Mineral Composition, Physical Properties, and Nutritive Values of Calcined Limestone and Bivalve Shell for Muscovy Duck Starter

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ABSTRACT
The mortality rate of muscovy duckling raised extensively was very high due to malnutrition. This study aimed to study the beneficial effects of calcination on mineral composition, physical properties of limestone and bivalve shells as mineral supplements for muscovy duck starter. Samples of limestones and bivalve shells were calcinated, and the products were analyzed for physical properties, particle size, and mineral content. Two complete mineral formulas were prepared by mixing the uncalcined and calcined products with other locally available materials. The mineral was mixed at 5% into the basal diet given to 180-day-old muscovy ducklings raised by 16 muscovy broods for six weeks. There were four dietary treatments: control diet (P0), basal diet + 5% uncalcined mineral (P1), basal diet + 5% calcined mineral (P2), and basal diet + 5% commercial mineral premix (P3), respectively. Parameters measured included feed intake, body weight gain, FCR, mortality, and mineral status of blood and tibia bones. Results show calcination increased calcium concentration, tapped and specific densities in both limestone and bivalve shells. Calcination significantly reduced particle size and bulk density of bivalve shell meal. Mineral supplementation using calcined limestone and bivalve shell meal significantly improved feed intake and reduced duckling mortality. The results suggested that calcination enhanced physical properties and nutritional values of limestone and bivalve shell meal shell for Muscovy duck starter.

Keywords: *Muscovy duckling, local mineral, calcination, limestone, bivalve shell, physical properties.*

1. INTRODUCTION

Muscovy duck (*Cairina moschata*) has its own market segment in West Sumatra. Muscovy duck's meat and eggs are commonly used for traditional Minangkabau dishes and liners known as "green chili duck curry" ("gulai itik cabe hijau") and "egg tea" ("teh telur"), respectively. Muscovy duck carcass raised by traditional farms meets the requirements of the consumers due to higher portion of breast meat and a lower content of subcutaneous and abdominal fat in the carcass [1]. Egg tea is a traditional and nutritious energy drink made from fresh egg yolk, mixed with sugar, lime, salt, and brewed with hot tea. Consumers believe the use of duck eggs has several advantages, such as distinctive aroma and taste, rich in vitamins, and remarkable effects on stamina and health [2]. The unique flavor and aroma of the duck meat and egg allegedly related to the raising and feeding practices, where the duck is generally raised extensively by scavenging during the day and consumed various natural feed.

Muscovy duck and egg price is higher than that of kampong chicken and laying ducks due to limited supply. The supply of duck and eggs in the local market still comes from smallholder farms in rural areas. Muscovy ducks are mostly not confined and allowed to roam around the yard with limited provision of supplementary feed. Our previous field study on the most common traditional free-range system found that the average

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number of Muscovy ducks raised was 11-21 ducks/farm. The ducks laid eggs 2-3 times per year with an average of 12 eggs/duck/laying period. The hatchability of eggs was about 84 %, but the mortality of young ducks during the starter period was found very high, ranged from 14 to 42% [3,4]. After hatching, ducklings are usually freed with their mother (muscovy hen) to scavenge around the yard to find their feed. Some farmers supplemented by using rice bran and commercial broiler starter diet high energy and protein but low mineral. We suggested that the imbalanced nutrient density has also been the leading cause of inadequate bone development, which has a significant effect on the weight gain and walking ability of poultry [5]. Ducklings cannot meet their dietary needs and suffer from malnutrition which quickly identifies their physical appearance and poor feather development. Consequently, ducklings strolling, unable to follow the mother, and eventually die due to exposure to rain and predators.

The duckling for an extensive free-range system requires diets with sufficient and balanced nutrients and minerals to normalize the skeleton, growth, and health status. Diet for the starter duck needs mineral supplement with a high mineral concentration and easily digested and absorbed by the young duckling, which still has a limited feed intake capacity and nutrient digestibility. The mineral supplement for duckling could be produced using limestone and bivalve shells mixed with other locally available materials to make a cheap complete mineral. The West Sumatra region, as a part of the Bukit Barisan cluster and located along the coast of the Indian ocean, abounds natural limestone and waste oyster shells. Limestone derived from different natural deposits contains large high calcium (30-40%) and several essential trace elements Mn, Fe, Mn, and Se [6]. Dried oyster shells derived from shellfish living in various fresh water and terrestrial habitats of lakes, rivers, estuarine, and marine represented about 47-56 % of the total body weight of the shellfish and contained calcium of about 31-36% [7]. Calcium (Ca) is one of the essential minerals plays a critical role in the development of bone and its strength for Muscovy duckling [8].

The limestone and oyster shells need to be processed by calcination to increase the concentration of some minerals and improve physical properties before mixture in the diet of young Muscovy duckling. The primary purpose of calcination by high temperature is to eliminate impurities and to decompose the calcium carbonate present into calcium dioxide (CaO_2) [9]. Calcination increased essential mineral concentration and acceptable particle percentage [10], which might have a beneficial effect on intake, digestibility, and important mineral absorption by young ducklings. Some physical property parameters related to intake capacity and digestibility include bulk density, tapped density, specific density, and particle size.

Moreover, calcium oxide, the main component, is a thermo-dynamically stable chemical compound and has antimicrobial effects [11,12]. According to Sadeghi et al [12] calcined seashell had antibacterial effect against *Escherichia coli* and *Staphylococcus aureus.* We hypothesized that calcined limestone and oyster shell as the main component of the mineral supplement is to have beneficial effects on starter duckling health. It consequently enhances feed intake and growth rate, to minimize the mortality rate of starter duckling. There is also limited study on calcined limestone and bivalve shells as a mineral supplement for Muscovy duckling. The purpose of this research is to study the effect of calcination of limestone and shell on mineral composition and physical properties and to evaluate the beneficial effects of using the calcines as a component of mineral supplement in the diets on the performances of Muscovy duckling raised under free-ranged feeding system during starter period.

2. MATERIALS AND METHODS

2.1 Collection and Calcination of Limestone and Shell

We collected samples of limestone in the form of chunks (@ 100 kg) and flour (@ 50 kg) from a local rock mining company PT. Bakapindo (Kamang Mudik, Agam district) processes large natural deposit rock by crushing and grinding it into calcite flour. Samples of bivalve shells derived from the fresh water of lake mussel (Corbicula moltkiana). The shell part of mussels was separated and prepared according to the procedures described by Khalil et al [7].

We calcinated the samples of limestone and shell in chunks and intact form of about 20 and 10 kg each by burning in a modified furnace made from metal drums. Calcination lasted for about 48-72 hours with a temperature of 800-900 ºC until the limestone, and the shell turns white, and the chunks become brittle. We break the calcined limestone and shell down into smaller pieces and particles, then ground them into meal form. Three samples of each product of calcined limestone and bivalve shell meal along with raw or non-calcine limestone and oyster shell meal were taken and then analyzed for minerals, physical properties, and particle size. The mineral content studied included: Ca, P, Mg, Cu, Zn, and Mn by using a spectrophotometer (AAS) according to the standard method described by AOAC [13].

The physical properties measured included: bulk density, tapped bulk density, and specific density. A 100-mm determined bulk and tapped density graduated cylinder according to the method described by Ruttloff [14]. Bulk density is the ratio of the weight of the sample (w) with the volume of space filled by the samples (v1). In contrast, tapped bulk density is the ratio of the weight of the sample (w) with the volume of space filled by the sample after compacted (v2). Bulk and tapped bulk density (g/ml) calculated by using the following formula: w/v1 and w/v2 in g/ml, respectively. Specific density was measured by using a 25-ml Piknometer Pyrex.

Particle size was measured by sieve analysis by using a sieve shaker Retsch VS 1000 (Retch GmbH, Germany). About 300 g samples were sieved for 10 minutes by using a set of sieves with discrete size ranges of 500-1000 µm and classified into four different levels: coarse (>1000 µm), medium (1000-710 µm), small (710-500 µm), and fine (<500 µm). The detained parts in each sieve were weighed. Percentage of each particle size was calculated by dividing the weight of detained part with total weight of dried sample and the multiplied 100%.

2.2 Feeding Trial

We prepared two complete mineral formulas by mixing uncalcined and calcined limestone and bivalve shell meals with bone meal, dicalcium phosphate, iodized kitchen salt, and then enriched with micro-mineral compounds of Zn and Cu ($ZnSO_4.7H_2O$ and $CuSO_4.5H_2O$). The first formula was uncalcined Mineral which was composed of raw limestone and bivalve shell meals. The second was Calcined Mineral by using calcined limestone and oyster shell. We set up the mineral concentration of the formulas to meet the standard of mineral supplement for poultry according to NRC [15] and Weinreich et al. [16]. The formulas were analyzed by using AAS, and their mineral composition is presented in Table 1.

The mineral formulas were mixed with a basal diet composed of corn, rice bran, soybean meal, fish meal, coconut, and palm oil meal. There were four experimental diets: P0 (basal diet without mineral supplement), P1 (basal diet + 5% non-calcined mineral), P3 (basal diet + 5% calcined mineral), and P4 (basal diet + 5% commercial mineral premix). We justified the nutrient and energy compositions to meet the standard requirements of starting and finishing female muscovy ducks recommended by INRA [17]. The formula of the experimental diets and their energy and analyzed nutrient contents is presented in Table 2. The commercial mineral premix used was mineral mix special for duck (Mineral Bebek®) (produced by Eka Farma, Semarang, Indonesia). The mineral composition as stated in the label was: Ca: 48.7%, Mg: 0.29%, I: 0.005%, Fe: 0.3%, Cu: 0.02%, Zn: 0.25%, and Mn: 0.4%.

Table 1. Composition of mineral formulas

Minerals	Unit	Non-calcined Mineral	Calcined Mineral
Ca	%	34.71	36.25
P	%	6.54	6.77
Mg	%	0.77	0.74
Cu	ppm	170.61	161.84
Zn	ppm	2007.48	2265.48
Mn	ppm	140.51	142.71

We feed the experimental diets to sixteen groups of newly hatched ducklings (day-old duck) with mother (Muscovy duck hens). There were in total 180 ducklings with an average body weight of 50.50 g/duckling. Each mothered duck nursed an average of 11.25 ducklings. Each treatment consisted of 4 groups of ducks as replication. The ducklings and their hens were housed in double space pens measuring 2.8 m x 2.6 m x 0.9 m each. The first part is shielded. The floor was covered with rice straw; the walls are made of plywood and a tin roof. This space is intended for rest at night and protection from adverse weather. The second room is a space for a playground, covered with a transparent plastic net and equipped with feeding and drinking facilities. The experimental diets were offered twice a day for six weeks of the starter period. Ducklings were weighed weekly. In the week 5 and 6, duckling with their mother freed outside the pen for 2-3 jam hours per day to scavenge and play in a small pond.

Table 2. Experimental diet formulas and energy and nutrient composition

Feedstuffs	Control diet (no mineral supplement)	Experimental diets supplemented with complete minerals:		
		Uncalcined Mineral	Calcined Mineral	Commercial premix (P3)
	P0	P1	P2	P3
Corn	44.0	42.5	42.5	42.5
Rice bran	5.0	5.0	5.0	5.0
Fish meal	10.0	10.0	10.0	10.0
Soybean meal	16.0	22.0	22.0	22.0
Coconut oil	4.0	5.0	5.0	5.0
Copra meal	10.0	5.0	5.0	5.0
Palm kernel meal	10.0	5.0	5.0	5.,0
Premix (Top mix)	0.5			
Kitchen salt	0.5			
Calcite Mineral		5.0		
Calcinated Mineral			5.0	
Commercial mineral mix				5.0
Energy and nutrient composition				
Metabolizable energy (kcal/kg)*	2.912	2.912	2.900	2.900
Crude protein (%)	17.2	18.7	19.5	18.8
Crude fat (%)	5.7	5.3	5.5	5.3
Crude fiber (%)	8.4	7.6	5.0	6.5
Crude ash (%)	6.8	11.0	10.7	9.9
Calcium (%)	3.0	3.0	3.0	3.0
Phosphorus (%)	0.6	0.6	0.6	0.6
Dry matter (%)	94.7	94.9	95.2	94.7

2.3 Parameter

The performance parameters measured were feed intake, body weight gain, feed conversion ratio (FCR), mortality rate, and mineral status of blood and tibia bones. At the end of the starter period, one duckling per treatment was selected and fasted for about 12 h. The selected ducklings were slaughtered by placing in a blood cone for collecting blood. About 3-4 ml blood was immediately taken using 5-mL disposable syringes, transferred to heparinized vials, then centrifuged at 3000 rpm (LMC-3000, Grant Instrument, UK) for 15 min. The serum was collected in a sterile vial and preserved at -20°C until analysis for Ca, P, and Mg minerals. The weight and dimension (length and diameter) of tibia bones were measured. Tibia bones were then dried, ground, and analyzed for crude and minerals of Ca, P, and Mg. The minerals of blood serum and tibia bone were determined using AAS at the Chemical Laboratory of National Veterinary Service Institute in Baso, Bukittinggi, West Sumatra, Indonesia.

Statistical analysis: The data obtained were expressed as mean and standard deviation (mean ± S.D.). Data were statistically analyzed using one-way variance analysis (ANOVA) in a completely randomized design using IBM.

SPSS Software v 7.0. The Least Significant Difference (LSD) was applied to separate means. Differences were considered at $P<0.05$ [18].

3. RESULTS AND DISCUSSION

3.1 Effect of Calcination on Mineral Composition

Data on the effect of calcination on the macro and trace minerals of limestone and bivalve shell meals are presented in Table 3. Calcium concentration increased in calcined products, but there was no significant difference due to high data variation. In a good calcination process, limestone contained approximately 97 % CaO and low impurities. Bivalve shell hat slightly higher Ca content than that of limestone. This finding was supported by Ha et al [19], who reported that the composition of calcium oxide in seashells was higher than that of limestone. Phosphorus and magnesium concentration was considerably low, ranged between 0.00 to 0.12 g/kg) and not significantly affected by the calcination process. Data on trace minerals showed high variation, especially by Zn and Mn. Cu and Mn concentration reduced by calcination. Calcination significantly increased Zn concentration by the shell. Calcined bivalves found Calcined the highest Zn concentration. The trace mineral composition of bivalve species shows a considerable variation, presumably due to their differences in crystalline structure and the nature of impurities.

According to Boynton [20], there are many factors affected the quality of calcined products i.e., crystallinity degree, impurities, calcination duration and temperature, and chemical reactivity. There is an optimum calcination temperature and speed of heating for every limestone [21]. Limestone derived from different sources varied considerably in their chemical compositions and physical structure [22].

Table 3. Mineral composition of un- and calcined limestone and bivalve shell meal

Minerals	Limestone		Bivalve shell	
	Uncalcined	Calcined	Uncalcined	Calcined
Macrominerals (g/kg)				
- Ca	398.95±30.56	428.41±10.33	402.56±20.77	420.73±16.16
- P	0.12±0.13	0.12± 0.02	0.00± 0.01	0.00±0.11
- Mg	3.79±1.38	1.68±0.08	2.32± 1.43	3.55± 3.68
Trace minerals (ppm)				
- Cu	2.23±0.50	1.69±0.60	3.54±2.59	2.96±2.33
- Zn	13.90±1.57	8.09±2.23	13.09±5.69	191.34±15.07
- Mn	37.16±5.39	19.56±3.81	246.08±358.46	30.49±5.55

3.2 Effect of Calcination on Physical Properties and Particle Size

Table 4 presents mean data on physical properties and particle size distribution of calcines compared to raw limestone and shells, except for the bulk density of bivalve shells. Calcination significantly increased bulk taped and bulk densities. Raw and calcined limestones were dominated by fine particles (< 500 µm) composed of more than 90%. There was no significant effect of calcination on the particle size of limestone. The fine particles of calcines were even lower than that of the raw limestone, which limestone mining companies processed. On the other hand, calcination significantly reduced the particle size of the shell. Calcination decreased the percentage of coarse particles from 31.7% of raw meal to 2.8% of calcined products, while the portion of the fine particle increased from 37.1% to 78.2%.

Physical characteristics are closely related to the mineral composition, crystal structure, and particle size. The oyster shells are largely composed of aragonite and calcite, which have higher strengths and densities than limestone powder [23]. Moreover, the oyster shell comprises small prisms and irregularly shaped folia of calcite with a loose texture, whereas the calcite texture in limestone is crystalline and compact [19]. Bulk density is the relevant chemical composition of the limestone. Bulk density increases with an increase in % MgCO3 content [22]. The differences in particles size and distribution of particle size observed are due to the milling process. The grinding process in limestone mining companies consists of several stages with different grinding systems. On the other hand, calcined products and raw bivalve shells were ground by using a laboratory hammer mill. The specific density, which is related to the texture characteristic of calcines, is smaller for oyster shells than for limestone: large bivalve and seashell hat strong property. Furthermore, Faust [24] reported that particle size affects the temperature at which dissociation begins. Therefore, the difference in the physical properties and particle size of bivalve shells and limestone can be ascribed to the different textures of the samples. Oyster shells are composed of small prisms of calcite that are less than 10 nm thick [19,25].

Table 4. The effects of calcination on the physical properties and particle size of limestone and oyster meal

Minerals	Limestone		Oyster shell	
	Uncalcined	Calcined	Uncalcined	Calcined
Density:				
- Bulk density (g/ml)	0.95±0.03 c	1.43±0.01 a	1.43±0.02 a	1.33±0.01 b
- Tapped bulk density (g/ml)	1.48±0.04 c	1.79±0.00 a	1.63±0.02 b	1.76±0.03 a
- Specific density (g/ml)	2.55±0.02 b	2.61±0.02 a	1.74±0.05 c	2.57±0.05 b
Particle size (%):				
- Coarse	0.09±0.02 d	0.62±0.02 c	31.65±0.90 a	2.82±0.26 b
- Medium	0.09±0.03 d	1.51±0.01 c	14.76±0.22 a	6.98±0.50 b
- Small	0.14±0.08 d	4.21±0.14 c	16.52±0.13 a	11.99±0.28 b
- Fine	99.68±0.04 a	93.65±0.14 b	37.07±0.63 d	78.20±0.98 c

a,b,c,d values in the same row with different superscripts are significantly different

Table 5. Performances of ducklings fed diets supplemented with calcined minerals

Parameter	The control diet (no mineral supplement)	Experimental diets supplemented with complete minerals:		
		Uncalcined Mineral	Calcined Mineral	Commercial premix
	(P0)	(P1)	(P2)	(P3)
Feed intake:				
Total feed intake (g/duck)	1,404.27b (161.82)	2,173.28a (484.79)	1,939.02a (250.87)	1,511.06b (517.63)
Daily feed intake (g/duck/day)	33.43 b (3.85)	52.21 a (10.70)	44.76 a (6.99)	35.98 b (12.32)
Body weight of ducklings:				
Final body weight (g/duck)	424.39 (100.00)	696.81 (254.50)	626.10 (231.25)	482.26 (132.41)
Total body weight gain (g/duck)	381.00 (98.31)	634.96 (231.00)	571.88 (209.05)	439,69 (137.00)
Daily body weight gain (g/duck/day)	9.07 (2.34)	15.12 (5.51)	13.62 (4.98)	10.47 (3.26)
Feed conversion ratio	3.82 (0.85)	3.64 (0.96)	3.61 (0.92)	3.43 (0.28)
Mortality rate (%)	22.16 (23.92)	13.54 (19.65)	8.13 (10.29)	34.88 (26.47)

a,b values in the same row with different superscripts are significantly different

3.3 Effects of Mineral Supplementation on Duckling Performances

The data of mean feed intake, body weight, FCR, and mineral profile of blood and tibia bones of Muscovy duckling supplemented with different mineral formulas are presented in Table 5 and Table 6. Ducklings fed diets supplemented with complete mineral containing both raw and calcined limestone and oyster shell mean (P1 and P2) showed significantly higher feed intake than the ducks fed control diets (P0) and diets supplemented with commercial mineral (P3). There was no statistical difference in feed intake between raw (P1) and calcined minerals (P2). There was also a nonsignificant difference in feed intake between the duck feed diet supplemented with commercial mineral (P4) and those fed the control diets (P0).

There was no significant effect of mineral supplementation on body weight, body weight gain, FCR, and mortality due to high data variation. Numerically, duckling fed diets supplemented with complete mineral containing un- and calcined limestone and oyster shell meal (P1 and P2) had higher final body weight and daily weight gain than those of fed control diets (P0) and a diet supplemented with commercial mineral (P4). Final body weight of duckling supplemented with commercial mineral (P3) equals the control (P0). The highest absolute and body weight gain was found by the duckling supplemented with raw limestone and oyster shell (P1), but there was no significant difference with those supplemented calcines (P2). FCR ranged between 3.4 to 3.8. The best FCR was found by P1, followed by P3, P2, but there was no significant difference among the treatments.

The mortality rate of ducklings ranged between 8.1 to 34.9%. Duckling-fed diets supplemented with calcined limestone, and oyster meal (P2) showed the lowest mortality (8.1%), followed by P1 and P0. The highest mortality of 34.9% was found by duckling supplemented with commercial minerals (P3). There was no statistically significant difference in mortality rate due to considerable high data variability. Supplementation of the complete mineral containing the calcined limestone and lake bivalve shell meal gave no significantly different effects with the uncalcined formula on body weight gain and mineral composition in blood. However, the use of the calcines increased feed intake and bone mineralization, decreasing the mortality rate to 8.1% compared to 13.5% of uncalcined products or 22.2% and 34.5% of the control and commercial mineral, respectively. This indicates that the viability of Muscovy duckling during the starter period could be improved by supplementation of the starter diet with calcined limestone and waste shell. The best viability was presumably related to the better microbial condition in duckling's digestive tracts due to the antimicrobial activity of calcined minerals.

As shown in Table 6, there was no significant effect of mineral supplementation on the mineral concentration of blood. However, the tibia bones of duckling supplemented with calcined limestone and oyster shell had the highest Ca and P concentration and length and diameter sizes. The mean Ca and P concentration of 11.7-14.7 and 8.5-10.2 mg/dL in the present study was higher than the 8.0, and 5.6 ml/dL, respectively, reported by Okeudo et al. [26] for local muscovy duck reared extensively in Nigeria. The Mg level of 2.0-2.4 mg/dL was found in the range of the average plasma magnesium concentration in laying hens which ranged between 2.4 and 4.8 mg/dL as reported by Stafford and Edwards [27]. However, the tibia bones of duckling supplemented with calcined limestone and oyster shell had the highest Ca and P concentration and length and diameter sizes. The Ca level of 19.8-21.7% was higher than 11.3-15.7% reported by Costa et al. [28] for Muscovy duck in housing.

Table 6. DM weight, length, and diameter of tibia bones, and mineral profile of tibia bone and blood samples of ducklings fed diets supplemented with different complete minerals.

Parameter	The control diet (no mineral supplement)	Experimental diets supplemented with complete minerals:		
		Uncalcined Mineral	Calcined Mineral	Commercial premix
	(P0)	(P1)	(P2)	(P3)
DM weight and dimension of tibia bones:				
- DM (g/duck)	2.90 (1.22) [b]	5.04 (1.83) [a]	5.26 (2.18) [a]	2.85 (0.93) [b]
- Length (mm)	9.64 (1.14)	11.28 (1.45)	11.74 (1.93)	10.10 (1.08)
- Diameter (mm)	0.86 (0.09) [bc]	0.98 (0.11) [ab]	1.00 (0.16) [a]	0.84 (0.08) [c]
DM and mineral composition of tibia bones (%):				
- Ca	19.84 (0.69) [b]	20.44 (0.41) [b]	21.73 (0.63) [a]	19.91 (0.92) [b]
- P	1.29 (0.47) [b]	1.33 (0.81) [b]	3.27 (0.87) [a]	1.39 (0.64) [b]
- Mg	0.75 (0.03)	0.75 (0.01)	0.78 (0.02)	0.71 (0.15)
Blood mineral profiles (mg/dL):				
- Ca	14.70 (1.25)	12.58 (1.51)	12.08 (1.01)	11.68 (1.41)
- Mg	2.23 (0.32)	2.20 (0.12)	2.05 (0.51)	2.38 (0.19)
- P	9.35 (1.43)	8.53 (1.20)	10.20 (2.78)	9.19 (1.47)

[a,b] values in the same row with different superscripts are significantly different

4. CONCLUSION

Calcination of limestone and bivalve improved calcium concentration and physical properties in bulk density, compacted bulk density, specific density, and particle size. The calcines' use as the main component of complete mineral in the starter diets positively affected feed intake, body weight gain, feed utilization efficiency, and improved viability of Muscovy ducklings.

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