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The Effect of Fungicidal Treatment on Selected Quality Parameters of Barley and Malt

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Protection of barley grain against contamination by fungi such as *Fusarium* spp., particularly by those producing mycotoxins, secondary metabolites with adverse health effects, is of principal importance. Fungicides applied immediately after full heading of spring barley is one method of direct protection. In this work, extensive two-year field experiments combined with a detailed chemical laboratory analysis (barley and malt) were performed with the aim to study the effect of previous crops, different fungicides, and other conditions on the selected barley and malt quality parameters (content of β-glucans, pentosans, oxalic acid, deoxynivalenol, and gushing), while the main task was to follow the effect of the fungicide (used as a treatment to protect against pathogens, mostly *Fusarium*) on changes of the chemical composition in barley and malt, and gushing. It was found that the relationship between the studied factors and the parameters usually applied to the evaluation of barley and malt quality is quite complex and not straightforward. The responses show typical features of a multifactorial influence with both positive and negative correlations resulting in a decrease or increase in grain quality (concentrations of β-glucans, pentosans, deoxynivalenol, and other studied parameters). The role of previous crops was also found to be important. The fungicides should be applied at the time of heading but not at the very beginning of this period.

KEYWORDS: Spring barley; Fusarium in ear; application of fungicides; malt quality parameters; deoxynivalenol

INTRODUCTION

During the growing season, plants are exposed to changing environmental conditions which may inhibit cellular functions, damage plant organs, or cause plant death. Plants are also at risk from pathogenic microorganisms (viruses, bacteria, fungi). Pathogenic fungi have a number of very effective lytic exoenzymes which facilitate host cell wall penetration (*1*). The attack and penetration of pathogenic microorganisms into barley grains may be associated with phenomena that manifest themselves in the course of further processing (for example, during beer production), thus reducing quality.

Recently, considerable attention has been devoted to diseases occurring in the ear, the most significant of which are those caused by fungi of the species *Fusarium*. The intensity of the damage caused by the disease depends on many circumstances, the most significant being the previous crop, course of the weather, and the variety grown.

Application of fungicides may protect the plant against *Fusarium* spp. and prevent damage to the grain.

Fungicides are classified according to their effect: systemic, quasisystemic, and nonsystemic (contact). The pesticides with systemic effects penetrate through the leaf cuticle and are dispersed throughout the whole plant (e.g., epoxiconazol, metconazol, etc.). Mobility of substances in preparations with quasi-systemic effects is lower, and cuticle penetration is limited (e.g., cresoxim-methyl, prochloraz). Fungicides in the third category, contact pesticides, exhibit a local effect on sites of their surface deposits (e.g., carbendazim).

Fungicidal mechanisms are highly heterogeneous (depending on the chemical structure of the active ingredient) and may attack not only hyphae of fungi, but also spores. Triazol fungicides (with the active ingredients epoxiconazol, metconazol, tebuconazol, triadimefon, flusilazole, etc.) are among the most commonly used. Publications have described the inhibition

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of ergosterol by triazole fungicides. Strobilurin-based fungicides (e.g., azoxystrobin, kresoxim-methyl, famoxadone) are the second most widely used group of fungicides. These substances prevent mitochondrial transport of electrons in the process of cellular respiration (by the inhibition of cytochrome c oxidoreductase). The third group of fungicides is based on benzimidazol (carbendazim). Fungicides may contain just one ingredient or a suitable combination of active ingredients to improve their efficacy (*2*, *3*).

Chemical protection against the attack of barley by *Fusarium* spp. is much more complicated than protection against foliar diseases. The fungicide should only be applied after full heading of the ear. The morphology of the ear (with awns) requires careful spray treatment with a small quantity of water. Various adjuvants have also been tested. The application of adjuvants together with some fungicides can improve the degree of coverage (which is important mainly for the ear protection), and resistance to rain or dew washing off increases (*4*). Appropriate fungicide selection is important, too, as some exhibit only partial efficacy. Fungicide application may reduce visual infestation, but it may also increase mycotoxin content (e.g., deoxynivalenon [DON] produced by *F. graminearum* and *F. culmorum*) or interfere in the biochemical development of the grain, which can manifest itself by a change in grain quality. Such changes may include the content of β-glucans, pentosans, DON content, an increase in gushing and level of oxalic acid, and other parameters that indicate the malting quality of barley.

β-glucans are an important component of plant cell walls. Barley endospermal cell walls contain about 75% of β-glucans; 20% are pentosans. Brewing technology requires low β-glucan content in malt and wort. That means nearly complete decomposition of this polysaccharide. The negative influence of β-glucans shows itself in the increased viscosity of wort and beer, reduced brewing yield, poor beer filterability, and prolonged lautering time. Some β-glucans, however, are required, as they contribute positively to the mouth feel, body, and foam of the beer. On the other hand, β-glucans act favorably against such diseases as cardiovascular diseases and carcinomas of the alimentary tract. They reduce cholesterol and improve activity of the alimentary organs (*5*, *6*). For these reasons, it is important to adjust the β-glucan levels in barley and malt so that the requirements of beer producers are fulfilled while retaining nutritiously valuable substances.

Arabinoxylans (pentosans) of barley are noncellulose polysaccharides. Estimates of the arabinoxylan content of barley grain ranges from 4 to 7 wt % (*7*). The arabinoxylans are concentrated in the outer protective layers of the grain. Henry (*8*) reported that only 22% of total barley arabinoxylan is found in the endosperm. Small grains have a higher arabinoxylan content, presumably because most arabinoxylan is located in the outer layers of the grain, and small grains contain relatively less endosperm than larger grains (*7*). Arabinoxylans form only about 1.5% of the barley endosperm weight, but their capacity to form highly viscous solutions can considerably influence barley technological utilization. The most common problems relating to the extraction, filtration, and product stability in malting and brewing are ascribed to β-glucans, but non-decomposed arabinoxylans extracted from the malting grain can also influence extract viscosity, filtration, and possibly the formation of certain types of beer hazes.

The production of trichothecenes has been identified in 24 strains of the fungi of *Fusarium* spp. (*F. crookwellense*, *F. culmorum*, *F. graminearum*, *F. moniliforme*, *F. solani*, *F. oxysporum*, etc.). Besides fungi of *Fusarium* spp., trichothecenes

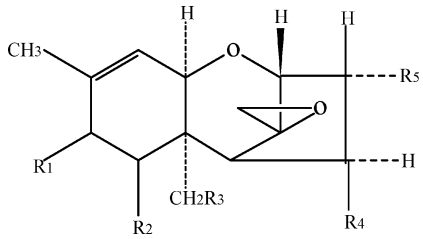

Figure 1. Chemical structure of trichothecenes of type B (deoxynivalenol: R_1 =O, R_2 –OH, R_3 –OH, R_4 –H, R_5 –OH).

are also produced by *Trichoderma*, *Trichothecuim*, and *Stachybotrys* spp. Their basic structures are cyclic sesquiterpenes with a double bond between C-9 and C-10 and an epoxy bond between C-12 and C-13. Their levels vary from tens to thousands of μg/kg in cereals. Deoxynivalenol (DON), belonging to type B trichothecenes (**Figure 1**), is the most frequently occurring trichothecene. It is often identified as a marker for the presence of other trichothecenes and potential health risks, although in terms of toxicity, it does not belong to the most dangerous (it is 10× less toxic than T-2 toxin, but it can cause digestive problems in livestock, even at low concentrations). Deoxynivalenol, unlike T-2 toxin, is less lipophilic and may not penetrate through lipophilic cellular membranes to the inner parts of cells in high concentration. According to IARC (*9*), DON, together with the other trichothecenes, is listed in a group of substances with insufficiently proven carcinogenic effect**.** The Czech Republic has so far only established the maximum level for deoxynivalenol. The maximum permissible concentrations are 0.5 mg/kg for cereals, 0.35 mg/kg for bread and pastry, and 0.1 mg/kg for cereal products for children's food products. DON levels in barley caryopses and malt in relation to barley protection were published in the study of Vanova et al. (*10*).

So-called "primary gushing" is one of the most frequent effects associated with the fungal disease called Fusarium Head Blight (FHB). The term gushing is common in both English and German literature and refers to the spontaneous overfoaming of beer from a bottle or can. It occurs mainly in beer, but it can also occur in nonalcoholic beverages. Basically, an immediate release of carbon dioxide (CO_2) is observed when a bottle is opened (*11*). Gushing incidence is connected with barley grains infested with species of *Fusarium*, *Aspergillus*, *Rhizopus*, *Penicillium*, and *Nigrospora*. However, the substances inducing gushing are not exactly known. It is suggested that these substances may be produced as a response to a previous stress of an organism either during growth or under certain conditions in the subsequent malting process.

Gushing, however, does not always have to relate to the presence of pathogens (i.e., *Fusarium* spp.). So-called "secondary gushing", which is not connected with malt quality, can be caused by some manufacturing factors, e.g., coarse bottle surface, oversaturation with carbon dioxide, among others. In addition, an increased content of oxalates (in the form of calcium oxalate) can contribute significantly to gushing. Oxalic acid plays a negative role from the aspect of both nutrition and brewing technology (*12*−*14*). The amount of oxalic acid in beer ranges from 4 to 32 mg/L. Although this is not a high concentration, it can cause, especially in the form of calcium oxalate, "oxalate haze" and the above-mentioned gushing.

The subject of this work was to study, in field experiments combined with detailed chemical analysis of barley and malt, the effect of fungicide preparations on the selected so-called "quality parameters" of barley and malts, including β-glucans, pentosans, oxalic acid, DON content, and gushing.

Table 1. Fungicides, Active Ingredients, and Contents

fungicide	active ingredients	content (g/L)
Amistar	azoxystrobin	250
Juwel	epoxyconazole	125
	Kresoxim-methyl	125
Charisma	famoxadone	100 l
	flusilazole	106.7
Sportak 45EC	prochloraz	450
Caramba	metconazole	60
Folicur BT	tebuconazole	125
	triadimefon	100
Orius	tebuconazole	250
Duett	carbendazim	125
	epoxyconazole	125
Adjuvant Silweet L-77	0.1 L + 250 L water in 2002	
	0.1 L + 150 L water in 2003	

MATERIALS AND METHODS

Field Experiments. Field trials were laid down in plots of the Agricultural Research Institute in Kroměříž, Ltd. (235 m above sea level, average annual temperature 8.7 °C, and annual precipitation sum 599 mm).

The variety Kompakt, which was very sensitive to FHB in other trials, was used in all the trials examined. Sugar beet and maize were the previous crops. The trials were analyzed as a complete randomized block design with four replications for each treatment.

To achieve sufficient disease severity every year, the plots were artificially inoculated with spores of *F. graminearum* and *F. culmorum*. Their ratio in the inoculum was 1:1. Fungal isolates were cultivated on solid nutrient media (sterile grain of winter wheat) after their pathogenicity was checked, and they were kept under UV light for 3−4 days following the sporulation stimulation. Then, the substrate was dried and stored for 3 months.

Conidial concentration in the inoculum was adjusted under a microscope to the amount of 1.0 million conidia per milliliter of suspension for both species of *Fusarium* present in the suspension. Inoculation with spore suspension was carried out on the particular varieties when about 75% of the ears reached full heading.

To avoid the infection of leaves by other pathogens, all plots were treated with a combination of Atlas or Cerelux (0.2 or 0.6 L/ha). Fungicides against FHB were applied at the beginning of spring barley anthesis (DC61-64, *15*). Artificial inoculation with a suspension of fusarial conidia was carried out 24 h later (in 2003) or 6 days later (in 2002). Eleven fungicides were tested. They were applied on the growth at one shot, always in the same month. The list of active substances is given in **Table 1**.

The content of Fusarium trichothecenes was evaluated in one fraction of kernels − diameter 2.5 mm − which is used in the malting technology process. Grain samples were taken from four replications, screened on a 2.5 mm sieve, and ground. Each sample was processed individually. 500 g of samples was used to measure mycotoxin, β-glucan, pentosan, and oxalate content.

2 kg of the screened samples was used for malting.

Malting Technology. Barley samples were micromalted, according to the adopted technology for the production of malts, and subjected to the gushing test. That means 2 days steeping (duration 48 h), 3−5 h in water (temperature 14 °C), 6 days germination (duration 144 h, temperature 14 °C) and kilning 1 × 22 h at kilning temperature of 80° C for 4 h.

The content of β-glucans, pentosans, and oxalates, DON concentration, and gushing were assessed in the starting material and the malt.

Determination of β-Glucans. Determination of β-glucans in barley, malt, and wort was carried out using the FIA (flow injection analysis) method. The principle of the FIA method requires the injection of a sample into a running bearing flow of buffer and agent. A complex is formed between the dye Calcofluor White M2R New, specific for β-glucosidic bond, and β-glucans contained in the barley, malt, and wort, which then shows an increase in fluorescent intensity recorded by a spectrofluorimeter (*16*). The exact mechanism for this reaction is not known, but it is probably caused by a hydrophobic interaction (*17*).

Determination of Pentosans. For pentosan determination, the modified spectrophotometric method of Douglas (*18*) was used. About 5 mg of flour (barley, malt) was blended with 10 mL of an extract solution (glacial acetic acid, hydrochloric acid, phloroglucinol, and glucose). The intensity of the orange-red color was measured at A_{510} and A_{552}.

Determination of Deoxynivalenol. Deoxynivalenol levels in 10 g of homogenized ground barley and malt samples were determined using the method of capillary gas chromatography coupled with a detector of electron catcher (GC/ECD) published by Radova et al. (*19*). For purification of the extract (extraction for 60 min with 100 mL of mixture acetonitrile-water, 84:16, v/v), the method of solid-phase extraction (SPE) with blended sorbent MycoSep 225 was used. Derivation with trifluoroacetanhydride of acetic acid (TFAA) was carried out prior to the analytic terminal of the GC/ECD. Detection limit for DON was 5 μg/kg.

Gushing. The Carlsberg three-day test (*20*) was used for the determination of gushing in malt. The method is based on the assumption that markers of overfoaming are soluble in water, active and soluble after boiling, and active under the conditions prevailing in beer. The method includes the replacement of 50 mL of non-overfoaming finished beer with the malt extract, followed by a three-day shaking under the defined conditions. The volume of the foamed-up beer after the consequent bottle opening expresses the gushing value (mL).

Determination of Oxalates. The content of oxalic acid was determined by the method of capillary izotachophoresis (ITP, *21*). Conditions of ITP determination of oxalic acid were as follows: double capillary arrangement, leading electrolyte (LE) 10 mM HIS chloride + BTP + 0.1% m-HEC, pH = 6; terminating electrolyte (TE): 5 mM capronic acid + HIS, pH ≈ 5, current 250 μA preseparation column, 50 μA analytical column. For analysis, take 10 g of sample, add 90 mL of distilled water, and heat in water bath for 30 min at 65 °C. After cooling to room temperature, the solution is filtered and analyzed.

Statistical Evaluation. Efficacy of the fungicides (% rel.) was calculated using the formula $[(K - P)/K] \times 100$, where K = DON (β-glucans, pentosans, oxalates, gushing) content in the nontreated control and P = DON (β-glucans, pentosans, oxalates, gushing) content after the application of a fungicide or a mixture of fungicides. The relation between DON content and gushing in malt was assessed by correlation analysis. The efficacy of fungicides in both years and after both previous crops was assessed using analysis of variance and differences among the individual fungicides by testing the significance of simple contrasts using the LSD method.

RESULTS AND DISCUSSION

In previous years, great attention has been paid to minimizing the presence of fungi mycelia and mycotoxins in agricultural products. Comparison of various fungicide activities to DON levels in barley caryopses and malt is given in the study of Vanova et al. (*10*).

In the years of the study (2002 and 2003), fungicides were applied with the adjuvant Silwet L-77 (**Table 1**). Better results were obtained in 2003 where adjuvant Silwet L-77 was used, and there was a low water content per hectare (150 L/ha) (*10*). The maximum reduction of mycotoxins was achieved using a combination of azole fungicides with tebuconazole or metconazole (or their mixture) with the addition of Silwet L-77 and a low rate of water. Orius fungicides with active compounds tebuconazol and Caramba with metconazol as an active compound belong to a group of fungicides based on triazols which inhibit the biosynthesis of ergosterol. In 2002, a solo application of the preparation Amistar or Juwell was the least successful. In comparison to the control, it did not reduce the levels of DON. On the contrary, in the variety Kompakt, DON content

Table 2. Correlative Dependence between Content of Gushing in Malt and DON in Barley and Malt

year	2002–2003	2002	2003	2002–2003	2002–2003
previous crop	sugar beet maize	sugar beet maize	sugar beet maize	sugar beet	maize
	correlation coefficient				
gushing – DON barley	0.093	0.0371	0.5305**	0.029	0.0683
gushing – DON malt	–0.0162	–0.0663	0.3843*	–0.0617	–0.1141
DON barley – DON malt	0.8890***	0.5017*	0.8228***	0.9217***	0.7927***

year	2002	2002	2003	2003
previous crop	sugar beet	maize	sugar beet	maize
	correlation coefficient			
gushing – DON barley	–0.1064	0.1988	0.3295	0.3624
gushing – DON malt	0.1503	–0.227	–0.0621	0.5073
DON barley – DON malt	0.5147	0.1648	0.6013*	0.8775***

Table 3. Efficacy of Fungicide Treatment (%) on the Decrease of Gushing in Barley Grain and Malt

	2002				2003			
	barley		malt		barley		malt	
fungicide	sugar beet	maize	sugar beet	maize	sugar beet	maize	sugar beet	maize
control	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Amistar	×	×	27.27	98.85	33.33	0.00	63.10	55.77
Amistar + Caramba	×	×	–172.73	31.03	44.44	100.00	53.57	100.00
Amistar + Duett	×	×	–104.55	94.25	55.56	×	15.48	51.92
Caramba	×	×	54.55	77.01	–55.56	60.00	55.95	88.46
Folicur BT	×	×	–427.27	–4.60	22.22	×	5.95	38.46
Folicur BT + Sportak 45EC	×	×	–113.64	–2.30	61.11	–120.00	40.48	57.69
Charisma	×	×	–350.00	94.25	38.89	20.00	45.24	69.23
Charisma + Caramba	×	×	100.00	77.01	66.67	×	73.81	–13.46
Charisma + Sportak 45EC	×	×	–381.82	6.90	44.44	×	82.14	23.08
Juwel	×	×	–50.00	88.51	38.89	0.00	72.62	73.08
Orius	×	×	18.18	–5.75	22.22	–140.00	100.00	59.62

in barley and malt increased after both previous crops (*10*). In 2003, the DON content was lower in comparison to the control after the application of all of the fungicides, both in the barley grain and malt and after both previous crops (*10*).

There was a significant increase in DON concentration in all samples after malting (*10*). Favorable conditions for fungal mycelium growth during the malting process (higher humidity, optimum temperature) and thus higher mycotoxin production can be the reason for the increased DON levels. At the same time, trichothecenous mycotoxins may be released from the matrix, probably because of enzymatic reactions during malting. These results are supported by the study of Schwarz et al. (*22*), who also studied changes in the content of the selected mycotoxins during malting.

As is evident from **Table 2**, no correlation between the content of DON and gushing was established, although both parameters are connected with a microbial attack (mycotoxins − secondary metabolites of fungi, new substances arising after a pathogenic attack of a caryopsis can cause over-foaming of beer − gushing).

Only in 2003 was compliance between gushing in malt and DON in barley found (**Table 2**) after both previous crops; also in 2003, after the previous crop maize, compliance between gushing in malt and DON in malt was found (**Table 2**). The presence and quantity of DON in samples of barley and malt cannot be explicitly identified as a direct factor determining gushing, but as mentioned above, mycotoxins belong to the principal indicators of the fungal mycelium incidence.

In terms of the efficacy of different combinations of fungicides on gushing in malt, in 2003 a zero gushing value was attained only after the application of the fungicide Amistar + Caramba after the previous crop maize (**Table 3**, **Figure 2**) and after application of the fungicide Orius after the previous crop sugar beet (**Table 3**, **Figure 3**). In 2002, after the previous crop maize, the fungicide Amistar was the best (**Table 3**, **Figure 2**), and Charisma + Caramba 0.5 were the best after the previous crop sugar beet (**Table 3**, **Figure 3**). On the basis of the total evaluation of the fungicide efficacy on the gushing value in malt (years 2002 and 2003 after both previous crops) using the analysis of variance, Amistar, Caramba, and Juwel (**Table 4**) (*23*), or the combination of Charisma + Caramba 0.50, are all effective preparations. The fungicides Amistar and Juwell, selected according to the DON content, were ineffective in the reduction of the level of the selected mycotoxin (*10*).

Application of some fungicides tends to increase the gushing value versus the control (**Table 3**). Especially in 2002, the efficacy of the fungicides applied was lower for barley grown after both previous crops. Efficacy increased (**Table 3**) in 2003 when Silwet L-77 adjuvant and low water rate (150 L/ha) were used (*10*). The use of the adjuvant with fungicides ensures a good covering of the ears and penetration into the ear tissue. The amount of the active substance penetrating through the plant

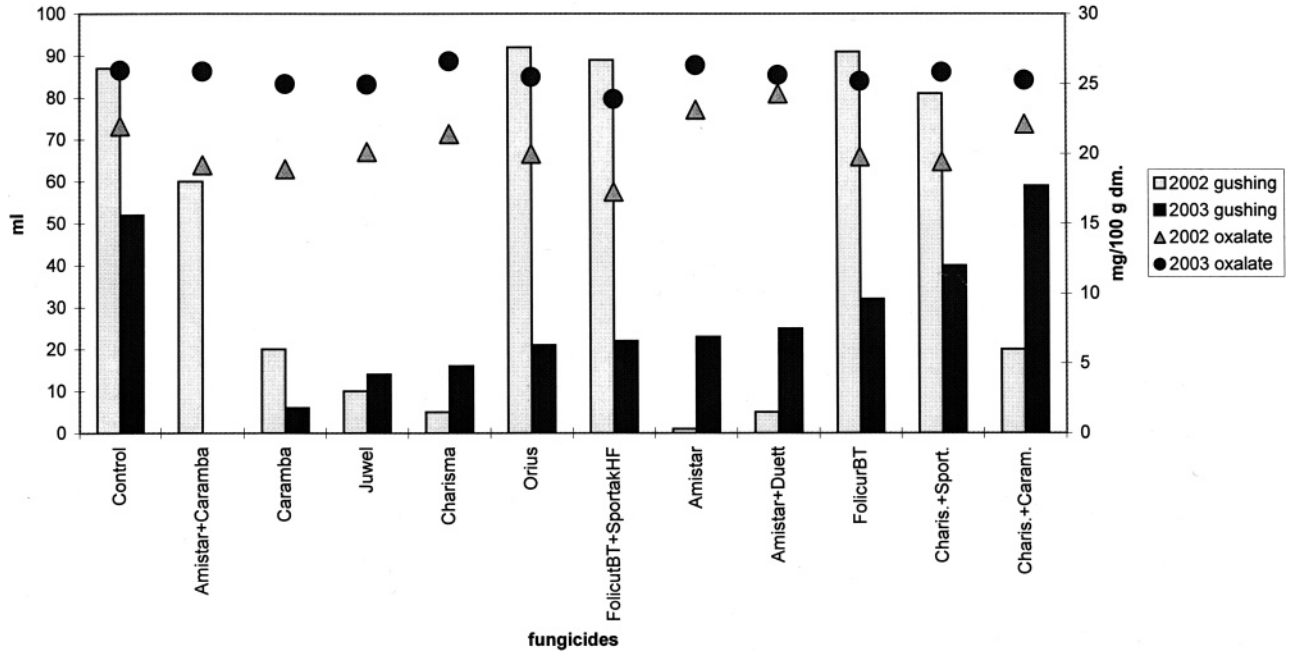

Figure 2. Comparison of gushing values and oxalate content in malt for the variety Kompakt: effect of fungicide treatment, previous crop maize.

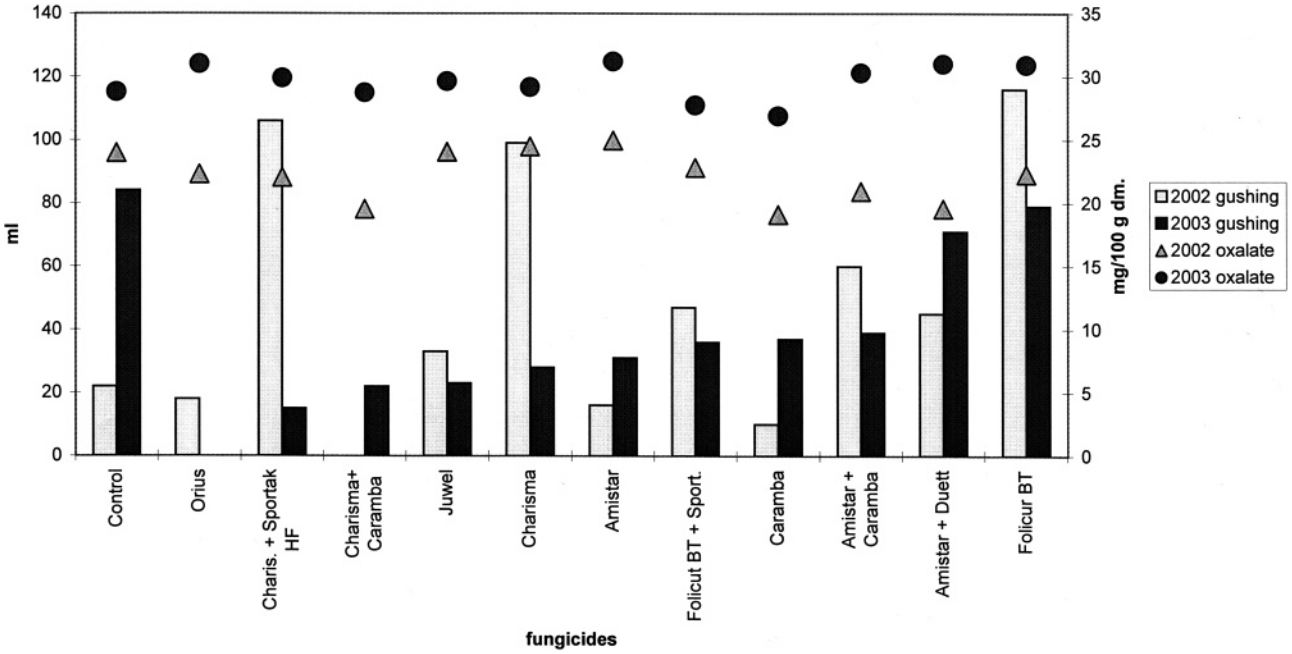

Figure 3. Comparison of gushing values and oxalate content in malt for the variety Kompakt: effect of fungicide treatment, previous crop sugar beet.

surface depends on the plant characteristics, properties of the solution, and environmental factors (*4*).

The analysis of samples showed that the application of fungicides could also change other parameters such as the content of oxalates, β-glucans, and pentosans.

The optimum concentration of oxalates in barley and malt should be as low as possible, considering the problems which their presence in barley and barley products can cause (origin of secondary gushing). The optimum concentration in malt to reduce the incidence of gushing is up to ca. 15 mg/100 g of d.m.

After the application of some fungicides, an increased oxalate level in barley and malt, in comparison with the control, was observed in barley grown after both previous crops and in both years (**Table 5**). Total evaluation by analysis of variance (years 2002 and 2003 for barley grown after both previous crops) showed an increase of oxalate content in barley versus the control after application of Amistar + Duet, Folicur BT + Sportak HF, Charisma + Caramba, and Folicur BT (**Table 8**), and in malt after application of the fungicides Charisma and Amistar (**Table 8**).

The limit for β-glucan content is 150−200 mg/L in wort. Generally, it was observed that, after the application of fungicides, the β-glucan content, mainly in wort, was increased versus the control in both years (**Tables 6**, **8**). Similarly, increased levels were detected in 2003 (**Table 6**) when the adjuvant Silwet L-77 and low water rate (150 L/ha) were applied to ensure better efficacy of the fungicides used for minimization of the incidence of fungal mycelia. The total evaluation by analysis of variance (years 2002 and 2003 on barley grown after both previous crops) showed an increase of β-glucan content in the barley versus the control only after application of

Table 4. Statistical Assessment of Fungicide Efficacy in All Variants, after Both Previous Crops and in Both Years Studied Multiple Range Analysis for Gushing in Malt

method: 95% Tukey HSD Level	count	LS mean	homogeneous groups
Amistar 1.0 L	4	17.750	X
Caramba 1.5 L	4	18.250	XX
Juwel 0.8 L	4	20.000	XXX
Charisma 1.0 L + Caramba 0.5 L	4	25.250	XXXX
Orius 1.0 L	4	32.750	XXXXXX
Amistar 0.5 L + Duett 0.5 L	4	36.500	XXXXXXX
Amistar 0.6 L + Caramba 0.7 L	4	39.750	XXXXXXXX
Charisma 1.5 L	4	41.500	XXXXXXXX
Folicur BT 0.7 L + Sportak 45EC 0.5 L	4	52.000	XXXXXXXX
Charisma 1.0 L + Sportak 45EC 0.5 L	4	60.500	XXXXXX
Control	4	61.250	XXXXXX
Folicur BT 1.0 L	4	79.500	X
year			
2003	28	33.679	X
2002	24	47.262	X
previous crop			
maize	26	34.624	X
sugar beet	26	46.316	X

Table 5. Efficacy of Fungicide Treatment (%) on Oxalate Content in Barley Grain and Malt

	2002				2003			
	barley		malt		barley		malt	
fungicide	sugar beet	maize	sugar beet	maize	sugar beet	maize	sugar beet	maize
control	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Amistar	–13.35	12.99	–4.13	–5.37	7.73	2.06	–8.33	–1.42
Amistar + Caramba	–42.23	25.04	12.72	12.74	5.40	14.21	–5.21	0.35
Amistar + Duett	–3.36	16.19	18.43	–10.65	–11.15	–7.09	–7.64	1.27
Caramba	–4.67	30.15	20.35	13.97	20.49	21.14	6.59	3.77
Folicur BT	–29.39	–6.59	7.09	9.92	–3.88	2.94	–7.39	2.96
Folicur BT + Sportak 45EC	3.79	–6.71	4.84	21.39	–5.82	–1.54	3.61	7.89
Charisma	–21.08	28.39	–2.09	2.55	–10.06	2.65	–1.28	–2.50
Charisma + Caramba	–62.80	–14.82	18.60	–0.73	21.31	0.46	0.24	2.70
Charisma + Sportak 45EC	–27.06	19.93	8.17	11.61	19.85	1.76	–3.82	0.50
Juwel	–2.63	17.08	–0.25	8.38	–6.52	12.15	–2.88	3.89
Orius	–29.61	–4.06	7.05	9.01	9.70	21.46	–7.71	1.81

Table 6. Efficacy of Fungicide Treatment (%) on β-Glucan Content in Barley Grain and Malt

	2002				2003			
	barley		wort		barley		wort	
fungicide	sugar beet	maize	sugar beet	maize	sugar beet	maize	sugar beet	maize
control	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Caramba	–29.37	20.80	–15.48	–20.81	–12.60	–2.99	–184.78	–131.82
Folicur BT + Sportak 45 EC	10.58	18.44	–13.10	7.38	–7.35	–11.49	–241.30	–105.94
Charisma + Caramba	–16.67	18.44	–119.05	–28.19	–11.81	–1.38	–141.30	2.80
Charisma	2.91	15.37	33.33	–16.11	–8.92	–3.91	–60.87	–76.92
Juwel	–6.88	14.42	16.67	36.24	–2.36	–1.38	–141.30	–77.62
Charisma + Sportak 45 EC	–3.70	19.62	–77.38	–14.77	–7.87	–6.67	–139.13	16.08
Amistar + Caramba	–0.26	21.99	–76.19	–19.46	0.00	–1.84	–289.13	–90.91
Folicur BT	9.79	18.20	–7.14	0.00	–3.94	–7.36	–228.26	–75.52
Amistar + Duett	–6.61	16.31	–64.29	16.78	2.36	2.30	–334.78	–16.78
Orius	24.60	26.48	46.43	10.07	0.26	–4.14	–600.48	–140.91
Amistar	4.76	20.57	20.24	37.58	–1.84	–0.46	–202.17	–40.56

Charisma + Caramba and after a solo application of the fungicide Caramba (**Table 8**).

High concentrations of pentosans and β-glucans can contribute to problems with the technological process of beer production. Maltsters therefore try to produce malts with lower values of not only β-glucans but also pentosans.

According to the table of efficacy (**Table 7**) and total evaluation of the results achieved by analysis of variance in both years 2002 and 2003 (**Table 8**), concentration of pentosans in barley caryopses and in wort versus the controls increased after the application of most fungicides in barley grown after both previous crops in both years. Similarly, like β-glucan

Table 7. Efficacy of Fungicide Treatment (%) on Pentosan Content in Barley Grain and Wort

	2002				2003			
	barley		wort		barley		wort	
fungicide	sugar beet	maize	sugar beet	maize	sugar beet	maize	sugar beet	maize
control	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Caramba	–2.11	–12.31	–13.35	–29.77	9.10	–7.46	–11.68	–16.94
Folicur BT + Sportak 45EC	17.04	–11.61	8.74	–11.13	24.04	–17.94	–18.10	–27.96
Charisma + Caramba	9.35	1.21	–12.74	–20.38	22.76	–7.64	–3.34	–12.26
Charisma	28.36	–14.38	–13.23	–50.58	8.25	4.26	2.31	–24.10
Juwel	22.62	0.87	–1.33	–6.79	14.51	–7.99	–27.21	–14.19
Charisma + Sportak 45EC	23.53	–2.43	11.29	–32.66	–7.11	–31.44	–4.75	–18.32
Amistar + Caramba	–9.05	–11.27	–19.90	7.23	11.10	–23.27	–29.40	–23.42
Folicur BT	–8.60	–17.16	–3.52	–11.71	–4.69	–32.86	–13.99	–22.04
Amistar + Duett	2.26	4.16	9.71	–1.45	0.85	–28.06	–29.14	–15.70
Orius	17.65	2.77	–13.96	4.62	22.76	4.62	–38.77	–19.01
Amistar	–21.12	6.93	13.11	8.53	4.69	–20.43	–29.14	–21.21

Table 8. Results of Statistical Assessment of Fungicide Efficacy in All Variants, after Both Previous Crops and in Both Years Studied for All Studied Parameters[a]

parameters	oxalate	β-glucan	pentosan	gushing	oxalate	β-glucan.	pentosan
fungicides	barley	barley	barley	malt	malt	wort	wort
Amistar + Duett	–	+	–	+	+	–	–
Amistar + Caramba	+	+	–	+	+	–	–
Amistar	+	+	–	+	–	–	–
Caramba	+	–	–	+	+	–	–
Folicur BT + Sportak 45EC	–	+	+	+	+	–	–
Folicur BT	–	+	–	–	+	–	–
Charisma + Caramba	–	–	+	+	+	–	–
Charisma + Sportak 45EC	+	+	–	+	+	–	–
Charisma	+	+	+	+	–	–	–
Juwel	+	+	+	+	+	–	–
Orius	+	+	+	+	+	–	–

[a] + means decrease of the value of parameter after application of the fungicide versus control. – means increase of the value of parameter after application of the fungicide versus control.

content, higher values of pentosans in wort versus the control, were determined after the application of all the fungicides in barley grown after the previous crop maize in 2003. With the previous crop sugar beet, after the application of the fungicides Charisma and Orius, lower values of the studied parameter were achieved.

Fungicides interfere in the biochemical mechanism of a caryopsis development and thus negatively or positively influence the activity of the enzymatic system that participates in catabolism of the polysaccharides, e.g., β-glucans and pentosans. They also interfere in the chemical cycle of oxalic acid conversion. The selected malting technology also contributes to the increased concentration of oxalates and DON in malt (*23*), and so, the increased levels sometimes observed can be due to malting and not to the use of fungicides.

Application of fungicides protects the plant against microorganisms, reduces their activity and subsequent devaluation, and increases quality of the infected material. It was found here that the use of most fungicides selected by us varies the levels of β-glucans, pentosans, and other studied parameters in barley caryopsis to a different extent and typically has a multifactorial effect with both a decrease and an increase in some parameters being observed. Sometimes an increased concentration of mycotoxin deoxynivalenol and increased levels of gushing observed might be caused by malting technology.

In conclusion, successful application of a fungicide for plant protection requires choosing a suitable fungicide, but it is necessary to consider the chemical status of the active substance contained in the given individually selected fungicide, growing conditions of barley, such as previous crop, barley variety, and its susceptibility to fusarium infections. Effective fungicide application also requires keeping the prescribed time scale and manner of fungicide application on the growth. It is also necessary to apply the fungicide at the time of full heading, but not at the very beginning of this period. This fact is often neglected, and an improperly timed application can minimize the efficacy of the fungicides.

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