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Acridone Alkaloids. VI.[1] The Constituents of *Citrus depressa*. Isolation and Structure Elucidation of New Acridone Alkaloids from *Citrus* genus[2]

TIAN-SHUNG WU,[a] CHANG-SHENG KUOH,[b] and HIROSHI FURUKAWA*,[a]

Faculty of Pharmacy, Meijo University,[a] Yagoto, Tempaku, Nagoya 468, Japan and Chia-Nan Junior College of Pharmacy,[b] Tainan, Taiwan, R. O. C.

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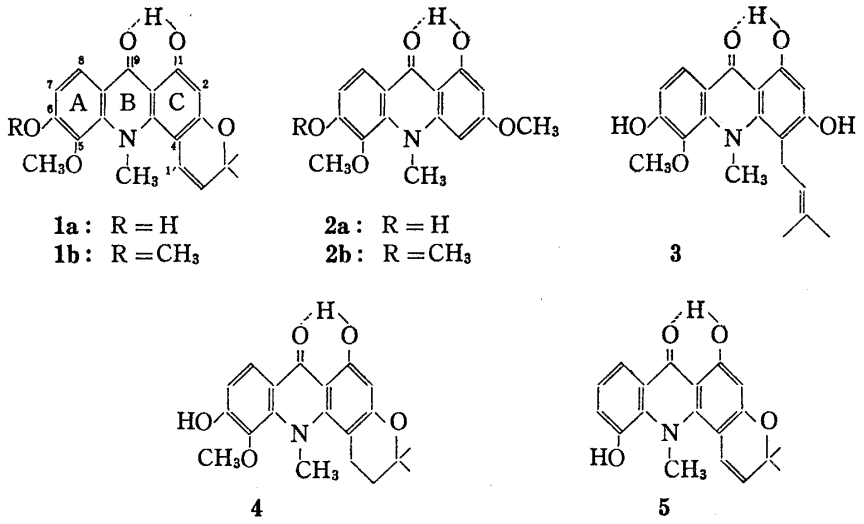
Five new acridone alkaloids, citracridone-I (**1a**), -II (**1b**), citpressine-I (**2a**), -II (**2b**), and prenylcitpressine (**3**) along with a known acridone alkaloid, 5-hydroxynoracronycine (**5**), and three known coumarins, clausarin (**6**), suberosin (**7a**), and xanthyletin (**8**) were isolated from the root bark of *Citrus depressa* (Rutaceae) collected in Taiwan and characterized. This is the first report of isolation of acridone alkaloids from *Citrus* species. In the structure elucidations, the use of nuclear Overhauser effect (NOE) experiment on the *O*-methoxymethyl derivatives of phenolic acridone alkaloids was shown to be useful for the determination of the location of the phenolic hydroxyl groups.

Keywords——*Citrus depressa*; Rutaceae; acridone alkaloid; coumarin; citracridone-I; citracridone-II; citpressine-I; citpressine-II; prenylcitpressine; ^{1}H-NMR

Citrus depressa (Rutaceae) is a small green tree, and the peel is popularly used as the source of Chen-pi, an important Chinese drug in Taiwan, which has been used for treating heartburn, abdominal pain, diarrhea, tussis, vomiting and inappetence, and as an expectorant.[3] In a preliminary communication,[2] we described the isolation and structures of five new acridone alkaloids contained in *C. depressa*. The full details of the structure elucidation are now presented in this paper.

The ethanolic extract of the root bark of *C. depressa*, which grows naturally in Taiwan, was treated by the procedure described in the experimental section, and five new acridone alkaloids named citracridone-I, -II, citpressine-I, -II, and prenylcitpressine along with a known acridone alkaloid, 5-hydroxynoracronycine (**5**),[4] and three known coumarins, clausarin (**6**), suberosin (**7a**), and xanthyletin (**8**), were isolated and characterized.

Citracridone-I was obtained as orange plates from acetone, mp 275—278°C. Mass spectrometry and microanalysis established the molecular formula $C_{20}H_{19}NO_5$ for this alkaloid. The ultraviolet (UV) spectrum showed typical absorption associated with a 9-acridone nucleus[5,6] (see Experimental), and a bathochromic shift was observed on addition of sodium methoxide ($NaOCH_3$) or aluminium chloride ($AlCl_3$), indicating the presence of phenolic hydroxyl groups.[4] The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed the presence of two one-proton singlets at δ 14.52 and 9.33 due to two hydroxyl protons, indicating that at least one of them was strongly hydrogen bonded. Hydrogen bonding of the 1-hydroxyl group in the 9-acridone nucleus is well known to occur.[5] The ^{1}H-NMR data for citracridone-I are shown in Table I. The AB-type quartets at δ 6.63 and 5.61 (J=10 Hz) and a six-proton singlet at δ 1.53 reflect the presence of a dimethylpyran system attached to ring C since the lower signal of this AB quartet had a long range coupling (J=1 Hz) with the doublet at δ 6.23 (H-2). An NMR nuclear Overhauser effect (NOE) study gave a 9.5% enhancement of the signal at δ 6.63 on irradiation at the frequency corresponding to the *N*-methyl protons at δ 3.75, allowing the assignment of an angular orientation of the dimethylpyran ring. The ^{13}C-NMR spectrum of citracridone-I also supported these conclusions, and signals of an *N*-methyl carbon and the olefinic C-1′ of the dimethylpyran ring appeared at δ 48.6 and 120.8, respectively.[7,8] An additional AB-type signal (J=9 Hz) at δ 7.00 and 8.01 in the ^{1}H-NMR spectrum was assigned to mutually *ortho*-located protons; the lower field signal could be assigned to H-8 on the basis of the deshielding by the C-9 carbonyl moiety.



1a: R = H
1b: R = CH_3

2a: R = H
2b: R = CH_3

3

4

5

Chart 1

In addition, the absence of NOE between the H-7 signal at δ 7.00 and the methoxyl signal at δ 3.91 suggested the location of a methoxyl and a hydroxyl group at C-5 and C-6, respectively.

To confirm these assignments, a deuterium exchange reaction of the *ortho* (and *para*)-located proton to the phenolic hydroxyl group was attempted. However, all attempts using general methods[10] were unsuccessful. Then, an NOE experiment (Chart 2) was carried out for the *O*-methoxymethyl derivative of citracridone-I prepared by treatment of citracridone-I with chloromethylmethyl ether and sodium hydroxide in the presence of phase-transfer catalyst.[11] Irradiation of the methylene protons of the methoxymethyl ether moiety at δ 5.30 gave a 14.9% enhancement of H-7 at δ 7.09. Irradiation of the *N*-methyl signal at δ 3.70 produced a 12.3% enhancement of the signal at δ 6.52 due to H-1′. These data were consistent with the structure **1a** for citracridone-I.

NOE measurement for the methoxymethyl derivatives of phenolic alkaloids is considered to be a useful method for the determination of the location of the phenolic hydroxyl groups.

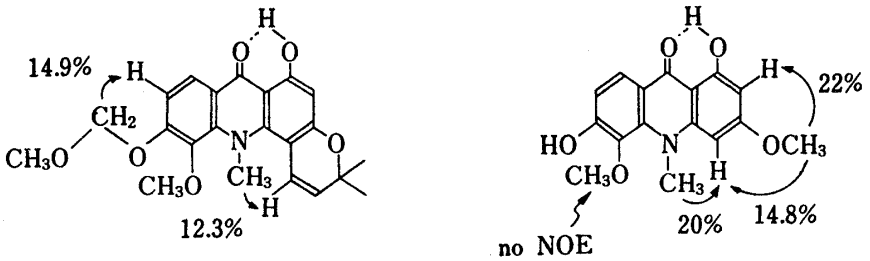


Chart 2

Next, methylation of **1a** with diazomethane furnished a mono-*O*-methyl ether, which still showed a hydrogen-bonded hydroxyl proton at δ 14.35 in the ^{1}H-NMR spectrum. Thus, the structure of this product was assigned as **1b**. Citracridone-II, mp 161—163°C, $C_{21}H_{21}NO_5$ (M^+: *m/z* 367) was shown to be identical with this *O*-methyl ether by infrared (IR), UV, ^{1}H-NMR and mass spectral comparisons, and mixed mp determination.

Citpressine-I, mp 183—185°C, and citpressine-II, mp 168—170°C, have the molecular formulae $C_{16}H_{15}NO_5$ (M^+: *m/z* 301) and $C_{17}H_{17}NO_5$ (M^+: *m/z* 315), respectively, and showed UV spectra typical of a 9-acridone nucleus.[5,6] The ^{1}H-NMR spectra (Table I) of these alkaloids showed similar signal patterns, except for an additional methoxyl signal in that of citpressine-II. Treatment of citpressine-I with diazomethane gave a mono-*O*-methyl ether, which was identical

with citpressine-II. The presence of a hydroxyl group being still hydrogen bonded in citpressine-II was indicated by the IR (3430 cm^{-1}) and ^1H-NMR spectra (1H singlet at δ 14.71). In the aromatic proton region of the ^1H-NMR spectrum of citpressine-I, *meta*-coupled proton signals at δ 6.25 and 6.51 (each 1H, d, $J=2$ Hz), and *ortho*-coupled proton signals at δ 8.10 and 6.99 (each 1H, d, $J=9$ Hz) were observed. The lower *ortho*-coupled proton signal at δ 8.10 is characteristic of H-8 in a 9-acridone system. An NOE experiment (Chart 2) showed that the signal at δ 6.51, one of the *meta*-coupled protons, exhibited 14.8% and 20% enhancements on irradiation of the methoxyl signal at δ 3.97, and of the *N*-methyl signal at δ 4.10, respectively. At the same time, irradiation of the methoxyl at δ 3.97 gave a 22% enhancement of the other *meta*-coupled proton signal at δ 6.25. However, on irradiation of the methoxyl at δ 3.83, no NOE was observed at any proton signal. These data led to the structures **2a** and **2b** for citpressine-I and -II, respectively.

TABLE I. ^1H-NMR Spectra Data for Acridone Alkaloids from *Citrus depressa*

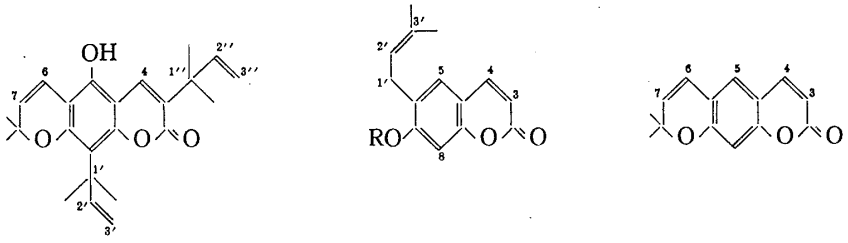
	1a	**1b**	**2a**
1-OH	14.52 (1H, s)[a]	14.35 (1H, s)[a]	14.85 (1H, s)[a]
2-H	6.23 (1H, d; 1)	6.26 (1H, s)	6.25 (1H, d; 2)
3-OCH_3			3.97 (3H, s)
4-H			6.51 (1H, d; 2)
N-CH_3	3.75 (3H, s)	3.74 (3H, s)	4.10 (3H, s)
5-OR	3.91 (3H, s)	3.90 (3H, s)	3.83 (3H, s)
6-OR	9.33 (1H, s)[a]	4.01 (3H, s)	2.83 (1H, s)[a]
7-H	7.00 (1H, d; 9)	7.01 (1H, d; 9)	6.99 (1H, d; 9)
8-H	8.01 (1H, d; 9)	8.13 (1H, d; 9)	8.10 (1H, d; 9)
1′-H	6.63 (1H, dd; 1, 10)	6.62 (1H, d; 10)	
2′-H	5.61 (1H, d; 10)	5.58 (1H, d; 10)	
3′-$(CH_3)_2$	1.53 (6H, s)	1.51 (6H, s)	

	2b	**3**	**5**
1-OH	14.71 (1H, s)[a]	14.31 (1H, s)[a]	14.57 (1H, s)[a]
2-H	6.22 (1H, d; 2)	6.30 (1H, s)	6.18 (1H, s)
3-OCH_3	3.96 (3H, s)	3.06 (1H, s)[a]	
4-H	6.46 (1H, d; 2)		
N-CH_3	4.04 (3H, s)	3.64 (3H, s)	3.87 (3H, s)
5-OR	3.84 (3H, s)	3.91 (3H, s)	2.90 (1H, s)[a]
6-OR	4.06 (3H, s)	9.32 (1H, br)	7.40 (1H, dd; 2, 7)
7-H	7.16 (1H, d; 9)	6.94 (1H, d; 9)	7.25 (1H, t; 7)
8-H	8.12 (1H, d; 9)	7.92 (1H, d; 9)	7.88 (1H, dd; 2, 7)
1′-H		3.58 (2H, m)	6.81 (1H, d; 10)
2′-H		5.36 (1H, m)	5.73 (1H, d; 10)
3′-$(CH_3)_2$		1.71 (3H, s)	1.51 (6H, s)
		1.81 (3H, s)	

Taken in acetone-d_6, except for **1a** ($CDCl_3$+DMSO-d_6) and **1b** ($CDCl_3$).
Values are in ppm. Multiplicities are indicated by the usual symbols: s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet. Figures in parentheses are coupling constants in Hz.
a) These signals disappeared on addition of D_2O.

Prenylcitpressine was isolated as yellow needles from ether, mp 160—162°C, $C_{20}H_{21}NO_5$ (M^+: m/z 355). The UV and IR spectra (see Experimental) also showed absorptions characteristic of 9-acridones.[5,6] The ^1H-NMR studies revealed the presence of a strongly intramolecularly hydrogen bonded proton at δ 14.31 assignable to the C-1 hydroxyl group of an acridone molecule. In addition, two hydroxyl protons at δ 9.32 and 3.06, which disappeared with D_2O, were observed. Furthermore, the presence of an *N*-methyl, a methoxyl and a prenyl group in

this alkaloid was suggested by the ^{1}H-NMR spectrum (Table I), and aromatic protons appeared as an *ortho*-coupled AB-type quartet and a sharp one-proton singlet. Cyclization of this alkaloid with formic acid afforded yellow needles, mp 247—250°C. The IR, ^{1}H-NMR, UV, and mass spectra of this product were superimposable on those of **4** obtained by catalytic hydrogenation of **1a**. On the basis of these results, prenylcitpressine can be represented by the formula **3**.



6 **7a**: R = CH_3 **8**
7b: R = H

Chart 3

A known acridone alkaloid, 5-hydroxynoracronycine (**5**)[4] was also isolated from the same plant, and identified by comparison with an authentic sample. Among the non-alkaloidal components, clausarin (**6**),[12] suberosin (**7a**),[13,14] and xanthyletin (**8**)[13,15] were isolated and characterized.

Previous chemical investigation of the alkaloidal constituents of several species of the genus *Citrus* have revealed only the presence of simple alkylamines, quinolones and furoquinolines.[16] This is the first report of the presence of acridone alkaloids in *Citrus* genus.

Experimental

All melting points were measured on a micro melting point hot stage apparatus (Yanagimoto). ^{1}H- and ^{13}C-NMR spectra were recorded on PS-100 (JEOL) and FX-100 (JEOL) spectrometers, respectively in acetone-d_6 except where otherwise stated. Chemical shifts are given in ppm (δ) with tetramethylsilane (TMS) as an internal reference. Mass spectra (MS) were taken with an M-52 spectrometer (Hitachi) with a direct inlet system. UV spectra were determined in MeOH and infrared (IR) spectra were recorded in KBr tablets unless otherwise noted. Silica Gel GF_{254} (Merck) and Silica gel 60 (70—230 mesh ASTM) (Merck) were used for thin layer chromatography (TLC) and column chromatography, respectively. The abbreviations used are as follows: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet; br, broad; sh, shoulder.

Isolation of Acridone Alkaloids and Coumarins from *Citrus depressa*——The root bark of *Citrus depressa* HAYATA (250 g) collected on Orchid Island, Taiwan, was extracted with EtOH. The EtOH extract was partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ layer was separated, dried, and concentrated to give a brown syrup (9.0 g). This was subjected to silica gel column chromatography. Elution with acetone–benzene (1: 9) yielded five fractions (each 500 ml). Fraction 2 was rechromatographed on a silica gel column. Elution with hexane–EtOAc (4: 1) provided successively **6**, **7a**, **8**, β-sitosterol, **1b**, **2b**, **5**, and **1a**. Fraction 3 was also subjected to silica gel column chromatography and elution with $CHCl_3$–acetone (9: 1) gave successively **1a**, **2a**, and **3**.

Citracridone-I (1a)——Orange plates (380 mg) from acetone. mp 275—278°C. UV λ_{max} nm (log ε): 209 (4.28), 270 (4.67), 282 (sh, 4.63), 295 (sh, 4.58), 340 (4.05), 400 (3.57). UV λ_{max} (+$AlCl_3$) nm: 209, 215 (sh), 272, 290, 307, 363, 452. IR ν_{max} cm^{-1}: 3380, 1620, 1590, 1565. MS *m/z* (%): 353 (M^+, 33), 338 (100), 323 (35), 322 (32), 308 (9), 294 (15), 280 (20), 176 (15), 169 (15), 161 (32). *Anal.* Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96. Found: C, 67.94; H, 5.42; N, 3.78.

Citracridone-II (1b)——Yellow needles (10 mg) from ether. mp 161—163°C. UV λ_{max} nm (log ε): 209 (4.37), 268 (4.67), 283 (4.64), 341 (4.14), 405 (3.69). UV λ_{max} (+$AlCl_3$) nm: 248 (sh), 272, 292, 305 (sh), 365, 417. IR ν_{max} cm^{-1}: 1635, 1575, 1550. MS *m/z* (%): 367 (M^+, 40), 352 (100), 336 (11), 322 (20).

Citpressine-I (2a)——Yellow needles (54 mg) from acetone, mp 183—185°C. UV λ_{max} nm (log ε): 220 (4.09), 265 (sh, 4.64), 271 (4.65), 294 (sh, 4.06), 332 (3.96), 384 (3.58). UV λ_{max} (+$AlCl_3$) nm: 220, 273, 308 (sh), 352, 420. IR ν_{max} cm^{-1}: 3430, 1620, 1580, 1560. MS *m/z* (%): 301 (M^+, 100), 286 (65), 256 (14), 243

(18), 213 (9), 199 (6), 185 (12), 137 (44), 129 (27). *Anal.* Calcd for $C_{16}H_{15}NO_5 \cdot 1/2H_2O$: C, 61.93; H, 5.18; N, 4.51. Found: C, 61.86; H, 5.23; N, 4.30.

Citpressine-II (2b)——Yellow needles (153 mg) from ether, mp 168—170°C. UV λ_{max} nm (log ε): 220 (4.14), 270 (4.79), 300 (sh, 4.15), 333 (4.12), 382 (3.74). UV λ_{max} (+$AlCl_3$) nm: 230, 265 (sh), 277, 353, 428. IR ν_{max} cm^{-1}: 1650, 1590. MS *m/z* (%): 315 (M^+, 100), 300 (72), 285 (18), 257 (17). *Anal.* Calcd for $C_{17}H_{17}NO_5$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.81; H, 5.47; N, 4.27.

Prenylcitpressine (3)——Yellow plates (12 mg) from ether, mp 160—162°C. UV λ_{max} nm (log ε): 222 (4.29), 262 (4.51), 269 (4.49), 334 (4.18), 387 (3.76). UV λ_{max} (+$AlCl_3$) nm: 234, 250 (sh), 265 (sh), 279, 368, 433. IR ν_{max} ($CHCl_3$) cm^{-1}: 3500, 3230, 1620, 1590, 1555. MS *m/z* (%): 355 (M^+, 54), 340 (100), 310 (52). *Anal.* Calcd for $C_{20}H_{21}NO_5 \cdot 1/2H_2O$: C, 65.92; H, 6.09; N, 3.84. Found: C, 66.20; H, 6.53; N, 3.86.

5-Hydroxynoracronycine (5)——Red needles (92 mg) from acetone, mp 268—270°C. UV λ_{max} nm: 209, 236, 267, 284, 295 (sh), 323, 344 (sh), 418. IR ν_{max} cm^{-1}: 3250, 1630, 1550. MS *m/z*: 323 (M^+), 308 (100%), 293, 280, 264, 161, 154, 146, 132, 118. This was shown to be identical with an authentic sample of **5** by IR, ^{1}H-NMR, and MS comparisons, and mixed mp determination.

Methylation of Citracridone-I (1a)——Compound **1a** (25 mg) was treated with CH_2N_2 in ether at room temp. overnight. Evaporation of the solvent left a solid, which was crystallized from ether to give yellow needles, mp 161—163°C. The IR, ^{1}H-NMR, UV, and mass spectra were superimposable on those of citracridone-II (**1b**).

Hydrogenation of Citracridone-I (1a)——A solution of **1a** (30 mg) in EtOH (25 ml) was shaken under H_2 gas in the presence of PtO_2 (50 mg) at room temp. for 6 h. The solution was filtered and the filtrate was concentrated. The residue was crystallized from ether to give yellow needles (**4**) (30 mg), mp 248—250°C. UV λ_{max} nm: 225, 266, 270, 336, 382. IR ν_{max} cm^{-1}: 3380, 1635, 1580, 1552. MS *m/z* (%): 355 (M^+, 100), 340, 326, 310, 300, 288, 272, 256. ^{1}H-NMR δ: 1.45 (6H, s, 3′-$(CH_3)_2$), 1.86 (2H, t, J=7 Hz, 2′-H), 2.82 (1H, s, 6-OH), 2.95 (2H, t, J=7 Hz, 1′-H), 3.72 (3H, s, N–CH_3), 3.94 (3H, s, 5-OCH_3), 6.08 (1H, s, 2-H), 6.98 (1H, d, J=9 Hz, 7-H), 7.94 (1H, d, J=9 Hz, 8-H), 14.17 (1H, s, 1-OH). *Anal.* Calcd for $C_{20}H_{21}NO_5 \cdot 1/2H_2O$: C, 65.92; H, 6.09; N, 3.84. Found: C, 66.13; H, 5.91; N, 3.73.

Methylation of Citpressine-I (2a)——Treatment of **2a** (20 mg) with CH_2N_2 in the usual way afforded yellow needles (20 mg), mp 168—170°C. The product was shown to be identical with citpressine-II (**2b**) by IR, and ^{1}H-NMR comparisons and mixed mp determination.

Cyclization of Prenylcitpressine (3)——A solution of **3** (7 mg) in HCOOH (85%, 1 ml) was heated at 80—90°C for 3 h, and then left at room temp. overnight. Water was added and the solution was extracted with $CHCl_3$. The $CHCl_3$ layer was washed with aqueous $NaHCO_3$ and H_2O, then dried and concentrated. The residue was chromatographed on silica gel and eluted with diisopropyl ether. Fractions (each 5 ml) were collected and monitored by TLC. Fraction 18—23 left yellow residues after evaporation, and the residues were recrystallized from ether to afford yellow needles, mp 247—250°C. The IR, ^{1}H-NMR, UV and MS were superimposable on those of **4**.

Methoxymethylation of Citracridone-I (1a)——A mixture of **1a** (30 mg), CH_2Cl_2 (10 ml), 1% NaOH aq. sol. (10 ml), and phase transfer catalyst (Adogen 464 from Aldrich, 2 mg) was stirred at room temp. for 30 min, and then chloromethylmethyl ether (1.0 ml) was added. After 1 h, the aqueous layer was separated and extracted with CH_2Cl_2. The CH_2Cl_2 layers were combined, dried with $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a silica gel column and elution with benzene–acetone (9: 1) afforded yellow plates, which were recrystallized from ether. mp 205—207°C. UV λ_{max} nm: 235, 269, 285, 295 (sh), 313 (sh), 342, 405. IR ν_{max} ($CHCl_3$) cm^{-1}: 1622, 1580, 1550. MS *m/z*: 397 (M^+), 382 (100%), 338, 322, 294. ^{1}H-NMR ($CDCl_3$) δ: 1.51 (6H, s, 3′-$(CH_3)_2$), 3.52 (3H, s, OCH_3), 3.70 (3H, s, N–CH_3), 3.87 (3H, s, 5-OCH_3), 5.30 (2H, s, O–CH_2–O), 5.50 (1H, d, J=10 Hz, 2′-H), 6.16 (1H, s, 2-H), 6.52 (1H, d, J=10 Hz, 1′-H), 7.09 (1H, d, J=9 Hz, 7-H), 7.95 (1H, d, J=9 Hz, 8-H), 14.12 (1H, s, 1-OH).

Suberosin (7a)——Colorless needles (30 mg) from MeOH, mp 88—90°C. UV λ_{max} nm: 210, 224, 255 (sh), 298 (sh), 333. IR ν_{max} cm^{-1}: 1705, 1605. ^{1}H-NMR ($CDCl_3$) δ: 1.72 (3H, s, CH_3), 1.78 (3H, s, CH_3), 3.32 (2H, d, J=8 Hz, H-1′), 3.92 (3H, s, OCH_3), 5.33 (1H, m, H-2′), 6.25 (1H, d, J=10 Hz, H-3), 6.80 (1H, s, H-5), 7.20 (1H, s, H-8), 7.64 (1H, d, J=10 Hz, H-4). MS *m/z*: 244 (M^+), 229 (100%), 201, 175. This was shown to be identical with an authentic sample prepared from demethylsuberosin (**7b**) by IR, ^{1}H-NMR, and MS comparisons, and mixed mp determination.

Xanthyletin (8)——Colorless plates (250 mg) from EtOH. mp 130—132°C. UV λ_{max} nm: 225, 265, 304 (sh), 348. IR ν_{max} cm^{-1}: 1705, 1622. ^{1}H-NMR ($CDCl_3$) δ: 1.47 (6H, s, 2×CH_3), 5.72 (1H, d, J=10 Hz, H-7), 6.25 (1H, d, J=10 Hz, H-3), 6.37 (1H, d, J=10 Hz, H-6), 6.76 (1H, s, H-5), 7.07 (1H, s, H-10), 7.60 (1H, d, J=10 Hz, H-4). MS *m/z*: 228 (M^+), 213 (100%), 200, 199, 185. This was shown to be identical with an authentic sample by IR, ^{1}H-NMR, and MS comparisons, and mixed mp determination.

Clausarin (6)——Colorless rod (30 mg) from acetone. mp 208—210°C. UV λ_{max} nm: 212, 229, 280, 337. IR ν_{max} cm^{-1}: 3150, 1715, 1665, 1640. ^{1}H-NMR δ: 1.42 (6H, d, 2×CH_3), 1.44 (6H, s, 2×CH_3), 1.63 (6H, s, 2×CH_3), 4.70 (1H, q, J=1.5 and 10 Hz, H-3′), 4.90 (1H, q, J=1.5 and 18 Hz, H-3′), 5.05 (1H, q, J=1.5 and 18 Hz, H-3″), 5.08 (1H, q, J=1.5 and 10 Hz, H-3″), 5.66 (1H, d, J=10 Hz, H-7), 6.18 (1H, q, J=10 and 18 Hz, H-2″), 6.28 (1H, q, J=10 and 18 Hz, H-2′), 6.72 (1H, d, J=10 Hz, H-6), 7.95 (1H, s, H-4), 8.37 (1H, br s, 5-OH). MS *m/z*: 380 (M^+), 365 (100%), 337, 309, 297. This was shown to be identical

with an authentic sample by IR, ^{1}H-NMR, and MS comparisons, and mixed mp determination.

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