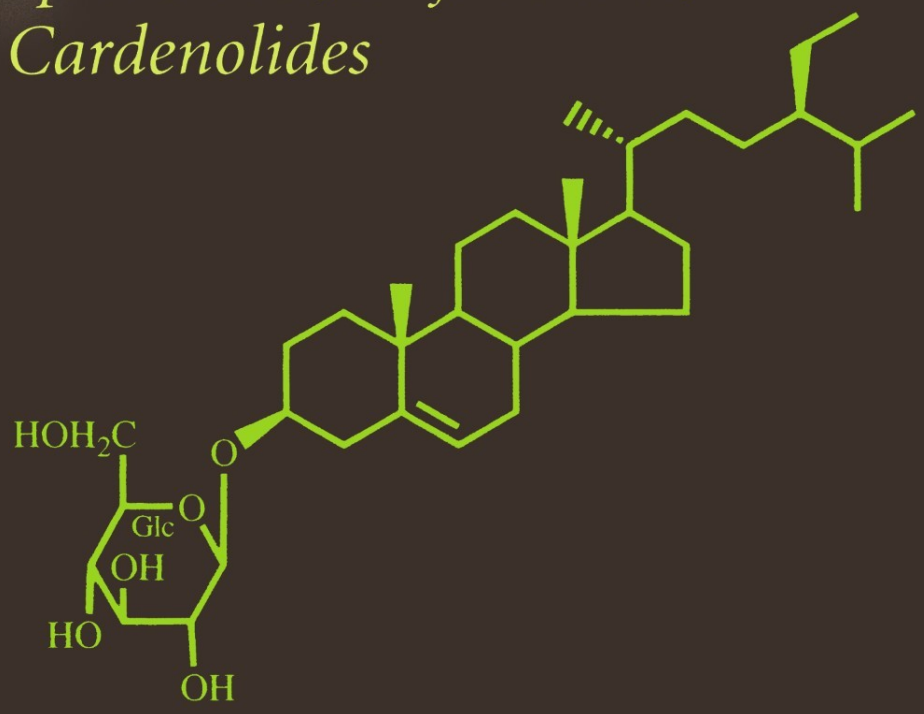
Spectroscopic Data of Steroid Glycosides

Volume 3

Spirostanes, Bufanolides, Cardenolides



Viqar Uddin Ahmad
Anwer Basha

Springer

Spectroscopic Data of Steroid Glycosides: Spirostanes, Bufanolides, Cardenolides

Volume 3

Volume 1
SPECTROSCOPIC DATA OF STEROID GLYCOSIDES: CHOLESTANES, ERGOSTANES, WITHANOLIDES, STIGMASTANE
Edited by Viqar Uddin Ahmad and Anwer Basha

Volume 2
SPECTROSCOPIC DATA OF STEROID GLYCOSIDES: STIGMASTANES, FUROSTANES, SPIRTOSTANES
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SPECTROSCOPIC DATA OF STEROID GLYCOSIDES: SPIROSTANES, BUFANOLIDES, CARDENOLIDES
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Spectroscopic Data of Steroid Glycosides: Spirostanes, Bufanolides, Cardenolides

Volume 3

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PREFACE

The present volumes reproduce the spectroscopic data of naturally occurring steroidal glycosides as far as they are available in the chemical literature published until the end of 2004. Steroids have the basic skeleton of cyclopentanoperhydrophenanthrene. Generally they do not have methyl groups attached to C-4 and thus differ from triterpenes. Many of the steroidal glycosides, or saponins, have interesting biological activities and constitute the active principles of the natural drugs. The cardiac glycosides (cardenolides) included in the present work act as life-saving medicines in certain ailments.

Not included in this work are the glycosides of steroidal alkaloids. However, the compounds which contain a nitrogen atom in the sugar or in the ester moiety (e.g. nicotinoyl moiety) are included.

The steroidal glycosides are arranged according to the class of their aglycones (steroidal parts). Within each class increasing molecular weight is taken as the basis for this arrangement. If the compounds of the same class have the same molecular weight, then the glycosides with lesser number of carbon atoms come earlier than those with more carbon atoms. Finally, if all these factors are the same, then the compounds are arranged in alphabetical order.

The chemical shifts in the proton nuclear magnetic resonance (PMR) spectral data are arranged according to the increasing δ (ppm) values. Each signal represents one proton unless indicated otherwise. The small alphabets used as superscript in PMR and ^{13}C-NMR (CMR)-spectral data mean that the assignments are ambiguous and may be reversed with signals having the same superscripts. The signals masked by solvent peaks or by other signals of the compound are marked by an asterisk.

Compounds can be easily located in this book with the help of the four indexes at the end of the last volume. The trivial names of the compounds given by the original authors are used as the heading of the compound. If no trivial name has been given, then the name of the plant from which the glycoside has been isolated followed by the word "saponin" or "glycoside" and then the numerical order are used as the main heading. For the subheading, the name of the aglycone (trivial names if available) followed by names of the sugars are used with clear indication of glycosidic linkages and branching of the sugar chain if present.

I am very grateful to Ms. Judy Watson of Chemical Abstract Service who has helped me greatly in finding the registry numbers of several compounds. This work would not have been possible without the help of literature surveyors Dr. Akbar Ali, Dr. Hidayat M. Khan, Dr. M. Athar Abbasi, Mr. Touseef Ali Khan, Mr. Umair Quyyum Khan, Miss. Humera Zaheer, Miss. Rukhsana Kausor, Miss Husna Qamar, Miss. Fouzia Shamim,

Ms. Zeenat Siddiqui, Muhammad Zubair, Afsar Khan, and Shazia Yasmeen to whom my sincere thanks are due. The whole book has been typed, composed, and structures drawn by Mr. Rafat Ali, Mr. Shabbir Ahmed, and Tariq Ilyas and I wish to express my sincere thanks to them.

ABBREVIATIONS

Aco	Acofrose
Afr	Acrofriose
Agl	Aglycone
All	Allose
Alt	Altrose
Ang	Angeloyl
Ant	Antirose
Ara	Arabinose
Boi	Boivinose
Ben	Benzoyl
Can	Canarose
Cin	Cinnamoyl
CMR	^{13}C-Nuclear Magnetic Resonance
Cym	Cymarose
DAC	4-Deoxy-4-aminocymarose
DMC	4-Deoxy-4-methylaminocymarose
Dal	6-Deoxyallose
Ddg	Dideoxygulopyranoside
Def	2-Deoxyfucose
Dex	6-Deoxy-D-glycero-L-threo-4-hexosulose
DHMP	2,3-Dihydroxy-3-methylpentanoyl
DMB	Dimethoxybenzoyl
DMC	4-Deoxy-4-methylaminocymarose
Dil	Digitalose
Din	Diginose
Dix	Digitoxose
Dma	Deoxymethylallose
DMP	3,4-Dimethyl-2(*E*)-pentenoyl
DMX	Dimethylxylose
EI	Electron ionization
ESI	Electro-spray ionization
F	Furanosyl
FAB	Fast Atom Bombardment
FD	Field desorption
Fuc	Fucose
Gal	Galactose

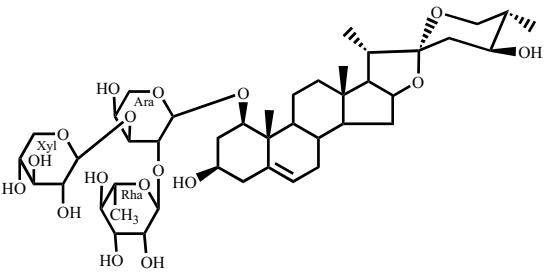
Glc	Glucose
Glum	6-Deoxy-α-L-glucopyranoside
Gum	Gulomethylose
HMB	Hydroxymethoxybenzoyl
HMG	Hydroxymethylglutaroyl
HR	High resolution
Ike	Ikemoyl (3,4-dimethyl-2-pentenoyl)
LD	Laser Desorption
Meb	2-Methylbutanoyl
MeXyl	Methylxylose
MGl	Methylglucose
Neg	Negative
Nic	Nicotinoyl
Ole	Oleandrose
Oli	Olivose
PMB	*Para* -methoxybenzoyl
Pos	Positive
PMR	Proton Magnetic Resonance
Qui	Quinovose
Rha	Rhamnose
Sar	Sarmentose
Tam	Talomethylose
Tar	Triacetylarabinose
The	Thevetose
TMB	Trimethoxybenzoyl
TOF	Time of flight
Xyl	Xylose

CONTENTS

ORNITHOGALUM THYRSOIDES SAPONIN 13

(24*S*,25*S*)-Spirost-5-ene-1β,3β,24-triol 1-O-{α-L-rhamnopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside}

Source : *Ornithogalum thyrsoides* (Liliaceae)
Mol. Formula : $C_{43}H_{68}O_{17}$
Mol. Wt. : 856
$[\alpha]_D^{26}$: -48.0° (c=0.10, MeOH)
Registry No. : [790300-61-7]



IR (film) : 3386 (OH), 2950, 2928 and 2905 (CH), 1047 cm^{-1}.

PMR (C_5D_5N, 500 MHz) : δ 0.85 (s, 3xH-18), 1.08 (d, *J*=6.5 Hz, 3xH-27), 1.12 (d, *J*=6.9 Hz, 3xH-21), 1.42 (s, 3xH-19), 1.74 (d, *J*=6.2 Hz, 3xH-6 of Rha), 1.82 (m, H-25), 1.97 (dd, *J*=12.7, 12.1 Hz, H-23ax), 2.30 (dd, *J*=12.7, 4.7 Hz, H-23eq), 3.59 (dd, *J*=11.4, 11.3 Hz, H-26ax), 3.71 (dd, *J*=11.3, 11.3 Hz, H-26eq), 3.83 (dd, *J*=12.0, 3.9 Hz, H-1), 3.88 (m, *W*½=2.0 Hz, H-3), 4.01 (ddd, *J*=12.1, 10.3, 4.7 Hz, H-24), 4.54 (q-like, *J*=7.4 Hz, H-16), 4.74 (d, *J*=7.4 Hz, H-1 of Ara), 4.98 (d, *J*=7.5 Hz, H-1 of Xyl), 5.58 (br d, *J*=5.7 Hz, H-6), 6.34 (br s, H-1 of Rha).

CMR (C_5D_5N, 125 MHz) : δ C-1) 83.8 (2) 37.5 (3) 68.2 (4) 43.8 (5) 139.5 (6) 124.7 (7) 32.4 (8) 33.1 (9) 50.3 (10) 42.9 (11) 24.0 (12) 40.3 (13) 40.2 (14) 56.8 (15) 31.9 (16) 81.5 (17) 62.6 (18) 16.7 (19) 14.9 (20) 42.2 (21) 15.0 (22) 111.8 (23) 41.8 (24) 70.6 (25) 40.0 (26) 65.3 (27) 13.6 **Ara** (1) 100.5 (2) 74.2 (3) 84.5 (4) 69.6 (5) 67.1 **Rha** (1) 101.8 (2) 72.5 (3) 72.5 (4) 74.1 (5) 69.5 (6) 19.2 **Xyl** (1) 106.5 (2) 74.6 (3) 78.3 (4) 71.0 (5) 67.0.

Mass (E.S.I., Positive ion, H.R.) : *m/z* 879.4302 [$(M+Na)^+$, calcd. for 879.4354].

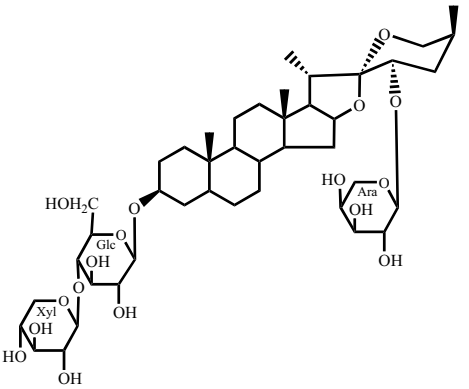
Reference

1. M. Kuroda, Y. Mimaki, K. Ori, H. Sakagami and Y. Sashida, *J. Nat. Prod.*, **67**, 1690 (2004).

ASPAROSIDE A'

(25*S*)-Spirostan-3β,23α-diol 3-O-[β-D-xylopyranosyl-(1→4)-β-D-glucopyranoside]-23-O-α-L-arabinopyranoside

Source : *Asparagus meioclados* (Liliaceae)
Mol. Formula : $C_{43}H_{70}O_{17}$
Mol. Wt. : 858
M.P. : 196-198°C
$[\alpha]_D$: -50.4° (c=2.13, MeOH-$CHCl_3$ 1:1)
Registry No. : [500761-43-3]



IR (KBr) **:** 980, 918, 900, 850 (intensity 918>900, 25*S*-spirostanol) cm^{-1}.

PMR (C_5D_5N, 500 MHz) **:** δ 0.78 (s, C*H*$_3$), 1.02 (s, C*H*$_3$), 1.14 (d, *J*=6.6 Hz, 3xH-27), 1.22 (d, *J*=6.7 Hz, 3xH-21), 1.85 (H-25), 1.90 (H-17), 2.20 (H-24A), 2.40 (H-24B), 3.00 (H-20), 3.28 (d, *J*=10.2 Hz, H-26A), 3.64 (H-5A of Xyl), 3.82 (H-5A of Ara), 3.84 (H-5 of Glc), 4.00 (H-2 of Xyl), 4.04 (H-2 of Glc), 4.05 (m, H-26B), 4.10 (H-4 of Xyl), 4.22 (H-5B of Xyl, H-3 of Ara), 4.24 (H-23, H-3 of Xyl), 4.26 (H-3 of Glc), 4.28 (H-5B of Ara), 4.32 (H-4 of Glc), 4.34 (H-4 of Ara), 4.40 (H-2 of Ara), 4.44 (H-6A of Glc), 4.54 (H-6B of Glc), 4.60 (H-16), 4.88 (d, *J*=7.7 Hz, H-1 of Glc), 4.92 (d, *J*=7.7 Hz, H-1 of Ara), 5.13 (d, *J*=7.6 Hz, H-1 of Xyl).

CMR (C_5D_5N, 125 MHz) **:** δ C-1) 30.8 (2) 26.8 (3) 75.2 (4) 30.6 (5) 36.9 (6) 26.9 (7) 26.7 (8) 35.3 (9) 40.1 (10) 35.2 (11) 21.1 (12) 40.7 (13) 41.3 (14) 56.2 (15) 31.8 (16) 81.4 (17) 62.8 (18) 17.2 (19) 23.8 (20) 36.2 (21) 14.5 (22) 111.2 (23) 72.3 (24) 34.6 (25) 30.4 (26) 64.0 (27) 17.7 **Glc** (1) 102.8 (2) 74.5 (3) 76.8 (4) 80.9 (5) 76.5 (6) 61.8 **Xyl** (1) 105.5 (2) 74.4 (3) 78.5 (4) 70.7 (5) 67.3 **Ara** (1) 106.2 (2) 72.1 (3) 74.3 (4) 68.6 (5) 65.8.

Mass (E.S.I.) **:** *m/z* 876 $[M+H_2O]^+$, 859 $[M+H]^+$, 841 $[M+H-H_2O]^+$, 727 [M+H-Pentose]$^+$, 577 $[M+H_2O$-H-2xPentose$]^+$, 565 [M-Pentose-Glc]$^+$, 432 [M-132-132-162]$^+$, 415 $[M+H$-2xPentose-Glc-$H_2O]^+$.

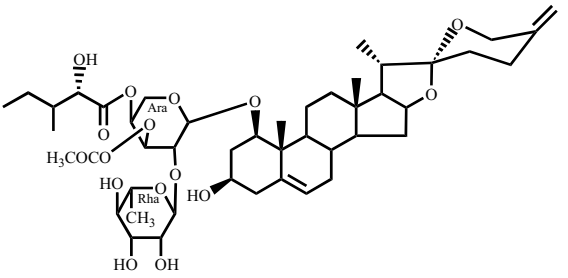
Reference

1. J. Feng, D.-F. Chen, Q.-Z. Sun, N. Nakamura, M. Hattori, *J. Asian Nat. Prod. Res*., **4**, 221 (2002).

RUSCUS ACULEATUS SAPONIN 11

Neoruscogein 1-O-{α-L-rhamnopyrranosyl-(1→2)-[3-O-acetyl-4-O-(2*S*,3*S*)-2-hydroxy-3-methylpentanoyl]-α-L-arabinopyranoside}

Source : *Ruscus aculeatus* L. (Liliaceae)
Mol. Formula : $C_{46}H_{70}O_{15}$
Mol. Wt. : 862
$[\alpha]_D^{26}$:.-40.0° (c=0.10, MeOH)
Registry No. : [205191-12-4]



IR (KBr) : 3430 (OH), 2930 (CH), 1740 (C=O), 1045 cm^{-1}.

PMR (C_5D_5N, 400 MHz) : δ 0.97 (s, 3xH-18), 1.14 (t, *J*=7.5 Hz, 3xH-5 of HMP), 1.17 (d, *J*=7.2 Hz, 3xH-21), 1.30 (d, *J*=6.9 Hz, 3xH-6 of HMP), 1.40 (s, 3xH-19), 1.75 (d, *J*=6.2 Hz, 3xH-6 of Rha), 2.00 (s, OCOC*H*$_3$), 4.77 (d, *J*=7.4 Hz, H-1 of Ara), 4.78 and 4.81 (each 1H, br s, 2xH-27), 5.44 (dd, *J*=9.7, 3.3 Hz, H-3 of Ara), 5.60 (br d, *J*=5.5 Hz, H-6), 5.66 (d, *J*=1.0 Hz, H-1 of Rha), 5.67 (br dd, *J*=3.3, 2.1 Hz, H-4 of Ara).

CMR (C_5D_5N, 100 MHz) : δ C-1) 83.2 (2) 37.2 (3) 68.1 (4) 43.7 (5) 139.3 (6) 124.8 (7) 31.9 (8) 33.2 (9) 50.3 (10) 42.8 (11) 24.3 (12) 40.4 (13) 40.6 (14) 57.0 (15) 32.4 (16) 81.5 (17) 63.2 (18) 16.9 (19) 15.0 (20) 42.0 (21) 15.0 (22) 109.5 (23) 33.3 (24) 29.0 (25) 144.5 (26) 65.0 (27) 108.6 **Ara** (1) 99.5 (2) 73.2 (3) 74.9 (4) 70.1 (5) 64.1 **Rha** (1) 102.1 (2) 72.3 (3) 72.5 (4) 73.9 (5) 69.5 (6) 19.0 **HMP** (1) 174.7 (2) 75.6 (3) 39.7 (4) 24.7 (5) 12.2 (6) 16.1 **Ac** (1) 170.1 (2) 20.7.

Mass (FAB, Negative ion) : *m/z* 861 $[M-H]^-$.

Biological Activity : It showed potent cytostatic activity on growth of Leukemia HL 60 cells, and 98.2% inhibition at 10 μg/ml sample concentration. Its IC_{50} value is 3.0 μg/ml.

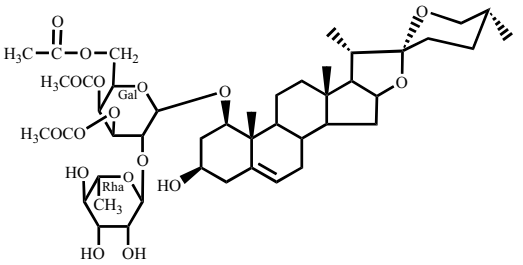
Reference

1. Y. Mimaki, M. Kuroda, A. Kameyama, A. Yokosuka and Y. Sashida, *Chem. Pharm. Bull*., **46**, 298 (1998).

RUSCUS ACULEATUS SAPONIN 17

Ruscogenin 1-O-{α-L-rhamnopyranosyl-(1→2)-3,4,6-tri-O-acetyl-β-D-galactopyranoside}

Source : *Ruscus aculeatus* L. (Liliaceae)
Mol. Formula : $C_{45}H_{68}O_{16}$
Mol. Wt. : 864
$[\alpha]_D^{25}$: -78.0° (c=0.10, MeOH)
Registry No. : [211036-50-9]



IR (KBr) **:** 3430 (OH), 2945 (CH), 1755 (C=O), 1455, 1375, 1235, 1140, 1075, 1055, 980, 965, 920, 900, 865, 835, 810 cm^{-1}.

PMR (C_5D_5N, 400 MHz) **:** δ 0.69 (d, *J*=4.8 Hz, 3xH-27), 0.97 (s, 3xH-18), 1.14 (d, *J*=6.7 Hz, 3xH-21), 1.40 (s, 3xH-19), 1.78 (d, *J*=6.1 Hz, 3xH-6 of Rha), 1.95 (s, OCOC*H*$_3$), 1.97 (s, OCOC*H*$_3$), 2.08 (s, OCOC*H*$_3$), 3.50 (dd, *J*=10.3, 10.3 Hz, H-26A), 3.58 (dd, *J*=10.3, 2.6 Hz, H-26B), 3.77 (dd, *J*=12.0, 3.7 Hz, H-1), 3.81 (m, H-3), 4.22 (br dd, *J*=6.9, 6.1 Hz, H-4 of Gal), 4.30 (dd, *J*=9.5, 9.5 Hz, H-4 of Rha), 4.32 (dd, *J*=11.3, 6.1 Hz, H-6A of Gal), 4.43 (dd, *J*=9.8, 7.7 Hz, H-2 of Gal), 4.48 (dd, *J*=9.5, 3.4 Hz, H-3 of Rha), 4.51 (br d, *J*=3.4 Hz, H-2 of Rha), 4.56 (dd, *J*=11.3, 6.9 Hz, H-6B of Gal), 4.58 (q-like, H-16), 4.75 (dq, *J*=9.5, 6.1 Hz, H-5 of Rha), 4.86 (d, *J*=7.7 Hz, H-1 of Gal), 5.49 (dd, *J*=9.5, 3.4 Hz, H-3 of Gal), 5.62 (br d, *J*=5.4 Hz, H-6), 5.69 (br s, H-1 of Rha), 5.76 (br d, *J*=3.4 Hz, H-4 of Gal).

CMR (C_5D_5N, 100 MHz) **:** δ C-1) 84.4 (2) 37.9 (3) 68.1 (4) 43.6 (5) 139.2 (6) 124.9 (7) 31.9 (8) 33.1 (9) 50.4 (10) 42.7 (11) 24.4 (12) 40.5 (13) 40.4 (14) 57.2 (15) 32.4 (16) 81.2 (17) 63.3 (18) 17.5 (19) 15.0 (20) 42.0 (21) 14.9 (22)

109.3 (23) 31.9 (24) 29.3 (25) 30.6 (26) 66.9 (27) 17.3 **Gal** (1) 99.8 (2) 75.2 (3) 75.2 (4) 68.5 (5) 70.8 (6) 62.2 **Rha** (1) 102.2 (2) 72.3 (3) 72.4 (4) 73.8 (5) 70.1 (6) 19.0 (O*C*OCH$_3$) 170.4, 170.1, 170.1 (OCO*C*H$_3$) 20.6, 20.5, 20.3.

Mass (FAB, Negative ion) **:** *m/z* 863 $[M-H]^-$, 821 $[M\text{-Acetyl}]^-$, 779 $[M\text{-Rha-Acetylx2}]^-$, 591 $[M\text{-Rha-Acetylx3}]^-$.

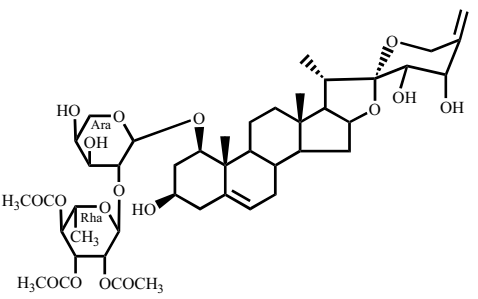
Biological Activity : Potent cytotatic activity on leukemia HL-60 cells, show 98.2% inhibition at 10 μg/ml. Its IC_{50} value is 3.1 μg/ml^{-1}.

Reference

1. Y. Mimaki, M. Kuroda, A. Kameyama, A. Yokosuka and Y. Sashida, *Phytochemistry*, **48**, 485 (1998).

DRACONIN A

(23*S*,24*S*)-Spirosta-5,25(27)-diene-1β,3β,23,24-tetrol 1-O-[2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside]



Source : *Dracaena draco* (Dracaenacea)
Mol. Formula : $C_{44}H_{64}O_{17}$
Mol. Wt. : 864
$[\alpha]_D^{20}$: -70° (c=1.5, EtOH
Registry No. : [565205-14-3]

IR (film, KBr) : 2380, 1740 (C=O) 1230 cm^{-1}.

PMR (C_5D_5N, 500 MHz) : δ 0.85 (s, 3xH-18), 0.94 (d, *J*=7.0 Hz, 3xH-21), 1.06 (s, 3xH-19), 1.15 (m, H-14), 1.17 (m, H-12A), 1.22 (d, *J*=6.3 Hz, 3xH-6 of Rha), 1.24 (H-9), 1.30 (H-11), 1.52 (H-7A, H-15A), 1.55 (m, H-8), 1.72 (m, H-12), 1.73 (dd, *J*=6.7, 8.6 Hz, H-17), 1.84 (dd, J-2 ax), 1.96 (H-15B), 1.97 (H-7B), 1.88 (s, OCOC*H*$_3$), 2.05 (s, OCOC*H*$_3$), 2.15 (s, OCOC*H*$_3$), 2.19 (m, H-2 eq), 2.23 (m, H-4A), 2.34 (m, H-4B), 2.65 (m, H-20), 3.37 (dd, *J*=4, 11.7 Hz, H-1), 3.50 (H-3 and H-23), 3.62 (dd, *J*=7.7, 8.5 Hz, H-2 of Ara), 3.68 (dd, *J*=7.0, 3.1 Hz, H-3 of Ara), 3.80 (br s, H-4 of Ara), 3.85 (d, *J*=12.9 Hz, H-26 eq), 3.94 (dd, *J*=12.8, 2.2 Hz, H-5A of Ara), 4.26 (m, H-24), 4.26 (d, *J*=7.6 Hz, H-1 of Ara), 4.30 (m, H-5 of Rha), 4.32 (m, H-5B of Ara), 4.35 (d, *J*=12.0 Hz, H-26B), 4.50 (dd, *J*=7.2, 15.4 Hz, H-16), 5.05 (br s, H-27A), 5.05 (dd, *J*=10.0, 9.8 Hz, H-4 of Rha), 5.11 (br s, H-27B), 5.21 (dd, *J*=3.2, 1.8 Hz, H-2 of Rha), 5.46 (d, *J*=1.9 Hz, H-1 of Rha), 5.46 (dd, *J*=10.1, 3.4 Hz, H-3 of Rha), 5.57 (d, *J*=5.8 Hz, H-6).

CMR (C_5D_5N, 125 MHz) : δ C-1) 85.07 (2) 39.87 (3) 67.84 (4) 42.49 (5) 137.54 (6) 125.60 (7) 31.49 (8) 32.53 (9) 50.10 (10) 42.14 (11) 23.39 (12) 39.87 (13) 40.52 (14) 56.69 (15) 31.86 (16) 83.32 (17) 60.81 (18) 16.54 (19) 14.31 (20) 36.08 (21) 14.03 (22) 112.42 (23) 68.42 (24) 74.08 (25) 143.07 (26) 60.15 (27) 114.21 **Ara** (1) 100.21 (2) 73.64

(3) 75.10 (4) 69.35 (5) 66.20 **Rha** (1) 96.21 (2) 69.91 (3) 68.78 (4) 71.58 (5) 66.20 (6) 17.35 ($OCOCH_3$) 169.89, 170.13, 170.76 ($OCOCH_3$) 20.81, 20.81, 20.97.

Mass (FAB, Positive ion) : *m/z* 865 $[M+H]^+$, 847 $[M+H-H_2O]^+$, 592 $[M\text{-Rha }(OAc)_3)^+]$.

Biological Activity : Inhibits the growth of HL-60 cells with IC_{50} 9.7 ± 2.7 μm.

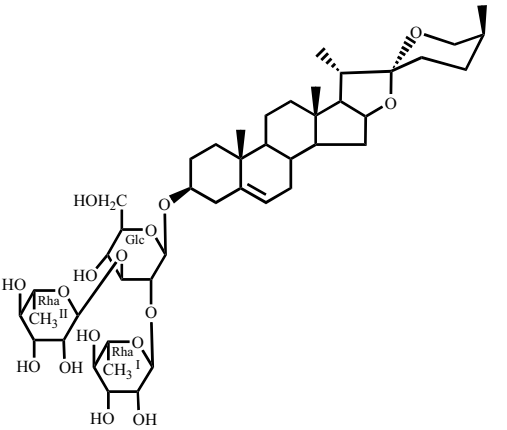
Reference

1. A.G. Gonzalez, J.C. Hernandez, F. Leon, J.I. Padron, F. Estever, J. Quintana and J. Bermejo, *J. Nat. Prod*., **66**, 793 (2003).

ASPARAGUS PLUMOSUS SAPONIN 2, HYPOGLAUCIN A

Yamogenin 3-O-{α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→3)]-β-D-glucopyranoside}

Source : *Asparagus plumosus*[1] (Liliaceae), *Dioscorea collettii* Hook. f. var. *hypoglauca* (Polibin) Pei et Ting
Mol. Formula : $C_{45}H_{72}O_{16}$
Mol. Wt. : 868
M.P. : 295-296°C
$[\alpha]_D^{25}$: -99° (c=0.9, $CDCl_3$-MeOH)
Registry No. : [93528-39-3]



IR (KBr)[1] **:** 3400 (OH), 1650 (C=O), 988, 921, 900, 885 cm^{-1} (intensity 921>900, 25*S*-Spiroketal).

CMR[2] : δ C-1) 37.5 (2) 30.3 (3) 77.2 (4) 38.8 (5) 140.7 (6) 121.3 (7) 31.7 (8) 32.5 (9) 50.4 (10) 37.1 (11) 21.1 (12) 39.9 (13) 40.4 (14) 56.6 (15) 29.3 (16) 81.0 (17) 62.6 (18) 14.7 (19) 19.3 (20) 42.5 (21) 16.2 (22) 109.6 (23) 26.2 (24) 27.6 (25) 26.4 (26) 66.8 (27) 14.8 **Glc** (1) 99.8 (2) 78.2 (3) 89.4 (4) 70.2 (5) 76.1 (6) 61.1 **Rha I** (1) 101.5 (2) 71.7 (3) 72.1 (4) 73.1 (5) 69.1 (6) 18.3 **Rha II** (1) 102.5 (2) 71.7 (3) 72.1 (3) 73.3 (4) 70.2 (6) 81.1.

Mass (F.D.)[1] : *m/z* (rel.intens.) 1015 [(M+H+146)$^+$, 11.4], 891 [(M+Na)$^+$, 5.6], 869 [(M+H)$^+$, 100], 868 [(M)$^+$, 49.7], 850 [(M-H_2O)$^+$, 4.5], 722 [(M-Rha)$^+$, 32.5], 576 [(M-2xRha)$^+$, 2.8], 415 [(M+H-2xRha-Glc)$^+$, 24.1].

Mass (FAB, Positive ion)[1] : *m/z* (rel.intens.) 869 [(M+H)$^+$, 0.57], 723 [(M+H-Rha)$^+$, 0.32], 415 [(M+H-2xRha-Glc)$^+$, 3.1], 139 [(Genin)$^+$, 44.2], 105 [(Genin)$^+$, 100].

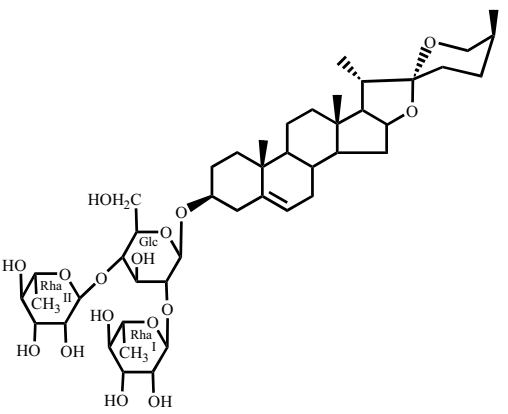
References

1. O.P. Sati and G. Pant, *Phytochemistry*, **24**, 123 (1985).
2. S. Tang and Z. Pang, *Zhiwu Xuebao*, **26**, 419 (1984).

COLLETTINSIDE III, TUBEROSIDE D (SOLANUM)

Yamogenin 3-O-[α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranoside]

Source : *Liriope platyphylla* Wang. et Tang.[1] (Liliaceae), *Dioscorea collectti* Hook.f.[2] (Dioscoreaceae), *Solanum tuberosum* L.[3] (Solanaceae), *Brachiaria decumbens* Stapf[4] (Graminae). Isolated admixed with its C-25-epimer (dioscin)
Mol. Formula : $C_{45}H_{72}O_{16}$
Mol. Wt. : 868
Registry No. : [60478-68-4]



IR (KBr)[2] : 3400 (OH), 1040 (OH), 982, 915 > 898, 830 (25*S*-spiroketal) cm^{-1}.

PMR (C_5D_5N, 500 MHz)[4] **:** δ 0.89 (H-9), 0.97 (H-1A), 1.03 (H-14), 1.05 (3xH-19), 1.06 (3xH-18), 1.07 (H-12A), 1.12 (3xH-27), 1.13 (3xH-21), 1.34 (H-24A), 1.42 (2xH-11), 1.44 (H-23A), 1.45 (H-7A), 1.55 (H-8), 1.62 (d, 3xH-6 of Rha II), 1.66 (H-12A), 1.72 (H-1B), 1.75 (3xH-6 of Rha), 1.77 (H-17), 1.80 (H-25), 1.84 (H-2A, H-7B), 1.87 (H-20, H-23B), 2.01 (2xH-15), 2.06 (H-2B), 2.13 (H-24B), 2.75 (2xH-4), 3.34 (H-26A), 3.62 (H-5 of Glc), 3.86 (H-6), 4.03 (H-26B), 4.08 (H-6A of Glc), 4.18 (H-3 of Glc), 4.21 (H-6B of Glc), 4.22 (H-2 of Glc), 4.33 H-4 of Rha II), 4.37 (H-4 of Rha I), 4.39 (H-4 of Glc), 4.48 (H-16), 4.53 (H-3 of Rha), 4.62 (H-2 of Rha II), 4.67 (H-3 of Rha I), 4.84 (H-2 of Rha I), 4.93 (H-5 of Rha II), 4.95 (H-1 of Glc, H-5 of Rha I), 5.30 (H-6), 5.85 (H-1 of Rha II), 6.39 (H-1 of Rha I).

CMR (C_5D_5N, 125 MHz)[4] **:** δ C-1) 37.6 (2) 30.3 (3) 78.1 (4) 39.1 (5) 140.9 (6) 121.9 (7) 32.4 (8) 31.8 (9) 50.4 (10) 37.2 (11) 21.2 (12) 39.9 (13) 40.5 (14) 56.7 (15) 32.3 (16) 81.2 (17) 63.0 (18) 16.4 (19) 19.5 (20) 42.5 (21) 15.0 (22) 109.4 (23) 26.5 (24) 26.3 (25): 27.6 (26) 65.2 (27) 15.2 **Glc I** (1) 100.4 (2) 77.9 (3) 78.2 (4) 78.6 (5) 77.0 (6) 61.3 **Rha** (1) 102.1 (2) 72.6 (3) 72.7 (4) 74.2 (5) 69.6 (6) 18.8 **Glc II** (1) 103.0 (2) 72.9 (3) 72.8 (4) 74.0 (5) 70.5 (6) 18.6.

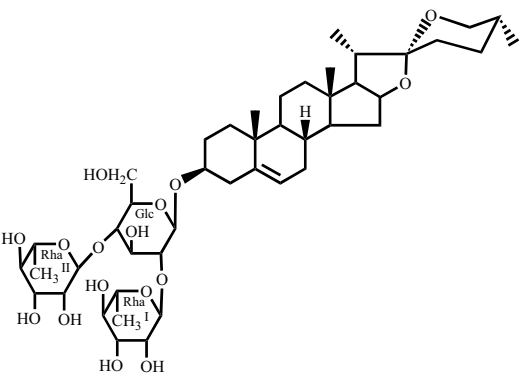
References

1. Y. Watanabe, S. Sanada, Y. Ida and J. Shoji, *Chem. Pharm. Bull*., **31**, 1980 (1983).
2. C.-L. Liu, Y.Y. Chen, S.-B. Ge and B.-G. Li, *Yaoxue Xuebao* (*Acta Pharm. Sin*.), 18, 597 (1983).
3. P.K. Kintya and T.I. Prasol, *Khim. Prir. Soedin*, 586 (1991); *Chem. Nat. Comp*., 27, 515 (1991).
4. V.S. Pires, A.T. Taketa, G. Gosmann and E.P. Schenkel, *J. Braz. Chem. Soc*., **13**, 135 (2002).

DIOSCIN, COLLETTISIDE III

Diosgenin 3-O{α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranoside}

Source : *Dioscorea tokoro* Makino[1] (Dioscoraceae), *Dioscorea colletti* var. *hypoglauca*[2] (Dioscoraceae), *Heloniopsis orientalis* (Thunb.) C. Tanaka[3] (Liliaceae), *Trillium*, *grandiflorum* (Michx.) Salisb.[4] (Liliaceae), *Paris dunniana* var. *oligophylla*[5] (Liliaceae), *Paris polyphylla* Sm.[6] (Liliaceae), *Allium ampeloprasum* Linn.[7] (Liliaceae) etc.
Mol. Formula : $C_{45}H_{72}O_{16}$
Mol. Wt. : 868
M.P. : 275-277°C (decomp.)[8]
$[\alpha]_D^{13}$: -115.0° (c=0.373, EtOH)[8]
Registry No. : [19057-60-4]



IR (KBr)[2] **:** 3422, 2937, 1637, 1454, 1381, 1044, 912 < 899 (25*R*-spiroketal), 812 cm^{-1}.

IR (Nujol)[7] **:** 3390, 2945, 2920, 2850, 1455, 1375, 1240, 1130, 1040, 980, 919, 895 and 810 cm^{-1}.

PMR (C_5D_5N, 500/600 MHz)[7] **:** δ 0.68 (d, *J*=5.8 Hz, 3xH-27), 0.80 (s, 3xH-18), 0.85 (t, *J*=7.5 Hz, H-9), 0.95 (t, *J*=13.1 Hz, H-1α), 1.02 (s, 3xH-19), 1.04 (m, H-14), 1.09 (m, H-12α), 1.11 (d, *J*=6.9 Hz, 3xH-21), 1.42 (m, H-11α, H-15α), 1.45 (m, H-8), 1.54 (m, H-25), 1.55 (m, H-24α), 1.55 (d, *J*=6.2 Hz, 3xH-6 of Rha II), 1.61 (m, H-23β), 1.67 (m, H-12β), 1.68 (m, H-23α), 1.71 (m, H-1β), 1.75 (d, *J*=6.2 Hz, H-6A), 1.76 (dd, *J*=6.9, 7.7 Hz, H-17), 1.77 (dd, *J*=13.9, 2.8 Hz, H-2α), 1.84 (m, H-7α), 1.92 (dq, *J*=6.9, 6.9 Hz, H-20), 2.01 (m, H-15β), 2.02 (m, H-2β), 2.64 (dd, *J*=12.7, 13.3 Hz, H-4β), 2.73 (ddd, *J*=3.5, 13.3, 1.0 Hz, H-4α), 3.46 (dd, *J*=10.8, 10.8 Hz, H-26α), 3.54 (dd, *J*=10.8, 2.0 Hz, H-26β), 3.57 (br d, *J*=9.6 Hz, H-5 of Glc), 3.82 (m, H-3), 4.03 (m, H-6A of Glc), 4.15 (m, H-2 and H-3 of Glc), 4.17 (m, H-6B of Glc), 4.25 (m, H-4 of Rha II), 4.27 (m, H-4 of Rha I), 4.31 (m, H-4 of Glc), 4.46 (dd, *J*=8.5, 1.5 Hz, H-3 of Rha II), 4.50 (dd, *J*=7.7, 8.1 Hz, H-16), 4.54 (dd, *J*=8.9, 1.5 Hz, H-3 of Rha I), 4.61 (br s, H-2 of Rha II), 4.76 (br s, H-2 of Rha I), 4.84 (dq, *J*=9.6, 6.2 Hz, H-5 of Rha II), 4.86 (d, *J*=7.7 Hz, H-1 of Glc), 4.89 (dq, *J*=9.6, 6.2 Hz, H-5 of Rha I), 5.29 (d, *J*=3.9 Hz, H-6), 5.77 (br s, H-1 of Rha II), 6.31 (br s, H-1 of Rha I), 6.39 (br, OH of Rha I), 6.49 (br, O*H* of Rha II), 6.59 (br, O*H* of Rha I), 6.68 (br, O*H* of Rha II), 6.69 (br, O*H* of Glc), 6.70 (br, O*H* of Glc and Rha I), 6.71 (br, O*H* of Rha II).

CMR (C_5D_5N, 50 MHz)[3] **:** δ C-1) 37.3 (2) 30.0 (3) 77.8 (4) 38.9 (5) 140.8 (6) 121.6 (7) 32.2 (8) 31.6 (9) 50.3 (10) 37.0 (11) 21.0 (12) 39.8 (13) 40.4 (14) 56.6 (15) 32.1 (16) 81.0 (17) 62.8 (18) 16.2 (19) 19.3 (20) 41.9 (21) 14.9 (22) 109.1 (23) 31.6 (24) 29.2 (25) 30.5 (26) 66.8 (27) 17.2 **Glc** (1) 100.2 (2) 78.9 (3) 76.6 (4) 78.1 (5) 77.7 (6) 61.3 **Rha I** (1) 101.8 (2) 72.5 (3) 72.2 (4) 73.7 (5) 69.3 (6) 18.5 **Rha II** (1) 102.7 (2) 72.6 (3) 72.2 (4) 73.9 (5) 70.3 (6) 18.3.

Mass (FAB, Positive ion)[3] **:** *m/z* 891 $[M+Na]^+$.

Mass (FAB, Positive ion)[2] **:** *m/z* 869 $[M+H]^+$, 723 $[M+H\text{-}Rha]^+$, 577 $[M+H\text{-}2xRha]^+$, 415 $[M+H\text{-}2xRha\text{-}Glc]^+$.

Mass (FAB, Negative ion, H.R.)[7] **:** *m/z* 867.4747 $[(M-H)^-$, requires 867.4742].

Mass (F.D.)[9] **:** *m/z* 907 $[M+K]^+$, 891 $[M+Na]^+$, 761 $[M+K\text{-}Rha]^+$, 745 $[M+Na\text{-}Rha]^+$, 729 $[M+Na\text{-}(O\text{-}Rha)]^+$, 457 $[M+2xNa]^{++}$.

Biological Activity : Antifungal activity against *Candida albicans, Aspergillus flavus* and other fungi.[4] Causes morphological abnormality of *Pyricularia oryzae* mycelia,[2] exhibits cytotoxic activity against the cancer cell line K 562 *in vitro*.[2] The compound shows antifungal and hemolytic activity.[10]

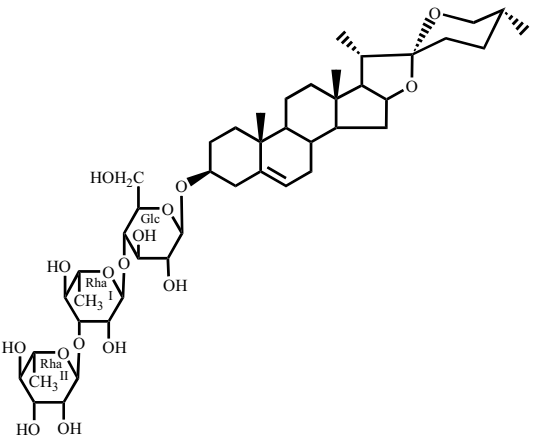
References

1. R.E. Marker, T. Tsukamoto and D.L. Turrner, *J. Am. Chem. Soc*., **62**, 2525 (1940).
2. K. Hu, A. Dong, X. Yao, H. Kobayashi and S. Iwasaki, *Planta Med.*, **62**, 573 (1996).
3. K. Nakano, K. Murakami, Y. Takaishi, T. Tomimatsu and T. Nohara, *Chem. Pharm. Bull*., **37**, 116 (1989).
4. C.D. Hufford, S. Liu and A.M. Clark, *J. Nat. Prod.*, **51**, 94 (1988).
5. W.-K. Huang, *Yao Hsueh Hsueh Pao*, **12**, 657 (1965); *Chem. Abstr*., **64**, 11553 g (1966).
6. A. Singh, S.N. Srivastava and L.D. Kapoor, *Indian J. Chem*., **4**, 460 (1966).
7. N. Sata, S. Matsunaga, N. Fusetani, H. Nishikawa, S. Takamura and T. Saito, *Biosci. Biotechnol. Biochem*., **62**, 1904 (1998).
8. T. Tsukamoto, T. Kawasaki and T. Yamauchi, *Chem. Pharm. Bull*., **4**, 35 (1956).
9. H.-R. Schulten, T. Komori and T. Kawasaki, *Tetrahedron*, **33**, 2595 (1977).
10. M. Takechi, S. Shimada and Y. Tanaka, *Phytochemistry*, **30**, 3943 (1991).

FLORIBUNDASAPONIN C

Diosgenin 3-O-[α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranoside]

Source : *Dioscorea floribunda* Mart. et Gal. (Dioscoreaceae)
Mol. Formula : $C_{45}H_{72}O_{16}$
Mol. Wt. : 868
M.P. : 255-258°C
$[\alpha]_D$: -93.6° (C_5H_5N)
Registry No. : [68406-04-2]



IR (Nujol) **:** 3330, 918, 978, 898, 868, 840, 815 cm^{-1}.

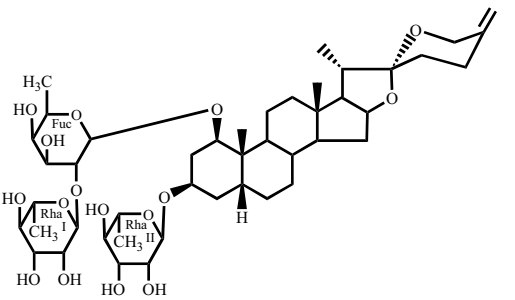
Reference

1. S.B. Mahato, N.P. Sahu and B.C. Pal, *Indian Journal of Chemistry*, **16**(B), 350 (1978).

REINECKIA CARNEA SAPONIN 1

Convallamarogenin 1-O-[α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranoside]-3-O-α-L-rhamnopyranoside

Source : *Reineckia carnea* Kunth (Liliaceace)
Mol. Formula : $C_{45}H_{72}O_{16}$
Mol. Wt. : 868
M.P. : 223-225°C (decomp.)
$[\alpha]_D^{36}$: -81.9° (c=1.05, MeOH)
Registry No. : [108382-81-6]



IR (KBr) : 3500-3300 (OH), 980, 945, 915, 895, 875, 830 cm^{-1} ($\Delta^{25\,(27)}$-spiroketal).

PMR (C_5D_5N, 80.0 MHz) : δ 0.84 (s, 3xH-18), 1.06 (d, *J*=7.0 Hz, 3xH-21), 1.25 (s, 3xH-19), 1.45 (d, *J*=6.5 Hz, sec. CH_3), 1.58 (d, *J*=5.8 Hz, sec. CH_3), 1.66 (d, *J*=5.4 Hz, sec. CH_3), 5.32 (s, anomeric H), 6.36 (s, anomeric H).

CMR (, 20.0 MHz) : C-1) 77.5 (2) 29.7 (3) 70.0 (4) 33.9 (5) 30.9 (6) 26.9[a] (7) 26.6[a] (8) 34.6 (9) 45.7 (10) 39.6 (11) 22.1 (12) 40.3 (13) 40.6 (14) 56.9 (15) 32.2 (16) 81.4 (17) 63.1 (18) 16.7 (19) 17.0 (20) 41.8 (21) 15.0 (22) 109.4 (23) 33.2[b] (24) 28.9[b] (25) 144.4 (26) 65.0 (27) 108.7 **Fuc** (1) 99.1[c] (2) 77.0 (3) 74.6 (4) 73.4 (5) 71.4 (6) 17.0 **Rha I** (1) 101.2[c] (2) 72.1[d] (3) 72.7[d] (4) 74.0 (5) 69.0 (6) 18.8[e] **Rha II** (1) 99.3 (2) 72.2 (3) 72.2 (4) 73.9 (5) 69.9 (6) 18.7.

Mass (F.D.) : *m/z* 892 $[M+H+Na]^+$, 869 $[M+H]^+$, 147 $[C_6H_{10}O_4]^+$.

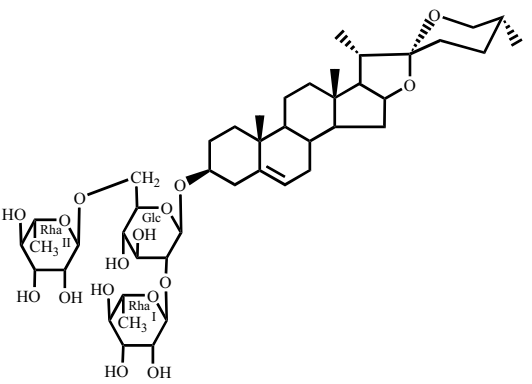
Reference

1. K. Iwagoe, T. Konishi and S. Kiyosawa, *Yakugaku Zasshi*, **107**, 140 (1987).

SPRENGERININ D

(25*R*)-Spirost-5-en-3β-ol-3-O-{α-L-rhamnopyranosyl-(1→2)-[α-L-rhmnopyransyl-(1→6)]-β-D-glucopyranoside}

Source : *Asparagus sprengeri* Regel (Liliaceae)
Mol. Formula : $C_{45}H_{72}O_{16}$
Mol. Wt. : 868
M.P. : 250-255°C (MeOH)
$[\alpha]_D^{20}$: -85.2° (c=1.0, Pyridine)
Registry No. : [88861-92-1]



IR (KBr) : 3400 (OH), 2840 (C=CH), 1045, 986, 920, 898 (intensity 898 > 920, 25*R*-spiroketal), 850 cm^{-1}.

PMR (DMSO-d_6, 100 MHz) : δ 4.85 (d, *J*=6.5 Hz, H-1 of Glc), 4.98 (br s, H-1 of Rha), 5.25 (d, *J*=2.0 Hz, H-1 of Rha).

Mass (FD) (Silicone emitter 25.5-29 MA) : *m/z* (rel.intens.) 907 $[M+K]^+$ (92), 891 $[M+Na]^+$ (100), 869 $[M+H]^+$ (3), 868 $[M]^+$ (2), 745 $[(M+Na)-146]^+$ (11), 723 $[(M+H)-146]^+$ (20), 599 $[(M+Na)-292]^+$ (3.5), 577 $[(M+H)-292]^+$ (20), 457 $[M+2Na]^{2+}$ (19), 413 $[genin]^+$ (45), 397 [spirostadiene $+H]^+$ (20).

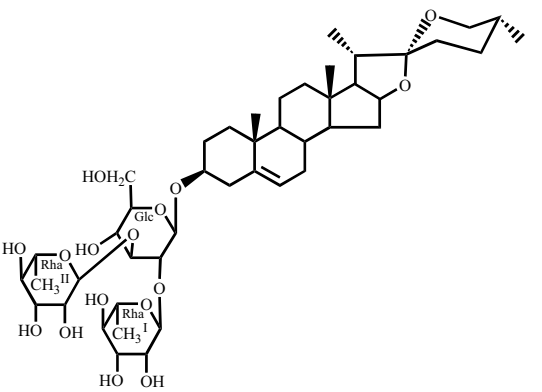
Reference

1. S.C. Sharma, R. Sharma and R. Kumar, *Phytochemistry*, **22**, 2259 (1983).

TACCAOSIDE, COLLETTISIDE IV

Diosgenin 3β-O-[α-L-rhamnopyranosyl-(1→2)]-[α-L-rhamnopyranosyl-(1→3)]-β-D-glucopyranoside

Source : *Tacca cheancer*[1], *Tacca chantrieri* Andre.[2] (Taccaceae)
Mol. Formula : $C_{45}H_{72}O_{16}$
Mol. Wt. : 868
M.P. : 276-278°C[2]
$[\alpha]_D^{25}$: -102° (c=0.10, MeOH)[2]
Registry No. : [75055-90-2



IR (KBr)[2] : 3450 (OH), 1620, 1130, 1035, 1010 (C-O-C), 920, 900, 867, 840, 810 cm^{-1} (920<900, 25*R*-spiroketal).

CMR (C_5D_5N)[2] : δ C-1) 37.5 (2) 30.0 (3) 77.9 (4) 38.7 (5) 140.8 (6) 121.7 (7) 32.2 (8) 31.7 (9) 50.3 (10) 37.1 (11) 21.1 (12) 39.8 (13) 40.5 (14) 56.7 (15) 32.2 (16) 81.1 (17) 62.9 (18) 16.3 (19) 19.3 (20) 42.0 (21) 15.0 (22) 109.2 (23) 31.7 (24) 29.3 (25) 30.5 (26) 66.9 (27) 17.3 **Glc** (1) 99.9 (2) 78.2 (3) 87.5 (4) 70.5 (5) 77.9 (6) 62.2 **Rha I** (1) 102.4 (2) 72.3 (3) 72.6 (4) 73.4 (5) 69.7 (6) 18.5 **Rha II** (1) 103.7 (2) 72.3 (3) 72.6 (4) 73.4 (5) 69.9 (6) 18.3.

Mass (F.D.)[2] : *m/z* 869 $[M+H]^+$.

References

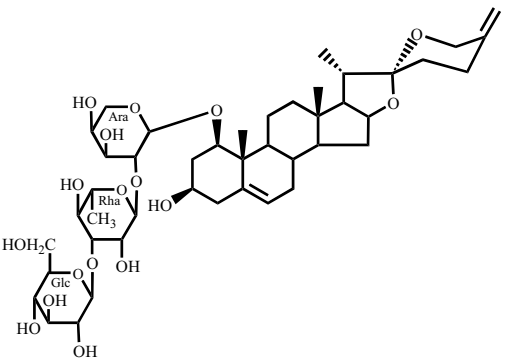
1. F.M. Ngok, A.N. Kel'ginbaev, M.B. Gorovits and N.K. Abubakirov, *Khim. Prir. Soedin*., 352 (1980); *Chem. Nat. Comp*., **16**, 262 (1980).

2. J. Zhou, C. Chen, R. Liu and C. Yang, *Zhiwu Xuebao* (*Acta Bot. Sin.*), **25**, 568 (1983).

RUSCUS ACULEATUS SAPONIN 5, RUSCOPONTICOSIDE D, RUSCIN

Neoruscogenin 1-O-{β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside}

Source : *Ruscus aculeatus* L.[1] (Liliaceae)
Mol. Formula : $C_{44}H_{68}O_{17}$
Mol. Wt. : 868
$[\alpha]_D^{26}$: -64.0° (c=0.10, MeOH)[2]
Registry No. : [39491-41-3]



PMR (C_5D_5N, 400 MHz)[2] : δ 0.86 (s, 3xH-18), 1.05 (d, *J*=6.9 Hz, 3xH-21), 1.47 (s, 3xH-19), 1.69 (d, *J*=6.1 Hz, 3xH-6 of Rha), 4.14 (2H, overlapping, H-3 and H-4 of Ara), 4.63 (d, *J*=7.6 Hz, H-1 of Ara), 4.78 and 4.81 (each 1H, br s, 2xH-27), 5.58 (br d, *J*=5.5 Hz, H-6), 5.67 (d, *J*=7.8 Hz, H-1 of Glc), 6.38 (d, *J*=1.1 Hz, H-1 of Rha).

CMR (C_5D_5N, 100 MHz)[2] : δ C-1) 84.8 (2) 38.1 (3) 68.2 (4) 43.8 (5) 139.6 (6) 124.8 (7) 32.0 (8) 33.1 (9) 50.5 (10) 43.0 (11) 23.9 (12) 40.3 (13) 40.2 (14) 56.9 (15) 32.4 (16) 81.5 (17) 63.0 (18) 16.7 (19) 15.1 (20) 41.8 (21) 15.0 (22) 109.5 (23) 33.2 (24) 29.0 (25) 144.5 (26) 65.0 (27) 108.6 **Ara** (1) 101.4 (2) 74.3 (3) 76.1 (4) 70.3 (5) 67.7 **Rha** (1) 101.2 (2) 72.1 (3) 82.7 (4) 73.3 (5) 69.3 (6) 18.7 **Glc** (1) 106.5 (2) 76.1 (3) 78.3 (4) 71.7 (5) 78.4 (6) 62.6.

Mass (E.S.I., Positive ion)[3] : *m/z* 891 $[M+Na]^+$, 869 $[M+H]^+$, 707 $[M+H\text{-}Glc]^+$, 561 $[M+H\text{-}Glc\text{-}Rha]^+$, 429 $[Agl+H]^+$, 411 $[Agl+H\text{-}H_2O]^+$.

Mass (FAB, Negative ion, ESI)[2] : *m/z* 867 $[M\text{-}H]^-$.

Biological Activity : It possesses cytostatic activity on growth of Leukemia HL 60 cells and shows 16.8% inhibition at 10 µg/ml sample concentration.[2]

References

1. E. Bombardelli, A. Bonati, B. Gabetta and G. Mustich, *Fitoterapia*, **42**, 127 (1971).

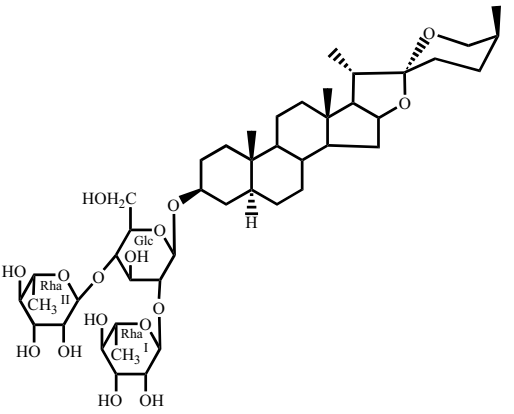
2. Y. Mimaki, M. Kuroda, A. Kameyama, A. Yokosuka and Y. Sashida, *Chem. Pharm. Bull*., **46**, 298 (1998).

3. E. de Combarieu, M. Falzoni, N. Fuzzati, A. Giori, M. Lovati and R. Pace, *Fitoterapia*, **73**, 583 (2002).

NICOTIANOSIDE C

(25*S*)-5α-Spirostan-3β-ol-3-O-{α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranoside}

Source : *Nicotiana tabacum* L. (Solanceae)
Mol. Formula : $C_{45}H_{74}O_{16}$
Mol. Wt. : 870
M.P. : 268-269°C
$[\alpha]_D^{22}$: -73° (c=1.0, CH_3OH)
Registry No. : [174761-03-6]



PMR (C_5D_5N, 300/250 MHz) : δ 0.71 (s, 3xH-18), 0.76 (s, 3xH-19), 1.03 (d, $J_{25,27}$=7.0 Hz, 3xH-27), 1.06 (d, $J_{20,21}$=7.0 Hz, 3xH-21), 1.52 ($J_{6,5}$=7.0 Hz, H-6 of Rha II), 1.64 (d, $J_{6,5}$=6.5 Hz, H-6 of Rha I), 3.30 (br d, H-26A), 3.50 (m, H-5 of Glc), 3.62 (m, $J_{26A,26B}$=11.0 Hz, H-26B), 3.82 (m, H-3), 3.90 (dd, $J_{6A,AB}$=12.5 Hz, H-6A of Glc), 4.00 (t, $J_{2,3}$=7.3 Hz, H-2 of Glc), 4.06 (dd, $J_{3,4}$=9.8 Hz, H-3 of Glc), 4.18 (t, $J_{4,5}$=9.5 Hz, H-4 of Rha I), 4.19 ($J_{4,5}$=9.5 Hz, H-4 of Rha II), 4.38 (t, $J_{4,5}$=10.0 Hz, H-4 of Glc), 4.40. (dd, $J_{3,4}$=9.5 Hz, H-3 of Rha II), 4.42 ($J_{3,4}$=9.5 Hz, H-3 of Rha I), 4.50 ($J_{2,3}$=3.5 Hz, H-2 of Rha II), 4.62 (dd, $J_{2.3}$=3.5 Hz, H-2 of Rha I), 4.72 (dq, $J_{5.6}$=6.5 Hz, H-5 of Rha I), 4.73 ($J_{5,6}$=7.0 Hz, H-5 of Rha II), 4.82 (d, $J_{1.2}$=7.5 Hz, H-1 of Glc), 5.65 ($J_{1,2}$=1.5 Hz, H-1 of Rha II), 6.12 (d, $J_{1.2}$=1.5 Hz, H-1 of Rha I).

CMR (C_5D_5N, 125 MHz) : δ C-1) 37.1 (2) 29.9 (3) 78.0 (4) 34.3 (5) 44.8 (6) 28.9 (7) 31.9 (8) 34.8 (9) 54.1 (10) 35.3 (11) 21.2 (12) 40.4 (13), 40.6 (14) 56.5 (15) 32.1 (16) 80.6 (17) 61.9 (18) 16.4 (19) 12.0 (20) 42.3 (21) 14.6 (22) 109.2 (23) 27.1 (24) 25.9 (25) 26.1 (26) 65.1 (27) 16.2 **Glc** (1) 100.0 (2) 79.0 (3) 77.4 (4) 78.4 (5) 77.1 (6) 61.6 **Rha I** (1) 102.3 (2) 72.6 (3) 72.8 (4) 74.2 (5) 70.6 (6) 18.6 **Rha II** (1) 103.0 (2) 72.6 (3) 72.8 (4) 74.0 (5) 69.7 (6) 18.8.

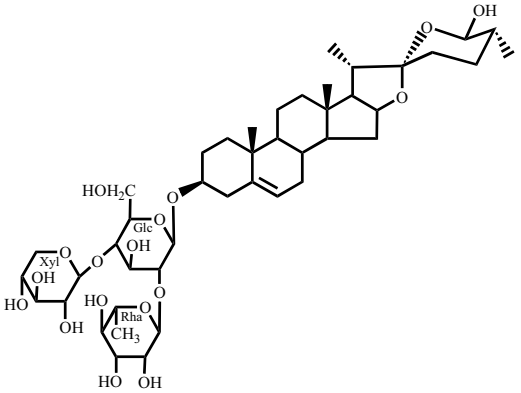
Reference

1 S.A. Shvets, P.K. Kintya, O.N. Gutsu, and V.I. Grishkovets, *Khim. Prir. Soedin.*, **31,** 396 (1995); *Chem. Nat. Comp.*, **31**, 332 (1995).

ANGUIVIOSIDE C

(25*R*,26*R*)-Spirost-5-en-3β,26-diol 3-O-[α-L-rhamnopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucopyranoside]

Source : *Solanum anguivi* (Solanaceae)
Mol. Formula : $C_{44}H_{70}O_{17}$
Mol. Wt. : 870
$[\alpha]_D^{26}$: -67.4° (c=0.27, MeOH)
Registry No. : [276680-83-2]



PMR (C_5D_5N, 500 MHz) : δ 1.01 (s, 3xH-18 and 3xH-19), 1.15 (d, *J*=3.1 Hz, 3xH-27), 1.27 (d, *J*=6.7 Hz, 3xH-21), 1.74 (3xH-6 of Rha I), 3.67 (br t, *J*=10.7 Hz, H-5 of Xyl), 3.84 (m, H-5 of Glc), 4.00* (H-2 of Xyl, H-4 of Glc), 4.10 (br t, *J*=9.2 Hz, H-3 of Xyl), 4.11* (H-2 and H-3 of Glc I, H-4 and H-5 of Xyl), 4.26* (H-6 of Glc and H-4 of Rha), 4.45 (br t, *J*=12.2 Hz, H-6 of Glc), 4.56 (m, H-16), 4.70 (br, *J*=7.9 Hz, H-3 of Rha), 4.86 (br s, H-2 of Rha), 4.91 (m, H-5 of Rha), 4.97* (H-1 of Glc I and Xyl). * overlapped signals.

CMR (C_5D_5N, 100 MHz) : δ C-1) 37.5 (2) 30.1 (3) 77.9 (4) 38.7 (5) 140.8 (6) 121.9 (7) 32.3 (8) 31.4 (9) 50.3 (10) 37.1 (11) 21.1 (12) 40.2 (13) 41.0 (14) 56.6 (15) 32.1 (16) 81.7 (17) 62.6 (18) 19.4 (19) 16.6 (20) 41.6 (21) 14.8 (22)

113.5 (23) 32.3 (24) 30.1 (25) 36.2 (26) 96.1 (27) 17.4 **Glc** (1) 99.9 (2) 77.4 (3) 88.2 (4) 69.5 (5) 77.7 (6) 62.3 **Rha** (1) 102.4 (2) 72.4 (3) 72.8 (4) 74.0 (5) 69.6 (6) 18.7 **Xyl** (1) 105.4 (2) 74.6 (3) 78.3 (4) 70.6 (5) 67.2.

Mass (FAB, Positive ion) **:** *m/z* 910 $[M+K+H]^+$.

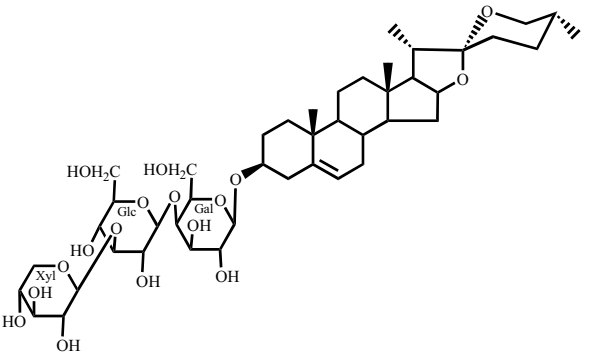
Reference

1. X-H. Zhu, T. Ikeda and T. Nohara, *Chem. Phram. Bull.*, **48**, 568 (2000).

CAPSICOSIDE C_3

Diosgenin 3-O-[β-D-xylopyranosyl-(1→3)-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside]

Source : *Capsicum annum* L. (Solanaceae)
Mol. Formula : $C_{44}H_{70}O_{17}$
Mol. Wt. : 870
M.P. : 263-265°C
$[\alpha]_D^{20}$: -60.0° (c=1.0, CH_3OH)
Registry No. : [125456-10-2]



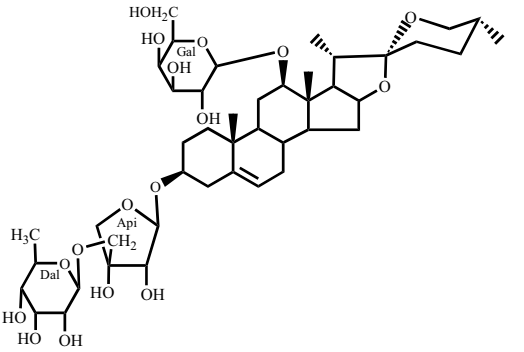
Reference

1. E.V. Gutsu and P.K. Kintya, *Khim. Prir. Soedin*., 582 (1989); *Chem. Nat. Comp*., **25**, 500 (1989).

HELONIOPSIS ORIENTALIS SAPONIN 2

Heloniogenin 3-O-[β-D-6-deoxyallopyranosyl-(1→5)-β-D-apiofuranopyranoside]-12-O-[β-D-galactopyranoside]

Source : *Heloniopsis orientalis* (Thunb.) C. Tanaka (Liliaceae)
Mol. Formula : $C_{44}H_{70}O_{17}$
Mol. Wt. : 870
$[\alpha]_D^{24}$: -41.0° (c=1.0, MeOH)
Registry No. : [121795-63-9]



IR (KBr) **:** 3400 (OH), 980, 960, 912, 900, 860, 840 cm^{-1}. 900 > 912 cm^{-1} (25*R*-spiroketal).

CMR (C_5D_5N, 200 MHz) **:** δ C-1) 37.1 (2) 30.1 (3) 77.5 (4) 39.3 (5) 141.2 (6) 121.5 (7) 32.0 (8) 31.7 (9) 49.0 (10) 36.8 (11) 27.5 (12) 82.6 (13) 44.8 (14) 44.3 (15) 32.0 (16) 80.9 (17) 53.0 (18) 17.0 (19) 19.2 (20) 42.2 (21) 15.2 (22) 109.3 (23) 32.0 (24) 29.3 (25) 30.6 (26) 66.8 (27) 17.3 **Api** (1) 108.0 (2) 78.3 (3) 78.9 (4) 74.6 (5) 72.9 **Dal** (1) 102.5 (2) 74.1 (3) 72.3 (4) 72.7 (5) 69.8 (6) 18.5 **Gal** (1) 107.1 (2) 72.9 (3) 75.4 (4) 70.5 (5) 76.6 (6) 62.0.

Mass (FAB, Positive ion) **:** *m/z* 893 $[M+Na]^+$.

Mass (E.I.) **:** *m/z* 592, 430, 412, 394, 298, 139.

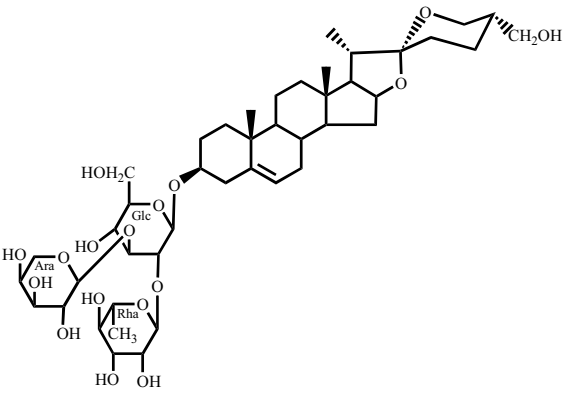
Reference

1. K. Nakano, K. Murakami, Y. Takaishi, T. Tomimatsu and T. Nohara, *Chem. Pharm. Bull*., **37**, 116 (1989).

LILIUM LONGIFLORUM SAPONIN 2

(25*S*)-Spirost-5-ene-3β,27-diol 3-O-{α-L-rhamnopyranosyl-(1→2)-[α-L-arabinopyranosyl-(1→3)]-β-D-glucopyranoside}

Source : *Lilium longiflorum* (Liliaceae)
Mol. Formula : $C_{44}H_{70}O_{17}$
Mol. Wt. : 870
$[\alpha]_D^{28}$: -58.0° (c=0.10, MeOH)
Registry No. : [159690-18-3]



IR (KBr) : 3370 (OH), 2920 (CH), 1445, 1370, 1245, 1040, 955, 905, 860, 830, 805, 775 cm^{-1}.

PMR (C_5D_5N, 400 MHz) **:** δ 0.85 (s, 3xH-18), 1.06 (s, 3xH-19), 1.17 (d, *J*=6.9 Hz, 3xH-21), 1.75 (d, *J*=6.1 Hz, 3xH-6 of Rha), 3.66 (dd, *J*=11.0, 7.3 Hz, H-27A), 3.74 (dd, *J*=11.0, 5.0 Hz, H-27B), 3.90 (dd, *J*=11.1, 11.1 Hz, H-26A), 4.03 (overlapping, H-26B), 4.91 (d, *J*=7.5 Hz, H-1 of Glc), 4.97 (d, *J*=7.0 Hz, H-1 of Ara), 5.34 (br d, *J*=4.1 Hz), 6.28 (br s, H-1 of Rha).

CMR (C_5D_5N, 100.6 MHz) **:** δ C-1) 37.5 (2) 30.1 (3) 77.8[a] (4) 38.7 (5) 140.8 (6) 121.9 (7) 32.3[b] (8) 31.7 (9) 50.3 (10) 37.2 (11) 21.1 (12) 39.9 (13) 40.5 (14) 56.7 (15) 32.4[b] (16) 81.2 (17) 63.0 (18) 16.4 (19) 19.4 (20) 42.1 (21) 15.1 (22) 109.7 (23) 31.6 (24) 24.1 (25) 39.2 (26) 64.1 (27) 64.4 **Glc** (1) 100.0 (2) 78.0 (3) 88.1 (4) 69.7[c] (5) 77.7[a] (6) 62.5 **Rha** (1) 102.5 (2) 72.5 (3) 72.9 (4) 74.2 (5) 69.4 (6) 18.7 **Ara** (1) 105.6 (2) 72.3 (3) 74.6 (4) 69.6[c] (5) 67.8.

Mass (FAB, Negative ion) : *m/z* 869 $[M-H]^-$.

Biological Activity : The compound shows 4.5% inhibition of the TPA-enhanced ^{32}P-incorporation into phosphopholipids of HeLa cells at a concentration of 50 $\mu g/ml^{-1}$.