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Review

Extraction and applications of cyanotoxins and other cyanobacterial secondary metabolites

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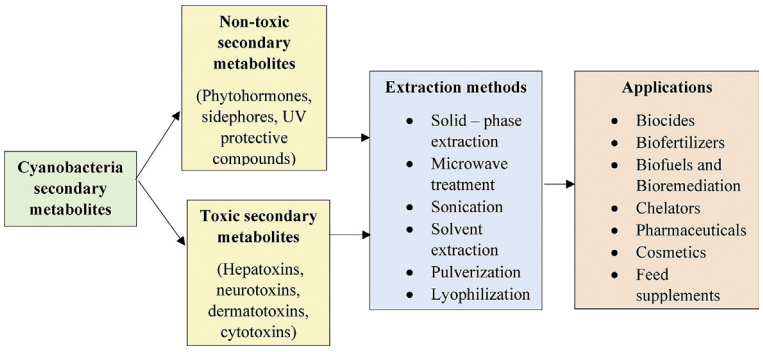
HIGHLIGHTS

- Cyanotoxins can be extracted and recovered to yield potentially useful bioproducts.
- Non-toxic secondary metabolites of cyanobacteria also find potential applications.
- Chemical, physical and intensified methods can extract secondary metabolites.
- Methods of extraction and recovery differ for toxic and non-toxic metabolites.
- Toxicity, nutritional value, energy content and chemical behavior also differ.

GRAPHICAL ABSTRACT



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ABSTRACT

The rapid proliferation of cyanobacteria in bodies of water has caused cyanobacterial blooms, which have become an increasing cause of concern, largely due to the presence of toxic secondary metabolites (or cyanotoxins). Cyanotoxins are the toxins produced by cyanobacteria that may be harmful to surrounding wildlife. They include hepatotoxins, neurotoxins and dermatotoxins, and are classified based on the organs they affect. There are also non-toxic secondary metabolites that include chelators and UV-absorbing compounds. This paper summarizes the optimal techniques for secondary metabolite extraction and the possible useful products that can be obtained from cyanobacteria, with additional focus given to products derived from secondary metabolites. It becomes evident that the potential for their use as biocides, chelators, biofuels, biofertilizers, pharmaceuticals, food and feed, and cosmetics has not yet been comprehensively studied or extensively implemented.

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1. Introduction

Cyanobacteria, or blue-green algae, are one of the oldest life forms that continue to exist on Earth (Gademann and Portmann, 2008). They are capable of oxygenic photosynthesis and nitrogen fixation (Berman-Frank et al., 2003). They are common in lakes, ponds, rivers and brackish waters (van Apeldoorn et al., 2007; Hamilton et al., 2014) as well as in desert soils (Richer et al., 2015). Overtime, cyanobacteria has evolved to produce various secondary metabolites to adapt to the changes in their surroundings due to high temperature, high pH, and high dissolved phosphorous and nitrogen (Descy et al., 2016; Dulić et al., 2016; Gademann and Portmann, 2008; Harke et al., 2016; Wood et al., 2017).

Cyanobacterial secondary metabolites may be toxic or non-toxic. Non-toxic secondary metabolites include phytohormones, siderophores and various UV-protective compounds such as mycosporine-like amino acids (MAAs) and scytonemin. Phytohormones play a vital role in surrounding plant growth, cell division and nutrient release (Sergeeva et al., 2002). Cyanobacteria commonly secrete siderophores that have the ability to chelate iron. This functions to help the cyanobacteria acquire sufficient iron (Gademann, 2007; Goldman et al., 1983; Kharangate-Lad and Bhosle, 2016). The UV absorbing compounds such as MAAs and scytonemin serve to protect the cyanobacteria from UV damage (Carreto and Carignan, 2011; Rastogi et al., 2010). On the other hand, toxic secondary metabolites are generally divided based on the organs they affect (Manganelli, 2016). There are hepatotoxins such as microcystins that affect the liver, neurotoxins such as anatoxin-a and saxitoxin that alter neuromuscular transmission, dermatotoxins, which cause skin irritation, cardiotoxins such as yessotoxin, as well as cytotoxins and irritant toxins (Campàs and Marty, 2007; Kleinteich et al., 2013; Merel et al., 2013; Msagati et al., 2006; Wiegand and Pflugmacher, 2005; Woodhouse et al., 2014).

Cyanobacteria often reach conditions of excessive growth, creating cyanobacterial blooms. These algal blooms are harmful due to the presence of toxic secondary metabolites. A highest concentration of toxic microcystin of 650 μg/l has been found in Ćelije reservoir, Serbia (Svirčev et al., 2014). It may result in mass mortalities of fish and birds (Drobac et al., 2016), as well as adverse health impacts on humans and animals (Hamilton et al., 2014; Johnk et al., 2008; Manganelli et al., 2010; Svirčev et al., 2017; Woodhouse et al., 2014). This paper summarizes (Fig. 1) the optimal techniques for secondary metabolite extraction and the possible useful bioproducts that can be obtained from cyanobacteria, with additional focus given to products derived from secondary metabolites.

2. Extraction of cyanobacterial secondary metabolites

In a cyanobacterial bloom, many species of cyanobacteria can be found, which in turn produce a variety of toxic and non-toxic secondary metabolites. This makes the process of isolating and identifying the secondary metabolites present in a particular bloom more difficult. With the rise in interest in secondary metabolites, analytical techniques have advanced. In order to minimize cost, chemical-free green extraction methods such as supercritical fluid extraction and pressurized liquid extraction have increased in popularity for secondary metabolite extraction (Mandal and Rath, 2015). The extraction method should provide sufficient purity for detection and quantification. The method selection depends on the target metabolite. Most of the non-toxic secondary metabolites are extracellular compounds, for example, scytonemins is not accumulated in the cytoplasm and is released into the extracellular sheath (Richter et al., 2006). Similarly MAAs are produced outside the cytoplasm (Singh et al., 2010). However, both endogenous and exogenous cytokinins can co-exist (Hussain et al., 2010). In contrast, toxic secondary metabolites are intracellular compounds and are normally extracted by first lysing the cell wall structure (Kim et al., 2009; Silva-Stenico et al., 2009). Hence, the extraction methods are also varied for toxic and non-toxic extractions.

2.1. Non-toxic secondary metabolite extraction

Various extraction techniques have been used to isolate non-toxic secondary metabolites, as shown in Table 1. Cytokinins and auxins were extracted by Hussain et al. (2010) using a Bieleski buffer followed by solid-phase extraction, which was more efficient than 80% ethanol as extractant. Cytokinins is present as cytokinin riboside phosphate, along with the enzyme phosphatases, which results in the degradation of cytokinins. The extraction of cytokinins (76% recovery) is increased by using the Bieleski buffer ($MeOH-CHCl_3-HCOOH-H_2O$, 12:5:1:2, v/v/v/v) because the $CHCl_3$ present in this buffer deactivates the phosphatase. However, it also extracts the lipophilic material along with cytokinin, which complicates further purification.

A study by Hoyerová et al. (2006) to extract cytokinins found

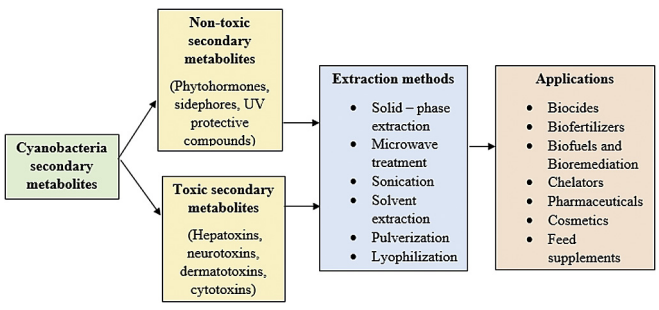

Fig. 1. Techniques for secondary metabolite extraction and their application.