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NEO-CLERODANE DITERPENOIDS FROM *SCUTELLARIA ORIENTALIS* SUBSP. *PINNATIFIDA*

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Key Word Index—*Scutellaria orientalis* subsp. *pinnatifida*; Labiatae; neo-clerodane diterpenes; scutorientalins A–C.

Abstract—Three new neo-clerodane derivatives, scutorientalins A–C, have been isolated from an acetone extract of the aerial parts of *Scutellaria orientalis* subsp. *pinnatifida*. The structures of the new diterpenoids, 19-acetoxy-6α-isobutyroyloxy-4α,18:8β,13*S*-diepoxy-neo-clerodan-15,16-olide (scutorientalin A); (11*S*)-11-acetoxy-8β, 19-dihydroxy-6α-isobutyroyloxy-4α, 18 epoxy-neo-cleroda-13-en-15,16-olide (scutorientalin B) and (11*R*)-11-hydroxy-19-acetoxy-6α-isobutyroyloxy-4α,18:8β,13*S*-diepoxy-neo-clerodan-15,16-olide (scutorientalin C), were established by chemical and spectroscopic means and by comparison with closely related compounds.

INTRODUCTION

The neo-clerodane diterpenes isolated from *Scutellaria* species possess interesting biological activities [1–5], in particular as insect antifeedants and against plant pathogenic fungi. In a continuation of our search for new neo-clerodanes in *Scutellaria* plants [6–9], we have now investigated *S. orientalis* subsp. *pinnatifida*. An acetone extract of the aerial parts of this plant provided three new neo-clerodane derivatives, scutorientalins A–C (**1–3**), whose structures were established by spectroscopic methods.

RESULTS AND DISCUSSION

Scutorientalin A (**1**) was assigned the molecular formula $C_{26}H_{38}O_8$ and its IR spectrum showed absorption for γ-lactone, ester and oxirane groups. The ^1H and ^{13}C NMR spectra of **1** (Tables 1 and 2) revealed the presence of an acetoxyl group and an isobutyroyloxy substituent (δ 2.40 *septet*, H-2′; 1.11*d*, 1.16*d*, 3H each) and showed the characteristic signals of a neo-clerodane diterpene possessing a 4α, 18-oxirane group [H-18 at δ 3.02 *dd* J_{gem} = 4.0 Hz; $J_{18B,3\alpha}$ = 2.3 Hz and 2.24 *d*, J = 4.0 Hz, δ_C = 65.0 *s* (C-4) and 48.6*t* (C-18)] [1, 2, 4, 6–10]. In addition to an 8, 13-ether bridge [Me-17 at δ 1.15 s; δ_C = 79.1 *s* (C-8), 76.6 *s* (C-13) and 24.4 *q* (Me-17) and a 13-spiro-15,16-lactone moiety (H-14 at δ 2.45 *d* and 2.92 *d*, J = 17.0 Hz; C-16 protons at δ 4.11 *d* and 4.24 *d* J = 8.7 Hz; δ_C 44.3 *t* (C-14), 175.7 *s* (C-15) and 76.7 *t* (C-16) as found in other neo-clerodane derivatives previously isolated from *Scutellaria* plants [6–8, 10–15]. All these protons must be assigned to a 4α, 18: 8,13-diepoxy-neo-clerodan-15,16-olide derivative. The attachment of the acetate and isobutyroyloxy groups to the neo-clerodane nucleus was shown by two one-proton signals, which appeared as an AB*q* (δ 4.47 *d* and δ 4.71 *d*, J = 12.2 Hz) which we have assigned to C-19 methylene protons, and a one-proton signal (δ 5.08 *dd*, J_1 = 11.3 Hz; J_2 = 5.1 Hz), which we have assigned to C-6 [7, 10–15]. The position of the acetate and isobutyroyloxy groups and the relative configuration of **1** were deduced from a NOESY experiment. The axial H-6β proton showed NOEs with H-10β, H-7β and H_B-18. The H_A-18 proton showed NOEs with H-3β, whereas H_A-19 showed cross-peaks with the acetoxyl group. This last result established that this ester group is placed at C-19; consequently, the isobutyroyloxy group must be placed at the C-6 equatorial position.

Treatment of **1** with HCl [16, 17] gave **2** in which the ^1H NMR signal (Table 1) of H-6β was paramagnetically shifted at δ 5.38 (*dd*, $J_{6\beta,7\alpha}$ = 10.7 Hz; $J_{6\beta,7\beta}$ = 4.9 Hz), which established that the proton at C-6β and -CH_2Cl group at C-4 were β-oriented. In a NOESY experiment, the Me-20 protons showed NOEs with the H-7α, Me-17 and 2H-19. The relative stereochemistry of the spiran centre at C-13 was secured, because NOE cross-peaks were observed between Me-17 and C-16 methylene protons [6–8, 10, 11). These results established that the B/C ring junction of **1** is *cis*, and its H-7α and C-19, C-16 methylene groups are α- oriented, possessing *cis*-spatial relationships with the C-17 and C-20 methyl groups [6-8, 10, 11]. The axial H-6β and 13-spiro-15,16-γ-lactone moiety were also confirmed by comparison of the ^1H and ^{13}C NMR data for **1** with these reported for closely related compounds [6–8, 10–15].

Table 1. ^{1}H NMR spectral data for compounds **1–3** (250 MHz, $CDCl_3$)*

H	1	2	3†
1α	—	—	*ca* 1.48‡
1β	—	—	*ca* 1.91‡
2α	—	—	*ca* 1.86‡
2β	—	—	*ca* 1.65‡
3α	—	—	*ca* 2.38‡
3β	1.05 *m*	—	*ca* 1.17‡
6β	5.08 *dd*	5.38 *dd*	5.23 *dd*
7α	1.77 *dd*	—	1.90 *dd*
7β	1.58 *dd*	—	1.58 *dd*
10β	2.16 *dd*	2.16 *dd*	2.14 *dd*
11α	—	—	5.52 *br d*
12A	—	—	2.51 *dd*‡
12B	—	—	3.53 *br d*
14A	2.45 *d*‡	2.44 *d*‡	
			5.84 *br s*
14B	2.92 *d*	2.87 *d*	
16A	4.11 *d*	4.16 *d*	4.64 *dd*
16B	4.24 *d*	4.25 *d*	4.84 *dd*
Me-17	1.15 *s*	1.17 *s*	1.29 *s*
18A§	2.24 *d*		2.28 *d*
		4.00 *s*	
18B‖	3.02 dd		2.97 dd
19A	4.47 *d*	4.68 *d*	4.12 *t*¶
19B	4.71 *d*	4.90 *d*	4.30 *d*
Me-20	0.83 *s*	0.89 *s*	0.70 *s*
2′	2.40 *sept*‡	2.45 *sept*‡	2.49 *sept*‡
3′	1.11 *d*	1.13 *d*	1.15 *d*
4′	1.16 *d*	1.15 *d*	1.18 *d*
OAc	2.11 *s*	2.10 *s*	1.99 *s*

J (Hz)	1	2	3
6β, 7α	11.3	11.3	11.7
6β, 7β	5.1	4.7	4.4
7α, 7β	14.6	14.4	14.3
10β, 1β	3.8	3.2	2.4
10β, 1α	13.5	12.1	12.7
11α, 12A	—	—	10.9
11α, 12B	—	—	<0.6
14A, 14B	17.0	17.2	15.4
14, 16A	—	—	1.7
14, 16B	—	—	1.7
16A, 16B	8.7	8.8	17.4
18A, 18B	4.0	—	3.7
18B, 3α	2.3	—	2.2
19A, 19B	12.2	13.1	11.8
19A, OH	—	—	9.9
2′,3′; 2′,4′	6.9	6.9	6.9

*Spectral parameters were obtained by first-order approximation. All assignments were confirmed by double resonance experiments.

†Assignments in agreement with ^{1}H–^{13}C COSY spectra.

‡Overlapped signal.

§Exo hydrogen with respect to ring B.

‖Endo hydrogen with respect to ring B.

¶Collapsed into a *d* after addition of D_2O.

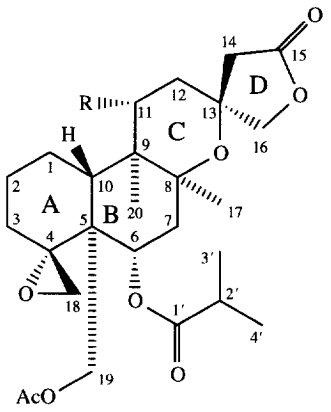
Table 2. ^{13}C NMR spectral data for compounds **1**, **3** and **5** (62.9 MHz, $CDCl_3$)

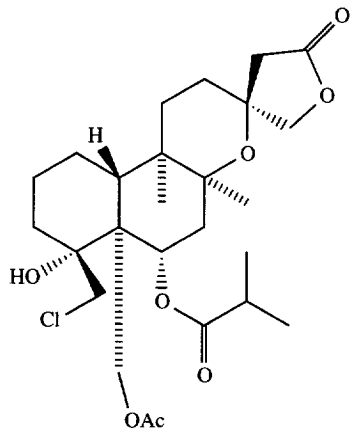
C	1	3	5
1	20.7	23.0	26.9
2	25.2	24.7	28.3*
3	32.6	32.5	28.9*
4	65.0	65.1	61.2
5	44.8	46.1*	44.6
6	68.4	71.2*	68.8*
7	38.2	39.7	39.7
8	79.1	76.1	79.0
9	37.9	46.3*	36.3
10	42.2	43.0	34.0
11	27.1	74.2*	66.2*
12	28.7	33.2	38.1
13	76.6	168.1	76.4
14	44.3	116.4	44.2
15	175.7	175.8	175.8
16	76.7	73.1	76.9
17	24.2	26.4	24.1
18	48.7	47.6	50.3
19	61.9	61.1	61.9
20	18.9	15.8	18.8
1′	173.6*	173.9*	174.1*
2′	34.1	34.2	34.1
3′	20.4*	18.7*	20.2*
4′	20.7*	18.8*	21.0*
OAc	171.1*	170.0*	171.0*
	21.2	20.7	21.2*

*Assignments may be reversed, but those given are considered to be the most likely.

Scutorientalin B (**3**) was assigned the molecular formula $C_{26}H_{38}O_9$. Its IR spectrum showed bands for hydroxyls, α, β-unsaturated γ-lactone groups and ester groups. The ^{1}H and ^{13}C NMR spectra of **3** (Tables 1 and 2) were almost identical with those of scutalpins B and C isolated from *S. alpina* subsp. *javalambrensis* (Spain) [7], scutalpins H and I from *S. alpina* (Italy) [10] and compound **4** isolated from *S. alpina* (Japan) [18]. In fact the observed differences were consistent with the existence in the former of an isobutyroyloxy group instead of the tigloyloxy substituent present in the latter (**4**). The assignments of all protons and carbon resonances of **3** were achieved by double resonance experiments as well as from the ^{1}H–^{13}C COSY spectra. The triplet at δ 4.12 (J = 9.9 Hz) collapsed into a doublet (J = 11.8 Hz) after addition of D_2O, thus confirming that one of the hydroxyl groups of **3** was a primary one, which must be at C-19, whereas the tertiary hydroxyl group must be at the C-8β position, because the Me-17 protons were paramagnetically shifted at δ 1.29 *s* and δ_C 26.4 *q* (C17) [7, 10, 18].

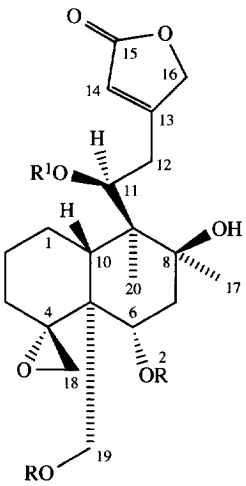
The positions of the acetoxyl and isobutyroyloxy groups in **3** were confirmed to be at C-11 and C-6, respectively, because the ^{1}H NMR resonances (Table 1) at δ 5.52 (*br d*) and 5.23 (*dd*) were the same as those in **4** [18]. NOE experiments confirmed that **3** possessed the same stereochemistry [7, 18] because irradiation at δ 0.70 (*s*, Me-20) caused a positive NOE enhancement of the signals of the H-1α, H-11α, Me-17, H_A-19 and H_B-19 protons, whereas a positive NOE of the H-7β, H_A-12 and Me-20 protons was observed when the Me-17 protons (δ 1.29) were irradiated. Irradiation at

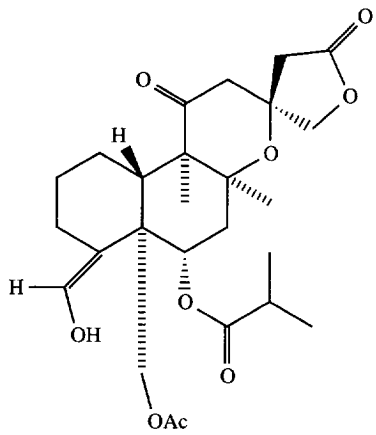




1 R = H
5 R = OH
6 R = OAc

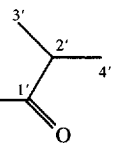
2



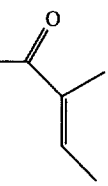


7

3 R = H; R^1 = Ac; R^2 =



4 R = H; R^1 = Ac; R^2 =



δ 5.23 (H-6β) produced a positive NOE enhancement of the signals at δ 1.58 (H-7β), 2.14 (H-10β), 2.97 (H_B-18) and 2.49 *septet* (H-2′), and a negative NOE enhancement in the signal of the other H_A-18 at δ 2.28 [6]. Irradiation at δ 1.16 (Me-3′,4′) caused a positive NOE enhancement of the signals of the H-3α, H-7β, H_A-18 and H-2′. These two last experiments confirmed the close spatial relationship between the oxirane group, H-6β and H-2′ of the isobutyroyloxy group of scutorientalin B, as well as the equatorial C-6 position of the last one. From all of the above data, it was evident that scutorientalin B had the structure depicted in **3**.

The third diterpenoid, scutorientalin C (**5**) ($C_{26}H_{38}O_9$), gave rise to ^{1}H and ^{13}C NMR spectra almost identical with those of **1** (Tables 3 and 2, respectively). In fact, the only difference between the ^{1}H NMR spectra of **5** and **1** was the presence in the

Table 3. ^{1}H NMR spectral data for compounds **5**–**7** (250 MHz, $CDCl_3$, TMS as int. standard)*

H	5	6	7	Δ (ppm)†
6β	5.12 *dd*	5.13 *dd*	5.23 *dd*	+0.11
7β	1.72 *dd*	1.60 *dd*	1.59 *dd*	−0.13
7α	1.77 *dd*	1.74 *dd*	1.74 *dd*	−0.03
10β	2.75 *dd*	2.63 *dd*	—	—
11β	4.33 *t*	5.30 *t*	—	—
12A	—	—	2.29 *d*	—
12B	—	—	2.70 *d*	—
14A	2.47 *d*	2.34 *d*†	2.48 *d*	+0.01
14B	2.90 *d*	2.96 *d*	2.90 *d*	0
16A	4.10 *d*	4.12 *d*	4.14 *d*	+0.04
16B	4.21 *d*	4.25 *d*	4.26 *d*	+0.02
Me-17	1.08 *s*	1.10 *s*	1.19 *s*	+0.11
18A§	2.44 *d*	2.31 *d*	6.42 *br s*	—
18B‖	3.10 *dd*	3.13 *dd*	—	—
19A	4.45 *d*	4.48 *d*	4.41 *d*	−0.04
19B	4.70 *d*	4.68 *d*	4.75 *d*	+0.05
Me-20	0.80 *s*	0.83 *s*	1.03 *s*	+0.23
2′	2.38 *sept*	2.39 *sept*‡	2.56 *sept*	+0.18
3′	1.12 *d*	1.14 *d*	1.20 *d*	+0.08
4′	1.14 *d*	1.16 *d*	1.22 *d*	+0.08
OAc	2.08 *s*	2.06 *s*	1.98 *s*	−0.10
OAc	—	2.11 *s*	—	—
OH¶	2.43 *s*	—	2.78 *s*	—

J (Hz)	5	6	7
6β, 7α	11.3	11.4	11.3
6β, 7β	5.0	5.3	4.8
10β, 1α	13.0	13.0	—
10β, 1β	3.0	3.0	—
11β, 12α	2.6	2.6	—
11β, 12β	2.6	2.6	—
12A, 12B	—	—	12.9
14A, 14B	17.2	17.1	17.2
16A, 16B	8.7	8.8	8.8
18A, 18B	3.6	4.2	—
18B, 3α	1.9	2.0	—
19A, 19B	12.3	12.5	12.3
2′, 3′	6.9	6.8	6.9
2′, 4′	6.9	6.8	6.9

*Spectral parameters were obtained by first-order approximation. All assignments were confirmed by double resonance experiments.

†Between 5 and 7.

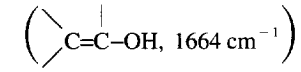
‡Overlapped signal.

§Exo hydrogen with respect to ring B.

‖Endo hydrogen with respect to ring B.

¶Disappeared after addition of D_2O.

former of a one-proton signal at δ 4.33 (*t*, *J* = 2.6 Hz) assigned to H-11β, instead of the methylene protons of **1**. Acetic anhydride–pyridine treatment of **5** yielded a derivative (**6**), the IR spectrum of which was devoid of hydroxyl absorption and whose ^{1}H NMR spectrum (Table 3) showed a paramagnetically shifted signal of H-11β (δ 5.30 *t*, *J* = 2.6 Hz). Furthermore, treatment of **5** with CrO_3–pyridine gave compound **7**, in which the ^{1}H NMR signals (Table 3) of Me-20 and the C-12 methylene protons were paramagnetically shifted at δ 1.03 (*s*) and 2.70 (*d*), respectively. Thus, showing unambiguously that the keto group in **7** was at the C-11 position. According to the small coupling constant of **5** (*J* = 2.6 Hz), the proton at C-11 was equatorial and the hydroxyl group was axial and ring C was in the chair conformation [7, 10, 11]. It is notable that in the same oxidation reaction the 4α,18-oxirane ring in **5** was transformed into a C-4-C-18 vinyl alcohol in **7**. The closure of this vinyl alcohol was revealed by a one-proton singlet at δ 6.42, the 4, 18 double bond was also confirmed by the IR spectrum



The stereochemistry of the 4, 18-double bond must be

Z, because in the ^{1}H NMR spectrum of **7** the signals for H-6β and H-2′ were paramagnetically shifted (Δ + 0.11 ppm and Δ + 0.18 ppm, respectively) (Table 3). This fact showed unambiguously that the isobutyroyloxy group in **5** is at C-6 equatorial position. The vinyl alcohol is stabilized by a hydrogen bond between the hydroxyl group and the adjacent oxygen atom from the isobutyroyloxy group at C-6. The relative stereochemistry of the spiran centre at C-13 of **5** must be the same as in **1** because both compounds showed almost identical chemical shifts for their C-14 and C-16 methylene protons (Tables 1 and 3). If **5** differs from **1** in the stereochemistry at C-13, then strong chemical shift differences for H_2-14 must be expected [8, 11]. All the above data were in complete agreement with a structure such as **5** for scutorientalin C. This neo-clerodane diterpene is the first to be isolated from a *Scutellaria* species with a free hydroxyl group in ring C at the C-11 axial position [6–8, 10, 11].

The absolute configurations of **1**, **3** and **5** were not ascertained. However, on biogenetic grounds, it may be supposed that **1**, **3** and **5** belong to the neo-clerodane series like the other diterpenoids isolated from *Scutellaria* species [6–8, 10–15, 18].

EXPERIMENTAL

Mps: uncorr. Plant materials were collected in June 1994 near Zemen (Bulgaria) and voucher specimens are deposited in the Herbarium of the Higher Institute of Agriculture at Plovdiv, Bulgaria.

Extraction and isolation of the diterpenoids. Dried and powdered aerial parts of *S. orientalis* subsp. *pinnatifida* (950 g) were extracted with Me_2CO (3 × 4 l) at room temp. for 6 days. The combined extracts were evapd *in vacuo* to near-dryness, MeOH (500 ml) was added and the soln extracted with petrol (5 × 150 ml). The MeOH phase was concd, yielding a residue (26 g) to which H_2O was added and the mixt. extracted with $CHCl_3$. The organic extract was dried and the solvent removed to yield 6 g of a gum, which was subjected to CC on silica gel (Merck No. 7734, deactivated with 15% H_2O (w/w), 250 g). Elution with petrol–EtOAc mixs yielded the following compounds in order of increasing chromatographic polarity: **1** (72 mg), **3** (217 mg) and **5** (207 mg).

Scutorientalin A (**1**). Mp 150–152° (from EtOAc–*n*-hexane); $[\alpha]_D^{20}$ −10.3° ($CHCl_3$; *c* 0.321). *IR* ν_{max} (KBr) cm^{-1}: 3058, 2974, 2948, 2879, 1789, 1728 br, 1472, 1422, 1391, 1367, 1288, 1254, 1240, 1193, 1159, 1128, 1116, 1104, 1090, 1028, 995, 913, 806, 719; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 478 $[M]^+$ (0.3), 448 (12), 407 (10), 335 (8), 316 (20), 301 (5), 214 (19), 201 (22), 189 (14), 187 (19), 185 (10), 183 (10), 182 (11), 159 (18), 155 (15), 123 (12), 119 (11), 111 (3), 105 (10), 97 (5), 95 (7), 93 (8), 91 (11), 81 (5), 79 (11), 71 (49), 67 (13), 43 (100). Found: C, 65.74; H, 7.91, $C_{26}H_{38}O_8$ requires: C, 65.25; H, 8.00%.

Conversion of compound **1** *into compound* **2**. A soln of **1** (25 mg) in $CHCl_3$ (8 ml) at room temp. was treated with aq. conc. HCl (1 ml) for 8 min with stirring. The reaction mixt. was then diluted with H_2O (15 ml) and extracted with $CHCl_3$ (3 × 15 ml). The extract was dried (Na_2SO_4) and evapd to dryness, giving a residue that was purified by CC over silica gel (hexane–EtOAc, 3:1, as eluent) giving **2** (18 mg), amorphous solid, mp 83–87°; $[\alpha]_D^{20}$ −4.81° ($CHCl_3$; *c* 0.302); IR ν_{max} (KBr) cm^{-1}: 3454, 2973, 1788, 1732 br, 1471, 1440, 1390, 1371, 1286, 1244, 1200, 1162, 1101, 1084, 1025, 956, 862, 808, 746, 692, 605; ^{1}H NMR: Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 497 $[M - H_2O]^+$ (2), 424 (5), 319 (8), 183 (10), 172 (11), 119 (14), 97 (8), 95 (12), 81 (8), 71 (48), 43 (100). Found: C, 60.21; H, 7.51; Cl, 6.71, $C_{26}H_{39}O_9Cl$ requires: C, 60.58; H, 7.63; Cl, 6.89%).

Scutorienlalin B (**3**). Mp 218–220° (from EtOAc–*n*-hexane); $[\alpha]_D^{20}$ −12.1° ($CHCl_3$; *c* 0.312). IR ν_{max} (KBr) cm^{-1}: 3577, 3528, 3451, 3115, 2974, 2945, 1779, 1737 br, 1638, 1472, 1453, 1374, 1290, 1237, 1206, 1148, 1117, 1094, 1086, 1063, 1025, 964, 896, 844, 609; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; EIMS (70 eV, direct inlet) *m/z* (rel. int.): $[M]^+$ absent 476 $[M - H_2O]^+$ (0.6), 468 (0.4), 393 (0.6), 285 (10), 219 (11), 201 (10), 189 (20), 171 (18), 145 (8), 131 (10), 127 (11), 107 (10), 105 (12), 93 (11), 79 (14), 71 (40), 43 (100). (Found: C, 63.67; H, 7.69, $C_{26}H_{38}O_9$ requires: C, 63.14; H, 7.75%).

Scutorientalin C (**5**). Amorphous solid, mp 93–97°; $[\alpha]_D^{20}$ 0° ($CHCl_3$; *c* 0.337); IR ν_{max} (KBr) cm^{-1}: 3490 (OH), 3061 (epoxide), 1786 (spiro-γ-lactone), 1733 br, 1241 (esters), 2974, 2945, 1472, 1451, 1390, 1375, 1207, 1191, 1165, 1126, 1106, 1078, 1025, 998, 966, 857, 823, 769, 630; ^{1}H NMR: Table 3; ^{13}C NMR: Table 2; EIMS (70 ev, direct inlet) *m/z* (rel. int.): 494 $[M]^+$ (0.5), 464 (0.6), 434 $[M - HOAc]$ (0.9), 352 (0.7), 213 (11), 187 (10), 185 (11), 183 (14), 173 (10), 172 (12), 169 (20), 119 (10), 98 (10), 95 (8), 93 (7), 91 (9), 71 (40), 43 (100). (Found: C, 62.91; H, 7.62; $C_{26}H_{38}O_9$ requires: C, 63.14; H, 7.75%).

Acetylation of **5**. Compound **5** (25 mg) was treated with a mixt. of Ac_2O (0.8 ml) and pyridine (1 ml) at room temp. for 48 hr. Work-up in the usual manner gave **6** (23 mg). Amorphous solid, mp 86–90°, $[\alpha]_D^{20}$ +1.37° ($CHCl_3$; *c* 0.297) IR ν_{max} (KBr) cm^{-1}: 3060, 2974, 1789, 1735 br, 1472, 1451, 1376, 1239, 1186, 1166, 1126, 1080, 1026, 964, 912, 857, 822, 749, 607; ^{1}H NMR Table 3; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 536 $[M]^+$ (0.8), 501 (0.6), 476 $[M–HOAc]^+$ (10), 352 (3), 316 (12), 301 (14), 187 (10), 185 (12), 183 (16), 172 (10), 169 (21), 97 (8), 95 (9), 91 (11), 43 (100). (Found: C, 62.38; H, 7.61; $C_{28}H_{40}O_{10}$ requires: C, 62.67; 7.51%).

Oxidation of **5**. Treatment of **5** (38 mg) in pyridine (1.5 ml) with CrO_3 (45 mg) in the usual manner yielded **7** (18 mg), amorphous solid, mp 109–111°; $[\alpha]_D^{20}$ +6.21° ($CHCl_3$; *c* 0.378). IR ν_{max} (KBr) cm^{-1}: 3476, 2975, 2963, 1786, 1738 br, 1664, 1471, 1457, 1377, 1291, 1235, 1186, 1156, 1104, 1070, 1026, 964, 916, 858, 824, 731, 693, 648, 602; ^{1}H NMR: Table 3; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 492 $[M]^+$ (2), 432 (7), 319 (10), 301 (10), 187 (14), 183 (17), 172

(10), 119 (13), 97 (8), 95 (10), 91 (12), 81 (7), 71 (57), 43 (100). (Found: C, 63.27; H, 4.48 $C_{26}H_{36}O_9$, requires: C, 63.40; H, 7.37%).

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