

## STUDYING THE INFLUENCE OF EXTRACTANTS NATURE IN THE PROCESS OF THIN-FILM VAPOR-PHASE EXTRACTION ON COMPOSITION, DEGREE OF EXTRACTION AND FORM OF OBTAINED PRODUCTS

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*The technique of thin-film vapor-phase extraction of vegetable raw material has been described. By the example of birch bark the efficiency of the technique for obtaining extractive substances especially of triterpeneoid nature is shown.*

As a result of activity of wood-processing enterprises large quantity of cortex wastes the volume of which amounts to 10...15 % of all resources of processed wood is formed at the adjacent territories annually. At long-term storage crust may be a source of a number of phenolic compounds which are washed off with meteorological precipitations and melt water contaminating environment [1].

Common birch bark (*Betula Pendula* Roth) is known as a source of triterpenoid [2]. Their total content achieves 315 g/kg in terms of bone-dry raw material [2]. Triterpenoid composition is represented by the following compounds: betulinal (78,1 %), lupeol (7,9 %), methyl ether of betulinic acid (4,3 %), erythrodiol (2,8 %), methyl ether of oleanolic acid (2,0 %), betulinic aldehyde (1,2 %). About 3,7 % accounts for the rest of triterpenic compounds [2].

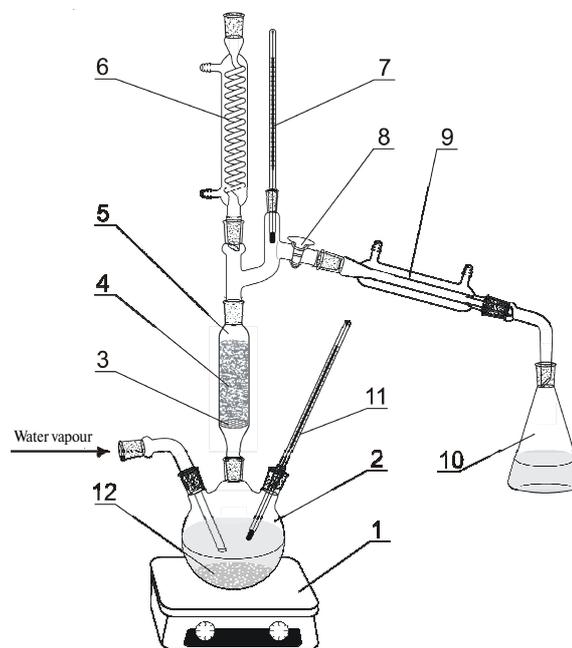
Betulinal possesses antivirus, antineoplastic and antiseptic properties, displays antioxidant activity. Betulinal derivative – betulinic acid – depresses growth of black cancer and other cancer cells [3].

Thus, betulinal accessibility and biological activity range it with valued natural source for using both in native state and in the form of different transformation products. Perspectives of betulinal versatile application in medicine, pharmacy, veterinary science, paint and varnish industry require the development of efficient techniques of its obtaining from wastes of wood-processing industry.

Extraction is one of the main methods of separating vegetable raw material into individual components or their complexes. Extractants are chosen on the basis of physicochemical properties of extracted compounds. Selectivity of extraction is achieved by selecting corresponding solvent.

Simple in work and resultant methods are used more often: maceration, digestion, percolation, perforation and extraction [4]. Distinguished boundary could not be often drawn between these processes. Technological and instrument extraction process arrangement is various: from applying the devices in all its varieties and percolation in separating funnels to more widely spread extraction technique by carrying out sequential single processing of a part of raw material with fresh solvent at normal temperature (20...25 °C) (maceration) or with heating (digestion) with gathering and combining obtained solutions for further solvent distillation from extractant.

Efficiency of any type of extraction of solid substance with liquid depends first of all on its solubility and transition rate from one phase into another. Solubility may be changed selecting corresponding solvent into which the required substance mainly transfers and present impurities stay in solid phase. Transition rate of a substance from solid phase into solution is mainly determined by the rate of liquid penetration into solid phase, diffusion rate of the substance in liquid and removal rate of the substance from phase boundary. In comparison with the system of two liquid phases the equilibrium on the boundary of solid and liquid phases occurs very slowly. It is possible to accelerate the approach to the equilibrium increasing solid phase surface owing to sample grinding or constant supply of fresh solvent to the phase boundary. Besides, it is possible to accelerate equilibrium achieving by simple mixing (at maceration and digestion) or due to countercurrent (at percolation).



**Figure.** Installation diagram: 1) heater, 2) accumulator, 3) metal lath, 4) birch bark, 5) extraction column, 6) backflow condenser, 7-11) thermometer, 8) cock, 9) direct condenser, 10) capacity for gathering regenerated solvent, 12) grained extractant

On the basis of defects analysis of existing extraction techniques and physicochemical regularities of extraction

process we developed the new high-performance extraction technique – thin-film vapor-phase extraction [5].

Birch bark stocked in Tomsk neighborhood, ground to the particles with the size of 3...5 mm, dried to the constant mass at temperature 105 °C was used as the original raw material. Extraction process was carried out in extractor (Figure). Extractor represents extraction column – 5, the backflow condenser – 6 is attached above and below there is an accumulator – 2 with a choke for introduction of direct water vapor. The accumulator is heated with the heater – 1. The ground birch bark – 4 is loaded into extraction column. Extractant (two-component mixture from easy-to-boil solvent with boiling temperature lower than 100 °C and water) is loaded into accumulator. The accumulator is heated by water vapor introduced into it or the heater. Extractant vapors pass through the layer of ground birch bark and condensed in the backflow condenser – 6. Condensate sprays the layer of the ground birch bark passing through its layer; enriched with extractive substances and flows down into accumulator. In this case extractant evaporates and returns to the extraction column and dissolved extract precipitates in the form of granulated material – 12.

At the end of extraction the backflow condenser is changed into direct one – 9 and easy-boiling solvent is distilled from accumulator and ground birch bark in extraction column with direct water vapor or accumulator temperature increase. The sediment is separated by filtration and dried. Regenerated easy-boiling solvent is used repeatedly.

Extraction took 2...4 h. The obtained extract samples were analyzed at HPLC-chromatographer HP 1100, column – Microbore 2×250, mobile phase: 95 % – CH<sub>3</sub>OH, 5% – H<sub>2</sub>O, acidulous H<sub>3</sub>PO<sub>4</sub> in terms of 0,2 ml/l H<sub>2</sub>O. Detector – diode array, range 180...700 nm. Peaks were identified according to the standard and UV-absorption spectra.

In the given paper the dependence of betulin yield (total extract) and content of betulinol in it on extractant nature was studied to determine the influence of solvent nature on extraction intensity and selectivity (Table).

**Table.** Dependence of extraction product yield on time and extractant nature

Easy-boiling solvent	Suggested method			Method [6]	
	Extract total yield, % (betulinol content, %)	Betulinol yield relative to crust, %		Extract total yield, % (betulinol content, %)	Betulinol yield relative to crust, %
		2 h	4 h		
Ethanol	11,8 (65,8)	7,76	8,19	–	–
Propanol-2	15,7 (36,6)	5,75	7,69	20,6 (46,0)*	9,48
Hexane	6,0 (92,1)	5,53	7,49	10,5 (90,1)**	9,46
Ethyl acetate	18,3 (34,5)	6,31	7,76	15,5 (60,0)*	9,30

\* Extraction time 10...12 h

\*\* Extraction time 30 h

It is seen from table data analysis that the choice of easy-boiling solvent determines to a considerable degree both qualitative and quantitative composition of the obtained product. So using hexane more pure betulinol is managed to be obtained to the prejudice of the rest extractive substances. Using ethyl acetate extract qualitative composition expands and completeness of extracting betulinol remains. Therefore, extraction process selectivity may control the selection of extractant composition. It was stated in [6] that at birch bark exhaustive extraction the betulinol yield 9,30...9,48 % may be achieved, however, after two hours of extraction about 58,5...67,8 % of betulinol is extracted of its total content in birch bark. And after four hours it is 81,1...83,4 %. Further process carrying out results in increasing product extraction completeness but in this case process costs growth significantly.

It was also stated that extraction temperature condition influences the ratio of extractant components in extraction column and in accumulator. It determines to a considerable degree the qualitative composition of the obtained product and its mechanical properties.

The important fact is that it is water presence as one of extractant components that promotes granulation of the formed sediment in the accumulator that results ultimately in simplifying further technological processing stages such as filtration and drying of the end product. The range of water and easy-boiling solvent ratio in the accumulator for which stable granulation is observed was found.

So it was stated for two-component extractant ethanol-water that extraction optimal conditions are achieved at liquid phase temperature in the accumulator equal 83...85 °C and temperature inside the extraction column – 82...84 °C, ethanol mass fraction in accumulator amounts to 22 %. Following these parameters the extract comes out in the form of granulated sediment handy for further processing. Decreasing ethanol concentration in the accumulator the extract represents flaky mass that complicates further filtration. If alcohol content is higher than 22 % then fine-dispersed suspension is formed.

When using the solvent immiscible with water, for example, hexane the ratio of the components does not considerably influence product composition and appearance. In this case coagulation occurs on hexane-water boundary at regeneration of easy-boiling solvent.

Thus, the method of thin-film vapor-phase extraction of vegetable raw material was developed by the example of birch bark. The main regularities of the influence of nature of easy-boiling extractant component on composition, extraction degree and form of the obtained extracts were determined. It was shown that extraction process intensification is stipulated by carrying out the process in thin layer at spraying birch bark layer with extractant condensate as well as owing to the raised gradient of extractive substance concentration in the system extractant-birch bark.

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## REDUCTION OF SOME CYCLIC DERIVATIVES OF DIPHENIC ACID WITH SODIUM BORANE IN ALCOHOLS

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*Reduction of heptamerous cyclic imides with sodium borane has been carried out for the first time by the example of some imides of diphenic acid. In this case for the first time amides of 2'-hydroxymethylphenyl-2-carboxylic acid which are potentially valued bioactive compounds were obtained. It was shown that the nature of substituent at nitrogen atom influences the reaction products yields and composition. The reduction of diphenic acid anhydride with sodium borane in simple alcohols occurs with the formation of reduction products – 7H-dibenzo[c,e]oxepin-5-on (36...46 %) as well as products of diphenic acid alcoholysis-monoester (29...36 %). In this case the nature of alcohol influences weakly reaction products ratio.*

Imides of diphenic (biphenyl-2,2'-dicarboxylic) acid are of practical interest as semi-products for obtaining new nitrogen-containing biologically active substances – derivatives 2,2'-substituted biphenyls [1]. Recently new synthesis methods of these compounds based on reaction of diphenic acid with ureas were proposed [2, 3]. For further functionalisation of the above stated imides their reduction with sodium borohydride in methanol medium was studied in the given paper.

The analysis of literary data showed that reduction of dicarboxylic acid cyclic imides with alkalis borohydrides is known only by the example of penta- and hexamerous cycles [4–8] in this case succinimide, phthalimide, glutarimide and their derivatives served as a rule as substrates. There is no information about similar reactions for heptamerous cyclic imides in scientific literature.

Earlier unsubstituted imide of diphenic acid **Ia** was reduced with zinc amalgam in hydrochloric acid and with lithium aluminum hydride in ether. In the first case 6,7-dihydrodibenzo[c,e]azepine-5-on was obtained, in the second – 6,7-dihydro-5H-dibenzo[c,e]azepine (with outputs of 13 and 29 % respectively) [9].

We studied sodium borohydride influence on some imides of diphenic acid in methanol. For this purpose a number of imides containing substituents of different nature at nitrogen atom was selected. They are: hydrogen (R=H, **Ia**), alkyl (R=CH<sub>3</sub>, **Ib**), aryl (R=Ph, **Ic**),

aralkyl (R=CH<sub>2</sub>Ph, **Id**), halogenalkyl (R=CH<sub>2</sub>CH<sub>2</sub>Cl, **Ie**) and hetaryl (R=antipyryl-4, **If**).

It was revealed that reduction starts at room temperature (20...25 °C) and finishes for 20...25 min.

It was shown that reduction of unsubstituted imide of diphenic acid **Ia** by 2 moles of NaBH<sub>4</sub> in methanol results in forming mixture of four products. Only the main reaction product which is the amide of 2'-hydroxymethylbiphenil-2-carboxylic acid **IIa** was extracted individually (Fig. 1). Compound **IIa** was obtained with the output (32 %).

One more product of this reaction by the data of thin-layer chromatography (TLC), is probably 7H-dibenzo[c,e]oxepine-5-on **III**. The rest products could not be identified by the moment.

N-substituted imides **Ib-e** are reduced with 2 moles of NaBH<sub>4</sub> in methanol exclusively to acyclic N-substituted amides of 2'-hydroxymethylbiphenil-2-carboxylic acid **IIb-e**. Yields of reduction products with such substituents as methyl **IIb**, phenyl **IIc** and benzyl **IId** amount to 84, 85 and 88 % respectively. N-(2-chloroethan)imide **Ie** forms respective amide **IIe** only with the yield of 63 %. Reduced yield of the product **IIe**, may be evidently explained by the fact that imide **Ie**, in comparison with imides **IIb-d** contains reactive substituent – CH<sub>2</sub>CH<sub>2</sub>Cl, the chlorine atom in which may undergo various reactions of substitution or removal in the given