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EUDESMANOLIDES, TRICHOMATOLIDES B–E, AND A HELIANGOLIDE FROM *CALEA TRICHOMATA*

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Key Word Index—*Calea trichomata*, Asteraceae, Heliantheae, sesquiterpene lactones, eudesmanolides, heliangolide

Abstract—*Calea trichomata* gave in addition to four known 1β-hydroxy-8β-tigloyloxy-11(13)-eudesmen-6α,12-olide derivatives a new heliangolide, 3-deoxy-2,3-dehydroheliangin, and four new eudesmanolides, trichomatolides B–E The structures of the new compounds were established by chemical and spectral methods

INTRODUCTION

In continuation of our biochemical systematic study of the subtribe Galinsoginae, tribe Heliantheae, we have further investigated *Calea trichomata* from Chiapas, Mexico for their sesquiterpene lactone constituents Besides the known eudesmanolides trichomatolide A and four 1β-hydro-8β-tigloyloxy eudesman-6α,12-olide derivatives, previously isolated from *Calea trichomata* [1], *Calea rotundifolia* [2], and *Liatris laevigata* [3], we also isolated a new heliangolide, 3-deoxy-2,3-dehydroheliangin (**1**), and four new eudesmanolides, trichomatolides B–E (**2**, **3**, **5** and **7**) 3-Deoxy-2,3-dehydroheliangin (**1**) represents only the third 1(10)-*trans*,2-*cis*,4-*cis*-germacratrienolide derivative so far isolated, and the first one from the genus *Calea* The new compounds were characterized by chemical and spectral methods

RESULTS AND DISCUSSION

3-Deoxy-2,3-dehydroheliangin (**1**), $C_{20}H_{24}O_5$, is a gum which exhibited in the ^{1}H NMR spectrum two one-proton doublets at δ6 37 (H-13a) and 5 79 (H-13b), and a narrow multiplet at 2 97 (H-7) suggesting an α-methylene-γ-lactone A strong IR absorption at 1755 cm^{-1} corroborated the presence of a γ-lactone moiety Further IR absorptions at 1705 and 1650 cm^{-1} indicated the presence of an unsaturated ester and double bond(s) The ester side chain was assigned to a tiglate group on the basis of typical ^{1}H NMR signals, a one-proton quartet of quartets at δ6 83, and two three-proton signals, a broad singlet at 1 78 and broadened doublet at 1 76, together with strong mass spectral peaks at *m/z* 83 (A^1) and 55 (A^2) Assignments of all proton signals of the basic ring skeleton of **1** were deduced from extensive ^{1}H NMR double irradiation experiments, the results being summarized in Table 1 The ^{1}H NMR parameters are in good agreement with a germacranolide skeleton containing a 2,3-double bond Furthermore, the small coupling constants ($J_{7,13a}$ = 2 0 Hz, $J_{7,13b}$ = 1 8 Hz, $J_{6,7}$ = 1 5 Hz) are characteristic for heliangolides which typically contain a 12,6α-*trans*-lactone and a 4,5-*cis*-double bond [5] The presence of a conjugated diene system in **1** was also supported by the UV spectrum which exhibited a shoulder at 235 nm (ε = 7 24 × 10^3) superimposed on a strong absorption maximum at 216 nm due to the methylene lactone The small coupling constant ($J_{7,8}$ ~ 1 5 Hz) suggested an α-orientation of H-8, and therefore a β-configuration of the tiglate side chain

The chemical shifts of H-1 (δ3 28) and the C-10-Me (δ1 38), together with the multiplicities and coupling constants of H-3, H-2 and H-1 (Table 1), were in full accord with the presence of a 1,10-epoxide in 3-deoxy-2,3-dehydroheliangin (**1**) as in punctatin [5] and 15,5′-bisdeoxypunctatin [6] The ^{1}H NMR data of 15,5′-bisdeoxypunctatin and 3-deoxy-2,3-dehydroheliangin were nearly identical, differing only in the signals due to the side chain proton absorption, and the chemical shift of H-7 ‡

Trichomatolide B (**2**), $C_{20}H_{26}O_6$, is a gum with an IR spectrum showing the presence of hydroxyl group(s) (absorption bands at 3600 and 3480 cm^{-1}), a γ-lactone moiety (1765 cm^{-1}), an α,β-unsaturated ester (1705 cm^{-1}), and double bonds (1650 and 1605 cm^{-1}) The presence of an α-methylene-γ-lactone was corroborated by the ^{1}H NMR spectrum of **2** which showed two one-proton doublets at δ6 15 (H-13a) and 5 48 (H-13b), and a doublet of quartets at δ2 90 (H-7) The nature of the ester side chain was evident from the ^{1}H NMR data a one-proton quartet of quartets at δ6 81, and two three-proton signals, a broad singlet at δ1 82 and a broad doublet at 1 79 which are typical of a tiglic ester moiety Further confirmation of this was obtained from the strong mass spectral peaks at *m/z* 83 (A^1) and 55 (A^2) Assignment of all ^{1}H NMR signals of **2** were deduced from double irradiation experiments (Table 1) On the basis of the ^{1}H NMR data, together with the IR and mass spectral evidence, the structure of trichomatolide B can be formulated as an eudesmanolide with a tigloyloxy group at C-8, and an hydroxyl group on C-1 and C-3, as shown in **2** exclusive of stereochemistry Based on the biogenetic

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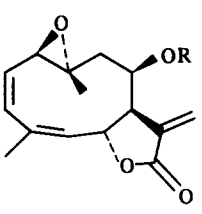
‡The reported chemical shift for H-7 of 15, 5′-bisdeoxypunctatin [6] is δ 2 17 and differs significantly from H-7 in **1** (δ 2 97).

Table 1 ^{1}H NMR spectral data* of compounds **1**, **2**, **3**, **5**, **6** and **8** (200 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**	**3**	**5**	**6**	**8**
H-1	3 28 *dd* (7 4, 4 5)*	3 94 *dd* (12 0, 4 5)	3 86 *dd* (12 0, 6 0)	3 54 *dd* (11 2, 4 8)*	4 79 *dd* (11 2, 5 0)	4 79 *dd* (11 5, 6 0)
H-2a H-2b	5 55 *dd* (11 4, 7 4)	2 06 *m* 1 65–1 85†	1 80–1 96†	1 20–1 90†	0 90–2 00†	0 90–1 72†
H-3	6 14 *br d* (11 4)	4 39 *br t* (3 0)	4 05 *br d* (2 5, 2 5)	1 20–1 90†	0 90–2 00†	1 80–2 20†
H-5	5 31 *dq* (10 5, 1 5)	2 87 *br d* (11 5)	—	2 28 *br d* (11 0)	2 38 *br d* (11 0)	2 38 *br d* (11 0)
H-6	5 13 *dd* (10 5, 1 5)	4 52 *dd* (11 5, 11 5)	5 15 *br d* (12 5)	4 53 *dd* (11 0, 11 0)	4 51 *dd* (11 0, 11 0)	4 51 *dd* (11 0, 11 0)
H-7	2 97 *m* (1 5)	2 90 *dddd* (11 5, 3 2, 3 2, ~ 3)	3 02 *dddd* (12 5, 3 5, 3 2, ~ 3)	2 88 *dq* (11 0, 3 0)	2 86 *br d* (11 0)	2 85 *dq* (11 5, 3 0)
H-8	5 20 *m*	5 81 *ddd* (4 0, 2 5, ~ 3)	5 81 *ddd* (4 0, 5, ~ 3)	5 84 *br t* (3 0)‡	5 80 *br q* (3 0)	5 79 *br q* (3 0)
H-9a	2 81 *dd* (15 0, 4 5)	2 38 *dd* (15 5, 2 5)	2 43 *dd* (16 0, 2 5)	2 42 *dd* (15 5, 2 5)	2 17 *dd* (16 5, 2 5)	1 94 *dd* (15 5, 2 5)
H-9b	1 39 *dd* (15 0, 3 0)	1 65 *dd* (15 5, 4 0)	1 66 *dd* (16 0, 4 0)	1 64 *dd* (15 5, 4 0)	1 63 *dd* (16 5, 3 8)	1 63 *dd* (15 5, 4 0)
H-13a	6 37 *d* (2 0)	6 15 *d* (3 2)	6 24 *d* (3 5)	6 17 *d* (3 0)	6 18 *d* (3 0)	6 16 *d* (3 0)
H-13b	5 79 *d* (1 8)	5 48 *d* (3 2)	5 55 *d* (3 2)	5 47 *d* (3 0)	5 47 *d* (3 0)	5 46 *d* (3 0)
H-14	1 38 *s*	0 95 *s*	1 21 *s*	0 99 *s*	1 07 *s*	1 06 *s*
H-15a H-15b	1 88 *d* (1 5)	5 22 *br s* 5 12 *d* (1 5)	2 07 *d* (1 2)	5 04 *br s* 4 97 *br s*	5 06 *br s* 4 98 *br s*	5 06 *br s* 4 99 *br s*
OTig	6 83 *qq* (7 2, 1 8)	6 81 *qq* (7 2, 1 8)	6 82 *qq* (7 4)	4 61 *q* (6 8)	5 69 *q* (7 0)	7 13 *q* (7 5)
H-4′	1 78 *br s*	1 82 *br s*	1 81 *br s*	1 38 *d* (6 8)	1 38 *br d* (7 0)	1 97 *d* (7 5)
H-5′	1 76 *br s*	1 79 *s*	1 78 *s*	6 13 *br s*, 5 88 *br s*	6 22 *d* (2 0), 5 87 *br s*	4 88 *d* (12 0), 4 77 *d* (12 0)
OAc	—	—	—	—	2 06 s, 2 04 s	2 05 s, 2 00 *s*

*Figures in parentheses are coupling constants in Hz. Signals are designated as follows *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet and *br* = broadened
†Obscured by other signals
‡m ($W_{\frac{1}{2}}$ = 6 Hz)



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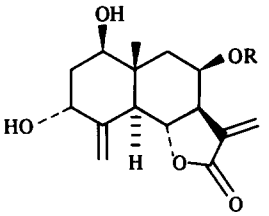

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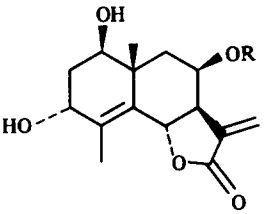

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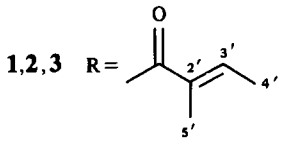
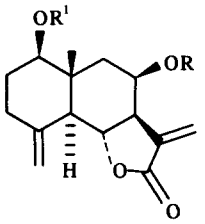
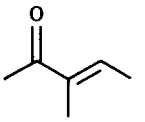


1,2,3 R=





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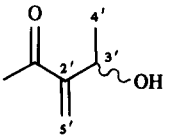

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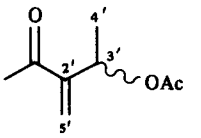

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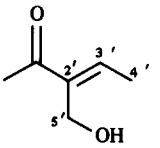

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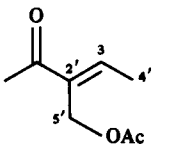


8 R¹= OAc, R=

assumption that H-7 adopts an α-configuration [7], H-6 should be β-oriented since the coupling constant ($J_{6,7}$ = 11 5 Hz) suggests an antiperiplanar arrangement of H-6 and H-7 Similarly, the large coupling constant ($J_{5,6}$ = 11 5 Hz) also indicates an antiperiplanar arrangement of H-5 and H-6, and therefore H-5 has an α-orientation The configuration of the tiglate ester side chain at C-8 was formulated as β on the basis of the small coupling constant ($J_{7,8} \sim 3$ Hz) which suggested an equatorial disposition of H-8 The stereochemistry at C-1 was deduced from the coupling constants of H-1 and the protons at C-2, whose magnitudes were in accord with a *trans*-diaxial relationship between the H-2β and H-1 and with a *cis*-equatorial-axial relationship between H-2α and H-1 Based on the same arguments, the small coupling constant $J_{2,3a} = J_{2,3b} = 3$ Hz indicated an α-orientation of the hydroxyl group at C-3 The structural and stereochemical assignments were corroborated by ^{1}H NMR spectral comparison of **2** with data described for synthetic 1β,3α-dihydroxylated eudesmanolide analogues [8, 9]

Trichomatolide C (**3**), $C_{20}H_{26}O_6$, displayed in the ^{1}H NMR spectrum two one-proton doublets at δ6 24 (H-13a) and 5 55 (H-13b), and a multiplet at δ3 02 (H-7) that are characteristic of α,β-unsaturated-γ-lactones Its IR spectrum with an absorption band at 1765 cm^{-1} corroborated the presence of a γ-lactone moiety, and also showed bands which indicated an unsaturated ester (1705 cm^{-1}), double bond(s) (1650 and 1605 cm^{-1}), and hydroxyl group(s) (3595 and 3445 cm^{-1}) The ^{1}H NMR spectrum of compound **3** (Table 1) is very similar to that of **2**, and in agreement with the 1β,3α-dihydroxy-8β-tigloyloxy eudesmanolide type of sesquiterpene lactone as compound **2**, except for the following differences (a) the H-6 signal did not appear as a doublet of doublets as in compound **2**, but as a broad doublet at δ5 15 (J = 12 5 Hz), (b) there was no H-5 signal in the spectrum of **3**, (c) the two olefinic signals of the exocyclic methylene group at C-4 were missing, and instead a three-proton narrow doublet at δ2 07 was found, indicating a C-4 methyl group These differences between the ^{1}H NMR spectra of trichomatolide B and C suggested an isomeric relationship between the two compounds, with trichomatolide C having an endocyclic 4,5-double bond as shown in structure **3**

Trichomatolide D (**5**), $C_{20}H_{26}O_6$, showed in the ^{1}H NMR spectrum two one-proton doublets at δ6 17 (H-13a) and 5 47 (H-13b), and a doublet of quartets at 2 88 (H-7) typical of an α,β-unsaturated γ-lactone The IR spectrum of **5** showed absorption bands indicating the presence of hydroxyl group(s) (3600 and 3515 cm^{-1}), an α,β-unsaturated γ-lactone (1765 cm^{-1}) and an unsaturated ester (1715 cm^{-1}) The ^{1}H NMR spectrum was assigned by extensive double irradiation experiments and the results are given in Table 1 Major portions of the ^{1}H NMR spectrum of compound **5** were nearly identical with the known eudesmanolide (**4**) previously found in *Calea rotundifolia* [2] and *Calea trichomata* [1] Obvious differences were detected for signals due to the different side chains The methylene group at C-4 (H-15) produced singlets at δ5 04 (H-15a) and 4 97 (H-15b), broadened by small allylic and geminal couplings The stereochemistry at C-5, C-6 and C-7 was deduced from the large coupling constants $J_{5,6} = J_{6,7} = 11\,0$ Hz which indicated an antiperiplanar arrangement of H-5, H-6 and H-7 Similarly, the small coupling constant $J_{7,8} = 3\,0$ Hz suggested a β-orientation for the ester side chain at C-8 The chemical shift of H-1 (δ3 54) suggested the presence of a hydroxyl group at C-1, and the coupling constant $J_{1,2\beta} = 11\,2$ Hz clearly demonstrated a *trans*-diaxial relationship between H-1 and H-2β, and therefore an equatorial position for the β-hydroxyl on C-1 The assignment of H-1 was further corroborated by its downfield shift ($\Delta\delta = 1\,25$) upon acetylation of compound **5**

Instead of the typical tiglate signals in the ^{1}H NMR spectrum of **4** [1, 2], the spectrum of trichomatolide D (**5**) showed a one-proton quartet at δ4 61 ($J = 6\,8$ Hz), two one-proton broad singlets at 6 13 and 5 88, and a three-proton doublet at 1 38 ($J = 6\,8$ Hz) This pattern of signals, together with the characteristic mass spectral peaks at m/z 99 (**B**^{1}), 81 [**B**$^1 - H_2O$], 71 [**B** − **B**^{3}] and 55 [**B**$^2 - H_2O$], clearly indicated the presence of a 3-hydroxy-[2-ethylacrylate] moiety

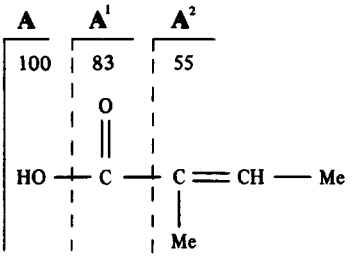
Acetylation of **5** with acetic anhydride–pyridine gave compound **6**, $C_{24}H_{30}O_8$, which lacked the hydroxyl absorptions in the IR spectrum, but instead showed an additional carbonyl band at 1740 cm^{-1} which was assigned to the acetate groups The ^{1}H NMR spectrum of the diacetate **6** (Table 2) showed two sharp methyl singlets at δ2 06 and 2 04, together with paramagnetic acetylation shifts for H-1 from 3 54 in **5** to 4 79 in **6** and for H-3′ from 4 61 in **5** to 5 69 in the acetate **6** These paramagnetic shifts confirmed the presence of hydroxyl groups on C-1 and C-3′ in trichomatolide D (**5**)

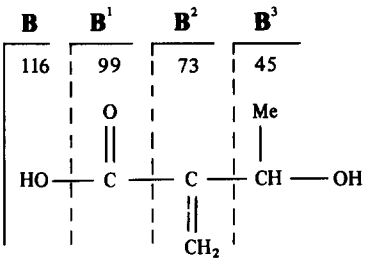
The ^{1}H NMR spectrum of the acetate **6** showed a well-separated double pattern of the signals corresponding to H-6, H-8, H-13a, H-13b, and H-3′, which are slightly shifted as shown in Table 1 This splitting pattern became more evident when the spectrum was obtained in acetone-d_6 Here the C-10 methyl singlet was also split These data indicated a mixture of two very similar compounds, most likely diasteroisomers differing only in the chirality at C-3′ of the side chain Similar findings were previously reported in the tetraludin series [10] Attempts to separate the mixture were not successful and in Table 1 the data for the diasteromeric pair are reported

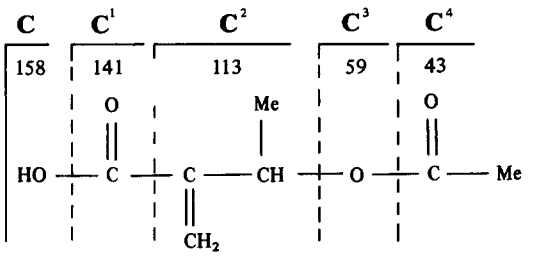
Trichomatolide E (**7**), $C_{20}H_{26}O_6$, was an impure gum which could only be separated from trichomatolide D (**5**) through conversion to the diacetate **8** on which the identification was performed The IR spectrum of **8** showed strong absorptions at 1765 cm^{-1} (α,β-unsaturated γ-lactone), 1735 cm^{-1} (acetate), broad band at 1720 cm^{-1} (unsaturated ester) and 1650 cm^{-1} (double bond) The presence of two acetate groups in **8** was indicated by two three-proton singlets at δ2 05 and 2 00, and a mass spectral base peak at m/z 43 The ^{1}H NMR parameters of compound **8** were obtained by detailed decoupling experiments and are summarized in Table 1

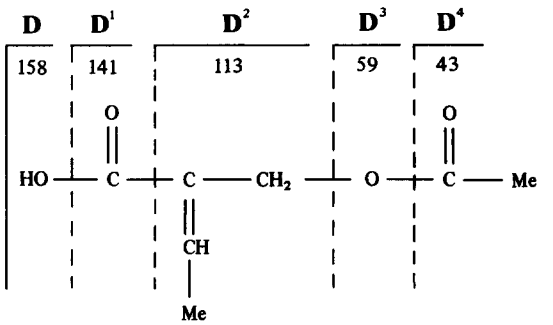
Compound **8** showed a ^{1}H NMR spectrum nearly identical with the one of **6**, but gave different side chain signals The spectrum of **8** displayed a one-proton quartet at δ7 13 (H-3′), a two-proton AB pattern ($J = 12$ Hz) at 4 88 (H-5′a) and 4 77 (H-5′b), and a three-proton doublet at 1 97 These signals together with strong mass spectral peaks at m/z 141 [**D**^{1}] and 99 [**D** − **D**^{3}] are diagnostic of the sarracinic acid acetate moiety

On the basis of the great similarities of the ^{1}H NMR









spectral data of compounds **8** and **6**, the stereochemical structure of the eudesmanolide skeleton of **8** must be as in **6**. In addition, the sarracinoyl acetate moiety is attached to C-8. Since the ^{1}H NMR spectrum of the eudesmanolide mixture previous to acetylation lacked acetate signals, it can be assumed that compounds **5** and **7** are the natural products.

EXPERIMENTAL

Calea trichomata was collected on 29 July, 1978 in Chiapas, Mexico 2.8 miles south of La Trinitaria along Highway 190 (L. Urbatsch, No. 3335, voucher deposited at LSU, USA). The air-dried plant material was extracted and worked up as previously described [1]. Fractions 16–18 contained eudesmanolides on which we have previously reported [1]. Rechromatography of less polar fractions led the isolation of the new trichomatolides B–E. Fractions 6–7 (120 mg) were purified by preparative TLC on silica gel with Et_2O–petrol (7:3), yielding 10 mg of **1** as a gum. Fractions 24–25 (900 mg) were rechromatographed on a 250 g silica gel column using mixtures of petrol–EtOAc of increasing polarity as eluant (60 fractions of 50 ml each). Fractions 22–25 of this second column chromatographic run (Me_2CO–$CHCl_3$, 8:2), after further purification by preparative TLC, provided 90 mg of trichomatolide D (**5**). Fractions 26–27 (1.1 g) were fractionated over 250 g silica gel with Me_2CO–$CHCl_3$ mixtures of increasing polarity, yielding 50 fractions of 50 ml each. From these, fractions 38–40 (19 mg) were rechromatographed by preparative TLC (Me_2CO–$CHCl_3$, 7:3) affording 8 mg of pure trichomatolide C (**3**). With a similar purification procedure, fractions 42–44 (24 mg) gave 11 mg of trichomatolide B (**2**).

3-Deoxy-2,3-dehydrohelianginn (**1**) $C_{20}H_{24}O_5$, gum, UV λ_{max}^{MeOH} nm 216 (ε 7.41 × 10^3), 235 (ε 3.86 × 10^3), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1755 (γ-lactone), 1705 (conj. ester), 1650 (double bond), EIMS (probe) (rel. int.) 344 $[M]^+$ (0.3), 244 $[M-A]^+$ (1.5), 229 $[M-A-Me]^+$ (1.5), 216 $[M-A-CO]^+$ (1.3), 211 $[M-A-CO-Me]^+$ (4), 83 $[A^1]^+$ (100), 55 $[A^2]^+$ (54). CIMS (isobutane) *m/z* 345 $[M+1]$.

Trichomatolide B (**2**) $C_{20}H_{26}O_6$, gum, UV λ_{max}^{MeOH} nm 216 (ε 4.93 × 10^2), 225 (ε 3.63 ×10^2), 240 (ε 2.19 × 10^2), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 3480 (OH), 1765 (γ-lactone), 1705 (conj. ester), 1650 (double bond), 1605 (double bond), EIMS (probe) *m/z* (rel. int.) 362 $[M]^+$ (7), 344 $[M-H_2O]^+$ (0.5), 262 $[M-A]^+$ (2), 244 $[M-A-H_2O]^+$ (6), 229 $[M-A-H_2O-Me]^+$ (2), 226 $[M-A-2H_2O]^+$ (2), 216 $[M-A-H_2O-CO]^+$ (4), 201 $[M-A-H_2O-Me-CO]^+$ (4), 83 $[A^1]^+$ (100), 55 $[A^2]^+$ (45). [Found (MS) 362.1726 $C_{20}H_{26}O_6$ requires 362.1729.]

Trichomatolide C (**3**) $C_{20}H_{26}O_6$, gum, UV λ_{max}^{MeOH} nm 220 (ε 9.53 × 10^3), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3595 (OH), 3445 (OH), 1765 (γ-lactone), 1705 (conj. ester), 1650 (double bond), 1605 (double bond), EIMS (probe) *m/z* (rel. int.) 362 $[M]^+$ (0.5), 344 $[M-H_2O]^+$ (0.5), 262 $[M-A]^+$ (8), 247 $[M-A-Me]^+$ (16), 244 $[M-A-H_2O]^+$ (12), 229 $[M-A-H_2O-Me]^+$ (8), 216 $[M-A-H_2O-CO]^+$ (8), 201 $[M-A-H_2O-Me-CO]^+$ (7), 83 $[A^1]^+$ (100), 55 $[A^2]^+$ (95). [Found (MS) 362.1719 $C_{20}H_{26}O_6$ requires 362.1729.]

Trichomatolide D (**5**) $C_{20}H_{26}O_6$, gum, UV λ_{max}^{MeOH} nm 215 (ε 7.24 × 10^3); IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3600 (OH), 3515 (broad, OH), 1765 (γ-lactone), 1715 (conj. ester), 1650 (weak, double bond), EIMS (probe) *m/z* (rel. int.) 362 $[M]^+$ (2), 344 $[M-H_2O]^+$ (2), 326 $[M-2H_2O]^+$ (1), 246 $[M-A]^+$ (22), 228 $[M-A-H_2O]^+$ (40), 213 $[M-A-H_2O-Me]^+$ (25), 202 $[M-A-CO_2]^+$ (42), 200 $[M-A-H_2O-CO]^+$ (16), 185 $[M-A-H_2O-CO-Me]^+$ (23), 99 $[B^1]^+$ (38), 81 $[B^1-OH]^+$ (96), 71 $[B-B^3]^+$ (27), 55 $[B^2-OH]^+$ (39). [Found (MS) 362.1730 $C_{20}H_{26}O_6$ requires 362.1729.]

Trichomatolide D acetate (**6**) Acetylation of 40 mg **5** in pyridine–Ac_2O for 10 hr, followed by usual work-up, gave the acetate **6**, $C_{24}H_{30}O_8$, gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1760 (γ-lactone), 1740 (acetate), 1730 (acetate), 1720 (conj. ester), EIMS (probe) *m/z* (rel. int.) 446 $[M]^+$ (0.3), 386 $[M-HOAc]^+$ (6), 326 $[M-2HOAc]^+$ (3), 288 $[M-C]^+$ (1), 228 $[M-C-HOAc]^+$ (28), 213 $[M-C-HOAc-Me]^+$ (12), 200 $[M-C-HOAc-CO]^+$ (8), 185 $[M-C-HOAc-CO-Me]^+$ (10), 141 $[C^1]^+$ (59), 115 $[C-C^4]^+$ (7), 99 $[C-C^3]^+$ (17), 82 $[C^1-C^3]^+$ (18), 54 $[C^2-C^3]^+$ (10), 43 $[CH_3CO]^+$ (100).

Trichomatolide E acetate (**8**) The above acetylation of **5** gave after preparative TLC purification (petrol–Me_2CO, ×2) beside the acetate **6**, 9 mg of acetate **8**, $C_{24}H_{30}O_8$, gum, UV λ_{max}^{MeOH} nm 218 (ε 6.51 × 10^2), 225 (ε 5.51 × 10^2), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1765 (γ-lactone), 1735 (acetate), 1725 (acetate), 1715 (conj. ester), 1650 (double bond), EIMS (probe) *m/z* (rel. int.) 446 $[M]^+$ (0.4), 386 $[M-HOAc]^+$ (6), 326 $[M-2HOAc]^+$ (1), 288 $[M-D]^+$ (1), 228 $[M-D-HOAc]^+$ (34), 213 $[M-D-HOAc-Me]^+$ (14), 200 $[M-D-HOAc-CO]^+$ (8), 141 $[D^1]^+$ (82), 99 $[D-D^3]^+$ (25), 53 $[D^2-D^3]^+$ (9), 43 $[CH_3CO]^+$ (100). [Found (MS) 446.1942 $C_{24}H_{30}O_8$ requires 446.1938.]

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