

A NEW FUROCLERODANE FROM ERIGERON CANADENSIS L.

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ABSTRACT

The re-investigation of *Erigeron canadensis* L. (*Conyza canadensis* L.) afforded two conycephaloid derivatives, in addition to β -sitosterol, stigmasterol, caryophyllene epoxide and oleanolic acid. The structures of these compounds were established on basis of spectral methods and comparison with reference compounds.

INTRODUCTION

The plant genus *Erigeron* (*Conyza*) is a genus belonging to tribe Astereae (Asteraceae). In Libya, this genus is represented by only three species⁽¹⁾. The current literature concerning *Erigeron canadensis* L. described the isolation of acetylenic derivatives, tetrahydromethyl farnesene and α - trans bergamotene⁽²⁾. Recently there has been eight identified sesquiterpene hydrocarbons⁽³⁾.

Until the twenties of this century *E. canadensis* was an official drug in the USA and in the countries of the British Commonwealth. Besides its use in folk medicine, it used to be recommended in official medicine, as a haemostyptic, diuretic, antidiarrhoeic, astringent and anthelmintic⁽⁴⁻⁶⁾. Of particular interest are however, reports that *E. canadensis* had a favourable effect on spondylarthritis and chronic arthrosis of the spine⁽³⁾, acting in these cases also as diuretical. Good results were obtained with it, also in other rheumatic diseases and in gout. In a recent study, it was found that the petroleum ether and ethanolic extracts have a significant anti-inflammatory effect⁽³⁾. Therefore it seemed to be necessary to carry out the present work.

EXPERIMENTAL

Material and Methods :

The air dried plant material was collected in February 1991 from Tripoli, Libya. It was authenticated by Prof. Dr. A. El-Gadi, Botany Departement, Faculty of Science, Al-Fateh University. Voucher specimen of the identified plants was kept at the Pharmacognosy Dept., Faculty of Pharmacy, Zagazig University.

$^1\text{Hnmr}$ spectra were recorded in CDCl_3 , with Bruker WM400. The ms spectra were recorded by Varian MAT 711, 70 ev, direct inlet. The ir spectra were recorded by Bechmann IR-9 (CCl_4).

Extraction and isolation :

The air dried material (1kg) was extracted at room temperature by maceration with a mixture of methanol - ether (1:3) affording 30g. The obtained extract was fractionated by using column chromatography (silica gel) into four fractions .

Fraction I : eluted with petroleum ether (100%) .

Fraction II : eluted with Petroleum ether - ether (1:1) .

Fraction III : eluted with ether (100%) .

Fraction IV : eluted with ether - methanol (9:1) .

Fraction I contained some sesquiterpene hydrocarbons⁽³⁾ .

Fraction II afforded by PTLC (SiO_2 , GF 254, sys petroleum ether- ether, 1:1) 30 mg of **1** (R_f 0.52) and 50 mg of β - sitosterol and stigmasterol (R_f 0.73).

Fraction III afforded by PTLC (SiO_2), using ether-chloroform- benzene. (1:1:1) 60 mg of **2** (R_f 0.59) and 20 mg of **3** (R_f 0.37).

Fraction IV afforded by PTLC (SiO_2 , system: chloroform - methanol (9.5: 0.5) 18 mg of **4** (R_f 0.43).

RESULTS AND DISCUSSION

Re-investigation of the aerial parts of *Erigeron canadensis* L. by chromatographic methods resulted in the isolation of β -sitosterol, stigmasterol, 5 β -6 α -epoxy - 5,6 dihydrocaryophyllene **1**, oleanolic acid **2**; 17-oxo, 8,17-dihydroconycephaloide **3** and the new compound 1-hydroxy-17-oxo-8,17-dihydroconycephaloide **4**. In addition, compounds **1**, **2** and **3** are isolated for the first time from this plant.

The structure of these compounds could be confirmed unambiguously by the high field $^1\text{Hnmr}$ (Tables 1,2), ms, ir spectra, m.p. and CO-TLC.

The structure of compound **3** followed from the $^1\text{Hnmr}$ spectrum (Table 1) and spin decoupling. The typical downfield signals at δ - 7.51 (H-15, dd), 7.1 (H-16, dd) and 6.43 (H-14, dd) clearly indicated the presence of a β -substituted furan, while the signals at δ -6.81 (H-3, dd), 4.67 (H-19, dd) 4.30 (H-19', dd), 2.13 (H-10, dd) indicated the similarity of this compound with furanoditerpene lactone⁽⁷⁻⁸⁾.

The chemical shift of H-12 (δ -5.63) required an oxygen function at C-12, which following the typical coupling of H-12, could be present as a lactone ring.

However, the ir spectrum displayed a band at 1790 cm^{-1} due to 18,19-lactone, and band at 1735 cm^{-1} indicating the presence of another lactone⁽⁹⁾, the band at 880 cm^{-1} for the β -substituted furan. The ms spectrum showed that the molecular formula of this compound is ($\text{C}_{20}\text{H}_{22}\text{O}_5$); m/z (rel.int.) 342 (M^+ , 5%), 337 ($\text{M}^+ - \text{Me}$, 2%) 94 ($\text{C}_5\text{H}_2\text{O}_2$). All the previous data, confirmed that compound **3** is 17-oxo-8,17-dihydroconycephaloid⁽⁷⁾.

The ms spectrum of compound **4** (M^+ , 358), indicated an additional oxygen compared to **3**. This must be presented as a hydroxyl group.

Also the missing of H-1 α and the downfield shift of H-1 β indicate the position of the hydroxyl group at C-1. The spin decoupling confirmed this assumption. All the other signals were nearly similar to those of **3**.

Table 1 : $^1\text{Hnmr}$ spectral data of compounds **2** and **3** (400 MHz, CDCl_3 , TMS as Int. standard).

Hydrogen	Compound 3 (δ)	Compound 4 (δ)
H-1 α	1.34 dddd	-
H-1 β	1.90 dddd	4.49 dd
H-2 α	2.53 dddd	2.54 dd
H-2 β	2.30 dddd	2.5 dd
H- 3	6.81 dd	6.79 dd
H- 6 α	1.8 m	1.8 m
H- 6 β	1-3 m	1.3 m
H-10	1.73 dd	1.87 d
H- 11 α	2.12 dd	2.17 dd
H- 11 β	1.72 dd	2.08 dd
H- 12	5.63 dd	5.40 dd
H-14	6.43 dd	6.43 dd
H- 15	7.51 dd	7.51 dd
H-16	7.1 dd	7.1 dd
H-19	4.67 dd	4.67 dd
H- 19'	4.30 dd	4.30 d
H-20	1.10 s	1.1 s

J (Hz) 1 α , 1 β = 13; 1 α , 2 α = 4; 1 α , 2 β = 12; 1 α , 10=12; 1 β , 2 α = 2.5; 1 β , 2 β = 5; 1 β , 10 = 2; 2 α 12 β = 17; 2 α , 3 = 7; 2 β , 3=2; 6 α , 6 β = 16, 6 α , 19 = 2, 11 α , 11 β = 13; 11 α , 12 = 12; 11 β , 12 = 2.5; 14, 15 = 15, 16 = 1.5; 14, 16 = 1.

Table 2 : $^1\text{Hnmr}$ spectral data of compound **1** (400 MHz, CDCl_3 , TMS as int. stand.)

Hydrogen	δ	Hydrogen	δ
H-1	2.63 dd	H-10 α	1-68dd
H-3 α	2.30 m	H-10 β	1.70dd
H-3 β	1.77 m	H-12	4.87 brs
H-4 α	2.30 m	H-12	4.99 brs
H-4 β	1-42 m	H-13	1.02 brs
H-5	2.89 dd	H-14	1.00 s
H-7 α	2.09 ddd	H-15	1.45 s
H-7 β	1.94 dd		
H-8	1.44 m		
H-9	1.58 ddd		

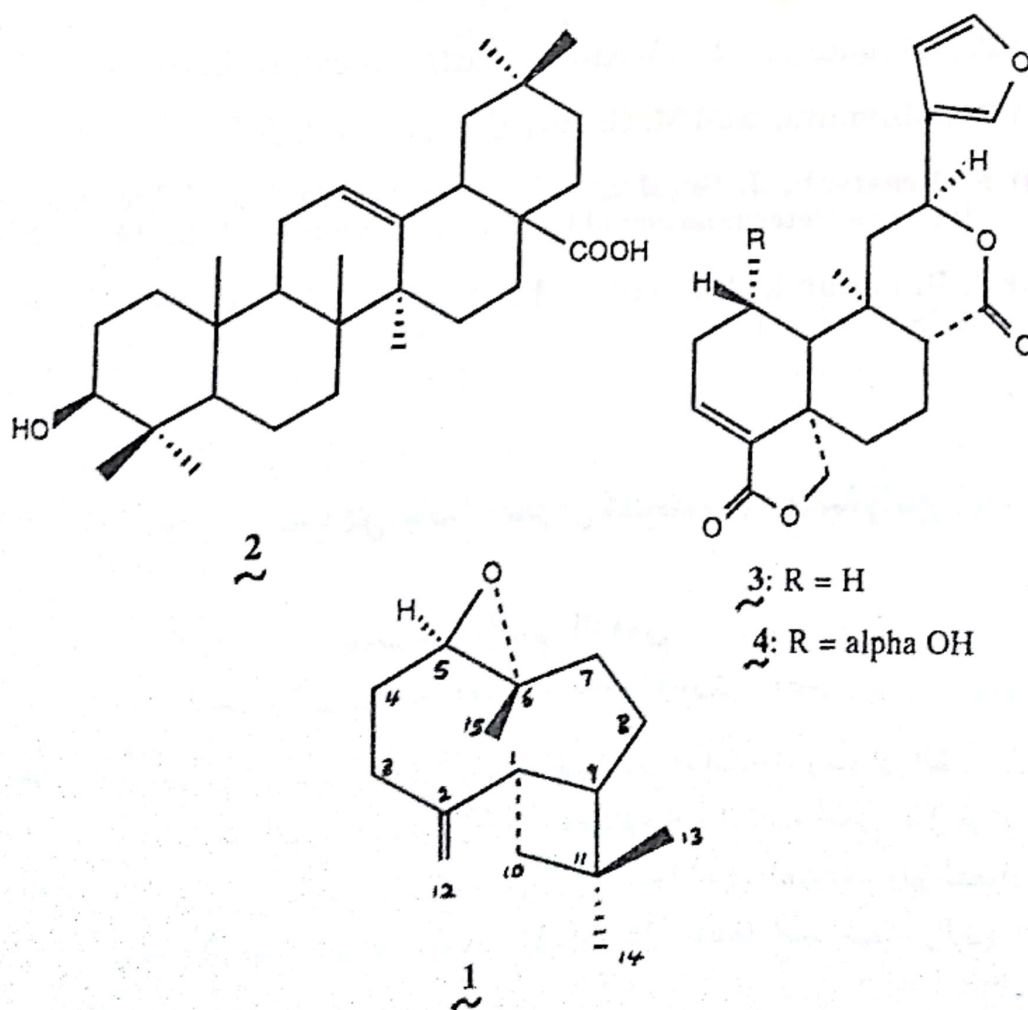
J (Hz) : 1,9 = 1,10 α = 9; 1,10 β = 11; 5, 4 α = 4; 5,4 β =11; 4 β , 3 α = 11; 4 β , 4 α = 14; 4 β , 3 β = 3; 7 α , 7 β = 12; 7 α , 8 = 2.

The ir spectrum of 4 showed the same bands of ir spectrum of 3 in addition to band at 3500 cm^{-1} for a hydroxyl group. Ms spectrum showed: m/z (rel. int.) 358.14 ($\text{C}_{20}\text{H}_{22}\text{O}_6$), 328 (100%) ($\text{M}^+ - \text{CH}_2\text{O}$), 312(30%), 94 (45%) ($\text{C}_5\text{H}_2\text{O}_2$)⁺

Compound 2 is a crystalline compound with m.p. ($310\text{-}311^\circ\text{C}$) and $^1\text{Hnmr}$ spectral data indicated that this compound is oleanolic acid. The Co-TLC confirmed this assumption.

The structure of compound 1 was easily deduced from the $^1\text{Hnmr}$ spectrum (Table 2), which showed signals characteristic for caryophyllene⁽¹⁰⁾.

The downfield shift of the H-15 at δ -1.45 indicates that H-15 is an epoxy methyl group; which confirmed by the upfield shift of H-5 (δ -2.89).



ACKNOWLEDGEMENT

The author thanks Dr. J. Jakupovic, TU. Berlin. Germany, for running the $^1\text{Hnmr}$ and ms. spectra .

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فيوروكليز ودان جديد من نبات إيريجرون كندينسيس (عشبة زامورا)

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يتم نبات إيريجرون كندينسيس (عشبة زامورا) في ليبيا وله استخدام واسع في الطب الشعبي . وفي هذا البحث تم دراسة هذا النبات كيميائياً وبطرق الكروماتوجرافيا المختلفة أمكن فصل مركب جديد من نوع التربينات الثنائية . بالإضافة إلى عدد من المركبات الأخرى المعروفة . وتم التعرف علي التركيب الكيميائي لهذه المركبات بإجراء الدراسات الطيفية مثل الأشعة تحت الحمراء والرنين النووي المغناطيسي ومطياف الكتلة وكذلك مقارنتها بعينات أصلية نقية من المواد المعروفة .