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Nitrogen-Affected Florasulam and Pinoxaden Metabolism in Winter Wheat

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Aim. To create environmentally friendly technologies for agrochemicals' integrated application, pinoxaden and florasulam metabolism at the nitrogen action were tested in wheat plants. **Methods**. High performance liquid chromatography (HPLC) of pinoxaden, florasulam and their metabolites in wheat plants. **Results.** The application of the Derby herbicide combined with Axial graminicide and nitrogen does not lead to an increase in residual amounts of florasulam and DE 570 BIH metabolite, while the application of Axial in mixtures with Derby herbicide and nitrogen does not cause an increase in residual amounts of major pinoxaden M04, M06 and M10 metabolites in winter wheat grain. **Conclusions**. The herbicidal composition of Derby, Axial and carbamide was established to be safe for use in crop production. It also efficiently controls main types of deleterious weeds in winter wheat fields.

Keywords: metabolism, herbicides, graminicides, weeds, winter wheat.

INTRODUCTION

Wee infestation on crops is one of the important disincentives prohibiting from high yields. At the same time, weed control has still been a complicated and expensive constituent of the winter wheat sowing protection technology [1].

The discovery of the phytotoxic action of the herbicides – the acetolactate synthase inhibitors – that belong to the sulfonamides significantly strengthened the weeds-killing on spiked cereals sowing. The derivatives of N-arylthiazole-[1,5-c]-pyrymidine sulfonamides include herbicides: chloransulam-methyl, dichlorsulam, florasulam, methylsulam and others, also triazole-pyrymidine sulfonamides – penoxulam and pyroxulam [2–4].

For the weed-killing in wheat sowing the selective herbicide for the spiked cereals protection from annual and some perennial dicotyledonous weeds Derby 175 s. c. (suspension containing 100 g/l of flumethylsulam and 75 g/l of florasulam (Syngenta, Switzerland) is widely used in doses of 0.050–0.070 l/ha. This systemic post-emergent herbicide controls the wide spectrum of annual and some perennial (sow-thistle) dicotyledonous weeds, in particular resistant to others anti-dicotyledonous preparations. Cleavers (*Gallum aparine* L.), cornflowers (*Centaurea cyanus* L.), consolidas (*Consolida ambigua* (L.) P.W. Ball & Heywood), and other malicious forms of dicotyledonous weeds manifest high sensitivity to the action of this composition. By the mechanism of action the herbicide's components relate to the acetolactate synthase inhibitors. Florasulam is an important component of the Derby herbicide. It is a derivative of triazol-pyrymidine sulfoanilide, anti-dicotyledonous herbicide, which is widely used in the world for the dicotyledonous post-emergent weed-killing in spiked cereals sowing in doses to 7.5 g/ha [5, 6]. Florasulam's selective ability is connected to the metabolic differences in the arable cereals and weeds. Thus, the half-life period of the florasulam molecule in the wheat is 2.4 h, while in the dicotyledonous weeds – from 19 h to > 48 h. The special features of florasulam metabolism were determined by dint of high performance liquid chromatography (HPLC) followed by the mass-spectrometric analysis of the carbon 14-labeled herbicide. According to the available data [7], florasulam is metabolized due to the hydroxylation of aniline ring with subsequent conjugation to glucose. The metabolism in the dicotyledonous weeds researched by the same scholars was such slow that the presence of the herbicide's metabolites could not be determined [7]. Therefore, hydroxylation was proposed as the basic way of florasulam's metabolism. Probably, 5-hydroxy-florasulam is the basic metabolite of florasulam in soil as well [8]. It should also be noted that the high level of esterase intensity in the gramineous plants' cells [9] can cause the metabolic destructive processes also as a result of the methyl group hydrolysis in 5-methoxy with the DE 570 BIH-metabolizing (Table 1).

Derby herbicide is frequently utilized in the mixtures with graminicides: pinoxaden or furore predominantly, and also with foliar application fertilizers: carbamide, first of all. At that, the influence of the working solutions components on the herbicide metabolism has not been established.

Graminicides are anti-monocotyledonous post-emergent herbicides widely used in the contemporary plant growing. They include three different in chemical nature classes of herbicides: aryl-oxy-phenoxy-propionic acid (AOPPK) derivatives, cyclohexane-1,3-dione, or cyclohexane oxime herbicides (CH) and phenylpyra-zoles. These are acetyl-CoA-carboxylase (ACC) selective inhibitors for the gramineous plants, and they compose together approximately 15 per cent of contemporary world herbicide market. The herbicides that belong to these classes are also used for the post-emergent cultivation of both dicotyledonous and monocotyledonous crops sowing aiming the selective destruction of annual and perennial gramineous weeds [1, 2, 10]. The phenylpyrazole family's amide derivatives were synthesized in early 1970-s for the first time. Four herbicides in this class are known: fluazolate, nipiroclofen, pyraflufen and pinoxaden [2, 11–13]. The graminicides are further continued to be developed with the high intensity.

The gramineous weeds control in winter wheat sowing is extremely crucial in connection to the domination of grain cereals in the crop rotations in all soil climatic zones of Ukraine and majority of other countries producing the grain all over the world. Therefore, the detection of phytotoxicity in the compounds of phenylpyrazole class and registration of Axial 045 EC c. e. in the leading countries of the world (the active gradient is pinoxaden, 45 g/l, and antidote is cloquintocet-mexyl) is the consequence of the task-oriented long-term explorations dedicated to graminicides' intensity and selectivity increase as for the wheat.

Axial is a translocated herbicide penetrating into the plant through leaves and being transported basi- and acropetal. It is an ACC inhibitor. The herbicide is post-emergent used against the annual gramineous weeds on winter wheat sowing from the beginning of the bunch-forming phase to the booting phase. The best influence is at the early development stages of weeds, but it can control them in the generative phase as well. The action of the agent is visually manifested in 3-15 days after application depending on weather conditions and form of weeds. The essential drawback of the graminicides – ACC inhibitors – is the difficulty in achieving of high phytotoxicity and selectivity in the working mixtures with other pesticides: for example, with the herbicides of anti-auxin class (2,4-D derivatives, benzoic acid and other), and monooxygenases inhibitors (organic phosphorus insecticides), and so forth. It should be noted that pinoxaden is expedient to be used predominantly in the mixtures with anti-dicotyledonous agents and foliar nutrition fertilizers. The prospect of the Axial application in combination with the Derby anti-dicoty ledonous herbicide and carbamide has already been determined [10, 14].

Pinoxaden metabolism in the plants was studied in wheat and barley sowing in France, Germany, Italy, Spain, Australia and the USA [2]. In particular, analytical methods for determining of pinoxaden metabolites content, both free and bound, SYN 505164 (M04) and NOA 407854 (M02), in water, soil and plants are described. It is revealed that the greater quantity of pinoxaden disappears in the plants sufficiently rapidly after treatment, whereas its metabolites – M02, M04, M06 and M10 – appear. The data available in the literature allow making a conclusion about the relatively insignificant stability of this herbicide and its metabolites in spiked cereals sowing within various agrarian-climatic zones (Dr. A. V. Blagaya, 2012, personal information). In this case the influence of the working solutions' components, subject to the combined treatment of pinoxaden together with the anti-dicotyledonous herbicides and fertilizers on the metabolism of graminicides has not been established yet.

Table 1. Florasulam Metabolism in the Wheat Plants at the Action of Pinoxaden and Carbamide

Herbicide, Metabolite	Derby	Derby + Axial	Derby + Axial + + Carbamide	Compound Content, mg/kg	
				Flag Leaf Phase	Grain
Florasulam	+	–	–	0.07 ± 0.02	undefined
Florasulam	–	+	–	0.11 ± 0.04	undefined
Florasulam	–	–	+	0.12 ± 0.04	undefined
DE 570 BIH Metabolite	+	–	–	0.11 ± 0.04	undefined
DE 570 BIH Metabolite	–	+	–	0.11 ± 0.07	undefined
DE 570 BIH Metabolite	–	–	+	0.19 ± 0.05	undefined

The aim of the current research was to investigate the special features of pinoxaden and florasulam metabolism in the wheat plants, including subject to combined action in the combination of Derby with Axial and carbamide, and also to determine the decomposition rate of pinoxaden and florasulam in the conditions of field experiment.

MATERIALS AND METHODS

The tests were performed on the full-scale sowing of winter wheat *(Triticum aestivum* L.*)* of the Smuhlianka variety in the Vinnytsia region (the Komora Agrarian Firm, Trostianets town, the Zernoprodukt MKHP Private Company, PJSC (the enterprise of Myronivskyi Khliboprodukt) and the Experimental Farm of the Institute of Plant Physiology and Genetics NAN of Ukraine in Glevakha settlement, Vasylkivskyi District, Kyiv Region in 2011–2012. The test was repeated six times in the plot of 50 m^2.

During the plants' vegetation the fertilization, pests and diseases control, and also phenological observations were provided. Seeds were treated before sowing with Selest Top protectant (1.5 l/t). The working solution was enriched with complex fertilizers on the basis of mono-potassium phosphate (2 kg/t of seeds). During the vegetation the plants were treated with Alto Super (0.5 l/ha) and Amistar Extra (0.7 l/ha) fungicides, Engio (0.2 l/ha) insecticide, in particular, in the boting, flag-leaf and anthesis phases. The Derby (0.070 l/ha) and Axial (1.0 l/ha) herbicides were applied in the booting to the basic area of field, while 0.2–0.3 ha sections were left herbicide-free for experiment. The dose of carbamide for the foliage application was 10 kg/ha. Spraying was performed in the evening hours at the air temperature of 20–24 °C and absence of wind.

The florasulam and its metabolite DE 570 BIH content was determined by the HPLC method [10]. Chromatographic conditions were as follows: the liquid chromatograph Shimadzu (Japan) with the UV detector, wave length – 260 nm, column – Nucleosil C18, mobile phase – mixture of acetonitrile and twice-distilled water with 0.1 g/l of trifluoracetic acid (35:65), confinement time conformed to standards. Florasulam (DE 570) and its metabolite (DE 570 BIH) were obtained from the Dow AgroSciences Company (USA). The florasulam and its DE 570 BIH metabolite both in plants and grain were determined after acetone (flag leaves) and mixture of acetone with 1 per cent solution of acetic acid (10:1) (grain) extraction. Further on, the extracts were cleaned in the hexane–water (pH 3.0) system with acetic acid, whereas the extracts of green parts were additionally refined on the TFE C18 cartridges (Waters, USA).

The determination of pinoxaden and its M01 (NOA 407855), M02 (NOA 407854), M04 (SYN 505164), M06 (SYN 502836), and M10 (NOA 447204) metabolites content was carried out by the HPLC method [14]. Pinoxaden and its metabolites control in the winter wheat plants, in the gramineous weed predominant over the planted area – silky bent grass *(Apera spica-venti* L.*),* and also in the wheat grain was performed after extracting with the mixture of hydrochloric acid 1N and acetonitrile (M02) and hydrochloric acid 1N (M04, M06, M10) at boiling and sequential cleaning of the extract aliquot by redistribution in the immiscible solvents system on the column with the aluminum oxide, and further - in the concentrating cartridges Oazis (R) HLB (M2) or twice – Oazis (R) MCX (M04, M06, M10) (the concentrating cartridges of the Waters Company, USA). Chromatographic conditions were as follows: the liquid chromatograph Shimadzu with the UV detector, column – Nucleosil C18, mobile phase – mixture of acetonitrile and twice-distilled water (70:30), confinement time conformed to standards. M02, M04, M06 and M10 metabolites were of the Syngenta Company.

Statistical data processing was conducted involving the professional software specially designed for the statistical analysis – Statistica 8.0, according to standard procedures, and using the Microsoft Excel software.

RESULTS AND DISCUSSION

It is established that upon condition of the Derby heavy treatment (70 ml/ha) within the flag leaf phase of the low levels of florasulam residual quantities are fixed in the wheat plants. The Derby heavy application (50 ml/ha and more) are caused by the need for strengthening the effect of composition on the sow-thistle plants, especially on those being in the generative phase of development. The application of Derby with Axial can contribute to an increase in the florasulam content in the plants, probably, due to the components of preparative form strengthening the income of the herbicides' active gradients to the plants.

It has already been determined in the greenhouse experiment [15] that the heavy treatment of sulfonamide flumetsulam, which is like in structure to florasulam resulted in the following content of the former: 0.031 mg/kg in grain and 0.045 mg/kg in soil. The field tests subject to the Derby high dose (70 ml/ha) no residues either of florasulam, or its DE 570 BIH metabolite were detected in grain (Table 1).

It should be noted that the low DE 570 BIH metabolite content in the wheat plants was also observed in the flag leaf phase. The simultaneous usage of the Derby together with the Axial and nitrogenous fertilizer can contribute to exasperation of this metabolite accumulation in the plants.

It is known that the florasulam half-life period in the winter wheat plants comprises less than twenty-four hours. This fact is confirmed with the results of the herbicide remainders detection. At the same time low content of the DE 570 BIH metabolite in the plants can give evidences on the fact that hydroxylation with subsequent carbohydrate conjugation is more probable way of florasulam metabolism in the plants.

Moreover, pinoxaden was fixed at extremely low levels in the winter wheat plants in 24 hour after treatment. Whereas the maximum allowable level for the spiked cereals grain is 0.2 mg/kg, in the week after treatment the pinoxaden content was below the level of quantification (LOQ).

The pinoxaden content was clearly recorded in the gramineous weed plants with the increasing tendency in the week after treatment. Furthermore, the pinoxaden influence on the *A. spica - venti* L. plants was manifested in the phytotoxicity and rapid decrease in the weed's fresh in the later periods (Table 2).

The results of the Axial metabolism investigation in the winter wheat plants give evidences on the fact that even in the flag leaf phase pinoxaden (M01) is just a secondary component – relatively to other residuals' amount. Immediately after treatment, the active gradient of the Axial – pinoxaden (M01) is rapidly hydrolyzed to M02, the basic metabolite in the wheat plants even in the first days after spraying. M02, in its turn, is hydrolyzed generating M04, the key metabolite in the wheat plants in 7–14 days after spraying. The M04 metabolism is possible in three following basic ways: 1) by the M04 glucose compound, what causes the M05 generation, which was detected in all tests of wheat after spraying by some scholars [5–7], 2) by the M04 oxidation to the acidic metabolite M06, which portion is relatively small among other metabolites (less than 10 per cent) in the majority of the selection and analysis cases, and 3) by the M04 hydroxylation with subsequent M10 generating, the secondary metabolite in all wheat samples, except for the straw (Table 3).

Table 2. Pinoxaden Content in the Winter Wheat and Silky Bent Grass Plants

Post-Treatment Time, Days	Content, mg/kg	
	Winter Wheat	Silky Bent Grass
1	0.07 ± 0.01	0.09 ± 0.03
7	< 0.01	0.15 ± 0.03
15	undefined	undefined**

Note: undefined** − no trace of pinoxaden were detected in test samples due to total killing of the gramineous weed plants.

It has been established that the addition of the antidicotyledonous herbicide Derby to the Axial solutions does not influence on the pinoxaden metabolism. Instead, upon condition of the carbamide and Derby addition to the Axial solutions somewhat higher accumulation of the M02 metabolite is observed in the wheat plants within the flag leaf phase. M04 metabolite accumulation increase after the carbamide addition was statistically uncertain. Only small quantities of M04 and M10 metabolites were detected in the grain.

Taking into account the established value of the pinoxaden allowable daily dose (ADD) for the man at the level 0.005 mg/kg of the body weight, the proposed MAD of pinoxaden in the bread cereals grain – 0.2 mg/kg – showed reliable guarantee of active gradient safety in course of safety tests. According to the physiological consumption rates of grain products a human being can consume up to 380 g of such products per day. It means that subject to the pinoxaden rate in the bread cereals grain at 0.2 mg/kg, the maximum pinoxaden daily income will be 0.076 mg. The obtained data give evidences on the fact that the products made

Table 3. Derby Herbicide and Carbamide Influence on Pinoxaden Accumulation in the Winter Wheat Plants

Variant, Compound	Axial	Axial + Derby	Axial +Derby + + Carbamide	Compound Content, mg/kg	
				Flag Leaf Phase	Grain
Pinoxaden	+	−	−	< 0.01	undefined
Pinoxaden	−	+	−	< 0.01	undefined
Pinoxaden	−	−	+	< 0.01	undefined
M2 Metabolite	+	−	−	0.21 ± 0.06	< 0.01
M2 Metabolite	−	+	−	0.20 ± 0.04	< 0.01
M2 Metabolite	−	−	+	0.29 ± 0.04	< 0.01
M4 Metabolite	+	−	−	0.15 ± 0.04	0.03 ± 0.01
M4 Metabolite	−	+	−	0.15 ± 0.03	0.03 ± 0.01
M4 Metabolite	−	−	+	0.19 ± 0.04	0.04 ± 0.01
M6 Metabolite	+	−	−	0.05 ± 0.01	< 0.01
M6 Metabolite	−	+	−	0.06 ± 0.01	< 0.01
M6 Metabolite	−	−	+	0.06 ± 0.01	< 0.01
M10 Metabolite	+	−	−	0.07 ± 0.01	0.02 ± 0.01
M10 Metabolite	−	+	−	0.07 ± 0.01	0.02 ± 0.01
M10 Metabolite	−	−	+	0.09 ± 0.02	0.03 ± 0.01

of the bread cereals grain provide not more than 10–15 per cent of possible pinoxaden income into the human organism. Thus, the established value of pinoxaden MAD in the bread cereals grain at 0.2 mg/kg guarantees safety of the agricultural production grown with the Axial treatment for the human being.

CONCLUSIONS

It is established that the treatment of the anti-dicotyledonous herbicide Derby 175 SC, s. c. in combinations with the graminicide Axial 045 EC, c. e. and carbamide never causes an increase in the florasulam and DE 570 BIH metabolite residual quantities in the wheat grain. In case of applying the Derby together with graminicide and nitrogenous fertilizer the florasulam and its metabolite content slightly raises in the wheat plants within the flag leaf phase. This exasperation of the herbicide accumulation in the plants can be connected to the fixed increase in the phytotoxicity of this composition to the malicious forms of weeds in wheat sowing [10].

The application of graminicide Axial in the mixtures with the herbicide Derby and carbamide does not cause an increase in the pinoxaden basic metabolites – M04, M06 and M10 – residual quantities in the winter wheat grain. It has been established that this very composition is safe for the application in the plant growing; it also efficiently controls basic species of malicious weeds in the winter wheat and barley sowing.

Метаболізм композиції піноксадену та флорасуламу за дії азоту в рослинах озимої пшениці

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Мета. Для створення екологічно безпечних технологій комплексного застосування агрохімікатів дослідити особливості метаболізму піноксадену та флорасуламу за дії азоту в рослинах пшениці. **Методи**. Високоефективна рідинна хроматографія піноксадену, флорасуламу та їх метаболітів у рослинах пшениці. **Результати**. Виявлено, що застосування протидводольного гербіциду Дербі у композиціях з грамініцидом Аксіал й азотом не призводить до підвищення залишкових кількостей флорасуламу і метаболіту DE 570 BIH, а застосування Аксіалу в сумішах з гербіцидом Дербі та азотом не спричиняє зростання залишкових кількостей основних метаболітів піноксадену M04, M06 і M10 у зерні озимої пшениці. **Висновки**. Встановлено, що дана композиція є безпечною для застосування у рослинництві та з високою ефективністю контролює основні шкодочинні види бур'янів у посівах озимої пшениці.

Ключові слова: метаболізм, гербіциди, грамініциди, бур'яни, озима пшениця.

Метаболизм композиции пиноксадена и флорасулама при действии азота в растениях озимой пшеницы

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Цель. Для создания экологически безопасных технологий комплексного применения агрохимикатов исследовать особенности метаболизма пиноксадена и флорасулама при действии азота в растениях пшеницы. **Методы**. Высокоэффективная жидкостная хроматография пиноксадена, флорасулама и их метаболитов в растениях пшеницы. **Результаты**. Выявлено, что применение противодводольного гербицида Дерби в композициях с граминицидом Аксиал и азотом не приводит к повышению остаточных количеств флорасулама и метаболита DE 570 OH, а использование Аксиала в смесях с гербицидом Дерби и азотом не вызывает возрастания остаточных количеств основных метаболитов пиноксадена M04, M06 и M10 в зерне озимой пшеницы. **Выводы**. Установлено, что данная композиция является безопасной для применения в растениеводстве и с высокой эффективностью контролирует основные вредоносные виды сорняков в посевах озимой пшеницы.

Ключевые слова: метаболизм, гербициды, граминициды, сорняки, озимая пшеница.

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