

## 11-HYDROXYJASIONONE, A NEW SESQUITERPENE TYPE FROM *JASONIA MONTANA*

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**Key Word Index**—*Jasonia montana*; Compositae; Inuleae; sesquiterpenes; new skeleton; monoterpene; geranyl acetate derivative.

**Abstract**—The aerial parts of *Jasonia montana* afforded, in addition to known compounds, a sesquiterpene with a new carbon skeleton and a derivative of geranyl acetate. The structures have been established by high field NMR techniques and a possible biogenetic pathways for the new compounds are discussed.

### INTRODUCTION

From the small genus *Jasonia*, (subtribe Inulinae) three species have been studied [1-4]. From two species eudesmanes were reported [1, 4]. The roots from *J. montana* (Vahl.) Botsch. also gave such compounds [4]. We have now studied the aerial parts. The results are discussed in this paper.

### RESULTS AND DISCUSSION

The aerial parts of *J. montana* gave the thymol derivative **1**, isointermedeol [5], costic acid and the derived ketones **2** and **3** [6], the geraniol derivatives **4** [7] and **5**, luteolin-7,3-dimethyl ether [8], the seco-eudesmane derivative **6** [9] and the unusual eight-membered ring ketone **7** named 11-hydroxyjasonione.

The structure of the acetate **5** was easily deduced from its <sup>1</sup>H NMR spectrum (Experimental) which showed the typical signals of a prenyl acetate residue and those of an E-double bond. The chemical shifts of H-8 and H-9 required an oxygen function at C-7 and the broadened doublet at  $\delta$  2.81 (2H) indicated a methylene group which must be placed between two double bonds. Thus a geranyl acetate derivative was present where by allylic rearrangement a 7-hydroxy group was introduced.

The <sup>1</sup>H NMR spectrum of **7** (Table 1), the molecular formula ( $C_{15}H_{24}O_2$ ) and the <sup>13</sup>C NMR spectrum indicated that a bicyclic sesquiterpene was present. The <sup>13</sup>C NMR data showed the presence of a keto group ( $\delta$  212.9 s), a tertiary hydroxy group ( $\delta$  73.1 s) and a trisubstituted double bond ( $\delta$  126.8 d and 145.2 s). Furthermore, all <sup>1</sup>H NMR signals could be assigned by spin decoupling. Irradiation of the threefold doublet at  $\delta$  5.40, obviously due to an olefinic proton, changed the signal at  $\delta$  2.29(m) and sharpened the broadened doublet at  $\delta$  3.16, which itself was geminally coupled with the doublet at  $\delta$  3.43. The former showed a long range coupling with the threefold doublet at  $\delta$  2.36, which itself coupled geminally with the double doublet at  $\delta$  2.78. The chemical shifts of these four proton required one methylene group between a double bond and a keto group and a second one next to

Table 1. <sup>1</sup>H NMR spectral data of compound **7** ( $CDCl_3$ , 400 MHz)

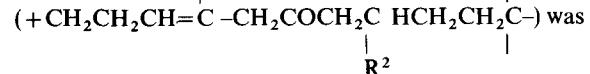
H	H
1 $\alpha$	1.95 ddd
1 $\beta$	1.56 ddd
2	2.29 m
3	5.40 ddd
6 $\alpha$	2.78 dd
6 $\beta$	2.36 ddd
7	2.59 dddd
8 $\alpha$	1.87 dddd
8 $\beta$	8 $\beta$
9 $\alpha$	9 $\alpha$
9 $\beta$	9 $\beta$
12	12
13	13
14	14
15 $\alpha$	15 $\alpha$
15 $\beta$	15 $\beta$

$J$  [Hz]: 1 $\alpha$ , 1 $\beta$  = 13; 1 $\alpha$ , 2 $\alpha$  = 1 $\alpha$ , 2 $\beta$  = 11; 1 $\beta$ , 2 $\alpha$  = 4; 1 $\beta$ , 2 $\beta$  = 7.5; 2 $\alpha$ , 3 = 2 $\beta$ , 3 = 3,15 $\beta$  ~ 2.5; 6 $\alpha$ , 6 $\beta$  = 15; 6 $\beta$ , 15 $\alpha$  = 1.5; 6 $\alpha$ , 7 = 4; 6 $\beta$ , 7 = 11.5; 7,8 $\alpha$  = 4; 7,8 $\beta$  = 11.5 8 $\alpha$ , 8 $\beta$  = 14; 8 $\alpha$ , 9 $\alpha$  = 4; 8 $\alpha$ , 9 $\beta$  = 12; 8 $\beta$ , 9 $\alpha$  = 8 $\beta$ , 9 $\beta$  ~ 4; 9 $\alpha$ , 9 $\beta$  = 15; 15 $\alpha$ , 15 $\beta$  = 15.5.

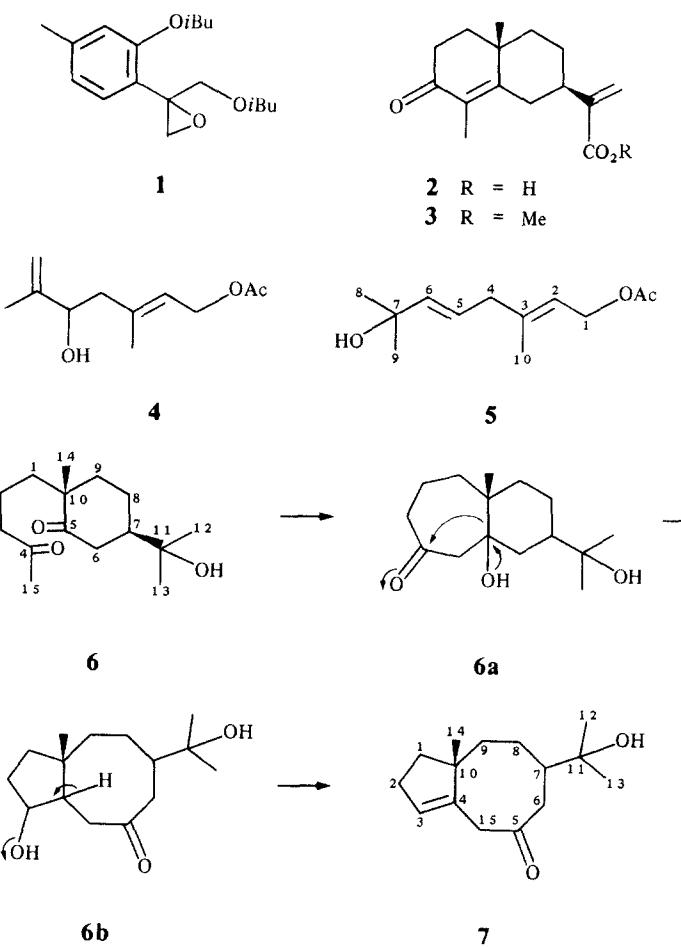
a keto group. The corresponding proton showed further couplings with a fourfold doublet at  $\delta$  2.59 (H-7) which itself was coupled with a pair of fourfold doublets at  $\delta$  1.87 and 1.32. Irradiation of these two signals collapsed the geminal coupled signals at  $\delta$  1.48 and 1.67 to double doublets. As these signals showed no further couplings next to the corresponding methylene group a quaternary carbon was present. Furthermore, the coupling partner of the olefinic proton ( $\delta$  2.29 m) was coupled with a pair of threefold doublets at  $\delta$  1.95 and 1.56 which both collapsed to doublets on irradiation at  $\delta$  2.29. This showed that the quaternary carbon was present next to the corresponding methylene group. Thus the complete sequence

R<sup>1</sup>

|



established. As three methyl singlets ( $\delta$  0.99, 1.11 and 1.21) as well as a tertiary hydroxy group was present, R<sup>1</sup> and R<sup>2</sup> could only be a methyl and a hydroxyisopropyl group.



The relative position of these groups followed from the NOE's on irradiation at  $\delta$  1.21. Clear effects were observed with H-6 $\alpha$ , H-6 $\beta$ , H-7 and H-8 $\alpha$ . Thus R<sup>2</sup> was the position of the isopropyl group and therefore the whole structure was settled. The relative configuration at C-7 and C-10 followed from NOEs between H-14, H-9 $\alpha$ , H-9 $\beta$ , H-1 $\beta$  and H-15 $\beta$  which itself, as already mentioned showed a long range coupling (*W*) with H-6. These results together with couplings observed (Table 1) required a configuration and conformation as given in 7A. Thus compound 7, which we have named 11-hydroxyjasionone, is a sesquiterpene with a carbon skeleton which seems to be new. Most likely it is formed via the aldol condensation product of 6 as shown in the Scheme. Accordingly, for the numbering of 7 that of 6 was used. Furthermore, the proposed formation of 7 would lead to these configurations. These results again showed that highly oxygenated eudesmanes are characteristic for *Jasonia*.

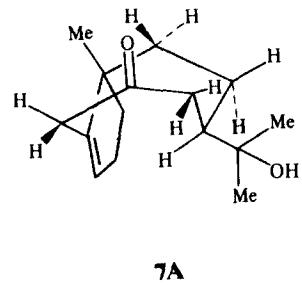
#### EXPERIMENTAL

The air-dried plant material (1 kg, collected in August 1985) in the Northern part of Sinai peninsula, identified by Prof. Dr El-Hadidi, Dept. of Botany, Cairo University, Egypt) was extracted with  $\text{Et}_2\text{O}$ – $\text{EtOH}$ – $\text{CH}_2\text{Cl}_2$  (1:1:1) and the extract obtained was separated by repeated CC (silica gel) and TLC as reported

elsewhere [10]. Finally 7 mg 1, 2.5 mg isointermideol, 6 mg costic acid, 150 mg 2, 60 mg 3, 10 mg 4, 4 mg luteolin-7,3'dimethyl ether, 3 mg 5, 4 mg 6 and 2 mg 7 were obtained.

**1-Acetoxy-7-hydroxy-3,7-dimethylocta-2E,5E-diene (5).** Colourless oil; IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$ : 3600 (OH), 1750 (OAc); MS  $m/z$  (rel. int.): 152.120 [ $\text{M} - \text{HOAc}$ ]<sup>+</sup> (22) (calc. for  $\text{C}_{10}\text{H}_{16}\text{O}$ : 152.120), 137 (44), 119 (45), 109 (100), 95 (94), 81 (94), 67 (84), 55 (84); <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  4.57 (*br d*, H-1), 5.41 (*br t*, H-2), 2.81 (*br d*, H-4), 5.54 (*dt*, H-5), 5.64 (*dt*, H-6), 1.31 (s, H-8, H-9), 1.74 (*br s*, H-10), 2.05 (s, OAc); *J* [Hz]: 1, 2 = 4, 5 = 7; 5, 6 = 16; 4, 6 = 1.

**11-Hydroxyjasionone (7).** Colourless oil; IR  $\nu_{\text{max}}^{\text{CCl}_4}$   $\text{cm}^{-1}$ : 3590 (OH), 1700 (CO); MS  $M/z$  (rel. int.): 236.176 [ $\text{M}^+$ ]<sup>+</sup> (4) (calc. for



7A

$C_{15}H_{24}O_2$ : 236.176), 221 (4), 218 (4), 203 (2), 176  $[M - C_3H_8O]^+$  (3), 161 (6), 95  $[C_7H_{11}]^+$  (100);  $^{13}C$  NMR ( $CDCl_3$ , C-1-C-15): 34.6 *t*, 35.8 *t*, 126.8 *d*, 145.2 *s*, 212.9 *s*, 44.5 *t*, 43.8 *d*, 29.1 *t*, 25.4 *t*, 49.4 *s*, 73.1 *s*, 26.5 *q*, 28.6, 25.4 *q*, 44.8 *t*, (some signals may be interchangeable).

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