Available online at www.sciencedirect.com
SCIENCE DIRECT
European Journal of Medicinal Chemistry 41 (2006) 586–591
EUROPEAN JOURNAL OF MEDICINAL CHEMISTRY
http://france.elsevier.com/direct/ejmech

Original article

Microwave assisted synthesis of fragrant jasmone heterocyclic analogues

Anna Pawełczyk, Lucjusz Zaprutko *

Chair and Department of Organic Chemistry, Poznan University of Medical Sciences, Grunwaldzka 6, 60-780 Poznań, Poland

Received 16 May 2005; received in revised form 1 September 2005; accepted 8 September 2005
Available online 24 March 2006

Abstract

cis-Jasmone, from jasmonoid group, is an important jasmine odor fragrance compound. The syntheses of new heterocyclic analogues of jasmone were described. Five analogues of this compound were prepared under microwave irradiation and the results of the microwave assisted syntheses were compared with classical, thermally initiated reactions in solvent. Microwave reactions were carried out successfully, and reaction times were significantly reduced to a few minutes. Three of five obtained analogues, pyrrolidinone, oxazolidinone and thiazolidinone demonstrated an interesting, specific odor which was compared with floral, typical jasmine odor of jasmone.

Keywords: *cis*-Jasmone; Heterocyclic analogues; Microwave synthesis; Fragrance compounds; Odor evaluation

1. Introduction

cis-Jasmone (**1**) and methyl jasmonate (**2**), which belong to jasmonoid group, are a well appreciated flower fragrances and valuable perfume ingredient known since the ancient times. Jasmine extract is mainly obtained from flowers of *Jasminum grandiflorum* (*Oleaceae*) and contains a complex bouquet of more than hundred volatiles comprising *cis*-jasmone at the amount of 2–3%, together with methyl jasmonate, jasmolactone, dihydrojasmone and *trans*-jasmone. All of these compounds have to be considered as late metabolites of the same lipid peroxidation process which begins with the conversion of linolenic and linoleic acids. Jasmine oil is usually produced from fresh flowers by means of the extraction process, known as "enfleurage" [1–3]. *cis*-Jasmone has been found in the oils of jonquil, orange flowers and also in different species of mint. Jasmonoids exhibit not only characteristic fragrance properties but they also play a key role as phytohormones in plants. These compounds enable the plants to communicate with their surroundings as well as generate defense responses against insects. Jasmonoids are crucial in defense-related and developmental processes occurring in plants e.g. the production of enzymes and stimulation of biosynthesis process. Besides, they act as signal transducers in cellular response and regulate important vital functions, the growth for example [3–5] (Fig. 1).

cis-Jasmone (**1**) is one of the most important representatives of jasmine fragrance which was isolated from jasmine absolute [2]. Jasmine has a tonic effect on human organism, fosters better concentrations and increases human ability to work. Jasmine is regarded as calming, antidepressant, antiseptic and anti-inflammatory agent. This compound is produced on a large scale by using synthetic methods; however, the manufacture price is still very high [6]. Thus, research focused on finding new, cheaper fragrance and structural analogues is to be conducted. Many structural jasmone analogues which exhibit interesting odor have been described in literature [3,7,8] but according to our knowledge, odor of heterocyclic analogues, containing heteroatom(s) in the ring have not been examined yet. Now, the preparation of five jasmone heterocyclic analogues with saturated chain and pyrrolidinone **7**, oxazolidinone **8**, pyrazolidinone **9**, pyrazolinone **10a** and thiazolidinone **11**

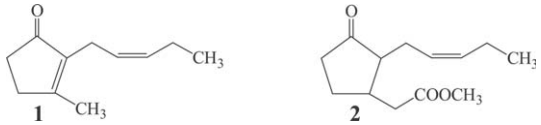


Fig. 1. Structure of main jasmonoides.

* Corresponding author. Tel.: +48 61 8546 670; Fax: +48 61 4546 680.
E-mail address: zaprutko@amp.edu.pl (L. Zaprutko).

0223-5234/$ - see front matter © 2006 Elsevier SAS. All rights reserved.
doi:10.1016/j.ejmech.2005.09.012

rings are described. Their odor evaluations are presented also. All of these compounds were obtained by using not only the microwave assisted method but also the classical one. The use of microwave irradiation to the synthesis of five-membered heterocyclic compounds, which had a common structure knowing from many biologically important compounds, has become very popular in the pharmaceutical field, due to the fact that it is a new technology of drugs discovery and development. Microwave irradiation has been used to assist many organic syntheses and it is known as a modern, highly yielding, environmental friendly and economical synthetic technique [9,10].

2. Results and discussion

2.1. Syntheses

Almost all jasmone analogues were prepared successfully from acyclic compounds by connecting classical and microwave assisted synthesis. Reactions were performed in two steps: condensation and alkylation, except the thiazolidinone analogue **11**, which was obtained in one stage. Microwave reactions were carried out according to two optional procedures, dependent on the type of reaction:

- *N*-alkylation and *C*-alkylation in "solvent-free" conditions;
- cyclocondensation in polar, high microwave absorbing solvent solutions.

The results of these microwave assisted reactions (MWA) were compared with classical, thermally initiated ones (Fig. 2).

Five heterocyclic derivatives of jasmone were obtained. The structure and classical preparation of compounds **8** [11] and odorless **10a** [12] were described in the literature sources, but in the case of compounds **7**, **9** and **11** no data have been found.

Necessary reaction times for the microwave reactions proceeding were reduced significantly in comparison with the respective times in conventional conditions. Microwave cyclocondensation of ethyl acrylate with methylhydrazine leading to heterocyclic compound **5** was more efficient and much faster than the appropriate reaction in conventional conditions, which requires 24 h. Ethyl 2-acetylheptanoate (**6**) was prepared by *C*-alkylation of ethyl acetoacetate. Classical *C*-alkylation has been carried out for 6–10 h [13], while the reaction under microwave irradiation required only 4 min [14]. The preparation of oxazolidinone **4** from aminoalcohol and dimethyl carbonate requires the removal of the alcohol appearing from the reaction mixture. In the classical method it was accomplished by using distillation method. It takes about 4 h at 100–140 °C [15] and the final yield of oxazolidinone **4** was 78%. The application of microwave irradiation was rather unsuccessful because reaction time was not reduced significantly and even after 1 h under the microwave irradiation the yield of final product was only 20%.

Heterocyclic compounds **3** and **4** under microwave irradiation react remarkably fast with alkyl halide resulting respective *N*-alkyl derivatives **7** and **8** with good yields. The yield of *N*-alkylated pyrazolidinone **9**, which had been obtained from **5**, was somewhat lower (38%) because apart from the main product also by-products were formed in reaction conditions. Microwave alkylation reactions were performed in "solvent-free" conditions with use of different solid supports: K_2CO_3, K_2CO_3/KOH, SiO_2/KOH. Optimal results were obtained in the case of K_2CO_3/KOH mixture. The application of K_2CO_3 only required more time and was not always successful. The addition of KOH is very advantageous to *N*-alkylation reaction rate. Microwave reactions were carried out by simple mixing of reagents, catalytic amount of TBAB as a phase transfer catalyst, potassium carbonate and potassium hydroxide [16]. *N*-Alkylation in dry DMF solution was carried out at room temperature for 24–48 h [17]. The classical *N*-alkylation of heterocyclic compounds bearing an acidic hydrogen atom at tached to nitrogen is generally accomplished by the treatment of these compounds with an appropriate base. An alternative is to perform the reaction under phase transfer catalysis (PTC) conditions. Classical *N*-alkylation is a time-consuming process and results in a lower selectivity of reaction; while microwave assisted alkylation on basic solid support is realized faster and more efficiently.

The pyrazolone analogue **10a** was synthesized from monoalkylated ethyl acetoacetate (**6**) and hydrazine hydrate in ethanolic solution. Classical reaction has been refluxed for 1–2 h [12], while the application of microwave irradiation required only 5–10 min (160 W). The **10a** and **10b** structures are tautomeric forms and according to the literature data [18], in polar medium, the **10a** structure is the more stable form. The suggested structure of pyrazolinone analogue is confirmed by

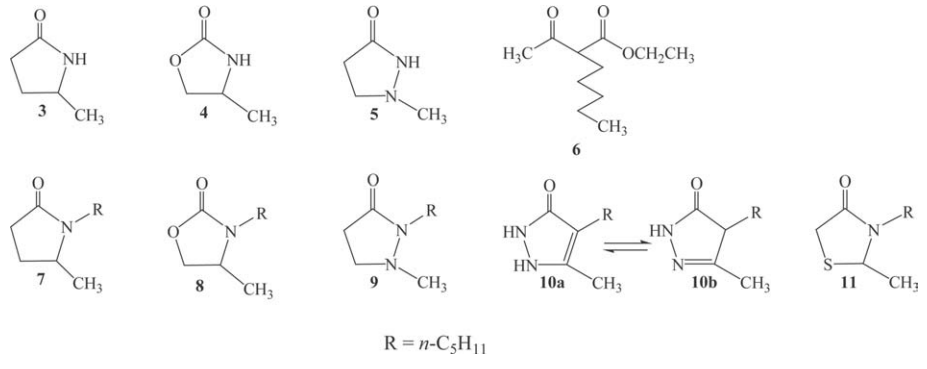


Fig. 2. Formula picture.

Table 1
The results of heterocyclic jasmone analogues synthesis

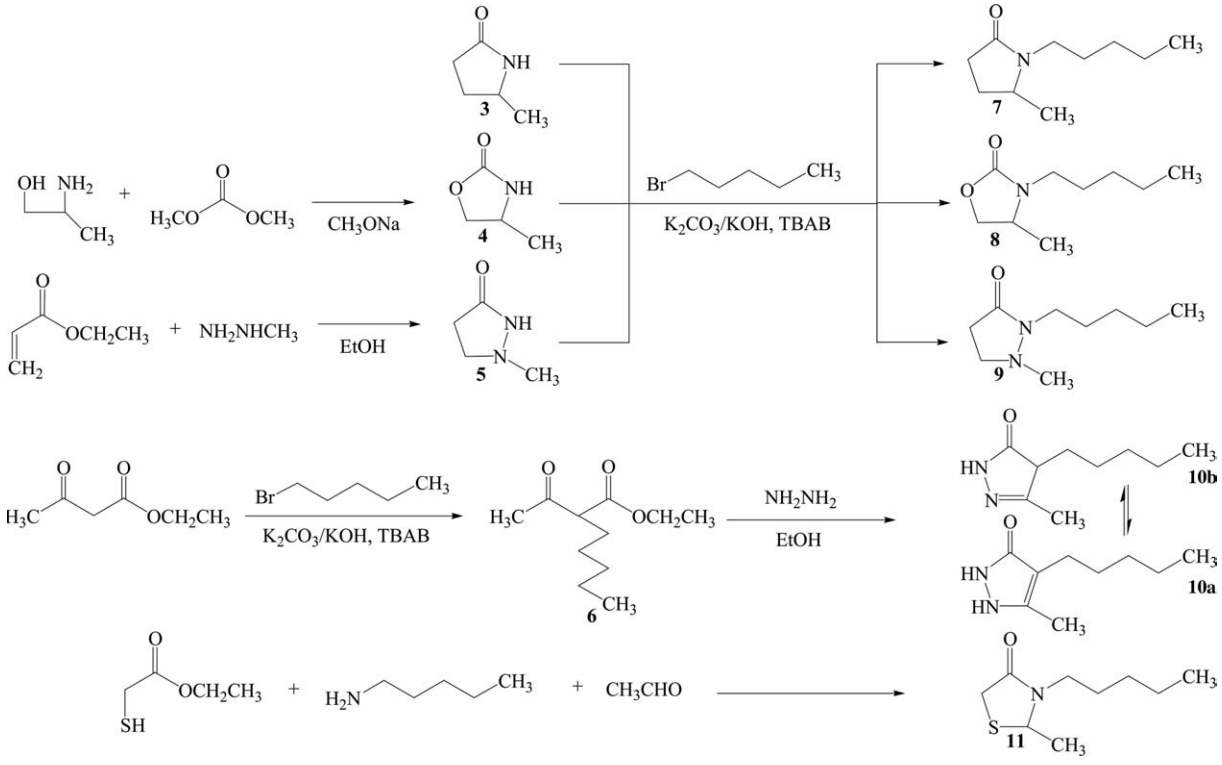
Compound	Classical method			Microwave assisted method			
	Temperature (°C)	Time (h)	Yield (%)	Temperature (°C)	Power (W)	Time (min)	Yield (%)
4	100–120	4	78	–	–	–	–
5	Reflux	24	62	78–80	160	5	72
6	Reflux	6–10	56	100–105	400	4	83
7	rt	24–48	Below 20	100–105	450	4	90
8	rt	24–48	Below 20	100–105	450	4	54
9	rt	24–48	Below 20	100–105	450	4	38
10a	Reflux	1–2	41	80–82	160	5–10	58
11	60	15	58	60	160	5	85

rt: room temperature.

spectral data. The ^{1}H-NMR spectra shows the broad singlet at 10.3 ppm which corresponds with two protons attached to nitrogen atoms. Besides, two signals at 100.79 and 136.33, characteristic to unsaturated carbon atoms, were observed in ^{13}C-NMR spectra. The **10a** structure can be additionally confirmed by the optical rotation measurement. The lack of optical activity for this compound can be a proof of the absence of asymmetrical carbon atoms in molecule of pyrazolone analogue.

It has been found that microwave irradiation is also applicable to synthesis of the thiazolidinone analogue **11**. Until now, one pot synthesis in toluene solution is a very popular procedure that leads to thiazolidinone system [19]. In this paper, microwave solventless thiazolidinone synthesis from pentylamine, acetaldehyde and ethyl thioglycolate resulted in good yields. The reaction time of this process was reduced significantly from several dozen to 10 min in comparison with conventional heating, but the main aim of the microwave technique is to eliminate solvents, especially low polar solvents, and replacing them with the more environmental friendly e.g. ethanol [20]. The obtained results and comparison of the main parameters of syntheses for all compounds are presented in Table 1.

The products were identified by some spectral methods. The IR absorption bands at about 1600–1720 cm^{-1} indicate the presence of a carbonyl group, which is also confirmed on ^{13}C-NMR spectra as a signal at lower fields about 160–174 ppm. The respective molecular ions [M^{+}] were detected in the mass spectra of all synthesized compounds. The fragmentation way exhibited a loss of the one of CH_3 groups as the first fragment and subsequent loss of the alkyl side chain, which was cut step by step. Optical rotation of final compounds **7**, **8** and **11** with asymmetric carbon atom were close to null. This indicates a racemic structure of mentioned products, which is in agreement with the racemic structure of substrates **3** and **4**. (Scheme 1).



Scheme 1. Microwave synthesis of jasmone heterocyclic analogues.

2.2. Odor evaluation

Jasmine fragrance compounds are very expensive materials. The discovery of structure–odor correlation was very helpful in projecting cheaper and more easily available jasmine-odor compounds. Characteristic jasmine odor of jasmonates is determined by the presence of three different groups around a five-membered carbon cycle: a strongly polar functional group e.g. carbonyl function, an alkyl side chain (five or six carbon atoms) and a weakly polar functional group e.g. lower alkyl [21]. The unsaturated *cis*-double bond, presents in the alkyl side chain in position 2 in jasmone, play very important role in fragrance properties; odor of *trans*-jasmone and dihydrojasmone is less floral than *cis*-jasmone. Present investigation showed the influence of the exchange of carbon(s) atom(s) on heteroatom(s) e.g. nitrogen, oxygen and sulfur on olfactory properties of obtained analogues.

Characteristic odor and odor durability of five heterocyclic analogues of jasmone were examined and the results are demonstrated in Table 2. The majority of obtained compounds exhibit specific olfactory properties. Their odors were compared with typical jasmine floral, warm and spicy odor of *cis*-jasmone. The **8** and **11** analogues are the strongest smelling compounds. The **7** and **8** analogues demonstrate strong, sweet coconut note. Compounds **7** and **11** exhibited jasmone note in the background.

The original jasmine character was significantly decreased for **7** and **11** analogues. Odor of **8** and **9** analogues lacked of jasmine note. Compound **9** showed only very weak, not very characteristic odor. Compound **10a** was odorless.

We tried confronting the number and the kind of heteroatoms introduced into the cycle with fragrance properties of obtained compounds. In the case of compounds which contain two adjoin nitrogen atoms the odor is very weak (**9**) or has not been detected (**10a**). On the other hand, the most intensive odor has been observed for analogues comprising two different heteroatoms in five-membered ring (**8**, **11**) or only one heteroatom (**7**). The **8** and **11** analogues have been characterized as the most tenacious fragrances which exhibited high odor durability. After 24 h the odor of these compounds is the more tenacious than odor of *cis*-jasmone.

In conclusion, the introduction of heteroatoms into the five-membered ring was undesirable for both, the jasmine odor and its intensity, but odor durability of the analogues **7**, **8** and **11** was increased in comparison with *cis*-jasmone odor durability.

3. Experimental protocols

The MWA were carried out using a microwave reactor "Plazmatronika RM 800" with maximum power of 800 W, the inert magnetic stirrer and the temperature control with IR method. The progress of reaction and purity of products were controlled with TLC method on silica gel plates (60 F_{254} from Merck). The spots on the plates were visualized with UV method or developed by the use of iodine or Dragendorff reagent. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini NMR-spectrometer (respectively, 300 and 75 MHz) in $CDCl_3$ or DMSO solutions. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) used as internal standard. Infrared (IR) spectra were performed on a "Specord 71-IR" as a film for liquid samples and as KBr tablets for solid samples and were expressed in cm^{-1} scale. Mass spectra were recorded on an AMD 402 spectrometer. Melting points were determined in an open capillary and were uncorrected. Products purification processes were performed with use of column chromatography method on silica gel 60 (70–230 mesh) and appropriate solvent mixtures as an eluent. Solid product was purified in the crystallization process. Analytical data of C, H, N assay for all new compounds were within less than ± 0.3% of the theoretical values and are in the good agreement with the proposed structures. Among five-membered heterocyclic ketones which were used as substrates, the racemic 5-methyl pyrrolidinone **3** was purchased from Aldrich as commercial product.

3.1. Classical syntheses

The classical syntheses were carried out according to the methods described in literature or with the use of some modifications of these procedures. Oxazolidinone **4** was prepared from racemic 2-amino-1-propanol and dimethyl carbonate in the presence of catalytic amount of sodium methoxide [15]. Pyrazolidinone **5** was prepared from ethyl acrylate and excess of methylhydrazine in ethanolic solution [22,23]. Ethyl 2-acetylheptanoate **6** was prepared by *C*-alkylation of ethyl acetoacetate using pentyl bromide in the presence of sodium ethoxide in ethanolic solution [13]. Analogues **7**–**9** were prepared by *N*-alkylation of appropriate heterocyclic compounds **3**–**5** using pentyl bromide in dry dimethylformamide in the presence of potassium carbonate in room temperature [16]. Pyrazolinone **10a** was synthesized from **6** and hydrazine hydrate in ethanolic solution [12]. Thiazolidinone **11** was prepared from pentylamine, acetaldehyde and ethyl thioglycolate in one pot synthesis

Table 2
Odor evaluation of jasmone analogue

Compound	Odor	Odor durability		
		After 1 h	After 6 h	After 24 h
7	Medium-intensive, sweet, reminiscent of jasmone with coconut note	++++	+++	++
8	Medium-intensive, tenacious, sweet, coconut, lack of jasmine odor	++++	++++	+++
9	Weak, not characteristic	+	–	–
10a	Odorless	–	–	–
11	Intensive, strong, spicy, tenacious, with sulfuric note, weak jasmone note in the background	++++	++++	+++
cis-Jasmone	Intensive, floral, warm, typical jasmine	+++++	++++	+

according to the well known method used to form thiazolidinone ring [24].

3.2. Microwave assisted syntheses

3.2.1. 1-Methyl-3-pyrazolidinone (5)

One gram (10 mmol) of ethyl acrylate and 0.69 g (15 mmol) of methyl hydrazine was dissolved in 20 ml of ethanol. The mixture was refluxed under microwave conditions with 160 W power of microwaves for 5 min. After concentration in vacuo, the crude product was obtained as orange oil, which was purified by a column chromatography using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.72 g (72%) of pale yellow oil. Results of spectral and elemental analysis were in agreement with the literature data [23].

3.2.2. Ethyl 2-acetylheptanoate (6)

0.65 g (5 mmol) of ethyl acetoacetate and subsequently 0.8 ml (6 mmol) of pentyl bromide were added to pulverized mixture of 0.16 g (0.5 mmol) of tetrabutylammonium bromide (TBAB), 3.59 g (26 mmol) of potassium carbonate and 0.39 g (7 mmol) of potassium hydroxide. Reagents, in a flask with condenser, were irradiated for 4 min with 450 W power of microwaves. The product was extracted with ether and the obtained organic solution was concentrated in vacuo. The residued yellow oil was purified by a column chromatography, using a mixture of hexane and ether 6:1 as an eluent, yielding 0.83 g (83%) of colorless oil. All analytical data were in agreement with the literature results [11].

3.2.3. 5-Methyl-1-pentyl-2-pyrrolidinone (7)

0.49 g (5 mmol) of **3** and subsequently 0.9 ml (7.5 mmol) of pentyl bromide were added to pulverized mixture of 0.16 g (0.5 mmol) of TBAB, 2.76 g (20 mmol) of potassium carbonate and 1.12 g (20 mmol) of potassium hydroxide. Reagents, in a flask with condenser, were irradiated for 4 min with 450 W power of microwaves. The crude product was extracted with chloroform and the obtained organic solution was filtered and concentrated in vacuo. The residued yellow oil was purified by column chromatography, using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.76 g (90%) of **7** as pale yellow oil. IR (film): $\nu = 1680$. MS: *m/z* (rel. int. %) = 169 (15.8) [M^+], 154 (13.4), 140 (12.2), 126 (6.1), 112 (100.0), 98 (15.9), 84 (39.6), 67 (5.8), 55 (25.3), 41 (26.6). ^{1}H-NMR ($CDCl_3$): $\delta = 0.91$ (t, $J = 7.0$ Hz, 3H, CH_3 in pentyl), 1.21 (d, $J = 6.3$ Hz, 3H, CH_3), 1.26–1.39 (m, 4H, $2 \times CH_2$), 1.41–1.63 (m, 2H, CH_2), 2.13–2.28 (m, 2H, H-4), 2.31–2.40 (m, 2H, H-3), 2.89–2.96 (m, 1H, N–CH_2), 3.52–3.62 (m, 1H, N–CH_2), 3.67–3.76 (m, 1H, H-5). ^{13}C-NMR ($CDCl_3$): $\delta = 13.49$ (CH_3 in pentyl), 19.27 (CH_3), 21.89/26.29/26.58 ($3 \times CH_2$), 26.59 (C-3), 29.83 (C-4), 39.42 (C-5), 57.73 (N–CH_2), 174.12 (C=O). $[\alpha]_D^{20} = \sim 0°$.

3.2.4. 4-Methyl-3-pentyl-2-oxazolidinone (8)

0.50 g (5 mmol) of **4** was *N*-alkylated as described above for compound **7**. The residued pale yellow oil was purified by a column chromatography, using a mixture of ethyl acetate and hexane 1:1 as an eluent, yielding 0.46 g (54%) of **8** as colorless oil. IR (film): $\nu = 1720$. MS: *m/z* (rel. int. %) = 171 (6.5) [M^+], 156 (46.3), 142 (36.4), 128 (6.6), 114 (100.0), 100 (8.1), 86 (21.3), 70 (49.5). ^{1}H-NMR ($CDCl_3$): $\delta = 0.90$ (t, $J = 6.9$ Hz, 3H, CH_3 in pentyl), 1.27 (d, $J = 5.8$ Hz, 3H, CH_3), 1.30–1.39 (m, 4H, $2 \times CH_2$), 1.47–1.60 (m, 2H, CH_2), 3.00–3.09 (m, 1H, N–CH_2), 3.36–3.46 (m, 1H, N–CH_2), 3.79–3.92 (m, 2H, H-5), 4.39 (t, $J = 7.7$ Hz, 1H, H-4). ^{13}C-NMR ($CDCl_3$): $\delta = 13.90$ (CH_3 in pentyl), 18.08 (CH_3), 22.27/26.99/28.79 ($3 \times CH_2$), 41.49 (C-4), 50.71 (N–CH_2), 68.80 (C-5), 158.12 (C=O). $[\alpha]_D^{20} = \sim 0°$.

3.2.5. 1-Methyl-2-pentyl-3-pyrazolidinone (9)

0.50 g (5 mmol) of **5** was *N*-alkylated as described above for compound **7**. The residued orange oil was purified by a column chromatography, using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.32 g (38%) of **9** as yellow oil. IR (KBr): $\nu = 1680$. MS: *m/z* (rel. int. %) = 170 (100.0) [M^+], 155 (1.7), 141 (2.6), 127 (2.4), 113 (54.8), 99 (23.8), 85 (8.6), 70 (25.2), 57 (70.5). ^{1}H-NMR ($CDCl_3$): $\delta = 0.91$ (t, $J = 6.9$ Hz, 3H, CH_3 in pentyl), 1.27–1.39 (m, 4H, $2 \times CH_2$), 1.65–1.78 (m, 2H, CH_2), 2.57 (m, 2H, H-4), 3.28 (s, 3H, N–CH_3), 3.47–3.56 (m, 2H, N–CH_2), 3.79–3.88 (m, 2H, H-5). ^{13}C-NMR ($CDCl_3$): $\delta = 13.87$ (CH_3 in pentyl), 22.36/26.85/28.66 ($3 \times CH_2$), 43.20 (CH_3), 50.54 (C-5), 51.95 (N–CH_2), 63.81 (C-4), 168.78 (C=O). $[\alpha]_D^{20} = \sim 0°$.

3.2.6. 3-Methyl-4-pentyl-5-pyrazolinone (10a)

0.50 g (10 mmol) of hydrazine hydrate was added to the solution of 1.00 g (5 mmol) of **6** in ethanol. Reagents, in a flask with condenser, were irradiated for 10 min with 160 W power of microwaves. The obtained solution was concentrated in vacuo, yielding 0.49 g (58%) of white crystals. The crude product was purified by a crystallization from benzene, m.p. 198–200 °C (Ref. [12]: m.p. 186–187 °C). IR (film): $\nu = 1600$, MS: *m/z* (rel. int. %) = 168 (18.9) [M^+], 153 (1.0), 139 (0.5), 125 (0.5), 111 (100.0), 97 (1.5), 83 (1.1), 68 (2.0), 55 (3.2), 41 (5.5). ^{1}H-NMR (DMSO): $\delta = 0.85$ (t, $J = 7.0$ Hz, 3H, CH_3 in pentyl), 1.25–1.33 (m, 4H, $2 \times CH_2$), 1.34–1.43 (m, 2H, CH_2), 2.03 (s, 3H, CH_3), 2.17 (t, $J = 7.4$ Hz, 2H, H-1′), 10.31 (br s, 2H, NH). ^{13}C-NMR (DMSO): $\delta = 9.87$ (CH_3), 14.03 (CH_3 in pentyl), 21.33/22.03/29.57 ($3 \times CH_2$), 31.00 (C-1′), 100.79 (C-4), 136.33 (C-3), 159.82 (C=O). $[\alpha]_D^{20} = \sim 0°$.

3.2.7. 2-Methyl-3-pentyl-4-thiazolidinone (11)

0.96 g (11 mmol) of *n*-pentylamine was cooled to 0 °C, and mixed with 0.53 g (12 mmol) of acetaldehyde. The mixture was stirred at room temperature under condenser. After 1 h 0.60 g (5 mmol) of ethyl thioglycolate (or thioglycolic acid) was added. Reagents, were irradiated for 5 min with 160 W power of microwaves in a flask with condenser. The obtained product was dissolved in ethyl acetate, and solution was washed successively with diluted hydrochloric acid and water, it was subsequently dried with $MgSO_4$ and concentrated in vacuo. The residued yellow oil was purified by a column chromatography, using a mixture of ethyl acetate and hexane 1:1 as

an eluent, yielding 0.79 g (85%) of **11** as pale yellow oil. IR (film): ν = 1680. MS: *m/z* (rel. int. %) = 187 (51.9) [M^+], 172 (100.0), 158 (2.7), 144 (3.4), 130 (13.6), 116 (6.5), 102 (61.0), 74 (12.0), 56 (15.2). ^{1}H-NMR ($CDCl_3$): δ = 0.90 (t, J = 7.0 Hz, 3H, CH_3 in pentyl), 1.24–1.38 (m, 4H, 2 × CH_2), 1.48–1.60 (m, 2H, CH_2), 1.54 (d, J = 6.0 Hz, 3H, CH_3), 2.97–3.07 (m, 1H, N–CH_2), 3.52–3.60 (m, 1H, N–CH_2), 3.61–3.70 (m, 2H, H-5), 4.76 (q, J = 6.1 Hz, 1H, H-2). ^{13}C-NMR ($CDCl_3$): δ = 13.96 (CH_3 in pentyl), 23.17 (CH_3), 22.32/26.86/28.93 (3 × CH_2), 32.39 (C-2), 42.21 (C-5), 56.41 (N–CH_2), 170.36 (C=O). $[\alpha]_D^{20}$ = ~0°.

3.3. Test of odor evaluation

Tests of odor evaluation were performed using 10% (v/v for fluids and w/v for solid) EtOH solutions of samples **7**–**9**, **10a** and **11**. Three drops of prepared solution were absorbed on a smelling blotter (thin strip of highly absorbent paper). When the ethanol was evaporated the strips with the sample were performed to organoleptic analyses by non-professional perfumers. The odor characteristic and intensity of each sample were compared with the sample of *cis*-jasmone similar solution (commercial product from Aldrich). Durability of the scents was studied after 1, 6 and 24 h.

Acknowledgements

This study was partially supported by Polish State Committee for Scientific Research (Grant No. 2 PO5F 031 29).

References

[1] K. Bauer, D. Garbe, H. Surburg, in: Common Fragrance and Flavor Materials: Preparation, Properties and Uses, third ed, Wiley-VCH, Germany, 1997, p. 94 (200).
[2] D.H. Pybus, C.S. Sell, in: The Chemistry of Fragrances, RSC, Cambridge, UK, 1999, pp. 32–39.
[3] A. Kurek, L. Zaprutko, Pol. J. Cosmet. 3 (2004) 140–153.
[4] J.G. Turner, C. Ellis, A. Devoto, Plant Cell 14 (2002) 153–164.
[5] T. Koch, K. Bandemer, W. Boland, Helv. Chim. Acta 80 (1997) 838–851.
[6] a) W.J. Wiegers, J.B. Hall, US Patent no. 4045 489, Aug 30, 1981, acc. C.A. 87 (1977) 5396q, b) W.J. Wiegers, J.B. Hall, US Patent no. 4265 836, May 5, 1981, acc. C.A. 95 (1981) 61459q.
[7] P. Weyerstahl, A. Schenk, Flavour Frag. J. 11 (1996) 141–144.
[8] H. Kiyota, T. Koike, E. Higashi, T. Oritani, Flavour Frag. J. 16 (2001) 175–179.
[9] P. Lidström, J. Tierney, B. Wathey, J. Westman, Tetrahedron 57 (2001) 9225–9283.
[10] Y. Xu, Q.X. Guo, Heterocycles 4 (2004) 903–974.
[11] M.T. Hancock, A.R. Pinhas, Tetrahedron Lett. 44 (2003) 5457–5460.
[12] M.M. Bouveault, R. Loquin, Bull. Soc. Chim. Fr. 31 (1904) 588–593.
[13] P.E. Sum, L. Weiler, Can. J. Chem. 56 (1978) 2301–2304.
[14] D. Runhua, W. Yuliang, J. Yaozhong, Synth. Commun. 24 (1) (1994) 111–115.
[15] P. Alewood, M. Benn, R. Reinfried, Can. J. Chem. 52 (1974) 4083–4089.
[16] D. Bogdal, J. Pielichowski, K. Jaskot, Heterocycles 45 (1997) 715–722.
[17] D.R. Adamus, A.F. Barnes, F. Cassidy, M. Thompson, J. Chem. Soc. PT1 (1984) 2061–2067.
[18] A.R. Katritzky, C.W. Rees, Comp. Heterocycl. Chem. 5 (1984) 36–37.
[19] A. Rao, A. Carbone, A. Chimirri, E. De Clercq, A.M. Monforte, P. Monforte, C. Pannecouque, M. Zappala, Farmaco 58 (2003) 115–120.
[20] V. Gududuru, V. Nguyen, J.T. Dalton, D.D. Miller, Synlett 13 (2004) 2357–2358.
[21] K.J. Rossiter, Chem. Rev. 96 (1996) 3201–3240.
[22] L.A. Carpino, J. Am. Chem. Soc. 80 (1958) 601–604.
[23] R.F. Smith, L.A. Dennis, W.J. Ryan, G. Rodriguez, K.A. Brophy, J. Heterocycl. Chem. 29 (1) (1992) 181–183.
[24] M. Mąkosza, M. Sypniewski, T. Glinka, Tetrahedron 52 (1996) 3189–3194.