DEVELOPMENT OF INCLUSION COMPLEXES BASED ON ESSENTIAL OILS AND CYCLODEXTRIN FOR NATURAL FUR TREATMENT

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Essential oils are liquid substances, with oily appearance, insoluble in water, soluble in alcohol and organic solvents, with specific odour and are known for their remarkable perfume and their therapeutic qualities. Inclusion complexes of any plant extract with cyclodextrins may be used in several areas: medicine, pharmacy, perfumery, textiles, the food industry, as well as in the leather and fur industry. The paper presents the spectrometric method (FT-IR) of characterizing inclusion complexes based on essential oils and β-cyclodextrin, to highlight the obtained inclusion complexes that will be used for finishing woolen sheepskin, in order to prolong the perfuming effect of volatile oils.

Key words: woolen sheepskin, finishing, essential oils, cyclodextrin

INTRODUCTION

Improvement of fur processing technologies is closely related to chemical auxiliaries used in various operations, in order to increase processing yield and to delay or prevent unwanted phenomena that affect the quality of furs and fur items (Chirita *et al*.,1999; Maier *et al*., 2010; Bălău Mândru *et al*., 2011; Niculescu *et al*., 2014; Niculescu *et al*., 2015; Niculescu *et al*., 2015)

Essential oils are liquid substances, with oily appearance, insoluble in water, soluble in alcohol and organic solvents, with specific odour and are known for their remarkable perfume and their therapeutic qualities (Ciulei *et al*., 1993; Constantinescu *et al*., 2004; European Pharmacopeia, 2005).

Cyclodextrins (CD) are unstable compounds and usually combine with other chemicals to form a stable aqueous compound. Inclusion complexes of any plant extract with cyclodextrins may be used in several areas: medicine, pharmacy, perfumery, textiles, the food industry, as well as in the leather and fur industry.

There is particular interest in the use of cyclodextrins to prepare bioproducts with long-term effect. Some researchers have used β-CD and encapsulated complex materials, such as oleoresins, essential oils (sage, jasmine, rose, etc.) and fatty acid compounds (linoleic acid) with cyclodextrin (Chen *et al*., 2009; Cabrales *et al*., 2012; Chen *et al*., 2011).

The paper presents the spectrometric method (FT-IR) of characterizing inclusion complexes based on essential oils and β-cyclodextrin, to highlight the obtained inclusion complexes that will be used for finishing woolen sheepskin, in order to prolong the perfuming effect of volatile oils.

EXPERIMENTAL

Materials

Lavender oil (Solaris, Romania), containing 33% linalyl acetate, 29% linalool, 4% lavandulyl acetate, terpinene, ocimene, caryophyllene etc.; Orange oil (Solaris, Romania), containing 94% limonene, pinene, myrcene, octanal, linalool, etc.; Ethanol (Chemical Company, Germany), colorless liquid, boiling point 78.37°C, density - 0.79g/cm^3; β-cyclodextrin (Redox, Romania), white powder, purity > 99,0%, melting point 290-300°C.

Methods

Synthesis of materials based on plant extracts for biological protection and fragrance of fur was conducted in a glass flask using a heating and homogenization installation (Velp) and an ultrasonic bath (Elmasonic S 15 H).

Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements were run with a Jasco instrument (model 4200), in the following conditions: wavenumber range – 600-4000 cm^{-1}; data pitch – 0.964233 cm^{-1}; data points – 3610: aperture setting – 7.1 mm; scanning speed – 2 mm/s; number of scans – 30; resolution – 4 cm^{-1}; filter – 30 kHz; angle of incident radiation – 45° (Coates *et al*., 2000; Moldovan, 2001).

Obtaining the Inclusion Complexes Based on Essential Oils and β-cyclodextrin

The receipts and methodology for obtaining the inclusion complexes based on essential oils and β-cyclodextrin the inclusion complexes based on essential oils and β-cyclodextrin are described in (Arama *et al*., 2012).

Inclusion complexes were prepared by co-precipitation method, using lavender essential oil (labelled LAV) and β-CD, orange essential oil (labelled POR) and β-CD, and a mechanical mixture from the same components, namely LAV and β-CD, and POR and β-CD was prepared as control.

A. Mechanical Mixture

A mechanical mixture was prepared as control (labelled AM-LAV-CD) from lavender oil: β-CD by mixing in a glass flask for 5 minutes to get a homogeneous mixture. It was labelled LAV-CD. A mechanical mixture was prepared as control (labelled AM-POR-CD) orange oil: β-CD by mixing in a glass flask for 5 minutes to get a homogeneous mixture. It was labelled POR-CD.

B. Inclusion Complex

The inclusion complex of the lavender oil: β-CD was prepared by co-precipitation. The same method was used to prepare the inclusion complex of orange oil: β-CD.

For good homogenization of mixture component and precipitates, a heating and homogenization equipment and an ultrasonication device were used. Flasks were kept at 40°C, for 48 hours in the water bath. Filtration led to the microcrystalline precipitate, that was dried in the oven at 40°C for 48 hours. The same method was used to prepare products based on orange oil.

Lavender oil was added to screw cap vials containing β-CD in 5 ml ethanol:water solution (25:75 v/v). The ratio was 1-5 parts lavender oil (or orange oil): 1 part β-CD in 5 ml ethanol:water solution (25:75 v/v), according to data and labels presented in Table 1.

Table 1. Amounts of essential oils and β–CD used to obtain precipitates

Precipitate label	LAV or POR ratio	β–CD ratio
LAV-CD-1	LAV -1	1
LAV-CD-2	LAV- 2	1
LAV-CD-3	LAV-3	1
LAV-CD-4	LAV-4	1
LAV-CD-5	LAV-5	1
POR-CD-1	POR-1	1
POR-CD-2	POR-2	1
POR-CD-3	POR-3	1
POR-CD-4	POR-4	1
POR-CD-5	POR-5	1

RESULTS AND DISCUSSION

Characterization of Inclusion Complexes Based on Essential Oils and β-cyclodextrin Pigment Pastes by Spectroscopy (FT-IR)

FT-IR spectra of samples are presented in Figure 1 for: a-lavender oil (LAV), b-β-cyclodextrin (CD), c-mechanical mixture of lavender oil-β-cyclodextrin (AM), d- co-precipitate obtained from lavender oil-β-cyclodextrin, in a ratio of 1:5, by co-precipitation (CO). Figure 2 presents FT-IR spectra for: a-orange oil (POR), b-mechanical mixture of orange oil-β-cyclodextrin (AM), c-co-precipitate obtained from orange oil-β-ciclodextrin, in a ratio of 1:5, by co-precipitation (CO).

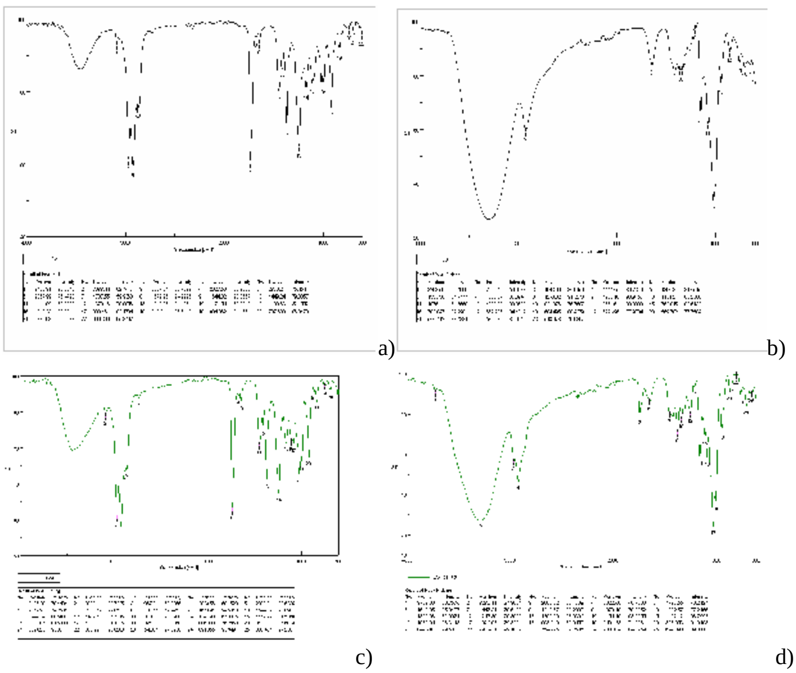
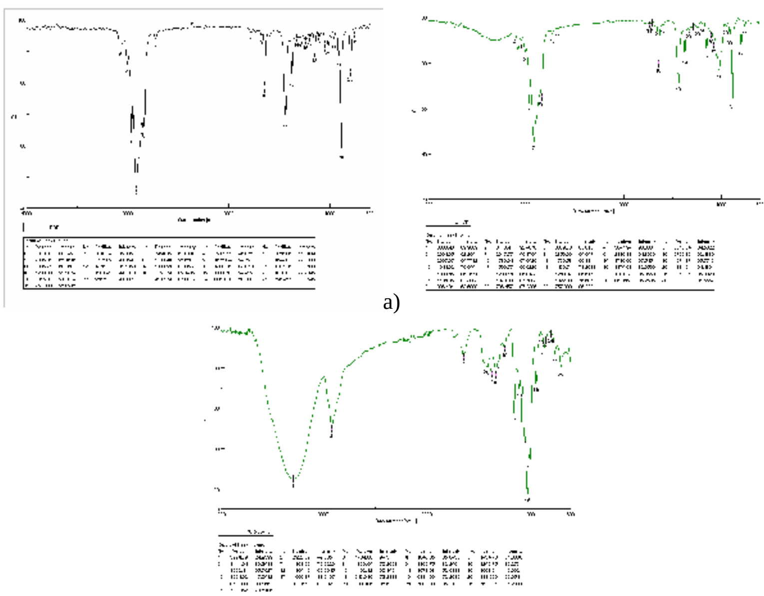


Figure 1. a) FT-IR spectrum for LAV; b) FT-IR spectrum for CD; c) FT-IR spectrum for AM (LAV-β-CD); d) FT-IR spectrum for CO (LAV-β-CD, 5:1)

Prominent spectra for lavender oil are: 3455, 2967, 2923, 1737, 1449, 1370, 1240 and 918 cm^{-1}. In general, the stretching region of the hydroxyl group, O-H, was observed in the 3200-3600 cm^{-1} range. The band at 3455 cm^{-1} indicates the presence of hydroxyl group in lavender. The band of alkanes (C-H) is noticed at 1350-1512 cm^{-1}. The band of lavender oil at 1370 cm^{-1} indicates the presence of C-H group. Stretched bands at 1000-1260 cm^{-1} indicate the presence of the ether group (C-O). The band of lavender oil at 1240 cm^{-1} indicates the presence of C-O group. The peaks of carbonyl group band (C=O) appeared in the range of 1700 to 1750 cm^{-1}. The band of lavender oil at 1737 cm^{-1} indicates the presence of C=O group (Fig. 1.a.). Prominent spectra of β-CD are: 3298, 1643 and 1020 cm^{-1}. The band at 3298 cm^{-1} indicates the presence of the hydroxyl group in β-CD, and the band at 1643 cm^{-1} indicates the presence of the CD ring (Fig. 1.b.).

FT-IR spectra of the mechanical mixture consisting of lavender oil and β-CD overlap and intensities of characteristic peaks of lavender oil are higher (Fig. 1.c.). FT-IR spectra of inclusion complexes differ from that of the mechanical mixture consisting of lavender oil and β-CD (Fig. 1.d.).

The characteristic peaks of lavender oil, C=O stretching vibrations at 1737 cm^{-1} shifted to 1736 cm^{-1} and are of much lower intensity. The characteristic peaks of lavender oil, C-O stretching vibrations at 1240 cm^{-1} disappeared and can no longer be seen. Water in β-CD led to the broad peak of O-H masking the presence of O-H in lavender oil. The absorption band at 1412 cm^{-1} due to deformation vibration of O-H bond appeared as a result of the band at 1449 cm^{-1} shifting, due to the increasing number of O-H groups, with the introduction of β-CD into the system. The wavelength of the vibration of CD ring from 1643 cm^{-1} was shifted to 1645 cm^{-1}, which shows that the lavender molecule was incorporated into the hydrophobic cavity of the CD (Fig. 1.d.).



a) b) c)

Figure 2. a) FT-IR spectrum for POR; b) FT-IR spectrum for AM (POR-β-CD); c) FT-IR spectrum for CO (POR-β-CD, 5:1)

Prominent spectra of orange oil are: 2964, 2917, 1644, 1436, 1375 and 886 cm^{-1}. The band of orange oil at 1644 cm^{-1} indicates the presence C=O group. The band of alkanes (C-H) is noticed at 1350-1512 cm^{-1}. The band of orange oil at 1375 cm^{-1} indicates the presence of alkane C-H group (Fig. 2.a.). FT-IR spectra of the mechanical mixture consisting of orange oil and β-CD overlap and intensities of peaks characteristic to orange oil are lower (Fig. 2.b).

FT-IR spectra of inclusion complexes differ from that of the mechanical mixture consisting of orange oil and β-CD (Fig. 2.c.). The transition of C-H band in the orange oil from 1375 cm^{-1} to higher wave numbers, 1410 cm^{-1}, indicates that C-H strengthened and participated in complexation (Fig. 2.c.). The presence of water in β-CD led to the broad peak of O-H, masking the presence of O-H in the orange oil. The wavelength of the CD ring vibration from 1643 cm^{-1} shifted to 1644 cm^{-1}, which shows that the orange oil molecule was incorporated into the hydrophobic cavity of the CD (Fig. 2.c.).

Treatment of natural fur (sheep suede) with fragrance materials was carried out by wetting the surface of fur.

CONCLUSIONS

- Inclusion complexes of essential oils and β-cyclodextrin were prepared: inclusion complex of lavender oil and β-cyclodextrin, and orange oil and β-cyclodextrin, both prepared using the co-precipitation method.
- Methods of treating natural furs with new fragrant materials and with essential oils as such (in the float or by wetting the surface of fur) were established.
- The fragrance effect on fur treated with inclusion complexes based on lavender oil and β-CD and orange oil and β-CD is better and lasts much longer compared to fur treated with essential oils as such.
- Depending on the amount of product applied to the surface of fur, the fragrance effect is different, the higher the amount of product applied on the fur, the stronger the scent.

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