

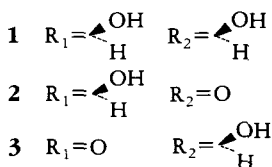
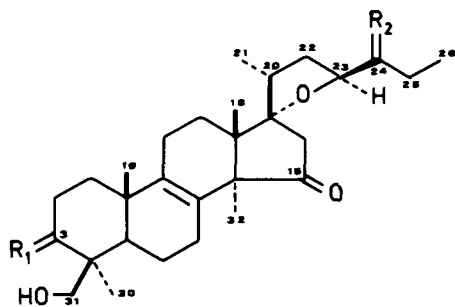
TRITERPENES FROM BULBS OF *MUSCARI COMOSUM*, 4. THE STRUCTURE OF FURTHER NOVEL NORTRITERPENE COMPONENTS¹

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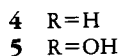
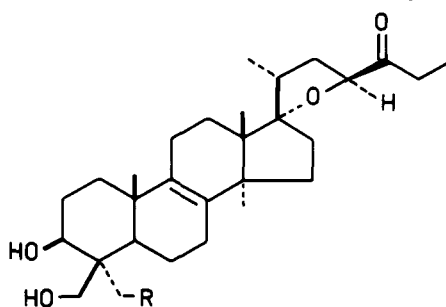
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The bulbs of *Muscari comosum* Mill. have been shown to be a source of several interesting products. In addition to some glycosides (1) and homoisoflavanones (2), we have isolated a series of 27-norlanostane triterpenes (3-7) either as free compounds or as aglycone moieties of the glycosides, all having the peculiar structural feature of a spirofused tetrahydrofuran ring at C-17. Following a more detailed investigation, we have isolated two novel free nortriterpenes, **1** and **4**, and have elucidated their structures on the basis of chemical and spectral evidence.

binolic proton resonates at δ 3.331 and is coupled with the protons 23-H and 25-H₂, as shown by pertinent decoupling experiments. The signal of the 25-H₂ in the spectrum of **1** appears at a higher field than in the spectrum of **2** because of the change in functionality at C-24. On the other hand, the 23-H, 24-H, and 25-H₂ signals of **1** are closely comparable to those of compound **3** (Table 1), which possesses a side-chain identical to that assumed for **1** on the grounds of the above data. Owing to the scarcity of material, the cmr spectrum of **1** could not be recorded to find further support



Compound **1** possesses the molecular formula C₂₉H₄₆O₅ (hrms). The mass spectral fragmentation pattern resembled that of **2** (8); the presence of the peak at *m/z* 343 of the ion **6** is particularly diagnostic (8) of a structure similar to that of **2**. Inspection of the pmr spectrum of **1**, summarized in Table 1, as well as that of **2**, indicated that **1** is the 24-alcohol corresponding to **2**: the car-



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for its structure, but definitive evidence was easily obtained by conversion of **3** into **1** through the selective reduction of the 3-keto function (NaBH₄/MeOH at room temperature); this also allowed the determination of the chirality at C-24 of **1** as S (3). Compound **4** possesses the molecular formula C₂₉H₄₆O₄ (hrms). In contrast to all the other nortriterpenes found in the bulbs of *M. comosum*, both as free compounds and as aglycones, **4** possesses

¹For Part 3, see Adinolfi, *et al.* (5).

TABLE 1. Pmr (270 MHz) Chemical Shifts (Selected Data) in CDCl_3^a

	1	2(4)	3(3)	4	5(6)
18-H ₃	0.924 s	0.931 s	0.953 s	0.961 s	0.896 s
19-H ₃	0.949 s	0.951 s	1.068 s	0.949 s	0.959 s
30-H ₃	1.277 s	1.267 s	1.282 s	1.255 s	
30-H ₂					3.700, 4.148 ABq ^m , $J_{AB}=10.29$
32-H ₃	1.252 s	1.384 s	1.305 s	1.229 s	1.226 s
21-H ₃	1.121 d	1.125 d	1.128 d	1.058 d	1.055 d
	$J_{20,21}=6.99$	$J_{20,21}=6.62$	$J_{20,21}=6.80$	$J_{20,21}=6.99$	$J_{20,21}=6.75$
31-H ₂	3.346, 4.229	3.375 b, 4.242	3.462, 4.011	3.354, 4.247	3.750, 4.344
	ABq, $J_{AB}=11.70$	ABq, $J_{AB}=11.27$	ABq, $J_{AB}=11.21$	ABq, $J_{AB}=11.03$	ABq ^m , $J_{AB}=11.03$
3-H	3.456 dd ^b	3.468 dd ^e		3.468 dd ⁱ	3.7 ^k
20-H	2.20 m	2.35 m	2.20 m		
23-H	4.002 m ^c	4.674 t ^f	4.033 m ^g	4.530 dd ^l	4.540 dd ^l
24-H	3.331 m ^d		3.347 m ^h		
25-H ₂	1.40 m	2.495 q	1.35 m	2.553 q	2.557 q
		$J_{25,26}=7.35$		$J_{25,26}=7.35$	$J_{25,26}=7.35$
26-H ₂	0.996 t	1.076 t	1.009 t	1.071 t	1.068 t
	$J_{25,26}=6.94$	$J_{25,26}=7.35$	$J_{25,26}=7.35$	$J_{25,26}=7.35$	$J_{25,26}=7.35$
16-H ₂	2.342, 2.689	2.207, 2.774	2.358, 2.717		
	ABq, $J_{AB}=19.12$	ABq, $J_{AB}=19.42$	ABq, $J_{AB}=19.49$		

^aAll chemical shift values are given in δ relative to TMS. Coupling constants are given in Hz and were inferred from pertinent decoupling experiments.

^bX part of an ABX system ($J_{AB}+J_{BX}=16.45$).

^cEight-line pattern: X quartet ($J_{AX}+J_{BX}=16.70$) of an ABX system, further split ($J=7.72$) by coupling with the 24-H.

^dSix-line pattern: X quartet ($J_{AX}+J_{BX}=11.33$) of an ABX system, further split ($J=7.72$) by coupling with the 23-H.

^eX part of an ABX system ($J_{AX}+J_{BX}=15.20$).

^fX part of an ABX system ($J_{AX}+J_{BX}=18.92$).

^gBuried with a 31-H₂ signal. When shifted by Eu(dpm)₃ it appears as a six-line pattern: X quartet ($J_{AX}+J_{BX}=15.5$) of an ABX system, further split ($J=7.92$) by coupling with the 24-H.

^hSix-line pattern: X quartet ($J_{AX}+J_{BX}=12.19$) of an ABX system, further split ($J=7.92$) by coupling with 23-H.

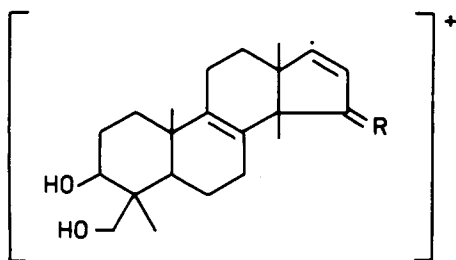
ⁱX part of an ABX system ($J_{AX}+J_{BX}=16.92$).

^jX part of an ABX system ($J_{AX}+J_{BX}=17.90$).

^kBuried with the 31-H₂ signal.

^lX part of an ABX system ($J_{AX}+J_{BX}=17.62$).

^mInterchangeable signals.



6 R=O

7 R=H₂

only four oxygen atoms in its structure: whereas the 24-keto, the 17,23-epoxy, the 3- and the 31-hydroxy functions are present, **4** lacks both the 15-keto and the 30-hydroxy functions. This could be quite safely concluded by inspection of the pmr and cmr spectra, whose signals could be assigned as in Tables 1 and 2, respectively, by comparison with those of the other nortriterpene components of the bulbs, mainly **2** and **5**. In the pmr spectrum of **4**, the absence of the low-field AB quartet of the 16-CH₂ protons

present in the spectrum of **2** at δ 2.207, 2.774 could be noted (as in the spectrum of **5**). Furthermore, the signal of the 30-CH₂OH protons was absent (in contrast to the spectrum of **5**), while the signal of the 30-CH₃ protons was observed (as in the spectrum of **2**). Accordingly, in the cmr spectrum of **4**, the C-14, C-15, C-16, and C-17 carbons have chemical shifts similar to those of **5** (and different from those of **2**), and the C-30 and C-4 carbons have chemical shifts similar to those of **2** (and different from those of **5**). The mass spectrum was also in complete accord with the structure **4**, as all the relevant peaks can be explained (see Experimental), including the peak at m/z 329, which is attributable (8) to the fragment **7**.

Finally, it may be noteworthy that, while all the other nortriterpenes we have hitherto isolated from the bulbs may be divided into two main structural

TABLE 2. Cmr (67.88 MHz) Chemical Shifts in CDCl₃^a

	4	2(4)	5(6)		4	2	5
C-1	35.35	35.39	35.30	C-16	39.64	51.85	39.70
C-2	28.31	28.28	27.41	C-17	91.65	91.19	97.18
C-3	80.68	80.73	77.86	C-18	19.56	20.43	19.51
C-4	42.84	42.86	45.96	C-19	19.20	19.80	19.23
C-5	51.20	50.78	47.29	C-20	43.57	43.46	43.63
C-6	18.29	18.26	18.72	C-21	17.19	17.17	17.18
C-7	26.46	26.28	26.24	C-22	36.80	36.78	36.77
C-8	134.03	133.19	134.07	C-23	81.41	81.71	81.52
C-9	135.28	135.99	135.45	C-24	213.36	212.03	213.63
C-10	36.80	37.30	36.50	C-25	32.26	32.40	32.30
C-11	20.76	20.52	20.78	C-26	7.50	7.38	7.39
C-12	24.90	22.97	24.91	C-30	22.23	22.28	71.27
C-13	48.66	47.57	48.69	C-31	64.37	64.41	63.83
C-14	50.50	57.84	50.55	C-32	25.85	23.78	25.91
C-15	31.71	215.08	31.70				

^aChemical shift values are given in δ relative to TMS

groups according to oxygenation at the 30- or 15-position, **4** is the only compound that does not belong to either group.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURE.—Procedures used are those described by Adinolfi et al. (3).

ISOLATION PROCEDURE.—The isolation procedure previously described (3) for fresh bulbs of *M. comosum* (Liliaceae), collected in autumn (1982) in Puglia, Italy, and authenticated by the Botanical Garden of the University of Naples, where a voucher specimen has been deposited, was repeated with a 5 kg amount of material. Crystallization of fraction *e* [Rf value lower than that of fraction *d*, (3)] from Me₂CO gave compound **1** (1 mg) and crystallization of fraction *a'* [Rf value falling between those of fractions *a* and *b*, (3)] from MeOH gave compound **4** (3 mg).

Compound **1** had mp 234–236°; ms, *m/z* 474.3337 (M⁺; calcd for C₂₉H₄₆O₅, 474.3345), 456 (M⁺-18, H₂O), 416 (M⁺-58, CH₃CH₂CHO), 343 (6), 303, 290, 183, 157. Pmr: Table 1. Cmr: Table 2.

Compound **4** had mp 195–197°; [α]_D -22° (c 0.3, CHCl₃); ms, *m/z* 458.3388 (M⁺; calcd for C₂₉H₄₆O₄, 458.3396), 443 (M⁺-15, CH₃), 425 (433-H₂O), 401 (M⁺-57, CH₃CH₂CO), 383 (401-H₂O), 329 (7), 304, 289, 255. Pmr: Table 1. Cmr: Table 2.

REDUCTION OF **3**.—A sample of **3** (2 mg) was dissolved in MeOH (0.5 ml) and treated with NaBH₄ (traces) at room temperature for 30 min. Usual work-up gave a solid (2 mg); preparative tlc

(silica gel, C₆H₆-Et₂O, 3:7, three runs) gave **1** (1 mg), identical (pmr) to the sample isolated from the bulbs as above.

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