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PHYTOCHEMICAL INVESTIGATION OF CENTAUREA ARANEOSA GROWING IN EGYPT.

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ABSTRACT

The petroleum ether extract of Centaurea araneosa afforded : Lupeol acetate , long chain acid ($C_{30}H_{60}O_2$) , Lupeol , β - sitosterol- stigmasterol mixture and a waxy substance. The chloroform fraction yielded three methoxylated flavonoid aglycones of rare occurrence in Compositae namely : velutin, hispidulin and cirsmaritin in addition to apigenin. The ethyl acetate fraction yielded β - sitosterol glucoside , apigenin 7-0- glucoside and luteolin 7- 0 - glucoside. Extraction of the sesquiterpene lactones yielded only cnicin. The structure of these compounds was determined through spectral analysis and chemical interconversion as well as comparison with reported data.

INTRODUCTION

Genus Centaurea (Family Compositae) is represented in Egypt by 13 species (1) . Many of these plants are widely used in folk medicine (2) as antitumor , hypoglycemic , hypotensive and diuretic. Also it has been reported that some Centaurea plants are incorporated in cosmetic preparations (3) and for hair scalp preparations (4). Obviously , this genus is rich with chemical constituents such as sesquiterpene lactones (5- 8), flavonoids (9-11), steroids and triterpens (12) as well as ,alkaloids (13), carboxylic acids (14) and acetylenic compounds (15) previously reported. Current literature indicated no reports on the chemistry or biological activity of Centaurea araneosa which is a wild plant indigenous to Egypt, where it is known by the Arabic name"Sennariya" . Therefore, we were encouraged in studing this plant for its biological and chemical importance .

EXPERIMENTAL

Plant Material :

The wild flowering plant Centaurea araneosa Boiss was collected in May 1988 from Sinai proper , south of El - Tih desert , Egypt. The identification was kindly established by Prof. Dr. Nabil El-Hadidi, Professor of Taxonomy , Facutly of Science , Cairo University. A voucher specimen is deposited at the Department of Pharmacognosy, Faculty of Pharmacy, University of Zagazig, Egypt.

Methods and Apparatus :

All solvents were analytical grade; Melting points were determined on Buchi B 5/2 and are uncorrected ; IR was determined on Pye Unicam and Perkin - Elmer 580 IR ; UV on Shimadzu UV - 260; the mass spectra were determined on LKB - 9000 and the NMR were determined on a Varian VSR - 300 spectrometer with TMS as internal standard .

GC/MS Finnigan Mat. G/MS system series 5100. The TLC was developed with :

System I = Methylene chloride :Light petroleum (1:1)

System II = Chloroform : Methanol (98: 2)

System III = Chloroform : Methanol (90 : 10)

System IV = Chloroform : Methanol - Water (7. 5 : 2.5 : 3 drops)

System V = n - Butanol - Acetic acid - Water (4:1:5)

Extraction and Fractionation :

The air - dried whole plant (1 kg) was successively extracted with light petroleum , chloroform , ethyl acetate and finally with ethanol 95% using soxhlet extractor (96 h.) .The extraction processes afforded 27 g of light petroleum extract , 26 g of chloroformic extract , 3.8 g of ethyle acetate and 72 g of ethanol extract .

Chromatography of the Light Petroleum Extract :

The light petroleum extract (27 g) was partitioned between n - hexane (440 ml) and acetonitrile (4 x 110 ml), the two solvents were presaturated with each other. The two phases were separately evaporated in vacuo to provide a dark green greasy residue (hexane) 22 g and a greenish oily residue (acetonitrile) 4. 2 g .

Investigation of the Hexane Phase :

10 g of the dried hexane phase was chromatographed on acolumn of silica gel (600 g , 90 x 6 cm) packed in light petroleum. Gradient elution was adopted using light petroleum and the

polarity was increased with CH_2Cl_2. The eluted fractions (200 ml each),were monitored by TLC using system I and anisaldehyde - H_2SO_4 spray reagent . Similar fractions were pooled together to yield 4 fractions (H_1 , H_2 , H_3 , H_4)

Compound 1 :

Fraction H_2 (0.8 g) eluted with light petroleum - methylene chloride (8 : 2) was rechromatographed on a column of silica gel (100 g , 50 x 2 cm) and eluted with light petroleum and increased with methylene chloride . The fraction eluted with (7 : 3) upon evaporation and crystallization (CH_2Cl_2 - MeOH) provided 75 mg of needle shaped crystals with R_f 0.45 (sys. 1) m. p. 212 - 214°C, it gave positive results with Liebermann's and Salkowski's tests ; IR (kBr) : ν 3010 - 2800 , 1730 , 1630 , 1465 , 1375 , 1250 and 1020 cm^{-1} , MS m/z (% rel. int.) : 468 (M^+ , 5.1) , 543 (1.1) , 408 (1.0) , 409 (0.7) , 220 (16.1) , 218 (100) , 205 (5.9) , 203 (30) & 189 (13) . ^{1}HNMR (ppm) ($CDCl_3$, 80 MHz): δ 5.2 (2H, br .s, CH_2) , 4.6 (1H, t, H3) , 1. 98 (3H, s, - CO - CH_3) , 1.2 (3H, s, CH_3) ,1.0 (3H,s, CH_3) , 0.85 (3H, s, CH_3) ,0.70 (12H, s, 4 CH_3). Hydrolysis (25 mg , 10 % alc. KOH) yielded a white needle crystals having m.p. 214 - 216 ° C.

Compound 2 :

Fraction H_4 (1.5 g) eluted with mixture (4 : 6) , was rechromatographed on silica gel column (150 g , 40 X 2 cm) , packed with light petroleum and the polarity was increased with chloroform . Fraction eluted with light petroleum : chloroform (1:1) , yielded 120 mg of white needle crystals ($CHCl_3$: MeOH) with R_f 0.16 (sys. 1) , m. p. 60 - 64° C ; gave negative Liebermann's and Salkowski's tests. IR (KBr) : ν 3450 , 1710 , 1470 , 1375, 1180 cm^{-1} , MS : m/z (rel . int. %) 452 (M^+ , 2.9) , 437 (0.6) , 434 (0.6) , 408 (0.4) , 60 (3.2) , 59 (100) , 57 (7.8) .

Investigation of the Acetonitrile Phase :

4 g acetonitrile soluble phase was chromatographed on a column of silica gel (200 g, 50 x 2 cm) eluted with methylene chloride and the polarity was increased with acetonitrile to yield several fractions (100 ml each) examined by TLC and pooled together to yield the following compounds :

Compound 3 :

Fractions eluted with methylene chloride : acetonitrile (97: 3) yielded (145 mg) white needle shaped crystals (145 mg) from ($CHCl_3$ - MeOH) with R_f 0.5 (system II) ; m. p. 212-215 °C and positive Liebermann's and Salkowski's tests . IR (KBr) : ν 3450 , 1990 , 1460 , 1380 cm -1 ; MS m/z (rel . int . %) 426 (M^+ , 5.6) , 407 (4.0) , 303 (1.6) , 248 (49.8) , 218

(100) , 207 (44.3) , 205 (20.4) , 189 (16.60 , 135 (28.0) , 95 (23.9). The acetate derivative was also prepared (acetic anhydride + pyridine) to show m. p . 217 - 218° C .

Compound 4 :

Fractions eluted with methylene chloride: acetonitrile, (90 : 10) yielded after recrystallization (70 mg) needle crystals from (CHCl 3 - MeOH) with R_f 0.4 (sys . II , tailed dark pink spot) ; m.p. 128 - 132° C; positive Liebermann's and Salkwoski's tests. IR (kBr) : ν 3600 - 3200, 2860 , 3010 , 1630 , 1380 , 1480 , 1070 cm^{-1} ; MS : m/z (rel . int . %) 414 (23.4) , 412 (100) , 399 (4.9) , 397 (0.4) , 396 (4.5) , 394 (10.1) , 383 (0.7) , 381 (4.4) , 329 (6.6), 327 (5.0), 303 (4.5) , 301 (8.1) , 271 (39.3), 273(13.0), 255 (45.6) , 213 (18.7) . Acetyl derivative was prepared (35 mg , pyridine + acetic anhydride) and purfied by repeated crystallization from a mixtare of $CHCL_3$ - MeOH. TLC impregnated with 10 % aqueous Ag NO_3 developed with light petroleum - methylene chloride - acetic acid (8: 2 : 2 drops) , and antimony trichloride spray reagent revealed two adjacent violet spots .

Compound 5 :

Fractions eluted with methylene chloride : acetonitrile (90 : 10) yielded a greenish oily residue (1.4 g) , rechromatographed on a silica gel column (150 g, 60 x 2 cm) eluted with light petroleum - ether - acetic acid (50 : 50 : 0.2) and fractions 20 ml each were collected . Distillation gave 800 mg of colourless waxy material with R_f 0.4 (sys. II) , m. p . 53 - 56 ° C. IR (CH Cl 3 and / or nujol): ν 3550 - 3350 , 1730 , 1470 , 1380 , 1210 cm^{-1} . GC / MS analysis of this wax using the following conditions : megabore fused - silico capillary column (30 m x 0.5 mm) , coated with DB-5, 5 % phenylmethyl (varian , film thickness 1.5 μ); Helium flow rate 40 ml/min. Temp ; initial 50 ° C for 5 min. then 10 % min. to 270° C and isothermal for 5 min.

The composition of the components (table 1) was based on the mass fragmentation pattern [16,17] of each component and confirmation was achieved through computer matching with stored spectra of authentic reference materials.

Chromatography of the Chloroform Extract :

20 g of the chloroformic extract was chromatographed on silica gel columm (700 g , 115x7cm) packed in and eluted with light petroleum. Polarity was incereased with chloroform and methanol to yield several fractions (200 ml each) , monitored by TLC using (sys. III) , ammonia , UV and anisaldehyde- H_2SO_4 for visulization. The similar fractions were pooled, concentrated to give the following compounds :

Compound 6 :

Fractions eluted with 60 % $CHCl_3$ were concentrated to give (1.1g). This residue was rechromatographed through flash chromatography on silica gel column (40 x 3 cm) using $CHCl_3$ - Et_2O - Me OH (90 : 2 : 8) . The fast running bluish band (UV lamp) was eluted and crystallized from ethyl acetate to yield 38 mg yellow needles with R_f 0.67 (sys. III) ; mp 224 - 226 ° C ; gave positve flavonoid tests IR (KBr) : ν 3420 , 1655 , 1610 , 1025 cm^{-1} ; UV (MeOH) λ 265 and 342 nm displaced by addition of Na OMe and Al Cl_3 / HCl (table2). MS : m/z (rel . int . %) 314 (M^+ , 100), 313 (10.1) , 286 93.9) , 285 (17.8) , 284 (3.8) , 167 (9.0) , 166 (1.2) , 148 (3.0) , 138 (3.3) , 137 (1.3).The 2 D ^1H / ^1H COSY and ^1H / ^{13}C HETCOR are illustrated in table 3.

Compounds 7 and 8 :

Fractions eluted with chloroform showed two flavonoidal spots (syst. III) with R_f 0.59 and 0.48 respectively. Rechromatography of the residue (0.9 g) on silica gel column (50 g , 50 x 1 cm) eluted with benzene - methanol (9:1) resulted in the elution of compound 7 followed by 8 .

Compound 7 :

Was purified by PTLC (silica gel , benzene - methanol , 9: 1) which provided 14 mg of pale yellow micro needles (methanol) wiht m.p. 259 - 262 ° C . It gave brown colour with $FeCl_3$. yellow colour with NaOH (T.S.) and reddish with Mg /HCl. This compound did not reduce Fehling's solution neither before or after hydrolysis. IR (KBr) : ν 3550 - 3300 , 1660 , 1605 , 1365 cm. $^{-1}$ MS : m/z (rel . int. %) 314 (M^+ , 100) , 313 (22.6) , 299 (84.2) , 119 (14.2) , 118 (3.2) , 69 (10.5) ; UV (MeOH : λ 272 and 340 nm displaced by the addition of NaOMe , $AlCl_3$ and NaOAc (Table 4) .

Compound 8 :

The pooled fractions containing compound 8 was subjected to crystallization (MeOH) to yield 56 mg of pale yellow flakes, R_f 0.48 (sys. III) m.p. 284 - 276° C , it gave yellow colour with NaOH and $AlCl_3$ solutions and did not reduce Fehling's solution before or after hydrolysis . IR(KBr) : ν 3310 , 1650 , 1610 , 1370 cm^{-1} .MS : m/z (rel. int . %) 300 (M^+, 48.7) , 299 (3.7) , 285 (30.1) , 282(25.0) , 257 (38.6) , 139 (13.9) , 121 (5.5) , 119 (13.81) , 118 (9.2), 69 (100) , 53 (12 .1) . UV (Me OH) : λ 272 and 332 nm displaced by the addition of NaOMe , Al Cl_3 / HCl and NaOAc , (Table 2) .

The ^1H and ^{13}C NMR spectral data of compound 8 are shown in Table 4 .

Compound 9 :

Fractions eluted with 4% methanol yielded upon crystallization (MeOH) 20 mg of yellow needle crystales with R_f 0.45 (sys. III) ; m. p . 348 ° C ; gave positive results with the flavonoidal tests and negative Fehling's solution test before and after hydrolysis. IR (KBr) : ν 3300, 1660 , 1610 , 1035 cm^{-1} ; MS : m/z (rel . int . %) 270 (M^+ , 100) , 269 (14.9) , 242 (15.6) , 153 (20.2) , 152 (11.8) , 124 (11.3) , 123 (2.6) , 121 (3.3) , 118 (9.1) ; UV (MeOH) : λ 265 and 330 nm displaced by the addition of Na OMe , Al Cl 3 / HCl and NaOAc (Table2) .

Chromatography of the Ethyl Acetate Extract :

About 3.8 g of the ethyl acetate extract was chromatographed on silica gel column (200 g , 60 x 3 cm) eluted with ethyl acetate and the polarity was increased by methanol. The pooled fractions were monitored by TlC using (system IV) anisaldehyde - H_2SO_4 and ammonia vapours for visualization. Similar fractions were pooled, concentrated to yield the following compounds :

Compound 10 :

Fractions eluted with (5% methanol) yielded 720 mg of white granular powder (Me OH) with R_f 0. 59 (sys. IV) ; m.p. 280 - 282° C ; gave positive Molish's , Liebermann's and Salkowski's tests ; also reduced Fehling's solution after acid hydrolysis . IR (KBr) : ν 3550 - 3100 , 2940 & 2910, 1635 , 1470 , 1375 , 1170 , 1090 , 1030 cm^{-1} . MS : m/z (rel . int . %) 414 (M^+). Acid hydrohysis (50 mg , 7 % H_2SO_4) yielded an aglycone (20 mg) white needles ($CHCl_3$ / MeOH) with m. p . 140° C . The aqueous solution was chromatographed against authentic sugars (PC Whatmann NO.1, system V and aniline phthalate as detecting reagent) .

Compounds 11 and 12 :

Fractions eluted with methanol (10 %) showed two major flavonoidal sposts with R_f 0.37 and 0. 25 (sys. IV). The residue (1.4 g) was rechromatographed on silica gel column (100 g , 50 x 2 cm) eluted with ethyl acetate and increased with methanol to provide two major fractions I & II .

Compound 11 :

This compound was isolated and purified from fraction 1 (4% Me OH) by preparative HPLC on a resolve C_{18} column . (30 m x 7.8 mm) using acetonitrile - water (26: 74) as a mobile phase at a flow rate 3ml / min and a UV detector set at 254 nm , yielded 25 mg of yellow micro needles (Me OH) showing m.p. 227 - 229° C , gave posilve Fehlings solution test after hydrolysis. I R (KBr) : ν 3500 - 3100 , 1650 , 1600 , 1070 , 1030 , 990 cm^{-1} .MS .

m/z (rel . int . %) 269 (M^+, 17) , 242 (21) , 153 (19) , 152 (12) , 124 (15) , 121 (12) and 118 (14) ; UV (Me OH) : λ 265 and 335 nm displaced by the addition of NaOMe ,$AlCl_3$ - HCl and Na OAC (Table 2) .Acid hydralysis yielded an aglycone showing m.p. 348° C.

Compound 12 :

Fraction II (6% methanol) was subjected to crystallization to give 15 mg of yellow granular compound with R_f 0.25 (sys. IV) ; m.p . 238° C ; gave postive Fehling's solution test after acid hydrolysis . IR (KBr) : ν 3450 , 1655 , 1090 , 1050 , 1025 cm^{-1} . MS : m/z (rel . int . %) 286 (M^+ , 100) , 258 (21) , 153 (28) , 152 (7) , 134 (14) . UV (Me OH) : λ 252 and 345 nm displaced by the addition of Na OMe , $AlCl_3$-HCl and NaOAc- H_3BO_3 (Table2). Acid hydrolysis yielded an aglycone showing m. p. 325 - 327° C.

Investigation of the Sesquiterpene Lactones :

A sample of air-dried whole plant (1 Kg) was extracted with a mixture of methanol - ether - light petroleum (10 L ,1: 1:1) . The residue (41 g) was dissolved in 500 ml of methanol and kept in refrigerator for 48 hrs then filtered. The filterate was concentrated under vacuo (35°C) and the residue (29g) was chromatographed on silica gel column (900 g , 80 x 7 cm), eluted with light petroleum and increased with ether then methanol. The pooled fractions were examined by TLC (sys. IV) and, similar fractions were collected together .

Compound 13 :

Fractions eluted with 10% methanol was concentrated and rechromatographed over a silica gel column (30 x 3.5 cm) developed by ether-methanol (98 : 2) to afford two main fractions. The second fraction was (tlc promising) subjected to further purification using charcoal followed by crystallization from methanol-light petroleum to furnish 160 mg of colourless needle crystals with R_f 0.5 (sys. IV) ; m. p. 145 - 146 °C ; IR (KBr): ν 3340 - 3300, 1760 , 1700 , 1655 cm^{-1} . The ^1H and ^{13}C NMR and the 2 D ^1H / ^1H COSY and ^1H / ^{13}C HETCOR are presented in Table 5 .

RESULTS AND DISCUSSION

The powdered plant Centaurea araneosa, was successively extracted with light petroleum , chloroform , ethyl acetate and ethanol 95% .

Colum chromatography of the light petroleum extract yielded five compounds : lupeal acetate 1 and lupeol 3 . Compound 2 was found to be a long chain acid . The identity of these compounds was based on the IR & MS data (16,17) .

Compound 4 was found to be a mixture of stigmasterol and β - sitosterol with a predominance of the former. Data obtained from mixture of reference samples of stigmasterol and β-sitosterol showed great similarity with compound 4 (TLC,IR & MS) . Similar mixtares have been encountered in many species of Centaurea [18,19] . Compound 5 showed low m.p. and negative Liebermann's and Salkowski's tests which suggested the presence of long chain hydrocarbon having a carboxylic function in its structure. The IR spectrum revealed the presence of C = O (17 30cm $^{-1}$) , - OH (3550 - 3350 cm $^{-1}$) besides CH_3 and CH_2 groups (1380 and 1470 cm $^{-1}$) .Tthe GC /Ms analysis (Table 1) revealed that compound 5 is a mixture of long chain hydrocarbons and acids (Tetradecanoic acid, Pentadecanoic acid Hexadecanoic acid Heptadecanoic acid , Dodeconoic acid, Tetradecane and Tridecane).

Chromatographic fractionation of the chloroform extract on silica gel column yielded four yellowish compounds. The colour reactions with NH_4OH and UV [20] as well as $FeCl_3$ and Mg / HCl indicated the flavonoidal nature of these compounds. They all gave negative Fehling's solution indicating their aglycone nature . Compound 6 showed a parent ion m/z 314 ($C_{17}H_{14}O_6$) and fragment ions m/z 167 , 166 and 148 which suggested the presence of one - OCH_3 and one - OH group in ring A&B [21]. The UV spectrum (MeOH) showed (Table 2) two absorption bands at 265 and 342 nm also the main and secondary absorptions were similar to those reported for tetrasubstituted flavones[22]. The crucial placement of hydroxyl group in both rings at 4` and 5 was indicated by the UV shifts with NaOMe and Al Cl_3 (Table 2). Heteronuclear $^1H/^{13}C$ correlation (HETCOR, Table 3) gave full structural assignments for compound 6 to be verified as velutin. The obtained data also were compared with those reported (m. p. , IR, MS) for velutin previously isolated from Ceanothus velutinus [23,24] .This is the first report about the occurrance of such a structure in the genus Centaurea .

Compound 7 was identified as cirsimaritin through MS and IR analysis and the structure was confirmed by comparison with the reported data for cirsimaritin [25,26] .

Compound 8 was identified as hispidulin. Its UV (MeOH) spectrum showed two absoption bands at 272 and 332 nm which suggested flavone skeleton ,displaced by NaOMe, $AlCl_3$ - HCl and NaOAc (Table 2) which indicated the presence of free - OH at C - 4` , 5 and 7 and also implied C - 6

oxygenation as well as the absence of band II shift in $AlCl_3$,$AlCl_3$- HCl suggested that the B- ring has no O-dihydroxy substitution. The MS showed a parent ion m/z 300 (C_{16} H_{12} O_6) and fragment ions at m/z 282 , 257 , 121 . The ^1H and ^{13}C NMR were basically the same as those reported for hispidulin [27,28]. Compound 9 was identified as apigenin through direct comparison of its (m.p, TLC, IR, MS and U V) with those of authentic apigenin .

Chromatographic fractionation of the ethyl acetate extract led to the isolation of three compounds . The three compounds are glycosides as they gave postive Molish's test . Compound 10 was identified as β . Sitosterol glucoside . A cid hydrolysis yielded an aglycone identical to β - sitosterol by direct comparison (m.p., co -TLC , IR & MS) with authentic β - sitosterol , and the sugar was identified as glucose . Compounds 11 & 12 were found to be apigenin 7-O-glucoside and luteolin 7-O-glucoside. Acid hydrolysis yielded glucose and aglycones identical to apigenin and luteolin (compared with m.p. , TLC , IR , MS and UV) with authentic samples.

Finally the powdered plant was extracted with a mixture of methanol - ether -light petroleum (1:1:1) and the chromatographic fractionation led to the isolation of a sesquiterpene lactone. The IR showed γ - lactone (1760 cm^{-1}) - OH group (s) (3340 - 3300 cm^{-1}), ester C = O (1700 cm^{-1}) as well as C = C (1655 cm^{-1}) . The NMR spectra showed typical signals for cnicin, a germacranolide sesquiterpene lactone. The structure was confirmed by ^1H and ^{13}C (HETCOR, Table 5) and direct comparison (m.p.IR,^{1}HNMR) with those reported for cnicin [6,8&19] previously isolated from several Centaurea species.

This , to our knowledge is the first report about the constituents of Centaurea araneosa .

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Table (1) : GC/ MS of Compound 5 .

Peak No	Scan time	M+	Important ions m/z	Mol. formula	Name
1	120	-	-		Not identified
2	215	184	43,57,71,85 99 , 169 , 170.	$C_{13}H_{28}$	Tridecane
3	303	184	iso		
4	384	198	as before+169, 183.	$C_{14}H_{30}$	Tetradecane
5	462	-	-	-	Not identified
6	535	200	43,59,60,73,85, 155,183.	$C_{12}H_{24}O_2$	Dodecanoic acid
7	589	-	-	-	Not identified
8	668	228	43,59,60,73,71, 183, 211.	$C_{14}H_{28}O_2$	Tetradecanoic acid
9	723	242	43,59,60,71,73, 197, 225.	$C_{15}H_{30}O_2$	Pentadecanoic acid
10	816	256	43,59,60,71,73, 211, 239.	$C_{16}H_{32}O_2$	Hexadecanoic
11	887	270	43,59,60,71,73, 225, 253.	$C_{17}H_{34}O_2$	Heptadecanoic acid
12	942	-	-	-	Not identified
13	1029	-	-	-	Not identified

Table (2): The UV Spectral Data of the Flavonoidal Compounds.

Comp.	MeOH	MeOH+ NaOMe	MeOH+ Al Cl 3	MeOH+AlCl3 - HCl	MeOH NaOAc	MeOH+ NaOAc -H3BO3
6 Band I	342	400	383	383	345,400	345
6 Band II	265	256	270	270	263	263
7 Band I	340	395	366	355	395	345
7 Band II	272	265,270	276	276	270	270
8 Band I	332	392	357	352	328	340
8 Band II	272	272	276,300	280,300	275	272
9 Band I	330	320,390	345,380	337,378	340	335
9 Band II	265	270	270,297	270,293	267	265
11 Band I	335	380	345,380	340,380	345	340
11 Band II	265	265	270,295	272,295	265	263
12 Band I	345	390	420	355,385	365	365
12 Band II	252	260	270	270	255	255

Table (3): The NMR Spectral Data of Compound 6

Position	COSY	H [ppm, J (H3)]	HETCOR	C*
2			(no correlation)	161.37,s
3		6.97,s		115.75,d
4			(no correlation)	181.95,s
4a			(no correlation)	104.66,s
5			(no correlation)	163.99,s
6		6.38,d,j=2.1		97.97,d
7			(no correlation)	165.09,s
8		6.81,d,J = 2.1		92.69,d
8a			(no correlation)	157.23,s
1'			(no correlation)	121.32,s
2'		7.61,m		120.47,d
6'				110.21,d
3'			(no correlation)	148.03,s
4'			(no correlation)	150.88,s
5'		6.94,d,J=8.7		103.33,d
7 - OCH_3		3.90,s		65.05,d
3' -OCH_3		3.88,s		55.98,d
5-OH		12.98,s		
4'-OH		3.34, br.s		

*Multiplicities were determined by APT pulse sequence.

Table (4): ^{1}H and ^{13}CNMR Spectral Data of Compound 8

Position	H J in H_z	C*
2	-	163.74,s
3	6.61,s	94.19,d
4	-	182.06,s
4a	-	152.75,s+
5	-	152.36,s+
6	-	131.29,s
7	-	157.17,s
8	6.78,s	102.32,d
8a	-	104.04,s
1'	-	121.20,s
2',6'	7.93,d(8.9)	128.37,dx 2
3',5'	6.95,d.(8.9)	115.90,dx 2
4'	-	161.11,s
6-OMe	3.79,s	59.90,q
5-OH	10.54,s	-

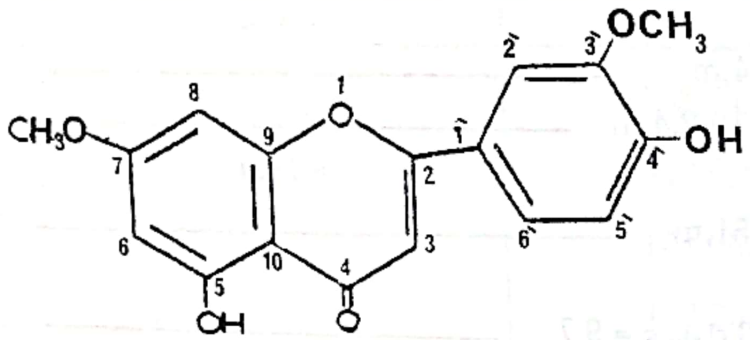
* Multipicites were determined by APT and DEPT pulse sequencies , Assignments were made by 2 D ^{1}H / ^{1}H COSy and ^{1}H / ^{13}C HETCOR experiments .

+Assignments may be interchanged

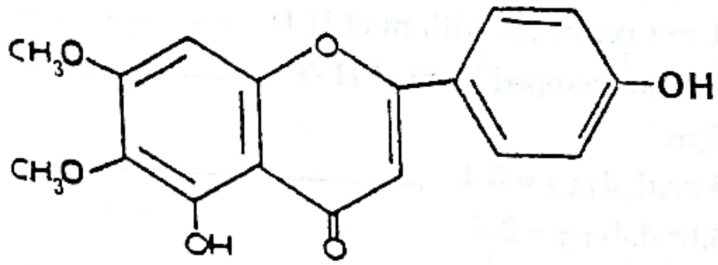
Table(5): NMR Spectral Data for Compound 13

H	^{1}H-^{1}H COSY	δ (J, Hz)	HETCOR	C*
1		5.04,m		129.14,d
2		2.10-2.4,m		25.56,t
2'				
3		2.51,m		33.77,t
3'				
5		4.89,d,$J_{5,6}$ = 9.7		127.49,d
6		5.24,dd,$J_{6,5}$=9.7,$J_{6,7}$=8.4		76.19,d
7		3.27,m (coincides with m of H - 4`` b)		51.62,d
8		5.01,m (coincides with m of H-1)		72.52,d
9		2.43,m overlapped by m of H -3		47.69,t
9`		1.86,m		
13		6.08,br.d, $J_{13,7}$ = 3.4		123.55,t
13`		5.73,br.d,$J_{13`,7}$ = 2.6		
14		1.45,s		16.34,q
15		4.09,dd,$J_{15,15`}$ =13.9 , $J_{15,OH}$ = 4.8 (after exchange br. d,J=13.9)		
15`		3.88,dd,$J_{15`,15}$=13.9,$J_{15`,OH}$ =5.6(after exchange br.d, J=13.9)		58.98
15 - OH		4.93,d		
3``		4.37,m		70.05,d
3``OH		5.16,d,$J_{OH,3``}$ = 5.2		
4``a		3.49,m (after exchange dd, J 4`` a ,b = 10.5,$J_{4``a,3``}$= 5.3)		
4``b		3.27 ,m (coincides with m of H-7)		65.31,t
4`` -OH		4.7,t		
5``a		6.23,d,$J_{5``a,b}$ = 1.6		
5``b		5.98, br.s		125.56,t

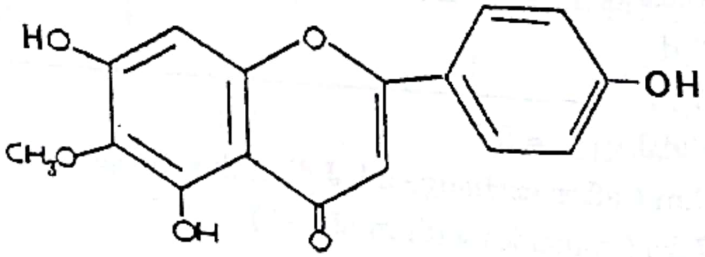
*multiplicities were determined by APT and DEPT pulse sequences + six singlets at 169.44 (CO), 164.78 (CO), 144.19,141.59, 136.16 and 131.79.



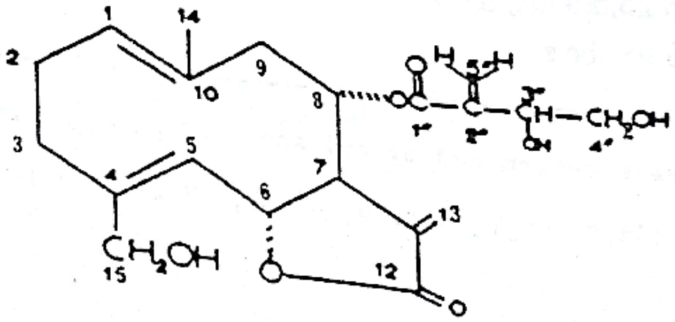
Velutin



Cirsimaritin



Hispidulin



Cnicin,

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دراسة المحتويات الكيميائية لنبات سنتاوريا أرانيوزا « سناريه » الذي ينمو فى مصر

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في هذا البحث تم استخلاص النبات وتجزئة الخلاصة الي خلاصة ألاثير البترولي وخلاصة الكلورفورم وخلاصة خلات الاثيل والكحول ولقد تم تحليل هذه الخلاصات باستخدام كروماتوجرافيا العمود كلا علي حده ومن ثم فقد تم فصل خمسة مركبات من خلاصة الأثير البترولي وهي خلات اللوبيول ، اللوبيول . حمض دهني طويل السلسلة وخليط ستيرول ومادة شمعية تم تحليلها باستخدام جهاز كروماتوجرافيا الغاز المتصلة بجهاز طيف الكتلة.

ومن خلاصة الكلوروفورم أمكن فصل أربعة مركبات فلافونيدية بعضها تم فصله لأول مرة من جنس النبات وهذه المركبات هي ڤلتين ، هيسبديولين ، كيرسمارتين وأبيجنين .

ومن خلاصة خلات الأيثيل تم فصل ثلاثة جلوكوزيدات وهي بيتا سيتو ستيرول جلوكوزيد، ابيجنين - ٧- جلوكوزيد - وليتيولين -٧- جلوكوزيد.وكذلك تم فصل سيسكويتربين لاكتون كنيسين .

ولقد تم التعرف علي هذه المركبات وتحديد التركيب الكيميائي لها بمقارنتها بعينات أصلية نقية وكذلك باستخدام التحاليل الطبيعية المختلفة متمثلة في التحليل الطيفي بالأشعة تحت الحمراء ، طيف الكتلة ، الرنين النووي المغناطيسي للهيدروجين والكربون -١٣ متمثلة في التحاليل ذات البعد الواحد وذات البعدين.

وهذا البحث هو أول تقرير عن محتويات هذا النبات الذي ينمو في مصر .