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Limonoids and Quinolone Alkaloids from *Evodia rutaecarpa* BENTHAM

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Four new limonoids and five new quinolone alkaloids were isolated from the fruit of *Evodia rutaecarpa* BENTHAM (Rutaceae), together with seven known limonoids and four known quinolone alkaloids, and their structures were determined on the basis of spectral data and chemical reactions.

Keywords—limonoid; quinolone alkaloid; *Evodia rutaecarpa*; 12 α -hydroxylimonin; 12 α -hydroxyevodol; 1-methyl-2-[(*Z*)-6-undecenyl]-4(1*H*)-quinolone; 1-methyl-2-[(*Z*)-10-pentadecenyl]-4(1*H*)-quinolone; 1-methyl-2-[(*Z*)-6-pentadecenyl]-4(1*H*)-quinolone; 1-methyl-2-[(6*Z*,9*Z*)-6,9-pentadecadienyl]-4(1*H*)-quinolone; 1-methyl-2-[(4*Z*,7*Z*)-4,7-tridecadienyl]-4(1*H*)-quinolone

In the course of our studies on the biologically active compounds of Rutaceous plants, we have investigated in particular the limonoids and quinolone alkaloids in *Evodia rutaecarpa* BENTHAM. Limonoids were detected as brown-orange spots on thin layer chromatography (TLC) with Ehrlich's reagent, which reacts with the furan ring.¹⁾ From the fruit of this plant, seven known limonoids, limonin (I),²⁾ rutaevine (II),³⁾ evodol (III),⁴⁾ obacunone (IV),⁵⁾ jangomolide (V),⁶⁾ rutaevine acetate (VI)⁷⁾ and graucin A (VII),⁸⁾ were isolated together with new limonoids, 12 α -hydroxylimonin (VIII), 12 α -hydroxyevodol (IX), 6 α -acetoxy-5-epilimonin (X) and 6 β -acetoxy-5-epilimonin (XI). Compounds X and XI were reported in our

Chart 1

previous paper.⁹⁾ This paper describes two new limonoids, VIII and IX, and quinolone alkaloids.

12 α -Hydroxylimonin (VIII) was obtained as a colorless powder, $[\alpha]_D^{20} -134.0^\circ$ ($c=1.00$, CHCl_3). The infrared (IR) spectrum showed the presence of hydroxyl (3475 cm^{-1}), lactone (1750 cm^{-1}) and ketone (1720 cm^{-1}) groups. The electron impact mass spectrum (EI-MS) showed fragment ion peaks at m/z 485 ($\text{M}-\text{H}$)⁺, 471 ($\text{M}-\text{CH}_3$)⁺. The proton nuclear magnetic resonance (^1H -NMR) spectrum exhibited signals due to four tertiary methyl groups at δ 0.96, 1.13, 1.16 and 1.28, two singlet signals at δ 3.80 (15-H) and 5.44 (17-H), an AX quartet ($J=13\text{ Hz}$) at δ 4.40 (19-H _{α}) and 4.82 (19-H _{β}), a β -substituted furan at δ 6.46 (22-H) and 7.50 (2H, 21-, 23-H), and a carbinol methine signal at δ 3.94 (d, $J=5\text{ Hz}$, 12-H). These ^1H -NMR spectral features closely resembled those of limonin (I) except for the presence of the signals due to an additional hydroxyl group. In the carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectrum, the signals of the C-ring of VIII were similar to those of VII compared with rutaevine (II)⁸⁾ (see Fig. 1). Compound VIII was substituted with a hydroxyl group at the 12-position of limonin. In order to decide the stereostructure at 12-C, VIII was acetylated. In the ^1H -NMR spectrum, the acetyl methyl signal of VIII acetate was observed at δ 1.76, because the acetyl methyl was shielded heavily by paramagnetic anisotropy of the furan ring⁸⁾ (see Fig. 2). Thus, the hydroxyl group of at 12-C was α .

12 α -Hydroxyevodol (IX) was obtained as an amorphous solid, $[\alpha]_D^{20} -114.0^\circ$ ($c=0.48$, MeOH). The IR spectrum showed the presence of hydroxyl (3450 cm^{-1}), lactone (1750 cm^{-1}) and conjugated ketone (1690 cm^{-1}) groups. The EI-MS showed the M^+ peaks at m/z 500 and a fragment ion peak at m/z 485 ($\text{M}-\text{CH}_3$)⁺. The ^1H -NMR spectrum exhibited signals due to four tertiary methyl groups at δ 1.02, 1.10, 1.51 and 1.57, three singlet signals at δ 4.10 (15-H), 5.46 (17-H) and 4.67 (2H, 19-H₂), a β -substituted furan at δ 6.46 (22-H) and 7.54 (2H, 21-, 23-H), and a carbinol methine signal at δ 3.94 (d, $J=5\text{ Hz}$, 12-H). These ^1H -NMR spectral features closely resembled those of evodol (III) except for the presence of the signals due to an additional hydroxyl group (see Fig. 1). The ^{13}C -NMR spectrum showed the hydroxyl group attached at the 12-position of III, as in VIII. The α configuration was suggested, because the acetyl methyl signal at 12-C of IX acetate was observed at δ 1.74.

Fig. 1. Difference of ^{13}C -NMR Chemical Shifts on the C-Ring between 12-Hydroxy Derivatives and Base Compounds

Fig. 2. Partial Structure of 12 α -Acetoxy Limonoids

rearrangement of the molecular ion at m/z 173, from displacement rearrangement of the molecular ion at m/z 186, and elimination of the ketene at m/z 144¹⁰⁾ (see Fig. 4). The ¹H-NMR spectrum exhibited signals due to the quinolone skeleton, *i.e.*, N-methyl group at δ 3.73, conjugated olefinic proton at δ 6.22 (1H, s, 3-H), aromatic protons at δ 7.3—7.8 (3H, m, 6-, 7-, 8-H), aromatic peri-proton at δ 8.41 (1H, dd, $J=8$, 2 Hz, 5-H), and olefinic protons at δ 5.35 (2H, m, 6'-, 7'-H). On catalytic hydrogenation, XVI was converted to XIV. This suggested that the side chain carbon number was eleven. On Lemieux-Johnson oxidation, XVI produced pentanal which was identified by comparing its 2,4-dinitrophenylhydrazone with an authentic sample. This suggested that the double bond of the side chain existed at the 6'-position, and it was considered to be in *Z*-form based on the ¹³C-NMR chemical shift of the allyl carbon (δ 27.0).

Compound XVII was obtained as a colorless oil. The UV and ¹H-NMR spectra exhibited signals due to the quinolone skeleton. The EI-MS showed the M^+ peak at m/z 367 and fragment ion peaks at m/z 186, 173, 144. The ¹H-NMR spectrum also exhibited a signal due to olefinic protons at δ 5.40 (2H, br t, $J=5$ Hz). On catalytic hydrogenation, XVII was converted to XV. This suggested that the side chain carbon number was fifteen. However, the ¹³C-NMR spectrum indicated that XVII consisted of two compounds. This was proved by

TABLE I. ¹H-NMR Chemical Shifts of Limonoids

	I ^{a,i)}	II ^{b,j)}	III ^{a,i)}	IV ^{a,i)}	V ^{a,i)}	VI ^{a,j)}	VII ^{b,j)}	VIII ^{a,j)}	IX ^{a,j)}
1	4.04 (brs)	4.54 (brs)	4.07 ₂ (brs)	6.51 (d, 11)	6.52 (d, 10)	4.40 (brs)	4.37 (brs)	4.80 (brs)	4.12 (brs)
2 α	2.68 (dd, 17, 2)	2.64 (dd, 15, 3)	2.84 (dd, 17, 5)	5.97 (d, 11)	6.13 (d, 10)	2.64 (dd, 16, 3)	— ^{k)}	— ^{k)}	— ^{k)}
2 β	2.98 (dd, 17, 4)	2.92 (dd, 15, 3)	2.97 (dd, 17, 5)			2.90 (dd, 16, 2.5)	— ^{k)}	— ^{k)}	— ^{k)}
5	2.23 (dd, 15, 3)	2.86 (s)		2.61 (dd, 11, 4)	2.68 (t, 6)	3.06 (s)	2.95 (s)	— ^{k)}	
6 α	2.47 (dd, 14, 3)			2.30 (dd, 11, 4)	2.70 (d, 6)			— ^{k)}	
6 β	2.86 (dd, 15, 14)			2.99 (t, 11)				— ^{k)}	
7		4.25 (d, 4.5)				5.63 (s)	5.81 (d, 5)		
9	2.55 (dd, 12, 3)	— ^{k)}	2.64 (dd, 13, 3)	2.15 (dd, 8.5, 3.5)	2.66 (t, 8)	— ^{k)}	— ^{k)}	— ^{k)}	— ^{k)}
12 β	— ^{k)}	— ^{k)}	— ^{k)}	— ^{k)}	— ^{k)}	— ^{k)}	4.93 (d, 4)	3.94 (d, 5)	3.94 (d, 5)
15	4.04 (s)	4.00 (s)	4.12 (s)	3.66 (s)	3.99 (s)	3.84 (s)	4.01 (s)	3.80 (s)	4.10 (s)
17	5.48 (s)	5.48 (s)	5.43 (s)	5.46 (s)	5.53 (s)	5.50 (s)	5.59 (s)	5.44 (s)	5.46 (s)
19 α	4.46 (d, 13)		4.62 (d, 13)			4.16 (d, 13)		4.40 (d, 13)	
19 β	4.77 (d, 13)	4.3 (brs)	4.66 (d, 13)	1.24 (s)	6.07 (s)	4.34 (d, 13)	3.9 4.3 (d, 13)	4.82 (d, 13)	4.67 (s)
21	7.41	7.70	7.41 ^{c)}	7.43	7.40	7.44	7.84 ^{e)}	7.50	7.54
22	6.38	6.55	6.38	6.37	6.32	6.38	6.61	6.46	6.46
23	7.40	7.77	7.40 ^{c)}	7.40	7.41	7.44	7.73 ^{e)}	7.50	7.54
18	1.17 (s)	1.35 (s)	1.04 (s)	1.12 (s)	1.16 (s)	1.32 (s) ^{d)}	1.18 (s) ^{f)}	1.16 (s) ^{g)}	1.51 ^{h)}
28	1.30 (s)	1.13 (s)	1.54 (s)	1.46 (s)	1.36 (s)	1.32 (s) ^{d)}	1.13 (s) ^{f)}	1.13 (s) ^{g)}	1.57 ^{h)}
29	1.18 (s)	1.25 (s)	1.49 (s)	1.51 (s)	1.30 (s)	1.40 (s) ^{d)}	1.28 (s) ^{f)}	1.28 (s) ^{g)}	1.10 ^{h)}
30	1.07 (s)	0.57 (s)	1.16 (s)	1.51 (s)	1.30 (s)	0.80 (s) ^{d)}	0.56 (s) ^{f)}	0.96 (s) ^{g)}	1.02 ^{h)}

a) In CDCl₃. b) In DMSO-*d*₆. c-h) Assignments may be interchanged in each column. i) Measured at 400 MHz. j) Measured at 90 MHz. k) Could not be assigned.

TABLE II. ^{13}C -NMR Chemical Shifts of Limonoids

	I ^{a)}	II ^{b)}	III ^{b)}	IV ^{a)}	V ^{a)}	VI ^{b)}	VII ^{b)}	VIII ^{a)}	IX ^{b)}
1	79.1	81.9	78.7	156.8	150.7	81.8	81.8	78.9	79.0
2	35.7	35.9	35.0	123.0	119.0	35.8	35.9	35.7 ^{b)}	35.0
3	169.1	170.9	169.8	166.9 ^{e)}	160.3	170.6	170.7	169.7	169.7
4	80.3	81.4	81.8	84.0	86.3	81.5	81.5	80.2	81.1
5	60.5	64.5	140.7	57.4	53.3	64.4	64.7	61.1	140.3
6	36.4	207.2	142.3	40.0	37.7	200.4	207.2	36.5 ^{b)}	141.9
7	206.2	81.4	195.3	207.5	209.6	81.5	81.8	206.0	195.3
8	51.3	48.6 ^{c)}	47.1 ^{d)}	53.0	49.3	48.3 ^{f)}	48.1 ^{g)}	52.3	47.3
9	48.1	45.3 ^{c)}	46.2	49.3	41.8	43.8 ^{f)}	41.2	45.0	42.8
10	45.9	45.6 ^{c)}	46.6 ^{d)}	43.3	49.3	46.0 ^{f)}	45.8 ^{g)}	45.8	46.9
11	18.9	19.3	18.7	17.1	19.2	19.1	31.2	30.7	31.9
12	30.8	31.0	30.0	32.8	29.1	30.8	65.9	68.5	65.9
13	37.9	37.2	36.8	37.5	38.5	37.2	42.9	43.6	42.2
14	65.7	65.9	65.7	65.1	67.2	65.4	65.9	64.4	64.4
15	53.9	50.8	51.9	53.4	54.2	50.2	50.6	52.4	50.6
16	166.9	166.9	166.7	166.7 ^{e)}	166.6	166.5	166.8	166.2	166.5
17	77.8	77.5	77.2	78.0	77.9	77.5	77.0	76.8	76.6
19	65.4	69.8	69.5	—	104.0	69.3	70.1	65.9	69.3
20	120.0	120.0	119.8	120.0	120.0	119.7	119.8	120.0	119.7
21	141.1	141.6	141.6	141.1	141.2	141.6	141.7	141.6	141.6
22	109.7	110.3	110.0	109.8	109.7	110.1	110.6	109.6	110.4
23	143.2	143.4	143.4	143.3	143.3	143.4	143.0	144.3	142.9
C-Methyls	17.6	14.7	17.5	16.5	15.7	14.6	14.1	13.4	12.9
	20.7	20.5	19.8	19.6	20.2	20.3	14.7	16.7	17.5
	21.4	23.8	24.9	21.2	24.9	23.3	23.8	21.5	25.0
	30.2	28.8	25.5	26.9	31.9	28.5	28.7	30.1	25.5
				32.1					
Acetate carbonyl						169.5			
Acetate methyl						20.0			

a) In CDCl_3 . b) In $\text{DMSO}-d_6$. c—h) Assignments may be interchanged in each column.

Lemieux–Johnson oxidation, in which XVII produced pentanal and nonanal in the proportion of 2 : 3. The double bond was elucidated as *Z*-form based on the ^{13}C -NMR chemical shifts of allyl carbon (δ 26.9, 27.0). Consequently, XVII was a mixture of 1-methyl-2-[(*Z*)-10-pentadecenyl]-4(1*H*)-quinolone and 1-methyl-2-[(*Z*)-6-pentadecenyl]-4(1*H*)-quinolone in the proportion mentioned above.

1-Methyl-2-[(6*Z*,9*Z*)-6,9-pentadecadienyl]-4(1*H*)-quinolone (XVIII) was obtained as a colorless oil. The UV and ^1H -NMR spectra again exhibited signals due to the quinolone skeleton. The EI-MS showed the M^+ peak at m/z 365 and the fragment ion peaks at m/z 186, 173 and 144. In addition, the ^1H -NMR spectrum exhibited the signals due to olefinic protons at δ 5.40 (4H, m, 6'-, 7'-, 9'-, 10'-H). On catalytic hydrogenation, XVIII was converted to XV. This suggested that the side chain carbon number was fifteen. On Lemieux–Johnson oxidation, XVIII produced hexanal and malonaldehyde. This suggested that the double bonds of the side chain existed at the 6'- and 9'-positions, and were showed *Z*-form, based on the ^{13}C -NMR spectrum chemical shifts of allyl carbon (δ 26.9, 25.5 and 27.0), as in linoleic acid.

1-Methyl-2-[(4*Z*,7*Z*)-4,7-tridecadienyl]-4(1*H*)-quinolone (XIX) was obtained as a colorless oil. Each spectral data showed similarity between XIX and XVIII. On catalytic hydrogenation, XIX was converted to XIII. This suggested that the side chain carbon number was thirteen. On Lemieux–Johnson oxidation, XIX produced hexanal and malonaldehyde.

TABLE III. ^{13}C -NMR Chemical Shifts of Quinolone Alkaloids and Linoleic Acid in CDCl_3

	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	Linoleic acid
2	154.5	154.7	154.7	155.2	154.6	154.7	154.5	154.5	1 180.2
3	110.5	111.1	111.1	111.1	111.2	110.7	110.7	111.2	2 34.2
4	177.3	177.7	177.7	178.0	177.8	177.4	177.4	177.9	3 24.8
4a	— ^{a)}	— ^{a)}	— ^{a)}	— ^{a)}	— ^{a)}	— ^{a)}	— ^{a)}	— ^{a)}	4 29.2 ^{r)}
5	126.0	126.6	126.6	126.8	126.7	126.2	126.2	126.8	5 29.2 ^{r)}
6	122.8	123.2	123.2	123.5	123.3	123.0	122.9	123.4	6 29.2 ^{r)}
7	131.7	132.0	132.0	132.2	132.0	131.8	131.7	132.1	7 29.7 ^{r)}
8	115.2	115.3	115.3	115.4	115.3	115.3	115.2	115.3	8 27.3
8a	141.6	142.0	142.0	142.0	142.0	141.7	141.7	— ^{a)}	9 130.0 ^{s)}
									10 127.4 ^{s)}
N-CH ₃	33.8	34.1	34.1	34.3	34.1	34.0	33.9	34.2	11 25.8
									12 128.2 ^{s)}
1'	34.3	34.7	34.7	34.9	34.7	34.5	34.5	34.2	13 130.3 ^{s)}
2'	28.1 ^{b)}	28.5	28.5	28.7	28.6 ^{b)}	28.3 ^{j)}	28.2 ^{m)}	28.6	14 27.3
3'	28.8 ^{b)}	29.3 ^{e)}	29.3 ^{f)}	29.4 ^{g)}	28.9 ^{h)}	28.8 ^{j)}	28.7 ^{m)}	26.8 ^{p)}	15 29.4 ^{r)}
4'	28.9 ^{b)}	29.3 ^{e)}	29.3 ^{f)}	29.4 ^{g)}	29.4 ^{h)}	29.1 ^{j)}	29.1 ^{m)}	130.7 ^{q)}	16 31.6
5'	23.9 ^{b)}	29.3 ^{e)}	29.3 ^{f)}	29.4 ^{g)}	27.0	29.1 ^{j)}	26.9 ⁿ⁾	127.4 ^{q)}	17 22.7
6'	29.4 ^{b)}	29.5 ^{e)}	29.5 ^{f)}	29.7 ^{g)}	129.2 ⁱ⁾	29.3 ^{j)} (129.1)	129.3 ^{o)}	25.8	18 14.1
7'	26.6 ^{c)}	29.6 ^{e)}	29.6 ^{f)}	29.7 ^{g)}	130.2 ⁱ⁾	29.3 ^{j)} (129.7)	127.5 ^{o)}	128.2 ^{q)}	
8'	129.3 ^{d)}	29.6 ^{e)}	29.6 ^{f)}	29.7 ^{g)}	27.0	29.6 ^{j)}	25.5	130.1 ^{q)}	
9'	129.7 ^{d)}	29.6 ^{e)}	31.9	29.7 ^{g)}	32.0	26.9 ^{k)}	128.2 ^{o)}	27.4 ^{p)}	
10'	26.9 ^{c)}	23.6 ^{e)}	22.7	29.7 ^{g)}	22.4	129.7 ⁱ⁾	130.1 ^{o)}	29.4	
11'	31.7	31.9	14.1	29.7 ^{g)}	14.0	130.3 ^{j)}	27.0 ⁿ⁾	31.6	
12'	22.1	22.7		29.9 ^{g)}		27.0 ^{k)}	29.1 ^{m)}	22.6	
13'	13.8	14.1		32.0		31.8	31.3	14.1	
14'				22.8		22.5 (22.2)	22.8		
15'				14.2		14.0 (13.9)	13.9		

a) This signal was not observed. b—s) Assignments may be interchanged in each column.

This suggested that the double bonds of the side chain existed at the 4'- and 7'-positions, and were *Z*-form, based on the ^{13}C -NMR chemical shifts of allyl carbon (δ 26.8, 25.8 and 27.4).

The biological activities of these compounds will be reported in the future.

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined with a JASCO DIP-140 digital polarimeter, IR spectra were run on a JASCO A-202 grating infrared spectrometer and UV spectra on a Shimadzu UV-360 spectrometer. MS were recorded on JEOL JMS D-100 instruments. Circular dichroism (CD) spectra were measured on a JASCO J-20A spectrometer. ^1H - and ^{13}C -NMR spectra were recorded on a JEOL JNM-FX 90Q FT (90 MHz and 22.5 MHz, respectively) and on a JEOL JNM-GX 400 (399.5 MHz). Chemical shifts are given on the δ (ppm) scale with tetramethylsilane (TMS) as an internal standard (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad). TLC was carried out on precoated Silica gel 60 F₂₅₄ plates (Merck). Column chromatography was carried out on Silica gel type 60 (Merck). HPLC was run on JASCO 880-PC and UVDEC-100V instruments.

Isolation—The dried fruits of *E. rutaecarpa* (10 kg) were extracted twice with MeOH under reflux to give the MeOH extract (1.4 kg), which was partitioned between AcOEt and water to give an AcOEt-soluble fraction (550 g). The AcOEt-soluble fraction was partitioned between benzene and water to give the benzene-soluble fraction (280 g). The benzene-soluble fraction was absorbed on Celite and eluted with MeOH-H₂O (50:50) to give eluate 1 and with MeOH-H₂O (75:25) to give eluate 2. Eluate 1 was passed through a Mitsubishi Diaion HP-20 column, and the absorbed material was eluted with MeOH-H₂O (75:25) to give fraction 1. Fraction 1 was chromatographed on a silica gel column [solvent, benzene-AcOEt (85:15)] to give a limonoid mixture. The mixture was purified by HPLC [column, YMC-Pack D-ODS-7; CH₃CN-H₂O (50:50)] to give compounds I—XI. Eluate 2 was concentrated under reduced pressure and the residue was chromatographed on a silica gel column [solvent, benzene-acetone (85:15)] to

give a quinolone alkaloid mixture. The mixture was purified by HPLC [column, Nomura Chemical Develosil C8-10; MeOH-H₂O (90:10)] to give compounds XII–XIX.

Limonin (I)—Colorless crystals (45 mg), mp 271–275 °C (AcOEt). *Anal.* Calcd for C₂₆H₃₀O₈: C, 66.37; H, 6.43. Found: C, 66.65; H, 6.48. $[\alpha]_D^{20}$ –127.3° (c = 1.21, acetone). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 1765, 1715, 1315, 1290, 1270, 1170, 1035, 1020, 920, 895, 880, 740, 620, 600. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 208 (3.77). MS m/z : 470 (M)⁺, 455 (M–CH₃)⁺, 347 (M–C₆H₃O₃)⁺. CD (c = 0.011, MeOH) $[\theta]$ (nm): –16000 (228), –9300 (291). ¹H- and ¹³C-NMR: Tables I and II.

Rutaevine (II)—Colorless needles (26 mg), mp 274–276 °C (CHCl₃–AcOEt). *Anal.* Calcd for C₂₆H₃₀O₉: C, 64.19; H, 6.21. Found: C, 64.38; H, 6.26. $[\alpha]_D^{20}$ –132.0° (c = 0.50, CH₃CN). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 1775, 1745, 1715, 1390, 1290, 1180, 1110, 1060, 1030, 1005, 955, 905, 880, 825, 730, 700, 600. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 206 (3.78). MS m/z : 486 (M)⁺, 471 (M–CH₃)⁺, 363 (M–C₆H₃O₃)⁺. CD (c = 0.006, MeOH) $[\theta]$ (nm): –13000 (221), –1900 (298). ¹H- and ¹³C-NMR: Tables I and II.

Evodol (III)—Colorless powder (11 mg). $[\alpha]_D^{20}$ –156.4° (c = 1.04, CHCl₃–MeOH (1:1)). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 1750, 1690, 1660, 1360, 1290, 1050, 1030, 915, 875, 600. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 206 (3.82), 276 (3.95). MS m/z : 484 (M)⁺, 469 (M–CH₃)⁺, 361 (M–C₆H₃O₃)⁺. CD (c = 0.005, MeOH) $[\theta]$ (nm): –15000 (230), +62000 (275), –48000 (319). ¹H- and ¹³C-NMR: Tables I and II.

Obacunone (IV)—Colorless rods (14 mg), mp 216–222 °C (EtOH). $[\alpha]_D^{20}$ –48.0° (c = 0.417, CHCl₃). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 1750, 1710, 1400, 1290, 1170, 1125, 1080, 1035, 1000, 930, 890, 835, 815, 615. MS m/z : 454 (M)⁺, 439 (M–CH₃)⁺, 331 (M–C₆H₃O₃)⁺. CD (c = 0.005, MeOH) $[\theta]$ (nm): +11000 (220), –12700 (247), –9000 (288). ¹H- and ¹³C-NMR: Tables I and II.

Jangomolide (V)—Colorless crystals (30 mg), mp 258.5–259.5 °C (CHCl₃–EtOH). *Anal.* Calcd for C₂₆H₂₈O₈: C, 65.61; H, 6.29. Found: C, 65.62; H, 6.07. $[\alpha]_D^{20}$ +20.3° (c = 0.62, CHCl₃–MeOH (1:1)). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 1720, 1385, 1345, 1285, 1270, 1060, 1020, 980, 920, 875, 810, 600. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 209 (4.20). MS m/z : 468 (M)⁺, 453 (M–CH₃)⁺, 345 (M–C₆H₃O₃)⁺. CD (c = 0.005, MeOH) $[\theta]$ (nm): –39000 (220), +7000 (303). ¹H- and ¹³C-NMR: Tables I and II.

Rutaevine Acetate (VI)—Colorless crystals (43 mg), mp 183–186 °C (EtOH). $[\alpha]_D^{20}$ –104.0° (c = 1.00, CH₃CN). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 1760, 1720, 1395, 1375, 1290, 1230, 1180, 1110, 1060, 1030, 1010, 960, 910, 880, 770, 700, 605. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 206 (3.81). MS m/z : 528 (M)⁺, 513 (M–CH₃)⁺, 468 (M–CH₃COOH)⁺, 363 (M–C₆H₃O₃–CH₂CO)⁺. CD (c = 0.006, MeOH) $[\theta]$ (nm): –21000 (224), –1700 (290). ¹H- and ¹³C-NMR: Tables I and II.

Graucina A (VII)—Colorless crystals (30 mg), mp 314–316 °C (CH₃CN). $[\alpha]_D^{20}$ –110.0° (c = 0.20, CH₃CN). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 3475, 1775, 1750, 1705, 1405, 1375, 1300, 1185, 1170, 1110, 1075, 1055, 1015, 960, 880, 820, 775, 760, 610. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 206 (3.55). MS m/z : 502 (M)⁺, 487 (M–CH₃)⁺, 379 (M–C₆H₃O₃)⁺. CD (c = 0.007, MeOH) $[\theta]$ (nm): –9100 (224), –1500 (290). ¹H- and ¹³C-NMR: Tables I and II.

12 α -Hydroxylimonin (VIII)—Colorless powder (27 mg), $[\alpha]_D^{20}$ –134.0° (c = 1.0, CHCl₃). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 3475, 1750, 1720, 1285, 1165, 1045, 1020, 940, 910, 900, 875, 810, 620, 600, 580. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 205 (3.76). MS m/z : 485 (M–H)⁺, 471 (M–CH₃)⁺, 363 (M–C₆H₃O₃)⁺. CD (c = 0.005, MeOH) $[\theta]$ (nm): –12200 (227), –6300 (290). ¹H- and ¹³C-NMR: Tables I and II.

12 α -Hydroxyevodol (IX)—Amorphous solid (6 mg), $[\alpha]_D^{20}$ –114.0° (c = 0.48, MeOH). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 3450, 1750, 1690, 1385, 1355, 1285, 1050, 1030, 880, 600. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 205 (3.84), 276 (3.67). MS m/z : 500 (M)⁺, 485 (M–CH₃)⁺. CD (c = 0.005, MeOH) $[\theta]$ (nm): –8800 (228), +27800 (275), –22200 (320). ¹H- and ¹³C-NMR: Tables I and II.

6 α -Acetoxy-5-epilimonin (X)—Colorless rods (31 mg), mp 256–258 °C (MeOH). *Anal.* Calcd for C₂₈H₃₂O₁₀: C, 63.64; H, 6.10. Found: C, 63.49; H, 6.14. $[\alpha]_D^{20}$ –93.5° (c = 1.0, CHCl₃). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 1765, 1750, 1740, 1380, 1295, 1250, 1180, 1060, 1025, 1005, 980, 915, 880, 810, 605. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 208 (3.76). MS m/z : 528 (M)⁺, 513 (M–CH₃)⁺, 453 (M–CH₃COOH)⁺, 387 (M–C₆H₃O₃)⁺. CD (c = 0.007, MeOH) $[\theta]$ (nm): –19000 (225), –4000 (287). ¹H-NMR (CDCl₃) (400 MHz) δ : 1.14 (3H, s, 18-H₃), 1.22 (3H, s, 30-H₃), 1.27 (3H, s, 28-H₃), 1.37 (3H, s, 29-H₃), 1.48 (1H, ddd, J = 15.5, 7, 3.5 Hz, 12-H₂), 1.70 (1H, dddd, J = 15.5, 7, 4, 2 Hz, 11-H₂), 1.87 (1H, dddd, J = 15.5, 12, 7.5, 3.5 Hz, 11-H₂), 1.88 (1H, ddd, J = 15.5, 7.5, 4 Hz, 12-H₂), 2.21 (3H, s, CH₃CO), 2.61 (1H, dd, J = 15.5, 3.5 Hz, 2-H₂), 2.85 (1H, dd, J = 15.5, 2.5 Hz, 2-H₂), 2.92 (1H, dd, J = 12, 2 Hz, 9-H), 3.08 (1H, dd, J = 3.5, 3.2 Hz, 1-H), 4.23 (1H, d, J = 12 Hz, 19-H₂), 4.64 (1H, d, J = 12 Hz, 19-H₂), 5.44 (1H, s, 17-H), 6.05 (1H, d, J = 10 Hz, 6-H), 6.35 (1H, dd, J = 1.8, 1 Hz, 22-H), 7.40 (1H, t, J = 1.8 Hz, 23-H), 7.42 (1H, dd, J = 1.8, 1 Hz, 21-H). ¹³C-NMR: See the previous paper.⁹⁾

6 β -Acetoxy-5-epilimonin (XI)—Colorless crystals (36 mg), mp 229–231 °C (MeOH). *Anal.* Calcd for C₂₈H₃₂O₁₀: C, 63.64; H, 6.10. Found: C, 63.37; H, 6.09. $[\alpha]_D^{20}$ +41.0° (c = 1.0, CHCl₃). IR $\nu_{\max}^{\text{KBr}}$ cm^{–1}: 1770, 1750, 1385, 1285, 1240, 1155, 1055, 1020, 980, 880, 805, 600. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 206 (3.78). MS m/z : 513 (M–CH₃)⁺, 453 (M–CH₃–CH₃COOH)⁺. CD (c = 0.010, MeOH) $[\theta]$ (nm): –11500 (230), +12000 (295), +11000 (303). ¹H- and ¹³C-NMR: See the previous paper.⁹⁾

Acetylation of II—Acetic anhydride (2 drops) was added to a solution of II (11 mg) in pyridine (0.5 ml), and the reaction mixture was left for 3 h at room temperature. After evaporation of the solvent, the product was purified by HPLC using a reversed-phase column to give the acetate (II-Ac) as colorless crystals (9 mg). II-Ac was identical

with VI by $^1\text{H-NMR}$ spectral comparison.

Acetylation of III—III (4 mg) was acetylated in the same way as II, giving the acetate (III-Ac) as colorless crystals (4 mg). $^1\text{H-NMR}$ (CDCl_3) δ : 1.00, 1.16, 1.46, 1.46 (3H, s, 18-, 28-, 29-, 30- H_3), 2.28 (3H, s, 6-OAc), 4.06 (1H, s, 15-H), 4.18 (1H, br t, $J=2.5$ Hz, 1-H), 4.70 (2H, s, 19- H_2), 5.46 (1H, s, 17-H), 6.38 (1H, br s, 22-H), 7.45 (2H, br s, 21-, 23-H).

Acetylation of VII—VII (10 mg) was acetylated in the same way as II, giving the acetate (VII-Ac) as colorless crystals (8 mg). $^1\text{H-NMR}$ (CDCl_3) δ : 0.79, 1.33, 1.42, 1.42 (3H, s, 18-, 28-, 29-, 30- H_3), 1.83 (3H, s, 12-OAc), 2.30 (3H, s, 7-OAc), 2.56 (1H, dd, $J=16$, 3 Hz, 2- H_2), 2.90 (1H, dd, $J=16$, 2.5 Hz, 2- H_β), 3.09 (1H, br d, $J=11$ Hz, 9-H), 3.12 (1H, s, 5-H), 3.84 (1H, s, 15-H), 4.06 (1H, d, $J=13$ Hz, 19- H_2), 4.24 (1H, d, $J=13$ Hz, 19- H_β), 5.02 (1H, d, $J=5$ Hz, 12-H), 5.56 (1H, s, 17-H), 5.67 (1H, s, 7-H), 6.39 (1H, br s, 22-H), 7.46, 7.48 (1H, br s, 21-, 23-H).

Acetylation of VIII—VIII (10 mg) was acetylated in the same way as II, giving the acetate as a colorless powder (VIII-Ac) (4.5 mg). $^1\text{H-NMR}$ (CDCl_3) δ : 1.01, 1.18, 1.31, 1.31 (3H, s, 18-, 28-, 29-, 30- H_3), 1.83 (3H, s, 12-OAc), 4.86 (1H, d, $J=5$ Hz, 12-H), 5.50 (1H, s, 17-H), 6.40 (1H, br s, 22-H), 7.43 (2H, br s, 21-, 23-H).

Acetylation of IX—IX (3 mg) was acetylated in the same way as II, giving the acetate (IX-Ac) as a colorless powder (2.5 mg). $^1\text{H-NMR}$ (CDCl_3) δ : 1.06, 1.20, 1.45, 1.49 (3H, s, 18-, 28-, 29-, 30- H_3), 1.74 (3H, s, 12-OAc), 2.28 (3H, s, 6-OAc), 4.12 (1H, s, 15-H), 4.42 (1H, d, $J=13$ Hz, 19- H_2), 4.86 (1H, d, $J=13$ Hz, 19- H_β), 5.02 (1H, d, $J=5$ Hz, 12-H), 5.46 (1H, s, 17-H), 6.38 (1H, br s, 22-H), 7.42, 7.44 (1H, br s, 21-, 23-H).

Alkali Hydrolysis of X—Aqueous 0.1 N KHCO_3 (0.5 ml) was added to a solution of X (5 mg) in MeOH (4.5 ml). The mixture was stirred for 24 h at room temperature. After being diluted with water, the mixture was passed through a Mitsubishi Diaion HP-20 column, which was washed with water, then eluted with MeOH. The MeOH eluate was purified by HPLC using a reversed-phase column to give a colorless amorphous product (X-C) (0.31 mg). X-C was identical with III by $^1\text{H-NMR}$ spectral comparison.

Alkali Hydrolysis of XI—XI (5 mg) was hydrolyzed in the same way as X, giving a colorless amorphous product (X-IC) (0.25 mg), which was identical with III by $^1\text{H-NMR}$ spectral comparison.

Evocarpine (XII)—Colorless oil (457 mg). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2960, 2940, 2860, 1635, 1605, 1505, 1475, 1180, 775, 760. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 213 (4.41), 239 (4.47), 321 (4.14), 333 (4.15). MS m/z : 339 (M^+) (26), 186 ($\text{M}-\text{C}_{11}\text{H}_{21}$) $^+$ (100), 173 ($\text{M}-\text{C}_{12}\text{H}_{22}$) $^+$ (93), 144 ($\text{M}-\text{C}_{13}\text{H}_{23}\text{O}$) $^+$ (12). $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, br t, $J=6$ Hz, 13'- H_3), 1.35 (12H, m, 2'-, 3'-, 4'-, 5'-, 6'-, 11'- H_2), 1.70 (2H, m, 12'- H_2), 2.72 (2H, br t, $J=8$ Hz, 1'-H), 3.76 (3H, s, N- CH_3), 5.40 (2H, br t, $J=5$ Hz, 8'-, 9'-H), 6.26 (1H, s, 3-H), 7.3—7.8 (3H, m, 6-, 7-, 8-H), 8.50 (1H, dd, $J=8$, 2 Hz, 5-H). $^{13}\text{C-NMR}$: Table III.

Dihydroevocarpine (XIII)—Colorless powder (21.8 mg), mp 74.5—75.5 $^\circ\text{C}$ (AcOEt). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2960, 2930, 2860, 1645, 1605, 1575, 1500, 1475, 1180, 775, 760. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 213 (4.40), 239 (4.46), 321 (4.13), 333 (4.15). MS m/z : 341 (M^+) (12), 186 ($\text{M}-\text{C}_{11}\text{H}_{23}$) $^+$ (100), 173 ($\text{M}-\text{C}_{12}\text{H}_{24}$) $^+$ (96), 144 ($\text{M}-\text{C}_{13}\text{H}_{25}\text{O}$) $^+$ (16). $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, br t, $J=6$ Hz, 13'- H_3), 1.27 (20H, br s, 2'-, 3'-, 4'-, 5'-, 6'-, 7'-, 8'-, 9'-, 10'-, 11'- H_2), 1.60 (2H, br m, 12'- H_2), 2.70 (2H, br t, $J=8$ Hz, 1'- H_2), 3.76 (3H, s, N- CH_3), 6.24 (1H, s, 3-H), 7.3—7.8 (3H, m, 6-, 7-, 8-H), 8.50 (1H, dd, $J=8$, 2 Hz, 5-H). $^{13}\text{C-NMR}$: Table III.

1-Methyl-2-undecyl-4(1H)-quinolone (XIV)—Colorless powder (19 mg), mp 69—70 $^\circ\text{C}$ (AcOEt-ether). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2960, 2940, 2860, 1645, 1600, 1575, 1500, 1475, 1180, 775, 760. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 213 (4.40), 239 (4.46), 321 (4.13), 333 (4.15). MS m/z : 313 (M^+) (20), 186 ($\text{M}-\text{C}_9\text{H}_{13}$) $^+$ (100), 173 ($\text{M}-\text{C}_{10}\text{H}_{20}$) $^+$ (100), 144 ($\text{M}-\text{C}_{11}\text{H}_{21}\text{O}$) $^+$ (16). $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, br t, $J=6$ Hz, 11'- H_3), 1.27 (18H, br s, 2'-, 3'-, 4'-, 5'-, 6'-, 7'-, 8'-, 9'-, 10'- H_2), 2.73 (2H, br t, $J=8$ Hz, 1'- H_2), 3.78 (3H, s, N- CH_3), 6.28 (1H, s, 3-H), 7.3—7.8 (3H, m, 6-, 7-, 8-H), 8.50 (1H, dd, $J=8$, 2 Hz, 5-H). $^{13}\text{C-NMR}$: Table III.

1-Methyl-2-pentadecyl-4(1H)-quinolone (XV)—Colorless powder (7 mg), mp 65—66 $^\circ\text{C}$ (AcOEt-ether). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2960, 2930, 2860, 1645, 1605, 1575, 1505, 1475, 1180, 775, 760. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 213 (4.40), 239 (4.46), 321 (4.13), 333 (4.15). MS m/z : 369 (M^+) (24), 186 ($\text{M}-\text{C}_{13}\text{H}_{27}$) $^+$ (100), 173 ($\text{M}-\text{C}_{14}\text{H}_{28}$) $^+$ (93), 144 ($\text{M}-\text{C}_{15}\text{H}_{29}\text{O}$) $^+$ (5). $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, br t, $J=6$ Hz, 15'- H_3), 1.28 (24H, br s, 2'-, 3'-, 4'-, 5'-, 6'-, 7'-, 8'-, 9'-, 10'-, 11'-, 12'-, 13'- H_2), 1.64 (2H, br m, 14'- H_2), 2.76 (2H, br t, $J=8$ Hz, 1'- H_2), 3.79 (3H, s, N- CH_3), 6.26 (1H, s, 3-H), 7.3—7.8 (3H, m, 6-, 7-, 8-H), 8.50 (1H, dd, $J=8$, 2 Hz, 5-H). $^{13}\text{C-NMR}$: Table III.

1-Methyl-2-[(Z)-6-undecenyl]-4(1H)-quinolone (XVI)—Colorless oil (10 mg). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2960, 2940, 2860, 1635, 1605, 1575, 1505, 1470, 1180, 775, 760. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 213 (4.43), 239 (4.49), 321 (4.16), 333 (4.17). MS m/z : 311 (M^+) (30), 186 ($\text{M}-\text{C}_9\text{H}_{17}$) $^+$ (100), 173 ($\text{M}-\text{C}_{10}\text{H}_{18}$) $^+$ (79), 144 ($\text{M}-\text{C}_{11}\text{H}_{19}\text{O}$) $^+$ (20). $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, br t, $J=6$ Hz, 11'- H_3), 1.2—1.8 (10H, br m, 2'-, 3'-, 4'-, 9'-, 10'- H_2), 1.9—2.3 (4H, br m, 5'-, 8'- H_2), 2.71 (2H, br t, $J=8$ Hz, 1'- H_2), 3.73 (3H, s, N- CH_3), 5.35 (2H, m, 6'-, 7'-H), 6.22 (1H, s, 3-H), 7.3—7.8 (3H, m, 6-, 7-, 8-H), 8.41 (1H, dd, $J=8$, 2 Hz, 5-H). $^{13}\text{C-NMR}$: Table III.

Compound XVII {1-Methyl-2-[(Z)-10-pentadecenyl]-4(1H)-quinolone (XVIIa)+1-Methyl-2-[(Z)-6-pentadecenyl]-4(1H)-quinolone (XVIIb)}—Colorless oil (47 mg). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2960, 2940, 2860, 1630, 1605, 1505, 1470, 1180, 760. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 214 (4.40), 239 (4.47), 321 (4.13), 333 (4.14). MS m/z : 367 (M^+) (30), 186 ($\text{M}-\text{C}_{13}\text{H}_{25}$) $^+$ (100), 173 ($\text{M}-\text{C}_{14}\text{H}_{26}$) $^+$ (82), 144 ($\text{M}-\text{C}_{15}\text{H}_{27}\text{O}$) $^+$ (12). $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, br m, 15'- H_3), 1.32 (18H, br m), 2.70 (2H, br t, $J=8$ Hz, 1'- H_2), 3.74 (3H, s, N- CH_3), 5.40 (2H, br t, $J=5$ Hz), 6.25 (1H, s, 3-H), 7.3—7.8 (3H, m, 6-, 7-, 8-H), 8.48 (1H, dd, $J=8$, 2 Hz, 5-H). $^{13}\text{C-NMR}$: Table III.

1-Methyl-2-[(6Z,9Z)-6,9-pentadecadienyl]-4(1H)-quinolone (XVIII)—Colorless oil (45 mg). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2960, 2940, 2860, 1630, 1605, 1505, 1470, 1180, 760. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 214 (4.41), 239 (4.50), 321 (4.11), 333 (4.13). MS m/z : 365 (M^+) (39), 186 ($\text{M}-\text{C}_{13}\text{H}_{23}$)⁺ (100), 173 ($\text{M}-\text{C}_{14}\text{H}_{24}$)⁺ (86), 144 ($\text{M}-\text{C}_{15}\text{H}_{25}\text{O}$)⁺ (19). $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, br t, $J=6$ Hz, $15'\text{-H}_3$), 1.40 (12H, br m, $2', 3', 4', 12', 13', 14'\text{-H}_2$), 2.08 (4H, br m, $5', 11'\text{-H}_2$), 2.70 (4H, m, $1', 8'\text{-H}_2$), 3.69 (3H, s, N-CH_3), 5.40 (4H, m, $6', 7', 9', 10'\text{-H}$), 6.15 (1H, s, 3-H), 7.25–7.8 (3H, m, 6-, 7-, 8-H), 8.44 (1H, dd, $J=8, 2$ Hz, 5-H). $^{13}\text{C-NMR}$: Table III.

1-Methyl-2-[(4Z,7Z)-4,7-tridecadienyl]-4(1H)-quinolone (XIX)—Colorless oil (9 mg). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2980, 2960, 2890, 1635, 1610, 1515, 1480, 1180, 765. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 213 (4.41), 240 (4.45), 321 (4.10), 334 (4.12). MS m/z : 337 (M^+) (38), 186 ($\text{M}-\text{C}_{11}\text{H}_{19}$)⁺ (92), 173 ($\text{M}-\text{C}_{12}\text{H}_{20}$)⁺ (100), 144 ($\text{M}-\text{C}_{13}\text{H}_{21}\text{O}$)⁺ (23). $^1\text{H-NMR}$ (CDCl_3) δ : 0.90 (3H, br t, $J=6$ Hz, $13'\text{-H}_3$), 1.2–1.4 (6H, br m, $10', 11', 12'\text{-H}_2$), 1.80 (2H, m, $2'\text{-H}$), 2.0–2.2 (4H, m, $3', 9'\text{-H}$), 2.7–2.8 (4H, m, $1', 6'\text{-H}_2$), 3.73 (3H, s, N-CH_3), 5.40 (4H, m, $4', 5', 7', 8'\text{-H}$), 6.24 (1H, s, 3-H), 7.3–7.7 (3H, m, 6-, 7-, 8-H), 8.44 (1H, dd, $J=8, 2$ Hz, 5-H). $^{13}\text{C-NMR}$: Table III.

Catalytic Hydrogenation of Quinolone Alkaloids—A mixture of a solution of each compound (about 1 mg) in EtOH (1 ml) and 10% Pd-C (10 mg) as a catalyst was stirred for 12 h under hydrogen and then the catalyst was filtered off. The solution was concentrated and the product was identified as the side chain saturated compound by TLC [solvent, benzene-AcOEt (85:15)] and HPLC [column, Develosil C8-7 (4.6 $\times$ 250 mm); solvent, MeOH-H₂O (90:10); wavelength, 321 nm] comparisons.

Lemieux-Johnson Oxidation of Quinolone Alkaloids—Osmium tetroxide (1 mg) and sodium periodate (10 mg) in H₂O (1 ml) were added to a solution of each compound (about 1 mg) in H₂O (1 ml). The mixture was stirred for 24 h and extracted with ether. The ether layer, after being dried over anhydrous sodium sulfate, was treated with a saturated ether solution of 2,4-dinitrophenylhydrazine in large excess, and with concentrated HCl. After washing of the reaction mixture with water twice, the ether was evaporated off, and the residue was dissolved in MeOH and shown to be identical with standard hydrazone, produced from an authentic sample of the aldehydes, by HPLC [column, YMC-Pack R-ODS-7 (4.6 $\times$ 250 mm); solvent, MeOH-H₂O (90:10); wavelength, 360 nm] comparison.

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References

- 1) T. Reichstein, *Helv. Chim. Acta*, **15**, 1100 (1932).
- 2) S. Arnott, A. W. Davie, and J. M. Robertson, *J. Chem. Soc.*, **1961**, 4183.
- 3) D. L. Dreyer, *J. Org. Chem.*, **32**, 3442 (1967).
- 4) Y. Hirose, *Chem. Pharm. Bull.*, **11**, 535 (1963).
- 5) T. Kubota, T. Kamikawa, T. Tokoroyama, and T. Matsuura, *Tetrahedron Lett.*, **1961**, 325.
- 6) J. Ahmad, K. Wizarat, K. M. Shamsuddin, and J. D. Connolly, *Phytochemistry*, **23**, 1269 (1984).
- 7) R. D. Bennett and S. Hasegawa, *Tetrahedron*, **37**, 17 (1981).
- 8) M. Nakatani, H. Takao, T. Iwashita, and H. Naoki, *Bull. Chem. Soc. Jpn.*, **60**, 2503 (1987).
- 9) T. Sugimoto, A. Ueno, S. kadota, C. Cui, and T. Kikuchi, *Chem. Pharm. Bull.*, **36**, 1237 (1988).
- 10) R. Tschesche and W. Werner, *Tetrahedron*, **23**, 1873 (1967).
- 11) T. Kimimado, C.-F. Chang, S. Murakoshi, A. Sakurai, and S. Tamura, *Agric. Biol. Chem.*, **40**, 605 (1976).