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# Short communication

# Microwave assisted synthesis of unsaturated jasmone heterocyclic analogues as new fragrant substances

# Anna Pawełczyk, Lucjusz Zaprutko\*

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

## A R T I C L E I N F O

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# ABSTRACT

Taking the rising interest in jasmone structure based fragrant compounds into account it has been decided to take up an attempt to synthesize the new heterocyclic derivatives of this 2,3-disubstituted cyclopentenone, which could be characterized by the ability of interaction with the same receptors with which jasmone affects. Obtained structures of unsaturated heterocyclic derivatives are based on pyrrolidinone, oxazolidinone, pyrazolidinone, pyrazolone and thiazolidinone systems with 2-double or 2triple unsaturated five-carbon side chain. The rapid, highly yielding and ecofriendly microwave assisted organic syntheses (MAOS) have been used to obtain compounds mentioned above. Odor evaluation and relationships between their structure and osmic properties for all synthesized fragrant compounds have been studied. It has been shown that the majority of the obtained compounds have exhibited interesting, very intensive and fixative fragrant properties.

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## 1. Introduction

Jasmine extract is mainly obtained from jasmine flowers of the species Jasminum grandiflorum from the olive family (Oleaceae). The extract of jasmine flowers contains over 250 components. The number and diversity of these compounds are enormous. In the jasmine absolute in addition to benzyl alcohol, benzyl acetate. linalool, indole, methyl anthranilate, also ketonic compounds, such as jasmone and methyl jasmonate have been discovered. Those carbonyl compounds, called jasmonoids, are derived from polyunsaturated fatty acids as a result of biosynthesis, which probably proceeds in the same way as the biosynthesis of prostaglandins in higher organisms. Jasmone is a well-known component of plant volatiles and is a very important substance determining the odor of jasmine flowers. This compound can be obtained from the natural extract or by using different synthetic methods [1,3]. From the chemical point of view, it is a 2,3-disubstituted derivative of cyclopentenone with 2-pentenyl side chain in  $\alpha$ -position to carbonyl function [2–5]. The natural jasmine extract contains two geometrical isomers of jasmone: *cis*-jasmone **1** and *trans*-jasmone 2 (Fig. 1).

The jasmine fragrances, in particular jasmonoids, are invaluable in perfumery industry. These compounds are also produced on a large scale using synthetic methods; however, the cost of their production is still very high. Thus, the search for cheaper fragrances and new structural analogues of natural fragrant substances is continued and many structural jasmone analogues exhibiting interesting odor have been described [2,6,7]. New heterocyclic furanone analogues of jasmone compounds with oxygen atom introduced into the five-membered ring have been also developed [8].

Recently, we have reported [9] microwave synthesis of some fragrant structural jasmone heteroanalogues containing saturated alkyl side chain with five-carbon atoms (Fig. 2).

It has been shown that saturated jasmone derivatives **3**, **4** and **7** represented interesting, very intensive and long-lasting fragrant properties such as aniseed, coconut and vanilla. Flower jasmine note, characteristic of standard note of *cis*-jasmone, together with structural correlation was also kept. Pyrazolidinone **5** showed very weak odor, while odor of pyrazolone **6** was not detected. Now, the preparation of series succeeding jasmone heterocyclic analogues with pyrrolidinone, oxazolidinone, pyrazolidinone, pyrazolone and thiazolidinone cycles and 2-unsaturated alkyl side chain is described. Their odor evaluations are also investigated. The rapid, highly yielding and ecofriendly microwave assisted organic syntheses (MAOS) were used to obtain fragrant jasmone hetero-analogues. The majority of microwave assisted reactions was conducted in solvent-free conditions with the use of solid support or in polar, highly microwave absorbing solvents.

High-speed synthesis with microwaves has attracted a considerable amount of attention in recent years [10]. Microwave assisted





<sup>\*</sup> Corresponding author. Tel.: +48 61 8546 670; fax: +48 61 8546 680.

*E-mail addresses:* apaw@ump.edu.pl (A. Pawełczyk), zaprutko@ump.edu.pl (L. Zaprutko).

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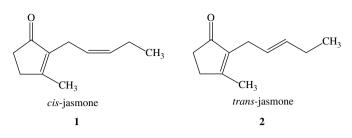


Fig. 1. Isomers of natural jasmone.

chemistry is based on efficient heating of materials by "microwave dielectric heating" effects and especially by two mechanisms: dipolar polarization and ionic conduction. This phenomenon is dependent on the ability of dielectric properties of reagents or solvents to absorb microwave energy and convert it into heat [11]. Presently, most scientists agree that in the majority of cases the reason for the observed rate enhancements are purely thermal/ kinetic effects, which are a consequence of high temperature that can rapidly be attained when irradiating polar materials in a microwave field. In addition to effects mentioned above, microwave specific effects must also be considered e.g., superheating effect of solvent at the atmospheric pressure, the selective heating of selected reaction components, the molecular radiators formation, the elimination of wall effects caused by inverted temperature gradients compared to classical heating [11,12]. The main benefits of performing reaction under microwave irradiation conditions are the significant rate enhancements and higher product yields that can frequently be observed.

### 2. Results and discussion

# 2.1. Chemistry

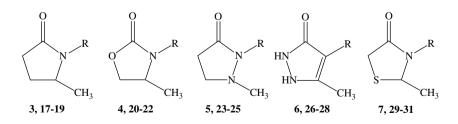
The series of unsaturated heterocyclic analogues of jasmone with 2-double and 2-triple unsaturated five-carbon side chain was prepared. Obtained structures of unsaturated heterocyclic derivatives are based on pyrrolidinone, oxazolidinone, pyrazolidinone, pyrazolone and thiazolidinone systems, which contain one or two heteroatoms in the five-membered ring, such as nitrogen, oxygen or sulfur and also 2-*trans*-pentenyl, 2-*cis*-pentenyl and 2-pentynyl side chain (Fig. 2).

Microwave assisted reactions were optimized and adjusted to obtain planned products, and also introduction of different modifications was indispensable in many cases, not only displacement of conventional reaction to microwave conditions. Recently [9], in the case of the synthesis of saturated heterocyclic jasmone analogues **3–7**, we have compared the results of some of the microwave assisted syntheses with classical, thermally initiated reactions in organic solvent. Necessary reaction times for the microwave reaction proceedings were reduced significantly in comparison with the respective times in conventional conditions. The most of the reactions were more efficient, much faster and generally more advantageous than the appropriate classical reactions.

Almost all jasmone analogues were prepared successfully from acyclic compounds with the use of new or known from literature sources MAOS methods. Among heterocyclic ketones which were used as substrates, only 5-methyl-2-pyrrolidinone (8) was purchased from Aldrich as commercial product. First, compounds necessary to obtain the planned heterocyclic derivatives such as 4methyl-2-oxazolidinone (9) [9,13], 1-methyl-3-pyrazolidinone (10) [9,14], respective C-alkyl derivatives of ethyl acetylacetate 11–13 [9,15] and 2-mercaptoacetic acid amides 14-16 [16] were synthesized. The preparation of oxazolidinone 9 from appropriate aminoalcohol and dimethyl carbonate requires the removal of the alcohol appearing from the reaction mixture and it was accomplished by using distillation process [13]. Microwave cyclocondensation of ethyl acrylate with methylhydrazine in ethanolic solution [9] was conducted during 10 min and has been leading to heterocyclic pyrazolidinone 10.

Pyrrolidinones **17–19**, oxazolidinones **20–22** and pyrazolidinones **23–25** were obtained as a result of *N*-alkylation reaction of **8–10**, according to the procedure described by Bogdal et al. [16] with the use of appropriate alkyl bromide. Heterocyclic pyrrolidinone **8** and oxazolidinone **9** under microwave irradiation react remarkably fast (5 min) with alkyl halides, resulting respective *N*-alkyl derivatives with good yields. The yield of *N*-alkylated pyrazolidinones **23–25**, which have been obtained from **10**, was somewhat lower (25–33%) because apart from the main product, dialkylated by-products were also formed in the reaction conditions. Alkyl derivatives of ethyl acetylacetate **11–13** and 2-mercaptoacetic acid amides **14–16** were cyclized under microwave conditions. As a result of these processes, the 2-unsaturated in the alkyl side chain heterocyclic analogues of jasmone **17–31** were obtained.

A majority of compounds used as factors supplying characteristic for jasmine five-carbon chains were purchased as commercial products. However, in order to obtain full structural analogy to natural jasmone which contains 2-*cis*-pentenyl substituent, the commercially not available 1-bromo-2-*cis*-penten was prepared. This compound was synthesized from 2-*cis*-penten-1-ol on the way of the substitution reaction of hydroxyl function by bromide atom with the use of PBr<sub>3</sub>, in the mixture of petroleum ether and pyridine [17,18].



3, 4, 5, 6, 7; R = -*n*-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> 17, 20, 23, 26, 29; R = -*trans*-CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>3</sub> 18, 21, 24, 27, 30; R = -*cis*-CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>3</sub> 19, 22, 25, 28, 31; R = -CH<sub>2</sub>C≡CCH<sub>2</sub>CH<sub>3</sub>

Fig. 2. Structures of heterocyclic derivatives of jasmone.

Microwave alkylation processes were performed for about 5 min in solvent-free conditions usually with the use of equimolar mixture of K<sub>2</sub>CO<sub>3</sub>/KOH as a solid support and catalytic amount of tetrabutylammonium bromide (TBAB).

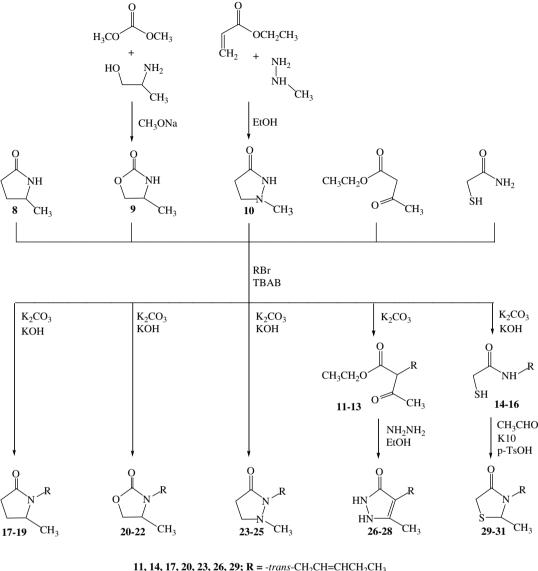
Pyrazolone analogues 26-28 were synthesized by the cyclocondensation reactions of obtained C-alkvl derivatives of ethyl acetvlacetates **11–13** with hydrazine hydrate in ethanolic solution for about 10 min [9.19]. Respective alkyl derivatives of ethyl acetylacetate such as ethyl 2-acetyl-4-heptenoates (11,12) and ethyl 2-acetyl-4-heptynoate (**13**) were prepared by *C*-alkylation of ethyl acetylacetate with the use of 2-unsaturated alkyl bromides under microwave irradiation and required solvent-free condition with the use of K<sub>2</sub>CO<sub>3</sub> as a solid support for 4 min. According to the literature sources [20] pyrazolone compounds exhibit tautomerism ability. The suggested structure of pyrazolone analogues was confirmed by spectral data. The <sup>1</sup>H NMR spectra shows the broad bands at 9.5– 11.2 ppm which correspond with two protons attached to nitrogen atoms. Besides, two signals at the range 98–137 ppm, characteristic to unsaturated carbon atoms, were observed in <sup>13</sup>C NMR spectra. This structure can be additionally confirmed by the optical rotation measurement. The lack of optical activity for these compounds can be a proof of the absence of asymmetric carbon atom in molecule of pyrazolone analogues.

It has been found that microwave irradiation is also successfully applicable to synthesis of the thiazolidinone compounds. Until now, one pot synthesis in toluene solution has been a very popular procedure that leads to thiazolidinone system [21]. Recently, we have reported [9] microwave solvent less thiazolidinone synthesis from pentylamine, acetaldehyde and ethyl 2-mercaptoacetate resulted in good yields. The reaction time of this process was significantly reduced from hours to 10 min relatively to conventional heating. It has not managed to employ formula cited above to synthesis of thiazolidinones with unsaturated side chain, because appropriate unsaturated pentylamines induced great synthetic difficulties. Thiazolidynone derivatives 29-31 were obtained as a result of cyclocondensation of acetaldehyde with mono-alkylated 2-mercaptoacetamide derivatives **14–16**. First, five-carbon chains were introduced into acyclic amide of 2-mercaptoacetic acid by the use of general N-alkylation process [16] and next the obtained N-mono-substituted amides were reacted with acetaldehyde, yielding final disubstituted thiazolidinones. Amide alkylation with the use of appropriate alkyl bromide realized both in classical and microwave conditions was processed very fast but not selective. Many of the alkylated derivatives of 2-mercaptoacetamide were found in the reaction mixture. The mono-alkylated derivatives were separated using chromatography method. Microwave cyclocondensation process was carried in solvent-free conditions with the use of montmorilonite K10-clay and catalytic amount of *p*-toluenesufonic acid. General synthesis methods of all prepared compounds were presented on Scheme 1.

The obtained products were identified by some spectral methods. The IR absorption bands at about 1600–1720 cm<sup>-1</sup> indicate the presence of a carbonyl group, which is also confirmed on <sup>13</sup>C NMR spectra as a signal at lower fields about 160-174 ppm. The respective molecular ions [M<sup>+</sup>] were detected in the mass spectra of all synthesized compounds. The fragmentation way exhibited by the loss of one of the CH<sub>3</sub> groups as the first fragment and subsequent loss of the fragments of alkyl side chain. In the recorded spectra, except characteristic signals for appropriate heterocyclic moiety, signals of characteristic 2-unsaturated side chains were also observed. Carbon signals for 2-pentenyl group CH=CH were observed as well at the range of 120-140 ppm and in case of 2-pentynyl group C $\equiv$ C at the range of 70–85 ppm. Additionally, proton signals at the range of 5.0–6.0 ppm for CH=CH were well affirmed by appropriate carbon signals on <sup>13</sup>C NMR spectra. All of the prepared compounds were submitted sufficient spectral analysis. Purity of final compounds was determined with the use of thin layer chromatography (TLC) method. The fundamental physico-chemical properties, such as boiling or melting point and optical rotation were also measured. Optical rotation of pyrrolidinones, oxazolidinones and thiazolidinones which can contain asymmetric carbon atom was close to null. This indicates racemic structure of the products, which is in agreement with racemic structure of substrates used.

# 2.2. Odor evaluation

"Jasmine chemistry" is a very dynamically developing direction of organic chemistry and research focused on finding cheaper synthesis methods of jasmone [3] and other jasmine odor compounds or new fragrance and structural analogues of natural fragrant substances are to be conducted [2]. Lately [9], we have examined fragrant properties of saturated structural jasmone heteroanalogues. The present investigation has shown fragrant properties of series of following new, unsaturated structural and functional heterocyclic analogues of natural jasmone. Structural similarity gets through introduction of one or two heteroatoms into the five-membered cycle of jasmone molecule or its closest analogues. It is known that usually heterocyclic analogues of natural origin substances show interesting properties, which often are similar to their mother substances but differently directed. It also has been observed in the case of jasmone heteroanalogues. The influence of the exchange of carbon(s) atom(s) on heteroatom(s) e.g., N, O and S on olfactory properties of obtained analogues was examined. Chemical modifications of 2-unsaturated side chain were also in question. Organoleptic analysis of the odor and relationships between their structure and osmic properties for all fragrant compounds were performed. Their odors were compared with typical jasmine floral, warm and spicy odor of *cis*-jasmone. Characteristics of the odor and odor durability of these heterocyclic jasmone derivatives were presented in Table 1. It has been shown that the majority of the obtained compounds were exhibited interesting, very intensive and extremely durable odor, in some cases considerably exceeding durability odor of jasmone, such as aniseed, coconut and vanilla. In many cases, flower jasmine note, characteristic for standard odor of cis-jasmone, together with structural correlation was also kept. Pyrrolidinones (17-19), oxazolidinones (20-22) and thiazolidinones (29-31) exhibited the most interesting osmic properties, while pyrazolidinones (23-25) and pyrazolones (26-28) showed very weak odor or were odorless. This new group of obtained fragrances, despite close structural correlation with jasmone, represents new, somewhat different odor notes respectively to standard jasmone. Most probably the heteroatoms which have been introduced into five-membered ring are responsible for these interesting and specific olfactory properties. As a result of conduced sensory analysis it has been found that most of the received compounds exhibited interesting fragrant properties. Based on the group of obtained fragrant compounds it takes attempts to coherence of their structural and osmic features, the influence of exchanging one or two carbon atoms in fivemembered cycle on heteroatoms such as: N, O or S and also influence their amount and kinds of fragrant impressions. In the case of compounds which contain two adjoining nitrogen atoms the odor is very weak and not characteristic or has not been detected. It was observed in pyrazolidinones (23-25) and pyrazolones (26-28). On the other hand, the most intensive and durable odors were exhibited by compounds including two different heteroatoms in the ring, such as oxazolidinones (**20–22**) with nitrogen and oxygen atoms and thiazolidinones (29-31) with nitrogen and sulfur atoms in the ring. The pyrrolidinones, containing only one heteroatom, exhibited quite interesting fragrant properties also. A similar odorstructure correlation was observed in the case of saturated heterocyclic derivatives of jasmone (3-7) [9]. Odor of selected



**11, 14, 17, 20, 23, 26, 29; R =** *-trans*-CH<sub>2</sub>CH=CHCH<sub>2</sub>CH

**12, 15, 18, 21, 24, 27, 30; R** = -*cis*-CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>3</sub>

13, 16, 19, 22, 25, 28, 31;  $\mathbf{R} = -CH_2C \equiv CCH_2CH_3$ 

Scheme 1. Microwave assisted synthesis of unsaturated heteroanalogues of jasmone.

compounds is more durable than odor durability of pattern jasmone after 24 h, but odor of pyrrolidinone **18** and oxazolidinone **21** is smelt after 6 days even.

Taking structure–odor relationship into consideration, the structural modifications in five-carbon, 2-unsaturated alkyl side chain must be also pointed out. The introduction of double bond for classic, low molecular weight ketones usually results in the increase of intensity of odor which sometimes accompanied by spicy note, but with increase of molecular weight, the spicy odor a character was vanished and floral note was appeared [22]. The unsaturated *cis*-double bond, present in the alkyl side chain in position 2 in natural *cis*-jasmone plays very important role in the fragrance properties; odor of *trans*-jasmone and dihydrojamone is less floral than *cis*-jasmone [2]. The introduction of double bond into heterocyclic jasmone analogues, both *cis* and *trans*, leads to the increase of odor intensity relatively to their saturated hetero-analogues. Presence of triple bond in the structure of compounds resulted in the increase of spicy and diffusivity of odor and also in

decline or decrease of floral-jasmine odor participation. However, a new spicy and burned note appeared.

# 3. Experimental protocols

#### 3.1. General

The microwave assisted reactions were carried out using a microwave reactor PLAZMATRONIKA RM 800 with operating frequency 2.45 GHz, maximum power of microwave 800 W and equipped with the inert magnetic stirrer, the temperature control through IR sensor, the post-reaction cooling system, the module for small-scale experiments (below 30 ml), the computer software control system. The progress of reaction and purity of products were controlled with TLC method on silica gel plates (60 F<sub>254</sub> from Merck). The spots on the plates were visualized with UV method or developed by the use of iodine vapour or Dragendorff reagent. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini

#### Table 1

Odor evaluation of 2-unsaturated ja	asmone heteroanalogu	les
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Compound	Odor	Int. <sup>a</sup>	Odor durability			
			1 h	6 h	24 h	Remarks
Jasmone	Floral, warm, typical jasmine	3	+++++	++++	+	
Pyrrolidinones						
17	Floral, aniseed, with lightly cucumber note, reminiscent of cis-jasmone	2	++++	+++	++	
18	Floral, aniseed, reminiscent of cis-jasmone, very intensive	3	+++++	++++	+++	Smelt after 6 days
19	First note lightly acidic and burned, the next reminiscent of cis-jasmone	2	++++	++	+	
Oxazolidinones						
20	Sweet with aniseed, coconut and vanilla note, the lack of jasmine character	3	+++++	+++	++	
21	Sweet with coconut, vanilla and caramel note, then jasmine-floral, very intensive	3	+++++	++++	+++	Smelt after 6 days
22	First note lightly acidic and burned, the next reminiscent of cis-jasmone	2	+++	++	+	
Pyrazolidinones						
23-25	Very weak, not characteristic	-	+	-	-	
Pyrazolones						
26–28	Odorless	-	-	-	-	
Thiazolidinones						
29	With significant floral-jasmine note, weak fatty, aniseed and pepper	3	+++++	+++	++	
30	With significant floral-jasmine note, spicy, aniseed and pepper	3	+++++	++++	+++	
31	Lightly acidic, spicy, then reminiscent of <i>cis</i> -jasmone	2	++	++	+	

NMR-spectrometer (resp. 300 and 75 MHz) in CDCl<sub>3</sub> or DMSO solutions. Chemical shifts are given in parts per million, relatively 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<sup>-1</sup> scale. Mass spectra were recorded on an AMD 402 spectrometer (70 eV, EI). The optical rotation  $[\alpha]_D^{20}$  was measured on a PERKIN-ELMER 242B polarimeter using 1 dm glass tube at wavelength  $\lambda = 598 \,\mu\text{m}$ . Melting and boiling points were determined with the use of certified apparatus BÜCHI B-545 with warmup time 1 °C/min. Melting points were automatically determined in an open melting point capillary and were uncorrected. Boiling points were determined with sample observation in an open boiling point tubes with plunged capillaries. Product purification processes were performed with the use of column chromatography method on silica gel 60 (70-230 mesh) and appropriate solvent mixtures as an eluent. Solid products were purified in the crystallization process. Analytical data of C, H, N assays for all new compounds were analyzed on a VARIO EL III elementary analyzer and were within less than  $\pm 0.3\%$  of the theoretical values. The results were in the good agreement with the proposed structures.

### 3.2. Microwave assisted synthesis (MAOS)

Based on our earlier experiences [9], conditions of reactions conducted have been optimized both in the view of microwave power and reaction time as well as a composition of solid support.

# 3.2.1. Synthesis of pyrrolidinone, oxazolidinone and pyrazolidinone heteroanalogues of jasmone

3.2.1.1. General procedure for N-alkylation of compounds **8–10**. To the pulverized mixture of 0.5 mmol of TBAB, 20 mmol of potassium carbonate and 20 mmol of potassium hydroxide, 5 mmol of respective azole (**8**, **9** or **10**) and subsequently 7.5 mmol of appropriate 2-unsaturated pentyl bromide were added. Reagents, in a calibrated flask (transparent to microwave irradiation) with condenser, were irradiated for 4 min with 450 W power of microwaves. The crude product was extracted two times with the use of 20 ml of methylene chloride and the obtained organic solution was filtered and concentrated in vacuo. The residued crude oil was purified by a column chromatography, with the use of appropriate eluent, yielding pure product.

3.2.1.1.1. 5-Methyl-1-(2-trans-pentenyl)-2-pyrrolidinone (17). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide 0.49 g of 8 and subsequently 1.12 g of 1-bromo-2-trans-pentene were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.80 g (94%) of 17 as pale yellow oil (b.p. 262-266 °C).  $R_f = 0.71$  (chloroform:ethanol 10:1). MS, m/z (%): 167 (35) [M<sup>+</sup>], 152 (28), 138 (82), 125 (9), 112 (57); 98 (92), 84 (100), 69 (97), 56 (49). IR (cm<sup>-1</sup>): 1685 ( $\nu$  C=0). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.98 (t, I = 7.5 Hz, 3H, CH<sub>3</sub>-5'), 1.19 (d, I = 6.0 Hz, 3H, CH<sub>3</sub>), 1.56–1.62 (m, 2H, CH2-4), 2.02-2.10 (m, 2H, CH2-4'), 2.13-2.22 (m, 2H, CH2-3), 2.25-2.41 (m, 1H, CH<sub>2</sub>-1'), 3.41-3.50 (m, 1H, CH<sub>2</sub>-1'), 3.64-3.74 (m, 1H, CH-5), 5.27-5.37 (m, 1H, trans-CH=), 5.62-5.72 (m, 1H, trans-CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 13.32 (CH<sub>3</sub>), 22.04 (CH<sub>3</sub>-5'), 25.26 (C-4'), 31.28 (C-3), 32.93 (C-4), 38.63 (C-5), 67.78 (C-1'), 123.47/135.97 (*trans*-CH=CH), 170.20 (C=O).  $C_{10}H_{17}NO$  (167.2).  $[\alpha]_D^{20} = \sim 0^\circ$ .

3.2.1.1.2. 5-Methyl-1-(2-cis-pentenyl)-2-pyrrolidinone (18). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide 0.49 g of 8 and subsequently 1.12 g of 1-bromo-2-cis-pentene were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.65 g (78%) of **18** as pale yellow oil (b.p. 266-270 °C).  $R_f = 0.76$  (chloroform:ethanol 10:1). MS, m/z (%): 167 (34) [M<sup>+</sup>], 152 (27), 138 (82), 125 (9), 112 (58), 98 (91), 84 (100), 69 (98), 56 (49). IR (cm<sup>-1</sup>): 1685 ( $\nu$  C=0). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.99 (t, J = 7.5 Hz, 3H, CH<sub>3</sub>-5'), 1.20 (d, J = 6,3 Hz, 3H, CH<sub>3</sub>), 1.55–1.64 (m, 2H, CH2-4), 2.02-2.11 (m, 2H, CH2-4'), 2.13-2.27 (m, 2H, CH2-3), 2.32-2.49 (m, 1H, CH<sub>2</sub>-1'), 3.59-3.73 (m, superimposed bands: 1H (CH-5) and 1H (CH<sub>2</sub>-1')), 5.21–5.37 (m, 1H, cis-CH=), 5.51–5.72 (m, 1H, cis-CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 13.60 (CH<sub>3</sub>), 22.18 (CH<sub>3</sub>-5'), 25.28 (C-4'), 31.52 (C-3), 32.97 (C-4), 38.57 (C-5), 67.72 (C-1'), 123.39/134.12 (*cis*-CH=CH), 171.20 (C=O).  $C_{10}H_{17}NO$  (167.2).  $[\alpha]_D^{20} = \sim 0^\circ$ .

3.2.1.1.3. 5-Methyl-1-(2-pentynyl)-2-pyrrolidinone (**19**). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide, 0.49 g of **8** and subsequently 1.10 g of 1-bromo-2-pentyne were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.72 g (87%) of **19** as pale yellow oil (b.p. 281–285 °C).  $R_f = 0.66$  (chloroform:ethanol 10:1). MS, m/z (%): 165 (32)

 $[M^+], 150 (58), 136 (6), 124 (19), 112 (25), 98 (27), 84 (100), 70 (23), 55 (46), 41 (51). IR (cm^{-1}): 1685 ($\nu$ C=0). $^1H$ NMR (CDCl_3): $\delta$ = 1.12 (t,$ *J* $= 7.5 Hz, 3H, CH_3-5'), 1.25 (d,$ *J* $= 6.6 Hz, 3H, CH_3), 1.45-1.58 (m, 1H, CH_2-4'), 2.13-2.25 (m, superimposed bands: 2H (CH_2-4) and 1H (CH_2-4')); 2.52-2.74 (m, 2H, CH_2-3), 3.80-3.87 (m, 2H, CH_2-1'), 4.04-4.16 (m, 1H, CH-5). $^{13}C$ NMR (CDCl_3): $\delta$ = 12.52 (CH_3), 13.77 (CH_3-5'), 19.64 (C-4'), 22.02 (C-3), 31.39 (C-4), 38.36 (C-5), 67.97 (C-1'), 74.07/84.89 (C=C), 170.10 (C=O). $C_{10}H_{15}NO$ (165.1). $[\alpha]_{D}^{20} = ~0^{\circ}. $$ 

3.2.1.1.4. 4-Methyl-3-(2-trans-pentenyl)-2-oxazolidinone (20). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide 0.50 g of **9** and subsequently 1.12 g of 1-bromo-2-trans-pentene were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of hexane and ethyl acetate 1:1 as an eluent, yielding 0.73 g (85%) of 20 as colorless oil (b.p. 294-299 °C).  $R_f = 0.67$  (hexane:ethyl acetate 1:1). MS, m/z (%): 169 (26) [M<sup>+</sup>], 154 (11), 140 (84), 127 (2), 114 (78), 100 (6), 86 (17), 70 (23), 69 (36), 56 (36), 41 (100). IR (cm<sup>-1</sup>): 1685 ( $\nu$  C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.99$  (t, J = 7.5 Hz, 3H, CH<sub>3</sub>-5'), 1.25 (d, J = 6.0 Hz, 3H, CH<sub>3</sub>), 2.01– 2.16 (m, 2H, CH2-4'), 3.52-3.60 (m, 1H, CH2-1'), 3.79-3.93 (m, superimposed bands: 1H (CH<sub>2</sub>-1') and 2H (CH<sub>2</sub>-5)), 4.40 (t, *I* = 7.7 Hz, 1H, CH-4), 5.32–5.42 (m, 1H, *trans*-CH=), 5.58–5.79 (m, 1H, trans-CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 12.81 (CH<sub>3</sub>), 17.46 (CH<sub>3</sub>-5'), 24.62 (C-4'), 43.15 (C-4), 49.89 (C-1'), 68.34 (C-5), 121.94/136.03 (trans-CH=CH), 157.16 (C=O). C<sub>9</sub>H<sub>15</sub>NO<sub>2</sub> (169.0).  $[\alpha]_D^{20} = \sim 0^\circ$ .

3.2.1.1.5. 4-Methyl-3-(2-cis-pentenyl)-2-oxazolidinone (21). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide 0.50 g of 9 and subsequently 1.12 g of 1-bromo-2-cis-pentene were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of hexane and ethyl acetate 1:1 as an eluent, yielding 0.61 g (73%) of 21 as colorless oil (b.p. 297-302 °C).  $R_f = 0.76$  (hexane:ethyl acetate 1:1). MS, m/z (%): 169 (28) [M<sup>+</sup>], 154 (14), 140 (85), 127 (3), 114 (100), 100 (9), 86 (25), 70 (41), 69 (70), 56 (60). IR (cm<sup>-1</sup>): 1685 ( $\nu$  C=0). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.00  $(t, J = 7.5 \text{ Hz}, 3H, CH_3-5'), 1.26 (d, J = 6.0 \text{ Hz}, 3H, CH_3), 2.01-2.19 (m, J)$ 2H, CH<sub>2</sub>-4'), 3.72-3.90 (m, superimposed bands: 1H (CH<sub>2</sub>-1') and 2H (CH<sub>2</sub>-5)), 4.01–4.12 (m, 1H, CH<sub>2</sub>-1'), 4.39 (t, J = 7.5 Hz, 1H, CH-4), 5.28–5.42 (m, 1H, *cis*-CH=), 5.57–5.78 (m, 1H, *cis*-CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 13.82$  (CH<sub>3</sub>), 17.83 (CH<sub>3</sub>-5'), 24.86 (C-4'), 43.45 (C-4), 50.27 (C-1'), 68.65 (C-5), 122.31/135.85 (cis-CH=CH), 157.74 (C=O).  $C_9H_{15}NO_2$  (169.1).  $[\alpha]_D^{20} = \sim 0^\circ$ .

3.2.1.1.6. 4-Methyl-3-(2-pentynyl)-2-oxazolidinone (22). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide, 0.50 g of 9 and subsequently 1.10 g of 1bromo-2-pentyne were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of hexane and ethyl acetate 1:1 as an eluent, yielding 0.67 g (80%) of 22 as colorless oil (b.p. 310-315 °C).  $R_f = 0.62$  (hexane:ethyl acetate 1:1). MS, m/z (%):167 (20) [M<sup>+</sup>], 152 (9), 138 (1), 126 (27), 114 (11), 100 (8), 86 (100), 70 (21), 67 (45), 56 (16), 42 (84). IR (cm<sup>-1</sup>): 1685 ( $\nu$  C=0).<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.12$  (t, J = 7.5 Hz, 3H, CH<sub>3</sub>-5'), 1.28 (d, J = 6.6 Hz, 3H, CH<sub>3</sub>), 2.14– 2.24 (m, 2H, CH<sub>2</sub>-4'), 3.73-3.80 (m, 2H, CH<sub>2</sub>-5), 3.84-3.94 (m, 1H,  $CH_2-1'$ ), 4.19–4.28 (m, 1H,  $CH_2-1'$ ), 4.45 (t, J = 7.5 Hz, 1H, CH-4). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 12.60$  (CH<sub>3</sub>), 13.79 (CH<sub>3</sub>-5'), 21.38 (C-4'), 43.24 (C-4), 62.09 (C-1'), 73.37 (C-5), 75.67/77.42 (C=C), 163.82 (C=O).  $C_9H_{13}NO_2$  (167.1).  $[\alpha]_D^{20} = \sim 0^\circ$ .

3.2.1.1.7. 1-Methyl-2-(2-trans-pentenyl)-3-pyrazolidinone (**23**). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide, 0.50 g of **10** and subsequently 1.12 g of 1-bromo-2-*trans*-pentene were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.28 g (33%) of **23** as yellow oil (b.p. 228–234 °C).

 $R_{\rm f} = 0.66$  (chloroform:ethanol 10:1). MS, m/z (%): 168 (16) [M<sup>+</sup>], 153 (1), 139 (10), 126 (1), 113 (100), 99 (23), 85 (7), 69 (20), 57 (47). IR (cm<sup>-1</sup>): 1660 ( $\nu$  C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.90$  (t, J = 6.9 Hz, 3H, CH<sub>3</sub>-5'), 1.87–1.99 (m, 2H, CH<sub>2</sub>-4'), 2.58–2.67 (m, 2H, CH<sub>2</sub>-4), 3.30 (s, 3H, CH<sub>3</sub>), 3.45–3.54 (m, 2H, CH<sub>2</sub>-1'), 3.79–3.88 (m, 2H, CH<sub>2</sub>-5), 5.22–5.29 (m, 1H, *trans*-CH=), 5.58–5.64 (m, 1H, *trans*-CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 13.98$  (CH<sub>3</sub>-5'), 22.47 (C-4'), 43.20 (CH<sub>3</sub>), 50.54 (C-5), 58.97 (C-4), 65.18 (C-1'), 121.68/136.57 (*trans*-CH=CH), 167.64 (C=O). C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O (168.1).  $[\alpha]_D^{20} = \sim 0^{\circ}$ .

3.2.1.1.8. 1-Methyl-2-(2-cis-pentenyl)-3-pyrazolidinone (24). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide, 0.50 g of **10** and subsequently 1.12 g of 1-bromo-2-cis-pentene were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.25 g (30%) of **24** as yellow oil (b.p. 219–225  $^{\circ}$ C).  $R_{\rm f} = 0.70$  (chloroform:ethanol 10:1). MS, m/z (%): 168 (10) [M<sup>+</sup>], 153 (5), 139 (13), 126 (2), 113 (70), 99 (100), 85 (9), 69 (22), 57 (41). IR (cm<sup>-1</sup>): 1670 ( $\nu$  C=0). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.10 (t, J = 6.9 Hz, 3H, CH<sub>3</sub>-5'), 2.17-2.23 (m, 2H, CH<sub>2</sub>-4'), 2.62-2.68 (m, 2H, CH<sub>2</sub>-4), 3.32 (s, 3H, CH<sub>3</sub>), 3.40-3.51 (m, 2H, CH<sub>2</sub>-1'), 3.81-3.92 (m, 2H, CH<sub>2</sub>-5), 5.25–5.31 (m, 1H, *cis*-CH=), 5.59–5.65 (m, 1H, *trans*-CH=). <sup>13</sup>C NMR  $(CDCl_3): \delta = 13.86 (CH_3-5'), 22.52 (C-4'), 43.45 (CH_3), 50.87 (C-5),$ 59.03 (C-4), 65.23 (C-1'), 121.88/136.67 (cis-CH=CH), 167.87 (C=O).  $C_9H_{16}N_2O$  (168.1).  $[\alpha]_D^{20} = \sim 0^\circ$ .

3.2.1.1.9. 1-Methyl-2-(2-pentynyl)-3-pyrazolidinone (**25**). To the mixture of 0.16 g of TBAB, 2.76 g of potassium carbonate and 1.12 g of potassium hydroxide 0.50 g of **10** and subsequently 1.10 g of 1-bromo-2-pentyne were added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography, using a mixture of chloroform and ethanol 10:1 as an eluent, yielding 0.20 g (25%) of **25** as yellow oil (b.p. 234–240 °C). *R*<sub>f</sub> = 0.63 (chloroform:ethanol 10:1). MS, *m/z* (%): 166 (2) [M<sup>+</sup>], 151(3), 137 (6), 125 (3), 113 (100), 99 (11), 81 (41), 67 (25). IR (cm<sup>-1</sup>): 1680 ( $\nu$  C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.92 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>-5'), 1.85–1.97 (m, 2H, CH<sub>2</sub>-4'), 2.54–2.65 (m, 2H, CH<sub>2</sub>-4), 3.33 (s, 3H, CH<sub>3</sub>), 3.81–3.92 (m, superimposed bands: 2H (CH<sub>2</sub>-1') and 2H (CH<sub>2</sub>-5)). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 13.89 (CH<sub>3</sub>-5'), 2.63 (C-4'), 43.53 (CH<sub>3</sub>), 50.91 (C-5), 60.23 (C-4), 65.76 (C-1'), 75.62/77.31 (CH≡CH), 168.03 (C=O). C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O (166.1). [α]<sub>2</sub><sup>D</sup> = ~0°.

#### 3.2.2. Synthesis of pyrazolone heteroanalogues of jasmone

Compounds **11–13**, necessary to obtain pyrazolone heteroanalogues, were prepared according to the method described earlier [9].

3.2.2.1. General procedure for cyclocondensation to pyrazolone cycles. To the solution of 5 mmol of ethyl 2-alkyl acetylacetate (**11**, **12** or **13**) in 20 ml of anhydrous ethanol, 10 mmol of 99% hydrazine hydrate was added. Reagents, in a calibrated flask with condenser, were irradiated for 10 min with 160 W power of microwaves. The obtained solution was concentrated in vacuo, yielding crude product, which was purified by crystallization from benzene.

3.2.2.1.1. 5-Methyl-4-(2-trans-pentenyl)-1,2-dihydro-3-pyrazolone (**26**). To the solution of 0.99 g of **11** in 20 ml of anhydrous ethanol, 0.50 g of 99% hydrazine hydrate was added. Reagents were irradiated in the microwave reactor. The crude product was isolated and crystallized from benzene yielding 0.50 g (60%) of white crystals (m.p. 178–182 °C). MS, m/z (%): 166 (9) [M<sup>+</sup>], 151 (3), 137 (23), 124 (2), 111 (100), 97 (4), 82 (5), 69 (13), 53 (7), 41 (16). IR (cm<sup>-1</sup>): 1600 ( $\nu$  C=O). <sup>1</sup>H NMR (DMSO):  $\delta$  = 0.85 (t, *J* = 6.8 Hz, 3H, CH<sub>3</sub>-5'), 2.02 (s, 3H, CH<sub>3</sub>), 2.01–2.09 (m, 2H, CH<sub>2</sub>-4'), 3.25–3.30 (m, 2H, CH<sub>2</sub>-1'), 5.30–5.38 (m, 2H, *trans*-CH=CH), 9.21 (br s, 1H, NH), 10.99 (br s, 1H, NH). <sup>13</sup>C NMR (DMSO):  $\delta$  = 9.91 (CH<sub>3</sub>), 14.04 (CH<sub>3</sub>-5'), 2.02 (C-4'), 24.80 (C-2'), 98.73 (C-4), 127.84/130.71 (*trans*-CH=CH), 136.52 (C-5), 159.15 (C=O). C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O (166.1). [ $\alpha$ ]<sub>D</sub><sup>D</sup> =  $\sim$ 0°.

3.2.2.1.2. 5-Methyl-4-(2-cis-pentenyl)-1,2-dihydro-3-pyrazolone (**27**). To the solution of 0.99 g of **12** in 20 ml of anhydrous ethanol, 0.50 g of 99% hydrazine hydrate was added. Reagents were irradiated in the microwave reactor. The crude product was isolated and crystallized from benzene yielding 0.42 g (51%) of white crystals (m.p. 180–183 °C). MS, *m*/*z* (%): 166 (9) [M<sup>+</sup>] 151 (2), 137 (23), 124 (3), 111 (100), 97 (4), 82 (4), 69 (12), 53 (7), 41 (15). IR (cm<sup>-1</sup>): 1600 ( $\nu$  C=O). <sup>1</sup>H NMR (DMSO):  $\delta$  = 0.91 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>-5'), 2.01 (s, 3H, CH<sub>3</sub>), 1.91–2.20 (m, 2H, CH<sub>2</sub>-4'), 2.89–2.94 (m, 2H, CH<sub>2</sub>-1'), 5.27–5.42 (m, 2H, *cis*-CH=CH), 10.24 (br s, 1H, NH), 10.96 (br s, 1H, NH). <sup>13</sup>C NMR (DMSO):  $\delta$  = 9.95 (CH<sub>3</sub>), 14.02 (CH<sub>3</sub>-5'), 19.09 (C-4'), 24.78 (C-2'), 98.74 (C-4), 127.63/130.48 (*cis*-CH=CH), 136.53 (C-5), 159.16 (C=O). C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O (166.1). [ $\alpha$ ]<sub>D</sub><sup>D</sup><sup>0</sup> = ~0°.

3.2.2.1.3. 5-Methyl-4-(2-pentynyl)-1,2-dihydro-3-pyrazolone (**28**). To the solution of 0.98 g of **13** in 20 ml of anhydrous ethanol, 0.50 g of 99% hydrazine hydrate was added. Reagents were irradiated in the microwave reactor. The crude product was isolated and crystallized from benzene yielding 0.44 g (54%) of white crystals (m.p. 189–194 °C). MS, *m*/*z* (%): 164 (93) [M<sup>+</sup>], 149 (45), 135 (100), 123 (21), 111 (23), 97 (11), 77 (21), 67 (28), 55 (7), 41 (38). IR (cm<sup>-1</sup>): 1600 ( $\nu$  C=O). <sup>1</sup>H NMR (DMSO):  $\delta$  = 1.02 (t, *J* = 7.5 Hz, 3H, CH<sub>3</sub>-5'), 2.09 (s, 3H, CH<sub>3</sub>), 2.02–2.15 (m, 2H, CH<sub>2</sub>-4'), 3.37 (m, 2H, CH<sub>2</sub>-1'), 9.53 (br s, 1H, NH), 11.15 (br s, 1H, NH). <sup>13</sup>C NMR (DMSO):  $\delta$  = 10.10 (CH<sub>3</sub>), 11.20 (C-4'), 11.78 (C-2'), 14.20 (CH<sub>3</sub>-5'), 78.02/80.35 (C=C), 96.40 (C-4), 102.38 (C-5), 158.55 (C=O). C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>O (164.1). [ $\alpha$ ]<sup>D</sup><sub>2</sub> = ~0°.

#### 3.2.3. Synthesis of thiazolidinone heteroanalogues of jasmone

Compounds **14–16**, necessary to obtain thiazolidinone heteroanalogues, were prepared by using the general *N*-alkylation method [16].

3.2.3.1. General procedure for cyclocondensation to thiazolidinone cycles. In 10 ml of methylene chloride, 2 mmol of appropriate *N-mono*-substituted 2-mercaptoacetamide (14, 15 or 16) and catalytic amount of *p*-toluenesulfonic acid were dissolved. To the obtained solution, 2 g montmorilonite K10-clay was added and mixed. After evaporation of solvent, to the dry mixture 10 mmol of acetaldehyde was added. Reagents, in a calibrated flask (transparent to microwave irradiation) with condenser, were irradiated for 5 min with 200 W power of microwaves. The crude product was extracted two times with the use of 20 ml of methylene chloride and the obtained organic solution was filtered and concentrated in vacuo. The residued crude oil was purified by a column chromatography, with the use of mixture of hexane and ethyl acetate 1:1 as an eluent, yielding pure product.

3.2.3.1.1 2-Methyl-3-(2-trans-pentenyl)-4-thiazolidinone (**29**). To the prepared dry mixture of 0.32 g of **14**, 2 g of K10-clay and *p*-toluenesulfonic acid, 0.44 g of acetaldehyde was added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography yielding 0.23 g (65%) of **29** as pale yellow oil (b.p. 278–283 °C).  $R_f$ = 0.59 (hexane:ethyl acetate 1:1). MS, *m*/*z* (%): 185 (9) [M<sup>+</sup>], 170 (6), 156 (10), 143 (2), 130 (2), 116 (3), 101 (3), 84 (10), 69 (100), 56 (14). IR (cm<sup>-1</sup>): 1680 (*v* C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.88 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>-5'), 1.61 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 2.01–2.12 (m, 2H, CH<sub>2</sub>-4'), 3.51–3.62 (m, 2H, CH<sub>2</sub>-1'), 3.70–3.81(m, 2H, CH<sub>2</sub>-5), 4.92 (q, *J* = 6.2 Hz, 1H, CH-2), 5.32–5.42 (m, 1H, *trans*-CH=), 5.58–5.79 (m, 1H, *trans*-CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 13.54 (CH<sub>3</sub>-5'), 22.25 (CH<sub>3</sub>), 23.87 (C-4'), 46.25 (C-2), 49.63 (C-5), 58.21 (C-1'), 127.84/130.71 (*trans*-CH=CH), 173.63 (C=O). C<sub>9</sub>H<sub>15</sub>NOS (185.1). [ $\alpha$ ]<sup>D</sup><sup>D</sup><sup>2</sup> =  $\sim$ 0°.

3.2.3.1.2. 2-Methyl-3-(2-cis-pentenyl)-4-thiazolidinone (**30**). To the prepared dry mixture of 0.32 g of 15, 2 g of K10-clay and *p*-toluenesulfonic acid, 0.44 g of acetaldehyde was added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography yielding 0.24 g (66%) of **30** as

pale yellow oil (b.p. 270–275 °C).  $R_f = 0.65$  (hexane:ethyl acetate 1:1). MS, m/z (%): 185 (7) [M<sup>+</sup>], 170 (10), 156 (12), 143 (4), 130 (7), 116 (9), 101 (5), 84 (13), 69 (100), 56 (11). IR (cm<sup>-1</sup>): 1680 ( $\nu$  C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.90$  (t, J = 7.1 Hz, 3H, CH<sub>3</sub>-5'), 1.63 (d, J = 6.2 Hz, 3H, CH<sub>3</sub>), 2.00–2.08 (m, 2H, CH<sub>2</sub>-4'), 3.50–3.58 (m, 2H, CH<sub>2</sub>-1'), 3.67–3.77 (m, 2H, CH<sub>2</sub>-5), 4.94 (q, J = 6.0 Hz, 1H, CH-2), 5.28–5.39 (m, 1H, *cis*-CH=), 5.47–5.69 (m, 1H, *cis*-CH=). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 13.49$  (CH<sub>3</sub>-5'), 22.00 (CH<sub>3</sub>), 23.83 (C-4'), 46.21 (C-2), 49.60 (C-5), 58.18 (C-1'), 127.80/130.61 (*cis*-CH=CH), 173.63 (C=O). C<sub>9</sub>H<sub>15</sub>NOS (185.1).  $[\alpha]_D^{20} = \sim 0^{\circ}$ .

3.2.3.1.3. 2-Methyl-3-(2-pentynyl)-4-thiazolidinone (**31**). To the prepared dry mixture of 0.32 g of **16**, 2 g of K10-clay and *p*-tolue-nesulfonic acid, 0.44 g of acetaldehyde was added. Reagents were irradiated in the microwave reactor. The crude product was purified by a column chromatography yielding 0.22 g (60%) of **31** as pale yellow oil (b.p. 319–325 °C).  $R_f$ = 0.50 (hexane:ethyl acetate 1:1). MS, m/z (%): 183 (29) [M<sup>+</sup>], 168 (62), 154 (15), 142 (20), 130 (8), 117 (16), 100 (20), 86 (100), 67 (77). IR (cm<sup>-1</sup>): 1680 ( $\nu$  C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.10 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>-5'), 1.60 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 2.09–2.16 (m, 2H, CH<sub>2</sub>-4'), 3.64–3.75 (m, 2H, CH<sub>2</sub>-5), 3.83–3.94 (m, 2H, CH<sub>2</sub>-1'), 4.93 (q, *J* = 6.2 Hz, 1H, CH-2). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 13.49 (CH<sub>3</sub>-5'), 22.00 (CH<sub>3</sub>), 23.83 (C-4'), 46.57 (C-2), 48.96 (C-5), 64.19 (C-1'), 74.81/86.71 (C=C), 174.43 (C=O). C<sub>9</sub>H<sub>13</sub>NOS (183.2). [ $\alpha$ ]<sub>D</sub><sup>D</sup><sup>0</sup> =  $\sim$ 0°.

#### 3.3. Test of odor evaluation

Fragrant properties of the obtained compounds were performed according to the Polish Standard Methodology PN-ISO 5496, which is in accordance with the International Standard ISO 5496:1992(E). Direct sniffing strips methodology was employed to the odor analysis. Tests of odor evaluation were performed using 10% (v/v for fluids and w/v for solid) ethanol solutions of samples 17-31. Three drops of prepared solution were absorbed on a Whatman smelling blotter (thin strip of highly absorbent paper) and take care of it so that they did not touch. When the ethanol evaporated, the strips with the sample were performed for organoleptic analyses by nontraining assessors. The evaluating panel is a group of persons recognized to have normal olfaction sensitivity. Odor-assessors were over 18 years old and both sex. The odor was evaluated by sniffing the air under the testing strip gently moving them few centimeters in front of the nose, to such manner so that it did not touch the nose. The odor characteristic and intensity of each sample were compared with the sample of *cis*-jasmone (commercial product of Aldrich) similar solution. Durability of the scents was studied after 1, 6 and 24 h. In the case of highest odor durability samples 18 and 21, which smelt after 6 days even, additionally the odor durability was determined after next 24 h to their odor decline. The testing strips were held on a special holder stand in well ventilated work-room. The test of odor evaluation was repeated to confirm the results.

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