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WITHANOLIDES OF EGYPTIAN WITHANIA SOMNIFERA L. DUNAL

PART II: 20, 28-dihydroxy-1-oxo-witha-2,5,8(14), 24-tetraenolide

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ABSTRACT

The isolation of the title compound was reported in a previous publication. It is now characterized by NMR and mass spectral data as 20, 28-dihydroxy-1-oxo-witha-2,5,8 (14), 24-tetraenolide. This confirms the predominant character of chemotype III in the Egyptian wild plant.

INTRODUCTION

In a previous publication[1], the isolation of three withanolides from the alcoholic extract of Egyptian Withania somnifera L. (Dun) wild plant was reported. Two of such compounds were characterized as derivatives of 5B, 6B-epoxy-1-oxo-witha-2, 24-dienolide: substance A being 14,17, 20-trihydroxy derivative and substance C,4,14,17,20-tetrahydroxy derivative.

The present report deals with the characterization of substance B.

EXPERIMENTAL

Plant Material:

The material used in this investigation was the overground parts of Withania somnifera L. (Dunal)[1].

Isolation of Substance B:

The method of isolation of this compound was reported previously[1].

Characterization of the Compound:

NMR (CD_3OD) ppm (δ): 1.1 (s, 3H, 18-CH_3), 1.21 (s, 3H, 19-CH_3), 1.31 (s, 3H, 21-CH_3), 2.15 (s, 3H, 28-CH_3), 4.4 (s, 2H, C_{27}-CH_2), 4.25 (dt, 1H, 22-H), 5.7 (dd, 1H, 6-H), 5.9(d, 1H, 2H) and 6.9 (m, 1H, 3-H).

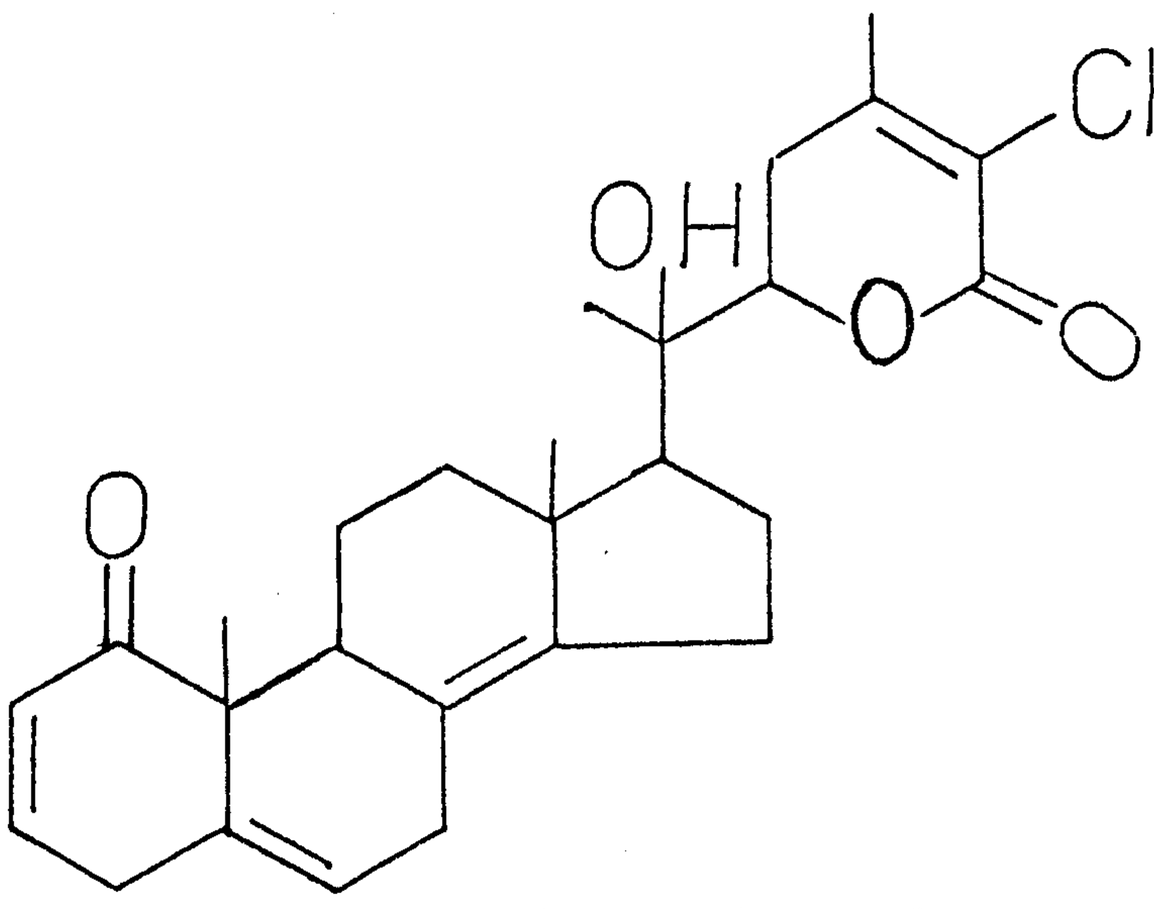
Mass Spectrum (m/e): (452, M^+), 434, 402, 372, 355, 312, 294, 268, 249, 238, 209, 185, 171, 155, 141, 124, 107, 96,79, 67 (100%, base peak).

DISCUSSION

The structure of Substance B was determined primarily through NMR and mass spectral studies. NMR proved the presence of 4 methyl groups corresponding to positions 18, 19, 21 and 28. The chemical shift of 21-CH_3 at 1.31 ppm indicated the presence of C_{20}-OH group[2,3] and the chemical shift of 28-CH_3 indicated Δ^{24} double bond. C_{27} Hydrogens appeared as a singlet at 4.4 integrating for 2 protons indicative of C_{27}-OH group. The appearance of C_{22}-H as muliplet (dt) at 4.25 is consistent with the absence of C_{17}-OH. This fact together with the appearance of the chemical shift of 18-CH_3 at 1.1 indicated

the presence of $\Delta^{8(14)}$ double bond[2,3]. Other evidence from the NMR indicated the Δ^{5} double bond (6-H as dd at 5.7) and Δ^{2} double bond (2-H and 3-H at 5.9 and 6.9 respectively).

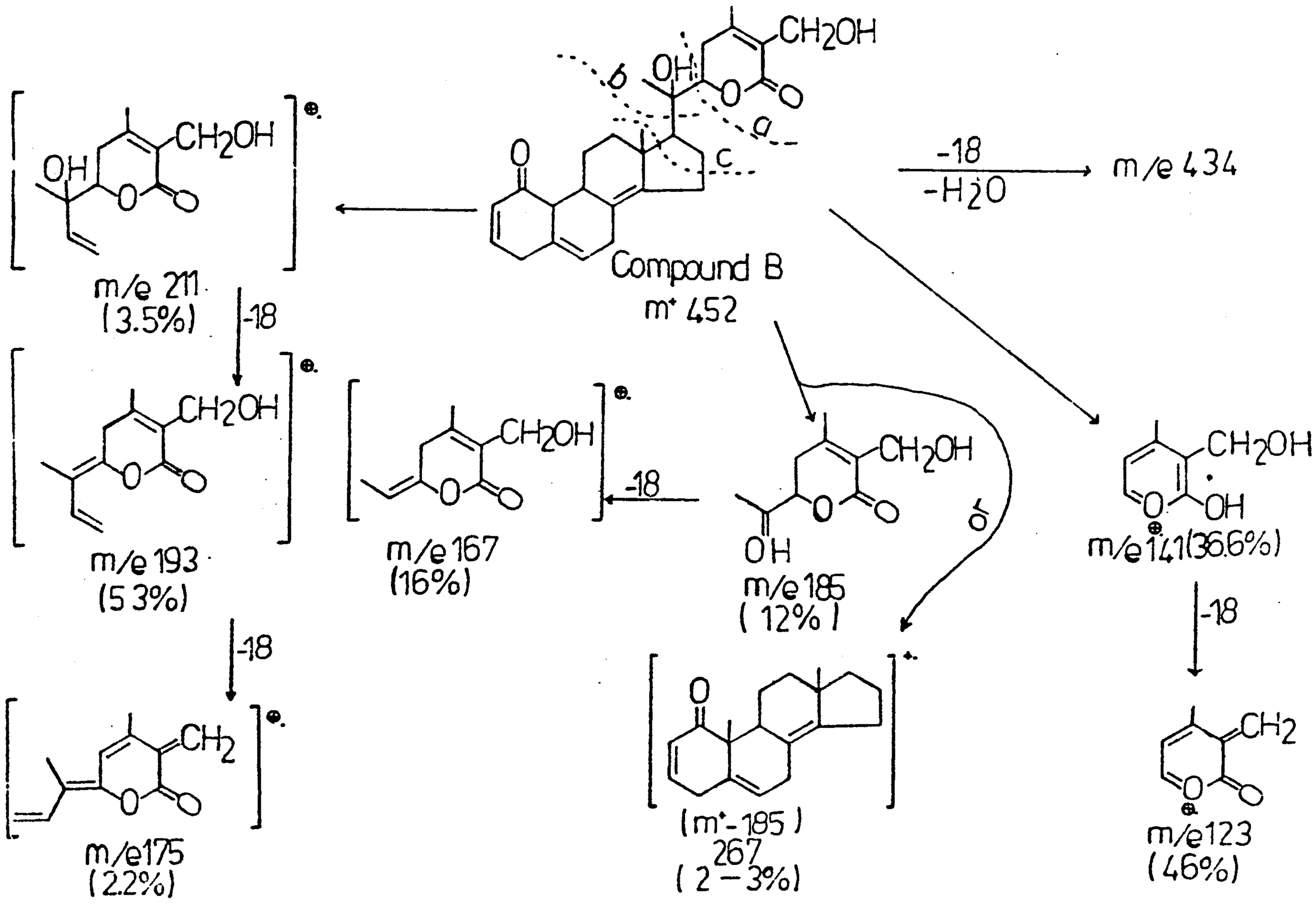
Mass Spectral (EI) data gave support of the structure proposed from NMR spectral analysis. M^{+} appeared at m/e 452, corresponding to $C_{28}H_{36}O_{5}$, with peaks as 434 (M^{+}-18), and main peaks at m/e 267, 211, 185, 167, 141 and 123. The proposed fragmentation pattern is shown in Fig. I and corresponds to pathways proposed for fragmentations of withanolides in the mass spectrum[2,4]. Thus substance B is identified as 20, 28-dihydroxy-1-oxo-witha-2, 5, 8 (14) 24-tetraenolide.



This structural type is typical for chemotype III of Withania somnifera L. (Dunal)[5,6], and confirms that the Egyptian wild Withania somnifera has predominantly chemotype III character.

It is noteworthy, that Abraham et al[5]. reported the isolation of a compound of similar gross structure to compound B, but did not give the data of their structural elucidation procedures used. Presentation of our characterization procedures is thus warranted.

Fig.I-Fragmentation Pattern Of Substance B



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الويثانوليدات من نبات ويثانيا سومنيفيـــــــــــرا

الجزء الثانى "٢٠ ،٢٨ ـ ثنائى ايدروكسى ـ ١ ـ أوكســـــو ـ
وثيا ـ ٢ ،٨،٥ (١٤) ،٢٤ ـ رباعى أنيولـيـــــــــــد

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تم وصف طريقة فصل المركب المذكور من الخلاصه الكحوليه لنبات ويثانيـا سـومنيفيرا فى نشرة سابقه ٠٠ وسمى مركـــب ب ٠

وقد تم التعرف عليه بواسطة دراسه خواصه الطيفيه باستخدام الرنيـــن النووى المغناطيسى وطيف الكتله وتبين أن تركيبه الكيميائى هو " ٢٠ ،٢٨ ـ ثنائى أيدروكسى ـ ١ ـ أوكســو ويثا ـ ٢ ،٥ ،٨ (١٤) ،٢٤ ـ رباعى أنيوليد"٠

ومن هذا مع ماسبق ذكره عن المركبين أ ،جـ فى النشرة السابقه يتضـــح أن نبات ويثانيا ســومينفيرا الذى ينمو بريا فى مصر ينتمى الى النـــــوع الكيميائى الثالث للنبـــــات ٠

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