

Abstracts of

International Baltic Sea Region Scientific Conference

Interdisciplinary Research for Higher Socioeconomic Value of Forests

June 10-12, Riga, Latvia



norden

Nordic Forest Research
Co-operation Committee (SNS)



EFI ASSOCIATED EVENT

LATVIJAS VALSTS MEŽI

Main session

ISOLATION OF SUBERINIC ACIDS FROM EXTRACTED OUTER BIRCH BARK DEPENDING ON THE APPLICATION PURPOSES

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The research applies to silviculture and the utilization of wood material (bark) for obtaining of triterpenes and saturated higher fatty acids, containing reactive hydroxyl and epoxy groups, which are used to synthesize high added value derivatives for pharmacy, cosmetics, agriculture, the spirits industry, emulsion production, the polymer industry, etc. Therefore, the application of the results of our investigation has synergy with material science. The aim of the investigation was to increase the utilization efficiency of birch bark and to inform the audience about the wide scope of high added value products, which could be produced from this valuable raw material.

In Latvia's plywood factories, along with veneer shorts, birch bark is burned up in boiler-houses for steam and heat production. Silver birch (*Betula pendula* Roth.) outer bark comprises 2.0% of the veneer blocks' mass. For producing 1 m³ of veneer, on the average, 2.7 m³ of veneer blocks are necessary, of which 28.6 kg is o.d. outer birch bark. If the plywood export was 246.1 thousand m³ in 2012, the total annual potential of such a valuable raw material can reach 7000 t in Latvia. Besides triterpenes, about 45% of the outer bark mass is polyester - suberine, formed by higher saturated oxyfatty acids with a unique and rarely naturally found location of functional groups in the molecule. Simultaneously with producing 1 m³ of plywood, it is possible to obtain also about 17 kg of suberine from outer birch bark. Epoxy-hydroxy stearic acid or "HEPA" (18-hydroxy-9,10-epoxy-octadecanoic acid), which comprises 27-28% of the total suberinic acids' mass, can be obtained by alkaline depolymerisation. HEPA is an interesting raw material for organic synthesis, because it is encountered seldom in nature, and it is very difficult to obtain it synthetically. It can be used as a starting substance of the fragrance ambretolide (oxocyclopentadec-10-en-2-one), with application in domestic chemistry and in shampoo production.

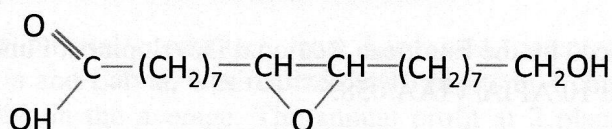


Figure 1. Structural formula of 18-hydroxy-9,10-epoxy-octadecanoic acid.

The extracted outer birch bark, left-over from the isolation of triterpenes, was depolymerised in alkaline (NaOH or KOH) solutions in water or an alcohol-water mixture. The use of different alkaline solutions was determined by the necessity to preserve the reactive epoxy groups present in the obtained individual suberinic acids. In the water medium, most of the epoxy groups are formed by the hydroxyl groups at the C-9 and C-10 atoms. Two methods for obtaining of suberinic acids were compared. Three parallel depolymerisation experiments were made for each method and two parallel aliquots of each sample were analysed by triple procedures. The results represent the average values of each experimental method, which do not exceed a 5% variation for both the indices between the parallel aliquots and those between the parallel aliquots of the same sample. To be acceptable for practical use, a method should be chosen, depending on the application purpose. If it is necessary to retain epoxy groups or positioned hydroxyl groups in a suberinic acid molecule, or isolated fractions of individual suberinic acids such as HEPA, certain pH and temperature ranges are required, which certainly makes the process more complex and time consuming. However, the

resulting products, namely, individual suberic acids show valuable properties in the application purposes related to organic synthesis. The fractionation of suberic acids by sedimentation in certain ranges of the solution pH made it possible to obtain suberic acids with the HEPA content up to 58% o.d. total suberic acids (Table 1).

Table 1. Yield and properties of fractionated suberic acids

pH of the solution	Yield, % o.d. extracted outer birch bark	Acid number, mg KOH/g	HEPA content, % o.d. total suberic acids
6.0	19.3	138.1	58.0
4.7	11.3	75.3	57.3
2.1	4.9	165.9	3.3

If it is planned to use salts of suberic acids as an additive in surfactant compositions, or as a component in an acidic form for polyurethane synthesis, there is no need to retain all functional groups (hydroxyl or epoxy) during the preparation process. Therefore, also the technological process does not require precisely fixed pH and temperature ranges. After the acidification of sodium suberates, it was possible to obtain a mixture of suberic acids (45-50% o.d. extracted outer birch bark) with the acid number 189.7 mg KOH/g and the HEPA content 21.1%. The mixture of suberic acids was successfully used as a hydroxyl groups containing component in polyurethane synthesis. The obtained polyurethane foams showed very good mechanical and dimensional stability properties, which can be developed into novel “green” composite materials with tailored properties.

Looking for the utilisation of the process waste waters, the possibility of using potassium hydroxide instead of sodium hydroxide in the neutralisation operation was envisaged. It may be advantageous to use nitric acid in the acidification process, because then a potassium nitrate solution can be obtained as a by-product and used as a fertiliser in gardening and floriculture.

Keywords: *Birch bark, depolymerisation, suberic acids, 18-hydroxy-9,10-epoxy-octadecanoic acid.*

The work has been financed by the European Regional Development Fund, contract No. 2010/0289/2DP/2.1.1.1.0/10/APIA/VIAA/058.

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