Research on Obtaining Products for Fragrance and Biological Protection on Natural Leathers and Furs

OLGA NICULESCU[1,2]*, MINODORA LECA[1], ZENOVIA MOLDOVAN[1], DANA CORINA DESELNICU[3]

[1] University of Bucharest, Faculty of Chemistry, 36-46 Mihail Kogalniceanu Blvd., 050107, Bucharest, Romania

[2] National Research and Development Institute for Textiles and Leather – Division Leather and Footwear Research Institute Bucharest, 98 I. Minulescu Str., 031215, Romania

[3] University Politehnica of Bucharest, 313 Splaiul Independentei, 060042, Bucharest, Romania

During the various stages of processing or subsequently during use or storage, finished fur products may be damaged due to external factors and insects. These effects can be controlled or corrected by finishing and maintenance treatment of fur and fur products. Chemical insecticides used against insects are toxic to humans. Essential oils are known both for their fragrance and particularly for their therapeutic qualities. They can be used for disinfection and repellence of harmful insects. The paper refers to obtaining and their characterization by physico-chemical, spectral and CG/MS analyses new products based on natural oils (essential oil of lavender and orange), ethyl alcohol, non-ionogenic surfactants from the category of polyethoxylated fatty alcohols and polyethylene glycols, and cationic surfactants (quaternary ammonium salts), which improve resistance of fur and fur garments to biological factors (moths), while providing fur with fragrance and increasing the quality of fur garments.

Keywords: finishing natural fur, essential oils, quality, FT-IR spectrometry, Gas Chromatography Mass Spectrometry (CG/MS)

In fur processing technologies, finishing can be done in two ways, namely: treatment applied directly in the float and treatment by pressing the follicle sheath to obtain special effects and increase the quality of fur and fur garments [1].

During use or storage, finished fur products may be damaged due to external factors and insects. These effects can be controlled or corrected by finishing and maintenance treatment of fur and fur products.

Degradation of wool garments and fur may occur due to insects (moths) and to their larvae, which can break down keratin substances in their intestines and use them as food.

Moths are small butterflies whose larvae attack various vegetable or animal products (flour, cereals, grape vines, wax, tobacco, wool, silk, cotton, etc.). They are part of the Order Lepidoptera, Pyralidae family and are categorized as clothing moths and house moths (Tineola Bisselliella and Tinea pellionella).

As temporary measures to fight moths the following can be listed:

- spraying fluid insecticides on wool in the storage location;
- storing wool in closed rooms where volatile substances make the atmosphere unfriendly for pests.

Substances used to destroy moth larvae have temporary action and efficacy. Some spray products must be used again from time to time to maintain a permanent and effective action on moths. Moths have become immune to volatile substances used (paradichlorobenzene, naphthalene), rendering them ineffective.

A permanent treatment against wool moths is the use of synthetic products, substituted sulfonic acids with a partial chlorine content (colorless), producing heavy keratin digestion in the intestine of the larvae, hindering the ability of pests to devour wool fibers. These products can be used in a hot bath treatment, for example, during the dyeing process.

Essential oils are liquid substances with oily appearance, insoluble in water, soluble in alcohol and organic solvents, with the characteristic odor of volatile substances they contain.

In terms of chemistry, essential oils are complex mixtures of aliphatic and aromatic hydrocarbons, aldehydes, alcohols, esters, and other constituents. [2,3]

Aromatic essences extraction is done by three methods: cold pressing, solvent extraction and water vapor distillation.

Volatile oils can be extracted from various parts of the plant, from flowers, seeds, leaves, stems, peels, roots, rhizomes, tubers, flower buds, etc. [4-9].

Essential oils are very concentrated in active chemical elements and have various properties: they are antiseptic, antibacterial, immunostimulant, etc. [10,11].

Lavender essential oil is extracted from the flowers.

It is a fragrant and colorless volatile oil. The main chemical components of lavender essential oil are: linalyl acetate, linolol, geraniol, linalool valerate, boreol, coumarin, herniarin, cineol, nerol, furfural, alpha pimen, caryophyllene.

Sweet orange essential oil is extracted from orange peel by cold pressing.

It has a sweet, slightly sour odour, and it is coloured yellow-orange. The main cchemical components of essential oil of orange are a-pinene, sabinene, myrcene, limonene, linalool, citronella, neral and geraniol. Orange essential oil is widely used in food industry, pharmaceutical industry, cosmetics, aromatherapy, etc.

These essential oils (lavender, orange) can be used for protection against damage caused by insects and to provide fur with fragrance.

This paper presents the process of obtaining and their characterization by physico-chemical, spectral and CG/MS analyses new products based on natural oils (essential oil of lavender and orange), ethyl alcohol, non-ionogenic

* email: o_niculescu@yahoo.com; Tel.: 0743747994

surfactants from the category of polyethoxylated fatty alcohols and polyethylene glycols, and cationic surfactants (quaternary ammonium salts), which improve resistance of fur and fur garments to biological factors (moths), while providing fur with fragrance and increasing the quality of fur garments.

Experimental part

Materials and methods

- 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;
- Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (Elton Corporation, Romania), density: 0.95 g/cm^3 at 40°C, *p*H (10% solution): 7-8;
- Polyethylene Glycol 600 (Merck, Germany), density - 1.13 g/cm^3 at 20°C, flash point - 270°C; *p*H (10% solution): 4-7; melting point: 17 to 22°C, hygroscopic, flashpoint - 380°C;
- Hexadecyl-trimethyl ammonium bromide (Merck, Germany), water solubility of 3g/L, *p*H (10% solution): 5-7, melting point 237-243°C, hygroscopic.

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^o.

Gas Chromatography Mass Spectrometry (GC/MS) Analysis:

Analysis of the essential oils carried out by using Agilent 7890 A GC System equipped with Agilent 5795 C MS, and HP-5 MS (0.25 mm x 30 m i.d., film thickness 0.25). The carried gas helium (99.9%) at a flow rate of 1 mL/ min; ionization energy was 70 eV. Mass range m/z 50-650 amu. Data acquisition was scan mode. MS transfer line temperature was 250 ^{0}C, MS Ionization source temperature was 230 ^{0}C, the injection port temperature was 250 ^{0}C. The samples were injected with 250 split ratio. The injection volume was 1 µL. Oven ttemperature was programmed in the range of 50 to 250 ^{0}C at 3^{0}C/ min. The structure of each compound was identified by comparison with their mass spectrum (Nist 05 and Wiley 7 library).

Obtaining fragrant products based on essential oils

The following components were added to the mixing vessel: 10% lavender essential oil, 10% orange essential oil, 20% ethyl alcohol, 10% lauric alcohol ethoxylate with seven moles of ethylene oxide, 9-10% polyethylene glycol 600 (non-ionogenic), 1% hexadecyltrimethylammonium bromide (cationic) and deionized water. Components were homogenised using a mechanical stirrer, on an electrically heated installation, at the temperature of 30-35^{0}C, for 15-20 min. In order to homogenise components, an ultrasound bath was used, in which the glass flask was inserted, at the temperature of 25^{0}C, for 10 min. The product with fragrance properties was marked P-LP.

Results and discussions

Characterisation of components used to obtain fragrant products

Essential oils used to obtain fragrant products were analysed using GC-MS [12-14].

Chromatograms for lavender and orange oil are shown in figure 1 and 2, and identification of compounds in their composition is presented in tables 1 and 2.

The following compounds are found in the highest amount: linalol, 36.57%, linalyl acetate, 35.60% and alpha - terpineol, 7.67%.

GC-MS analysis of orange essential oil shows that the limonene compound is predominant, in proportion of 94.7%.

Characterisation of fragrant products obtained

FT-IR spectra of analysed samples, lavender oil, orange oil and fragrance product P-LP 3 are shown overlapping in figure 3a-c.

The main bands of lavender oil are (fig. 3.a): 3455 cm^{-1} – indicating the presence of hydroxyl groups, 2967 and 2923 cm^{-1} – given by aliphatic CH_2 groups, 1737 cm^{-1} – indicating the presence of C=O group from ester, 1449 and 1370 cm^{-1} – assigned to the C-H group, 1240 cm^{-1} and 918 cm^{-1} given by the C-O group from ether.

Orange oil has the following main bands (fig.3.b): 2964 and 2917 cm^{-1}, indicating the presence of aliphatic CH_2 group, 1675 cm^{-1} assigned to the presence of C=O group, 1436 cm^{-1} and 1375 cm^{-1} – due to C-H group fro alkanes, 886 cm^{-1} – for C=C groups from alkenes.

In the spectrum of fragrance product P-LP (fig.3.c) a large intense band is noticed, centered at 3385 cm^{-1} due to

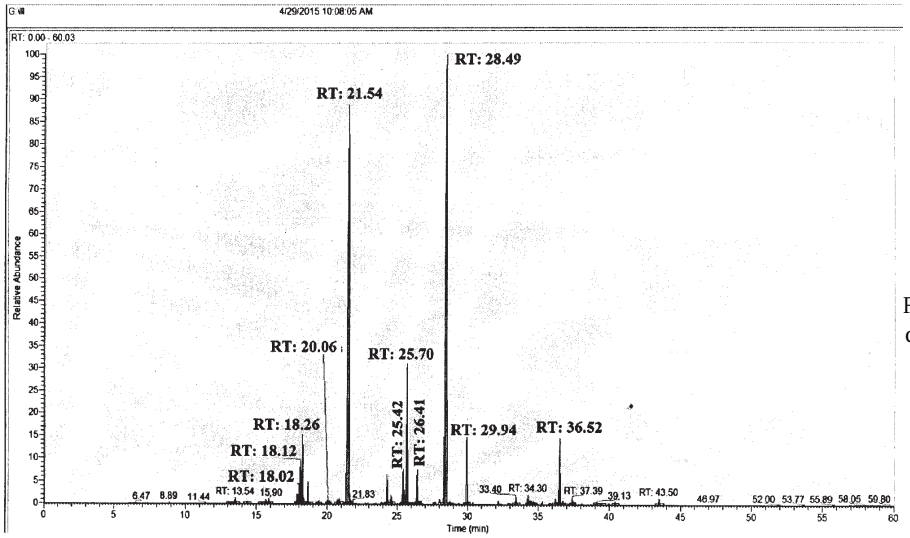

Fig.1. Chromatogram of organic compounds in the lavender oil

Table 1

IDENTIFICATION OF ORGANIC COMPOUNDS IN THE LAVENDER ESSENTIAL OIL BY GC-MS

No.	RT	Amount, %	Compounds
1	13.54	0.25	1Rα-Pinen
2	15.9	0.18	α-Myrcene
3	17.86	0.4	O-Cymene
4	18.02	0.64	Limonene
5	18.12	1.41	2α-Pinen
6	18.26	2.52	Cineole
7	18.65	0.89	γ-Carene
8	20.06	0.35	Linalool oxid
9	21.54	36.57	Linalol
10	24.27	1.25	Camphor
11	24.56	0.46	Levandulol
12	25.42	1.5	Borneol L
13	25.7	7.67	Terpineol
14	26.41	1.45	α-Terpineol
15	28.49	35.60	Linalyl acetate
16	29.94	2.77	Lavandulyl acetate
17	36.52	2.81	Caryophylene

Table 2

IDENTIFICATION OF ORGANIC COMPOUNDS IN THE ORANGER ESSENTIAL OIL BY GC-MS

No.	RT	Amount, %	Compounds
1	13.8	1.4	1R alpha Pinene
2	16.06	1.3	alpha Myrcene
3	18.26	94.7	dl - limonene
4	21.61	1.38	l - linalool
5	25.9	0.39	4 - terpineol
6	28.57	0.95	linalyl acetate

hydrogen bonds formed by water in the fragrance product and the mentioned bands for component essential oils, of much lower intensity due to dilution.

Characterisation of fragrant leather assortments obtained

Fragrance product preparations – P-LP – contain 10% lavender essential oil, 10% range essential oils, 10% ethyl alcohol, 10% lauric alcohol ethoxylate with seven moles of ethylene oxide, 10% polyethylene glycol 600 (non-ionogenic), 1% hexadecyltrimethyl ammonium bromide (cationic emulsifier) and deionized water. [15-18]

Leather samples were treated with various amounts of fragrance products applied on the surface of finished leathers in the final dressing composition, and on the surface of leathers not covered with film.

The finished leather samples were additionally treated with polyurethane final dressing in the composition of which the P-LP product was added in different proportions.

Fragrance products were tested using the sensory test, monitoring the fragrance effect and the concentration of the fragrance volatilized from leathers treated with the prepared products.

The most fragrant leathers are those treated with fragrance products in proportion of 100%.

The subject was also studied in [19-22].

Conclusions

In the spectrum of fragrance product P-LP a large intense band is noticed, centered at 3385 cm^{-1} due to hydrogen bonds formed by water in the fragrance product and the mentioned bands for component essential oils, of much lower intensity due to dilution.

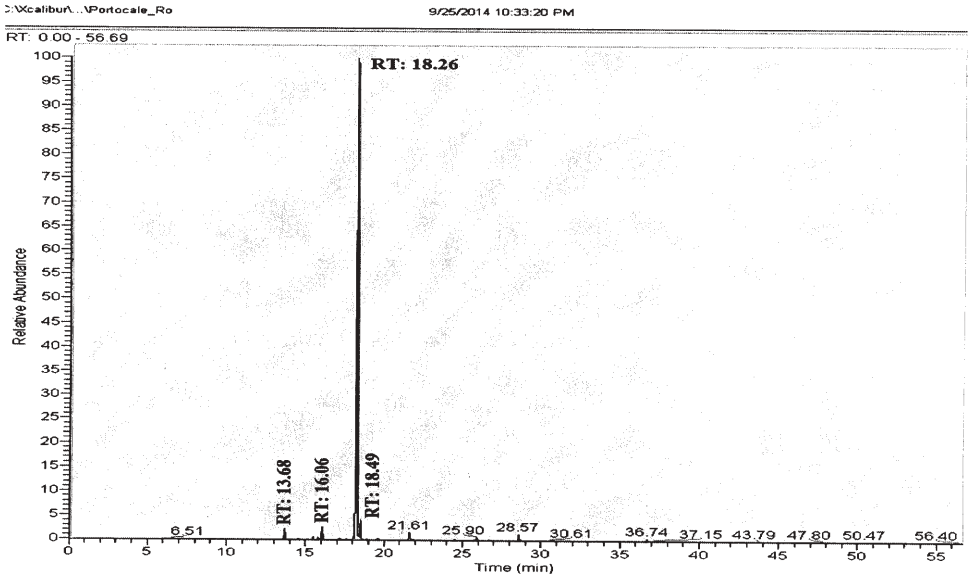

Fig.2. Chromatogram of compound separation in the orange oil

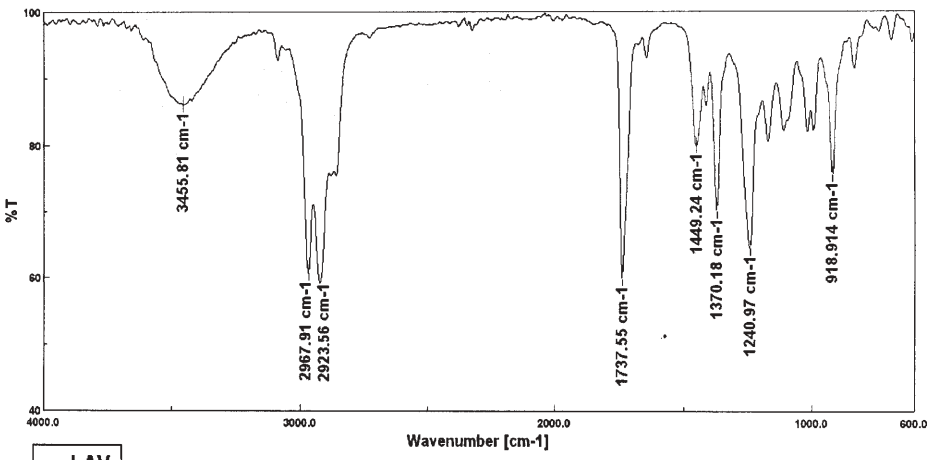

Fig. 3.a. FT-IR spectra of lavender essential oil (LAV)

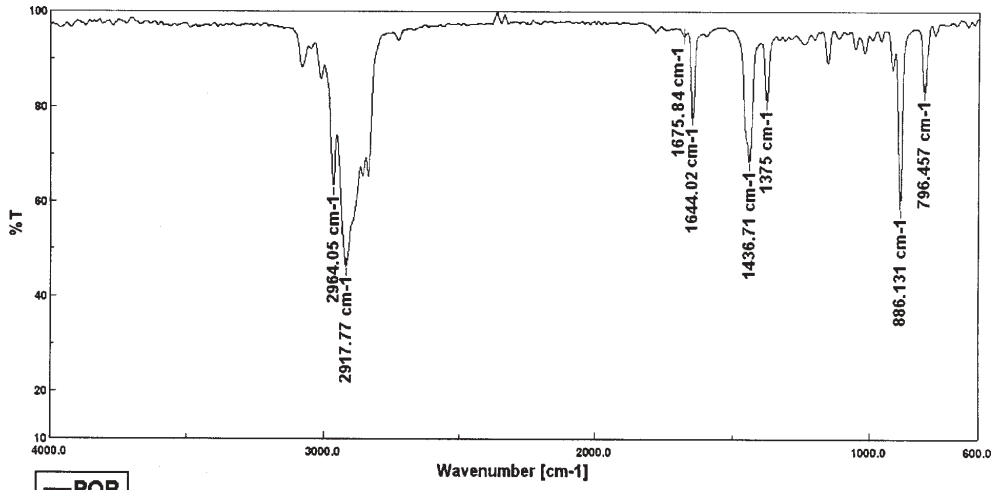

Fig. 3.b. FT-IR spectra of orange essential oil (POR)

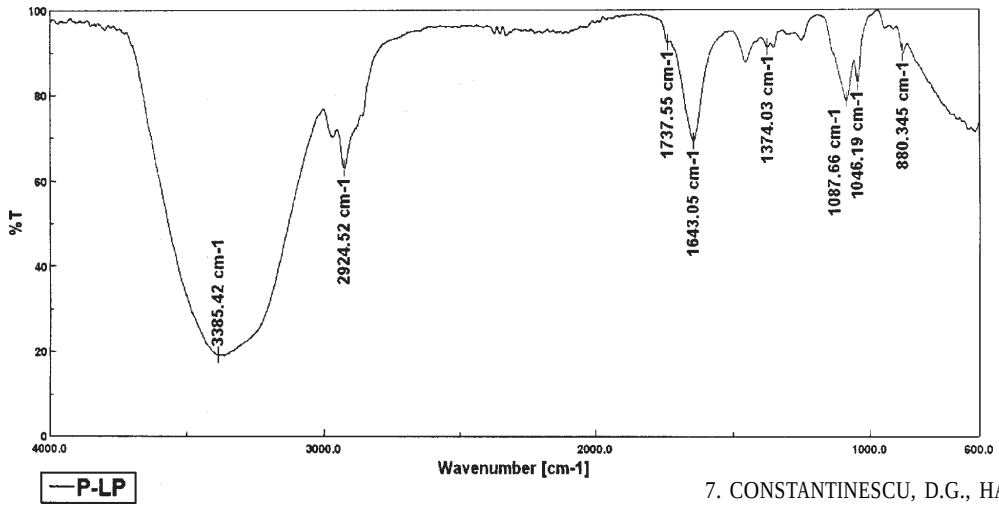

Fig. 3.c. FT-IR spectra of film obtained from the fragrance product P-LP

Samples treated with fragrance products in proportion of 100% are the most fragrant (fragrance lasts for 10 -15 days).

The P-LP product can be used (in proportion of 100%) in surface finishing of sheepskins with buffed grain to obtain a waxy feel and a fragrant effect of the dermal substrate.

Treatment using these products can be repeated from time to time by spraying or dabbing with a textile cloth or sponge. The products can be used to treat film-covered leathers in proportion of 50-80% in the composition of the polyurethane final dressing.

Products can be used for surface treatment of finished leathers and leather products in the composition of the polyurethane final dressing to obtain a pleasant fragrant effect (products are compatible with materials used in the final dressing and are spread uniformly on the leather surface).

Using fragrance products based on vegetable extracts with insecticidal action (lavender, citrus) in the leather and fur finishing process can lead to obtaining garments with durable fragrance and to the biological protection of garments during storage.

References

1. CHIRITA, Gh., CHIRITA, M., „Tratat de chimia ºi tehnologia pieilor ºi blãnurilor”, vol. I, Ed. Gh. Asachi, Iaºi 1999.
2. Farmacopeea Românã, ediþia a X-a, Ed. Medicalã, Bucureºti, 1998.
3. European Pharmacopeia, vol. II, ESCOP Strasbourg, Council of Europe, 2005.
4. CIULEI, I., GRIGORESCU, E., STANESCU, U., Plante medicinale, fitochimie ºi fitoterapie, vol. 2, Ed. Medicalã, Bucureºti, 1993.
5. PALADE, M., Botanica farmaceuticã, Ed. Tehnicã, Bucureºti, 1998.
6. PARVU, C., Enciclopedia plantelor. Plante din flora României, Bucureºti, Editura Tehnicã, 2002.
7. CONSTANTINESCU, D.G., HATIEGANU, E., BUSURICU, F., Plante medicinale utilizate în terapeuticã, Bucureºti, Editura Medicalã, 2004.
8. STANESCU, U., MIRON, A., HANCIANU, M., APROTOSOAIE, C., Plante medicinale de la A la Z, Iaºi , Editura Gr. T. Popa, 2004.
9. ARDELEAN, A., MOHAN, G., Flora medicinalã a României, Bucureºti, Editura All, 2008.
10. S. RAMEZANI, F. RAMEZANI, M. GHASEMI,M. H. FOTOKIAN, Res. J. Biol. Sci., 2009, 4, 103.
11. E. SVAJDLENKA, P. MARTONFI, I. TOMASKO, D. GRANCAI, M. NAGY, J. Essent. Oil Res., 1999, 11, 532.
12. MOLDAVAN, Z., Metode de monitorizare a substanþelor toxice. Note de curs ºi aplicaþii, Ed. Universitãþii din Bucureºti, 2012.
13. DAVID,V., MEDVEDOVICI, A., Metode de separare ºi analizã cromatograficã, ediþia a II-a, Ed. Universitãþii din Bucureºti, 2008.
14. *** http://cachescan.bcub.ro/2008_05_28/cap_10_1_148_159
15. *** wikipedia.ro
16. BALAU MANDRU, NICULESCU, O., PRUNEANU, M., MAIER, V., Product with antistatic-antifelting effect for fur treatment, Patent OSIM 127298/2014.
17. NICULESCU, O., MACOVESCU, G., COARA, G., TONEA, S., Film-like composition and finishing process for nappalan sheep leathers, Patent Aplication OSIM A/00923/2010.
18. NICULESCU, O., TONEA, R.A., TONEA, S, Product for biological protection and fragrance of furs and fur garment, Patent Aplication OSIM A/00395/2014
19. NICULESCU, O., LECA, M., MOLDOVAN, Z., CHELARU, C., GURAU, D., BERECHET, D. M., Rev. Chim. (Bucharest), **66**, no. 8, 2015, p. 1173
20. NICULESCU, O., LECA, M., STAICU, T., MOLDOVAN, Z., CHELARU, C., BERECHET, D.M., Rev. Chim. (Bucharest), **66**, no. 9, 2015, p. 1278
21. NICULESCU, O., LECA, M., STAICU, T., MICUTZ, M., MOLDOVAN, Z., Rev. Chim. (Bucharest), **66**, no. 10, 2015, p. 1549
22. NICULESCU, O., LECA, M., MOLDOVAN, Z., DESELNICU, D.C., Rev. Chim. (Bucharest), **66**, no. 11, 2015, p. 1133

Manuscript received: 24.11.2014