Seasonal Variations of yeso sika Deer Skin and its Vegetable Tanned Leather

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Abstract: Yeso sika deer is one of the red deer species inhabited Hokkaido and exhibits seasonal molt twice a year. We investigated seasonal variations of morphological and biochemical characteristics of yeso sika deer skin as well as physical, chemical and morphological properties of its vegetable tanned leather. Morphologically, in spring and autumn, which is just active phase of molting cycle, yeso sika deer skins had thick hair fibers, therefore there is many hair follicular spaces in the skin, and many inter fiber spaces were observed by SEM. From biochemical analysis, water, ash and fat content did not vary with the seasons. Protein content of skins in spring and autumn was higher than winter or summer skins, which is just resting phase of molt. Inversely collagen content of these skins was lower than winter or summer skins. Although raw skins showed some seasonal variation in its characteristics, vegetable tanned leathers of yeso sika deer were not so different with the seasons in its tensile strength, shrinkage temperature. Overall, yeso sika deer leather has high degree of water absorption. Our findings suggest that yeso sika deer skin is good material for leather manufacture.

Key words: Yeso sika deer; skin; vegetable tanned leather; seasonal variation

1 Introduction

Yeso sika deer (*Cervus nippon yesoensis*) is one of the red deer species inhabited Hokkaido Island, in recent years, increased their number got to be in trouble. Hokkaido prefecture now attempts to control their quantity and explore how to utilize captured them effectively in which not only meats but also by-products including the skin. We previously reported that their skin has many similarities to calf skin including its size or biochemical composition but has some unique characteristics especially collagen fiber and fiber bundle structure and would be a good material for leather manufacture ^[1,2].

Yeso sika deer exhibits a typical seasonal molting, which occurs in spring and autumn (active molting phase), and shows different coat color in summer and winter (resting phase of molt). In general, molt is a phenomenon in which new hairs are growing and old hairs are shedding. However, it is not only hair production but total skin event including histological and biochemical changes. So we investigated seasonal variations of morphological and biochemical characteristics of yeso sika deer skin and then physical, chemical and morphological properties of its vegetable tanned leather.

2 Experimental

2.1 Materials

Three years old male yeso sika deer were used to experiment. Skin samples of 20 cm x 20 cm in size were cut from the central back portion taken at the time of spring molt (June), summer coat (August), autumn molt (November), and winter coat (February). In each season, three deer skin were used to experiment (n=3).

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2.2 Vegetable Tannage

Fleshed and washed skin samples were limed with 1.5% Na₂S and 5% lime powder, calculated on the basis of skin weight, for 4 days. After liming, scudded pelts were delimed with 3% NH₄Cl and washed with water and then analyzed as delimed pelts. Delimed pelts were immersed in a solution of quebracho powder (BASF Japan, Tokyo) for 2 weeks with adjusting pH and specific gravity. After tannage, leathers were washed and dried at room temperature for analysis.

2.3 Composition of skin and leather

Skin and vegetable tanned leather were crushed in liquid nitrogen, and the content of water, ash, lipid, crude protein, and collagen were measured. Lipid was extracted by the Soxhlet's extractor, protein content was measured by the Kjeldahl method and collagen content was measured by the method of Bergman and Loxley ^[3] as the content of hydroxyproline and multiplying the content 7.52. Vegetable tannin content was calculated by the subtraction of water, ash, lipid and protein contents from total leather weight.

2.5. Scanning electron microscopy

For scanning microscopic observation, samples were prepared according to the method of cell maceration ^[4]. Briefly, skin specimens cut into 5 x 5 mm were prefixed in 2.5% glutaraldehyde in 0.1 M phosphate buffer (pH 7.4), washed with distilled water and immersed in 10% NaOH (alkali treatment). Then the specimens were immersed in 1% tannic acid followed by immersion in 1% OsO₄. Subsequently, the specimens were dehydrated with graded alcohol and lyophilized with t-butyl alcohol. Leathers were directly dehydrated and lyophilized. After mounted on a metal stubs, each lyophilized samples were coated with osmium and observed with scanning electron microscope (JSM-6301F, JOEL, Tokyo).

2.6 Physical properties

Shrinkage temperature, tensile strength and degree of water absorption were measured according to the methods of Japanese Industrial Standards K6550.

3 Results and Discussion

3.1 Morphological aspects

Fig. 1 shows the grain (dermal surface) of skin and vegetable tanned leather of Yeso sika deer. The pore of guard hair and underfur were located transversally to the median line of the animal body.

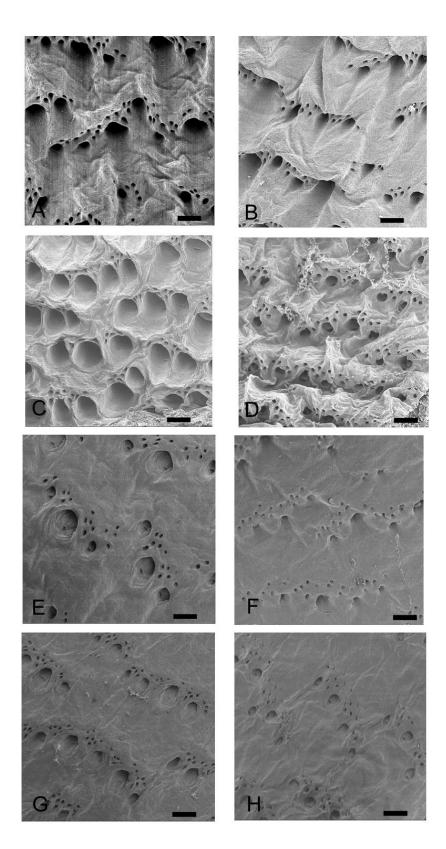


Fig. 1 SEM views of yeso sika deer skin and vegetable tanned leather grain Raw skin (A-D), vegetable tanned leather (E-H), spring (A, E); summer (B, F); autumn (C, G); winter (D, H) Scale bar; 0.3 mm (A-D), 0.2 mm (E-H)

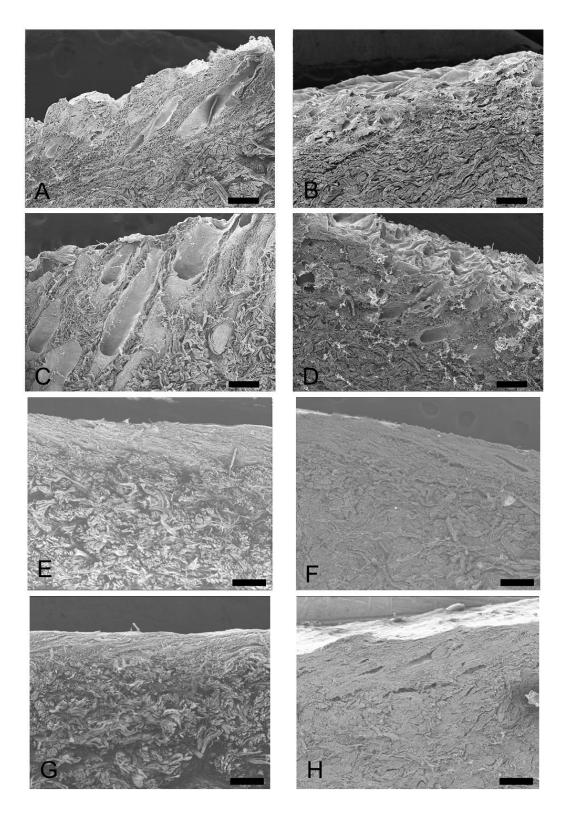


Fig. 1 SEM views of Yeso sika deer skin and vegetable tanned leather saggital plane Raw skin (A-D), vegetable tanned leather (E-H), spring (A, E); summer (B, F); autumn (C, G); winter (D, H) Scale bar; 0.3 mm

Pore size of guard hair in molting phase (Fig. 1A, C) was larger than summer and winter skin (Fig. 1 B, D), so pore occupied large amount of dermal surface. In vegetable tanned leather, dermal surface was flattened and occupancy of pore was decreased (Fig. 1 E~H). Fig. 2 shows the saggital plane of skin and vegetable tanned leather of Yeso sika deer. In molting phase, many developed hair follicle space were observed and collagen fiber bundles had many and wide inter spaces and bundled loosely (Fig. 2 A, C). It was same as in vegetable tanned leather (Fig. 2 E, G), but individual fiber thickness and density of fibrils were not different between seasons (data not shown).

3.2 Chemical composition

Protein and collagen content of Yeso sika deer skin and leather were shown in Tab. 1. Water, ash and crude fat contents of raw skins were not so different between seasons. These contents of vegetable tanned leather were also not different between seasons and tannin content of leathers was 25.7 to 28.4% (data not shown). Protein content was higher in February than other seasons and the proportion of collagen in total protein was higher in resting phase (i.e. skin of August and February). It is thought that in molting phase, many large hair follicles were in dermis and higher content of keratin, major hair component, reflected in this result. However, in vegetable tanned leather, seasonal variation in proportion of collagen in total protein was decreased. It would be resulted from beamhouse process in that removed hair and other non-collagenous proteins. Overall, compared to raw skin, seasonal variations of vegetable tanned leather were decreased in morphologically and chemically. Therefore, it is thought that yeso sika deer skin throughout a year could be used for tannage as same manner.

Season	Protein	Collagen	Proportion of collagen	Protein	Collagen	Proportion of collagen
	(%)	(%)	in total protein (%)	(%)	(%)	in total protein (%)
Spring	28.93	19.87	68.67	63.90	51.37	83.00
Summer	27.30	19.43	71.15	62.22	56.11	87.82
Autumn	27.21	16.47	60.52	62.95	52.67	84.77
Winter	31.15	24.86	79.81	61.89	54.99	87.37

Tab. 1 Protein and collagen content of Yeso sika deer skin and vegetable tanned leather

Tab. 2 shows physical properties of vegetable tanned leather of yeso sika deer. Shrinkage temperature was about 80C°, not so different within the seasons and the all leathers have sufficient heat resistance. Tensile strength was highest in leather made from winter skin and lowest in spring, but its lowest value, 17.25MPa is sufficient for practical leather. Inversely, the degree of water absorption was highest in spring and summer and lower in autumn and winter. It is inconsistent with SEM observations of saggital plane. But at higher magnification of grain, many small-bulged structures were observed (data

not shown), so it may increase the surface area and change the hydrophilicity. We previously reported that yeso sika deer leather has higher water absorption than calf skin, and now we found that seasonal variation in water absorption.

Season	Shrinkage temperature	Tensile strength	Degree of water absorption	
	(C°)	(MPa)	(%)	
Spring	80.4	17.25	152.90	
Summer	80.7	18.45	149.41	
Autumn	80.7	18.72	132.16	
Winter	80.7	22.57	120.39	

Tab. 2 Physical properties of yeso sika deer vegetable tanned leather

We previously reported that vegetable tannage increased resistances to chemical reagents and proteases ^[2]. It was confirmed in this study and these increase not different between seasons (data not shown).

Our results showed that vegetable tanned leather of yeso sika deer is adequate to practical use regardless of season. Having some variation in leathers properties, utilization to leather should consider taking advantage of these properties.

4 Conclusions

Seasonal variation of yeso sika deer skin could be distinguished between active molting phase and resting phase from its morphological and biochemical characteristics. Morphologically, greater hair pore, hair follicle were observed when molting phase. At the same time, protein content was higher but collagen content was lower. But after vegetable tannage, its variation was decreased, especially collagen content and its proportion to total protein. Physical properties of vegetable tanned leather of yeso sika deer have sufficient properties for practical use of leather regardless of season. So, yeso sika deer skin provides a good material for leather manufacture. Further study is needed to elucidate yeso sika deer leather characteristics in detail.

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