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TETRAHEDRON: *ASYMMETRY*

# Stereochemistry of terpene derivatives. Part 2:[1] Synthesis of new chiral amino acids with potential neuroactivity

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**Abstract**

The syntheses and stereochemistry of two new amino acids obtained from the monoterpene ketones (–)-*cis*-caran-*trans*-4-one and (–)-menthone via appropriate lactams are presented. The configuration of all stereogenic centers is confirmed by X-ray crystallography. 

## 1. Introduction

Terpenes are known as useful chiral synthons in syntheses of a variety of optically active compounds displaying interesting biological properties such as local anesthetics[2,3] or anti-arrythmics and cardiodepressive compounds,[4,5] insect growth regulators[6,7] or pyrethroids.[8,9]

In this paper we present the possibility of using terpene substrates as synthons for the preparation of ten-carbon amino acids with predetermined stereogenic centers. These compounds might be considered as structural analogues of GABA and thus are expected to be of interest as potential inhibitors of GABA neuroreceptors.

The starting materials used in these syntheses were two naturally occurring terpenes: (+)-3-carene—a bicyclic hydrocarbon (a popular component of gum turpentine)—and the monocyclic alcohol (–)-menthol.

## 2. Results and discussion

(–)-c*is*-Caran-4-one **1**, readily available from (+)-3-carene by a two step pathway (stereoselective borohydration–oxidation[10] followed by the Brown–Garg oxidation[11] of crystalline (–)-*cis*-caran-*trans*-4-ol) was used as starting material. Reaction of **1** with hydroxylamine hydrochloride

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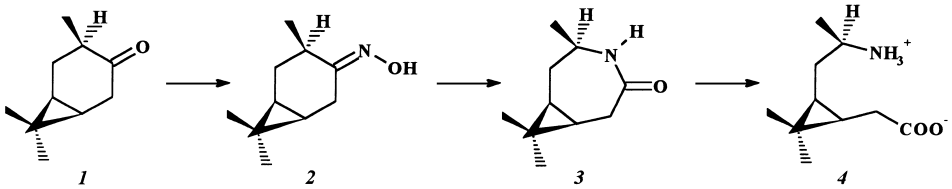
afforded the known (–)-*cis*-caran-4-one oxime **2** in good yield (76%, Scheme 1), which was then subjected to a Beckmann rearrangement in tetrahydrofuran–water solution with tosyl chloride as the inducing agent, resulting in lactam **3**.[12] The lactam **3** was then hydrolyzed under basic conditions at elevated temperatures (100°C) yielding (1*R*,2*S*,2′*R*)-(+)-2-(2-amino-1-propyl)-3,3-dimethylcycloprop-1-ylacetic acid **4**.[13]




Scheme 1.

The absolute configuration of the stereogenic center at C-7† was determined from the X-ray structures of both lactam **3** and amino acid **4** in relation to the known chirality of C-3 and C-5 positions in the starting material (Fig. 1).

Analogously, the reaction outlined in Scheme 2 afforded lactam **7**,[15] which upon hydrolysis in alkaline conditions at 170°C gave (3*R*,6*S*)-(–)-6-amino-3,7-dimethyloctanoic acid (amino acid **8**).[16]

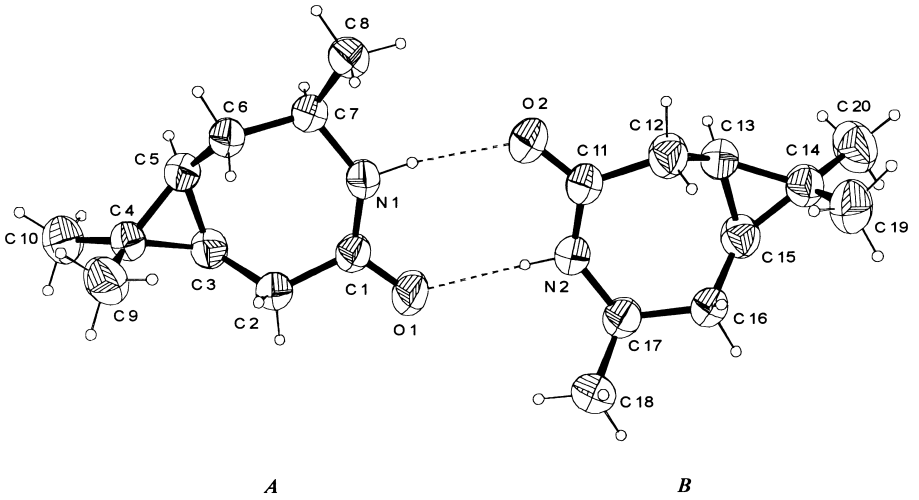
The absolute configuration at the C-6 center of this amino acid **8** was also determined by means of X-ray crystallographic studies in relation to the known chirality of the C-3 position in the starting (–)-menthol **5** (Fig. 2).

The structures of amino acids **4** and **8** indicated that the amino acid molecules appear as zwitterions. In all the crystals studied a network of medium and weak intermolecular N–H···O hydrogen bonds occurs. They are listed in Tables 1–3 for compounds **4**, **8** and **3**, respectively. Interestingly, in the case of lactam **3** molecular dimers are formed due to the existence of these hydrogen bonds (Fig. 1). Two molecules (**A** and **B**) form the asymmetric unit of the crystal cell and they differ slightly from each other in the conformation of seven-membered rings. The torsion angle C(2)–C(3)–C(5)–C(6) in the molecule **A** corresponds to the C(12)–C(13)–C(15)–C(16) angle in the molecule **B** with values of 4.8° and 0.0°, respectively. Moreover the ring of molecule **B** is more flattened in comparison with the ring of molecule **A**, especially within the C(12)–C(11)–N(2)–C(17)–C(16) fragment.

NMR spectra of both amino acids **4** and **8** showed strong dependence on pH. However, the examination of coupling constants and application of the Pachler[17] approach indicated that this unusual phenomenon does not result from the change in population of conformers (these molecules appeared to be conformationally flexible independent of pH) but from the change in chemical character of both amino and carboxylic group versus pH.

The results described above identified cyclic chiral lactams, easily available by three-step procedure from popular terpene ketones, as useful synthons for the preparation of new amino acids with six carbon atoms between both functional groups. Moreover, absolute configurations of the stereogenic centers of these amino acids are strictly fixed by the structure of the substrates

† For clarity of presentation the carbon atoms in lactam **3** and amino acid **4** are numbered according to the numbers used in crystallographic data and do not agree with common IUPAC nomenclature. In the Experimental, the names of compounds synthesized are given according to the principal IUPAC rules.

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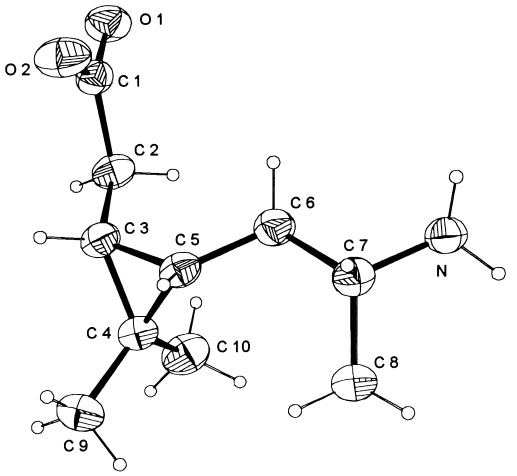
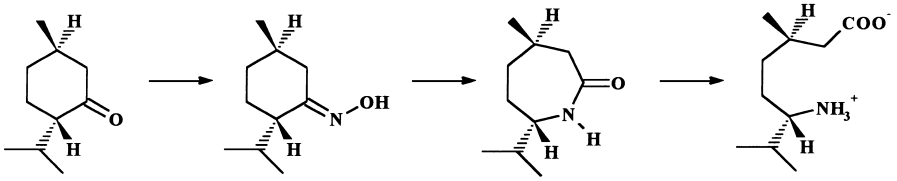
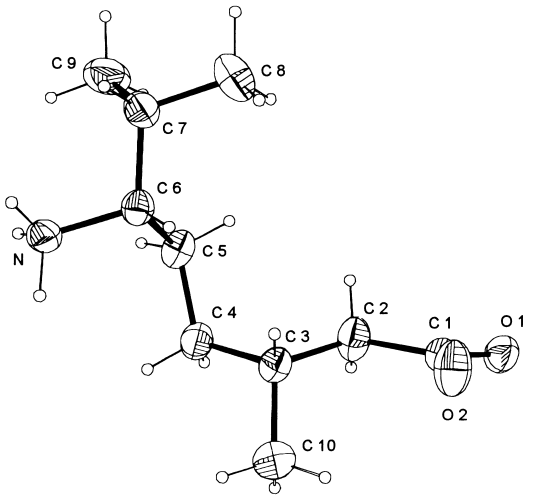



4

Figure 1. ORTEP-III[14] view of molecular structures of lactam **3** and amino acid **4**. Thermal ellipsoids are drawn at the 50% probability level. The H atoms are shown as spheres with a fixed radius




Scheme 2.




*8*

Figure 2. ORTEP-III[14] view of molecular structures of amino acid **8**. Thermal ellipsoids are drawn at the 50% probability level. The H atoms are shown as spheres with a fixed radius

Table 1
Hydrogen-bonds for **4**

| D-H...A | d(D-H) (Å) | d(D...A) (Å) | d(H...A) (Å) | <(DHA) (°) |
|---|---|---|---|---|
| N-HNA...O1(1) | 0.932 | 2.756 | 1.824 | 177.40 |
| N-HNB...O2(2) | 0.914 | 2.768 | 1.895 | 159.17 |
| N-HNB...O1(2) | 0.914 | 3.406 | 2.646 | 141.01 |
| N-HNC...O2(3) | 0.906 | 2.918 | 2.038 | 163.70 |

Symmetry equivalent atoms: (1) x-1, y+1, z; (2) –x+2, y+1/2, -z+1; (3) x-1, y, z.

Table 2
Hydrogen-bonds for **8**

| D-H...A | d(D-H) (Å) | d(D...A) (Å) | d(H...A) (Å) | <(DHA) (°) |
|---|---|---|---|---|
| N-HN1...O1(1) | 0.909 | 2.772 | 1.865 | 176.37 |
| N-HN2...O1(2) | 0.884 | 2.880 | 2.010 | 167.51 |
| N-HN3...O2(3) | 0.989 | 2.796 | 1.811 | 173.46 |
| N-HN3...O1(3) | 0.989 | 3.263 | 2.566 | 127.42 |

Symmetry equivalent atoms: (1) –x+2, y+1/2, -z+1/2; (2) –x+3/2, -y+2, z+1/2; (3) –x+1, y+1/2, -z+1/2.

Table 3
Hydrogen-bonds for **3**

| D-H...A | d(D-H) (Å) | d(D...A) (Å) | d(H...A) (Å) | <(DHA) (°) |
|---|---|---|---|---|
| N1-HN1...O2 | 0.882 | 2.969 | 2.130 | 158.64 |
| N2-HN2...O1 | 0.832 | 2.932 | 2.105 | 172.64 |

used with the Beckmann rearrangement occurring without inversion of configuration at the adjacent carbon atom.[12,15] Preliminary studies on the influence of both acids on behavior of mice indicated their potential usefulness as nootropic compounds (i.e. those which stimulate brain functioning).

## 3. Experimental

The course of all reactions and purities of the products were checked by means of thin-layer chromatography (TLC) and gas chromatography (GC). TLC was carried out on silica gel DC-Alufolien Kieselgel 60 $F_{254}$ (Merck). Chromatograms were developed with mixtures of hexane, acetone and ethyl acetate applied in various ratios and detected with 20% ethanolic $H_2SO_4$ with an admixture of 0.1% of anisaldehyde. Analytical GC was performed on a Hewlett–Packard 5890 (seria II) using capillary column HP-1, length 25 m, temperature 120–280°C. Melting points (uncorrected) were determined on a Boetius apparatus. IR spectra were taken for liquid films or in KBr on a Perkin–Elmer 621 spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded for $CDCl_3$ or $D_2O$ solutions on a Bruker Avance DRX 300 apparatus, with TMS as the internal standard. Optical rotation was measured on an Autopol IV automatic polarimeter (Rudolph) in methanol, concentrations denoted in g/100 ml. Monocrystalline samples of **4** and **8** were grown from ethanol, and single crystals of **3** were obtained from hexane. The X-ray data were collected at room temperature, on the Kuma Diffraction diffractometer (Kuma, Wrocław, Poland) equipped with a CCD camera which was positioned at 46 mm from the crystal. Graphite-monochromatized MoK$\alpha$ radiation was employed. Numbers of frames were: 888 (**3**), 740 (**4**) and 888 (**8**). The frames were measured at 0.5° (**3**, **8**) or 0.6° (**4**) $\omega$ widths with 15 s (**3**), 10 s (**4**) or 20 s (**8**) exposure times. The intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. The data reduction was performed with the Kuma KM4CCD Software. Unit cell parameters were determined by least-squares refinements using reflections in the $2\theta$ ranges: 6.799–44.538°, 6.81–43.774°, 7.563–57.086° for **3**, **4** and **8**, respectively. The structures were solved by direct methods using the SHELXS program and refined on $F^2$ values by full-matrix least squares using the SHELXL program from the SHELXL-97 package[18] with anisotropic displacement parameters for non-hydrogen atoms. Positions of hydrogen atoms were found from $\Delta F$ syntheses or calculated geometrically using the riding model and refined isotropically. Crystallographic data for structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

### 3.1. Substrates

(+)-3-Carene (Institute of Chemical Industry, Warsaw), b.p. 79°C/28 mmHg, $n_D^{20} = 1.4732$, $[\alpha]_D^{20} = +14.7$, was transformed, via crystalline (–)-*cis*-caran-*trans*-4-ol [m.p. 32°C, b.p. 76–79/2 mmHg, $[\alpha]_D^{20} = -63.0$ (c = 10.0, EtOH); lit.[10] b.p. 78°C/2 mmHg, $[\alpha]_D^{20} = -69.5$ (c = 3.3, EtOH)], to the (–)-*cis*-caran-4-one **1** (b.p. 74–76/4.5 mmHg, $n_D^{20} = 1.4680$, $[\alpha]_D^{20} = -135.8$; lit.[19] b.p. 98–99°C/19 mmHg, $n_D^{20} = 1.4703$, $[\alpha]_D^{20} = -133.2$) according to the known procedure.[10,11]

(–)-Menthol (commercially available, Merck), m.p. +43°C, $[\alpha]_D^{20} = -50 \pm 1$ (c = 10.0, EtOH), $n_D^{20} = 1.4600$, b.p. 215°C, was oxidized[11] yielding (–)-menthone **5** [b.p. 207–209°C, $n_D^{20} = 1.4500$, $[\alpha]_D^{20} = -23.0$, lit.[20] b.p. 83–84°C/11 mmHg, $n_D^{20} = 1.4501$, $[\alpha]_D^{20} = -23.0$ (c = 8.7, MeOH)].

### 3.2. General procedure for the preparation of oximes

A mixture of appropriate ketone (0.05 mol), sodium hydrogen carbonate (6.00 g, 0.07 mol) and hydroxylamine hydrochloride (4.48 g, 0.07 mol) in 40 ml methanol and 5 ml distilled water was heated to 65°C for 3 h. After completion of the reaction (as detected by TLC) the mixture was diluted with 50 ml distilled water and then extracted three times with hexane. The extract was washed successively with 5% $NaHCO_3$ and saturated NaCl solutions and dried over $MgSO_4$. After evaporation of solvent the crude product was distilled under reduced pressure. Distillation in vacuo gave 0.04 mol (76%) of appropriate oxime.

#### 3.2.1. (–)-cis-*Caran-4-one oxime* **2**

M.p. 42°C, b.p. 95–102°C/4 mmHg, $[\alpha]_D^{20} = -45.1$ (c = 1.8, MeOH); lit.[12] m.p. 40–43°C, $[\alpha]_D^{20} = -6.8$ (neat); $^{13}$C NMR ($\delta$): 14.57 (q, C-9), 16.03 (q, C-8), 18.25 (s, C-7), 19.14 (d, C-1), 20.05 (t, C-2), 20.33 (d, C-6), 27.95 (q, C-10), 29.23 (t, C-5), 34.32 (d, C-3), 163.09 (s, C-4).

#### 3.2.2. (–)-*Menthone oxime* **6**

M.p. 54–56.5°C, $[\alpha]_D^{20} = -57.0$ (c = 10.0, MeOH); lit.[15] m.p. 57°C, $[\alpha]_D^{20} = -52.8$ (c = 5.7, MeOH).

### 3.3. Beckmann rearangement—general procedure

Oxime (0.02 mol) was added to 2.40 g (0.06 mol) NaOH in 15 ml distilled water and 15 ml THF solution. A mixture was stirred for 8 h with cooling under 10°C. Then 6.50 g of tosyl chloride (0.04 mol) in 5 ml of THF mixture was added dropwise. Reaction mixture was additionally stirred with cooling for 4 h and then for 2 h at 50°C. After evaporation of solvent the mixture was diluted with distilled water and extracted with diethyl ether. Extract was washed with 5% $NaHCO_3$ solution and then with saturated NaCl. Removal of solvent gave crude product which was recrystallized from hexane.

#### 3.3.1. (1S,3R,7R)-(–)-3,8,8-*Trimethyl-4-azabicyclo[5.1.0]octan-5-one* **3**

M.p. 136–140°C, $[\alpha]_D^{20} = -110$ (c = 10.0, MeOH); lit.[12] m.p. 130–131°C, $[\alpha]_D^{20} = -114.7$ (c = 5.0, MeOH). IR (KBr, cm$^{-1}$): 3212 (m), 3076 (w), 2924 (m), 1652 (v s), 1458 (m), 1375 (m), 1328 (s), 844 (m). $^1$H NMR ($CDCl_3$), $\delta$: 0.74–0.95 (m, 2H at C-3 and C-5); 1.03 and 1.08 (2s, 6H, *gem*-Me); 1.17 (d, J = 6.50 Hz, 3H at C-8); 1.36–1.57 (m, 1H at C-6); 1.87–1.98 (m, 1H at C-6); 2.36 (d/d, J = 15.80/9.82 Hz, 1H at C-2); 2.64 (d/d/d, J = 15.80/5.76/1.30 Hz, 1H at C-2); 3.57 (m, 1H at C-7); 6.04 (s, 1H from -NH); $^{13}$C NMR ($\delta$): 12.25 (q, C-10), 16.66 (s, C-4), 19.09 (d, C-5), 21.50 (d, C-3), 21.86 (q, C-9), 25.76 (q, C-8), 27.85 (t, C-6), 30.45 (t, C-2), 48.13 (d, C-7), 172.58 (s, C-1). Elemental analysis: calculated for $C_{10}H_{17}NO$ (167.25): 8.37% N, 71.81% C, 10.24% H. Found: 8.30% N, 71.73% C, 10.31% H. Crystal data: $C_{10}H_{17}NO$, $M_w = 167.25$, $T = 298$K, monoclinic, space group $P2_1$, $a = 6.769(1)$ Å, $b = 8.246(2)$ Å, $c = 17.591(4)$ Å, $\beta = 90.43(3)°$, $V = 981.9(4)$ Å$^3$, $Z = 4$, $D_c = 1.131$ Mg/m$^3$, $\mu = 0.072$ mm$^{-1}$, $F(000) = 368$, crystal size $0.89 \times 0.38 \times 0.18$ mm, diffractometer Kuma KM4CCD, $2\theta \leq 63.8$, 8724 refl. measured, 6032 unique refl., 5112 refl. with $I > 2s(I)$, 226 parameters.

#### 3.3.2. (2S,5R)-(–)-2-*Isopropyl-5-methyl-1-azacycloheptan-7-one* **7**

M.p. 121–122°C, $[\alpha]_D^{20} = -57.0$ (c = 10.0, MeOH); lit.[15] m.p. 118–120°C, $[\alpha]_D^{20} = -56.7$ (c = 5.5, MeOH); IR (KBr, cm$^{-1}$): 3232 (m), 3084 (w), 2952 (s), 2924 (s), 1666 (v s), 1636 (s), 1456 (m),

1374 (m), 774 (m); $^1$H NMR ($CDCl_3$), $\delta$: 0.95 (2d, J = 6.72 Hz, 6H at C-9 and C-10); 1.01 (d, J = 6.64 Hz, 3H at C-11); 1.16–1.47 (m, 2H at C-5 and C-8); 1.67–2.01 (m, 4H at C-3 and C-4); 2.22–2.50 (m, 2H at C-6); 3.12–3.22 (m, 1H at C-2); 5.95 (s, 1H from -NH); $^{13}$C NMR ($\delta$): 15.28 (q, C-8), 15.88 (q, C-9), 21.80 (q, C-10), 27.43 (t, C-4), 29.51 (d, C-3), 29.96 (d, C-7), 36.29 (t, C-5), 41.98 (t, C-2), 56.23 (d, C-6), 174.15 (s, C-1). Elemental analysis: calculated for $C_{10}H_{19}NO$ (169.27): 8.28% N, 70.96% C, 11.31% H. Found: 8.21% N, 70.88% C, 11.39% H.

### 3.4. General procedure for alkaline hydrolysis of lactams

A mixture of 0.02 mol of lactam, 1.71 g (0.04 mol) NaOH, 10 ml distilled water and 25 ml ethanol was heated for 5–10 h. After acidification to neutral pH, solution was filtered off and solvents was evaporated under reduced pressure. The crude product was recrystallized from ethanol.

#### 3.4.1. (1R,2S,2′R)-(+)-2-(2-Amino-1-propyl)-3,3-dimethylcycloprop-1-ylacetic acid **4**

M.p. 225°C, $[\alpha]_D^{20} = +15.0$ (c = 10.0, MeOH); IR (KBr cm$^{-1}$): 3041 (m), 2949 (s) and 2929 (s), 2163 (w), 1623 (m), 1558 (v s), 1458 (m), 1386 (s), 707 (m); $^1$H NMR ($D_2O$), $\delta$: 0.5 (d/d/d, J = 6.88/5.10/6.92 Hz, 1H at C-5); 0.83 (d/d/d, J = 7.30/5.10/8.32 Hz, 1H at C-3); 0.88 and 1.02 (2s, 6H *gem*-Me); 1.27 (d, J = 6.64 Hz, 3H at C-8); 1.44–1.63 (m, 2H at C-6); 2.04 (d/d, J = 16.08/8.34 Hz, 1H at C-2); 2.17 (d/d, J = 16.07/7.00 Hz, 1H at C-2); 3.26–3.38 (m, 1H at C-7); $^{13}$C NMR ($\delta$): 14.25 (q, C-10), 16.63 (s, C-4), 17.62 (q, C-9), 22.02 (d, C-5), 22.56 (d, C-3), 27.80 (q, C-8), 29.08 (t, C-6), 32.46 (t, C-2), 48.61 (d, C-7), 183.03 (s, C-1). Elemental analysis: calculated for $C_{10}H_{19}NO_2$ (185.26): 7.56% N, 64.83% C, 10.34% H. Found: 7.50% N, 64.76% C, 10.41% H. Crystal data: $C_{10}H_{19}NO_2$, $M_w = 185.26$, $T = 298$K, monoclinic, space group $P2_1$, $a = 6.295(1)$ Å, $b = 6.713(1)$ Å, $c = 12.836(3)$ Å, $\beta = 100.20(3)°$, $V = 533.86(17)$ Å$^3$, $Z = 2$, $D_c = 1.153$ Mg/m$^3$, $\mu = 0.079$ mm$^{-1}$, $F(000) = 204$, crystal size 0.90×0.67×0.18 mm, diffractometer Kuma KM4CCD, $2\theta \leq 63.18$, 4585 refl. measured, 3238 unique refl., 3087 refl. with $I > 2\sigma(I)$, 131 parameters.

#### 3.4.2. (3R,6S)-(−)-6–amino-3,7-dimethyloctanoic acid **8**

M.p. 211.5°C, $[\alpha]_D^{20} = -36.0$ (c = 10.0, MeOH); IR (KBr, cm$^{-1}$): 3006 (m), 2943 (s), 2890 (s), 2147 (w), 1623 (s), 1525 (v s), 1418 (m), 1396 (s), 1261 (m), 917 (m), 676 (m); $^1$H NMR ($D_2O$), $\delta$: 0.81 (d, J = 6.63 Hz, 3H at C-10); 0.85 and 0.86 (2d, J = 6.93 Hz, 6H at C-8 and C-9); 1.04–1.19 (m, 1H at C-4); 1.21–1.35 (m, 1H at C-4); 1.35–1.52 (m, 1H at C-5); 1.55–1.70 (m, 1H at C-5); 1.67–1.80 (m, 1H at C-3); 1.80–1.93 (m, 1H at C-7); 1.89 (d/d, J = 13.53/7.83 Hz, 1H at C-2); 2.07 (d/d, J = 13.50/6.81 Hz, 1H at C-2); 2.98 (t/d, J = 9.03/7.92 Hz, 1H at C-6); $^{13}$C NMR ($\delta$): 17.00 (q, C-8), 17.71 (q, C-9), 19. 43 (q, C-10), 27.01 (t, C-4), 29.77 (d, C-3), 31.14 (d, C-7), 32.14 (t, C-5), 45.53 (t, C-2), 57.96 (d, C-6), 183.30 (s, C-1). Elemental analysis: calculated for $C_{10}H_{21}NO_2$ (187.28): 7.48% N, 64.13% C, 11.30% H. Found: 7.42% N, 64.06% C, 11.40% H. Crystal data: $C_{10}H_{21}NO_2$, $M_w = 187.28$, $T = 298$ K, orthorhombic, space group $P2_12_12_1$, $a = 5.719(1)$ Å, $b = 10.923(2)$ Å, $c = 17.389(3)$ Å, $V = 1086.3(3)$ Å$^3$, $Z = 4$, $D_c = 1.145$ Mg/m$^3$, $\mu = 0.078$ mm$^{-1}$, $F(000) = 416$, crystal size 0.59×0.13×0.15 mm, diffractometer Kuma KM4CCD, $2\theta \leq 63.73$, 9332 refl. measured, 4365 unique refl., 3182 refl. with $I > 2\sigma(I)$, 132 parameters.

## Acknowledgements

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