Mansoura Journal of Chemistry Vol. 38 (2), December, 2011.

GC/MS ANALYSIS OF SESQUITERPENES IN SYNADENIUM GRANTII

Abdel-Aziz M. Dawidar, Eman M. Keshk, Hamada H. Saad and Mamdouh Abdel-Mogib^a Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

(Received: 15/9/2011)

ABSTRACT

The phytochemical investigation of Synadenium grantii has led to the isolation of several known compounds including β sitosterol, stigmasterol, β -amyrinone and quercetin besides the identification of volatile components of petroleum ether fraction which are characterized by high content of various skeletons of sesquiterpenes that did not be reported previously either from the species or from the genus.

Keywords: Euphorbiaceae, Synadenium grantii, β-Sitosterol, Stigmasterol, β-Amyrinone, Quercetin, Sesquiterpenes.

INTRODUCTION

The Euphorbiaceae family consists of about 6,900 species but only a few species are worth considering as commercial sources of compounds. When the stems of many members including *Synadenium grantii* Hook. f. are cut, exude a milky sap (white latex) which has an unpleasant taste and is toxic when ingested in significant quantities [Judd *et al.*, (1999)].

S. grantii (Euphorbiaceae), commonly called African milkbush, is a shrubby plant native to tropical Africa. The principal utilization of the shrub is for live fences. Often they cause injury to cattle, producing redness and edema of the mucous membranes and eyes, and also blistered areas of the skin [Bagavathi et al., (1988)]. In India and different countries of Africa the latex of S. grantii is very commonly used as an analgesic, an anti-inflammatory [Bagavathi et al., (1988)] and antitumor agent by the Midwestern region Brazilians [Nogueira et al., (2008)]. S. grantii latex contains toxic

^a Corresponding author: E-mail mamdouh_m@mans.edu.eg, Tel.: +2 0502242388

constituents responsible for the high irritant activity which provides health hazards to both humans as well as to grazing live stock [Bagavathi et al., (1988)].

The phytochemical investigation of *S. grantii* revealed the presence of diterpenoids [Kinghorn *et al.*, (1980) & Bagavathi *et al.*, (1988)], triterpenoids [Nielsen *et al.*, 1979)], and anthocyanins with unusual furanose sugar [Andersen *et al.*, (2010)].

In this article, we present the phytochemical investigation results of Synadenium grantii highlighting the presence of sesquiterpenes in the genus Synadenium.

RESULTS AND DISCUSSION

The separation of the dried aerial part extracts of Synadenium grantii afforded some known natural products, including euphol 1 and tirucallol 2 which are previously reported from this species [Nielsen *et al.*, (1979)]. Their structures were proven by ¹H NMR data which agreed with the compared one from the literature [Rondon *et al.*, (2003) & Bartlett *et al.*, (1990)], respectively.

The 'H NMR spectrum of compound 3 revealed the presence of six methyl groups in the up field region showing that the compound may be steroidal or triterpenoidal compound. The spectrum indicated the presence of a multiplet signal at δ 3.51 ppm, which was assigned for H-3 of steroids. An olefinic proton appeared as broad doublet at 5.33 ppm, was assigned for H-6 in ring B suggesting the presence of a Δ^5 -3-hydroxy sterol. The spectrum indicated the presence of two tertiary methyl signals at 0.66 and 0.99 ppm, corresponding to Me-18 and Me-19, respectively. The side chain signals appeared at δ 0.90 (3H, d, J= 6.9 Hz, Me-21), 0.80 (3H, d, J= 6.9 Hz, Me-26), 0.80 (3H, d, J= 6.9 Hz, Me-27), 0.83 (3H, t, J= 7.65 Hz, Me-29), suggesting that the sterol has a stigmast-5-en-3-ol skeleton. By comparing these data with the literature [Weng *et al.*, (2003)] compound 3 was identified as β -sitosterol.

The ¹H NMR spectrum of compound 4 was found to be identical with the spectrum of compound 3 in addition to two olefinic proton signals appeared as a pair of double doublet at δ 5.13, 5.00 ppm, which were assigned for H-22 and H-23, respectively. The spectrum suggesting the presence of a $\Delta^{5.22}$ -3-hydroxy sterol. Thus, all the previous data and the compared one from literature [Chung *et al.*, (2005)] support that the compound 4 is stigmast-5, 22-dien-3-ol which is known as stigmasterol.

The IR spectrum of compound 5 revealed an absorption band at 1706 cm⁻¹ due to the presence of a carbonyl group. The ¹H NMR data showed the presence of eight singlet methyl group signals at the up field (from 0.83 to 1.13 ppm). This indicated that it may belong to oleanane series. The characteristic (H-12) signal appears as a broad doublet at 5.18 ppm. The absence of the (H-3) signal in the ¹H NMR spectrum indicated that the hydroxyl group (at H-3) was replaced by a carbonyl group which was confirmed by the IR spectrum. The mass spectrum confirmed this suggestion by showing the molecular ion peak at m/z 424 (6.30%) corresponding to $C_{30}H_{48}O$. Additionally an ion peak appeared at m/z 218 (76%) which is characteristic for the triterpenoids with C_{12} -

 C_{13} double bond [Shiojima et al., (1992)]. By comparing these data with the literature [Valea et al., (2005) & Júnior et al., (2005)] compound 5 was identified as β -amyrinone.

The ¹H-NMR spectral data of compound 6 was characteristic of flavonoids. Ring A was apparently 5,7-disubstituted by two meta-oriented protons at δ 6.15 ppm (1H, brs, H-6) and δ 6.39 ppm (1H, brs, H-8). On the other hand, the observation of ABX system at δ 7.63 ppm (1H, brs, H-2), δ 6.85 ppm (1H, d, J= 8.4 Hz, H-5) and δ 7.51 ppm (1H, dd, J= 8.4 Hz, H-6) suggested a 3,4-disubstituted ring B. It also showed signals for five hydroxyl groups at δ 12.44 ppm (1H, s, 5-OH), δ 10.80 ppm (1H, brs, 7-OH), δ 9.60 ppm (1H, brs, 4-OH) and 9.30 (2H, brs, 3-OH and 3-OH). By comparing these data with the literature [Miyazawa et al., (2003)] compound 6 was identified as quercetin.

The volatile components of petroleum ether fraction were analyzed by GC/MS technique to give thirty compounds which were stated in Table (1.) These compounds are characterized by high percent of different sesquiterpenes.

EXPERIMENTAL

General:

The ¹H NMR spectra were recorded on a 500 MHz spectrometer (JEOL) at Faculty of Science, Alexandria University. Chemical shifts were given in ppm relative to TMS as internal standard. Infrared spectra were recorded on a Mattson 5000 FT-IR spectrophotometer at Faculty of Science, Mansoura University. GC/MS analysis were performed on a Varian GC interfaced to Finnegan SSQ 7000 Mass selective Detector (SMD) with ICIS V2.0 data system for MS identification of the GC components. The column used was DB-5 (J&W Scientific, Folosm, CA) cross-linked fused silica capillary column (30 m. long, 0.25mm. internal diameter) coated with poly dimethylsiloxane (0.5 µm. film thickness). The oven temperature was programmed from 50°C for 3 min., then heating by 7°C /min. to 250 °C and isothermally for 10 min., at 250°C. Injector temperature was 200°C and the volume injected was 0.5µl. Transition-line and ion source temperature were 250°C and 150°C, respectively. The mass spectrometer had a delay of 3 min. to avoid the solvent peak and then scanned from m/z 50 to m/z 300. Ionization energy was set at 70 eV at Chemistry Department, Faculty of Science, Mansoura University. Thin layer chromatography and preparative thin layer chromatography (PTLC) were performed on silica gel (Kieselgel 60, GF 254) of 0.25mm thickness. Solvents: petroleum ether (60-80), diethyl ether, hexane, methylene chloride, ethyl acetate, acetone and methanol were obtained from Adwic Company.

Plant material:

Synadenium grantii Hook. f. was collected from Mansoura University Horticulture, Mansoura, Egypt in July (2010) and identified by Prof. Dr. Ibrahim Mashaly, Botany Department, Faculty of Science, Mansoura University.

Processing of plant material:

The aerial parts of the plant were air dried in shade at room temperature and ground to give 1000 gm of dried powder material. The dried ground plant material was extracted by a soxhlet extractor using different solvents; petroleum ether $60-80^{\circ}$ C, methylene chloride and ethyl acetate, respectively to obtain three fractions; pet. ether fraction (39.00 g, 3.9% w/w), methylene chloride fraction (10.00 g, 1% w/w) and ethyl acetate fraction (11.70 g, 1.17% w/w).

The petroleum ether fraction was dissolved in cold methanol to obtain methanol insoluble fraction (16.50 g, hydrocarbons fraction) and methanol soluble one (22.50 g).

The methanol soluble fraction (20.00 g of which) was subjected to silica gel column chromatography using hexane/acetone solvent as an eluent with increasing polarity. The fraction obtained by hexane/acetone 4:1 (0.25 g), was separated on TLC using hexane/acetone 7:3 as an eluent to give euphol and tirucallol ($R_f = 0.7, 30$ mg).

The fraction obtained by hexane/acetone 3:1 (0.35 g), was separated on TLC using hexane/acetone 7:3 as an eluent to give β -sitosterol and stimgasterol ($R_f = 0.6$, 18 mg).

The methylene chloride fraction (10.00 g) was dissolved in cold methanol to obtain a methanol insoluble fraction (3.47 g, hydrocarbons fraction) and a methanol soluble fraction (6.53 g).

The methanol soluble fraction of methylene chloride fraction was subjected to silica gel column chromatography using petroleum ether/ethyl acetate solvent system as an eluent with increasing polarity. The fraction obtained by petroleum ether/ethyl acetate 19:1(0.38 g), was separated on TLC using petroleum ether/ethyl acetate 47:3 as an eleunt to give β -amyrinone ($R_f = 0.6, 35$ mg). The fraction obtained by elution with petroleum ether/ethyl acetate 17:3(0.40 g), gave by TLC with petroleum ether/ethyl acetate 9:1 β -sitosterol and stigmasterol ($R_f = 0.2, 20$ mg).

The ethyl acetate fraction (11.70 g) was subjected to silica gel column chromatography using methylene chloride/methanol solvent system with increasing polarity. The fraction obtained by elution with methylene chloride/ methanol 83:17(0.34 g), gave by TLC using methylene chloride/methanol 22:3 as an eluent quercetin ($R_f = 0.3, 17 \text{ mg}$).

Isolation of the volatile components of petroleum ether fraction:

A sample from the methanol soluble fraction of petroleum ether extract was dissolved in diethyl ether to be analyzed by the GC/MS technique

Euphol 1. White powder, ¹H NMR (CDCl₃): $\delta_{\rm H}$ 5.08 (1H, brs, H-24), 3.21 (1H, dd, H-3), 1.67 (3H, s, Me-27), 1.59 (3H, s, Me-26), 0.98 (3H, s, Me-29), 0.94 (3H, s, Me-18), 0.85 (3H, d, Me-21), 0.83 (3H, s, Me-28), 0.79 (3H, s, Me-30), 0.74 (3H, s, Me-19).

Tirucallol 2. White powder, ¹H NMR (CDCl₃): δ_{H} 5.07 (1H, brs, H-24), 3.21 (1H, dd, H-3), 1.67 (3H, s, Me-27), 1.59 (3H, s, Me-26), 0.98 (3H, s, Me-29), 0.94 (3H, s, Me-18), 0.89 (3H, d, Me-21), 0.84 (3H, s, Me-28), 0.78 (3H, s, Me-30), 0.74 (3H, s, Me-19).

β-Sitosterol 3. White powder, ¹H NMR (CDCl₃): $\delta_{\rm H}$ 5.33 (1H, brd, H-6), 3.51 (1H, m, H-3), 0.99 (3H, s, Me-19), 0.90 (3H, d, Me-21), 0.83 (3H, t, Me-29), 0.80 (3H, d, Me-26), 0.80 (3H, d, Me-27), 0.66 (3H, s, Me-18).

Stigmasterol 4. White powder, ¹H NMR (CDCl₃): $\delta_{\rm H}$ 5.33 (1H, brd, H-6), 5.13 (1H, dd, H-22), 5.00 (1H, dd, H-23), 3.51 (1H, m, H-3), 0.99 (3H, s, Me-19), 0.90 (3H, d, Me-21), 0.83 (3H, t, Me-29), 0.80 (3H, d, Me-26), 0.80 (3H, d, Me-27), 0.66 (3H, s, Me-18).

β-Amyrinone 5. Colorless needles, IR cm⁻¹; 1706 (Carbonyl group). MS; m/z (rel. int.) 424 (6.3%) [M⁺], 409 (4.2%) [M-CH₃]⁺, 218 (76%) [M-C₁₄H₂₄O]⁺, 203 (40%) [C₁₅H₂₃]⁺, 189 (14.3%) [C₁₄H₂₁]⁺; ¹H NMR (CDCl₃): $\delta_{\rm H}$ 5.19 (1H, brd, H-12), 2.53(1H, dddd, H-2a), 2.36 (1H, dddd, H-2b), 1.13 (3H, s, Me-27), 1.08 (3H, s, Me-23), 1.06 (3H, s, Me-25), 1.04 (3H, s, Me-24), 1.01 (3H, s, Me-26), 0.86 (6H, s, Me-29 and Me-30), 0.83 (3H, s, Me-28).

Quercetin 6. Yellow powder, ¹H NMR (DMSO): δ_{H} 12.44 (1H, s, 5-OH), 10.80 (1H, brs, 7-OH), 9.60 (1H, brs, 4-OH), 9.30 (2H, brs, 3-OH and 3-OH), 7.63 (1H, brs, H-2), 7.51 (1H, brd, H-6'), 6.85 (1H, d, H-5'), 6.39 (1H, brs, H-8), 6.15 (1H, brs, H-6).

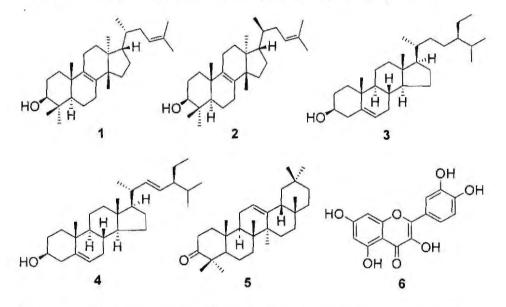


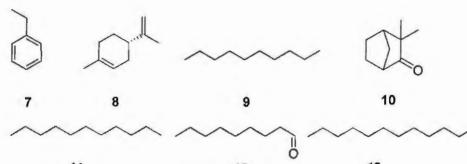
Table (1): volatile constituents of methanol soluble fraction of petroleum ether extract

No.	Compound	R	Area %	M.F	m/z (ret. Int. %)
7	Ethyl benzene	6.82	0.32	CaHio	106 (81.58) [M ⁺], 91 (100) [M- CH ₃] ⁺ , 77 (47.37) [C ₆ H ₃] ⁺ , 64 (18.42) [C ₅ H ₄] ⁺
8	Limonene	11.51	0.29	C10H16	136 (5.26) [M ⁺], 121 (13.16) [M- CH ₃] ⁺ , 91 (26.32) [C ₇ H ₉] ⁺ , 68 (100) [C ₅ H ₈] ⁺ , 67 (92.11) [C ₅ H ₇] ⁺
9	n-Decane	12.09	0.38	C10H22	113 (2.63) $[C_{6}H_{17}]^{+}$, 99 (5.26) $[C_{7}H_{13}]^{+}$, 85 (30.26) $[C_{6}H_{13}]^{+}$, 71 (47.37) $[C_{5}H_{11}]^{+}$, 57 (52.63) $[C_{4}H_{9}]^{+}$, 43 (100) $[C_{3}H_{7}]^{+}$
10	2-Camphenilone	12.37	0.69	C ₉ H ₁₈ O	138 (21.21) [M ⁺],109 (21.21) [M- CO-H] ⁺ , 95 (63.64) [C ₇ H ₁₁] ⁺ , 69 (100) [C ₅ H ₉] ⁺ , 69 (100) [C ₄ H ₅ O] ⁺
11	n-Undecane	13.52	1.39	C ₁₁ H ₂₄	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
12	n-Nonaldehyde	13.98	0.66	C9H18O	98 (26.31) $[C_6H_{10}O]^+$, 70 (26.31) $[C_5H_{10}]^+$, 57 (63.16) $[C_4H_9]^+$, 43 (84.21) $[C_3H_7]^+$, 41 (100) $[C_3H_5]^+$
13	n-Dodecane	16.41	1.27	C ₁₂ H ₂₆	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$
14	Estragole	16.68	0.71	C10H12O	148 (100) $[M^+]$, 133 (7.89) $[M-CH_3]^*$, 121 (26.32) $[C_8H_9O]^*$, 105 (31.58) $[C_7H_5O]^*$, 91 (39.47) $[C_6H_3O]^*$, 77 (44.74) $[C_6H_5]^*$
15	Octahydro-5,5,8a- trimethyl-4- methylene-2H-1,4a- methano-naphthalen- 3-ol	17.70	2.33	C15H24O	220 (50) [M ⁺], 202 (41.18) [M-H ₂ O] ⁺ , 187 (52.94) [M-H ₂ O- CH ₃] ⁺ , 117 (100) [C ₉ H ₉] ⁺

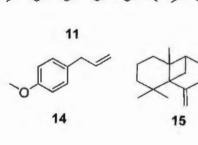
No.	Compound	R	Area %	M.F	m/z (ret. Int. %)
16	2,6,10-Trimethyl tetradecane	18.40	2.07	C ₁₇ H ₃₆	155 (2.63) $[C_{11}H_{23}]^{+}$, 142 (13.16) $[C_{10}H_{22}]^{+}$, 141 (10.53) $[C_{10}H_{21}]^{+}$, 127 (2.63) $[C_{9}H_{19}]^{+}$, 85 (26.32) $[C_{6}H_{13}]^{+}$, 71 (42.11) $[C_{5}H_{11}]^{+}$, 57 (39.47) $[C_{4}H_{9}]^{+}$, 43 (100) $[C_{3}H_{7}]^{+}$
17	(2E,4E)-2,4- Decadienol	18.69	1.44	C ₁₀ H ₁₆ O	$\begin{array}{c} 121 (1.32) [C_8H_9O]^+, 107 (1.32) \\ [C_7H_9O]^+, 95 (10.52) [C_6H_7O]^+, 81 \\ (100) [C_5H_5O]^+, 55 (21.05) \\ [C_3H_3O]^+, 43 (18.42) [C_3H_7]^+, 41 \\ (44.74) [C_2H_3]^+ \end{array}$
18	(+)-Cyclosativene	19.34	7.79	C ₁₅ H ₂₄	204 (39.47) [M ⁺], 189 (11.84) [M- CH ₃] ⁺ , 175 (2.63) [M- C ₂ H ₆] ⁺ , 134 (7.89) [C ₁₀ H ₁₄] ⁺ , 133 (19.73) [C ₁₀ H ₁₃] ⁺ , 119 (47.36) [C ₉ H ₁₁] ⁺ , 105 (89.47) [C ₈ H ₉] ⁺ , 91 (100) [C ₇ H ₇] ⁺ , 65 (13.16) [C ₉ H ₅] ⁺
19	(+)-Epi-bicyclo sesquiphellandrene	20.44	0.67	C15H24	204 (5.26) [M ⁺], 161 (100) [M- C ₃ H ₇] ⁺ , 135 (0.30) [C ₁₀ H ₁₃] ⁺ , 105(26.32) [C ₈ H ₉] ⁺ , 91 (21.05) [C ₇ H ₇] ⁺ , 65 (13.16) [C ₃ H ₅] ⁺
20	Trans- geranylacetone	20.77	0.64	C13H22O	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
21	Aromadendrene	21.12	0.51	C15H24	204 (17.86) [M ⁺], 203 (10.71) [M- H] ⁺ , 189 (10.71) [M- CH ₃] ⁺ , 175 (3.57) [C ₁₃ H ₁₉] ⁺ , 133 (25) [C ₁₀ H ₁₃] ⁺ , 119 (28.57) [C ₉ H ₁₁] ⁺ , 105 (64.29) [C ₈ H ₉] ⁺ , 91 (100) [C ₇ H ₇] ⁺ , 65 (17.86) [C ₅ H ₅] ⁺
22	a-Amorphene	21.40	8,45	C15H24	204 (17.11) $[M^+]$, 189 (2.63) $[M^-$ CH ₃] ⁺ , 161 (100) $[M- C_3H_7]^+$, 133 (18.42) $[C_{10}H_{13}]^+$, 119 (31.58) $[C_9H_{11}]^+$, 105 (43.42) $[C_3H_9]^+$, 91 (69.73) $[C_7H_7]^+$, 65 (10.53) $[C_3H_3]^+$
23	Cadina-4,9-diene	22.00	16.39	C15H24	204 (23.68) [M ⁺], 189 (7.89) [M- CH ₃] [*] , 161 (57.89) [M- C ₃ H ₇] [*] , 133 (10.53) [C ₁₀ H ₁₃] [*] , 119 (21.05) [C ₉ H ₁₁] [*] , 105 (100) [C ₈ H ₉] [*] , 91 (64.47) [C ₇ H ₇] [*] , 65 (10.53) [C ₃ H ₅] [*]

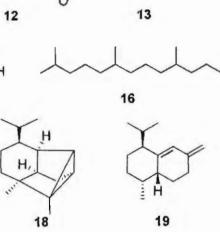
No.	Compound	R,	Area %	M.F	m/z (ret. Int. %)
24	4,5,9,10-Dehydro isolongifolene	23.27	0.18	C15H20	232 (2.63) [M ⁺], 201(7.89) [M- OCH ₃] ⁺ , 200(34.21) [M-OCH ₃ -H] ⁺ , 175 (10.53) [M- C_3H_7] ⁺ , 157 (100) [$C_{12}H_{13}$] ⁺ , 142 (34.21) [C_9H_{18} O] ⁺ , 85 (23.68) [C_3H_9 O] ⁺ , 71 (26.32) [C_4H_7 O] ⁺
25	Caryophyllene oxide	23.57	1.11	C13H24O	202 (7.89) $[C_{13}H_{22}]^*$, 135 (13.16) $[C_{10}H_{13}]^*$,119 (10.53) $[C_9H_{11}]^*$, 79 (36.84) $[C_6H_7]^*$, 67 (34.21) $[C_3H_7]^*$, 54 (13.16) $[C_3H_2O]^*$, 43 (100) $[C_3H_7]^*$, 41 (63.16) $[C_3H_5]^*$
26	Trans-Z-α- bisabolene epoxide	23.83	0.53	C15H24O	220 (13.16) $[M^+]$, 203 (5.26) $[C_{15}H_{23}]^+$, 149 (34.21) $[C_{11}H_{17}]^+$, 91 (89.47) $[C_7H_7]^+$, 77 (60.53) $[C_6H_5]^+$, 43 (100) $[C_3H_7]^+$
27	n-Cetyl alcohol	24.46	6.52	C ₁₆ H ₃₄ O	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
28	Spathulenol	24.70	6.16	C15H24O	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
29	8,14-Cedranoxide	25.69	1.30	C ₁₅ H ₂₄ O	220 (5.26) $[M^+]$, 204 (5.26) $[C_{15}H_{24}]^*,135$ (15.79) $[C_{10}H_{15}]^*,$ 107 (13.10) $[C_8H_{11}]^*,$ 93 (13.16) $[C_7H_9]^*,$ 79 (26.32) $[C_6H_7]^*,$ 69 (13.16) $[C_5H_9]^*,$ 55 (10.52) $[C_4H_7]^*,$ 43 (100) $[C_3H_7]^*$
30	Octahydro-2,2,7a- trimethyl-4- methylene-1,3a- ethano-3aH-inden-5- ol	26.20	1.15	C15H24O	220 (7.89) [M ⁺], 205 (6.58) [M- CH ₃] ⁺ , 202 (2.63) [M ⁺ -H ₂ O] ⁺ , 106 (67.1) [C ₈ H ₁₀] ⁺ , 105 (57.89) [C ₈ H ₉] ⁺ , 93 (63.16) [C ₇ H ₉] ⁺ , 41 (100) [C ₃ H ₅] ⁺

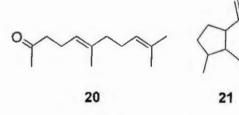
No.	Compound	R	Area %	M.F	m/z (ret. Int. %)
31	a-Cadinol	27.46	4.03	C ₁₅ H ₂₆ O	222 (1.32) [M ⁺], 204 (5.26) [M- H_2O] ⁺ , 161 (28.94) [C ₁₁ $H_{13}O$] ⁺ , 135 (15.79) [C ₁₀ H_{15}] ⁺ , 95 (57.89) [C ₇ H_{11}] ⁺ , 67 (21.05) [C ₅ H_7] ⁺ , 43 (100) [C ₃ H_7] ⁺
32	Tau-muuroloi	28.06	4.86	C ₁₅ H ₂₆ O	222 (2.63) [M ⁺], 204 (10.53) [M- H_2O] ⁺ , 161 (28.95) [C ₁₁ $H_{13}O$] ⁺ , 135 (5.26) [C ₁₀ H_{13}] ⁺ , 95 (68.42) [C ₇ H_{11}] ⁺ , 67 (14.47) [C ₅ H_7] ⁺ , 43 (100) [C ₃ H_7] ⁺
33	Cadalene	28.95	1.15	C15H18	198 (65.79) [M ⁺], 183 (97.37) [M- CH ₃] ⁺ , 168 (26.32) [M- C_2H_6] ⁺ , 154 (28.95) [C_9H_{12}] ⁺ , 41 (100) [C_3H_5] ⁺
34	Aromadendrene oxide	29.80	2.66	C13H24O	220 (10.53) [M ⁺], 131 (18.42) [$C_{10}H_{11}$] ⁺ , 122 (26.32) [$C_{9}H_{14}$] ⁺ , 91 (44.74) [$C_{7}H_{7}$] ⁺ , 69 (13.16) [$C_{5}H_{9}$] ⁺ ,66 (15.79) [$C_{5}H_{6}$] ⁺ , 55 (39.47) [$C_{4}H_{7}$] ⁺ , 41 (100) [$C_{3}H_{5}$] ⁺
35	Deoxy sericealactone	30.08	0.98	C ₁₆ H ₂₀ O ₄	147 (13.16) $[C_{11}H_{17}]^+$, 133 (31.58) $[C_{10}H_{13}]^+$, 117 (26.32) $[C_{9}H_{9}]^+$, 105 (23.68) $[C_{8}H_{9}]^+$, 93 (42.11) $[C_{7}H_{9}]^+$, 77 (36.84) $[C_{6}H_{5}]^+$, 55 (36.84) $[C_{3}H_{3}O]^+$, 43 (100) $[C_{3}H_{7}]^+$
36	Di-epi-a-cedrene epoxide	30.98	0.58	C₁₃H₂₄O	220 (18.42) $[M^+]$, 151 (23.68) $[C_{10}H_{15}O]^+$, 133 (26.32) $[C_{10}H_{13}]^+$, 118 (47.37) $[C_9H_{10}]^+$, 105 (100) $[C_8H_9]^+$, 92 (47.37) $[C_6H_4O]^+$, 71 (84.21) $[C_5H_{11}]^+$, 70 (81.58) $[C_3H_{10}]^+$, 69 (73.68) $[C_3H_9]^+$

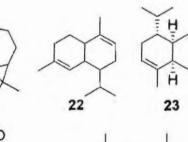


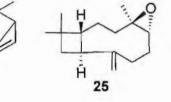
OH





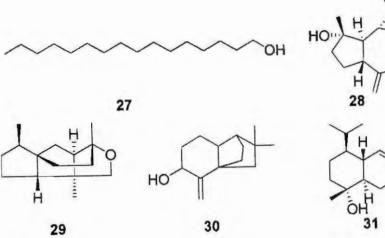


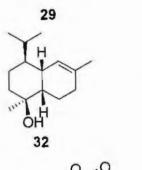


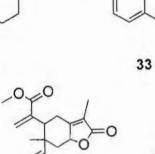


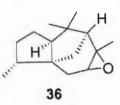
n

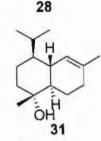


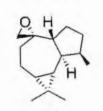














REFERENCES

Andersen, O. M.; Jordheim, M.; Byamukama, R.; Mbabazi, A.; Ogweng, G.; Skaar, I. and Kiremire, B. (2010) Anthocyanins with unusual furanose sugar (apiose) from leaves of *Synadenium grantii* (Euphorbiaceae). Phytochemistry **71**(13): 1558-1563.

Bagavathi, R.; Sorg, B. and Hecker, E. (1988) Skin irritant principles of Euphorbiaceae. Part XIV. Tigliane-type diterpene esters from *Synadenium grantii*. Planta Med. 54(6): 506-10.

Bartlett, W. R.; Johnson, W. S.; Plummer, M. S. and Small, V. Jr. (1990) Biomemtic polyene cyclizations. Cationic cyclization of a substrate having an internal acetylinic bond. Synthesis of euphol and tirucallol. J. Org. Chem. 55(7): 2215-24.

Chung, I. M.; Kong, W. S.; Lee, O. K.; Park, J. S. and Ahmad, A. (2005) Cytotoxic chemical constituents from the mushroom of Pholiota adipose. Food Sci. Biotechnol. 14(2): 255-258.

Judd, W. S.; Campbell, C. S.; Kellogg, E. A.; Stevens, P. F. (1999). Plant systematics: a phylogenetic approach, Sinauer, Sunderland, MA USA. pp. 464.

Júnior, G.M.V.; Souza, C.M.L. and Chaves, M.H. (2005) Resina de *Protium heptaphyllum*: Isolamento, caracterização estrutural e avaliação das propriedades térmicas. Quim. Nova 28(2): 183-187.

Kinghorn, A. D. (1980) Major skin-irritant principle from Synadenium grantii. J. Pharm. Sci. 69(12): 1446-7.

Miyazawa, M. and Hisama, M. (2003) Antimutagenic activity of flavonoids from *chrysanthemum morifolium*. Biosci. Biotechnol. Biochem. 67(10): 2091-2099.

Nielsen, P. E.; Nishimura, H.; Liang, Y. and Calvin, M. (1979). Steroids from *Euphorbia* and other latex-bearing plants. Phytochemistry 18(1): 103-4.

Nogueira, L. A.; Leao, A. B.; Vieira, M. S.; Benfica, P. L.; Cunha, L. C. and Valadares, M. C. (2008) Antitumoral and antiangiogenic activity of *Synadenium umbellatum* Pax. J. Ethnopharmacol. 120(3): 474-8.

Rondon, M.; Morales, A.; Bahsas, A.; Rojas, J. and Buitrago, D. (2003) A new glycoside isolated from the latex of *Euphorbia cotinifolia* L. Rev. Latinoam. Quim. 31(1): 10-15.

Shiojima, K.; Arai Y.; Masuda K.; Takase Y.; Ageta T. and Ageta H. (1992) Mass spectra of pentacyclic triterpenoids. Chem. Pharm. Bull. 40(7): 1683-1690.

Valea, A.E.; Davida, J.M.; Brandão, H.N. and David J.P. (2005) A New Flavonol Glycoside Derivative from Leaves of *Moldenhawera nutans*. Z. Naturforsch. C. 60(1/2): 45-49.

Weng, J. R.; Su, H. J.; Yen, M. H.; Won, S. J. and Lin, C. N. (2003) The cytotoxic constituents of *Euphorbia makinoi*. Chin. Pharm. J. (Taipei, Taiwan) 55(4): 267-272.

الملخص العربى

التحليل الكروماتوجرافي الغازي المزود بمطياف الكتله للتربينات نصف الثلاثيه من نبات السينادينم جرانتي

عبد العزيز دويدار، إيمان كثنك، حمادة سعد، ممدوح عبد المجيب قسم الكيمياء، كلية العلوم، جامعة المنصورة، المنصورة، مصر

أدى الفحص الفيتوكيمياني لنبات سينادينم جرانتي إلى فصل العديد من المركبات المعروفة بما في ذلك بيتاسيتواستيرول واستجماستيرول وبيتا أميرين وكوارستين، بالإضافة إلى تعريف المكونات المتطايرة لخلاصة الإيثر البترولي، والتي تميزت بمحتوى عالى من أنواع مختلفة من التربينات نصف الثلاثية والتي لم نتشر سابقاً لا من هذا النوع ولا حتى من الجنس.

