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Research advances for the extraction, analysis and uses of anthraquinones: A review

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ABSTRACT

A current economic trend is to highlight natural resources, and many plant species are rich sources of anthraquinones. The latter are natural compounds that have various biological properties with subsequent positive and/or negative effects, and have found industrial application as natural dyes. The potential of anthraquinones to inhibit or prevent fungal and bacterial growth are two interesting biological properties, but many other properties are attributed to them, such as antioxidant, anticancer, anti-inflammatory, laxative and many others. Each biological property attributed to anthraquinone derivatives is listed with several research works. These last ones are described in terms of materials and results.

The intensity of research focused on natural compounds valuation from natural and suitable substances has been growing over the past few decades. In term of publications, anthraquinones have been the most studied in China with around 1/2 of publications (44%).

The article mainly provides a handy overall of different extraction methods, analysis techniques, whereas bioactive properties and industrial applications from various plant species containing anthraquinone derivatives are also reported.

Numerous extraction and analysis methods are reviewed: Ultrasonic assisted, microwave, pressurisated fluid and supercritical fluid extraction, for the first, capillary electrophoresis, thin layer, liquid, gaseous, countercurrent and supercritical fluid chromatography for the second. Each technique is fundamentally explained and several studies dedicated to anthraquinones have been explored, describing both the part of the studied plant in which are located the anthraquinones (roots, leaves, seeds, flowers) and the physico-chemical properties of these compound (volatility, acidity). The influence of parameters to optimize extraction and analysis methods are carefully described, and advantages of modern approaches are reported with regards to traditional ones, in terms of time and solvent consuming and efficiency. Finally, the most of the studied plants containing anthraquinone derivatives were from mainly 3 families (81%): *Polygonaceae*, *Rubiaceae* and *Fabaceae*. The best known as anthraquinones are: rhein, aloe emodin, emodin, physcion, chrysophanol that are described in most studies and given as responsible of several biological properties. For industrial applications, these compounds are used as natural dyes to replace synthetic chemicals in formulation in order to prevent some side effects.

Abbreviations: EPA, environmental protect agency; AOAC, association of analytical communities; SFE, supercritical fluid extraction; UAE, ultrasonic assisted extraction; PLE, pressurized liquid extraction; MWE, microwave extraction; CE, capillary electrophoresis; SFC, supercritical fluid chromatography; LC, liquid chromatography; HPLC, high pressure liquid chromatography; GC, gas chromatography; CCC, counter current chromatography; CPC, centrifugal partition chromatography; TLC, thin layer chromatography; HPTLC, high performance thin layer chromatography; RP-LC, reversed-phase liquid chromatography; NARP-LC, non aqueous reversed-phase liquid chromatography; LSER, linear solvation energy relationships; UV, ultraviolet; FLD, fluorimeter; ECD, electron capture detector; MS, mass spectrometry; FID, flame ionization detector; DAD, diode array detector; CZE, capillary zone electrophoresis; MEKC, micellar electrokinetic chromatography; cITP, capillary isotachophoresis; IR, infra-red; NMR, nuclear magnetic resonance; IPrOH, isopropyl alcohol; MeOH, methanol; ACN, acetonitrile; EtOH, ethanol.

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Contents

1. Introduction

Various natural products have been isolated from plants species and have remarkable bioactive properties such as fungicides, insecticides, growth regulators or antioxidants. Numerous applications such as pesticide, cosmetic, food-processing or pharmaceutical field have been found for the valuation of these natural compounds. In addition, with the sustainable development, natural products represent an attractive economical option due to their biodegradable nature and production from renewable resources. Consequently, the valuation of vegetable resources is an important topic and challenge for corporations (Gupta et al., 2015; Rostagno and Prado, 2013).

The analysis of natural compounds is a fascinating challenge. Extracts from natural resources such as terrestrial or marine plants are inherently complex as each extract can be composed of hundreds of individual compounds. Moreover, the individual concentration of each compound in an extract can vary in a large range, further complicating the analytical task. In addition, changes in growing conditions, harvesting techniques, or postharvest processing can lead to noticeable phytochemical differences (nature and proportion of metabolites) from lot to lot (Dayan and Kromidas, 2011). Metabolites are organic compounds synthesized by plants using enzyme-mediated chemical reactions called metabolic pathways. These reactions occur for two different purposes:

- primary metabolites, including amino acids, lipids, and carbohydrates, support growth and development of the plant;
- secondary metabolites provide other varied biological functions that are essential in all plants.

Secondary metabolites are variously distributed in the plant kingdom, and their biological functions are specific to the plants in which they are found. They are often responsible for color, fragrance and flavor and they typically mediate the interaction between the plant and its environment. Some of them (polyphenols, alkaloids, terpenes, polyketides, and hormones) are related to defense and signaling mechanisms (Wolfender et al., 2015). As a result, molecular structures with large chemical diversity are available in the nature. Anthraquinones constitute one family of such compounds which occur naturally in some plants. Natural anthraquinones are interesting due to their wide spectrum of applications and bioactive properties.

Anthraquinone derivatives are the largest group of natural quinones. Other natural quinones are naphthoquinones and benzoquinones. Anthraquinones also constitute the largest group of natural pigments with about 700 compounds described, in which the compounds most frequently reported are emodin, physcion, catenarin and rhein (Fig. 1). Around 200 of these compounds are issued from flowering plants while the rest of them are produced by lichens and fungi (Seigler, 2012). They can be found in all parts of the plants: roots, rhizomes, fruits, flowers and leaves. Most of these compounds are derivatives of the basic structure 9,10-anthracenedione, a tricyclic aromatic organic compound with formula $C_{14}H_8O_2$. The latter is a yellow solid crystalline powder that absorbs visible light and is the basic structure of a large class of dyes and pigments (Dave and Ledwani, 2012). Glycosylated anthraquinones are also present within the plant, for instance in rhizomes to favour their accumulation and storage in the plant (Pandith et al., 2014), but they are converted into aglycone anthraquinones by β-glucosidases or oxidative processes. How-