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Reactions of β-Pinene Epoxide with Some Amines under the Action of the Microwave Radiation

S. S. LAEV, V. V. FOMENKO, N. I. KOMAROVA, D. V. KORCHAGINA and N. F. SALAKHUTDINOV

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 9, Novosibirsk 630090 (Russia)

E-mail: anvar@nioch.nsc.ru

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Abstract

Interaction of β-pinene epoxide with some amines (butylamine, diethylamine, piperidine, morpholine) under the action of the microwave radiation was studied. It was established that in all the cases opening of the epoxide cycle occurs, and mainly the pair of isomeric aminoalcohols is formed – 2-(aminomethyl)-6,6-dimethyl-bicyclo[3.1.1]heptane-2-ols. In all the experiments, one of the isomers was isolated and characterized by means of column chromatography; in the case of piperidine both isomers were isolated. In the experiment with butylamine, 1-*para*-menthene-7,8-diol was isolated from the reaction mixture, and in the case of diethylamine the amino alcohol of menthane structure was isolated.

Key words: β-pinene epoxide, amines, amino alcohols, chromatography

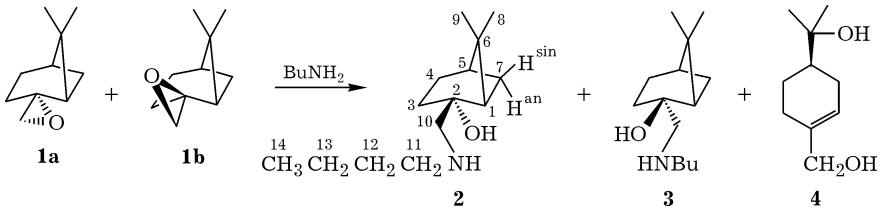
INTRODUCTION

The interaction of amines with epoxides is well studied and important because it is one of the most convenient methods to synthesize vicinal amino alcohols used as construction blocks in designing the molecules of natural and biologically active compounds [1–11]. The promising character of studies in the area of synthesis of amino derivatives of terpene series is due to their valuable practical properties, in particular antiviral, antifidant, pesticide activity accompanied by low toxicity for warm-blooded organisms [6]. However, the interaction of β-pinene epoxide **1** with amines has been studied by present only for the example of reaction with diethyanolamine [12]. This may be due to the structural features and the elevated tendency to opening the epoxide cycle of compound **1**. In this connection, it seems interesting to carry out the interaction of β-pinene epoxide with some amines to establish the regularities of the reaction and outcome to new promising compounds.

The interaction of an epoxide with an amine is usually carried out at elevated temperature in the presence of water [1–3, 5–11]. Nevertheless, carrying out the reaction of compound **1** with piperidine at 120–150 °C in the pre sence of water and without using water we obtained rather complicated mixtures of products with low content of amino alcohol (less than 40 %). The formation of amino alcohols through the interaction of some epoxides with aqueous ammonia under the microwave activation was described in [13]. Because of this, we studied the interaction of compound I with some amines (butylamine, diethylamine, piperidine, morpholine) under activation in the home microwave oven.

RESULTS AND DISCUSSION

Results of the analysis of the reaction mixture by means of gas chromatography/mass spectrometry (GC-MS)provide evidence that the interaction of β-pinene epoxide **1** with butylamine (Scheme 1) under the microwave acti-



Scheme 1.

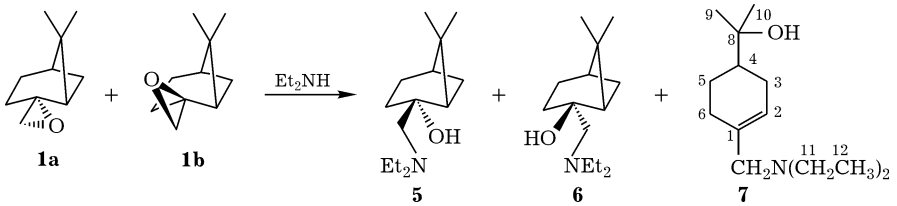
vation leads predominantly to the formation of a mixture of isomeric amino alcohols (2-{[butylamino]-methyl}-6,6-dimethyl-bicyclo[3.1.1.]-heptane-2-ols) **2** and **3** in the total amount of 56 % (according to the GC-MS data), 1-*para*-menthene-7,8-diol **4** that is present in minor amount (9 %), and a small amount (~6 %) of the products of transformation of compound **1** (nopynone, perillic alcohol, *cis*- and *trans*-myrtanal).

The reaction mixture also contains unreacted initial compound (13 %). The formation of product **4** has unexpected character because it is known to be formed mainly in the interaction of compound **1** with water in the presence of a weakly acidic catalyst [14]. In our case the reaction is carried out in the basic medium. The reaction may apparently proceed further on at the N–H group of compounds **2** and **3** because, according to the GC-MS data, the mixture contains the product with mass 357 (up to 10 %) corresponding to the addition of two epoxide molecules to the amine. It was established that the content of this product increases with an increase in the time of activation. Compounds **2** and **4** were isolated in the individual form by means of column chromatography on silica gel; the yield was 19 and 6 %, respectively (calculated for the charged epoxide). The structure of compound **2** was completely confirmed by the data of ^{1}H and ^{13}C NMR spectra. Compound **3** was obtained in mixture with compound **2** and characterized on the basis of some signals in ^{1}H and ^{13}C NMR spectra; its mass spectrum is almost identical with the mass spectrum of compound **2**; the molecular mass (225) of the obtained substance corresponds to compound **3**, retention time is comparable with the retention time for compound **2**.

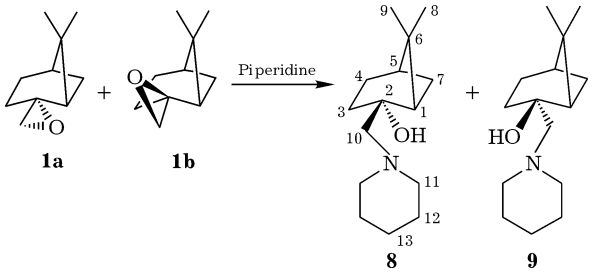
In the reaction of compound **1** with diethylamine (Scheme 2) also a mixture of isomeric amino alcohols is formed: (2-{[bis-(ethyl)-amino]-methyl}-6,6-dimethyl-bicyclo[3.1.1]heptane-3-ols) **5** and **6** in the total amount of about 50 %, 1-*para*-menthene-7-(diethylamino)-8-ol **7** (8 %), as well as the products of isomerization of compound **1** (~14 %).

In this case, the interaction proceeds somewhat slower than in the case of butylamine. This is evidenced by the fact that the concentration of unreacted initial compound in the reaction mixture turned out to be higher (25 %). Compounds **5** and **7** were isolated in the individual form with the yield of 20 and 5 %, respectively (calculated for the charged epoxide). Compound **6** was obtained in mixture with compound **5** and characterized on the basis of some signals in the ^{1}H and ^{13}C NMR spectra, its mass spectrum is almost identical with the mass spectrum of compound **5**, the molecular mass (225) of the compound corresponds to that of compound **6**, while retention time is close to the retention time for compound **5**.

In the reaction of compound **1** with piperidine (Scheme 3), a mixture of isomeric amino alcohols is formed: (2-{piperidinylmethyl}-6,6-dimethyl-bicyclo[3.1.1]heptane-2-ols **8**, **9** with the total content of ~80 %, the products of isomerization of compound **1** (~6 %), as well as



Scheme 2.



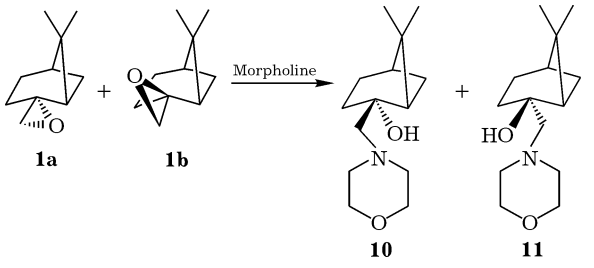
Scheme 3.

the product (9 %)the mass of which is smaller by 18 units than the mass of amino alcohols. This compound seems to be the product of dehydration of the formed amino acids **8** and **9**.

In this case, the interaction proceeds faster in comparison with the case of aliphatic amines, which is evidenced by the presence of unreacted initial compound (~1 %). Using two different versions of column chromatography, compounds **8** and **9** were isolated in the individual form with the yield of 25 and 12 %, respectively (calculated for the charged epoxide). We failed to isolate the product with the mass of 219 (the product of dehydration of the formed amino alcohols **8** and **9**). This failure may be due to the irreversible sorption of the product on the column.

In the reaction of compound **1** with morpholine (Scheme 4), also mainly the mixture of isomeric amino alcohols is formed: (2-{morpholinylmethyl}-6,6-dimethyl-bicyclo[[3.1.1]-heptane-2-oles) **10**, **11** in the total amount of ~60 %, the products of isomerization of compound **1** (~15 %) and the product (13 %) with the molecular mass smaller by 18 units than the molecular mass of amino alcohols. It is likely to be the product of dehydration of the formed amino alcohols **10** and **11**.

The reaction mixture also contains unreacted initial compound (0.5 %). Using column chromatography, we isolated compound **10** in the



Scheme 4.

individual form with a yield of 19 % (calculated for the charged epoxide). We failed to isolate compound **11** in the individual form, but its presence in the reaction mixture is indicated by the molecular mass (239), the mass spectrum which is almost identical to that of compound **10**, and the position of the peak in GC-MS spectrum corresponding to this compound. It should also be noted that compound **11** is present in chromatographic fractions in mixture with amino alcohol **10**. The product with the mass 221 could not be isolated, too; it seems to be sorbed irreversibly on the column.

So, we studied the interaction of β-pinene epoxide **1** with some amines (butylamine, diethylamine, piperidine, morpholine) under heating in a home microwave oven. In all the cases, opening of the epoxide cycle occurs; predominantly a pair of isomeric amino alcohols is formed – (2-{aminomethyl}-6,6-dimethyl-bicyclo[3.1.1]heptane-2-ols. In all the experiments, one of the isomers was isolated by means of column chromatography and characterized; in the case of piperidine, both isomers were isolated. In general, the results obtained open new possibilities for carrying out amination processes and transformations of the epoxides of natural compounds with good selectivity.

EXPERIMENTAL

In the present work, we used β-pinene epoxide (a mixture of compounds **1a** and **1b** at a ratio of 1 : 4, according to the data of ^{1}H NMR spectroscopy) obtained by the interaction of β-pinene with the aqueous solution of H_2O_2 [15]. Butylamine, ethylamine, piperidine and morpholine were commercial reagents of the ch. reagent grade.

Aminolysis reaction was carried out in a home microwave oven of Techno Co. (rated output power 800 W). A sealed ampoule with β-pinene epoxide **1** (0.23 g, 1.5 mmol), amine (10 mmol) and water (0.54 g, 30 mmol) (the reagent mixture occupied 1/4 of the ampoule volume) was placed in the oven and activated in the mode of 50 % power for 4 h; temperature was not measured; no ballast (vessels with water, aluminium oxide *etc.*) was used. The reac-

tion mixture was taken out of the ampoule; 8 mL of water was added. Extraction with diethyl ether was carried out three times (10 mL each). The organic layer was dried above magnesium sulphate, the solvent was removed. The residue was analyzed by means of gas chromatography/mass spectrometry with the gas chromatograph Hewlett-Packard 5890/II with the quadrupole mass spectrometer (HP MSD 5971) as detector. Quartz column HP-5 was used (copolymer 5 % diphenyl–95 % dimethylsiloxane), it was 30 m long, its inner diameter was 0.25 mm and thickness of the immobile phase film was 0.25 mm. The content of components was determined on the basis of the areas of gas chromatographic peaks without using correcting coefficients. The optical activity of the products was measured using a WXQ4 and Polamat A polarimeters; concentration is indicated in grams per 100 mL of the solvent (chloroform).

From the experiments involving the interaction of compound **1** with butylamine, we obtained a mixture containing (according to the GC-MS data) compound **2** (31 %), compound **3** (25 %), compound **4** (9 %) and initial compound **1** (13 %). By means of chromatography with silica gel (Silosorb-600 grade, particle size 40–100 mm, elutriator: a mixture of methylene chloride and ethanol at a ratio of 100 : 7), we isolated 0.061 g of oil-like compound **2** and 0.015 g of oil-like compound **4** (the yield of the compounds was 18 and 6 %, respectively).

From the experiments involving the interaction of compound **1** with diethylamine, we obtained a mixture containing compound **5** (34 %), compound **6** (17 %), compound **7** (8 %) and initial compound **1** (25 %). By means of chromatography with silica gel (Silosorb-600 grade, particle size 40–100 mm, elutriator: a mixture of methylene chloride and acetonitrile at a ratio of 10 : 1), we isolated 0.067 g of oil-like compound **5** and 0.017 g of oil-like compound **7** (the yield of the compounds was 20 and 5 %, respectively).

From the experiments involving the interaction of compound **1** with piperidine, we obtained a mixture containing compound **8** (57 %), compound **9** (24 %). By means of chromatography with silica gel (elutriator: a mixture of methylene chloride and ethanol at a ratio of 100 : 7), we isolated 0.039 g of oil-like compound **8**. By means of chromatography with silica gel (Silosorb-600 grade, particle size 40–100 mm, elutriator: a mixture of methanol and water at a ratio of 1 : 1), we isolated 0.044 g (yield 12 %) of oil-like compound **9**.

From the experiments involving the interaction of compound **1** with morpholine, we obtained a mixture containing compound **10** (33 %), compound **11** (29 %) and initial compound **1** (6 %). By means of chromatography with silica gel (Silosorb-600 grade, particle size 40–100 mm, elutriator: a mixture of hexane and diethyl ether at a ratio of 3 : 2), we isolated 0.068 g of oil-like compound **10** (yield 19 %).

The ^{1}H and ^{13}C NMR spectra of the synthesized compounds were recorded with spectrometers AM-400 (working frequencies 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C) and Bruker AV-300 (300.13 and 100.61 MHz, respectively) for solutions in the mixture of CCl_4–$CDCl_3$ (1 : 1 by volume) or in $CDCl_3$. The signals of chloroform (δ_H 7.24, δ_C 76.90) were used as the internal standard. The structure of compounds was established on the basis of the data of analysis of ^{1}H NMR spectra, the spectra of ^{1}H–^{1}H double resonance, as well as ^{13}C spectra using the standard procedures to record spectra in the mode of J-moludation (JMOD), with the off-resonance suppression of protons, two-dimensional ^{13}C–^{1}H correlation spectra on direct constants (CH–COSY, $^{1}J_{C,H}$ 135 Hz) and one-dimensional ^{13}C–^{1}H correlation spectra on far-field constants ($^{2,3}J_{C,H}$ 10 Hz). Atom numbering in compounds shown in Schemes 1–3 corresponds to atom numbering in the NMR spectra. High-resolution mass spectra were recorded with Thermo Scientific DFS (Double Focusing Sector Mass Spectrometer).

Compound **2**. NMR ^{1}H spectrum, δ, ppm: 0.88 t ($C^{14}H_3$, $J_{14,13}$ 7 Hz), 1.00 d (H^{7an}, $J_{7an,7sin}$ 10 Hz), 1.08 s ($C^{9}H_3$), 1.19 s ($C^{8}H_3$), 1.24–1.37 m ($2H^{13}$), 1.39–1.54 m (H^{5}, $2H^{12}$), 1.65–2.02 m (H^{1}, $2H^{3}$, $2H^{4}$), 2.14 dddd (H^{7sin}, $J_{7sin,7an}$ 10, $J_{7sin,1}$ 6, $J_{7sin,5}$ 6, $J_{7sin,4sin}$ 2 Hz), 2.42 d (H^{10}, $J_{10,10'}$ 12 Hz), 2.62 m ($2H^{11}$), 2.68 d ($H^{10'}$, $J_{10',10}$ 12 Hz). NMR ^{13}C spectrum, δ, ppm: 49.42 d (C^{1}), 75.37 s (C^{2}), 29.22 t (C^{3}), 24.00 t (C^{4}), 40.76 d (C^{5}), 38.32 s (C^{6}), 26.96 t (C^{7}), 27.43 q (C^{8}), 23.36 q (C^{9}), 58.80 t (C^{10}), 49.75 t (C^{11}), 31.17 t (C^{12}), 20.12 t (C^{13}),

13.77 q (C^{14}). NMR spectrum, *m/z* (I_{rel}, %): 225 (1) $[M]^+$, 182 (2), 142 (3), 139 (4), 121 (4), 93 (2), 88 (8), 87 (25), 86 (68), 83 (6), 79 (2), 70 (2), 69 (10), 57 (5), 55 (7), 44 (100), 43 (10), 41 (13), 30 (17). Retention time in the GC-MS spectrum 29.6 min. Found: $[M-H_2O]^+$ 207.2000, $C_{14}H_{25}N$. Calculated: $[M-H_2O]^+$ 207.1980. $[\alpha_D^{23.2}] = -6.7$ (s 0.21).

Compound **3**. Spectrum was recorded for the mixture with compound **2** at a ratio of 2 : 3. NMR ^{1}H spectrum, δ, ppm: 0.89 t ($C^{14}H_3$, $J_{14,13}$ 7 Hz), 0.91 s (C^9H_3), 1.21 s (C^8H_3),1.52 d (H^{7an}, $J_{7an,7sin}$ 10 Hz), 2.58 d (H^{10}, $J_{10,10'}$ 12 Hz), 2.60 m ($2H^{11}$), 2.74 d ($H^{10'}$, $J_{10',10}$ 12 Hz). NMR ^{13}C spectrum δ, ppm: 74.61 s (C^2), 30.72 t (C^3), 24.71 t (C^4), 40.76 d (C^5), 38.02 s (C^6), 27.01 t (C^7), 27.40 q (C^8), 23.46 q (C^9), 50.20 t (C^{11}), 30.95 t (C^{12}). The signals of other protons and carbon atoms in the spectra are superimposed with the signals from compound **2**. Mass spectrum, *m/z* (I_{rel}, %): 225 (1) $[M]^+$, 182 (2), 142 (5), 139 (3), 121 (3), 93 (2), 88 (6), 87 (18), 86 (59), 83 (5), 79 (2), 70 (2), 69 (9), 57 (5), 55 (7), 44 (100), 43 (10), 41 (12), 30 (19). Retention time in the GC-MS spectrum 29.7 min.

Compound **4**. NMR ^{1}H, δ, ppm: 1.17 s and 1.19 s (C^9H_3, $C^{10}H_3$), 1.25 d.d.d.d (H^{5a}, $J_{5a,5e}$ 12, $J_{5a,6a}$ 12, $J_{5a,4a}$ 11, $J_{5a,6e}$ 5 Hz), 1.52 dddd (H^{4a}, $J_{4a,3a'}$ 12.5, $J_{4a,5a}$ 11, $J_{4a,3e'}$ 5, $J_{4a,5e}$ 2.2 Hz), 1.77–1.99 m ($H^{3a'}$, H^{5e}), 2.01–2.21 m ($H^{3e'}$, $2H^6$), 3.92–4.05 m ($2H^7$), 5.67 m (H^2). NMR ^{13}C spectrum, δ, ppm: 137.42 s (C^1), 122.38 d (C^2), 26.48 t (C^3), 45.03 d (C^4), 23.52 t (C^5), 26.48 t (C^6), 67.08 t (C^7), 72.52 s (C^8), 26.32 q and 27.36 q (C^9, C^{10}). Mass spectrum, *m/z* (I_{rel}, %): 152 (11), 137 (3), 121 (12), 119 (4), 109 (27), 108 (16), 94 (18), 93 (21), 91 (18), 81 (13), 79 (95), 77 (12), 67 (10), 59 (100), 55 (11), 53 (8), 43 (64), 41 (24), 39 (13), 31 (21). $[\alpha_D^{23.2}] = -64$ (s 0.25).

Compound **5**. NMR ^{1}H, δ, ppm: 0.97 t ($2C^{12}H_3$, $J_{12,11}$ 7 Hz), 1.00 d (H^{7an}, $J_{7an,7sin}$ 10 Hz), 1.08 s (C^9H_3), 1.19 s (C^8H_3), 2.11 d.d.d.d (H^{7sin}, $J_{7sin,7an}$ 10, $J_{7sin,1}$ 6, $J_{7sin,5}$ 6, $J_{7sin,4sin}$ 2Hz), 2.24 d (H^{10}, $J_{10,10'}$ 13 Hz), 2.52 d ($H^{10'}$, $J_{10',10}$ 13 Hz), 2.53 q ($2C^{11}H_2$, $J_{11,12}$ 7 Hz), 3.90 brs (OH). The signals of other protons are observed as overlapping multiplets in the region 1.57–2.02 ppm. NMR ^{13}C spectrum, δ, ppm: 50.86 d (C^1), 74.82 s (C^2), 29.92 t (C^3), 24.26 t (C^4), 40.53 d (C^5), 38.11 s (C^6), 26.57 t (C^7), 27.55 q (C^8), 23.33 q (C^9), 64.44 t (C^{10}), 48.79 t ($2C^{11}$), 12.13 q ($2C^{12}$). Mass spectrum, *m/z*: (I_{rel}, %): 225 (1) $[M]^+$, 142 (3), 114 (1), 87 (9), 86 (100), 72 (10), 58 (7), 41 (2), 30 (3). Retention time in the GC-MS spectrum 25.9 min. Found: $[M-H_2O]^+$ 207.2147, $C_{14}H_{25}N$. Calculated: $[M-H_2O]^+$ 207.1980. $[\alpha_D^{27.4}] = -60$ (s 0.10).

Compound **6**. Spectrum was recorded for the mixture with compound **5** at a ratio of 5 : 6. NMR ^{1}H, δ, ppm: 0.92 s (C^9H_3), 0.98 t ($2C^{12}H_3$, $J_{12,11}$ 7 Hz), 1.20 s (C^8H_3), 1.53 d (H^{7an}, $J_{7an,7sin}$ 10 Hz), 2.36 d (H^{10}, $J_{10,10'}$ 13 Hz), 2.55 q ($2C^{11}H_2$, $J_{11,12}$ 7 Hz), 2.58 d ($H^{10'}$, $J_{10',10}$ 13 Hz). Signals of other protons are superimposed with the signals of compound **5**. NMR ^{13}C spectrum, δ, ppm: 51.88 d (C^1), 73.98 s (C^2), 30.28 t (C^3), 25.05 t (C^4), 40.71 d (C^5), 37.98 s (C^6), 27.23 t (C^7), 27.36 q (C^8), 23.72 q (C^9), 64.63 t (C^{10}), 48.74 t ($2C^{11}$), 12.02 q ($2C^{12}$). Mass spectrum, *m/z*: (I_{rel}, %): 225 (1) $[M]^+$, 142 (10), 114 (2), 87 (9), 86 (100), 72 (11), 58 (3), 41 (2), 30 (2). Retention time in the GC-MS spectrum 26.2 min.

Compound **7**. NMR ^{1}H, δ, ppm: 1.17 s и 1.18 s (C^9H_3, $C^{10}H_3$), 1.18 t ($2C^{12}H_3$, $J_{12,11}$ 7 Hz), 1.26 m (H^{5a}), 1.52 d.d.d.d (H^{4a}, $J_{4a,3a'}$ 13, $J_{4a,5a}$ 11, $J_{4a,3e'}$ 5, $J_{4a,5e}$ 2.2 Hz), 1.84 m ($H^{3a'}$), 1.94 m (H^{5e}), 2.00–2.20 m ($H^{3e'}$, $2H^6$), 3.45 q ($2C^{11}H_2$, $J_{11,12}$ 7 Hz), 3.91–4.05 m ($2H^7$), 5.67 m (H^2). NMR ^{13}C spectrum, δ, ppm: 137.38 s (C^1), 122.34 d (C^2), 26.45 t (C^3), 44.99 d (C^4), 23.48 t (C^5), 26.45 t (C^6), 67.02 t (C^7), 72.54 s (C^8), 26.26 q and 27.29 k (C^9, C^{10}), 65.73 t ($2C^{11}$), 15.14 q ($2C^{12}$). Mass spectrum, *m/z*: (I_{rel}, %): 152 (8), 137 (3), 121 (10), 119 (3), 109 (22), 108 (13), 94 (16), 93 (19), 91 (18), 81 (9), 79 (85), 77 (11), 67 (11), 59 (100), 55 (10), 53 (8), 43 (58), 41 (25), 39 (12), 31 (19). Found: $[M-H_2O]^+$ 207.1471, $C_{14}H_{25}N$. Calculated: $[M-H_2O]^+$ 207.1980. $[\alpha_D^{22.5}] = -173.3$ (s 0.45).

Compound **8**. NMR ^{1}H, δ, ppm: 0.97 d (H^{7an}, $J_{7an,7sin}$ 10 Hz), 1.07 s (C^9H_3), 1.19 s (C^8H_3), 2.10 dddd (H^{7sin}, $J_{7sin,7an}$ 10, $J_{7sin,1}$ 6, $J_{7sin,5}$ 6, $J_{7sin,4sin}$ 2 Hz), 2.16 d (H^{10}, $J_{10,10'}$ 13 Hz), 2.42 d ($H^{10'}$, $J_{10',10}$ 13 Hz), 2.42–2.58 m ($4H^{11}$). Signals of other protons are observed as overlapping multiplets in the region 1.35–2.00 ppm. NMR ^{13}C spectrum, δ, ppm: 50.78 d (C^1), 75.36 s (C^2), 29.94 t (C^3), 24.35 t (C^4), 40.75 d (C^5), 38.37 s (C^6), 26.77 t (C^7), 27.76 q (C^8), 23.52 q (C^9), 68.87 t (C^{10}), 56.92 t ($2C^{11}$), 26.32 t ($2C^{12}$), 23.92 t (C^{13}). Mass spectrum, *m/z*: (I_{rel}, %): 237

(1) $[M]^+$, 154 (2), 99 (13), 98 (100), 84 (3), 83 (1), 70 (3), 69 (2), 56 (2), 55 (6), 53 (1), 43 (3), 42 (6), 41 (10), 39 (2),30 (2). $[\alpha_D^{22.6}] = +2.0$ (s 0.40). Found: C 75.52, H 10.80, N 5.52. $C_{15}H_{27}NO$. Calculated: C 75.90, H 11.46, N 5.90.

Compound **9**. NMR ^{1}H, δ, ppm: 0.89 s (C^9H_3), 1.19 s (C^8H_3), 1.38 m ($2H^{13}$), 1.52 d (H^{7an}, $J_{7an,7sin}$ 10 Hz), 1.51–1.58 m ($4H^{12}$), 1.59–1.89 m ($2H^3$, $2H^4$, H^5), 1.91 m (H^1), 2.14 ddd (H^{7sin}, $J_{7sin,7an}$ 10, $J_{7sin,1}$ 6, $J_{7sin,5}$ 6 Hz), 2.30 d (H^{10}, $J_{10,10'}$ 13 Hz), 2.52 d ($H^{10'}$, $J_{10',10}$ 13 Hz), 2.46–2.58 m ($4H^{11}$). NMR ^{13}C spectrum, δ, ppm: 51.50 d (C^1), 74.43 s (C^2), 30.03 t (C^3), 24.94 t (C^4), 40.63 d (C^5), 37.96 s (C^6), 27.11 t (C^7), 27.33 q (C^8), 23.72 q (C^9), 68.96 t (C^{10}), 56.74 t ($2C^{11}$), 26.16 t ($2C^{12}$), 23.72 t (C^{13}). Mass spectrum, m/z: (I_{rel}, %): 237 (1) $[M]^+$, 154 (3), 99 (11), 98 (100), 84 (6), 83 (2), 70 (4), 69 (3), 56 (3), 55 (5), 53 (3), 43 (4), 42 (6), 41 (13), 39 (3),30 (2). $[\alpha_D^{22.6}] = -37.3$ (s 0.15). Found: $[M]^+$ 237.2093, $C_{15}H_{27}NO$. Calculated: M 237.2095.

Compound **10**. NMR ^{1}H, δ, ppm: 0.99 d (H^{7an}, $J_{7an,7sin}$ 10 Hz), 1.08 s (C^9H_3), 1.19 s (C^8H_3), 1.60–1.80 m ($2H^3$, H^{4an}), 1.85 dd (H^1, $J_{1,5}$ 6, $J_{1,7sin}$ 6 Hz), 1.89 m (H^5), 1.95 ddddd (H^{4sin}, $J_{4sin,4an}$ 12.5, $J_{4sin,3an}$ 7, $J_{4sin,3sin} = J_{4sin,5} = J_{4sin,7sin}$ 2 Hz), 2.12 dddd (H^{7sin}, $J_{7sin,7sin}$ 10, $J_{7sin,1}$ 6, $J_{7sin,5}$ 6, $J_{7sin,4sin}$ 2 Hz), 2.22 d (H^{10}, $J_{10,10'}$ 13 Hz), 2.48 d ($H^{10'}$, $J_{10',10}$ 13 Hz), 2.50–2.61 m ($4H^{11}$), 3.66 t ($4H^{12}$, $J_{12,11}$ 4.5 Hz). NMR ^{13}C spectrum, δ, ppm: 50.65 d (C^1), 75.79 s (C^2), 29.67 t (C^3), 24.11 t (C^4), 40.56 d (C^5), 38.18 s (C^6), 26.66 t (C^7), 27.51 q (C^8), 23.33 q (C^9), 68.63 t (C^{10}), 55.63 t ($2C^{11}$), 67.12 t ($2C^{12}$). Mass spectrum, m/z: (I_{rel}, %): 239 (1) $[M]^+$, 156 (2), 139 (1), 121 (1), 102 (3), 101 (38), 100 (100), 86 (1), 83 (2), 71 (7), 70 (3), 69 (3), 67 (1), 57 (1), 56 (7), 55 (4), 43 (6), 42 (3), 41 (5), 30 (1). Retention time in GC-MS spectrum 32.6 min. Found: $[M]^+$ 239.1885, $C_{14}H_{25}NO_2$. Calculated: M 239.1886.

Compound **11**. Mass spectrum, m/z (I_{rel}, %): 239 (1) $[M]^+$, 170 (8), 139 (1), 121 (1), 102 (2), 101 (21), 100 (100), 86 (3), 83 (1), 71 (7), 70 (2), 67 (4), 57 (2), 56 (5), 55 (2), 43 (8), 42 (3), 41 (3), 30 (1). Retention time in GC-MS spectrum 33.0 min.

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