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# GERMACRANOLIDES FROM *MELAMPODIUM AMERICANUM* AND *MELAMPODIUM PILOSUM**

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**Key Word Index**—*Melampodium americanum*; *Melampodium pilosum*; Compositae; Heliantheae; sesquiterpene lactones; germacrolide; melampolides.

**Abstract**—Chemical analysis of *Melampodium americanum* yielded, besides the known melampodinin A, four new melampolides, melampodinin B, melampodinin C, 9-desacetoxymelampodinin A and 11,13-dihydromelampodin A-9[2-methylbutanoate]. The germacrolide 15-desacetoxymelfusin was found as a minor constituent. *Melampodium pilosum* yielded melampodin A and melfusin.

## INTRODUCTION

In our continued biochemical systematic study of the subtribe Melampodiinae, we have analysed aerial parts of *Melampodium americanum* L. and *M. pilosum* Stuessy of section Melampodium [1] for their chemical constituents. Besides the known antineoplastic sesquiterpene lactone melampodinin A (**1**)‡ [2], four related melampolides and a germacrolide were isolated from *M. americanum*. From *M. pilosum*, the known melampodin A (**5**)‡ [3–5] and melfusin (**8**) [6] were obtained. The structure elucidations of the five new compounds involved spectral methods (NMR, MS, CD) and chemical transformations.

## RESULTS AND DISCUSSION

### *Melampodinin B*

Melampodinin B (**2**), $C_{28}H_{36}O_{12}$, mp 205–206.5°, showed sharp doublets at $\delta$ 5.82 (H-13a) and 6.23 (H-13b), a multiplet 2.70 (H-7) and an IR absorption at 1770 $cm^{-1}$ typical of an $\alpha,\beta$-unsaturated $\gamma$-lactone. Further $^1H$ NMR signals, assigned by extensive spin-decoupling experiments, were very similar to those of melampodinin A (**1**) [2] with the exception that the acetate signal in **1** was replaced by signals characteristic of 2-methylbutanoate (Table 1). The low-resolution MS supported the $^1H$ NMR assignments. Besides the parent peak at *m/z* 564, compound **2** exhibited peaks at *m/z* 462, $M^+ - C_5H_{10}O_2$ ($M^+ - C$), 85 ($C_1$), 57 ($C_2$) and 29 ($C_3$) due to the presence of the 2-methylbutanoate moiety **C**. Further strong peaks at *m/z* 389 ($M^+ - C_7H_{11}O_5$), 176 (**A**) and 131 ($A_2$) indicated the presence of the $C_7$ ester moiety **A**, at the medium ring skeleton of **2** [2]. Side-chains $A_1$ and $C_1$ in **2** could either be attached to C-8 and C-9, respectively, or vice versa. Specific removal of the C-9 ester function under mild solvolysis with NaOME–MeOH at 0° [7] was attempted with the readily available melampodinin A (**1**). Reaction of **1** under the above conditions led to removal of both ester groups and an opening of the 2,3-epoxide function and thus precluded an assignment of the site of attachment of the two ester moieties.

### *Melampodinin C*

Melampodinin C (**3**), $C_{28}H_{34}O_{12}$, a minor constituent which was not obtained completely free of **2**, exhibited $^1H$ NMR parameters very similar to those of melampodinin B (**2**). The two compounds differed in the $C_5$ ester side-chain with melampodinin C showing $^1H$ NMR signals and MS peaks typical for the tiglate moiety (**D**). i.e. Two three-proton signals, a broadened singlet at $\delta$ 1.91 (C-2″-Me), a doublet at 1.79 (C-3″-Me) and a broadened one-proton quartet at 6.83 together with MS peaks at *m/z* 462 ($M^+ - C_5H_8O_2$), 100 ($C_5H_8O_2$, $D_2$), 83 ($D_1$) and 55 ($D_2$).

### 9-*Desacetylmelampodinin* A

9-Desacetylmelampodinin A (**4**), $C_{23}H_{28}O_{11}$, was a minor constituent from the polar chromatographic fractions of *M. americanum*. Spin-decoupling experiments clearly suggested structure **4** with the $C_7$ ester $A_1$ attached to C-8 (H-8, $\delta$ 6.37, $J_{8,9}$ = 8.5 Hz) and a hydroxyl group at C-9 (H-9, $\delta$ 4.16, $J$ = 8.5 Hz). Plans to correlate **4** chemically with melampodinin A (**2**) by acetylation required extraction of more plant material. However, in a repeated extraction and work-up of a second batch of the same plant collection, compound **4** could not be obtained. This suggested that 9-desacetylmelampodinin A (**4**) possibly represented an artifact formed during the first isolation procedure. We have recently observed in our laboratory [7] that treatment of melcanthin B [8] under the conditions used in our isolation procedure [9], that is,

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‡ The *in vivo* inhibitory activity against lymphocytic leukemia P-388 (PS) was assayed under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, NIH. Melampodinin A (NSC No. 294600) exhibited an optimum % T/C 140 at 12 mg/kg, melampodin A (NSC No. 155619) a T/C 128 at 12 mg/kg and melampodin A acetate (NSC No. 294602) T/C 133 at 6 mg/kg.

Table 1. $^1$H NMR data for compounds **2**–**4**, **6** and **7** (200 MHz, TMS as internal standard)

| Signal | **2** ($CDCl_3$) | **3** ($CDCl_3$) | **3** ($C_6D_6$) | **4** ($Me_2CO$-$d_6$) | **6** ($CDCl_3$) | **7** ($CDCl_3$) | **7** ($C_6D_6$) |
|---|---|---|---|---|---|---|---|
| H-1 | 7.00 *d* (2.0)* | 7.02 *d* (2.0) | 6.75 *d* (2.0) | 6.73 *dd* (3.0; 1.0) | 6.96 *d* (2.0) | 5.69 *s* (*br*)† | 5.45 *s* (*br*) |
| H-2 | 3.67 *dd* (3.5; 2.5) | 3.68 *dd*† | 3.22 *dd*† | 3.65 *dd* (2.0; 2.0) | 3.64 *dd* (4.0; 2.0) | 5.94 *d* (10.0) | 5.62 *d* |
| H-3 | 3.75 *d* (3.5) | 3.76 *d* (4.0) | 3.13 *d*† | 3.69 *d* (2.0) | 3.69 *d* (4.0) | 5.27 *d* (10.0) | 5.11 *d* |
| H-5 | 5.34 *dd* (10.5; 1.5) | 5.34† *s* | 5.40 *dd*† | 5.32–5.01† | 5.20 *d* (10.5) | 3.04 *d*† (11.5) | 2.99 *d* |
| H-6 | 5.23 *dd* (9.5; 10.5) | 5.23 *dd* (10.0) | 5.41 *d* (10.0) | | 5.50 *dd*† (10.5) | 4.55 *dd* (11.5) | 4.39 *dd* |
| H-7 | 2.70 *d tr* (*br*) (9.5; 3.0) | 2.66 *m*† | 2.39 *m*† | 2.85 *m*† | 2.24 *dd* (*br*) (10.5; 8.0) | 3.36 *dq* (*br*) (11.5; 3.0) | 2.89 *m* |
| H-8 | 6.68 *d* (*br*) (9.0) | 6.73 *d* (10.0) | 7.03 *d* (10.0) | 6.37 *dd* (8.5; 1.5) | 6.39 *d* (*br*) (8.0) | 5.67 *dd*† | 5.25 *d* |
| H-9 | 5.36 *d* (9.0) | 5.41 *d* (9.0) | 5.52 *d* (9.0) | 4.16 *d* (8.5) | 5.24 *d* (8.0) | 4.39 *s* (*br*) | 3.83 *s* (*br*) |
| H-13a | 5.82 *d* (3.0) | 5.80 *d* (3.0) | 5.76 *d* (3.0) | 5.69 *d* (3.0) | — | 5.42 *d* (3.0) | 5.02 *d* |
| H-13b | 6.23 *d* (3.0) | 6.22 *d* (3.0) | 6.14 *d* (3.0) | 6.05 *d* (3.0) | | 6.17 *d* (3.0) | 5.98 *d* |
| C-4-Me | 2.21 *d* (1.5) | 2.21 *d* (2.0) | 1.86 *s* (*br*) | 2.15 *d* (1.5) | 2.17 *d* (2.0) | 2.03 *s* | 2.03 *s* |
| COOMe | 3.83 *s* | 3.82 *s* | 3.28 *s*† | 3.75 *s*† | 3.81 *s* | 3.73 *s* | 3.30 *s* |
| H-3′ | 5.18 *q* (6.0) | 5.18 *q* (6.0) | | | 3.08 *q* (6.0) | 3.03 *q*† | 2.46 *q* |
| C-2′-Me | 1.26 *s* | 1.14 *s* | 1.10 *s* | 1.34 *s* | 1.53 *s* | 1.53 *s* | 1.14 *s* |
| C-3′-Me | 1.26 *d* (6.0) | 1.23 *d*† | 1.10 *d* (6.0) | 1.20 *d* (6.0) | 1.26 *d* (6.0) | 1.26 *d* (6.0) | 0.96 *d* |
| Ac | 1.92 *s* | 1.90 *s* | 1.66 *s* | 1.81 *s* | | | |
| C-2″-Me | 1.06 *d* (7.0) | 1.91 *s* | 1.63 *s* | | 1.03 *s* (7.0) | | |
| C-3″-Me | 0.81 *tr* (7.0) | 1.79 *d*† | 1.21 *d* (8.0) | | 0.79 *tr* (8.0) | | |
| H-2″/H-3″ | 2.34 *q* (7.0) | 6.83 *q* (*br*) (7.0) | 6.81 *q* (*br*) (8.0) | — | 2.3 *h* | | |
| H-11 | | | | | 2.74 *p* (8.0) | | |
| C-11-Me | | | | | 1.19 *d* (8.0) | | |

* Figures in parentheses are coupling constants or line separation in Hz.
† Obscured by other signals.

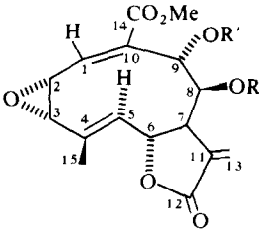
stirring with 5% $Pb(OAc)_2$ in EtOH–$H_2O$ (1:1) for 24 hr at room temperature, led to specific hydrolysis of the C-9 acetate function. However, treatment of melampodinin A (**1**) under similar experimental conditions did not provide compound **4**.

11,13-*Dihydromelampodin* A 9-[2-*methylbutanoate*]

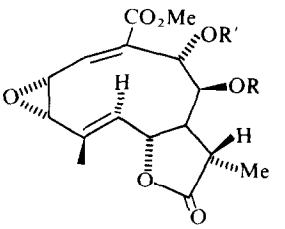
11,13-Dihydromelampodin A 9-[2-methylbutanoate] (**6**), $C_{26}H_{34}O_{10}$, mp 187–188°, exhibited an IR band at 1775 $cm^{-1}$ which suggested a γ-lactone but doublets near δ 6 typical for an α-methylene-γ-lactone were missing. Instead, the presence of a three-proton doublet at δ 1.19 (C-11-Me, $J_{11,13} \approx 8.0$ Hz) indicated an 11,13-dihydrolactone. Two three-proton absorptions, a singlet at δ 1.53 and a doublet 1.26 ($J$ = 6.0 Hz), together with a quartet at 3.08 suggested an epoxyangelate side-chain in **6** and prominent MS peaks at $m/z$ 390 ($M^+ - C_5H_8O_3$), 116 ($C_5H_8O_3$, **B**), 99 ($C_5H_7O_2$, $\mathbf{B}_1$) and 71 ($C_4H_7O$, $\mathbf{B}_2$) verified the above $^1$H NMR assignments. Further intense MS peaks at $m/z$ 404 ($M^+ - C_5H_{10}O_2$), 102 ($C_5H_{10}O_2$), 85 ($C_5H_9O$), 57 ($C_6H_9$) and 29 ($C_2H_5$) and a three-proton singlet at δ 1.03 (C-2″-Me) together with a triplet at 0.79 (C-3″-Me) were diagnostic of 2-methylbutanoate as the second ester in **6**. Spin-decoupling experiments, which are summarized in Table 1, established the structure of the medium ring skeleton exclusive of stereochemistry and the sites of attachment of the two ester groups at C-8 and C-9. Comparison of the $^1$H NMR parameters of **6** with data of melampolides of similar oxidation patterns suggested that **6** should exhibit the same configurations at C-2, C-3 and C-6 to C-9 as melampodin A (**5**) the absolute configuration of which had previously been established [3–5]. The coupling data also indicated that the conformation of the medium ring portion of **6** was not

affected by the bio-reduction of the 11,13-methylene bond and should be as in melampodin A (**5**). The stereochemistry at C-11 was tentatively assigned based on correlations between $J_{7,11}$ and the two possible dihedral angles between H-7/H-11α (45°) and H-7/H-11β (160°) obtained from stereomodels. The experimentally observed coupling ($J_{7,11}$ = 8 Hz) was in better agreement with the nearly antiperiplanar arrangement of H-7 and H-11 suggesting a H-11β in **6**. No chemical evidence could be provided for the attachments of the two ester functions. Nearly identical $^1$H NMR shifts of the epoxyangelate absorptions in **6** and melampodin A (**5**) [3] were used as arguments to tentatively assign structure **6** for the new 11,13-dihydro compound.

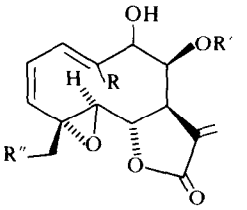
Melampolides with a skeletal arrangement represented by melampodin A (**5**) and the melampodinin-type compounds exhibit a strong broad positive CD band near 250 nm. Application of the Stöcklin–Waddell–Geissman rule [10] for the assignment of lactonization of the 6,12-γ-lactone group would predict a *cis*-lactone function in all compounds which is contrary to the data obtained from X-ray [4] and NMR studies [3]. Failure of the lactone rule for these types of melampolides seems to be most strongly influenced by the presence of a second chromophore, the α,β-unsaturated methyl ester. Indeed, the 11,13-dihydrocompound **6** still exhibited a strong positive absorption at 249 nm which suggested that the major contribution to the positive bands in compounds **1** to **6** stems from the n → π*-transition of the α,β-unsaturated methyl ester [7]. It should be pointed out, however, that the melampolides melampolidin [2], uvedalin and polydalin [11], which resemble the same skeletal type as the above compounds, but have no 2,3-epoxide function, exhibit negative bands near 250 nm.



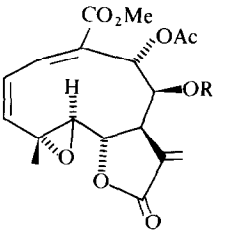
| | R | R′ |
|---|---|---|
| Melampodinin A (**1**) | $A_1$ | Ac |
| Melampodinin B (**2**)* | $A_1$ | $C_1$ |
| Melampodinin C (**3**)* | $A_1$ | $D_1$ |
| 9-Desacetylmelampodinin A (**4**) | $A_1$ | H |
| Melampodin A (**5**) | $B_1$ | H |



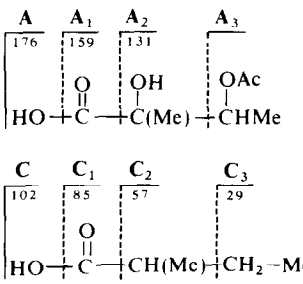
11, 13-Dihydromelampodin A, 9-[3-methylbutanoate] (**6**)*
R = $B_1$; R′ = $C_1$

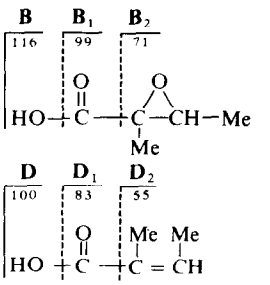


15-Desacetoxymelfusin (**7**)
R = $CO_2Me$; R′ = $B_1$; R″ = H
Melfusin (**8**) R = $CO_2Me$; R′ = **B**; R″ = OAc



Leucanthin A (**9**)
R = $B_1$





* Tentatively assigned on basis of NMR correlations of compounds **2**, **3** and **6** with those of known melampolides. The ester side chains at C-8 and C-9 might have to be reversed. Except in **B** of compound **5**, the chiralities of the asymmetric centres of the ester moities **A**, **B** and **C** are unknown.

*15-Desacetoxymelfusin*

15-Desacetoxymelfusin (**7**), $C_{21}H_{24}O_9$, mp 150–152°, exhibited spectral absorptions typical of an α-methylene-γ-lactone (IR at 1765 $cm^{-1}$ and $^1H$ NMR doublets at δ 5.42 and 6.17). Further IR absorptions at 3570, 1745, 1730 and 1715 $cm^{-1}$ indicated the presence of hydroxyl(s) and ester function(s), respectively. The assignments of the basic skeletal arrangement of **7** were mainly deduced from $^1H$ NMR spectral data obtained at 200 MHz in $CDCl_3$ and $C_6D_6$, and from MS fragmentation patterns. A series of MS peaks at *m/z* 116 (**B**), 99 ($\mathbf{B}_1$) and 71 ($\mathbf{B}_2$) in combination with diagnostic NMR absorptions (a one-proton quartet at δ 3.03; two methyl absorptions, a singlet at 1.53 and a doublet at 1.26) were in accord with the presence of an epoxyangelate moiety in **7**. Detailed double resonance $^1H$ NMR experiments (Table 1) supported a germacranolide skeleton for the new compound. The NMR parameters suggest a skeletal arrangement and oxidation pattern of the medium ring portion similar to the known melampolide leucanthin A (**9**) [9]. A singificant difference existed between the H-1 absorption at δ 5.69 in **7** and H-1 in leucanthin A which exhibited a signal near δ 7.0 diagnostic of the melampolides of type **1**–**5**. The appearance of H-1 in **7** below δ 6.0 indicated *trans*-attachment of H-1 and the carbomethoxy group at C-10 suggesting the presence of a 1(10)-*trans*-double bond in compound **7**. Comparison of the NMR and MS spectral data of **7** with the germacrolide melfusin (**8**) which has recently been isolated from *M. diffusum* [6] revealed gross similarities. A major difference between melfusin (**8**) and the new compound existed for C-15 which in **8** represented an acetoxymethylene function and had to be a Me group in **7** as indicated by the three-proton singlet at δ 2.03. Since the spectral and chemical arguments for configurational and conformational assignments of melfusin (**8**) have been outlined in great detail [6], we refrain from repeating the assignment of 15-desacetoxy-melfusin (**7**) which due to the scarcity of material was solely determined on the basis of NMR and MS correlations between the two compounds.

## EXPERIMENTAL

*Melampodium pilosum* (Hartman & Funk, No. 4265, collected on Sept. 5, 1976, 23 miles west of La Huacana, Michoacan, Mexico; voucher deposited at O.S., U.S.A.). Aerial parts (70 g) were extracted with 100 ml $CH_2Cl_2$. Standard work-up [9] yielded 120 mg crude terpenoid syrup which was chromatographed by prep. TLC providing 3 mg **5**, 2 mg **8** and 3 mg of a mixture of melampolides ($^1H$ NMR) which could not be further separated due to the lack of material.

*Melampodium americanum* (Hartman & Funk, No. 4175, collected on August 25, 1976 in Chiapas, Mexico; voucher deposited at O.S., U.S.A.). Aerial parts (1 kg) were extracted with 2 l. $CH_2Cl_2$. Standard work-up [9] yielded 5.0 g crude syrup which was chromatographed over 280 g of Si gel, starting with a mixture of $CHCl_3$–*n*-PrOAc (7:3) followed with mixtures of eluants of increasing polarity ($CHCl_3$–*n*-PrOAc, 1:1, 2:3, 1:2, 0:1, and 100% $Me_2CO$) taking 20-ml fractions obtaining a total of 238 fractions. Fractions 6–16 contained 133 mg **6**. From fractions 17–42, 150 mg **1**, 81 mg **2** and 2.3 mg of a mixture of **2** and **3** were isolated by repeated prep. TLC. Compounds **2** and **6** were recrystallized from *iso*-PrOH. Fractions 55–80 provided 11.5 mg **7** which was recrystallized from *n*-hexane. Fractions 171–172 contained 10 mg **4**.

*Melampodinin B* (**2**), $C_{28}H_{36}O_{12}$, mp 205–206.5°; UV $\lambda_{max}^{MeOH}$ nm: 203 ($\varepsilon$ 3.6 × $10^4$); CD (MeOH; *c* 4.0 × $10^{-4}$), $[\theta]_{248}$ + 3.8 × $10^4$, $[\theta]_{216}$ −1.7 × $10^5$; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1770 (γ-lactone), 1750, 1740, 1730, 1720 (esters), 1650, 1670, (double bonds); MS (probe) 70 eV *m/z* (rel. int.): 564 (0.4) $[M]^+$, 479 (1.6) $[M - C_4H_7O_2]^+$, 462 (1.0) $[M - C_5H_{10}O_2]^+$, 389 (1.0) $[M - C_7H_{11}O_5]^+$, 286 (19.1) $[M - C_7H_{12}O_5 - C_5H_{10}O_2]^+$, 227 (15.1) $[M - C_7H_{12}O_5 - C_5H_{10}O_2 - C_2H_3O_2]^+$, 176 (11.0) $[C_7H_{12}O_5]^+$, 131 (27.4) $[C_6H_{11}O_3]^+$, 85 (39.2) $[C_5H_{11}O_3]^+$, 57 (91.4) $[C_4H_9]^+$, 43 (100) $[C_2H_3O]^+$, 29 (52.5) $[C_2H_5]^+$. [Calc. for $C_{28}H_{36}O_{12}$: 564.2207. Found: (MS) 564.2200.]

*Melampodinin C* (**3**), $C_{28}H_{34}O_{12}$, gum, which could not be completely sepd from **2**. UV $\lambda_{max}^{MeOH}$, 204 nm; CD (MeOH), max at 248 nm, min at 216 nm; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1765 (γ-lactone), 1710, 1720, 1745 (esters), 1645, 1665 (double bonds); MS (probe) 70 eV *m/z* (rel. int.): 462 (0.4) $[M - C_5H_8O_2]^+$, 303 (4.4) $[M - C_5H_8O_2 - C_7H_{11}O_4]^+$, 286 (24.9) $[M - C_5H_8O_2 - C_7H_{12}O_5]^+$, 227 (28.1) $[M - C_5H_8O_2 - C_7H_{12}O_5 - C_2H_3O_2]^+$, 176 (15.6) $[C_7H_{12}O_5]^+$, 159 (4.2) $[C_7H_{11}O_4]^+$, 131 (22.3) $[C_6H_{11}O_3]^+$, 100 (1.0) $[C_5H_8O_2]^+$, 87 (3.1) $[C_4H_7O_2]^+$, 83 (100) $[C_4H_7O]^+$, 55 (29.8) $[C_4H_7]^+$. [Calc. for $C_{23}H_{26}O_{10}$(M − **D**): 462.1526. Found: (MS) 462.1510.]

*9-Desacetylmelampodinin A* (**4**), $C_{23}H_{28}O_{11}$, gum. MS (probe) 70 eV *m/z* (rel. int.): 480 (1.3) $[M]^+$, 462 (2.2) $[M - H_2O]^+$, 304 (5.7) $[M - C_7H_{12}O_5]^+$, 286 (12.3) $[M - C_7H_{12}O_5 - H_2O]^+$, 227 (13.4) $[M - C_7H_{12}O_5 - H_2O - C_2H_3O_2]^+$, 176 (26.7) $[C_7H_{12}O_5]^+$, 159 (12.3) $[C_7H_{11}O_4]^+$, 131 (48.0) $[C_6H_{11}O_3]^+$, 87 (13.3) $[C_4H_7O_2]^+$, 43 (100) $[C_2H_3O]^+$.

*11,13-Dihydromelampodin A, 9-[2-methylbutanoate]* (**6**), $C_{26}H_{34}O_{10}$, mp 187–188°, UV $\lambda_{max}^{MeOH}$ 199 nm ($\varepsilon$ 2.3 × $10^4$); CD (MeOH) $[\theta]_{249}$ +3.5 × $10^4$, $[\theta]_{215}$ −1.7 × $10^5$; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1775 (γ-lactone), 1760, 1755, 1730, 1720, 1710 (ester), 1670, 1645 (double bonds); MS (probe) 70 eV *m/z* (rel. int.): 404 (5.2) $[M - C_5H_{10}O_2]^+$, 390 (0.6) $[M - C_5H_8O_3]^+$, 305 (2.2) $[M - C_5H_{10}O_2 - C_5H_7O_2]^+$, 288 (29.8) $[M - C_5H_{10}O_2 - C_5H_8O_3]^+$, 273 (20.5) $[M - C_5H_{10}O_2 - C_5H_8O_3 - Me]^+$, 116 (2.7) $[C_5H_8O_3]^+$, 102 (0.8) $[C_5H_8O_3]^-$, 99 (4.3) $[C_5H_7O_2]^+$, 85 (82.2) $[C_5H_9O]^+$, 71 (19.7) $[C_4H_7O]^+$, 57 (100) $[C_4H_9]^+$, 29 (5.7) $[C_2H_5]^+$. [Calc. for $C_{26}H_{34}O_{10}$: 506.2152. Found: (MS) 506.2155.]

*Melfusin, 15-desacetoxy* (**7**), $C_{21}H_{24}O_9$, mp 150–152°, UV $\lambda_{max}^{MeOH}$ nm: end absorption at 200 ($\varepsilon$ 4.5 × $10^4$), 265 ($\varepsilon$ 1.1 × $10^4$); CD (MeOH; *c* 3.4 × $10^{-3}$); $[\theta]_{272}$ +4.4 × $10^4$, $[\theta]_{218}$ −3.9 × $10^4$; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3670 (OH), 1765 (γ-lactone), 1745, 1730, 1715 (esters), 1640, 1650 (double bonds); MS (probe) 70 eV *m/z* (rel. int.): 404 (3.5) $[M - O]^+$, 270 (1.1) $[M - O - C_5H_8O_3 - H_2O]^+$, 255 (1.5) $[M - O - C_5H_8O_3 - H_2O - Me]^+$, 239 (1.7) $[M - O - C_5H_8O_3 - H_2O - OMe]^+$, 211 (24.5) $[M - O - C_5H_8O_3 - H_2O - C_2H_3O]^+$, 116 (6.1) $[C_5H_8O_3]^+$, 99 (2.7) $[C_5H_7O_2]^+$, 71 (12.5) $[C_4H_7O]^+$. [Calc. for $C_{21}H_{24}O_8$: 404.1469 (M − O). Found: (MS) 404.1478.]

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