Nine Triterpene Dimers from *Maytenus chuchuhuasca*

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Nine regioisomeric and stereoisomeric triterpene dimers, named xuxuarine Hα (**1**), xuxuarine Hβ (**2**), xuxuarine Iα (**3**), xuxuarine Iβ (**4**), isoxuxuarine Hα (**5**), 7,8-dihydroisoxuxuarine Hα (**6**), 7,8-dihydroisoxuxuarine Iα (**7**), xuxuarine Jα (**8**), and xuxuarine Kα (**9**), were isolated from the Brazilian medicinal plant 'xuxuá' (*Maytenus chuchuhuasca* RAYMOND-HAMET et COLAS). Their structures were elucidated on the basis of several spectroscopic analyses including 2D-NMR experiments, mass spectra, and circular dichroism (CD) studies.

Introduction. – Plants belonging to the genus *Maytenus* (Celastraceae) are widely used in folk medicines in South America [1], and they are rich sources of terpenoids including dihydro-β-agarofuran sesquiterpenes [2], highly oxidized friedelane triterpenes [3], and several types of triterpene dimers [4–6]. The triterpene dimers comprise quite a unique class of compounds, which are composed of two quinonemethide-derived triterpenes, such as pristimerin, tingenone, 22β-hydroxytingenone, and their congeners[4]), joined by two ether linkages between the A rings or between the A and B rings of quinoid and aromatic triterpenes [5]. The triterpene dimers have been isolated exclusively from Celastraceae plants, mainly from *Maytenus* species, and have been reported by only two groups, *González* and co-workers [4] and our group [5][6]. We have already reported four triterpene dimers obtained from the Paraguayan folk medicinal plant 'cangorosa' (*M. ilicifolia* MART.) [6], and nineteen dimers from a Brazilian 'xuxuá' (*M. chuchuhuasca* RAYMOND-HAMET et COLAS) [5]. We have established a general methodology for elucidating their regioisomeric and stereoisomeric structures based on several spectroscopic procedures including comparisons of ^{1}H- and ^{13}C-NMR chemical shifts, NOE (or ROE) correlations in NOESY (ROESY)

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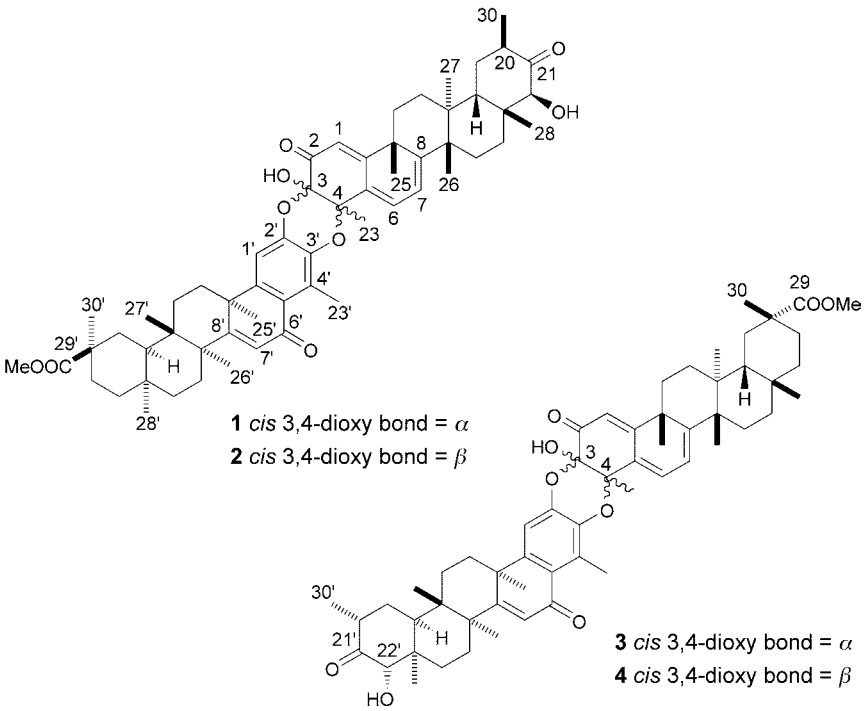
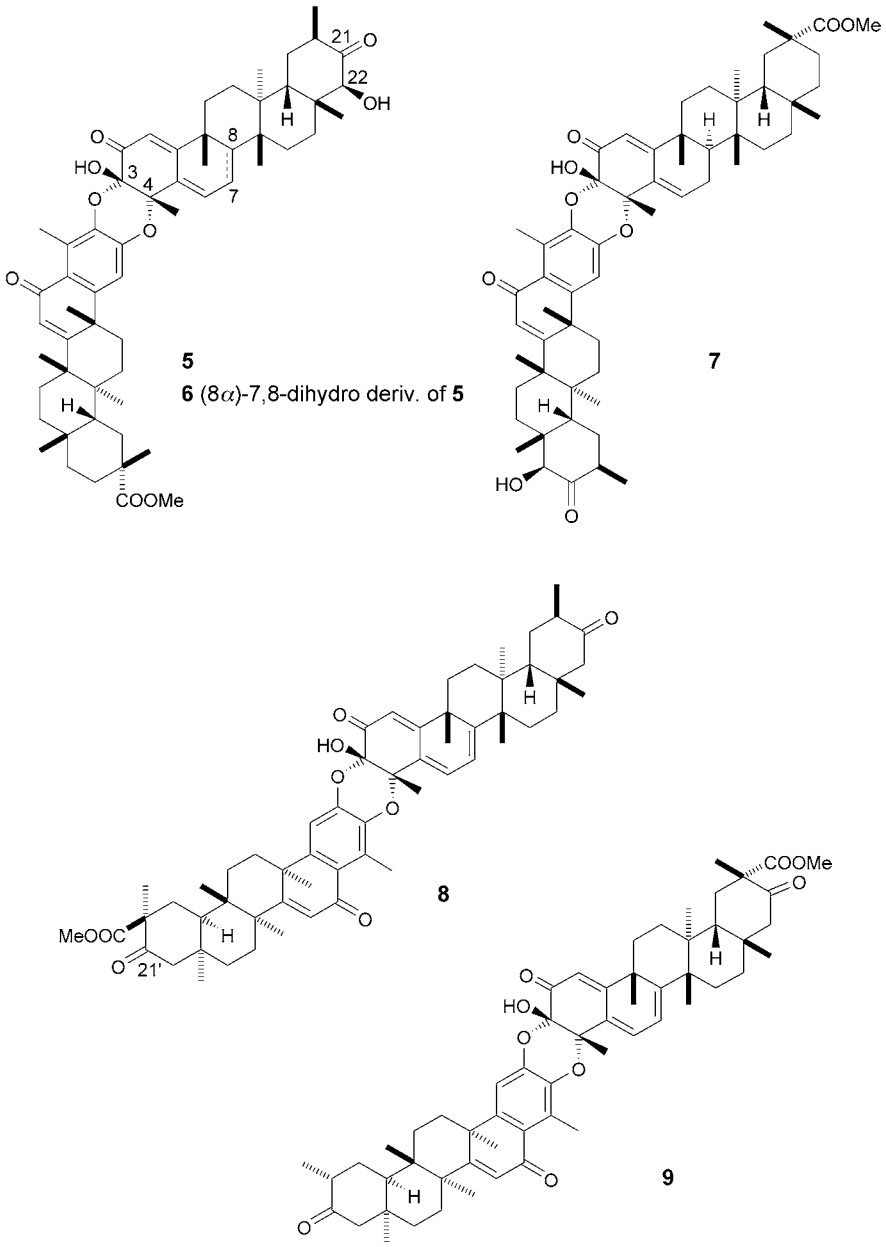
4) Pristimerin = (9β,13α,14β,20α)-3-hydroxy-9,13-dimethyl-2-oxo-24,25,26-trinoroleana-1(10),3,5,7-tetraen-29-oic acid methyl ester; tingenone = (9β,13α,14β,20β)-3-hydroxy-9,13-dimethyl-24,25,26,30-tetranoroleana-1(10),3,5,7-tetraene-2,21-dione.

plots, *retro-Diels–Alder*-type fragmentations in mass spectra, and exciton couplings in circular dichroism (CD) spectra [5].

We have isolated another nine triterpene dimers from 'xuxuá' [7]: xuxuarines Hα (**1**), Hβ (**2**), Iα (**3**), Iβ (**4**), isoxuxuarine Hα (**5**), 7,8-dihydroisoxuxuarine Hα (**6**), 7,8-dihydroisoxuxuarine Iα (**7**), xuxuarines Jα (**8**), and Kα (**9**). We report their structure elucidation by spectral analyses.

Results and Discussion. – Compounds **1**–**5** were obtained as yellow amorphous solids. They all give FAB-MS with an $[M+H]^+$ ion peak at *m*/*z* 915.5, and they all have the molecular formula $C_{58}H_{74}O_9$ based on HR-FAB-MS analyses. Their ^{1}H- and ^{13}C-NMR spectral data (*Tables 1* and *2*) indicate that they are triterpene dimers composed of a pristimerin-type triterpene unit and a 22β-hydroxytingenone-type triterpene unit[4]), one in quinoid form and the other in aromatic form. Their NMR chemical shifts are typical of triterpene dimers of this class [5]. We have already proposed [5] how the noticeable differences in ^{1}H- and ^{13}C-NMR chemical shifts can be interpreted to elucidate their regioisomeric (xuxuarine-type and isoxuxuarine-type) and stereoisomeric (α- and β-type) structures regarding the connecting *cis* 3,4-dioxy bonds. From the spectral evidence, we can conclude that **1**–**5** are xuxuarines Hα (**1**), Hβ (**2**), Iα (**3**), Iβ (**4**), and isoxuxuarine Hα (**5**), respectively.





Typically for the dimers **1**–**5**, two *s*, two *d*, and one *dd* appear in the low-field region (δ 6–7) of their ^{1}H-NMR spectra, which are assignable to H–C(1′), H–C(7′), H–C(1), H–C(7), and H–C(6), respectively, besides a D_2O-exchangeable signal of OH–C(3) around δ 5. Moreover, the following signals typical of pristimerin-type triterpenes are present: Me ester signals at δ 3.5–3.6 and high-field-shifted Me signals around δ 0.55 assignable to COOMe at C(20) and Me(27), respectively. They have the following shifts typical of 22β-hydroxytingenone-type triterpenes: Me *d* signals at δ 1.05, pairs of CH *d* and D_2O-exchangeable signals at δ 4.5

Table 1. *Typical ^{1}H-NMR Chemical Shifts of* **1**–**9**[a]). δ in ppm, J in Hz.

1	**2**	**3**	**4**	
H–C(1)	6.10 ($d, J = 1.6$)	6.10 ($d, J = 1.7$)	6.09 ($d, J = 1.6$)	6.08 ($d, J = 1.7$)
OH–C(3)	5.09 (s)	5.13 (s)	5.10 (s)	5.16 (s)
H–C(6)	6.29 ($dd, J = 1.6, 6.6$)	6.57 ($dd, J = 1.7, 7.0$)	6.25 ($dd, J = 1.6, 6.6$)	6.53 ($dd, J = 1.7, 6.8$)
H–C(7)	6.00 ($d, J = 6.6$)	6.14 ($d, J = 7.0$)	5.95 ($d, J = 6.6$)	6.09 ($d, J = 6.8$)
H_α–C(19)	–	–	2.40 ($d, J = 16.1$)	2.38 ($d, J = 16.5$)
H_α–C(20)	2.63 (m)	2.64 (m)	–	–
H_α–C(22)	4.48 (br. $d, J = 4.4$)	4.51 (br. $d, J = 4.4$)	–	–
OH_β–C(22)	3.59 ($d, J = 4.4$)	3.63 ($d, J = 4.4$)	–	–
Me(23)	1.60 (s)	1.60 (s)	1.59 (s)	1.59 (s)
Me(25)	1.49 (s)	1.44 (s)	1.43 (s)	1.34 (s)
Me(26)	1.27 (s)	1.27 (s)	1.18 (s)	1.16 (s)
Me(27)	1.00 (s)	0.97 (s)	0.55 (s)	0.53 (s)
Me(28)	0.84 (s)	0.83 (s)	1.07 (s)	1.06 (s)
Me(30)	1.06 ($d, J = 6.2$)	1.06 ($d, J = 6.4$)	1.17 (s)	1.17 (s)
COOMe	–	–	3.60 (s)	3.59 (s)
H–C(1′)	6.80 (s)	6.75 (s)	6.80 (s)	6.75 (s)
H–C(7′)	6.25 (s)	6.22 (s)	6.30 (s)	6.26 (s)
H_α–C(19′)	2.40 ($d, J = 15.4$)	2.40 ($d, J = 15.6$)	–	–
H–C(20′)	–	–	2.65 (m)	2.61 (m)
H_α–C(22′)	–	–	4.53 (br. $d, J = 4.2$)	4.52 (br. $d, J = 4.5$)
OH_β–C(22′)	–	–	3.62 ($d, J = 4.2$)	3.62 ($d, J = 4.5$)
Me(23′)	2.75 (s)	2.74 (s)	2.75 (s)	2.75 (s)
Me(25′)	1.49 (s)	1.49 (s)	1.57 (s)	1.55 (s)
Me(26′)	1.27 (s)	1.27 (s)	1.38 (s)	1.37 (s)
Me(27′)	0.54 (s)	0.55 (s)	0.99 (s)	1.00 (s)
Me(28′)	1.09 (s)	1.09 (s)	0.86 (s)	0.86 (s)
Me(30′)	1.16 (s)	1.16 (s)	1.05 ($d, J = 6.2$)	1.03 ($d, J = 6.4$)
COOMe	3.54 (s)	3.49 (s)	–	–

	5	**6**	**7**	**8**	**9**
H–C(1)	6.11 ($d, J = 1.7$)	5.99 (br. s)	5.98 (s)	6.12 ($d, J = 1.7$)	6.12 ($d, J = 1.7$)
OH–C(3)	4.98 (s)	4.92 (s)	4.93 (s)	5.10 (s)	5.10 (s)
H–C(6)	6.37 (dd, $J = 1.7, 6.6$)	6.37 (br. s)	6.26 (br. s)	6.29 (dd, $J = 1.7, 6.6$)	6.27 (dd, $J = 1.7, 6.6$)
H–C(7)	6.01 ($d, J = 6.6$)	–	–	5.99 ($d, J = 6.6$)	5.97 ($d, J = 6.6$)
H_α–C(19)	–	–	–	–	2.78 ($d, J = 15.0$)
H–C(20)	2.65 (m)	2.70 (m)	–	2.47 (m)	2.49 (m)
H_α–C(22)	4.47 (br. d, $J = 4.4$)	4.49 (br. d, $J = 4.4$)	–	2.85 (d, $J = 14.7$)	3.16 (d, $J = 14.3$)
OH_β–C(22)	3.63 ($d, J = 4.4$)	3.63 ($d, J = 4.4$)	–	–	–
Me(23)	1.59 (s)	1.49 (s)	1.47 (s)	1.61 (s)	1.60 (s)
Me(25)	1.50 (s)	1.13 (s)	1.06 (s)	1.49 (s)	1.47 (s)
Me(26)	1.28 (s)	1.06 (s)	0.97 (s)	1.26 (s)	1.25 (s)
Me(27)	0.99 (s)	1.23 (s)	0.75 (s)	1.00[b]) (s)	0.77 (s)
Me(28)	0.83 (s)	0.82 (s)	1.05 (s)	1.00[b]) (s)	0.98 (s)
Me(30)	1.05 ($d, J = 6.4$)	1.07 ($d, J = 6.4$)	1.18 (s)	0.99 ($d, J = 6.0$)	1.34 (s)
COOMe	–	–	3.64 (s)	–	3.63 (s)
H–C(1′)	7.01 (s)	6.97 (s)	6.97 (s)	6.81 (s)	6.81 (s)
H–C(7′)	6.22 (s)	6.23 (s)	6.27 (s)	6.26 (s)	6.29 (s)
H_α–C(19′)	2.47 ($d, J = 15.5$)	2.45 ($d, J = 16.0$)	–	2.78 ($d, J = 15.7$)	–
H–C(20′)	–	–	2.66 (m)	–	–
H_α–C(22′)	–	–	4.55 (br. $d, J = 4.4$)	3.21 ($d, J = 14.5$)	2.91 ($d, J = 14.3$)
OH_β–C(22′)	–	3.63 ($d, J = 4.4$)	–	–	
Me(23′)	2.49 (s)	2.53 (s)	2.54 (s)	2.75 (s)	2.75 (s)
Me(25′)	1.55 (s)	1.55 (s)	1.60 (s)	1.53 (s)	1.55 (s)
Me(26′)	1.30 (s)	1.30 (s)	1.40 (s)	1.34 (s)	1.36 (s)
Me(27′)	0.63 (s)	0.62 (s)	1.07 (s)	0.74 (s)	0.98 (s)
Me(28′)	1.11 (s)	1.11 (s)	0.88 (s)	0.99[b]) (s)	1.00 (s)
Me(30′)	1.19 (s)	1.19 (s)	1.05 ($d, J = 5.8$)	1.33 (s)	0.98 ($d, J = 6.0$)
COOMe	3.60 (s)	3.56 (s)	–	3.57 (s)	–

[a]) All measurements were made in $CDCl_3$ at 400 MHz, 300 K; assignments from HSQC and HMBC.
[b]) Assignments may be reversed.

Table 2. *^{13}C-NMR Chemical Shifts of* **1**–**9**[a]). δ in ppm.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
C(1)	115.5 (*d*)	115.0 (*d*)	115.2 (*d*)	114.6 (*d*)	116.0 (*d*)	113.0 (*d*)	113.1 (*d*)	115.5 (*d*)	115.5 (*d*)
C(2)	190.3 (*s*)	189.5 (*s*)	190.2 (*s*)	189.4 (*s*)	190.4 (*s*)	191.6 (*s*)	191.4 (*s*)	190.2 (*s*)	189.5 (*s*)
C(3)	92.0 (*s*)	91.0 (*s*)	92.0 (*s*)	91.1 (*s*)	91.8 (*s*)	91.3 (*s*)	91.3 (*s*)	92.0 (*s*)	92.0 (*s*)
C(4)	79.4 (*s*)	76.8[d]) (*s*)	79.4 (*s*)	77.2[d]) (*s*)	79.3 (*s*)	79.4 (*s*)	79.5 (*s*)	79.4 (*s*)	79.4 (*s*)
C(5)	130.3 (*s*)	132.1 (*s*)	129.8 (*s*)	131.8 (*s*)	130.9 (*s*)	134.3 (*s*)	134.1 (*s*)	130.3 (*s*)	130.2 (*s*)
C(6)	126.6 (*d*)	128.7 (*d*)	126.8 (*d*)	128.9 (*d*)	126.2 (*d*)	134.1 (*d*)	133.8 (*d*)	126.6 (*d*)	126.5 (*d*)
C(7)	116.3 (*d*)	117.3 (*d*)	116.1 (*d*)	117.2 (*d*)	116.4 (*d*)	24.2 (*t*)	24.2 (*t*)	116.2 (*d*)	116.3 (*d*)
C(8)	160.1 (*s*)	163.0 (*s*)	161.5 (*s*)	164.4 (*s*)	159.9 (*s*)	41.1 (*d*)	41.6 (*d*)	160.4 (*s*)	160.5 (*s*)
C(9)	41.6 (*s*)	43.7[b]) (*s*)	42.0 (*s*)	44.0 (*s*)	41.4 (*s*)	37.3 (*s*)	37.4 (*s*)	41.7 (*s*)	41.8 (*s*)
C(10)	173.8 (*s*)	173.0 (*s*)	174.3 (*s*)	173.2 (*s*)	173.2 (*s*)	169.8 (*s*)	170.0 (*s*)	173.7 (*s*)	173.6 (*s*)
C(11)	33.4 (*t*)	33.3 (*t*)	32.9 (*t*)	32.8 (*t*)	33.5 (*t*)	30.7 (*t*)	32.0 (*t*)	33.2 (*t*)	32.8 (*t*)
C(12)	29.9[b]) (*t*)	29.9 (*t*)	29.5 (*t*)	29.6[b]) (*t*)	29.9[b]) (*t*)	29.7 (*t*)	29.4 (*t*)	29.8 (*t*)	29.5 (*t*)
C(13)	39.4 (*s*)	39.8 (*s*)	38.1 (*s*)	38.6 (*s*)	39.5 (*s*)	40.0[b]) (*s*)	40.1 (*s*)	39.4 (*s*)	38.5 (*s*)
C(14)	44.0 (*s*)	43.6[b]) (*s*)	44.7 (*s*)	44.4 (*s*)	43.9 (*s*)	39.9[b]) (*s*)	38.9 (*s*)	44.3 (*s*)	44.2 (*s*)
C(15)	28.0 (*t*)	28.2 (*t*)	28.4 (*t*)	28.6 (*t*)	28.1 (*t*)	27.7 (*t*)	28.3 (*t*)	28.3 (*t*)	28.4 (*t*)
C(16)	29.5 (*t*)	29.5 (*t*)	36.3 (*t*)	36.4 (*t*)	29.5[c]) (*t*)	29.3 (*t*)	36.0 (*t*)	35.4 (*t*)	35.5 (*t*)
C(17)	44.7 (*s*)	45.0 (*s*)	30.5 (*s*)	30.5 (*s*)	44.7 (*s*)	44.7[c]) (*s*)	30.1 (*s*)	38.2 (*s*)	37.1 (*s*)
C(18)	44.9 (*d*)	44.8 (*d*)	44.1 (*d*)	44.3 (*d*)	44.9 (*d*)	45.4 (*d*)	44.6 (*d*)	43.4 (*d*)	43.6 (*d*)
C(19)	32.1 (*t*)	31.9 (*t*)	30.9 (*t*)	30.8 (*t*)	32.1 (*t*)	31.7 (*t*)	30.5 (*t*)	32.1 (*t*)	34.2[b]) (*t*)
C(20)	40.8 (*d*)	40.9 (*d*)	40.4 (*s*)	40.4 (*s*)	40.8 (*d*)	41.2 (*d*)	40.5 (*s*)	41.9 (*d*)	53.6 (*s*)
C(21)	213.6 (*s*)	213.5 (*s*)	29.8 (*t*)	30.1[c]) (*t*)	213.5 (*s*)	213.8 (*s*)	29.7 (*t*)	213.6 (*s*)	209.4 (*s*)
C(22)	76.5 (*t*)	76.4 (*t*)	34.7 (*t*)	34.7 (*t*)	76.5 (*t*)	77.2 (*t*)	36.0 (*t*)	52.5 (*t*)	51.9 (*t*)
C(23)	22.2 (*q*)	24.6 (*q*)	22.2 (*q*)	24.6 (*q*)	22.2 (*q*)	22.8 (*q*)	22.7 (*q*)	22.3 (*q*)	22.3 (*q*)
C(25)	35.6 (*q*)	40.1 (*q*)	34.9 (*q*)	39.1 (*q*)	35.8 (*q*)	23.0 (*q*)	22.1 (*q*)	35.6 (*q*)	35.2 (*q*)
C(26)	22.4 (*q*)	22.3 (*q*)	22.5 (*q*)	22.4 (*q*)	22.4 (*q*)	15.8 (*q*)	16.0 (*q*)	22.3 (*q*)	22.8 (*q*)
C(27)	20.9 (*q*)	20.4 (*q*)	18.7 (*q*)	18.2 (*q*)	20.9 (*q*)	18.9 (*q*)	16.8 (*q*)	20.0 (*q*)	18.2 (*q*)
C(28)	25.0 (*q*)	25.0 (*q*)	31.6 (*q*)	31.6 (*q*)	25.0 (*q*)	25.1 (*q*)	31.7 (*q*)	32.6 (*q*)	32.6 (*q*)
C(29)	–	–	178.9 (*q*)	178.8 (*s*)	–	–	179.0 (*s*)	–	175.1 (*s*)
C(30)	14.8 (*q*)	14.8 (*q*)	32.7 (*q*)	32.8 (*q*)	14.7 (*q*)	14.9 (*q*)	32.3 (*q*)	15.1 (*q*)	25.1 (*q*)
COO*Me*	–	–	51.6 (*q*)	51.6 (*q*)	–	–	51.7 (*q*)	–	52.6 (*q*)
C(1′)	111.3 (*d*)	110.6 (*d*)	111.4 (*d*)	110.5 (*d*)	110.6 (*d*)	110.6 (*d*)	110.4 (*d*)	111.4 (*d*)	111.4 (*d*)
C(2′)	144.6 (*s*)	145.1 (*s*)	144.7 (*s*)	145.2 (*s*)	144.4 (*s*)	144.5 (*s*)	144.5 (*s*)	144.7 (*s*)	144.6 (*s*)
C(3′)	137.6 (*s*)	137.5 (*s*)	137.7 (*s*)	137.6 (*s*)	138.3 (*s*)	138.2 (*s*)	138.4 (*s*)	137.7 (*s*)	137.6 (*s*)
C(4′)	127.7 (*s*)	128.4 (*s*)	127.8 (*s*)	128.6 (*s*)	129.3 (*s*)	129.3 (*s*)	129.6 (*s*)	127.8 (*s*)	127.8 (*s*)
C(5′)	124.5 (*s*)	123.9 (*s*)	124.5 (*s*)	123.9 (*s*)	123.4 (*s*)	123.7 (*s*)	123.4 (*s*)	124.5 (*s*)	124.5 (*s*)
C(6′)	187.8 (*s*)	187.3 (*s*)	187.7 (*s*)	187.2 (*s*)	187.2 (*s*)	187.2 (*s*)	187.0 (*s*)	187.7 (*s*)	187.7 (*s*)
C(7′)	126.2 (*d*)	126.1 (*d*)	126.1 (*d*)	126.2 (*d*)	126.2 (*d*)	126.3 (*d*)	126.3 (*d*)	126.2 (*d*)	126.1 (*d*)
C(8′)	171.6 (*s*)	171.7 (*s*)	170.4 (*s*)	169.9 (*s*)	171.1 (*s*)	171.1 (*s*)	169.7 (*s*)	170.8 (*s*)	170.7 (*s*)
C(9′)	39.9 (*s*)	40.0 (*s*)	39.7 (*s*)	39.7 (*s*)	40.8 (*s*)	40.1 (*s*)	39.7 (*s*)	39.8 (*s*)	39.8 (*s*)
C(10′)	150.5 (*s*)	151.2 (*s*)	150.4 (*s*)	151.1 (*s*)	151.8 (*s*)	151.8 (*s*)	151.7 (*s*)	150.3 (*s*)	150.4 (*s*)
C(11′)	34.2 (*t*)	34.0 (*t*)	34.5 (*t*)	34.3 (*t*)	34.3 (*t*)	34.3 (*t*)	34.6 (*t*)	34.1 (*t*)	34.3[b]) (*t*)
C(12′)	29.9[b]) (*t*)	29.9 (*t*)	30.2 (*t*)	30.1[c]) (*t*)	29.8[b]) (*t*)	29.9 (*t*)	29.8 (*t*)	29.9 (*t*)	30.1 (*t*)
C(13′)	39.0 (*s*)	39.0 (*s*)	40.1 (*s*)	40.1 (*s*)	39.0 (*s*)	39.0 (*s*)	40.1 (*s*)	39.2 (*s*)	40.2 (*s*)
C(14′)	44.9 (*s*)	44.7 (*s*)	44.0 (*s*)	43.9 (*s*)	44.9 (*s*)	44.8[c]) (*s*)	44.0 (*s*)	44.3 (*s*)	44.3 (*s*)
C(15′)	28.5 (*t*)	28.5 (*t*)	28.2 (*t*)	28.2 (*t*)	28.6 (*t*)	28.6 (*t*)	28.2 (*t*)	28.6 (*t*)	28.4 (*t*)
C(16′)	36.4 (*t*)	36.4 (*t*)	29.6 (*t*)	29.5[b]) (*t*)	36.4 (*t*)	36.4 (*t*)	29.6 (*t*)	35.7 (*t*)	35.5 (*t*)
C(17′)	30.5 (*s*)	30.5 (*s*)	44.9 (*s*)	44.9 (*s*)	30.5 (*s*)	30.5 (*s*)	44.9[b]) (*s*)	37.1 (*s*)	38.2 (*s*)
C(18′)	44.3 (*d*)	44.2 (*d*)	45.0 (*d*)	45.0 (*d*)	44.3 (*d*)	44.3 (*d*)	45.0[b]) (*d*)	43.9 (*d*)	43.5 (*d*)
C(19′)	30.8 (*t*)	30.9 (*t*)	32.0 (*t*)	31.9 (*t*)	31.1 (*t*)	31.1 (*t*)	30.1 (*t*)	34.2 (*t*)	32.0 (*t*)
C(20′)	40.4 (*s*)	40.5 (*s*)	40.9 (*d*)	40.9 (*d*)	40.7 (*s*)	40.6 (*s*)	40.9 (*d*)	53.6 (*s*)	41.9 (*d*)
C(21′)	29.8[b]) (*t*)	29.7 (*t*)	213.7 (*t*)	213.6 (*s*)	29.7[c]) (*s*)	29.7 (*t*)	213.6 (*s*)	209.4 (*s*)	213.7 (*s*)
C(22′)	34.8 (*t*)	35.0 (*t*)	76.5 (*t*)	76.7 (*t*)	35.0 (*t*)	35.0 (*t*)	76.1 (*d*)	51.9 (*t*)	52.6 (*t*)
C(23′)	13.0 (*q*)	13.2 (*q*)	13.0 (*q*)	13.2 (*q*)	13.3 (*q*)	13.4 (*q*)	13.4 (*q*)	13.0 (*q*)	13.0 (*q*)
C(25′)	37.6 (*q*)	37.7 (*q*)	38.7 (*q*)	38.9 (*q*)	37.7 (*q*)	37.6 (*q*)	38.9 (*q*)	38.2 (*q*)	38.4 (*q*)
C(26′)	20.8 (*q*)	20.9 (*q*)	20.9 (*q*)	20.9 (*q*)	20.8 (*q*)	20.8 (*q*)	20.9 (*q*)	21.2 (*q*)	20.8 (*q*)
C(27′)	18.3 (*q*)	18.5 (*q*)	20.6 (*q*)	20.7 (*q*)	18.6 (*q*)	18.6 (*q*)	20.8 (*q*)	17.8 (*q*)	19.7 (*q*)
C(28′)	31.6 (*q*)	31.6 (*q*)	25.0 (*q*)	25.0 (*q*)	31.6 (*q*)	31.6 (*q*)	25.0 (*q*)	32.6 (*q*)	32.6 (*q*)
C(29′)	178.8 (*s*)	179.1 (*s*)	–	–	179.4 (*s*)	179.4 (*s*)	–	175.0 (*q*)	–
C(30′)	32.7 (*q*)	32.9 (*q*)	14.8 (*q*)	14.7 (*q*)	33.0 (*q*)	33.0 (*q*)	14.8 (*q*)	25.1 (*q*)	15.1 (*q*)
COO*Me*	51.6 (*q*)	51.4 (*q*)	–	–	51.8 (*q*)	51.7 (*q*)	–	52.5 (*q*)	–

[a]) All measurements were made in $CDCl_3$ at 100 MHz, 300 K; assignments from HSQC and HMBC. [b])[c]) Corresponding assignments may be reversed. [d]) Signals superimposed on solvent signals.

and 3.6, each assignable to Me(30), H_α–C(22), and OH_β–C(22). Comparisons of small differences in the chemical shifts of Me(23′), *i.e.*, δ(H) 2.7 for the xuxuarine-type and δ(H) 2.5 for the isoxuxuarine-type [5], and of C(3), C(4), and C(23) and H–C(6), *i.e.*, δ(C) 92, 79, and 22 and δ(H) 6.3 for the α-type, and δ(C) 91, 77, and 24 and δ(H) 6.5 for the β-type [5], can be used to elucidate the structure of **1**–**5**. The chemical shifts assignable to C(3), C(4), and C(23), and H–C(6) and Me(23′) appear at: δ(C) 92.0, 79.4, and 22.2, and δ(H) 6.29 and 2.75 for **1**; δ(C) 91.0, 76.8, and 24.6, and δ(H) 6.57 and 2.74 for **2**; δ(C) 92.0, 79.4, and 22.2, and δ(H) 6.25 and 2.75 for **3**; δ(C) 91.1, 77.2, and 24.6 and δ(H) 6.53 and 2.75 for **4**; δ(C) 91.8, 79.3, and 22.2, and δ(H) 6.37 and 2.49 for **5**. Thus, **1**–**4** are xuxuarine-type regioisomers, while **5** is an isoxuxuarine-type regioisomer, and **1**, **3**, and **5** have α-type configuration, while **2** and **4** have β-type configuration. The regioisomer and stereoisomer attributions are confirmed by ROESY and CD spectra, as follows: On one hand, cross-peaks are observed between H–C(6) and Me(23′) for **1**–**4**, and between H–C(6) and H–C(1′) for **5** in their ROESY plot, on the other hand, a positive first *Cotton* effect for **1**, **3**, and **5**, and a negative first *Cotton* effect for **2** and **4** are observed in their CD spectrum. In the FAB-MS, **1**, **2** and **5** have *retro-Diels–Alder*-type fragmentation-ion peaks at *m*/*z* 437 and 481, while **3** and **4** have fragmentation-ion peaks at *m*/*z* 451 and 464, indicating that the 22β-hydroxytingenone-type and pristimerin-type unit is in the quinoid and aromatic form, respectively, in **1**, **2**, and **5**, and in the aromatic and quinoid form, respectively, in **3** and **4**.

Compounds **6** and **7** were obtained as pale-yellow amorphous solids. Both compounds exhibit $[M+H]^+$ ion peaks at *m*/*z* 917.5 in the FAB-MS, and have the molecular formula $C_{58}H_{74}O_9$, as determined by HR-FAB-MS analyses. From their ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*), **6** and **7** are both triterpene dimers composed of a pristimerin-type triterpene unit and a 22β-hydroxytingenone-type unit[4]), similarly to **1**–**5**. However, the disappearance of the low-field H–C(7) signal and the breadth of the H–C(6) signal in the ^{1}H-NMR spectra suggest that the quinoid triterpene unit in each molecule is partially saturated, *i.e.*, saturation between C(7) and C(8). Therefore, they should be 7,8-dihydro derivatives of xuxuarines or isoxuxuarines of H or I class. Further spectral data confirm that **6** and **7** are 7,8-dihydroisoxuxuarine Hα and 7,8-dihydroisoxuxuarine Iα, respectively.

The sets of chemical shifts of **6** and **7**, assignable to C(3), C(4), C(23), H–C(6), and Me(23′) (δ(C) 91.3, 79.4, and 22.8, and δ(H) 6.37 and 2.53 for **6**; δ(C) 91.3, 79.5, and 22.7, and δ(H) 6.26 and 2.54 for **7**) indicate that they both have isoxuxuarine-type conjugation with α orientation about the *cis* 3,4-dioxy bond. This is confirmed by their ROESY and CD spectra, with a ROE correlation between H–C(6) and H–C(1′) and a positive first *Cotton* effect for both compounds. The ROESY plots also show a ROE correlation between H–C(8) and Me(27), confirming the α orientation of H–C(8) in **6** and **7**. In the MS, *retro-Diels–Alder*-type fragmentation peaks are at *m*/*z* 439 and 481 for **6** and at *m*/*z* 452 and 466 for **7**.

Compounds **8** and **9** are both pale-yellow amorphous solids. They both have a $[M+H]^+$ ion peak at *m*/*z* 913.5 in the FAB-MS, and a molecular formula $C_{58}H_{72}O_9$, as determined by HR-FAB-MS. Their ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) show that they are composed of a tingenone-type triterpene unit and a pristimerin-like triterpene unit[4]), connected *via* a xuxuarine-α-type linkage. CD and ROESY data confirm the regioisomeric xuxuarine structure and the α-type configuration of the *cis* 3,4-dioxy bond of **8** and **9**, which we name xuxuarines Jα, and Kα, respectively. To the best of our knowledge, their new triterpene unit, namely 21-oxopristimerin, has not been reported in the literature.

The molecular formula and the CH *d* at δ(H) 3.2 and carbonyl C=O at δ(C) 209 in the NMR spectra of **8** and **9** indicate that the triterpene skeleton is oxidized. The oxidation site was determined by HMBC experiments. In the spectra, the signal at δ(C) 209 correlates with the CH *d* at δ(H) 3.2 and a Me signal at δ(H) 1.3, and the latter signal correlates with the ester carbonyl signal, *i.e.*, with C(29). Therefore, the oxidation site is

at C(21) of the pristimerin-type triterpene unit. The MS fragment patterns established whether the units are in quinoid or aromatic forms. The *retro-Diels–Alder*-type fragmentation peaks are at *m/z* 421 and 495 in **8**, and at *m/z* 437 and 479 in **9**.

We have already proposed biosynthesis routes for triterpene dimers of this class, and have explained the diverse formation of the regioisomers and stereoisomers of triterpene dimers [5]. That is, a 2,3-dioxo-type triterpene, which is in equilibrium with its quinoid form, approaches from the front or the reverse direction to the counterpart triterpene molecule from the upper or the lower side to form *Diels–Alder*-type adducts. There are at least three kinds of well-known quinoid triterpenes, *i.e.*, tingenone, 22β-hydroxytingenone, and pristimerin[4]), and formation of dimers from themselves gives the xuxuarines of the A, B, and E series, respectively. These dimers can have two types of stereoisomers, the α- and β-types, and two types of regioisomers, the xuxuarine- and isoxuxuarine types. There are $3 \times 3 \times 2 \times 2 = 36$ permutations of forming triterpene dimers by using all three kinds of quinoid triterpenes. There are some other kinds of quinoid triterpenes [3], 7,8-dihydro derivatives, and undiscovered derivatives such as 21-oxopristimerin in xuxuarines Jα (**8**) and Kα (**9**). There are also triterpene dimers of the cangorosin A class, which are composed of one quinoid and one aromatic triterpene unit joined between the A and B rings [6]. Thus, the chemical diversity of triterpene dimers is enormous.

Experimental Part

General. The procedures have been described previously [5]; otherwise specified as follows. HPLC: *Supelcosil-ABZ + Plus* columns (4.6 mm i.d. × 250 mm for anal., 21.2 mm i.d. × 250 mm for prep.; *Supelco*, USA) packed with 5-μm *ABZ + Plus* gel, and *Fluofix-120E* columns (4.6 mm i.d. × 250 mm for anal., 20 mm i.d. × 250 mm for prep.; *NEOS, Co.*, Japan) packed with 5-μm silica gel with a branched-fluorocarbon-bonded phase. CD: λ ($\Delta\varepsilon$) in nm. UV: λ_{max} (log ε) in nm. IR: in cm^{-1}. NMR: *Varian Unity-Plus-400*; ^1H (400 MHz), ^{13}C (100 MHz). MS: in *m/z* (rel. %).

Plant Material. The specification and the location of the voucher specimen have been described previously [5].

Extraction and Isolation. The extraction and primary fractionation processes have been described previously [5]. The triterpene dimers have been isolated from the *Fr. IV*, *V*, and *VI*, previously. The granddaughter fractions derived from the above three fractions were re-checked by reversed-phase TLC (MeCN); the fractions containing triterpene dimers appeared as pale-yellow spots, usually with R_f *ca.* 0.1 – 0.5, and were further purified. Primary HPLC analysis (80 → 100% aq. MeCN), and then conventional *ODS*-HPLC columns each in isocratic mode were run. Good separations of the triterpene dimers were difficult; however, a couple of brands of *ODS*-HPLC columns were tried; changing the eluting solvents was not helpful for many cases. Among several types of packing gels for HPLC columns, a *Supelcosil ABZ + Plus* column gave better separations for most of the dimers. Although a *Fluofix* column also gave different separation patterns from the *ODS* column, base-line separation was not good enough in most cases. Continuous purification steps of several granddaughter fractions by using *ABZ + Plus* and *Fluofix* prep. HPLC columns in combination finally gave the nine new triterpene dimers: xuxuarine Hα (**1**; 0.00008% *w/w*), xuxuarine Hβ (**2**; 0.00004%), xuxuarine Iα (**3**: 0.0001%), xuxuarine Iβ (**4**; 0.00007%), isoxuxuarine Hα (**5**; 0.0001%), 7,8-dihydroisoxuxuarine Hα (**6**; 0.00004%), dihydroisoxuxuarine Iα (**7**; 0.00004%), xuxuarine Jα (**8**; 0.00005%), and xuxuarine Kα (**9**; 0.00003%).

*Xuxuarine Hα (= Methyl (3*S*,4*S*,9′*R*,13*S*,13′*S*,14*S*,14′*S*,17*R*,17′*S*,18*S*,18′*R*,20*R*,20′*R*,22*S*)-3,22-Dihydroxy-2,6′,21-trioxo-2′,3′:3′,4-dioxy-29-nordi(friedela)-1(10),1′,3′,5,5′(10′),7,7′-heptaen-29′-oate*[5]) *= Methyl (1*S*,3*R*,4a*S*,4b*S*,6a*R*,8a*S*,10b*R*,12a*S*,12b*R*,14*R*,16a*S*,18a*S*,22a*S*,24b*S*,26a*R*)-1,2,3,4,4a,4b,5,6,6a,8,8a,10b,11,12,12a,12b,13,14,15,16,16a,17,18,18a,20,22a,24b,25,26,26a-Triacontahydro-1,8a-dihydroxy-3,4b,6a,10b,12a,14,16a,*

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[5]) Friedelane = (4β,5β,8α,9β,10α,13α,14β)-5,9,13-trimethyl-24,25,26-trinoroleanane.

*18a,21,22a,24b,26a-dodecamethyl-2,8,20-trioxodipiceno[2,3-*b*:4′,3′-*e*][1,4]dioxin-14-carboxylate*; **1**): Yellow amorphous solid. CD (MeOH): 357 (+17.1), 300 (+10.8), 268 (−0.8), 246.5 (−27.2). UV (MeOH): 253 (4.21), 295.5 (4.03), 379.5 (3.89). IR (KBr): 3443, 2946, 1711, 1676, 1649, 1582, 1460, 1379, 1308, 1200, 1150, 1061, 995, 870, 583. ^{1}H-NMR ($CDCl_3$): *Table 1.* ^{13}C-NMR ($CDCl_3$): *Table 2*. FAB-MS: 915.5 (28, $[M+H]^+$), 481.3 (3), 436.3 (6). HR-FAB-MS: 915.5433 ($C_{58}H_{75}O_9^+$; calc. 915.5411).

Xuxuarine Hβ (= *Methyl (3*R,*4*R,*9*R,*9′*R,*13*S,*13′*S,*14*S,*14′*S,*17*R,*17′*S,*18*S,*18′*R,*20*R,*20′*R,*22*S*)-3,22-Dihydroxy-2,6′,21-trioxo-2′,3 : 3′,4-dioxy-29-nordi(friedela)-1(10),1′,3′,5,5′(10′),7,7′-heptaen-29′-oate*[5]) = *Methyl (1*S,*3*R,*4a*S,*4b*S,*6a*R,*8a*R,*10b*R,*12a*S,*12b*R,*14*R,*16a*S,*18a*S,*22a*R,*24b*S,*26a*R*)-1,2,3,4,4a,4b,5,6,6a,8,8a,10b,11,12,12a,12b,13,14,15,16,16a,17,18,18a,20,22a,24b,25,26,26a-Triacontahydro-1,8a-dihydroxy-3,4b,6a,10b,12a,14,16a,18a,21,22a,24b,26a-dodecamethyl-2,8,20-trioxodipiceno[2,3-*b*:4′,3′-*e*][1,4]dioxin-14-carboxylate*; **2**): Yellow amorphous solid. CD (MeOH): 396 (−9.1), 330 (+10.3), 261.5 (−48.0). UV (MeOH): 254 (4.23), 298.5 (4.04), 385 (3.97). IR (KBr): 3457, 2946, 1711, 1649, 1597, 1541, 1460, 1379, 1308, 1204, 1155, 1103, 1091, 995, 870, 584. ^{1}H-NMR ($CDCl_3$): *Table 1.* ^{13}C-NMR ($CDCl_3$): *Table 2:* FAB-MS: 915.6 (23, $[M+H]^+$), 481.4 (5), 437.3 (6). HR-FAB-MS: 915.5395 ($C_{58}H_{75}O_9^+$; calc. 915.5411).

Xuxuarine Iα (= *Methyl (3*S,*4*S,*9*R,*9′*R,*13*S,*13′*S,*14*S,*14′*S,*17*S,*17′*R,*18*R,*18′*S,*20*R,*20′*R,*22′*S*)-3,22′-Dihydroxy-2,6′,21′-trioxo-2′,3 : 3′,4-dioxy-29′-nordi(friedela)-1(10),1′,3′,5,5′(10′),7,7′-heptaen-29-oate*[5]) = *Methyl (3*R,*4a*R,*4b*S,*6a*R,*8a*S,*10b*R,*12a*S,*12b*S,*14*R,*16*S,*16a*R,*18a*S,*22a*S,*24b*S,*26a*S*)-1,2,3,4,4a,4b,5,6,6a,8,8a,10b,11,12,12a,12b,13,14,15,16,16a,17,18,18a,20,22a,24b,25,26,26a-Triacontahydro-8a,16-dihydroxy-3,4b,6a,10b,12a,14,16a,18a,21,22a,24b,26a-dodecamethyl-8,15,20-trioxodipiceno[2,3-*b*:4′,3′-*e*][1,4]dioxin-3-carboxylate*; **3**): Yellow amorphous solid. CD (MeOH): 358 (+17.3), 299 (+13.7), 246.5 (−26.9). UV (MeOH): 253 (4.24), 296.5 (4.09), 382.5 (3.90). IR (KBr): 3470, 2944, 1711, 1676, 1651, 1597, 1460, 1379, 1306, 1202, 1146, 1092, 1061, 995, 870, 577. ^{1}H-NMR ($CDCl_3$): *Table 1.* ^{13}C-NMR ($CDCl_3$): *Table 2*. FAB-MS: 915.5 (25, $[M+H]^+$), 464.3 (5), 450.3 (6). HR-FAB-MS: 915.5420 ($C_{58}H_{75}O_9^+$; calc. 915.5411).

Xuxuarine Iβ (= *Methyl (3*R,*4*R,*9*R,*9′*R,*13*S,*13′*S,*14*S,*14′*S,*17*S,*17′*R,*18*R,*18′*S,*20*R,*20′*R,*22′*S*)-3,22′-Dihydroxy-2,6′,21′-trioxo-2′,3 : 3′,4-dioxy-29′-nordi(friedela)-1(10),1′,3′,5,5′(10′),7,7′-heptaen-29-oate*[5]) = *Methyl (3*R,*4a*R,*4b*S,*6a*R,*8a*R,*10b*R,*12a*S,*12b*S,*14*R,*16*S,*16a*R,*18a*S,*22a*R,*24b*S,*26a*S*)-1,2,3,4,4a,4b,5,6,6a,8,8a,10b,11,12,12a,12b,13,14,15,16,16a,17,18,18a,20,22a,24b,25,26,26a-Triacontahydro-8a,16-dihydroxy-3,4b,6a,10b,12a,14,16a,18a,21,22a,24b,26a-dodecamethyl-8,15,20-trioxodipiceno[2,3-*b*:4′,3′-*e*][1,4]dioxin-3-carboxylate*; **4**): Yellow amorphous solid. CD (MeOH): 397.5 (−7.3), 332 (+10.1), 261 (−42.1). UV (MeOH): 254 (4.18), 296.5 (3.98), 387 (4.00). IR (KBr): 3441, 2942, 1711, 1653, 1597, 1541, 1460, 1379, 1306, 1204, 1152, 1086, 1061, 1020, 858, 590. ^{1}H-NMR ($CDCl_3$): *Table 1.* ^{13}C-NMR ($CDCl_3$): *Table 2*. FAB-MS: 915.5 (14, $[M+H]^+$), 464.4 (6), 451.3 (4). HR-FAB-MS: 915.5462 ($C_{58}H_{75}O_9^+$; calc. 915.5411).

Isoxuxuarine Hα (= *Methyl (3*S,*4*S,*9*R,*9′*R,*13*S,*13′*S,*14*S,*14′*S,*17*R,*17′*S,*18*S,*18′*R,*20*R,*20′*R,*22*S*)-3,22-Dihydroxy-2,6′,21-trioxo-3,3′:2′,4-dioxy-29-nordi(friedela)-1(10),1′,3′,5,5′(10′),7,7′-heptaen-29′-oate*[5]) = *Methyl (1*S,*3*R,*4a*S,*4b*S,*6a*R,*8a*S,*12b*S,*14a*S,*17*R,*18a*R,*18b*S,*20a*R,*22a*S,*24b*S,*26a*R*)-1,2,3,4,4a,4b,5,6,6a,8,8a,11,12b,13,14,14a,15,16,17,18,18a,18b,19,20,20a,22a,24b,25,26,26a-Triacontahydro-1,8a-dihydroxy-3,4b,6a,10,12b,14a,17,18b,20a,22a,24b,26a-dodecamethyl-2,8,11-trioxodipiceno[2,3-*b*:3′,4′-*e*][1,4]dioxin-17-carboxylate*; **5**): Yellow amorphous solid. CD (MeOH): 340 (+20.3), 302 (+19.8), 254 (−32.4). UV (MeOH): 253 (4.26), 298.5 (4.08), 379.5 (3.97). IR (KBr): 3457, 2946, 1711, 1676, 1649, 1595, 1466, 1379, 1308, 1202, 1148, 1065, 1020, 858, 604. ^{1}H-NMR ($CDCl_3$): *Table 1.* ^{13}C-NMR ($CDCl_3$): *Table 2*. FAB-MS: 915.5 (45, $[M+H]^+$), 481.4 (5), 436.3 (7). HR-FAB-MS: 915.5429 ($C_{58}H_{75}O_9^+$; calc. 915.5411).

7,8-Dihydroisoxuxuarine Hα (= *Methyl (3*S,*4*S,*8*R,*9*R,*9′*R,*13*S,*13′*S,*14*R,*14′*S,*17*R,*17′*S,*18*S,*18′*R,*20*R,*20′*R,*22*S*)-3,22-Dihydroxy-2,6′,21-trioxo-3,3′:2′,4-dioxy-29-nordi(friedela)-1(10),1′,3′,5,5′(10′),7′-hexaen-29′-oate*[5]) = *Methyl (1*S,*3*R,*4a*S,*4b*S,*6a*R,*8a S,*12b*S,*14a*S,*17*R,*18a*R,*18b*S,*20a*R,*22a*S,*24a*R,*24b*R,*26a*R*)-1,2,3,4,4a,4b,5,6,6a,8,8a,11,12b,13,14,14a,15,16,17,18,18a,18b,19,20,20a,22a,24,24a,24b,25,26,26a-Dotriacontahydro-1,8a-dihydroxy-3,4b,6a,10,12b,14a,17,18b,20a,22a,24b,26a-dodecamethyl-2,8,11-trioxodipiceno[2,3-*b*:3′,4′-*e*][1,4]dioxin-17-carboxylate*; **6**): Yellow amorphous solid. CD (MeOH): 326 (+13.8), 294.5 (+19.6), 255 (−14.8). UV (MeOH): 250.5 (4.15), 296 (4.16). IR (KBr): 3453, 2946, 1713, 1682, 1649, 1595, 1458, 1381, 1308, 1202, 1144, 1026, 872, 600. ^{1}H-NMR ($CDCl_3$): *Table 1.* ^{13}C-NMR ($CDCl_3$): *Table 2*. FAB-MS: 917.5 (78, $[M+H]^+$), 481.3 (13), 439.3 (8). HR-FAB-MS: 917.5550 ($C_{58}H_{77}O_9^+$; calc. 917.5568).

7,8-Dihydroisoxuxuarine Iα (= *Methyl (3*S,*4*S,*8*R,*9*R,*9′*R,*13*S,*13′*S,*14*R,*14′*S,*17*S,*17′*R,*18*R,*18′*S,*20*R,*20′*R,*22′*S*)-3,22′-Dihydroxy-2,6′,21′-trioxo-3,3′:2′,4-dioxy-29′-nordi(friedela)-1(10),1′,3′,5,5′(10′),7′-hexaen-29-oate*[5]) = *Methyl (3*R,*4a*R,*4b*S,*6a*R,*8a*S,*12b*S,*14a*R,*15*S,*17*R,*18a*S,*18b*S,*20a*R,*22a*S,*24a*R,*24b*R,*26a*S*)-1,2,3,4,4a,4b,5,6,6a,8,8a,11,12b,13,14,14a,15,16,17,18,18a,18b,19,20,20a,22a,24,24a,24b,25,26,26a-Dotriacontahydro-8a,15-dihydroxy-3,4b,6a,10,12b,14a,17,18b,20a,22a,24b,26a-dodecamethyl-8,11,16-trioxodipiceno[2,3-*b*:3′,4′-*e*][1,4]dioxin-3-carboxylate*; **7**): Yellow amorphous solid. CD (MeOH): 324 (+14.2), 294 (+22.5), 251.5 (−12.1). UV

(MeOH): 251 (4.185), 297 (4.19). IR (KBr): 3468, 2936, 1711, 1684, 1649, 1595, 1460, 1381, 1306, 1208, 1140, 1026, 868, 598. ^{1}H-NMR ($CDCl_3$): *Table 1*. ^{13}C-NMR ($CDCl_3$): *Table 2*. FAB-MS: 917.5 (13, $[M+H]^+$), 466.3 (3), 452.3 (2). HR-FAB-MS: 917.5546 ($C_{58}H_{77}O_9^+$; calc. 917.5568).

Xuxuarine Jα (= *Methyl (3*S*,4*S*,9*R*,9′*R*,13*S*,13′*S*,14*S*,14′*S*,17*S*,17′*S*,18*R*,18′*R*,20*R*,20′*S*)-3-Hydroxy-2,6′,21,21′-tetraoxo-2′,3 :3′,4-dioxy-29-nordi(friedela)-1(10),1′,3′,5,5′(10′),7,7′-heptaen-29′-oate*[5]) = *Methyl (3*R*,4a*R*,4b*S*,6a*R*,8a*S*,10b*R*,12a*S*,12b*R*,14*S*,16a*S*,18a*S*,22a*S*,24b*S*,26a*S*)-1,2,3,4,4a,4b,5,6,6a,8,8a,10b,11,12,12a,12b,13,14,15,16,16a,17,18,18a,20,22a,24b,25,26,26a-Triacontahydro-8a-hydroxy-3,4b,6a,10b,12a,14,16a,18a,21,22a,24b,26a-dodecamethyl-2,8,15,20-tetraoxodipiceno[2,3*-b :*4′,3′*-e*][1,4]dioxin-14-carboxylate*; **8**): Yellow amorphous solid. CD (MeOH): 356 (+18.4), 299.5 (+13.1), 247 (−32.3). UV (MeOH): 253 (4.27), 295 (4.09), 382 (3.96). IR (KBr): 3449, 2953, 1713, 1676, 1649, 1597, 1458, 1379, 1308, 1200, 1148, 1084, 1059, 1005, 870, 577. ^{1}H-NMR ($CDCl_3$): *Table 1*. ^{13}C-NMR ($CDCl_3$): *Table 2*. FAB-MS: 913.7 (17, $[M+H]^+$), 495.4 (2), 421.3 (6). HR-FAB-MS: 913.5244 ($C_{58}H_{73}O_9^+$; calc. 913.5255).

Xuxuarine Kα (= *Methyl (3*S*,4*S*,9*R*,9′*R*,13*S*,13′*S*,14*S*,14′*S*,17*S*,17′*S*,18*R*,18′*R*,20*S*,20′*R*)-3-Hydroxy-2,6′,21,21′-tetraoxo-2′,3 :3′,4-dioxy-29′-nordi(friedela)-1(10),1′,3′,5,5′(10′),7,7′-heptaen-29-oate*[5]) = *Methyl (3*S*,4a*R*,4b*S*,6a*R*,8a*S*,10b*R*,12a*S*,12b*R*,14*R*,16a*S*,18a*S*,22a*S*,24b*S*,26a*S*)-1,2,3,4,4a,4b,5,6,6a,8,8a,10b,11,12,12a,12b,13,14,15,16,16a,17,18,18a,20,22a,24b,25,26,26a-Triacontahydro-8a-hydroxy-3,4b,6a,10b,12a,14,16a,18a,21,22a,24b,26a-dodecamethyl-2,8,15,20-tetraoxodipiceno[2,3*-b :*4′,3′*-e*][1,4]dioxin-3-carboxylate*; **9**): Yellow amorphous solid. CD (MeOH): 355 (+14.8), 299.5 (+11.6), 247.5 (−27.1). UV (MeOH): 252 (4.23), 295 (4.04), 379 (3.88). IR (KBr): 3453, 2953, 1711, 1676, 1649, 1597, 1458, 1379, 1306, 1202, 1150, 1092, 1059, 1017, 870, 575. ^{1}H-NMR ($CDCl_3$): *Table 1*. ^{13}C-NMR ($CDCl_3$): *Table 2*. FAB-MS: 913.5 (100, $[M+H]^+$), 479.2 (23), 437.3 (20). HR-FAB-MS: 913.5245 ($C_{58}H_{73}O_9^+$; calc. 913.5255).

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Received February 27, 2004