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Acridone Alkaloids. VII.[1] Constituents of *Citrus sinensis* Osbeck var. *brasiliensis* Tanaka. Isolation and Characterization of Three New Acridone Alkaloids, and a New Coumarin

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Fractionation and chromatography of the acetone extract of the root bark of *Citrus sinensis* Osbeck var. *brasiliensis* Tanaka (Rutaceae) afforded three new acridone alkaloids namely citrusinine-I, -II and citbrasine and a new coumarin, ethylsuberenol. The structures of citrusinine-I -II, and citbrasine, and ethylsuberenol were characterized as **1a**, **2a**, **3**, and **6**, respectively. Citracridone-I (**4**), suberenol (**7**), suberosin (**8**), crenulatin (**9**), xanthoxyletin (**10**), xanthyletin (**11**), nordentatin (**12**), elemol (**13**), and *p*-hydroquinone were also isolated.

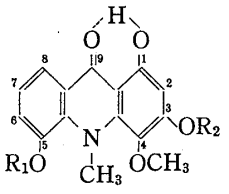
Keywords——*Citrus sinensis* var. *brasiliensis*; Rutaceae; acridone alkaloid; coumarin; citrusinine-I; citrusinine-II; citbrasine; ethylsuberenol; elemol; *p*-hydroquinone

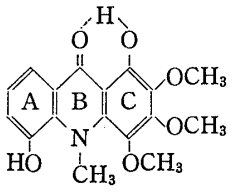
In the preceding paper,[1,2] we reported the first isolation of acridone alkaloids from *Citrus* genus (Rutaceae). In continuing our investigation of the constituents of this genus, we examined the constituents of the root bark of *Citrus sinensis* Osbeck var. *brasiliensis* Tanaka collected in Taiwan. Yen *et al.*[3] reported the isolation of some steroids and xanthyletin (**11**) from this plant. In our present study, the acetone extract of the plant was treated by the procedure described in Experimental, and seventeen substances were isolated. Four of them were proved to be three new acridone alkaloids and a new coumarin.

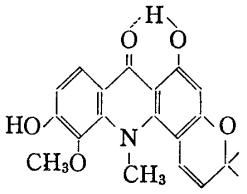
Citrusinine-I (**1a**) was obtained as orange needles, mp 206—207°C. This alkaloid showed the molecular ion peak at *m/z* 301 in the mass spectrum (MS), and microanalysis established the formula as $C_{16}H_{15}NO_5$. The ultraviolet (UV) spectrum (λ_{max} 234, 265, 320, 334, and 418 nm) showed absorptions typical of a 9-acridone nucleus.[4] A positive reaction with ferric chloride ($FeCl_3$), an infrared (IR) band at 3220 cm^{-1}, and proton nuclear magnetic resonance (^{1}H-NMR) peaks at δ 14.05 and 9.16 which disappeared with deuterium oxide (D_2O), indicated the presence of phenolic hydroxyl groups. The lower field signal at δ 14.05 together with an IR band at 1625 cm^{-1} was indicative of a chelated C-1 hydroxyl group in a 9-acridone.[4] The ^{1}H-NMR spectrum of citrusinine-I showed three sharp singlets (each three protons) at δ 3.71, 3.77, and 3.92 due to *N*-methyl and/or methoxyl groups. ABC pattern signals at δ 7.04 (1H, t, J=8 Hz), 7.19 (1H, dd, J=2 and 8 Hz), and 7.68 (1H, dd, J=2 and 8 Hz) were assigned to H-7, H-6, and H-8, respectively. The deshielding of H-8 is reasonable because it lies in the *peri*-position with respect to the 9-carbonyl moiety. A sharp one-proton singlet at δ 6.30 could be attributed to a lone aromatic proton at H-2 (or H-4). In the ^{13}C-NMR spectrum of citrusinine-I, an *N*-methyl carbon signal at δ 45.98 suggested that both *peri*-positions (C-4 and C-5) relative to the *N*-methyl moiety in the 9-acridone nucleus were substituted.[5] Treatment of citrusinine-I with chloromethylmethyl ether and sodium hydroxide in the presence of phase-transfer catalyst (Adogen 464, Aldrich) afforded the corresponding methoxymethyl ether (**1b**) as orange plates, mp 148—150°C. The ^{1}H-NMR spectrum of this still showed a hydrogen bonded 1-hydroxyl signal at δ 13.99 together with methoxymethyl signals at δ 3.55 (3H, s) and 5.31 (2H, s). A nuclear Overhauser effect (NOE) experiment gave an 8.1% enhancement of the signal at δ 7.44 (H-6, one of the ABC-type protons) on irradiation of the methylene protons at δ 5.31. Thus, the hydroxyl group in citrusinine-I was located at C-5. Further, a 12.8%

enhancement of the signal at δ 6.37 (H-2) on irradiation of the C-3 methoxyl protons at δ 3.95 was observed, but there was no NOE on irradiation at δ 3.78 (due to C-4 methoxyl and *N*-methyl proton signals). These observations suggested the location of two methoxyls at C-3 and C-4. Thus, citrusinine-I should be represented by the formula **1a**.

Citrusinine-II (**1a**) was obtained as yellow needles, mp 244—246°C, $C_{15}H_{13}NO_5$ (M^+, *m/z*



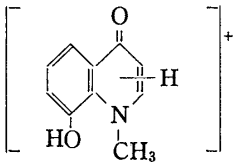




1a: R_1=H, R_2=CH_3
1b: R_1=CH_2OCH_3, R_2=CH_3
1c: R_1=CH_3, R_2=CH_3

3 **5**

2a: R_1=R_2=H
2b: R_1=R_2=CH_2OCH_3



5 *m/z* 174

Chart 1

TABLE I. ^{1}H-NMR Spectra Data for Acridone Alkaloids and Their Derivatives

	1a	**1b**	**1c**
1-H	14.05 (s)[a]	13.99 (s)[a]	13.91 (s)[a]
2-H/OCH_3	6.30 (1H, s)	6.37 (1H, s)	6.34 (1H, s)
3-OH/OCH_3	3.92 (3H, s)	3.95 (3H, s)	3.94 (3H, s)
4-OCH_3	3.77 (s)[b]	3.78 (s)	3.74 (s)[b]
N-CH_3	3.71 (s)[b]	3.78 (s)	3.71 (s)[b]
5-OH/OCH_3	9.16 (1H, br)[a]		4.00 (3H, s)
6-H	7.19 (dd, 2 and 8)	7.44 (dd, 2 and 8)	7.31 (dd, 2 and 8)
7-H	7.04 (t, 8)	7.19 (t, 8)	7.16 (t, 8)
8-H	7.68 (dd, 2 and 8)	7.98 (dd, 2 and 8)	7.76 (dd, 2 and 8)
OCH_2OCH_3		5.31 (2H, s)	
		3.55 (3H, s)	

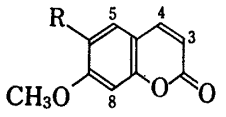
	2a	**2b**	**3**
1-H	13.94 (s)[a]	13.78 (s)[a]	13.99 (s)[a]
2-H/OCH_3	6.15 (1H, s)	6.58 (1H, s)	4.13 (3H, s)[b]
3-OH/OCH_3	9.12 (1H, br)[a]		3.95 (3H, s)[b]
4-OCH_3	3.80 (s)	3.80 (s)	3.81 (s)[b]
N-CH_3	3.71 (s)	3.80 (s)	3.84 (s)[b]
5-OH/OCH_3	9.12 (1H, br)[a]		7.12 (1H, br)[a]
6-H	7.20 (dd, 2 and 7)	7.45 (dd, 2 and 8)	7.19 (dd, 2 and 8)
7-H	7.06 (t, 7)	7.20 (t, 8)	7.07 (t, 8)
8-H	7.69 (dd, 2 and 7)	7.99 (dd, 2 and 8)	7.85 (dd, 2 and 8)
OCH_2OCH_3		5.32 (4H, s)	
		3.54 (3H, s)	
		3.56 (3H, s)	

Taken in acetone-d_6 (**1a**, **1c**, and **2a**) or in $CDCl_3$ (**1b**, **2b**, an **3**).
Values are in ppm (δ). Figures in parentheses are coupling consants in Hz.
a) These signals disappeared on D_2O.
b) Assignments may be interchanged.

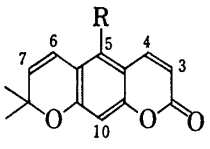
287). Methylation of the compound with diazomethane gave an *O,O*-dimethyl ether, $C_{17}H_{17}NO_5$ (M^+, *m/z* 315), which was identical with **1c** derived from citrusinine-I (**1a**) on the basis of comparisons of their IR, ^{1}H-NMR, and MS. To confirm the location of the two hydroxyl groups, citrusinine-II was methoxymethylated as in the case of citrusinine-I (**1a**) to furnish **2b** as yellow needles, mp 99—101°C, $C_{19}H_{21}NO_7$ (M^+, *m/z* 375). The ^{1}H-NMR spectrum revealed two methoxymethyl signals at δ 3.54 (3H, s), 3.56 (3H, s), and 5.32 (4H, s) together with a hydrogen-bonded hydroxyl proton signal at δ 13.78. In the NOE experiment, 11.1% and 19.3% enhancements of the signals at δ 7.45 (H-6) and 6.58 (H-2) were observed on irradiation at the frequency corresponding to the two methylene protons at δ 5.32. These results led to the location of the two hydroxyl groups at C-3 and C-5. The above evidence confirmed the structure **2a** for citrusinine-II.

Citbrasine (**3**), red plates from ether, mp 154—156°C, $C_{17}H_{17}NO_6$ (M^+, *m/z* 331). The UV spectrum showed absorption bands at λ_{max} 209, 225, 262, 272, 325 and 426 nm, which are typical of a 9-acridone nucleus.[4] A dark green color reaction with $FeCl_3$, bathochromic shifts of the UV bands with sodium methoxide ($NaOCH_3$) or aluminium chloride ($AlCl_3$), IR bands at 3250 and 1622 cm^{-1}, and ^{1}H-NMR signals at δ 13.99 and 7.12 which disappeared with D_2O indicated the presence of two phenolic hydroxyl groups in citbrasine, at least one of them being chelated with the 9-carbonyl moiety. The ^{1}H-NMR spectrum of this alkaloid showed four three-proton singlets at δ 3.81, 3.84, 3.95, and 4.13 due to methyl groups attached to oxygen and/or nitrogen. In the aromatic proton region, ABC type proton signals appeared at δ 7.19 (1H, dd, J=2 and 8 Hz), 7.07 (1H, t, J=8 Hz), and 7.85 (1H, dd, J=2 and 8 Hz). The lower signal at δ 7.85 is characteristic of H-8 in 9-acridone. The mass spectrum of citbrasine showed, among other fragment peaks, a characteristic peak at *m/z* 174 due to the ion **5** which resulted from the cleavage of ring C and associated transfer of hydrogen as in the case of glyfoline.[6] This fragmentation is characteristic of 1,2,3,4-tetra-*O*-substituted acridone alkaloids.[7] From the above results, we suggest the structure **3** for citbrasine.

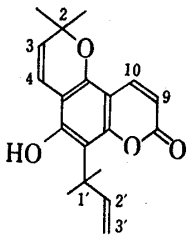
Together with those three new acridone alkaloids, citracridone-I (**4**), previously isolated from *Citrus depressa* by us,[1,2] was also obtained.



6 : R=CH=CH-C(CH$_3$)$_2$(OC$_2$H$_5$)
7 : R=CH=CH-C(CH$_3$)$_2$(OH)
8 : R=CH$_2$CH=C(CH$_3$)$_2$
9 : R=CHO



10 : R=OCH$_3$
11 : R=H



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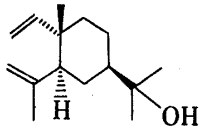

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Chart 2

Ethylsuberenol (**6**) was isolated as colorless needles from ether, mp 154—155°C, $C_{15}H_{20}O_4$ (M^+, *m/z* 288). The UV absorption bands at λ_{max} 257, 295, 306, and 343 nm, and IR bands at ν_{max} 1710, 1605, and 1555 cm^{-1} were very similar to those of suberenol (**7**), one of the coumarins

isolated from the same plant. The ^{1}H-NMR spectrum of this compound showed an AB quartet at δ 6.15 and 7.51 (each 1H, d, J=10 Hz) due to H-3 and H-4, respectively. The chemical shifts value of the downfield H-4 signal at δ 7.51 suggested the absence of anoxygenated function at C-5 in coumarins.[8] Two one-proton singlets at δ 6.67 and 7.37 were assigned to H-8 and H-5, respectively. A methoxyl group appeared as a three-proton singlet at δ 3.83. The remaining signals, arising from the side-chain protons were a six-proton singlet at δ 1.36 corresponding to two methyl groups, ethoxyl group signals at δ 3.34 (2H, q, J=7 Hz) and 1.16 (3H, t, J=7 Hz), and an AB quartet at δ 6.65 (H-1′), 6.10 (H-2′) (each 1H, d, J=16 Hz) due to *trans* olefinic protons. The mass fragmentation pattern of this compound was very similar to that of suberenol.[11] These spectral data suggested the structure of **6** for ethylsuberenol.

As known compounds, suberosin (**8**),[8,12] xanthoxyletin (**10**),[9] xanthyletin (**11**),[8,13] nordentatin (**12**),[9] elemol (**13**),[10] and *p*-hydroquinone were isolated and identified by IR, ^{1}H-NMR, and MS comparisons, mixed mp determination, and/or gas chromatography with authentic samples. Physical constants and spectroscopic data (UV, IR, and ^{1}H-NMR) of **7** and **9** were in agreement with those of suberenol,[11] and crenulatin[11] respectively. However, direct comparisons could not be made. Studies of other minor compounds isolated (a, b, c, and d in Experimental) are in progress.

Experimental

All melting points were measured on a micromelting 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 $CDCl_3$ 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 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; sh shoulder.

Extraction and Separation——The dry powdered root bark (0.5 kg) of *C. sinensis* Osbeck var. *brasiliensis* Tanaka, collected in Taiwan was extracted twice with acetone. The acetone extract was concentrated and the residue dissolved in $CHCl_3$–H_2O (1: 1). The $CHCl_3$ layer was separated and evaporated to a brown syrup. On cooling, a crystalline mass (5.3 g, **11**) was deposited. This was separated by filtration and purified by recrystallization from EtOH. The mother liquor was distilled *in vacuo* (bp 116°C/4 mmHg) to afford **13** (11 g). The residue was chromatographed on a silica gel column with benzene–acetone (9: 1) as the eluent to yield five fractions. Fraction 1 was rechromatographed on a silica gel column with hexane–EtOAc (4: 1) to afford successively **8** (8.7 g), **10** (12 g), **11** (20 g), a (0.05 g), b (0.005 g), c (0.01 g), and d (0.012 g). Fraction 2 was treated similarly to give successively **8** (3.1 g), **11** (2.5 g), **12** (0.15 g), **9** (0.03 g), **4** (0.2 g), **1a** (0.04 g), and **3** (0.007 g). Fraction 3 was also subjected to silica gel column chromatography and elution with $CHCl_3$–acetone (9: 1) yielded successively **7** (0.35 g), **6** (0.03 g), *p*-hydroxyquinone (0.04 g), and **2a** (0.02 g).

Citrusinine-I (**1a**)——mp 206—207°C. Orange needles (acetone). A dark green color reaction with $FeCl_3$. UV λ_{max} nm: 234, 265, 320, 334, 418. IR ν_{max} cm^{-1}: 3220, 1610, 1540. MS *m/z*: 301 (M^+), 286 (100%), 271, 174. ^{13}C-NMR (DMSO-d_3+$CDCl_3$) δ: 181.94 (s), 159.95 (s), 159.42 (s), 148.19 (s), 141.87 (s), 137.19 (s), 129.76 (s), 124.14 (s), 122.45 (d), 119.93 (d), 115.72 (d), 105.83 (s), 93.49 (d), 59.97 (q), 55.99 (q), 45.98 (q). *Anal.* Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 64.02; H, 4.97; N, 4.58.

Citrusinine-II (**2a**)——mp 244—246°C. Yellow needles (acetone). A dark green color reaction with $FeCl_3$. UV λ_{max} nm (log ε): 209 (4.15), 223 (4.16), 265 (4.59), 285 (sh, 4.25), 319 (4.08), 334 (sh, 4.00), 412 (3.55). UV λ_{max} (+$AlCl_3$) nm: 209, 223, 283 (sh), 291, 355, 462. UV λ_{max} (+$NaOCH_3$) nm: 209, 236, 263, 292, 362, 420. IR ν_{max} cm^{-1}: 3280, 1630, 1595, 1530. MS *m/z* (%): 287 (M^+, 38), 272 (100), 258 (6), 244 (82), 239 (12), 301 (9), 174 (6), 145 (15). *Anal.* Calcd for $C_{15}H_{13}NO_5$: C, 62.71; H, 4.56; N, 4.88. Found: C, 62.12; H, 4.58; N, 4.61.

Citbrasine (**3**)——mp 154—156°C. Red plates (ether). A dark green color reaction with $FeCl_3$. UV λ_{max} nm (log ε): 209 (4.18), 225 (4.08), 262 (sh, 4.51), 272 (4.58), 325 (3.96), 426 (3.59). UV λ_{max} (+$AlCl_3$) nm: 209, 233, 257, 289, 355, 488. UV λ_{max} (+$NaOCH_3$) nm: 211, 273, 333, 440. IR ν_{max} ($CHCl_3$) cm^{-1}: 3250, 1622, 1590, 1555. MS *m/z* (%): 331 (M^+, 36), 316 (100), 301 (9), 300 (7), 286 (16), 272 (6), 258 (15), 244 (9), 174 (25).

***O*-Methylcitrusinine-I** (**1c**)——1) Compound **1a** (15 mg) in ether (5 ml) was treated with an excess of ethereal CH_2N_2 and left at room temperature overnight. The mixture was concentrated and chromatography

of the residue on silica gel using benzene: acetone=9: 1 gave **1c** as an amorphous gum. UV λ_{max} nm: 224, 264, 318, 332 (sh), 415. IR ν_{max} ($CHCl_3$) cm^{-1}: 1620, 1585, 1560. MS *m/z*: 315 (M^+), 300 (100%), 285, 270, 257, 242.

2) Treatment of **2a** (3 mg) as described above 1) afforded an uncrystallizable gum, which was found to be identical with **1c** by IR, ^{1}H-NMR, MS, and TLC comparisons.

Methoxymethylation of Citrusinine-I (1a)——A mixture of citrusinine-I (**1a**) (15 mg) in CH_2Cl_2 (10 ml) and 0.1% NaOH (10 ml) was stirred at room temp. for 20 min in the presence of a phase-transfer catalyst (Adogen 464, Aldrich, 5 mg), then excess chloromethylmethyl ether was added. After 1 h, the aqueous phase was separated and extracted with CH_2Cl_2. The combined organic extract was washed with H_2O, dried, and evaporated to dryness. The residue was chromatographed on a silica gel column and elution with benzene–acetone (9: 1) yielded **1b** as orange plates, which were recrystallized from ether. mp 148—150°C. UV λ_{max} nm: 225, 268, 317, 334 (sh), 415. IR ν_{max} ($CHCl_3$) cm^{-1}: 1630, 1590, 1560. MS *m/z*: 345 (M^+), 330 (100%), 300, 298, 286, 285, 284.

Methoxymethylation of Citrusinine-II (2a)——Treatment of **2a** (10 mg) as described for citrusinine-I (**1a**) afforded **2b** as yellow needles. mp 99—101°C. UV λ_{max} nm: 222, 267, 318, 332 (sh), 412. IR ν_{max} ($CHCl_3$) cm^{-1}: 1625, 1590, 1562. MS *m/z*: 375 (M^+), 360 (100%), 344, 330, 329, 328, 316, 298, 286, 285, 284, 270, 258, 242.

Ethylsuberenol (6)——mp 154—155°C. Colorless needles (ether). UV λ_{max} nm (log ε): 257 (4.52), 295 (3.98), 306 (3.98), 343 (4.15). IR ν_{max} ($CHCl_3$) cm^{-1}: 1710, 1605, 1555. ^{1}H-NMR δ: 1.16 (3H, t, J=7 Hz, CH_3), 1.36 (6H, s, 2×CH_3), 3.34 (2H, q, J=7 Hz, CH_2), 3.83 (3H, s, 7-OCH_3), 6.10 (1H, d, J=16 Hz, H-2′), 6.15 (1H, d, J=10 Hz, H-3), 6.65 (1H, d, J=16 Hz, H-1′), 6.67 (1H, s, H-8), 7.37 (1H, s, H-5), 7.51 (1H, d, J=10 Hz, H-4). MS *m/z* (%): 288 (M^+, 35), 273 (100), 259 (4), 245 (23), 243 (37), 229 (13), 227 (9), 217 (40), 213 (14), 203 (42), 201 (6), 199 (6), 189 (9), 187 (7), 186 (7), 185 (9), 175 (7), 171 (5), 158 (6), 128 (15).

Suberenol (7)——mp 172—173°C. Pale yellow plates (acetone). UV λ_{max} nm: 212, 256, 296, 306, 345. IR ν_{max} cm^{-1}: 3400, 1720, 1675, 1600. ^{1}H-NMR (acetone-d_6) δ: 1.34 (6H, s, 2×CH_3), 3.68 (1H, s, OH), 3.91 (3H, s, OCH_3), 6.13 (1H, d, J=9.5 Hz, H-3), 6.35 (1H, d, J=16 Hz, H-2′), 6.80 (1H, d, J=16 Hz, H-1′), 6.81 (1H, s, H-8), 7.61 (1H, s, H-5), 7.78 (1H, d, J=9.5 Hz, H-4). MS *m/z*: 260 (M^+), 245, 242, 227, 203, 189 (100%), 159, 131.

Crenulatin (9)——mp 254—255°C. Colorless needles (acetone). UV λ_{max} nm: 217, 257, 298 (sh), 310, 332, 343 (sh). IR ν_{max} cm^{-1}: 1715, 1670, 1610. ^{1}H-NMR δ: 3.97 (3H, s, OCH_3), 6.26 (1H, d, J=10 Hz, H-3), 6.83 (1H, s, H-8), 7.63 (1H, d, J=10 Hz, H-4), 7.91 (1H, s, H-5), 10.33 (1H, s, -CHO). MS *m/z*: 204 (M^+, 100%), 186, 175, 159, 158.

Xanthoxyletin (10)——Colorless elongated prisms from acetone. mp 131—132°C. UV λ_{max} nm: 226, 258, 268, 322, 347. IR ν_{max} cm^{-1}: 1720. ^{1}H-NMR δ: 1.45 (6H, s, 2×CH_3), 3.82 (3H, s, OCH_3), 5.65 (1H, d, J=10 Hz, H-7), 6.13 (1H, d, J=10 Hz, H-3), 6.47 (1H, d, J=10 Hz, H-6), 6.52 (1H, s, H-10), 7.97 (1H, d, J=10 Hz, H-4). MS *m/z*: 258 (M^+), 243 (100%). This product was shown to be identical with an authentic sample by IR, ^{1}H-NMR, and MS comparisons, and mixed mp determination.

Xanthyletin (11)——Colorless plates from EtOH. mp 130—131°C. UV λ_{max} nm: 225, 265, 304 (sh), 348. IR ν_{max} cm^{-1}: 1705, 1622. ^{1}H-NMR 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 product was shown to be identical with an authentic sample by IR, ^{1}H-NMR, and MS comparisons, and mixed mp determination.

Nordentatin (12)——Pale yellow prisms from acetone. mp 180—182°C. UV λ_{max} nm: 225, 279, 337. IR ν_{max} cm^{-1}: 3200—3280, 1700, 1675. ^{1}H-NMR (acetone-d_6) δ: 1.44 (6H, s, 2-$C(CH_3)_2$), 1.63 (6H, s, 1′-$C(CH_3)_2$), 4.78 (1H, q, J=1.5 and 10 Hz, H-3′), 4.88 (1H, q, J=1.5 and 18 Hz, H-3′), 5.69 (1H, d, J=10 Hz, H-3), 6.03 (1H, d, J=10 Hz, H-9), 6.29 (1H, q, J=10 and 18 Hz, H-2′), 6.73 (1H, d, J=10 Hz, H-4), 8.08 (1H, d, J=10 Hz, H-10), 8.75 (1H, s, OH). MS *m/z*: 312 (M^+), 297 (100%). This product was shown to be identical with an authentic sample by IR, ^{1}H-NMR, and MS comparisons, and mixed mp determination.

Elemol (13)——Colorless needles from hexane. mp 48—48.5°C. $[\alpha]_D$ −2° (c=1.0, $CHCl_3$). IR ν_{max} cm^{-1}: 3580, 1620, 900, 885. ^{1}H-NMR δ: 0.98 (3H, s, CH_3), 1.21 (6H, s, 2×CH_3), 1.71 (3H, dd, J=1 and 2 Hz, C=C-CH_3), 4.56—4.96 (4H, m), 5.78 (1H, dd, J=10 and 18 Hz, CH=CH_2). MS *m/z*: 222 (M^+), 204, 189, 161, 149, 135, 121, 107. This product was shown to be identical with an authentic sample by IR, ^{1}H-NMR, and MS comparisons, and gas chromatography (column, 5% Apiezon L, at 190°C; flow rate, 40 ml/min, retention time, 12.4 min; Shimadzu 7A).

***p*-Hydroquinone**——Colorless prisms from acetone. mp 169—170°C. UV λ_{max} nm: 227, 295. IR ν_{max} cm^{-1}: 3150, 1600, 1500. ^{1}H-NMR (acetone-d_6) δ: 6.64 (4H, s), 7.67 (2H, s, 2×OH), MS *m/z*: 110 (M^+), 81, 53, 39 (100%). This product was shown to be identical with an authentic sample by IR and ^{1}H-NMR comparisons, and mixed mp determination.

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References and Notes

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