Alternative Natural Deliming Agents[1]

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Abstract

This study elucidates whether the herbal extracts can be used instead of various chemical substances used in the process of deliming. To that end, the extracts of christ's thorn seed (*Paliurus spina-christi*), red radish (*Raphanus sativus var. radicula*) and black radish (*Raphanus sativus var. niger*) were employed in the deliming process. Calcium content of the leathers has been identified with Perkin Elmer Optima 2100 DV ICP-OES (Inductively Coupled Plasma- Optical Emission Spectrometry). As a result of the controls carried out, it was concluded that red radish and especially black radish extract have a considerable deliming effect. SEM images of the grain surface are also shown in this paper.

Keywords: Leather, deliming, *Raphanus sativus var. niger*, *Raphanus sativus var. radicula*.

1. Introduction

The purpose of deliming is to neutralise the alkali, lime etc. from the liming process thus causing the skin to become flaccid by releasing the bound water from the swollen protein fibre. Generally ammonium sulphate is used due to its low-cost. [1] Ammonium sulphate is a white color fertilizer with ($(NH_4)_2SO_4$) phsiological acid character and also containing 21% nitrogenous plant nutrient. It has very high buffering capacity, gives also very clean pelts with fine grain and will not cause problems if overdosed. During deliming with ammonium salts the PH is reduced for bating to use pancreatic bating agents at pH 8.0-9.0. Ammonia is however a pollutant both in the waste water and as an atmospheric pollutant due to the free ammonia released during deliming and bating.[1] The excessive mixing of ammonium sulphate to soil and water causes to the pollution of ground and surface waters, to air pollution with nitrogen oxide emission, to the deformation of soil structure, modification of soil reactions and damaging the balance of the elements in the soil, and in this context, to damaging the macro and micro fauna in the soil. In addition, when these compounds with nitrogen content diffuse in the environment excessively, the nitrate amount on the leaf reaches a level which threatens the human health especially on the vegetables with edible leaves . [2]

Together with the diffusion of these compounds into soil at high quantities, their conversion into nitrate by nitrification due to microorganisms, and because of the negative charge of nitrate, they are washed from the soil, thus causing to a high amount of nitrogen in ground waters. This increases the acidity of the soils with low acidity and acidic reaction, thus also increasing the solubility of the elements such as Al and Mn, and causing to the appearance of toxicity of these elements in the plant .[3] In addition, they accumulate in the soil and expand the size of soil pollution. The importance of the excessive mixing of these nitric compounds into soil in terms of soil microbiology is that they negatively impact the activities of symbiotic microorganisms which fix the free nitrogen in air such as ***Rhizobium* sp.** In this case, the way of benefitting from the free nitrogen of air is blocked. As a result, the nitrogen compounds which mix in soil at high amounts limits the activities of nitrification bacteria, and damages the second source of nitrogen which is ready and cost-free (the free nitrogen in air). [4]

[1] This study has partially been extracted from Mümin Çolakoğlu, Murat Kaplan and Demet Şahin's bachelor dissertation study which entitled 'Bazı Bitki Ekstraktlarının Kireç Giderme İşleminde Kullanılabilirliğinin Araştırılması'

Currently, the processes under the title ecologic leather products include natural products which do not harm the environment and human health, and alternative technologies are being developed. Although the use of chemicals is highly common during the deliming stage, which is one of the steps of leather processing, the studies for the use and development of different products for a sustainable ecological production are conducted .[1, 5, 6, 7]

In this research, herbal extracts have been used instead of the chemical agents used during the deliming stage, and their deliming effects have been examined. For this purpose, Christ's torn seed, red radish and black radish extracts have been employed in the study. Historically this plants have been used as medicinal foods for a variety of ailments such as kidney stone expellers and gallstone expellers.[8,9,10,11] Setting up from here, the study aims to identify the deliming activities of the mentioned herbal agents in the leather industry.

2. Materials and Methods

2.1. Materials

2.1.1.Plant Extracts

Radishes (*Raphanus sativus* L.) are members of the cruciferous vegetable family which contain many classes of biologically active phytochemicals. There is a great diversity in the cruciferous vegetable family, and radishes themselves are available in varieties that differ in terms of size, shape, and colour. In this study black (*Raphanus sativus var. niger)* and red radishes *(Raphanus sativus var. radicula)* were used. For the aims of the study, the squeezed juice was obtained from radishes and dried. These extracts were used for the experiments. In folk medicine the black and red radishes have been used since antiquity as a natural drug against abdominal inflation, insufficient digestion and for the inhibition of gallstone formation etc.[12] It was reported that these plants contain sulfur-containing secondary metabolites known as glucosinolates (GLs) and /or their derivatives (isothiocyanates, nitriles, cyano-epithioalkanes formed during hydrolises catalysed by myrosinase), essential oils, flavanoids and other polyphenolic compounds.[13,14,12]

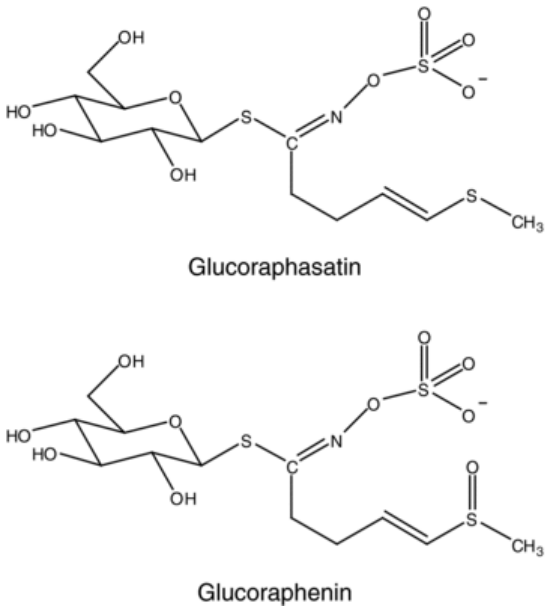


Figure 1. Structures of the primary glucosinolates found in radish varieties .[13]

It was reported that black radish root contains a high level of different glucosinolates (1029 mg/100g)[15] but some researchers reported that they found only glucotropaeolin and it is supposed that during processing and storage, the enzyme myrosinase is activated and all the glucosinolates are hydrolysed to degradation products such as bisothicyanates, nitriles,thiocyanates, oxazolidinetthiones, sulphate and glucose .[12,16] Recently, a number of studies have demonstrated that radishes or radish extracts have biological activity including antioxidant [10,17] antimutagenic [18] and fungitoxic activity .[19]

The christ's thorn plant used in the study was picked in the Ege University (Izmir) campus area. The collected seeds were dried in a damp-free room without being exposed to sunlight. The seeds were grinded and destructed, and the grinded seeds of the christ's torn plant were placed on a heater together with a stirrer, and thus the extraction was realized. Then the extract was powderized.

2.1.2. Skin

In the study, sheep raw skins (wet-salted) were used. The applications were carried out on the leathers with two different structures. Of these leathers, the first one is thick and strict in structure, and the second one is thin and limp in structure.

Table-1. The conditions of ICP-OES

Wavelength (Ca^{+2}) nm	Plasma (L/min)	Aux (L/min)	Neb (L/min)	Power Watts	Plasma View	View Dist
317.933	17	0,20	0,80	1450	Axial	15

2.2. Methods

2.2.1. Processing of raw skin

The leathers were processed in compliance with a standard recipe until the deliming process. After that, each of the prepared extracts was used at 4% in the deliming process. At the end of 90 and 120 minutes, the control was made with phenolfitalein and the effectiveness of the used extracts were examined.

2.2.2. Calcium Analysis of leathers

The leathers weighed at around 0.5 gr precision, were processed through concentrated HNO_3 5 ml and concentrated $HClO_4$ wet decomposition process and the Ca^{2+} amount in the samples diluted to 25 ml was identified with Perkin Elmer Optima 2100 DV ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) at recommended parameters and wavelengths. The operating conditions of the instrument are provided in Table 1.

Leather sample	*Ca^{2+} Content (ppm)*	*Thickness (mm)*
Control sample (Thick)	945.7	1.78
Control sample (Thin)	920.1	1.53
Paliurus spina-christi (Thick)	974.5	2.34
Paliurus spina-christi (Thin)	934.8	1.47
Raphanus sativus var. radicula (Thick)	900.3	1.95
Raphanus sativus var. radicula (Thin)	880.4	0.93
Raphanus sativus var. niger (Thick)	853.2	1.81
Raphanus sativus var. niger (Thin)	772.4	1.13
Ammonium sulphate (Thick)	795.7	1.14
Ammonium sulphate (Thin)	797.5	0.85
Deliming agent (Thick)	749.7	1.46
Deliming agent (Thin)	749.6	1.04

At the figures: 1-Control sample ,2- *Paliurus spina-christi* , *3-Raphanus sativus var. radicula ,4-Raphanus sativus var. Niger,* 5-Ammonium sulphate ,6-Deliming agent

The analyses have been repeated twice on both thick and thin leathers and deliming with ammonium sulphate was compared with the commercially available Mixture of inorganic salts, acids and buffering ammonium salts based deliming agent, and the control sample.

2.2.2.3. Identification of Thickness of Leathers

Satra thickness gauge is used.

2.2.4. Scanning Electron Microscope (SEM)

Hitachi Model TM-1000 Tabletop Microscope was used to obtain SEM images.

3.Results and Discussion

The calcium content and leather thicknesses identified on the leathers with ICP-OES are listed on Table 1.

Figure 2. Calcium content of thick leathers

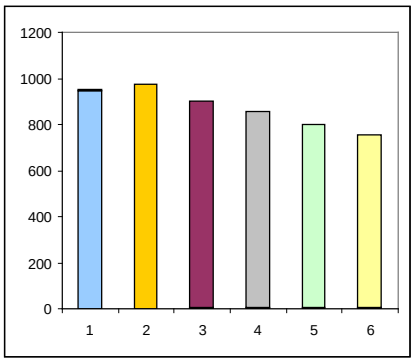
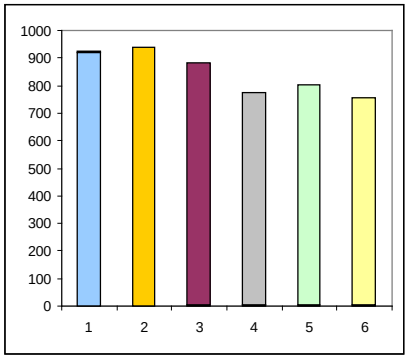


Figure 3. Calcium content of thin leathers



On the 90th and 120th minutes of deliming process, deliming activities were checked with phenolphtalein, and the results obtained accordingly are shown on Table 3, 4, 5 and 6.

Table 3. The effect of used plant extracts on thick leathers at the end of 90 minutes

Extract type	pH value after process	Cross section color (Control with phenolfitalein)	Deliming effect
Paliurus spina-christi	>8.2	Pink	None
Raphanus sativus var.radicula	>8.2	Light pink	Little
Raphanus sativus var. niger	>8.2	Very light pink	Good
Control (wash only with water)	>8.2	Dark pink	Bad
Ammonium sulphate (1,5 %)	8.2	Colorless	Very good
Deliming agent (1,5 %)	8.2	Colorless	Very good

Table 4. The effect of used plant extracts on thick leathers at the end of 120 minutes

Extract type	pH value after process	Cross section color (Control with phenolfitalein)	Deliming effect
Paliurus spina-christi	>8.2	Light pink	Little
Raphanus sativus var.radicula	>8.2	Very light pink	Little
Raphanus sativus var. niger	<8.2	Colorless	Very good
Control (wash only with water)	>8.2	Dark pink	Bad
Ammonium sulphate (1,5 %)	8.2	Colorless	Very good
Deliming agent (1,5%)	8.2	Colorless	Very good

Table 5. The effect of used plant extracts on thin leathers at the end of 90 minutes

Extract type	pH value after process	Cross section color (Control with phenolfitalein)	Deliming effect
Paliurus spina-christi	>8.2	Light pink	Little
Raphanus sativus var. radicula	>8.2	Light pink	Little
Raphanus sativus var. niger	>8.2	Very light pink	Good
Control (wash only with water)	>8.2	Dark pink	Bad
Ammonium sulphate (1,5 %)	8.2	Colorless	Very good
Deliming agent (1,5 %)	8.2	Colorless	Very good

Table 6. The effect of used plant extracts on thin leathers at the end of 120 minutes

Extract type	pH value after process	Cross section color (Control with phenolfitalein)	Deliming effect
Paliurus spina-christi	>8.2	Very light pink	Good
Raphanus sativus var. radicula	<8.2	Colorless	Very good
Raphanus sativus var. niger	<8.2	Colorless	Very good
Control (wash only with water)	>8.2	Dark pink	Bad
Ammonium sulphate (1,5 %)	8.2	Colorless	Very good
Deliming agent (1,5 %)	8.2	Colorless	Very good

During the researches conducted, SEM images of the leathers were obtained through enlarging by 80 times. Especially, as also clearly noted on the images, certain changes occurred on the skin structure of thin and thick leathers depending on the

given agent. Especially, a thickening of the leather and coarsening on the leather skin was observed as anticipated when *Paliurus spina-christi* extract in polyphenolic structure was given to the leather during the deliming stage. As a result of deliming of the leather with water, deliming could not be realized completely, and cracks occurred on the surface, especially veining occurred on thick leather. Herbal agents give the leather their own peculiar colors, while a thin, leaning and clean leather was obtained after the process done with ammonium sulphate and commercial deliming agent. As a result of processing with black radish, a thin skin was obtained, but it gave the skin a yellowish color.

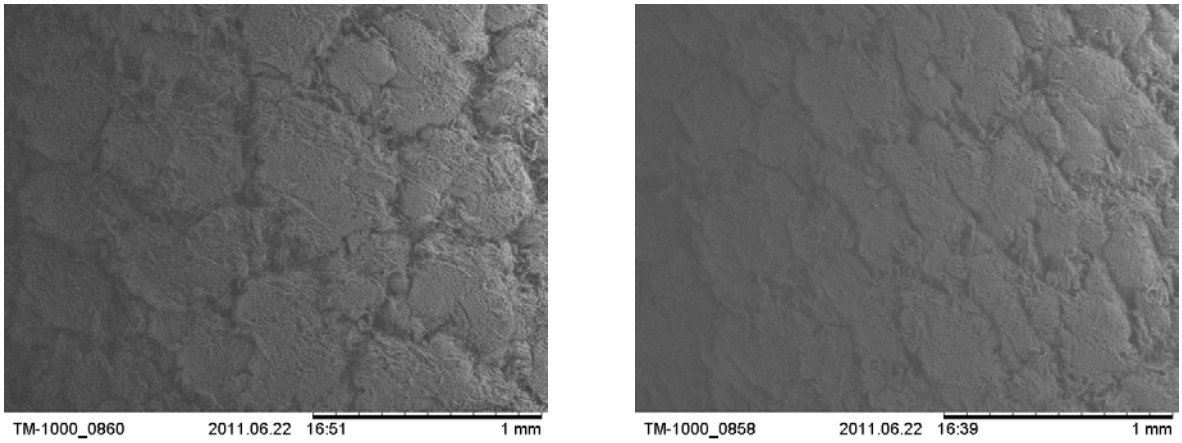


Figure 4: Deliming with ammonium sulphate thin and thick leathers SEM images x80

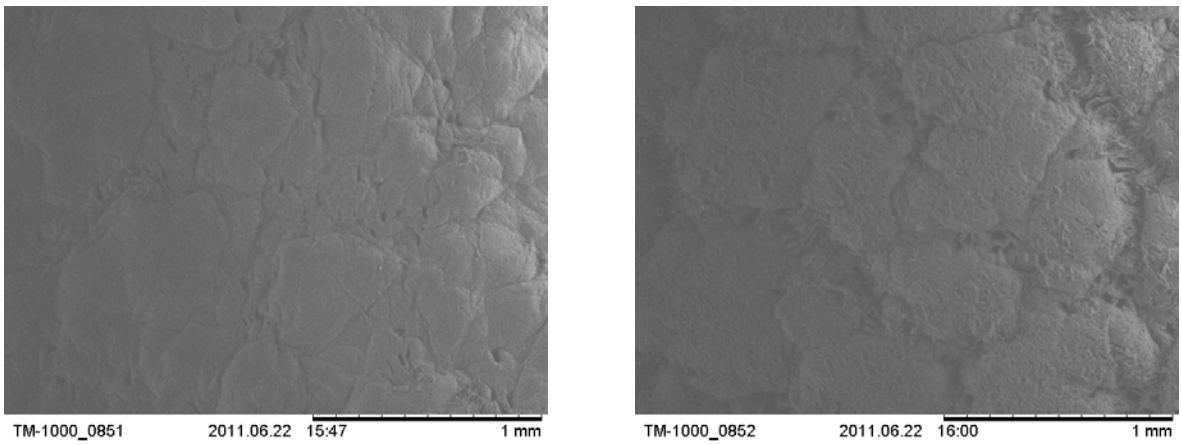


Figure 5: Deliming with *Raphanus sativus var. niger* thin and thick leathers SEM images x80

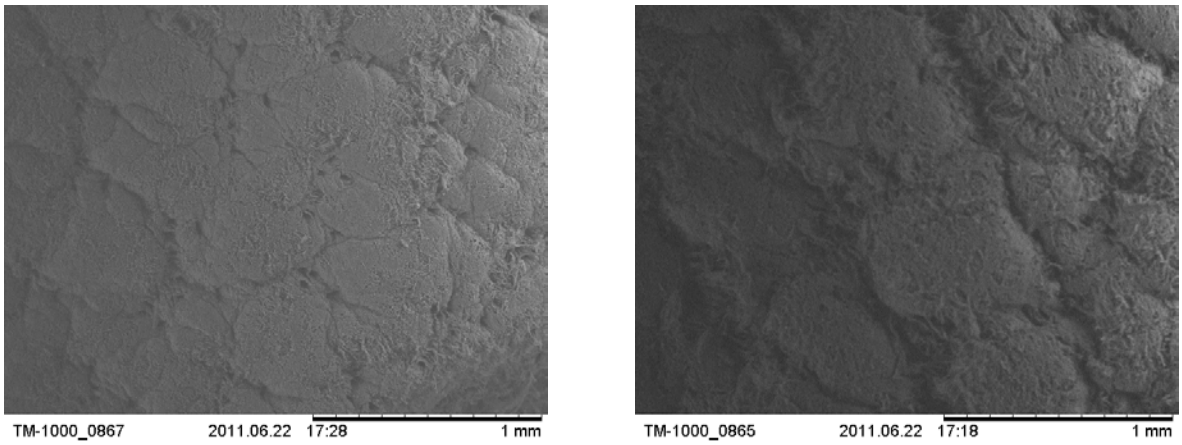


Figure 6: Deliming with *Raphanus sativus var. radicula* thin and thick leathers SEM images x80

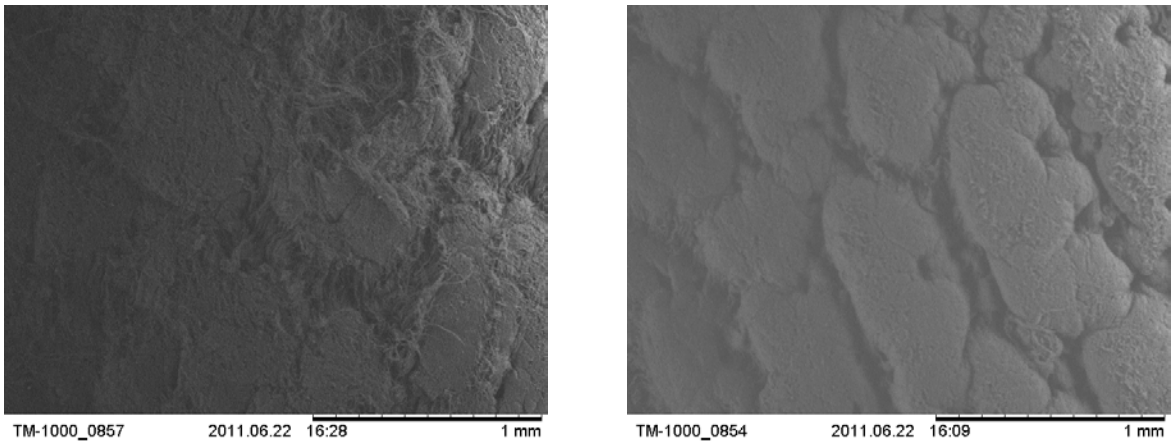


Figure 7: Control groups- Deliming with water thin and thick leathers SEM images x80

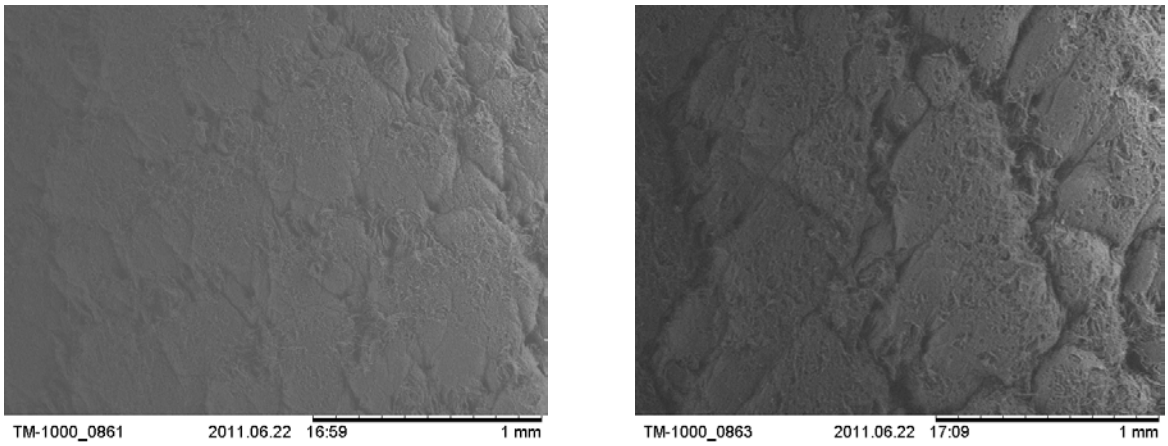


Figure 8: Deliming with industrial deliming agent thin and thick leathers SEM images x80

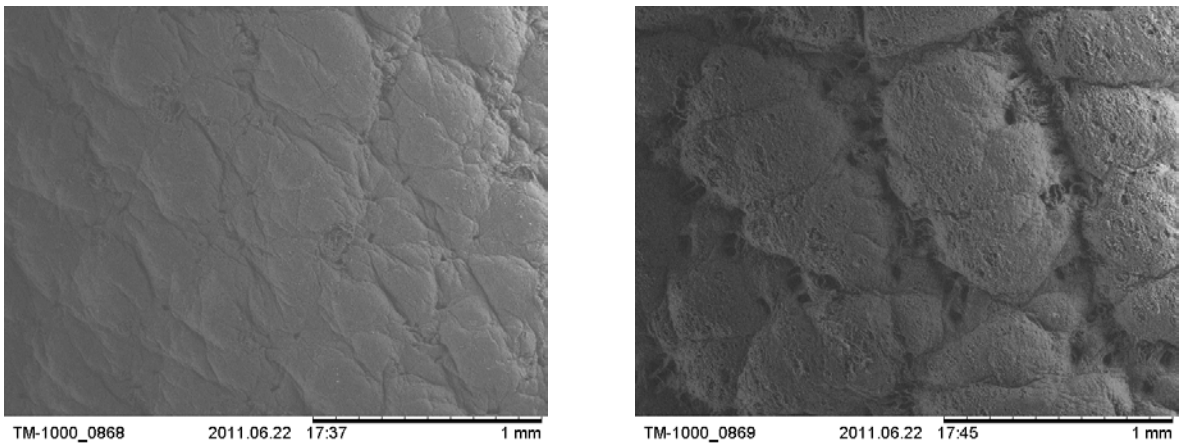


Figure 9: Deliming with *Paliurus spina-christi* thin and thick leathers SEM images x80

Conclusions

Industrialization rapidly accelerates as a result of the never-stopping advancement of modern technologies in our era, and global competition among countries climbs day by day. However the human life- and environment-threatening extent of the waste amount, which has been highlighted prominently in recent years, has become a serious issue that requires measures being taken. The use of natural products instead of the chemical agents used in processes for the sake of protecting the human- and environmental-health is being researched and tried to be implemented also in the leather industry similar to all other branches of industry. This study inspected whether natural agents would be used instead of chemical preparations during

deliming process as one of leather processing steps, and reached certain positive results. It has been identified that the black radish extract has a high deliming impact, while red radish extract is also effective, but not as much as black radish. Especially for the leather types without thick structures, black radish extract may be an alternative to other commercially available preparations. According to the literature study we conducted, it is known from many

researches that radish extracts contain glucosinolates (GLs). Glucosinolates are important thiosaccaridic metabolites and the researches on their synthetic production are currently ongoing. As a further step to this study, the active compound in the radish extract should be identified, and synthetic means of production of this substance, its economic worth, environmental importance, advantage and disadvantage for leather industry should be scrutinized.

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