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A FURTHER NEW EUDESMAN DERIVATIVE FROM BROCCHIA CINEREA DEL. GROWING IN EGYPT

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ABSTRACT

Reinvestigation of the aerial parts of Brocchia cinerea Del. afforded a new eudesman sesquiterpene derivative : 11- Carboxymethyl-6 α- angeloyloxy - 1β, 4α, 8α-trihydroxy eudesm- 11(13)-ene. In addition, three known compounds have also been isolated. The structure of these compounds were established on basis of spectroscopic methods.

INTRODUCTION

Brocchia cinerea Del. represents one of the monotypic Anthemideae genera of the family Compositae which are characteristic of the north African flora[1]. The chemistry of the genus Brocchia has been previously investigated. Spiroketal, enolether polyines[1,2], coumarins linked with sesquiterpenes, several sesquiterpene lactones[2,3] and flavones[4,5] have been reported from this species.

EXPERIMENTAL

Plant Material :

The air dried aerial parts (about 500 g) collected from the eastern desert of Egypt, in April 1990. The plant was kindly idetified by Prof. N. El-Hadidi, Faculty of Science, Cairo University. A voucher specimen deposited in the faculty of Pharmacy, Zagazig University, Egypt .

Extraction and Fractionation :

The powder (500 g) was extracted with methanol: Diethyl ether: petroleum ether (1:1:1) and the extract was worked up as reported previously[7].

The CC fraction eluted with ether: methanol (3:1) was segregated over a silica gel column and eluted successively to yield three major fractions : I-Ether: Petrooleum ether (3:1), II-Ether and III-Ether: Methanol (4:1). PTLC (chloroform-methanol, 10:1) of fraction I afforded 10 mg of 8α, 13-diacetoxy -7,11-dehydro-11,13-dihydroanhydroverlotorin (R_f 0.8). Fraction II was purified by PTLC (Chloroform - Methanol, 10:1) to yield 15 mg of 13-acetoxy - 8 α - hydroxy - 7, 11 - dehydro - 11, 13 - dihydroanhydroverlotorin (R_f 0.3). PTLC (Ether) of fraction III afforded 20 mg 6α-angeloyloxy - 1β, 4α-dihydroeudesm-11(13)-en-8α, 12 olid (R_f 0.6) and -10 mg of compound 1 (R_f 0.2).

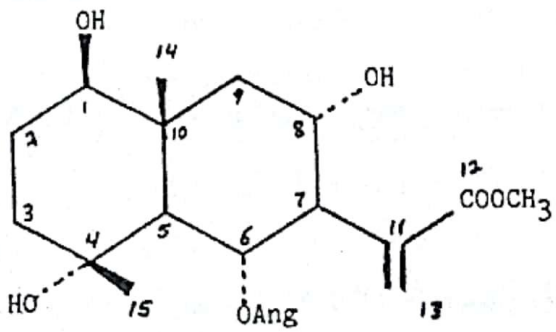
11-Carboxymethyl-6α-angeloyloxy-1β, 4α, 8α - trihydroxyeudesm -11 (13) ene. (Compound 1): colourless oil; ^{1}Hnmr: ($CDCl_3$: 400 MHz) : δ 3.42 (H-1, brdd, 7= 5, 11Hz); 1.74 (H-2α, dddd, j= 5,13,2 Hz); 1.64 (H-2B, dddd, j= 5, 11, 13: Hz); 1.57(H - 3α, br ddd, J= 5, 13 Hz); 1.77 (H-3 β, ddd, j=5, 13, 2 Hz); 1.89 (H - 5, d, j=10.5 Hz); 5.84 (H - 6, dd, J=10.5 Hz); 2.45 (H - 7, dddd, J=10.5, 3.5, 3 Hz); 4.40 (H - 8 β, ddd, J=10.5, 13,3.5 Hz); 1.16(H - 9α, brdd, J=13 Hz); 2.32 (H - 9β, dd, J=13, 3.5 Hz); 6.30 (H - 13, brs); 5.71 (H - 13, brs); 1.10 (H - 14, s); 1.21 (H -15, s); 3.80(-OCH_3, S); O-Ang: 6.05 qq, 1.92 dq, 1.83 dq.

MS m/z (rel. int.): 378 [M-H_2O] $^+$ [5] Calc. for C_{21} H_{30} O_6: 378], 279 [378 - O-Ang]$^+$ [1.5], 278 [378 - Ang OH]$^+$ [2], 261 [279 - H_2O]$^+$ [10]. 83 [C_4 H_7 CO]$^+$ [100]. 55 [83-CO]$^+$ [82]. IR $\lambda_{max}^{CCl_4}$: ν 3630 (OH), 1720 (C=CCO_2 R).

RESULTS AND DISCUSSION

The ^{1}Hnmr spectral data of compound I showed signals at δ 4.40 ddd (H-8β), δ1.10 S (H-14), δ1.21 S (H-15), δ5.84 dd (H-6) in addition to two broad singlets at δ 6.30 and 5.71 (H-13 and 13). Furthermore the presence of an angelate followed from the typical signals at δ 6.05 qq, 1.92 dq. and 1.83 dq. The down field shift of H-8β and the arise of a methly signal at δ 3.8 S indicated the presence of α - Oll at C-8 and a carboxymethyl group (- COO CH_3) at C-11. Spin decoupling allowed the assignment of all signals which led to the proposed structure. The configuration at C - 4 and C - 8 was deduced by comparing the chemical shifts with those of similar compounds[3,6]. Accordingly this compound was confirmed to be 11-carboxymethy1-6α-angeloyloxy-Iβ, 4 α, 8α–trihydroxyeudesm-11(13)-ene. The M S provided a supporting evidence for such structure with a molecular ion peak at m/z 378 [M^+ - H_2O] which fits nicely with the proposed structure.

In addition, structures of the known compounds were established to be 8α, 13 - Diacetory - 7, 11 - dehydro - 11,13 - dihydronanhy droverlotorin; 13 acetoxy-8α-hydroxy-7,11- dehydro - 11,13 - dihydroanhydroverlotorin and 6α - angeloyloxy - 1β, 4α-dihydroeudesm - 11(13) - en - 8α,12-Olide by direct comparison of their ^{1}H N M R data with those of authentic samples[2,3]



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مشتق سيسكويتيربينى يودزمانى جديد من نبات البروشيا سنيريا الذى ينمو فى مصر

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فى هذا البحث تم فحص و تجزئة خلاصة الاجزاء الهوائية لهذا النبات. ثم عن طريق كروماتوجرافيا العمود تم الحصول على ثلاثة اجزاء عرضت الى الفحص و التجزئة على كروماتوجرافيا الطبقة السميكة للحصول على اربعة مركبات ثبت ان احدهم جديد و تم تحديد تركيبة الكيميائى بواسطة الرنين النووى المغناطيسى (٤٠٠ ميجاهرتز) و طيف الكتلة و الاشعة تحت الحمراء ليتضح أنه:

١١ - كربوكسى ميثيل - ٦ الفا - انجيلويل أوكس - ١ بيتا ، ٤ الفا ، ٨ الفا - ثلاثى هيدروكس إيودزم - ١١(١٣) - إين.

اما المواد الثلاثة التى فصلت والمعروفة سابقا هى :

٨ ألفا ، ١٣ - داى اسيتوكس - ٧ ، ١١ - ديهيدو - ١١ ، ١٣ - دايهيدرو أنهيدروفرلوتورين.

والمركب الثانى : ١٣ - أسيتوكس - ٨ الفا - هيدروكس - ٧ ، ١١ - ديهيدو - ١١ ، ١٣ - داى هيدو أنهيدروفرلوتورين.

والمركب الثالث : ٦ ألفا - انجيلو بل أوكسى - ١ بتيا ، ٤ ألفا - داى هيدروإيودزم - ١١(١٣) - إين - ٨ الفا ، ١٢ - أوليد.