ISSN 0012-5008, Doklady Chemistry, 2008, Vol. 423, Part 1, pp. 299–304. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © S.V. Chernov, E.E. Shul'ts, M.M. Shakirov, Yu.V. Gatilov, G.A. Tolstikov, 2008, published in Doklady Akademii Nauk, 2008, Vol. 423, No. 3, pp. 350–354.

CHEMISTRY

Synthesis of Diterpene Alkaloids of a New Structural Type from Maleopimaric Acid

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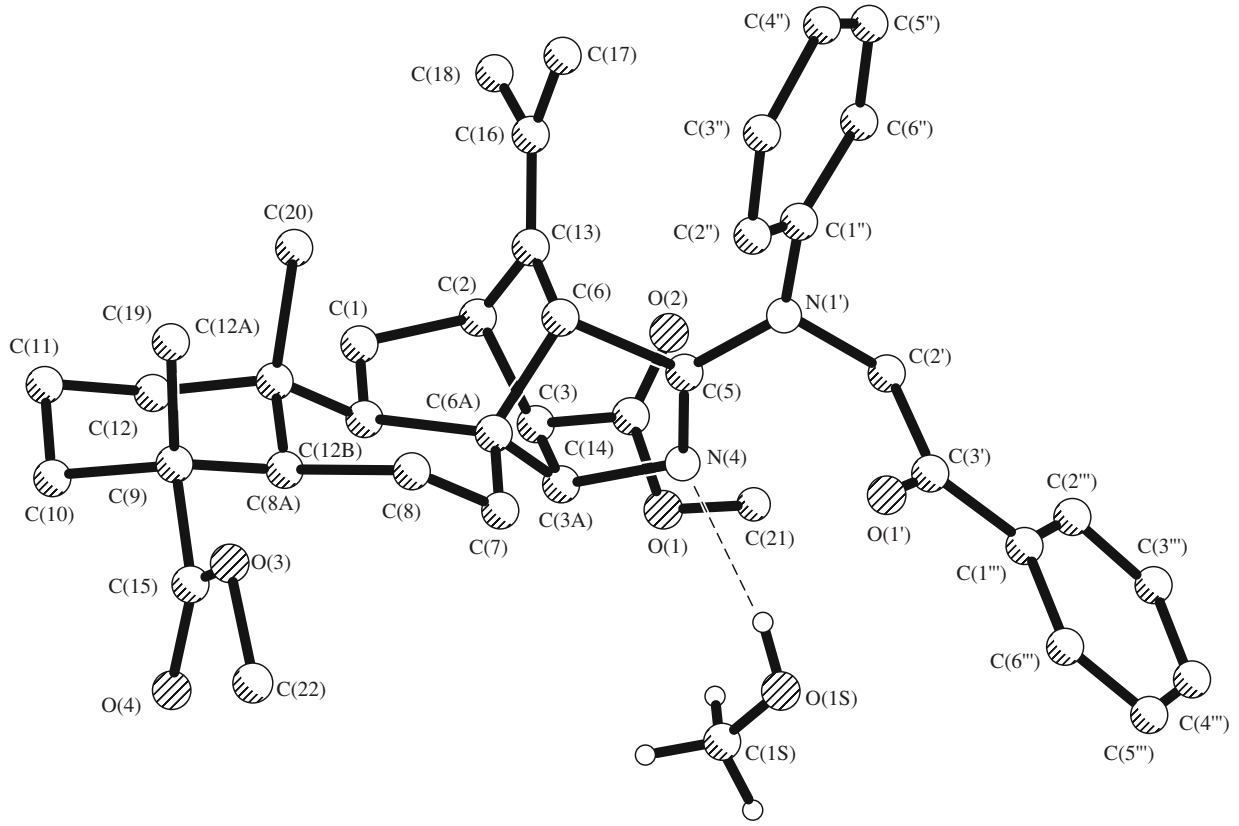
Received June 10, 2008

DOI: 10.1134/S0012500808110098

The adduct of levopimaric acid with maleic anhydride, maleopimaric acid (**1**), widely used in the technology of paint and varnish and polymeric materials [1, 2], is considered as a promising starting material for the synthesis of biologically active compounds [3–5] and chiral ligands [6]. In this paper, we suggest a general approach to the synthesis of diterpene alkaloids of a new structural type based on maleopimaric acid. A nitrogen-containing group, which indicates that the new compounds are alkaloids, is represented by the amidine structural fragment.

The suggested approach (Scheme 1) is based on the sequential use of the Lossen rearrangement and the intramolecular Vilsmeier reaction. Methyl maleopima-



Perspective view of the structure of compound **9**.

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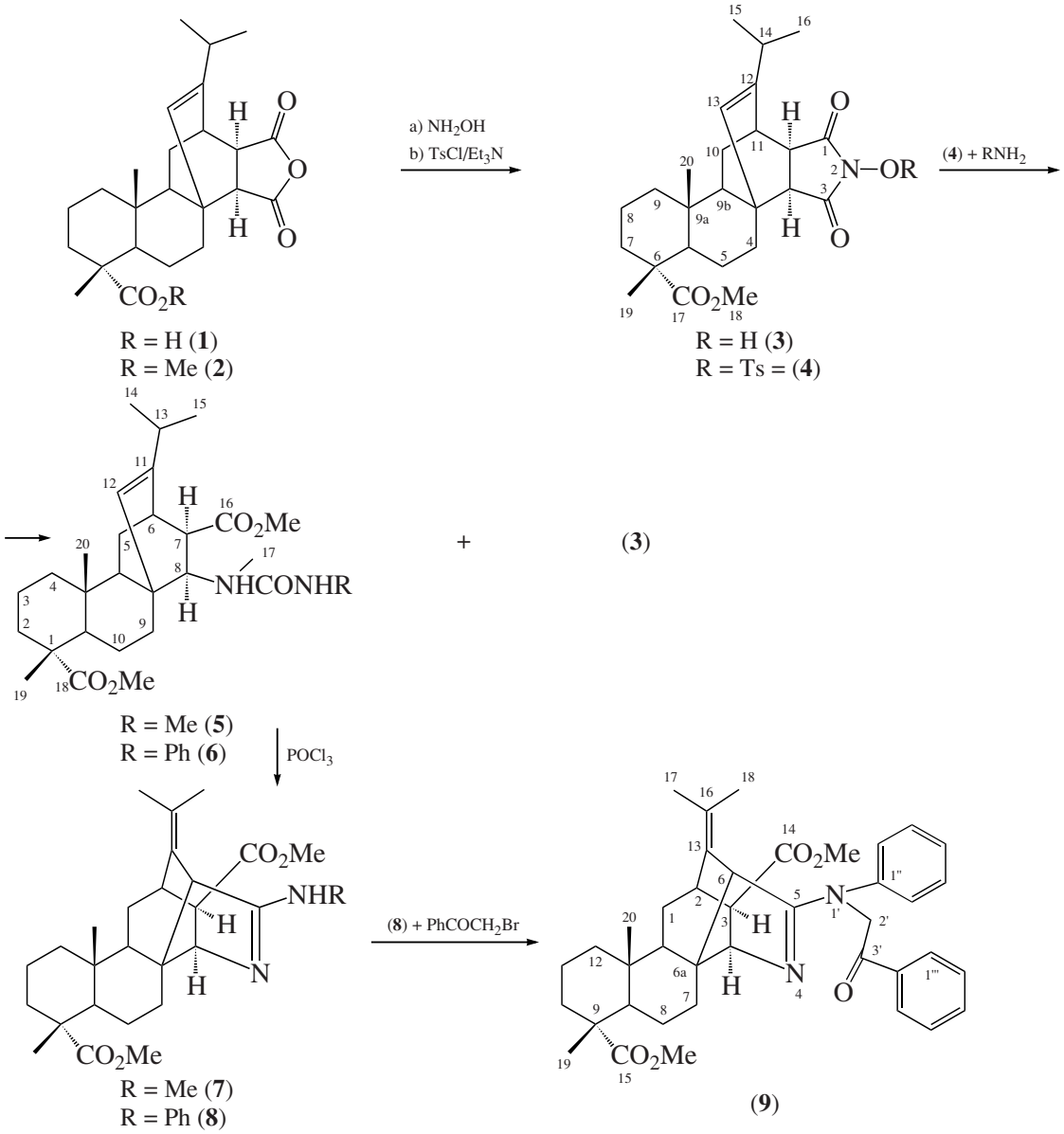
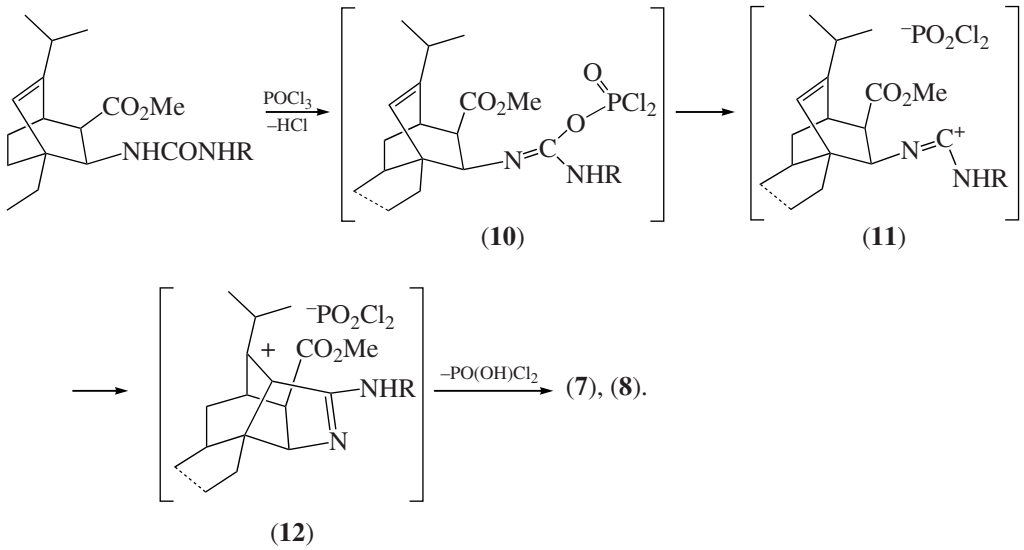
rate (**2**) was treated with hydroxylamine in an alcohol solution to give *N*-hydroxy derivative (**3**), converted into toluenesulfonate (**4**). The latter undergoes rearrangement under the action of amines (methylamine or aniline) in a methanol solution to form ureido esters (**5**, **6**) in 43 and 53% yields, respectively. The by-product in both cases is *N*-hydroxy maleopimarimide (**3**) (34–44%), readily separable by treatment with aqueous alkali because it is a hydroxamic ester.

We have found that the treatment of ureido esters **5**, **6** with $POCl_3$ in benzene leads to cyclic amidines (**7**) and (**8**), whose structure is confirmed by spectral data. The reaction of *N*-phenylamidine (**8**) with bromoacetophenone gives a phenacyl derivative (**9**). Its structure is confirmed by X-ray diffraction (Fig. 1).



Scheme 1.

We may consider that the cyclization of ureido esters **5** and **6** proceeds further through the formation of intermediates **10**–**12** (Scheme 2).



Scheme 2.

EXPERIMENTAL

NMR spectra of compounds were obtained in $CDCl_3$ solutions on a Bruker AV-300 spectrometer operating at 300.13 (^{1}H) and 75.47 MHz (^{13}C) and a Bruker DRX-500 spectrometer operating at 500.13 (^{1}H) and 125.76 MHz (^{13}C). Signal assignment in NMR spectra was made with the use of different types of proton–proton and carbon–proton shift correlation spectroscopy (COSY, COLOC) and 2D ^{1}H NMR nuclear Overhauser effect spectroscopy (NOESY) (for compounds **5**, **6**, **8**, and **9**). Mass spectral analysis and molecular weight and elemental composition determination were carried out on a Finnigan MAT-8200 high-resolution mass spectrometer with ionizing voltage 70 eV (injector temperature 270–300°C). Melting points were determined on a Kofler heating bench. Specific rotations $[\alpha]_D^{20}$ were measured on a Pol AAr3005 polarimeter in chloroform at ambient temperature. X-ray diffraction data were obtained on a Bruker P4 diffractometer ($2\theta < 52°$, 3990 reflections, $R_{int} = 0.0331$). The reaction course was monitored by TLC on Silufol UV-254 plates.

Methyl maleopimarate (**2**) was obtained as described in [7].

Methyl (3a*R*,6*R*,9a*R*,11a*R*)-2-hydroxy-6,9a-dimethyl-1,3-dioxo-3b,11-(12-isopropyletheno)hexadecahydro-^{1}H-naphtho[2,1-*e*]isoindole-6-carboxylate (3). A concentrated ammonia solution was added dropwise to a solution of hydroxylamine hydrochloride (4.0 g, 58 mmol) in 15 mL of water to pH ≈ 9. To the resulting solution, 70 mL of ethanol and 22.0 g (53 mmol) of methyl maleopimarate (**2**) were added. The reaction mixture was heated on a water bath until dissolution, 10 mL of water was added, and the mixture was cooled to ambient temperature. The resulting crystals were filtered off and washed with cold ethanol to give 18.6 g of hydroxyimide **3** (yield 82.4%), mp 277°C (decomp.) (from MeOH).

Methyl (3a*R*,6*R*,9a*R*,11a*R*)-6,9a-dimethyl-1,3-dioxo-3b,11-(12-isopropyletheno)-2-(*p*-toluenesulfonyloxy)hexadecahydro-^{1}H-naphtho[2,1-*e*]isoindole-6-carboxylate (4). Toluenesulfonyl chloride (9.0 g, 47 mmol) and 5.0 mL of triethylamine were added successively with stirring to a suspension of 20 g (46.5 mmol) of *N*-hydroxyimide **3** in 50 mL of methylene chloride. The substance dissolved. After completion of the reaction, the mixture was washed with 3% aqueous HCl and water and concentrated. Crystallization from a methanol–methylene chloride mixture gave 24.8 g (91%) of tosylate **4**, mp 162–164°C, $[\alpha]_D^{20}$ –32° (*c* 2.26). ^{1}H NMR ($CDCl_3$ δ, ppm, *J*, Hz): 0.53 (s, 3H, (C-20)H_3), 0.88 (dt, 1H, H-9, *J* 12.8 and 3.6), 0.93 and 0.95 (both d, 6H, (C-15)H_3 and (C-16)H_3, *J* 6.9), 1.15 (s, 3H, (C-19)H_3), 1.13 (dm, 1H, H-5, J_{gem} 13.2), 1.21 (m, 1H, H-10), 1.32–1.52 (m, 6H, H-7,8,8,9,9b,10), 1.55–1.71 (m, 4H, H-4,5,5a,7), 2.18 (m, 1H, H-14), 2.33 (m, 1H, H-4, J_{gem} 12.0), 2.41 (s, 3H, CH_3 at C-4'), 2.48 (d, 1H, H-3a, *J* 6.8), 2.87 (dd, 1H, H-11a, *J* 6.8 and 2.0), 3.04 (d, 1H, H-11, *J* 2.0), 3.57 (s, 3H, OCH_3), 5.40 (s, 1H, H-13), 7.32 (d, 2H, H-3',5', *J* 8.0), 7.82 (d, 2H, H-2',6', *J* 8.0). ^{13}C NMR (δ, ppm): 15.39 (q, C-20), 16.59 (q, C-19), 16.76 (t, C-8), 19.50 and 20.32 (both

q, C-15,16), 21.42 (t, C-5), 21.66 (q, CH_3 at C-4'), 27.13 (t, C-10), 32.38 (d, C-14), 34.73 (t, C-4), 35.04 (d, C-11), 36.43 (t, C-7), 37.50 (t, C-9), 37.75 (s, C-9a), 40.59 (s, C-3b), 42.41 (d, C-11a), 46.86 (s, C-6), 49.17 (d, C-9b), 49.46 (d, C-3a), 51.75 (q, C-18), 53.83 (d, C-5a), 124.15 (d, C-13), 129.14 and 129.70 (both d, C-2',3',5',6'), 131.07 (s, C-4'), 142.62 (s, C-1'), 147.07 (s, C-12), 168.77 and 169.81 (both s, C-1,3), 178.90 (s, C-17).

For $C_{32}H_{41}NO_7S$ anal. calcd. (%): C, 65.84; H, 7.08; N, 2.40; S, 5.49.

Found (%): C, 65.48; H, 7.18; N, 2.28; S, 5.63.

Dimethyl (1*R*,4a*R*,7*R*,8*R*)-1,4a-dimethyl-6,8a-(11-isopropyletheno)-8-(3-methylureido)tetradecahydrophenanthrene-1,7-dicarboxylate (5) . A mixture of 2.0 g (3.43 mmol) of tosylate **4**, 20 mL of methanol, and 2 mL of 10% methylamine solution in methanol was stirred until complete dissolution (2 h). The solution was concentrated to half volume, 50 mL of ether was added, and the mixture was washed with 3% NaOH solution (2 × 15 mL) and water and concentrated. The residue was crystallized from a methylene chloride–methanol mixture to give 0.70 g (43%) of ureide **5**. The aqueous solution was acidified with hydrochloric acid, and the resulting precipitate was extracted with methylene chloride. The extract was washed with water and concentrated, and the residue was crystallized from aqueous methanol to give 0.65 g (44%) of *N*-hydroxy maleopimarimide (**3**). Compound **5**, mp 235–237°C. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 0.44 (s, 3H, (C-20)H_3), 0.79 (dt, 1H, H-4, *J* 12.8 and 2.8), 0.87 and 0.94 (both d, 6H, (C-14)H_3 and (C-15)H_3, *J* 7.0), 0.82–0.99 (m, 3H, H-3,5,10), 0.98 (s, 3H, (C-19)H_3), 1.24–1.45 (m, 7H, H-2,3,4,5,9,10,10a), 1.52–1.65 (m, 2H, H-2,4b), 1.82 (m, 1H, H-9, J_{gem} 13.0), 2.37 (m, 1H, H-13), 2.49 (s, 1H, H-6), 2.50 (d, 3H, NCH_3, *J* 7.0), 2.86 (d, 1H, H-7, *J* 7.6), 3.39 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.91 (t, 1H, NH, *J* 7.0), 4.55 (d, 1H, H-8, *J* 7.6), 4.95 (m, 1H, NH), 5.22 (s, 1H, H-12). ^{13}C NMR (δ, ppm): 15.28 (q, C-20), 16.49 (q, C-19), 16.70 (t, C-3), 19.37 and 20.66 (both q, C-14,15), 21.31 (t, C-10), 21.45 (q, CH_3), 28.43 (t, C-5), 32.41 (d, C-13), 33.44 (t, C-9), 36.10 (t, C-2), 36.12 (d, C-8), 36.91 (s, C-4a), 37.82 (t, C-4), 41.30 (s, C-8a), 46.80 (s, C-1), 48.77 (d, C-4b), 49.82 (d, C-10a), 50.74 (d, C-7), 50.75 (q, CH_3), 51.52 (q, CH_3), 57.46 (d, C-6), 122.07 (d, C-12), 150.15 (s, C-11), 158.40 (s, C-17), 173.41 (s, C-16), 178.77 (s, C-18).

Dimethyl (1*R*,4a*R*,7*R*,8*R*)-1,4a-dimethyl-6,8a-(11-isopropyletheno)-8-(3-phenylureido)tetradecahydrophenanthrene-1,7-dicarboxylate (6). A mixture of 1.2 g (2.06 mmol) of tosylate **4**, 0.7 g (7.5 mmol) of aniline, 1 mL of triethylamine, and 15 mL of methanol was heated under reflux for 2 h. The reaction mixture was washed with 3% HCl solution, 3% NaOH solution (2 × 20 mL), and water and concentrated. The residue was crystallized from methanol to give 0.59 g (43%) of ureide **6**. Acidification of the aqueous solution, extraction with methylene chloride, and crystallization from aqueous methanol afforded 0.26 g (34%) of *N*-hydroxy maleopimarimide (**3**). Compound **6**, mp 256–258°C, $[\alpha]_{580}$ +14° (*c* 2.12). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 0.52 (s, 3H, (C-20)H_3), 0.88 (dt, 1H, H-4, *J* 13.0 and 2.6), 0.93 and 0.96 (both d, 6H, (C-14)H_3 and (C-15)H_3, *J* 7.0), 1.01–1.07 (m, 3H, H-3,5,10), 1.08 (s, 3H, (C-19)H_3), 1.27–1.50 (m, 7H, H-2,3,4,5,9,10,10a), 1.61–1.71 (m, 2H, H-2,4b), 1.93 (m, 1H, H-9), 2.43 (m, 1H, H-13), 2.59 (s, 1H, H-6), 3.00 (d, 1H, H-7, *J* 7.4), 3.46 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 3.65 (m, 1H, NH), 4.12 (dd, 1H, H-8, *J* 7.4 and 2.0), 5.19 (m, 1H, NH), 5.24 (s, 1H, H-12), 6.95 (m, 1H, Ph), 7.22 (m, 3H, Ph), 7.45 (m, 1H, Ph). ^{13}C NMR (δ, ppm): 15.45 (q, C-20), 16.69 (q, C-19), 16.85 (t, C-3), 19.47 and 20.83 (both q, C-14,15), 21.45 (t, C-10), 28.52 (t, C-5), 32.61 (d, C-13), 33.64 (t, C-9), 36.21 (t, C-2), 36.37 (d, C-8), 37.08 (s, C-4a), 37.93 (t, C-4), 41.37 (s, C-8a), 46.92 (s, C-1), 48.83 (d, C-4b), 50.87 (d, C-7), 51.03 (q, CH_3), 51.53 (d, C-10a), 51.69 (q, CH_3), 57.54 (d, C-6), 120.20 (d, C-2',6'), 121.98 (d, C-12), 122.91 (d, C-4'), 128.84 (d, C-3',5'), 138.84 (s, C1'), 150.56 (s, C-11), 155.38 (s, C-17), 173.38 (s, C-16), 178.24 (s, C-18).

Dimethyl (3*R*,3a*R*,9*R*,12a*R*)-9,12a-dimethyl-2,6-(13-isopropylidenemethano)-5-(methylamino)-1,2,3,3a,6,7,8,8a,9,10,11,12,12a,12b-tetradecahydronaphtho[2,1-*d*]indole-3,9-dicarboxylate (7). A mixture of 0.65 g (1.38 mmol) of compound **5** and 0.5 mL of $POCl_3$ in 8 mL of benzene was heated under reflux for 30 min until HCl evolution ceased. The reaction mixture was diluted with ether and washed with 5% aqueous ammonia solution and water. The solvent was evaporated, and the residue was crystallized from an ethyl acetate–petroleum ether mixture to give 0.41 g (64%) of amidine **7**. Mp 195–197°C. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 0.62 (s, 3H, (C-20)H_3), 0.80 (dt, 1H, H-12, *J* 13.2 and 2.8), 0.91 (m, 1H, H-8), 1.00 (s, 3H, (C-19)H_3), 1.18–1.27 (m, 1H, H-1), 1.30–1.42 (m, 2H, H-7,8), 1.45–1.56 (m, 4H, H-10,11,11,12), 1.59 and 1.62 (both s, 6H, (C-17)H_3 and (C-18)H_3), 1.58–1.71 (m, 4H, H-1,8a,7,10), 2.56 (d, 1H, H-3, *J* 6.4), 2.57 (s, 3H, NCH_3), 2.83 (br s, 1H, H-12b), 2.90 (m, 1H, H-2), 2.93 (s, 1H, H-6), 3.46 (d, 1H, H-3a, *J* 6.4), 3.48 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 4.65 (m, 1H, NH). ^{13}C NMR (δ, ppm): 13.18 (q, C-20), 16.18 (q, C-19), 16.94 (t, C-11), 19.30 and 20.30 (both q, C-17,18), 21.48 (t, C-8), 29.30 (q, CH_3), 30.02 (t, C-1), 31.96 (d, C-2), 34.45 (t, C-7), 36.47 (t, C-10), 37.19 (s, C-12a), 37.44

(t, C-12), 46.33 (d, C-8a), 46.86 (s, C-9), 47.28 (d, C-3), 48.46 (s, C-6a), 49.76 (d, C-12b), 50.14 (d, C-6), 50.63 (q, CH_3), 51.43 (q, CH_3), 68.16 (d, C-3a), 123.47 (s, C-13), 127.19 (s, C-16), 170.09 (s, C-5), 172.94 (s, C-14), 178.68 (s, C-15). MS calcd. for $C_{27}H_{40}N_2O_4$ 456.29879, found $[M]^+$ 456.31559.

Dimethyl (2*S*,3*R*,3a*R*,6a*S*,9*R*,12a*R*)-9,12a-dimethyl-2,6-(13-isopropylidenemethano)-5-(phenylamino)-1,2,3,3a,6,7,8,8a,9,10,11,12,12a,12b-tetradecahydronaphtho[2,1-*d*]indole-3,9-dicarboxylate (8). A mixture of 0.22 g of ureide **6** and 0.5 mL of $POCl_3$ in 8 mL of toluene was heated under reflux for 30 min. The reaction mixture was diluted with ether and washed with 5% aqueous ammonia solution and water. The solvent was evaporated, and the residue was chromatographed on alumina (ethyl acetate as eluent) to give 0.16 g (73%) of amidine **8**. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 0.77 (s, 3H, (C-20)H_3), 0.81 (dt, 1H, H-12, *J* 13.2 and 2.8), 0.95 (m, 1H, H-8), 1.09 (s, 3H, (C-19)H_3), 1.26 (m, 1H, H-1), 1.32–1.60 (m, 4H, H-1,7,8,11), 1.60–1.72 (m, 5H, H-8a,10,10,11,12), 1.76 and 1.83 (both s, 6H, (C-17)H_3 and (C-18)H_3), 1.58–1.71 (m, 1H, H-7), 2.61 (d, 1H, H-3, *J* 5.4), 3.13 (br s, 1H, H-12b), 3.22 (m, 1H, H-2), 3.30 (s, 1H, H-6), 3.54 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 3.59 (d, 1H, H-3a, *J* 5.4), 4.65 (m, 1H, NH), 6.69 (m, 2H, Ph), 6.86 (t, 1H, H-4', *J* 8.4), 7.13 (m, 2H, Ph). ^{13}C NMR (δ, ppm): 13.53 (q, C-20), 16.18 (q, C-19), 16.97 (t, C-11), 20.04 and 20.98 (both q, C-17,18), 21.48 (t, C-8), 29.70 (t, C-1), 30.68 (d, C-2), 34.24 (t, C-7), 36.64 (t, C-10), 37.34 (s, C-12a), 37.56 (t, C-12), 44.60 (s, C-9), 46.14 (d, C-3), 46.94 (s, C-6a), 48.18 (d, C-12b), 48.79 (d, C-8a), 49.86 (d, C-6), 51.56 (q, CH_3), 51.64 (q, CH_3), 64.17 (d, C-3a), 121.42 and 122.08 (both d, C-2',6'), 126.47 (s, C-13), 128.01 (s, C-16), 128.33 (d, C-4'), 128.83 (d, C-3',5'), 150.51 (s, C-1'), 162.77 (s, C-5), 172.09 (s, C-14), 178.80 (s, C-15). MS calcd. for $C_{32}H_{42}N_2O_4$ 518.29, found $[M]^+$ 518.32.

Dimethyl (2*S*,3*R*,3a*R*,6a*S*,9*R*,12a*R*)-9,12a-dimethyl-2,6-(13-isopropylidenemethano)-5-[(2-oxo-2-phenylethyl)(phenyl)amino]-1,2,3,3a,6,7,8,8a,9,10,11,12,12a,12b-tetradecahydronaphtho[2,1-*d*]indole-3,9-dicarboxylate (9). A mixture of 0.15 g (0.29 mmol) of amidine **8** and 0.15 g (0.75 mmol) of bromoacetophenone in 10 mL of toluene was heated under reflux for 2 h. The solvent was evaporated, the residue was chromatographed on alumina (petroleum ether–ethyl acetate, 1 : 1, as eluent), and the product was crystallized from aqueous methanol to give 0.13 g (70%) of compound **9**, mp 158–160°C, $[\alpha]_{580}$ –295° (*c* 3.0). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 0.79 (s, 3H, (C-20)H_3), 0.99 (s, 3H, (C-19)H_3), 1.01 (m, 1H, H-12), 1.29 (s, 3H, (C-17)H_3), 1.38 (m, 2H, H-1,8), 1.50–1.68 (m, 6H, H-7,8,10,11,11,12), 1.78 (s, 3H, (C-18)H_3), 1.70–1.96 (m, 4H, H-1,8a,10,12b), 2.41 (dd, 1H, H-7, J_{gem} 12.4), 2.78 (d, 1H, H-3, *J* 5.8), 3.12 (br s, 1H, H-2), 3.46 (s, 1H, H-6), 3.61 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.80 (d, 1H, H-3a, *J* 5.8), 5.12 (d, 1H, H-2', *J* 8.8), 5.26 (d, 1H, H-2', *J* 8.8), 7.22 (m, 3H, H-2",4",6"), 7.38–7.46 (m, 2H, H-3",5"), 7.48–7.60 (m, 3H, H-3"',4"',5"'), 7.98 (d, 2H, H-2"',6"', *J* 8.4). ^{13}C NMR (δ, ppm): 13.05 (q, C-20), 16.22 (q, C-19), 16.78 (t, C-11), 19.32 and 21.46 (both q, C-17,18), 22.08 (t, C-8), 30.68 (t, C-1), 32.56 (d, C-2), 34.96 (t, C-7), 37.05 (t, C-10), 37.64 (s, C-12a), 37.83 (t, C-12), 45.18 (d, C-3), 45.22 (d, C-8a), 47.14 (s, C-9), 48.06 (d, C-12b), 49.98 (s, C-6a), 51.02 (q, OCH_3), 51.86 (d, C-6), 52.11 (q, OCH_3), 58.18 (t, C-2'), 71.48 (d, C-3a), 124.75 (d, C-4"), 125.28 (s, C-13), 125.82 (d, C-2",6"), 126.52 (s, C-16), 127.87 (d, C-2"',6"'), 128.26 (d, C-3"',5"'), 128.61 (d, C-3",5"), 132.88 (d, C-4"'), 135.91 (s, C-1"'), 145.08 (s, C-1"), 173.17 (s, C-5), 173.55 (s, C-14), 178.82 (s, C-15), 194.21 (s, C-3'). MS calcd. for $C_{40}H_{48}N_2O_5$ 636.43, found $[M]^+$ 636.43.

X-ray crystallographic data for compound 9. $C_{40}H_{48}N_2O_5$ and CH_3OH, *M* 668.85, colorless orthorhombic crystals, space group $P2_12_12_1$, *a* = 10.8425(13), *b* = 12.3700(19), *c* = 27.616(4) Å, *V* = 3703.9(9) Å^3, *Z* = 4, d_{calc} = 1.199 g cm^{-3}, λ(MoK_α) = 0.71073 Å, μ(MoK_α) = 0.080 mm^{-1}, *T* = 296 K.

The structure of compound **9** was solved by direct methods using the SIR2002 software and refined by least squares in the anisotropic–isotropic (for hydrogen atoms) approximation using the SHELXL-97 software [8, 9]. A correction for absorption was applied empirically (transmission 0.96–0.98). Hydrogen atoms were introduced into ideal positions and refined as riding on their bonded atoms. Final refining parameters: wR_2 0.1507, R_1 = 0.08855, and GOOF = 1.016 for all 3871 reflections (*R* 0.0519 for 2538 > 2σ(*I*)), absolute structure parameter, –0.06(14).

The structure of compound **9** was deposited with the Cambridge Crystallographic Data Center (CCDC 682150); X-ray diffraction data are available at http://www.ccdc.cam.uk/conts/retrieving.html

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 06–03–32150 and 08–03–00340).

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