Spectroscopic Data of Steroid Glycosides: Pregnanes, Androstanes, and Miscellaneous

Volume 5

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

Volume 2
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Volume 6
SPECTROSCOPIC DATA OF STEROID GLYCOSIDES: MISCELLANEOUS STEROIDS AND INDEXES
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Spectroscopic Data of Steroid Glycosides: Pregnanes, Androstanes, and Miscellaneous

Volume 5

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Library of Congress Control Number: 2006922481

ISBN-10: 0-387-31164-5
ISBN-13: 978-0387-31164-7
Set ISBN: 0-387-34348-2

9 8 7 6 5 4 3 2 1

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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

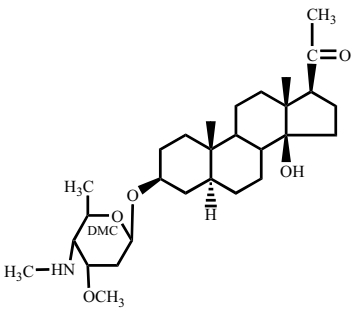
Aco	Acofrose
Afr	Acrofriose
Agl	Aglycone
All	Allose
Alt	Altrose
Ang	Angeloyl
Ant	Antirose
Ara	Arabinose
Boi	Boivinose
Ben	Benzoyl
Can	Canarose
Cin	Cinnamoyl
CMR	^{13}C-Nuclear Magnetic Resonance
Cym	Cymarose
DAC	4-Deoxy-4-aminocymarose
DMC	4-Deoxy-4-methylaminocymarose
Dal	6-Deoxyallose
Ddg	Dideoxygulopyranoside
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

HOLACURTINE

3β,14-Dihydroxypregnan-20-one 3-O-[(4-deoxy-4-methylamino)cymaropyranoside]



Source : *Holarrhena curtisii* King and Gamble[1,2,3] (Apocynaceae)
Mol. Formula : $C_{29}H_{49}NO_5$
Mol. Wt. : 491
M.P. : 162°C[2]; 165-166°C[2]
$[\alpha]_D$: +40.7° (c=0.18, $CHCl_3$)[2]
Registry No. : [17934-63-3]

IR (Nujol)[2] **:** 3300-3600 (br) (NH, OH), 1697 (C=O) cm^{-1}.

PMR ($CDCl_3$, 400 MHz)[3] **:** δ 0.79 (s, 3xH-19), 0.83 (m, H-3), 0.90 (m, H-1A), 0.96 (s, 3xH-18), 1.03 (m, H-5, H-7A), 1.30 (m, H-4A, H-6A, H-6B, H-11A, H-12A), 1.32 (d, *J*=6.0 Hz, 3xH-6 of DMC), 1.5 (m, H-2A, H-11B, H-12B, H-2A of DMC), 1.56 (m, H-8), 1.63 (m, H-4B), 1.72 (dt, *J*=13.0, 4.0 Hz, H-1B), 1.77 (m, H-15A), 1.89 (m, H-2B, H-16A), 1.99 (m, H-16B), 2.09 (m, H-15B), 2.14 (m, H-7B), 2.19 (m, H-2B of DMC), 2.23 (s, 3xH-21), 2.26 (m, H-4 of DMC), 2.45 (s, N-C*H*$_3$), 2.90 (dd, *J*=9.0, 4.5 Hz, H-17), 3.41 (s, C*H*$_3$), 3.64 (m, H-3, H-5 of DMC), 3.78 (m, H-3 of DMC), 4.35 (br s, 14-O*H*), 4.81 (dd, *J*=9.5, 2.0 Hz, H-1 of DMC).

CMR ($CDCl_3$, 67.5 MHz)[3] **:** δ C-1) 37.1 (2) 29.1 (3) 76.6 (4) 34.1 (5) 44.2 (6) 28.5 (7) 27.5 (8) 39.6 (9) 49.2 (10) 35.7 (11) 20.6 (12) 38.9 (13) 49.0 (14) 84.6 (15) 33.6 (16) 24.7 (17) 62.1 (18) 15.1 (19) 12.0 (20) 217.6 (21) 33.1 **DMC** (1) 95.0 (2) 33.8 (3) 73.0 (4) 63.7 (5) 70.3 (6) 19.1 (O*C*H$_3$) 56.7 (N-*C*H$_3$) 33.8.

Mass (E.I., 100°, 70 eV)[2] **:** *m/z* 491 (4), 416 (29), 317 (100), 299 (84) metastable ion *m/z* 282 (calc. 317→299 m* 282), 281 (18), 177 (33), 158 (29), 87 (98).

Mass (E.I., H.R.)[3] *: m/z* 491.3614 [M^+, calcd. for 491.3611].

Biological Activity : Significant cytotoxic and leishmanicidal activity.[3]

References

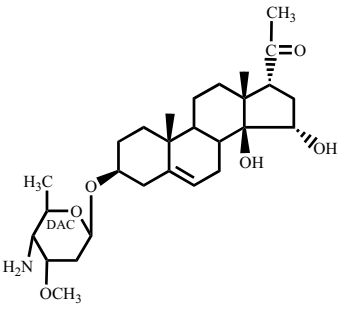
1. M.M. Janot, P. Devissaguet, Q. Khuong-Huu, J. Parello, N.G. Bisset and R. Goutarel, Compt. Rend., **266 c**, 388 (1968).

2. J.R. Cannon, E.L. Ghisalberti and V. Lojanapiwatna, *J. Sci. Soc. Thailand*, **6**, 81 (1980).

3. T.-S. Kam, K.-M. Sim, T. Koyano, M. Toyoshima, M. Hayashi and K. Komiyama*, J. Nat. Prod.*, **61**, 1332 (1998).

HOLOCURTINOL

3β,14β,15α-Trihydroxypregn-5-en-20-one 3-O-[(4-deoxy-4-amino)-cymaropyranoside]



Source : *Holarrhena curtisii* King and Gamble (Apocynaceae)
Mol. Formula : $C_{28}H_{46}NO_6$
Mol. Wt. : 491
$[\alpha]_D$: 30° (c=0.05, $CHCl_3$)
Registry No. : [215595-76-9]

IR (dry film) : 3392 (NH, OH), 1694 (C=O), 1693 (C=C) cm^{-1}.

PMR ($CDCl_3$, 400 MHz) : δ 0.96 (s, 3xH-18 and 3xH-19), 1.02 (m, H-9), 1.10 (m, H-1A), 1.24 (d, *J*=6.0 Hz, 3xH-6 of DAC), 1.32 (m, H-11 A and H-12A) 1.5 (m, H-2A, H-11B, H-12B, H-2A of DAC), 1.76 (m, H-1B, H-8), 1.88 (m, H-2B, H-16A) 2.16 (m, H-4A, H-4B, H-7A, H-2B of DAC), 2.24 (s, 3xH-21), 2.38 (m, H-7B, H-16B, H-4 of DAC), 3.13 (dd, *J*=9.0, 4.5 Hz, H-17), 3.40 (s, O*CH*$_3$ of DAC), 3.56 (m, H-3, H-3 of DAC, H-5 of DAC), 4.37 (d, *J*=6.0 Hz, H-15), 4.80 (dd, *J*=9.5, 2.0 Hz, H-1 of DAC), 5.42 (br d, *J*=5.0 Hz, H-6).

CMR ($CDCl_3$, 67.5 Hz) : δ C-1) 36.9 (2) 29.6 (3) 78.8 (4) 37.4 (5) 140.2 (6) 121.8 (7) 36.9 (8) 36.5 (9) 45.3 (10) 37.3 (11) 20.1 (12) 38.7 (13) 48.3 (14) 84.9 (15) 81.9 (16) 27.2 (17) 61.2 (18) 16.1 (19) 18.6 (20) 217.5 (21) 33.4 **DAC** (1) 95.5 (2) 34.7 (3) 77.2 (4) 56.3 (5) 71.8 (6) 18.7 (O*CH*$_3$) 57.4.

Mass (E.I.) : *m/z* (rel.intens.) 491 [$(M)^+$, 8], 330 (100), 312 (68), 294 (42).

Mass (H.R.) : *m/z* 491.3240 [$(M)^+$, requires 491.3247].

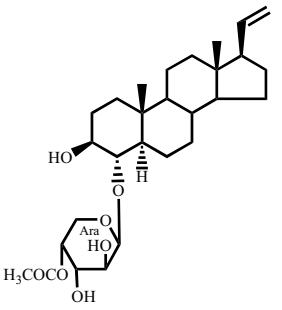
Biological Activity : Significant cytotoxic and leishmanicidal activity.

Reference

1. T.-S. Kam, K.-M. Sim, T. Koyano, M. Toyoshimo, M. Hayashi and K. Komiyama, *J. Nat. Prod.*, **61**, 1332 (1998)

4'-O-ACETYLPREGNEDIOSIDE A

3β,4α-Dihydroxy-5α-pregn-20-ene 4-O-[4'-O-acetyl-β-D-arabinopyranoside]



Source : *Alcyonium* sp. (Xeniidae), soft coral
Mol. Formula : $C_{28}H_{44}O_7$
Mol. Wt. : 492
M.P. : 199°C
$[\alpha]_D$: -96° ($CHCl_3$)
Registry No. : [92679-04-4]

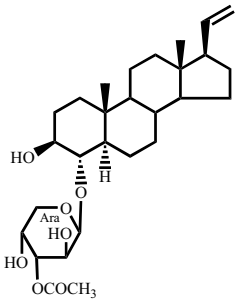
CMR (C_5D_5N, 22.5 MHz) : δ C-1) 36.5 (2) 29.1 (3) 76.3 (4) 88.7 (5) 50.3 (6) 23.6 (7) 32.1 (8) 35.4 (9) 55.0[a] (10) 38.0 (11) 20.9 (12) 37.8 (13) 43.8 (14) 55.8[a] (15) 24.9 (16) 27.5 (17) 55.6[a] (18) 13.1 (19) 13.6 (20) 140.1 (21) 114.8 **Ara** (1) 103.5 (2) 71.1 (3) 68.5 (4) 73.3 (5) 62.2.

Reference

1. M. Kobayashi, Y. Kiyota, S. Orito, Y. Kyogoku and I. Kitagawa, *Tetrahedron Lett.,* **25**, 3731 (1984).

3'-O-ACETYLPREGNEDIOSIDE A

3β,4α-Dihydroxy-5α-pregn-20-ene 4'-O-[(3'-O-acetyl)-β-D-arabinopyranoside]



Source : *Alcyonium* sp. (Xeniidae), soft coral
Mol. Formula : $C_{28}H_{44}O_7$
Mol. Wt. : 492
M.P. : 126°C
$[\alpha]_D$: -148° ($CHCl_3$)
Registry No. : [92679-05-5]

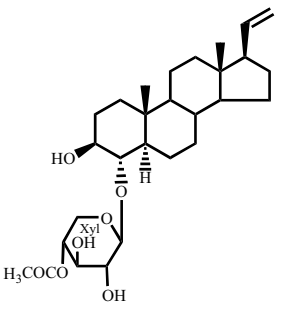
CMR (C_5D_5N, 22.5 MHz) : δ C-1) 36.5 (2) 29.3 (3) 76.2 (4) 88.6 (5) 50.3 (6) 23.6 (7) 32.1 (8) 35.4 (9) 55.0[a] (10) 38.0 (11) 21.0 (12) 37.8 (13) 43.8 (14) 55.8[a] (15) 25.0 (16) 27.5 (17) 55.6[a] (18) 13.1 (19) 13.6 (20) 140.1 (21) 114.8 **Ara** (1) 103.9 (2) 68.0 (3) 74.7 (4) 68.0 (5) 65.0.

Reference

1. M. Kobayashi, Y. Kiyota, S. Orito, Y. Kyogoku and I. Kitagawa, *Tetrahedron Lett.*, **25**, 3731 (1984).

4'-O-ACETYLPREGNEDIOSIDE B

3β,4α-Dihydroxy-5α-pregn-20-ene 4-O-(4'-O-acetyl) xylopyranoside



Source : *Alcyonium* sp. (Xeniidae), soft coral
Mol. Formula : $C_{28}H_{44}O_7$
Mol. Wt. : 492
M.P. : 193°C
$[\alpha]_D$: -2.2° ($CHCl_3$)
Registry No. : [92679-06-6]

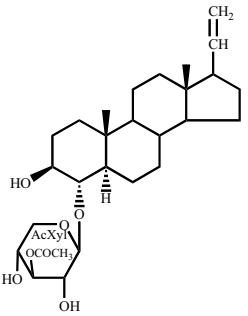
CMR (C_5D_5N, 22.5 MHz) : δ C-1) 36.6 (2) 29.0 (3) 76.0[a] (4) 87.7 (5) 50.1 (6) 23.5 (7) 32.1 (8) 35.5 (9) 55.0[b] (10) 37.9 (11) 20.9 (12) 37.7 (13) 43.7 (14) 55.6[b] (15) 24.9 (16) 27.5 (17) 55.6[b] (18) 13.1 (19) 13.7 (20) 140.1 (21) 114.7 **Xyl** (1) 106.8 (2) 75.2 (3) 76.5[a] (4) 72.8 (5) 63.4.

Reference

1. M. Kobayashi, Y. Kiyota, S. Orito, Y. Kyogoku and I. Kitagawa, *Tetrahedron Lett.,* **25**, 3731 (1984).

LOBOPHYTUM GLYCOSIDE 1

Pregn-20-en-3β,4α-diol 4-O-[(3-O-acetyl)-β-D-xylopyranoside]



Source : *Lobophytum* species (soft coral)
Mol. Formula : $C_{28}H_{44}O_7$
Mol. Wt. : 492
M.P. : 212-214°C
$[\alpha]_D^{20}$: +150.6° (c=0.02, MeOH)
Registry No. : [419572-94-4]

IR (KBr) : 3353, 2934, 1754, 1638, 1056, 992, 908 cm^{-1}.

PMR (C_5D_5N, 500 MHz) : δ 0.56 (s, 3xH-18), 0.80 (s, 3xH-19), 1.93 (s, OCOC*H*$_3$), 2.01 (m), 2.55 (m), 3.70 (dd, *J*=11.5, 1.0 Hz, H-5A of AcXyl), 3.71 (dd, *J*=10.0, 9.5 Hz, H-4β), 3.85 (m, H-3α), 4.10 (dd, *J*=10.0, 8.0 Hz, H-2 of AcXyl), 4.23 (m, H-4 of AcXyl), 4.34 (dd, *J*=11.0, 5.5 Hz, H-5B of AcXyl), 5.06 (m, 2xH-21), 5.15 (d, *J*=8.0 Hz, H-1 of AcXyl), 5.74 (dd, *J*=10.0, 9.5 Hz, H-3 of AcXyl), 5.82 (m, H-20).

CMR (C_5D_5N, 125 MHz) : δ C-1) 36.6 (2) 29.3 (3) 76.4 (4) 87.8 (5) 50.3 (6) 23.6 (7) 32.2 (8) 35.6 (9) 55.0 (10) 37.8 (11) 20.9 (12) 37.9 (13) 43.8 (14) 55.6 (15) 25.0 (16) 27.5 (17) 55.6 (18) 13.1 (19) 13.8 (20) 140.2 (21) 114.8 **AcXyl** (1) 107.0 (2) 73.9 (3) 79.6 (4) 69.1 (5) 67.3 (O*C*OCH$_3$) 170.6 (OCO*C*H$_3$) 21.1.

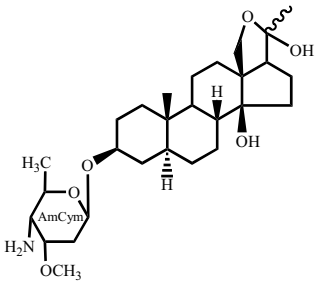
Mass (FAB, Positive ion) : *m/z* 515 $[M+Na]^+$.

Reference

1. X.-X. He, J.-Y. Su, L.-M. Zeng, X.-P. Yang and Y.-J. Liang, *Huaxue Xuebao* (*Acta Chim. Sin.*), **60**, 334 (2002).

HOLANTOSINE A

Holantogenin 3-O-[4-deoxy-4-amino-β-D-cymaropyranoside]



Source : *Holarrhena antidysenterica* (Roxb.) (Apocynaceae)
Mol. Formula : $C_{28}H_{47}NO_6$
Mol. Wt. : 493
Registry No. : [28719-38-2]

N-Acetate :

M.P. : -260-261°C; **$[\alpha]_D^{20}$:** -28° ($CHCl_3$)

IR (Nujol) : 3320, 1650, 1540 cm^{-1} (secondary amide).

PMR ($CDCl_3$, 60 MHz) : δ 0.74 (s, 3xH-19), 1.19 (d, *J*=5.0 Hz, 3xH-6 of sugar), 1.40 (s, 3xH-21), 2.00 (s, OCOC*H*$_3$), 3.40 (s, OC*H*$_3$), 3.53 and 4.16 (ABq, *J*=9.0 Hz, 2xH-18), 4.78 (dd, *J*=10.0, 2.0 Hz, H-1 of AmCym), 3.30 and 4.20 (H-3 and H-3, H-4, H-5 of AmCym), 5.75 (N*H*-Ac).

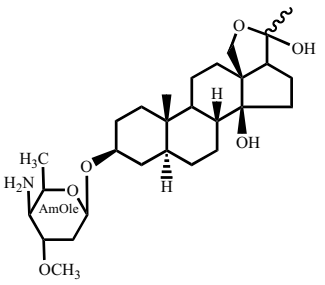
Mass (E.I.) : *m/z* (rel.intens.) 517 $[(M-H_2O)^+$, 0.12], 457 $[M-H_2O$-AcOH$]^+$, 3.59 (0.6), 3.15 (1.0), 115 (60.0), 96 (1.8).

Reference

1. M.M. Janot, Q. Khuong-Huu, C. Monneret, I. Kaboré, J. Hildesheim, S.D. Gero and R. Goutarel, *Tetrahedron*, **26**, 1695 (1970).

HOLANTOSINE C

Holantogenin 3-O-[4-deoxy-4-amino-α-L-oleandropyranoside]



Source : *Holarrhena antidysenterica* (Roxb.) (Apocynaceae)
Mol. Formula : $C_{28}H_{47}NO_6$
Mol. Wt. : 493
Registry No. : [34312-24-8]

N-Acetate :

M.P. : -245°C; **$[\alpha]_D$:** -73° ($CHCl_3$-MeOH 7:3)

IR (Nujol) : 3360, 1680, 1540 ($NHCOCH_3$), 3320 (OH) cm^{-1}.

PMR ($CDCl_3$, 60 MHz): δ 0.73 (s, 3xH-19), 1.18 (d, *J*=6.0 Hz, 3xH-6 of AmOle), 1.46 (s, 3xH-21), 2.0 (s, $NHCOCH_3$), 3.30 (s, OCH_3), 3.53 (d, *J*=9.0 Hz, H-18A), 4.16 (d, *J*=9.0 Hz, H-18B), 4.95-5.18 (H-1 of AmOle), 5.35-5.60 (NH), 3.43-3.91 (H-3, H-4, H-5 of AmOle, H-3 of Agl).

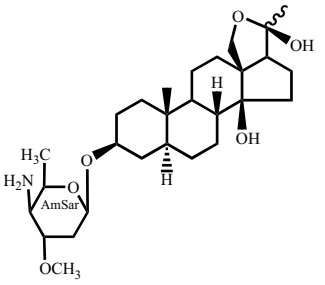
Mass (E.I.) : *m/z* 517 [trace, $M-H_2O]^+$, 315, 298, 255, 115, 96.

Reference

1. Q. Khuong-Huu, C. Monneret, I. Kabore, P. Choay, J.M. Tekam and R. Goutarel, *Bull. Soc. Chim. Fr.*, 864 (1971).

HOLANTOSINE E

Holantogenin 3-O-[4-deoxy-4-amino-β-D-sarmentopyranoside]



Source : *Holarrhena antidysenterica* (Roxb.) (Apocynaceae)
Mol. Formula : $C_{28}H_{47}NO_6$
Mol. Wt. : 493
Registry No. : [40738-39-4]

N-Acetate :

M.P. : -152°C; **$[\alpha]_D$:** -47° (c=1.0, $CHCl_3$)

IR (Nujol) : 3290 (sec. amide and alcohol), 1650, 1540 (secondary amide) cm^{-1}.

PMR ($CDCl_3$, 60 MHz) : δ 0.74 (s, 3xH-19), 1.40 (s, 3xH-21), 1.17 (d, *J*=6.0 Hz, 3xH-6 of Am Sar), 2.02 (s, NH-CO*C*H_3), 3.43 (s, OC*H*$_3$), 3.53 (d, *J*=9.0 Hz, H-18A), 4.16 (d, *J*=9.0 Hz, H-18B), 4.80 (dd, *J*=9.0, 2.5 Hz, H-1 of AmSar).

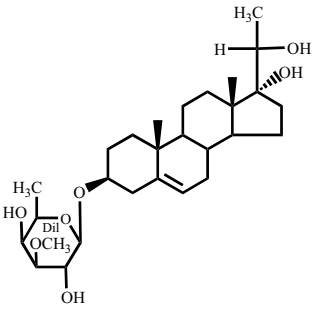
Mass (E.I.) : *m/z* 359 (1.0), 315 (1.5), 297 (0.5), 255 (1.0), 186 (4.0), 172 (1.0), 143 (1.5), 126 (5.0), 115 (36.0), 96 (7.0).

Reference

1. R. Goutarel, C. Monneret, P. Choay, I. Kabora and Q. Khuong-Huu, *Carbohydr. Res*., **24**, 297 (1972).

PERIPLOCOSIDE L

Pregn-5-ene-3β,17α,20(*S*)-triol 3-O-β-D-digitalopyranoside



Source : *Periploca sepium* (Asclepiadaceae)
Mol. Formula : $C_{28}H_{46}O_7$
Mol. Wt. : 494
M.P. : 238-240°C
$[\alpha]_D$: -53.3° (c=0.06, MeOH)
Registry No. : [116709-66-1]

PMR ($CDCl_3$, 400 MHz) **:** δ 0.75 (s, 3xH-18), 1.01 (s, 3xH-19), 1.19 (d, *J*=6.3 Hz, 3xH-21), 1.36 (3H, d, *J*=6.5 Hz, 3xH-6 of Dil), 3.21 (dd, *J*=7.8, 10.35 Hz, H-3 of Dil), 3.52 (3H, s, OCH_3), 3.84 (q, *J*=6.3 Hz, H-20), 4.32 (d, *J*=7.8 Hz, H-1 of Dil), 5.36 (m, H-6).

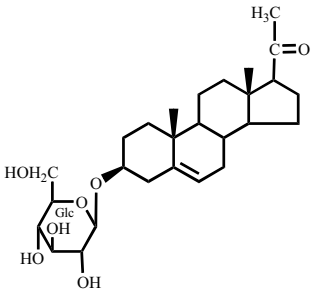
CMR ($CDCl_3$, 100 MHz) **:** δ C-1) 37.35 (2) 29.64 (3) 78.64 (4) 38.91 (5) 140.80 (6) 121.84 (7) 31.96 (8) 31.89 (9) 49.77 (10) 36.78 (11) 20.55 (12) 31.11 (13) 45.71 (14) 51.46 (15) 23.57 (16) 37.72 (17) 85.77 (18) 14.04 (19) 19.39 (20) 72.37 (21) 18.62 **Dil** (1) 101.20 (2) 70.63 (3) 82.96 (4) 68.08 (5) 70.43 (6) 16.50 (OCH_3) 57.44.

Reference

1. H. Itokawa, J. Xu and K. Takeya, *Chem. Pharm. Bull*., **36**, 2084 (1988).

CARUMBELLOSIDE II

3β-Hydroxypregn-5-en-20-one 3-O-β-D-glucopyranoside



Source : *Caralluma umbellata* Haw. (Asclepiadaceae)
Mol. Formula : $C_{27}H_{42}O_8$
Mol. Wt. : 494
M.P. : 274-276°C
$[\alpha]_D$: -17.3° (c=0.15, MeOH)
Registry No. : [155740-23-1]

UV (MeOH) : λ_{max} 216 (log ε, 3.99) nm.

IR (KBr) : 3400, 2920, 1670, 1050 cm^{-1}.

PMR (C_5D_5N, 500.1 MHz) **:** δ 0.86 (s, 3xH-19), 1.02 (dt, *J*=10.5, 3.0 Hz, H-1α), 1.08 (s, 3xH-18), 1.13 (m, H-9α), 1.23 (dt, *J*=13.0, 5.0 Hz, H-12β), 1.31 (m, 2xH-11), 1.41 (br d, H-12α), 1.72 (m, H-1β and 2β), 1.85 (m, H-8β and H-15β), 1.87 (m, H-7β), 1.92 (m, H-16β), 2.03 (m, H-15α, H-16α), 2.17 (br d, *J*=10.5 Hz, H-2α), 2.21 (s, 3xH-21), 2.43 (br t, *J*=12.5 Hz, H-4β), 2.53 (dq, *J*=3.5, 10.5 Hz, H-7α), 2.69 (dd, *J*=12.5, 4.0 Hz, H-4α), 2.82 (dd, *J*=8.5, 4.5 Hz, H-17α), 3.95 (m, H-3α), 3.96 (H-5 of Glc), 4.05 (t, *J*=8.5 Hz, H-2 of Glc), 4.26 (t, *J*=8.5 Hz, H-4 of Glc), 4.29 (t, *J*=8.5 Hz, H-3 of Glc), 4.40 (dd, *J*=11.5, 5.0 Hz, H-6A of Glc), 4.56 (d, *J*=11.5 Hz, H-6B of Glc), 5.04 (d, *J*=8.5 Hz, H-1 of Glc), 5.37 (d, *J*=3.5 Hz, H-6).

CMR (C_5D_5N, 90.8/125.8 MHz) : δ C-1) 37.5 (2) 30.3 (3) 78.1 (4) 39.2 (5) 139.6 (6) 122.6 (7) 27.9 (8) 37.2 (9) 46.3 (10) 37.6 (6) 122.6 (7) 27.9 (8) 37.2 (9) 46.3 (10) 37.6 (11) 21.2 (12) 38.9 (13) 49.4 (14) 85.1 (15) 34.6 (16) 24.6 (17) 63.2 (18) 15.6 (19) 19.6 (20) 216.8 (21) 31.6 **Glc** (1) 102.6 (2) 75.2 (3) 78.7 (4) 71.8 (5) 78.6 (6) 62.9.

Mass (FAB, Positive ion) : *m/z* (rel.intens.) 495 $[(M+H)^+$, 4], 477 $[(M+H-H_2O)^+$, 78], 333 $[(M+H-Glc-H_2O)^+$, 4], 315 (53), 299 (28), 298 (25), 797 (100), 207 (11), 157 (21), 115 (20).

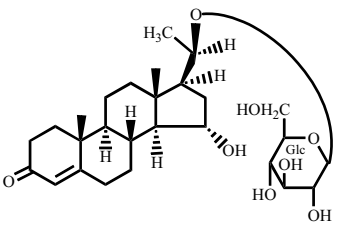
Mass (FAB, Positive ion, H.R.) : *m/z* 477.2852 $[(M+H-H_2O)^+$, calcd. 477.2862].

Reference

1. L.-J. Lin, L.-Z. Lin, R.R. Gil, G.A. Cordell, M. Ramesh, B. Srilatha, B. Reddy and A.V.N.A. Rao, *Phytochemistry*, **35**, 1549 (1994).

CENTAUREA MOSCHATA SAPONIN 1

(20*R*)-15α-Hydroxypregn-4-en-3-one 20-O-β-D-glucopyranoside



Source : *Centaurea moschata* L. (Compositae)
Mol. Formula : $C_{27}H_{42}O_8$
Mol. Wt. : 494
Registry No. : [222417-30-3]

UV (EtOH) : λ_{max} 241 nm.

PMR (CD_3OD, 400 MHz) : δ 0.89 (s, 3xH-18), 0.97 (m, H-9α), 1.05 (dd, *J*=9.5 Hz, H-14α), 1.11 (d, *J*=6.0 Hz, 3xH-21), 1.22 (m, H-12α), 1.24 (s, 3xH-19), 1.25 (m, H-7α), 1.42 (m, H-11β), 1.51 (m, H-16β), 1.52 (m, H-11α), 1.65 (m, H-8α), 1.78 (m, H-17α), 1.80 (m, H-1α), 1.85 (m, H-16α), 2.10 (m, H-1β), 2.20 (m, H-7β), 2.25 (m, H-12β), 2.30 (m, H-6α), 2.35 (m, H-2α), 2.45 (m, H-2β), 2.45 (m, H-2β), 2.50 (m, H-6β), 3.13 (t, *J*=7.7 Hz, H-2 of Glc), 3.25 (m, H-4 and H-5 of Glc), 3.35 (H-3 of Glc), 3.65 (m, H-6β of Glc), 3.85 (d, *J*=12.8 Hz, H-6α of Glc), 3.90 (m, H-20α), 3.95 (m, H-15), 4.33 (d, *J*=7.7 Hz, H-1 of Glc), 5.70 (m, H-4).

CMR (CD_3OD, 100 MHz) : δ C-1) 35.4 (2) 33.3 (3) 201.0 (4) 122.4 (5) 174.3 (6) 32.7 (7) 32.2 (8) 35.2 (9) 54.5 (10) 38.7 (11) 20.4 (12) 39.3 (13) 42.7 (14) 62.5 (15) 72.9 (16) 37.7 (17) 53.7 (18) 11.9 (19) 16.4 (20) 73.7 (21) 17.3 **Glc** (1) 99.3 (2) 73.9 (3) 76.8 (4) 70.8 (5) 76.4 (6) 61.9.

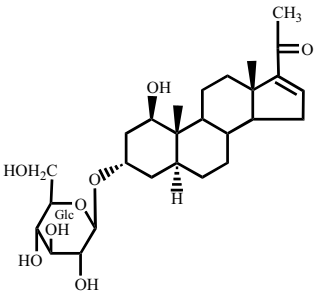
Mass (C.I.) : *m/z* 512 $[M+H+NH_3]^+$, 495 $[M+H]^+$, 479, 439, 391, 361, 333 $[M+H-Glc]^+$ 315, 297, 279, 256, 196, 186, 164, 146, 124, 113.

Reference

1. S.D. Sarker, R. Lafont, J.-P. Girault, V. Sik and L. Dinan, *Pharmaceutical Biol.*, **36**, 202 (1998).

CORDYLINE STRICTA SAPONIN 8

1β,3α-Dihydroxy-5α-pregn-16-en-20-one 3-O-β-D-glucopyranoside



Source : *Cordyline stricta* (Agavaceae)
Mol. Formula : $C_{27}H_{42}O_8$
Mol. Wt. : 494
$[\alpha]_D^{27}$: +43.2° (c=0.13, MeOH)
Registry No. : [194143-98-1]

UV (MeOH) **:** λ_{max} 241 (log ε, 3.94) nm.

IR (KBr) **:** 3400 (OH), 2920 (CH), 1650 (C=O), 1580 (C=C), 1440, 1420, 1360, 1315, 1225, 1195, 1155, 1070, 1025, 990, 930, 890, 840, 825, 815 cm^{-1}.

PMR (C_5D_5N, 400 MHz) **:** δ 0.99 (s, 3xH-18), 1.07 (s, 3xH-19), 2.21 (s, 3xH-21), 3.91 (ddd, *J*=8.9, 4.9, 2.5 Hz, H-5 of Glc), 4.06 (dd, *J*=8.9, 7.7 Hz, H-2 of Glc), 4.24 (dd, *J*=8.9, 8.9 Hz, H-4 of Glc), 4.28 (overlapping, H-1), 4.29 (dd, *J*=8.9, 8.9 Hz, H-3 of Glc), 4.34 (br s, H-3), 4.41 (dd, *J*=11.7, 4.9 Hz, H-6A of Glc), 4.54 (dd, *J*=11.7, 2.5 Hz, H-6B of Glc), 4.95 (d, *J*=7.7 Hz, H-1 of Glc), 6.59 (dd, *J*=3.1, 1.7 Hz, H-16).

CMR (C_5D_5N, 100 MHz) **:** δ C-1) 73.5 (2) 37.1 (3) 74.0 (4) 35.1 (5) 39.3 (6) 28.6 (7) 32.1 (8) 34.5 (9) 55.6 910) 42.7 (11) 24.9 (12) 36.0 (13) 46.2 (14) 56.8 (15) 32.5 (16) 144.5 (17) 155.8 (18) 16.3 (19) 6.5 (20) 196.2 (21) 27.1 **Glc** (1) 102.7 (2) 75.3 (3) 78.7 (4) 71.7 (5) 78.3 (6) 62.9.

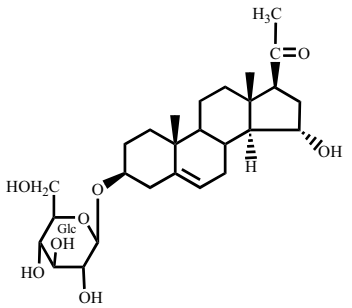
Mass (FAB, Negative ion) : *m/z* 493 $[M-H]^-$.

Reference

1. Y. Mimaki, Y. Takaashi, M. Kuroda and Y. Sashida, *Phytochemistry*, **45**, 1229 (1997).

RUBUS AMABILIS SAPONIN 1

3β,15α-Dihydroxypregn-5-en-20-one-3-O-β-D-glucopyranoside



Source : *Rubus amabilis* Focke (Rosaceae)
Mol. Formula : $C_{27}H_{42}O_8$
Mol. Wt. : 494
M.P. : 290-292°C
$[\alpha]_D^{20}$: +110° (c=0.25, C_5D_5N)
Registry No. : [312930-63-5]

IR (KBr) : 3434, 2939, 2871, 1696, 1447, 1365, 1278, 1224, 1162, 1120, 1073, 1018, 898, 803, 637 cm^{-1}.

PMR (CD_3OD, 400 MHz) : δ 0.73 (s, 3xH-18), 0.91 (dd, *J*=11.0, 5.4 Hz, H-14), 0.95 (m, H-9), 0.96 (s, 3xH-19), 1.00 (m, H-1α), 1.38 (m, H-12α), 1.40 (m H-11β), 1.46 (m, H-2β), 1.51 (m, H-7B), 1.55 (m, H-11α), 1.72 (m, H-8), 1.81 (br d, *J*=11.0 Hz, H-1β), 1.81 (br d, *J*=11.0 Hz, H-2α), 1.93 (br d, *J*=6.2 Hz, H-12β), 1.98 (m, H-16α)[a], 2.00 (m, H-16β)[a], 2.04 (s, 3xH-21), 2.12 (br t, *J*=12.4 Hz, H-4β), 2.23 (br d, *J*=18.9 Hz, H-7α), 2.38 (dd, *J*=12.5, 4.0 Hz, H-4α), 2.46 (t, *J*=9.3 Hz, H-17), 2.88 (br t, *J*=7.9 Hz, H-2 of Glc), 3.00 (br t, *J*=8.5 Hz, H-4 of Glc), 3.05 (m, H-5 of Glc), 3.11 (br t, *J*=8.2 Hz, H-3 of Glc), 3.40 (dd, *J*=11.4, 5.5 Hz, H-6A of Glc), 3.46 (m, H-3), 3.64 (br d, *J*=11.4 Hz, H-6B of Glc), 4.04 (br, H-15), 4.21 (d, *J*=7.6 Hz, H-1 of Glc), 5.40 (d, *J*=2.0 Hz, H-6).

CMR (CD_3OD, 100 MHz) : δ C-1) 36.9 (2) 29.3 (3) 76.7 (4) 38.3 (5) 140.3 (6) 121.3 (7) 30.3 (8) 27.4 (9) 49.7 (10) 36.3 (11) 20.6 (12) 39.1 (13) 43.0 (14) 60.5 (15) 68.1 (16) 35.5 (17) 63.0 (18) 15.4 (19) 19.0 (20) 208.0 (21) 31.2 **Glc** (1) 100.8 (2) 73.4 (3) 76.9 (4) 70.1 (5) 76.7 (6) 61.1.

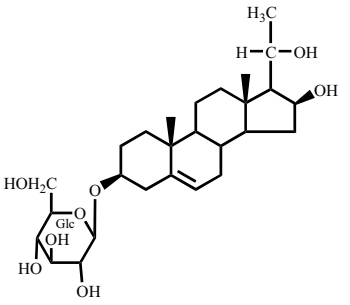
Mass (FAB) : *m/z* 517 $[M+Na]^+$, 315 $[M+H\text{-}Glc]^+$, 297 $[315\text{-}H_2O]^+$.

Reference

1. X. Chen, Q. Zhu, Z. Jia, *Planta Med.*, **67**, 270 (2001).

BALANITES AEGYPTIACA SAPONIN 1

Pregn-5-en-3β,16β,20(*R*)-triol 3-O-[β-D-glucopyranoside]



Source : *Balanites aegyptiaca* Del. (Balanitaceae)
Mol. Formula : $C_{27}H_{44}O_8$
Mol. Wt. : 496
M.P. : 220-222°C
$[\alpha]_D^{23}$: +17.5° (c=0.15, MeOH)
Registry No. : [171828-53-8]

PMR (C_5D_5N, 400 MHz) **:** δ 0.90 (s, 3xH-18), 1.01 (s, 3xH-19), 1.20 (d, *J*=6.4 Hz, 3xH-21), 5.2 (d, *J*=7.0 Hz, H-1 of Glc).

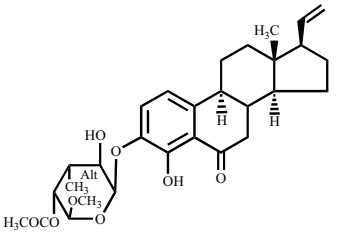
CMR (C_5D_5N, 100 MHz) : δ C-1) 37.1 (2) 30.0 (3) 78.0 (4) 37.1 (5) 140.9 (6) 121.8 (7) 31.6[a] (8) 31.3[a] (9) 50.8 (10) 36.9 (11) 21.0 (12) 38.9 (13) 41.6 (14) 54.8 (15) 35.3 (16) 73.8 (17) 62.9 (18) 15.6 (19) 19.0 (20) 67.0 (21) 23.9 **Glc** (1) 105.2 (2) 75.4 (3) 78.4 (4) 71.8 (5) 78.3 (6) 61.8.

Reference

1. M.S. Kamel and A. Koskinen, *Phytochemistry*, **40**, 1773 (1995).

HAPAIOSIDE

3,4-Dihydroxy-19-norpregna-1,3,5(10),20-tetraen-6-one 3-O-[4-O-acetyl-6-deoxy-β-L-altropyranoside]



Source : *Cribrochalina olemda* (Niphatidae)
Mol. Formula : $C_{28}H_{36}O_8$
Mol. Wt. : 500
$[\alpha]_D$: -34.8° (c=0.028, MeOH)
Registry No. : [159397-70-3]

UV (MeOH) : λ_{max} 218 (ε 3321), 268 (ε, 1894), 346 (ε, 793) nm

IR (neat) : 3416, 2941, 1735, 1634, 1446, 1245, 1087, 1026 cm^{-1}.

PMR ($CDCl_3/CD_3OD$, 500 MHz) : δ 0.63 (s, 3xH-18), 1.06 (d, *J*=6.6 Hz, 3xH-6 of Alt), 1.27 (m, H-15A), 1.37 (m, H-12A), 1.39 (m, H-14), 1.61 (m, H-11), 1.62 (m, H-16A), 1.77 (br d, *J*=6.8, 2.4 Hz, H-15B), 1.83 (m, H-16B), 1.85 (m, H-12B), 1.91 (m, H-8), 2.1 (s, OCOC*H*$_3$), 2.05 (m, H-17), 2.30 (m, H-11), 2.36 (dd, *J*=17.3, 13.3 Hz, H-7A), 2.45 (dt, *J*=4.5, 11.6 Hz, H-9), 2.72 (dd, *J*=17.3, 3.6 Hz, H-7B), 3.86 (dd, *J*=10.2, 3.7 Hz, H-2 of Alt), 4.18 (dd, *J*=10.2, 3.5 Hz, H-3 of Alt), 4.32 (dq, *J*=6.6 Hz, H-5 of Alt), 4.98 (br d, *J*=12.9 Hz, H-21), 5.22 (dd, *J*=3.5 Hz, H-4 of Alt), 5.45 (d, *J*=3.7 Hz, H-1 of Alt), 5.74 (ddd, *J*=17.0, 12.9, 9.0 Hz, H-20), 6.84 (dd, *J*=8.4, 1.3 Hz, H-1), 7.31 (d, *J*=8.4 Hz, H-2).

CMR ($CDCl_3/CD_3OD$, 125.0 MHz) : δ C-1) 116.2 (2) 125.1 (3) 144.1 (4) 154.3 (5) 118.0 (6) 206.5 (7) 45.1 (8) 40.6 (9) 44.0 (10) 143.2 (11) 25.9 (12) 37.5 (13) 44.2 (14) 55.2 (15) 24.7 (16) 27.8 (17) 55.9 (18) 13.0 (20) 139.7 (21) 115.5 **Alt** (1) 100.5 (2) 69.8 (3) 69.1 (4) 74.7 (5) 67.1 (6) 16.5 (OCO*C*H_3) 172.4, 20.8.

Mass (FAB, Positive ion) : *m/z* 501 $[M+H]^+$.

Mass (FAB, Positive ion, H.R.) : *m/z* 501.2503 $[M+H]^+$.

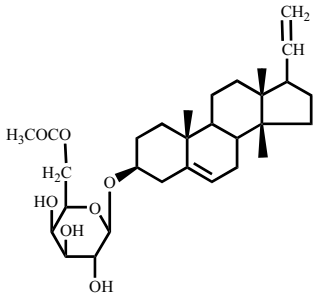
Mass (FAB, Positive ion) : *m/z* 189.1 [(M^+-$C_{20}H_{25}O_3$), 90].

Reference

1. B.K.S. Yeung, M.T. Hamann, P.J. Scheuer, M. Kelly-Borges, *Tetrahedron*, **50**, 44, 12593 (1994).

EUNICEA LACINIATA GLYCOSIDE 1

Pregnadienol 3-O-[(6-O-acetyl)-β-D-galactopyranoside]



Source : *Eunicea laciniata* Duchassaing and Michelotti (Octocoral)
Mol. Formula : $C_{29}H_{44}O_7$
Mol. Wt. : 504
M.P. : 245-250°C (decomp.)
$[\alpha]_D$: -193.7 (c=0.09, $CHCl_3$)
Registry No. : [656250-28-1]

IR (film) : 3417, 1740, 1462 cm^{-1}.

PMR ($CDCl_3$, 500 MHz) : δ 0.61 (s, 3xH-18), 0.95 (m, H-9), 1.02 (m, H-14), 1.02 (s, 3xH-19), 1.07 (m, 2xH-12), 1.22 (m, H-15A), 1.43 (m, H-11A), 1.48 (s, H-7A), 1.56 (m, H-11β), 1.58 (m, H-16A), 1.63 (m, H-2A), 1.69 (m, H-

15B), 1.72 (m, H-8), 1.80 (m, H-16B), 1.88 (ddd, *J*=12.5, 7.5, 2.5 Hz, H-1B), 1.96 (m, H-2B), 1.96 (m, H-17), 2.02 (m, H-7B), 2.02 (s, OCOC*H*$_3$), 2.27 (m, H-4A), 2.38 (m, H-4B), 3.57 (m, H-3), 3.62 (m, H-3), 3.68 (t, *J*=6.2 Hz, H-4 of Gal), 3.89 (s, H-4 of Gal), 4.29 (dd, *J*=11.4, 6.6 Hz, H-6A of Gal), 4.34 (d, *J*=7.7 Hz, H-1 of Gal), 4.38 (m, H-6A of Gal), 4.97 (d, *J*=7.4 Hz, H-21A), 4.98 (d, *J*=8.6 Hz, H-21B), 5.38 (br d, *J*=5.2 Hz, H-6), 5.77 (ddd, *J*=16.5, 10.5, 7.7 Hz, H-20).

CMR ($CDCl_3$, 125 MHz) : δ C-1) 37.2 (2) 29.7 (3) 79.4 (4) 38.8 (5) 140.5 (6) 122.1 (7) 32.0 (8) 37.3 (9) 50.5 (10) 36.9 (11) 20.7 (12) 37.4 (13) 43.4 (14) 55.9 (15) 25.0 (16) 27.3 (17) 55.4 (18) 12.7 (19) 19. (20) 139.8 (21) 114.6 **Gal** (1) 101.4 (2) 72.0 (3) 73.4 (4) 68.2 (5) 72.1 (6) 62.9 (O*C*OCH$_3$) 171.1 (OCO*C*H$_3$) 21.0.

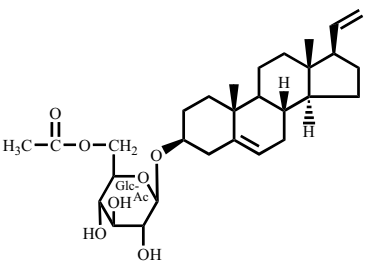
Mass (FAB, Positive ion, H.R.) : *m/z* 527.3109 [$(M+Na)^+$, calcd. for 527.3087].

Reference

1. K.I. Marville, W.F. Reynolds, R.. Sealy and W.F. Tinto, *Heterocycles*, **63**, 107 (2004).

MURICEA GLYCOSIDE 2

Pregna-5,20-dien-3β-ol 3-O-[6-O-acetyl-β-D-glucopyranoside]



Source : *Muricea austera* (gorgonian, horny coral)
Mol. Formula : $C_{29}H_{44}O_7$
Mol. Wt. : 504
M.P. : 175-178°C

IR (KBr) : 3408, 2942, 1720, 1638, 1457, 1371, 1265, 1090, 1036, 904 cm^{-1}.

PMR ($CDCl_3$, CD_3OD, 1:1, 300 MHz) : δ 0.63 (s, 3xH-18), 0.99 (m, H-9), 1.03 (s, 3xH-19), 1.09 (m, H-14), 1.13 (s, H-1A and H-15A), 1.44 (m, H-11A), 1.51 (m, H-8), 1.55 (m, H-11B, H-16A), 1.62 (m, H-2A), 1.63 (m, H-7A), 1.72 (m, H-12A), 1.74 (m, H-15B), 1.76 (m, H-16B), 1.86 (m, H-1B), 1.92 (m, H-12B), 1.94 (m, H-2B), 1.98 (m, H-7B, H-17), 2.04 (s, OCOC*H*$_3$), 2.29 (m, H-4A), 2.42 (m, H-4B), 3.21 (dd, *J*=8, 7.7 Hz, H-2 of Glc-Ac), 3.32 (m, H-3 of Glc-Ac), 3.35 (m, H-4 of Glc-Ac), 3.45 (m, H-5 of Glc-Ac), 3.55 (m, H-3), 4.23 (dd, *J*=6.3, 12.0 Hz, H-6A of Glc-Ac), 4.37 (dd, *J*=2.4, 12.0 Hz, H-6B of Glc-Ac), 4.39 (d, *J*=7.7 Hz, H-1 of Glc-Ac), 4.95 (d, *J*=14.7 Hz, H-21A), 4.96 (d, *J*=12.3 Hz, H-21B), 5.38 (br d, *J*=5.4 Hz, H-6), 5.75 (m, H-20).

CMR ($CDCl_3$-CD_3OD, 1:1, 100 MHz) : δ C-1) 38.2 (2) 30.4 (3) 80.2 (4) 39.5 (5) 141.2 (6) 122.3 (7) 32.8 (8) 32.9 (9) 51.5 (10) 37.6 (11) 21.5 (12) 38.2 (13) 44.1 (14) 56.8 (15) 25.6 (16) 28.0 (17) 56.3 (18) 13.1 (19) 19.8 (20) 140.1 (21) 114.7 **Glc-Ac** (1) 102.2 (2) 74.6 (3) 77.4 (4) 71.2 (5) 74.7 (6) 64.5 ($OCOCH_3$) 172.2 ($OCOCH_3$) 20.9.

Mass (E.S.I., Positive ion) : *m/z* 527 $[M+Na]^+$, 505 $[M+H]^+$, 283 [M-Acetyl glucose]$^+$, 230 (4).

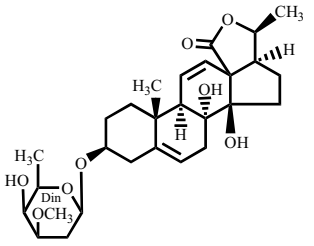
Biological Activity : Moderate in vitro cytotoxic activity against HCT-116 human colon carcinoma (IC_{50}-17.3 μg/ml).

Reference

1. J.I. Murillo-Alvarez and R. Encarnacion-Dimayuga, *Pharm. Biol*., **41**, 531 (2003).

AMALOSIDE D

(20*S*)-3β,8α,14β-Trihydroxypregn-5,11-diene-18-oic acid γ-lactone 3-O-β-D-diginopyranoside



Source : *Amalocalyx yunnanensis* Tsiang (Apocynaceae)
Mol. Formula : $C_{28}H_{40}O_8$
Mol. Wt. : 504
M.P. : 240-242°C
Registry No. : [150677-82-0]

PMR ($CDCl_3$, 400 MHz) : δ 1.17 (s, 3xH-19), 1.29 (d, *J*=6.4 Hz, 3xH-6 of Din), 1.35 (d, *J*=6.7 Hz, 3xH-21), 1.6 (m, H-16A), 1.8 (m, 2xH-2), 1.9 (m, H-7A), 1.9 (m, 2xH-15), 1.9 (m, H-16B), 2.18 (br s, H-9α), 2.3 (m, 2xH-1), 2.3 (m, 2xH-4), 2.65 (ddd, *J*=7.4, 6.8, 2.3 Hz, H-17α), 2.92 (br d, *J*=17.7 Hz, H-7B), 3.29 (dt *J*=10.0, 2.8 Hz, H-3 of Din), 3.35 (s, OCH_3), 3.41 (br q *J*=6.4 Hz, H-5 of Din), 3.58 (tt, *J*=10.4, 5.2 Hz, H-3α), 3.65 (t, *J*=2.8 Hz, H-4 of Din), 4.49 (dd, *J*=9.8, 2.0 Hz, H-1 of Din), 4.71 (dq, *J*=6.8, 6.7 Hz, H-20), 5.32 (d, *J*=6.5 Hz, H-6), 5.60 (dd, *J*=10.4, 3.2 Hz, H-11), 5.89 (dd, *J*=10.4, 1.8 Hz, H-12).

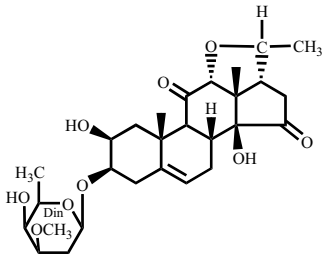
CMR ($CDCl_3$, 100.6 MHz) : δ C-1) 37.1 (2) 29.9 (3) 78.2 (4) 38.4 (5) 140.5 (6) 117.3 (7) 29.9 (8) 76.3 (9) 46.8 (10) 38.4 (11) 129.0 (12) 126.7 (13) 62.9 (14) 85.9 (15) 36.3 (16) 22.4 (17) 55.1 (18) 176.8 (19) 23.0 (20) 75.3 (21) 16.3 **Din** (1) 97.9 (2) 31.9 (3) 77.9 (4) 67.0 (5) 70.3 (6) 16.7 (OCH_3) 55.6.

Reference

1. X.-L. Shen, Y.-J. Hu, Y.-L. An and Q.-Z. Mu, *Phytochemistry*, **33**, 687 (1993).

DIGIFOLEIN

Digifologenin 3-O-β-D-diginopyranoside



Source : *Digitalis purpurea* L.[1], *D. lanata* Ehrh.[1,2], *D. canariensis* L.[3], *D. thopsi* L.[3] (Scrophulariaceae)
Mol. Formula : $C_{28}H_{40}O_8$
Mol. Wt. : 504
M.P. : 198-202°C[2]
$[\alpha]_D^{20}$: -220° (c=1.0, $CHCl_3$)
Registry No. : [6877-39-0]

UV $(EtOH)^4$: λ_{max} 309 (log ε, 1.94) nm.

IR $(KBr)^4$: 3500 (OH), 1743 (C=O), 1723 (C=O), 1655 (C=C), 1092, 1083, 1070, 1032, 898, 870, 845 cm^{-1}.

PMR $(CDCl_3, 60\ MHz)^2$: δ 1.58 (s, 3xH-18), 1.22 (s, 3xH-19), 1.28 (d, *J*=6.5 Hz, 3xH-21), 1.37 (d, *J*=6.4 Hz, 3xH-6 of Din), 3.4 (s, OCH_3 of Din).

CD $(Dioxan)^2$: λ_{max} 316 nm, $\Delta\varepsilon_{max}$ -6.25.

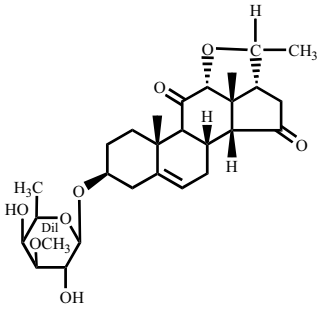
ORD $(MeOH)^2$: 286 (ϕ+ 10300), 331 (ϕ - 15500).

References

1. R. Tschesche and G. Grimmer, *Chem. Ber.*, **88**, 1569 (1955).
2. C.W. Shoppee, R.E. Lack and S. Sternhell, *J. Chem. Soc.*, 3281 (1963).
3. R. Tschesche and G. Buschauer, *Ann.*, **603**, 59 (1957).
4. C.W. Shoppee, R.E. Lack and A.V. Robertson, *J. Chem. Soc.*, 3610 (1962).

DIGITALONIN

Diginigenin 3-O-β-D-digtalopyranoside



Source: *Digitalis purpurea* L., *D. lanata* Ehrh. (Scrophulariaceae)
Mol. Formula : $C_{28}H_{40}O_8$
Mol. Wt. : 504
M.P. : 208-213°C
$[\alpha]_D$: -167.1° (c=0.74, MeOH)

UV (EtOH) : λ_{max} 310 (log ε, 1.97) nm.

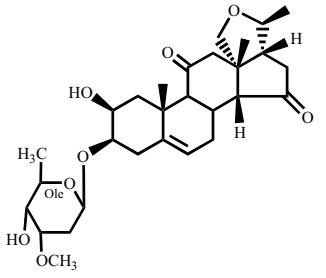
Biological Activity: No cardiotonic activity.

Reference

1. D. Sato, H. Ishii, Y. Oyama, T. Wada and T. Okumura, *Chem. Pharm. Bull*., **4**, 284 (1956).

LANAFOLEIN

Digifologenin 3-O-β-D-oleandroside



Source : *Digitalis lanata* Ehrh.[1], *D. canariensis* L. var. *isobelliana* (Webb) Lindler[2] (Scrophulariaceae)
Mol. Formula : $C_{28}H_{40}O_8$
Mol. Wt. : 504
M.P. : 178-181°C[1]
$[\alpha]_D^{19..5}$: -204° (MeOH)[1]

UV (EtOH)[3] : λ_{max} 310 (log ε, 1.91) nm.

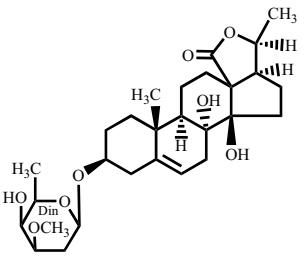
IR (KBr)[3] : 3480 (OH), 1743 (C=O), 1715 (C=O), 1653 (C=C) cm^{-1}.

References

1. R. Tschesche and G. Buschauer, *Ann*., **603**, 59 (1957).
2. S.K. Pavanaram, P. Hofer, H. Linde and K. Meyer, *Helv. Chim. Acta*, **46**, 1377 (1963).
3. C.W. Shoppe, R.E. Lack and A.V. Robertson, *J. Chem. Soc.*, 3610 (1962).

AMALOSIDE C

(20*S*)-3β,8α,14β-Trihydroxypregn-5-ene-18-oic acid-γ-lactone 3-O-β-D-diginopyranoside



Source : *Amalocalyx yunnanensis* Tsiang (Apocynaceae)
Mol. Formula : $C_{28}H_{42}O_8$
Mol. Wt. : 506
M.P. : 186°C
Registry No. : [150677-81-9]

PMR ($CDCl_3$, 400 MHz) : δ 1.02 (s, 3xH-19), 1.27 (d, *J*=6.5 Hz, 3xH-6 of Din), 1.35 (d, *J*=6.7 Hz, 3xH-21), 2.83 (ddd, *J*=7.4, 6.8, 2.1 Hz, H-17α), 3.30 (dt *J*=10.0, 2.8 Hz, H-3 of Din), 3.34 (s, OCH_3), 3.39 (br q *J*=6.5 Hz, H-5 of Din), 3.53 (tt, *J*=10.4, 5.2 Hz, H-3α), 3.64 (t, *J*=2.8 Hz, H-4 of Din), 4.48 (dd *J*=9.8, 2.0 Hz, H-1 of Din), 4.65 (dq, *J*=6.8, 6.7 Hz, H-20), 5.33 (d, *J*=6.5 Hz, H-6).

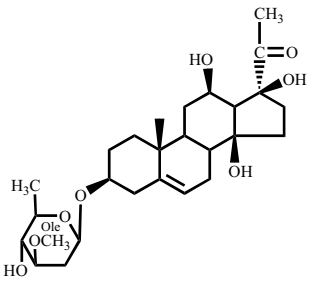
CMR ($CDCl_3$, 100.6 MHz) : δ C-1) 38.3[a] (2) 29.6[b] (3) 78.0 (4) 38.2[a] (5) 140.8 (6) 117.7 (7) 34.9 (8) 76.1 (9) 47.8 (10) 38.3 (11) 21.9 (12) 29.8[b] (13) 57.8 (14) 86.4 (15) 37.9 (16) 24.5 (17) 52.1 (18) 178.4 (19) 22.2 (20) 76.1 (21) 16.7 **Din** (1) 97.6 (2) 31.8 (3) 77.9 (4) 67.0 (5) 70.3 (6) 17.1 (OCH_3) 55.6.

Reference

1. X.-L.Shen, Y.-J. Hu, Y.L. An and Q.-Z. Mu, *Phytochemistry*, **33**, 687 (1993).

CYNANFORMOSIDE C

Pergularin 3-O-[β-D-oleandropyranoside]



Source : *Cynanchum formosanum* (Asclepiadaceae)
Mol. Formula : $C_{28}H_{44}O_8$
Mol. Wt. : 508
M.P. : 118-121°C
$[\alpha]_D^{20}$: -44.5° (c=2.5, $CHCl_3$)
Registry No. : [137708-25-9]

IR (KBr) **:** 3419 (OH), 3053 (C=C), 1699 (C=O), 1653 (C=C) cm^{-1}.

PMR ($CDCl_3$) **:** δ 0.97 (s, 3xH-18), 1.12 (s, 3xH-19), 1.30 (d, *J*=6.0 Hz, 3xH-6 of Ole), 2.32 (s, 3xH-21), 3.37 (s, OC*H*$_3$), 3.07-3.65 (H-3, H-12, H-3', H-4' and H-5' of Ole), 4.58 (br d, *J*=9.5 Hz, H-1 of Ole), 5.37 (br s, H-6).

CMR ($CDCl_3$) **:** δ C-1) 38.5 (2) 29.4 (3) 75.4 (4) 36.8 (5) 139.5 (6) 121.3 (7) 32.2 (8) 36.7 (9) 43.0 (10) 37.1 (11) 26.0 (12) 71.5 (13) 59.9 (14) 88.6 (15) 31.5 (16) 30.3 (17) 91.6 (18) 5.8 (19) 19.4 (20) 213.2 (21) 28.1 **Ole** (1) 97.6 (2) 35.6 (3) 80.8 (4) 77.5 (5) 68.8 (6) 17.9 (O*C*H$_3$) 56.2.

Mass (E.I.) : *m/z* 348 [(M-Ole)$^+$, 3], 328 [(M-Ole-OH)$^+$, 2], 303 [(M-Ole-CH_3CO)$^+$, 20], 145 [(Ole-OH)$^+$, 100], 113 [(Ole-OH-MeOH)$^+$, 70].

Reference

1. Z.-S. Chen, J.-S. Lai and Y.-I. Kuo, *Chem. Express*, **6**, 559 (1991).