Pergamon

PII: S0031-9422(98)00445-2

*Phytochemistry* Vol. 49, No. 8, pp. 2443–2447, 1998

Printed in Great Britain
0031-9422/98/$ - see front matter

# AREPTINS A AND B TWO NEW NEO-CLERODANE DITERPENOIDS FROM *AJUGA REPTANS*

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(*Received in revised form* 3 *April* 1998)

**Key Word Index**—*Ajuga reptans*; Labiatae; *neo*-clerodane diterpenoids; areptins A and B.

**Abstract**—Two new *neo*-clerodane derivatives, areptins A and B, have been isolated from the acetone extract of the aerial parts of *Ajuga reptans*, in addition to the previously known diterpenes, ajugareptansin, ajugorientin, ajugachin A and iridoid glucosides, 8-acetylharpagide and harpagide. The structures of the new compounds were established by chemical and spectroscopic means as: (11*S*,13*R*,16*S*)-2α,6α,19-triacetoxy-3β-(2-methylbutyryloxy)-4α, 18:11, 16:15, 16-triepoxy-*neo*-clerodan-1β-ol (areptin A); (11*S*,13*S*,16*S*), 6α-19-diacetoxy-1β [(*E*)-2-methyl-2-butenoyloxy]-4α, 18:11, 16:15, 16-triepoxy-*neo*-cleroda-14-en-3β-ol) (areptin B). 

## INTRODUCTION

In continuation of our studies on the diterpenes from *Ajuga* species [1–5], we have now investigated the aerial parts of *A. reptans*. From the acetone extract of this plant we have isolated two new *neo*-clerodane diterpenes, areptins A (**1**) and B (**2**), besides the already known diterpenes ajugareptansin [6], ajugachin A [1], ajugorientin (**5**) [7] and iridoid glucosides, 8-acetylharpagide and harpagide [8–10]. The structures of **1** and **2** were established by chemical and spectroscopic means and by comparison with those of closely related compounds [1–3, 7, 11, 12].

## RESULTS AND DISCUSSION

Areptin A (**1**) had a molecular formula $C_{31}H_{46}O_{12}$ and its IR spectrum was consistent with the presence of hydroxyl (3454 $cm^{-1}$) and ester groups (1746 br, 1234 *br* $cm^{-1}$). The $^1H$ NMR spectrum (Table 1) showed signals for three acetate groups (δ 1.94 *s*, 2.05 *s* and 2.15 *s*), a 2-methylbutyric ester function (δ 2.18 *m*, 1.40 *m*, 1.06 *d*, *J* = 6.6 Hz; 0.85 *t*, *J* = 7.5 Hz) [2, 6], together with characteristic signals of a *neo*-clerodane structure (Me-17 at δ 0.99 *d*, *J* = 6.3 Hz; Me-20 at δ 1.08 *s*) possessing a 4α,18-oxirane (δ 2.73 *d* and 2.83 *d*, *J* = 4.0 Hz) and hexahydrofurofuran moiety (see the H-11, H-13, $H_2$-15 and H-16 proton resonances in Table 1), which was also confirmed by the significant peaks at *m/z* 113, 111, 83 and 69 in the mass spectrum of **1** like other *neo*-clerodane derivatives previously isolated from *Ajuga* plants [1–7]. The attachment of the above mentioned functions was revealed by the following signals due to six protons on carbon atoms bearing oxygen atoms: δ 5.06 *dd* (1H, $J_1$ = 10.4 Hz; $J_2$ = 8.4 Hz), 5.53 *d* (1H, *J* = 10.5 Hz), 4.33 *d* and 4.79 *d*, $J_{gem}$ = 12.6 Hz), 4.67 *dd* (1H, $J_1$ = 11.5; $J_2$ = 4.7 Hz) and 4.18 *m* (2H, overlapped signals with H-11α). In addition the $^1H$ NMR spectrum of **1** showed an one-proton doublet at δ 1.81 (*J* = 10.5 Hz), which collapsed into a singlet when the multiplet at δ 4.18 was irradiated. This result clearly established that the hydroxyl group of areptin A (**1**) was at C-1β (equatorial position) like in ajugavensin C a *neo*-clerodane diterpene isolated from *A. genevensis* [2, 3]. The chemical shifts and the behaviour of the signals at δ 4.67 *dd*, 4.73 *d* br, and 4.79 *d* were the same as these at H-6β and $H_2$-19, respectively [1–4, 6, 7]. Moreover the signals at δ 5.06 *t* and 5.33 *d* are reciprocally coupled ($J_{2\beta,3\alpha} = J_{2\beta,1\alpha}$ = 10.4 Hz), *trans*-diaxial coupling), which was revealed by double resonance experiments, and they must be assigned to a *neo*-clerodane possessing two ester groups at the C-2α and C-3β equatorial positions. On the other hand the multiplet at δ 4.18 and the doublet at δ 1.81 clearly showed that **1** possessed a >CH–CHOH–CHOR–CHOR–C≡ structural part in the ring A, which was also confirmed by the $^{13}C$ NMR data (Table 2), δ 66.8 *d*(C-1), 70.2 *d*(C-2) and 76.8

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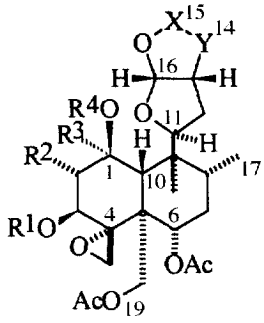
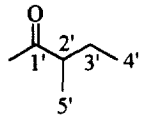
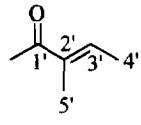
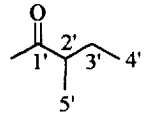
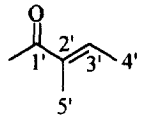
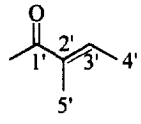


| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | X-Y |
|---|---|---|---|---|---|
| 1 |  | OAc | H | H | $CH_2$—$CH_2$ |
| 2 | H | H | H |  | CH=CH |
| 3 |  | OAc | | O | $CH_2$—$CH_2$ |
| 4 | Ac | H | H |  | CH=CH |
| 5 | H | H | H |  | $CH_2$—$CH_2$ |

*d*(C-3). According to the coupling constants of above structural part (10.4 Hz) the ring A should be in a chair conformation [2, 3].

In agreement with above conclusion areptin A (**1**) was treated with $CrO_3$-pyridine and derivative **3** was obtained, in which $^1H$ NMR spectra (Table 1) the signal of the proton of hydroxyl group at $\delta$ 5.45 had disappeared. The signals for H-10$\beta$ and H-2$\beta$ were paramagnetically shifted to $\delta$ 2.87 and $\delta$ 5.20 and transformed into a singlet and doublet, respectively. Moreover the signals for H-3 $\alpha$ ($\delta$ 5.53), $H_A$-18 ($\delta$ 2.73) and $H_B$-18 ($\delta$ 2.83) were also paramagnetically shifted to $\delta$ 5.75, 2.94 and 3.13, respectively, whereas the multiplet for 2H-15 was diamagnetically shifted and split at $\delta$ 3.68 *ddd* and 3.80 *ddd*. The location of the 2-methylbutyryl group in areptin A(**1**) was established from the hetero-nuclear multiple bond connectivity (HMBC) spectrum, which showed correlation between the carbonyl carbon of the 2-methylbutyryl moiety ($\delta_C$ 175.0) and the H-3$\alpha$ ($\delta$ 5.53 *d*) proton, whereas the carbonyl carbons of the three acetoxyl groups ($\delta_C$ 170.6 *s*, 170.2 *s* and 170.0 *s*) were connected with the 2$\beta$ H ($\delta$ 5.06), 6$\beta$ H ($\delta$ 4.67) and 2H-19 ($\delta$ 4.33 and 4.79) protons, thus establishing the positions of the 2-methylbutyryl group (C-3 equatorial) and the three acetoxy (C-2, C-6 equatorial and C-19) groups. The relative configuration of **1** was deduced from a NOESY experiment. The axial H-6$\beta$ showed NOE's with H-10$\beta$, $H_B$-18 and H-8$\beta$. Moreover, the H-10$\beta$ showed NOE's with $H_A$-18, H-2$\beta$ and 1$\beta$-OH. The H-3$\alpha$ showed cross-peaks with $H_A$-19 and the acetoxyl group at C-2$\alpha$. The Me-20 group showed NOE's with H-11$\alpha$ and $H_B$-19, whereas H-16$\beta$ showed cross-peaks with H-13$\beta$ and 1$\beta$-OH, consequently areptin A (**1**) possessed the same stereochemistry as ajugavensin C [2, 3].

Table 1. $^1$H NMR data of compounds **1** and **3** (250 MHz, $CDCl_3$, TMS as int. standard, chem. shifts in ppm, $J$ in Hz)*

| H | 1 | 3 | $J_{H,H}$ | 1 | 3 |
|---|---|---|---|---|---|
| 1α | 4.18 *m*† | – | 1α, 10β | 10.5 | – |
| 2β | 5.06 *t* | 5.20 *t* | | | |
| 3β | 5.53 *d* | 5.75 *d* | 2β, 10β | – | < 1 |
| 6β | 4.67 *dd* | 4.86 *dd* | | | |
| 7α | ~1.50† | – | 2β, 1α | 10.4 | 10.1 |
| 7β | ~1.58† | – | 3α, 2β | 10.4 | 10.1 |
| 8β | ~1.55† | – | 6β, 7α | 11.5 | 11.4 |
| 10β | 1.81 *d* | 2.87 *s* | 6β, 7β | 4.7 | 4.9 |
| 11α | 4.16 *m*† | 4.27*dd* | 11α, 12A | – | 10.0 |
| 12A | ~1.53† | – | 11α, 12B | – | 6.0 |
| 12B | ~2.28† | – | 15A, 15B | – | 8.7 |
| 13β | 2.95§ | 2.75 § | 15A, 14B | – | 6.5 |
| 14A | ~1.68† | – | 15A, 14A | – | 3.4 |
| 14B | ~2.20† | – | 15B, 14A | – | 6.6 |
| 15 (2H) | 3.89‡ | 15A 3.68 *ddd* | 15B, 14B | – | 3.3 |
| | | 15B 3.80 *ddd* | | | |
| 16β | 5.63 *d* | 5.62 *d* | 16β, 13β | 5.2 | 5.0 |
| Me-17 | 0.99 *d* | 0.80 *d* | 17, 8β | 6.3 | 6.6 |
| | | | 18A, 18B | 4.0 | 3.8 |
| 18 A | 2.73 *d* | 2.94 *d* | 19A, 19B | 12.6 | 12.9 |
| 18 B | 2.83 *d* | 3.13 *d* | 4′, 3′ | 7.5 | 7.4 |
| 19 A | 4.33 *br d* | 4.27 *d* | 2′, 5′ | 6.6 | 7.2 |
| 19 B | 4.79 *d* | 4.62 *d* | | | |
| Me-20 | 1.08 *s* | 1.02 *s* | | | |
| OAc | 1.94 *s* | 1.91 *s* | | | |
| | 2.05 *s* | 1.96 *s* | | | |
| | 2.15 *s* | 2.0 *s* | | | |
| OH | 5.45 *br s* | – | | | |
| 2′ | 2.18 *m*† | 2.27 *sept* | | | |
| 3′ | 1.40 *m*† | 1.42 *m* | | | |
| 4′ | 0.85 *t* | 0.81 *t* | | | |
| 5′ | 1.06 *d* | 1.03 *d* | | | |

*Spectral parameters were obtained by first-order approximation. All assignments were confirmed by double resonance experiments.
†Overlapped signals.
‡$W_{1/2}$ = 17 Hz.
§$W_{1/2}$ = 17.2 Hz.

Table 2. $^{13}$C NMR spectral data of compounds **1**, **2** and **4** (62.9 MHz, $CDCl_3$, TMS as int. standard)*

| C | 1 | 2 | 4 |
|---|---|---|---|
| 1 | 66.8 *d* | 70.2 *d*† | 69.4 *d*† |
| 2 | 70.2 *d* | 34.0 *t*† | 34.9 *t*† |
| 3 | 76.8 *d* | 66.7 *d* | 66.4 *d* |
| 4 | 62.4 *s* | 64.0 *s* | 64.1 *s* |
| 5 | 44.8 *s* | 44.7 *s* | 44.7 *s* |
| 6 | 69.3 *d* | 71.3 *d*† | 70.9 *d*† |
| 7 | 31.7 *t* | 33.7 *t*† | 33.5 *t*† |
| 8 | 36.6 *d* | 34.3 *d* | 35.1 *d* |
| 9 | 42.3 *s* | 41.0 *s* | 40.8 *s* |
| 10 | 49.9 *d* | 52.2 *d* | 52.1 *d* |
| 11 | 84.9 *d* | 83.9 *d* | 84.4 *d* |
| 12 | 33.0 *t* | 32.6 *t* | 31.9 *t* |
| 13 | 41.3 *d* | 45.7 *d* | 45.6 *d* |
| 14 | 32.5 *t* | 102.0 *d* | 102.4 *d* |
| 15 | 69.3 *t* | 146.2 *d* | 146.4 *d* |
| 16 | 107.8 *d* | 107.1 *d* | 108.2 *d* |
| 17 | 16.5 *q* | 17.3 *q* | 16.8 *q* |
| 18 | 42.7 *t* | 43.6 *t* | 44.4 *t* |
| 19 | 61.7 *t* | 61.6 *t* | 62.2 *t* |
| 20 | 17.3 *q* | 14.8 *q* | 15.5 *q* |
| OAc | 170.0 *s* | 170.2 *s* | 170.2 *s* |
| | 170.2 *s* | 169.8 *s* | 169.4 *s* |
| | 170.6 *s* | 20.0 *q* | 169.6 *s* |
| | 21.0 *q* | 21.0 *q* | 20.8 *q* |
| | 21.0 *q* | – | +21.0 *q* |
| | 21.1 *q* | – | +21.1 *q* |
| 1′ | 175.0 *s* | 166.3 *s* | 166.3 *s* |
| 2′ | 41.9 *d* | 128.8 *s* | 128.7 *s* |
| 3′ | 26.5 *t* | 137.4 *d* | 137.2 *d* |
| 4′ | 11.4 *q* | 14.4 *q* | 14.4 *q* |
| 5′ | 14.1 *q* | 12.1 *q* | 12.0 *q* |

*Multiplicities were determined by DEPT pulse sequence.
†Assignments may be reversed.

The second diterpenoid areptin B (**2**), had a molecular formula of $C_{29}H_{40}O_{10}$ from elemental analysis and mass spectroscopy. Its IR spectrum was consistent with the presence of hydroxyl group (3473 $cm^{-1}$), ester groups (1738, 1707, 1256 $cm^{-1}$), a tigloyloxy moiety (1651 $cm^{-1}$), a vinyl ether function (1620 and 734 $cm^{-1}$) and an oxirane ring (3078 $cm^{-1}$). The $^1$H and $^{13}$C NMR spectra (Tables 1 and 2) were almost identical with those of ajugorientin (**5**) [4]. In fact the observed differences between these spectra were consistent with the presence in compound **2** of a double bond between C-14–C-15 in the furofuran moiety, [($\delta$ 4.70 *t*, $J$ = 2.1 Hz, 6.36 *dd*, $J_1$ = 2.5; $J_2$ = 2.1 Hz); carbon atoms resonances at $\delta_C$ 102.0 *d* and 146.2 *d* [1]] instead of the hexahydrofurofuran part. Moreover, the signals of H-13β ($\delta$ 3.31 *m*) and H-16β ($\delta$ 5.87 *d*, $J$ = 6.2 Hz) were paramagnetically shifted ($\Delta$ + 0.66 ppm and $\Delta$ + 0.31 ppm, respectively), in comparison with those of the compound **5** [7]. The identical chemical shifts of the H-1α, H-6β and C-19 methylene protons of **2** in comparison with **5** [2, 3, 7] supported the same arrangement of the ester substituents in both compounds.

The presence of the hydroxyl group was confirmed by the acetylation of **2** yielding the derivative **4**, the IR spectrum of which was devoid of hydroxyl absorption (see Experimental) and whose $^1$H NMR spectrum (Table 3) showed a paramagnetically shifted signal of H-3α (5.53 *dd*, $J_{3\alpha,2\beta}$ = 7.3 Hz; $J_{3\alpha,2\alpha}$ = 4.2 Hz).

Important information about the conformation of the ring A of compound **2** was obtained from the vicinal coupling constants at $\delta$ 5.78 for H-1α (*ddd*, $J_{1\alpha,10\beta}$ = 8.0 Hz, $J_{1\alpha,2\alpha}$ = 4.0 Hz, $J_{1\alpha,2\beta}$ = 4.8 Hz) and $\delta$ 4.32 for H-3α (*dd*, $J_{3\alpha,2\beta}$ = 7.2; $J_{3\alpha,2\beta}$ = 4.2 Hz). Such behaviour of the above mentioned protons in the $^1$H NMR spectra of the decaline part in **2** can be explained with distorted boat conformation of the ring A like other *neo*-clerodane diterpenoids [3, 6, 7]. All the above data were in complete agreement with structure such as **2** for areptin B. The absolute configurations of **1** and **2** were not ascertained. However, on biogenetic grounds, one could suppose that **1** and **2** belong to the *neo*-clerodane series like the other diterpenoids isolated from *Ajuga* species [1–7, 11, 12].

## EXPERIMENTAL

Mps: uncorr. Plant materials was collected in August 1995, at Pirin Mountains near chalet rest-

Table 3. $^1$H NMR data of compounds **2** and **4** (250 MHz, $CDCl_3$, TMS as int. standard, chem. shifts in ppm, $J$ in Hz)*

| H | 2 | 4 | $J_{H,H}$ | 2 | 4 |
|---|---|---|---|---|---|
| 1α | 5.78 *ddd* | 5.85 *m*† | 1α, 2α | 4.0 | 4.0 |
| 2α | ~1.67† | ~1.69† | 1α, 2β | 4.8 | 4.4 |
| 2β | 2.45 *ddd* | 2.52 *ddd* | 1α, 10β | 8.0 | 5.3 |
| 3α | 4.32 *dd* | 5.53 *dd* | 2α, 2β | 10.2 | 8.4 |
| 6β | 4.79 *dd* | 4.79 *dd* | 2β, 3α | 7.2 | 7.3 |
| 7α | ~1.72† | ~1.74† | 3α, 2α | 4.1 | 4.2 |
| 7β | 2.01 *t* | 2.03 *t* | 6β, 7β | 4.8 | 4.9 |
| 8β | ~1.52† | ~1.55† | 6β, 7α | 12.4 | 12.6 |
| 10β | 2.21 *d* | 2.23 *d* | 8β, 17 | 6.1 | 6.0 |
| 11α | 4.28 *ddd* | 4.17 *dd* | 11α, 12A | 11.7 | 11.7 |
| 13β | 3.31§ | 3.26‡ | 11α, 12B | 5.0 | 4.9 |
| 14 | 4.70 *t* | 4.72 *t* | 13β, 14 | 2.5 | 2.5 |
| 15 | 6.36 *dd* | 6.37 *dd* | 13β, 15 | 2.1 | 2.3 |
| 16β | 5.87 *d* | 5.85 *d*† | 13β, 16β | 6.2 | 6.2 |
| Me-17 | 0.89 *d* | 0.86 *d* | 14, 15 | 2.5 | 2.5 |
| 18A | 2.91 *d* | 2.93 *d* | 18A, 18B | 4.4 | 4.3 |
| 18B | 3.02 *d* | 2.99 *d* | 19A, 19B | 12.3 | 12.7 |
| 19A | 4.17 *br d* | 4.13 *d* | 19A, 6β | <0.3 | <0.2 |
| 19B | 5.02 *d* | 5.06 *d* | 3′, 4′ | 6.9 | 6.8 |
| Me-20 | 0.94 *s* | 0.99 *s* | 3′, 5′ | 1.3 | 1.2 |
| OAc | 2.11 *s* | 2.13 *s* | 4′, 5′ | 0.9 | 0.8 |
| | 1.95 *s* | 1.94 *s* | | | |
| | – | 1.92 *s* | | | |
| 3′ | 6.77 *qq* | 6.80 *qq* | | | |
| 4′ | 1.81 *m* | 1.80 *m* | | | |
| 5′ | 1.84 *m* | 1.83 *m* | | | |

*Spectral parameters were obtained by first-order approximation. All assignments were confirmed by double resonance experiments.
†Partially overlapped signals.
‡$W_{1/2}$ = 18 Hz.
§$W_{1/2}$ = 21 Hz.

house-"Banderitza" at 1998 msl (Bulgaria) and voucher specimens (No. 32723) are deposited in the Herbarium of the Department of the Botanica at the Higher Institute of Agriculture at Plovdiv, Bulgaria.

*Extraction and isolation of the compounds*

Dried and powdered *Ajuga reptans*, aerial parts (1.1 kg) were extracted with $Me_2CO$ (7 l) at room temp. for 7 days. After removal of the solvent, the residue (48 g) was dissolved in 800 ml 60% aq $Me_2CO$ then cooled at 2–4° for 24 h and filtered. This process was repeated 3×. The combined filtrates were extracted first with $CHCl_3$ (100 ml × 4) and the extract was washed with $H_2O$, dried ($Na_2SO_4$) and evapd. *in vacuo* giving a residue (5 g). This residue was chromatographed on a silica gel column (Merck, No. 7734, deactivated with 10% $H_2O$, 110 g), eluted with $CHCl_3$–petrol (9:1) yielded areptin A (**1**, 41 mg) and with $CHCl_3$–areptin B (**2**, 28 mg), ajugareptansin (500 mg). Further elution with $CHCl_3$–MeOH (9.5:0.5) yielded ajugachin A (31 mg) and ajugorientin (**5**, 47 mg). Second, the combined extracts were extracted with *n*-BuOH (5 × 100 ml). The *n*-BuOH-extract (4.8 g) was chromatographed (CC. Merck, No. 7734, 10% $H_2O$, 115 g). Elution with $CHCl_3$–MeOH mixtures yielded crude 8-acetylharpagide (78 mg) and harpagide (43 mg). The previously known compounds were identified by their spectroscopic (IR, $^1$H and $^{13}$C NMR) data and by comparison (mmp, TLC) with authentic samples.

*Areptin A (**1**)*

Mp 169–172° (EtOAc-*n*-hexane); $[\alpha]_D$ 20° 0° ($CHCl_3$, *c* 0.225); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3454, 3078, 2973, 2880, 1746 br, 1448, 1463, 1372, 1234 br, 1180, 1149, 1078, 1046, 1027, 984, 621. $^1$H NMR (Table 1), $^{13}$C NMR (Table 2). EIMS (70 eV, direct inlet) *m/z* (rel. int): $[M]^+$ absent, 592 $[M-H_2O]^+$ (0.01), 509(0.1), 506(0.6), 420(0.3), 395(0.8), 318(0.5), 312(1), 225(4), 187(6), 185(4), 113(100), 111(28), 102(18), 101(15), 83(21), 69(19), 43(28). (Found: C 61.12; H 7.73. $C_{31}H_{46}O_{12}$ requires: C 60.98; H 7.54%).

*Oxidation of **1** to **3***

$CrO_3$–pyridine oxidation of **1** (22 mg) in the usual manner yielded **3** (16 mg) as an amorphous solid, mp. 89–92°, $[\alpha]_D$ 20°–3.7° ($CHCl_3$, *c* 0.227), IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3072, 2977, 2882, 1744 br, 1721, 1446, 1460, 1362, 1247, 1172, 1127, 1067, 1028, 981, 603. $^1$H NMR (Table 1). EIMS (70 eV, direct inlet) *m/z* (rel. int): 608 $[M]^+$ (0.01), 529(0.03), 507(0.4), 506(0.3), 497(0.7), 495(0.8), 404(0.6), 393(1), 314(2), 236(6), 185(7), 113(60), 111(21), 102(16), 101(14), 83(28), 69(27), 43(100). (Found: C 61.47; H 7.58. $C_{31}H_{44}O_{12}$ requires: C 61.18; H 7.23%).

*Areptin B (**2**)*

An amorphous solid mp. 91–95°, $[\alpha]_D$ 20–21.2° ($CHCl_3$, *c* 0.211); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3473 (OH), 3078, 1707, 1651 (tigloyloxy), 1620, 734 (vinyl ether), 1738, 1256 (OAc and tigloyloxy), 2967, 2938, 2878, 1462, 1373, 1187, 1150, 1110, 1068, 1034, 905, 804. $^1$H NMR (Table 3), $^{13}$C NMR (Table 2). EIMS (70 eV, direct inlet) *m/z* (rel. int): 548 $[M]^+$ (0.01), 489(0.02), 449$[M-OTig]^+$(0.06), 448$[M-HOTig]^+$ (0.1), 437(0.7), 338(0.5), 332(0.9), 278(1), 216(3), 198(4), 111(85), 83(50), 69(70), 55(40), 43(100). (Found: C 63.02; H 7.11. $C_{29}H_{40}O_{10}$ requires: C 63.50; H 7.30%).

*Acetylation of **2** to **4***

Compound **2** (25 mg) was treated with a mixt. of $Ac_2O$ (0.8 ml) and pyridine (1 ml) at room temp. for 48 h. Work-up in the usual manner gave **4** (22 mg). Amorphous solid, mp. 86–89°, $[\alpha]_D$ 20–18.09° ($CHCl_3$, *c* 0.257); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3061, 2971, 2934, 1741, 1707, 1652, 1618, 1445, 1369, 1250, 1143, 1093, 1071, 1037, 1011, 949, 899, 735.$^1$H NMR (Table 3), $^{13}$C NMR (Table 2). EIMS (70 eV, direct inlet) *m/z* (rel. int): 548 $[M]^+$ absent, 499$[M-OTig]^+$(0.02), 498(0.01), 489$[M-C_6H_7O_2]^+$ (0.01), 390(0.2), 387(0.3), 314(0.3), 258(2), 111(70), 83(58), 69(40), 55(38), 43(100). (Found: C 63.27; H 7.41. $C_{31}H_{42}O_{11}$ requires: C 63.05; H 7.12%).

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