

# 11-HYDROXYJASONONE, 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-hydroxyjasonone.

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 δ 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.

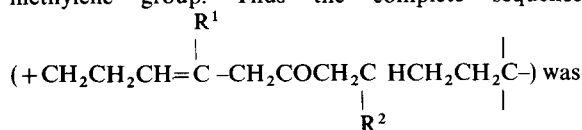
The <sup>1</sup>H NMR spectrum of 7 (Table 1), the molecular formula (C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>) and the <sup>13</sup>C NMR spectrum indicated that a bicyclic sesquiterpene was present. The <sup>13</sup>C NMR data showed the presence of a keto group (δ 212.9 s), a tertiary hydroxy group (δ 73.1 s) and a trisubstituted double bond (δ 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 δ 5.40, obviously due to an olefinic proton, changed the signal at δ 2.29(*m*) and sharpened the broadened doublet at δ 3.16, which itself was geminally coupled with the doublet at δ 3.43. The former showed a long range coupling with the threefold doublet at δ 2.36, which itself coupled geminally with the double doublet at δ 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<sub>3</sub>, 400 MHz)

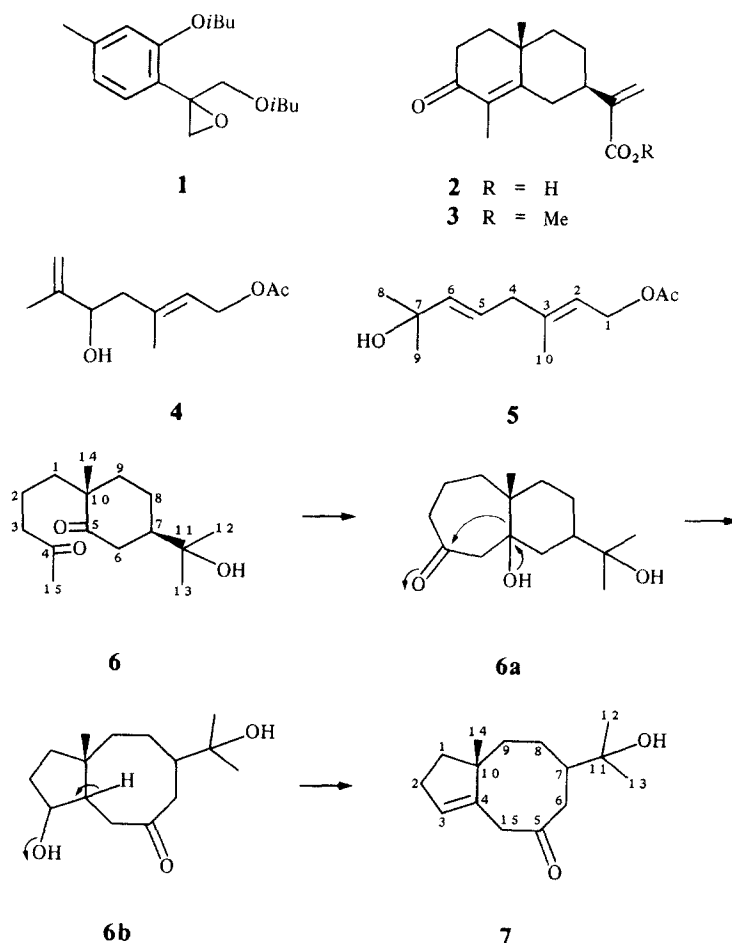
H		H	
1α	1.95 <i>ddd</i>	8β	1.32 <i>dddd</i>
1β	1.56 <i>ddd</i>	9α	1.48 <i>ddd</i>
2	2.29 <i>m</i>	9β	1.67 <i>ddd</i>
3	5.40 <i>ddd</i>	12	1.11 <i>s</i>
6α	2.78 <i>dd</i>	13	1.21 <i>s</i>
6β	2.36 <i>ddd</i>	14	0.99 <i>s</i>
7	2.59 <i>dddd</i>	15α	3.43 <i>br d</i>
8α	1.87 <i>dddd</i>	15β	3.16 <i>br d</i>

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

a keto group. The corresponding proton showed further couplings with a fourfold doublet at δ 2.59 (H-7) which itself was coupled with a pair of fourfold doublets at δ 1.87 and 1.32. Irradiation of these two signals collapsed the geminal coupled signals at δ 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 (δ 2.29 *m*) was coupled with a pair of threefold doublets at δ 1.95 and 1.56 which both collapsed to doublets on irradiation at δ 2.29. This showed that the quaternary carbon was present next to the corresponding methylene group. Thus the complete sequence



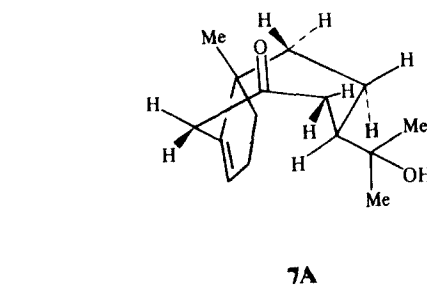
established. As three methyl singlets (δ 0.99, 1.11 and 1.21) as well as a tertiary hydroxy group was present, R<sup>1</sup> and R<sup>2</sup> could only be a methyl and a hydroxyisopropyl group.



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-hydroxy-yjasione, 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 Et<sub>2</sub>O-EtOH-CH<sub>2</sub>Cl<sub>2</sub> (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 isointermedeol, 6 mg cistic 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  $\nu_{\text{max}}^{\text{CCl}_4}$  cm<sup>-1</sup>: 3600 (OH), 1750 (OAc); MS *m/z* (rel. int.): 152.120 [M-HOAc]<sup>+</sup> (22) (calc. for C<sub>10</sub>H<sub>16</sub>O: 152.120), 137 (44), 119 (45), 109 (100), 95 (94), 81 (94), 67 (84), 55 (84); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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-Hydroxy-yjasione (7).** Colourless oil; IR  $\nu_{\text{max}}^{\text{CCl}_4}$  cm<sup>-1</sup>: 3590 (OH), 1700 (CO); MS *M/z* (rel. int.): 236.176 [M]<sup>+</sup> (4) (calc. for

$C_{15}H_{24}O_2$ : 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).

## REFERENCES

1. De Pascual Teresa, J., Barrero, A., Feliciano, A. and Medarde, M. (1980) *Phytochemistry* **19**, 2155.
2. De Pascual Teresa, J., Barrero, A., Medarde, M. san Feliciano, A. and Grande, M. (1978) *An. Quim.* **74**, 1536.
3. De Pascual Teresa, J., San Feliciano, A., Barrero, A. and Medarde, M. (1979) *An. Quim.* **75**, 422.
4. Eid, F., El-Dahmy, S. and Gupta, R. K. (1987) *Pharmazie* **42**, 423.
5. Thappa, R. K., Dhar, K. L. and Atel, C. K. (1979) *Phytochemistry* **18**, 671.
6. Bohlmann, F., Jakupovic, J. and Lonitz, M. (1977) *Chem. Ber.* **110**, 301.
7. Zdero, C., Bohlmann, F., King, R. M. and Robinson, H. (1986) *Phytochemistry* **25**, 509.
8. Fraser, A. W. and Lewis, J. R. (1973) *Phytochemistry* **12**, 1787.
9. Zdero, C., Bohlmann F and Müller, M. (1987) *Phytochemistry* **26**, 2763.
10. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.