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Extraction of cinnamic alcohol from Rhodiola rosea using deep eutectic solvents

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Abstract. The aim of this study is to assess the possibility of using deep eutectic solvents (DES) for the extraction of components of essential oils and biologically active substances from the rhizomes of Rhodiola rosea. Cinnamic alcohol was obtained obtained in aqueous, methanol, ethanol and DES extracts by maceration. Content of the alcohol in extracts was assessed. For preparation of DES, choline chloride was used as an hydrogen bonds acceptor, and malonic acid and glycerol were used as hydrogen bonds donors. Analysis was performed by gas chromatography-mass spectrometry using a GCMS-QP2010 instrument (SHIMADZU) with NIST 27.147 databases. It has been established that the mixture of choline chloride + glycerin + water extracts more than 2 times more cinnamic alcohol than ethanol, and more than 5 times more than methanol.

1. Introduction

Rhodiola rosea is a well-known medicinal plant in scientific and traditional medicine that is widespread in the Arctic, on the coasts and sea cliffs. In Russia, it grows in the Mountain Altai, the Polar Urals, in the Murmansk region and some other regions [1,2]. Glycosides of p-tyrosol and cinnamic alcohol (salidroside, rosavin, etc.) from Rhodiola rosea are biologically active substances [7,8]. These alcohols, along with geraniol, myrtenol, 1-octanol, etc., are part of the essential oils contained in its rhizomes [1]. The use of Rhodiola Rosea for the production of various medicines, dietary supplements and cosmetics is quite an urgent task [9–11] for high-tech developments in Russia.

The use of deep eutectic solvents (deep eutectic solvents, DES) [12–17] is one of the actively developing areas in the field of extraction of biologically active and fragrant substances from plants. DES is a mixture of two substances: hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA). The mixture melting point is significantly lower than that of each individual component. This class of solvents was described for the first time in 2003 in the work of A.Abbott [18]. Different combinations of HBD and HBA form a large number of various compositions of DES, differing somewhat in their properties, in particular, in their ability to extract certain plant metabolites. DES has been successfully applied to the extraction of quercetin glycosides (rutin), malvidin, camferol, etc. [17].

DES is similar in properties to ionic liquids, some of which were used to extract biologically active glycosides from Rhodiola rosea [19,20].

Based on the available data, it can be assumed that DES can be effectively used for the extraction of both the specific glycosides of Rhodiola rosea (salidroside, rosavin, etc.), as well as their aglycones – cinnamic alcohol and p-tyrosol.

The aim of this study is to assess the possibility of using deep eutectic solvents for the extraction of components of essential oils and biologically active substances from the rhizomes of Rhodiola rosea, in particular cinnamic alcohol.

2. Materials and methods

2.1. Materials

Dried roots and rhizomes of Rhodiola Rosea (Company "Travy i Korni", Russia) was used as initial raw material. Choline chloride (99%, RONGSHENG BIOTECH) was used as an HBA for DES, malonic acid (99.5%, Chemical Line) and glycerol (99.0%, Vekton) were used as HBDs. Distilled water, methanol (MeOH, 99.0%, Vekton) ethanol (EtOH, 95.0%, Vekton) were used as reference solvents.

2.2. Extraction procedure

DES were prepared by mixing of choline chloride with malonic acid in molar ratio 1:1, and choline chloride with glycerol in molar ratio 1:2. To obtain homogeneous liquids, the mixtures of HBA and HBD were kept during the day in air thermostat at 50°C. To decrease viscosity of DES and affect their extraction properties, pure DESs were mixed with reference solvents (water, methanol or ethanol) in volume ratio 1:1.

Extraction was performed by the maceration. Powdered dried rhizomas of Rhodiola rosea and extragent were mixed in mass/volume ratio 1:20 in the sealed glass vials and were kept during the day at 50°C. Obtained extracts were centrifuged using ELMI Multi Centrifuge CM 6M and then were filtered by forcing through the syringe with filter paper inside it.

2.3. GS-MS analysis

Analysis of the extracts was performed with GCMS- QP2010 (SHIMADZU) equipped with capillary column HP-5MS 30m length. Sample volume was 0.1 μl, flow division – 1:20. Samples were previously diluted with the methanol in volume ratio 1:1. Signal registration was made in SIM-regime for ions with atomic masses 51, 78, 92, 105 and 134, which are characteristic for cinnamic alcohol. Substance identification was made due to NIST 27.147 database.

3. Results and Discussion

Estimation of the content of cinnamic alcohol in the obtained extracts was carried out by integrating the chromatogram peaks (figure.1) of extracts that showed the highest content of the target substance, and comparing the peak areas obtained for each extract. The results are shown in table 1.

Extracts prepared using water, methanol and ethanol contain a noticeable amount of cinnamon alcohol. Among the analyzed extracts obtained using DES1, a significant amount of cinnamic alcohol was found for a sample treated with a mixture of DES1 + methanol. In extracts obtained using DES2, the highest content of cinnamic alcohol was recorded for a mixture of choline chloride, glycerol and water.

From the data of semi-quantitative analysis, according to the peak areas of cinnamic alcohol, it can be concluded that cinnamon alcohol is best extracted with a mixture of DES2 and water. Its concentration in the extract is almost 2 times higher than in ethanol extract, and more than 5 times higher than in methanol extract.

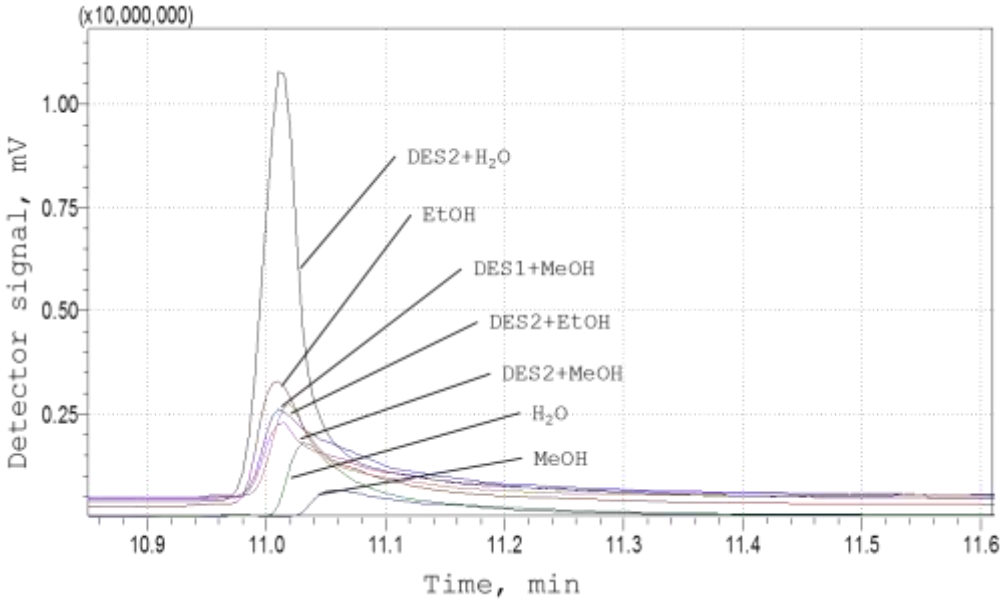

Figure.1. GS-MS analysis of Rhodiola rosea extracts in SIM regime.

Table 1. Peak areas (S) of GS-MS signal for cinnamic alcohol detected in SIM regime.

Extragent	$S \times 10^{-2}$, mV×min
H_2O	9807
MeOH	5394
EtOH	15740
DES1 + MeOH	14914
DES2 + H_2O	27973
DES2 + MeOH	14680
DES2 + EtOH	16780

4. Conclusions

The results of a comparison of the efficiency of extractants based on deep eutectic solvents for the extraction of cinnamic alcohol from the rhizomes of Rhodiola Rosea according to a semi-quantitative gas chromatographic analysis with mass spectrometry were obtained. It has been established that the extractant based on a mixture of choline chloride and glycerol (in a molar ratio of 1: 2), diluted with water (in a ratio of 1: 1 by volume) almost twice as efficiently extracts cinnamon alcohol, compared to ethanol. The data obtained are a significant contribution to the development of research in the field of application of deep eutectic solvents for the extraction of various components of medicinal plants.

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