Selectivity of Pyribenzoxim and Bispyribac-sodium Between *Echinochloa crus-galli* and Rice (*Oryza sativa*)

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피와 벼에 대한 피리벤족심과 비스피리백-소디움의 선택성

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ABSTRACT Dose-response studies were conducted to compare herbicidal activity and rice selectivity of pyribenzoxim and bispyribac-sodium. When tested with formulations at the constant adjuvant concentration regardless of herbicide dose, the GR_{90} value (the rate required to inhibit growth by 90%) of pyribenzoxim for barnyardgrass was 8.7 g ai ha^{-1}, while that of bispyribac-sodium was 7.7 g ai ha^{-1}. The GR_{10} values (the rate required to inhibit growth by 10%) of pyribenzoxim and bispyribac-sodium were 93.3 g and 2.9 g ai ha^{-1} for Japonica rice and 185.8 and 23.9 g ai ha^{-1} for Indica rice, respectively. The selectivity indices (GR_{10} for rice/GR_{90} for barnyardgrass) of pyribenzoxim for Japonica and Indica rice were 10.7 and 21.3, respectively, while those of bispyribac-sodium were 0.4 and 3.1, respectively. Therefore, selectivities of pyribenzoxim were 6.8 and 28.0 folds greater for Japonica and Indica rice, respectively, than those of bispyribac-sodium. In addition, the selectivity indices of technical ingredients of pyribenzoxim and bispyribac-sodium were 1.5 and 0.5, respectively, showing about 3 folds difference. The selectivity indices of their formulations tested with no adjustment of adjuvant concentration were 1.2 and 0.5, respectively, showing 2 folds difference. These results thus demonstrate that although pyribenzoxim and bispyribac-sodium are similar in herbicidal activity to barnyardgrass, pyribenzoxim is a vastly advanced herbicide in rice selectivity.

Key words: bispyribac-sodium; barnyardgrass; dose-response; pyribenzoxim; rice selectivity.

INTRODUCTION

Pyribenzoxim (Pyanchor®) is a rice herbicide belonging to pyrimidinyloxybenzoate chemistry and known to provide broad-spectrum weed control in rice (Cho et al. 1997; Koo et al. 1997). It inhibits

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acetolactate synthase, a key enzyme in biosynthesis of branched amino acids, like sulfonylurea and imidazolinone herbicides (Bae et al. 1997; Lim et al. 1997). According to Koo et al. (1997), pyribenzoxim was safe to rice, wheat, and zoysiagrass and by foliar application showed good efficacy against not only grass weeds, *Alopecurus myosuroides, Digitaria sanguinalis, Echinochloa crus-galli*, and *E. colona*, at 10~30 g ai ha^{-1} but also broadleaf weeds, *Aeschynomene indica, Amaranthus retroflexus, Bidens frondosa, Cirsium arvense, Galium aparine, Persica hydropiper, Solanum nigrum, Stellaria media*, and *Xanthium strumarium*. In comparison with propanil, pyribenzoxim can control *E. crus-galli* up to 6.5 leaf stage when its dose rate was increased to 30 g ai ha^{-1}, demonstrating its wider application window than propanil (Koo et al. 1997). However, pyribenzoxim is known to have no soil activity (Koo et al. 1997).

Bispyribac-sodium (Nominee®) also belongs to pyrimidinyloxybenzoate chemistry developed prior to pyribenzoxim and has been widely used in many countries. This herbicide also inhibits acetolacthate synthase (Shimizu 1997) and has shown good efficacy against *Echinochloa* species, and annual or perennial grass, sedge, and broadleaf weeds, i.e., *Cyperus diffusa, C. iria, Fimbristyllis* spp., *Leersia oryzoides, Murdania* sp., *Panicum distichum, Polygonum* sp., *Sagittaria* spp., *Scirpus* spp., and *Sphenoclea zeylanica* (Braverman and Jordan 1996; Han 2001; Kobayashi et al. 1995; Shinohara et al. 1994; Tachikawa et al. 1997; Yokohama et al. 1993).

Herbicide selectivity is a key element to determine if a new herbicide is applicable for a practical use for a specific crop in controlling weeds in the crop field. The applicability of the new herbicide depends not only efficacy against weeds but also crop safety at a selected dose range. Selectivity means that the herbicide shows sufficient enough weed control at a selected dose but no or acceptably low phytotoxicity to crop at a greater dose than the selected dose for weed control. This dose difference between the dose (A) required to achieve an acceptable weed control and the other dose (B) required to give an acceptable crop safety determines the selectivity of herbicide. We assumed that the ratio (B/A) between these doses is an index to represent selectivity between weed and crop to the herbicide, i.e., “selectivity index”, which can be used as a measure of herbicide selectivity. Herbicide selectivity is determined by differences in morphological, physiological, biochemical and genetic characteristics of crop and weeds. Even a small difference in chemistry of herbicides may result in a large difference in herbicide dose-response and give different selectivity. In the cases of pyribenzoxim, and bispyribac-sodium, although they have a similar chemical structure and are known to be similarly effective in controlling weeds and safe to rice, no comparison between them has been conducted. Therefore, it is worthwhile to directly compare dose-responses of the same plants to these herbicides to differentiate these herbicides. This study was thus conducted to investigate a differential aspect of the two herbicides, in particular, emphasizing rice selectivity.

MATERIALS AND METHODS

Pot experiments were conducted in a glasshouse maintained at 30/23 (day/night)±3℃. Japonica rice variety (*Oryza sativa* L. cv. Ilpoom) or Indica rice variety (cv. MTL250), and barnyardgrass (*E. crus-galli* var. *crus-galli* L.) were grown until about 3 and 4 leaf stages, respectively, in a plastic pot (200 cm^2) containing a sandy loam soil. Spray was made using a CO_2-pressurized belt-driven sprayer (R&D Sprayer, USA) equipped with an 8001E flat fan nozzle (Spraying System Co., USA) adjusted to deliver 300 L ha^{-1}. The plants were then returned to the glasshouse and watered by sub-irrigation as needed. Shoot fresh weight was measured at 20 days after application. The experiment consisted of three replicates in a completed randomized design.

Comparison of technical ingredients

The technical ingredients of pyribenzoxim (98.7%) and bispyribac-sodium (98.0%) dissolved in 20% N-methylpyrrolidone (NMP) and 30% acetone solution containing 1,000 ppm adjuvant of Tween20 were treated to Japonica rice (cv. Ilpoom) and barnyardgrass. Application rates were 0.047~30 g ai ha^{-1} for barnyardgrass and 22.5~720 g ai ha^{-1} for rice. Solvent without herbicide applied to plants was regarded as untreated control. Application timing was approximately 3.8 and 3.2 leaf stages for barnyardgrass and rice, respectively.

Comparison of formulated products

Pyribenzoxim formulated as 3% EC (Pyanchor®, LG Life Sciences, Ltd., Korea) and bispyribac-sodium formulated as 10% SC (Nominee®, Kumiai Chemical, Japan) were applied to Japonica rice (cv. Ilpoom) and barnyardgrass at 3 and 3.5 leaf stages, respectively. As pyribenzoxim was formulated with built-in adjuvant, adjuvant concentration in the spray solution was sequentially diluted as its dose rate decreased. In the case of bispyribac-sodium, which was formulated in twin packs (the one pack for SC containing bispyribac-sodium and the other for its adjuvant), the SC and adjuvant were tank-mixed with 1 : 1 ratio at the top dose and sequentially diluted. Application rates of both herbicides were 3.75~60 g ai ha^{-1} and 15~480 g ai ha^{-1} for barnyardgrass and rice, respectively. Application timing was approximately 3.5 and 3.2 leaf stages for barnyardgrass and rice, respectively.

Comparison of formulated products at the same adjuvant concentration

Adjuvant-free pyribenzoxim 3% EC and bispyribac-sodium 10% SC were dissolved in water containing their relevant adjuvants at 1,000 ppm. Application was made at 4 leaf stage of barnyardgrass and 3.2 and 3.1 leaf stages of Japonica rice cv. Ilpoom and Indica rice cv. MTL250 (Thailand), respectively. Application rates for barnyardgrass were 0.047~30 g ai ha^{-1} for both herbicides, while for rice they were 7.5~ 480 g ai ha^{-1} and 2.5~320 g ai ha^{-1} for pyribenzoxim and bispyribac-sodium, respectively.

Statistical analysis

All measurements were initially subjected to analysis of variance (ANOVA). Non-linear regression analysis was used to fit the standard dose-response model (Streibig 1980) to fresh weights of rice and barnyardgrass. All statistical analyses were conducted using Genstat 5 (Genstat Committee 1993).

RESULTS AND DISCUSSION

Dose-response to technical ingredients

To compare the innate selectivity of pyribenzoxim with that of bispyribac-sodium, pyribenzoxim and bispyribac-sodium were applied after dissolving their active ingredients in solution containing 20% NMP, 30% acetone, and 50% distilled water. Both herbicides showed very good efficacy against barnyardgrass with GR_{50} values of pyribenzoxim and bispyribac-sodium being 3.1 and 2.1 g ai ha^{-1}, respectively (Fig. 1A). The estimated GR_{90} value of pyribenzoxim was 19.2 g ai ha^{-1}, while that of bispyribac-sodium was 11.4 g ai ha^{-1}. Although bispyribac-sodium was slightly more active than pyribenzoxim, the difference was within the variation. In the case activity against rice, bispyribac-sodium caused severe damage on rice,

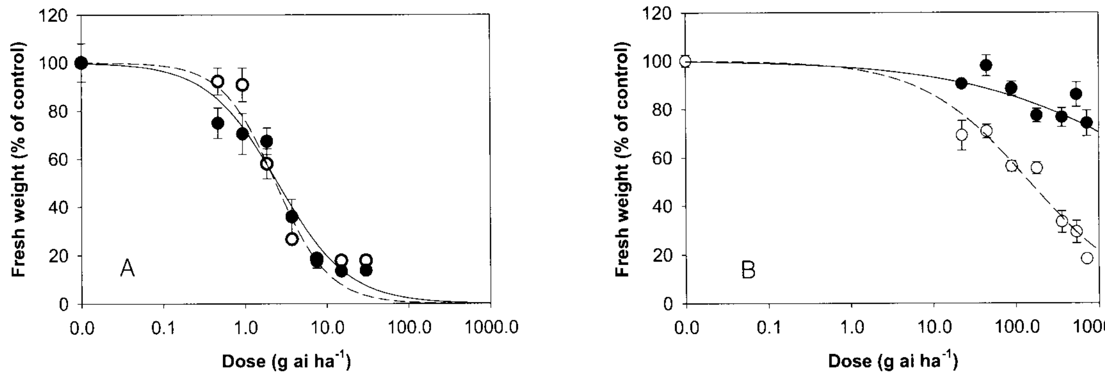

Fig. 1. Dose-responses for fresh weights of barnyardgrass (A) and Japonica rice cv. Ilpoom (B) to pyribenzoxim (●) and bispyribac-sodium (○) dissolved in 20% NMP and 30% acetone solution containing 1,000ppm Tween20.

much greater than that caused by pyribenzoxim, with GR_{50} values of bispyribac-sodium and pyribenzoxim being 145.8 g and 9701.0 g ai ha^{-1}, respectively (Fig. 1B). The estimated GR_{10} value of pyribenzoxim was 28.1 g ai ha^{-1}, while that of bispyribac-sodium was 5.7 g ai ha^{-1}. The selectivity index, estimated by comparing GR_{90} values for barnyardgrass and GR_{10} values for rice, was 1.5 and 0.5 for pyribenzoxim and bispyribac-sodium, respectively (Table 1). This result clearly demonstrates that pyribenzoxim is more selective to rice than bispyribac-sodium with similar efficacy against barnyardgrass.

Dose-response to formulated products

In a practical field condition, rice growers use formulated products based on recommendation provided by manufacturers or distributors. To compare directly those formulated pyribenzoxim and bispyribac-sodium, pyribenzoxim (3% EC, Pyanchor®) and bispyribac-sodium (10% SC, Nominee®) were tested with rice and barnyardgrass. Against barnyardgrass, both herbicides performed well and achieved complete control of barnyardgrass at their recommended dose of 30 g ai ha^{-1} although bispyribac-sodium showed a little better efficacy at lower doses (Fig. 2A). The GR_{50} and GR_{90} values of pyribenzoxim were 10.3 and 16.9 g ai ha^{-1}, respectively, while those of bispyribac-sodium were 3.3 and 9.7 g ai ha^{-1}, respectively. Against rice, both herbicides caused more damage as compared with the above test but bispyribac-sodium

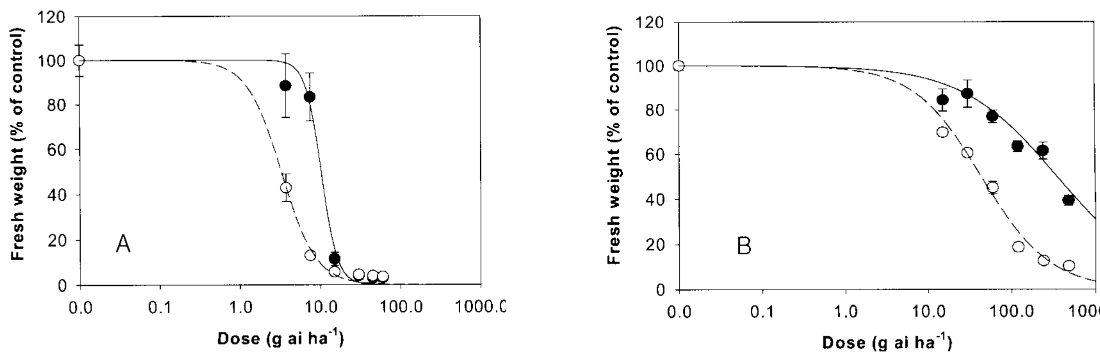

Fig. 2. Dose-responses for fresh weights of barnyardgrass (A) and Japonica rice cv. Ilpoom (B) to pyribenzoxim 3% EC (●) and bispyribac-sodium 10% SC (○).

caused much more severe damage than pyribenzoxim (Fig. 2B). The GR_{50} and GR_{10} values of pyribenzoxim were 351.1 and 19.7 g ai ha^{-1}, respectively, while those of bispyribac-sodium were 43.6 and 5.5 g ai ha^{-1}, respectively. As a result, the selectivity index of pyribenzoxim was 1.2, while that of bispyribac-sodium was 0.5 (Table 1). This result again proves that when tested with formulated products, pyribenzoxim is safe to rice but the bispyribac-sodium is not safe enough for practical use.

Dose-response to formulated products at the same adjuvant concentration

In general, herbicidal activity is determined by not only herbicide itself but also other ingredients in formulation, particularly adjuvant, which improves herbicide penetration into plants and thus increases herbicidal activity (Bunting et al. 2004; Grichar and Sestak 2000; McWhorter 1992). When they were tested without their tank-mix adjuvants, no or very little herbicidal activity was observed in our preliminary test (data not shown). In the above test, the concentration of adjuvant was changed sequentially as herbicide dose rate changed. We thus assumed that this change in adjuvant concentration affected dose-responses to the herbicides. To eliminate the effect of adjuvant on the dose-response, it is necessary to give the same adjuvant concentration in the spray solution regardless of application dose rate. Therefore, pyribenzoxim and bispyribac-sodium were tested at a constant concentration (1,000 ppm) of their relevant adjuvants.

Both herbicides showed very good efficacy against barnyardgrass, whose dose-response to pyribenzoxim was very similar to that of bispyribac-sodium (Fig. 3). The GR_{90} values of pyribenzoxim and bispyribac-sodium were 8.7 and 7.7 g ai ha^{-1}, respectively. By comparison, the dose-response of rice to pyribenzoxim was very significantly different from that to bispyribac-

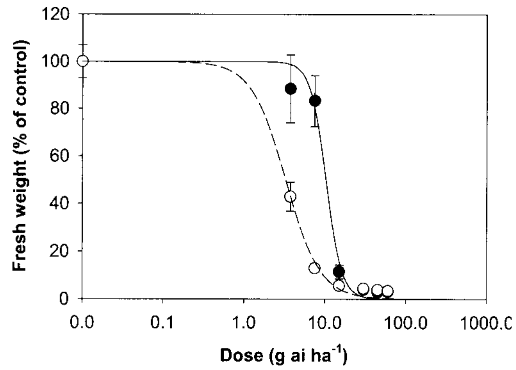

Fig. 3. Dose-responses for fresh weights of barnyardgrass to pyribenzoxim 3% EC (●) and bispyribac-sodium 10% SC (○) treated at the constant adjuvant concentration of 1000 ppm.

sodium, particularly in the case of Japonica rice (Fig. 4). The GR_{10} values of pyribenzoxim were 94.0 g and 185.8 g ai ha^{-1} for Japonica and Indica rice, respectively, while those of bispyribac- sodium were 2.9 and 23.9 g ai ha^{-1}, respectively. As a result, the selectivity indices of pyribenzoxim were 10.7 and 21.3 for Japonica and Indica rice, respectively, while those of bispyribac-sodium were 0.4 and 3.1, respectively (Table 1), indicating that bispyribac-sodium is safe to Indica rice, while pyribenzoxim safe to both Japonica and Indica rice. Therefore, our results clearly demonstrate that pyribenzoxim has greater selectivity between rice and barnyardgrass than bispyribac-sodium.

General discussion and conclusion

The selectivity index was estimated by comparing relative herbicidal activities to weed (GR_{90}) and crop (GR_{10}). It is assumed that if the index is greater than 1, the herbicide tested can be used to manage the weed in the crop cultivation. However, if it is less than 1, the herbicide cannot be used practically due to high risk of crop damage. In this study, our results clearly demonstrated that pyribenzoxim had better safety to rice than bispyribac-sodium but performed similarly in controlling barnyardgrass.

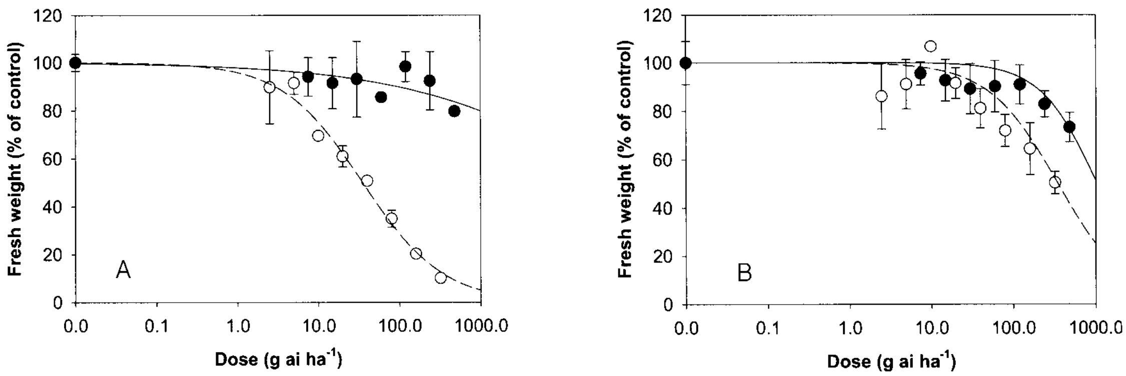

Fig. 4. Dose-responses for fresh weights of Japonica rice cv. Ilpoom (A) and Indica rice cv. MTL250 (B) to pyribenzoxim 3% EC (●) and bispyribac-sodium 10% SC (○) at the constant adjuvant concentration of 1,000 ppm.

Regardless of rice cultivars, the selectivity index of pyribenzoxim was always greater than 1, indicating that pyribenzoxim can be used for Japonica and Indica rice (Table 1). However, the index of bispyribac-sodium was about 0.5 for Japonica rice and only greater than 1 for Indica rice. Therefore, it can be concluded that this better selectivity of pyribenzoxim may allow pyribenzoxim to be more safely used for weed management in rice cultivation than bispyribac-sodium.

It is generally accepted that herbicide selectivity is due to differences in uptake, translocation, and metabolism related with plant species and application timing (Eberlein and Behrens 1984; Leafe 1962). In order for herbicide to reach the target site, it has to overcome many obstacles such as stoma, cuticle layer, epidermis, cell wall, cell membrane, which also gives different selectivity (Fang 1958) and whose characteristics depend on plant species (Choi et al. 1999). Herbicide action in plants requires the herbicide to be translocated to its target site in the plant (Crafts 1966), and the

Table 1. GR_{90} and GR_{10} values for barnyardgrass and rice, respectively, of pyribenzoxim (PBX) and bispyribac-sodium (BPB), and their selectivity indices based on different test methods.

Test method [c]	GR_{90} for barnyardgrass [a] (A)		GR_{10} for rice [b] (B)		Selectivity index (B/A)	
	PBX	BPB	PBX	BPB	PBX	BPB
Test 1	19.2	11.4	(J) 28.1	5.7	1.5	0.5
Test 2	16.9	9.7	(J) 19.7	5.5	1.2	0.5
Test 3	8.7	7.7	(J) 94.0	2.9	10.7	0.4
			(I) 185.8	23.9	21.3	3.1

[a] GR_{90} represents a dose required to inhibit the growth of barnyardgrass by 90%, GR_{10} represents a dose required to inhibit the growth of rice by 10%, and the selectivity index was estimated by dividing GR_{10} value by GR_{90} value.
[b] J and I in parentheses represent Japonica and Indica rice, respectively.
[c] Test 1, 2, and 3 represent methods for comparison of technical ingredients, formulated products, and formulated products at the same adjuvant concentration, respectively.

translocation rate of the herbicide depends on plant species and growth conditions, so difference in translocation thus gives herbicide selectivity between crop and weed (Slife et al. 1962). Metabolic decomposition of herbicide absorbed in plants is also an important cause of selectivity and these phenomena depend on herbicides (Hatzios and Penner 1982; Leafe 1962; Weimer et al. 1988). In this sense, there should be some mechanisms why pyribenzoxim and bispyribac-sodium showed such differences in selectivity between rice and barnyardgrass in glasshouse condition. Therefore, it can be speculated that rice tolerance of pyribenzoxim significantly greater than bispyribac-sodium may be related with differences in herbicide uptake, translocation, and metabolism. Early watergrass (*E. oryzoides*) and late watergrass (*E. phyllopogon*) relatively tolerant to bispyribac-sodium showed greater activity of cytochrome P-450 monooxygenase, which is known to metabolize and thus detoxify herbicide in plant, than sensitive *Echinochloa* species (Fischer et al. 2000; Yun et al. 2005). Activities of cytochrome P-450 monooxygenase to pyribenzoxim and bispyribac-sodium may also be a mechanism of such selectivity difference. Particular interests arise from the finding that pyribenzoxim showed similar safety to both Japonica and Indica rice but bispyribac-sodium showed better safety to Indica rice than Japonica rice. Therefore, it is worth of investigating mechanisms related with selective response of Indica and Japonica rice to pyribenzoxim and bispyribac-sodium and we are currently working on this.

요 약

피리벤족심과 비스피리백-소디움에 대한 피와 벼의 농도반응을 비교하여 이들의 선택성을 비교하고자 포트시험을 온실에서 수행하였다. 피에 대한 제초효과는 비스피리백-소디움이 피리벤족심보다 약간 높았지만 그 차이는 매우 작았으며, 벼에 대한 약해는 두 제초제 간 현저한 차이가 있어 피리벤족심이 자포니카 벼에는 약 5~30배, 인디카 벼에는 약 8배 안전하였다. 피리벤족심과 비스피리백-소디움에 대한 피의 GR_{90}값과 벼의 GR_{10}값을 상대적으로 비교한 선택성지수를 계산한 결과 원제에 대한 선택성 지수는 피리벤족심이 1.5, 비스피리백-소디움이 0.5로써 피리벤족심이 약 3배 선택성이 높았으며, 제제를 직접 비교한 결과 피리벤족심이 1.2, 비스피리백-소디움이 0.5으로 여전히 피리벤족심이 2배 이상 선택성이 높았다. 특히, 전착제 농도를 일정하게 한 조건에서 비교한 결과 자포니카 벼의 경우 피리벤족심의 선택성지수는 10.7, 비스피리백-소디움은 0.4로 약 28배의 선택성의 차이가 났으며, 인디카 벼의 경우 피리벤족심이 21.3, 비스피리백-소디움이 3.1로 약 7배의 선택성 차이가 났다. 결론적으로 피리벤족심과 비스피리백-소디움은 피에 대해 유사한 제초활성을 갖지만, 벼에 대한 안전성은 피리벤족심이 매우 높았으며, 따라서 피리벤족심의 선택성이 아주 높았다.

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