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TEN HOMOISOFLAVANONES FROM TWO *MUSCARI* SPECIES

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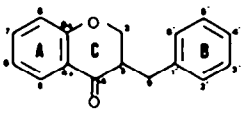
Key Word Index -*Muscari armeniacum*; *M. botryoides*; Liliaceae; homoisoflavanones.

Abstract From the bulbs of *Muscari armeniacum* and of *M. botryoides* 10 novel homoisoflavanones were isolated. All these new 3-benzyl-4-chromanones were substituted with hydroxy or methoxy groups in the 3'- and 4'-positions.

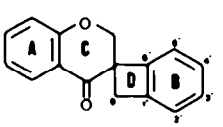
INTRODUCTION

We have recently [1-3] described the isolation and the structure elucidation of a number of homoisoflavanones of 3-benzyl-4-chromanone and scillascillin type [4] from bulbs of *Muscari comosum* Miller (Liliaceae). The extension of this study to bulbs of other *Muscari* species, namely *Muscari armeniacum* Leicht and *Muscari botryoides* Miller, gave 10 novel homoisoflavanones of both types (**1**-**7** and **13**-**15**) in addition to some 3-benzyl-4-chromanones (**8**-**12**) already found in *Muscari comosum* [1-3]. The distribution of homoisoflavanones in the bulbs of the two plants examined is shown in Table 1. Its noteworthy that all the novel 3-benzyl-4-chromanones described in this paper bear oxygen functions at both positions 3' and 4'. This constitutes a unusual substitution pattern of the B ring [1-6].

The structures of the novel compounds **1**-**7** and **13**-**15** were elucidated by spectral analysis (^{1}H and ^{13}C NMR, MS and UV). The known compounds **8**-**12** were identified by comparison of their physical properties with those of authentic samples.



	5	6	7	8	3'	4'
1	OH	OMe	OH		OH	OH
2	OH	OMe	OH		OMe	OH
3	OH	OMe	OH		OH	OMe
4	OH		OMe	OH	OH	OH
5	OH		OH		OH	OH
6	OMe		OH		OH	OH
7	OMe		OH		OH	OMe
8	OH	OMe	OH			OH
9	OH		OH		OH	OMe
10	OH		OMe	OH		OH
11	OH	OMe	OMe	OH		OH
12	OH		OH			OH



	5	7	3'	4'
13	OH	OMe	OH	OH
14	OH	OMe	OH	OMe
15	OH	OH	OH	OMe
16	OH	OH	OMe	OH

RESULTS AND DISCUSSION

The molecular formulae of all the compounds described in this paper have been established by high resolution mass spectrometry.

Elucidation of the carbon skeleton of **1**-**7** *and* **13**-**15**

The 3-benzyl-4-chromanone structure of compounds **1**-**7** was deduced from the presence in their ^{1}H NMR spectra (Table 2) of the signals of the -(2)CH_2 (3)CH (9)CH_2 grouping, which were clearly seen as eight lines at δ 4.0-4.3 [AB of ABX, (2)CH_2], one multiplet at δ2.5-2.9 [(3)CH] and two double doublets centred in the ranges δ2.5-2.7 and δ3.0-3.1 [(9)CH_2], respectively. On the other hand, the methylene protons at C-2 and C-9 in scillascillinoids **13**, **14** and **15** appeared as two AB quartets (the former was centred at δca 4.5; the signals of the latter were centred at δca 3 and δca 3.5 with $J_{AB} = ca$ 13 Hz), due to the absence of a proton at C-3. The signal of the 3-carbon appeared as a singlet (δca 55) in the ^{13}C off-resonance NMR spectra (Table 3; compare with the known compound **16**).

Elucidation of the B ring substitution pattern of **1**-**7**

The B ring of 3-benzyl-4-chromanones **1**-**7** bears two oxygenated functions. In fact, the base peak in the mass

Table 1. Homoisoflavanones in *M. armeniacum* and *M. botryoides*

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
M. armeniacum	×	×	×	×	×	×	×	×	×			×	×		×
M. botryoides									×	×	×		×	×	×

Table 2. Proton shifts of homoisoflavanones in CD_3OD*

Compound	2-H_2	3-H	5-H	6-H	8-H	7-H	9-H_2	4'-H	2'-H	3'-H	5'-H	6'-H
1	4.08, 4.25 AB of ABX (4.3, 7.3, 11.4)	2.79 *m*	12.22 *s*	3.80 *s*	5.92 *s*	10.66 *s*	2.60 *dd* (10.0, 13.5) 3.06 *dd* (4.3, 13.5)	8.72 s†	6.70 *d* (1.8)	8.79 s†	6.73 *d* (8.1)	6.56 *dd* (1.8, 8.1)
2	4.08, 4.24 AB of ABX (4.0, 7.0, 11.0)	2.83 *m*	12.22 *s*	3.77 *s*	5.91 *s*	10.5 *br*	2.66 *dd* (10.3, 13.6) 3.10 *dd* (4.8, 13.6)	8.78 *s*	6.80 *d* (1.8)	3.83 *s*	6.73 *d* (8.1)	6.65 *dd* (1.8, 8.1)
3	4.06, 4.23 AB of ABX (4.1, 7.3, 11.4)	2.81 *m*	12.22 *s*	3.77 *s*	5.91 *s*	9.87 *s*	2.62 *dd* (9.9, 13.6) 3.06 *dd* (4.8, 13.6)	3.82 *s*	6.71 *d* (1.8)	8.75 *s*	6.85 *s* (8.1)	6.66 *dd* (1.8, 8.1)
4	4.11, 4.28 AB of ABX (4.4, 7.3, 11.4)	2.80 *m*	11.82 *s*	6.10 *s*	8.17*s*	3.87 *s*	2.56 *dd* (10.3, 13.6) 3.04 dd (4.4, 13.6)	8.73 s†	6.69 d (1.8)	8.80 s†	6.70 *d* (8.1)	6.54 *dd* (1.8, 8.1)
5	4.08, 4.24 AB of ABX (4.6, 7.3, 11.4)	2.76 m	12.17 *s*	5.86	5.83 AB (2.2)	10.76 *s*	2.57 *dd* (10.3, 13.5) 3.02 *dd* (4.5, 13.5)	8.72 s†	6.67 *d* (1.8)	8.79 s†	6.70 *d* (8.1)	6.54 *dd* (1.8, 8.1)
6	4.02, 4.18 AB of ABX (4.4, 7.2, 11.4)	2.58 *m*	3.79 *s*	6.04	5.93 AB (1.8)	10.48 *s*	2.50 *dd* (10.7, 13.0) 2.96 *dd* (4.4, 13.0)	8.67 s†	6.66 *d* (1.8)	8.76 s†	6.69 *d* (8.1)	6.52 *dd* (1.8, 8.1)
7	4.05, 4.21 AB of ABX (3.7, 6.6, 11.4)	2.66 *m*	3.81 *s*	6.07	5.97 AB (1.8)	10.48 *s*	2.58 *dd* (10.7, 12.5) 3.00 *dd* (3.6, 12.5)	3.82 *s*	6.69 *d* (1.8)	8.80 *s*	6.84 *d* (8.1)	6.65 *dd* (1.8, 8.1)
13	4.50 *s*		12.05 *s*	6.05	6.03 AB (2.2)	3.81 *s*	2.93, 3.48 AB (13.5)	8.82 s†	6.48 s‡	8.79 s†	6.64 s‡	
14	4.54, 4.56 AB (9.0)	—	12.09 *s*	6.08	6.05 AB (2.2)	3.83 *s*	2.99, 3.51 AB (13.2)	3.76 *s*	6.68 *s*	8.88 *s*	6.65 *s*	
15	4.51, 4.53 AB (9.0)	—	12.12 *s*	5.93	5.90 AB (2.2)	10.82 *s*	2.97, 3.49 AB (13.2)	3.77 *s*	6.68 *s*	8.86 *s*	6.65 *s*	-
16§	4.50 *s*	—	12.11 *s*	5.91	5.89 AB (1.8)	8.5–9.3	2.98, 3.51 AB (13.2)	8.5–9.3	6.82 *s*	3.83 *s*	6.51 *s*	

*Chemical shifts are given in δ(ppm) relative to TMS. Coupling constants (in parentheses) are given in Hz. The signals of the hydroxyl protons, which were not detected in CD_3OD owing to deuteron–proton exchange, are reported for solutions in DMSO-d_6.

†‡Interchangeable values.

§Ref. [2].

Table 3. Carbon shifts of homoisoflavanones in CD_3OD*

C	1	2	3	4	5	6	7	8†	10†	13	14‡	15	16†
2	70.2	70.4	70.3	70.5	70.1	70.2	69.9	70.2	70.5	75.0	74.4	74.9	74.7
3	§	§	§	§	§	50.7	§	49.1	48.8	55.3	54.8	55.3	55.2
4	200.1	199.5	200.0	200.1	199.4	194.5	194.0	199.9	200.1	198.5	197.7	198.4	197.9
4a	102.9	103.0	103.0	103.2	102.8	105.6	105.4	102.7	103.2	103.2	102.8	102.6	102.4
5	156.8	156.7	156.8	158.2	165.8	166.9	166.8	156.7	158.2	165.6	164.9	165.9	165.8
6	130.5	130.8	129.2	93.5	97.1	97.1	96.8	130.4	93.5	95.8	95.6	97.3	97.3
7	160.9	160.8	160.9	158.0	168.2	167.3	166.8	161.1	158.1	169.6	168.8	168.4	168.5
8	95.8	95.8	95.8	127.6	95.8	94.6	94.6	95.9	127.6	94.7	94.6	96.0	96.0
8a	160.1	159.8	160.1	149.3	164.7	164.9	164.6	160.0	149.2	164.8	164.0	165.0	165.0
9	33.2	33.5	33.1	33.0	33.2	34.0	33.6	32.9	32.8	35.6	35.9	36.0	35.9
1′	130.9	130.6	132.3	131.0	130.9	131.7	132.9	130.0	130.2	134.0	134.7	135.7	134.1
2′	117.1	113.7	117.0	117.2	117.1	117.5	117.1	131.0	131.1	112.0	111.7	112.1	109.0
3′	146.4	148.9	147.8	146.4	146.4	146.8	147.8	116.3	116.4	148.4	148.8	149.6	150.8
4′	145.1	146.1	147.8	145.1	145.1	145.4	147.6	157.1	157.2	146.7	148.8	149.6	148.1
5′	116.5	116.3	112.9	116.5	116.5	116.8	113.1	116.3	116.4	110.1	106.5	107.3	110.1
6′	121.5	122.7	121.3	121.5	121.5	121.8	121.4	131.0	131.1	135.9	134.7	135.7	137.2
5-OCH_3	—	—	—			56.6	56.5	—					
6-OCH_3	61.0	61.0	61.0	-	-			60.9		—	—	—	—
7-OCH_3			-	56.7	—	—		-	56.7	56.3	56.6	—	-
3′-OCH_3	--	56.5	—	--	—	—	—	—	—			-	56.7
4′-OCH_3			56.4				56.2	—	—	—	56.1	56.9	—

*Chemical shifts are given in δ(ppm) relative to TMS.
†Ref. [7].
‡Measured in 9: 1 CD_3OD $CDCl_3$.
§Buried with solvent signals.

spectra was due to the dihydroxytropylium fragment (*m/z* 123) in the case of **1**, **4**, **5** and **6**, and to the hydroxymethoxytropylium fragment (*m/z* 137) in the case of **2**, **3** and **7**. None of the two oxygenated functions is *ortho* to the 1'-position and therefore they are at positions 3' and 4' since in the ^{13}C NMR spectra the signal of the 1'-carbon was at δ 130–133, which is the same chemical shift range of the 1'-carbon of the 3-benzyl-4-chromanones bearing a 4'-hydroxyl group only [7]. The signals of the three protons at positions 2' (*d*, J_{meta} = 1.8 Hz), 5' (*d*, J_{ortho} = 8.1 Hz) and 6' (*dd*, J_{meta} = 1.8 Hz, J_{ortho} = 8.1 Hz) were clearly discerned in the zone δ6.5–6.8. The NOE enhancements of the 5'-proton signal of **3** and of **7** and the 2'-proton signal of **2** upon irradiation of the methoxyl proton signal at δ3.82 (**3**), δ3.82 (**7**) and δ3.83 (**2**), respectively, indicated the attachment position of the B ring methoxyl group in the compounds.

Elucidation of the A ring substitution pattern of **1**–**7**

Compounds **1**–**3** bear one methoxyl and two hydroxyl substituents. This was indicated by the presence in the mass spectra of the peak *m/z* 183, due to hydrogen shift and retro-Diels–Alder cleavage of the chromone fragment [4]. One of the hydroxyl proton signals appears at δ12.22 (5-OH, chelated). The assignment of the second A ring hydroxyl group at the 7-position of **1**, **2** and **3** was indicated by the chemical shifts of the A ring methine hydrogen (δ < 6.00) and carbon (δ95.8–95.9) atoms [7]. The methoxyl group must be at C-6 and the 8-position must be unsubstituted since the ^{13}C NMR signal of the 5-carbon was displayed at δ156.7–156.8, in good agreement with the value expected on the basis of substituent effects [7]. Accordingly, the chemical shifts of the remaining A ring carbons were very similar to those of known **8**.

The mass peak at *m/z* 167, derived from hydrogen shift and RDA cleavage of the chromone fragment, indicated that both **6** and **7** bear one methoxyl and one hydroxyl substituent at the A ring. The UV absorptions at 284 nm (**6**) and at 285 nm (**7**) remained unaffected upon addition of aluminium chloride (absence of 5-OH, confirmed by the absence of proton signals at δ > 11), but were shifted (+ 30 nm) upon addition of sodium acetate (presence of a free hydroxyl at C-7) [8]. The NMR signals of the two A ring methine protons appear as an AB system with *J* = 1.8 Hz in both compounds indicating their *meta* location and therefore that the methoxyl group is at position 5. Interestingly, although both **6** and **7** bear a free hydroxyl group at C-7, their NMR spectra display the signals of one of the two A ring methine protons at δ > 6.00 [7]. This is clearly due to its *ortho* location with the 5-methoxyl as deduced by the NOE enhancement of its signal upon irradiation at the 5-methoxyl proton frequency.

The presence of two free hydroxyl groups as the only substituents of the A ring of **5** was deduced from the MS peak *m/z* 153. One hydroxyl group is located at C-5 (proton NMR signal at δ12.17). The location of the second was established to be position 7 on the basis of the chemical shift values of the 6- and 8-protons and of the 5-, 6- and 8-carbons [7].

The peak *m/z* 183 in the mass spectrum of **4** indicated that the A ring bears two hydroxyl and one methoxyl group. The NMR signals of the hydroxyl proton at δ12.5 and of the A ring methine proton at δ > 6.00 revealed that one hydroxyl group is at C-5 and the methoxyl group at C-7. The chemical shifts of the A ring carbons are very similar to those of **10**. Therefore, the remaining hydroxyl group is linked at C-8.

Elucidation of the substitution pattern of **13**–**15**

The A ring substitution pattern was deduced from the mass peaks *m/z* 167 (**13** and **14**) and *m/z* 153 (**15**), from the hydroxy-proton NMR signals at δca 12 (**13**–**15**, 5-OH) and from the chemical shifts of the A ring proton and carbon atoms [7].

The mass spectra of **14** and **15** displayed the ((2)C-ring D-ring B) peak at *m/z* 162 which is also present in the spectrum of **16** and is indicative of one methoxyl and one hydroxyl B ring substituent [2]. The singlet appearance of the NMR signals of the two B ring protons revealed their *para* location. The NMR signals of the two methoxyl groups of **14** were distinguished by measuring the NOE enhancement of the signals of the two protons at C-6 and C-8 (δ6.08, δ6.05, ABq) and the B ring proton at δ6.65 upon irradiation at δ3.83 and δ3.76, respectively. In addition, upon irradiation of the methoxyl signal at δ3.77 of **15** an NOE enhancement was measured for the singlet at δ6.65. For both **14** and **15** a long-range 2D-homonuclear correlation experiment revealed the coupling of the δ6.68 B ring proton with the 9-protons. Therefore, the ring-B methoxyl group must be at the 4'-position and the hydroxyl group at the 3'-position in both compounds.

A mass peak *m/z* 148 (two B ring hydroxyl groups) for the ((2)C-ring D-ring B) fragment and the singlet appearance of the two ring-B protons (location at 2' and 5') could be considered convincing evidence for the B ring substitution pattern of **13**.

Assignment of ^{13}C *chemical shifts*

The assignments of the ^{13}C chemical shifts of compounds **1**–**7** and **13**–**15** were based on comparison with other homoisoflavanones [7] and on consideration of known substituent effects [9, 10]. In some cases additional experiments were required. They are described below.

For the 3' 4'-dihydroxy compounds **1**, **4**, **5** and **6**, by a carbon–proton long-range 2D shift correlation experiment the 3'- and 4'-carbon lines were found to be correlated to the 5'- and to the 2'- and 6'-proton lines, respectively. This experiment was unsuccessful in assigning the remaining B ring methine carbon signals owing to the close proximity of the relevant signals in the proton spectra. However, the signal at δca 116 was safely assigned to 5'-carbon since it did not display a $J^3_{C,H}$ in the gated fully coupled spectra of the four compounds. Distinction between the 2'- and 6'-carbon lines was made easy by consideration of the shielding effect of the *ortho*-hydroxy group. The signal of the methoxy-bearing 3'-carbon of **2** was distinguished from that of the 4'-carbon since it exhibited coupling with the methoxy protons in a gated coupled spectrum.

Appropriate NMR experiments were needed for the assignment of all the B ring carbons of **13**. A selective INEPT experiment with irradiation at δ2.93 (upfield signal of 9-H_2) led to the identification of the 3'-carbon line (δ148.4) through correlation *via* $J^4_{C,H}$ coupling and,

consequently, to the assignment of the 4'-carbon line (δ 146.7). Distinction between the signals of C-1' and C-6' and of C-2' and C-5' was obtained by analysis of the signal multiplicity in a gated fully coupled spectrum.

EXPERIMENTAL

^{13}C and ^{1}H spectra were recorded in CD_3OD (when not otherwise specified) solutions at 30° and 67.88/270.13 MHz ($^{13}C/^{1}H$) with a WH-270 FT NMR spectrometer (Bruker) equipped with a dual-probe. One-dimensional spectra were typically obtained with 3000 Hz (^{1}H) and 13000 Hz (^{13}C) spectral widths. Nuclear Overhauser enhancements were obtained in the difference mode as reported in ref. [11]. Fully coupled spectra were measured in the gated mode at 67.88 MHz using a pulse width of 4 μsec, a sweep width of 13000 Hz and blocks of 32 k data points of memory.

Selective INEPT [12] experiments were performed with the Bruker INEPTRD microprogram using delays $D_2 = D_3 = 30$ msec corresponding to $J_{C,H} = 8$ Hz. Long-range 2D carbon proton shift correlation [13] experiments were performed with the Bruker XHCORR microprogram using delay $D_3 = 100$ msec corresponding to $J_{C,H} = 5$ Hz. Long-range 2D proton-proton shift correlation [14] experiments were performed with the Bruker COSYLR microprogram using delay $D_2 = 80$ msec corresponding to $J_{H,H} = 3$ Hz.

Isolation of homoisoflavanones. Fresh bulbs (18 kg) of *Muscari armeniacum* Leicht (purchased from Stassen Italiana, Como, Italy, and authenticated by the Botanical Garden of the University of Naples) were homogenized in a mechanical stirrer, freeze-dried and extracted in a Soxhlet with light petrol (12 hr), with Et_2O (12 hr) and then with MeOH (12 hr).

The Et_2O extract was evapd (5 g) and chromatographed on a silica gel (120 g) column with a gradient mixture of hexane Et_2O and then of Et_2O–MeOH. Homoisoflavanones were contained in the fractions eluted with 100% Et_2O (fraction A, 1.5 g) and with 9:1 Et_2O MeOH (fraction B, 800 mg).

Fraction B was further purified by CC (silica gel; 19:1 $CHCl_3$ MeOH) and HPLC (LiChroCart-NH_2 7 μm (Merck), 250 × 4 mm, 60 atm, UV 260 nm; 1:1 $CHCl_3$ MeOH) to give compound **6** (26 mg). Fraction A on rechromatography (hexane with increasing amounts of Me_2CO) yielded fractions A1 (4:1 hexane Me_2CO; 200 mg), A2 (7:3; 80 mg) and A3 (3:2; 60 mg). The latter was crystallized from MeOH–hexane to give compound **4** (54 mg). HPLC (conditions as above; 7:3 MeOH $CHCl_3$) of fraction A2 yielded compound **5** (24 mg) and compound **1** (22 mg). HPLC (conditions as above; 3:2 MeOH $CHCl_3$) of fraction A1 gave two main fractions, A1A (90 mg) and A1B (102 mg). By repetitive PLC (silica gel; 98:2 $CHCl_3$ Me_2CO) compounds **15** (6 mg), **13** (60 mg), **9** (12 mg) and **12** (15 mg) were obtained from the former and compounds **8** (12 mg), **2** (6 mg) and **3** (5 mg) from the latter.

The MeOH extract of the bulbs was evapd (9.5 g) and submitted to CC (silica gel). The fractions eluted with 9:1 $CHCl_3$ MeOH were evapd (103 mg) and then purified by subsequent CC (silica gel; 9:1 $CHCl_3$ AcOEt) and HPLC (conditions as above; 3:7 MeOH $CHCl_3$) to yield compound **7** (7 mg).

A similar isolation procedure was adopted to obtain homoisoflavanones from bulbs of *Muscari botryoides* Miller (2 kg; collected in May 1985 near Formia, Lazio, Italy and authenticated by the Botanical Garden of the University of Naples). Compounds **9** (15 mg), **10** (10 mg), **11** (24 mg), **13** (52 mg), **14** (43 mg) and **15** (23 mg) were isolated.

On TLC (silica gel; 4:1 C_6H_6 AcOEt) homoisoflavanones **1**–**15** exhibited the following increasing polarity order: **6** > **4** > **7** > **5** > **1** > **13** > **2** > **3**, **12** > **10**, **11** > **9** > **15** > **8** > **14**.

Compound **1** had mp 179–181° (from $CHCl_3$–MeOH), $[\alpha]_D$ −65° (MeOH, c = 0.6). EIMS, 70 eV, *m/z* (rel. int.): 332.0885 ([M]$^+$; calc. for $C_{17}H_{16}O_7$ 332.0896) (80), 210 (100), 209 (50), 195 (60), 183 (40), 167 (30), 149 (70), 123 (85).

Compound **2** had mp 205–206° (from MeOH–hexane), $[\alpha]_D$ −37° (MeOH, c = 0.5). EIMS, 70 eV, *m/z* (rel. int.): 306.1044 ([M]$^+$; calc. for $C_{18}H_{18}O_5$ 346.1052) (25), 210 (45), 209 (20), 195 (20), 183 (30), 167 (20), 149 (35), 137 (100).

Compound **3** was a powder. EIMS, 70 eV, *m/z* (rel. int.): 346.1049 ([M]$^+$; calc. for $C_{18}H_{18}O_5$ 346.1052) (30), 210 (50), 209 (20), 195 (40), 183 (40), 167 (20), 149 (30), 137 (100).

Compound **4** had mp 138–141° (from MeOH–hexane), $[\alpha]_D$ −43 (MeOH, c = 0.7). EIMS, 70 eV, *m/z* (rel. int.): 332.0899 ([M]$^+$; calc. for $C_{17}H_{16}O_7$ 332.0896) (95), 210 (100), 195 (15), 183 (50), 167 (35), 149 (20), 123 (95).

Compound **5** was an oil. EIMS, 70 eV, *m/z* (rel. int.): 302.0781 ([M]$^+$; calc. for $C_{16}H_{14}O_6$ 302.0790) (65), 180 (100), 179 (80), 153 (50), 123 (85).

Compound **6** was a vitreous solid, $[\alpha]_D$ −59° (MeOH, c = 0.6). UV λ_{max}^{MeOH} nm (log ε): 284 (4.2), shifted to 314 upon addition of NaOAc. EIMS, 70 eV, *m/z* (rel. int.): 316.0939 ([M]$^+$; calc. for $C_{17}H_{16}O_6$ 316.0947) (25), 194 (40), 193 (40), 167 (100), 123 (40).

Compound **7** was a powder. UV λ_{max}^{MeOH} nm (log ε): 285 (4.2), shifted to 315 upon addition of NaOAc. EIMS, 70 eV, *m/z* (rel. int.): 330.1095 ([M]$^+$; calc. for $C_{18}H_{18}O_6$ 330.1103) (30), 193 (10), 167 (95), 137 (100).

Compound **13** was a powder. EIMS, 70 eV, *m/z* (rel. int.): 314.0785 ([M]$^+$; calc. for $C_{17}H_{14}O_6$ 314.0790) (20), 167 (25), 148 (100).

Compound **14** had mp 187–188° (from MeOH), $[\alpha]_D$ +9° (MeOH, c = 0.2). EIMS, 70 eV, *m/z* (rel. int.): 328.0940 ([M]$^+$; calc for $C_{18}H_{16}O_6$ 328.0947) (40), 167 (100), 162 (15).

Compound **15** had mp 209–211° (from MeOH–hexane), $[\alpha]_D$ +11 (MeOH, c = 0.4). EIMS, 70 eV, *m/z* (rel. int.): 314.0788 ([M]$^+$; calc. for $C_{17}H_{14}O_6$ 314.0790) (65), 162 (40), 153 (100).

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