Spectroscopic Data of Steroid Glycosides: Miscellaneous Steroids and Indexes

Volume 6

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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Volume 3
SPECTROSCOPIC DATA OF STEROID GLYCOSIDES: SPIROSTANES, BUFANOLIDES, CARDENOLIDES
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Volume 4
SPECTROSCOPIC DATA OF STEROID GLYCOSIDES: CARDENOLIDES AND PREGNANES
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Volume 5
SPECTROSCOPIC DATA OF STEROID GLYCOSIDES: PREGNANES, ANDROSTANES, AND MISCELLANEOUS
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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

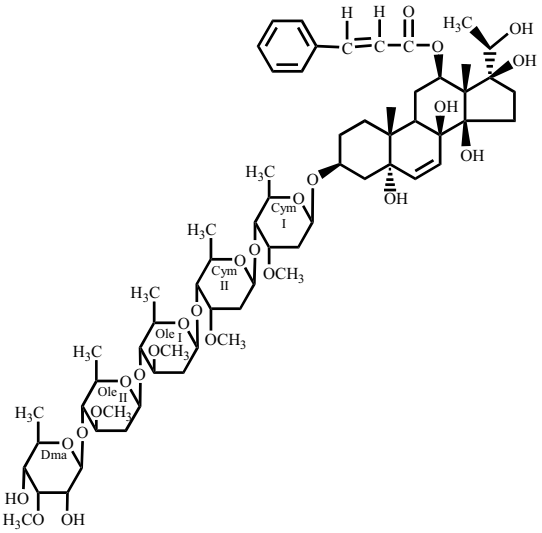
Glc	Glucose
Glum	6-Deoxy-α-L-glucopyranoside
Gum	Gulomethylose
HMB	Hydroxymethoxybenzoyl
HMG	Hydroxymethylglutaroyl
HR	High resolution
Ike	Ikemoyl (3,4-dimethyl-2-pentenoyl)
LD	Laser Desorption
Meb	2-Methylbutanoyl
MeXyl	Methylxylose
MGl	Methylglucose
Neg	Negative
Nic	Nicotinoyl
Ole	Oleandrose
Oli	Olivose
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

GYMNEPREGOSIDE O

12-O-(*Z*)-Cinnamoyl-(20*S*)-pregn-6-ene-3β,5α,8β,12β,14β,17β,20-heptaol 3-O-[(6-deoxy)-3-O-methyl-β-D-allopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside]

Source : *Gymnema alternifolium* (Asclepiadaceae)
Mol. Formula : $C_{65}H_{100}O_{21}$
Mol. Wt. : 1216
M.P. : 112-114°C
$[\alpha]_D^{25}$: +12.8° (c=1.1, $CHCl_3$)
Registry No. : [238420-73-0]



UV (MeOH) : λ_{max} 200 (log ε, 4.50), 276 (log ε, 4.11) nm.

IR (film) : 3450, 1705, 1635, 1585, 1120 cm^{-1}.

PMR (C_5D_5N, 600 MHz) : δ 1.35 (d, *J*=6.6 Hz, 3xH-6 of Cym I), 1.35 (d, *J*=6.9 Hz, 3xH-6 of Cym II), 1.36 (d, *J*=6.3 Hz, 3xH-21), 1.42 (d, *J*=5.7 Hz, 3xH-6 of Ole I), 1.54 (d, *J*=5.5 Hz, 3xH-6 of Dma), 1.57 (s, 3xH-19), 1.68 (d, *J*=5.7 Hz, 3xH-6 of Ole II), 2.02 (s, 3xH-18), 3.42 (s, OC*H*$_3$ of Ole I), 3.43 (dd, *J*=9.8, 2.6 Hz, H-4 of Cym II), 3.45 (m, H-4

of Cym I), 3.47 (m, H-4 of Ole I), 3.53 (s, OC*H*$_3$ of Ole II), 3.55 (s, OC*H*$_3$ of Cym I and Cym II), 3.62 (m, H-4 of Ole II), 3.82 (s, OC*H*$_3$ of Dma), 4.06 (q, *J*=6.3 Hz, H-20), 4.15 (m, H-3), 4.67 (dd, *J*=9.6, 1.5 Hz, H-1 of Ole I), 4.87 (dd, *J*=9.8, 1.5 Hz, H-1 of Ole II), 5.10 (dd, *J*=9.5, 1.5 Hz, H-1 of Cym II), 5.14 (dd, *J*=9.1, 1.5 Hz, H-1 of Cym I), 5.25 (dd, *J*=11.2, 4.2 Hz, H-12), 5.30 (d, *J*=7.6 Hz, H-1 of Dma), 5.89 (d, *J*=10.2 Hz, H-6), 6.20 (d, *J*=10.2 Hz, H-7), 6.36 (d, *J*=12.8 Hz, H-8 of *Z*-Cin), 7.00 (d, *J*=12.8 Hz, H-7 of *Z*-Cin), 7.31 (dt, *J*=7.5, 7.5, 1.5 Hz, H-4 of *Z*-Cin), 7.36 (t, *J*=7.5, Hz, H-3, H-5 of *Z*-Cin), 7.88 (dd, *J*=7.5, 1.5 Hz, H-2, H-6 of *Z*-Cin).

CMR (C_5D_5N, 125 MHz) : δ C-1) 27.6 (2) 26.6 (3) 74.2 (4) 39.1 (5) 74.7 (6) 136.2 (7) 127.7 (8) 73.8 (9) 37.0 (10) 39.7 (11) 23.7 (12) 75.9 (13) 57.9 (14) 88.8 (15) 33.4 (16) 33.4 (17) 87.9 (18) 12.6 (19) 21.6 (20) 70.7 (21) 19.4 ***Z*-Cin** (1) 134.9 (2) 130.4 (3) 128.3 (4) 129.3 (7) 143.4 (8) 121.0 (9) 166.2 **Cym I** (1) 97.7 (2) 36.8 (3) 77.9 (4) 83.0 (5) 69.1 (6) 18.4 (O*C*H$_3$) 58.7 **Cym II** (1) 100.4 (2) 36.8 (3) 77.7 (4) 83.1 (5) 68.9 (6) 18.4 (O*C*H$_3$) 58.9 **Ole I** (1) 101.9 (2) 37.6 (3) 79.0 (4) 82.7 (5) 71.6 (6) 18.6 (O*C*H$_3$) 57.3 **Ole II** (1) 100.0 (2) 37.6 (3) 79.5 (4) 82.9 (5) 72.1 (6) 19.0 (O*C*H$_3$) 57.2 **Dma** (1) 102.0 (2) 73.3 (3) 84.0 (4) 74.6 (5) 71.0 (6) 18.6 (O*C*H$_3$) 62.0.

Mass (FAB, Negative ion) : *m/z* 1263 $[M-H]^-$.

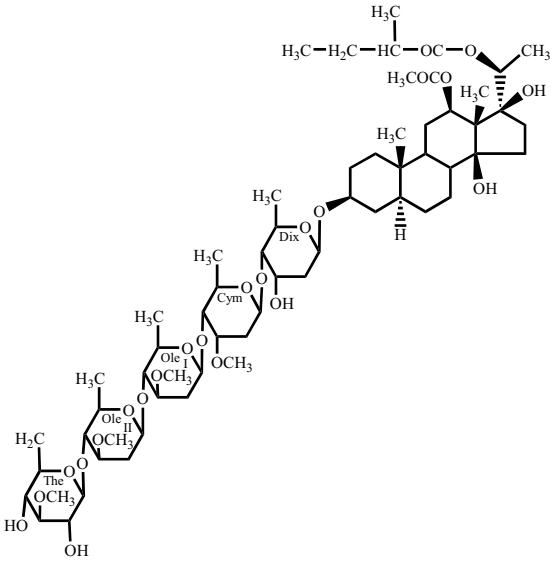
Reference

1. K. Yoshikawa, K. Matsuchika, K. Takahashi, M. Tanaka, S. Arihara, H-C. Chang and J-D. Wang, *Chem. Pharm. Bull.*, **47**, 798 (1999).

TELOSMOSIDE A_{11}

Telosmogenin I 3-O-[β-D-thevetopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranoside]

Source : *Telosma procumbens* (Hance.) Merr. (Asclepiadaceae)
Mol. Formula : $C_{62}H_{104}O_{23}$
Mol. Wt. : 1216
$[\alpha]_D^{31}$: -7.0° (c=1.85, MeOH)
Registry No. : [343781-70-4]



PMR (C_5D_5N, 400/500 MHz) : δ 0.68 (s, 3xH-19), 0.81 (t, *J*=7.4 Hz, 3xH-4 of Meb), 1.21 (d, *J*=6.8 Hz, 3xH-5 of Meb), 1.30 (d, *J*=6.1 Hz, 3xH-6 of Cym), 1.38 (d, *J*=6.1 Hz, H-21), 1.39 (d, *J*=6.1 Hz, 3xH-6 of Ole I), 1.43 (d, *J*=6.3 Hz, 3xH-6 of Dix), 1.55 (d, *J*=5.9 Hz, 3xH-6 of The), 1.60 (s, 3xH-18), 1.68 (d, *J*=6.1 Hz, 3xH-6 of Ole II), 2.20 (s, OCO*CH*$_3$), 2.39 (m, H-2 of Meb), 3.45 (s, OC*H*$_3$ of Ole I), 3.51 (s, OC*H*$_3$ of Ole II), 3.54 (s, OC*H*$_3$ of Cym), 3.80 (m, H-3), 3.85 (s, OC*H*$_3$ of The), 4.64 (dd, *J*=9.7, 1.5 Hz, H-1 of Ole I), 4.85 (dd, *J*=9.8, 1.7 Hz, H-1 of Ole II), 4.90* (H-20), 4.91* (H-12), 4.91 (d, *J*=7.5 Hz, H-1 of The), 5.13 (dd, *J*=9.5, 1.5 Hz, H-1 of Cym), 5.42 (dd, *J*=9.3, 1.5 Hz, H-1 of Dix). * overlapped signals.

CMR (C_5D_5N, 100/125 MHz) : δ C-1) 36.7 (2) 29.9 (3) 76.5 (4) 34.7 (5) 44.3 (6) 28.7 (7) 26.9 (8) 40.3 (9) 45.7 (10) 35.7 (11) 27.8 (12) 74.5 (13) 55.6 (14) 87.8 (15) 30.8[a] (16) 33.8[a] (17) 87.3 (18) 9.5 (19) 12.1 (20) 74.6 (21) 15.3 (O*C*OCH$_3$) 171.3 (OCO*C*H$_3$) 22.3 **Meb** (1) 175.7 (2) 41.2 (3) 27.0 (4) 11.6 (5) 16.4 **Dix** (1) 95.9 (2) 39.0 (3) 67.5 (4) 83.4[b] (5) 68.5 (6) 18.7[c] **Cym** (1) 99.7 (2) 36.9 (3) 77.7 (4) 83.1[b] (5) 69.0 (6) 18.4[c] (O*C*H$_3$) 58.4 **Ole I** (1) 101.9 (2) 37.7[d] (3) 79.0 (4) 82.7[b] (5) 71.6 (6) 18.7[c] (O*C*H$_3$) 57.3 **Ole II** (1) 100.0 (2) 37.5[d] (3) 79.4 (4) 83.2[b] (5) 72.1 (6) 18.9[c] (O*C*H$_3$) 57.3 **The** (1) 104.1 (2) 75.2 (3) 88.1 (4) 76.0 (5) 72.8 (6) 18.5[c] (O*C*H$_3$) 60.9.

Mass (FAB, Negative ion, H.R.) : *m/z* 1215.6879 [(M-H)$^-$, calcd for 1215.6890].

Mass (FAB, Negative ion) : *m/z* 1216 [M-H]$^-$, 1056 [M-The]$^-$, 912 [M-(The-Ole)]$^-$.

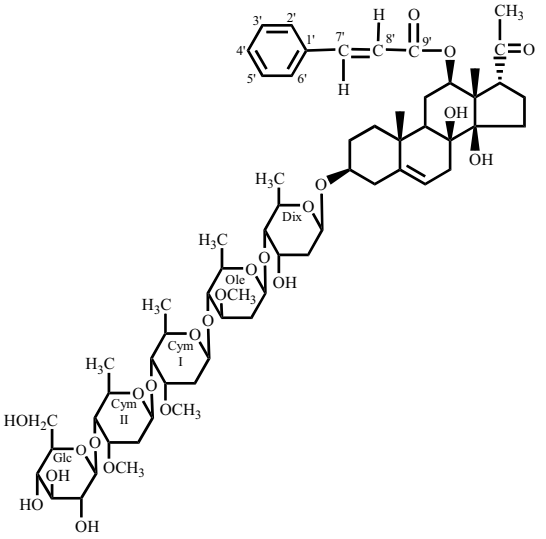
Reference

1. V.D. Huan, K. Ohtani, R. Kasai, K. Yamasaki and N.V. Tuu, *Chem. Pharm. Bull.*, **49**, 453 (2001).

ASCLEPIAS FRUTICOSA SAPONIN 12

Ikemagenin 3-O-[β-D-glucopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranoside]

Source : *Asclepias fruticosa* L. (Syn. *Gomphocarpus fruticosus* L. R.Br.) (Asclepiadaceae)
Mol. Formula : $C_{63}H_{94}O_{23}$
Mol. Wt. : 1218
$[\alpha]_D^{27}$: +20.8° (c=0.38, MeOH)
Registry No. : [162584-75-0]



PMR (C_5D_5N, 400 MHz) : δ 1.34 (d, *J*=6.0 Hz, 3xH-6 of Cym I), 1.36 (d, *J*=6.0 Hz, 3xH-6 of Ole), 1.47 (d, *J*=6.0 Hz, 3xH-6 of Dix), 1.61 (d, *J*=6.0 Hz, 3xH-6 of Cym II), 3.42 (t, *J*=9.0 Hz, H-4 of Ole), 3.43 (dd, *J*=9.0, 3.0 Hz, H-4 of Cym I), 3.51 (dd, *J*=9.0, 2.0 Hz, H-4 of Dix), 3.52 (s, OC*H*$_3$), 3.53 (s, OC*H*$_3$), 3.61 (s, OC*H*$_3$), 3.66 (dd, *J*=10.0, 2.0 Hz, H-4 of Cym II), 3.98 (m, H-5 of Glc), 4.00 (dd, *J*=8.0, 9.0 Hz, H-2 of Glc), 4.05 (br s, H-3 of Cym I), 4.11 (br s, H-3 of Cym II), 4.17 (t, *J*=9.0 Hz, H-4 of Glc), 4.20 (m, H-5 of Cym I), 4.23 (t, *J*=9.0 Hz, H-3 of Glc), 4.24 (m, H-5 of Cym II), 4.30 (m, H-5 of Dix), 4.38 (dd, *J*=12.0, 6.0 Hz, H-6 of Glc), 4.57 (br d, *J*=12.0 Hz, H-6B of Glc), 4.62 (br s, H-3 of Dix), 4.73 (dd, *J*=9.0, 1.0 Hz, H-1 of Ole), 4.93 (d, *J*=8.0 Hz, H-1 of Glc), 5.08 (dd, *J*=10.0, 1.0 Hz, H-1 of Cym II), 5.26 (br d, *J*=10.0 Hz, H-1 of Cym I), 5.48 (dd, *J*=9.0, 1.0 Hz, H-1 of Dix).

CMR (C_5D_5N, 100 MHz) : **Dix** δ C-1) 96.3 (2) 39.1 (3) 67.5 (4) 83.6 (5) 68.4 (6) 18.6 **Ole** (1) 101.3 (2) 37.5 (3) 78.7 (4) 82.6 (5) 71.7 (6) 18.5[a] **Cym I** (1) 98.3 [b](2) 37.1[c] (3) 78.0[d] (4) 83.1 (5) 69.2 (6) 18.6[a] (O*C*H$_3$) 58.8[e] **Cym II** (1) 100.3[b] (2) 36.7[c] (3) 77.9[d] (4) 83.6 (5) 69.3 (6) 18.4[a] (O*C*H$_3$) 58.6[e] **Glc** (1) 106.5 (2) 75.3 (3) 78.3 (4) 71.8 (5) 78.3 (6) 63.0.

Mass (FAB, Positive ion, H.R.) : *m/z* 1241.6089 [$(M+Na)^+$, calcd. for 1241.6084].

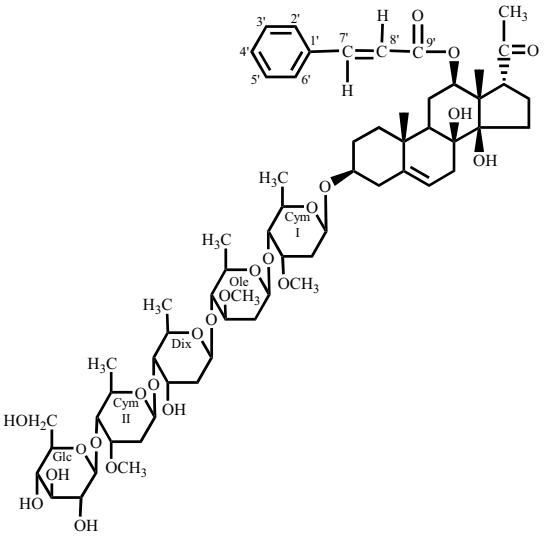
Reference

1. F. Abe, Y. Mori, H. Okabe and T. Yamauchi, *Chem. Pharm. Bull.*, **42,** 1777 (1994).

ASCLEPIAS FRUTICOSA SAPONIN 13

Ikeamgenin 3-O-[β-D-glucopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranoside]

Source : *Asclepias fruticosa* L. (Syn. *Gomphocarpus fruticosus* L. R.Br.) (Asclepiadaceae)
Mol. Formula : $C_{63}H_{94}O_{23}$
Mol. Wt. : 1218
$[\alpha]_D^{28}$: +24.08° (c=0.23, MeOH)
Registry No. : [162584-76-1]



PMR (C_5D_5N, 400 MHz) : δ 1.38 (d, *J*=6.0 Hz, 3xH-6 of Dix), 1.44 (d, *J*=6.0 Hz, 3xH-6 of Cym I and 3xH-6 of Ole), 1.55 (d, *J*=6.0 Hz, 3xH-6 of Cym II), 3.43 (dd, *J*=9.0, 2.0 Hz, H-4 of Dix), 3.50 (dd, *J*=9.0, 3.0 Hz, H-4 of Cym I), 3.51 (t, *J*=9.0 Hz, H-4 of Ole), 3.52 (s, OC*H*$_3$), 3.55 (s, OC*H*$_3$), 3.58 (s, OC*H*$_3$), 3.60 (dd, *J*=9.0, 2.0 Hz, H-4 of Cym II), 3.95 (m, H-5 of Glc), 3.99 (dd, *J*=8.0, 9.0 Hz, H-2 of Glc), 4.05 (br s, H-3 of Cym I), 4.09 (br s, H-3 of Cym II), 4.15 (t, *J*=9.0 Hz, H-4 of Glc), 4.22 (t, *J*=9.0 Hz, H-3 of Glc), 4.36 (dd, *J*=12.0, 6.0 Hz, H-6A of Glc), 4.56 (dd, *J*=12.0, 2.0 Hz, H-6B of Glc), 4.59 (br s, H-3 of Dix), 4.69 (br d, *J*=10.0 Hz, H-1 of Ole), 4.91 (d, *J*=8.0 Hz, H-1 of Glc), 5.12 (br d, *J*=10.0 Hz, H-1 of Cym II), 5.27 (br d, *J*=10.0 Hz, H-1 of Cym I), 5.46 (br d, *J*=10.0 Hz, H-1 of Dix).

CMR (C_5D_5N, 100 MHz) : **Cym I** C-1) 96.3 (2) 37.2 (3) 77.8 (4) 82.8[a] (5) 68.9 (6) 18.6[b] (O*C*H$_3$) 58.8 **Ole** (1) 101.9 (2) 37.5 (3) 78.8 (4) 82.9[a] (5) 71.7 (6) 18.4[b] (O*C*H$_3$) 57.4 **Dix** (1) 98.4 (2) 38.9 (3) 67.5 (4) 83.4[a] (5) 68.7 (6) 18.6[b] **Cym II** (1) 99.6 (2) 36.4 (3) 77.9 (4) 83.0[a] (5) 69.4 (6) 18.5[b] (O*C*H$_3$) 58.6 **Glc** (1) 106.4 (2) 75.3 (3) 78.3 (4) 71.8 (5) 78.4 (6) 63.0.

Mass (FAB, Positive ion, H.R) : *m/z* 1241.6077 [(M+Na)$^+$, calcd. for 1241.6084].

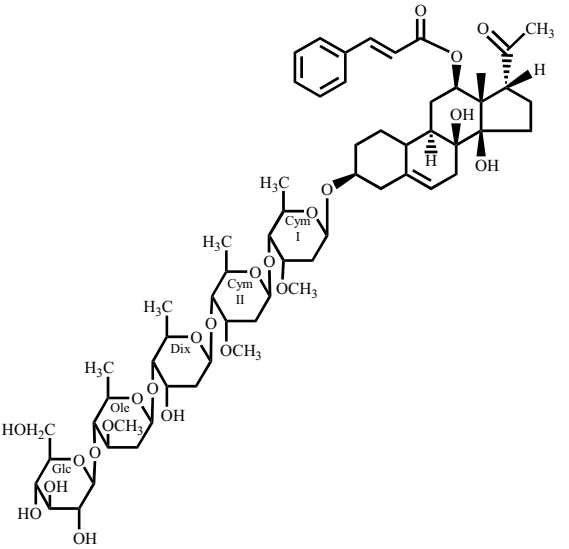
Reference

1. F. Abe, Y. Mori, H. Okabe and T. Yamauchi, *Chem. Pharm. Bull.*, **42,** 1777 (1994).

ASCLEPIAS INCARNATA SAPONIN 78

Ikemagenin 3-O-[β-D-glucopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digtoxopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside]

Source : *Asclepias incarnata* L. (Asclepiadaceae)
Mol. Formula : $C_{63}H_{94}O_{23}$
Mol. Wt. : 1218
$[\alpha]_D^{25}$: +15.1° (c=1.26, MeOH)
Registry No. : [531553-09-3]



UV (MeOH) : λ_{max} 216 (log ε, 4.17), 222 (log ε, 4.08), 278 (log ε, 4.35) nm.

PMR (C_5D_5N, 400 MHz) : δ 1.33 (d, *J*=6.5 Hz, 3xH-6 of Cym II), 1.39 (d, *J*=6.5 Hz, 3xH-6 of Cym I), 1.42 (d, *J*=6.5 Hz, 3xH-6 of Dix), 1.65 (d, *J*=6.0 Hz, 3xH-6 of Ole), 3.43 (dd, *J*=9.5, 3.0 Hz, H-4 of Dix), 3.48 (dd, *J*=9.5, 3.0 Hz, H-4 of Cym II), 3.50* (H-4 of Cym I), 3.52 (s, OCH_3), 3.62 (s, 2xOCH_3), 3.63* (H-3 of Ole), 3.64* (H-5 of Ole), 3.65* (H-4 of Ole), 3.93 (m, H-5 of Glc), 3.99 (t, *J*=8.0 Hz, H-2 of Glc), 4.07 (q, *J*=3.0 Hz, H-3 o f Cym I and Cym II), 4.16 (dq, *J*=9.5, 6.5 Hz, H-5 of Cym II), 4.17* (H-4 of Glc), 4.20* (H-3 of Glc), 4.21 (dq, *J*=9.5, 6.5 Hz, H-4 of Cym I), 4.27 (dq, *J*=9.5, 6.5 Hz, H-5 of Dix), 4.33 (dd, *J*=11.5, 5.5 Hz, H-6A of Glc), 4.52 (dd, *J*=11.5, 2.5 Hz, H-6B of Glc),

4.59 (q, *J*=3.0, Hz, H-3 of Dix), 4.73 (dd, *J*=9.5, 2.0 Hz, H-1 of Ole), 5.10 (d, *J*=8.0 Hz, H-1 of Glc), 5.12 (dd, *J*=9.5, 2.0 Hz, H-1 o f Cym II), 5.27 (dd, *J*=9.5, 2.0 Hz, H-1 of Cym I), 5.30 (dd, *J*=9.5, 2.0 Hz, H-1 of Dix).

CMR (C_5D_5N, 100.40 MHz) : δ **Cym I** C-1) 96.5 (2) 37.3 (3) 78.0 (4) 83.4 (5) 69.0 (O*C*H_3) 59.0 **Cym II** (1) 100.5 (2) 37.2 (3) 78.0 (4) 83.2 (5) 69.0 (O*C*H_3) 58.9 **Dix** (1) 100.5 (2) 39.0 (3) 67.5 (4) 83.2 (5) 68.5 **Ole** (1) 101.4 (2) 37.1 (3) 79.3 (4) 83.2 (5) 72.1 (O*C*H_3) 57.2 **Glc** (1) 104.5 (2) 75.7 (3) 78.7 (4) 72.1 (5) 78.2 (6) 63.2 (C-6 of sugars) 18.8, 18.6x2, 18.4.

The CMR data of the aglycone moiety are in good agreement with those of Asclepias Incarnata Saponin 67 (q.v.).

Mass (FAB) : *m/z* 1241 $[M+Na]^+$.

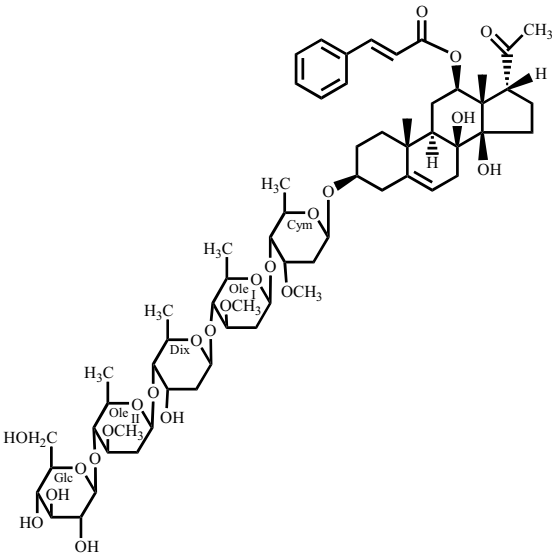
Reference

1. T. Warashina and T. Noro, *Chem. Pharm. Bull.,* **48,** 516 (2000).

ASCLEPIAS INCARNATA SAPONIN 93

Ikemagenin-3-O-[β-D-glucopyranosyl-(1→4)-β-D-oleanderopyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranoside]

Source : *Asclepias incarnata* L. (Asclepiadaceae)
Mol. Formula : $C_{63}H_{94}O_{23}$
Mol. Wt. : 1218
$[\alpha]_D^{25}$: $+1.4^o$ (c=0.53, MeOH)
Registry No. : [272444-26-5]



UV (MeOH) : λ_{max} 217 (log ε, 4.23), 222 (log ε, 4.15), 278 (log ε, 4.38) nm.

PMR (C_5D_5N, 400 MHz) : δ 1.44* (H-6 of Cym, Ole I and Dix), 1.65 (d, *J*=6.0 Hz H-6 of Ole II), 3.45 (dd, *J*=9.5, 3.0 Hz, H-3 of Dix), 3.51 (s, OC*H*$_3$), 3.51* (H-3 of Cym), 3.52* (H-5 of Ole I), 3.54* (H-4 of Ole II), 3.56 (s, OC*H*$_3$), 3.58 (s, OC*H*$_3$), 3.59* (H-3 of Ole I), 3.65* (H-3, H-4 and H-5 of Ole II), 3.93 (m, H-5 of Glc), 3.99 (t, *J*=8.0 Hz, H-2 of Glc), 4.05 (q, *J*=3.0 Hz, H-3 of Cym), 4.17* (H-4 of Glc), 4.19* (H-3 of Glc), 4.23 (dq, *J*=9.5, 6.5 Hz, H-5 of Cym), 4.29 (dq, *J*=9.5, 6.5 Hz, H-5 of Dix), 4.33 (dd, *J*=11.5, 5.5 Hz, H-6A of Glc), 4.52 (dd, *J*=11.5, 2.5 Hz, H-6B of Glc), 4.61 (q, *J*=3.0 Hz, H-3 of Dix), 4.70 (dd, *J*=9.5, 2.0 Hz, H-1 of Ole I), 4.73 (dd, *J*=9.5, 2.0 Hz, H-1 of Ole II), 5.10 (d, *J*=8.0 Hz, H-1 of Glc), 5.28 (dd, *J*=9.5, 2.0 Hz, H-1 of Cym), 5.48 (dd, *J*=9.5, 2.0 Hz, H-1 of Dix). * overlapped signals.

CMR (C_5D_5N, 100.40 MHz) : δ C-1) 39.0 (2) 29.9 (3) 77.7 (4) 39.4 (5) 139.5 (6) 119.2 (7) 35.2 (8) 74.6 (9) 44.8 (10) 37.6 (11) 25.0 (12) 73.4 (13) 55.9 (14) 87.5 (15) 34.2 (16) 22.0 (17) 60.5 (18) 15.8 (19) 18.2 (20) 209.3 (21) 32.2 **Ester moiety** (1) 165.9 (2) 119.3 (3) 144.9 (4) 135.1 (5) 128.6 (6) 129.3 (7) 130.6 (8) 129.3 (9) 128.6 **Cym** (1) 96.5 (2) 37.8 (3) 77.9 (4) 82.8 (5) 69.0 (O*C*H$_3$) 58.9 **Ole I** (1) 102.0 (2) 37.3 (3) 78.9 (4) 83.3 (5) 71.8 (O*C*H$_3$) 57.5 **Dix** (1) 98.5 (2) 39.0 (3) 67.7 (4) 83.5 (5) 68.7 **Ole II** (1) 101.4 (2) 37.2 (3) 79.4 (4) 83.2 (5) 72.1 (O*C*H$_3$) 57.2 **Glc** (1) 104.4 (2) 75.7 (3) 78.7 (4) 72.1 (5) 78.2 (6) 63.2 (C-6 of sugars) 18.8, 18.7x2, 18.6.

Mass (FAB) : *m/z* 1241 $[M+Na]^+$.

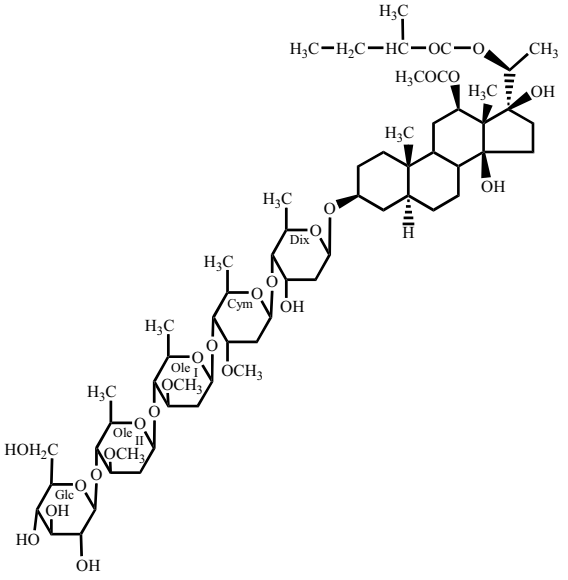
Reference

1. T. Warashina and T. Noro, *Chem. Pharm. Bull.,* **48**, 516 (2000).

TELOSMOSIDE A_{12}

Telosmogenin I 3-O-[β-D-glucopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-digitoxopyranoside]

Source : *Telosma procumbens* (Hance) Merr. (Asclepiadaceae)
Mol. Formula : $C_{61}H_{102}O_{24}$
Mol. Wt. : 1218
$[\alpha]_D^{30}$: -5.0° (c=2.38, MeOH)
Registry No. : [343781-71-5]



PMR (C_5D_5N, 400/500 MHz) : δ 0.70 (s, 3xH-19), 0.82 (t, *J*=7.4 Hz, 3xH-4 of Meb), 1.21 (d, *J*=7.1 Hz, 3xH-5 of Meb), 1.32 (d, *J*=5.8 Hz, 3xH-6 of Cym), 1.41 (d, *J*=5.7 Hz, 3xH-6 of Ole I), 1.42 (d, *J*=5.7 Hz, 3xH-21), 1.46 (d, *J*=6.1 Hz, 3xH-6 of Dix), 1.64 (s, 3xH-18), 1.72 (d, *J*=5.6 Hz, 3xH-6 of Ole II), 2.23 (s, OCOC*H*$_3$), 2.42 (m, H-2 of Meb), 3.48 (s, OC*H*$_3$ of Ole I), 3.54 (s, OC*H*$_3$ of Cym), 3.59 (s, OC*H*$_3$ of Ole II), 3.82 (m, H-3), 4.67 (dd, *J*=9.8, 1.5 Hz, H-1 of Ole I), 4.88 (dd, *J*=9.6, 1.5 Hz, H-1 of Ole II), 4.90* (H-20), 4.92* (H-12), 5.11 (d, *J*=7.6 Hz, H-1 of Glc), 5.17 (dd, *J*=9.5, 1.5 Hz, H-1 of Cym), 5.47 (dd, *J*=9.6, 1.5 Hz, H-1 of Dix). * overlapped signals.

CMR (C_5D_5N, 100/125 MHz) : δ C-1) 36.7 (2) 30.0 (3) 76.5 (4) 34.7 (5) 44.3 (6) 28.7 (7) 26.9 (8) 40.3 (9) 45.7 (10) 35.7 (11) 27.9 (12) 74.5 (13) 55.6 (14) 87.8 (15) 30.9[a] (16) 33.8[a] (17) 87.3 (18) 9.5 (19) 12.1 (20) 74.6 (21) 15.3 (O*C*OCH$_3$) 171.3 (OCO*C*H$_3$) 22.3 **Meb** (1) 175.8 (2) 41.2 (3) 27.1 (4) 11.6 (5) 16.4 **Dix** (1) 95.9 (2) 39.1 (3) 67.6 (4) 83.4[b] (5) 68.6 (6) 18.7[c] **Cym** (1) 99.7 (2) 36.9 (3) 77.7 (4) 83.2[b] (5) 69.0 (6) 18.5[c] (O*C*H$_3$) 58.9 **Ole I** (1) 102.0 (2) 37.6 (3) 79.0 (4) 82.7[b] (5) 71.6[d] (6) 18.7[c] (O*C*H$_3$) 57.3 **Ole II** (1) 100.0 (2) 37.6 (3) 79.6 (4) 82.4[b] (5) 72.1[d] (6) 18.9[c] (O*C*H$_3$) 57.3 **Glc** (1) 104.5 (2) 75.7 (3) 78.7 (4) 72.0[d] (5) 78.1 (6) 63.1.

Mass (FAB, Negative ion, H.R.) : *m/z* 1217.6680 [(M-H)$^-$, calcd for 1217.6683].

Mass (FAB, Negative ion) : *m/z* 1218 [M-H]$^-$, 1056 [M-Glc]$^-$, 912 [M-(Glc-Ole)]$^-$, 767 [M-(Glc-Ole-Ole)]$^-$.

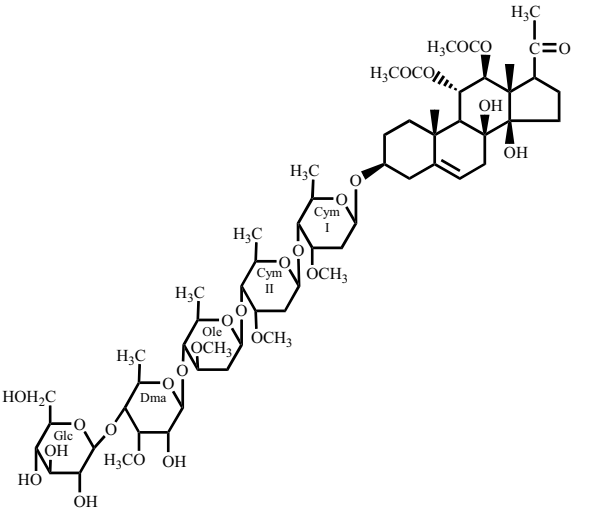
Reference

1. V.D. Huan, K. Ohtani, R. Kasai, K. Yamasaki and N.V. Tuu, *Chem. Pharm. Bull.*, **49**, 453 (2001).

HOYACARNOSIDE K

11,12-Di-O-acetyl-17β-marsdenin 3-O-[β-D-glucopyranosyl-(1→4)-(6-deoxy-3-O-methyl)-β-D-allopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside]

Source : *Hoya carnosa* R.Br. (Asclepiadaceae)
Mol. Formula : $C_{59}H_{94}O_{26}$
Mol. Wt. : 1218
$[\alpha]_D^{24}$: +31.5° (c=2.03, MeOH)
Registry No. : [246040-89-1]



PMR (C_5D_5N, 500 MHz) **:** δ 1.34 (d, *J*=6.0 Hz, 3xH-6 of Cym I), 1.36 (d, *J*=6.0 Hz, 3xH-6 of Cym II), 1.59 (d, *J*=6.0 Hz, 3xH-6 of Ole), 1.64 (d, *J*=6.0 Hz, 3xH-6 of Dma), 1.70 (m, H-2A of Ole), 1.79 (m, H-2A of Cym II), 1.89 (m, H-2A of Cym I), 2.27 (m, H-2B of Cym II), 2.32 (m, H-2B of Cym I), 2.46 (m, H-2B of Ole), 3.41 (dd, *J*=9.0, 3.0 Hz, H-4 of Cym II), 3.48 (dd, *J*=9.0, 3.0 Hz, H-4 of Cym I), 3.50-3.60 (m, H-3 and H-5 of Ole), 3.51 (s, OCH_3), 3.54 (s, OCH_3), 3.55 (t, *J*=9.0 Hz, H-4 of Ole), 3.63 (s, OCH_3), 3.73 (dd, *J*=9.0, 3.0 Hz, H-4 of Dma), 3.81 (br d, *J*=8.0 Hz, H-2 of Dma), 3.83 (s, OCH_3), 3.97 (m, H-5 of Glc), 3.99 (q, *J*=3.0 Hz, H-3 of Cym II), 4.01 (dd, *J*=8.0, 9.0 Hz, H-2 of Glc), 4.08 (q, *J*=3.0 Hz, H-3 of Cym I), 4.14 (m, H-5 of Cym II), 4.18 (t, *J*=9.0 Hz, H-4 of Glc), 4.20 (m, H-5 of Cym I), 4.23 (t, *J*=9.0 Hz, H-3 of Glc), 4.25 (dq, *J*=9.0, 6.0 Hz, H-5 of Dma), 4.35 (dd, *J*=12.0, 5.0 Hz, H-6A of Glc), 4.47 (t, *J*=3.0 Hz, H-3 of Dma), 4.52 (dd, *J*=12.0, 2.0 H,z H-6B of Glc), 4.66 (dd, *J*=10.0, 2.0 Hz, H-1 of Ole), 4.96 (d, *J*=8.0 Hz, H-1 of Glc),5.09 (dd, *J*=10.0, 2.0 Hz, H-1 of Cym II), 5.25 (d, *J*=8.0 Hz, H-1 of Dma), 5.29 (dd, *J*=9.0, 2.0 Hz, H-1 of Cym I).

CMR (C_5D_5N, 125 MHz) : δ **Cym I** C-1) 96.2 (2) 37.2 (3) 78.0 (4) 83.3 (5) 68.9[a] (6) 18.5 **Cym II** (1) 100.4 (2) 37.0 (3) 77.7 (4) 83.1 (5) 68.8 (6) 18.4 **Ole** (1) 101.8 (2) 37.5 (3) 79.2 (4) 82.8 (5) 71.9 (6) 18.8 **Dma** (1) 101.8 (2) 72.6 (3) 83.1 (4) 83.3 (5) 69.5 (6) 18.2 **Glc** (1) 106.5 (2) 75.4 (3) 78.3 (4) 71.9 (5) 78.0 (6) 63.0 (O*C*H_3) 57.3, 58.8, 58.8, 61.6.

Mass (FAB-HR, Positive ion) : *m/z* 1241.5929 [$(M+Na)^+$, requires 1241.5931].

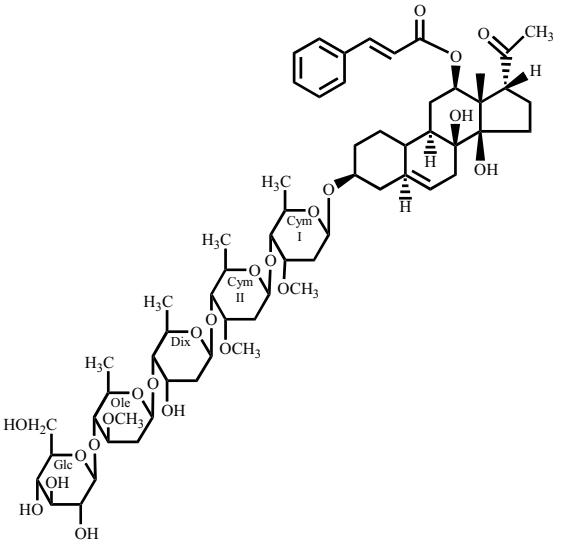
Reference

1. F. Abe, H. Fujishima, Y. Iwase, T. Yamauchi, K. Kinjo and S. Yaga, *Chem. Pharm. Bull.*, **47**, 1128 (1999).

ASCLEPIAS INCARNATA SAPONIN 79

5α,6-Dihydroikemagenin 3-O-[β-D-glucopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digtoxopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside]

Source : *Asclepias incarnata* L. (Asclepiadaceae)
Mol. Formula : $C_{63}H_{96}O_{23}$
Mol. Wt. : 1220
$[\alpha]_D^{24}$: +13.3° (c=0.87, MeOH)
Registry No. : [272444-20-9]



UV (MeOH) : λ_{max} 202 (log ε, 4.31), 217 (log ε, 4.23), 222 (log ε, 4.18), 278 (log ε, 4.36) nm.

The PMR and CMR data of the aglycone moiety and the sugar moiety are in good agreement with those of Asclepias Incarnata Saponin 69 and Asclepias Incarnata Saponin 78, respectively (q.q.v.).

Mass (FAB) : *m/z* 1243 $[M+Na]^+$.

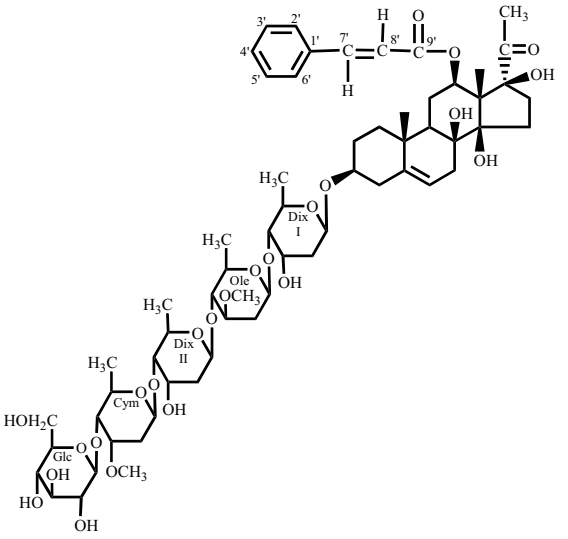
Reference

1. T. Warashina and T. Noro, *Chem. Pharm. Bull.,* **48**, 516 (2000).

ASCLEPIAS FRUTICOSA SAPONIN 16

Kidjolanin 3-O-[β-D-glucopyranosyl-(1→4)-β-D-cymaropyranoeyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-oleandropyranosyl (1→4)-β-D-digitoxopyranoside]

Source : *Asclepias fruticosa* L. (Syn. *Gomphocarpus fruticosus* L. R.Br.) (Asclepiadaceae).
Mol. Formula : $C_{62}H_{92}O_{24}$
Mol. Wt. : 1220
$[\alpha]_D^{26}$: +24.3° (c=0.38, MeOH)
Registry No. : [162584-79-4]



PMR (C_5D_5N, 400 MHz) : δ 1.35 (s, 3xH-19), 2.03 (s, 3xH-18), 2.50 (s, 3xH-21), 3.89 (m, H-3), 5.19 (dd, *J*=12.0, 4.0 Hz, H-12), 5.30 (br s, H-6), 6.81 (d, *J*=16.0 Hz, H-8'), 7.33-7.36 (H-2', H-3' and H-4'), 7.61–7.63 (H-2' and H-6'), 8.00 (d, *J*=16.0 Hz, H-7'). Sugar signals are in good agreement with those of Asclepias fruticosa glycoside 10 (qv.).

CMR (C_5D_5N, 100 MHz) : δ C-1) 38.8 (2) 29.8 (3) 77.7 (4) 39.2 (5) 139.4 (6) 119.1 (7) 33.8[a] (8) 74.3 (9) 44.5 (10) 37.4 (11) 25.0 (12) 73.3 (13) 55.8 (14) 89.4 (15) 34.7[a] (16) 33.0 (17) 92.4 (18) 10.6 (19) 18.2 (20) 209.7 (21) 27.6 **Cinnamoyl** (1') 135.0 (2')128.5 (3') 130.5 (4') 130.5 (5') 129.2 (6') 128.5 (7') 144.8 (8') 119.2 (9') 165.8 Sugar signals in good agreement with those of Asclepias fruticosa glycoside 10 (qv.)

Mass (FAB, Positive ion, H.R.) : *m/z* 1243.5874 [calcd. for $(M+Na)^+$ requires 1243.5876].

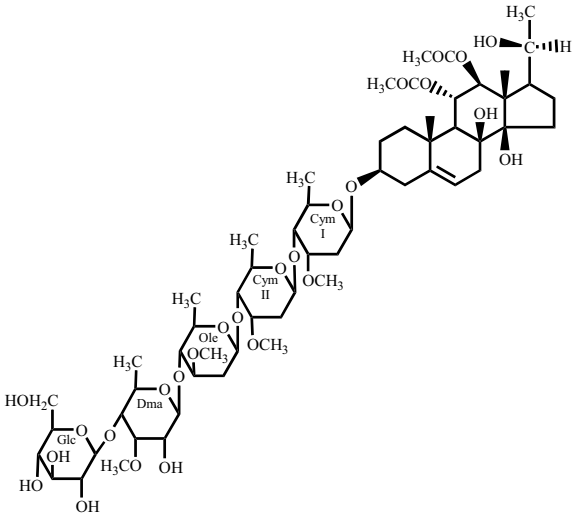
Reference

1. F. Abe, Y. Mori, H. Okabe and T. Yamauchi, *Chem. Pharm. Bull.,* **42,** 1777 (1994).

HOYACARNOSIDE T

11,12-Di-O-acetylmarsectohexol 3-O-[β-D-glucopyranosyl-(1→4)-(6-deoxy-3-O-methyl)-β-D-allopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside]

Source : *Hoya carnosa* R.Br. (Asclepiadaceae)
Mol. Formula : $C_{59}H_{96}O_{26}$
Mol. Wt. : 1220
$[\alpha]_D^{26}$: +16.3° (c=2.10, MeOH)
Registry No. : [246042-02-4]



PMR (C_5D_5N, 500 MHz) **:** δ 1.34 (d, *J*=6.0 Hz, 3xH-6 of Cym I), 1.36 (d, *J*=6.0 Hz, 3xH-6 of Cym II), 1.59 (d, *J*=6.0 Hz, 3xH-6 of Ole), 1.64 (d, *J*=6.0 Hz, 3xH-6 of Dma), 1.70 (m, H-2A of Ole), 1.79 (m, H-2A of Cym II), 1.89 (m, H-2A of Cym I), 2.27 (m, H-2B of Cym II), 2.32 (m, H-2B of Cym I), 2.46 (m, H-2B of Ole), 3.41 (dd, *J*=9.0, 3.0 Hz,

H-4 of Cym II), 3.48 (dd, *J*=9.0, 3.0 Hz, H-4 of Cym I), 3.50-3.60 (m, H-3 and H-5 of Ole), 3.51 (s, OCH_3), 3.54 (s, OCH_3), 3.55 (t, *J*=9.0 Hz, H-4 of Ole), 3.63 (s, OCH_3), 3.73 (dd, *J*=9.0, 3.0 Hz, H-4 of Dma), 3.81 (br d, *J*=8.0 Hz, H-2 of Dma), 3.83 (s, OCH_3), 3.97 (m, H-5 of Glc), 3.99 (q, *J*=3.0 Hz, H-3 of Cym II), 4.01 (dd, *J*=8.0, 9.0 Hz, H-2 of Glc), 4.08 (q, *J*=3.0 Hz, H-3 of Cym I), 4.14 (m, H-5 of Cym II), 4.18 (t, *J*=9.0 Hz, H-4 of Glc), 4.20 (m, H-5 of Cym I), 4.23 (t, *J*=9.0 Hz, H-3 of Glc), 4.25 (dq, *J*=9.0, 6.0 Hz, H-5 of Dma), 4.35 (dd, *J*=12.0, 5.0 Hz, H-6A of Glc), 4.47 (t, *J*=3.0 Hz, H-3 of Dma), 4.52 (dd, *J*=12.0, 2.0 H,z H-6B of Glc), 4.66 (dd, *J*=10.0, 2.0 Hz, H-1 of Ole), 4.96 (d, *J*=8.0 Hz, H-1 of Glc),5.09 (dd, *J*=10.0, 2.0 Hz, H-1 of Cym II), 5.25 (d, *J*=8.0 Hz, H-1 of Dma), 5.29 (dd, *J*=9.0, 2.0 Hz, H-1 of Cym I).

CMR (C_5D_5N, 125 MHz) : δ **Cym I** C-1) 96.2 (2) 37.2 (3) 78.0 (4) 83.3 (5) 68.9[a] (6) 18.5 **Cym II** (1) 100.4 (2) 37.0 (3) 77.7 (4) 83.1 (5) 68.8 (6) 18.4 **Ole** (1) 101.8 (2) 37.5 (3) 79.2 (4) 82.8 (5) 71.9 (6) 18.8 **Dma** (1) 101.8 (2) 72.6 (3) 83.1 (4) 83.3 (5) 69.5 (6) 18.2 **Glc** (1) 106.5 (2) 75.4 (3) 78.3 (4) 71.9 (5) 78.0 (6) 63.0 (O*C*H_3) 57.3, 58.8, 58.8, 61.6.

Mass (FAB, Positive ion, H.R.) : *m/z* 1243.6086 [$(M+Na)^+$, requires 1243.6087].

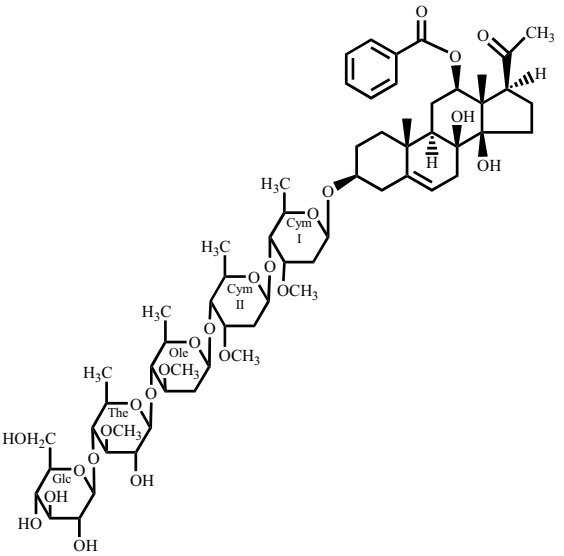
Reference

1. F. Abe, H. Fujishima, Y. Iwase, T. Yamauchi, K. Kinjo and S. Yaga, *Chem. Pharm. Bull*., **47**, 1128 (1999).

ASCLEPIAS INCARNATA SAPONIN 92

12-O-Benzoylisolineolon 3-O-[β-D-glucopyranosyl-(1→4)-β-D-thevetopyranosyl-(1→4)-β-D-oleanderopyranosyl-(1→4)-β-D-cymaropyranoyl-(1→4)-β-D-cymaropyranoside]

Source : *Asclepias incarnata* L. (Asclepiadaceae)
Mol. Formula : $C_{62}H_{94}O_{24}$
Mol. Wt. : 1222
$[\alpha]_D^{25}$: +24.0° (c=1.01, MeOH)
Registry No. : [272439-12-0]



UV (MeOH) : λ_{max} 230 (log ε, 4.16), 273 (log ε, 2.93) nm.

The PMR and CMR data of the aglycone moiety and the sugar moiety are in good agreement with those of Asclepias Incarnata Saponin 71 and Asclepias Incarnata Saponin 90, respectively (q.q.v.).

Mass (FAB) : *m/z* 1245 $[M+Na]^+$.

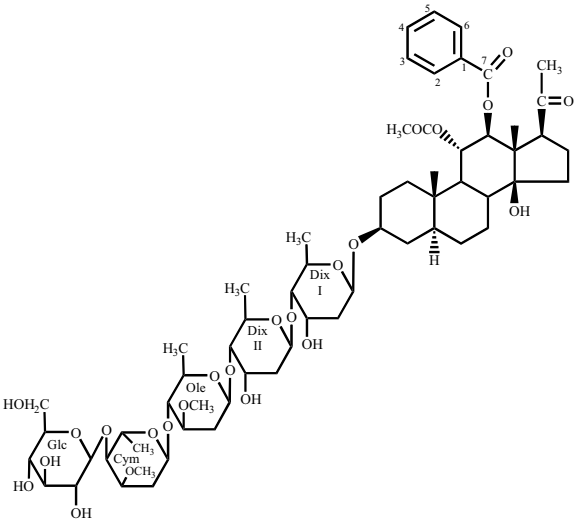
Reference

1. T. Warashina and T. Noro, *Chem. Pharm. Bull.,* **48**, 516 (2000).

CYNAFOSIDE D

Cynafogenin 3-O-[β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-digitoxopyranoside]

Source : *Cynachum africanum* R.Br. (Asclepiadaceae)
Mol. Formula : $C_{62}H_{94}O_{24}$
Mol. Wt. : 1222
M.P. : 153-155°C
$[\alpha]_D^{16}$: +12.8° (c=1.00)
Registry No. : [117479-85-3]



UV (EtOH) : λ_{max} 230 (log ε, 3.68), 275 (log ε, 2.39), 282 (log ε, 2.39) nm.

IR ($CHCl_3$) : 3400, 1730, 1710, 1600, 1580, 1490, 1160 cm^{-1}.

PMR ($CDCl_3$, 500 MHz) : δ 0.95 (s, 3xH-19), 1.15 (s, 3xH-18), 1.22, 1.23, 1.25, 1.27 (d, *J*=5.9 Hz, 3xH-6 of sugar), 1.51 (ddd, *J*=12.5, 11.0, 9.8 Hz, H-2ax of Ole), 1.64 (s, C*H*$_3$CO$_2$), 1.68, 1.71 (ddd, *J*=13.7, 9.3, 2.9 Hz, H-2ax of Dix), 1.79 (ddd, *J*=15.0, 4.8, 3.7 Hz, H-2ax of Cym), 2.06 (s, 3xH-21), 2.04, 2.12 (each dt, *J*=13.7, 2.4 Hz, H-2eq of Dix I and Dix II), 2.22 (ddd, *J*=15.0, 3.3, 1.5 Hz, H-2eq of Cym), 2.35 (ddd, *J*=12.5, 4.4, 2.2 Hz, H-2eq of Ole), 3.12 (t, *J*=9.3 Hz, H-4 of Ole), 3.19, 3.22 (each dd, *J*=9.3, 2.9 Hz, H-4 of Dix I and Dix II), 3.26 (ddd, *J*=11.0, 8.8, 4.4 Hz, H-

3 of Ole), 3.31 (dq, *J*=8.8, 5.9 Hz, H-5 of Ole), 3.36, 3.37 (each s, OC*H*$_3$ of Cym and Ole), 3.54 (dd, *J*=9.3, 2.9 Hz, H-4 of Cym), 3.73 (ddd *J*=3.7, 3.3, 2.9 Hz, H-3 of Cym), 3.77, 3.83 (each dq, *J*=9.3, 5.9 Hz, H-5 of Dix I and Dix II), 3.80, 3.88 (each dd, *J*=11.5, 4.6 Hz, and *J*=11.5, 3.3 Hz respectively, 2xH-6 of Glc), 4.22 (ddd, *J*=3.0, 3.0, 2.9 Hz, H-3 of Dix), 4.25 (dq, *J*=9.3, 5.9 Hz, H-5 of Cym), 4.38 (d, *J*=7.3 Hz, H-1 of Glc), 4.52 (dd, *J*=9.8, 2.0 Hz, H-1 of Ole), 4.87 (dd, *J*=3.0, 1.0 Hz, H-1 of Cym), 4.89, 4.91 (each dd, *J*=10.0, 2.0 Hz, H-1 of Dix I and Dix II), 4.99 (d, *J*=9.8 Hz, H-12), 5.41 (t, *J*=9.8 Hz, H-11), 7.49 (t, *J*=7.3 Hz, H-3 and H-5 of Benz), 7.62 (t, *J*=7.3 Hz, H-4 of Benz), 8.05 (d, *J*=7.3 Hz, H-2 and H-6 of Benz).

CMR ($CDCl_3$, 67.5 MHz) : δ C-1) 38.1 (2) 30.4 (3) 76.0 (4) 35.5 (5) 44.6 (6) 29.3[a] (7) 28.4[a] (8) 40.0 (9) 50.1 (10) 38.0 (11) 71.6 (12) 79.1[b] (13) 54.9 (14) 83.9 (15) 33.9 (16) 24.3 (17) 58.4 (18) 11.8 (19) 12.4 (20) 213.4 (21) 31.7 (CH_3-*C*O) 170.4 (H_3*C*-CO) 21.3 **Benz** (1) 130.1 (2) 130.1 (3) 129.2 (4) 133.9 (5) 129.2 (6) 130.1 (7) 166.7 **Dix I** (1) 96.0 (2) 39.0 (3) 68.7[c] (4) 83.4[d] (5) 67.5[e] (6) 18.7[f] **Dix II** (1) 99.8 (2) 37.7 (3) 68.7[c] (4) 83.2[d] (5) 67.4[e] (6) 18.6[f] **Ole** (1) 101.4 (2) 36.8 (3) 79.0[b] (4) 81.6[d] (5) 72.1 (6) 18.4[f] (O*C*H_3) 56.4[g] **Cym** (1) 97.3 (2) 32.2 (3) 73.6 (4) 79.0[b] (5) 64.7 (6) 18.4[f] (O*C*H_3) 56.9[g] **Glc** (1) 102.3 (2) 75.3 (3) 78.4[b] (4) 73.8 (5) 78.6[b] (6) 62.9.

Mass (F.D.) : *m/z* 1245 $[M+Na]^+$.

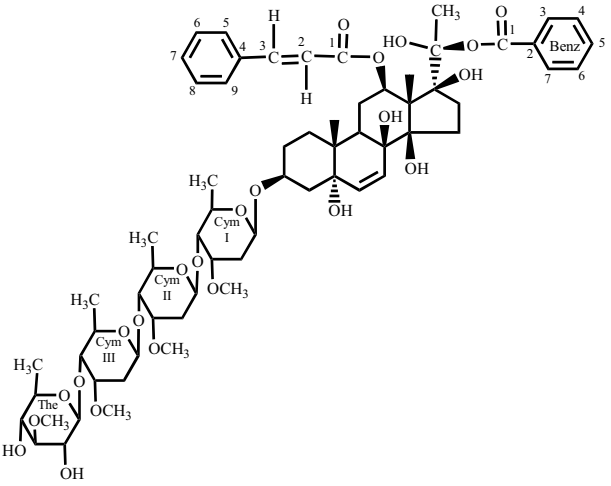
Reference

1. S. Tsukamoto, K. Hayashi, K. Kaneko, H. Mitsuhashi, F.O. Snyckers and T.G. Fourie, *J. Chem. Soc. Perkin Trans. 1*, 2625 (1988).

ARAUJIA SERICIFERA GLYCOSIDE 16

20-O-Benzoyl-12-O-(*E*)-cinnamoyl-3β,5α,8β,12β,14β,17β,20-heptahydroxy-20-(*S*)-pregn-6-ene 3-O-[β-D-thevetopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-thevetopyranoside]

Source : *Araujia sericifera* (Asclepiadaceae)
Mol. Formula : $C_{65}H_{92}O_{22}$
Mol. Wt. : 1224
$[\alpha]_D^{22}$: +141° (c=1.67, MeOH)
Registry No. : [645396-37-8]



UV (MeOH) : λ_{max} 201 (log ε, 4.84), 220 (log ε, 4.69), 223 (log ε, 4.71), 231 (sh), 279 (log ε, 4.65) nm.

PMR (C_5D_5N, 400 MHz) : δ 1.50 (s, 3xH-19), 1.55 (d, *J*=6.0 Hz, 3xH-21), 2.16 (s, 3xH-18), 4.16* (H-3), 5.15 (dd, *J*=9.5, 2.0 Hz, H-1 of Cym I), 5.27 (q, *J*=6.0 Hz, H-20), 5.34 (dd, *J*=10.0, 4.5 Hz, H-12), 5.92 (d, *J*=10.5 Hz, H-6), 6.21 (d, *J*=10.5 Hz, H-7), 6.48 (d, *J*=16.0 Hz, H-2 of Cin), 7.29 (br t, *J*=8.0 Hz, H-4 and H-6 of Benz), 7.49 (br t, *J*=8.0 Hz, H-5 of Benz), 7.89 (d, *J*=16.0 Hz, H-3 of Cin), 8.19 (br d, *J*=8.0 Hz, H-3 and H-7 of Benz).

The PMR signals and their chemical shifts of the sugar moiety are identical to those of Araujia Sericifera Glycoside 1 (qv).

CMR (C_5D_5N, 100.4 MHz) : δ C-1) 27.7 (2) 26.6 (3) 74.9[a] (4) 39.2 (5) 74.8[a] (6) 136.8 (7) 127.3 (8) 74.1 (9) 36.8 (10) 39.7 (11) 23.7 (12) 75.8 (13) 58.2 (14) 88.3 (15) 33.2 (16) 34.3 (17) 87.8 (18) 12.4 (19) 21.5 (20) 75.4 (21) 15.6 Cin (1) 166.8 (2) 120.3 (3) 144.6 (4) 135.0 (5) 128.6 (6) 129.2 (7) 130.1 (8) 129.1 (9) 128.6 **Benz** (1) 165.9 (2) 131.3 (3) 130.2 (4) 128.7 (5) 133.1 (6) 128.7 (7) 130.2 **Cym I** (1) 97.8.

The CMR chemical shifts of the sugar moiety are identical to those of Araujia Sericifera Glycoside 1 (qv).

Mass (FAB, Positive ion) : *m/z* 1247 $[M+Na]^+$.

Mass (FAB, Positive ion, H.R.) : *m/z* 1247.5989 $[(M+Na)^+$, calcd. for 1247.5978].

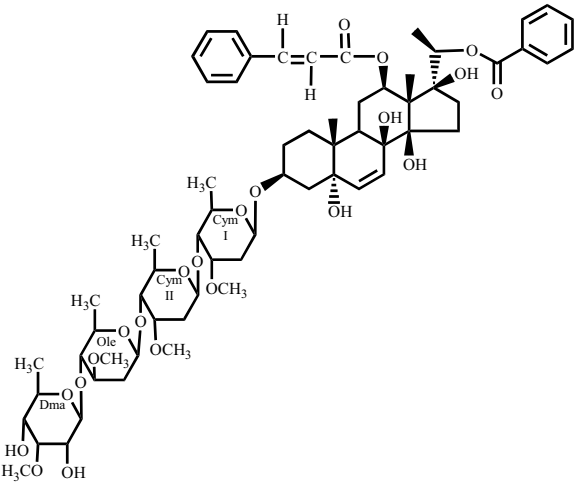
Reference

1. T. Warashina and T. Noro, *Chem. Pharm. Bull*., **51**, 1036 (2003).

GYMNEPREGOSIDE L

12-O-(*E*)-Cinnamoyl-20-O-benzoyl-(20*S*)-pregn-6-ene-3β,5α,8β,12β,14β,17β,20-heptaol-6-deoxy-3-O-methyl-β-D-allopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside

Source : *Gymnema alternifolium* (Asclepiadaceae)
Mol. Formula : $C_{65}H_{92}O_{22}$
Mol. Wt. : 1224
M.P. : 146-148°C
$[\alpha]_D^{25}$: +93.5° (c=0.7, $CHCl_3$)
Registry No. : [238420-59-2]



UV (MeOH) : λ_{max} 222 (log ε, 4.34), 236 (log ε, 4.17), 278 (log ε, 4.32) nm.

IR (film) : 3440, 1715, 1640, 1100 cm^{-1}.

PMR (C_5D_5N, 400 MHz) : δ 1.52 (s, 3xH-19), 1.54 (d, *J*=6.1 Hz, 3xH-21), 2.19 (s, 3xH-18), 4.15 (m, H-3), 5.27 (q, *J*=6.1 Hz, H-20), 5.37 (dd, *J*=10.1, 4.1 Hz, H-12), 5.92 (d, *J*=10.4 Hz, H-6), 6.24 (d, *J*=10.4 Hz, H-7), 6.49 (d, *J*=15.8 Hz, H-8 of Cin), 7.28 (t, *J*=8.0 Hz, H-3 of Tig), 7.34 (t, *J*=7.2, 6.7 Hz, H-3, H-5 of Cin), 7.34 (dt, *J*=7.2, 6.7, 1.6 Hz, H-4 of Cin), 7.36 (dd, *J*=7.2, 1.5 Hz, H-2, H-6 of Cin), 7.49 (t, *J*=8.0 Hz, H-4 of Tig), 7.80 (d, *J*=15.8 Hz, H-7 of Cin), 8.19 (d, *J*=8.0 Hz, H-2 of Tig).