Chemistry of Natural Compounds, Vol. 47, No. 2, May, 2011 [*Russian original No. 2, March-April, 2011*]

SYNTHESIS FROM (+)-α-PINENE OF OPTICALLY ACTIVE MACROCYCLES CONTAINING CYCLOBUTANE, ESTER, AZINE, OR HYDRAZIDE GROUPS

G. Yu. Ishmuratov,* G. R. Mingaleeva, O. O. Shakhanova, R. R. Muslukhov, M. P. Yakovleva, L. P. Botsman, and A. G. Tolstikov

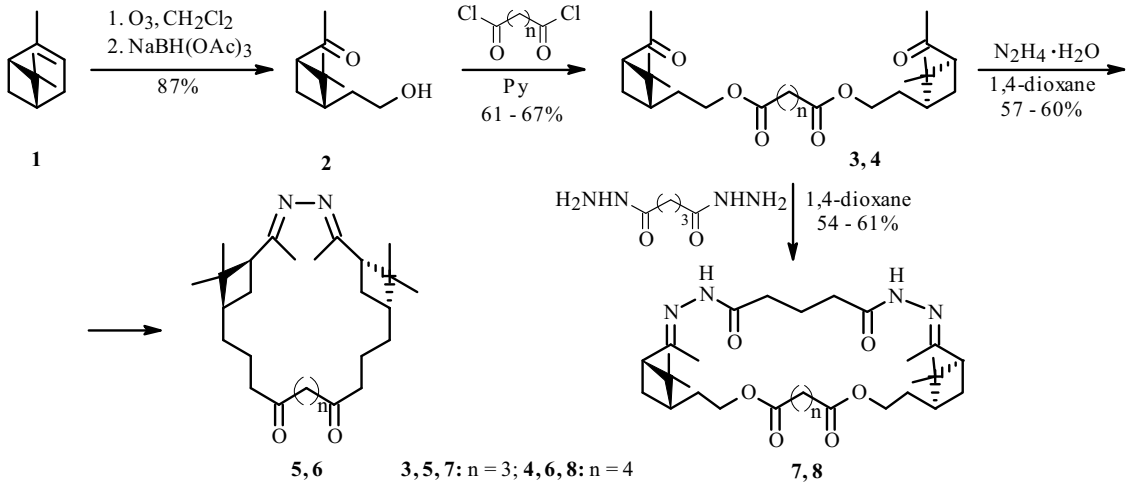
UDC 547.447+547.451+547.598.5

Optically active symmetric macrocyclic diesterazines and diesterdihydrazides were synthesized efficiently from the available natural monoterpene (+)-α-pinene (de 50%) using a [2+1]-reaction of 1′-[(1S,3S)-3-(2-hydroxyethyl)-2,2-dimethylcyclobutyl]ethanone and glutaric and adipic acid chlorides followed by [1+1]-condensation of the intermediate diketodiesters with hydrazine hydrate or glutaric acid dihydrazide.

Keywords: (+)-α-pinene, 1′-[(1*S*,3*S*)-3-(2-hydroxyethyl)-2,2-dimethylcyclobutyl]ethanone, *bis*{2‴-[(1′*S*,3′*S*)-3′-acetyl-2′,2′-dimethylcyclobutyl]ethyl}pentanedioate, *bis*{2‴-[(1′*S*,3′*S*)-3′-acetyl-2′,2′-dimethylcyclobutyl]ethyl}hexanedioate, optically active macrocyclic azinodiesters and diesterdihydrazides, synthesis.

We reported previously the synthesis from tetrahydropyran [1–4], 4-methyltetrahydropyran [2, 3, 5], and *l*-menthol [6] of several macrocyclic compounds containing ester, azine, or hydrazide groups. Antibacterial activity *in vivo* and *in vitro* was observed among them [4].

Herein we propose a short and efficient synthesis in three steps from the available monoterpene (+)-α-pinene (**1**) (*de* 50%) of 23- (**5**), 24- (**6**), 30- (**7**), and 31-membered (**8**) chiral macrocyclic compounds containing cyclobutane, ester, azine, or hydrazide groups with potential biological and pharmacological activity. The synthetic scheme included ozonolytic cleavage of starting cycloolefin (**1**) to the ketoalcohol (**2**), its [2+1]-condensation with glutaric or adipic acid dichlorides, and final cyclization of the intermediate diketodiesters (**3**, **4**) using hydrazine hydrate or glutaric acid dihydrazide in 1,4-dioxane at room temperature and a reagent:solvent mole ratio of 1:70.



Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, 450054, Ufa, fax: (347) 235 60 66, e-mail: insect@anrb.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 195–198, March–April, 2011. Original article submitted July 22, 2010.

 0009-3130/11/4702-0210

The structures of products **5**–**8** were established using IR, PMR, and ^{13}C NMR spectroscopy and GC/MS.

IR spectra of **5**–**8** lacked absorption bands characteristic of the ketones in the key diketodiesters (1701 cm^{-1} in **3** and 1705 in **4**). The appearance of bands in the IR spectra at 1633 cm^{-1} for **5** and 1637 for **6**, typical of an azine group; and at 1647, 1690, and 3392 cm^{-1} for **7** and 1644, 1683, and 3326 for **8**, characteristic of a hydrazide group, proved that macrocycles with azine and hydrazide groups, respectively, had formed.

NMR spectra of **5**–**8** were compared with those of starting diketodiesters **3** and **4** and glutaric acid dihydrazide. Because starting natural (+)-α-pinene (**1**) was a mixture (3:1) of diastereomers and subsequent transformations did not affect its asymmetric centers, the ratio of stereoisomers was preserved. ^{13}C NMR spectra of **5**–**8** lacked a resonance for the carbonyl C atom of the starting acyclic compounds (207.18 ppm in **3** and 207.32 in **4**). PMR spectra of macrocycles **5** and **6** lacked a resonance (~6.90) for the C=N–NH_2 group; macrocycles **7** and **8**, (~4.90) for the hydrazide group. This indicated that the products were not linear substitution products.

The ^{13}C NMR spectra of **5** and **6** contained a resonance for the C atom of the ester (170.92 ppm in **5** and 173.07 in **6**), a singlet for the azine (159.08 ppm in **5** and 159.01 in **6**), and a strong-field quartet (14.36 ppm in **5** and 14.32 in **6**) of two magnetically equivalent CH_3 groups. The strong-field chemical shift of the Me groups indicated that they were *cis*-oriented. Therefore, the double bonds in the macrocycles had the *trans-trans* configuration.

Analogously to **5** and **6**, ^{13}C NMR spectra of **7** and **8** had resonances for ester C atoms (170.82 ppm in **7** and 173.13 in **8**) and for NH–C=O C atoms (175.53 in **7** and 175.73 in **8**) that were shifted compared with starting gluaric acid dihydrazide (171.89) and a singlet for a C=N group (151.43 in **7** and 151.12 in **8**) and two quartets for CH_3 groups (15.65 in **7** and 15.76 in **8**), the chemical shifts of which corresponded to C atoms of two magnetically equivalent CH_3–C=N groups. This indicated that the double bonds in the macrocycles had the *trans-trans* configuration.

PMR spectra of macrocycles **7** and **8** had weak-field resonances (9.08 ppm in **7** and 8.46 in **8**), the chemical shifts and integrated intensities of which corresponded to two protons of NHC=O groups in the macrocycles. Resonances of NHC=O C atoms in the ^{13}C NMR spectra of these compounds were noticeably broadened compared with those of the corresponding C atoms in the starting glutaric acid dihydrazide. This was probably due to intramolecular interactions of the functional groups.

Thus, the strong-field chemical shift of the two methyl groups in **5**–**8** was consistent with the *trans-trans* configuration of the double bonds. Three conformers with *diexo*-, *diendo*-, and *exo,endo*-orientations of the methyl groups were possible for them. The appearance of only one resonance for the methyl groups and C atoms of the double bonds in NMR spectra of **5**–**8** indicated that other stereoisomeric and conformational combinations were absent. However, the NMR spectral data were insufficient to confirm unambiguously which of them was most probable.

All spectral data pointed to the formation of macrocycles **7** and **8**. This was confirmed by the mass spectra. Compounds **5**–**8** were studied using atmospheric pressure chemical ionization (APCI) with detection of positive and negative ions (20 eV). The capability for protonation and solvation by H_2O is well known in the chemistry of amides and hydrazides [7], because of which the APCI method was used. Mass spectra of **3**–**8** showed very strong peaks for protonated MH^+ and deprotonated $[M - H]^-$ ions in addition to their 1÷2 ionic associates with H_2O molecules. This could be considered proof of the existence of compounds with the corresponding molecular weights.

EXPERIMENTAL

IR spectra were recorded from thin layers on a Shimadzu Prestige-21 instrument. NMR spectra were taken in $CDCl_3$ solutions with TMS internal standard on a Bruker AM-300 (operating frequency 300.13 MHz for ^1H and 75.47 MHz for ^{13}C). Resonances in NMR spectra were assigned and proton–proton SSCC were determined using two-dimensional correlation spectroscopy COSY (C–H) and COSY (H–H) and double resonance. Chromatographic analysis was carried out in a Chrom-5 instrument [column length 1.2 m, stationary phase silicone SE-30 (5%) on Chromaton N-AW-DMCS (0.16–0.20 mm), operating temperature 50–300°C] with He carrier gas. Column chromatography used Lancaster SiO_2 (70-230) (England). TLC monitoring used Sorbfil SiO_2 (Russia). Elemental analyses of all compounds agreed with those calculated. Mass spectra of **3**–**8** were measured in a Shimadzu LC/MS 2010 EV under APCI conditions at electron energy 20 eV with detection of positive and negative ions. The liquid mobile phase was water at flow rate 0.03 mL/min.

1′-[(1*S*,3*S*)-3-(2-Hydroxyethyl)-2,2-dimethylcyclobutyl]ethanone (2). A solution of **1** (1.95 g, 14.4 mmol) and glacial AcOH (1.64 mL, 28.7 mmol) in CH_2Cl_2 (40 mL) was stirred (from –4°C to –2), purged with an O_3–O_2 mixture (ozonator production 40 mmol O_3/h) until 15 mmol of O_3 was absorbed, purged with Ar, diluted with CH_2Cl_2 (20 mL), stirred (10°C), added to a

previously prepared suspension of $NaBH(OAc)_3$ [prepared by adding a solution of glacial AcOH (11.9 g, 198 mmol) in CH_2Cl_2 (20 mL) to a suspension of $NaBH_4$ (2.5 g, 66 mmol) in CH_2Cl_2 (100 mL) with subsequent stirring for 2 h], heated to room temperature, stirred for 3 h, cooled to 10°C, and treated with NaOH solution (4.5 g in 100 mL H_2O). The organic layer was separated, washed successively with saturated NH_4Cl solution and H_2O, dried over Na_2SO_4, and evaporated to afford ketoalcohol **2**. Yield 2.42 g (87%), 99% purity (GC), $[\alpha]_D^{20}$ +41.2° (*c* 0.4, CH_3OH) [8]. IR and PMR spectra of **2** were practically identical to those published earlier [9, 10].

^{13}C NMR spectrum (75.47 MHz, $CDCl_3$, δ, ppm): 17.12 (20.88) (q, CH_3-2-*cis*), 22.74 (22.55) (t, C-4), 24.55 (29.98) (q, CH_3-2-*trans*), 30.27 (q, C-2′), 32.90 (33.67) (t, C-1′), 38.47 (38.87) (d, C-3), 43.18 (s, C-2), 54.21 (54.10) (d, C-1), 60.82 (t, C-2″), 208.27 (208.02) (s, C-1′).

General Method for Preparing Diketodiesters 3 and 4. A solution of hydroxyketone **2** (2.0 mmol) in anhydrous Py (1 mL) was stirred, treated with a solution of the appropriate dicarboxylic acid chloride (1.0 mmol) [11] in anhydrous Et_2O (1 mL), treated after 48 h (TLC monitoring) with CH_2Cl_2 (10 mL), washed successively with HCl solution (5%, 3 × 1.5 mL) and saturated NaCl solution (3 × 1.5 mL), dried over $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2, petroleum ether:MTBE (*tert*-butyl methyl ether), 5:1) to afford the corresponding diketodiester.

***Bis*{2‴-[(1′*S*,3′*S*)-3′-acetyl-2′,2′-dimethylcyclobutyl]ethyl}pentanedioate (3).** Yield 0.14 g (67%), $[\alpha]_D^{20}$ +1.86° (*c* 5.73, CH_2Cl_2), R_f 0.69. IR spectrum (KBr, ν, cm^{-1}): 1735 (O=C–O), 1701 (C=O).

PMR spectrum (300.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.91 (1.05) (6H, s, CH_3-2′-*cis*), 1.07 (1.19) (6H, s, $2CH_3$-2′-*trans*), 1.60–1.72 (4H, m, H-2‴), 1.75–1.88 (2H, m, H-3), 1.87 (2H, dt, J = 10.1, 8.5, H-4′-*cis*), 1.90–2.02 (4H, m, H-1′, H-4′), 2.07 (6H, s, H-2″), 2.37 (4H, t, J = 7.0, H-2, H-4), 2.82 (2H, dd, J = 10.0, 7.3, H-3′), 4.02 (4H, t, J = 6.8, H-1‴).

^{13}C NMR spectrum (75.47 MHz, $CDCl_3$, δ): 16.86 (20.59) (q, CH_3-2′-*cis*), 19.81 (t, C-3), 22.70 (22.29) (t, C-4′), 28.68 (29.45) (t, C-2‴), 29.75 (24.75) (q, CH_3-2′-*trans*), 29.76 (q, C-2″), 32.92 (t, C-2, C-4), 38.67 (37.92) (d, C-1′), 42.77 (41.10) (s, C-2′), 53.81 (52.29) (d, C-3′), 62.00 (t, C-1‴), 170.58 (s, C-1, C-5), 207.18 (s, C-1″).

Mass spectrum (APCI, 20 eV, *m*/*z*): 437 $[M + H]^+$, 454 $[M + H_2O]^+$, 435 $[M - H]^-$.

***Bis*{2‴-[(1′*S*,3′*S*)-3′-acetyl-2′,2′-dimethylcyclobutyl]ethyl}hexanedioate (4).** Yield 0.13 g (61%), $[\alpha]_D^{20}$ +1.66° (*c* 3.74, CH_2Cl_2), R_f 0.70. IR spectrum (KBr, ν, cm^{-1}): 1734 (O=C–O), 1705 (C=O).

PMR spectrum (300.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.87 (1.00) (6H, s, CH_3-2′-*cis*), 1.29 (1.21) (6H, s, CH_3-2′-*trans*), 1.46–1.58 (4H, m, H-3, H-4), 1.62–1.68 (4H, m, H-2‴), 1.89 (2H, dt, J = 10.1, 8.5, H-4′-*cis*), 2.03 (6H, s, H-2″), 2.30 (4H, t, J = 7.2, H-2, H-5), 2.83 (2H, dd, J = 10.1, 7.2, H-3′), 4.0 (4H, t, J = 6.9, H-1‴).

^{13}C NMR spectrum (75.47 MHz, $CDCl_3$, δ): 16.95 (24.40) (q, CH_3-2′-*cis*), 22.76 (22.38) (t, C-4′), 24.08 (t, C-3, C-4), 28.76 (29.39) (t, C-2‴), 29.40 (q, C-2″), 29.54 (24.83) (q, CH_3-2′-*trans*), 33.58 (t, C-2, C-5), 38.70 (38.00) (d, C-1′), 42.86 (41.18) (s, C-2′), 53.89 (53.37) (d, C-3′), 62.67 (t, C-1‴), 172.95 (s, C-1, C-6), 207.32 (s, C-1″).

Mass spectrum (APCI, 20 eV, *m*/*z*): 451 $[M + H]^+$, 468 $[M + H_2O]^+$, 449 $[M - H]^-$.

General Method for Preparing macrocycles 5 and 6. Diketodiester (**3** or **4**, 1.0 mmol) in anhydrous dioxane (6.2 mL) was stirred vigorously, treated slowly dropwise with hydrazine hydrate (1.0 mmol, 92%), and stirred for 24 h (TLC monitoring). The dioxane was evaporated at reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL), washed with H_2O (3 × 3 mL), dried over $MgSO_4$, and evaporated. The resulting residue was stirred, treated successively with anhydrous CH_2Cl_2 (1 mL) and hexane (10 mL), and stored until the layers separated, the upper of which was decanted. The residue was washed with hexane (3 mL) and evaporated *in vacuo*.

(1*S*,6*S*,8*S*,20*S*)-2,5,7,7,21,21-Hexamethyl-11,17-dioxa-3,4-diazatricyclo[18.1.1.1^{6,8}]tricosa-2,4-dien-12,16-dione (5). Yield 0.25 g (57%), $[\alpha]_D^{20}$ +9.50° (*c* 1.46, CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 1734 (O=C–O), 1633 (C=N).

PMR spectrum (300.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.87 (0.99) (6H, s, CH_3-7-*cis*, CH_3-21-*cis*), 1.51–1.75 (4H, m, H-9, H-19), 1.21 (1.16) (6H s, CH_3-7-*trans*, CH_3-21-*trans*), 1.68 (6H, s, CH_3-2, CH_3-5), 1.89–2.03 (6H, m, H-8, H-20, H-22, H-23), 1.90–2.15 (2H, m, H-14), 2.35 (4H, t, J = 6.8, H-13, H-15), 2.62 (2H, dd, J = 10.0, 6.9, H-1, H-6), 3.99 (4H, t, J = 6.9, H-10, H-18).

^{13}C NMR spectrum (75.47 MHz, $CDCl_3$, δ): 14.36 (q, CH_3-2, CH_3-5), 16.91 (24.62) (q, CH_3-7-*cis*, CH_3-21-*cis*), 19.30 (t, C-14), 23.32 (23.13) (s, C-22, C-23), 28.92 (29.77) (t, C-9, C-19), 30.33 (24.62) (q, CH_3-7-*trans*, CH_3-21-*trans*), 32.60 (t, C-13, C-15), 38.70 (37.88) (d, C-8, C-20), 42.34 (42.48) (s, C-7, C-21), 49.94 (49.29) (d, C-1, C-6), 63.16 (t, C-10, C-18), 159.08 (c, C-2, C-5), 170.92 (s, C-12, C-16).

Mass spectrum (APCI, 20 eV, *m*/*z*): 433 $[M + H]^+$, 451 $[M + H + H_2O]^+$, 431 $[M - H]^-$.

(1*S*,6*S*,8*S*,21*S*)-2,5,7,7,22,22-Hexamethyl-11,18-dioxa-3,4-diazatricyclo[19.1.1.1^{6,8}]tetracosa-2,4-dien-12,17-dione (6). Yield 0.27 g (60%), $[\alpha]_D^{20}$ +12.20° (*c* 1.81, CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 1735 (O=C–O), 1637 (C=N).

PMR spectrum (300.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.81 (6H, s, CH_3-7-*cis*, CH_3-22-*cis*), 1.22 (6H, s, CH_3-7-*trans*, CH_3-22-*trans*), 1.45–1.63 (4H, m, H-14, H-15), 1.61–1.70 (4H, m, H-9, H-20), 1.91 (2H′, dt, J = 10.1, 8.4, H-23, H-24), 1.92–2.30 (2H, m, H-8, H-21), 2.04 (2H″, dt, J = 10.1, 10.0, H-23, H-24), 2.31 (4H, t, J = 6.8, H-13, H-16), 2.58 (2H, dd, J = 10.1, 7.0, H-1, H-6), 3.99 (4H, t, J = 7.0, H-10, H-19).

^{13}C NMR spectrum (75.47 MHz, $CDCl_3$, δ): 14.32 (q, CH_3-2, CH_3-5), 16.92 (q, CH_3-7-*cis*, CH_3-22-*cis*), 24.23 (t, C-14, C-15, C-23, C-24), 28.85 (t, C-9, C-20), 30.27 (q, CH_3-7-*trans*, CH_3-22-*trans*), 33.62 (t, C-13, C-16), 38.52 (38.78) (d, C-8, C-21), 42.22 (s, C-7, C-22), 49.81 (50.05) (d, C-1, C-6), 62.95 (t, C-10, C-19), 159.01 (s, C-2, C-5), 173.07 (s, C-12, C-17).

Mass spectrum (APCI, 20 eV, *m/z*): 575 $[M + H]^+$, 592 $[M + H_2O]^+$, 573 $[M – H]^–$, 590 $[M + H_2O – 2H]^–$, 608 $[M + 2H_2O – 2H]^–$.

General Method for Preparing Macrocycles 7 and 8. Diketoester (**3** or **4**, 1.0 mmol) in anhydrous dioxane (6.2 mL) was stirred vigorously, treated slowly with glutaric acid dihydrazide (0.16 g, 1.0 mmol) [11], and stirred for 48 h (TLC monitoring). The dioxane was evaporated. The residue was dissolved in CH_2Cl_2 (20 mL), washed with H_2O (3 × 5 mL), dried over $MgSO_4$, and evaporated. The resulting residue was stirred, treated successively with anhydrous CH_2Cl_2 (1 mL) and hexane (10 mL), and stored until the layers separated, the upper of which was decanted. The residue was washed with hexane (5 mL) and evaporated.

(1*S*,13*S*,15*S*,27*S*)-2,12,14,14,28,28-Hexamethyl-18,24-dioxa-3,4,10,11-tetraazatricyclo[25.1.1.1^{13,15}]triaconta-2,11-dien-5,9,19,23-tetrone (7). Yield 0.34 g (61%), $[\alpha]_D^{20}$ +2.00° (*c* 1.83, CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 3292 (NH), 1735 (O=C–O), 1690 (CONH), 1647 (C=N).

PMR spectrum (300.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.79 (6H, s, CH_3-14-*cis*, CH_3-28-*cis*), 1.17 (6H, s, CH_3-14-*trans*, CH_3-28-*trans*), 1.65 (6H, s, CH_3-2, CH_3-12), 1.67–1.80 (4H, m, H-16, H-26), 1.78–1.97 (2H, m, H-15, H-27), 1.97–2.10 (4H, m, H-7, H-21), 2.23 (4H, t, J = 6.9, H-6, H-8), 2.41 (4H, t, J = 6.7, H-20, H-22), 2.63 (2H, dd, J = 9.9, 7.0, H-1, H-13), 4.08 (4H, t, J = 6.7, H-17, H-25), 9.08 (2H, br.s, NH).

^{13}C NMR spectrum (75.47 MHz, $CDCl_3$, δ): 15.65 (q, CH_3-2, CH_3-12), 16.81 (q, CH_3-14-*cis*, CH_3-28-*cis*), 19.41 (t, C-7), 20.60 (t, C-21), 22.96 (t, C-29, C-30), 28.75 (t, C-16, C-26), 29.58 (q, CH_3-14-*trans*, CH_3-28-*trans*), 31.93 (t, C-6, C-8), 33.02 (t, C-20, C-22), 38.75 (37.50) (d, C-15, C-27), 42.39 (s, C-14, C-28), 49.97 (49.32) (d, C-1, C-13), 62.93 (t, C-17, C-25), 151.43 (s, C-2, C-12), 170.82 (s, C-19, C-23), 175.53 (s, C-5, C-9).

Mass spectrum (APCI, 20 eV, *m/z*): 561 $[M + H]^+$, 579 $[M + H + H_2O]^+$, 597 $[M + H + 2H_2O]^+$, 599 $[M – H]^–$, 577 $[M + H_2O – H]^–$, 595 $[M + 2H_2O – H]^–$.

(1*S*,13*S*,15*S*,28*S*)-2,12,14,14,29,29-Hexamethyl-18,25-dioxa-3,4,10,11-tetraazatricyclo[26.1.1.1^{13,15}]hentriaconta-2,11-dien-5,9,19,24-tetrone (8). Yield 0.31 g (54%), $[\alpha]_D^{20}$ +2.30° (*c* 1.94, CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 3326 (NH), 1734 (O=C–O), 1683 (CONH), 1644 (C=N), .

PMR spectrum (300.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.87 (6H, s, CH_3-14-*cis*, CH_3-29-*cis*), 1.19 (6H, s, CH_3-14-*trans*, CH_3-29-*trans*), 1.48–1.54 (4H, m, H-21, H-22), 1.61–1.70 (2H, m, H-7), 1.63–1.74 (4H, m, H-16, H-27), 1.82–1.98 (6H, m, H-15, H-28, H-31, H-30), 2.28 (4H, t, J = 6.9, H-6, H-8), 2.30 (4H, t, J = 6.8, H-20, H-23), 2.69 (2H, dd, J = 9.8, 6.6, H-1, H-13), 4.15 (4H, t, J = 4.1, H-17, H-26), 8.48 (2H, br.s, NH).

^{13}C NMR spectrum (75.47 MHz, $CDCl_3$, δ): 15.76 (q, CH_3-2, CH_3-12), 16.86 (q, CH_3-14-*cis*, CH_3-29-*cis*), 19.42 (t, C-7), 24.13 (t, C-21, C-22), 24.38 (s, C-30, C-31), 28.90 (t, C-16, C-27), 30.11 (q, CH_3-14-*trans*, CH_3-29-*trans*), 31.66 (t, C-6, C-8), 33.67 (t, C-20, C-23), 38.38 (d, C-15, C-28), 42.45 (c, C-14, C-29), 50.05 (d, C-1, C-13), 63.84 (t, C-17, C-26), 151.12 (s, C-2, C-12), 173.13 (s, C-19, C-24), 175.73 (s, C-5, C-9).

Mass spectrum (APCI, 20 eV, *m/z*): 575 $[M + H]^+$, 593 $[M + H_2O + H]^+$, 611 $[M + 2H_2O + H]^+$, 573 $[M – H]^–$, 591 $[M + H_2O – H]^–$, 609 $[M + 2H_2O – H]^–$.

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