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EFFECT OF OXYGEN INCORPORATION INTO CYCLOHEXANONE RING ON ANTIFEEDANT ACTIVITY

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Abstract: The behaviour of the peach potato aphid *Myzus persicae* (Sulz.) was studied during settling on plants. The experiment involved observing peach potato aphid activity after the application of some natural and synthetic cyclohexanones and the, respective ε-lactones and epoxy-ε-lactones which were obtained from the cyclohexanones. Stereochemistry, and the number and position of methyl substituents were important for the biological activity of the starting compounds: only trimethyl-substituted cyclohexanones were active, *i.e.* 3.3.5-trimethylcyclohexanone (deterrent) and 2.2.6-trimethylcyclohexanone (attractant). The effect of oxygen incorporation into the cyclohexanone ring on deterrent activity varied depending on the starting compound. The ε-lactones that derived from saturated cyclohexanones were either weak attractants or were inactive, except the deterrent ε-lactone with three methyl groups at positions 3.7.7. None of the products of unsaturated ketone isophorone (weak deterrent) oxidation, *i.e.* epoxy isophorone, epoxy lactone, or unsaturated lactone, affected aphid settling. Of the two epoxy ketones obtained from (+)-dihydrocarvone that was inactive, only (2S, 5S)-2-methyl-5-((S)-1-methyloxiranyl)-cyclohexanone was a strong deterrent. Both epoxy-ε-lactones that derived from (+)-dihydrocarvone were strong deterrents.

Key words: *Myzus persicae*, feeding deterrents, ε-lactones, epoxy-ε-lactones

INTRODUCTION

The peach potato aphid *Myzus persicae* (Sulz.) is a polyphagous aphid species that feeds on secondary hosts of over 40 different plant families. It is also the most important insect vector of more than 100 plant viruses (Capinera 2004). At present, aphid control depends mainly on the use of insecticides. Due to the repeated applications, many aphid species have developed resistance to several chemical aphicides. The peach potato aphid has developed an especially strong resistance to aphicides. Therefore, a more specific alternative method of aphid control is needed. The use of targeted chemicals that would repell aphids or deter their feeding is one of the most promising approaches. The reduced feeding may, in consequence, cause the rejection of a plant or affect aphid development, fecundity, and longevity, which finally leads to collapse. The most interesting discoveries for insect control include ajugarin, azadirachtin, and polygodial. The sesquiterpenoid polygodial was successfully applied in the field against bird cherry-oat aphid *Rhopalosiphum padi*. Sesquiterpenoid polygodial gave similar outcomes to the results obtained with cypermethrin (Pickett *et al*. 1994).

Insect feeding deterrents (antifeedants) belong to different chemical groups and were initially found in natural sources (Wawrzyniak 1996; Klein Gebbinck *et al*. 2002; Wawrzeńczyk *et al*. 2002). Compounds with the lactone moiety are commonly occurring natural products and frequently exhibit antifeedant properties against insects (Picman 1986). The use of natural compounds on a wide scale, however, is costly. For this reason, there is a strong demand for synthetic, behaviour modyfing chemicals which are simple to obtain in the laboratory. In the present work we were interested in whether the incorporation of oxygen into the cyclohexanone ring creating a lactone moiety, would affect the biological activity. We were especially interested in the starting compound's antifeedant activity against aphids. We studied the behaviour of *M. persicae* during settling on plants. The study concerned settling after the application of natural and synthetic cyclohexanones, and the respective ε-lactones and epoxy-ε-lactones of the cyclohexanones.

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MATERIALS AND METHODS

Chemical compounds

The chemical compounds: 2-Methylcyclohexanone (1a), 3-methylcyclohexanone (1b), 4-methylcyclohexanone (1c), 3.3.5-trimethylcyclohexanone (1e) were purchased from Sigma–Aldrich Chemical Co. The chemical compounds: 2.2.6-trimethylcyclohexanone (1d), 2-isopropyl-5-methylcyclohexanone (1f), isophorone (1g) and (+)-dihydrocarvone (1h) were purchased from Fluka BioChemika.

The racemic (2a–f, 3b, 3e, 3g, 4g) and optically active (2h, 3h) ε-lactones were prepared by the oxidation of corresponding ketones (1a–h) with *m*-chloroperbenzoic acid (*m*-CPBA) in dichloromethane according to the method described by us earlier (Ratuś *et al*. 2006; Ratuś *et al*. 2009). The yields, physical and spectral data of lactones 2b, 3b, 2c, 2e, 3e, 2f, 4g, epoxy lactones 2h, 3h, epoxy ketones 4h, 5h were presented in Ratuś *et al*. (2009), and lactones 2a, 2d, epoxy ketone 2g and epoxy lactone 3g in Ratuś *et al*. (2006). The purity of the tested compounds was higher than 97% as determined by gas chromatography using capillary columns: Thermo TR-5 (30 m x 0.32 mm x 1.0 μm) and Agilent DB-17 (30 m x 0.25 mm x 0.25 μm).

Biological tests

Aphids (*M. persicae*) and plants (Chinese cabbage *Brassica pekinensis*) were reared in the laboratory at 20°C, 65% RH, and L16 : 8D photoperiod. All experiments were carried out under the same conditions.

The compounds were applied to the adaxial surface of a leaf as 0.1% ethanolic solutions, on 0.01 ml/cm^2 of the leaf, according to the method described by Polonsky *et al.* (1989). All biological tests were performed 1 hour after the application of the compounds, to allow for the evaporation of the solvent.

The feeding deterrence was assessed by a choice-test, in which the aphid settling on plants was observed. The compounds were applied on one half of the leaf. The other side of the leaf midrib was treated with ethanol and acted as the control. Aphids had a choice between treated and control surfaces. Aphids that settled, *i.e.* they did not move and the position of their antennae indicated feeding (Hardie *et al*. 1992) on each side of the midrib were counted at 1h, 2h, and 24h intervals after access to the leaf (8 replicates, 20 viviparous apterous females/replicate). The data were analyzed using the Mann-Whitney U-test (STATISTICA 6.1. package). If aphids showed a clear preference for the half of the leaf treated with the tested compound ($p < 0.05$), the compound was described as having **attractant** properties. If aphids settled mainly on the control half of the leaf ($p < 0.05$), the compound tested in the respective choice-test was stated a feeding **deterrent**. From the data thus obtained, the relative (R) coefficient of deterrence was calculated using the formula according to Nawrot *et al.* (1982):

$$R = (C–T/C+T)$$

Where:

C – the number of aphids settled on the control half of the leaf

T – the number of aphids settled on the half of the leaf treated with the tested compound.

Negative values of R indicated attractant properties and positive R values – the deterrent ones.

RESULTS AND DISCUSSION

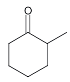
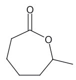
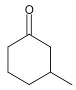
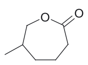
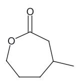
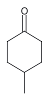
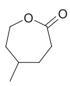
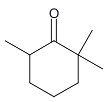
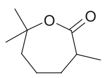
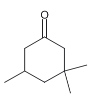
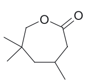
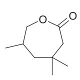
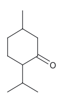
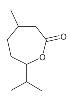
The Baeyer-Villiger oxidation of methyl and trimethyl substituted saturated cyclohexanones (1a–1f) with *m*–CPBA gave respective ε-lactones (2a–2f, 3b, and 3e) (Table 1). It is noteworthy, that in the reaction of cyclohexanones with alkyl substituents in the α position to carbonyl group, only one product was formed. The regioselectivity of Baeyer-Villiger oxidation was lower in the reaction of cyclohexanones with methyl substituents in β positions. From the ketones 1b and 1e**,** the mixtures of two products 2b, 3b and 2e, 3e**,** respectively, were obtained. More complex mixtures of products were formed in the oxidation of unsaturated ketones 1g and 1h. The oxidation of isophorone (1g) with application of 1.1 or 2.2 equiv. of *m*-CPBA per 1 equiv. of ketone, afforded mixture of epoxy ketone 2g, epoxy lactone 3g and unsaturated ε-lactone 4g. The oxidation of (+)-*R*-dihydrocarvone (1h) with 1.1 or 2.2 equiv. of *m*-CPBA led to a mixture of diastereoisomeric epoxy ketones 4h, 5h and epoxy lactones 2h, 3h. The increase in the amount of *m*-CPBA to 3.0 equiv. per 1 equiv. of unsaturated ketone led to the formation of only epoxy lactones 2h and 3h. The analysis of the composition of reaction mixture, in the course of the process, indicated that the epoxy ketones 4h and 5h were formed first and then they were transformed into epoxy lactones 2h and 3h.

The starting compounds, *i.e.* methyl and trimethyl substituted cyclohexanones, varied in biological activity. Ketones 1a and 1b did not affect aphid behaviour either at the beginning or at the end of the experiment. Ketone 1c showed attractant activity 24 hours after application (R = –0.5) (Table 1, Fig. 1A). Ketone 1d showed deterrent activity at the beginning of the experiment and attractant 24 hours later (Fig. 1A). Ketone 1e was a deterrent, whose index of deterrence reached 0.6 in the first hour of the experiment. Later, its activity slightly decreased but remained relatively high (R = 0.4) until the end of experiment (24 hours after application).

The ε-lactones, that derived from respective cyclohexanones, also differed in biological activity. Generally, the incorporation of oxygen into methyl and trimethyl substituted cyclohexanones did not have any significant effect on biological activity, except for the oxidation of ketones 1a and 1e. The oxidation of ketone 1a led to lactone 2a that had weak attractant properties (R value after 24 hours: –0.2), and the oxidation of ketone 1e reduced its deterrent activity dramatically. Lactone 2d showed weak deterrent activity (R = 0.2 throughout the experiment). Neither of the lactones, 2e and 3e had any effect on aphid settling (Table 1, Fig. 1A).

The naturally occurring unsaturated cyclic ketone isophorone 1g showed deterrent properties 24 hours after

Table 1. Deterrent effect of methyl and trimethyl substituted cyclohexanones 1a–1f and products of their oxidation, the respective ε-lactones 2a–2f, 3b and 3e. Numbers represent means ±SE of 8 replications; statistically significant differences in aphid settling behaviour at $p < 0.05$ according to Mann-Whitney U-test

Compound	Symbol/Name		Number of aphids		
			1 h	2 h	24 h
	1a	control	7.6±0.9	7.1±0.9	4.8±0.9
	2-methylcyclohexanone	test	8.0±1.1	6.0±1.1	2.6±0.7
		P	0.7871	0.4453	0.0731
	2a	control	2.4±0.9	3.1±1.1	4.2±0.5
	7-methyl-1-oxepan-2-one	test	5.6±1.0	6.6±0.8	6.0±0.5
		P	0.0316	0.0195	0.0256
	1b	control	5.6±1.1	6.3±1.5	5.1±1.2
	3-methylcyclohexanone	test	4.5±0.5	5.0±0.7	7.1±1.1
		P	0.3563	0.4599	0.2503
	2b	control	7.4±1.1	7.6±1.2	8.2±1.1
	6-methyl-1-oxepan-2-one	test	10.0±1.1	9.9±0.9	10.2±1.1
		P	0.1165	0.1660	0.2250
	3b	control	8.5±1.1	6.9±0.9	5.5±0.9
	4-methyl-1-oxepan-2-one	test	10.0±1.2	11.1±0.6	6.6±1.4
		P	0.3779	0.0026	0.5163
	1c	control	7.0±1.3	5.3±1.3	2.3±0.3
	4-methylcyclohexanone	test	8.9±1.3	6.6±0.6	6.1±0.6
		P	0.3195	0.3623	0.0004
	2c	control	7.4±1.0	7.6±0.9	7.9±0.7
	5-methyl-1-oxepan-2-one	test	6.1±1.1	6.4±1.0	9.2±0.6
		P	0.4164	0.3601	0.1692
	1d	control	8.5±1.2	5.8±0.9	2.5±0.3
	2.2.6-trimethylcyclohexanone	test	3.8±0.5	3.9±1.0	5.9±1.7
		P	0.0041	0.0359	0.7336
	2d	control	8.2±0.9	10.4±1.3	10.1±1.3
	3.7.7-trimethyl-1-oxepan-2-one	test	5.4±0.8	6.1±0.7	6.6±0.7
		P	0.0336	0.0123	0.0355
	1e	control	13.3±1.3	13.3±1.2	13.8±1.1
	3.3.5-trimethylcyclohexanone	test	3.8±0.9	4.5±1.1	5.9±0.9
		P	0.0000	0.0001	0.0001
	2e	control	9.1±0.9	9.9±0.9	9.7±0.9
	4.6.6- trimethyl-1-oxepan-2-one	test	8.7±0.9	8.2±1.1	7.6±1.3
		P	0.7814	0.2746	0.2024
	3e	control	9.1±0.9	9.4±0.8	9.2±0.7
	4.4.6- trimethyl-1-oxepan-2-one	test	8.0±0.4	8.1±0.6	7.5±0.9
		P	0.2266	0.2268	0.1540
	1f	control	6.3±1.2	6.5±1.3	3.4±0.7
	2-isopropyl-5-methylcyclohexanone	test	6.3±0.8	5.5±0.7	3.0±0.6
		P	1.0000	0.5091	0.7079
	2f	control	8.6±1.4	9.3±1.0	7.2±0.7
	7-isopropyl-4-methyl-1-oxepan-2-one	test	7.1±1.4	5.0±1.0	5.4±1.1
		P	0.4664	0.00 83	0.1642

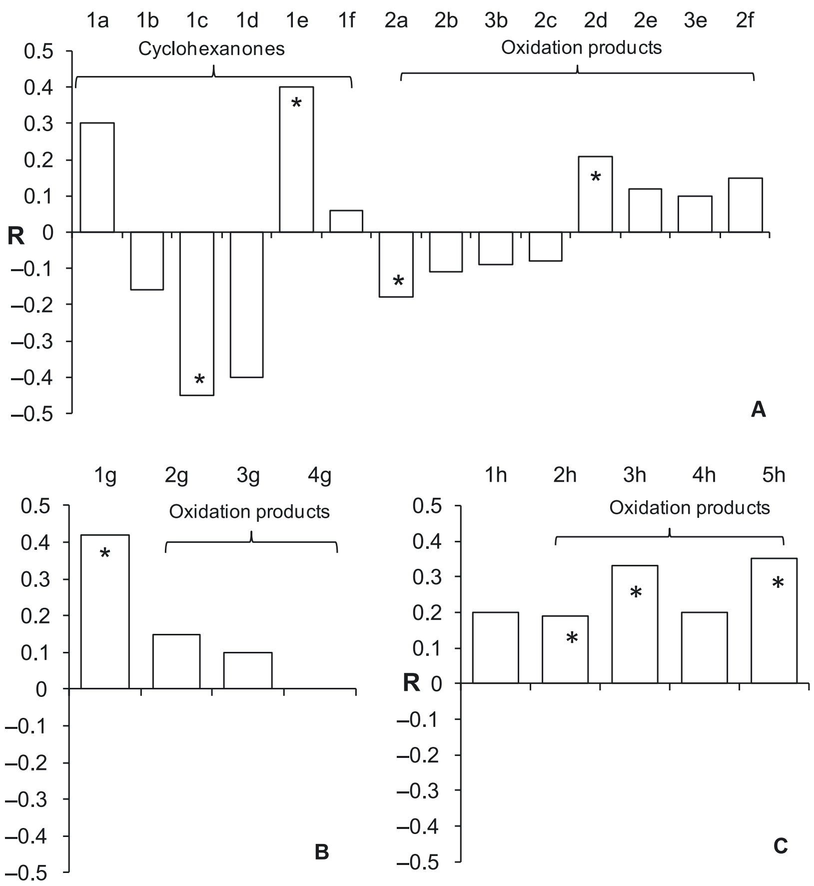


Fig. 1. Index of deterrence (R) for cyclohexanones and products of their oxidation. A – Methyl and trimethyl substituted cyclohexanones 1a–1f and products of their oxidation, the respective ε-lactones 2a–2f, 3b and 3e. B – Isophorone 1g and products of its oxidation, the respective lactone 4g, epoxy ketone 2g and epoxy lactone 3g. C - (+)-Dihydrocarvone 1h and products of its oxidation, the respective epoxy ketones 4h–5h and epoxy lactones 2h–3h. Asterisks indicate statistically significant biological activity according to the Mann-Whitney U-test results ($p < 0.05$): $R < 0$ – attractant, $R > 0$ – deterrent

Table 2. Deterrent effect of isophorone 1g and products of its oxidation, the respective lactone 4g, epoxy ketone 2g, and epoxy lactone 3g. Numbers represent means ±SE of 8 replications; statistically significant differences in aphid settling behaviour at $p < 0.05$ according to Mann-Whitney U-test

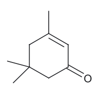
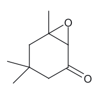
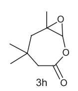
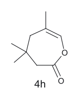
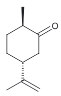
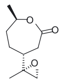
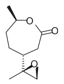
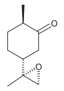
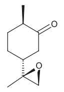
Compound	Symbol/Name		Number of aphids		
			1 h	2 h	24 h
	1g 3.5.5-trimethyl-cyclohex-2-en-1-one	control	1.4±0.2	3.9±0.6	4.4±0.8
		test	2.6±0.5	4.4±0.7	1.8±0.4
		P	0.0335	0.6076	0.0098
	2g 4.4.6-trimethyl-7-oxabicyclo[4.1.0]heptan-2-one	control	1.7±0.6	7.3±0.9	6.1±0.7
		test	0.8±0.4	4.0±1.2	4.5±1.6
		P	0.1566	0.0507	0.3760
	3g 5.5.7-trimethyl-2.8-dioxabicyclo[5.1.0]octan-3-one	control	6.5±0.9	6.5±0.8	6.5±1.1
		test	6.7±0.9	7.4±1.1	5.4±0.9
		P	0.8493	0.5270	0.4393
	4g 4.4.6-trimethyl-1-oxepan-6-en-2-one	control	6.5±1.1	4.1±0.8	0.9±0.3
		test	4.9±1.1	2.6±1.2	0.9±0.4
		P	0.3162	0.3083	1.0000

Table 3. Deterrent effect of (+)-dihydrocarvone 1h and products of its oxidation, the respective epoxy ketones 4h–5h and epoxy lactones 2h–3h. Numbers represent means ±SE of 8 replications; statistically significant differences in aphid settling behaviour at $p < 0.05$ according to Mann-Whitney U-test

Compound	Symbol/Name		Number of aphids		
			1 h	2 h	24 h
	1h	control	11.1±1.3	5.3±1.1	4.5±1.2
	2R.5R-5-iso-propenyl-2-methylcyclohexanone	test	5.4±1.1	4.9±1.1	3.0±0.8
		P	0.0049	0.8122	0.3149
	2h	control	10.4±0.8	11.2±0.7	10.9±0.9
	(4S. 7S)-7-methyl-4-((R)-1-methyloxiranyl)-1-oxepan-2-one	test	5.7±0.5	6.2±0.5	7.4±1.0
		P	0.0003	0.0000	0.0186
	3h	control	9.2±0.9	10.2±0.8	11.7±0.9
	(4S. 7S)-7-methyl-4-((S)-1-methyloxiranyl)-1-oxepan-2-one	test	4.6±0.7	4.9±0.7	5.9±0.5
		P	0.0013	0.0002	0.0000
	4h	control	8.6±0.9	6.6±1.0	6.5±1.4
	(2S. 5S)-2-methyl-5-((R)-1-methyloxiranyl)-cyclohexanone	test	7.4±0.8	5.6±0.8	4.3±0.9
		P	0.3007	0.4524	0.2011
	5h	control	12.3±1.3	10.4±1.9	10.1±2.1
	(2S. 5S)-2-methyl-5-((S)-1-methyloxiranyl)-cyclohexanone	test	5.5±1.1	3.8±0.7	4.9±0.7
		P	0.0015	0.0048	0.0313

application (R = 0.4). The oxidation of 1g caused the loss of this activity. Neither the epoxy ketone 2g, the epoxy lactone 3g nor the unsaturated ε-lactone 4g had any effect on aphid settling (Table 2, Fig. 1B).

(+)-Dihydrocarvone (1h) showed deterrent properties only at the beginning of the experiment (R = 0.3; 1 hour after application) (Table 3, Fig. 1C). Both epoxy lactones 2h and 3h, reduced aphid settling for 24 hours after application. The epoxy ketone 4h did not affect aphid settling, while its stereoisomer 5h had a strong negative effect on aphid settling behaviour (R = 0.4 throughout the experiment) (Table 3, Fig. 1C.).

The biological activity of cyclohexanones and products of their oxidation was monitored at three time intervals during the experiment, *i.e.* 1, 2, and 24 hours after aphids had access to the treated leaves. Ketone 1e, lactone 2d and compounds with epoxy group (2h, 3h, and 5h) showed the most stable strong deterrent activity. However, in some cases there were differences in aphid response to various substances in the course of time (*e.g.* 1b, 1c, 1d, 1g, and 3g). In the case of ketones 1d and 1g, the switch from negative aphid response (deterrent activity of the compound) to positive (attractant activity of the compound) or otherwise, respectively, was statistically significant (Tables 1, 2).

In conclusion, as far as the structure-activity aspect of this study is concerned, our experiments showed that in the case of alkyl-substituted cyclohexanones, the number and position of alkyl substituents and stereochemistry of cyclohexanone molecule was important for the deterrent activity: only trimethyl-substituted cyclohexanones were biologically active. 3.3.5-trimethylcyclohexanone (1e) was an active deterrent and 2.2.6-trimethylcyclohexanone (1d) was a weak attractant. In the case of the unsaturated ketone isophorone 1g, none of the derived products: epoxy isophorone (2g), epoxy lactone 3g, and unsaturated lactone 4g showed biological activity. Of the two epoxy ketones 4h and 5h that were obtained from (+)-dihydrocarvone, [(2S, 5S)-2-methyl-5-(R)-1-methyloxiranyl]-cyclohexanone (4h) was inactive, while [(2S,5S)-2-methyl-5-(S)-1-methyloxiranyl]-cyclohexanone (5h) was a strong deterrent. The ε-lactones showed either weak attractant properties (2a, 3b) or were inactive (2b, 2c, 2e, 3e, 2f). The only active deterrent was ε-lactone 2d with three methyl groups at positions 3.3.7. On the contrary, both epoxy-ε-lactones 2h and 3h that derived from (+)-dihydrocarvone were strong deterrents.

The results of the experiments presented here illustrate three major aspects of biological activity of the studied compounds, *i.e.* the variation in the stability of deterrent effect, a switch from attractant to deterrent properties or otherwise, and the importance of substituents, and stereochemistry of the molecule. These aspects seem characteristic of feeding deterrents because similar observations were made during analogous studies on natural and synthetic aphid antifeedants (Halarewicz-Pacan 2003; Dancewicz *et al*. 2005, 2006, 2008; Wawrzeńczyk *et al*. 2003). The change in stability and nature of the behavioural effect of exogenously applied chemicals may be caused by the alteration of local conditions in the plant tissues. These are changes that take place in the course of time due to plant and aphid metabolism. The chemicals may became less concentrated in plant tissues and the phloem sap, the pH of the sap may change, *etc*. Moreover, the compounds may be detoxified by enzymes present in aphid saliva or by aphid symbionts (Leszczyński 2001). On the other hand, it is very well documented that natural antifeedants are lactones with one or more additional functional groups (Ley and Toogod 1990). Enantiomers of chiral compounds may differ significantly in respect to their interaction with biological receptors, thus resulting in a different biological activity (Juza *et al*. 2000).

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REFERENCES

Capinera J. 2004. Encyclopedia of Entomology. Vol. 1. Kluwer Academic Publishers, Dordrecht, 815 pp.

Dancewicz K., Gabryś B., Halarewicz-Pacan A., Grabarczyk M., Wawreńczyk C. 2005. Effect of terpenoid lactones with di- and trimethylcyclohexane systems on the behaviour of green peach aphid *Myzus persicae*. Pestycydy 4: 17–23.

Dancewicz K., Gabryś B., Halarewicz-Pacan A., Obara R., Wawrzeńczyk C. 2006. Alkilo podstawione γ- i δ-laktony jako deterenty pokarmowe w stosunku do mszyc. Prog. Plant Protection/Post. Ochr. Roślin 46 (1): 305–311.

Dancewicz K., Gabryś B., Dams I., Wawrzeńczyk C. 2008. Enantiospecific effect of pulegone and pulegone-derived lactones on *Myzus persicae* (Sulz.) settling and feeding. J. Chem. Ecol. 34 (4): 530–538.

Del Campo M.L., Via S., Caillaud M.C. 2003. Recognition of host-specific chemical stimulants in two sympatric host races of the pea aphid *Acyrthosiphon pisum*. Ecol. Entomol. 28: 405–412.

Gabryś B., Tjallingii W.F. 2002. The role of sinigrin in host plant recognition by aphids during initial plant penetration Entomol. Exp. Appl. 104 (1): 89–93.

Halarewicz-Pacan A., Gabryś B., Dancewicz K., Wawrzeńczyk C. 2003. Enantiospecific effect of limonene and limonene-derived bicyclic lactones on settling and probing behaviour of the peach potato aphid Myzus persicae (Sulz.). J. Plant Protection Res. 43 (2): 133–142.

Hardie J., Holyoak M., Taylor N.J., Griffiths D.C. 1992. The combination of electronic monitoring and video-assisted observations of plant penetration by aphids and behavioural effects of polygodial. Entomol. Exp. Appl. 62: 233–239.

Juza M., Mazzonti M., Morbidelli M. 2000. Simulated moving-bed chromatography and its application to chirotechnology. Trends Biotechnol. 18 (3): 108–118.

Klein Gebbinck E.A., Jansen B.J.M., Groot A.D. 2002. Insect antifeedant activity of clerodane diterpenes and related model compounds. Phytochemistry 61 (7): 737–770.

Leszczyński B. 2001. Rola allelozwiązków w oddziaływaniach owady – rośliny. p. 61–86. In: „Biochemiczne Oddziaływania Środowiskowe" (W. Oleszek, K. Głowniak, B. Leszczyński, eds.). Akademia Medyczna, Lublin.

Ley S.V., Toogood P.L. 1990. Insect antifeedants. Chem. Br. 1: 31–35.

Nawrot J., Błoszyk E., Grabarczyk M., Drożdż B. 1982. Deterrent properties of sesquiterpene lactones for the selected storage pests. Prace Nauk. Inst. Ochr. Roślin 24 (1), p. 27.

Pickett J.A., Wadhams L.J., Woodcock C.M. 1994. Attempts to control aphid pests by integrated use of semiochemicals. p. 1239–1246. In: Brighton Crop Protection Conference – Pests and Diseases. British Crop Protection Council, Thornton Heath, UK.

Picman A.K. 1986. Biological activities of sesquiterpene lactones. Biochem. Syst. Ecol. 14 (3): 255–281.

Polonsky J., Bhatnagar S.C., Griffits D.C., Pickett J.A., Woddcock C.M. 1989. Activity of quassinoids as antifeedants against aphids. J. Chem. Ecol. 15 (3): 993–998.

Ratuś B., Boratyński F., Nawrot J., Wawrzeńczyk C. 2009. Lactones Part XXXIII. Synthesis and antifeedant activity of alkyl substituted ε-lactones. Przemysł Chemiczny 88 (5): 557–562.

Ratuś B., Grudniewska A., Wawrzeńczyk C. 2006. Lactones 25 [1]. Baeyer-Villiger oxidation of cyclic ketones. p. 256–264. In: "Chemistry for Agriculture" (H. Górecki, Z. Dobrzański, P. Kafarski, eds.). Chech-Pol Trade: Prague, Brussels,

Wawrzeńczyk C., Paruch E., Olejniczak T. 2002. Terpenoid lactones as insect feeding deterrents. p. 206–213. In: "Chemical Products in Agriculture and Environment" (H. Górecki, Z. Dobrzański, eds.). Czech-Pol Trade: Prague.

Wawrzeńczyk W., Grabarczyk M., Szumny A., Gabryś B., Dancewicz K., Nawrot J., Prądzyńska A., Halarewicz-Pacan A. 2003. Lactones 19 [1]. Synthesis and antifeedant activity of lactones with methyl-, dimethyl- and trimethylcyclohexane system. p. 117–129. In: "Chemicals in Sustainable Agriculture. Chemistry for Agriculture Vol. 4". Czech-Pol Trade, Prague.

Wawrzeńczyk C., Dams I., Szumny A., Szczepanik M., Nawrot J., Prądzyńska A., Gabryś B., Dancewicz K., Magnucka E., Gawdzik B., Obara R., Wzorek A. 2005. Synthesis and evaluation of antifeedant, antifungal and antibacterial activity of isoprenoid lactones. Pol. J. Environ. Studies 14: 69–84.

Wawrzyniak M. 1996. The effect of selected plant extracts on the cabbage butterfly, *Pieris brassicae* L. (Lepidoptera). Pol. J. Entomol. 65 (1–2): 93–99.

POLISH SUMMARY

WPŁYW WPROWADZENIA ATOMU TLENU DO PIERŚCIENIA CYKLOHEKSANONU NA BIOLOGICZNĄ AKTYWOŚĆ

Badano zachowanie się mszycy brzoskwiniowej *Myzus persicae* (Sulz.) podczas zasiedlania roślin, po zastosowaniu wybranych naturalnych i syntetycznych cykloheksanonów oraz uzyskanych z nich odpowiednich ε-laktonów i epoksy-ε-laktonów. Struktura przestrzenna oraz liczba i pozycja grup funkcyjnych danego związku wyjściowego miały duże znaczenie dla poziomu aktywności biologicznej. Jedynie trójmetylopodstawione cykloheksanony były aktywne, tzn. 3.3.5-trimetylocyklheksanon (deterent) i 2.2.6-trimetylocyklheksanon (atraktant). Wpływ wbudowania atomu tlenu w pierścień cykloheksanonu na aktywność deterentną, zależał od związku wyjściowego. ε-Laktony pochodzące od nasyconych cykloheksanonów były albo słabymi deterentami, albo były nieaktywne, oprócz ε-laktonu z trzema grupami metylowymi w pozycjach 3.7.7. Żaden z produktów utleniania nienasyconego ketonu izoforonu (słaby deterent), tzn. epoksyizoforon, epoksylakton oraz nienasycony lakton, nie wpływał na zasiedlanie roślin przez mszyce. Spośród dwóch epoksyketonów uzyskanych z (+)-dihydrokarwonu, który był nieaktywny, jedynie (2S,5S)-2-metylo-5-((S)-1-metylooks:ranylo)-cykloheksanon, był silnym deterentem. Obydwa epoksy-ε-laktony pochodzące od (+)dihydrokarwonu były silnymi deterentami.