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Photochemical rearrangement of 5,6-epoxy derivatives of the Diels–Alder adduct of levoglucosenone and piperylene

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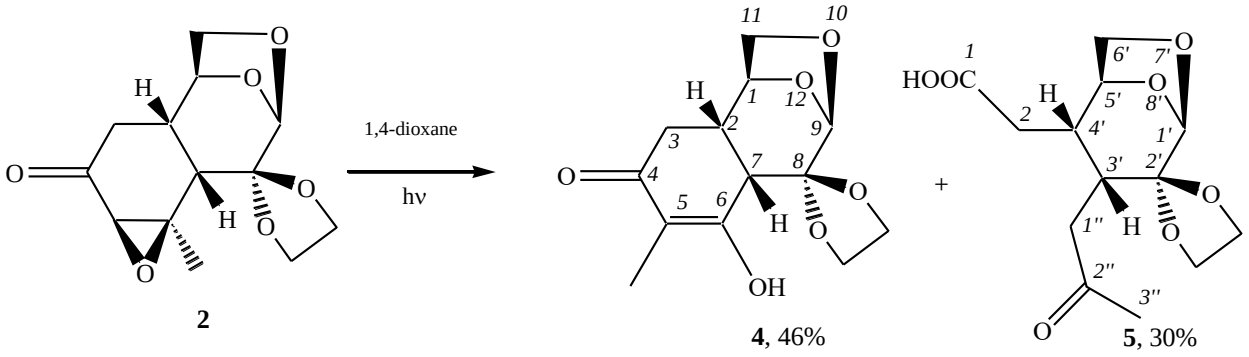
The spectral and analytical data were obtained using the equipment of the *Khimiya* Joint Center at the Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-300 (300 MHz for ^{1}H and 75.47 MHz for ^{13}C) and on a spectrometer Bruker Avance III, (500.13 MHz for ^{1}H and 125.47 MHz for ^{13}C). IR spectra were recorded on spectrophotometers Shimadzu IRPrestige-21 or Bruker Tensor 27 (from films or mulls in mineral oil). Mass spectra were measured on a GC-MS Hewlett Packard instrument, chromatograph HP 6890 with a mass-selective detector HP 5973. Optical rotation was determined on a polarimeter Perkin Elmer-341. Analytic TLC was carried out on Sorbfil plates of the grade PTSKh-AF-A ("Sorbpolymer" Co., Krasnodar). The melting points were measured on a Boëtius 05 heating stage. Photolysis was performed in a quartz tube using a high pressure mercury lamp DPT 220 (230 W) (radiant flux of 240-320 nm).



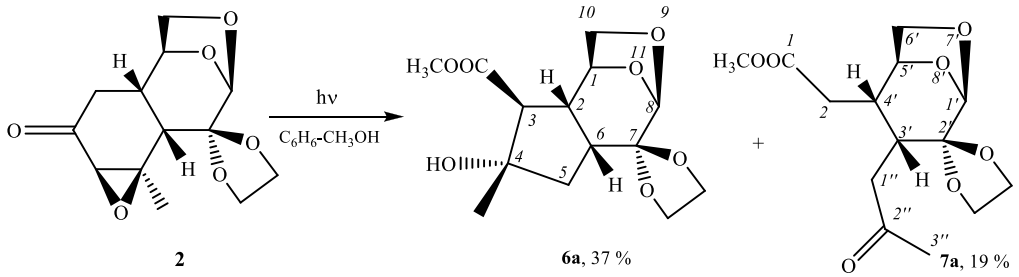
2 **4**, 46% **5**, 30%

(1*S*,2*S*,7*S*,9*R*)-6-Hydroxy-5-methyl-4*H*-spiro[10,12-dioxatricyclo[7.2.1.0^{2,7}]dodec-5-ene-8,2'-[1,3]dioxolan]-4-one (4) and {(1'*R*,3'*R*,4'*S*,5'*S*)-3'-(2-oxopropyl)spiro[7,8-dioxabicyclo[3.2.1]octane-2,2-[1,3]dioxolan]-4-yl}acetic acid (5). A solution of epoxide **2** (0.08 g,

0.03 mmol) in 1,4-dioxane (4 ml) and H_2O (0.04 ml) was irradiated at room temperature until the reaction was complete (ca 18 h). The solvent was distilled off under reduced pressure, and the residue was purified by chromatography on silica gel. Yield **4** 0.04 g (46%) and acid **5** 0.03 g (30%).

Compound **4**, colourless oil. $[\alpha]_D^{20}$ +41° (*c* 0.5, $CHCl_3$), R_f 0.4 (EtOAc). ^{1}H NMR ($CDCl_3$) δ: 2.08 (s, 3H, CH_3), 2.32 (m, 2H, H^2, H^{3B}), 2.92 (dd, 1H, H^{3A}, $^2J_{3A,3B}$ 15.8, $^3J_{3A,2}$ 11.4 Hz), 3.33 (d, 1H, H^7, $^3J_{7,2}$ 7.2 Hz), 3.45 (s, 1H, OH) 3.58 (m, 1H, OCH_2), 3.83 (m, 1H, OCH_2), 3.93 (dd, 1H, H^{11B}, $^2J_{11B,11A}$ 7.2 , $^3J_{11B,1}$ 4.6 Hz), 3.98 (m, 1H, OCH_2), 3.98 (d,1H, H^{11A}, $^2J_{11A,11B}$ 7.2 Hz), 4.04 (m, 1H, OCH_2), 4.52 (d, 1H, H^1, $^3J_{1,11B}$ 4.6 Hz), 5.04 (s, 1H, H^9). ^{13}C NMR ($CDCl_3$) δ: 19.63 (CH_3), 35.40 (C^3), 38.57 (C^2), 40.48 (C^7), 64.75 (OCH_2), 66.54 (OCH_2), 68.89 (C^{11}), 72.89 (C^1), 100.19 (C^9), 106.02 (C^8), 109.31 (C^5), 173.59 (C^6), 207.79 (C^4). Found, %: C 58.17, H 6.11 $C_{13}H_{16}O_6$. Calculated, %: C 58.20, H 6.01.

Compound **5**, colourless oil. $[\alpha]_D^{20}$ -80° (*c* 1.4, $CHCl_3$), R_f 0.1 (EtOAc). ^{1}H NMR ($CDCl_3$) δ: 2.15 (s, 3H, CH_3), 2.40 (m, 2H, $H^{4'}$, $H^{1''B}$), 2.49 (m, 1H, H^{2B}), 2.51 (m, 1H, $H^{1''A}$), 2.73 (dd, 1H, H^{2A}, $^2J_{2A,2B}$ 16.7, $^3J_{2A,4'}$ 9.1 Hz), 2.90 (dt, 1H, $H^{3'}$, $^2J_{3',1''B}$ 8.6, $^3J_{3',1''A}$ 5.3, $^3J_{3',4'}$ 5.5 Hz), 3.77 (dd, 1H, $H^{6'B}$, $^2J_{6'B,6'A}$ 7.5, $^3J_{6'B,5'}$ 5.4 Hz), 3.85 (m, 2H, OCH_2), 3.91 (m, 1H, OCH_2), 4.05 (d, 1H, $H^{6'A}$, $^2J_{6'A,6'B}$ 7.5 Hz), 4.08 (m,1H, OCH_2), 4.53 (dd,1H, $H^{5'}$, $^3J_{5',6'B}$ 5.4, $^3J_{5',4'}$ 1.3 Hz), 5.00 (s, 1H, $H^{1'}$), 9.51 (s, COOH). ^{13}C NMR ($CDCl_3$) δ: 29.65 (CH_3), 30.92 (C^2), 33.55 ($C^{3'}$), 36.99 ($C^{4'}$), 38.70 ($C^{1''}$), 64.60 (OCH_2), 66.34 (OCH_2), 67.60 ($C^{6'}$), 75.74 ($C^{5'}$), 99.79 ($C^{1'}$), 106.01 ($C^{2'}$), 177.59 (C=O), 206.94 (C=O). Found, %: C 54.59, H 6.03 $C_{13}H_{18}O_7$. Calculated, %: C 54.54, H 6.34.

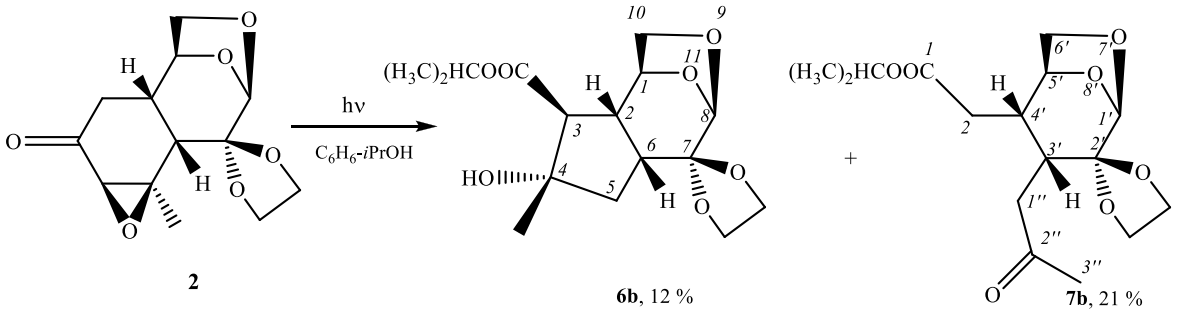


Methyl (1*S*,2*R*,3*R*,4*S*,6*S*,8*R*)-4-hydroxy-4-methylspiro[9,11-dioxatricyclo[6.2.1.0^{2,6}]-undecane-7,2'-[1,3]dioxolane]-3-carboxylate (6a) and methyl [(1'*R*,3'*R*,4'*S*,5'*S*)-3'-(2-oxopropyl)spiro[7,8-dioxabicyclo[3.2.1]octane-2,2'-[1,3]dioxolan]-4'-yl]acetate (7a). A solution of epoxide **2** (0.11 g, 0.04 mmol) in anhydrous C_6H_6 (84 ml) and MeOH (0.84 ml) was purged with argon for 10 min and then irradiated at room temperature until the reaction was complete (ca 18 h). The solvent was distilled off under reduced pressure, and the residue was

purified by chromatography on silica gel. Yield of cyclopentanone **6a** 0.04 g (37%), and compound **7a** 0.02 g (19%).

Compound **6a**. White crystals, mp. 185°C. $[\alpha]_D^{20}$ -124° (*c* 4.0, DMSO), R_f 0.19 (EtOAc–petroleum ether, 1:1). ^{1}H NMR (DMSO-d_6) δ: 1.37 (s, 3H, CH_3), 1.68 (dd, 1H, H^{5B}, $^2J_{5B,5A}$ 14.2, $^3J_{5B,6}$ 9.0 Hz), 1.77 (dd, 1H, H^{5A}, $^2J_{5A,5B}$ 14.2, $^3J_{5A,6}$ 2.1 Hz), 2.46 (ddd, 1H, H^6, $^3J_{6,5B}$ 9.0, $^3J_{6,2}$ 7.7, $^3J_{6,5A}$ 2.1 Hz), 2.60 (dd, 1H, H^2, $^3J_{2,3}$ 12.6, $^3J_{2,6}$ 7.7 Hz), 2.78 (d, 1H, H^3, $^3J_{3,2}$ 12.6 Hz), 3.60 (s, 3H, OCH_3), 3.65 (dd, 1H, H^{10B}, $^2J_{10B,10A}$ 7.0 , $^3J_{10B,1}$ 5.0 Hz), 3.78 (m, 1H, OCH_2), 3.79 (m, 1H, OCH_2), 3.88 (m, 2H, H^{10A}, OCH_2), 4.00 (m, 1H, OCH_2), 4.31 (d, 1H, H^1, $^3J_{1,10B}$ 5.0 Hz), 4.62 (s, 1H, OH), 4.99 (s, 1H, H^8). ^{13}C NMR (DMSO-d_6) δ: 27.97 (CH_3), 37.53 (C^6), 41.22 (C^5), 44.73 (C^2), 51.62 (OCH_3), 54.59 (C^3), 64.04 (OCH_2), 66.39 (OCH_2), 68.78 (C^{10}), 72.37 (C^1), 80.04 (C^4), 99.68 (C^8), 105.71 (C^7), 171.89 (C=O). Found, %: C 59.87, H 6.59 $C_{14}H_{20}O_7$. Calculated, %: C 59.94, H 6.66.

Compound **7a**, colourless oil. $[\alpha]_D^{20}$ -62° (*c* 0.4, $CHCl_3$), R_f 0.25 (EtOAc– petroleum ether, 1:1). ^{1}H NMR (CD_3OD) δ: 2.14 (s, 3H, CH_3), 2.35 (m, 1H, $H^{4'}$), 2.41 (dd, 1H, $H^{1''B}$, $^2J_{1''B,1''A}$ 17.0, $^3J_{1''B,3'}$ 8.7 Hz), 2.51 (dd, 1H, $H^{1''A}$, $^2J_{1''A,1''B}$ 17.0, $^3J_{1''A,3'}$ 5.5 Hz), 2.53 (dd, 1H, H^{2B}, $^2J_{2B,2A}$ 16.9 , $^3J_{2B,4'}$ 5.5 Hz), 2.69 (dd, 1H, H^{2A}, $^2J_{2A,2B}$ 16.9, $^3J_{2A,4'}$ 9.2 Hz), 2.83 (dt, 1H, $H^{3'}$, $^2J_{3',1''B}$ 8.7, $^3J_{3',1''A}$ 5.5, $^3J_{3',4'}$ 5.5 Hz), 3.67 (m, 3H, OCH_3), 3.77 (dd, 1H, $H^{6'B}$, $^2J_{6'B,6'A}$ 7.6, $^3J_{6'B,5'}$ 5.4 Hz), 3.88 (m, 2H, OCH_2), 3.93 (m, 2H, OCH_2), 4.03 (d, 1H, $H^{6'A}$, $^2J_{6'A,6'B}$ 7.6 Hz), 4.05 (m, 2H, OCH_2), 4.43 (dd, 1H, $H^{5'}$, $^3J_{5',6'B}$ 5.4, $^3J_{5',4'}$ 1.3 Hz), 4.99 (s, 1H, $H^{1'}$). ^{13}C NMR (MeOD) δ: 28.33 (CH_3), 30.79 (C^2), 33.38 ($C^{3'}$), 37.24 ($C^{4'}$), 38.27 ($C^{1''}$), 50.74 (OCH_3), 64.12 (OCH_2), 65.96 (OCH_2), 67.01 ($C^{6'}$), 75.86 ($C^{5'}$), 99.65 ($C^{1'}$), 105.91 ($C^{2'}$), 173.83 (C=O), 208.60 (C=O). Found, %: C 55.87, H 6.61 $C_{14}H_{20}O_7$. Calculated, %: C 55.94, H 6.66.



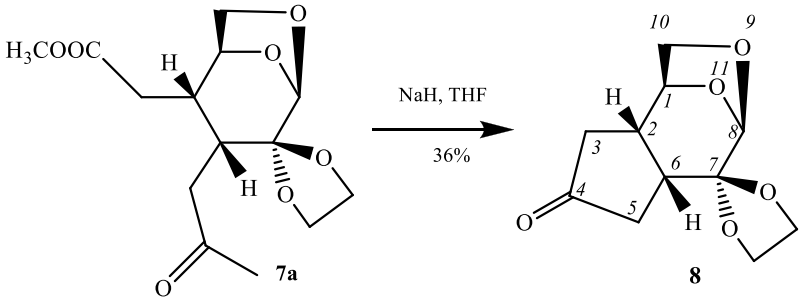
2 **6b**, 12 % **7b**, 21 %

Isopropyl (1*S*,2*R*,3*R*,4*S*,6*S*,8*R*)-4-hydroxy-4-methylspiro[9,11-dioxatricyclo-[6.2.1.0^{2,6}]undecane-7,2'-[1,3]dioxolane]-3-carboxylate (6b) and isopropyl {(1'*R*,3'*R*,4'*S*,5'*S*)-3'-(2-oxopropyl)spiro[7,8-dioxabicyclo[3.2.1]-octane-2,2'-[1,3]dioxolan]-4'-yl}acetate (7b). A solution of epoxide **2** (0.10 g, 0.04 mmol) in anhydrous C_6H_6 (84 ml) and *i*-

PrOH (0.84 ml) was purged with argon for 10 minutes and then irradiated at room temperature until the reaction was complete (ca 18 h). The solvent was distilled off under reduced pressure, and the residue was purified by chromatography on silica gel. Yield of cyclopentanone **6b** 0.015 g (12%), and compound **7b** 0.026 g (21%).

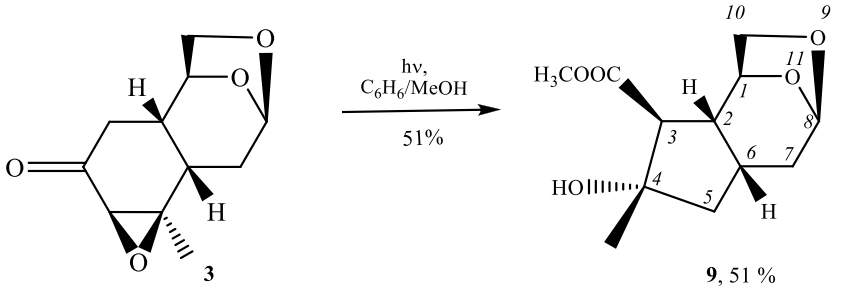
Compound **6b**, colourless oil. $[\alpha]_D^{20}$ -84.1° (*c* 0.5, CH_2Cl_2), R_f 0.23 (EtOAc– petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$) δ: 1.22 (m, 6H, CH_3), 2.47 (s, 3H, CH_3), 1.83 (m, 3H, OH, H^5), 2.63 (ddd, 1H, H^6, $^3J_{6,5B}$ 9.0, $^3J_{6,2}$ 7.7, $^3J_{6,5A}$ 2.1 Hz), 2.69 (dd, 1H, H^2, $^3J_{2,3}$ 12.6, $^3J_{2,6}$ 7.7 Hz), 2.93 (d, 1H, H^3, $^3J_{3,2}$ 12.7 Hz), 3.89 (dd, 1H, H^{10B}, $^2J_{10B,10A}$ 7.2 , $^3J_{10B,1}$ 4.9 Hz), 3.93 (m, 3H, OCH_2, H^{10A}, OCH_2), 4.0 (m, 1H, OCH_2), 4.12 (m, 1H, OCH_2), 4.58 (d, 1H, H^1, $^3J_{1,10B}$ 4.9 Hz), 5.05 (s, 1H, H^8), 5.12 (m, 1H, OCH). ^{13}C NMR ($CDCl_3$) δ: 21.93 (CH_3), 21.96 (CH_3), 27.56 (CH_3), 37.72 (C^6), 39.49 (C^5), 45.73 (C^2), 53.36 (C^3), 64.34 (OCH_2), 66.53 (OCH_2), 68.40 (OCH), 69.26 (C^{10}), 72.62 (C^1), 80.32 (C^4), 100.03 (C^8), 105.75 (C^7), 172.90 (C=O). Found, %: C 58.47, H 7.30 $C_{16}H_{24}O_7$. Calculated, %: C 58.52, H 7.37.

Compound **7b**, colorless oil. $[\alpha]_D^{20}$ -100.8° (*c* 0.4, CH_2Cl_2), R_f 0.34 (EtOAc– petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$) δ: 1.22 (t, 6H, CH_3, *J* 14.5, *J* 8.3, *J* 6.2 Hz), 2.14 (s, 3H, CH_3), 2.31-2.48 (m, 3H, H^4, $H^{1''B}$, H^{2B}), 2.52 (dd,1H, $H^{1''A}$, $^2J_{1''A,1''B}$ 17.1, $^3J_{1''A,3'}$ 5.5 Hz), 2.65 (dd, 1H, H^{2A}, $^2J_{2A,2B}$ 16.7, $^3J_{2A,4'}$ 9.2 Hz), 2.90 (dt, 1H, $H^{3'}$, $^2J_{3',1''B}$ 8.7, $^3J_{3',1''A}$ 5.5, $^3J_{3',4'}$ 5.5 Hz), 3.75 (dd, 1H, $H^{6'B}$, $^2J_{6'B,6'A}$ 7.6, $^3J_{6'B,5'}$ 5.4 Hz), 3.84 (m, 2H, OCH_2), 3.89 (m, 1H, OCH_2), 3.99 (d, 1H, $H^{6'A}$, $^2J_{6'A,6'B}$ 7.6 Hz), 4.09 (m, 1H, OCH_2), 4.52 (dd, 1H, $H^{5'}$, $^3J_{5',6'B}$ 5.4, $^3J_{5',4'}$ 1.3 Hz), 4.99 (m, 1H, OCH), 5.02 (s, 1H, $H^{1'}$). ^{13}C NMR ($CDCl_3$) δ: 21.81(CH_3), 21.84 (CH_3), 26.68 (CH_3), 31.50 (C^2), 33.68 ($C^{3'}$), 37.29 ($C^{4'}$), 38.96 ($C^{1''}$), 64.56 (OCH_2), 66.35 (OCH_2), 67.70 ($C^{6'}$), 67.95 (OCH) 75.78 ($C^{5'}$), 99.82 ($C^{1'}$), 106.10 ($C^{2'}$), 172.51 (C=O), 206.71 (C=O). Found, %: C 58.49, H 7.29 $C_{16}H_{24}O_7$. Calculated, %: C 58.52, H 7.37.



(1*S*,2*R*,6*R*,8*R*)-4*H*-Spiro[9,11-dioxatricyclo[6.2.1.0^{2,6}]undecane-7,2'-[1,3]dioxolan]-4-one (8). To a solution of ester **7a** (0.11 g, 0.38 mmol) in THF (5 ml) under argon was added sodium hydride (0.04 g, 1.52 mmol), and the mixture was refluxed until the initial compound

disappeared (TLC monitoring). The reaction mixture was treated with saturated aqueous solution of NH_4Cl, the reaction products were extracted with EtOAc (2×4.0 ml). The combined extracts were dried with $MgSO_4$, evaporated, the residue was chromatographed on silica gel. Yield: **8** 0.03 g (36%), white crystals, mp. 125°C. $[\alpha]_D^{20}$ +17° (*c* 0.26, CH_2Cl_2), R_f 0.2 (EtOAc–petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$) δ: 2.12 (dd, 1H, H^{5B}, $^2J_{5B,5A}$ 18.3, $^3J_{5B,6}$ 8.2 Hz), 2.24 (m, 2H, H^{3B}, H^{5A}), 2.42 (m, 1H, H^2), 2.67 (ddd, 1H, H^{3A}, $^2J_{3A,3B}$ 18.1, $^3J_{3A,2}$ 12.2, $^4J_{3A,5A}$ 1.0 Hz), 2.84 (dd, 1H, H^6, $^3J_{6,2}$ 8.0, $^3J_{6,5B}$ 8.0 Hz), 3.85 (m,1H, OCH_2), 3.88 (m, 2H, H^{10A}, OCH_2), 3.98 (m, 1H, H^{10B}), 4.01 (m, 1H, OCH_2), 4.05 (m, 1H, OCH_2), 4.32 (d, 1H, H^1, $^3J_{1,10B}$ 4.7 Hz), 5.04 (s, 1H, H^8). ^{13}C NMR ($CDCl_3$) δ: 36.86 (C^6), 37.98 (C^3), 39.61 (C^5), 40.48 (C^2), 64.67 (OCH_2), 66.61 (OCH_2), 68.60 (C^{10}), 73.08 (C^1), 99.55 (C^8), 105.59 (C^7), 216.97 (C=O). Found, %: C 58.27, H 6.15 $C_{11}H_{14}O_5$. Calculated, %: C 58.35, H 6.19.



3 **9**, 51 %

Methyl (1*S*,2*R*,3*S*,4*S*,6*S*,8*R*)-4-hydroxy-4-methyl-9,11-dioxatricyclo[6.2.1.0^{2,6}]-undecane-3-carboxylate (10) was obtained similarly to compounds **6a** and **7a** from epoxide **3** (0.06 g, 0.3 mmol). Yield 0.04 g (51%), colourless oily substance, $[\alpha]_D^{20}$ -62° (*c* 0.9, $CHCl_3$), R_f 0.5 (EtOAc– petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$) δ: 1.35 (ddd, 1H, H^{7B}, $^2J_{7B,7A}$ 14.0, $^3J_{7B,6}$ 10.3, $^3J_{7B,8}$ 1.4 Hz), 1.46 (s, 3H, CH_3), 1.48 (dd, 1H, H^{5B}, $^2J_{5B,5A}$ 14.4, $^3J_{5B,6}$ 2.8 Hz), 1.88 (ddd, 1H, H^{7A}, $^2J_{7A,7B}$ 14.0, $^3J_{7A,6}$ 7.9, $^3J_{7A,8}$ 1.4 Hz), 2.14 (dd, 1H, H^{5A}, $^2J_{5A,5B}$ 14.4, $^3J_{5A,6}$ 8.0 Hz), 2.51 (dd, 1H, H^2, $^3J_{2,3}$ 12.2, $^3J_{2,6}$ 7.6 Hz), 2.55 (m, 1H, H^6), 2.67 (d, 1H, H^3, $^3J_{3,2}$ 12.2 Hz), 3.77 (s, 3H, OCH_3), 3.84 (dd, 1H, H^{10B}, $^2J_{10B,10A}$ 7.1 , $^3J_{10B,1}$ 5.3 Hz), 3.92 (d, 1H, H^{10A}, $^2J_{10A,10B}$ 7.1 Hz), 4.55 (д, 1H, H^1, $^3J_{1,10B}$ 5.3 Hz), 5.46 (t, 1H, H^8, $^3J_{8,7A}$ 1.4, $^3J_{8,7B}$ 1.4). ^{13}C NMR ($CDCl_3$) δ: 27.92 (C^6), 29.12 (CH_3), 37.32 (C^7), 45.29 (C^2), 47.52 (C^5), 51.60 (OCH_3), 53.72 (C^3), 69.36 (C^{10}), 73.39 (C^1), 80.36 (C^4), 100.37 (C^8), 173.96 (C=O). Found, %: C 59.37, H 7.39 $C_{12}H_{18}O_5$. Calculated, %: C 59.44, H 7.43.