Secondary Metabolites from *Magnolia kachirachirai*

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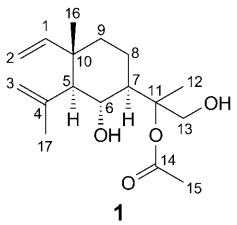
Investigation of the root bark of *Magnolia kachirachirai* led to the isolation of a new sesquiterpene, kachirachirain (**1**), and a new aporphine alkaloid, kachirachiranine (**2**), together with 20 known compounds, of which dimethyl 4,4′-methylenebis(4,1-phenylene)diurethane (**3**) was isolated for the first time from a natural source. Their structures were elucidated by spectroscopic analysis.

Introduction. – Magnoliaceous plants including seven genera and 200 species are distributed throughout temperate and tropical parts of East Asia, the South Eastern North United states, and southward through the West Indies, Central America, and North Eastern South America [1]. Most Magnoliaceous plants have been used as folk medicines [2]. Two genera, *Magnolia* and *Michelia*, with one species each, are native to Taiwan [1]. Alkaloids [3–18], terpenoids [6][8][17–19], steroids [6][7][17–19], lignans [6][7][17–21], amides [6][7][18], benzenoids [6][7][17][18], biphenyls [17], glyceride [17], chlorophylls [18], and fatty acids [22] have been isolated from these two species. Ushinsunine, which was isolated from *Michelia compressa*, showed antibacterial activity [3], and several sesquiterpenes exhibited cytotoxic activities [8].

M. kachirachirai (KANEHIRA & YAMAMOTO) DANDY is a large endemic evergreen tree growing in southeastern Taiwan [1]. Chemical constituents of the root bark of this species have not been studied previously, and the cytotoxicity of the root wood of this species has been reported in our previous study [17]. Investigation of neutral $CHCl_3$-soluble fraction of the root bark of this species has led to the isolation of two new compounds, **1** and **2**, with one compound, **3**, isolated for the first time from the nature, along with 19 known compounds. The structure elucidation of the three new isolates was described herein.



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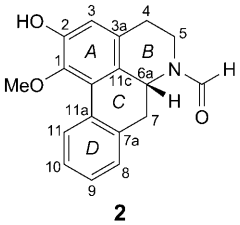

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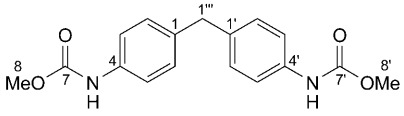

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Results and Discussion. – *Structure Elucidation*. Extensive chromatographic purification of the neutral $CHCl_3$-soluble fraction of the MeOH extract of the root bark of *M. kachirachirai* afforded 22 compounds. Compound **1** was isolated as a colorless oil, $[\alpha]_D^{25} = +11.0$ ($c = 0.18$, $CHCl_3$). The molecular formula, $C_{17}H_{28}O_4$, was determined by ESI-MS (*m/z* 319 ($[M + Na]^+$)) and HR-ESI-MS (*m/z* 319.1883 ($[M + Na]^+$; calc. 319.1885)). The IR spectrum showed absorption bands for OH groups at 3402 and for a CO group at 1738 cm^{-1}.

The ^{1}H-NMR spectrum of **1** (*Table 1*) revealed two pairs of signals for the terminal CH_2 groups: one at δ(H) 4.93 (*dd*, $J = 10.8, 1.2$, H_a–C(2)[1])) and 4.90 (*dd*, $J = 17.4, 1.2$, H_b–C(2)), forming an *AMX* system with the signal of an olefinic H-atom at δ(H) 5.73 (*dd*, $J = 17.4, 10.8$, H–C(1)). The other, at δ(H) 5.14 (br. *t*, $J = 1.5$, H_a–C(3)) and 4.77 (br. *s*, H_b–C(3)). These characteristic signals in the ^{1}H-NMR spectrum of **1** provided the clue to the structure of the isolate, as it was very similar to that of isoelemol [23], except that a OH group at C(6) (δ(C) 71.1) of **1** was in place of a H-atom at C(6) of isoelemol, and a 2-acetoxy-1-hydroxypropan-2-yl group (δ(H) 4.24 (*d*, $J = 11.1$, H_a–C(13)), 4.17 (*d*, $J = 11.1$, H_b–C(13)), 2.12 (*s*, Me(15)), 1.24 (*s*, Me(12))) at C(7) (δ(C) 52.6) of **1** was in place of a 2-hydroxypropan-2-yl group at C(7) of isoelemol. This was also supported by ^{13}C-NMR data and HMBC (*Table 1*) experiments, which showed correlations between both H–C(5) (δ(H) 1.99 (*d*, $J = 10.2$)) and H–C(7) (δ(H) 1.70 (*m*)), and C(6) (δ(C) 71.1); and between both H–C(6) (δ(H) 4.01 (*dd*, $J = 10.8, 10.2$)) and H_b–C(8) (δ(H) 1.40 (*m*)), and C(7) (δ(C) 52.6).

Table 1. *NMR Data of* **1**[1]). At 600 MHz in $CDCl_3$; δ in ppm, *J* in Hz.

	δ(H)	δ(C)	HMBC (H → C)
H–C(1)	5.73 (*dd*, $J = 17.4, 10.8$)	148.2	5, 9, 10, 16
H_a–C(2)	4.93 (*dd*, $J = 10.8, 1.2$)	110.9	10
H_b–C(2)	4.90 (*dd*, $J = 17.4, 1.2$)		1
H_a–C(3)	5.14 (br. *t*, $J = 1.5$)	114.2	4, 5, 17
H_b–C(3)	4.77 (br. *s*)		4, 5, 17
C(4)	–	143.7	
H–C(5)	1.99 (*d*, $J = 10.2$)	60.8	1, 3, 4, 6, 7, 10, 16, 17
H–C(6)	4.01 (*dd*, $J = 10.8, 10.2$)	71.1	4, 5, 7, 11
H–C(7)	1.67–1.72 (*m*)	52.6	6, 8, 11
H_a–C(8)	1.73–1.79 (*m*)	22.7	9, 10
H_b–C(8)	1.38–1.41 (*m*)		7
CH_2(9)	1.43–1.50 (*m*)	39.1	8
C(10)	–	40.8	
C(11)	–	73.9	
Me(12)	1.24 (*s*)	24.2	7, 11, 13
H_a–C(13)	4.24 (*d*, $J = 11.1$)	68.9	7, 11, 12, 14
H_b–C(13)	4.17 (*d*, $J = 11.1$)		7, 11, 12, 14
C(14)	–	171.2	
Me(15)	2.12 (*s*)	21.0	14
Me(16)	0.99 (*s*)	17.5	1, 5, 9, 10
Me(17)	1.77 (*s*)	26.3	3, 4, 5

[1]) Arbitrary atom numbering. For systematic names, see *Exper. Part.*

Furthermore, Me(16) (δ(H) 0.99 (*s*)) showed correlations with C(1) (δ(C) 148.2), C(5) (δ(C) 60.8), C(9) (δ(C) 39.1), and C(10) (δ(C) 40.8), indicating a Me group at C(10); Me(17) (δ(H) 1.77 (*s*)) showed correlations with C(3) (δ(C) 114.2), C(4) (δ(C) 143.7), and C(5) (δ(C) 60.8), confirming an isopropenyl group at C(5); Me(12) (δ(H) 1.24 (*s*)) showed correlations with C(7) (δ(C) 52.6), C(11) (δ(C) 73.9), and C(13) (δ(C) 68.9), suggesting a Me group at C(11); and H_a–C(13) (δ(H) 4.24) and H_b–C(13) (δ(H) 4.17) showed correlations with C(11) (δ(C) 73.9), suggesting a HO–CH_2 group (δ(C) 68.9, C(13)) at C(11). The relative configuration of **1** was determined by a NOESY spectrum (*Fig.*), where H–C(5) showed a correlation with H–C(7), confirming that H–C(5) and H–C(7) are on the same side of the molecule. Me(16) showed a correlation with H–C(6) but no correlation with H–C(5), suggesting that H–C(6) and Me(16) were on the opposite sides of the molecule compared to H–C(5) and H–C(7). Based on the ^{1}H- and ^{13}C-NMR (*Table 1*), COSY, HSQC, NOESY (*Fig.*), and HMBC (*Table 1*) experiments, the structure of **1** was elucidated and named kachirachirain.

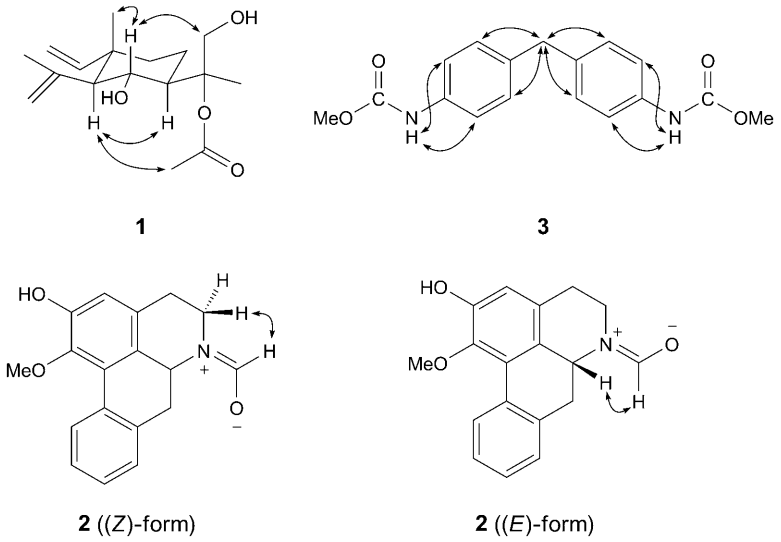

Figure. *Key NOESY* (H ↔ H) *correlations of* **1**–**3**

Kachirachiranine (**2**) was obtained as colorless needles. The ESI-MS displayed the *quasi*-molecular-ion ($[M+Na]^+$) peak at *m*/*z* 318, implying a molecular formula of $C_{18}H_{17}NO_3$, which was confirmed by the HR-ESI-MS (*m*/*z* 318.1107 $[M+Na]^+$; calc. 318.1106). UV Absorptions at 211, 272, and 312 nm indicated a highly conjugated system similar to that of asimilobine [24]. The IR spectrum showed absorption bands for a OH group at 3315 and for a formamide group at 1657 cm^{-1}.

The ^{1}H-NMR spectrum (600 MHz) of **2** was complex, due to the resonances of the two rotational isomers arising from restricted rotation about the N–CHO group. Two separate signals at δ(H) 8.26 and 8.39 represented the *N*-formyl H-atoms at a ratio of 2:1 ((*Z*)/(*E*)). The ^{1}H-NMR spectrum of **2** (*Table 2*) exhibited signals of three

mutually coupled aliphatic H-atoms of ring *C* at δ(H) 2.80 (br. *d*, J = 14.1, H_β–C(7)), 3.15 (*dd*, J = 14.1, 4.2, H_α–C(7)), and 4.90 (*d*, J = 13.8, 4.2, H–C(6a)) for the (*Z*)-isomer, and at δ(H) 2.77 (br. *d*, J = 14.1, H_β–C(7)), 3.12 (*dd*, J = 14.1, 14.1, H_α–C(7)), and 4.48 (*dd*, J = 13.8, 4.2, H–C(6a)) for the (*E*)-isomer. Signals of four mutually coupled aliphatic H-atoms of ring *B* were observed at δ(H) 2.74–2.76 (*m*, H_α–C(4)), 2.86–2.91 (*m*, H_β–C(4)), 3.40 (*ddd*, J = 12.9, 12.9, 2.9, H_α–C(5)), and 3.82 (*ddd*, J = 12.9, 4.2, 1.8, H_β–C(5)) for the (*Z*)-isomer, and at δ(H) 2.73–2.81 (*m*, H–C(4)), 3.12–3.17 (*m*, H_α–C(5)), and 4.40 (*ddd*, J = 12.9, 4.2, 4.2, H_β–C(5)) for the (*E*)-isomer. Among them, signals of H–C(6a) and H_β–C(5) were shifted downfield due to the anisotropic effect of the adjacent CO group. The ^{1}H-NMR spectrum showed five signals of aromatic H-atoms. One, at δ(H) 6.74 (*s*), was assigned to H–C(3) for ring *A* and the other four, at δ(H) 7.31 (*d*, J = 8.4, H–C(8)), 7.28–7.29 (*m*, H–C(9)), 7.33–7.34 (*m*, H–C(10)), and 8.31 (*d*, J = 7.8, H–C(11)), were assigned to ring *D* for the (*Z*)-isomer, and δ(H) 6.77 (*s*, H–C(3)), 7.23–7.34 (*m*, H–C(8), H–C(9), H–C(10)), and 8.34 (*d*, J = 8.4, H–C(11)) for the (*E*)-isomer. The ^{1}H-NMR spectrum of **2** also revealed the presence of two MeO groups with signals at δ(H) 3.57 (*s*, MeO–C(1)) and 3.63 (*s*, MeO–C(1)) for (*Z*)- and (*E*)-isomers, respectively; and two OH groups with signals at δ(H) 5.90 (br. *s*) for both of (*Z*)- and (*E*)-isomers. The disparity in geometry between the two isomers appeared clearly in a NOESY spectrum (*Fig.*). In particular, it was clearly evident that the proximity of the *N*-formyl H-atom, H_β–C(5) signal, (δ(H) 3.82) showed correlation with δ(H) 8.26 (*s*, NCHO) of the (*Z*)-isomer, and H–C(6a) signal (δ(H) 4.48) displayed correlation with that at δ(H) 8.39 (*s*, NCHO) of the (*E*)-isomer. The location of each substituent was further determined by HMBC (*Table 2*) and NOESY (*Fig.*) experiments. Its specific rotation is negative $[\alpha]_D^{25} = -169.3$ (c = 0.05, $CHCl_3$), so **2** possesses a (*R*)-configuration at C(6a) [25]. On the basis of the above results, the structure of kachirachiranine (**2**) was elucidated, which was further confirmed by ^{13}C-NMR (*Table 2*), COSY, HSQC, NOESY (*Fig.*), and HMBC (*Table 2*) experiments.

Dimethyl 4,4′-methylenebis(4,1-phenylene)diurethane (**3**) was isolated as a colorless solid. The molecular formula of **3** was determined as $C_{17}H_{18}N_2O_4$ by ESI-MS (*m*/*z* 337, ($[M+Na]^+$)) and HR-ESI-MS (*m*/*z* 337.1162 ($[M+Na]^+$)). UV Absorption maxima were at 207, 244, 281, and 365 nm. The ^{1}H-NMR spectrum (*Table 3*) of **3** showed two symmetrical *AA′XX′* systems at δ(H) 7.14 (J = 8.7, H–C(2), H–C(2′), H–C(6), H–C(6′)[1]) and 7.46 (J = 8.7, H–C(3), H–C(3′), H–C(5), H–C(5′)). The substituents in the aryl units were two (methoxycarbonyl)amino groups (δ(H) 8.54 (br. *s*, NH), 3.67 (*s*, H–C(8), H–C(8′))) and a CH_2 group (δ(H) 3.87 (*s*, CH_2(1‴))). This was also supported by the IR spectrum, which showed absorption bands for NH groups at 3328, and for CO groups at 1702 cm^{-1}, and ^{13}C-NMR spectrum (δ(C) 155.6 (C(7) and C(7′)), 52.7 (C(8) and C(8′))). From the HMBC spectrum (*Table 3*), the CH_2 group (CH_2(1‴)) showed correlations with C(2), C(2′), C(6), and C(6′), thus establishing that the CH_2 group is connected with two symmetrical benzenoid moieties. From the NOESY spectrum (*Fig.*), NH groups showed correlations with H–C(3), H–C(3′), H–C(5), and H–C(5′), confirming that two MeOCONH groups were connected at C(4) and C(4′). According to the ^{1}H- and ^{13}C-NMR (*Table 3*), COSY, HSQC, NOESY (*Fig.*), and HMBC (*Table 3*) experiments, the structure of **3** was elucidated. Compound **3** has been synthesized by reductive carbonylation of dinitroarene using a

Table 2. *NMR Data of* **2**. At 600 MHz in $CDCl_3$; δ in ppm, J in Hz.

	2 ((*Z*)-form)			**2** ((*E*)-form)
	δ(H)	δ(C)	HMBC (H → C)	δ(H)
C(1)	–	143.5		
C(2)	–	148.5		
H–C(3)	6.74 (*s*)	114.0	1, 11c, 2	6.77 (*s*)
C(3a)	–	129.9		
H_α–C(4)	2.74–2.76 (*m*)	30.7	11c, 3a	2.73–2.81 (*m*)
H_β–C(4)	2.86–2.91 (*m*)			2.73–2.81 (*m*)
H_α–C(5)	3.40 (*ddd*, J = 12.9, 12.9, 2.9)	42.1		3.12–3.17 (*m*)
H_β–C(5)	3.82 (*ddd*, J = 12.9, 4.2, 1.8)			4.40 (*ddd*, J = 12.9, 4.2, 4.2)
H–C(6a)	4.90 (*dd*, J = 13.8, 4.2)	49.5		4.48 (*dd*, J = 13.8, 4.2)
H_α–C(7)	3.15 (*dd*, J = 14.1, 4.2)	33.9	11c, 7a	3.12 (*dd*, J = 14.1, 14.1)
H_β–C(7)	2.80 (br. *d*, J = 14.1)		11c, 7a, 8	2.77 (br. *d*, J = 14.1)
C(7a)	–	136.1		
H–C(8)	7.31 (*d*, J = 8.4)	128.8	11a, 9	7.23–7.34 (*m*)
H–C(9)	7.28–7.29 (*m*)	127.4	7a, 11	7.23–7.34 (*m*)
H–C(10)	7.33–7.34 (*m*)	128.1		7.23–7.34 (*m*)
H–C(11)	8.31 (*d*, J = 7.8)	127.4	7a, 10	8.34 (*d*, J = 8.4)
C(11a)		131.1		
C(11b)	–	126.4		
C(11c)	–	124.8		
NCHO	8.26 (*s*)	162.2		8.39 (*s*)
*Me*O–C(1)	3.57 (*s*)	60.2	1	3.63 (*s*)
HO–C(2)	5.90 (br. *s*)		1, 2, 3	5.90 (br. *s*)

Table 3. *NMR Data of* **3**[1]). At 600 MHz in $CDCl_3$; δ in ppm, J in Hz.

	3		
	δ(H)	δ(C)	HMBC (H → C)
C(1)		137.5	
H–C(2)	7.14 (*d*, J = 8.7)	130.6	1‴, 4, 6
H–C(3)	7.46 (*d*, J = 8.7)	119.9	1
C(4)		138.9	
H–C(5)	7.46 (*d*, J = 8.7)	119.9	1
H–C(6)	7.14 (*d*, J = 8.7)	130.6	1‴, 2, 4
C(7)		155.6	
Me(8)	3.67 (*s*)	52.7	7
C(1′)		137.5	
H–C(2′)	7.14 (*d*, J = 8.7)	130.6	1‴, 4′, 6′
H–C(3′)	7.46 (*d*, J = 8.7)	119.9	1′
C(4′)		138.9	
H–C(5′)	7.46 (*d*, J = 8.7)	119.9	1′
H–C(6′)	7.14 (*d*, J = 8.7)	130.6	1‴, 2′, 4′
C(7′)		155.6	
Me(8′)	3.67 (*s*)	52.7	7′
CH_2(1‴)	3.87 (*s*)	41.7	2, 2′, 6, 6′
NH	8.54 (br. *s*)		

$PdCl_2$/Phen catalytic system [26]; however, this compound was isolated from a natural source for the first time.

The known isolates, *i.e.*, costunolide [17], α-cyclocostunolide [17], santamarin [6], 11β,13-dihydroreynosin [17], 11β,13-dihydrosantamarin [17], 11β,13-dihydrocostunolide [17], 2-oxo-T-cadinol [17], cyclocolorenone [27], 1-hydroxyaromadendr-4-en-3-one [28], *N*-acetylanonaine [17], *N*-acetyldehydroanonaine [17], lariciresinol [6], a mixture of β-sitosterol, and stigmasterol [17], a mixture of (24*R*)-stigmast-4-en-3-one and (22*E*,24*S*)-stigmasta-4,22-dien-3-one [17], ergosterol peroxide [29], β-amyrin acetate [30], and methyl 4-hydroxybenzoate [31] were readily identified by comparison with the data from the literature.

Conclusions. – Two genera with one species each of Formosan Magnoliaceous plants, *Magnolia kachirachirai* (KANEHIRA & YAMAMOTO) DANDY and *Michelia compressa* (MAXIM.) SARGENT are native to Taiwan. Formerly, *Michelia compressa* had been classified as belonging to the *Magnolia* genus, and was named *Magnolia compressa* MAXIM. in 1872. The external morphology of these two species is similar except that flowers of the latter are axillary, and those of the former are terminal [1]. However, both of these two species contain a large amount of costunolide from $CHCl_3$-soluble fractions (root wood of *M. compressa:* 5.4% [6]; root bark and root wood *M. kachirachirai:* 7.3 and 9.3%, resp. [17]). Sixty-six compounds have been isolated from *Michelia compressa*, including 20 sesquiterpenes, 15 aporphines, seven steroids, five lignans, four amides, eight benzenoids, two neolignans, two chlorophylls, one protoberberine, one triterpenoid, and one fatty acid [3–13][22], and 55 compounds, including 18 sesquiterpenes, eight aporphines, seven steroids, six lignans, ten neolignans, two biphenyls, one benzylisoquinoline, one glyceride, one triterpenoid, and one benzenoid, have been isolated from *Magnolia kachirachirai* in this and other studies [15–17][19–21]. The skeletons of the above components of these two species show a marked similarity. This observation may provide some information about the taxonomic position of these two species.

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Experimental Part

General. TLC: Silica gel *60 F_{254}* precoated plates (*Merck*). Column chromatography (CC): silica gel *60* (SiO_2; 70–230 or 230–400 mesh, *Merck*), silica gel (15–35 μm, *SILICYCLE*), and *Spherical C18 100A Reversed Phase Silica Gel* (*RP-C18*; 20–40 μm, *SILICYCLE*). M.p.: *Yanaco* micro-melting point apparatus; uncorrected. Optical rotations: *Jasco DIP-370* polarimeter; in $CHCl_3$. UV Spectra: *Jasco UV-240* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer-2000* FT-IR spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^1H-, ^{13}C-, and 2D-NMR spectra: *Varian Gemini*-200, *Varian Unity-Plus-400*, and *Varian VNMRS-600* spectrometers; δ in ppm rel. to Me_4Si, *J* in Hz. GC/MS: *Micromass Trio-2000* mass spectrometer; in *m*/*z* (rel. %). EI-MS: *VG-Biotech Quatro-5022* and *JEOL-JMS-HX 100* mass spectrometers; in *m*/*z* (rel. %). ESI- and HR-ESI-MS: *JEOL JMS-SX102A GC/LC/MS* and *Finnigan MAT-95XL* mass spectrometers; in *m*/*z*.

Plant Material. The root bark and the root wood of *M. kachirachirai* was collected from Mudan, Pingtung County, Taiwan in February 11, 2005, and identified by one of the author (*I.-S. C.*). A voucher specimen (No. Chen 6174) has been deposited with the Herbarium of the College of Pharmacy, Kaohsiung Medical University, Kaohsiung, Taiwan.

Extraction and Isolation. Dried root bark (4.3 kg) of *M. kachirachirai* was sliced and extracted with MeOH three times. The extract was concentrated under reduced pressure, and the residue (160 g) was partitioned between $CHCl_3/H_2O$ (1:1; 3×1500 ml) to provide a $CHCl_3$-soluble fraction and a H_2O-soluble fraction. The $CHCl_3$-soluble fraction was then extracted with 2% aq. H_2SO_4 to afford a neutral $CHCl_3$-soluble fraction (60 g) and an acid-soluble fraction. The acid-soluble fraction was basified with aq. NH_3 soln. and extracted with $CHCl_3$, then dried ($MgSO_4$) and evaporated *in vacuo* to afford the bases (17 g). The H_2O soln. was partitioned with BuOH to give a BuOH-soluble fraction (18 g), and a H_2O fraction (30 g).

The neutral $CHCl_3$-soluble fraction (60 g) was subjected to CC (2 kg of SiO_2, 70–230 mesh; hexane/acetone gradient) to obtain eleven fractions, *Frs. A1–A11*. *Fr. A2* (1.39 g) was subjected to CC (35 g of SiO_2, 230–400 mesh; hexane/acetone gradient): *Frs. A2.1–A2.4*. *Fr. A2.2* (68.2 mg) was recrystallized from MeOH to yield α-cyclocostunolide (54.0 mg). *Fr. A3* (1.55 g) was subjected to CC (40 g of SiO_2, 230–400 mesh; hexane/CH_2Cl_2 gradient): *Frs. A3.1–A3.6*. *Fr. A.3.3* (62.0 mg) was recrystallized from MeOH to give a mixture of (24*R*)-stigmast-4-en-3-one and (22*E*,24*S*)-stigmasta-4,22-dien-3-one (48.8 mg). *Fr. A4* (13.5 g) was washed with MeOH and filtered to afford costunolide (11.7 g) after recrystallization (MeOH). The mother liquid was concentrated under reduced pressure, and the residue (1.6 g) was submitted to CC (45 g of SiO_2, 230–400 mesh; hexane/acetone gradient): *Frs. A4.1–A4.5*, of which *Fr. A.4.3* (10.4 mg) was recrystallized from MeOH to produce a mixture of β-sitosterol and stigmasterol (6.2 mg). *Fr. A4.2* (0.2 g) was subjected to CC (5 g of SiO_2, 230–400 mesh; hexane/acetone 6:1): *Frs. A4.2.1–A4.2.3*, of which *Fr. A4.2.1* was purified by prep. TLC (SiO_2; hexane/acetone 3:1): 11β,13-dihydrocostunolide (22.4 mg). *Fr. A4.2.2* (0.05 g) was submitted to CC (5 g of SiO_2, 230–400 mesh; hexane/acetone 10:1): *Frs. A4.2.2.1–A4.2.2.3*, of which *Fr. A4.2.2.1* and *Fr. A4.2.2.3* were composed entirely of 11β,13-dihydroreynosin (8.6 mg) and 1-hydroxyaromadendr-4-en-3-one (3.7 mg), respectively. *Fr. A4.2.2.2* was purified by prep. TLC (SiO_2; CH_2Cl_2): 11β,13-dihydrosantamarin (6.7 mg) and cyclocolorenone (5.8 mg). *Fr. A4.5* (0.06 g) was subjected to CC (5 g of *RP-C18*, 20–40 μm; MeOH/H_2O 8:1): *Frs. A4.5.1–A4.5.5*, of which *Fr. A4.5.3* was purified by prep. TLC (SiO_2; hexane/CH_2Cl_2 2:1): ergosterol peroxide (3.1 mg). *Fr. A5* (1.58 g) was submitted to CC (40 g of SiO_2, 230–400 mesh; hexane/acetone gradient): *Frs. A5.1–Fr. A5.5*. *Fr. A5.4* (0.67 g) was subjected to CC (20 g of SiO_2, 230–400 mesh; hexane/acetone 1:3): *Frs. A5.4.1–Fr. A5.4.8*, of which *Fr. A5.4.1* and *Fr. A5.4.6* were composed entirely of methyl 4-hydroxybenzoate (1.3 mg) and 2-oxo-T-cadinol (3.3 mg), resp. *Fr. A7* (1.19 g) was subjected to CC (30 g of SiO_2, 230–400 mesh; $CHCl_3$/acetone gradient): *Frs. A7.1–A7.6*. *Fr. A.7.3* (0.7 g) was submitted to CC (18 g of SiO_2, 230–400 mesh; hexane/acetone 3:1): *Frs. A7.3.1–A7.3.6*. *Fr. A.7.3.4* (0.08 g) was subjected to CC (5 g of *RP-C18*, 20–40 μm; acetone/H_2O 1:1): *Frs. A7.3.4.1–A7.3.4.6*, of which *Fr. A7.3.4.2* was composed entirely of **1** (3.5 mg). *Fr. A7.3.6* (0.03 g) was subjected to CC (5 g of SiO_2, 230–400 mesh; CH_2Cl_2/hexane 9:1): *Frs. A7.3.6.1–A7.3.6.6*, of which *Fr. A7.3.6.4* and *Fr. A7.3.6.5* were composed entirely of *N*-acetyldehydroanonaine (1.8 mg) and santamarin (2.4 mg), resp. *Fr. A7.3.7* (18.5 mg) was subjected to CC (5 g of SiO_2, 230–400 mesh; CH_2Cl_2): *Frs. A7.3.7.1–A7.3.7.6*, of which fraction *Fr. A7.3.7.2* was composed entirely of **3** (1.0 mg). *Fr. 9* (1.88 g) was submitted to CC (50 g of SiO_2, 230–400 mesh; hexane/acetone gradient): *Frs. A9.1–A9.7*, of which *Fr. A.9.3* was composed entirely of *N*-acetylanonaine (9.8 mg). *Fr. A9.1* was purified by prep. TLC (SiO_2; CH_2Cl_2/hexane 2:1): β-amyrin acetate (3.2 mg). *Fr. 10* (0.27 g) was subjected to CC (8 g of SiO_2, 230–400 mesh; CH_2Cl_2/acetone gradient): *Frs. A10.1–A10.7*. *Fr. A.10.2* was purified by prep. TLC (*RP-C18*; MeOH/H_2O 5:1): **2** (2.2 mg). *Fr. A10.5* was purified by prep. TLC (SiO_2; hexane/acetone 1:1): lariciresinol (8.6 mg).

Kachirachirain (=*2-[*rel-*(1*R,*2*R,*3*S,*4*S)-4-Ethenyl-2-hydroxy-4-methyl-3-(prop-1-en-2-yl)cyclohexyl]-1-hydroxypropan-2-yl Acetate*; **1**). Colorless oil. $[\alpha]_D^{26} = +11.0$ ($c = 0.18$, $CHCl_3$). IR (neat): 3402 (OH), 1738 (C=O). ^{1}H- and ^{13}C-NMR: see *Table 1*. ESI-MS: 319 ($[M+Na]^+$). HR-ESI-MS: 319.1883 ($[M+Na]^+$, $C_{17}H_{28}NaO_4^+$; calc. 319.1885).

Kachirachiranine (=(*6a*R)*-4,5,6a,7-Tetrahydro-2-hydroxy-1-methoxy-6*H*-dibenzo[*de,g*]quinoline-6-carbaldehyde*; **2**). Colorless needles. M.p. 244–245°. $[\alpha]_D^{26} = -169.3$ ($c = 0.05$, $CHCl_3$). UV (MeOH): 312 (3.31), 272 (3.96), 211 (4.34). UV (KOH): 335 (3.33), 292 (3.73), 275 (3.90), 250 (4.08), 210 (4.46). IR (KBr): 3315 (OH), 1657 (C=O). ^{1}H- and ^{13}C-NMR: see *Table 2*. ESI-MS: 318 ($[M+Na]^+$). HR-ESI-MS: 318.1107 ($[M+Na]^+$, $C_{18}H_{17}NNaO_3^+$; calc. 318.1106).

Dimethyl 4,4′-Methylenebis(4,1-phenylene)diurethane (= *Dimethyl (Methanediyldibenzene-4,1-diyl)biscarbamate*; **3**). Colorless solid. M.p. 180–181°. UV (MeOH): 365 (2.18), 281 (2.88), 244 (3.44), 207 (3.63). IR (KBr): 3328 (NH), 1702 (C=O). ^{1}H- and ^{13}C-NMR: see *Table 3*. ESI-MS: 337 ($[M+Na]^+$). HR-ESI-MS: 337.1162 ($[M+Na]^+$, $C_{17}H_{18}N_2NaO_4^+$; calc. 337.1164).

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