Industrial Crops and Products 51 (2013) 100–106

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Volatility profiles of monoterpenes loaded onto cellulosic-based materials

Igor W.K. Ouédraogo[a,b], Julien De Winter[b], Pascal Gerbaux[b], Yvonne L. Bonzi-Coulibaly[a,*]

[a] Laboratoire de Chimie Organique: Structure et Réactivité, UFR-SEA, Université de Ouagadougou, 03 BP 7021, Ouagadougou 03, Burkina Faso
[b] Groupe de Recherche en Spectrométrie de Masse, Centre Interdisciplinaire de Spectrométrie de Masse, Université de Mons – UMONS, Place du Parc 23, B-7000 Mons, Belgium

ARTICLE INFO

Article history:
Received 8 June 2013
Received in revised form 21 July 2013
Accepted 9 August 2013

Keywords:
Monoterpene
Cellulose-based matrices
Impregnation
Volatility
Formulation

ABSTRACT

Monoterpene compounds were loaded onto pure cellulose and two cellulose-based matrices by impregnation method. The effects of initial ratio, structures of volatile compounds and polymers, i.e. cellulose, acetate cellulose and rice husk, on the release profiles were investigated. Four monoterpenes, namely α-pinene, citronellal, carvone and terpinen-4-ol, were tested as volatile compound models. In the case of carvone loaded onto cellulose, we observed that the release of the volatile molecule increases with increasing initial ratio in the formulation. Using different cellulose-based matrix to study the volatility of monoterpene models, the lowest release rates was obtained with rice husk formulations, with highly retention capacity over 50% for carvone, terpinen-4-ol and citronellal after 20 days at 21 °C.

It was also concluded that the impregnation of terpinen-4-ol and carvone into cellulose and cellulose acetate respectively, could effectively help in prolonging the retention of these volatiles. α-Pinene, a highly hydrophobic molecule showed no significant retention. These results indicate that cellulose-based matrices could be potentially used as good carriers of active compounds for ecological pesticides formulation for postharvest applications.

1. Introduction

Essential oils from aromatic plants are mainly monoterpene derivatives and are involved in a wide range of applications in sanitary, cosmetic, agricultural, pharmaceutical and food industries. Successful uses of essential oils against agricultural pests and food-borne microorganisms are also convincingly (Isman et al., 2011; Nguemtchouina et al., 2010; Sacchetti et al., 2005) reported. One important point to consider in the different applications is the capability of the used formulations to release the active constituent(s) in a controlled manner. This is even more problematic when considering essential oils given the really high volatility of the constituting monoterpene compounds. Given the low vapor pressure (high boiling point) and their molecular structures, monoterpenes are prone to rapid evaporation and easy degradation, respectively (Hoskovec et al., 2005; Lai et al., 2006). Various reactions such as oxidation or Norrish type II photofragmentation (Rochat et al., 2000) are well known to limit their use over time. Different strategies have then been developed to protect the monoterpene constituents from degradation and/or to control their release and diffusion. Most of the procedures involve neighboring-group participation (De Saint Laumer et al., 2003), profragrances formation (Levrand et al., 2006), encapsulations (Cevallos et al., 2010; Luo et al., 2011) or nitrile and oxime-based derivations (Narula, 2004; Dikusar et al., 2008; Ouédraogo et al., 2009). Those methods were demonstrated to prolong the long-lasting effect of volatile compounds and, as an additional benefit, to increase their stability in aggressive media (air oxidation, light, moisture and higher temperatures).

Intensive studies have been conducted to consider bio-based materials, i.e. cellulose, as adsorbents of many inorganic or organic compounds in the context of water treatment (Ji et al., 2012; Wojnárovits et al., 2010; Wang and Li, 2013; Takács et al., 2012). Also various biopolymers have been used as matrix for entrapping different active compounds for medical or food purposes (Soottitantawat et al., 2005; Sánchez-González et al., 2011a,b; Tongnuanchan et al., 2012). Incorporation of essential oils into polymer matrices for fruit protection or against food borne pathogens has been showed to represent a successful approach (Marcuzzo et al., 2010; Paula et al., 2011; Bosquez-Molina et al., 2010; Woranuch and Yoksan, 2013). Sánchez-González et al. (2011b) prepared antimicrobial films by incorporating various essential oils from bergamot, lemon and tea tree, into chitosan and hydroxypropylmethylcellulose films. The association of these bio-based

---

* Corresponding author. Tel.: +226 50 30 70 64; fax: +226 50 30 72 42.
E-mail addresses: pascal.gerbaux@umons.ac.be (P. Gerbaux), bonziy@univ-ouaga.bf (Y.L. Bonzi-Coulibaly).

0926-6690/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.indcrop.2013.08.032

materials with adsorbed essential oils improves the physical and biological/chemical properties of the film. In addition, when adsorbed on the biopolymer, the volatility of the essential oil constituents is reduced and the activity time of the essential oil is of course prolonged.

Cellulose-based materials could be promising materials for natural volatile molecule formulation in crops protection strategies against insects or fungi. In the context of seed protection, feedstocks could be selected and serve as low-cost adsorbents. Indeed, rice husk and derivative products like cellulose and cellulose acetate are interesting polymers given several recognized properties such as no toxicity, availability, biodegradability (Sun et al., 2004; Liu et al., 2007; Asadi et al., 2008). Rice husks are an important by-product of rice milling process. According to the statistical data of Food and Agriculture Organization (FAO), the world annual paddy production is approximately 582 million tons and rice husk represent 22–25% of the rice grain. Rice husk as described in the literature is mainly composed of cellulose (32.24–42.8%), hemicellulose (21.34–32.7%), lignin (11.96–24.5%) and mineral ash (15.05–18.86%) which is in large amount of silica (SiO_2) (Genieva et al., 2008; Abbas and Ansumali, 2010; Osman et al., 2010; Wan Ngah and Hanafiah., 2008; Adel et al., 2011; Chaudhary and Jollands, 2004; Saha et al., 2005; Saha and Cotta, 2007). Thus, due to the availability, attention has been focused on sorbents production from rice husk. In this context, we decided to probe the adsorption capabilities of some cellulosic-based matrices toward some typical monoterpene compounds.

For the present work, cellulose, cellulose acetate and rice husk have been selected as model matrices for the adsorption of four monoterpenes used as volatile compound candidates. The selected molecules are (+)-α-pinene (unsaturated hydrocarbon), citronellal (aldehyde), carvone (ketone) and terpinen-4-ol (alcohol). The release behaviors of the four compounds loaded onto cellulosic-based materials will be investigated by gas chromatography–mass spectrometry (GC–MS) analyses.

2. Materials and methods

2.1. Materials

Cellulose powder (DS-0), for thin layer chromatography (TLC) was purchased from Sigma–Aldrich. Cellulose acetate (average M.W. 100.000) was obtained from ACROS Organics. Monoterpene chemical used were (+)-α-pinene (purity >98%, Alfa Aesar), carvone (purity >99%, ACROS Organics), citronellal (purity >93%, ACROS Organics) and terpinen-4-ol (purity >95%, Aldrich). Rice husk was obtained from local rice collected in Burkina Faso. All other reagents used throughout the study were analytical grade.

2.2. Rice husk preparation and characterization

The dried material of rice husk (size fractions of 0.063–0.125 mm) was successively washed with deionized water, ethanol and acetone several times to remove dust and fines. Afterwards, the collected material was dried in an oven at 60 °C for 24 h. The material was characterized by Fourier transform-infrared (FT-IR) analysis on a Perkin Elmer BX II spectrophotometer employing the KBr pellet method. The specific surface area of rice husk was determined in comparison with cellulose and cellulose acetate by N_2 adsorption at 77 K using an ASAP 2020 Micromeritics instrument and the Brunauer–Emmett–Teller (BET) method (Sing et al., 1985).

FT-IR spectra: 3600–3200 cm^{-1} O—H stretching, 1732 cm^{-1} C=O stretching (hemicellulose), 1606 and 1515 cm^{-1} aromatic rings of lignin, 799 cm^{-1} Si—O—Si bond, 465–485 cm^{-1} O—Si—O bending vibration.
Specific surface area: 7.1 m^2/g.

2.3. Volatile compound formulations and volatility studies

Formulation of monoterpenes loaded onto cellulose-based matrices was carried out by impregnation: 1 mg of each monoterpene was first diluted with 200 μL of acetone and then added to 100 mg of cellulose into glass vials (inner diameter × height: 20 mm × 40 mm). The volatility study was performed by using different amounts, expressed as weight of volatile molecule per 100 g of cellulose-based matrix. For the study of the influence of the adsorbent nature, 0.25 mg of each monoterpene was mixed to get 1 mg of a mixture of monoterpenes. This mixture was diluted with 200 μL of acetone (for cellulose or rice husk formulations) or hexane (for cellulose acetate formulation) and then added to 100 mg of cellulose-based matrix into glass vials (inner diameter × height: 20 mm × 40 mm). The resulting mixtures were left uncovered for solvent and monoterpene evaporation. Monitoring was carried out under room temperature (21 ± 2 °C). Each experiment was replicated 3 times and the mean (average) values are reported. Monoterpenes (without cellulose-based matrix) were also diluted with 200 μL of acetone and exposed for monitoring the volatilization.

2.4. Extraction method

At set time intervals, the amount of the residual volatile molecules was determined. The remaining volatile molecules were extracted from the cellulose matrices by 5 mL of dry ethanol. The suspension was vigorously shaken with vortex apparatus (Fisher Scientific) for 15 s and sonicated for 15 min. The solid phase was then separated from the ethanolic mixture by centrifugation (Eppendorf centrifuge, 5417R) at 7000 rpm for 10 min at 21 °C. The supernatant containing the volatile molecules was collected and the monoterpene compound contents were quantified by gas chromatography–mass spectrometry (GC–MS). The extraction procedure was demonstrated to be quantitative by measuring the extracted amounts of the four monoterpene compounds, directly after the adsorption onto the three different matrices.

The amount of remaining monoterpenes was expressed as the relative retention (%) and was determined using the following equation:

$$\text{Relative retention}\,(\%) = \frac{M_t}{M_0} \times 100$$

where M_t and M_0 are respectively the amount (mg) of monoterpene in sample at time t and initial time t_0. For each formulation, the relative retention at t_0 was measured to be equal to the unity, i.e. the extraction procedure must be quantitative.

2.5. Gas chromatography–mass spectrometry analysis (GC–MS)

Each extraction sample was diluted in 1 mL of chloroform and 1 μL was directly injected into the GC–MS apparatus.

The GC–MS analyses were performed using a Waters GCT Premier (from Waters Corporation company, Manchester, England) instrument based on a time-of-flight analyzer. The gas chromatograph was equipped with a Restek Rtx-5Sil MS column (30 m length, 0.25 mm inner diameter and 0.25 μm film thickness). Typical GC conditions were: injector temperature, 250 °C; splitless mode; Helium carrier gas flow rate, 1 mL/min; interface temperature: 250 °C. The temperature program was as follow: initial temperature, 55 °C; 1 °C/min ramp; final temperature, 150 °C;