Analytica Chimica Acta 789 (2013) 65–73

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Sequential determination of fat- and water-soluble vitamins in *Rhodiola imbricata* root from trans-Himalaya with rapid resolution liquid chromatography/tandem mass spectrometry

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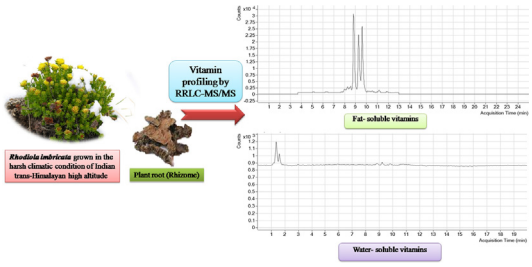
HIGHLIGHTS

- First study reporting on the vitamin profile of *Rhodiola imbricata* root.
- A rapid method to analyze sequentially fat and water-soluble vitamins was developed.
- The method was based on rapid resolution liquid chromatography/tandem mass spectrometry (RRLC–MS/MS).
- Electrospray ionization source in multiple reaction monitoring mode was used.
- The quantification of several free vitamins in the plant root was achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 October 2012
Received in revised form 26 May 2013
Accepted 31 May 2013
Available online 11 June 2013

Keywords:
Rhodiola imbricata
Fat-soluble vitamins
Water-soluble vitamins
Rapid resolution liquid chromatography
Tandem mass spectrometry
Sequential determination

ABSTRACT

A rapid method was developed to determine both types of vitamins in *Rhodiola imbricata* root for the accurate quantification of free vitamin forms. Rapid resolution liquid chromatography/tandem mass spectrometry (RRLC–MS/MS) with electrospray ionization (ESI) source operating in multiple reactions monitoring (MRM) mode was optimized for the sequential analysis of nine water-soluble vitamins (B_1, B_2, two B_3 vitamins, B_5, B_6, B_7, B_9, and B_{12}) and six fat-soluble vitamins (A, E, D_2, D_3, K_1, and K_2). Both types of vitamins were separated by ion-suppression reversed-phase liquid chromatography with gradient elution within 30 min and detected in positive ion mode. Deviations in the intra- and inter-day precision were always below 0.6% and 0.3% for recoveries and retention time. Intra- and inter-day relative standard deviation (RSD) values of retention time for water- and fat-soluble vitamin were ranged between 0.02–0.20% and 0.01–0.15%, respectively. The mean recoveries were ranged between 88.95 and 107.07%. Sensitivity and specificity of this method allowed the limits of detection (LOD) and limits of quantitation (LOQ) of the analytes at ppb levels. The linear range was achieved for fat- and water-soluble vitamins at 100–1000 ppb and 10–100 ppb. Vitamin B-complex and vitamin E were detected as the principle vitamins in the root of this adaptogen which would be of great interest to develop novel foods from the Indian trans-Himalaya.

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1. Introduction

Plant-derived foods for example fruits, vegetables, grains, oils, nuts and many more have become an essential part of the human diet for their beneficial health promoting effects [1,2]. The Indian

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http://dx.doi.org/10.1016/j.aca.2013.05.062

sub-continental diets, in particular, also consist of diverse foods such as cereals, pulses, green leafy vegetables, roots, tubers, fruits, oil seeds, spices and condiments [3]. These foods provide a large number of vital dietary components such as vitamins, antioxidant compounds, amino acids, and fatty acids that are essential for human health. Vitamins are characterized by a cluster of both chemically and analytically heterogeneous compounds those may exist in numerous chemically diverse but biologically inter convertible form. These are one of the essential micronutrients for human nutrition and a significant number of world populations are still prone to the health threats linked with low micronutrient ingestions even after taking balanced diet [4–8]. Therefore, intake of dietary supplements with optimum vitamin contents is a useful strategy in maintaining proper health.

Vitamins can be broadly classified in two major groups, water-soluble and fat-soluble vitamins. Water-soluble vitamins include B group vitamins *viz*. thiamine (B_1), riboflavin (B_2), niacin (B_3), pantothenic acid (B_5), pyridoxine (B_6), biotin (B_7), folic acid (B_9), cyanocobalamin (B_{12}) and ascorbic acid (C) while the fat-soluble vitamins are retinol (A), ergocalciferol (D_2), cholecalciferol (D_3), tocopherol (E), phylloquinone (K_1) and menaquinone (K_2). These vitamins play a number of vital functions in metabolism, and can cause health problems when they are either deficient or in surplus in human body [9].

Numerous analytical techniques such as spectrometric assays [10–13], volumetric assays [14], fluorimetry [15,16], chemiluminiscence [17,18], microbiological assays [19–21], capillary electrophoresis [22–24], thin layer chromatography [25], high performance liquid chromatography (HPLC) [9,26–28], and HPLC–mass spectrometry (HPLC–MS) and liquid chromatography–tandem spectrometry LC–MS/MS [29–34] have been reported for the analysis of vitamins in biological samples. Among these techniques rapid resolution liquid chromatography–tandem spectrometry (RRLC–MS/MS) is considered to be a powerful method for the concurrent determination of multiple vitamins in different foods and food products, nutraceutical, and pharmaceutical preparations.

Rhodiola imbricata (rose root or arctic root), belonging to the family Crassulaceae, is an important food crop and medicinal plant in the high altitude region of Indian trans-Himalayan cold desert. A number of metabolites like phenylpropanoids, phenylethanol derivatives, flavanoids, monoterpernes, triterpenes, and phenolic acids were found in good yield from *Rhodiola* sp. and some have been shown to possess useful biological activities [35–38]. Many pharmacological studies have demonstrated that *R. imbricata* exhibits cardioprotective, antiinflammatory, antipyretic, antistress and adaptogenic activities. It has also been found to possess antioxidant, antiaging, immunostimulant, antidepressant, radioprotective, and anticarcinogenic properties [39–42]. All these reports support its use in traditional system of medicine and in recent times, using this plant root, a number of products have been developed from our institute those were found to possess high nutritive properties and antioxidant capacities [43,44]. In our recent study, we have reported various volatile and semivolatile phytochemotypes from the underground part of this valuable medicinal plant [45]. However, there is lack of information regarding the vitamin profile of *R. imbricata* root which could play a vital role not only in the bio-activity and pharmacological properties but also could validate its use in the preparation of numerous pharmaceutical and nutritional preparations.

Previous reports on the simultaneous determination of numerous fat- and water-soluble vitamins in a single chromatographic run with diode array detector (DAD) and MS detectors to analyze the vitamin profile of functional drinks, nutritional beverages, pharmaceutical preparations, foodstuff and parenteral nutrition admixtures have already been published and amongst them, only a few methods could be referred to the complex food matrices [9,27,32,46]. In addition to that, very limited literature is available for the sequential estimation of water- and fat-soluble vitamins with triple quadrupole mass spectrometer (QQQ-MS) detector and there is no previous report on the vitamin profile of *R. imbricata* root which is used as an important ingredient in several nutraceutical, pharmaceutical and therapeutic preparations [43,44]. Hence, in the present investigation, our aim was to separate, identify and quantify the fat- and water-soluble vitamins in *R. imbricata* root by RRLC–MS/MS hyphenation.

2. Experimental

2.1. Materials and chemicals

Reference standards of fat-soluble vitamins: *trans*-retinol (A), ergocalciferol (D_2), cholecalciferol (D_3), D-α-tocopherol (E), phylloquinone (K_1), and menaquinone (K_2); water-soluble vitamins: thiamine hydrochloride (B_1), riboflavin (B_2), nicotinic acid (B_3), nicotinamide (B_3), D-pantothenic acid (B_5), pyridoxine hydrochloride (B_6), D-Biotin (B_7), folic acid (B_9), and cyanocobalamin (B_{12}) were procured from Sigma–Aldrich (Sigma–Aldrich, St. Louis, MO, USA). The solvents, acetonitrile and methanol were of gradient grade for liquid chromatography (MERCK KGaA, Darmstadt, Germany) and ultra pure water (MilliQ water) was prepared by a Milli-Q purification system (Millipore Corp., Bedford, MA, USA) for analysis. Potassium hydroxide was of analytical grade purchased from MERCK (MERCK, KGaA, Darmstadt, Germany). The chemicals and reagents used, were of HPLC and/or analytical grades. All solutions were passed through 0.45 μm Teflon membrane filters (MetaChem, Torrance, CA, USA) prior to analyses. The pH value of the solution was equilibrated with HI 8424 Portable pH/mV/°C meter (HANNA Instruments Inc., RI, USA) regularly calibrated with National Bureau of Standards (NBS) buffer solutions.

2.2. Plant materials

R. imbricata roots were collected from the trans-Himalayan region (Chang-La Top, altitude = 5330 m above mean sea level, Changthang valley, Ladakh) of India in the month of October, 2011 after the period of senescence, with prior permission from the local authority. The plant roots were washed thoroughly, and cut into small pieces and shade dried at room temperature for 15 days. Root dry matter content (DMC) was calculated as the percentage of dry weight relative to fresh weight [DMC (%) = Sample dry weight × 100/Sample fresh weight]. The DMC was 28–33%. Then they were finely powdered and used for further study.

2.3. Chromatographic apparatus and RRLC–MS/MS method details

Fat- and water-soluble vitamin detection and quantification were performed using the Agilent 1200 Series RRLC Binary modules interfaced to the Agilent 6410 B RRLC (G6410A, Agilent Technologies, Santa Clara, CA, USA) with HPLC-Chip Cube. The RRLC system was equipped with Agilent 1200 series vacuum micro degasser (G1322A), Agilent 1200 series binary pump system SL (G1312B), Agilent 1200 series High Performance Autosampler (HPALS) SL (G1367C), and Agilent 1200 series Thermostated Column Compartment (TCC) SL (G1316B). The Mass Spectrometer was equipped with an electrospray ionization (ESI) probe. The RRLC system was controlled by Agilent ChemStation module. Data acquisition and qualitative analysis were performed on MassHunter versions B.02.01 whereas quantitative analysis was carried out by using MassHunter versions B.03.01.

For RRLC–MS/MS determination, the separation of analytes were achieved on Agilent Poroshell 120 EC-C18 Narrow bore

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