienolide glycosides show much less variability in the kind of monosaccharides present. The sugar units mainly consist of glucose and rhamnose. In few compounds thevetose and 6-deoxyglucose were identified and xylose resp. digitalose are reported only in physodine C (**233**) and physodine A (**187**) [67]. More common is the occurrence of acetylated monosaccharides and of highly hydroxylated perhydropyrans, the latter usually connected by multiple ether bridges via 2α,3β-OH of the genin, mainly from the Crassulaceae.

Tables 3 and 4 contain a compilation of bufadienolides isolated from animal (Table 3) or plant (Table 4) sources. The compounds have been arranged according to the junction of rings A and B, the oxidation level at C-19 and the number and kind of substituents. Esterified bufadienolides of the same genin are cited in alphabetical order, glycosides of the same aglycone depending on the number of linked sugars, 6-deoxy sugars are mentioned first.

Table 3. Bufadienolides isolated from animal sources
19-nor-5-β-Bufadienolides

No.	Substance	Genin	Substituents*	Ref.
1	10-β-hydroxy-19-nor-cinobufagin	10-β-hydroxy-19-nor-cinobufagin	3-β, 10-β-OH, 16-β-OAc, 14,15β-epoxy	37
5-β-Bufadienolides with 19-CH_3-Group				
2	bufalin	bufalin	3-β, 14-β-OH	6–8, 14, 18, 28, 39
3	bufalin-3-*O*-adipoyl-arginine ester	bufalin	3-β, 14-β-OH, 3-*O*-adip	20, 26–28
4	bufalin-3-*O*-hemi-suberate	bufalin	3-β, 14-β-OH, 3-*O*-sub-1	33, 35, 39
5	bufalin-3-*O*-pimeloyl-arginine ester	bufalin	3-β, 14-β-OH, 3-*O*-pim	26 28
6	bufalin-3-*O*-succinoyl-arginine ester	bufalin	3-β, 14-β-OH, 3-*O*-succ-2	8, 9, 24, 27, 28
7	bufalin-3-*O*-sulphate	bufalin	3-β, 14-β-OH, 3-*O*-sul	13, 21, 28
8	bufalitoxin	bufalin	3-β, 14-β-OH, 3-*O*-sub-2	6, 10, 26–28
9	resibufogenin	resibufogenin	3-β-OH, 14,15β-epoxy	6–8, 14, 28 30, 39
10	resibufogenin-3-*O*-adipoylarginine ester	resibufogenin	3-β-OH, 14,15β-epoxy, 3-*O*-adip	27
11	resibufogenin-3-*O*-hemisuberate†	resibufogenin	3-β-OH, 14,15β-epoxy, 3-*O*-sub-1	33, 35, 39, 40
12	resibufogenin-3-*O*-pimeloyl-arginine ester	resibufogenin	3-β-OH, 14,15β-epoxy, 3-*O*-pim	27
13	resibufogenin-3-*O*-succinoyl-arginine ester	resibufogenin	3-β-OH, 14,15β-epoxy, 3-*O*-succ-2	9, 23, 27, 28
14	resibufogenin-3-*O*-sulphate	resibufogenin	3-β-OH, 14,15β-epoxy, 3-*O*-sul	11
15	resibufotoxin	resibufogenin	3-β-OH, 14,15β-epoxy, 3-*O*-sub-2	6, 10, 27
16	4-β-hydroxy-bufalin	4-β-hydroxy-bufalin	3-β, 4-β, 14-β-OH	37
17	telocinobufagin	telocinobufagin	3-β, 5-β, 14-β-OH	7, 13, 17, 18, 39
18	telocinobufagin-3-*O*-glutaroyl-arginine ester	telocinobufagin	3-β, 5-β, 14-β-OH, 3-*O*-glut	7
19	telocinobufagin-3-*O*-hemisuberate	telocinobufagin	3-β, 5-β, 14-β-OH, 3-*O*-sub-1	35
20	telocinobufagin-3-*O*-suberoylglutamine ester	telocinobufagin	3-β, 5-β, 14-β-OH, 3-*O*-sub-glut	5
21	telocinobufotoxin	telocinobufagin	3-β, 5-β, 14-β-OH, 3-*O*-sub-2	10, 11, 13, 17
22	3-*epi*-marinobufagin-glucuronide	3-*epi*-marinobufagin	3-α, 5-β-OH, 14,15β-epoxy, 3-*O*-β-D-glucuronide	13
23	marinobufagin	marinobufagin	3-β, 5-β-OH, 14,15β-epoxy	6–8, 14, 17, 18, 32, 36, 39
24	marinobufagin-3-*O*-glutaroyl-arginine ester	marinobufagin	3-β, 5-β-OH, 14,15β-epoxy, 3-*O*-glut	7
25	marinobufagin-3-*O*-pimeloyl-arginine ester	marinobufagin	3-β, 5-β-OH, 14,15β-epoxy, 3-*O*-pim	11
26	marinobufagin-3-*O*-suberoyl-glutamine ester	marinobufagin	3-β, 5-β-OH, 14,15β-epoxy, 3-*O*-sub-glut	4, 5
27	marinobufagin-3-*O*-succinoyl-arginine ester	marinobufagin	3-β, 5-β-OH, 14,15β-epoxy, 3-*O*-succ-2	7
28	marinobufagin-3-*O*-sulphate	marinobufagin	3-β, 5-β-OH, 14,15β-epoxy, 3-*O*-sul	11
29	marinobufotoxin	marinobufagin	3-β, 5-β-OH, 14,15β-epoxy, 3-*O*-sub-2	10, 11, 17, 27
30	gamabufotalin	gamabufotalin	3-β, 11-α, 14-β-OH	7, 8, 18, 28, 39, 42
31	gamabufotalin-3-*O*-adipoyl-arginine ester	gamabufotalin	3-β, 11-α, 14-β-OH, 3-*O*-adip	19, 27, 28
32	gamabufotalin-3-*O*-hemisuberate	gamabufotalin	3-β, 11-α, 14-β-OH, 3-*O*-sub-1	28, 35, 38
33	gamabufotalin-3-*O*-pimeloyl-arginine ester	gamabufotalin	3-β, 11-α, 14-β-OH, 3-*O*-pim	24, 27, 28
34	gamabufotalin-3-*O*-succinoyl-arginine ester	gamabufotalin	3-β, 11-α, 14-β-OH, 3-*O*-succ-2	8, 19, 27, 28
35	gamabufotalin-3-*O*-sulphate	gamabufotalin	3-β, 11-α, 14-β-OH, 3-*O*-sul	11, 25, 28
36	gamabufotalitoxin	gamabufotalin	3-β, 11-α, 14-β-OH, 3-*O*-sub-2	8, 22, 27, 28

37	15-β-hydroxy-bufalin	15-β-hydroxy-bufalin	3-β, 14-β, 15-β-OH	37
38	desacetyl-bufotalin	desacetyl-bufotalin	3-β, 14-β, 16-β-OH	14
39	desacetyl-cinobufagin	desacetyl-cinobufagin	3-β, 16-β-OH, 14,15β-epoxy	39
40	desacetyl-cinobufagin-3-*O*-hemisuberate	desacetyl-cinobufagin	3-β, 16-β-OH, 14,15β-epoxy, 3-*O*-sub-1	35
41	desacetyl-cinobufagin-3-*O*-hemisuccinate	desacetyl-cinobufagin	3-β, 16-β-OH, 14,15β-epoxy, 3-*O*-succ-1	28
42	bufotalin	bufotalin	3-β, 14-β-OH, 16-β-OAc	6–8, 14, 29, 39
43	bufotalin-3-*O*-hemisuberate	bufotalin	3-β, 14-β-OH, 16-β-OAc, 3-*O*-sub-1	35
44	bufotalin-3-*O*-suberoyl-L-histidine ester	bufotalin	3-β, 14-β-OH, 16-β-OAc, 3-*O*-sub-hist-1	15, 16
45	bufotalin-3-*O*-suberoyl-L-1-methyl-histidine ester	bufotalin	3-β, 14-β-OH, 16-β-OAc, 3-*O*-sub-hist-2	16
46	bufotalin-3-*O*-suberoyl-L-3-methyl-histidine ester	bufotalin	3-β, 14-β-OH, 16-β-OAc, 3-*O*-sub-hist-3	15, 16
47	bufotalin-3-*O*-succinoyl-arginine ester	bufotalin	3-β, 14-β-OH, 16-β-OAc, 3-*O*-succ-2	9
48	bufotalin-3-*O*-sulphate	bufotalin	3-β, 14-β-OH, 16-β-OAc, 3-*O*-sul	25, 28
49	vulgarobufotoxin	bufotalin	3-β, 14-β-OH, 16-β-OAc, 3-*O*-sub-2	6, 8, 10, 27, 28
50	cinobufagin	cinobufagin	3-β-OH, 14,15β-epoxy, 16-β-OAc	6, 8, 28, 39
51	cinobufagin-3-*O*-adipoyl-arginine ester	cinobufagin	3-β-OH, 14,15β-epoxy, 16-β-OAc, 3-*O*-adip	8, 20, 26–28
52	cinobufagin-3-*O*-glutaroyl-arginine ester	cinobufagin	3-β-OH, 14,15β-epoxy, 16-β-OAc, 3-*O*-glut	8
53	cinobufagin-3-*O*-hemisuberate	cinobufagin	3-β-OH, 14,15β-epoxy, 16-β-OAc, 3-*O*-sub-1	33, 34, 39
54	cinobufagin-3-*O*-pimeloyl-arginine ester	cinobufagin	3-β-OH, 14,15β-epoxy, 16-β-OAc, 3-*O*-pim	8, 26–28
55	cinobufagin-3-*O*-succinoyl-arginine ester	cinobufagin	3-β-OH, 14,15β-epoxy, 16-β-OAc, 3-*O*-succ-2	8, 9, 26–28
56	cinobufotoxin	cinobufagin	3-β-OH, 14,15β-epoxy, 16-β-OAc, 3-*O*-sub-2	8, 26–28
57	bufotalon	bufotalon	3-oxo, 14-β-OH, 16-β-OAc	37
58	3-α, 5-β, 11-α, 14-β-tetrahydroxy-5-β, 14-β-bufa-20, 22-dienolide	3-α, 5-β, 11-α, 14-β-tetrahydroxy-5-β, 14-β-bufa-20, 22-dienolide	3-α, 5-β, 11-α, 14-β-OH	41, 42
59	11α-hydroxy-telocinobufagin	11α-hydroxy-telocinobufagin	3-β, 5-β, 11-α, 14-β-OH	12, 13, 41, 42
60	11α-hydroxy-marinobufagin	11α-hydroxy-marinobufagin	3-β, 5-β, 11-α, 14,15β-epoxy	12, 13
61	3-α, 7-β, 11-α, 14-β-tetrahydroxy-5-β, 14-β-bufa-20, 22-dienolide	3-α, 7-β, 11-α, 14-β-tetrahydroxy-5-β,14-β-bufa-20,22-dienolide	3-α, 7-β, 11-α, 14-β-OH	41
62	3-β, 7-β, 11-α, 14-β-tetrahydroxy-5-β, 14-β-bufa-20, 22-dienolide	3-β, 7-β, 11-α, 14-β-tetrahydroxy-5-β, 14-β-bufa-20,22-dienolide	3-β, 7-β, 11-α, 14-β-OH	42
63	3-α, 5-β, 12-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide-3-*O*-β-D-glucuronide	3-α, 5-β, 12-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide	3-α, 5-β, 12-β-OH, 14,15-epoxy, 3-*O*-β-D-glucuronide	13
64	3-β, 5-β, 14-β, 16-β-tetrahydroxy-5-β, 14-β-bufa-20, 22-dienolide	3-β, 5-β, 14-β, 16-β-tetrahydroxy-5-β, 14-β-bufa-20, 22-dienolide	3-β, 5-β, 14-β, 16-β-OH	41, 42
65	3-α, 5-β, 16-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide	3-α, 5-β, 16-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide	3-α, 5-β, 16-β-OH, 14,15β-epoxy	42
66	3-β, 5-β, 16-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide	3-β, 5-β, 16-β-trihydroxy-14,15β-epoxy-5-β, 14-β-bufa-20, 22-dienolide	3-β, 5-β, 16-β-OH, 14,15β-epoxy	41, 42
67	3-β, 5-β, 16-β-trihydroxy-bufa-14, 20, 22-trienolide	3-β, 5-β, 16-β-trihydroxy-bufa-14, 20, 22-trienolide	3-β, 5-β, 16-β-OH, 14(15)-en	42
68	cinobufotalin	cinobufotalin	3-β, 5-β-OH, 14,15β-epoxy, 16-β-OAc	8

Table 3—*continued*

No.	Substance	Genin	Substituents*	Ref.
69	cinobufotalin-3-*O*-hemisuberate	cinobufotalin	3-β, 5-β-OH, 14,15β-epoxy, 16-β-OAc, 3-*O*-sub-1	35
70	cinobufotalitoxin	cinobufotalin	3-β, 5-β-OH, 14,15β-epoxy, 16-β-OAc, 3-*O*-sub-2	26–28
71	12-β-hydroxy-cinobufagin	12-β-hydroxy-cinobufagin	3-β, 12-β-OH, 14,15β-epoxy, 16-β-OAc	37
72	arenobufagin	arenobufagin	3-β, 11-α, 14-β-OH, 12-oxo	7, 17, 18, 28
73	arenobufagin-3-*O*-hemisuberate	arenobufagin	3-β, 11-α, 14-β-OH, 12-oxo, 3-*O*-sub-1	28, 35, 38
74	arenobufagin-3-*O*-sulphate	arenobufagin	3-β, 11-α, 14-β-OH, 12-oxo, 3-*O*-sul	25, 28
75	arenobufotoxin	arenobufagin	3-β, 11-α, 14-β-OH, 12-oxo, 3-*O*-sub-2	13, 17, 26–28
76	psi-bufarenogin	psi-bufarenogin	3-β, 12-α, 14-β-OH, 11-oxo	31
77	bufarenogin	bufarenogin	3-β, 12-β, 14-β-OH, 11-oxo	18
78	12-oxo-3-α, 5-β, 11-α, 14-β-tetrahydroxy-5-β, 14-β-bufa-20, 22-dienolide	12-oxo-3-α, 5-β, 11-α, 14-β-tetrahydroxy-5-β, 14-β-bufa-20, 22-dienolide	3-α, 5-β, 11-α, 14-β-OH, 12-oxo	41, 42
79	12-oxo-5-β, 11-α-dihydroxy-bufalin	12-oxo-5-β, 11-α-dihydroxy-bufalin	3-β, 5-β, 11-α, 14-β-OH, 12-oxo	42, 43
80	12-oxo-3-β-*O*-acetyl-5-β, 11-α-dihydroxy-bufalin	12-oxo-3-β-*O*-acetyl-5-β, 11-α-dihydroxy-bufalin	5-β, 11-α, 14-β-OH, 3-β-OAc, 12-oxo	43
81	11-oxo-5-β, 12-β-dihydroxy-bufalin	11-oxo-5-β, 12-β-dihydroxy-bufalin	3-β, 5-β, 12-β, 14-β-OH, 11-oxo	43
82	11-oxo-3-β-O-acetyl-5-β, 12-β-dihydroxy-bufalin	11-oxo-3-β-O-acetyl-5-β, 12-β-dihydroxy-bufalin	5-β, 12-β, 14-β-OH, 3-β-OAc, 11-oxo	43
83	12-oxo-3-β-*O*-acetyl-2-β, 5-β, 11-α-trihydroxy-bufalin‡	12-oxo-2-β, 11-α-trihydroxy-bufalin	2-β, 5-β, 11-α, 14-β-OH, 3-β-OAc, 12-oxo	44
84	12-oxo-2-β-*O*-acetyl-5-β, 11-α-dihydroxy-bufalin‡	12-oxo-2-β-*O*-acetyl-5-β, 11-α-dihydroxy-bufalin	3-β, 5-β, 11-α, 14-β-OH, 2-β-OAc, 12-oxo	44
85	12-oxo-2-β-*O*-acetyl-3-β-*O*-propionyl-5-β, 11-α-dihydroxy-bufalin‡	12-oxo-2-β-*O*-acetyl-5-β, 11-α-dihydroxy-bufalin	5-β, 11-α, 14-β-OH, 2-β-OAc, 3-β-*O*-propionyl, 12-oxo	44
86	12-oxo-2-β-*O*-acetyl-3-β-*O*-isobutyryl-5-β, 11-α-dihydroxy-bufalin‡	12-oxo-2-β-*O*-acetyl-5-β, 11-α-dihydroxy-bufalin	5-β, 11-α, 14-β-OH, 2-β-OAc, 3-β-*O*-isobutyryl, 12-oxo	44
87	12-oxo-2-β, 3-β-di-*O*-acetyl-5-β, 11-α-dihydroxy-bufalin‡	12-oxo-2-β-*O*-acetyl-5-β, 11-α-dihydroxy-bufalin	5-β, 11-α, 14-β-OH, 2-β, 3-β-OAc, 12-oxo	44

5-β-Bufadienolides with 19-CH_2OH-Group				
88	19-hydroxy-bufalin	19-hydroxy-bufalin	3-β, 14-β-OH	14, 18, 37
89	19-hydroxy-bufalin-3-*O*-suberoyl-L-histidine ester	19-hydroxy-bufalin	3-β, 14-β-OH, 3-*O*-sub-hist-1	16
90	19-hydroxy-bufalin-3-*O*-suberoyl-L-3-methylhistidine ester	19-hydroxy-bufalin	3-β, 14-β-OH, 3-*O*-sub-hist-3	16
91	resibufaginol	resibufaginol	3-β-OH, 14,15β-epoxy	40
92	hellebrigenol = 19-hydroxy-telocinobufagin	hellebrigenol = 19-hydroxy-telocinobufagin	3-β, 5-β, 14-β-OH	12–14, 29
93	19-hydroxy-marinobufagin	19-hydroxy-marinobufagin	3-β, 5-β-OH, 14,15β-epoxy	37
94	desacetyl-cinobufaginol	desacetyl-cinobufaginol	3-β, 16-β-OH, 14,15β-epoxy	37
95	11-α, 19-dihydroxy-telocinobufagin	11-α, 19-dihydroxy-telocinobufagin	3-β, 5-β, 11-α, 14-β-OH	12
96	11-α, 19-dihydroxy-marinobufagin	11-α, 19-dihydroxy-marinobufagin	3-β, 5-β, 11-α-OH, 14,15β-epoxy	12, 13
97	19-hydroxy-cinobufotalin	19-hydroxy-cinobufotalin	3-β, 5-β-OH, 14,15β-epoxy, 16-β-OAc	36
5-β-Bufadienolides with 19-CHO-Group				
98	resibufagin	resibufagin	3-β-OH, 14,15β-epoxy	32, 34, 36
99	hellebrigenin = bufotalidine	hellebrigenin = bufotalidine	3-β, 5-β, 14-β-OH	14, 17, 18, 39
100	hellebritoxin	hellebrigenin	3-β, 14-β-OH, 3-*O*-sub-2	10, 17
101	bufotalinin	bufotalinin	3-β, 5-β-OH, 14,15β-epoxy	17, 37
102	19-oxo-cinobufagin	19-oxo-cinobufagin	3-β-OH, 14,15β-epoxy, 16-β-OAc	34
103	19-oxo-desacetyl-cinobufotalin	19-oxo-desacetyl-cinobufotalin	3-β, 5-β, 16-β-OH, 14,15β-epoxy	37
104	19-oxo-cinobufotalin	19-oxo-cinobufotalin	3-β, 5-β-OH, 14,15β-epoxy, 16-β-OAc	34
105	marinosin	marinosin	3-β, 5-β, 14-β-OH, 11,19-halfacetal, 19-*O*-methyl	13

* Abbreviations for bufadienolides 1–105: ac = acetyl; adip = adipoyl-arginine ester; glut = glutarylarginine ester; met = methyl, pim = pimeloyl-arginine ester; sub-1 = hemisuberate; sub-2 = suberoyl-arginine ester; sub-hist-1 = suberoyl-L-histidine ester; sub-hist-2 = suberoyl-L-1-methylhistidine; sub-hist-3 = suberoyl-L-3-methylhistidine; sub-glut = suberoyl-glutamine ester; succ-1 = hemisuccinate; succ-2 = succinoyl-arginine ester; sul = sulphate.

† The substance was found in different cites under the names as follows: resibufogenin-3-*O*-hydrogensuberate, 3-*O*-suberoyl-resibufagenin.

‡ First bufadienolides from an invertebrate source. For the compounds the generic name lucibufagins is proposed [45].

Table 4. Bufadienolides isolated from plant sources

No.	Substance	Genin	Substituents*	Ref.
19-nor-Bufadienolides with 4(5) resp. 5(10)-double bond				
106	3-β, 14-β-dihydroxy-4-oxo-19-nor-bufa-5(10), 20, 22-trienolide-3-*O*-α-L-rhamnoside	3-β, 14-β-dihydroxy-4-oxo-19-nor-bufa 5(10), 20, 22-trienolide	3-β, 14-β-OH, 4-oxo, 5(10)-en, 3-*O*-α-L-Rha	55
107	3-β, 14-β-dihydroxy-4-oxo-16β-*O*-acetyl-19-nor-bufa-5(10), 20, 22-trienolide	3-β, 14-β-dihydroxy-4-oxo-16-β-*O*-acetyl-19-nor-bufa-5(10), 20, 22-trienolide	3-β, 14-β-OH, 4-oxo, 16-β-OAc, 5(10)-en	55
108	3-β, 10-β, 14-β-trihydroxy-19-nor-bufa-4, 20, 22-trienolide-3-*O*-α-rhamnoside	3-β, 10-β, 14-β-trihydroxy-19-nor-bufa-4, 20, 22-trienolide	3-β, 10-β, 14-β-OH, 4(5)en, 3-*O*-L-Rha	55
5-β-Bufadienolides with 19-CH_3-Group				
109	3-β-*O*-acetyl-bufalin	bufalin	14-β-OH, 3-β-OAc	110
110	telocinobufagin	telocinobufagin	3-β, 5-β, 14-β-OH	77
111	gamabufotalin-3-*O*-α-L-rhamnoside	gamabufotalin	3-β, 11-α, 14-β-OH, 3-*O*-α-L-Rha	47, 48, 51, 57, 62, 64
112	gamabufotalin-3-*O*-α-L-rhamnoside-β-D-glucoside	gamabufotalin	3-β, 11-α, 14-β-OH, 3-*O*-α-L-Rha-β-D-Glc	48, 62
113	11α-*O*-acetyl-gamabufotalin-3-*O*-α-L-rhamnoside-β-D-glucoside	11α-*O*-acetyl-gamabufotalin	3-β, 14-β-OH, 11-α-OAc, 3-*O*-α-L-Rha-β-D-Glc	63
114	daigredorigenin-3-acetate	daigredorigenin	1-β, 5-β, 14-β-OH, 3-β-OAc	83
115	bersamagenin-1-β, 3-β, 5-β-orthoacetate	bersamagenin-1-β, 3-β, 5-β-orthoacetate	1-β, 3-β, 5-β-ortho-Ac, 14-β-OH	87
116	5-β, 14-β-dihydroxy-3-β,6-*O*-diacetoxy-5-β, 14-β-bufa-6, 20, 22-trienolide	5-β, 14-β-dihydroxy-3-β, 6-*O*-diacetoxy-5-β, 14-β-bufa-6, 20, 22-trienolide	5-β, 14-β-OH, 3-β, 6-OAc, 6(7)-en	110
117	5-β, 16-β-dihydroxy-bufalin-3-*O*-β-D-glucoside	5-β, 16-β-dihydroxy-bufalin	3-β, 5-β, 14-β, 16-β-OH, 3-*O*-β-D-Glc	45
118	16-β-*O*-acetyl-gamabufotalin-3-*O*-α-L-rhamnoside	16-β-*O*-acetyl-gamabufotalin	3-β, 11-α, 14-β-OH, 16-β-OAc, 3-*O*-α-L-Rha	48, 62
119	arenobufagin-3-*O*-α-L-rhamnoside	arenobufagin-3-*O*-α-L-rhamnoside	3-β, 11-α, 14-β-OH, 12-oxo, 3-*O*-α-L-Rha	47
120	arenobufagin-3-*O*-α-L-rhamnosido-β-D-glucoside	arenobufagin	3-β, 11-α, 14-β-OH, 12-oxo, 3-*O*-α-L-Rha-β-D-Glc	65
121	16-β-*h*ydroxy-bersamagenin-1-β, 3-β, 5-β-*ortho*-acetate	16-β-*h*ydroxy-bersamagenin-1-β, 3-β, 5-β-*ortho*-acetate	14-β, 16-β-OH, 1-β, 3-β, 5-β-ortho-Ac	87
Bufadienolides with 19-CH_3-Group and 4,5-Double Bond				
122	scillarenin	scillarenin	3-β, 14-β-OH, 4(5)-en	49, 51, 54, 55, 57
123	proscillaridin A	scillarenin	3-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha	48, 49, 51, 53–55, 57, 59, 61, 62, 64
124	scillarenin-3-*O*-β-D-glucoside	scillarenin	3-β, 14-β-OH, 4(5)-en, 3-*O*-β-D-Glc	48, 49, 57, 64
125	scillaren A	scillarenin	3-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-β-D-Glc	49, 52 54, 59, 61, 62, 64
126	scillarenin-bis-rhamnoside	scillarenin	3-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-α-L-Rha	52
127	scillarenin-3-*O*-α-L-(2′, 3′-diacetoxy)-rhamnosido-β-D-glucoside	scillarenin	3-β, 14-β-OH, 4(5)-en 3-*O*-α-L-(2′, 3′-OAc)-Rha-4′-β-D-Glc	51

128	scillarenin-3-*O*-β-D-glucosido-β-D-glucoside	scillarenin	3-β, 14-β-OH, 4(5)-en 3-*O*-β-D-Glc-β-D-Glc	59
129	scillarenin-3-*O*-α-L-rhamnosido-3′-α-L-rhamnosido-4′-β-D-glucoside	scillarenin	3-β, 14-β-OH, 4(5)-en 3-*O*-α-L-Rha-3′-α-L-Rha-4′-β-D-Glc	50
130	scillarenin-3-*O*-α-L-rhamnosido-β-D-glucosido-3″-β-D-glucoside	scillarenin	3-β, 14-β-OH, 4(5)-en 3-*O*-α-L-Rha-β-D-Glc-3″-β-D-Glc	51
131	glucoscillaren A	scillarenin	3-β, 14-β-OH, 4(5)-en 3-*O*-α-L-Rha-β-D-Glc-β-D-Glc	49, 51, 59, 61, 62
132	scillarenin-3-*O*-α-L-rhamnosido-β-D-glucosido-6″-β-D-glucoside	scillarenin	3-β, 14-β-OH, 4(5)-en 3-*O*,-α-L-Rha-β-D-Glc-6″-β-D-Glc	49
133	scillarenin-3-*O*-α-L-(2′, 3′-*O*-diacetyl)-rhamnosido-β-D-glucosido-3″-β-D-glucoside	scillarenin	3-β, 14-β-OH, 4(5)-en 3-*O*-α-L-(2′, 3′-OAc)-Rha-β-D-Glc-3″-β-D-Glc	51
134	scillarenin-3-*O*-α-L-(2′, 3′-*O*-diacetyl)-rhamnosido-β-D-glucosido-β-D-glucoside	scillarenin	3-β, 14-β-OH, 4(5)-en 3-*O*-α-L-(2′, 3′-OAc)-Rha-β-D-Glc-β-D-Glc	51
135	scillirubrosidin	scillirubrosidin	3-β, 8-β, 14-β-OH, 4(5)-en	57
136	scillirubrosidin-3-*O*-α-L-rhamnoside	scillirubrosidin	3-β, 8-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha	57, 64
137	scillirubroside	scillirubrosidin	3-β, 8-β, 14-β-OH, 4(5)-en, 3-*O*-β-D-Glc	57, 64, 65
138	scillirubrosidin-3-*O*-D-glucosido-β-D-glucoside	scillirubrosidin	3-β, 8-β, 14-β-OH, 4(5)-en 3-*O*-β-D-Glc-β-D-Glc	59
139	scillirubrosidin-3-*O*-α-L-rhamnosido-β-D-glucosido-β-D-glucoside	scillirubrosidin	3-β, 8-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-β-D-Glc-β-D-Glc	59
140	12-*epi*-scilliphaeoside	12-*epi*-scilliphaeosidin	3-β, 12-α, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha	57, 62, 64
141	12-*epi*-scilliphaeosidin-3-*O*-β-D-glucoside	12-*epi*-scilliphaeosidin	3-β, 12-α, 14-β-OH, 4(5)-en, 3-*O*-β-D-Glc	64
142	12-*epi*-scilliphaeosidin-3-*O*-α-L-bisrhamnoside	12-*epi*-scilliphaeosidin	3-β, 12-α, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-α-L-Rha	64
143	12-*epi*-gluco-scilliphaeoside	12-*epi*-scilliphaeosidin	3-β, 12-α, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-β-D-Glc	64
144	scilliphaeosidin	scilliphaeosidin	3-β, 12-β, 14-β-OH, 4(5)-en	51, 57
145	scilliphaeoside	scilliphaeosidin	3-β, 12-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha	48, 51, 53–57, 59, 61, 62, 64
146	scilliphaeosidin-3-*O*-β-D-glucoside	scilliphaeosidin	3-β, 12-β, 14-β-OH, 4(5)-en, 3-*O*-β-D-Glc	48, 57, 59, 64
147	glucoscilliphaeoside	scilliphaeosidin	3-β, 12-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-β-D-Glc	56, 59, 61, 62, 64
148	scilliphaeosidin-3-*O*-α-L-rhamnosido-β-D-glucosido-3″-β-D-glucoside	scilliphaeosidin	3-β, 12-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-β-D-Glc-3″-β-D-Glc	51
149	scilliphaeosidin-3-*O*-α-L-rhamnosido-β-D-glucosido-β-D-glucoside	scilliphaeosidin	3-β, 12-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-β-D-Glc-β-D-Glc	51
150	3-oxo-scilliphaeosidin = anhydro-scilliphaeosidin	3-oxo-scilliphaeosidin = anhydro-scilliphaeosidin	3-oxo-12-β, 14-β-OH, 4(5)-en	53, 57
151	16-α-hydroxy-scillarenin-3-*O*-α-L-rhamnoside	16-α-hydroxy-scillarenin	3-β, 14-β, 16-α-OH, 4(5)-en, 3-*O*-α-L-Rha	55
152	16-β-hydroxy-scillarenin-3-*O*-α-L-rhamnoside	16-β-hydroxy-scillarenin	3-β, 14-β, 16-β-OH, 4(5)-en, 3-*O*-α-L-Rha	59
153	16-β-hydroxy-scillarenin-3-*O*-β-D-glucoside	16-β-hydroxy-scillarenin	3-β, 14-β, 16-β-OH, 4(5)-en, 3-*O*-β-D-Glc	59
154	16-β-hydroxy-scillarenin-3-*O*-α-rhamnosido-β-D-glucosido-β-D-glucoside	16-β-hydroxy-scillarenin	3-β, 14-β, 16-β-OH, 4(5)-en, 3-*O*-α-L-Rha-β-D-Glc-β-D-Glc	59
155	16-β-*O*-acetyl-scillarenin-3-*O*-α-L-rhamnoside	16-β-*O*-acetyl-scillarenin	3-β, 14-β-OH, 16-β-OAc, 4(5)-en, 3-*O*-α-L-Rha	59
156	16-β-*O*-acetyl-scillarenin-3-*O*-β-D-glucoside	16-β-*O*-acetyl-scillarenin	3-β, 14-β-OH, 16-β-OAc, 4(5)-en,3-*O*-β-D-Glc	59

Table 4—*continued*

No.	Substance	Genin	Substituents*	Ref.
157	16-β-*O*-acetyl-scillarenin-3-*O*-β-D-glucosido-β-D-glucoside	16-β-*O*-acetyl-scillarenin	3-β, 14-β-OH, 16-β-OAc, 4(5)-en, 3-*O*-β-D-Glc-β-D-Glc	59
158	16-β-*O*-acetyl-scillarenin-3-*O*-α-L-glucomethylosido-β-D-glucosido-β-D-glucoside	16-β-*O*-acetyl-scillarenin	3-β, 14-β-OH, 16-β-OAc, 4(5), 3-*O*-α-L-Glum-β-D-Glc-β-D-Glc	59
159	16-β-*O*-acetyl-scillarenin-3-*O*-α-L-rhamnosido-β-D-glucosido-β-D-glucoside	16-β-*O*-acetyl-scillarenin	3-β, 14-β-OH, 16-β-OAc, 4(5)-en, 3-*O*-α-L-Rha-β-D-Glc-β-D-Glc	59
160	12-β, 14-β-dihydroxy-2-α, 3-β-(tetrahydro-3′α, 5′β-dihydroxy-4′β-methoxy-6′-methyl-2-H-pyran-2′,4′-diyldioxy)-bufa-4, 20, 22-trienolide	2-α, 3-β, 12-β, 14-β-tetrahydroxy-bufa-4, 20, 22-trienolide	2-α, 3-β, 12-β, 14-β-OH, 4(5)-en, 2-α, 3-β-(tetrahydro-3′α, 5′β-OH-4′β-methoxy-6′-methyl-2H-pyran-2′,4′-diyldioxy)	49
161	2-α, 3-β, 14-β, 16-α-tetrahydroxy-14-β-bufa-4, 20, 22-trienolide	2-α, 3-β, 14-β, 16-α-tetrahydroxy-bufa-4, 20, 22-trienolide	2-α, 3-β, 14-β, 16-α-OH, 4(5)-en	55
162	6-desacetyl-scillirosidin	6-desacetyl-scillirosidin	3-β, 6-β, 8-β, 14-β-OH, 4(5)-en	57, 69
163	6-desacetyl-scillirosidin-3-*O*-α-L-rhamnoside	6-desacetyl-scillirosidin	3-β, 6-β, 8-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha	57
164	6-desacetyl-scilliroside	6-desacetyl-scillirosidin	3-β, 6-β, 8-β, 14-β-OH, 4(5)-en, 3-*O*-β-D-Glc	57–59, 64
165	scillirosidin	scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 4(5)-en	57, 58, 64
166	scilliroside	scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 4(5)-en, 3-*O*-β-D-Glc	45, 57–59, 64, 65
167	glucosyl-scilliroside	scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 4(5)-en, 3-*O*-β-D-Glc-β-D-Glc	58, 59
168	6-β, 11-β-dihydroxy-scillarenin	6-β, 11-β-dihydroxy-scillarenin	3-β, 6-β, 11-β, 14-β-OH, 4(5)-en	57
169	12-β-hydroxy-scillirubrosidin-3-*O*-α-L-rhamnoside	12-β-hydroxy-scillirubrosidin	3-β, 8-β, 12-β, 14-β-OH, 4(5)-en,3-*O*-α-L-Rha	59
170	3-oxo-12-β-hydroxy-scillirubrosidin	3-oxo-12-β-hydroxy-scillirubrosidin	3-oxo, 8-β, 12-β, 14-β-OH, 4(5)-en	69
171	16-β-*O*-acetyl-scillirubroside	16-β-*O*-acetyl-scillirubrosidin	3-β, 8-β, 14-β-OH, 16-β-OAc, 4(5)-en, 3-*O*-β-D-Glc	59
172	9-hydroxy-scilliphaeoside	9-hydroxy-scilliphaeosidin	3-β, 9, 12-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha	60
173	1-α, 2-α-epoxy-scillirosidin	1-α, 2-α-epoxy-scillirosidin	1-α, 2-α-epoxy, 3-β, 8-β, 14-β-OH, 6-β-OAc, 4(5)-en	85, 104
174	12-β-hydroxy-6-desacetyl-scillirosidin	12-β-hydroxy-6-desacetyl-scillirosidin	3-β, 6-β, 8-β, 12-β, 14-β-OH, 4(5)-en	69
175	12-β-hydroxy-6-desacetyl-scillirosidin-3-*O*-β-D-glucoside	12-β-hydroxy-6-desacetyl-scillirosidin	3-β, 6-β, 8-β, 12-β, 14-β-OH, 4(5), 3-*O*-β-D-Glc	59
176	12-β-hydroxy-scillirosidin	12-β-hydroxy-scillirosidin	3-β, 8-β, 12-β, 14-β-OH, 6-β-OAc, 4(5)-en	45, 59, 69
177	12-β-hydroxy-scilliroside	12-β-hydroxy-scillirosidin	3-β, 8-β, 12-β, 14-β-OH, 6-β-OAc, 4(5)-en, 3-*O*-β-D-Glc	45, 48, 59, 64, 69
178	3-oxo-12-β-hydroxy-scillirosidin	3-oxo-12-β-hydroxy-scillirosidin	3-oxo, 8-β, 12-β, 14-β-OH, 6-β-OAc, 4(5)-en	69
179	1-α, 2-α-epoxy, 12-β-hydroxy-scillirosidin	1-α, 2-α-epoxy, 12-β-hydroxy-scillirosidin	1-α, 2-α-epoxy, 3-β, 8-β, 12-β, 14-β-OH, 6-β-OAc, 4(5)-en	84, 104
180	6-β, 8-β, 12-β, 14-β-tetrahydroxy-2-α, 3-β-(tetrahydro-3′, 5′-dihydroxy-4′-methoxy-6′-methyl-2H-pyran-2′,4′-diyldioxy)-bufa-4, 20, 22-trienolide	2-α, 3-β, 6-β, 8-β, 12-β, 14-β-hexahydroxy-bufa-4, 20, 22-trienolide	2-α, 3-β, 6-β, 8-β, 12-β, 14-β-OH, 4(5)-en, 2-α, 3-β-(tetrahydro-3′α, 5′β-OH-4′-β-methoxy-6′-methyl-2H-pyran-2′α, 4′α-diyldioxy)	49

181	rubellin	2-α, 3-β, 6-β, 8-β, 11-α, 14-β-hexahydroxy-12-oxo-bufa-4, 20, 22-trienolide	2-α, 3-β, 6-β, 8-β, 11-α, 14-β-OH, 12-oxo, 4(5)-en, 2-α, 3-β-(tetrahydro-3′α, 5′β-OH,4′β-methoxy-6′-methyl-2-H-pyran-2′-α, 4′-α-diyldioxy)	68
5-β-Bufadienolides with 19-CH_2OH-Group resp. 19-CH_2OAc-group				
182	melianthusigenin	melianthusigenin	14-β-OH, 19-OAc, 1-β, 3-β, 5-β-ortho-Ac	103
183	bryotoxin B	bryotoxin B	11-α, 14-β, 19-OH, 1-β, 3-β, 5-β-ortho-Ac, 12-oxo	94
184	abyssinol B	abyssinol B	5-β, 19-OH, 3-α, 4-α-epoxy, 15-*O*-met, 14(15)-en	81
5-β-Bufadienolides with 19-CHO Group				
185	hellebrigenin	hellebrigenin	3-β, 5-β, 14-β-OH	46, 74, 77
186	deglucohellebrin = corelborin K	hellebrigenin	3-β, 5-β, 14-β-OH, 3-*O*-α-L-Rha	70, 73, 74, 77, 79
187	physodine A	hellebrigenin	3-β, 5-β, 14-β-OH, 3-*O*-β-D-Digt	67
188	hellebrigenin-3-*O*-β-D-glucoside	hellebrigenin	3-β, 5-β, 14-β-OH, 3-*O*-β-D-Glc	45, 46
189	hellebrin	hellebrigenin	3-β, 5-β, 14-β-OH, 3-*O*-α-L-Rha-β-D-Glc	73, 74, 76, 79
190	glucohellebrin	hellebrigenin	3-β, 5-β, 14-β-OH, 3-*O*-α-L-Rha-β-D-Glc-β-D-Glc	74, 76
191	hellebrigenin-3-*O*-acetate	hellebrigenin	3-β-OAc, 5-β, 14-β-OH	80, 86, 87, 106, 107, 109, 111
192	hellebrigenin-3-β, 5-β-diacetate	hellebrigenin	3-β, 5-β-OAc, 14-β-OH	86, 109
193	lanceotoxin B	5-*O*-acetyl-hellebrigenin	3-β, 14-β-OH, 5-β-OAc, 3-*O*-α-L-Rha	107
194	thesiuside	5-*O*-acetyl-hellebrigenin	3-β, 14-β-OH, 5-β-OAc, 3-*O*-β-D-Glc	113
195	lanceotoxin A	5-*O*-acetyl-hellebrigenin	3-β, 14-β-OH, 5-β-OAc, 3-*O*-(2′-α, 3′-β, 4′-β, 5′-α-OH)-hexanoyl	107
196	bersaldegenin-1-acetate	bersaldegenin	3-β, 5-β, 14-β-OH, 1-β-OAc	83
197	bersaldegenin-3-acetate	bersaldegenin	1-β, 5-β, 14-β-OH, 3-β-OAc	82, 83, 87, 92, 102
198	melianthugenin = bersaldegenin-1-β, 3β, 5-β-orthoacetate	melianthugenin = bersaldegenin-1-β, 3-β, 5-β-orthoacetate	14-β-OH, 1-β, 3-β, 5-β-*ortho*-Ac	83, 87, 102, 103
199	14-deoxy-15, 16β-epoxy-melianthugenin	14-deoxy-15β, 16-β-epoxy-melianthugenin	1-β, 3-β, 5-β-*ortho*-Ac, 15-β, 16-β-epoxy	100
200	kalanchoside	2-β-*O*-acetyl-hellebrigenin	3-β, 5β, 14-β-OH, 2-β-OAc, 3-β-*O*-β-D-(4′,6′-dideO)-altrose	101
201	physodine B	2-β-*O*-acetyl-hellebrigenin	3-β, 5-β, 14-β-OH, 2-β-OAc, 3-*O*-α-L-(2′-OAc)-Thev-β-D-Glc	67
202	11-α-hydroxy-desglucohellebrin	11-α-hydroxy-hellebrigenin	3-β, 5-β, 11-α, 14-β-OH, 3-*O*-α-L-Rha	79
203	16-β-hydroxy-hellebrigenin	16-β-hydroxy-hellebrigenin	3-β, 5-β, 14-β, 16-β-OH	45
204	16-β-hydroxy-hellebrigenin-3-*O*-β-D-glucoside	16-β-hydroxy-hellebrigenin	3-β, 5-β, 14-β, 16-β-OH, 3-*O*-β-D-Glc	45
205	6-β-*O*-acetyl-melianthugenin	6-β-*O*-acetyl-melianthugenin	14-β-OH, 6-β-OAc, 1-β, 3-β, 5-β-*ortho*-Ac	112
206	6-β-*O*-acetyl-14-deoxy-15, 16-β-epoxy-melianthugenin	6-β-*O*-acetyl-14-deoxy-15-β, 16-β-epoxy-melianthugenin	6-β-OAc, 1-β, 3-β, 5-β-*ortho*-Ac, 15-β, 16-β-epoxy	100
207	bryophyllin A = bryotoxin C	11-α-hydroxy-melianthugenin	11-α, 14-β-OH, 1-β, 3β, 5-β-*ortho*-Ac	82, 92, 94
208	bryophyllin B	bersaldegenin-11, 19-halfacetal	1-β-OAc, 3-β, 5-β, 14-β-OH, 11, 19-half acetal	82
209	16-β-hydroxy-bersaldegenin-3-acetate	16-β-hydroxy-bersaldegenin	1-β, 5-β, 14-β, 16-β-OH, 3-β-OAc	87
210	16-β-hydroxy-melianthugenin	16-β-hydroxy-melianthugenin	14-β, 16-β-OH, 1-β, 3-β, 5-β-*ortho*-acetate	87
211	bryotoxin A	3-β, 5-β, 11-α, 14-β-tetrahydroxy, 12-oxo-5-β, 14-β-bufa-20, 22-dienolide	3-β, 5-β, 11-α, 14-β-OH, 12-oxo, 3-*O*-(3′-OAc, 4′-6′-dideO)-altrose	94, 105

Table 4—*continued*

No.	Substance	Genin	Substituents*	Ref.
212	daigremontianin	daigremontianin	11-α, 14-β-OH, 1-β, 3-β, 5-β-*ortho*-Ac, 12-oxo	83
213	abyssinol A	abyssinol A	5-β-OH, 3-α-, 4-α-epoxy, 16-oxo, 14(15)-en	81
214	abyssinol C	abyssinol C	5-β-OH, 1-β, 3-β-OAc, 15-Omet, 16-oxo, 14(15)-en	81
215	abyssinin	abyssinin	5-β-OAc, 3-α, 4-α-epoxy, 15-Omet, 16-oxo, 14(15)-en	81
5-β-Bufadienolides with 19-CHO Group- and 3,4-Double Bond				
216	scilliglaucogenin	scilliglaucogenin	5-β, 14-β-OH, 3(4)-en	64
217	scilliglaucoside	scilliglaucogenin	5-β, 14-β-OH, 3(4)-en, 5-*O*-β-D-Glc	48, 57, 62, 64, 65
218	bersenogenin	bersenogenin	5-β, 14-β, 16-β-OH, 3(4)-en	80
219	scillicyanogenin	scillicyanogenin	5-β, 14-β-OH, 16-β-OAc, 3(4)en	55
220	scillicyanoside	scillicyanogenin	5-β, 14-β-OH, 16-β-OAc, 3(4)-en, 5-*O*-β-D-Glc	48, 55, 62
Bufadienolides with 19-CHO Group- and 4, 5-Double Bond				
221	scilliglaucosidin	scilliglaucosidin	3-β, 14-β-OH, 4(5)-en	46, 57, 80
222	scilliglaucosidin-3-*O*-α-L-rhamnoside	scilliglaucosidin	3-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha	46, 54, 55, 57
223	altosid	scilliglaucosidin	3-β, 14-β-OH, 4(5)-en, 3-*O*-β-D-Glc	46, 50, 54
224	scilliglaucosidin-3-*O*-α-L-rhamnosido-3′-α-L-rhamnosido-4′-β-D-glucoside	scilliglaucosidin	3-β, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha-3′-α-L-Rha-4′-β-D-Glc	50
225	scilliglaucosidin-3-one	scilliglaucosidin-3-one	3-oxo, 14-β-OH, 4(5)-en	46
226	11-α-hydroxy-scilliglaucosidin-3-*O*-α-L-rhamnoside	11-α-hydroxy-scilliglaucosidin	3-β, 11-α, 14-β-OH, 4(5)-en, 3-*O*-α-L-Rha	51, 59
227	12-β-hydroxy-scilliglaucosidin-3-*O*-D-glucoside	12-β-hydroxy-scilliglaucosidin	3-β, 12-β, 14-β-OH, 4(5)-en, 3-*O*-β-D-Glc	64
228	3-epi-berscillogenin	3-epi-berscillogenin	3-α, 14-β, 16-β-OH, 4(5)-en	80
229	berscillogenin	berscillogenin	3-β, 14-β, 16-β-OH, 4(5)-en	80
230	scillicyanosidin	scillicyanosidin	3-β, 14-β-OH, 16-β-OAc, 4(5)-en	55
231	scillicyanosidin-3-*O*-β-D-glucoside	scillicyanosidin	3-β, 14-β-OH, 16-β-OAc, 4(5)-en, 3-*O*-β-D-Glc	50, 55
5-β-Bufadienolides with 19-COOH Group				
232	5-β, 14-β-dihydroxy-10-carboxy-5-β, 14-β-bufa-3, 20, 22-trienolide-5-*O*-β-D-glucoside	5-β, 14-β-dihydroxy-10-carboxy-5-β, 14-β-bufa-3, 20, 22-trienolide	5-β, 14-β-OH, 3(4)-en, 5-*O*-β-D-Glc	55, 64
5-α-Bufadienolides with 19-CH_3 Group				
233	physodine C	3-β-hydroxy-12-α-*O*-acetyl-5-α, 14-α-bufadienolide	3-β-OH, 12-α-OAc, 3-*O*-α-L-Rha(4 → 1)-β-D-Xyl	67
234	physodine D	3-β-hydroxy-12-α-*O*-acetyl-5-α, 14-α-bufadienolide	3-β-OH, 12-α-OAc, 3-*O*-α-L-(4′-OAc)-Rha(3 → 1)-β-D-Glc	67

235	5-α-4, 5-dihydro-proscillaridin A	5-α-4, 5-dihydro-scillarenin	3-β, 14-β-OH, 3-*O*-α-L-Rha	62
236	5-α-4, 5-dihydro-glucoscillaren A	5-α-4, 5-dihydro-scillarenin	3-β, 14-β-OH, 3-*O*-α-L-Rha-β-D-Glc-β-Glc	62
237	5-α-bufalon	5-α-bufalon	3-oxo, 14-β-OH	78
238	cotyledoside	2-α, 3-β, 14-β-trihydroxy-7β, 8β-epoxy-5-α, 14-β-bufa-20, 22-dienolide	2-α, 3-β, 14-β-OH, 7β, 8β-epoxy, 2-α, 3-β-(tetrahydro-3′-α, 5′-β-OH, 4′-β-methoxy, 6′-methyl-2H-pyran, 2′-α, 4′-α-diyldioxy)	88
239	5-α-4, 5-dihydro-scillirosidin-3-*O*-α-L-thevetoside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Thev	59
240	5-α-4, 5-dihydro-scillirosidin-3-*O*-β-D-glucoside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-β-D-Glc	59
241	5-α-4, 5-dihydro-scillirosidin-3-*O*-α-L-glucomethyloside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Glum	59
242	5-α-4, 5-dihydro-scillirosidin-3-*O*-α-L-rhamnosido-β-D-glucoside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Rha-β-D-Glc	59
243	5-α-4, 5-dihydro-scillirosidin-3-*O*-α-L-thevetosido-β-D-glucoside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Thev-β-D-Glc	59, 62, 64
244	5-α-4, 5-dihydro-scillirosidin-3-*O*-α-L-glucomethylosido-β-D-glucoside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Glum-β-D-Glc	59
245	5-α-4, 5-dihydro-scillirosidin-3-*O*-α-L-rhamnosido-β-D-glucosido-β-D-glucoside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Rha-β-D-Glc-β-D-Glc	59
246	5-α-4, 5-dihydro-scillirosidin-3-*O*-α-L-thevetosido-β-D-glucosido-β-D-glucoside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Thev-β-D-Glc-β-D-Glc	48, 59
247	5-α-4, 5-dihydro-scillirosidin-3-*O*-α-L-glucomethylosido-β-D-glucosido-β-D-glucoside	5-α-4, 5-dihydro-scillirosidin	3-β, 8-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Glum-β-D-Glc-β-D-Glc	59
248	5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin	5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin	3-β, 8-β, 12-β, 14-β-OH, 6-β-OAc	69
249	5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin-3-*O*-α-L-thevetoside	5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin	3-β, 8-β, 12-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Thev	59
250	5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin-3-*O*-α-L-thevetosido-β-D-glucoside	5-α-4, 5-dihydro-12-β-hydroxy-scillirosidin	3-β, 8-β, 12-β, 14-β-OH, 6-β-OAc, 3-*O*-α-L-Thev-β-D-Glc	59, 66
251	5-α-4, 5-dihydro-16-β-hydroxy-scillirosidin-3-*O*-α-thevetoside	5-α-4, 5-dihydro-16-β-hydroxy-scillirosidin	3-β, 8-β, 14-β, 16-β-OH, 6-β-OAc, 3-*O*-α-L-Thev	59
252	5-α-4, 5-dihydro-16-β-*O*-acetyl-scillirosidin-3-*O*-α-L-thevetosido-β-D-glucoside	5-α-4, 5-dihydro-16-β-*O*-acetyl-scillirosidin	3-β, 8-β, 14-β-OH, 6-β, 16-β-OAc, 3-*O*-α-L-Thev-β-D-Glc	59
253	tyledoside F	2-α, 3-β, 11-α, 14-β-tetrahydroxy-7β, 8β-epoxy-5α, 14-β-bufa-20, 22-dienolide	2-α, 3-β, 11-α, 14-β-OH, 7β, 8β-epoxy, 2-α, 3-β-(tetrahydro-3′-β-OH, 4′-β-methoxy, 6′-methyl, 2H-pyran, 2′-α, 4′-α-diyldioxy)	90
254	tyledoside B	2-α, 3-β, 11-α, 14-β-tetrahydroxy-7β, 8β-epoxy-5α, 14-β-bufa-20, 22-dienolide	2-α, 3-β, 11-α, 14-β-OH, 7β, 8β-epoxy, 2-α, 3-β-(tetrahydro-3′-oxo, 4′-β-methoxy, 6′-β-methyl, 2H-pyran, 2′-α, 4′-α-diyldioxy)	90
255	tyledoside G	2-α, 3-β, 12-β, 14-β-tetrahydroxy-7β, 8β-epoxy-5α, 14-β-bufa-20, 22-dienolide	2-α, 3-β, 12-β, 14-β-OH, 7β, 8β-epoxy, 2-α, 3-β-(tetrahydro-3′-β-OH, 4′-β-methoxy, 6′-β-methyl, 2H-pyran, 2-α, 4-α-diyloxy)	90
256	tyledoside D	2-α, 3-β, 11-α, 14-β-tetrahydroxy-12-oxo-7β, 8β-epoxy-5α, 14-β-bufa-20, 22-dienolide	2-α, 3-β, 11-α, 14-β-OH, 7β, 8β-epoxy, 12-oxo, 2-α, 3-β-(tetrahydro, 3′-β-OH, 4′-β-methoxy, 6′-methyl, 2H-pyran, 2′-α, 4′-α-diyloxy)	90

Table 4—*continued*

No.	Substance	Genin	Substituents*	Ref.
257	tyledoside A	2-α, 3-β, 11-α, 14-tetrahydroxy-12-oxo-7β, 8β-epoxy-5-α, 14-β-bufa-20, 22-dienolide	2-α, 3-β, 11-α, 14-β-OH, 7β, 8β-epoxy, 12-oxo, 2-α, 3-β-(tetrahydro, 3′-oxo, 4′-β-methoxy, 6′-β-methyl, 2H-pyran, 2′-α, 4′-α-diyldioxy)	90, 93
258	tyledoside C = cotyledoside B	2-α, 3-β, 11-α, 14-β-tetrahydroxy-12-oxo-7β, 8β-epoxy-5-α-bufa-20, 22-dienolide	2-α, 3-β, 11-α, 14-β-OH, 7β, 8β-epoxy, 12-oxo, 2-α, 3-β-(tetrahydro, 3′-β-OH, 4′-α-OAc, 6′-α-methyl, 2H-pyran, 2′-α, 3′-α-diyldioxy)	89, 90
259	orbicuside B = cotyledoside C	2-α, 2-β, 3-β, 11-α, 12-β, 14-β-hexa-hydroxy-7β, 8β-epoxy-bufa-20, 22-dienolide	2-α, 2-β, 3-β, 11-α, 12-β, 14-β-OH, 7β, 8β-epoxy, 2-α, 2-β, 3-β-(tetrahydro, 6′-β-methyl, 2H-pyran, 2′-α, 3′-α, 4′-α-triyltrioxy)	89
260	orbicuside A = cotyledoside A	2-α, 2-β, 3-β, 11-α, 14-β-hydroxy-12-oxo-7β, 8β-epoxy-bufa-20, 22-dienolide	2-α, 2-β, 3-β, 11-α, 14-β-OH, 7β, 8β-epoxy, 12-oxo, 2-α, 2-β, 3-β-(tetrahydro, 6′-β-methyl, 2H-pyran, 2′-α, 3′-α, 4′-α-triyltrioxy)	89
261	orbicuside C = cotyledoside D	2-α, 2-β, 3-β, 6-β, 11-α, 14-β-hexa-hydroxy-12-oxo-7β, 8β-epoxy-bufa-20, 22-dienolide	2-α, 2-β, 3-β, 6-β, 11-α, 14-β-OH, 7β, 8β-epoxy, 12-oxo, 2-α, 2-β, 3-β-*O*-(tetrahydro, 6′-β-methyl, 2H-pyran, 2′-α, 3′-α, 4′-α-triyltrioxy	89
5-α-Bufadienolides with 19-CHO Group				
262	19-oxo-5-α-4, 5-dihydro-proscillaridin A	19-oxo-5-α-4, 5-dihydro-scillarenin	3-β, 14-β-OH, 3-*O*-α-L-Rha	62
263	16-β-hydroxy-bovogenin A	16-β-hydroxy-bovogenin A	3-β, 14-β, 16-β-OH	104, 108
264	16-β-formyloxy-bovogenin A	16-β-formyloxy-bovogenin A	3-β, 14-β-OH, 16-β-*O*-for	104, 108
265	3-dehydro-16-β-hydroxy-bovogenin A	3-dehydro-16-β-hydroxy-bovogenin A	14-β-OH, 16-β-OH, 3-oxo	108
Bufatettaenolides				
266	scillaridin	scillaridin	14-β-OH, 3(4), 5(6)-dien	49, 61
267	helleborogenone	3-oxo, 14-β-hydroxy-bufa-1, 4, 20, 22-tetraenolide	3-oxo, 14-β-OH, 1(2), 4(5)-dien	71–74

*Abbreviations: ac = acetyl; Cell = cellobiose (= D-glucose(1 → 4)-D-glucose); deO = deoxy; Digt = digitalose (= 6-deoxy-3-*O*-methyl-galactose); for = formyl; Gen = gentiobiose (= D-glucose (1 → 6)-D-glucose); Gentr = gentiotriose (= D-glucose (1 → 6)-D-glucose(1 → 6)-D-glucose); Glc = glucose; Glum = glucomethylose (= 6-deoxy-glucose); met = methyl; Rha = rhamnose; Thev- = thevetose; Xyl = xylose.

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