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GLYCOSIDES FROM *MUSCARI COMOSUM*—III

THE STRUCTURE OF FURTHER AUTHENTIC AGLYCONES†

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Abstract— From the glycosides mixture contained in the bulbs of *Muscari comosum* four aglycones were obtained by enzymatic hydrolysis. The structure of the two major ones, **1a** and **1b**, has been reported previously. This paper deals with the spectral and chemical evidence which led us to assign the two minor ones the structures **2a** and **3a**, with the same 27-norlanostane skeleton as **1a** and **1b**.

The extraction of a complex mixture of glycosides from the bulbs of *Muscari comosum* has been recently reported.[1] The structural elucidation of the acid-catalyzed methanolysis products allowed us to propose that one of the authentic aglycones could be already known[2] eucosterol **1a**. The latter was actually found among the products of the enzymatic hydrolysis of the glycosides mixture. Later on, another aglycone was assigned structure **1b**.[3] Two other minor aglycones had also been isolated by careful chromatographic fractionation of the enzymatic hydrolysis products. The present paper deals with the spectral and chemical evidence which led us to assign them structures **2a** and **3a**, with the same 27-norlanostane skeleton as **1a** and **1b**. However, they differ from these latter in lacking the ketonic function at C-15 and in having a hydroxymethylene group in place of the (30)CH_3 group.

Compound **2a**, $[\alpha]_D$ −27°, had the molecular formula $C_{29}H_{46}O_5$, as deduced by HRMS (*m/e* calc. 474.33450, found 474.33473). ^{13}C NMR (Table 1) and ^{1}H-NMR (Table 2) spectra exhibited signals whose chemical shifts and multiplicities were easily interpreted by comparison with the corresponding signals shown by the spectra of eucosterol **1a**. In agreement with the ^{13}C-spectrum, the proton spectrum of **2a** displayed the signals of only five methyl groups: of these three are tertiary (δ 0.896, s; 0.959, s; 1.226, s), one is secondary (δ 1.055, d) and one is primary (δ 1.068, t). In the lowest field zone, in addition to the signal due to the 23-H (δ 4.540, dd) the signals of two (and not one as in **1a**) CH_2OH groups as AB q's

Table 1. ^{13}C-NMR (67.88 MHz) chemical shifts of compounds **1a**, **1b**, **2a** and **3a** in $CDCl_3$[a]

	1a	1b	2a	3a		1a	1b	2a	3a
C-1	35.39 t	35.43 t	35.30 t	35.94 t	C-16	51.85 t	51.75 t	39.70 t	39.67 t
C-2	28.28 t	34.47 t	27.51 t	36.21 t	C-17	91.19 s	91.12 s	97.18 s	97.08 s
C-3	80.73 d	219.93 s	77.86 d	216.40 s	C-18	20.43 q	20.59 q	19.51 q	19.32 q
C-4	42.86 s	51.35 s	45.96 s	55.99 s	C-19	19.80 q	19.45 q	19.23 q	19.32 q
C-5	50.78 d	51.62 d	47.29 d	47.36 d	C-20	43.46 d	43.49 d	43.63 d	43.65 d
C-6	18.26 t	18.92 t	18.72 t	19.32 t	C-21	17.17 q	17.18 q	17.18 q	17.22 q
C-7	26.28 t	26.24 t	26.24 t	25.95 t	C-22	36.78 t	36.77 t	36.77 t	36.78 t
C-8	133.19 s	134.14 s	134.07 s	133.02 s	C-23	81.71 d	81.72 d	81.52 d	81.52 d
C-9	135.99 s	134.48 s	135.45 s	136.35 s	C-24	212.03 s	211.92 s	213.63 s	213.54 s
C-10	37.30 s	37.17 s	36.50 s	36.78 s	C-25	32.40 t	32.44 t	32.30 t	32.34 t
C-11	20.52 t	20.59 t	20.78 t	21.01 t	C-26	7.38 q	7.28 q	7.39 q	7.44 q
C-12	22.97 t	23.01 t	24.91 t	24.93 t	C-30	22.28 q	21.88 q	71.27 t	68.94 t
C-13	47.57 s	47.56 s	48.69 s	48.69 s	C-31	64.41 t	65.81 t	63.81 t	65.37 t
C-14	57.84 s	57.88 s	50.55 s	50.68 s	C-32	23.78 q	23.78 q	25.91 q	25.97 q
C-15	215.08 s	215.13 s	31.70 t	31.74 t					

[a] Chemical shifts are given in δ (ppm) relative to TMS. s = singlet, d = doublet, t = triplet, q = quartet in the off resonance spectra. The assignements of the signals of 2a and 3a are based on the comparison with the spectra of 1a and 1b. A detailed study of these latter has been reported in ref 3

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Table 2. ^{1}H-NMR (270 MHz) chemical shifts (selected data) in $CDCl_3$[a]

	3-H	18-H_3	19-H_3	21-H_3	23-H	25-H_2	26-H_3	30-H_2	31-H_2	32-H_3	Other signals
1a[b]	3.48 dd $J^{3\alpha,2\beta}$=11.1 $J^{3\alpha,2\alpha}$=4.1	0.94 s	0.96 s	1.13 d $J^{20,21}$=6.7	4.71 t $J^{22,23}$=9.46	2.51 q $J^{25,26}$=7.35	1.08 t		3.36 4.23 AB q J_{AB}=11.27	1.36 s	30-H_3 1.23 s 22-H_2 1.95 dd, $J^{22,23}$=9.46 $J^{20,22}$=3.1 16-H_2 2.22, 2.72 AB q J_{AB}=19.4 20-H 2.35
1b[c]		0.960 s	1.088 s	1.135 d $J^{20,21}$=6.82	4.698 t $J^{22,23}$=9.93	2.947 q $J^{25,26}$=6.99	1.069 t		3.469 4.021 AB q J_{AB}=11.40	1.407 s	30-H_3 1.271 s 22-H_2 1.994 dd, $J^{22,23}$=9.93 $J^{20,22}$=3.31 16-H_2 2.227, 2.798 AB q J_{AB}=19.12 20-H 2.35
2a	3.7[d]	0.896 s	0.959 s	1.055 d $J^{20,21}$=6.75	4.540 dd $J^{22,23}_{AX}$=7.36 $J^{22,23}_{BX}$=10.26	2.557 q $J^{25,26}$=7.35	1.068 t	3.700 4.148 AB q J_{AB}=10.29	3.750 4.344 AB q J_{AB}=11.03	1.226 s	
2b	4.87 dd $J^{3\alpha,2\beta}$=12 $J^{3\alpha,2\alpha}$=4.5	0.92 s	1.06 s	1.07 d $J^{20,21}$=6.7	4.53 dd $J^{22,23}_{AX}$=7.45 $J^{22,23}_{BX}$=10.31	2.57 q $J^{25,26}$=7.35	1.07 t	4.05 4.27 AB q J_{AB}=11.5	4.30 4.43 AB q J_{AB}=11.5	1.24 s	3xCH_3COO- 2.02 s 2.06 s 2.08 s
2c	3.867 dd[e] $J^{3\alpha,2\beta}$=11.03 $J^{3\alpha,2\alpha}$=5.68	0.896 s	0.944 s	1.061 d $J^{20,21}$=6.7	4.546 dd $J^{22,23}_{AX}$=6.99 $J^{22,23}_{BX}$=10.30	2.549 q $J^{25,26}$=7.35	1.070 t	3.598[f] 4.200 AB q J_{AB}=8.09	3.912[g] 4.337[h] AB q J_{AB}=8.46	1.234 s	$CH_3C(-O-)_3$ 1.446 s

2d	3.340 dd $J^{3\alpha,2\beta}$=12.05 $J^{3\alpha,2\alpha}$=3.66	0.910 s	0.910 s	1.062 d $J^{20,21}$=6.7	4.537 dd $J^{22,23}_{AX}$=7.41 $J^{22,23}_{BX}$=10.33	2.550 q	1.073 t $J^{25,26}$=7.4	3.601 3.914 AB q J_{AB}=12.13	3.844 3.964 AB q J_{AB}=12.13	1.232 s	$(CH_3)_2C$ 1.356 (6H)
3a		0.926 s	1.182 s	1.066 d $J^{20,21}$=6.75	4.548 dd $J^{22,23}_{AX}$=7.35 $J^{22,23}_{BX}$=10.29	2.549 q	1.070 t $J^{25,26}$=7.35	3.815 4.010 AB q J_{AB}=11.33	3.862 4.243 AB q J_{AB}=11.77	1.239 s	
3b		0.940 s	1.054 s	1.060 d $J^{20,21}$=6.7	4.543 dd $J^{22,23}_{AX}$=7.35 $J^{22,23}_{BX}$=10.29	2.555 q	1.070 t $J^{25,26}$=7.35	3.497 4.230 AB q J_{AB}=11.77	3.928 4.069 AB q J_{AB}=11.77	1.242s	$(CH_3)_2C$ 1.335 s 1.373 s

[a] All chemical shift values are given in δ (ppm) relative to TMS. Coupling constants values are given in Hz and were inferred from pertinent decoupling experiments. s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet.

[b] Reference 1.

[c] Reference 3.

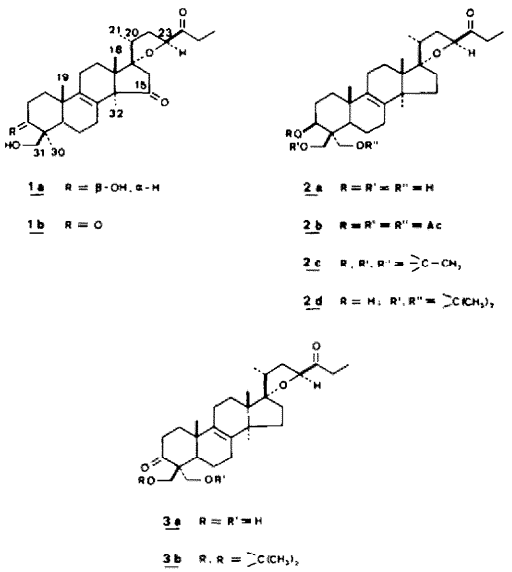
[d] Buried by the 3l-H_2 signal.

[e] Further split (J = 1.84 Hz) by coupling with one 3l-H (see text).

[f] Further split (J = 3.31 Hz) by coupling with one 3l-H (see text).

[g] Further split (J = 1.84 Hz) by coupling with the 3α-H (see text).

[h] Further split (J = 3.31 Hz) by coupling with one 30-H (see text).



1a R = β-OH, α-H

1b R = O

2a R = R' = R'' = H

2b R = R' = R'' = Ac

2c R, R', R' = >C-CH$_3$

2d R = H; R', R'' = >C(CH$_3$)$_2$

3a R = R' = H

3b R, R = >C(CH$_3$)$_2$

(δ 3.700, δ 4.148, J = 10.29 and δ 3.750, δ 4.344, J = 11.03) were present (corresponding ^{13}C-signals: δ 63.81, t and 71.27, t). One of the two AB q's overlapped the signal of the carbinolic proton at C-3 (corresponding ^{13}C-signal: δ 77.86, d). The presence of three hydroxyl groups in **2a** was confirmed by the formation of the tri-acetyl derivative **2b** upon treatment with Ac_2O/Py. In addition to the signals due to the three CH_3COO- groups the signals of the two pairs of acetoxymethylene protons (δ 4.05 and δ 4.27, AB q; δ 4.30 and δ 4.43, AB q) and of the 3α-H (δ 4.87, dd, $W_{1/2}$ = 17 Hz) can be easily distinguished in the ^{1}H-NMR spectrum of **2b** (Table 2).

The broad absorption in the IR spectrum of **2a** at 1725 cm^{-1} was shown to be due to only one keto group by the ^{13}C-spectrum (δ 213.63). The elimination of a propionyl radical in the mass spectrum (*m/e* 417, $M^+ - 57$) and the signals of an ethyl ketone in the ^{1}H-NMR spectrum (δ 2.557, q; δ 1.068, t; J_{vic} = 7.35 Hz) indicated the location of the keto group at C-24, as in **1a**.

Having been thus established the nature of four out of the five oxygen functions implied by the molecular formula of **2a**, the ethereal nature of the remaining oxygen atom was deduced from the ^{13}C-spectrum. This, in addition to the signals of the three carbinolic carbon atoms, exhibited two further signals (δ 97.18, s; δ 81.52, d) for carbon atoms adjacent to oxygen (C-17 and C-23, resp.), as for **1a**. The chemical shift of the C-17 atom (δ 97.18), moved downfield as compared to the resonance of the C-17 of **1a** (δ 91.19), is justified by the absence of the 15-keto group in **2a**.

The downfield shift of the ^{13}C line of the C-4 carbon of **2a** (δ 45.96) as compared with the line of the corresponding carbon of **1a** (δ 42.86) suggested that this carbon carries both hydroxymethylene groups in **2a**. Accordingly, the arrangement of the two primary hydroxyl groups was shown to be suitable for the closure of an orthoacetate structure with the 3α-OH, as an orthoacetate (m.p. 168–70°; MS, *m/e*: 498; ^{1}H-NMR, δ: 1.446, 3H, s, $CH_3C(-O-)_3$) was obtained upon treatment of **2a** with $CH_3C(OCH_3)_3$/pyridinium *p*-toluenesulfonate. Furthermore, from the ^{1}H-NMR spectrum of the orthoacetate evidence was achieved for the location of the two primary oxygen atoms at C-31 and C-30 and not at C-31 and C-19, this latter being the only other possibility left by the closure of the orthoester cage system. In fact, the 11.03 and 5.88 Hz values for $J_{3\alpha,2\beta}$ and $J_{3\alpha,2\alpha}$, respectively, are consistent only with the normal *trans*-diaxial and axial-equatorial relationship present in the structure **2c** (A-ring in a chair conformation, see Fig. 1), a severe distortion being implied by the alternative closure of the orthoacetate system at the positions 3α, 31 and 19. In addition, the 3α-proton gave rise to an eight-line signal centered at δ 3.867 as the four-line X-part of an ABX system with vicinal coupling constants of 5.88 and 11.03 Hz further split with an 1.84 Hz coupling constant. Also the AB q (J_{vic} = 8.46) due to one oxymethylene group was further split, the A-part (δ 4.337) with a J = 3.31 Hz and the B-part (δ 3.912) with a J = 1.84 Hz. The AB q (J_{vic} = 8.09 Hz) due to the second oxymethylene group presented its B-part (δ 3.598) further split with a J = 3.31 Hz, the A-part (δ 4.200) not being further split. Decoupling experiments showed the 3α proton and one proton of the former AB-system to be coupled with the J = 1.84 Hz and the second proton of the same AB-system and one proton of the other AB-system to be coupled with the J = 3.31 Hz. Each of these two couplings can be rationalized as a coupling across four single bonds in a planar W-path.[4] In the orthoacetate **2c** such a relationship occurs (see Fig. 1) between the 3α-proton and the 31-H_S and between the 31-H_R and the 30-H_S.

Further support to the structure **2a** came from the results of some decoupling experiments and NOE measurements carried out with acetonide **2d** (m.p. 123–5°; $[\alpha]_D$ −1.9°; MS, *m/e*: 514; ^{1}H-NMR, δ: 1.356, 6H, $(CH_3)_2C$<) obtained from **2a** upon treatment with dry acetone/$CuSO_4$. In the ^{1}H-NMR spectrum of **2d** (Table 2, Fig. 2a) the 3α-proton gives a dd at δ 3.340 with vicinal couplings of 12.00 and 3.68 Hz. The oxymethylene protons of the -CH_2O--C$(CH_3)_2$-$(CH_3)_2$-OCH_2- grouping appear as two AB q's, whose A and B lines (centered at δ3.601, δ3.914, J_{gem} = 12.13 Hz and δ3.844, δ3.964, J_{gem} = 12.13 Hz, respectively) were identified through pertinent decoupling experiments (successive irradiations at δ3.964, 3.914, 3.844 and 3.601 caused the signals at δ 3.844, 3.601, 3.964 and

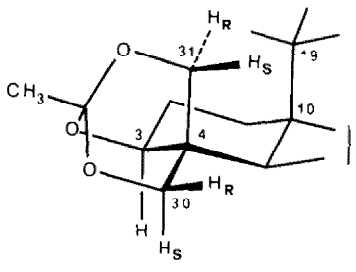


Fig. 1. Perspective view of the A ring of **2c**.

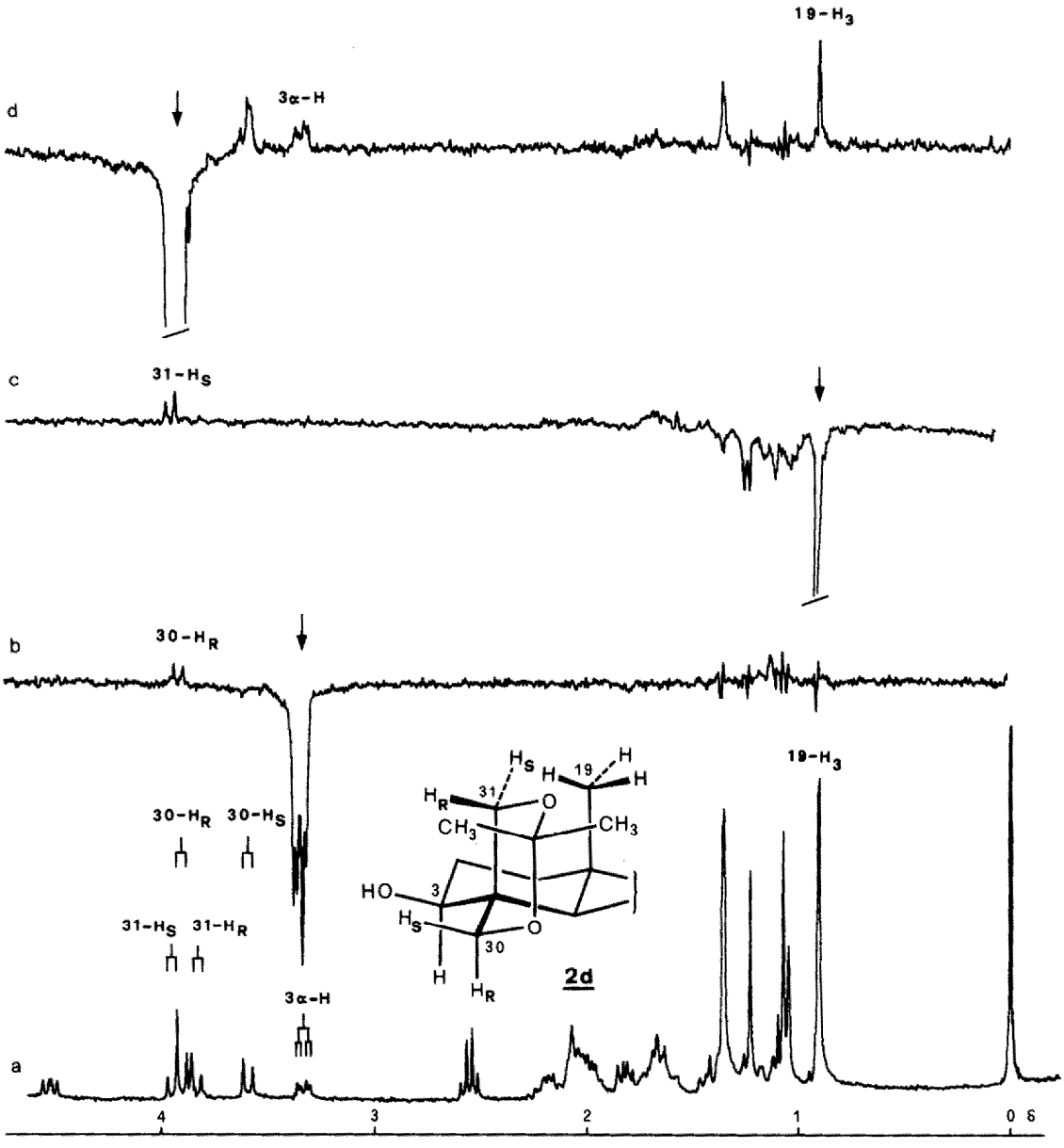


Fig. 2. ^{1}H-NMR (270 MHz) spectrum (a) of acetonide **2d** in $CDCl_3$ and NOE-difference spectra upon irradiation at δ 3.340 (b), δ 0.910 (c)[3] and δ 3.94 (d).

3.914, resp., to coalesce into singlets). Significant nuclear Overhauser effects were measured (Fig. 2b, c, d) between the signal centered at δ 3.914 and the 3α-H signal at δ 3.340 and between the signal centered at δ 3.964 and the angular methyl signal at δ 0.910. This result showing the spatial proximity of one oxymethylene group to the 3α-H and of the other to an angular methyl group is consistent only with the arrangement of the $-CH_2O-C(CH_3)_2-OCH_2-$ grouping in a spirane ring at the 4-carbon, the signal at δ 3.914 being due to the 30-H_R (and therefore the signal at δ 3.601 to the 30-H_S), the signal at δ 3.964 being due to the 31-H_S (and therefore the signal at δ 3.844 to the 31-H_R) and the signal of the 19-CH_3 being at δ 0.910.

Compound **3a**, m.p. 156–8°, $[\alpha]_D$ −33°, was assigned the molecular formula $C_{29}H_{44}O_5$ by HRMS (*m/e* calc. 472.31885, found 472.31898). The ^{1}H-NMR and ^{13}C-NMR evidence suggested that **3a** was the 3-keto counterpart of **2a**. In fact, in addition to a general correspondence of the signals in the proton spectrum (Table 2) the 3-H signal was absent and in the ^{13}C-spectrum (Table 1) a second line due to a ketonic carbon (δ 216.40) was present in addition to the (24)C = O line (δ 213.54). Decisive chemical evidence in this regard came from the formation of acetonide **3b** (m.p. 144–6°; $[\alpha]_D$ +9.3°; MS, *m/e*: 512) upon both treatment of **3a** with dry acetone/$CuSO_4$ and oxidation of **2d** with pyridinium chlorochromate.

The rather remote possiblity that **2a** and **3a** could have either an euphane or an *ent*-lanostane skeleton in spite of cooccurrence with the lanostane triterpenes **1a** and **1b** could be excluded as follows. The methyl singlet

at δ1.182 in the ^{1}H-NMR spectrum of **3a** was attributed to the (19)CH_3 as its irradiation caused the enhancement of the signal of one hydroxymethylene proton (δ4.243, A-part of an AB q) consequently identified as one 31-H. The enhancement of the methyl singlet at δ0.926 which must be assigned to the (18)CH_3 owing to its highest field position[2,5] was also detected. This latter result is consistent only with a lanostane skeleton for **3a**. Finally, the Horeau method[6] applied to **2d** allowed the determination of the chirality at C-3 as S. Therefore, the two novel 27-norlanostane triterpenes isolated from *Muscari comosum* have the same absolute configuration as **1a** and **1b**, as depicted in formulas **2a** and **3a**.

EXPERIMENTAL (with the assistance of Italo Giudicianni)

General. Mc. ps were determined on a Kofler block and are uncorrected. Reaction products were purified on silica gel thin layers (thickness 0.25 mm, Merck 60 F_{254}). IR spectra were measured in chloroform solutions on a Perkin Elmer mod. 399 spectrometer. Rotations were determined with chloroform solutions on a Perkin Elmer mod. 141 polarimeter. Mass spectra were measured on an AEI mod. 902 instrument. ^{1}H-NMR (270 MHz) and ^{13}C-NMR (67.88 MHz) spectra were recorded on a Fourier transform Bruker WH 270 spectrometer with ASPECT 2000 computer with 48 K memory (32 K data).

The nuclear Overhauser effect difference FID's were obtained by gated decoupling (decoupler on for 10 s before every scan) with a microprogram virtually identical with the one described in the Bruker Aspect 2000 NMR Software Manual 1 (4). For each measurement, 200 scans with irradiation off resonance were subtracted from those with irradiation on resonance. A decoupler amplitude up to 15 Hz was utilized. A flip angle of about 50° was applied. The sample concentration was 3÷6 mg in 0.5 ml $CDCl_3$ with TMS as internal reference.

Ketotriol **2a** *and diketotriol* **3a**. These compounds were obtained by silica gel column and preparative thin layer chromatography of the aglycone mixture prepared by enzymatic hydrolysis of the glycosides extracted from *Muscari comosum*, as described elsewhere.[1]

Ketotriol **2a** was an amorph solid. $[\alpha]_D$ −27° (c = 0.5). MS, *m/e*: 474.33473 (base peak, M^+, calc. for $C_{29}H_{46}O_5$ 474.33450), 459 (M^+ −15, CH_3), 441 (M^+ −15 −18, CH_3 + H_2O), 417 (M^+ −57, CH_3CH_2CO), 320, 305, 129. IR, cm^{-1}: 3625, 3500, 1725. ^{1}H-NMR: Table 2. ^{13}C-NMR: Table 1.

Diketotriol **3a** had m.p. 156 8° (from ethanol). $[\alpha]_D$ −33° (c = 0.5). MS, *m/e*: 472.31898 (M^+, calc. for $C_{29}H_{44}O_5$ 472.31885), 442 (M^+ −30, CH_2O), 424 (M^+ −30 −18, CH_2O + H_2O), 367 (base peak, M^+ −30 −18 −57, CH_2O + H_2O + CH_3CH_2CO), 255, 167. IR, cm^{-1}: 3620, 3520, 1725, 1695. ^{1}H-NMR: Table 2. ^{13}C-NMR: Table 1.

Triacetate **2b**. A solution of **2a** (10 mg) in dry pyridine (0.5 ml) and acetic anhydride (1 ml) was kept at room temperature overnight. Usual work up afforded triacetate **2b** (10 mg) as an amorph solid. $[\alpha]_D$ −11.5° (c = 0.4). MS, *m/e*: 600 (M^+, base peak), 585 (M^+ −15, CH_3), 543 (M^+ −57, CH_3CH_2CO), 483(M^+ −60 −57, CH_3COOH + CH_3CH_2CO), 446, 405, 363. IR, cm^{-1}: 1720. ^{1}H-NMR: Table 2.

Orthoacetate **2c**. To a solution of ketotriol **2a** (8 mg) in dry benzene (8 ml) pyridinium p-toluenesulfonate (traces) was added.[7] After benzene (2 ml) was distilled, methyl orthoacetate (0.3 ml, freshly distilled) was added. The solution was refluxed for 60 min. After 30 min benzene (2 ml) was distilled. To the cooled solution sat. $NaHCO_3$ and ether were added. Evaporation of the organic layer yielded a solid (10 mg). PLC (7:3 hexane/ether, 1 run) afforded pure orthoacetate **2c** (8 mg). M.p. 168 70° (from hexane). MS, *m/e*: 498 (M^+), 483 (M^+ −15, CH_3), 441 (base peak, M^+ −57, CH_3CH_2CO), 423, 167. IR, cm^{-1}: no hydroxyl bands, 1725, 1408, 1236. ^{1}H-NMR: Table 2.

Acetonide **2d**. A solution of ketotriol **2a** (6 mg) in dry acetone (8 ml) was stirred with anhydrous $CuSO_4$ (100 mg) at r.t. for 24 h. Filtration and evaporation gave a solid (6 mg). PLC (1:1 hexane/ether, 3 runs) afforded pure acetonide **2d** (6 mg). M.p. 123-5° (from hexane/benzene). $[\alpha]_D$ −1.9° (c = 0.3). MS, *m/e*: 514 (M^+), 457 (M^+ −57, CH_3CH_2CO), 441, 423, 345 (base peak). ^{1}H-NMR: Table 2.

Acetonide **3b**. (A) Diketotriol **3a** (8 mg) was treated with anhydrous $CuSO_4$ in dry acetone as above. Filtration and evaporation afforded a solid (8 mg). PLC (1:1 hexane/ether, 3 runs) yielded pure acetonide **3b** (6 mg). M.p. 144 6° (from hexane/benzene). $[\alpha]_D$ +9.3° (c = 0.4). MS, *m/e*: 512 (M^+). ^{1}H-NMR: Table 2.

(B) A solution of acetonide **2d** (4 mg) in dry dichloromethane (1 ml) was stirred with pyridinium chlorochromate (4 mg) at room temperature for 24 h. After addition of ether, filtration and evaporation, a solid (4 mg) was obtained. PLC (1:1 hexane/ether, 2 runs) gave acetonide **3b** (3 mg). M.p. 144–6 (from hexane/benzene), undepressed by mixture with a sample prepared as in A). MS, *m/e*: 512 (M^+).

Determination of the absolute configuration of C-3 in acetonide **2d**. A solution of **2d** (18 mg, 0.035 mM) and racemic α-phenylbutyric acid anhydride (58.5 mg, 0.188 mM) in pyridine (1 ml) was left at r.t. for 24 h. Work up as usual[6] afforded α-phenylbutyric acid (41 mg), $[\alpha]_D$ −1.1° (c = 0.9; benzene). Fully stereospecific esterification should yield $[\alpha]_D$ = 95.6/[2(5.371)-1] = −9.8°; therefore the optical yield is 11.2%. The neutral fraction contained no starting material (^{1}H-NMR).

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