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TERPENES, STEROIDS AND SHIKIIMATES IN *CALLIGONUM COMOSUM* L

Abdel-Aziz M. Dawidar, Mamdouh Abdel-Mogib, Ibrahim M. El-Sherbiny* and Ali A. Saeed
Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

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ABSTRACT

Further phytochemical investigation of *Calligonum comosum* L has led to the isolation of several known compounds including β-sitosterol, stigmasterol, betulin and *p*- hydroxy benzoic acid. Additional natural components, terpenoids, steroids and shikimates were identified and characterized by GC/MS technique from petroleum ether and methylene chloride fractions. Compounds **7-29** have not been reported previously as components from the species or from its genus.

Keywords: polygonaceae, *Calligonum comosum* L, monoterpenes, phytosterols, shikimates, 4- hydroxy benzoic acid, betulin.

INTRODUCTION

The polygonaceae family consists of about 40 genera and over 1000 species. *Calligonum comosum* L belongs to this family; it inhabits much plant of the North African desert, central and eastern Arabia and is commonly called Arta or Teep. It is a shrubby perennial plant **[Tackholm, (1974)]**.

The principal utilization of the different plant parts is in folk medicine. It is used by local healers to treat stomach ailments. The stems and leaves are chewed curing toothache **[Ghazanfar, (1994)]**. Moreover the plant has various biological activities **[El-Hawary & Kholief, (1990)]**.

Ethanol extract of the aerial parts of *C. comosum* significantly reduced the increase in hind paw oedema induced by carrageenan in rats and has a significant anti-inflammatory activity in the cotton pellet model [Liu *et al.*, (2001)].

Ethanolic, methanolic and acetonic extract from whole plant of *C. comosum* tissues except seeds, exhibited significant antibacterial activity. In addition, *C. comosum* organic extracts are probably useful in the control of food contamination by *listerial* species **[Hammami *et al.*, (2011)]**.

phytochemical analysis of *C. comosum* L. by previous workers have dealt with the isolation and identification of quercetin glycoside, kaempferol glycuronide and kaempferol **[Asayyad & Wagener, (1978)]**. Also anthraquinones **[El-Helah *et al.*, (1992)]**, violaxathin and neoxanthin **[Asayyad & Wagner, (1978)]**.

Eight compounds were isolated, purified, and identified from *C. comosum* L as (+)- catechin, dehydrodicatechin A, kaempferol-3-O-rhamnopyranoside, quercitrin (quercetin-3-O-rhamnopyranoside), β-sitosterol-3-O-glucoside, isoquercitrin (quercetin-3-O-glucopyranoside), kaempferol-3-O-glucuronide and mequilianin (quercetin-3- O-glucuronide) **[Badria *et al.*, (2007)]**.

In this article we present our phytochemical finding as a result of investigation of the lipophilic fractions of *C. comosum*.

RESULTS AND DISCUSSION

The separation of the extracts of the dried whole plant parts of *C. comosum* L afforded some known natural products, including **betulin 1 [Okasaka *et al.*, (2004)]**. The ^{1}H-NMR spectra of compound **(1)** showed five methyl group signals in the up-field. It was similar to the lupeol but the singlet of the H -28 methyl group (of lupeol at δ 0.76 ppm) was replaced by two doublets with geminal coupling of 10Hz at δ 3.48 and δ 3.46 ppm indicating the hydroxylation at C-28, in addition to that at C-3(indicated by H-3 signal as doublet of doublet at δ 3.18 ppm).The previous data suggested that product **1** is **betulin [20(29)-lupen-3β,28-diol]**. The mass spectrum of compound **1** showed the presence of molecular ion peak M^+ at m/z 442(1.3 %) which corresponding

($C_{30}H_{50}O_2$). By comparing these data with literature compound **1** was isolated before from *C. Leucocladum* **[Okasaka *et al.*, (2004)]**.

The ^{1}H-NMR spectrum of compound **2** 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 5.34 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 **[Toaima, *et al.*, (2007)]** compound **2** was identified as ***β*-sitosterol**.

The ^{1}H-NMR spectrum of compound **2** 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 5.11, 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 **3** is **stigmast-5, 22-dien-3-ol** which is known as **stigmasterol**.

The ^{1}H-NMR spectral data of compound **4** showed two doublet signals at δ 7.685 ppm and δ 6.649 ppm with coupling constant J=8.4Hz which were assigned to the a 1,4-disubstituted benzene ring. The singlet signal corresponding to a hydroxyl group was observed at δ 5.911 ppm. The down-field shift of the signal at δ 7.685 ppm indicated the presence of a deshielding COOH group. Thus **4-hydroxybenzoic acid** is probable, which was confirmed by comparing with literature **[EL-Rokh, (2007)]**.

The ^{1}H-NMR spectral data of compound **5** was characteristic of flavonoids. Ring A was apparently 6,8-disubstituted by two meta-oriented protons at δ 5.68 ppm (brs, H-6) and δ 5.89 ppm (brs, H-8). On the other hand, the observation of ABX system at δ 6.72 ppm (brs, H-2′), δ 6.65 ppm (d, *J*= 7.65 Hz, H-5′) and δ 6.56 ppm (1H, dd, *J*= 8.4 Hz, H-

6'). By comparing these data with the literature **[Badria *et al.*, (2007)]** compound **5** was identified as **Catechin.**

Compound **6** was isolated as yellow needles (15 mg), The spectroscopic data showed that compound **6** is a flavonol glycoside with free 5-, 7-, 4' -hydroxy groups **[Mabry *et al.*, (1970); Agrawal, (1989)]**. It gave an orange to yellow color after heating with Vanillin / Sulfuric acid spray reagent. This compound gave a positive Molisch's test indication its glycosidic nature. Its UV absorption in EtOH displayed absorption bands at 366 and 246 nm, indication that is has a flavones or a flavonol nucleous with 3-OH substituted **[Markham, (1982)]**.

This was proved by the ^{1}H-NMR spectrum, as it demonstrated two doublets at δ 6.93 ppm (d, *J*= 9.2 Hz) and δ 7.74 ppm (d, *J*= 9.2 Hz), each was integration for 2 protons that are corresponding to O-coupled protons H-3', H-5' and H-2', H-6' respectively. The oxygenation pattern of ring A was established from the ^{1}H-NMR signals at δ 6.17 ppm (br s) and δ 6.35 ppm (br s) for the meta-coupled protons of H-6 and H-8 respectively. The 3-OH position is substituted by a sugar moiety and it was identified by the ^{1}H-NMR signals at δ 0.89 ppm (d, *J*= 5.35 Hz, 3H), that is corresponding to H-6'' (methyl group); and δ 5.33 ppm (br s) that indicates anomeric proton H-1'', so the sugar moiety is suggested to be α- rhamnose **[Markham, (1982)]**. From the above results, compuond 6 is found to be **kaempferol-3-O-α-l- rhamnopyranoside.** By comparing these data with the literature **[Badria *et al.*, (2007)]** compound 6 was identified as **kaempferol-3-O-α-l- rhamnopyranoside.**

The volatile components of petroleum ether and methylene chloride fractions were analyzed by GC/MS technique to give twenty three compounds which were listed in **Table 1 and 2.** These compounds are classified as monoterpenes **(7-14)**, phytosterols **(15-23)** and shikimates **(24-29)**.

It is noteworthy to mention here that GC/MS analysis of the lipophlic fraction revealed the presence of high variation of stigmastane carbon skeleton derivatives in this species and this natural occurrence is very rare.

EXPERIMENTAL

General:

^{1}H NMR spectra were recorded on a 500 MHz spectrometer (JEOL) at National Research Center, Dokki, Cairo. 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 poloy dimethyl-siloxane (0.5µm. 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. (Agriculture Research Center, Dokki, Cairo).

Thin layer chromatography and preparative thin layer chromatography (PTLC) were performed on silica gel (Kieselgel 60, F 254) of 0.25mm thickness.

Solvents: petroleum ether (60-80), hexane, diethyl ether, methylene chloride, chloroform, ethyl acetate, acetone and methanol were obtained from Adwic Company.

Plant material:

Calligonum comosum was collected from Gamasa desert near Mansoura, Egypt, May, 2011. The authenticity of the plant was confirmed by Prof. Dr. Ibrahim Mashaly, Botany Department, Faculty of Science Mansoura University, Egypt, whom we acknowledged. The freshly collected plant material was air dried in shade at room temperature. The whole plant parts (roots, stems, flowers and leaves) were used for investigation.

Processing of *Calligonum comosum*:

The collected plant sample in July 2011 was cut into small pieces and was air dried in shade at room temperature. After drying the plant material, it was ground to give 1000 gm of dried powder material.

The plant material was extracted by a soxhlet extractor using three different solvents; petroleum ether 60-80°C, methylene chloride and ethyl acetate, respectively to obtain three fractions; Pet. ether fraction (5 g), methylene chloride fraction (5 g) and ethyl acetate fraction (10 g).

The methylene chloride extract (5 g) was subjected to silica gel column chromatography using petroleum ether/ethyl acetate solvent system as an eluent with increasing polarity.

Fraction 13 obtained by petroleum ether/ethyl acetate (65:35) (0.88 g), was separated on TLC using methylene chloride /methanol (98:2) as an eluent to give compound **1** (R_f = 0.8, 35 mg). Fraction 17 obtained by elution with petroleum ether/ethyl acetate (60:40) (0.40 g), gave by TLC with methylene chloride / methanol (94:6) a mixture of compounds **2** and **3** with the same (R_f = 085, 20 mg).

Ethyl acetate fraction (10 g) was subjected to silica gel column chromatography using chloroform/methanol solvent system with increasing polarity.

Fraction 5 obtained by elution with pet-ether / ethyl acetate (30:70) (0.84 g), gave by TLC using methylene chloride/methanol (19:1) as an eluent compound **4** (R_f = 0.35, 17 mg), Fraction 10 obtained by elution with pet-ether / ethyl acetate (10:90) (0.90 g), gave by TLC using methylene chloride/methanol (80:20) as an eluent compound **5** (R_f = 0.68). Fraction (27) was purified by Sephadex LH-20 Column using MeOH. Further purification by TLC using methylene chloride/methanol (80:20) as an eluent gave compound **6** as an oily homogenous material with R_f= 0.60.

Petroleum ether fraction (5 g) was dissolved in cold methanol to obtain two fractions. The first fraction is methanol insoluble (1.50 g, methanol insoluble fraction) and the second fraction is methanol soluble fraction (3.5 g). The second fraction (3.5 g) was subjected to silica gel

column chromatography using petroleum ether/ethyl acetate solvent system as an eluent with increasing polarity.

Fraction 26 obtained by petroleum ether /ethyl acetate (75:25) (1 g) as well as methylene chloride fraction were analyzed by GC/MS technique to identify their volatile components which are listed below in tables (1 and 2).

Betulin 1. White powder, MS; *m/z*(rel. int.) 442 (1.3%) $[M^+]$, 427 (5.0%) $[M\text{-}CH_3]^+$, 218 (36.2%) $[C_{16}H_{26}]^+$, 189 (40.2%) $[C_{14}H_{21}]^+$; 135 (44.7%) $[C_{10}H_{15}]^+$, 81 (62.6%) $[C_{15}H_{23}]^+$, 68 (33.2%) $[C_5H_8]^+$, 55 (100%) $[C_4H_7]^+$, ^{1}H NMR ($CDCl_3$): δ_H 3.18 (1H, dd, H-3,J=10HZ), 4.55(1H, s, H-29a), 4.67 (1H, s, H-29b), 3.46 (1H, d, H-28b), 3.48 (1H, d, H-28a), 1.66 (3H, s, Me-30), 1.015 (3H, s, Me-27), 0.98 (3H, s, Me-26), 0.95 (3H, s, Me-25), 0.81(3H, s, Me-24) 0.77 (3H, s, Me-23).

***ß*-Sitosterol 2.** White powder, ^{1}H-NMR ($CDCl_3$): δ_H 5.34 (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 3. White powder, ^{1}H-NMR ($CDCl_3$): δ_H 5.34 (1H, brd, H-6), 5.11 (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).

***P*-Hydroxy benzoic acid 4.** Yellow powder, The UV-visible spectrum in $CHCL_3$ presented tow maxima (246,292 nm) ^{1}H NMR (DMSO): δ_H 7.685 (1H, d, J=8.4,H-2), 7.668 (1H, d, J=8.4,H-6), 6.64 (1H, d, J=8.4,H-3), 6.63 (1H, d, J=8.4,H-5), 5.19 (1H, s-OH) .

Catechin 5. Yellow powder, UV-visible spectrum in $CHCl_3$ presented three maxima (286,358,402 nm) ^{1}H NMR (DMSO): δ_H 5.68 (brs, H-6), 5.89 (brs, H-8), 6.72 (brs, H-2'), 6.65 (1H, d, H-5'), 6.56 (dd, H-6'), 4.44 (1H, d, H-2), 3.78 (1H, m, H-3), 2.33,2.66 (dd, H-4) .

Kaempferol-3-O-α-l-rhamnopyranoside 6. Yellow powder, UV-visible spectrum in EtOH presented three maxima (246,366,394 nm) 1H NMR (CD3OD): δ H 6.17 (brs, H-6), 6.35 (brs, H-8), 7.74 (d, J=9.2, H-2'), 6.93 (d, J=9.2, H-3'), 6.93 (d, J=9.2, H-5'), 7.74 (d, J=9.2 H-6'), 5.33 (br s, H-1"), 4.20 (br s, H-2"), 3.28-3.58 (3",4",5"), 0.89 (d, J=5.35, H-6") .

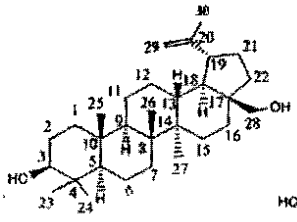
Table (1): volatile constituents of pet. ether fraction of *C. comosum*

No	Compound	R_t	Area%	M.F	m/z (ret. Int. %)
7	a-Myrcene	9.35	5.64	$C_{10}H_{16}$	136 (2.6) $[M^+]$, 137 (4.46) $[M+H]^+$, 121 (2.6) $[M-CH_3]^+$, 94.1 (10.7) $[M-C_3H_6]^+$, 93 (91.07) $[C_7H_9]^+$, 69 (8.9) $[C_5H_9]^+$, 41 (100) $[C_3H_5]^+$.
8	3-Thujene	10.59	20.2	$C_{10}H_{16}$	136 (3.57) $[M^+]$, 121 (3.57) $[M-CH_3]^+$, 93.1 (100) $[M-C_3H_7]^+$, 91 (60.7) $[C_7H_7]^+$, 77 (35.7) $[C_6H_5]^+$, 39 (30.35) $[C_3H_3]^+$.
9	*P*-Mentha-1,8-diene	11,51	11,7	$C_{10}H_{16}$	136 (5.35) $[M^+]$,121 (2.6) $[M-CH_3]^+$, 93.7 (7.14) $[M-C_3H_6]^+$, 93 (37.5) $[C_7H_9]^+$, 79 (53.57) $[C_6H_7]^+$, 68 (75) $[C_5H_8]^+$, 67 (100) $[C_5H_7]^+$.
10	Eucalyptol	6.60	0.39	$C_{10}H_{18}O$	154 (8.14) $[M^+]$, 139 (1.16) $[C_9H_{15}O]^+$, 96 (3.48) $[C_7H_{12}]^+$, 81 (32.55) $[C_6H_9]^+$, 55 (4.65) $[C_4H_7]^+$, 43 (100) $[C_3H_7]^+$, 41 (23.25) $[C_3H_5]^+$
11	*P*-Menthan-3-one,cis	8.62	4.70	$C_{10}H_{18}O$	154 (20.93) $[M^+]$, 139(37.20) $[C_9H_{15}O]^+$, 112.1 (72.09) $[C_7H_{12}O]^+$, 97 (30.23) $[C_6H_9O]^+$, 83 (20.93) $[C_5H_7O]^+$, 69 (79.74) $[C_4H_5O]^+$, 55 (65.1) $[C_3H_3O]^+$, 41 (100) $[C_2HO]^+$.
12	Borneol,	8.95	0.99	$C_{10}H_{18}O$	154 (1.16) $[M^+]$, 139 (2.32) $[C_9H_{15}O]^+$, 95 (100) $[C_7H_{11}]^+$, 81 (4.6) $[C_6H_{11}]^+$, 67(9.30) $[C_5H_7]^+$, 55 (9.3) $[C_4H_7]^+$, 43 (11.62) $[C_3H_7]^+$, 41 (23.25) $[C_3H_5]^+$.
13	Pulegone	9.89	8.93	$C_{10}H_{16}O$	152 (55.8) $[M^+]$, 137 (20.93) $[M-CH_3]^+$, 109 (43.02) $[C_8H_{13}]^+$, 95 (13.95) $[C_7H_{11}]^+$, 81 (100) $[C_6H_9]^+$, 67(88.37) $[C_5H_7]^+$, 53 (16.67) $[C_4H_5]^+$, 41(41.86) $[C_3H_5]^+$.
14	Cyclohexane, 1-methyl-4-(1-methylethylidene	15.93	0.06	$C_{10}H_{16}O$	138 (16.67) $[M^+]$, 137 (53.33) $[M-H]^+$, 95 (83.33) $[C_7H_{11}]^+$, 55 (100) $[C_4H_7]^+$.
15	*P*-Menth-8(10)-en-9-ol,cis	16.29	0.04	$C_{10}H_{18}O$	154 (13.33) $[M^+]$, 153 (16.67) $[M-H]^+$, 136 (30.00) $[C_{10}H_{16}]^+$, 83 (60) $[C_5H_7O]^+$, 55 (100) $[C_4H_7]^+$.
16	3β-Stigmasta-5, 22-dien-3-ol acetate	29.7	0.02	$C_{31}H_{50}O_2$	454 (3.33) $[M^+]$, 394 (40) $[C_{29}H_{45}]^+$, 355 (3.33) $[C_{26}H_{43}]^+$, 234 (3.33) $[C_{17}H_{30}]^+$, 195 (26.6) $[C_{14}H_{25}]^+$, 83 (59.44) $[C_6H_{11}]^+$, 69 (68.25) $[C_5H_9]^+$, 57 (63.99) $[C_4H_9]^+$, 55 (100) $[C_4H_7]^+$.

17	3β-Cholest-5-en-3-ol	30.63	0.01	$C_{27}H_{46}O$	386 (100) [M$^+$], 368 (46.66) [M-H_2O]$^+$, 353 (46.66) [$C_{26}H_{41}$]$^+$, 326 (10) [$C_{24}H_{38}$]$^+$, 255 (33.33) [$C_{19}H_{27}$]$^+$, 213 (43.33) [$C_{16}H_{21}$]$^+$, 159 (85.50) [$C_{12}H_{15}$]$^+$, 105 (43.33) [C_8H_9]$^+$, 81 (66.02) [C_6H_9]$^+$, 55 (72.35) [C_4H_7]$^+$.
18	(3β, 24R)Ergost-5-en-3-ol	31.79	0.65	$C_{28}H_{48}O$	400 (100) [M$^+$], 385 (33.33) [M-CH_3]$^+$, 382 (48.54) [M-H_2O]$^+$, 315 (59.44) [$C_{22}H_{35}O$]$^+$, 255 (30) [$C_{19}H_{27}$]$^+$, 231 (20) [$C_{16}H_{23}O$]$^+$, 213 (39.84) [$C_{16}H_{21}$]$^+$, 163 (20) [$C_{11}H_{15}O$]$^+$, 145 (36.66) [$C_{11}H_{13}$]$^+$, 123 (16.66) [$C_8H_{11}O$]$^+$, 105 (33.33) [C_8H_9]$^+$, 55 (33.33) [C_4H_7]$^+$.
19	3β-Stigmasta-5,22-dien-3-ol	32.17	0.68	$C_{29}H_{48}O$	412 (100) [M$^+$], 397 (16.66) [M-CH_3]$^+$, 394 (16.66) [M-H_2O]$^+$, 369 (16.66) [M-C_3H_7]$^+$, 351(33.3) [$C_{26}H_{39}$]$^+$, 327(3.33) [$C_{23}H_{35}O$]$^+$, 300 (40) [$C_{21}H_{32}O$]$^+$, 273 (13.33) [$C_{19}H_{29}O$]$^+$, 255 (61.46) [$C_{19}H_{27}$]$^+$, 231 (10) [$C_{16}H_{23}O$]$^+$, 213 (26.66) [$C_{16}H_{21}$]$^+$, 159 (43.33) [$C_{12}H_{15}$]$^+$, 105 (26.66) [C_8H_9]$^+$, 55 (64) [C_4H_7]$^+$.
20	γ-Sitosterol	33.24	9.09	$C_{29}H_{50}O$	414 (100) [M$^+$], 399 (34.70) [M-CH_3]$^+$, 396 (48.69) [M-H_2O]$^+$, 354 (6.67) [$C_{26}H_{41}$]$^+$, 329 (52.07) [$C_{23}H_{37}O$]$^+$, 273 (30.0) [$C_{19}H_{29}O$]$^+$, 255(30) [$C_{19}H_{27}$]$^+$, 231 (16.67) [$C_{16}H_{23}O$]$^+$, 213 (30) [$C_{16}H_{21}$]$^+$, 163 (20) [$C_{11}H_{15}O$]$^+$, 145 (23.33) [$C_{11}H_{13}$]$^+$, 123 (6.67) [$C_8H_{11}O$]$^+$, 105 (23.33) [C_8H_9]$^+$, 55 (16.67) [C_4H_7]$^+$.
21	Stigmastan-3,5-dien	33.79	0.18	$C_{29}H_{48}$	396 (100) [M$^+$], 381 (22.62) [M-CH_3]$^+$, 354(3.33) [$C_{26}H_{42}$]$^+$, 255 (10) [$C_{19}H_{27}$]$^+$, 213 (10) [$C_{16}H_{21}$]$^+$, 173 (3.33) [$C_{13}H_{17}$]$^+$, 147 (22.73) [$C_{11}H_{15}$]$^+$, 145 (20.26) [$C_{11}H_{13}$]$^+$, 105 (16.66) [C_8H_9]$^+$, 55 (16.66) [C_4H_7]$^+$.
22	Stigmasta-3,5-dien-7-one	34.30	0.15	$C_{29}H_{46}O$	410 (96.43) [M$^+$], 395 (6.67) [M-CH_3]$^+$, 368 (3.33) [$C_{26}H_{40}O$]$^+$, 269 (20) [$C_{19}H_{25}O$]$^+$, 227 (3.33) [$C_{16}H_{19}O$]$^+$, 174 (100) [$C_{12}H_{14}O$]$^+$, 134 (10) [$C_9H_{10}O$]$^+$, 55 (6.67) [C_4H_7]$^+$.
23	Stigmast-4-en-3-one	34.93	0.47	$C_{29}H_{48}O$	412 (72.16) [M$^+$], 397 (20) [M-CH_3]$^+$, 370 (26.6) [$C_{26}H_{42}O$]$^+$, 327 (10) [$C_{23}H_{35}O$]$^+$, 289 (34.92) [$C_{21}H_{37}$]$^+$, 271 (13.33) [$C_{19}H_{27}O$]$^+$, 229 (69.13) [$C_{16}H_{21}O$]$^+$, 147 (30) [$C_{11}H_{15}$]$^+$, 124 (100) [$C_8H_{12}O$]$^+$, 95 (20) [C_7H_{11}]$^+$, 55 (30) [C_4H_7]$^+$.

Table (2): volatile constituent's methylene chloride fraction of *C. comosum*

No.	Compound	Rt	Area%	M.F	m/z (ret. Int. %)
24	Vanillin	12.41	17.07	$C_8H_8O_3$	152 (86.04) $[M^+]$, 150.9 (100) $[M-H]^+$, 137 (3.48) $[C_7H_5O_3]^+$, 123 (9.30) $[C_7H_7O_2]^+$, 109 (23.25) $[C_6H_5O_2]^+$, 80.9 (46.51) $[C_5H_5O]^+$, 53 (18.60) $[C_4H_5]^+$.
25	Methyl paraben	13.0	4.28	$C_8H_8O_3$	152 (39.53) $[M^+]$, 121.2 (65.11) $[M-CH_3O]^+$, 107 (100) $[C_7H_7O]^+$, 93 (25.58) $[C_6H_5O]^+$, 65 (48.83) $[C_5H_5]^+$, 51 (2.32) $[C_4H_3]^+$.
26	4-Methoxy benzoic acid	13.47	0.26	$C_8H_8O_3$	152 (40.69) $[M^+]$, 120.9 (100) $[M-CH_3O]^+$, 93 (20.93) $[C_6H_5O]^+$, 65 (34.88) $[C_5H_5]^+$, 51 (2.32) $[C_4H_3]^+$.
27	3-Hydroxybenzoic acid methyl ester	13.58	2.71	$C_8H_8O_3$	152 (44.18) $[M^+]$, 121 (100) $[C_7H_5O_2]^+$, 93 (13.95) $[C_6H_5O]^+$, 65 (32.55) $[C_5H_5]^+$, 51 (1.16) $[C_4H_3]^+$.
28	4-hydroxy-3,5-dimethoxy-Benzaldehyed	15.46	46.61	$C_9H_{10}O_4$	182 (100) $[M^+]$, 181 (67.44) $[M-H^+]$, 166.9 (13.95) $[M-CH_3]^+$, 138.9 (16.27) $[C_7H_7O_3]^+$, 122.9 (4.65) $[C_6H_3O_3]^+$, 95 (9.30) $[C_5H_7O_2]^+$, 65 (18.60) $[C_5H_5]^+$
29	4-(3-hydroxy-1-propenyl)-2-methoxyPhenol	16.58	3.49	$C_{10}H_{12}O_2$	180 (66.27) $[M^+]$, 162 (4.65) $[M-H_2O]^+$, 147 (14) $[C_9H_7O_2]^+$, 137 (100) $[C_8H_9O_2]^+$, 124 (51) $[C_7H_8O_2]^+$, 107 (7) $[C_6H_3O_2]^+$, 106 (1.16) $[C_7H_6O]^+$,91 (78) $[C_6H_3O]^+$, 79 (20.93) $[C_5H_3O]^+$, 51 (18.60) $[C_4H_3]^+$.



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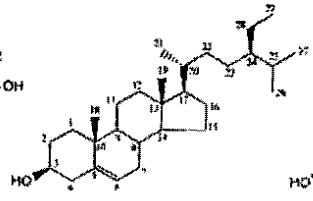

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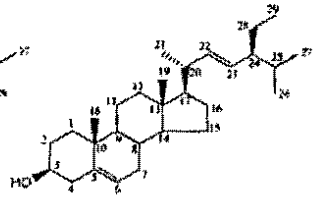

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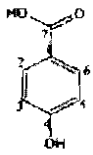

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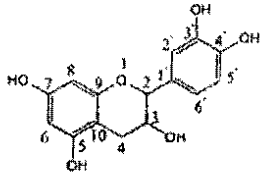

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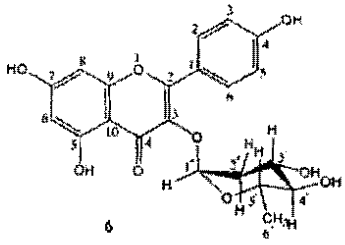

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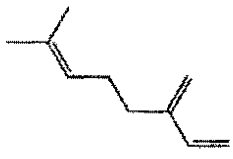

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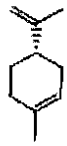

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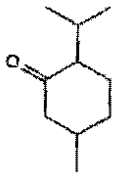

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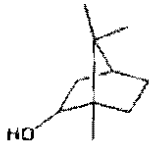

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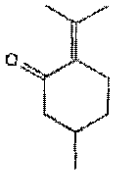

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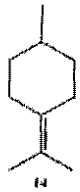

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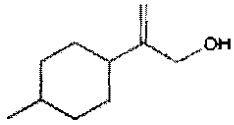

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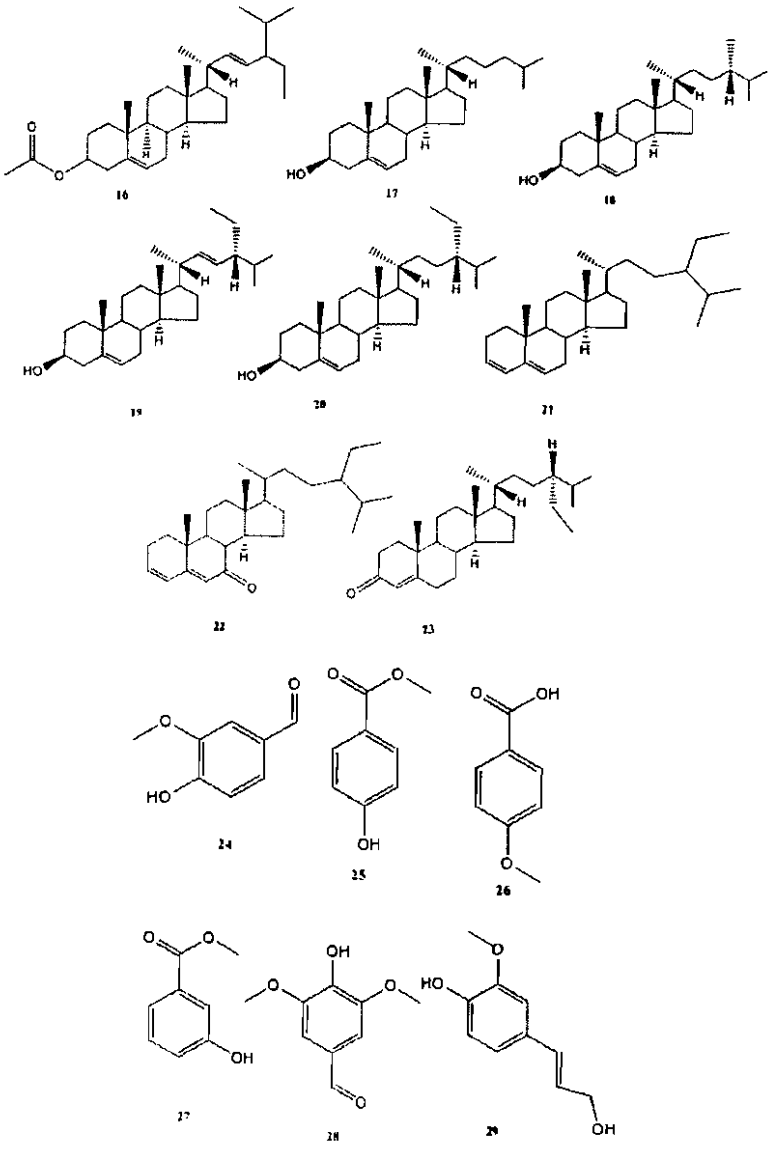
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تربينات، استيرويدات وشيكيمات فى كاليجونم كوموسم

عبد العزيز دويدار، ممدوح عبد المجيب ، ابراهيم الشربينى ، على سعيد
قسم الكيمياء، كلية العلوم، جامعة المنصورة، المنصورة، مصر

نتيجة للفحص الفيتوكيميائى لنبات كاليجونم كوموسم تم فصل العديد من المركبات المعروفة بالأضافة الى معرفة هوية المكونات المتطايرة لخلاصات الأيثير البترولى والمثيلين كلوريد حيث كانت مكونات خلاصة المذيب الأول هى تربينات أحادية وفيتوستيرولات والمذيب الثانى هى شيكيمات وذلك باستخدام تكنولوجيا جهاز غاز كروماتوجرافيا المقترن مع جهاز طيف الكتله وهذا أول تقرير عن وجود هذه المركبات فى هذا النوع النباتي وحتى الجنس.