Phytochemical Studies on *Sorbus cashmiriana*

[1]SADIA KHAN, [1]MEHDI HASSAN KAZMI*, [2]EJAZ AHMED** [3]ABDUL MALIK AND [2]AHSAN SHARIF

[1]*Department of Applied Chemistry and Chemical Technology, University of Karachi, Karachi, Pakistan.*
[2]*Institute of Chemistry, University of the Punjab, Quaid-e-Azam Campus, Lahore, 54590, Pakistan.*
[3]*International Centre for Chemical and Biological Sciences, H.E.J. Research Institute of Chemistry, University of Karachi, Karachi- 75270, Pakistan.*
mehdihkazmi@yahoo.com*, dr.ejaz.ahmed@gmail.com**

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Summary: Eleven compounds have been isolated for the first time from *Sorbus cashmiriana* namely ursolic acid (**1**), stigmasterol (**2**), myricadiol (**3**), taraxerol (**4**), 5*α*, 8*α*-epidioxyergosta -6, 22-diene-3*β*-ol (**5**), 3*β*, 5*α*-dihydroxy-6*β*-methoxyergosta-7, 22-diene **(6)**, betulonic acid (**7**), betulinic acid (**8**), *β*-sitosteryl acetate **(9)**, 5*α*, 8*α*-epidioxyergosta-6, 9 (11), 22-trien-3*β*-ol **(10)** stigmasterol 3-*O*-*β*-D-glucopyranoside **(11)**, respectively. Their structures have been elucidated by sophisticated spectroscopy techniques.

Introduction

The genus *Sorbus* comprises of about one hundred species widely distributed all over the world. Seven of these are found in Indo-Pakistan. One of these is Sorbus cashmiriana which is native to Kashmir and western Himalayas. Local medical practitioners used its water extract to treat nausea, heart diseases and to cleanse the blood. The berries of the plant are the source of vitamin C and use to cure Scurvy [1]. In-continuation of the previous work and the ethanopharmacological and chemotaxonomic importance of the *S. cashmiriana* led us to investigate the chemical constituents from the whole plant.

The methanolic extract of *Sorbus cashmiriana* showed strong toxicity in a brine shrimp lethality test [2]. On further fractionation a major toxicity was observed in the ethyl acetate soluble fraction. Herein we report the isolation and structure elucidation of ursolic acid (**1**) [3], stigmasterol (**2**) [4], myricadiol (**3**) [5], taraxerol (**4**) [6], 5*α*, 8*α*-epidioxyergosta -6, 22-diene-3*β*-ol (**5**) [7], 3*β*, 5*α*-dihydroxy-6*β*-methoxyergosta-7, 22-diene (**6**) [8], betulonic acid (**7**) [9], betulinic acid (**8**) [9], *β*-sitosteryl acetate (**9**) [4], 5*α*, 8*α*-epidioxyergosta-6, 9(11), 22-trien-3*β*-ol (**10**) [7] stigmasterol 3-*O*-*β*-D-glucopyranoside (**11**) [10], respectively from the ethyl acetate soluble fraction.

Results and Discussion

The methanolic extract of the whole plant was partitioned into *n*-hexane, chloroform, ethyl acetate, *n*-butanol and water soluble fractions. The ethyl acetate soluble fraction was subjected to column chromatography over silica gel eluting with *n*-hexane–ethyl acetate, ethyl acetate and ethyl-acetate - methanol in increasing order of polarity to obtain eleven compounds, reported for the first time from this specie. These could be identified as ursolic acid (**1**), stigmasterol (**2**), myricadiol (**3**), taraxerol (**4**), 5*α*, 8*α*-epidioxyergosta -6, 22-diene-3*β*-ol (**5**), 3*β*, 5*α*-dihydroxy-6*β*-methoxyergosta-7, 22-diene (**6**), betulonic acid (**7**), betulinic acid (**8**), *β*-sitosteryl acetate (**9**), 5*α*, 8*α*-epidioxyergosta-6, 9(11), 22-trien-3*β*-ol (**10**) stigmasterol 3-*O*-*β*-D-glucopyranoside (**11**), respectively, on the basis of their spectral data.

Experimental

General

Column Chromatography was carried out using silica gel (E-Merck, 230-400 mesh). TLC was performed over precoated silica gel G60-F_{254} preparative plates (20x20cm, 0.5mm thick, E Merck) and were visualized under UV light of (254 nm and 366 nm) and followed by ceric sulfate as spraying reagent in 10% H_2SO_4. Melting points were determined by Gallenkemp apparatus. Optical rotations were measured on a Jasco DIP-360 digital polarimeter. UV and IR spectra were recorded on Hitachi UV-3200 and Jasco-320A spectrometers respectively. El and HR-El-MS were measured in an electron impact mode on Finnigan MAT 12 or MAT 312 spectrometers and ions are given in *m/z* (%). ^{1}H and ^{13}C-NMR spectra was recorded on Bruker AMX-400 MHz spectrometer with TMS as an internal standard.

Plant Material

The whole plant (20 Kg) *Sorbus cashmiriana* Hedlund, Monog was collected in the month of July and August 2004 from Kashmir

*To whom all correspondence should be addressed.

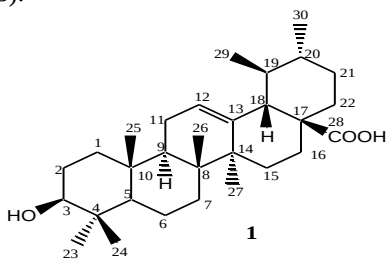
(Pakistan) and identified by Dr. Surraiya Khatoon, Plant Taxonomist, Department of Botany, University of Karachi, Karachi, Pakistan where a voucher specimen (No. KUH73/67760) has been deposited.

Isolation

The freshly collected whole plant material (20 kg) was cut into small pieces and extracted with methanol (3 x 30L). The combined methanolic extract was evaporated under reduced pressure to yield a residue (900 g), which was partitioned between *n*-hexane and water. The aqueous fraction was successively partitioned with chloroform (95 g), ethyl acetate (180 g), *n*-butanol (65 g), and water (48 g). The ethyl acetate soluble fraction (180 g) was subjected to column chromatography over silica gel eluting with *n*-hexane, *n*-hexane-ethyl acetate, ethyl acetate and ethyl acetate- methanol in increasing order of polarity to obtain 6 major fractions C_A-C_F. The fraction obtained from *n*-hexane- ethyl acetate (7.0: 3.0) were combined and re-chromatographed over silica gel using solvent system *n*-hexane- ethyl acetate (4.0: 6.0) and finally purified by PTLC solvent system (6.5: 3.5) to afford ursolic acid (**1**), stigmasterol (**2**) and myricadiol (**3**), respectively. The fraction obtained from *n*-hexane - ethyl acetate (5.0: 5.0) was further purified on PTLC with solvent system *n*-hexane- ethyl acetate (4.0: 6.0) to afford taraxerol (**4**), 5*α*, 8*α*- epidioxyergosta-6, 22-diene 3 *β*-ol (**5**) and 3*α*, 5*α* dihydroxy-6 *β*-methoxy ergosta-7, 22-diene (**6**), respectively. The fraction obtained from the *n*-hexane- ethyl acetate (4.0: 6.0) gave two spots on TLC which was further rechromatographed on PTLC using the solvent system *n*-hexane- ethyl acetate (3.2: 6.8) to give betulonic acid (**7**) and betulinic acid (**8**) respectively. The fraction obtained from the *n*-hexane- ethyl acetate (3.0: 7.0) were combined and rechromatographed over silica gel using solvent system *n*-hexane- ethyl acetate (2.0 : 8.0) and finally purified by PTLC using solvent system n-hexane- ethyl acetate (2.5: 7.5) to afford □-sitosteryl acetate **(9)** and 5*α*, 8*α*–epidioxy ergosta-6, 9 (11), 22 trien 3□–ol **(10)**. The fraction obtained from the ethyl acetate : methanol (9.0 : 1.0) was rechromatographed over silica gel eluting with ethyl acetate - methanol (9.5: 0.5) and final purification by PTLC using solvent system ethyl acetate - methanol (9.5: 0.5) to yield stigmasterol 3-*O*–□–D–glucopyranoside (**11**).

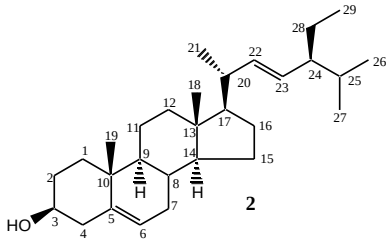
Ursolic acid (**1**)

Crystallized from EtOH (25 mg), m.p. 283-285 °C; $[\alpha]_D^{25}$ + 62.5° (*c* = 1.0, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3455, 3100, 1701, 1650, 825; ^{1}H-NMR ($CDCl_3$, 400 MHz) *δ*: 5.08 (1H, t, *J* = 6.1 Hz, H-12), 3.15 (1H, dd, *J* = 9.9 and 4.4 Hz, H-3), 1.19 (3H, s, H-27), 1.08 (3H, s, H-23), 0.95 (3H, s, H-25), 0.92 (3H, d, *J* = 6.8 Hz, H-30), 0.87 (3H, s, H-26), 0.82 (3H, s, H-24), 0.81 (3H, d, *J* = 6.6 Hz, H-29). ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ*: 176.5 (C-28), 139.1 (C-13), 126.0 (C-12), 79.3 (C-3), 55.5 (C-18), 52.6 (C-5), 48.1 (C-17), 47.7 (C-9), 41.9 (C-14), 39.9 (C-8), 38.8 (C-1), 36.9 (C-22), 37.5 (C-10), 33.6 (C-7), 30.9 (C-19), 30.7 (C-20), 29.7 (C-15), 27.8 (C-21), 24.2 (C-27), 27.6 (C-2), 23.9 (C-23, C-30), 24.1 (C-11), 23.9 (C-16), 22.8 (C-29), 18.5 (C-6), 17.5 (C-26), 16.1 (C-25), 15.8 (C-24). HREIMS *m/z*: 456.3560 (calcd. for $C_{30}H_{48}O_3$, 456.3603).



Stigmasterol (**2**)

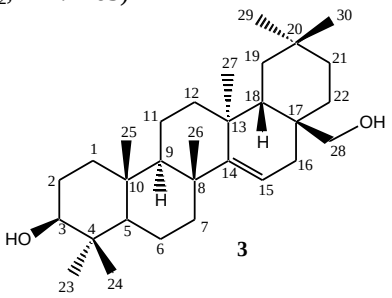
White crystalline solid (5 mg), m.p. 170-171 °C; $[\alpha]_D^{25}$ -51.5° (*c* = 1.5, $CHCl_3$). IR **(**KBr) ν_{max} cm^{-1}: 3432, 1648. ^{1}H-NMR ($CDCl_3$, 400 MHz), *δ*: 5.40 (1H, t, *J* = 8.1 Hz, H-6), 5.17 (1H, dd, *J* = 14.9, 8.5 Hz, H-22), 5.05 (1H, dd, *J* = 14.9, 8.2 Hz, H-23), 3.25 (1H, brm, H-3), 0.91 (3H, d, *J* = 6.4 Hz, Me-21), 0.84 (3H, d, *J* = 6.7 Hz, Me-26), 0.86 (3H, t, *J* = 7.1 Hz, Me-29), 0.82 (3H, d, *J* = 6.6 Hz, Me-27), 1.01 (3H, s, Me-19), 0.75 (3H, s, Me-18). ^{13}C-NMR ($CDCl_3$, 100 MHz) *δ*: 141.1 (C-5), 138.9 (C-22), 129.8 (C-23), 121.9 (C-6), 72.0 (C-3), 57.2 (C-14), 56.3 (C-17), 51.8 (C-24), 50.7 (C-9), 42.8 (C-13), 42.5 (C-4), 40.8 (C-20), 40.1 (C-12), 38.1 (C-1), 36.9 (C-10), 32.2 (C-8), 32.7 (C-25), 32.9 (C-7), 31.9 (C-2), 29.1 (C-16), 25.8 (C-28), 24.5 (C-15), 21.7 (C-27), 21.3 (C-21), 21.0 (C-11), 19.8 (C-19), 19.1 (C-26), 12.4 (C-18) and 12.2 (C-29). HREIMS *m/z*: 412.2929 (calcd. for $C_{29}H_{48}O$, 412.3925).



Myricadiol (**3**)

Crystallized from methanol (20 mg), m.p. 270-271°C ; $[\alpha]_D^{28}$ = +7.5° (c = 1.2, $CHCl_3$); IR ν_{max}

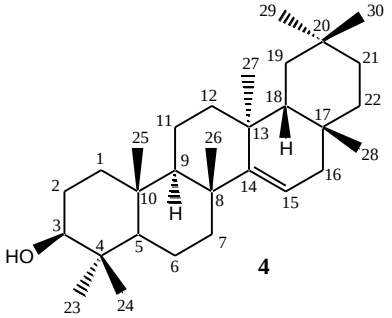
(KBr) cm^{-1}: 3550, 3050, 1640, 815; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 0.81 (3H, s, H-24), 0.91 (3H, s, H-23), 0.93 (3H, s, H-29), 0.96 (3H, s, H-25), 0.98 (3H, s, H-30), 1.00 (3H, s, H-27), 1.09 (3H, s , H-26), 3.33 (1H, brm, H-3), 3.80 (2H, s, H-28), 5.51 (1H, dd, J = 4.2, 7.4 Hz, H-15). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 158.7 (C-14), 119.1 (C-15), 78.4 (C-3), 64.1 (C-28), 55.9 (C-5), 49.5 (C-18), 45.9 (C-9), 41.5 (C-19), 41.2 (C-4), 39.2 (C-8), 38.4 (C-13), 38.3 (C-17), 38.0 (C-10), 37.8 (C-1), 36.3 (C-7), 33.9 (C-21), 33.7 (C-29), 32.9 (C-16), 30.1 (C-26), 32.0 (C-12), 28.8 (C-20), 28.6 (C-22), 28.4 (C-23), 27.8 (C-2), 26.1 (C-27), 22.1 (C-30), 19.2 (C-6), 17.7 (C-11), 16.6 (C-24), 15.6 (C-25). HREIMS *m/z*: 442.7102 (calcd for $C_{30}H_{50}O_2$, 442.7165)



3

Taraxerol (**4**)

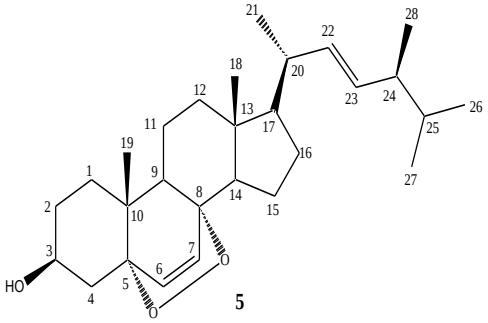
Crystallized from chloroform (32 mg), m.p. 279.5 ^{o}C; $[\alpha]_D^{28}$: +0.75 (c = 1.1, $CHCl_3$), IR (KBr) ν_{max} cm^{-1}: 3358, 1463, 815. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.55 (1H, dd, J = 4.1, 7.4 Hz, H-15), 3.19 (1H, dd, J = 9.1 and 5.3 Hz, H-3), 1.15 (3H, s, H-27), 1.05 (3H, s, H-23), 0.95 (3H, s, H-25), 0.97 (3H, s, H-24), 0.91 (3H, d, J = 6.8 Hz, H-30), 0.84 (3H, s, H-26), 0.82 (3H, s, H-29). ^{13}C-NMR ($CDCl_3$ 75 MHz) δ: 158.2 (C-14), 117.1 (C-15), 79.3 (C-3), 55.7 (C-5), 49.4 (C-18), 48.9 (C-9), 41.4 (C-19), 39.2 (C-4), 38.2 (C-1), 38.9 (C-8), 38.1 (C-17), 37.9 (C-10), 37.7 (C-13), 36.9 (C-16), 36.0 (C-12), 35.3 (C-7), 33.9 (C-21), 33.6 (C-29), 33.2 (C-22), 30.3 (C-28), 30.1 (C-26), 29.0 (C-20), 28.1 (C-23), 27.3 (C-2), 26.0 (C-27), 21.5(C-30), 19.0 (C-6), 17.7 (C-11), 15.6 (C-24), 15.4 (C-25). HREIMS *m/z*: 426.7125 (calcd for $C_{30}H_{50}O$, 442.7174)



4

5α, 8α-epidioxyergosta-6, 22-diene-3β-ol (**5**)

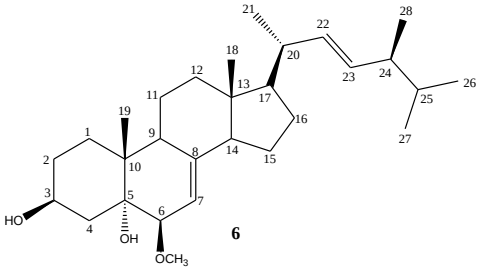
Crystallized from methanol (25 mg), m.p. 176-178 ^{o}C; $[\alpha]_D^{25}$: -31.5^o (c = 1.2, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}, 3400, 3021, 1650. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.51 (1H, d, J = 8.5 Hz, H-7), 6.25 (1H, d, J = 8.5 Hz, H-6), 5.24 (1H, dd, J = 14.9, 7.9 Hz, H-22), 5.15 (1H, dd, J = 14.9, 8.3 Hz, H-23), 3.98 (1H, m, H-3), 1.00 (3H, d, J= 7.0 Hz, H_3-21), 0.92 (3H, d, J = 6.8 Hz, H-28), 0.89 (3H, s, H-19), 0.84 (3H, d, J = 6.7 Hz, H-27), 0.62 (3H, s, H-18) and 0.82 (3H, d, J = 6.5 Hz, H-26). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 135.6 (C-6), 135.4 (C-22), 132.3 (C-23), 131.0 (C-7), 82.5 (C-5), 79.5 (C-8), 67.0 (C-3), 56.5 (C-17), 52.0 (C-14), 50.9 (C-9), 44.5 (C-13), 42.7 (C-24), 39.8 (C-20), 39.3 (C-12), 37.0 (C-4), 36.9 (C-10), 34.9 (C-1), 33.0 (C-25), 30.5 (C-2), 28.8 (C-16), 23.4 (C-15), 21.1 (C-21), 20.7 (C-11), 20.0 (C-27), 19.6 (C-26), 18.6 (C-19), 17.5 (C-28), 12.9 (C-18). HREIMS *m/z*: 428.3210 (calcd for $C_{28}H_{44}O_3$, 428.3290).



5

3β,5α-dihydroxy-6β-methoxyergosta-7,22-diene (**6**)

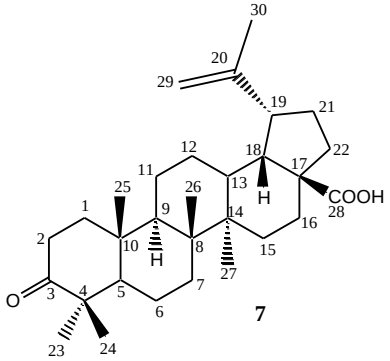
Crystallized from methanol (20 mg), m.p.173-176 ^{o}C; $[\alpha]_D^{28}$ -30.8^o (c = 1.1, $CHCl_3$). IR (KBr) ν_{max} cm^{-1} 3400, 1640, 1430. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 0.58 (3H, s, H-18), 0.93 (3H, d, J = 6.9 Hz, H-26), 0.82 (3H, d, J = 6.8 Hz, H-27), 0.88 (3H, d, J = 6.5 Hz, H-28), 0.95 (3H, s, H-19), 0.97 (3H, s, OMe), 3.9 (1H, m, H-3), 5.15 (2H, dd, J = 8.0, 16.1 Hz, H-22), 5.30 (2H, dd, J = 7.4, 16.1 Hz, H-23), 5.39 (1H, m, H-7). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 144.2 (C-8), 135.5 (C-23), 132.0 (C-22), 114.5 (C-7), 82.5 (C-6), 78.0 (C-5), 68.0 (C-3), 58.3 (OMe), 56.3 (C-17), 55.5 (C-14), 45.1 (C-13), 44.5 (C-9), 43.2 (C-24), 40.7 (C-20), 40.1 (C-4), 39.6 (C-12), 38.1 (C-10), 33.2 (C-25), 32.2 (C-1), 30.6 (C-2), 27.8 (C-16), 23.3 (C-15), 22.3 (C-11), 21.8 (C-27), 20.2 (C-21), 20.1 (C-26), 18.6 (C-19), 18.3 (C-28), 14.2 (C-18). HREIMS *m/z*: 444.3701 (calcd for $C_{29}H_{48}O_3$, 444.3726).



6

Betulonic acid **(7)**

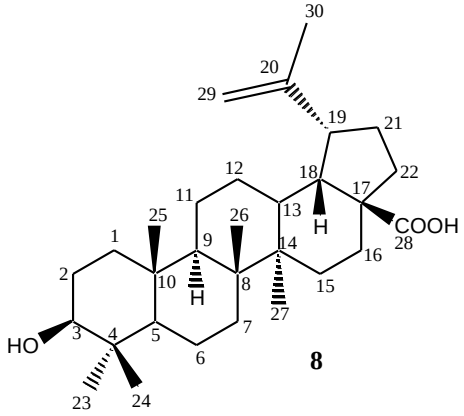
Crystallized from methanol (15 mg), m.p. 257-258°C; $[\alpha]_D^{28}$: + 30.2° (c = 1.0, $CHCl_3$) IR (KBr) ν_{max} cm^{-1}: 3020, 1700, 1640, 880. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.71 (1H, d, *J* = 2.1 Hz, H-29) and 4.61 (1H, d, *J* = 2.1 Hz, H-29), 1.66 (3H, s, H-30), 1.07 (3H, s, H-23), 1.01 (3H, s, H-25), 0.98 (3H, s, H-24), 0.96 (3H, s, H-26), 0.94 (3H, s, H-27). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 218.7 (C-3), 182.1 (C-28), 150.9 (C-20), 110.4 (C-29), 57.0 (C-17), 55.6 (C-5), 50.5 (C-9), 49.9 (C-18), 48.0 (C-4), 47.5 (C-19), 43.2 (C-14), 41.3 (C-8), 40.3 (C-1), 39.2 (C-13), 37.7 (C-10), 37.6 (C-22), 34.8 (C-2), 34.3 (C-7), 32.8 (C-16), 31.2 (C-15), 30.3 (C-21), 27.3 (C-23), 26.2 (C-12), 22.0 (C-11), 21.6 (C-24), 20.3 (C-6), 20.0 (C-30), 16.6 (C-25), 16.5 (C-26), 15.3 (C-27). HREIMS *m/z:* 454.6897 (calcd. for $C_{30}H_{46}O_3$, 454.6842).



7

Betulinic Acid **(8)**

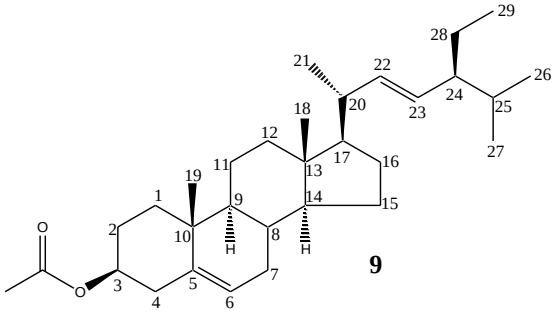
Crystallize from methanol (20 mg), m.p. 280-282°C; $[\alpha]_D^{25}$ + 27.5° (c = 1.3 $CHCl_3$). IR (KBr) ν_{max} cm^{-1}, 3020, 1697. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 4.88 (1H, d, *J* = 2.0 Hz, H-29), 4.69 (1H, d, *J* = 2.0 Hz, H-29), 3.55 (1H, dd, *J* = 8.9, 6.6 Hz, H-3), 1.81 (3H, s, H-30), 1.21 (3H, s, H-23), 1.07 (3H, s, H-25), 1.01 (3H, s, H-24), 0.99 (3H, s, H-26), 0.91 (3H, s, H-27). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 152.1 (C-20), 110.5 (C-29), 80.5 (C-3), 58.1 (C-17), 57.4 (C-5), 51.5 (C-9), 50.4 (C-19), 48.5 (C-18), 43.6 (C-14), 42.0 (C-8), 39.1 (C-1), 38.8 (C-4), 38.4 (C-13), 37.0 (C-22), 36.9 (C-10), 34.3 (C-7), 32.1 (C-16), 30.5 (C-15), 29.6 (C-21), 27.7 (C-2), 27.9 (C-23), 25.5 (C-12), 20.8 (C-11), 19.9 (C-30), 18.3 (C-6), 17.6 (C-28), 17.1 (C-24), 17.3 (C-25), 16.4 (C-26), 15.6 (C-27). HREIMS *m/z:* 456.6980 (calcd. for $C_{30}H_{48}O_3$, 456.7003).



8

β-Sitosteryl acetate (**9**)

Crystallized from methanol (40 mg), m.p. 119-121 °C; $[\alpha]_D^{25}$ –38.5° (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$) ν_{max} cm^{-1}, 3050, 1730, 1650 and 815. ^{1}H-NMR ($CDCl_3$, 400 MHz), δ: 3.55 (lH, m, H-3), 5.23 (lH, m, H-6), 2.05 (3H, s, C$\underline{H}_3$-COO),0.68 (3H, s,Me-18), 1.01 (3H, s, Me-19), 0.92 (3H, d, *J* = 6.2Hz, Me-21), 0.83 (3H, d, *J* = 6.5 Hz, Me-26), 0.81 (3H, d, *J* = 6.5Hz, Me-27), 0.84 (3H, t, *J* = 7.0 Hz, Me-29). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 172.8 ($\underline{C}$O), 139.8 (C-5), 122.6 (C-6), 77.2 (C-3), 56.7 (C-14), 56.2 (C-17), 50.1 (C-9), 45.8 (C-24), 42.6 (C-13), 42.4 (C-4), 40.0 (C-12), 37.1 (C-l), 36.6 (C-10), 36.2 (C-20), 34.0 (C-22), 33.1 (C-8), 32.0 (C-7), 31.8 (C-2), 29.3 (C-23), 28.2 (C-16), 26.2 (C-25), 24.3 (C-15), 23.1 (C-28), 21.1 (C-11), 20.1 ($\underline{C}H_3CO$), 19.4 (C-19), 19.8 (C-27), 19.1 (C-21), 18.8 (C-26), 12.2 (C-29), 11.9 (C-18). HREIMS *m/z*: 456.3930 (calcd for $C_{31}H_{52}O_2$, 456.3966).

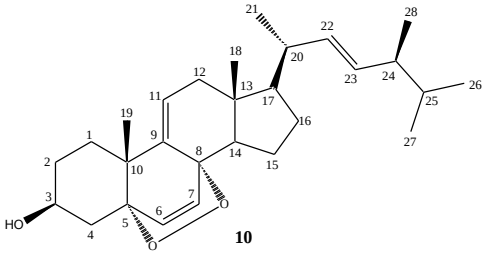


9

5α,8α-epidioxyergosta-6,9(11),22-trien-3β-ol (**10**)

Colorless crystals (20 mg); IR (KBr) ν_{max} cm^{-1}: 3440, 3024 and 1640. ^{1}H-NMR ($CDCl_3$, 500

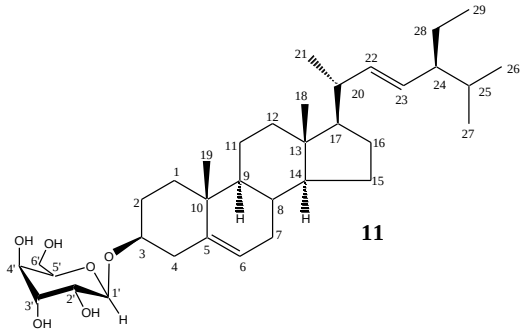
MHz), δ: 6.64 (1H, d, J = 8.9 Hz, H-7), 6.62 (1H, d, J = 8.9 Hz, H-6), 5.39 (lH, dd, J = 6.5, 2.7 Hz, H-11), 5.31 (1H, dd, J= 14.9, 8.5 Hz, H-22), 5.17 (1H, dd, J = 15.1, 8.5 Hz, H-23), 3.89 (1H, dt, J = 7.8, 8.5 Hz, H-3), 1.12 (3H, s, H-19), 1.05 (3H, d, J = 7.2 Hz, H-21), 0.94 (3H, d, J = 6.9 Hz, H-28), 0.83 (6H, d, J = 7.3 Hz, H-26 and H-27), 0.78 (3H, s, H-18). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ: 142.8 (C-9), 136.5 (C-22), 135.8 (C-7), 135.2 (C-6), 134.5 (C-23), 119.8 (C-11), 83.0 (C-5), 78.5 (C-8), 66.4 (C-3), 56.0 (C-17), 48.3 (C-14), 43.7 (C-13), 42.8 (C-24), 41.3 (C-12), 39.9 (C-20), 38.0 (C-10), 36.2 (C-4), 33.1 (C-25), 32.8 (C-1), 30.8 (C-2), 28.7 (C-16), 25.5 (C-19), 22.8 (C-15), 21.1 (C-21), 20.0 (C-27), 19.7 (C-26), 17.5 (C-28), 12.8 (C-18). HREIMS *m/z:* 426.6301 (calcd. for $C_{28}H_{42}O_3$, 426.6380).



10

Stigmasterol 3-O-β-D-glucopyranoside (**11**)

Crystallized from methanol (30 mg), m.p. 289-290 °C $[\alpha]_D^{25}$ –51.5° (c = 1.05, CH_3OH), IR (KBr) ν_{max} cm^{-1} 3454, 3024, 1646. ^{1}H-NMR (C_5D_5N, 400 MHz) δ: 5.23 (1H, br d, J = 5.9 Hz, H-6), 5.18 (1H, dd, J = 15.5, 8.0 Hz, H-22), 5.02 (1H, dd, J= 15.5, 8.4 Hz, H-23), 4.99 (1H, d, J = 6.9 Hz, H-1′), 4.10 (1H, dd, J = 14.0, 5.5 Hz, H-6_a'), 4.26 (1H, dd, J = 14.0, 2.9 Hz, H-6_b'), 3.85 (1H, m, H-3), 3.84-4.01 (4H, m, H-2′ - H-5′), 1.07 (3H, s, Me-19), 0.92 (3H, d, J = 7.2 Hz, Me-21), 0.83 (6H, d, J = 6.8 Hz, Me-26, Me-27), 0.81 (3H, t, J = 7.4 Hz, Me-29), 0.65 (3H, s, Me-18). ^{13}C-NMR (C_5D_5N, 125 MHz) δ: 141.8 (C-5), 139.1 (C-22), 130.1 (C-23), 121.8 (C-6), 103.1 (C-1'), 79.9 (C-3), 77.5 (C-3'), 77.1 (C-5'), 74.9 (C-2'), 71.2 (C-4'), 63.0 (C-6'), 57.2 (C-14), 56.7 (C-17), 52.9 (C-24), 51.1 (C-9), 44.2 (C-4), 43.8 (C-13), 41.0 (C-20), 40.1 (C-12), 38.5 (C-l), 37.7 (C-10), 33.7 (C-25), 33.4 (C-2), 32.4 (C-7), 33.9 (C-8), 29.5 (C-16), 26.1 (C-28), 25.0 (C-15), 22.2 (C-21), 23.0 (C-11), 20.1 (C-19), 18.7 (C-27), 18.5 (C-26), 12.8 (C-18), 13.1 (C-29). HRFABMS *m/z*: 575.4249 $[M+H]^+$(calcd for $C_{35}H_{59}0_6$, 575.4230).



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