Nine Regioisomeric and Stereoisomeric Triterpene Dimers from *Maytenus chuchuhuasca*

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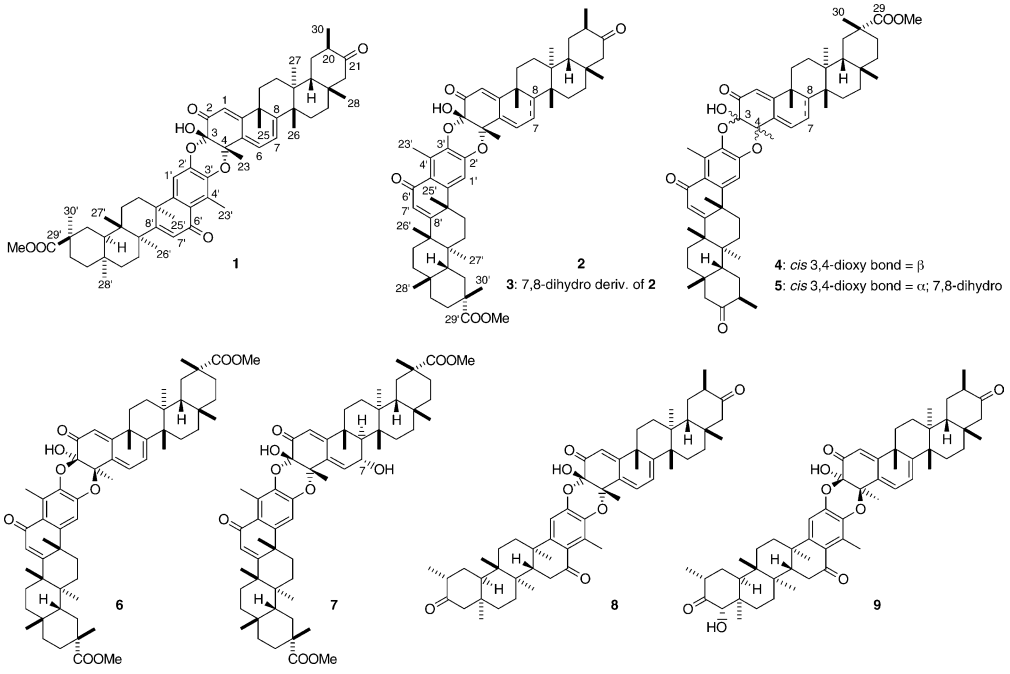
Nine regioisomeric and stereoisomeric triterpene dimers, namely xuxuarine Fα (1), isoxuxuarine Fα (2; cangorosin B), 7,8-dihydroisoxuxuarine Fα (3), isoxuxuarine Gβ (4), 7,8-dihydroisoxuxuarine Gα (5), isoxuxuarine Eβ (6), 7α-hydroxyisoxuxuarine Eα (7), 7′,8′-dihydroxuxuarine Aα (8), and 7′,8′-dihydroxuxuarine Dβ (9), were isolated from the Brazilian medicinal plant "xuxuá" (*Maytenus chuchuhuasca*). Their structures have been elucidated based on several spectroscopic analyses including 2D-NMR experiments, MS spectra and CD spectral studies.

Key words *Maytenus chuchuhuasca*; Celastraceae; triterpene dimer; xuxuá; xuxuarine

During the course of our studies on biologically active compounds from South American medicinal plants,[2)] we became interested in medicinal plants belonging to the genus *Maytenus* (Celastraceae). The plants of this genus are widely used in folk medicine in South America[3,4)] and are rich sources of terpenoids including dihydro-β-agarofuran sesquiterpenes,[5—10)] highly oxidized friedelane triterpenes,[11—20)] and several types of triterpene dimers.[21—30)] Among these, triterpene dimers constitute a rather unique class of compounds that are composed of two quinone-methide derived triterpenes such as pristimerin, tingenone, 22β-hydroxytingenone, and/or their congeners, joined by two ether linkages formed between the A rings or between the A and B rings of quinoid and aromatic triterpenes.[23)] At present, triterpene dimers have been reported exclusively by two groups of researchers, González *et al.* and us. A general methodology for elucidating the regioisomeric and stereoisomeric structures of triterpene dimers on the basis of a detailed comparison of ^{1}H- and ^{13}C-NMR chemical shifts, detection of NOE (or ROE) correlations in NOESY (ROESY), analysis of retro Diels–Alder type fragmentations in MS spectra, and interpretation of exciton couplings in CD spectra, has previously been established by us.[23,26,28)]

Continued investigations of the triterpene dimers obtained from the Brazilian medicinal plant "xuxuá" (*M. chuchuhuasca* Raymond-Hamet *et* Colas)[3,31)] have revealed the existence of additional minor triterpene dimers. Although the isolation and purification steps for these are difficult, several efforts during the preparative HPLC stages finally yielded nine triterpene dimers, xuxuarine Fα (**1**), isoxuxuarine Fα (**2**; cangorosin B), 7,8-dihydroisoxuxuarine Fα (**3**), isoxuxuarine Gβ (**4**), 7,8-dihydroisoxuxuarine Gα (**5**), isoxuxuarine Eβ (**6**), 7α-hydroxyisoxuxuarine Eα (**7**), 7′,8′-dihydroxuxuarine Aα (**8**), and 7′,8′-dihydroxuxuarine Dβ (**9**).



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We report their isolation using HPLC and elucidation by spectral analyses.

Results and Discussion

Triterpene dimers have previously been isolated from the fractions IV, V, and VI, which were three of twelve fractions came from CH_2Cl_2-soluble fraction of MeOH extract of "xuxuá".[23,26,28] The granddaughter fractions and great-granddaughter fractions derived from the above three fractions were re-checked by a reverse-phase TLC, and the fractions exhibited pale yellow spots, considered as triterpene dimers, were further proceeded to purification. For the primary HPLC analyses, a gradient elution of acetonitrile in water from 80% to 100% was performed; subsequently, each of the isocratic modes was performed with conventional ODS-HPLC columns. Reasonable separations of triterpene dimers were hard to achieve in some cases; however, a couple of brands of ODS-HPLC columns were examined, and it was observed that changing the elution solvents was not effective in such cases. After several types of packing gels for HPLC columns were tried, we finally found that Supelcosil ABZ+Plus column yielded better separation results for many cases. Although the Fluofix column also gave separation patterns that were different from the ODS column, it was not enough for baseline separation in most cases. Continuous purification steps for triterpene dimer contained fractions using ODS, ABZ+Plus and Fluofix preparative HPLC columns finally yielded nine triterpene dimers, xuxuarine Fα (**1**: 0.0001% w/w), isoxuxuarine Fα (**2**; cangorosin B: 0.0003%), 7,8-dihydroisoxuxuarine Fα (**3**: 0.0002%), isoxuxuarine Gβ (**4**: 0.00002%), 7,8-dihydroisoxuxuarine Gα (**5**: 0.00003%), isoxuxuarine Eβ (**6**: 0.00005%), 7α-hydroxyisoxuxuarine Eα (**7**: 0.00005%), 7′,8′-dihydroxuxuarine Aα (**8**: 0.0001%), and 7′,8′-dihydroxuxuarine Dβ (**9**: 0.00004%).

Compounds **1**, **2**, and **4** were obtained as yellow amorphous solids. Their FAB-MS spectra showed identical $[M+H]^+$ ion peaks at *m/z* 899. Further, based on HR-FAB-MS analyses, their molecular formulas were also found to be identical, $C_{58}H_{74}O_8$. Their ^{1}H- and ^{13}C-NMR spectral data (listed in Tables 1 and 2) indicated that these compounds were triterpene dimers that were composed of a pristimerin- and a tingenone-type triterpene, one of which was in quinoid form while the other was in aromatic form. Their noteworthy characteristics on the NMR spectra are pointed out as follows: Five proton signals in the low-field region {δ_H 5.99 (d), 6.11 (d), 6.25 (s), 6.28 (dd), and 6.80 (s) for **1**; δ_H 5.99 (d), 6.12 (d), 6.22 (s), 6.34 (dd), and 7.00 (s) for **2**; and δ_H 6.08 (d), 6.11 (d), 6.24 (s), 6.56 (dd), and 6.97 (s) for **4**}, assignable to H-7, H-1, H-7′, H-6, and H-1′, respectively, and these are typical values for this class of triterpene dimers.[23,24,26—28] Methyl ester signals {δ_H 3.54 (s) for **1**; δ_H 3.57 (s) for **2**; and δ_H 3.59 (s) for **4**} and high-field shifted methyl signals {δ_H 0.54 (s) for **1**; δ_H 0.63 (s) for **2**; and δ_H 0.53 (s) for **4**}, assignable to 20-COOMe and C-27, respectively, indicated that both these values corresponded with typical values of pristimerin-type triterpenes. Doublet methyl signals {δ_H 0.99 (J=6.8 Hz) for **1**; δ_H 0.98 (6.3 Hz) for **2**; and δ_H 1.00 (6.0 Hz) for **4**}, doublet methine signals {δ_H 2.85 (J=14.3 Hz) for **1**; δ_H 2.85 (14.1 Hz) for **2**; and δ_H 2.91 (14.3 Hz) for **4**}, and ketone carbon signals {δ_C 213.6 (s) for **1**; δ_C 213.6 (s) for **2**; and δ_C 214.7 (s) for **4**}, assignable to C-30, H-22α and C-21, respectively, indicated that these values corresponded with typical values of tingenone-type triterpenes. Thus, these compounds were similar to xuxuarines, *i.e.*, Fβ, Gα, and Gβ, which were also composed of a pristimerin-type and a tingenone-type triterpenes. With regards to **2**, most of the chemical shift values significantly resembled those of cangorosin B, which had been isolated from *M. ilicifolia*. We have already proposed the interpretations of ^{1}H- and ^{13}C-NMR chemical shift differences for elucidating their regioisomeric (xuxuarine-type and isoxuxuarine-type) and stereoisomeric (α- and β-types) structures regarding the *cis* 3,4-dioxy bonds. In other words, the detailed chemical shift comparisons of the H-23′ methyl group (δ_H 2.7 for the xuxuarine-type, δ_H 2.5 for the isoxuxuarine-type) and of C-3, C-4, C-23, and H-6 (δ_C 92, 79, 22, and δ_H 6.3 for the α-type; δ_C 91, 77, 24, and δ_H 6.5 for the β-type) can be used to elucidate the structure. It follows that the chemical shifts assignable to C-3, C-4, C-23, H-6, and H-23′ appeared at δ_C 92.0, 79.3, 22.3, δ_H 6.28, and 2.74 for **1**; δ_C 91.8, 79.4, 22.3, δ_H 6.34, and 2.48 for **2**; and δ_C 90.6, 76.9, 24.2, δ_H 6.56, and 2.44 for **4**; led to the conclusion that compound **1** as xuxuarine α type, **2** as isoxuxuarine α type, and **4** as isoxuxuarine β type, respectively. These assumptions on their regiochemistry and stereochemistry were authenticated by the ROESY and CD spectra (Fig. 1). In their ROESY spectrum, cross peaks were observed between H-6 and H-23′ signals for **1**, and between H-6 and H-1′ for **2** and **4**; and in their CD spectrum, a positive first Cotton effect for **1** and **2**, and a negative first Cotton effect for **4** were shown. Furthermore, the FAB-MS data enabled us to determine whether the pristimerin-type and the tingenone-type triterpene units were in the quinoid form or in the aromatic form (Fig. 2). The fragmentation ion peaks at *m/z* 421 and 481, which showed the tingenone-type triterpene to be in the quinoid form and the pristimerin-type to be in the aromatic form, were observed in **1** and **2**; and those at *m/z* 436 and 464, which suggested that the tingenone-type triterpene was in the aromatic form and the pristimerin-type in the quinoid form were observed in **4**. Based on these spectral evidences, it can be concluded that compounds **1**, **2**, and **4** were xuxuarine Fα, isoxuxuarine Fα (cangorosin B), and isoxuxuarine Gβ, respectively.

Compounds **3** and **5** were obtained as pale yellow amorphous solids. Both compounds exhibited $[M+H]^+$ ion peaks at *m/z* 901 in the FAB-MS spectra, and the fact that they had an identical molecular formula, $C_{58}H_{76}O_8$, was established by HR-FAB-MS analysis. Their ^{1}H- and ^{13}C-NMR spectra showed that both **3** and **5** were triterpene dimers composed of a pristimerin-type and a tingenone-type triterpene unit, similar to **1**, **2**, and **4**. However, the disappearance of the H-7 proton signal and the breadth of the H-6 methine proton signal suggested that the quinoid triterpene unit in each molecule was partially saturated between C-7 and C-8. Therefore, it is believed that these compounds were 7,8-dihydro derivatives of xuxuarines or isoxuxuarines belonging to the class F or G. The set of chemical shifts for **3** and **5** assignable to C-3, C-4, C-23, H-6, and H-23′ (δ_C 91.3, 79.5, 22.7, δ_H 6.35, 2.53 for **3**; δ_C 91.2, 79.5, 22.7, δ_H 6.26, 2.53 for **5**) suggested that both compounds involved isoxuxuarine type conjugation with α orientation about the *cis* 3,4-dioxy bond linkages. These judgments were confirmed by the ROESY and CD

Table 1. Typical ^{1}H-NMR Chemical Shifts (ppm, Multiplicity, and *J*/Hz) for **1**—**9**[a)]

Position	**1**	**2**	**3**	**4**	**5**
H-1	6.11 (d, 1.5)	6.12 (d, 1.5)	6.00 (s)	6.11 (d, 1.7)	5.98 (s)
3-OH	5.10 (s)	5.00 (s)	4.93 (s)	5.05 (s)	4.93 (s)
H-6	6.28 (dd, 1.5, 6.5)	6.34 (dd, 1.5, 6.5)	6.35 (br s)	6.56 (dd, 1.7, 7.0)	6.26 (br s)
H-7	5.99 (d, 6.5)	5.99 (d, 6.5)		6.08 (d, 7.0)	
H-19α				2.40 (d, 14.3)	2.34 (d, 13.2)
H-20	2.46 (m)	2.48 (m)	2.54 (m)		
H-22α	2.85 (d, 14.3)	2.84 (d, 14.1)	2.87 (d, 14.3)		
Me-23	1.60 (s)	1.58 (s)	1.49 (s)	1.56 (s)	1.47 (s)
Me-25	1.49 (s)	1.49 (s)	1.13 (s)	1.43 (s)	1.06 (s)
Me-26	1.26 (s)	1.27 (s)	1.05 (s)	1.20 (s)	0.97 (s)
Me-27	0.99 (s)	0.99 (s)	1.23 (s)	0.53 (s)	0.75 (s)
Me-28	0.98 (s)	0.97 (s)	0.96 (s)	1.07 (s)	1.05 (s)
Me-30	0.99 (d, 6.8)	0.98 (d, 6.3)	1.00 (d, 6.2)	1.18 (s)	1.17 (s)
COOMe				3.59 (s)	3.64 (s)
H-1′	6.80 (s)	7.00 (s)	6.97 (s)	6.97 (s)	6.98 (s)
H-7′	6.25 (s)	6.22 (s)	6.22 (s)	6.24 (s)	6.25 (s)
H-19′α	2.40 (d, 15.9)	2.46 (d, 15.0)	2.45 (d, 15.6)		
H-20′				2.50 (m)	2.50 (m)
H-22′α				2.91 (d, 14.3)	2.91 (d, 14.1)
Me-23′	2.74 (s)	2.48 (s)	2.53 (s)	2.44 (s)	2.53 (s)
Me-25′	1.49 (s)	1.55 (s)	1.54 (s)	1.61 (s)	1.60 (s)
Me-26′	1.27 (s)	1.30 (s)	1.30 (s)	1.37 (s)	1.38 (s)
Me-27′	0.54 (s)	0.63 (s)	0.61 (s)	0.98 (s)	1.06 (s)
Me-28′	1.09 (s)	1.11 (s)	1.11 (s)	1.01 (s)	1.02 (s)
Me-30′	1.16 (s)	1.19 (s)	1.19 (s)	1.00 (d, 6.0)	0.99 (d, 6.4)
COOMe	3.54 (s)	3.57 (s)	3.55 (s)		

Position	**6**	**7**	**8**	**9**
H-1	6.10 (d, 1.7)	5.99 (d, 1.0)	6.10 (d, 1.3)	6.11 (d, 1.7)
3-OH	5.02 (s)	4.89 (s)	5.12 (s)	5.12 (s)
H-6	6.56 (dd, 1.7, 7.0)	6.15 (dd, 1.0, 3.1)	6.25 (dd, 1.3, 6.5)	6.55 (dd, 1.7, 6.9)
H-7	6.08 (d, 7.0)	4.45 (ddd, 3.1, 9.2, 9.9)	5.99 (d, 6.5)	6.14 (d, 6.9)
7α-OH		0.83 (d, 9.9)		
H-19α	2.43[b)] (d, 14.8)	2.36 (br d, 11.9)		
H-20			2.47 (m)	2.49 (m)
H-22α			2.86 (d, 14.5)	2.88 (d, 14.3)
22β-OH				
Me-23	1.55 (s)	1.49 (s)	1.60 (s)	1.59 (s)
Me-25	1.42 (s)	1.12 (s)	1.48 (s)	1.43 (s)
Me-26	1.20 (s)	1.15 (s)	1.26 (s)	1.27 (s)
Me-27	0.54[c)] (s)	0.78 (s)	1.00 (s)	0.97 (s)
Me-28	1.09[d)] (s)	1.05 (s)	0.99 (s)	0.99 (s)
Me-30	1.17 (s)	1.18 (s)	0.99 (d, 6.0)	1.00 (d, 6.2)
COOMe	3.59[e)] (s)	3.65 (s)		
H-1′	6.96 (s)	6.98 (s)	6.64 (s)	6.60 (s)
H-7′	6.21 (s)	6.22 (s)	2.58 (m)	
			2.59 (m)	
H-8′			2.32 (dd, 6.2, 12.4)	
H-19′α	2.39[b)] (d, 13.0)	2.44 (d, 15.2)		
H-20′			2.57 (m)	2.69 (m)
H-22′α			2.93 (d, 14.1)	4.53 (br d, 4.0)
22′β-OH				3.63 (d, 4.6)
Me-23′	2.42 (s)	2.52 (s)	2.60 (s)	2.61 (s)
Me-25′	1.56 (s)	1.53 (s)	1.16 (s)	1.17 (s)
Me-26′	1.28 (s)	1.29 (s)	1.08 (s)	1.08 (s)
Me-27′	0.53[c)] (s)	0.58 (s)	1.26 (s)	1.25 (s)
Me-28′	1.07[d)] (s)	1.10 (s)	0.99 (s)	0.84 (s)
Me-30′	1.17 (s)	1.18 (s)	0.99 (d, 6.0)	1.04 (d, 6.4)
COOMe	3.55[e)] (s)	3.53 (s)		

a) All measurements were made in $CDCl_3$ at 400 MHz, 300 K. *b*—*e*) Assignments for values in each compound bearing the same superscript can be reversed.

Table 2. ^{13}C-NMR Chemical Shifts (ppm and Multiplicity) for **1**—**9**[a)]

C-No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
C-1	115.5 (d)	116.0 (d)	113.0 (d)	114.9 (d)	113.1 (d)	114.9 (d)	114.0 (d)	115.5 (d)	115.0 (d)
C-2	190.2 (s)	190.4 (s)	191.5 (s)	189.5 (s)	191.5 (s)	189.6 (s)	191.2 (s)	190.2 (s)	189.4 (s)
C-3	92.0 (s)	91.8 (s)	91.3 (s)	90.6 (s)	91.2 (s)	90.7 (s)	91.3 (s)	92.0 (s)	91.1 (s)
C-4	79.3 (s)	79.4 (s)	79.5 (s)	76.9[x)](s)	79.5 (s)	77.2[x)](s)	79.1 (s)	79.4 (s)	76.9[x)](s)
C-5	130.3 (s)	130.9 (s)	134.3 (s)	132.0 (s)	134.1 (s)	132.1 (s)	134.7 (s)	130.2 (s)	132.2 (s)
C-6	126.6 (d)	126.1 (d)	133.9 (d)	128.7 (d)	133.9 (d)	128.7 (d)	135.9 (d)	126.6 (d)	128.5 (d)
C-7	116.3 (d)	116.2 (d)	24.2 (t)	116.8 (d)	24.2 (t)	116.9 (d)	68.5 (d)	116.3 (d)	117.2 (d)
C-8	160.3 (s)	160.2 (s)	41.2 (d)	164.6 (s)	41.6 (d)	164.5 (s)	51.7 (d)	160.4 (s)	163.3 (s)
C-9	41.7 (s)	41.5 (s)	37.4 (s)	44.2 (s)	37.4 (s)	44.1 (s)	41.1 (s)	41.7 (s)	43.4 (s)
C-10	173.7 (s)	173.2 (s)	169.8 (s)	173.4 (s)	170.0 (s)	173.3 (s)	168.7 (s)	173.8 (s)	172.9 (s)
C-11	33.2 (t)	33.3 (t)	30.5 (t)	32.8 (t)	30.6 (t)	32.9 (t)	31.2 (t)	33.2 (t)	33.1 (t)
C-12	29.9[b)](t)	29.8[c)](t)	29.4 (t)	29.5 (t)	29.4 (t)	29.9[g)](t)	29.4 (t)	29.8[r)](t)	29.8 (t)
C-13	39.4 (s)	39.5 (s)	40.1[d)](s)	38.6 (s)	38.9 (s)	38.7 (s)	39.4 (s)	39.5[s)](s)	39.9 (s)
C-14	44.3 (s)	44.2 (s)	40.2[d)](s)	44.4[e)](s)	40.1 (s)	44.4 (s)	41.8 (s)	44.3 (s)	44.0 (s)
C-15	28.3 (t)	28.3 (t)	27.9 (t)	28.6 (t)	28.4[f)](t)	28.6[h)](t)	31.0 (t)	28.3 (t)	28.5 (t)
C-16	35.4 (t)	35.5 (t)	35.3 (t)	36.4 (t)	36.0 (t)	36.4 (t)	36.2 (t)	35.4[t)](t)	35.4 (t)
C-17	38.2 (s)	38.2 (s)	38.1 (s)	30.5 (s)	30.2 (s)	30.6 (s)	30.0 (s)	38.3[u)](s)	38.2 (s)
C-18	43.4 (d)	43.4 (d)	43.9 (d)	44.1 (d)	44.6 (d)	44.4[i)](d)	44.8 (d)	43.4 (d)	43.6 (d)
C-19	32.1 (t)	32.2 (t)	31.8 (t)	30.8 (t)	30.5 (t)	30.9[j)](t)	30.6 (t)	32.1 (t)	31.9 (t)
C-20	41.9 (d)	41.9 (s)	42.3 (d)	40.4 (s)	40.5 (s)	40.5[k)](s)	40.6[q)](s)	42.3 (d)	41.9 (d)
C-21	213.6 (s)	213.6 (s)	213.8 (s)	29.9 (t)	29.9 (t)	29.9[l)](t)	29.8 (t)	213.6 (s)	213.6 (s)
C-22	52.5 (t)	52.5 (t)	53.5 (t)	34.7 (t)	36.0 (t)	34.8[m)](t)	35.8 (t)	52.5 (t)	52.4 (t)
C-23	22.3 (q)	22.1 (q)	22.7 (q)	24.2 (q)	22.7 (q)	24.2 (q)	22.4 (q)	22.3 (q)	24.6 (q)
C-25	35.6 (q)	35.7 (q)	22.9 (q)	39.3 (q)	22.1 (q)	39.3 (q)	24.0 (q)	35.6 (q)	39.7 (q)
C-26	22.3 (q)	22.3 (q)	15.7 (q)	22.4 (q)	16.0 (q)	22.4 (q)	16.5 (q)	22.3 (q)	22.4 (q)
C-27	20.0 (q)	20.1 (q)	18.1 (q)	18.2 (q)	16.9 (q)	18.3[n)](q)	17.4 (q)	20.1 (q)	19.7 (q)
C-28	32.6 (q)	32.5 (q)	32.7 (q)	31.5 (q)	31.7 (q)	31.6[o)](q)	31.7 (q)	32.8[v)](q)	32.5 (q)
C-29				178.8 (s)	179.0 (s)	178.9[p)](s)	179.0 (s)		
C-30	15.1 (q)	15.1 (q)	15.2 (q)	32.7 (q)	32.3 (q)	32.8 (q)	32.4 (q)	15.2[w)](q)	15.1 (q)
COOMe				51.6 (q)	51.7 (q)	51.6 (q)	51.7 (q)		
C-1′	111.4 (d)	110.5 (d)	110.6 (d)	110.7 (d)	110.4 (d)	110.7 (d)	110.6 (d)	109.6 (d)	108.8 (d)
C-2′	144.6 (s)	144.4 (s)	144.5 (s)	144.3 (s)	144.5 (s)	144.2 (s)	144.2 (s)	145.0 (s)	145.3 (s)
C-3′	137.6 (s)	138.3 (s)	138.3 (s)	138.5 (s)	138.4 (s)	138.5 (s)	138.0 (s)	137.6 (s)	137.4 (s)
C-4′	127.6 (s)	129.3 (s)	129.4 (s)	128.3 (s)	129.5 (s)	128.2 (s)	129.3 (s)	129.0 (s)	129.7 (s)
C-5′	124.5 (s)	123.3 (s)	123.3 (s)	123.9 (s)	123.4 (s)	124.0 (s)	123.5 (s)	126.0 (s)	125.3 (s)
C-6′	187.9 (s)	187.2 (s)	187.2 (s)	187.6 (s)	187.1 (s)	187.8 (s)	187.2 (s)	201.1 (s)	200.0 (s)
C-7′	126.1 (d)	126.3 (d)	126.3 (d)	126.1 (d)	126.3 (d)	126.2 (d)	126.2 (d)	37.6 (t)	37.4 (t)
C-8′	171.7 (s)	171.0 (s)	171.0 (s)	170.4 (s)	170.0 (s)	171.5 (s)	171.0 (s)	41.9 (d)	41.8 (d)
C-9′	40.0 (s)	40.1 (s)	40.1[d)](s)	39.7 (s)	39.9 (s)	39.9 (s)	40.2 (s)	37.1 (s)	37.0 (s)
C-10′	150.5 (s)	151.8 (s)	151.8 (s)	151.0 (s)	151.7 (s)	151.1 (s)	151.9 (s)	151.7 (s)	152.2 (s)
C-11′	34.2 (t)	34.3 (t)	34.3 (t)	34.3 (t)	34.4 (t)	34.2 (t)	34.2 (t)	32.9 (t)	33.2 (t)
C-12′	29.9[b)](t)	30.0 (t)	29.9 (t)	30.2 (t)	30.2 (t)	29.6[g)](t)	29.9 (t)	29.7[r)](t)	29.5 (t)
C-13′	39.0 (s)	39.0 (s)	39.0 (s)	40.2 (s)	40.2 (s)	39.0 (s)	39.0 (s)	39.4[s)](s)	39.2 (s)
C-14′	44.7 (s)	44.7 (s)	44.7 (s)	44.3[e)](s)	44.3 (s)	44.7 (s)	44.7 (s)	40.0 (s)	39.8 (s)
C-15′	28.5 (t)	28.6 (t)	28.6 (t)	28.4 (t)	28.3[f)](t)	28.5[h)](t)	28.6 (t)	28.0 (t)	27.7 (t)
C-16′	36.4 (t)	36.4 (t)	36.4 (t)	35.5 (t)	35.5 (t)	36.4 (t)	36.4 (t)	35.3[t)](t)	29.3 (t)
C-17′	30.5 (s)	30.5 (s)	30.5 (s)	38.2 (s)	38.2 (s)	30.6 (s)	30.5 (s)	38.2[u)](s)	45.0 (s)
C-18′	44.3 (d)	44.3 (d)	44.3 (d)	43.5 (d)	43.5 (d)	44.3[i)](d)	44.3 (d)	44.0 (d)	45.3 (d)
C-19′	30.9 (t)	31.1 (t)	31.0 (t)	32.0 (t)	32.0 (t)	30.8[j)](t)	30.9 (t)	31.8 (t)	31.7 (t)
C-20′	40.4 (s)	40.6 (d)	40.6 (s)	41.9 (d)	41.9 (d)	40.4[k)](s)	40.5[q)](d)	41.9 (d)	41.3 (s)
C-21′	29.9[b)](t)	29.7[c)](t)	29.7 (t)	214.7 (s)	213.7 (s)	29.7[l)](t)	29.8 (t)	214.1 (s)	214.0 (s)
C-22′	34.7 (t)	35.0 (t)	35.0 (t)	52.6 (t)	52.7 (t)	34.7[m)](t)	35.0 (t)	53.6 (t)	77.2 (t)
C-23′	13.0 (q)	13.3 (q)	13.4 (q)	12.8 (q)	13.4 (q)	12.8 (q)	13.4 (q)	13.0 (q)	13.3 (q)
C-25′	37.6 (q)	37.6 (q)	37.7 (q)	38.9 (q)	38.7 (q)	38.0 (q)	37.6 (q)	26.2 (q)	26.5 (q)
C-26′	20.8 (q)	20.9 (q)	20.9 (q)	20.8 (q)	20.8 (q)	20.9 (q)	20.9 (q)	15.0 (q)	15.1 (q)
C-27′	18.3 (q)	18.5 (q)	18.5 (q)	19.7 (q)	20.0 (q)	18.2[n)](q)	18.4 (q)	18.2 (q)	19.0 (q)
C-28′	31.6 (q)	31.6 (q)	31.6 (q)	32.6 (q)	32.6 (q)	31.6[o)](q)	31.6 (q)	32.6[v)](q)	25.1 (q)
C-29′	178.7 (s)	179.3 (s)	179.3 (s)			178.7[p)](s)	179.0 (s)		14.8 (q)
C-30′	32.7 (q)	32.9 (q)	32.9 (q)	15.1 (q)	15.1 (q)	32.8 (q)	32.8 (q)	15.1[w)](q)	14.8 (q)
COOMe	51.6 (q)	51.6 (q)	51.6 (q)			51.6 (q)	51.7 (q)		

a) All measurements were made in $CDCl_3$ at 100 MHz, 300 K. *b*—*w*) Assignments for values in each compound bearing the same superscript can be reversed. *x*) Signals bearing this superscript were superimposed on solvent signals.

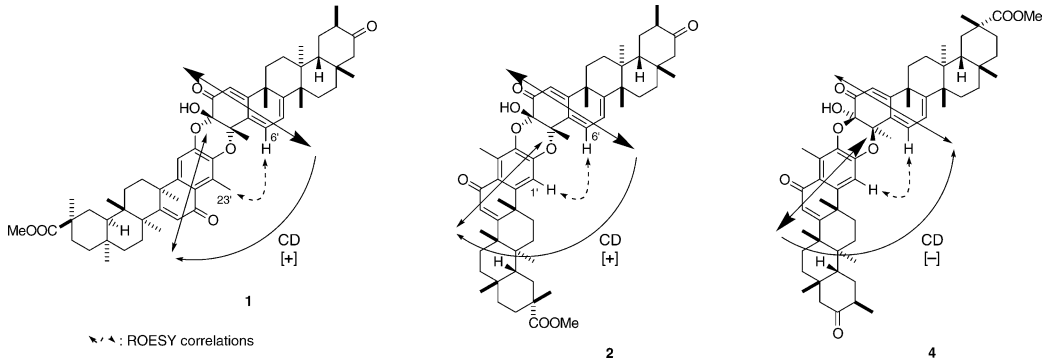

Fig. 1. ROESY Correlations and CD Exciton Couplings of **1**, **2**, and **4**

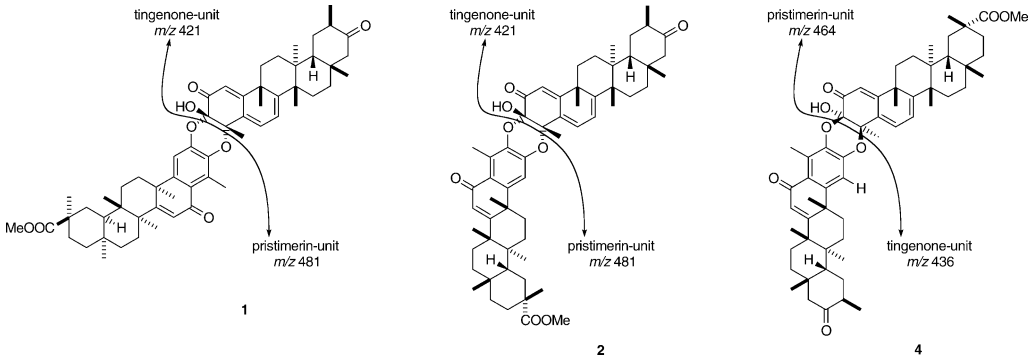

Fig. 2. MS Spectral Degradation Patterns of **1**, **2**, and **4**

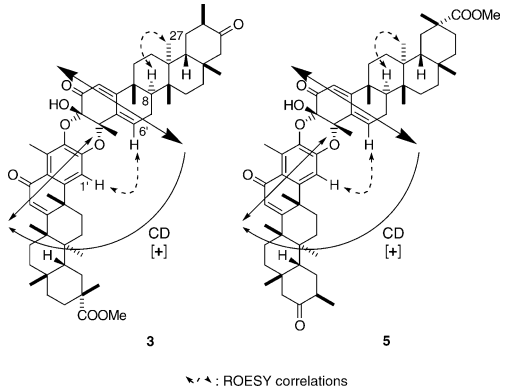

Fig. 3. ROESY Correlations and CD Exciton Couplings of **3** and **5**

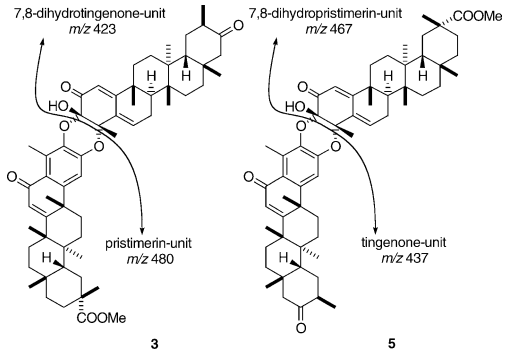

Fig. 4. MS Spectral Degradation Patterns of **3** and **5**

spectra, in which ROE correlations between H-6 and H-1′, and positive first Cotton effects were observed (Fig. 3). ROESY spectra also showed a ROE correlation between H-8 {δ_H 1.92 (m) for **3**; 1.81 (m) for **5**} and H-27 (δ_H 1.23 for **3**; 0.75 for **5**), thereby confirming the configuration of H-8 as α orientation. In the FAB-MS spectra (Fig. 4), **3** showed retro Diels–Alder type fragmentation peaks at *m*/*z* 423 and 480, while **5** showed them at *m*/*z* 437 and 467. These observations led to the conclusion that compounds **3** and **5** were 7,8-dihydroisoxuxuarine Fα and 7,8-dihydroisoxuxuarine Gα, respectively.

Compound **6**, a pale yellow amorphous solid, exhibited an $[M+H]^+$ ion peak at *m*/*z* 943 in the FAB-MS, and the molecular formula, $C_{60}H_{78}O_9$, was established by HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra of **6** showed two pristimerin-type triterpene units as its constituents, one of which was in the quinoid form while the other was in the aromatic form. These were similar to xuxuarine Eβ and isoxuxuarine Eα. The chemical shifts assignable to C-3, C-4, C-23, H-6, and H-23′ (δ_C 90.7, 77.2, 24.2, δ_H 6.56, 2.42) suggested the isoxuxuarine type conjugation with β orientation about the *cis* 3, 4-dioxy bond linkages, that is, isoxuxuarine Eβ. These estimations were validated by the CD and ROESY spectra (Fig. 5), for which a negative first Cotton effect (396 nm) was observed in the CD spectrum, and a cross peak was observed between the H-6 and H-1′ signals in the ROESY spectrum, confirming structure **6** to be an isoxuxuarines Eβ.

Compound **7**, a pale yellow amorphous solid, exhibited an $[M+H]^+$ ion peak at *m*/*z* 960 in the FAB-MS, and its molecular formula, $C_{60}H_{80}O_{10}$, was established by HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectra of **7** showed somewhat differ-

ent signal patterns in comparison with those of the xuxuarines, even though its components appeared to be two pristimerin derived triterpene units. The noteworthy characteristics on the NMR spectrum are indicated as follows: The H-6 methine proton (δ_H 6.15, dd, J=1.0, 3.1 Hz) showed different coupling constants from usual xuxuarines (J=*ca.* 2, 7 Hz). Instead of the disappearance of the H-7 proton signal from low-field region, one methine proton signal appeared at δ_H 4.45 (ddd, J=3.1, 9.2, 9.9 Hz). One deuterium exchangeable proton also appeared at δ_H 0.83 (d, J=9.9 Hz), which coupled with the methine proton at δ_H 4.45. Correspondingly, two olefinic carbons disappeared along with the appearance of two methine carbons at δ_C 68.5 and 51.7, which can be assigned as C-7 and C-8. These observations suggest that the conjugated ketone system of the quinoid triterpene units were hydroxylated at C-7. Similarly, the chemical shifts assignable to C-3, C-4, C-23, H-6, and H-23′ (δ_C 91.3, 79.1, 22.4, δ_H 6.15, 2.52) suggested compound **7** to be the isoxuxuarine type conjugation with α orientation about the *cis* 3,4-dioxy bond linkages. The ROESY spectrum of **7** showed a cross peak between H-6 and H-1′, which confirmed its isotype conjugation; and cross peaks between H-7 and H-25, H-7, and H-26; and H-8 (δ_H 1.68) and H-27, which revealed the stereochemistry at C-7 and C-8 to be 7α-hydroxyl and 8α-methine (Fig. 5). Finally, based on the CD spectrum (Fig. 5), in which a positive first Cotton effect (322 nm) was observed, it was concluded that the structure **7** is a 7α-hydroxyisoxuxuarines Eα.

Compounds **8** and **9** were obtained as pale yellow amorphous solids. In their FAB-MS spectra, **8** showed $[M+H]^+$ ion peak at *m/z* 857 whereas **9** showed it at *m/z* 873. Using HR-FAB-MS, the molecular formulae were established as $C_{56}H_{72}O_7$ for **8** and $C_{56}H_{72}O_8$ for **9**. Their NMR spectra indicated that **8** was composed of two tingenone-type triterpene units, while **9** was composed of a tingenone-type and a 22β-hydroxytingenone-type triterpene unit. However, the H-7′ olefinic proton and corresponding olefinic carbons of both compounds disappeared from low-field regions. Therefore, it was suggested that the aromatic triterpene unit in each molecule was partially saturated between C-7′ and C-8′, that is, they were 7′,8′-dihydro-type compounds. On the basis of the chemical shifts assignable to C-3, C-4, C-23, and H-6 (δ_C 92.0, 79.4, 22.3, δ_H 6.25 for **8**; δ_C 91.1, 76.9, 24.6, δ_H 6.55 for **9**, orientation of the *cis* 3,4-dioxy bond linkages were reported as an α orientation for **8** and a β orientation for **9**. The CD spectra (Fig. 5) showed a positive first Cotton effect (361.5 nm) for **8**, whereas it showed a negative first Cotton effect (394.5 nm) for **9**, proving the orientation determined by NMR chemical shifts. With respect to the configuration of the linkages, the chemical shift values of H-23′ were δ_H 2.60 for **8** and δ_H 2.61 for **9**; therefore, it was difficult to determine whether the compounds were of xuxuarine-type or the isoxuxuarine-type using 1D-NMR. In the ROESY spectra of **8** and **9**, ROE correlations between H-6 and H-23′ were observed (Fig. 5). Based on this, it was possible to assign a xuxuarine type configuration to both **8** and **9**. The ROESY spectra also showed a ROE correlation between H-8′ (δ_H 2.32 for **8**; 2.33 for **9**) and H-27′ in both compounds, confirming the configuration of H-8′ as being of an α orientation, based on their monomer triterpenes. With regard to the arrangement of the tingenone and the 22β-hydroxytingenone-type triterpene units of **9**, the retro Diels–Alder type fragmentation peaks at *m/z* 421 and 453 in the FAB-MS spectrum (Fig. 6) enabled to assign it to the xuxuarine D class. Based on these spectral evidences, it was concluded that compounds **8** and **9** were 7′,8′-dihydroxuxuarine Aα

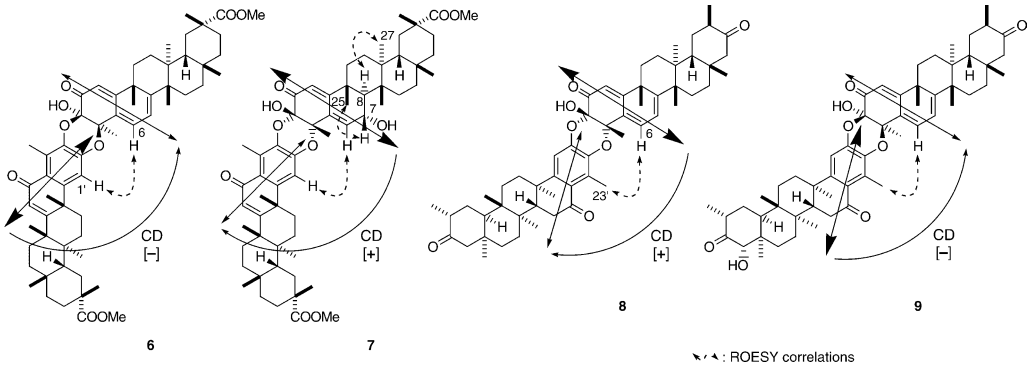

Fig. 5. ROESY Correlations and CD Exciton Couplings of **6**—**9**

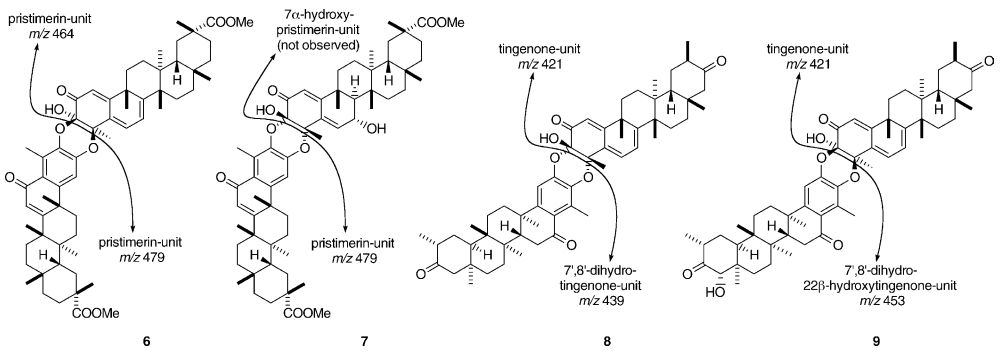

Fig. 6. MS Spectral Degradation Patterns of **6**—**9**

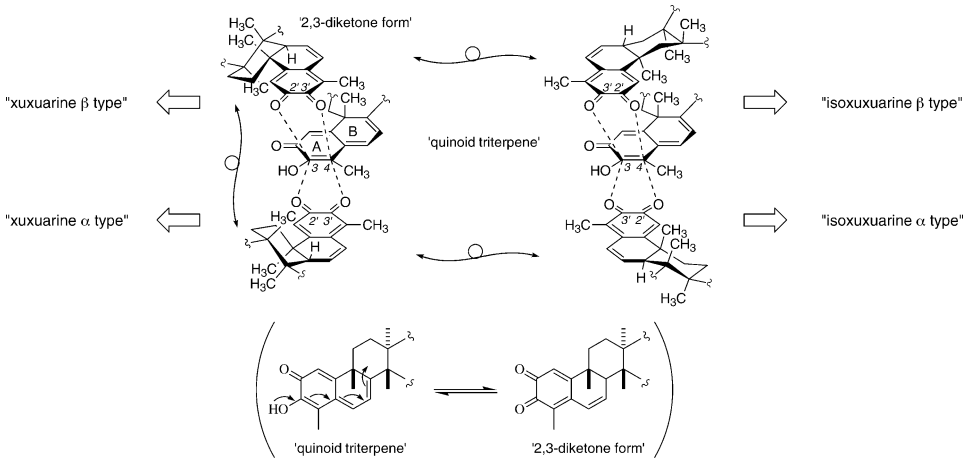

Fig. 7. Possible Biosynthetic Mechanism for Regioisomeric and Stereoisomeric Triterpene Dimers

and 7′,8′-dihydroxuxuarine Dβ, respectively.

Complete ^{1}H- and ^{13}C-NMR signal assignments of the nine triterpene dimers (**1**—**9**), which were done by means of HSQC and HMBC interpretations, are shown in Tables 1 and 2.

We have already proposed possible biosynthetic routes for triterpene dimers of this class, and explained their diverse formation toward the regiochemical and stereochemical isomers of triterpene dimers.[23] For example, a 2,3-diketone type triterpene, which is in an equilibrium state with its quinoid form, approaches from the front or the reverse direction to form the counterpart triterpene molecule or from the upper or the lower side to form Diels–Alder type adducts (Fig. 7). There are at least three kinds of well-known quinoid triterpenes: pristimerin, tingenone, and 22β-hydroxytingenone. When only one kind of quinoid triterpenes forms triterpene dimers, namely, xuxuarines A (from tingenone), B (from 22β-hydroxytingenone), and E series (from pristimerin), two types of stereochemical isomers of the α- and β-types, and two types of regiochemical isomers of the xuxuarine and isoxuxuarine-types were obtained. Similarly, when three kinds of quinoid triterpenes were used to form triterpene dimers, the diversity of triterpene dimers would increase in terms of number to $3\times3\times2\times2=36$. Some other kinds of quinoid triterpenes have also been reported.[11—20] 7,8-Dihydro[28] or 7′,8′-dihydro type triterpene dimers[23] and triterpene dimers of cangorosin A class that are composed of a quinoid and an aromatic triterpene unit joined in between A and B rings,[27] are also known. Thus, chemical diversity of triterpene dimers is believed to be enormous, it prefers a natural combinatorial library.

Experimental

General Experimental Procedures The experimental procedures were same as those described previously.[28] The other procedures are specified as follows: HPLC purification was performed using Inertsil PREP-ODS columns (5 mm i.d.×250 mm for analysis, 20 mm i.d.×250 mm for preparative; GL Science Inc., Japan) packed with 10 μm ODS gel, Supelcosil ABZ+Plus columns (4.6 mm i.d.×250 mm for analysis, 21.2 mm i.d.×250 mm for preparative; Supelco, U.S.A.) packed with 5 μm ABZ+Plus gel, and Fluofix 120E columns (4.6 mm i.d.×250 mm for analysis, 20 mm i.d.×250 mm for preparative; NEOS, Co., Japan) packed with 5 μm silica gel having a branched fluorocarbon bonded phase. ^{1}H (400 MHz), ^{13}C (100 MHz), and 2D NMR spectra were recorded on a Varian Unity Plus 400 spectrometer at 300 °K using Varian standard pulse sequences with standard parameters. Phase-sensitive ROESY experiments were conducted with a mixing time of 300 msec. Field gradient HSQC and HMBC experiments were performed with a 150 msec delay to optimize the one-bond correlation in HSQC spectra and suppress them in HMBC spectra, and with a 63 msec evolution delay for long-range couplings in HMBC spectra.

Plant Material Dark reddish brown stem barks of *Maytenus chuchuhuasca* Raymond-Hamet *et* Colas (5 kg), commonly known as "xuxuá", were purchased in São Paulo, Brazil in 1992. The botanical identification was made by Dr. William Antonio Rodrigues (Instituto Nacional de Pesquisas da Amazonia). A voucher specimen has been deposited in the herbarium of the Tokyo University of Pharmacy and Life Science.

Extraction and Isolation Crushed barks (5 kg) of *Maytenus chuchuhuasca* were extracted with hot MeOH (54 l) to give a MeOH extract (1.5 kg), which was partitioned between CH_2Cl_2 and H_2O. The CH_2Cl_2-soluble fraction (155 g) was subjected to silica gel cc using a CH_2Cl_2–EtOAc gradient system (1 : 0—0 : 1) following MeOH to give twelve fractions (Fr. I—XII). The fractions IV (7.1 g), V (9.9 g), and VI (13.5 g) were further subjected to ODS MPLC with CH_3CN–H_2O stepwise gradient system (8 : 2—1 : 0 for Fr. IV and VI; 7.5 : 2.5—1 : 0 for Fr. V) to give daughter fractions: 26 fractions (Fr. IV-A to Z) from Fr. IV; 20 fractions (Fr. V-A to T) from Fr. V; 19 fractions (Fr. VI-A to S) from Fr. VI, respectively. Each daughter fraction was further separated by silica gel MPLC using *n*-hexan–EtOAc gradient system or ODS MPLC using MeOH–H_2O gradient system. Several major components were isolated from above granddaughter fractions by preparative ODS HPLC using CH_3CN–H_2O or MeOH–H_2O isocratic systems, and were reported previously.[23,26,28] For example, Fr. V-G and Fr. VI-G gave tingenone; Fr. VI-N gave pristimerin; Fr. V-M gave xuxuarine Aα; Fr. V-L gave xuxuarine Aβ; Fr. VI-K-1 gave xuxuarine Bα, while Fr. VI-K-3 gave xuxuarines Cβ, and Dβ; Fr. VI-J-3 gave xuxuarine Bβ; Fr. IV-P gave xuxuarine Gβ; Fr. IV-R gave xuxuarine Gα. For the purpose of earning minor triterpene dimers, many of granddaughter fractions and great-granddaughter fractions, which were derived from the fractions IV, V, and VI, were re-checked by a reverse-phase TLC using 100% acetonitrile as a developing solvent. The fractions exhibited pale yellow spots, considered as triterpene dimers, usually having *Rf* values of *ca.* from 0.1 to 0.5 on the TLC, were further proceeded to purification. A gradient elution of 80 to 100% acetonitrile in water was conducted for the primary HPLC analysis; then each of isocratic modes was conducted with conventional ODS HPLC columns. Supelcosil ABZ+Plus column and Fluofix column were also conducted in some cases when reasonable separation of triterpene dimers were hard to obtain with conventional ODS HPLC column. Preparative ODS HPLC for one of granddaughter fractions, Fr. IV-O-28 (22.8 mg), eluting with 90% CH_3CN in H_2O gave compound **1** (6.5 mg). Compound **2** (17.1 mg) was obtained from Fr. IV-P-11-B (26.6 mg) by using ODS column with 93% CH_3CN elution, whereas **1** (1.4 mg) and **2** (0.8 mg) were obtained also from Fr. IV-P-11-A (6.3 mg) by using Fluofix column with 66% CH_3CN elution. Compound **3** (8.3 mg) was isolated from Fr. IV-Q-34 (35.9 mg) by using ODS column with 90% CH_3CN elution. One great-granddaughter fraction (27 mg) originated from Fr. V-T-10 was conducted on ODS column eluted with 90% CH_3CN to give **4** (0.7 mg) and **5** (1.0 mg) along with xuxuarines Gα and Gβ. Compound **6** (2.5 mg) was isolated from Fr. IV-W-9 (16 mg) by using ABZ+Plus column eluted with 93% CH_3CN. From one great-granddaughter

fraction (5.6 mg) originated from Fr. IV-R-8 gave **7** (2.7 mg) by using Fluofix column eluted with 65% CH_3CN. Compound **8** was isolated from Fr. IV-L-15 (11 mg) using ODS column with 85% CH_3CN elution. From Fr. V-K-2 (14 mg) using ODS column with 80% CH_3CN elution gave **9** (1.8 mg) along with xuxuarines Aα and Dβ.

Xuxuarine Fα (**1**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 253 (4.24), 295 (4.07), 382 (3.97). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 351 (+18.2), 302.5 (+14.3), 248 (−28.5). IR (KBr) cm^{-1}: 3449, 2942, 1711, 1676, 1649, 1597, 1460, 1379, 1308, 1202, 1150, 1084, 1061, 1019, 860, 606. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 899.3 (100, $[M+H]^+$), 481.1 (30), 421.2 (22). HR-FAB-MS *m/z*: 899.5461 (Calcd for $C_{58}H_{75}O_8$: 899.5462).

Isoxuxuarine Fα (Cangrosin B; **2**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 252.5 (4.28), 299.5 (4.14), 378 (3.99). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 341 (+25.5), 301.5 (+26.7), 253.5 (−37.4). IR (KBr) cm^{-1}: 3451, 2946, 1713, 1676, 1649, 1595, 1466, 1379, 1306, 1202, 1148, 1067, 1020, 845, 606. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 899.5 (55, $[M+H]^+$), 481.4 (4), 421.3 (7). HR-FAB-MS *m/z*: 899.5448 (Calcd for $C_{58}H_{75}O_8$: 899.5462).

7,8-Dihydroisouxuarine Fα (**3**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 251.5 (4.23), 297 (4.28). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 322.5 (+17.6), 294 (+27.7), 253.5 (−14.0). IR (KBr) cm^{-1}: 3459, 2944, 1711, 1684, 1649, 1595, 1460, 1381, 1308, 1202, 1144, 1105, 1028, 870, 600. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 901.5 (100, $[M+H]^+$), 480.3 (8), 423.3 (13). HR-FAB-MS *m/z*: 901.5617 (Calcd for $C_{58}H_{77}O_8$: 901.5618).

Isoxuxuarine Gβ (**4**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 252.5 (4.10), 299.5 (3.88), 385 (3.78). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 395.5 (−5.7), 338 (+1.9), 296 (−3.5), 262 (−19.2). IR (KBr) cm^{-1}: 3432, 2944, 1711, 1649, 1597, 1458, 1379, 1306, 1204, 1152, 1094, 1069, 1020, 841, 596. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 899.5 (30, $[M+H]^+$), 464.2 (4), 436.3 (2). HR-FAB-MS *m/z*: 899.5439 (Calcd for $C_{58}H_{75}O_8$: 899.5462).

7,8-Dihydroisouxuarine Gα (**5**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 250.5 (4.14), 297.5 (4.16). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 323 (+13.1), 293 (+20.0), 252 (−12.1). IR (KBr) cm^{-1}: 3449, 2944, 1711, 1686, 1649, 1597, 1458, 1381, 1306, 1206, 1140, 1026, 870, 598. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 901.5 (83, $[M+H]^+$), 467.2 (5), 437.3 (6). HR-FAB-MS *m/z*: 901.5595 (Calcd for $C_{58}H_{77}O_8$: 901.5618).

Isoxuxuarine Eβ (**6**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 254 (4.23), 298 (4.08), 385 (4.00). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 396 (−9.8), 338 (+3.8), 297 (−6.1), 262.5 (−25.7). IR (KBr) cm^{-1}: 3437, 2946, 1732, 1649, 1597, 1535, 1462, 1379, 1306, 1204, 1152, 1100, 1067, 1020, 841, 596. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 943.7 (54, $[M+H]^+$), 479.4 (4), 464.4 (5). HR-FAB-MS *m/z*: 943.5729 (Calcd for $C_{60}H_{79}O_9$: 943.5724).

7α-Hydroxyisoxuxuarine Eα (**7**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 254 (4.19), 295 (4.25). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 322 (+14.7), 292 (+27.3), 252 (−17.5). IR (KBr) cm^{-1}: 3464, 2949, 1730, 1686, 1949, 1583, 1464, 1379, 1306, 1262, 1204, 1148, 1028, 870, 804, 598. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 961.5 (54, $[M+H]^+$), 479.3 (7). HR-FAB-MS *m/z*: 961.5837 (Calcd for $C_{60}H_{81}O_{10}$: 961.5830).

7′,8′-Dihydroxuxuarine Aα (**8**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 234 (4.29), 277.5 (4.12), 382 (3.91). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 361.5 (+18.1), 287 (+10.2), 260.5 (−2.1), 247 (+7.3), 232.5 (−34.5). IR (KBr) cm^{-1}: 3451, 2946, 1711, 1686, 1649, 1595, 1460, 1381, 1308, 1204, 1144, 1105, 1028, 872, 600. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 857.3 (100, $[M+H]^+$), 439.3 (45), 421.3 (84). HR-FAB-MS *m/z*: 857.5352 (Calcd for $C_{56}H_{73}O_7$: 857.5356).

7′,8′-Dihydroxuxuarine Dβ (**9**): A yellow amorphous solid. UV λ_{max} (MeOH) nm (log ε): 234.5 (4.18), 277.5 (4.00), 385 (3.90). CD λ_{max} (MeOH) nm ($\Delta\varepsilon$): 394.5 (−7.3), 319 (+7.7), 256.5 (−25.2), 232.5 (+13.9). IR (KBr) cm^{-1}: 3463, 2936, 1711, 1672, 1595, 1458, 1381, 1306, 1263, 1206, 1152, 1086, 1019, 856, 571. ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR ($CDCl_3$): see Table 2. FAB-MS *m/z*: 873.5 (25, $[M+H]^+$), 453.2 (4), 421.3 (7). HR-FAB-MS *m/z*: 873.5279 (Calcd for $C_{56}H_{73}O_8$: 873.5305).

References and Notes

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