JOURNAL OF PLANT PROTECTION RESEARCH
Vol. 41, No. 3 2001

CHROMENES, CHROMANONES AND ALKYL SUBSTITUTED PHENOLS AS ANTIFEEDANTS TO STORAGE PESTS AND APHIDS

BEATA GABRYŚ[1], ALEKSANDRA HALAREWICZ-PACAN[1], JAN NAWROT[2], ALEKSANDRA PRĄDZYŃSKA[2], MIROSŁAW ANIOŁ[3], ANTONI SZUMNY[3], CZESŁAW WAWRZEŃCZYK[3]

[1]Agricultural University, Department of Agricultural Entomology,
Cybulskiego 32, 50-205 Wrocław, Poland
e-mail: begab@ozi.ar.wroc.pl
[2]Institute of Plant Protection, Miczurina 20, 60-318 Poznań, Poland
[3]Agricultural University, Department of Chemistry,
Norwida 25, 50-375 Wrocław, Poland
e-mail: c-waw@ozi.ar.wroc.pl

Accepted: May 30, 2001

Abstract: The aim of the work was to study the feeding deterrent activity of precocenes, their synthetic analogues, and some related compunds to storage pests: *Sitophilus granarius* L., *Tribolium confusum* Duv., *Trogoderma granarium* Ev., and aphids: *Myzus persicae* (Sulz.). Among all tested compounds precocenes I and II exhibited the best feeding deterrent activity against all tested insects. 4-Chromanols (16, 17 and 18), alcohols 19, 20 and 3-chromanone (15) showed high deterrence towards the larvae of *T. confusum*. The best antifeedant activity towards the adults of both *T. confusum* and *S. granarius* was observed for substituted phenols with methoxy group at benzene ring. The biological tests carried out on aphids showed that the presence of methoxy group in the molecule was a crucial structural factor for the appearance of antifeedant activity against these insects.

Key words: chromenes, chromanols, chromanones, methoxy phenols, antifeedants, *Sitophilus granarius* L., *Tribolium confusum* Duv., *Trogoderma granarium* Ev., *Myzus persicae* (Sulz.)

I. INTRODUCTION

Chromenes and chromanones are known for their biological activity. The most known are precocene I and precocene II, the methoxy analogues of 2,2-dimethylchromane, isolated from the plant *Ageratum houstonianum* Mill. They have originally been described as compounds that induce precocious metamorphosis in insects by selectively destroying the corpora allata glands and thus impeding the production of juvenile hormones (JH) (Bowers et al. 1976; Schooneveld 1981). This mechanism of anti-JH activity occurs essentially in hemimetabolous insects such as *Heteroptera* (bugs) and *Orthoptera* (grasshoppers and locusts) (Hendrick 1991). Precocene insensivity in holometabolous insects (e. g. *Lepidoptera*, *Coleoptera*) was attributed to the ability of sequestrating them by hemolymph proteins and subsequent metabolism, detoxification, or elimination (Binder and Bowers 1991). Indeed, *Heliothis zea* (Boddie) (*Lepidoptera*) metabolised 90% of a topical dose of precocene II in 20 hours, while *Oncopeltus fasciatus* (*Heteroptera*) metabolised only 10% of the dose in the same time period (Isman 1992). At the time of their discovery and on account of the anti-JH

activity these 2,2-dimetylchromenes were considered for practical application as insect control agents (Slama 1979). However, after several years the studies basing on the anti-JH activity of topically applied precocenes and their structural analogues were abandoned because these compounds appeared hepatoxic and nephrotoxic in vertebrates (Hendrick 1991).

Another line of studies on ageratochromenes refers to their toxicity and feeding deterrent activity (Wisdom et al. 1983; Darvas et al. 1989; Binder and Bowers 1991; 1992). Topical application of precocenes and their synthetic derivatives may have a lethal effect on treated insects (Fridman-Cohen et al. 1984; Darvas et al. 1989, 1993). Precocene I and II applied in artificfial diet deterred the feeding of *H. zea* larvae, which inhibited their growth and reduced survivorship (Wisdom et al. 1983). Binder and Bowers (1991) found that *H. zea* larvae did not discriminate between diets with precocene II and without it, but their growth and development were disrupted after precocene II ingestion and after topical treatments (Binder and Bowers 1991). Precocenes and their analogues exhibited toxicity and antifeedant and growth retardant activity also to larvae of *Pieris brassicae* and *Leptinotarsa decemlineata* in the treated food assay (Darvas et al. 1993).

The aim of the present work was to study the feeding deterrent activity of precocenes, their synthetic analogues, and some related compunds to storage pests: *Sitophilus granarius* L., *Tribolium confusum* Duv., *Trogoderma granarium* Ev., and aphids: *Myzus persicae* (Sulz.).

II. MATERIAL AND METHODS

1. Tested compounds

Precocenes I and II were purchased from Sigma-Aldrich. 6,7-Dimethoxy-1,4-diene analogue of precocene II (5) and methoxy-isopentenyl-phenols 21, 22, 23 were obtained as products of Birch reduction of precocene I, precocene II and 6-methoxy-2,2-dimethyl--2H-chromene (Anioł and Wawrzeńczyk 1994).

2,2-Dimethyl-4-chromanone (11) was obtained from 2-hydroxyacetophenone according to procedure described by Kabbe (1978). 2,2,7-Trimethyl-4-chromanone (10) and 7-methoxy-2,2-dimethyl-4-chromanone (9) were synthesized from m-cresol (Sebok et al. 1992) and resorcinol (Timar and Jaszberenyj 1988), respectively. Chromanones with partially reduced benzene ring (12, 13) and ketone 14 were isolated as products of Birch reduction (Li, liquid ammonia) of corresponding 4-chromanones in the presence of methyl alcohol as an additional source of protons (Anioł and Wawrzeńczyk 1997).

The reduction of 4-chromanones 9, 10, 11 in the conditions without alcohol provided mixtures of 4-chromanols 16, 17, 18 respectively, their analogues with partially reduced benzene ring (19, 20), 2-hydroxyalkyl-phenols (25, 26, 27) and 2-isovaleryl-phenol 28. The separation of these mixtures gave pure samples.

2,2-Dimethyl-3-chromanone (15) was obtained in two step synthesis from 2,2-dimethylchromene via its epoxide (Anastasis and Brown 1983).

2,2-Dimethyl 2*H*-chromene (3) and 2,2,4-trimethyl-2*H*-chromene (4) were synthesized from coumarin and 4-methylcoumarin, respectively, according to procedure described by Abou-Assali et al. (1976).

2,2-Dimethylchromane (3), its analogue with partially reduced benzene ring (7), and orto- isopentenyl phenol (24) were isolated from the products mixture obtained from Birch reduction of 2,2-dimethylchromene (6) (Anioł et al. 1994).

Ketone 14 was obtained in 80% yield from 7-methoxy-4-chromanol (19) as a product of its dehydration (TsOH, toluene) (Anioł 1996).

2. Rearing of insects

Storage pests: The test insects were *Sitophilus granarius* (adults), *Tribolium confusum* (adults and larvae), *Trogoderma granarium* (larvae). The insects were reared in the laboratory at 26°C ± 1°C and 60% ± 5% relative humidity on wheat grain or whole meal diet.

Aphids: *Myzus persicae* were reared on Chinese cabbage in the laboratory at 20°C ± 1°C, 60% ± 5% relative humidity, and 16 : 8 L : D photoperiod. For the tests only 1–3 days old adult apterous aphids were selected.

3. Biological tests

Storage pests: The compounds were tested as 1% acetone solutions applied to wheat wafer discs 1cm in diameter. The feeding of insects was recorded on control discs (saturated with the solvent), in a choice test (on discs with a possibility of choice between control and treated discs), and in a no-choice test (on discs saturated with the tested compounds). The wafer discs were weighed after drying in air for 30 min. before the experiments, and again after 5 days of feeding by beetles or larvae. The results were evaluated statistically using the analysis of variance at P = 0.05. The activity of the tested compounds was expressed by three coefficients of deterrence calculated from the weight of food consumed in the control (CC) and treated (PP) discs in the no-choice test, and in the choice test (C-P):

a) the absolute coefficient of deterrence:

$A = (CC-PP)/(CC+PP) \times 100$

b) the relative coefficient of deterrence:

$R = (C-P)/(C+P) \times 100$

c) the total coefficient of deterrence:

$T = A + R$

The total coefficient was used as the index of activity. Strong antifeedants had an index of 150–200.

Aphids: The tested chemicals were applied as 0.1% and 0.01% ethanol solutions painted on the leaf surface at ca. 0.01 ml/cm^2 on one side of the upper surface of Chinese cabbage leaves. The other side of the midrib was treated with solvent only. The insects (20 aphids per treatment) had a choice between equal areas of treated and control surfaces. Settled aphids were counted on both sides of the leaf after 24 hours. The results were examined

using analysis of variance at P = 0.05. The activity of the compounds was expressed as the relative coefficient of deterrence basing on numbers of aphids settled on treated (P) and control (C) sides of the leaf:

$R = (C-P)/(C+P) \times 100$

When $R < 0$ – the chemical was an attractant; $0 > R < 18$ – not active; $R > 18$ – acitve deterrent. The threshold index value of 18 was determined basing on the results of the statistical analysis.

Behavioural study: Aphid behaviour during the first contact with the substrate was monitored directly using a binocular according to a method described by Hardie et al. (1992). The whole leaves of Chinese cabbage were treated with the tested substance as described for screening tests above. The individual aphids were placed on a leaf 1 hour after application of the feeding deterrent selected in screening tests. Apart from ethyl alcohol control also clean cabbage leaves were used. Aphids were observed for 15 min. continuously and the following behaviours were recorded:

- walking,
- movement of antennae (the cessation of movement was recognised as the beginning of probing as reported by Hardie et al. [1992]).

From the data obtained in this experiment the following parameters could be calculated:

- total time spent on leaf
- total probing time
- number of probes
- mean probing time
- mean time to 1st probe

III. RESULTS AND DISCUSSION

The results of biological tests are presented in tables 1, 2, 3 and 4.

The values of total coefficients of deterrency of chromenes and products of their reduction (Tab. 1) indicate a high activity of both precocenes on storage pests as well as on aphids.

The coefficients of precocene II towards the storage insects are comparable with those observed for the most patent antifeedant, azadirachtin. Total coefficients determined for azadirachtin in the same manner, range from 174 to 194 (Nawrot et al. 1987).

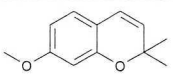
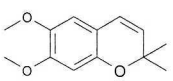
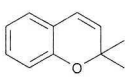
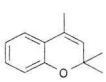
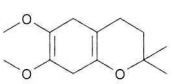
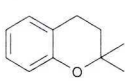
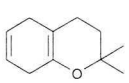
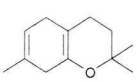
2,2-Dimethyl-2*H*-chromene (3) showed high deterrence against larvae of *T. confusum* and moderate against adults of this insect and *S. granarius*.

The introduction of additional methyl group at C-4 to 2,2-dimethyl-2*H*-chromene (compound 4) caused the decrease in antifeedant activity against all tested species.

Less active than precocenes and 2,2-dimethyl-2*H*-chromene (3) were also compounds with reduced C3-C4 double bond (6) and with partially reduced benzene ring (7, 8). Almost all reduced analogues of precocenes, chromane (6) and 2,2,4-trimethyl-chromene (4) were feeding atractants for the larvae of *T. granarium*.

Table 1

Feeding deterrent activity of chromenes and their analogues

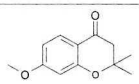
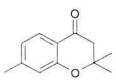
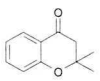
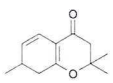
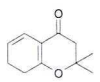
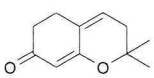
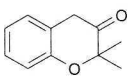
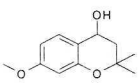
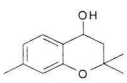
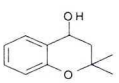
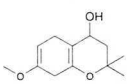
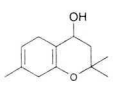
Compound	Total coefficient of deterrence				Relative coefficient of deterrence	
	granary weevil *Sitophilus granarius* adults	confused flour beetle *Tribolium confusum* adults	confused flour beetle *Tribolium confusum* larvae	Khapra beetle *Trogoderma granarium* larvae	peach-potato aphid *Myzus persicae* conc. 0.1%	peach-potato aphid *Myzus persicae* conc. 0.01%
1 	166.3	139.0	119.3	80.1	25.2	20.1
2 	189.4	194.2	165.8	198.6	25.8	20.5
3 	121.8	118.8	176.4	3.1	12.7	n.t.
4 	95.7	36.2	1.4	-44.9	-1.5	n.t.
5 	108.7	103.1	85.5	-13.3	3.2	n.t.
6 	5.6	-10.1	62.7	-53.2	-0.8	n.t.
7 	113.6	60.9	63.7	-57.8	2.2	n.t.
8 	55.7	24.9	83.5	17.1	5.0	n.t.
Azadirachtin	174.3	185.0	188.4	194.2	n. t.	n. t.

n. t. = not tested

Interesting results gave the tests carried out for chromanones and their reduced analogues, such as 4-chromanols and ketones with partially reduced benzene ring (Tab. 2). 4-Chromanones showed only weak deterrence against storage pests and except this one with methoxy group at C-7 (9) were not active towards aphids. Only 2,2-dimethyl--3-chromanone (15) exhibited high deterrence against the larvae of *T. confusum* and moderate activity against the adults of *T. confusum* and *S. granarius*.

Table 2

Feeding deterrent activity of chromanones and chromanols

Compound		Total coefficient of deterrence				Relative coefficient of deterrence	
		granary weevil	confused flour beetle	confused flour beetle	Khapr beetle	peach-potato aphid *Myzus persicae*	
		Sitophilus granarius adults	*Tribolium confusum* adults	*Tribolium confusum* larvae	*Trogoderma granarium* larvae	conc. 0.1%	conc. 0.01%
9		128.9	116.6	76.0	7.8	49.0	18.5
10		-45.9	72.4	1.5	-22.7	2.9	n.t.
11		82.2	31.3	38.8	39.1	-12.3	2.8
12		n. t.	154.9	156.0	162.6	2.9	n.t.
13		141.1	145.6	111.8	119.8	n. t.	n.t.
14		112.5	186.4	149.4	95.7	n. t.	n.t.
15		72.5	89.8	171.8	10.8	-1.2	n.t.
16		59.4	68.6	n. t.	-3.9	1.1	n.t.
17		104.0	91.1	n. t.	65.6	1.9	n.t.
18		106.4	91.2	n. t.	33.3	2.1	n.t.
19		86.8	174.6	159.3	3.6	n. t.	n.t.
20		83.1	120.5	169.2	135.4	n. t.	n.t.

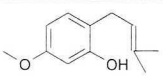
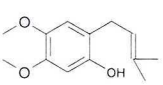
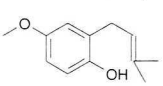
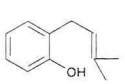
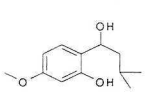
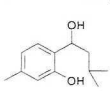
n. t. = not tested

More active against storage pests than 4-chromanone were products of their reduction: bicyclic ketones 12 and 13, chromanols 16, 17, 18 and alcohols 19, 20. The highest deterrency was observed against larvae of *T. confusum*. None of the chromanols was active towards aphids.

Table 3 contains the results of tests on feeding deterrent activity carried out for some reduction products of precocenes and chromenes. These compounds can be considered as alkyl, alkenyl hydroxyalkyl and methoxy phenols. Those with methoxy and isopentenyl groups (21, 22, 23, 25) showed quite good activity towards the storage pests. The two of

Table 3

Feeding deterrent activity of alkyl substituted phenols

Compound	Total coefficient of deterrence				Relative coefficient of deterrence	
	granary weevil *Sitophilus granarius* adults	confused flour beetle *Tribolium confusum* adults	confused flour beetle *Tribolium confusum* larvae	Khapr beetle *Trogoderma granarium* larvae	peach-potato aphid *Myzus persicae* conc. 0.1%	peach-potato aphid *Myzus persicae* conc. 0.01%
21 	151.9	180.6	194.1	128.6	n.t.	n.t.
22 	135.8	157.3	133.4	123.9	20.0	17.6
23 	161.1	162.4	147.5	90.1	19.5	16.1
24 	80.4	99.5	-11.5	63.0	1.3	n.t.
25 	72.5	89.8	n. t.	10.8	2.3	n.t.
26 	152.3	116.9	148.0	61.2	4.1	n.t.
27 	153.9	114.8	67.8	91.8	-17.1	n.t.
28 	81.3	34.8	-6.5	31.7	n. t.	n.t.

n. t. = not tested

them (22 and 23) were active against aphids too. Significant deterrence exhibited also hydroxy alkyl phenols 26 and 27.

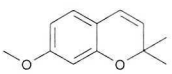
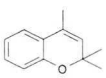
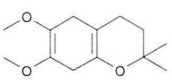
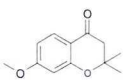
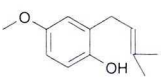
Phenolic compounds were more active against the adults of both *S. granarius* and *T. confusum* than against the larvae.

Table 4 contains the results of the behavioural study. All aphids spent similar time on the leaves. There was no significant difference in time before the first probes among aphids on either treated or control leaves. However, on treated leaves, aphids showed more probes than on ethanol treated or control leaves, but the total time of probing and a mean duration of a probe were shorter on treated than on ethanol treated or control leaves.

Both, the beetles and the aphids were not restrained from initial biting (beetles) or stylet penetration (aphids) of the supplied feeding substrate. The deterrent activity of the tested compounds was demonstrated after the insects had started feeding. In aphids the deterrent activity of precocenes and their derivatives was manifested in reduced total and mean probing time. Similar results were reported by Wisdom et al. (1983) for larvae of *Heliotis zea*. Binder and Bowers (1991) suggested that larval growth and development in *H. zea* were disrupted after precocene II ingestion, but not by preingestive discrimination by olfaction and gustation. The removal of gustatory receptors did not prevent the growth inhibition caused by larval consumption of precocene-containing diet. In the later work these

Table 4

Aphid behaviour on leaves treated and untreated with chromenes, chromanones, and alkyl substituted phenols. 15-min observations; 20 aphids / treatment. Values in columns followed by different letters show significant differences at P = 0.05; Kruskal-Wallis test

Parameter Compound	Total time spent on leaf minutes	Total time of probing minutes	Number of probes number	Mean probing time minutes	Mean time to 1st probe seconds
control	13.8	11.6 a	2.2 a	6.5 a	15.9
ethyl alcohol	15.0	13.0 a	2.5 a	7.3 a	16.1
1 	12.4	8.1 b	4.2 b	2.9 b	14.8
4 	13.7	9.6 b	3.9 b	3.7 b	18.1
5 	13.6	8.3 b	3.9 b	3.3 b	20.6
9 	13.6	9.3 b	4.2 b	2.9 b	16.2
23 	13.7	9.5 b	3.9 b	3.7 b	19.8

authors suggested that the inhibition of insect growth and feeding might possibly result from behavioural changes or disorder in physiological processes. They found significant reductions in rate of nutrient assimilation and conversion of ingested and digested food to body mass when larvae were fed precocene II. This was probably related to the disruption of midgut structure and function also discovered in their studies (Binder and Bowers 1992, 1994). Triseleva (1995) reported changes in midgut cells of *M. persicae* feeding on *Ageratum houstonianum*. The form and size of nuclei was changed and the height of epithelium was reduced. The disturbances were attributed to the influence of biologically active substances, the precocenes, which are known to occur in these plants. It is not unlikely that similar factors are responsible for the deterrent activity of precocenes and their analogues tested in our study. It can be particularly true for the aphids, which do not posess external gustatory receptors and can recognize the food source only after having sampled the sap of the plant. However, further research is needed to establish the functional mechanism of precocene antifeedant activity to these insects.

IV. CONCLUSIONS

1. Among all tested compounds precocenes I and II exhibited the best feeding deterrent activity against all tested insects.
2. 4-Chromanols (16, 17 and 18), alcohols 19, 20 and 3-chromanone (15) showed high deterrence towards the larvae of *T. confusum*.
3. The best antifeedant activity towards the adults of both *T. confusum* and *S. granarius* was observed for substituted phenols with methoxy group at benzene ring.
4. The biological tests carried out on aphids showed that the presence of methoxy group in the molecule was a crucial structural factor for the appearance of antifeedant activity against these insects.

V. REFERENCES

1. Abou-Assali M., Decoret C., Royer J., Dreux J. 1976. Etude de la reactivite des coumarines. Regioselectivite des reactifes de Grignard engages avec la coumarine. Tetrahedron 32: 1655–1659.
2. Anastasis P., Brown P.E. 1983. Studies of chromenes. Part 3. Routes to 2,2-dimethylchroman-3-ones and 4-ethoxycarbonyl-2,2-dimethylchromenes. Synthesis of stable chromenopyrazolinone. J. Chem. Soc. Perkin Trans., I: 1431–1437.
3. Anioł M. 1996. Reduction of chromenes and chromanones with metals in liquid ammonia. PhD Thesis (in Polish), 109 pp.
4. Anioł M., Łusiak P., Wawrzeńczyk C. 1994. The Birch reduction of coumarins and 2H-chromenes. Heterocycles 38: 981–1000.
5. Anioł M., Wawrzeńczyk C. 1984. The Birch reduction of precocene I and precocene II. Heterocycles 38: 2655–2622.
6. Anioł M., Wawrzeńczyk C. 1997. The Birch reduction of 2,2-dimethyl-4-chromanone and its 7-substituted analogues. Heterocycles 45: 1069–1079.
7. Binder B.F., Bowers W.S. 1991. Behavioral changes and growth inhibition in last instar larvae of *Heliothis zea* induced by oral and topical aaplication of Precocene II. Entomol. exp. appl., 59 (3): 207–217.

8. Binder B.F., Bowers W.S. 1994. Precocene II-induced changes in the anatyomy of midgut goblet cells of last instar larvae of *Helicoverpa zea* (Boddie) (*Lepidoptera, Noctuidae*). Int. J. of Insect Morphol. and Embryol., 23 (2): 127–134.
9. Binder B.F., Bowers W.S. 1992. Effects of precocene II on the nutritional physiology of last instar of *Heliothis zea* larvae. Arch. of Insect Bioch. and Physiol., 19 (4): 237–246.
10. Bowers W.S., Ohta T., Cleere J.S., Marsella P.A. 1976. Discovery of insect antijuvenile hormones in plants. Plants yield a potential fourth-generation insecticide. Science 193: 542–547.
11. Darvas B., Jaszberenyi J.C., Timar T., Fonagy A. 1993. Toxic activity of 2,2-dimethyl-3,4-dichloro- and 2,2-dimethyl-(1,2,3)-selenadiazolo-chromenes on *Pieris brassicae* and *Leptinotarsa decemlineata* larvae. J. of Pest. Sci., 18: 277–280.
12. Darvas B., Timar T., Varjas L., Kulcsar P., Hosztafi S., Bordas B. 1989. Synthesis of novel 2,2-dimethylchromene derivatives and their activity on larvae of *Pieris brassicae* (*Lep. Pieridae*) and *Leptinotarsa decemlineata* (*Col. Chrysomelidae*). Acta Phytopat. and Entomol. Hung., 24: 455–472.
13. Fridman-Cohen S., Staal G.B., Peber M.P. 1984. Quantitative studies on anti-allatin and lethal effects of a synthetic precocene in different larval instars of the desert locust. Entomol. exp. appl., 36: 115–124.
14. Hardie J., Holyoak M., Taylor N.J., Griffits D.C. 1992. The combination of electronic monitoring and video-assisted observation of plant penetration by aphids and behavioural effects of polygodial. Entomol. exp. appl., 62: 233–239.
15. Hendrick C.A., 1991. Juvenoids and anti-juvenile hormone agents: past and present. Proc. Conf. Insect Chemical Ecology, Tabor 1990: 429–452.
16. Isman M.B. 1992. A physiological perspective. p.156–176. In "Insect Chemical Ecology, An Evolutionary Approach" (B.D. Roitberg, M.B. Isman, eds.). Chapman and Hall.
17. Kabbe H. J. 1978. Eine einfache Synthese von 4-Chromanonen. Synthesis, p. 886.
18. Nawrot J., Harmatha J., Błoszyk E. 1987: Secondary plant metabolites with antifeeding activity and their effetcs on some stored product insects. p. 591–597. In "Proc 4th Int. Work. Conf. Stored-Product Protection" (E. Donahaye S., Navarro, eds.). Tel Aviv, Israel.
19. Schooneveld H. 1981. Effects of precocene on corpora allata of Locusta migratoria in vivo and in vitro. p. 377–388. In "Regulation of Insect Development and behaviour. International Conference" (F. Sehnal, A. Zabża, J.J., Men. B. Cymborowski, eds.). Karpacz, Poland, June 23–28 1980.
20. Sebok P., Jeko J., Timar J., Jaszbereny J. 1992. On the synthesis of substituted 2,2-dimethyl-4-chromanones and related compounds. Tetrahedron Letters 33: 2791–2794.
21. Sláma K. 1979. Insect Hormones and Antihormones in Plants. p.683-700. In: "Herbivores, Their Interaction with Secondary Plant Metabolites" (G.A. Rosenthal, D.H. Janzen, eds.). Academic Press.
22. Timar T., Jaszberenyj J. C. 1988: A novel synthesis of precocenes. Efficient synthesis and regioselective o-alkylation of dihydroxy-2,2-dimethyl-4-chromanone. J. Heterocycl. Chem., 25, p. 871.
23. Triseleva T. A. 1995: On the influence of feeding on different plants on the epithelium of midgut in *Myzodes persicae* and *Trialeurodes vaporariorum*. Zoologicheskii Zhurnal 74 (6): 76–82.
24. Wisdom C.S., Smiley J.T., Rodrigues E. 1983. Toxicity and deterrency of sesquiterpene lactones and chromenes to the corn earworm (*Lepidoptera, Noctuidae*). J. Econ. Entomol., 76(5): 993–998.

Beata Gabryś, Aleksandra Halarewicz-Pacan, Jan Nawrot, Aleksandra Prądzyńska, Mirosław Anioł, Antoni Szumny, Czesław Wawrzeńczyk

CHROMENY, CHROMANONY I ALKILO PODSTAWIONE FENOLE JAKO ANTYFIDANTY W STOSUNKU DO SZKODNIKÓW MAGAZYNOWYCH I MSZYC

STRESZCZENIE

Prekoceny i ich analogi oraz niektóre związki fenolowe poddano testom biologicznym na aktywność deterentną. Badania przeprowadzono na trzech szkodnikach magazynów zbożowych: larwach skórka zbożowego (*Trogoderma granarium* Ev.), larwach i chrząszczach trojszyka ulca (*Tribolium confusum* Duv.), chrząszczach wołka zbożowego (*Sitophilus granarius* L.) oraz na mszycy brzoskwiniowo-ziemniaczanej (*Myzus persicae* Sulz.). Testy wykazały, że najbardziej aktywnymi antyfidantami w stosunku do larw trojszyka ulca są 4-chromanole (16, 17 i 18), alkohole 19 i 20 oraz 3-chromanon (15). Fenole z grupami metoksylowymi wykazały wysoką aktywność zarówno w stosunku do larw, jak i chrząszczy trojszyka ulca. Połączenia te okazały się również, jako jedyne z testowanych, aktywne w stosunku do mszyc. Wskazuje to na grupy metoksylowe jako elementy strukturalne decydujące o aktywności deterentnej badanych połączeń fenolowych.