ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 1, pp. 67–75. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © S.V. Chernov, E.E. Shul'ts, M.M. Shakirov, G.A. Tolstikov, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 1, pp. 74–81.

Synthetic Transformations of Higher Terpenoids: XVI.* Synthesis of Decahydronaphtho[1,2-*g*]indoles from Lambertianic Acid

S. V. Chernov, E. E. Shul'ts, M. M. Shakirov, and G. A. Tolstikov

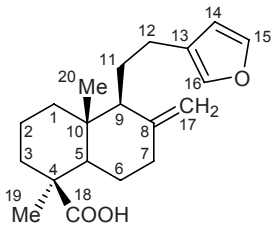
Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: schultz@nioch.nsc.ru

Received October 31, 2006

Abstract—Oxidative methoxylation of 8,17-isopropylidenedioxy derivative of lambertianic acid methyl ester with *N*-chlorobenzenesulfonamide in methanol, followed by hydrogenation over Raney nickel, gave rise to a 2,5-dimethoxytetrahydrofuran fragment which was converted into N-substituted pyrrole ring by the action of amines in acetic acid. The subsequent removal of the acetonide protection and periodate cleavage of the diols thus formed resulted in the formation of 17-nor-8-oxo derivatives, and the latter underwent smooth cyclization to decahydronaphtho[1,2-*g*]indoles in acid medium.

DOI: 10.1134/S1070428008010089

We previously [2] proposed a convenient procedure for the synthesis of pyrrole-containing labdanoids from lambertianic acid (**I**). We were interested in obtaining on this basis terpenoid indoles as analogs of tremorogenic indole alkaloids (such as penitrems and paspalines) [3] and biologically active polycyclic naphthocarbazoles [4–6]. For this purpose, we planned to use the transformation of dioxolane **II** which is readily available from lambertianic acid (**I**) [7] into the corresponding N-substituted pyrroles according to Clauson-Kaas [8] and their subsequent conversion into naphtho[1,2-*g*]indole derivatives.

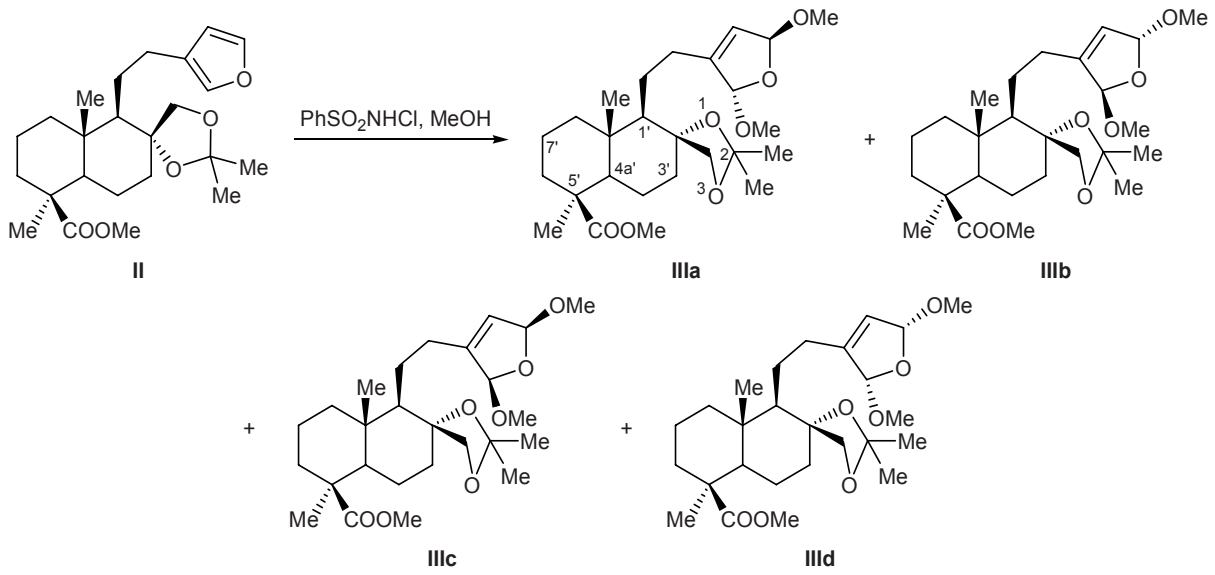


I

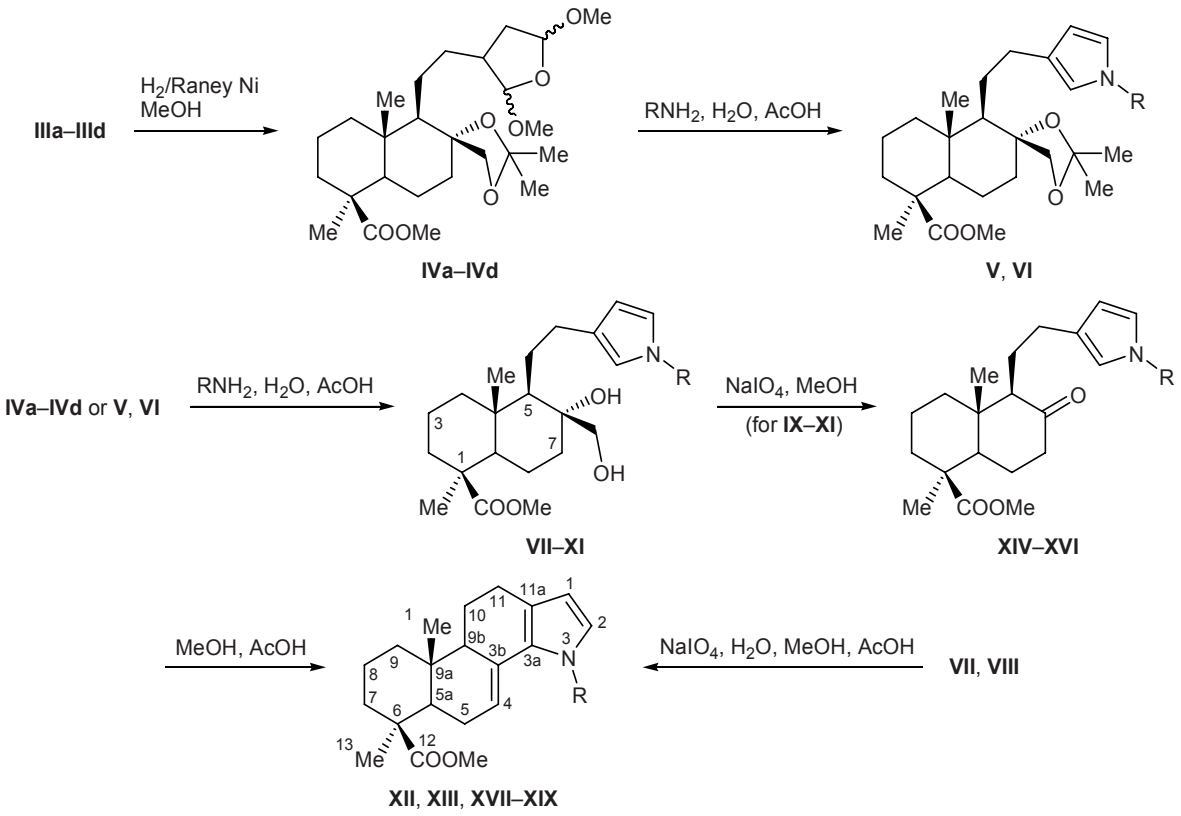
Compound **II** readily underwent oxidative methoxylation by the action of *N*-chlorobenzenesulfonamide in methanol, which produced a mixture of stereoisomeric 2,5-dimethoxydihydrofuran derivatives **IIIa**–**IIId** in almost quantitative yield (Scheme 1). The two *cis* and two *trans* stereoisomers were formed in equal amounts, as followed from the intensities of signals from methoxy protons and 14-H, 15-H, and 16-H in the ^{1}H NMR spectra (the atom numbering accepted for the labdane skeleton is used for compounds **I**–**XI**, **XIV**–**XVI**, and **XXI**). Hydrogenation of **IIIa**–**IIId** over Raney nickel afforded 2,5-dimethoxytetrahydrofuran derivatives **IVa**–**IVd** which reacted with primary amines in acetic acid to give 75–84% of the corresponding *N*-alkylpyrroles **V** and **VI**. Prolonged reaction resulted in the formation of diols **VII** and **VIII**. 8,17-Dihydroxy compounds **IX**–**XI** were synthesized in 51–75% yield by reaction of 2,5-dimethoxytetrahydrofurans **IVa**–**IVd** with allylamine, benzylamine, and aniline, respectively, on prolonged heating in acetic acid. By periodate oxidation of diols **VII** and **VIII** in methanol in the presence of acetic acid we obtained decahydronaphtho[1,2-*g*]indoles **XII** and **XIII** in a moderate yield (46–51%) as a result of cyclization of intermediate 8-oxo-17-norlabdanoids. The oxidation of **IX**–**XI** with sodium periodate under neutral conditions gave 8-oxo-17-nor derivatives **XIV**–**XVI** (yield 76–83%). Ketones **XIV**–**XVI** underwent intramolecular ring closure to N-substituted decahydronaphtho[1,2-*g*]-indoles **XVII**–**XIX** (yield 71–77%) on treatment with acetic acid in methanol (Scheme 2), as it was reported

* For communication XV, see [1].

Scheme 1.



Scheme 2.

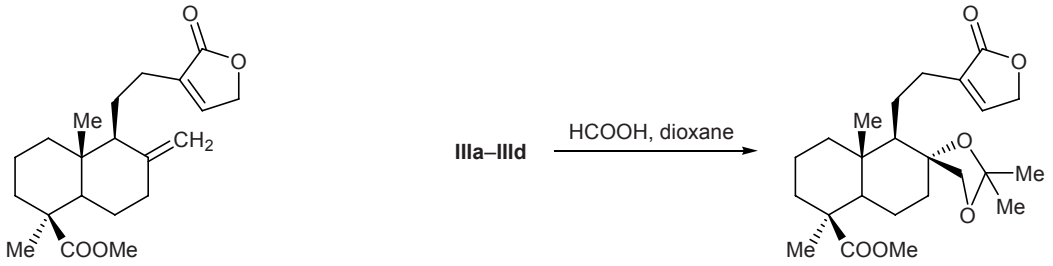


V, **VII**, **XII**, R = Me; **VI**, **VIII**, **XIII**, R = Et; **IX**, **XIV**, **XVII**, R = $PhCH_2$; **X**, **XV**, **XVIII**, R = CH_2=$CHCH_2$; **XI**, **XVI**, **XIX**, R = Ph.

previously for 8-oxo-17-norlambertianic acid methyl ester [7].

The natural labdane diterpenoid pinusolide (**XX**) was shown to act as effective and specific platelet aggregation inhibitor [9–11], as well as apoptosis-inducing agent [12]. We have studied the possibility for converting compounds **IIIa**–**IIId** into 8,17-isopropylidenedioxy pinusolide analog **XXI**. Our attempts to synthesize butenolide **XXI** from **IIIa**–**IIId** under the conditions described in [12] resulted in formation of

Scheme 3.



a mixture of products. Compound **XXI** was obtained in 65% yield by treatment of stereoisomeric 2,5-dimethoxydihydrofurans **IIIa**–**IIId** with 10% formic acid in dioxane (Scheme 3).

The structure of the newly synthesized compounds was determined on the basis of spectral data. Terpenoid pyrroles **V**–**XI** and **XIV**–**XVI** characteristically showed in the ^{1}H NMR spectra signals from protons in the pyrrole ring at δ 5.95 (14-H), 6.36 (16-H), and 6.46 ppm (15-H) (for compound **V**). The 12-H protons resonated in a weaker field (δ 2.35 and 2.63 ppm) than in the spectrum of **II** [7]. The formation of the naphtho[1,2-g]indole system (compounds **XII**, **XIII**, **XVII**–**XIX**) is confirmed by an appreciable upfield shift of signals from the bridgehead carbon atoms (C^{5a} and C^{9a}) in the ^{13}C NMR spectra ($\Delta\delta_C \approx 5$–9 ppm). The 9b-H and 11-H signals in the ^{1}H NMR spectra of these compounds are displaced downfield relative to the corresponding signals from 9-H and 12-H in the labdane fragment of the initial ketones. The 1-H and 2-H signals appear as doublets at δ 5.83 and 6.42 ppm, respectively (J = 2.7 Hz), and the 4-H proton gives a multiplet at δ 5.88 ppm.

The UV spectra of decahydronaphtho[1,2-g]indoles **XII**, **XIII**, and **XVII**–**XIX** contained absorption maxima at λ 265, 273, and 288 nm, indicating the presence of a vinylpyrrole fragment. The structure of the butenolide moiety in molecule **XXI** was determined on the basis of the INADEQUATE ^{13}C–^{13}C correlation spectrum. The C^{13} atom displayed three coupling constants with C^{16}, C^{14}, and C^{12} (J = 61.7, 67.6, and 46.8 Hz, respectively). Two coupling constants were observed for C^{14}, one with C^{13} (J = 67.6 Hz), and the other with C^{15} (J = 38.2 Hz). The C^{15} nucleus was coupled with C^{14} (J = 38.2 Hz), and C^{16} with C^{13} (J = 61.7 Hz). These values were consistent with the corresponding coupling constants of 3-substituted furan-2(5*H*)-ones [13] in support of the assumed structure of **XXI**.

Thus the application of the Clauson-Kaas method to a natural labdanoid, lambertianic acid, allowed us to develop procedures for the synthesis of N-substituted pyrroles of the labdane series and their two-step transformation into decahydronaphtho[1,2-*g*]indole derivatives.

EXPERIMENTAL

The mass spectra (electron impact, 70 eV) were recorded on a Finnigan MAT-8200 high-resolution mass spectrometer (vaporizer temperature 190–250°C). The ^{1}H and ^{13}C NMR spectra were measured on Bruker AC-200 (200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C) and Bruker DRX-500 instruments (500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C) from solutions in $CDCl_3$, CD_3OD, or CCl_4. Signals in the NMR spectra were assigned using various proton–proton, carbon–proton and carbon–carbon (**XXI**) shift correlation techniques (COSY, COLOC, and INADEQUATE). The UV spectra were obtained on an HP 8453 UV-Vis spectrophotometer from solutions in ethanol ($c = 10^{-4}$ M). The optical rotations ($[\alpha]_D^{20}$, deg ml g^{-1} dm^{-1}, c, g/100 ml) were determined using a Polamat A polarimeter (Carl Zeiss, λ 578 nm). The progress of reactions was monitored by TLC on Silufol UV-254 plates. The products were isolated by column chromatography on KSK silica gel or aluminum oxide.

Methyl (1′*R*,4*R*,4a′*R*,5′*S*,8a′*R*)-1′-[2-(2,5-dimethoxy-2,5-dihydrofuran-3-yl)ethyl]-2,2,5′,8a′-tetramethyloctahydro-1′*H*-spiro[[1,3]dioxolane-4,2′-naphthalene]-5′-carboxylate IIIa–IIId. A solution of 4.5 g (11.1 mmol) of dioxolane **II** and 1.5 ml of acetic acid in 30 ml of methanol was cooled below 10°C, and 2.4 g (11.3 mmol) of *N*-chlorobenzenesulfonamide sodium salt was added in portions under stirring. The mixture was stirred for 30 min (TLC), treated with 50 ml of a 3% sodium sulfite solution to decompose excess *N*-chloro amine, and extracted with diethyl ether. The extract was washed with a 3% solution of sodium hydroxide (2×15 ml) to remove $PhSO_2NH_2$ and with water and evaporated, and the residue was

subjected to chromatography on silica gel using petroleum ether–ethyl acetate (2:1) as eluent to isolate 4.9 g (95%) of a mixture of stereoisomers **IIIa**–**IIId** as a colorless oily substance. ^{1}H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 0.48 s and 0.51 s (3H, $C^{20}H_3$); 0.85–0.92 m (2H, 1-H, 3-H); 0.96–1.02 m (1H, 5-H); 1.12 m (1H, 2-H); 1.13 s and 1.14 s (3H, $C^{19}H_3$); 1.22–1.40 m (2H, 7-H, 9-H); 1.21 s and 1.31 s [3H each, $(CH_3)_2C$]; 1.45–1.57 m (2H, 2-H, 11-H); 1.62–1.75 m (3H, 1-H, 6-H, 11-H); 1.80–1.92 m (1H, 6-H); 2.00 m (1H, 7-H); 2.10 m (1H, 3-H); 2.16–2.40 m (2H, 12-H); 3.23 s, 3.24 s, 3.25 s, 3.28 s (6H, OCH_3); 3.54 d (1H, 17-H, *J* = 8.4); 3.57 s (3H, OCH_3); 3.68 d (1H, 17-H, *J* = 8.4); 5.26 br.s, 5.27 br.s, 5.38 br.s, and 5.37 br.s (1H, 16-H); 5.47 m, 5.50 m, 5.51 m, and 5.52 m (1H, 15-H); 5.58 m, 5.60 m, and 5.61 m (1H, 14-H). Mass spectrum, *m*/*z* (I_{rel}, %): 466 $[M]^+$ (2), 451 (22), 376 (66), 327 (42), 267 (28), 127 (100), 111 (47), 95 (25), 85 (27), 81 (33), 69 (36), 43 (42). Found: $[M]^+$ 466.28815. $C_{26}H_{42}O_7$. Calculated: *M* 466.29303.

Methyl (1′*R*,4*R*,4a′*R*,5′*S*,8a′*R*)-1′-[2-(2,5-dimethoxy-2,5-tetrahydrofuran-3-yl)ethyl]-2,2,5′,8a′-tetramethyloctahydro-1′*H*-spiro[[1,3]dioxolane-4,2′-naphthalene]-5′-carboxylates IVa–IVd. A solution of 4.66 g (10 mmol) of stereoisomer mixture **IIIa**–**IIId** in 30 ml of methanol was hydrogenated over Raney nickel (prepared from 5.0 g of 20% Ni–Al alloy) under atmospheric pressure. When the reaction was complete (3–4 h, TLC), the catalyst was filtered off, and the solvent was removed to obtain 4.6 g (98%) of stereoisomeric compounds **IVa**–**IVd** as an oily material. ^{1}H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 0.50 s and 0.52 s (3H, $C^{20}H_3$); 0.88–1.08 m (3H, 1-H, 3-H, 5-H); 1.06–1.12 m (2H, 2-H, 9-H); 1.15 s and 1.17 s (3H, $C^{19}H_3$); 1.25–1.40 m (2H, 7-H, 9-H); 1.20 s and 1.35 s [3H each, $(CH_3)_2C$]; 1.50–1.57 m (2H, 2-H, 11-H); 1.62–1.78 m (3H, 1-H, 6-H, 11-H); 1.86–1.99 m (2H, 6-H, 7-H); 2.10 m (1H, 3-H); 2.26–2.48 m (2H, 12-H); 3.24 s, 3.26 s, 3.29 s, and 3.38 s (6H, OCH_3); 3.30 m (1H, 13-H); 3.56 d (1H, 17-H, *J* = 8.4); 3.60 s (3H, OCH_3); 3.72 d (1H, 17-H, *J* = 8.4); 5.28 br.s, 5.32 br.s, 5.40 br.s, and 5.42 br.s (1H, 16-H); 5.48 m, 5.50 m, 5.51 m, and 5.55 m (1H, 15-H); 5.58 m, 5.62 m, and 5.64 m (1H, 14-H). Mass spectrum, *m*/*z* (I_{rel}, %): 468 $[M]^+$ (2), 453 (36), 390 (19), 376 (20), 347 (30), 329 (65), 287 (21), 269 (42), 135 (26), 127 (100), 109 (30), 107 (28). Found: $[M]^+$ 468.30842. $C_{26}H_{44}O_7$. Calculated: *M* 468.30868.

Methyl (1′*R*,4*R*,4a′*R*,5′*S*,8a′*R*)-2,2,5′,8a′-tetramethyl-1′-[2-(1-methyl-1*H*-pyrrol-3-yl)ethyl]octahydro-1′*H*-spiro[1,3-dioxolane-4,2′-naphthalene]-5′-carboxylate (V). Dimethoxytetrahydrofuran mixture **IVa**–**IVd**, 1.8 g (3.86 mmol), was dissolved in 15 ml of acetic acid, 3 ml of water and 3.0 ml of 25% aqueous methylamine were added, and the mixture was heated for 10 min at 80–85°C, cooled with water, and extracted with diethyl ether (3×20 ml). The extract was washed with a 5% solution of ammonia and evaporated, and the residue was subjected to chromatography on silica gel using petroleum ether–diethyl ether (2:1) as eluent. Yield 1.21 g (75%), oily substance, $[\alpha]_D^{20}$ = +2° (*c* = 5.9, chloroform). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.47 s (3H, $C^{20}H_3$), 1.01 d.t (1H, 3-H, *J* = 13.5, 4.3), 1.09 d.d.d (1H, 1-H, *J* = 13.5, 4.0. 2.3), 1.14 d.d (1H, 5-H, *J* = 12.6, 2.8), 1.18 s (3H, $C^{19}H_3$), 1.30 d.d (1H, 9-H, *J* = 12.7, 3.4), 1.38 s and 1.43 s (6H, CH_3), 1.35–1.48 m (2H, 2-H, 7-H), 1.60–1.72 m (2H, 2-H, 11-H), 1.78 m (3H, 1-H, 6-H, 11-H), 1.90 d.d.d (1H, 6-H, *J* = 12.8, 11.6, 3.6), 2.10 d.t (1H, 7-H, *J* = 12.8, 4.0), 2.15 m (1H, 3-H, ^2J = 13.5), 2.35 d.d.d (1H, 12-H, *J* = 13.6, 13.0, 4.8), 2.63 d.d.d (1H, 12-H, *J* = 13.5, 12.9, 5.6), 3.57 s (3H, CH_3N), 3.61 s (3H, CH_3O), 3.67 d.d (1H, 17-H, *J* = 8.4, 1.8), 3.77 d (1H, 17-H, *J* = 8.4), 5.95 d.d.d (1H, 14-H, *J* = 2.4, 2.1, 1.4), 6.36 d (1H, 16-H, *J* = 2.1), 6.46 m (1H, 15-H). ^{13}C NMR spectrum, δ_C, ppm: 12.31 (C^{20}), 18.95 (C^2), 21.92 (C^6), 26.78 (CH_3), 28.42 (C^{11}), 28.59 (CH_3), 30.56 (C^{12}), 35.78 (CH_3N), 37.71 (C^3), 38.76 (C^1), 39.44 (C^{10}), 39.52 (C^7), 43.61 (C^4), 51.08 (OCH_3), 55.75 (C^9), 56.51 (C^5), 68.39 (C^{17}), 85.03 (C^8), 106.67 ($C^{2'}$), 107.83 (C^{14}), 118.59 (C^{15}), 121.22 (C^{16}), 125.13 (C^{13}), 177.38 (C^{18}). Mass spectrum, *m*/*z* (I_{rel}, %): 417 $[M]^+$ (22), 326 (28), 121 (44), 109 (100). Found: $[M]^+$ 417.27669. $C_{25}H_{39}NO_4$. Calculated: *M* 417.27645.

Methyl (1′*R*,4*R*,4a′*R*,5′*S*,8a′*R*)-1′-[2-(1-ethyl-1*H*-pyrrol-3-yl)ethyl]-2,2,5′,8a′-tetramethyloctahydro-1′*H*-spiro[1,3-dioxolane-4,2′-naphthalene]-5′-carboxylate (VI). Stereoisomeric dimethoxytetrahydrofuran mixture **IVa**–**IVd**, 0.47 g (1 mmol), was dissolved in 10 ml of acetic acid, 2 ml of water and 0.5 ml of 50% aqueous ethylamine were added, and the mixture was heated for 20 min at 80–85°C, diluted with water, and extracted with diethyl ether. The extract was washed with a 5% solution of ammonia and evaporated, and the residue was subjected to chromatography on silica gel using petroleum ether–diethyl ether (2:1) as eluent. Yield 0.36 g (84%), oily substance, $[\alpha]_D^{20}$ = +20° (*c* = 4.8, chloroform). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.44 s (3H, $C^{20}H_3$), 0.90–1.10 m (3H, 1-H, 3-H, 5-H), 1.13 s (3H, $C^{19}H_3$), 1.18 t (3H, CH_3, *J* = 7.0), 1.28 s and 1.37 s (6H, CH_3),

1.40–1.80 m (4H, 2-H, 6-H, 7-H, 9-H), 1.80–1.95 m (3H, 2-H, 6-H, 11-H), 2.01 m (1H, 7-H), 2.09 m (1H, 11-H), 2.16–2.40 m (3H, 1-H, 3-H, 12-H), 2.50 m (1H, 12-H), 3.56 s (3H, OCH_3), 3.58 d (1H, 17-H, J = 8.5), 3.68 d (1H, 17-H, J = 8.5), 3.80 q (2H, CH_2), 5.72 d.d (1H, 14-H, J = 2.5, 2.0), 6.20 d.d (1H, 16-H, J = 2.5, 2.0), 6.30 m (1H, 15-H). ^{13}C NMR spectrum, δ_C, ppm: 12.51 (C^{20}), 16.67 (CH_3), 19.17 (C^2), 22.14 (C^6), 26.98 (CH_3), 28.24 (C^{12}), 28.77 (CH_3), 30.78 (C^{11}), 37.99 (C^7), 38.95 (C^3), 39.56 (C^{10}), 39.71 (C^1), 43.73 (C^4), 43.84 (CH_2), 51.03 (OCH_3), 56.05 (C^9), 56.65 (C^5), 68.45 (CH_2), 69.81 (C^{17}), 85.01 (C^8), 106.70 ($C^{2'}$), 108.03 (C^{14}), 116.79 (C^{15}), 119.35 (C^{16}), 124.94 (C^{13}), 176.92 (C^{18}). Mass spectrum, m/z (I_{rel}, %): 431 $[M]^+$ (15), 121 (53), 109 (100). Found: $[M]^+$ 431.30368. $C_{26}H_{41}NO_4$. Calculated: M 431.30354.

Methyl (1*S*,4a*S*,5*R*,6*R*,8a*S*)-6-hydroxy-6-hydroxymethyl-1,4a-dimethyl-5-[2-(1-methyl-1*H*-pyrrol-3-yl)ethyl]decahydronaphthalene-1-carboxylate (VII). Water, 3 ml, was added to a solution of 0.9 g (2.18 mmol) of pyrrole **V** in 15 ml of acetic acid, and the mixture was heated for 2 h at 80–85°C and extracted with diethyl ether. The extract was washed with a 5% solution of ammonia and evaporated, and the residue was purified by chromatography on aluminum oxide using methanol–diethyl ether (1:1) as eluent. Yield 0.61 g (75%), mp 61–63°C, $[\alpha]_D^{20}$ = +13° (c = 2.4, chloroform). ^{1}H NMR spectrum ($CDCl_3$–CCl_4), δ, ppm (J, Hz): 0.51 s (3H, $C^{20}H_3$), 0.98–1.05 (3H, 1-H, 3-H, 5-H), 1.15 s (3H, $C^{19}H_3$), 1.10–1.45 m (4H, 2-H, 6-H, 9-H, 11-H), 1.65–1.82 m (5H, 1-H, 2-H, 6-H, 7-H, 11-H), 2.08–2.18 m (1H, 7-H), 2.35 m (1H, 12-H), 2.50 m (1H, 3-H), 2.80 m (1H, 12-H), 3.40 d (1H, 17-H, J = 8.4), 3.48 s (3H, NCH_3), 3.51 d (1H, 17-H, J = 8.4), 3.55 s (3H, OCH_3), 5.78 m (1H, 14-H), 6.25 br.s (1H, 16-H), 6.30 d.d (1H, 15-H, J = 2.2, 1.8). ^{13}C NMR spectrum, δ_C, ppm: 13.21 (C^{20}), 19.03 (C^2), 21.41 (C^6), 26.80 (C^{11}), 28.53 (C^{19}), 30.40 (C^{12}), 35.53 (CH_3N), 37.46 (C^3), 37.80 (C^1) 39.17 (C^{10}), 39.63 (C^7), 43.47 (C^4), 50.76 (CH_3O), 56.51 (C^9), 59.12 (C^5), 62.19 (C^{17}), 74.54 (C^8), 108.43 (C^{14}), 118.64 (C^{15}), 120.79 (C^{16}), 124.67 (C^{13}), 176.35 (C^{18}). Mass spectrum, m/z (I_{rel}, %) (EI): 377 $[M]^+$ (23), 346 (16), 107 (100), 95 (85). Found: $[M]^+$ 377.25666. $C_{22}H_{35}NO_4$. Calculated: M 377.25659.

Methyl (1*S*,4a*S*,5*R*,6*R*,8a*S*)-5-[2-(1-ethyl-1*H*-pyrrol-3-yl)ethyl]-6-hydroxy-6-hydroxymethyl-1,4a-dimethyldecahydronaphthalene-1-carboxylate (VIII). A solution of 0.3 g of pyrrole **VI** in 5 ml of acetic acid and 1 ml of water was heated for 2 h at 80–85°C. The mixture was diluted with water and extracted with diethyl ether, the extract was washed with a 5% solution of ammonia and evaporated, and the residue was subjected to chromatography on aluminum oxide using methanol–diethyl ether (1:1) as eluent. Yield 0.19 g (70%), oily substance, $[\alpha]_D^{20}$ = +15 (c = 2.9, chloroform). ^{1}H NMR spectrum (CD_3OD), δ, ppm (J, Hz): 0.58 s (3H, $C^{20}H_3$), 0.98–1.08 m (2H, 1-H, 3-H), 1.12 d.d (1H, 5-H, J = 12.2, 2.8), 1.16 s (3H, $C^{19}H_3$), 1.17 t (3H, CH_3, J = 7.0), 1.32–1.48 m (3H, 2-H, 6-H, 9-H), 1.76–1.95 m (4H, 1-H, 2-H, 6-H, 11-H), 2.10 m (1H, 7-H), 2.16 m (1H, 3-H), 2.28 m (1H, 11-H), 2.38 m (1H, 12-H), 2.52 m (1H, 12-H), 3.38 d (1H, 17-H, J = 8.2), 3.49 d (1H, 17-H, J = 8.2), 3.61 s (3H, OCH_3), 3.82 q (2H, CH_2, J = 7.0), 5.80 m (1H, 14-H), 6.42 d.d (1H, 16-H, J = 2.6, 2.0), 6.50 m (1H, 15-H). ^{13}C NMR spectrum, δ_C, ppm: 13.24 ($C^{20}H_3$), 14.75 (CH_3), 16.41 (C^2), 21.80 (C^6), 27.60 (C^{11}), 28.59 (C^{19}), 31.09 (C^{12}), 37.61 (C^3), 38.08 (C^1), 39.66 (C^7), 40.25 (C^{10}), 43.94 (C^4), 50.89 (OCH_3), 57.09 (C^5), 60.27 (C^9), 62.54 (CH_2N), 64.03 (C^{17}), 75.39 (C^8), 107.74 (C^{14}), 117.29 (C^{15}), 119.73 (C^{16}), 125.04 (C^{13}), 178.51 (C^{18}). Mass spectrum, m/z (I_{rel}, %): 391 $[M]^+$ (22), 459 (4), 346 (3), 254 (12), 173 (100), 160 (59). Found: $[M]^+$ 391.32104. $C_{23}H_{37}NO_4$. Calculated: M 391.31444.

Methyl (1*S*,4a*S*,5*R*,6*R*,8a*S*)-5-[2-(1-benzyl-1*H*-pyrrol-3-yl)ethyl]-6-hydroxy-6-hydroxymethyl-1,4a-dimethyldecahydronaphthalene-1-carboxylate (IX). A mixture of 1.2 g (2.6 mmol) of stereoisomeric dimethoxytetrahydrofurans **IVa–IVd** and 0.5 ml of benzylamine in 15 ml of 80% acetic acid was heated for 3 h at 80–85°C, and the mixture was then treated as described above for compound **VII** to isolate 0.81 g (69%) of diol **IX** as an oily substance, $[\alpha]_D^{20}$ = +10° (c = 3.7, chloroform). ^{1}H NMR spectrum (CD_3OD), δ, ppm (J, Hz): 0.51 s (3H, $C^{20}H_3$), 0.98–1.05 (3H, 1-H, 3-H, 5-H), 1.15 s (3H, $C^{19}H_3$), 1.18–1.45 m (5H, 2-H, 6-H, 7-H, 9-H, 11-H), 1.65–1.92 m (3H, 2-H, 6-H, 11-H), 2.08–2.28 m (2H, 1-H, 7-H), 2.35 m (1H, 3-H), 2.50 m (1H, 12-H), 2.80 m (1H, 12-H), 3.40 d (1H, 17-H, J = 8.4), 3.68 d (1H, 17-H, J = 8.4), 3.65 s (3H, OCH_3), 4.88 s (2H, CH_2), 5.88 d.d (1H, 14-H, J = 2.2, 1.8), 6.35 br.s (1H, 16-H, J = 1.8), 6.52 d (1H, 15-H, J = 2.2), 7.11 m (2H, Ph), 7.30 m (3H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 13.21 ($C^{20}H_3$), 19.83 (C^2), 21.45 (C^6), 28.80 (C^{11}), 29.20 ($C^{19}H_3$), 29.58 (C^{12}), 38.46 (C^3), 38.92 (C^1), 39.43 (C^{10}), 40.63 (C^7), 43.47 (C^4), 50.76 (OCH_3), 53.86 (CH_2), 56.51 (C^9), 60.12 (C^5), 65.19 (C^{17}), 74.54 (C^8), 108.43 (C^{14}), 118.64 (C^{15}), 120.79 (C^{16}), 125.67 (C^{13}), 127.97 ($C^{2'}$, $C^{6'}$), 128.48 ($C^{4'}$), 130.04 ($C^{3'}$, $C^{5'}$), 139.97 ($C^{1'}$), 176.85 (C^{18}). Mass spectrum, m/z (I_{rel}, %): 453 $[M]^+$ (24), 422 (15),

345 (14), 183 (100), 170 (51), 91 (88). Found: $[M]^+$ 453.28717. $C_{28}H_{39}NO_4$. Calculated: *M* 453.28789.

Methyl (1*S*,4a*S*,5*R*,6*R*,8a*S*)-5-[2-(1-allyl-1*H*-pyrrol-3-yl)ethyl]-6-hydroxy-6-hydroxymethyl-1,4a-dimethyldecahydronaphthalene-1-carboxylate (X). Following a similar procedure, from 0.65 g (1.4 mmol) of stereoisomeric dimethoxytetrahydrofurans **IVa**–**IVd** and 0.5 ml of allylamine in 10 ml of 80% acetic acid we obtained 0.35 g (62%) of diol **X** as an oily substance, $[\alpha]_D^{20}$ = +18° (*c* = 1.8, chloroform). ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 0.60 s (3H, $C^{20}H_3$), 0.92 d.t (1H, 1-H, *J* = 13.3, 4.3), 0.96 d.d.d (1H, 3-H, *J* = 13.2, 12.8, 4.2), 1.12 s (3H, $C^{19}H_3$), 1.14 d.d (1H, 5-H, *J* = 12.7, 2.9), 1.40 d.d (1H, 9-H, *J* = 11.2, 3.0), 1.43–1.51 m (3H, 2-H, 7-H, 11-H), 1.66–1.80 m (4H, 1-H, 2-H, 6-H, 11-H), 1.90 m (1H, 6-H), 2.12 m (1H, 7-H, ^2J = 12.8), 2.18 d.d.d (1H, 3-H, *J* = 13.2, 4.0, 2.6), 2.38 m (1H, 12-H), 2.65 m (1H, 12-H), 3.54 d (1H, 17-H, *J* = 8.1), 3.62 s (3H, OCH_3), 3.77 d (1H, 17-H, *J* = 8.1), 4.50 m (2H, $C^{1'}H_2$), 5.14 m (2H, $C^{3'}H_2$), 5.90 m (1H, 14-H), 6.01 m (1H, 2′-H), 6.45 d (1H, 16-H, *J* = 2.0), 6.54 m (1H, 15-H). ^{13}C NMR spectrum, δ_C, ppm: 14.14 ($C^{20}H_3$), 19.57 (C^2), 22.67 (C^6), 28.39 (C^{11}), 29.12 ($C^{19}H_3$), 30.88 (C^{12}), 38.56 (C^3), 38.97 (C^1) 40.51 (C^{10}), 41.15 (C^7), 45.00 (C^4), 51.68 (OCH_3), 52.62 ($C^{1'}$), 57.97 (C^9), 61.11 (C^5), 64.88 (C^{17}), 76.17 (C^8), 109.04 (C^{14}), 116.82 ($C^{3'}$), 118.91 (C^{15}), 121.35 (C^{16}), 126.16 (C^{13}), 136.97 ($C^{2'}$), 179.21 (C^{18}). Mass spectrum, *m*/*z* (I_{rel}, %): 403 $[M]^+$ (15), 133 (100), 121 (96), 109 (27), 81 (30). Found: $[M]^+$ 403.27220. $C_{24}H_{37}NO_4$. Calculated: *M* 403.27224.

Methyl (1*S*,4a*S*,5*R*,6*R*,8a*S*)-6-hydroxy-6-hydroxymethyl-1,4a-dimethyl-5-[2-(1-phenyl-1*H*-pyrrol-3-yl)ethyl]decahydronaphthalene-1-carboxylate (XI) was synthesized in a similar way from 0.8 g (1.7 mmol) of stereoisomer mixture **IVa**–**IVd** and 0.5 ml of aniline in 10 ml of 80% acetic acid. Yield 0.38 g (51%), oily substance, $[\alpha]_D^{20}$ = +9° (*c* = 3.9, chloroform). ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 0.63 s (3H, $C^{20}H_3$), 0.90 d.t (1H, 1-H, *J* = 13.3, 4.3), 0.96 d.d.d (1H, 3-H, *J* = 13.2, 12.8, 4.2), 1.09 s (3H, $C^{19}H_3$), 1.16 d.d (1H, 5-H, *J* = 12.6, 2.9), 1.40 m (1H, 2-H), 1.47 m (1H, 11-H), 1.53 d.d (1H, 9-H, *J* = 11.1, 3.2), 1.72–1.88 m (4H, 1-H, 2-H, 6-H, 11-H), 1.90 m (2H, 6-H, 7-H), 2.19 m (1H, 3-H, ^2J = 13.2), 2.29 d.d.d (1H, 7-H, *J* = 12.7, 4.0, 2.6), 2.44 m (1H, 12-H), 2.63 m (1H, 12-H), 3.44 d (1H, 17-H, *J* = 8.1), 3.50 s (3H, OCH_3), 3.62 d (1H, 17-H, *J* = 8.1), 5.94 m (1H, 14-H), 6.45 d (1H, 16-H, *J* = 2.0), 6.54 m (1H, 15-H), 7.26–7.50 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.38 (C^{20}), 19.72 (C^2), 21.69 (C^6), 27.52 (C^{11}), 28.59 (C^{19}), 29.92 (C^{12}), 38.04 (C^3), 38.49 (C^7), 39.00 (C^1), 40.08 (C^{10}), 43.98 (C^4), 50.71 (OCH_3), 57.22 (C^9), 60.64 (C^5), 65.02 (C^{17}), 76.23 (C^8), 109.46 (C^{14}), 116.91 ($C^{4'}$), 119.08 (C^{15}), 122.03 (C^{16}), 125.88 (C^{13}), 128.67, 128.97 ($C^{3'}$, $C^{5'}$), 130.22 ($C^{2'}$, $C^{6'}$), 141.57 ($C^{1'}$), 179.20 (C^{18}). Mass spectrum, *m*/*z* (I_{rel}, %): 439 $[M]^+$ (16), 408 (9), 169 (100), 109 (28). Found: $[M]^+$ 439.27253. $C_{27}H_{37}NO_4$. Calculated: *M* 439.27224.

Methyl (6*S*,5a*R*,9a*R*)-3,6,9a-trimethyl-5,5a,6,7,-8,9,9a,9b,10,11-decahydro-3*H*-naphtho[1,2-*g*]indole-6-carboxylate (XII). A solution of 0.22 g (1.03 mmol) of sodium periodate in 2 ml of water was added dropwise to a solution of 0.38 g of diol **VII** in 8 ml of methanol containing 0.5 ml of acetic acid. The mixture was stirred for 3 min, diluted with water, treated with aqueous ammonia until alkaline reaction, and extracted with diethyl ether. The extract was evaporated, and the residue was subjected to chromatography on silica gel using petroleum ether–diethyl ether (1:1) as eluent. Yield 0.21 g (46%), mp 138–140°C (from petroleum ether–diethyl ether), $[\alpha]_D^{20}$ = +52° (*c* = 1.3, chloroform). UV spectrum, λ_{max}, nm (log ε): 203 (4.22), 265 (4.64), 273 (4.93), 288 (4.13). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.68 s (3H, $C^{14}H_3$), 1.05–1.12 m (2H, 7-H, 9-H), 1.22 s (3H, $C^{13}H_3$), 1.37 q.d (1H, 10-H, *J* = 12.5, 4.9), 1.46 d.d (1H, 5a-H, *J* = 12.2, 4.8), 1.51 m (1H, 8-H), 1.90–2.00 m (4H, 8-H, 9-H, 9b-H, 10-H), 2.17 d.d.d (1H, 7-H, *J* = 13.5, 3.2, 1.7), 2.40 d.d.d.d (1H, 5-H, *J* = 18.6, 5.8, 2.6, 2.2), 2.49 d.d.d (1H, 11-H, *J* = 15.5, 12.5, 4.5), 2.56 d.d.t (1H, 5-H, *J* = 18.6, 12.2, 2.4, 4.8), 2.65 d.d.d.d (1H, 11-H, *J* = 15.5, 4.9, 2.3), 3.67 s (3H, CH_3N), 3.71 s (3H, CH_3O), 5.83 d (1H, 1-H, *J* = 2.7), 5.88 d.d (1H, 4-H, *J* = 6.0, 2.5), 6.42 d (1H, 2-H, *J* = 2.7). ^{13}C NMR spectrum, δ_C, ppm: 12.90 (C^{14}), 19.62 (C^8), 24.21 (C^{11}), 24.58 (C^{10}), 24.59 (C^5), 28.83 (C^{13}), 35.57 (C^{9a}), 37.91 ($C^{1'}$), 38.06 (C^7), 39.63 (C^9), 43.70 (C^6), 50.74 (C^{5a}), 51.20 (CH_3O), 51.53 (C^{9b}), 105.22 (C^1), 114.48 (C^4), 121.52 (C^{11a}), 124.49 (C^2), 127.77 (C^{3a}), 128.76 (C^{3b}), 177.62 (C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 327 $[M]^+$ (100), 252 (44), 147 (71). Found: $[M]^+$ 327.21998. $C_{21}H_{29}NO_2$. Calculated: *M* 327.21982.

Methyl (6*S*,5a*R*,9a*R*)-3-ethyl-6,9a-dimethyl-5,5a,6,7,8,9,9a,9b,10,11-decahydro-3*H*-naphtho-[1,2-*g*]indole-6-carboxylate (XIII). A solution of 0.11 g (0.51 mmol) of sodium periodate in 2 ml of water was added dropwise to a solution of 0.2 g (0.45 mmol) of diol **VIII** in 5 ml of methanol containing 0.3 ml of acetic acid. The mixture was stirred for 5 min, diluted with water, treated with a 5% solution of

ammonia to alkaline reaction, and extracted with diethyl ether. The extracts were washed with water and evaporated, and the residue was purified by chromatography on silica gel using petroleum ether–diethyl ether (1:1) as eluent. Yield 0.09 g (51%), mp 121–123°C (from petroleum ether), $[\alpha]_D^{20}$ = +47° (*c* = 2.1, chloroform). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.67 s (3H, $C^{14}H_3$), 1.11 m (2H, 7-H, 9-H), 1.19 s (3H, $C^{13}H_3$), 1.37 t (3H, $C^{2'}H_3$, *J* = 7.0), 1.39–1.52 m (3H, 5a-H, 8-H, 10-H), 1.90–2.00 m (4H, 8-H, 9-H, 9b-H, 10-H), 2.15 m (1H, 7-H), 2.38–2.50 m (2H, 5-H, 11-H), 2.56–2.62 m (2H, 5-H, 11-H), 3.64 s (3H, OCH_3), 4.01 q (2H, $C^{1'}H_2$, *J* = 7.0), 5.69 m (1H, 4-H), 5.74 d (1H, 1-H, *J* = 2.1), 6.39 d (1H, 2-H, *J* = 2.0). ^{13}C NMR spectrum, δ_C, ppm: 13.09 (C^{14}), 16.53 ($C^{2'}$), 19.82 (C^8), 24.52 and 24.81 (C^{11}, C^{10}), 24.93 (C^5), 29.01 (C^{13}), 35.82 (C^{9a}), 38.31 (C^7), 39.89 (C^9), 43.81 (C^6), 43.83 ($C^{1'}$), 51.00 (CH_3O), 51.14 (C^{5a}), 51.95 (C^{9b}), 105.96 (C^1), 113.85 (C^4), 121.99 (C^{11a}), 122.93 (C^2), 126.87 (C^{3a}), 128.83 (C^{3b}), 177.11 (C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 341 $[M]^+$ (100), 326 (25), 266 (36), 161 (70). Found: $[M]^+$ 341.23551. $C_{22}H_{31}NO_2$. Calculated: *M* 341.22546.

Methyl (1*S*,4a*S*,5*R*,8a*S*)-5-[2-(1-benzyl-1*H*-pyrrol-3-yl)ethyl]-1,4a-dimethyl-6-oxodecahydronaphthalene-1-carboxylate (XIV). A solution of 0.24 g (1.12 mmol) of sodium periodate in 3 ml of water was added to a solution of 0.5 g (1.1 mmol) of diol **IX** in 10 ml of methanol. After 10 min, the mixture was diluted with water and extracted with diethyl ether. The extract was evaporated, and the residue was subjected to chromatography on aluminum oxide using diethyl ether as eluent. Yield 0.38 g (82%), oily substance, $[\alpha]_D^{20}$ = +14° (*c* = 4.4, chloroform). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.47 s (3H, $C^{20}H_3$), 0.88–0.96 m (2H, 1-H, 3-H), 1.08 d.d (1H, 5-H, *J* = 12.4, 2.6), 1.26 s (3H, $C^{19}H_3$), 1.45–1.55 m (3H, 2-H, 7-H, 11-H), 1.66–1.80 m (2H, 2-H, 6-H, 11-H), 1.92–2.04 m (3H, 1-H, 6-H, 7-H), 2.20 m (1H, 3-H), 2.28–2.36 m (1H, 12-H), 2.38–2.52 m (1H, 12-H), 3.55 s (3H, OCH_3), 4.91 s (2H, CH_2), 5.79 d.d (1H, 14-H, *J* = 2.5, 2.1), 6.43 d (1H, 16-H, *J* = 2.1), 6.64 d (1H, 15-H, *J* = 2.5), 7.14 m (2H, Ph), 7.29 m (3H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 13.79 (C^{20}), 20.82 (C^2), 24.37 (C^6), 26.99 and 27.03 ((C^{11}, C^{12}), 29.14 (C^{19}), 38.99 (C^3), 40.32 (C^1), 44.02 (C^{10}), 44.54 (C^7), 45.49 (C^4), 51.80 (OCH_3), 53.90 ($C^{1'}$), 55.88 (C^5), 62.85 (C^9), 109.45 (C^{14}), 119.73 (C^{15}), 122.17 (C^{16}), 125.27 (C^{13}), 128.03 ($C^{2'}$, $C^{6'}$), 128.39 ($C^{4'}$), 129.54 ($C^{3'}$, $C^{5'}$), 140.60 ($C^{1'}$), 178.68 (C^{18}), 213.26 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 421 $[M]^+$ (20), 362 (3), 183 (100), 171 (46), 90 (99). Found: $[M]^+$ 421.26151. $C_{27}H_{35}NO_3$. Calculated: *M* 421.26168.

Methyl (1*S*,4a*S*,5*R*,8a*S*)-5-[2-(1-allyl-1*H*-pyrrol-3-yl)ethyl]-1,4a-dimethyl-6-oxodecahydronaphthalene-1-carboxylate (XV). A solution of 0.11 g (0.51 mmol) of sodium periodate in 2 ml of water was added to a solution of 0.2 g (0.5 mmol) of diol **X** in 5 ml of methanol. After 10 min, the mixture was diluted with water and extracted with diethyl ether. The extract was evaporated, and the residue was subjected to chromatography on aluminum oxide using diethyl ether as eluent to isolate 0.14 g (76%) of ketone **XV** as an oily substance, $[\alpha]_D^{20}$ = +19° (*c* = 5.0, chloroform). ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 0.55 s (3H, $C^{20}H_3$), 1.12 d.t (1H, 3-H, *J* = 13.2, 4.2), 1.21 m (2H, 1-H, 5-H), 1.28 s (3H, $C^{19}H_3$), 1.45–1.55 m (3H, 2-H, 7-H, 11-H), 1.68–1.90 m (4H, 2-H, 6-H, 9-H, 11-H), 1.98 m (2H, 1-H, 6-H), 2.08–2.28 m (2H, 3-H, 7-H), 2.32–2.46 m (1H, 12-H), 2.45–2.52 m (1H, 12-H), 3.62 s (3H, OCH_3), 4.45 m (2H, 1′-H), 5.11 m (2H, 3′-H), 5.89 d.d (1H, 14-H, *J* = 2.5, 2.1), 6.01 m (1H, 2′-H), 6.40 d (1H, 16-H, *J* = 2.1), 6.56 d (1H, 15-H, *J* = 2.5). ^{13}C NMR spectrum, δ_C, ppm: 13.77 (C^{20}), 20.85 (C^2), 24.54 (C^6), 27.04 and 27.20 (C^{11}, C^{12}), 29.12 (C^{19}), 38.98 (C^3), 40.36 (C^1), 44.05 (C^{10}), 44.61 (C^7), 45.51 (C^4), 51.80 (OCH_3), 52.66 ($C^{1'}$), 55.85 (C^5), 63.13 (C^9), 109.13 (C^{14}), 116.70 ($C^{3'}$), 119.32 (C^{15}), 121.64 (C^{16}), 124.98 (C^{13}), 136.69 ($C^{2'}$), 178.71 (C^{18}), 214.68 (C^8).

Methyl (1*S*,4a*S*,5*R*,8a*S*)-1,4a-dimethyl-6-oxo-5-[2-(1-phenylpyrrol-3-yl)ethyl]decahydronaphthalene-1-carboxylate (XVI). A solution of 0.12 g (0.56 mmol) of sodium periodate in 2 ml of water was added to a solution of 0.25 g (0.55 mmol) of diol **XI** in 8 ml of methanol. After 10 min, the mixture was diluted with water and extracted with diethyl ether. The extract was evaporated, and the residue was subjected to chromatography on aluminum oxide using diethyl ether as eluent to isolate 0.20 g (83%) of ketone **XVI** as an oily substance, $[\alpha]_D^{20}$ = +8° (*c* = 2.2, chloroform). ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 0.53 s (3H, $C^{20}H_3$), 0.91–1.02 m (2H, 1-H, 3-H), 1.08 d.d (1H, 5-H, *J* = 12.4, 2.6), 1.26 s (3H, $C^{19}H_3$), 1.45–1.55 m (3H, 2-H, 6-H, 11-H), 1.66 m (1H, 9-H, 11-H), 1.70–1.80 m (2H, 2-H, 7-H), 1.98–2.04 m (1H, 6-H), 2.20 m (1H, 3-H), 2.30 m (3H, 1-H, 7-H, 12-H), 2.50 m (1H, 12-H), 3.62 s (3H, OCH_3), 5.91 d.d (1H, 14-H, *J* = 2.5, 2.1), 6.43 d (1H, 16-H, *J* = 2.1), 6.64 d (1H, 15-H, *J* = 2.5), 7.14 m (2H, Ph), 7.29 m (3H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 13.52 (C^{20}), 20.46 (C^2), 23.92 (C^6), 26.36 and 26.99 (C^{11},

C^{12}), 29.42 (C^{19}), 38.57 (C^3), 39.87 (C^1), 43.53 (C^{10}), 43.84 (C^7), 44.88 (C^4), 51.80 (OCH_3), 55.10 (C^5), 62.62 (C^9), 111.80 (C^{14}), 116.93 (C^{15}), 119.35 (C^{16}), 119.88 ($C^{2'}$, $C^{6'}$), 125.60 ($C^{4'}$), 127.33 (C^{13}), 130.41 ($C^{3'}$, $^{5'}$), 141.64 ($C^{1'}$), 178.60 (C^{18}), 211.07 (C^8).

Methyl (6*S*,5a*R*,9a*R*)-3-benzyl-6,9a-dimethyl-5,5a,6,7,8,9,9a,9b,10,11-decahydro-3*H*-naphtho-[1,2-*g*]indole-6-carboxylate (XVII). A solution of 0.2 g (0.48 mmol) of ketone **XIV** and 1 ml of acetic acid in 8 ml of methanol was kept for 2 h at room temperature. It was then diluted with water and extracted with diethyl ether. The extract was washed with a 5% solution of ammonia and evaporated, and the residue was subjected to chromatography on silica gel using petroleum ether–diethyl ether as eluent (2:1). Yield 0.13 g (71%), oily substance. ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 0.65 s (3H, $C^{14}H_3$), 0.88–0.96 m (2H, 7-H, 9-H), 1.13 s (3H, $C^{13}H_3$), 1.11–1.20 m (2H, 5a-H, 10-H), 1.30–1.52 m (3H, 8-H, 9b-H, 10-H), 1.90–2.01 m (2H, 8-H, 9-H), 2.11–2.25 m (3H, 5-H, 7-H, 11-H), 2.56 m (1H, 5-H), 2.68 d.d.d (1H, 11-H, *J* = 14.2, 6.2, 2.5), 3.62 s (3H, OCH_3), 5.23 s (2H, 1′-H), 5.56 m (1H, 4-H), 5.91 d (1H, 1-H, *J* = 1.8), 6.60 d (1H, 2-H, *J* = 1.8), 7.00 m (2H, Ph), 7.30 m (3H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 13.50 (C^{14}), 20.61 (C^8), 25.52 and 25.66 (C^{11}, C^{10}), 26.08 (C^5), 29.23 (C^{13}), 36.75 (C^{9a}), 39.19 (C^7), 40.79 (C^9), 44.95 (C^6), 51.75 (C^{5a}), 51.97 (CH_3O), 53.09 (C^{9b}), 53.38 ($C^{1'}$), 107.09 (C^1), 115.72 (C^4), 123.18 (C^{11a}), 126.14 (C^2), 126.64 ($C^{2''}$, $C^{6''}$), 127.83 ($C^{4''}$), 128.83 (C^{3a}), 129.32 (C^{3b}), 129.57 ($C^{3''}$, $C^{5''}$), 140.62 ($C^{1''}$), 179.29 (C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 403 $[M]^+$ (100), 328 (21), 223 (40), 91 (60). Found: $[M]^+$ 403.25132. $C_{27}H_{33}NO_2$. Calculated: *M* 403.25111.

Methyl (6*S*,5a*R*,9a*R*)-3-allyl-6,9a-dimethyl-5,5a,6,7,8,9,9a,9b,10,11-decahydro-3*H*-naphtho-[1,2-*g*]indole-6-carboxylate (XVIII). A solution of 0.15 g (0.40 mmol) of ketone **XV** and 1 ml of acetic acid in 8 ml of methanol was kept for 30 min, diluted with water, and extracted with diethyl ether. The extract was washed with a 5% solution of ammonia, the solvent was removed, and the residue was subjected to chromatography using petroleum ether–diethyl ether (2:1) as eluent. Yield 0.11 g (77%), oily substance. ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 0.70 s (3H, $C^{14}H_3$), 0.88–0.96 m (2H, 7-H, 9-H), 1.15 m (1H, 10-H), 1.13 s (3H, $C^{13}H_3$), 1.21–1.38 m (2H, 5a-H, 8-H), 1.52 m (1H, 8-H), 1.90–2.01 m (3H, 9-H, 9b-H, 10-H), 2.19 m (1H, 7-H), 2.38–2.55 m (3H, 5-H, 11-H), 2.68 d.d.d (1H, 11-H, *J* = 14.2, 6.2, 2.5), 3.65 s (3H, OCH_3), 4.60 m (1H, 3′-H), 4.83 m (2H, 1′-H), 5.16 m (1H, 3′-H), 5.70 m (1H, 4-H), 5.82 d (1H, 1-H, *J* = 2.8), 5.96 m (1H, 2′-H), 6.50 d (1H, 2-H, *J* = 2.8). ^{13}C NMR spectrum, δ_C, ppm: 13.50 (C^{14}), 20.80 (C^8), 25.49 and 25.77 (C^{11}, C^{10}), 26.41 (C^5), 29.67 (C^{13}), 36.80 (C^{9a}), 38.68 (C^7), 40.14 (C^9), 45.00 (C^6), 51.65 (C^{5a}), 52.09 (C^{9b}), 52.75 (CH_3O), 69.07 ($C^{1'}$), 106.86 (C^8), 115.05 (C^4), 116.60 ($C^{3'}$), 122.72 (C^{11a}), 125.27 (C^2), 128.56 (C^{3a}), 129.48 (C^{3b}), 136.73 ($C^{2'}$), 179.26 (C^{12}).

Methyl (6*S*,5a*R*,9a*R*)-6,9a-dimethyl-3-phenyl-5,5a,6,7,8,9,9a,9b,10,11-decahydro-3*H*-naphtho-[1,2-*g*]indole-6-carboxylate (XIX). A solution of 0.2 g (0.49 mmol) of ketone **XVI** and 0.2 ml of acetic acid in 8 ml of methanol was kept for 2 h, diluted with water, and extracted with diethyl ether. The extract was washed with a 5% solution of ammonia, the solvent was removed, and the residue was subjected to chromatography on silica gel using petroleum ether–diethyl ether (2:1) as eluent. Yield 0.14 g (75%), oily substance. ^{1}H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 0.68 s (3H, $C^{14}H_3$), 0.82–1.16 m (3H, 7-H, 9-H, 10-H), 1.14 s (3H, $C^{13}H_3$), 1.30–1.54 m (2H, 5a-H, 8-H), 1.92–2.06 m (4H, 8-H, 9-H, 9b-H, 10-H), 2.11 m (1H, 7-H), 2.25–2.36 m (2H, 5-H, 11-H), 2.55 d.d.d (1H, 5-H, *J* = 14.2, 6.2, 2.5), 2.72 d.d.d (1H, 11-H, *J* = 18.2, 4.8, 2.5), 3.62 s (3H, OCH_3), 4.98 m (1H, 4-H), 5.97 d (1H, 1-H, *J* = 2.8), 6.56 d (1H, 2-H, *J* = 2.8), 7.28 m (2H, Ph), 7.40 m (3H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 13.50 (C^{14}), 20.80 (C^8), 25.32 and 25.66 (C^{10}, C^{11}), 26.13 (C^5), 29.18 (C^{13}), 36.75 (C^{9a}), 39.19 (C^7), 40.73 (C^9), 44.98 (C^6), 51.64 (C^{5a}), 51.97 (CH_3O), 52.76 (C^{9b}), 107.64 (C^1), 115.05 (C^4), 116.42 ($C^{4'}$), 123.66 (C^{11a}), 126.34 (C^2), 128.14 and 128.19 ($C^{3'}$, $C^{5'}$), 128.39 (C^{3a}), 129.18 (C^{3b}), 130.17 ($C^{2'}$, $C^{6'}$), 143.99 ($C^{1'}$), 179.26 (C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 389 $[M]^+$ (100), 374 (43), 312 (34), 209 (32). Found: $[M]^+$ 389.23521. $C_{26}H_{31}NO_2$. Calculated: *M* 389.23546.

Methyl (1′*R*,4*R*,4a′*R*,5′*S*,8a′*R*)-2,2,5′,8a′-tetramethyl-1′-[2-(2-oxo-2,5-dihydrofuran-3-yl)ethyl]-octahydro-1′*H*-spiro[1,3-dioxolane-4,2′-naphthalene]-5′-carboxylate (XXI). Formic acid, 0.5 ml, was added to a solution of 0.2 g (0.43 mmol) of stereoisomeric 2,5-dimethoxydihydrofuran mixture **IIIa**–**IIId** in 5 ml of dioxane, and the mixture was kept for 2 h, diluted with water, and extracted with diethyl ether. The extract was washed with a 5% solution of ammonia and evaporated, and the residue was subjected to chromatography on silica gel using petroleum ether–diethyl ether (1:1) as eluent. Yield 0.11 g (65%), mp 151–153°C (from petroleum ether–acetone). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.41 s

(3H, $C^{20}H_3$), 0.92 d.d (1H, 3-H, J = 13.3, 4.3, 2.1), 0.96 d.d (1H, 1-H, J = 14.4, 4.8, 2.6), 1.06 d.d (1H, 5-H, J = 12.6, 2.8), 1.10 s (3H, $C^{19}H_3$), 1.26 d.d (1H, 9-H, J = 12.2, 3.0), 1.20 s and 1.30 s [3H each, $(CH_3)_2C$], 1.40–1.50 m (3H, 2-H, 11-H), 1.62 d.d.d.d (1H, 6-H, J = 14.6, 12.6, 3.8, 2.5), 1.66–1.75 m (3H, 1-H, 2-H, 7-H), 1.83 d.d.d (1H, 6-H, J = 14.6, 5.2, 2.8), 2.01 d.t (1H, 7-H, J = 12.8, 3.4), 2.07 d.d.d (1H, 3-H, J = 13.3, 4.6, 2.3), 2.17 m (1H, 12-H), 2.40 m (1H, 12-H), 3.52 d.d (1H, 17-H, J = 8.5, 1.7), 3.55 s (3H, OCH_3), 3.67 d (1H, 17-H, J = 8.5), 4.66 d (2H, 15-H, J = 1.8), 7.02 d (1H, 14-H, J = 1.8). ^{13}C NMR spectrum, δ_C, ppm: 12.41 (C^{20}), 18.96 (C^2), 21.87 (C^6), 23.36 (C^{11}), 26.73 (C^{19}), 28.38 (C^{12}), 28.48 and 28.63 (CH_3), 37.71 (C^3), 38.83 (C^1), 39.47 (C^7), 39.54 (C^{10}), 43.55 (C^4), 51.01 (CH_3), 55.79 (C^5), 56.11 (C^9), 68.26 (C^{17}), 69.57 (C^{15}), 84.71 (C^8), 106.60 ($C^{2'}$), 134.75 (C^{13}), 143.23 (C^{14}), 173.39 (C^{16}), 176.70 (C^{18}). Mass spectrum, m/z (I_{rel}, %): 420 $[M]^+$ (34), 405 (57), 362 (51), 345 (34), 285 (100), 237 (26), 127 (98), 121 (28), 109 (27), 105 (31), 95 (26), 81 (32), 72 (40). Found: $[M]^+$ 420.25101. $C_{24}H_{36}O_6$. Calculated: M 420.25117.

This study was performed under financial support by the Russian Foundation for Basic Research (project nos. 06-03-32150 and 05-03-32365) and by the President of the Russian Federation (program for support of leading scientific schools, project no. NSh 1589.3-06).

REFERENCES

1. Kharitonov, Yu.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2007, vol. 43, p. 839.
2. Chernov, S.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2006, vol. 42, p. 828.
3. Shults, E.E. and Tolstikov, G.A., *Selected Methods for Synthesis and Modification of Heterocycles*, Kartsev, V.G., Ed., 2006, vol. 4, p. 241.
4. Engler, T.A., Furness, K., Malhotra, S., Sanchez-Martinez, C., Shih, C., Xie, W., Zhu, G., Zhou, X., Conner, S., Faul, M.M., Sullivan, K.A., Kolis, S.P., Brooks, H.B., Patel, B., Schultz, R.M., DeHahn, T.B., Kirmani, K., Spencer, C.D., Watkins, S.A., Considine, E.L., Dempsey, J.A., Ogg, C.A., Stamm, N.B., Anderson, B.D., Campbell, R.M., Vasudevan, V., and Lytle, M.L., *Bioorg. Med. Chem. Lett*., 2003, vol. 13, p. 2261.
5. Ylikoski, J., Pirvola, U., Saarma, M., Walton, K., and Hudkins, R.L., World Patent Appl. no. WO 2000-018407; *Chem. Abstr*., 2000, vol. 132, no. 260705.
6. Router, S., Merour, J.-Y., Dia, N., Lansiaux, A., Bailly, C., Lozach, O., and Meijer, L., *J. Med. Chem*., 2005, vol. 49, p. 789.
7. Chernov, S.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2006, vol. 42, p. 36.
8. Fakstorp, J., Raleigh, D., and Schniepp, L.E., *J. Am. Chem. Soc*., 1950, vol. 72, p. 869.
9. Asili, J., Lambert, M., Ziegler, H.L., Stark, D., Sairafianpour, M., Witt, M., Asghari, G., Ibrahimi, I.S., and Jaroszewski, J.W., *J. Nat. Prod*., 2004, vol. 67, p. 631.
10. Kim, K.A., Moon, T.C., Lee, S.W., Chung, K.C., Han, B.H., and Chang, H.W., *Planta Medica*, 1999, vol. 65, p. 39.
11. Yang, H.O., Kang, Y.H., Suh, D.-Y., Kim, Y.C., and Han, B.H., *Planta Medica*, 1995, vol. 61, p. 519.
12. Shults, E.E., Velder, J., Schmalz, H.-G., Chernov, S.V., Rubalova, T.V., Gatilov, Y.V., Henze, G., Tolstikov, G.A., and Prokop, A., *Bioorg. Med. Chem. Lett*., 2006, vol. 16, p. 4228.
13. Kalinowski, H.-O., Berger, S., and Braun, S., *13C-NMR-Spektroskopie*, Stuttgart: Georg Thieme, 1984, pp. 455, 472.