

TRITERPENES FROM BULBS OF *MUSCARI COMOSUM*, 3. THE STRUCTURE OF TWO MINOR NOVEL NORTRITERPENE COMPONENTS<sup>1</sup>

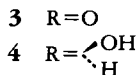
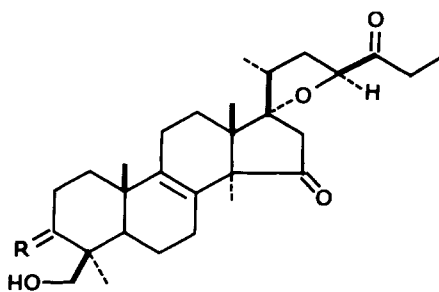
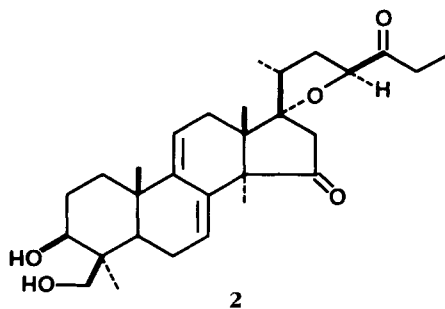
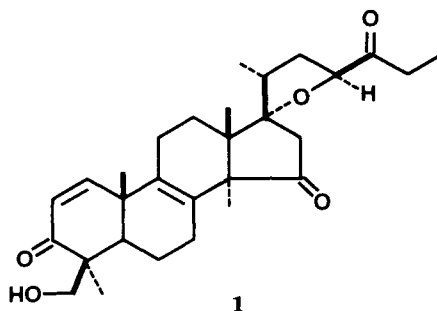
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We recently described the structural elucidation of five components of the triterpene mixture extracted from the bulbs of *Muscari comosum* Mill. (Liliaceae), all characterized by a spiro-fused tetrahydrofuran ring in their norlanostane skeleton (1, 2). We also pointed out (1) the presence of two minor components: the first, **1**, isolated from tlc fraction *a* of the mixture and the other, **2**, from tlc fraction *b*. This paper describes the determination of the structures of these two novel components.

Compound **1**, mp 181-183°, possesses the molecular formula C<sub>29</sub>H<sub>40</sub>O<sub>5</sub> (hrms). The pmr spectrum of **1** (Table 1) resembles that of compound **3**, a previously (1,3) characterized component of the same triterpene fraction. The most relevant feature of the spectrum of **1** as compared to that of **3** is the presence of the signals of two vinyl protons whose chemical shift and multiplicity ( $\delta$  7.313 and  $\delta$  5.959, ABq,  $J=10.56$  Hz) suggest that in ring A of **1** there is a  $\Delta^{1-3}$ -keto system (4,5). Accordingly, the uv spectrum displayed a maximum at 239 nm typical of steroid and terpenoid cyclohexen-3-one systems (6), and the ir spectrum showed the  $\alpha,\beta$ -unsaturated ketone band at 1665 cm<sup>-1</sup>. Conclusive evidence in favor of structure **1** was gained by the remarkably close similarity of the cmr spectra of **1** (Table 2) and **3** (3), the signals of A-ring carbons excepted. The C=C-C=O carbon resonances were found at  $\delta$  157.13, 126.53, and 206.07, respectively (7-9). In addition, the C-4 and C-5 resonances were shifted upfield and the C-10 resonance

downfield as a consequence of the introduction of the 1,2-double bond.<sup>2</sup>



Compound **2**, mp 221-224°, possesses the molecular formula C<sub>29</sub>H<sub>42</sub>O<sub>5</sub> (hrms). Uv absorption [EtOH,  $\lambda$  max 236, 241, and 250 (shoulder) nm] immediately suggests (10) the presence of the  $\Delta^{7,9(11)}$  diene chromophore. The

<sup>1</sup>Part 2: reference 2.<sup>2</sup>Cf. Compound A (8) and azadiradion (9).

TABLE 1. Pmr (270 MHz) Chemical Shifts in CDCl<sub>3</sub><sup>a</sup>

Compound	Protons						
	18-H <sub>3</sub>	19-H <sub>3</sub>	30-H <sub>3</sub>	32-H <sub>3</sub>	21-H <sub>3</sub>	31-H <sub>2</sub>	3-H
1 . . . . .	0.972s	1.234s	1.321s	1.402s	1.145d <i>J</i> <sub>20,21</sub> =6.64	3.544 3.899 ABq <i>J</i> <sub>AB</sub> =10.96	
2 . . . . .	0.836s	0.944s	1.262s	1.395s	1.211d <i>J</i> <sub>20,21</sub> =6.62	3.470 4.294 ABq <i>J</i> <sub>AB</sub> =10.99	3.47 <sup>b</sup>
	20-H	22-H <sub>2</sub>	23-H	25-H <sub>2</sub>	26-H <sub>3</sub>	16-H <sub>2</sub>	Others
1 . . . . .	2.30m	1.950dd <sup>c</sup>	4.694t <sup>d</sup>	2.487q <i>J</i> <sub>25,26</sub> =7.43	1.075t	2.224 2.823 ABq <i>J</i> <sub>AB</sub> =19.17	7.313 (1-H) 5.959 (2-H) ABq <i>J</i> <sub>1,2</sub> =10.56
2 . . . . .	2.3m	1.95m	4.684t <sup>d</sup>	2.501q <i>J</i> <sub>25,26</sub> =7.35	1.078t	2.175 2.798 ABq <i>J</i> <sub>AB</sub> =19.12	5.325m (11-H) 6.721bd (7-H)

<sup>a</sup>All chemical shift values are given in  $\delta$  (ppm) relative to TMS. Coupling constants are given in Hz and were inferred from pertinent decoupling experiments. Assignment of the methyl resonances was based mainly on comparison with the spectra of **3** and **4** (2).

<sup>b</sup>Buried within the 31-H<sub>2</sub> signal.

<sup>c</sup>AA' part of an AA'X system, further split (*J*=3.13) by coupling with 20-H.

<sup>d</sup>X part of an AA'X system (*J*<sub>AX</sub>+*J*<sub>A'X</sub>=18.00).

TABLE 2. Cmr (67.88 MHz) Chemical Shifts in CDCl<sub>3</sub> of 1<sup>a</sup>

C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
157.13	126.53	206.07	48.72	47.35	18.03	25.52	135.02	135.02	40.43
C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19	C-20
21.41	23.26	47.65	57.73	214.37	51.53	90.86	20.32	19.20	43.30
C-21	C-22	C-23	C-24	C-25	C-26	C-30	C-31	C-32	
17.08	36.66	81.55	211.70	32.29	7.29	21.88	64.90	24.23	

<sup>a</sup>Chemical shift values are given in  $\delta$  (ppm) relative to TMS. The assignments of the signals are based on the comparison with the spectrum of **3** (3).

pmr spectrum (Table 1), resembling that of **4** (2), supports this structural feature: 11-H and 7-H resonate at  $\delta$  5.325 and  $\delta$  6.721, respectively. The displacement to lower field of the signal of 7-H with respect to other lanosta-7,9(11)-

dienes (11) can be accounted for by the effect of the 15-keto group, since a similar chemical shift value has been reported (12) for the 7-H of another 15-keto lanosta-7,9(11)-diene. In spite of the absence of supporting cmr evidence,

due to the lack of a sufficient amount of material, structure **2** was readily confirmed by converting **4** into **2** by reaction with *m*-chloroperbenzoic acid followed by treatment with 80% aqueous HOAc, according to a simple modification of the well known procedure for the transformation of  $\Delta^8$  steroids and terpenoids into the  $\Delta^{7,9(11)}$  analogues (13).

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—See reference 1.

ISOLATION PROCEDURE.—Norritriterpenes **1** and **2** were obtained from fresh fractions *a* and *b*, respectively, isolated by the procedure described in reference 1 from the bulbs of *M. comosum*.

Compound **1** was the minor component isolated by tlc from the mother liquors of the crystallization of fraction *a* (1). It had mp 181-183° (from Me<sub>2</sub>CO); ms *m/z* 468.2863 (M<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>40</sub>O<sub>5</sub> 468.2876), 438 (base peak), 411 (M<sup>+</sup>-57, CH<sub>3</sub>CH<sub>2</sub>CO), 380, 268, 241; ir (CHCl<sub>3</sub>): 3300 (OH), 1735 (five ring C=O), 1715 (C=O), 1685 (C=C-C=O) cm<sup>-1</sup>; uv (EtOH), λ max 239 nm; pmr Table 1; cmr Table 2.

Compound **2** was the minor component isolated by tlc from the fraction *b* (1). It had mp 221-224° (from MeOH); ms *m/z* 470.3023 (M<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>42</sub>O<sub>5</sub> 470.3032), 413, 324 (base peak); ir (CHCl<sub>3</sub>): 3300 (OH), 1735 (five ring C=O), 1715 (C=O) cm<sup>-1</sup>; uv (EtOH), λ max 236, 241, 250 (shoulder) nm; pmr Table 1.

CONVERSION OF **4** INTO **2**.—A solution of **4** (1) (3 mg) and *m*-chloroperbenzoic acid (4 mg) in CHCl<sub>3</sub> (2 ml) was allowed to stand at room temperature for 40 h. The solution was then treated with solid KI (traces), acidified by addition of HOAc, washed with 0.1 N sodium metabisulphite, with 2 N NaOH and finally with H<sub>2</sub>O, and evaporated to dryness. The residue was dissolved in 80% aqueous HOAc (2 ml) and allowed to stand at room temperature for two days. The reaction mixture was diluted with CHCl<sub>3</sub>,

washed with saturated aqueous NaCl and evaporated. Tlc (silica gel; 8:2, EtOAc-CHCl<sub>3</sub>) of the residue gave a solid (2 mg) which was identical (tlc, pmr) to the sample of **2** isolated from the bulbs as above.

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