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GUAIANOLIDES AND CHROMENES FROM *CALEA* SPECIES

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Key Word Index—*Calea berteriana*; *C. prunifolia*; *C. solidaginea*; Asteraceae; Heliantheae; sesquiterpene lactones; guaianolides; heliangolides; 2,2-dimethylchromenes.

Abstract—Chemical analysis of *Calea berteriana* yielded, besides the known flavonoid acacetin and the sesquiterpene lactone calbertolide C, three new guaianolides, desacyl-8-tiglylsubcordatolide A and 8-epi-8-tiglylrupicolins A and B. *C. prunifolia* provided acacetin, calbertolide C, desacyl-8-tiglylsubcordatolide A, and two new chromenes, prunichromenes A and B. From *C. solidaginea* acacetin, heliangine, calbertolide C, 8-epi-8-tiglylrupicolin A and desacyl-8-tiglylsubcordatolide A were isolated. The structures of the new compounds were established by chemical and spectral methods.

INTRODUCTION

In continuation of our biochemical systematic study of the genus *Calea* [1–3], we have studied *C. berteriana* and *C. solidaginea* from Venezuela and *C. prunifolia* from Panama. All three species contained, besides the known flavonoid acacetin (**1**) [4] and the modified heliangolide calbertolide C (**3**) [2], a new guaianolide, desacyl-8-tiglylsubcordatolide A (**6**).

In a previous chemical investigation of another population of *C. berteriana* from Venezuela, the two 7,8-lactonized germacranolides calbertolides A and B and the modified heliangolide calbertolide C (**3**) were found [2], but no guaianolides could be detected. Here we describe the isolation and structure determination of three new guaianolides, 8-epi-8-tiglylrupicolins A (**4**) and B (**5**) and **6** from *C. berteriana*. *C. prunifolia* afforded, besides acacetin (**1**) and the lactones **3** and **6**, two new chromenes, prunichromenes A (**8**) and B (**9**). From *C. solidaginea*, the known lactone heliangine (**2**) [5, 6] and the two new guaianolides **4** and **6** were obtained. The identities of the known compounds (**1–3**) were established by ^{1}H NMR and mass spectral correlations with authentic samples. The new guaianolides **4–6** as well as the chromenes **8** and **9** were characterized by chemical and spectral methods.

RESULTS AND DISCUSSION

Calbertolide C (**3**), previously found in another Venezuelan population of *C. berteriana* [2], was characterized by comparison of its ^{1}H NMR, IR and mass spectral data with those of an authentic sample. Since the ^{13}C NMR data were not reported previously, they are presented in Table 2.

8-epi-8-Tiglylrupicolin A (**4**), $C_{20}H_{24}O_5$, is a gum which exhibited in the ^{1}H NMR spectrum two one-proton doublets at δ6.29 (H-13a) and 5.54 (H-13b), and a one-proton multiplet at δ3.41 (H-7) characteristic of an α-methylene-γ-lactone. This was further confirmed by an IR absorption at 1760 cm^{-1} which is typical of a γ-lactone moiety. Other bands in the IR spectrum indicated the presence of hydroxyl(s) (3580 and 3500 cm^{-1}), an unsaturated ester (1705 cm^{-1}) and a carbon–carbon unsaturation (1650 cm^{-1}). The ester side-chain was identified as a tiglate group on the basis of the characteristic ^{1}H NMR signals (a one-proton quartet of quartets at δ6.71, and two three-proton vinyl methyl signals at δ1.77 and 1.75), together with strong mass spectral peaks at *m/z* 83 (A^1) and 55 (A^2). Detailed spin decoupling experiments allowed the assignment of all ^{1}H NMR signals (Table 1). On the basis of the chemical shift of H-5 (δ2.80) and its multiplicity (*d*, $J_{5,6}$ = 11.2 Hz) and the splitting of H-6 (*dd*, $J_{5,6}$ = 11.2, $J_{6,7}$ = 9.0 Hz), together with the absence of angular methyl signals, we postulated a guaianolide-type skeleton for compound **4**.

Comparison of the ^{1}H NMR spectrum of **4** with the one of 8-epi-8-isobutyrylrupicolin A, which we previously isolated from *C. subcordata* [3], showed only minor differences for the skeletal proton signals, and differed mainly in the signals due to the side-chains. Based on the great similarity of the chemical shifts and splitting patterns, compound **4** must have the same configuration at C-1, C-5, C-7 and C-8 as 8-epi-8-isobutyrylrupicolin B [3], and therefore we propose a stereo-structure as shown in **4**.

8-epi-Tiglylrupicolin B (**5**), $C_{20}H_{24}O_5$, is a gum with an IR spectrum showing a tertiary alcohol (3570 and 1150 cm^{-1}), a γ-lactone (1765 cm^{-1}), an unsaturated ester (1705 cm^{-1}) and carbon–carbon unsaturation (1660 cm^{-1}). The ^{1}H NMR spectrum corroborated the presence of an α-methylene-γ-lactone moiety by exhibiting two one-proton doublets at δ6.26 (H-13a) and 5.54 (H-13b) and a multiplet at δ3.40 (H-7). As was the case in compound **4**, the ester side-chain was identified as a tiglate ester on the basis of the diagnostic ^{1}H NMR and mass spectral signals. Exhaustive decoupling experiments in different solvents allowed the assignments of the basic skeletal proton signals (Table 1). Comparison of the ^{1}H NMR spectra of compounds **4** and **5** showed significant differences only for the signals due to H-9 and H-14. The H-14 proton absorptions, which in **4** represented a three-proton broad singlet at δ1.97, appeared in **5** as two

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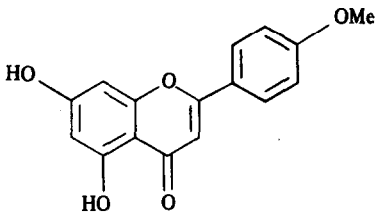

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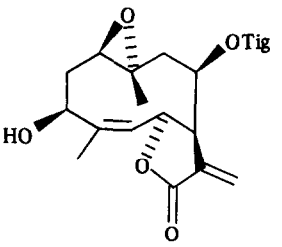

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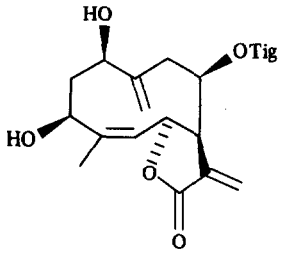

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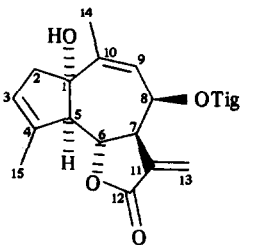

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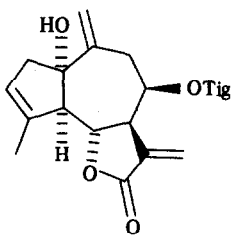

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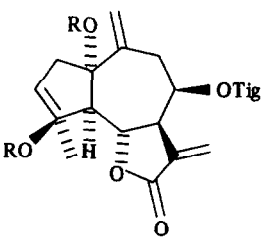

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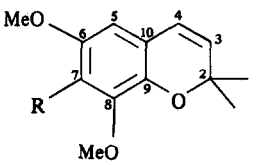
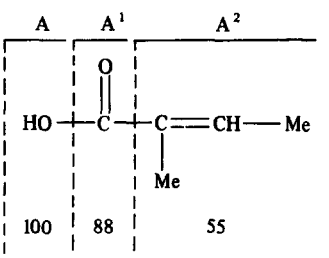
7 R = Ac



8 R = OMe

9 R = H



one-proton broadened singlets at δ5.18 (H-14a) and 4.96 (H-14b), which sharpened upon irradiation of the H-9 signals. This clearly indicated that compound **5** must possess an exocyclic methylene double bond at C-10. The H-9 proton signal, which in compound **4** was a one-proton doublet of doublets at δ5.65, appeared in **5** as two one-proton broadened doublets at δ3.07 (H-9a) and 2.49 (H-9b). Based on this isomeric relationship between compounds **4** and **5**, and by comparison of the ^{1}H NMR spectrum of **5** with the parameters of 8-epi-isobutyrylrupicolin A [3], we postulated for the new compound structure **5** and a stereochemistry as indicated in the formula.

Desacyl-8-tiglylsubcordatolide A (**6**), $C_{20}H_{24}O_6$, is a gum with an ^{1}H NMR spectrum suggesting an α-methylene-γ-lactone with two typical one-proton doublets at δ6.31 (H-13a) and 5.66 (H-13b), and a one-proton multiplet at δ3.58 (H-7). The IR spectrum indicated the presence of hydroxyl group(s) (3595 and 3460 cm^{-1}), a γ-lactone (1760 cm^{-1}), an unsaturated ester (1706 cm^{-1}) and carbon–carbon double bond(s) (1650 cm^{-1}). On the basis of the same arguments used for compounds **4** and **5**, the side chain in compound **6** was identified as a tiglate ester.

The chemical shifts and multiplicities of H-5 (δ2.51, *d*, $J_{5,6}$ = 11.2 Hz) and H-6 (δ4.73, *dd*, $J_{5,6}$ = 11.2, $J_{6,7}$

Table 1. ^{1}H NMR spectral data of guaianolides 4–7 (200 MHz, TMS)*

H	4	5	6	7
2a	2.65 m	2.92 *d* (*br*) (17.5)	5.64 *d* (6.0)	6.36 *d* (5.5)
2b		2.48 *d* (*br*) (17.5)		
3	5.52–5.57†	5.52–5.56†	6.02 *d* (6.0)	6.74 *d* (5.5)
5	2.80 *d* (*br*) (11.2)	2.80 *d* (*br*) (11.0)	2.51 *d* (11.2)	3.06 *d* (11.2)
6	4.46 *dd* (11.2; 9.0)	4.40 *t* (11.0)	4.73 *dd* (11.2; 9.2)	4.77 *dd* (11.2; 9.0)
7	3.41 *dddd* (9.0; 3.0; 3.4; 3.4)	3.40 *m*	3.58 *m*	3.40 *m*
8	5.84 *dd* (6.5; 3.0)	5.52–5.56†	5.65 *m*†	5.64 *m*
9a	5.65 *dd* (6.5; 1.5)	3.07 *dd* (15.0; 5.0)	3.18 *dd* (14.5; 4.0)	2.21 *dd* (14.5; 4.0)
9b		2.49 *dd* (15.0; 5.0)	2.46 *dd* (14.5; 2.5)	2.00–2.10†
13a	6.29 *d* (3.8)	6.26 *d* (4.0)	6.31 *d* (3.5)	6.35 *d* (3.3)
13b	5.54 *d* (3.4)	5.54 *d* (3.4)	5.66 *d* (3.5)	5.67 *d* (3.2)
14a	2.00 d (1.5)	5.18 *s* (*br*)	4.91 *s* (*br*)	5.01 *s* (*br*)
14b		4.96 *s* (*br*)	4.88 *s* (*br*)	4.99 *s* (*br*)
15	1.97 *br*	1.96 *s* (*br*)	1.41 *s*	1.61 *s*
OTig	6.71 *qq* (7.5; 1.8)	6.73 *qq* (7.2; 2.0)	6.76 *qq* (7.5; 2.0)	6.75 *qq*†
	1.77 *br*	1.76 *br*	1.80 *s* (*br*)	1.80 *br*
	1.75 *br*	1.74 *br*	1.77 *s* (*br*)	1.77 *br*
OAc				2.10 *s*
OAc′				2.05 *s*

*Coupling constants (*J*) or line separations in Hz are given in parentheses. Multiplets are given by the usual symbols.

†Obscured by other signals.

Table 2. ^{13}C NMR spectral data for compounds 3 and 6 (50.32 MHz, $CDCl_3$, ambient temp.)*

C	3	6
1	72.7† *d*	85.8† *s*
2	38.7‡ *t*	140.2‡ *d*
3	72.5† *d*	138.2‡ *d*
4	139.9 *s*	82.1† *s*
5	126.4 *d*	66.8§ *d*
6	74.8§ *d*	67.6§ *d*
7	47.5 *d*	46.4 *d*
8	76.8§ *d*	76.9§ *d*
9	36.4‡ *t*	36.0 *t*
10	143.2 *s*	134.8 *s*
11	144.4 *s*	144.1 *s*
12	171.0 *s*	169.8 *s*
13	125.4 *t*	122.6 *t*
14	118.7 *t*	116.9 *t*
15	23.7 *q*	24.0 *q*
1′	167.9 *s*	166.9 *s*
2′	138.2 *s*	138.8 *s*
3′	139.7 *d*	134.8 *d*
4′	15.4‖ *q*	14.4‖ *q*
5′	12.6‖ *q*	12.0‖ *q*

*Chemical shifts are given in ppm relative to TMS as determined by proton noise decoupling. Peak multiplicity was obtained by off-resonance decoupling (2.5 ppm above TMS).

†,‡,§,‖Assignments interchangeable.

= 9.2 Hz), together with the absence of angular methyl signals, again suggested a guaianolide-type skeleton. Comparison of the ^{1}H NMR and ^{13}C NMR spectral data (Table 2) of compound **6** with the data reported for subcordatolide A, a compound which we had previously isolated from *C. subcordata* [3], showed that both compounds have the same skeleton and substitution pattern, with structural differences only in the side-chain attached to C-8. The presence of two singlets at δ85.9 (C-1) and 82.1 (C-4) in the ^{13}C NMR spectrum of **6**, which correspond to quaternary carbons bearing a hydroxyl group, agreed with the presence of two tertiary hydroxyl groups in compound **6**.

Acetylation of **6** with acetic anhydride–4-dimethylaminopyridine [7] gave the diacetate (**7**), $C_{24}H_{28}O_8$, which lacked hydroxyl absorptions in the IR spectrum, but instead gave an additional broad carbonyl band at 1730 cm^{-1}. The ^{1}H NMR spectrum of **7** showed two three-proton singlets at δ2.10 and 2.05, clearly indicating the presence of two acetate groups.

On the basis of the close similarities of the ^{1}H NMR and ^{13}C NMR spectra of compound **6** and subcordatolide A [3], together with the paramagnetic acetylation shifts observed in the diacetate **7** for H-5 and H-15, we propose the structure and stereochemistry as shown in **6**.

Prunichromene A (**8**), $C_{14}H_{18}O_4$, is an oil with a ^{1}H NMR spectrum showing clearly a 2,2-dimethylchromene skeleton: a six-proton singlet at δ1.41 and a two-proton AB quartet (J = 10 Hz) at δ6.53 (H-4) and 5.48 (H-3). In addition, the ^{1}H NMR spectrum showed a broadened singlet at δ6.20 and three three-proton singlets at δ3.80, 3.81 and 3.88, corresponding to three methoxyl substituents on the aromatic ring. Double irradiation

Table 3. ^{1}H NMR spectral data of prunichromenes A (**8**) and B (**9**) (200 MHz, TMS)*

H	**8** ($CDCl_3$)	**8** (C_6D_6)	$\Delta\delta$†	**9** ($CDCl_3$)	**9** (C_6D_6)	$\Delta\delta$
3	5.48 (10.0)	5.26 *d*	−0.22	5.41 *d* (10.0)	5.23 *d*	−0.18
4	6.53 *d* (*br*) (10.0)	6.74 *d* (*br*)	0.31	6.57 *d* (*br*) (10.0)	6.90 *d* (*br*)	0.33
5	6.20 *s* (*br*)	6.27 *s* (*br*)	0.07	6.04 *d* (*br*) (2.5)	6.26 *d* (*br*)	0.18
7				6.01 *d* (2.5)	6.04 *d*	0.03
OMe	3.80 *s*	3.71 *s*	−0.09	3.78 *s*	3.29 *s*	−0.49
OMe′	3.81 *s*	3.75 *s*	−0.06	3.76 *s*	3.26 *s*	−0.50
OMe″	3.88 *s*	3.25 *s*	−0.63			
Me (6 H)	1.41 *s*	1.35 *s*	−0.06	1.41 *s*	1.35 *s*	−0.06

*Coupling constants (J) or line separations in Hz are given in parentheses.
†$\Delta\delta = \delta\,(C_6D_6) - \delta\,(CDCl_3)$.

experiments together with benzene-d_6 shift studies allowed the assignments of the ^{1}H NMR signals (Table 3). Saturation of the doublet at δ6.53 (H-4) collapsed the doublet at δ5.38 (H-3) to a singlet, and sharpened the broadened singlet at δ6.20. In return, double irradiation of the broadened singlet at δ6.20 sharpened the broadened doublet at δ6.53 (H-4), clearly indicating a long-range coupling between H-4 and the aromatic proton giving the broad singlet at δ6.20. Solvent shift studies in benzene-d_6, in which the association with the solvent molecules results in a diamagnetic shift of the methoxyl groups when at least one unsubstituted *ortho* position is present [8, 9], clearly showed (Table 3) that only one of the three methoxyl groups in chromene **8** experienced a large diamagnetic shift ($\Delta\delta = 0.63$ ppm). From these facts, together with the observed long-range coupling of H-4 with the aromatic proton at δ6.20, it must be concluded that prunichromene A is 6,7,8-trimethoxy-2,2-dimethylchromene as represented by structure **8**.

Further confirmation of the proposed structure for compound **8** was obtained from the ^{13}C NMR spectral data given in Table 4. The ^{13}C NMR spectrum showed three quartets corresponding to the three methoxyl groups present in **8** (δ61.5, 61.2 and 55.9), a large methyl signal at δ27.7 (C-10 and C-11), two doublets corresponding to C-3 (δ127.4) and C-4 (δ116.9), and one strongly shielded doublet at δ96.5 due to the aromatic carbon C-5. The assignments of these signals were established by single-frequency off-resonance decoupling (SFORD) (Table 4) and were in accord with a 6,7,8-trimethoxy-substitution pattern in chromene **8**.

Table 4. ^{13}C NMR spectral data for chromenes **8** and **9** (50.32 MHz, $CDCl_3$, ambient temp.)*

C	**8**	**9**
2	78.1 *s*	76.2 *s*
3	127.4 *d*	125.8 *d*
4	116.9 *d*	116.8 *d*
5	96.5 *d*	91.5 *d*
6	149.3 *s*†	156.2 *s*†
7	135.8 *s*	94.2 *d*
8	149.2 *s*†	154.8 *s*†
9	153.7 *s*	161.1 *s*
10	112.7 *s*	104.3 *s*
11 + 12	27.7 *q*	27.8 *q*
OMe	61.5 *q*	55.5 *q*
OMe	61.2 *q*	55.3 *q*
OMe	55.9 *q*	

*Chemical shifts are given in ppm relative to TMS as determined by proton noise decoupling. Peak multiplicity was obtained by off-resonance decoupling (2.5 ppm above TMS). Assignment of the doublets was done by single-frequency off-resonance decoupling.
†Assignments interchangeable.

Prunichromene B (**9**), $C_{13}H_{16}O_3$, is an oil with the typical ^{1}H NMR spectrum of a 2,2-dimethylchromene with a pair of AB-type doublets (J = 10 Hz) at δ5.41 (H-3) and 6.57 (H-4), and a six-proton singlet at δ1.41 for the geminal dimethyl group. The ^{1}H NMR spectrum of **9** was very similar to that of prunichromene A (**8**), except that compound **9** exhibited only two methoxyl signals in the ^{1}H NMR, but instead one extra aromatic signal at δ6.01.

Double irradiation of the doublet at δ6.57 (H-4) collapsed the doublet at 5.41 (H-3) to a singlet and sharpened the broadened doublet at δ6.04 (H-5) to a sharp doublet. Saturation of the broad doublet at δ6.04 (H-5) collapsed the doublet at δ6.01 (H-7) to a singlet and sharpened the doublet at δ6.57 (H-4). In return, saturation at δ6.01 (H-7) collapsed the doublet at δ6.04 (H-5) to a singlet. Irradiation at δ5.41 (H-3) collapsed the broadened doublet at δ6.57 (H-4) to a broad singlet. The same results were obtained by performing the decoupling experiments in C_6D_6, which gave better separations of the aromatic proton doublets. From the coupling constant (J = 2.5 Hz) of the aromatic protons at δ6.04 (H-5) and 6.01 (H-7), a *meta* disposition of these two aromatic protons can be derived. Solvent shift studies in benzene-d_6 (Table 3) further confirmed this conclusion, since the data indicated that both methoxyl groups had at least one free *ortho* position [8, 9]. These facts, together with the long-range coupling observed between H-4 and the aromatic proton at δ6.04 (H-5), led to the formulation of prunichromene B (**9**) as 6,7-dimethoxy-2,2-dimethylchromene.

The ^{13}C NMR spectrum of compound **9** was very similar to that of **8** (Table 4), except that C-7, which in **8**

was a singlet at δ135.8, appeared in **9** as a shielded doublet at δ94.2. In addition, only two methoxyl carbons were present in compound **9** (δ55.5 and 55.3). The other signals given in Table 4 were in agreement with the chemical shifts expected for the suggested substitution pattern.

EXPERIMENTAL

Calea solidaginea Kunth was collected on 12 December 1979 in Salom, Venezuela (L. Urbatsch, No. 3466, voucher deposited at L.S.U., U.S.A.). The air-dried plant material (728 g) was extracted and worked up as described previously [10], providing 8.0 g of crude syrup. The crude syrup was chromatographed on a silica gel column with hexane–Me_2CO mixtures of increasing polarity. Fifty fractions of 200 ml each were collected.

Fractions 9–11 (46 mg) were combined and rechromatographed on silica gel plates with $CHCl_3$–Me_2CO mixtures (19:1) yielding 7 mg 8-epi-8-tiglylrupicolin A (**4**). Fractions 15–18 gave 90 mg acacetin (**1**). Fractions 19–23 (80 mg) yielded 36 mg heliangine (**2**) after prep. TLC on silica gel plates with $CHCl_3$–Me_2CO (9:1). Prep. TLC on silica gel of fractions 24–29 (420 mg) with $CHCl_3$–Me_2CO (22:3) yielded 150 mg desacyl-8-tiglylsubcordatolide A (**6**), while the same procedure for fractions 30–35 (800 mg) gave 240 mg calbertolide C (**3**).

Calea berteriana DC. was collected on 10 December 1979 in Santa Merida, Venezuela, along Rio Chama towards Chiguara (L. Urbatsch, No. 3455, voucher deposited at L.S.U., U.S.A.). The air-dried plant material (968 g) was extracted and worked up as usual [10], giving 10.5 g of crude syrup. CC of the crude syrup over silica gel with petrol–Me_2CO mixtures of increasing polarity gave 50 fractions of 200 ml each.

Prep. TLC (silica gel) of fractions 10 and 11 with $CHCl_3$–Me_2CO (19:1) yielded 8 mg 8-epi-8-tiglylrupicolin A (**4**) and 4 mg 8-epi-8-tiglylrupicolin B(**5**). Fractions 14–17 gave 97 mg acacetin (**1**). Prep. TLC on silica gel plates of the combined fractions 25–28 (110 mg) with $CHCl_3$–Me_2CO (17:1) yielded 70 mg desacyl-8-tiglylsubcordatolide A (**6**). The same procedure applied to fractions 30–33 (260 mg) with $CHCl_3$–Me_2CO (4:1) gave 202 mg calbertolide C (**3**).

Calea prunifolia Kunth was collected on 8 August 1980 in Zorro Azul, Panama City, Panama (collected by A. J. Malcolm; voucher Malcolm No. 1 deposited to L.S.U., U.S.A.). The air-dried plant material (203 g) was extracted and treated following the usual procedure [10], providing 12.3 g crude syrup. CC (silica gel) of 1.3 g of the crude material with $CHCl_3$–Me_2CO mixtures of increasing polarity yielded 40 fractions of 100 ml each. Prep. TLC (silica gel) of fractions 13 and 14 (94 mg) with $CHCl_3$–Me_2CO (49:1) afforded 38 mg prunichromene B (**9**) and 23 mg prunichromene A (**8**). Rechromatography by prep. TLC of fractions 15–23 (90 mg) with $CHCl_3$–Me_2CO (9:1) yielded 17 mg calbertolide A (**3**), while the same procedure for fractions 24–30 (73 mg) gave 26 mg desacyl-8-tiglylsubcordatolide A (**6**). A yellow solid (13 mg) identified as acacetin (**1**) was obtained from fractions 15–23 by spontaneous crystallization.

8-epi-8-Tiglylrupicolin A (**4**). $C_{20}H_{24}O_5$, gum; UV λ_{max}^{MeOH} nm: strong end absorption; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 3500 (OH, broad), 1760 (γ-lactone), 1705 (unsaturated ester), 1650 (double bonds), 1145 (tertiary alcohol); EIMS (probe) *m/z* (rel. int.): 344 $[M]^+$ (0.2), 326 $[M-H_2O]^+$ (0.1), 244 $[M-A]^+$ (4.5), 229 $[M-A-Me]^+$ (2.1), 226 $[M-A-H_2O]^+$ (2.9), 201 $[M-A-Me-CO]^+$ (2.1), 198 $[M-A-H_2O-CO]^+$ (1.4), 83 $[A^1]^+$ (100.0), 55 $[A^2]^+$ (23.4).

8-epi-Tiglylrupicolin B (**5**). $C_{20}H_{24}O_5$, gum; UV λ_{max}^{MeOH} nm: strong end absorption; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3570 (OH), 1765 (γ-lactone), 1705 (unsaturated ester), 1662 (double bond), 1150 (tertiary alcohol); EIMS (probe) *m/z* (rel. int.): 344 $[M]^+$ (0.5), 326 $[M-H_2O]^+$ (0.4), 244 $[M-A]^+$ (7.9), 229 $[M-A-Me]^+$ (2.4), 226 $[M-A-H_2O]^+$ (3.9), 216 $[M-A-CO]^+$ (1.6), 201 $[M-A-Me-CO]^+$ (3.2), 198 $[M-A-H_2O-CO]^+$ (2.0), 83 $[A^1]^+$ (100.0), 55 $[A^2]^+$ (15.8).

Desacyl-8-Tiglylsubcordatolide A (**6**). $C_{20}H_{24}O_6$, gum; UV λ_{max}^{MeOH} nm: strong end absorption; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3595 (OH), 3460 (OH), 1760 (γ-lactone), 1705 (unsaturated ester), 1650 (double bond); EIMS (probe) *m/z* (rel. int.): 360 $[M]^+$ (0.3), 345 $[M-Me]^+$ (3.4), 260 $[M-A]^+$ (3.3), 245 $[M-A-Me]^+$ (2.4), 242 $[M-A-H_2O]^+$ (16.2), 227 $[M-A-H_2O-Me]^+$ (5.8), 199 $[M-A-H_2O-Me-CO]^+$ (6.7), 83 $[A^1]^+$ (100.0), 55 $[A^2]^+$ (27.4).

Diacetate (**7**). $C_{24}H_{28}O_8$, gum; IR $\lambda_{max}^{CHCl_3}$ cm^{-1}: 1765 (γ-lactone), 1730 (saturated ester), 1710 (unsaturated ester), 1660, 1645 (double bonds); EIMS (probe) *m/z* (rel. int.): 385 $[M-OAc]^+$ (0.5), 384 $[M-HOAc]^+$ (0.3), 344 $[M-A]^+$ (1.2), 343 $[M-OAc-CH_2{=}CO]^+$ (0.7), 342 $[M-HOAc-CH_2{=}CO]^+$ (1.5), 285 $[M-A-OAc]^+$ (0.6), 284 $[M-A-HOAc]^+$ (1.6), 243 $[M-A-AcO-CH_2{=}CO]^+$ (4.8), 242 $[M-A-HOAc-CH_2{=}CO]^+$ (16.5), 226 $[M-A-OAc-OAc]^+$ (5.2), 225 $[M-A-HOAc-OAc]^+$ (12.5), 224 $[M-A-HOAc-HOAc]^+$ (9.2), 83 $[A^1]^+$ (100.0), 55 $[A^2]^+$ (21.7), 43 $[Ac]^+$ (19.3).

Prunichromene A (**8**). $C_{14}H_{18}O_4$, oil; UV λ_{max}^{MeOH} nm (ε): 222 (4.44×10^4), 280 (1.53×10^4), 311 (1.04×10^4); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1608, 1505 (aromatic); EIMS (probe) *m/z* (rel. int.): 250 $[M]^+$ (21.2), 235 $[M-Me]^+$ (100.0), 220 $[M-2Me]^+$ (4.2), 219 $[M-MeO]^+$ (6.2), 205 $[M-3Me]^+$ (17.7), 189 $[M-2Me-MeO]^+$ (2.7); CIMS (isobutane): 251 $[M+1]^+$.

Prunichromene B (**9**). $C_{13}H_{16}O_3$, yellow oil; UV λ_{max}^{MeOH} nm (ε): 226 (6.27×10^4), 296 (1.18×10^4); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1608, 1580, 1498, 1465 (aromatic), 1125 (ether); EIMS (probe) *m/z* (rel. int.): 220 $[M]^+$ (15.6), 205 $[M-Me]^+$ (100.0), 190 $[M-2Me]^+$ (17.8), 189 $[M-MeO]^+$ (2.6); CIMS (isobutane): 221 $[M+1]^+$.

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