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NEW POLYACETYLENES, POLYENES AND TRITERPENOIDS FROM CARDUNCELLUS ERIOCEPHALUS

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ABSTRACT

The ethereal extract of Carduncellus eriocephalus was fractionated into methanol soluble and insoluble fractions. The methanol soluble residue was chromatographed on silica gel to afford : lupeol, lupeol acetate, taraxasterol and taraxasterol acetate. In addition, 1-pentene; 7,11-dimethyl-3-methylene-dodecan-1,6,10-triene; a new trans-5,16-diene-7-oxo-8,10,12,-14 tetrayne-octadecan-1-acetate-1,4-diol; cis-1,8-16-triene-11,13-diyne-heptadecan-15-ol and do deca-2E,4E,8Z,10Z teteraene, 1-oic isobutylamide were also isolated. The structure of these compounds was determined on the basis of their spectral characters and direct comparison with reference compounds.

INTRODUCTION

The plant genus Carduncellus is a scanty genus belonging to the tribe Cynareae (Asteraceae). In Egypt, this genus is represented by only two species; C. eriocephalus and C. mareoticus[1]. Previously, a tremendous work has been reported on the constituents of plants belonging to most of genera belonging to tribe Cynareae. Meanwhile several species from Silybum, Onopordon[2], Centaurea[2,6] and Atractylis[1,15] have demonstrated a reputed folkloric use and chemical or biological importance as well. However, only two reports have been recorded on plants belonging to the genus Carduncellus. Certainly, C. cearuleus[16] and C. monspeliesium[17] are the only two species which have been investigated among the genus. These findings, collectively encouraged us to undertake a phytochemical study of C. eriocephalus seeking a drug with potential pharamacological activity or chemical importance.

To our knowledge, this work is the first report about these constituents from this plant and the first isolation from the genus.

EXPERIMENTAL

Material and methods:

The plant material used in this study was the whole plant Carduncelllus eriocephalus Boiss var. albiflora. The plant was collected from Sinai (St. Catherine) in spring 1989 and kindly identified by Prof. Nabil El-Hadidi, Prof. of Taxonomy, Faculty of Science, Cairo University, Egypt. The plant was air dried, powdered and a voucher specimen was kept at the Department of Pharmacognosy, Faculty of Pharmacy, University of Zagazig, Egypt.

The ^{1}Hnmr spectra were recorded ($CDCL_3$/TMS) on Bruker WM400; MS were recorded on Varian MAT-711 (70 ev); UV spectra were recorded on Schimazadu UV-260; IR spectra were recorded on Beckmann 4210; Silica gel 30-60 μ Merck for flash column and Silica gel G F-254 for PTLC; all solvents were analytical reagents.

Extraction and fractionation:

The air dried plant (0.5 kg) was exhaustively extracted with a mixture of ether-light petroleum 40-60°C (1:1) by percolation (6 L) at room temperature. The combined extract was concentrated at reduced pressure to afford a viscous residue of 28 g. The latter was treated with five fold amount of methanol and kept at -15° for 24 h. The methanol filtrate was concentrated under vacuum to leave 22 g residue.

Column chromatography of extract:

The total residue (22.0 g) was charomatographed on Silica gel column, eluted by light petroleum and polarity was gradually increased with ether, collecting fractions 500 ml each, to afford 4 major fractions:

Fraction I: (4 g) eluted with light petroleum-ether (9:1), then subjected to PTLC, developed with light petroleum (100%) to give oily liquid compound **1** (20 mg); MS: m/z 70 (M^+, 60%).

Fraction II: Eluted with light petroleum-ether (8:2), showed 4 spots on TLC developed with light petroleum-ether (9.5-0.5). PLC, developed with the same solvent mixture (2 runs) yielded compound **2** as colourless oil (3 mg); R_f 0.82; MS: m/z 204 (M^+) and ^{1}Hnmr spectrum shown in (Table 1). Further elution of the PTLC gave an oily compound **3** (10 mg) with R_f 0.51; UV: 255, 272, 285, 310, 335, 360, 390, nm; ^{1}Hnmr spectrum shown in (Table 1) and MS: m/z 322 (M^+, 1%). Compound **4** (20 mg) with R_f 0.42; mp. 250-252°; MS: m/z 468 (M^+, 30%) identified as taraxasterol acetate. Further elution afforded compound **5** (12 mg); white powder, R_f 0.32; mp. 210-212° and MS: m/z 468 (M^+, 36%).

Fraction III: (7 g) eluted with light petroleum-ether (1:1) afforded compound **6** as needles (43 mg); mp 215-217°; MS: m/z: 426 (M^+, 90%) was identified as lupeol and compound **7** fine crystals (26 mg); mp 221-222°; M: m/z 426 (M^+, 46%).

Fraction IV: (3 g) was eluted with pure ether, and submitted to PTLC (light petroleum-ether 9:1, 2 developments) to yield compound 8 (Oily, 12 mg); MS: m/z 242 (M^+, 6%). Also, yielded compound **9** as colorless oil (3 mg); MS: m/z 247 and IR (CCl4): ν 3400-3395 (very weak, br) 2980-2820, 1640, 1580 cm^{-1}. Both compounds exhibited ^{1}Hnmr spectra (see Table 1) suggested the proposed structures.

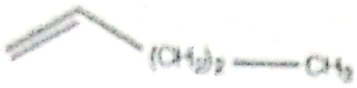
RESULTS AND DISCUSSION

Column chromatography followed by PTLC of the ethereal extract of C. eriocephalus yielded some known terpenoids; taraxasterol acetate **4**, lupeol acetate **5**, lupeol **6**, taraxasterol **7**, in addition to five olefins and polyacetylenes.

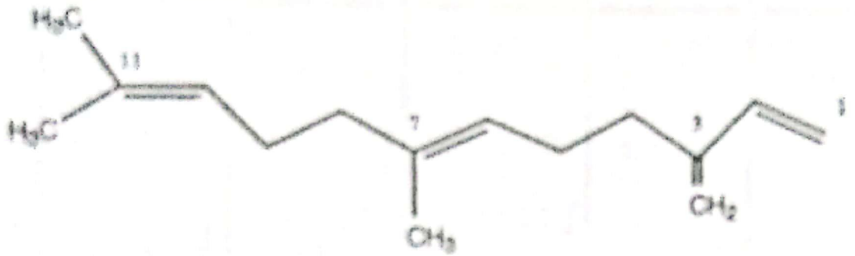
Compound **1** showed MS (m/z 70, M^+) suggestive of C_5H_{10} and ^{1}Hnmr spectrum confirmed the structure as 1-pentene.

Compound **2** exhibited MS (m/z 204, M^+) suggestive of $C_{15}H_{24}$. The ^{1}Hnmr showed three vinylic methyls (δ 1.68 s and δ 1.59 br,s); four methylenes (δ 2.22 m, 2.07 m); a terminal methylene (δ 5.24 dd, J = δ18.3 and 5.05 dd, J = 11,3.5); two vinylic protons (δ 6.37 br add, J = 18,11 and δ 5.09 m); a terminal methylene on a disubstituted double bond (δ 5.05 br s and δ 4.99 br,s). Identity was confirmed by comparison with spectra of similar compounds. Compound **3** showed MS (m/z 32, M^+) and ions collectively idicated an acetyl moiety; the UV spectrum indicated four sucessive acetylenic bonds with one double bond on each side[19]; identity was confirmed by comparison of data with spectra of homologous compouns. Screening the available literature[16,19], this compound to our knowledge, is a new natural product.

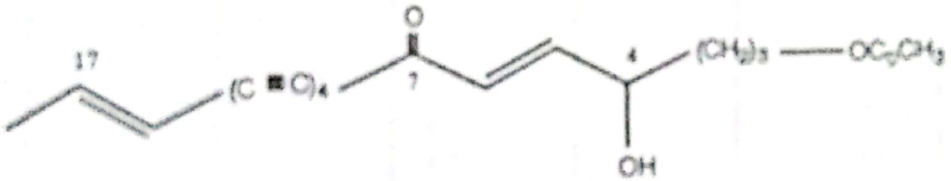
Similarly, compound **8** with MS (m/z 242, M^+) suggestive of $C_{17}H_{22}$). The ^{1}Hnmr indicated the presence of five adjacent (δ 1.9; H-4, H-5, H-6 and 2.01; H-3, H-7) two of them are allylic; two terminal methylenes (δ 4.93; 4.96; H-1, H-1` and 5.24, 5.46; H-17, H-17`); four vinylic protons (5.79, 5.39, 5.46, 5.92; H-2, H-8, H-9, H-16) with coupling constants ($C_{8\text{-}9}$ J = 11,7) indicative of the cis arrangement of $C_{8\text{-}9}$. The structure was proposed to be dehydrofalcarinol which may be the first in the genus. The final compound **9** with MS (m/z 247, M^+) informative of a nitrogenous substance and a suggested formula $C_{16}H_{25}NO$; the nitrogen was settled in an amide type from the very week IR (ν 3400-3395 and 1640 cm^{-1}); an N-isobutyl group was indicated by an N-methylene doublet at 3.16 (H-1`), a multiplet at 1.74 (H-2`) for a methine proton and a methyl doublet at 0.92 (H-3`, H-4`). A trans terminal vinylic methyl (1.77, dd, J = 7, 1.5) in conjugation with a cis double bond, with coupling constant (J = 10,11) obviously proved the cis placement of C_8-$_9$, while the large constants of C_9-C_{10}-C_{11} (J =15) together with a small constant of C_{11}-C_{12} (J =1.5) proved the cis-trans arrangement of C_8-C_9 and C_{10}-C_{11}. In addition. the coupling constant of $C_{2\text{-}3}$ (15 Hz), $C_{3\text{-}4}$ (10 Hz) and $C_{4\text{-}5}$ (15 Hz) indicated the trans structure of $C_{2\text{-}3}$ and $C_{4\text{-}5}$ double bonds. The structure was finally confirmed by comparison with a series of spectra of similar compounds.



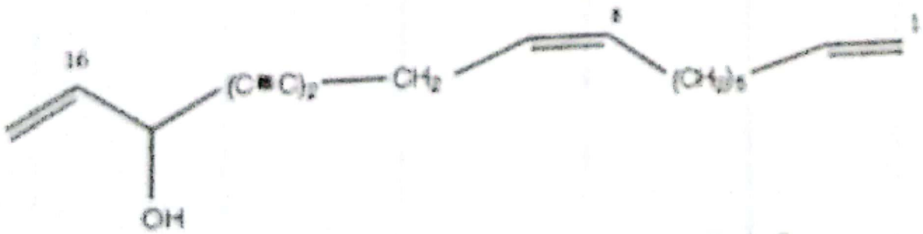
1-pentene: 1



7,11-dimethyl-3-methylene-dodeca-1,6,10-triene: 2



Trans 5,16-diene-7-oxo-8,10,12,14-tetrayne-octadecan-1,4-diol, 1-acetate: 3



Cis 1,8,16-triene-11,13-diyne-heptadecan-15-ol: 8

N-(isobutyl)-2,4,8,10-tetraene-dodecanoic acid amide: 9

Table (1): 400 MHz ^{1}Hnmr ($CDCl_3$, TMS) of the Olefinic and Acetylenic Compounds.

H	1	2	3	8	9
H-1 trans	4.93 ddt	5.24 dd	4.23 t	4.93 dd	
H-1 cis	4.49 ddt	5.05 dd		4.96 dd	
H-2	5.82 ddt	6.37 brdd	2.03 dt	5.79 ddt	5.57 brd
H-3				2.01 m	8.18 ddd
H-4		2.22 m	4.57 ddt		6.16 brdd
H-5	0.98 t		6.44 m	1.9 m	5.08 dt
H-6		5.16 brt	6.3 dd		
H-7				2.01 m	
H-8		2.07 m		5.39 dt	5.25 brdt
H-9				5.46 dt	5.96 dd
H10		5.09 m		3.02 brd	6.28 dd
H-11					5.67 dq
H-12					1.77 dd
H-13		1.59 br s			
H-14		5.05 br s			
H-14'		4.99 br s			
H-15		1.68 br s			
H-16				4.9 brd	
H-17			5.83 brd	5.92 ddd	
H-17'			5.53 brd	5.24 dd	
H-18				5.46 dd	
C-Ac			1.85 dd		
N-isobutyl:			2.09 s		
H-1'					
H-2'					3.16 d
H-3'					1.74 m
H-4'					0.92 d

J (Hz): Compund 1: 1t = 18; 1c = 3; 2=18,11; 3-4=7; 5=7. Compound 2: 1t = 18,3; 1c = 11,3.5; 2=18,11. Compound 3: 4=7; 5=16,7; 6=16,5; 16-14; 17=13,4; 18=13,3. Compound 8: 1-2t =17, 1-2c=11; 1:1=7; 8=11,7;9=7,11; 10=7; 15-16=7; 16-17 c= 11; 16-17 t = 17. 17:17=3. Compound 9: 2,3=15;3,4=10; 4,5=15,10; 5=15,7; 8=11,7; 9=10; 10=15; 11=15,7; 12=7,1.5.

Although, the amines and amides are reported in different genera of the Compositae[20], yet compound 9 appears to be unusual in the tribe Cynareae. Hence the plant alkamines content requires further investigation.

In comparison with C. caeruleus, which was previosuly investigated[18], it could be concluded that the chloroepoxy-, and the aldehyde derivatives of the acetylenes are not detected in the species C. eriocephalis.

To our knowledge, this is the first report about the chemistry of C. eriocephalus and the first isolation of these compounds from the genus. Meanwhile, isolation of the other constituents and screening for biological activity is in progress.

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مركب جديد من نوع عديد الاستيلينات بالإضافة إلى أوليفينات وتربينيات ثلاثية من نبات كاردينوسيلس إيريوسيفالس (الشاكسوكا)

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ينتمى هذا النبات إلى العائلة المركبة تحت فصلية السيناريا وهذه الفصيلة تشتهر بعدد كبير من النباتات التى تستخدم فى الطب الشعبى وحيث تم من قبل دراسة عدد كبير منها وفصل عدد من المركبات الهامة .

وفى هذه الدراسة تم فصل ٤ مركبات من نوع عديدة الاسيتلينات ثبت أن واحداً منها مركب جديد يفصل لأول مرة بالإضافة إلى عدد من المركبات المعروفة من نوع التربينات الثلاثية الإستيرولية والأوليفينات.

وتم اثبات التركيب البنائى لهذه المركبات باستخدام الطرق الطيفية والرنين النووى المغناطيسى (٤٠٠ ميجاهرنز) والجديد أيضاً أن هذه المركبات تفصل لأول مرة من هذا النبات.