

MULTIVARIATE SPECTROSCOPY ANALYSIS FOR CLASSIFICATION AND IDENTIFICATION OF MOLDAVIAN MATURED WINE DISTILLATES

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Abstract.

It is demonstrated that UV-Vis-NIR-spectroscopy can be used for solving the authenticity problem of matured wine distillates. Application of principal component analysis, classification trees and projection on latent structures to broadband transmission spectra allows determining the manufacturer and aging of wine distillates.

Keywords: chemical composition, classification trees, maturation, principal component analysis, projection on latent structures, transmission spectra, wine distillates.

1. Introduction

Currently an increasing number of consumers care about their health and want to buy natural and authentic food. Authenticity (originality) is an inherent constituent part of a food quality. It defines by a set of physical, chemical and biological parameters, whose absolute quantitative values and change intervals are validated by the natural properties of raw materials and an acceptable technological influence at the ready food manufacturing. Authentication is rather critical in manufacturing and quality control of cognacs and brandies produced from matured wine distillates. The main factors preventing falsification and manufacturing the low-quality product are the control of distillates' age and geographical origin and an identification of the manufacturer.

The only conventional optical characteristics of cognacs and brandies are optical densities at wavelengths 420 nm and 520 nm [5]. However there are different substances with similar optical properties in wine distillates. It impedes to infer about the quality and features of considered objects on the base of spectral measurements at a little number of assigned wavelengths. In this paper we apply the multivariate spectroscopy analysis to solving the problems of classification and identification of Moldavian matured wine distillates.

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2. Materials and methods

We have created an array of data on the physical and chemical composition of wine distillates' samples of different ages produced in Moldova by various manufacturers. The volatile components were determined by gas-liquid chromatography on the chromatograph GC HP 4890D with FID-detector, the decomposition products of lignin (aromatic aldehydes and acids) were determined on the liquid chromatograph Shimadzu LC-20A.

The typical example of distillates' transmission spectra is presented in Fig.1. It is registered by double-beam spectrophotometer Shimadzu PC 3101. Spectral resolution is 0.5 nm in the range from 190 to 480 nm and 1 nm in the range from 480 to 2600 nm. 1 mm optical path cuvette is used for spectral ranges from 190 to 480 nm and from 1100 to 2600 nm. 10 mm optical path cuvette is used for spectral range from 480 to 1100 nm. Spectra have been smoothed by 9-point cubic polynomial Savitzky-Golay filter after registration [4].

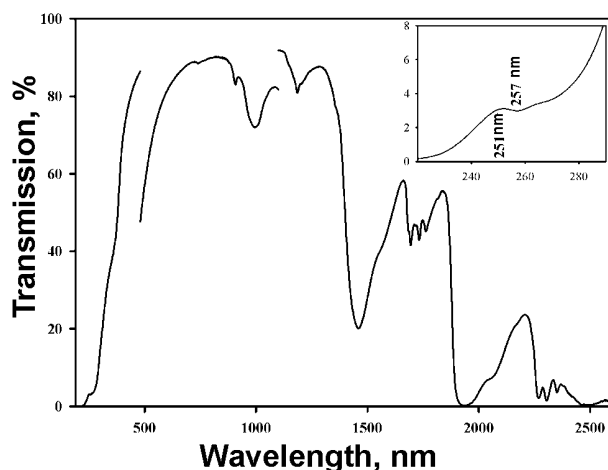


Fig. 1. Typical spectrum of matured wine distillate.
Spectral region of “cognac maximum” is shown in the inset.

In the seventies of the twentieth century the appearance of high-performance computers led to the possibility of effective multivariate data processing. Traditional analytical methods demand the great time expenses, high-priced equipment and consumed materials. It was found that they can be replaced by cheap formal and indirect methods operating the multivariate data. The real breakthrough was done in infrared spectroscopy, particular in the near infrared region. Formerly this region was of little use because of the intrinsic high noise. It is caused by intense water absorption and scattering in reflection spectra. The earliest applications of multivariate data processing methods were devoted to

modeling the spectroscopic data by principal component analysis (PCA) and projection on latent structures (PLS).

PCA [2] is designed to transform the original variables describing the considered set of samples into new, uncorrelated variables called the principal components that are linear combinations of the original variables. The direction of the first principal component lies along the maximum variance in the original variables. Each subsequent principal component describes smaller variance of original data than preceding ones. In terms of matrix notation the principal components are the eigenvectors of the covariance matrix of the original variables. Depending on the field of application, it is also named as the discrete Karhunen–Loève transform, the Hotelling transform, singular value decomposition and so on. In realization through singular value decomposition the I -by- J matrix X of initial data is decomposed to product of matrices U , S and transposed P :

$$X = USP^t.$$

Here I is the number of samples in the set, J is the number of original variables, U is the matrix from orthonormal eigenvectors u_r of the matrix X multiplied by the transposed matrix X :

$$XX^t u_r = \lambda_r u_r.$$

λ_r are the corresponding eigenvalues. P is the matrix from orthonormal eigenvectors p_r of the transposed matrix X multiplied by the matrix X :

$$X^t X p_r = \lambda_r p_r.$$

S is the diagonal matrix with square roots from λ_r in descending order. The classical presentation of PCA is $X = TP^t$, where matrix T of scores in PCA is the product of matrices U and S in singular value decomposition. This matrix contains the information about the samples. Matrix P of loadings contains the information about the original variables. The main purpose of PCA is to represent the location of the samples in a reduced coordinate system where instead of J -axes (corresponding to J original variables) only A principal components ($A < J, I$) can usually be used to describe the set with maximum possible information:

$$X = \sum_{a=1}^A t_a p_a^t + E = TP^t + E.$$

Here t_a are the principal components. Matrices T of scores and P of loadings have dimensions I -by- A and J -by- A . E is I -by- J matrix of remainders that contains irrelevant information.

PCA has been applied to the spectra of 42 samples of mature Moldavian wine distillates from 6 different manufacturers. Each spectrum consists of 2698 spectral data counts. PCA decomposes the multidimensional spectral counts space to low-dimensional space of principal components. Total explained variance of

distillates' transmission spectra is shown to be as much as 94.5% for 4-dimensional space of principal components.

The first aim of application of PCA to the studied spectra was the identification of distillates' age. PCA cannot find the apparent dependency of scores on age of samples considered. But the great value of the total explained variance allows suggesting the presence of another factor that is modeled by PCA. Fig. 2 presents the score plot where 6 manufacturers are marked differently. You can see that our hypothesis is confirmed. PCA models the belonging to the manufacturer in the first place.

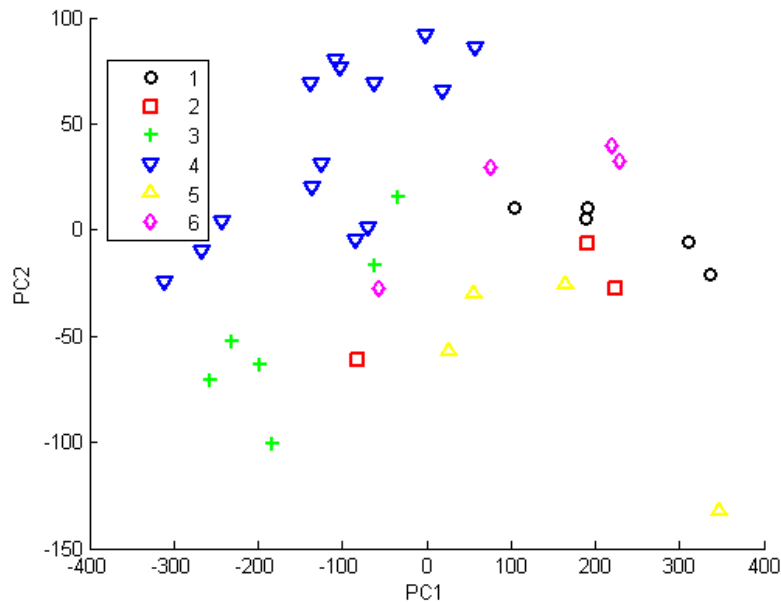


Fig. 2. Score plots in PC1-PC2 space.
Distillates' manufacturers are marked by different signs.

The classification trees making [3] can be applied in 3-dimensional space of principal components for identification of manufacturers. It is one of the kinds of supervised machine learning. The best results are presented in Fig. 3 and are obtained for the algorithm considering all possible combinations of 3-level predictor. Using 3 principal components this classification tree can identify 5 manufacturers from 6 ones considered.

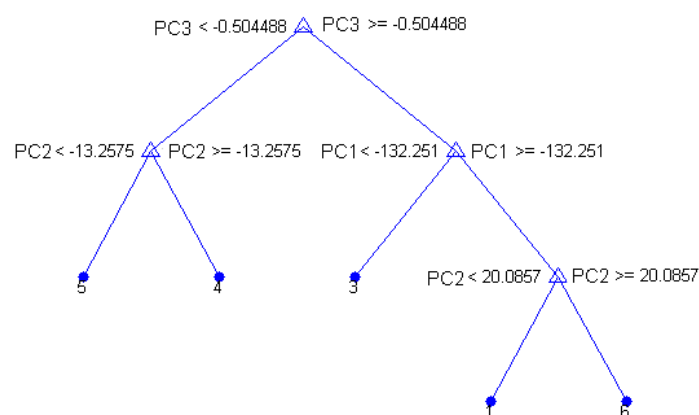


Fig. 3. Identification of distillates' manufacturers by classification tree in 3-dimensional space of principal components.

As you could see earlier PCA cannot identify the distillates' age. We use PLS for this purpose. PLS [1] is the bilinear statistical method in contrast to the linear PCA. It projects predictors (spectra in our case) and a response (sample age) into a new low-dimensional space of latent structures simultaneously.

21 latent structures give the regression factor of 0.98 on 42 samples of distillates. Results obtained by PLS are presented in Fig. 4 and show the unambiguous definition of distillates' age with relative errors being within 8% limits.

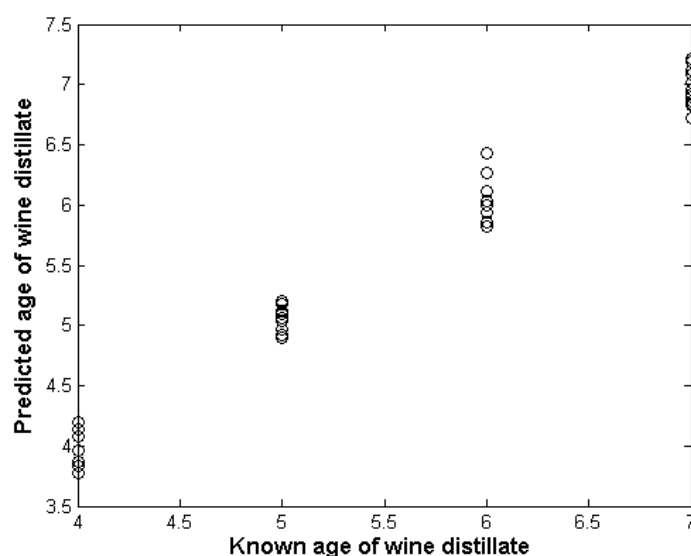


Fig. 4. Known age of wine distillates versus predicted age as the result of application of PLS to transmission spectra.

Conclusions

(1) In the result of these studies it was shown the possibility of using multivariate spectroscopy analysis for identification and classification of matured wine distillates. So the application of principal component analysis, classification trees and projection on latent structures to broadband transmission spectra allows defining the manufacturer and age of wine distillates. One of the possible ways is demonstrated for solving the authenticity problem of quality cognac and brandy manufacture. These analyses, along with the physical and chemical parameters and sensory evaluation of the product, can improve the accuracy of the results of the expert opinion in arbitration disputes.

(2) Part of the presented results is obtained in joint project № 13.820.14.07/BA of Moldavian Fond for Bilateral cooperation program between the Academies of Sciences and project № F13MLD-011 of the Belarusian Republican Foundation for Fundamental Research.

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HYDROMORPHIC SOILS - AS RESEARCH OBJECT OF AND UTILIZATION IN AGRICULTURE OF MOLDOVA

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Abstract.

In the paper are characterized hydromorphic soils of Moldova. The hydromorphic alluvial and non alluvial soils are an important group of soils as object of research for its use in agriculture and as an ecological niche for biodiversity conservation. Hydromorphic soils consists about 300 thousand ha or 8.4% of the total area of the land fund. The main degradation factors of hydromorphic soil are salinization, alkalization, compacting, gleyzation of middle and bottom part of the profile, swamping in terms of lack drainage, clogging by weak humus alluvia. Arable marshes are subject of intensive process of humus loss. Hydromorphic soils are influenced by extremely strong anthropogenic impact, therefore they must be included in the monitoring network of Moldova. Agricultural land use in accordance with the soil and climate resources of each agropedoclimatical zones, particularities of zonal and intrazonal soils will help guide Moldova's agriculture for subsistence in drought conditions.

Keywords: amelioration, hydromorphic, marshy, salinization, soil

1. Introduction

Republic of Moldova is characterized with a complex soil cover. Soil diversity is determined by climate change, topography and vegetation from north to south and vertical zonality of climate. The main soils of Moldova are chernozems, that occupies 2510 thousand ha or 70% of the land area and 78% of the agricultural land [1]. Under steppe and silvosteppe vegetation have formed zonal subtypes of chernozems: podzolic (3.5%); cambic (11.7%); typical (8.3%), common (18.8%); carbonate (19.9%); southern (0.1% of the land fund area) and intrazonal subtypes (7.3%), [2].

Under recent and previous forest vegetation (200-400 m of altitude) have evolved following zonal soils: grey (9.8%) and brown (0.8%) soils; chernozems xero-forestry (0.5% of the land fund).

Brown and grey soils, cambic chernozems of Central Moldova were formed as a result of vertical zonality and are distinguished from similar soils of Northern Moldova by a favorable temperature regime (amount $t^{\circ}>10^{\circ}= 3000-3150^{\circ}$).

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An important group of soils as object of use in agriculture and an ecological niche for biodiversity conservation are hydromorphic soils (300 thousand ha or 8.4% of the total area of the land fund). Hydromorphic class includes the soils influenced by moisture excess: chernozemlike, marshes and peaty [4, 6].

The main types and subtypes of soils were included in the monitoring network, which allows detecting changes in their quality status. For hydromorphic soils the network of monitoring polygons has not been established and information on their quality status is unknown.

The distribution of hydromorphic soils in the investigated area of land fund with agricultural destination is presented in Figure 1 and 2.

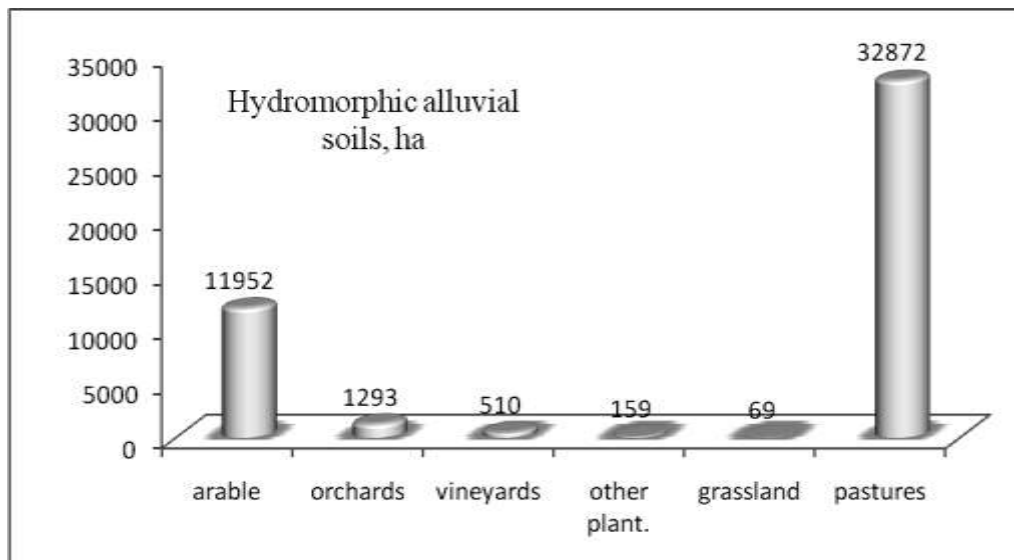


Fig. 1. Distribution of hydromorphic alluvial soils on land uses in the area of agricultural land

2. Hydromorphic soils

Hydromorphic soils divides into *non alluvial* and *alluvial*. They are represented by typical marshes, stratified marshes, swampy marshes, peaty soils, hydromorphic solonchaks and solonetz [3].

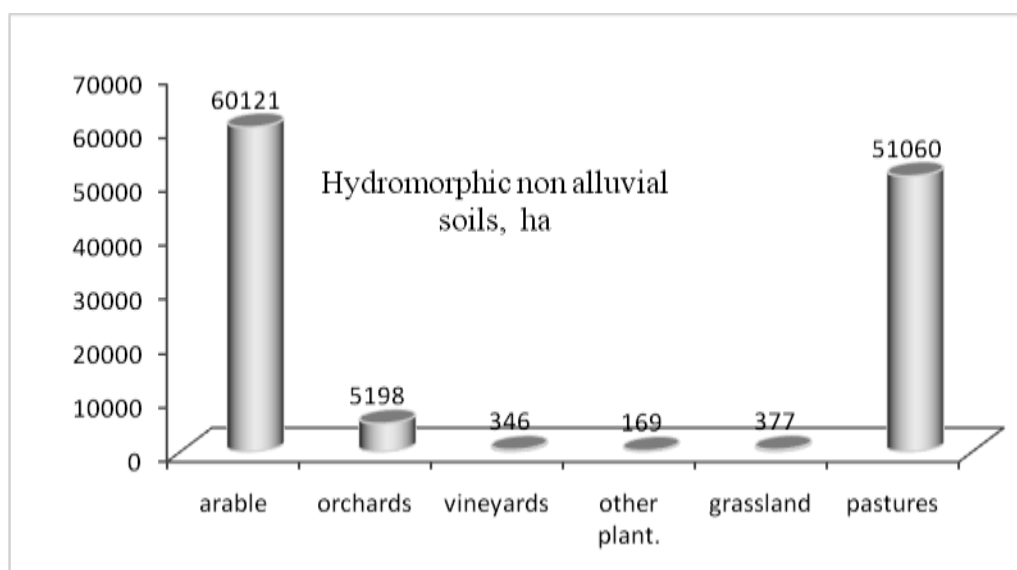


Fig. 2. Distribution of hydromorphic non alluvial soils on land uses in the area of agricultural land

Non alluvial hydromorphic soils occupies the area of 47 thousand ha or 2.54% and alluvial - 117.3 thousand ha or 6.3% of the investigated area of agricultural land [2]. These soils mostly in the past were irrigated. Currently the irrigation system can be achieved while restoring the drainage system regulating ground water level. As an object for use in agriculture the following hydromorphic soils are of interest: non alluvial and alluvial (fluvial) humiferous marshes, stratified marshes.

2.1. Non alluvial humiferous marshes

Non alluvial marshes area occupies 10.7 thousand ha or 0.58%. They are spread in all districts of Moldova. They were formed as a result of combination of humification and gleyzation accumulation processes in condition under permanent connection with groundwater. They are spread in the valleys, gullies, depressions, on the slopes and watershed in the form of small spots. They have a well-developed humus profile with thickness of 40-120 cm and signs of gleyzation in the middle and lower part of the profile. The humus content in the surface horizons of soils is 4-8% and in the arable layers - 3-5%. As a result of various share of precipitation and groundwater to wet these soils on seasons and years, the marshes formed a regularly percolating water regime which conditions the current instability of salinity profiles and properties, and also relatively rapid change in outcome improvement. This process lead to apparition on the comparatively small

territories, the combinations of hydromorphic soils, composed from marshes, swampy marshes and swampy soils [5].

2.2. Alluvial (fluvial) humiferous marshes

Together with the vertic marshes (8.8 thousand ha or 0.48%) these soils occupies the area of 52.5 thousand ha or 2.85%. They are spread in large river valleys of Dniester, Prut, Răut and small river floodplains. They were formed in the result of combining the humification, gleyzation and alluvial processes of accumulation in the floodplain of rivers. They were spread in the riverbed part, where alluvial regime manifests weakly and temporarily, or definitively ceased, and the accumulation of humus is pronounced. The shallow groundwater depth is 0.7 to 2.0 m and causes an intensive gleyzation in the middle and lower part of soils. They have a well-developed humus profile with thickness greater than 60-80 cm, sometimes more or less humus layers of buried soil, that differ by size composition [4,6].

They are characterized by high natural fertility, but their use as arable is possible only in the presence of drainage and protective dams. The main processes that cause their degradation are: salinization, alkalization, gleyzation, swampy at the irrigation without drainage, flooding in the case of floodwaters.

2.3. Stratified alluvial marshes

These marshes occupies 46.7 thousand ha or 2.52% [1]. It is more common in floodplains of Dniester, Prut and Răut rivers. They were formed on river stratified alluvium under intensive accumulation of alluvial deposits. The main criterion that distinguishes them is alternating layers of different texture and humus content in the profile. Soils are poorly evolved. Compared with alluvial humus marshes, they have a lighter color, lower humification, less developed structure, coarser texture. Morphological characteristics, composition and properties of these soils vary strongly in space. The humus content in arable layer is 1-3%, reaction - slightly alkaline. Natural fertility is low or medium. The degradation factors of stratified alluvial soils are the same as the fluvial typical marshes: salinization, alkalization, compaction, swamp at the irrigation without drainage, gleyzation [2].

3. Soil degradation by humidity excess

3.1. Periodic numidity excess and salinization processes of non alluvial marshes on the slopes and depressions

The formation and evolution of soils with excess moisture on the slopes and depressions is subject to prolonged stagnation of rainwater (from rainfall), the

appearance on the surface of coastal spring's water or groundwater, soil overeating with surface rain water and ground water.

The process of soil formation under hydromorphism is influenced by the content and composition of salts in ground water. In silvosteppe landscapes of Northern Moldova Plateau the ground waters have a low content of salts, the main component is calcium bicarbonate. In these conditions are formed non salinity marshes.

In Central and South Moldova landscapes predominate groundwater with high level of mineralization and the presence of toxic salts, under whose influence are formed the soils with different degrees of salinity and sodium enrichment.

The distribution of non alluvial marshes in Moldova is presented in the Table.

Table. Distribution of alluvial marshes in Moldova

Pedo-landscape Provinces	On the slopes		In depressions		Total	
	thousand ha	%	thousand ha	%	thousand ha	%
Silvosteppe of Northern Moldova	20.5	41.3	9.4	19.0	29.9	60.3
Silvosteppe of Central Moldova	6.5	13.1	2.8	5.6	9.3	18.7
Predanubian Steppe of South Moldova	4.2	8.5	4.1	8.3	8.3	16.8
Ukrainian Steppe of Southern Moldova	1.3	2.6	0.8	1.6	2.1	4.2
Total	32.5	65.5	17.1	34.5	49.6	100

The marshes on the slopes are distributed in the form of small spots with size from 0.1 ha to 1-5 ha. The mosaic of spots of hydromorphic soils on the arable land creates heterogeneity of soil cover of the plots, complicating the tillage and sustainable land use. In connection with the destruction of drainage facilities the surface of soil with humidity excess on the arable land increases intensive in recent years [3].

Marshes on the slopes have an area of 20 thousand ha, according to the land register are considered as arable and perennial plantation, however, the harvests on them, is practically impossible. Given the approximate cost of the annual harvest of 2 thousand lei per 1 ha, the annual loss caused by mosaic of marshes on the arable land reaches 40 ml. lei (\$ 3.64 million). Annual total loss for the whole area of non alluvial marshes as a result of salinization and water excess is 49 ml. lei (\$ 4.542 million), [2].

3.2. Periodic humidity excess and salinization processes of alluvial soils and marshes

The total area of alluvial soils and marshes is 259 thousand hectares, of which 99 thousand are salinization. Non salinization are soils in floodplains of small rivers from Northern Moldova and the most soils in the floodplain of Dniester river.

Salinization soils are widespread in the meadow of Middle and Lower Prut river and small meadow of Central and Southern Moldova. Ameliorative situation of these soils is very complicated. As a result of damming and regulation of flows by building ponds, restoring and deepening riverbeds have been excluded seasonal overflows that maintaining the saline balance in soil - groundwater system. Drainage facilities did not ensure evacuation of excess water and salts from the soils and lowering ground water level. In 75% of the floodplain soils groundwater depth is higher than the critical level, which favors evolution of salinization processes. Currently 47% of the alluvial soils are characterized by a satisfactory ameliorative status and 53% - unsatisfactory [3].

The annual loss of crops on alluvial soils with unsatisfactory ameliorative status (130 thousand ha) is 20-30%, equivalent to 500 lei per 1 ha and 66 million lei (\$ 6023 ml) over the entire area affected by degradation processes. The annually damage across the entire alluvial soils with excess moisture and salinization soils constitutes 111 ml. 309 thousand lei (\$10 ml.119 thousand), [2].

4. Amelioration of soils with humidity excess

Marshes, wetland marshes are found in all agropedoclimatical zones of Moldova on the slopes and depressions in the form of small spots. Mosaic of bogs on the slopes prevents the operation agricultural works. On the basis of the recovery and exploitation of soils with humidity excess are the drainage works, which include: rapid evacuation of stagnant water from the plane land; lowering the groundwater level in the landforms depression; capturing coastal springs and ground water. In the period 1970-1990 by drying-drainage works have been put in the agricultural circuit approximately 40 thousand ha (80%) of the total area of marshes. In the desiccation process of non salinization marshes they approach the zonal soils after quality status. Therefore, the models of improvement and rational use of hydromorphic soils will take into account only the relief particularities and salinization conditions.

Currently the system of soil drainage-drying with excess moisture on the slopes is partially or totally damaged and practically not functioning. Failure measures to restore and maintain the drainage-drying system, will lead to the exclusion from agricultural circuit about 40-50 thousand hectares of arable land [1].

Salinization soils with moisture excess from meadows are represented by alluvial (fluvial) marshes and alluvial soils (fluvisols) alkalization and salinization.

Ameliorative status of these soils, as a result of the demolition of the drainage system, worsened considerably, primarily in small river valleys and in the Prut meadow. Most arable land of small meadows has been converted from arable land into grassland. As a result of overgrazing the pasture has worsened and is characterized by low productivity.

Drainage facilities have not ensured lowering of water ground level, evacuation of water and salts excess from the soils. In these circumstances have become dominant halogen - salinization and alkalization processes. Currently over 99 thousand hectares are salinization, 20 thousand hectares - wetlands and about 10 thousand hectares became slitized (compacted). Over 75% of the floodplain soils have the depth above the critical groundwater level. According to the pedological, hydrological and biochemical indices, over 40% of the floodplain soils are characterized by favorable ameliorative status and 53% - unsatisfactory. Meadow soils in good condition are practically missing [2, 5].

Ameliorative works of alluvial salinization soil are integrated within the whole of the interventions to combat desertification and improve ameliorative condition of meadows territory in Moldova. Improving salinization soils is made based on projects developed for natural zones, river basins and is done in stages. Salinization soils require gypsum amendment, application of deep plowing, maximum fertilization. Without the application of mineral and organic fertilizers these soils cannot provide high yields being poor in humus, nutrients and low biological activity.

Conclusions

(1). The main degradation factors of marshes are salinization, alkalization, compacting, gleyzation of middle and bottom part of the profile, swamping in terms of lack drainage, clogging with weak humus silt. Arable marshes are influenced by intensive process of humus loss.

(2). The pedoameliorative measures for increasing production capacity of soils should include improvement of soils with humidity and salts excess, degraded as result of irrigation, in aim to combating drought and desertification.

(3). Monitoring polygons network of Moldova should be broadened and cover all pedoclimatical areas and vertical zones, and intrazonal soils (marshes, chernozemlike soils, solonetz, solonchaks, diluvial soils, alluvial soils, etc.) that are formed in all pedogeographic districts.

(4). Agricultural land use in accordance with the soil and climate resources of each agropedoclimatical area will contribute to the recovery of low productive lands (hydromorphic) and orientation the Moldova towards the subsistence of agriculture in drought conditions.

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BEHAVIOUR OF SOME NECTARINE VARIETIES TO MYCOTIC DISEASES

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Abstract.

Resistance of 20 nectarine varieties were studied during three years in an orchard on Prahova region. The diseases observations have carried out on *Sphaerotheca pannosa* var. *Taphrina deformans persicae*, *Stigmata carpophila*, *Monilinia laxa*, *Cytospora cincta* under treatments. Resistance of varieties and correlations of nectarifers glands with the resistance have been observed.

Key words: mycotic diseases, nectarine, *Prunus persica*, resistance

Introduction

Nectarine tree, like peach tree is affected every year by a number of phytopathogen agents as: *Sphaerotheca pannosa* var. *Taphrina deformans persicae*, *Stigmata carpophila*, *Monilinia laxa*, *Cytospora cincta*, a.s.o. for which to be treated farmers need a significant expenditure materials require the defendant to application of 13-15 treatments [1]. Treatments, though, besides the beneficial effect that consists in saving production, presents a number of drawbacks such as: environmental pollution, toxic residues in fruit, increasing production costs, etc. Due to these considerations the introduction in culture of nectarine varieties resistant to disease, is likely to diminish partial mentioned inconveniences.

Material and Method

The observations for the main diseases on nectarine were carried out during the period 2012-2014 on 20 varieties with 3 trees on 3 repetitions. The varieties have different origins (Romanian creations, American, Italian, French), under the application of phytosanitary treatments in a demonstrative plot in Prahova county. The differences noted are due exclusively to varieties and their reaction to pathogens.

For the detection of the attack caused by Mycosis in the orchard, under treatments observations have been made at: *Cytospora cincta* Sacc. (the percentage of tree branches to each subject, the average tree and variety).

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Taphrina deformans (Berk.) *Monilinia laxa* Tul. and *Sphaerotheca pannosa* var. *persicae* Woron. (noted F%, I% and GA% on 100 leaves, for every tree, then the average variety).

We used the grading system in the scale 0-6:

- 0-no attack;
- 1-attack is up to 3% of the body surface observed;
- 2-the attack between 5-10% of the body surface observed;
- 3-attack between 11 and 35% of the body surface observed;
- 4-attack of between 26 and 50% of the observed body;
- 5-attack between 51 and 75% of the observed body;
- 6-the attack between 75 and 100% of the observed body.

Mathematic formula for calculation is:

$$GA\% = \frac{F \times I}{100}$$

In order to detect resistance varieties of nectarine for *Stigmia carpophila* (Lev.) M.B.Ellis, *Monilinia laxa*, *Cytospora*, *cincta*, the length of the lesions produced by mycosis were analyzed and it was made a classification of varieties: 0-3 mm variety highly resistant (FR); 4-10 mm variety resistant (R); 11-25 mm medium variety resistant (MR); 26-50 mm sensitive variety (S); > 51 mm very sensitive variety (FS).

Results

A. *The behaviour of natural infections in terms of treatments.*

Assessment of the resistance to the main diseases of the nectarine was made in the conditions for carrying out plant-health treatments (8-10 per year).

a) In 2012 *Sphaerotheca pannosa* appears and has developed especially in the latter part of the period of vegetation, with a degree of attack between 0.71- 7, 61%. More sensitive proved to be American varieties, with a degree of attack greater than 5%. Climatic conditions of the year 2012 were not favourable to the development of the fungus *Sphaerotheca pannosa* product (Wallr) Lev. var. *persicae* Woron, so the varieties Fantasia, Tina and Mihaela, have shown traces of the attack. Maximum 2% attack registered Morton variety (Fig.1).

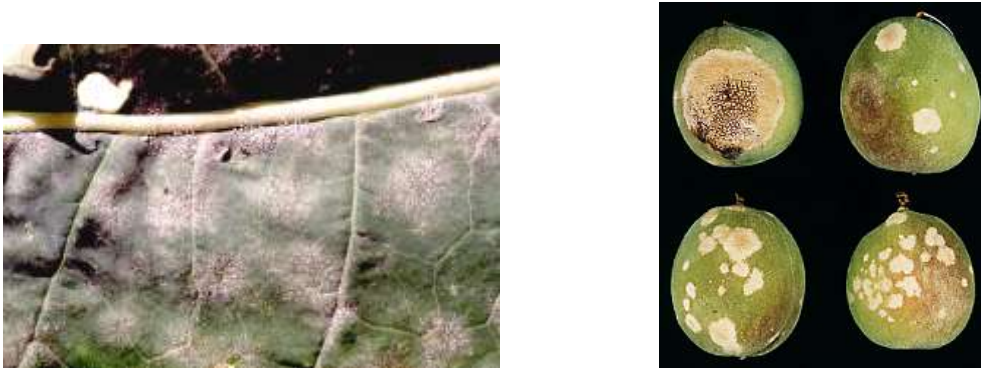


Fig.1 Symptoms of *Sphaerotheca pannosa var persicae* on leaves and fruit

In 2013, the attack was more intense, on the leaves and shoots and also on fruits, in percentages ranging between 1% (Harko) and 30, 0 % (Romamer I). Did not show symptoms: Hardyred, Regina, Tina.

Did not show symptoms of attack during the year 2014: Pocahontas, Morton, Harko, Nectared 7. A very good reaction (degree of attack under 1%) shown Morton, Harko and Armking.

b) Treatments applied to the fall of the foliage as well as the swelling buds, with copper-based products, have stopped the appearance with big intensity of the fungus *Taphrina deformans* (Berk.) Tulle.

In 2012 the fungus had good conditions of development, since the last decade of March until early June. In this context, on an untreated plot it was recorded a degree attack of 33% at Harko. Also in 2013, climatic conditions were favourable to the development of the fungus *Taphrina deformans*. On the treated plot, the attack has oscillated between 0 -1, 32%, (Fantasia, Flavortop and Nectared 7). In 2014, the attack was very low, being between: 0- 1, 13% (Tina, Mihaela, Pocahontas) and 5, 24% (Romamer I).

Degrees of attack, on the merits of treatments orchard over 1% had the varieties: Crimsongold, Independence, Morton. Did not show traces of the attack: Hardyred, Regina, Tina, Mihaela and Nectared 10.

Virtually no variety is not completely immune to *Taphrina deformans*, but some resistance can be observed on the varieties Hardyred, Regina, Nectared 10, Fairlane.

c) The first symptoms of attack of *Cytospora cincta* Sacc. were observed on the annual branches in 2012, in the fourth year after planting. The largest percentage of branches with symptoms of attack, of 3 %, had Flavortop variety.

His wounds produced by cuts, as well as wounds as a result of frosts, are input gates for the *Cytospora cincta* fungus.

Proof lies in the fact that in 2013, after the pruning time all the varieties have presented attack, the frequency oscillated between 5,0 %

(Romamer I, Fairlane) and 1,0 % (Armking). An attack under 2% was only to Mayred and Weinberger varieties.

Winter period of the years 2013-2014 was not too freezing and didn't favoured the appearance and evolution of *Cytospora cincta*, so the frequency of the attacked branches has not exceeded 2,4 % (Firebrite), and on some varieties the attack has not occurred at all: Tina, Mihaela, Weinberger and Nectared 10.

After three years of study we notice that have not been attacked or had along this period less than 3% attacks in terms of natural infection on the merits of treatments, the following varieties: Crimsongold, Romamer II, Independence, Mayred, Morton, Weinberger, Armking.

d) *Stigmia carpophila* (Lev.) M.B. Ellis appeared in 2012 on the branches, with frequent who oscillated between 0,30% (Armking) and 2,90% (Fairlane). In 2103, the degree of the attack increased to decisively swing between 1.8% and 8.3%. Following the attack of the two-year note, a better behaviour (the frequency below 9%) had the varieties: Romamer II, Nectared 4, Firebrite, Nectared Flavortop, Fairlane, Fantasia.

In the climatic conditions of the area of the South aerea of Prahova (long winters with minimal up to -19 ° C, large temperature fluctuations in the spring, drought), detection of resistant varieties to the attack of the disease presents a wide meaning.

e) The fungus *Monilinia laxa* (Aderh. et Ruhl), Honey has not caused serious natural infections in the field, during the three years of observations. *Monilinia laxa* may cause infections on nectarine branches throughout the year.

Optimal conditions for the development of the agent are in spring and autumn, when there is maximum of infected branches, with necrotic spots, 20-30 mm long.

In the summer, when air temperature exceeds 20 ° C the virulence of the pathogen agent decreases, and as a result is reduced the percentage of damaged branches. Necrotic lesions evolve slowly and in most cases the scars. Drying branches takes place after 5-6 months from the date of registration of the attack, in most cases fall.

In 2012 the length of necrosis, oscillated between 1,1 mm and 43,8 mm (Nectared 10). Serious injuries have submitted varieties: Pocahontas, Morton, Nectared 7, Crimsongold. In 2013 the dimensions oscillated between 7,5 mm and 100,5 mm.

It was observed that the most sensitive varieties are those with very late ripening (Nectared 7, Fantasia, Nectared 10).

Classifying the varieties after their resistance at *Monilinia laxa* the results are:

- resistant varieties: Hardyred;
- medium resistant varieties: Crimsongold, Romamer I, Tina, Romamer II, Mihaela, Independence, Pocahontas, Nectared 4, Firebrite, Flavortop, Fairlane, H, Weinberger (so about 75% of the varieties have an average resistance to attack by Monilia);
- sensitive varieties: Morton, Regina;
- highly sensitive varieties: Fantasia, Nectared 7, Nectared 10.

B. Presence of attack on fruit

The fruit's attacks were carried out observations on the fruit maturity harvest, known as the nectarine area extension is limited by the sensitivity of the fruit to diseases. With the intense virosis attacks on fruits, and also of various other attacks diminishes their capacity (spots of the epidermis, powdery mildew disease) made them virtually non commercial.

Observations on the behavior of fruit from *Monilinia laxa* and *Sphaerotheca pannosa* var. *persicae* has a special importance for detection of resistan: +++ very sensitive; ++ average sensitivity: -tolerant; 0-resistant.

a) *Monilinia laxa* expands after the infection very quickly, within 2-3 days and can affect the entire fruit. Observations made, for three years, show that most varieties are susceptible. Medium sensitivity had Flavortop and a good behavior: Hardyred, Regina, Tina, Mihaela and Armking. The resistant variety was Nectared 10.

b) *Sphaerotheca pannosa* var. *persicae* affects very often fruit and leaves, progressing rapidly and reducing in the end the quality of the fruit, making it non comercial. Good powdery mildew behaviour on the fruit presented: Armking, Nectared 10, Tina, Mihaela. Medium sensivity was observed on: Crimsongold, Hardyred, Morton, Flavortop, Nectared 7.

Greater sensitivity showed: Romamer II, Independence.

DISCUSSION

Before ripening fruits of some cultivars crashes on the seed through these opening and favouring the penetration of various pathogens in fruit. This flaw gathers in the varieties: Romamer I, Romamer II.

In the literature [3] (Simeone, A. M.1983), it mentions the fact that the varieties of nectarine with nectarifere kidney-shaped glands are very resistant to powdery mildew disease, those devoid of glands are very sensitive, and varieties with globular glands have a medium sensitivity.

Study of nectarifere glands at nectarine trees was conducted specifically for the detection of a positive correlation between the shape, size, number of nectarifere glands and resistance to disease [2].

The observations undertaken came as the number of nectarifere placed on the petiole glands at the base of the leaves, was not greater than 3, rule of 2, both of which are the same size. The form has varied depending on the variety.

Most of the varieties have nectarifere kidney-shaped glands placed 2 by 2 face to face. He attempted a classification of nectarifere foliar glands, as follows:

- free varieties of glands nectarifere: none;
- globular nectarifere: Flavortop;
- glands kidney-shaped nectarifere: shows most varieties, which is supposed to be correlated with a good resistance to *Sphaerotheca pannosa* var. *persicae*.

We believe that, although some varieties have been extensively damaged in natural conditions, but data are not completely conclusive, since phytosanitary treatments were applied, the reason for which, in order to discover resistant artificial inoculations must be carried out.

CONCLUSIONS

(1) Processing of data for a period of three years, allows submission of some nectarine varieties with a high degree of higher resistance compared to the main diseases:

1. *Taphrina deformans*: Hardyred, Regina, 10, Nectared Fairlane;
2. *Sphaerotheca pannosa*. var. *persicae*: Tina, Mihaela;
3. *Cytospora cincta*: Romamer II, Hardyred, Tina, Independence, Regina, Harko, Nectared, 10, Nectared 7, Crimsongold, Mihaela;
4. *Stigmina carpophila*: Romamer II, Tina, Fairlane, Mihaela;
5. *Monilinia laxa*: Hardyred, Nectared 10, Armking, Regina.

(2) Symptoms manifested by tuber rots, cancers, leakage gomes and finally drying partial or total, all components airline of the nectarine. They appear in particular as a result of low temperatures during winter period and of their fluctuation in the blooming period.

(3) Most of the fungus species are interference of wounds, forties in host tissues by injuries caused by frost, cuts, or physiological fall of the leaves (blind petiols).

(4) Diseases studied constitute only a link in the chain of those responsible factors for the development and the flow of the process of the decline of nectarine tree, together with the non parasitic factors (climatic factors, edafic factors, biological agents), they physiologically weak trees, being more sensitive to the attack by various parasites, as well as to frost and drought.

(5) Preventive treatments have proved to have a high efficiency curative, and for this reason, we recommend to pay a particular attention to carrying out their time and with recommended products.

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TOBACCO MARKET IN ROMANIA. MANIFESTATIONS, LIMITS AND CONSTRAINTS

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Abstract.

This paper assembly aims to identify the die circuit tobacco policy in Romania, which is the very market for this product (with reference to the production flow → processing → consumption). The paper has been played through the structural analysis that began with the planted areas and achieved yields, tobacco processors and labor input, Romania's foreign trade in tobacco products. The levels comparative analysis performed in the whole flow indicators of tobacco chain, was supplemented by appropriate statistical indicators (the arithmetic mean, the standard deviation, the coefficient of variation) of whose interpretive meaning captured variation elements of the period 2007-2012 dynamics.

Keywords: the foreign trade, the tobacco supply chain, the turnover.

1. Introduction

The whole work aims to show the results focused on the chain policy, through the manifestations of the tobacco market in the production flow → processing → consumption in Romania. The results observed in the structure of the work, itself plays an analysis with a structural shape that begins with the areas and production of the culture, processors, labor input and Romania's foreign trade in tobacco products.

In the first years after accession, the tobacco industry in Romania increased through subsidies [5]. Since 2010, the market collapsed, due to the fact that subsidies have declined substantially. It was a lack of communication between the authorities and farmers. Subsidies system was changed to grant subsidy per kg to the surface. In the present there are approx. 800 farmers in the APIA registers that want to access tobacco subsidy. Each of them have in the back 5-10 families for accomplishing the production.

From a national analysis it is shown that tobacco growers invest € 2,000 per

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hectare, with a profit of up to 700 euros [5] . But it can be mentioned that there are unused quantities of tobacco, on that basis - is supposed that tobacco does not has the quality which makes it refused to the takeover.

The tobacco growers believe that the subsidy of almost 1,300 euros per hectare is very low, given that until 2010 the aid was of 2,600 euros per hectare.

The investment for the cultivation of one hectare of tobacco amounts up to 2,000 euros and profit reaches 700 euros per hectare [5] .

The biggest crops are in the Transylvanian Plateau - the upper Mureş - , Carei area - Satu Mare - the Moldavian Plateau - from Suceava to Iaşi – but also Muntenia and Oltenia area. Over 60% of farmers cultivates tobacco Barley, which goes to export. In the country, they sell tobacco Virginia type [4].

2. Materials and methods

The paper aims the substantiation of a set of events in the sector of the tobacco market. The approach of the problem required the use of specific indicators (synthetic and derivatives) through which are known and presented specific problems at the national market chain within the period 2007-2012.

The calculation basis was the existing data of the National Institute of Statistics, pursuing a highlight of the levels achieved by processing the indicators and their interpretation.

Methodological, the synthetic and derived indicators were expressed quantitative and as a percentage, at which through comparative forms in the years succession were followed the yearly levels.

Were used the following statistical indicators: the arithmetic mean, the standard deviation, the coefficient of variation and the statistical significance of these indicators[1], [3].

The coefficient of variation can be: between 0-10% - little variation; 10-20% - medium variation; over 20% - big variation.

3. Results and discussions

a. Areas and productions on tobacco culture in Romania.

Growing tobacco is considered a profitable field agricultural activity. This follows from the comparative analysis, which in the agro food economy in Romania, shown in Table 1, regarding the tobacco industry, it can be seen:

Table 1)The Romania and the EU agro-food economy structure in 2012

Specification	The agro food economy structure in Romania		The agro food economy structure in EU	
	Total	PA / PAA	Total	PA / PAA
	%	%	%	%
Agriculture (PA)	60.70	0.58	25.00	3
Food Industry	(35.20)	x	(60.90)	x
Tobacco products industry	(4)	x	(7.90)	x
Fish farming	(0.10)	x	(6.20)	x
Total PAA	39.30	1	75.00	1
TOTAL	100.00	x	100.00	x

Source: Processed from The national strategic framework for the sustainable development of the agri-food sector and Romanian rural areas in the period 2014 - 2020 2030 CRPCIS, 2012 [10]

- From the analysis of the whole agri-food economy structure, as shown in the comparative values, we find that the share of agriculture in Romania is very high compared to the food industry (60.7% levels are compared to 25%). From the structure investigations we found that tobacco industry's share is 4%;

- Comparative with the structure of the economy of the whole EU, it is shown that the largest share has the agri-food industry (60.9%), agriculture is much below at this level (only 25%). Also tobacco industry accounts 7.9%, which is a lower level.

In part, these differences can be justified by the fact that for the tobacco growers in our country [5][6], it is found an insufficient number of processing companies. This constitutes a great deficiency, mentioning that at national there are approx. 800 growers. It could be also said that there are five types of tobacco - Oriental, semi-Oriental, Virginia, Burley and great consuming type, and after the privatization of the National Society of Romanian Tobacco, the market dropped and first-processing firms have shifted.

In Table 2 is presented the situation of tobacco production and areas from Romania where for the dynamics 2007-2012 it can be highlighted the following issues:

Table 2)The tobacco surfaces and productions in Romania

Specification	UM	2007	2008	2009	2010	2011	2012	Average / rhythm	Standard deviation	Variation Coefficient (%)
Area	thousand ha	1.1	1.2	0.9	1.5	1.7	1.3	1.3	0.3	22.3
	previous year		1.09	0.75	1.67	1.13	0.76	3.40	x	x
	% Compared to 2007	100	109.0	81.8	136.3	154.5	118.1	x	x	x
Total production	thousand tons	1.1	2.4	1.6	Three	2.6	1.3	2.0	0.8	38.6
	previous year		2.18	0.67	1.88	0.87	0.50	3.40	x	x
	% Compared to 2007	100	218.1	145.4	272.7	236.3	118.1	x	x	x
Average production	kg / ha	1025	1916	1842	1939	1939	1066	1621.2	447.5	27.6
	previous year		1.87	0.96	1.05	1.00	0.55	0.79	x	x
	% Compared to 2007	100	186.9	179.7	189.1	189.1	104	x	x	x

Source: Romanian Statistical Yearbook, INS, 2013 [9]

- The cultivated areas present oscillations, which annually are between 0.9 and 1.7 thousand hectares, but in comparison to 2007 there is an increasing trend, the annual average is of 1.3 thousand hectares. But these annual changes analyzed by the variation coefficient values fall in a high variation (over 20%);

- The analysis of total and average productions, frame annual variation levels that tend to increase in comparison to 2007. The values fluctuations analyzed according to the variation coefficient highlight also a great variation (over 20%), indicating that the values that express this variation are much higher than those of the areas.

b. The tobacco processing enterprises and their results in the activity.

Understanding the main characteristics of the tobacco market in Romania throughout the chain defines the following segments [5] : a) first segment is represented in by the tobacco producers. They are not allowed to make processing

and production, but to cultivate and harvested tobacco for the market intermediaries; *b*) the intermediaries that interpose between growers and manufacturers of cigarettes, they are being called also as first processors (which is the second segment of market), which are responsible for the preparation of tobacco production: *c*) companies that produce cigarettes through specific technologies (which is the third segment) and for which the processing and cultivation of tobacco is prohibited [2].

Mainly, for the tobacco processing sector the question is of knowledge both the number of firms that produce tobacco, and especially their results. In *Table 3* for the period 2007-2011 are given the turnover and the number of enterprises, significantly based on the following:

Table 3 - Number of enterprises and their turnover technology tobacco products in Romania

Specification	UM	2007	2008	2009	2010	2011	Average /rhythm	Standard deviation	Variation Coefficient (%)
Number of enterprises	Number	18	16	15	13	9	11.8	6.6	55.4
	Compared to the previous year								
	%		0.89	0.94	0.87	0.69	-100.00	x	x
Total turnover	thousand lei Total	3,395	4,136	2,390	2,166	2,314	2,880.2	853.4	29.6
	Compared to the previous year								
	%		1.22	0.58	0.91	1.07	-9.14	x	x
The average turnover per firm	Thousand lei / enterprise	188.6	258.5	159.3	166.6	257.1	x	x	x
	Compared to the previous year	x	137.06	61.62	104.58	154.32	x	x	x
	%	100	137.06	84.46	88.33	136.32	x	x	x

Source: SMEs in the Romanian economy, INS, Romania, 2010-2013[9]

- Regarding the number we can observe a significant decrease (the existence of a number of 18 in 2007, in 2011 there are only 9). Comparisons with the previous year, especially compared to 2007, are inferior. Annual oscillation based on these annual reductions determined by the coefficient of variation (over 20%), being at the 55.4% level;

- The turnover still plays on its total an annual decrease, but whose rate is

much lower than the decrease in the number of enterprises. The coefficient of variation on the same indicator falls into the great scale (over 20%), which is below the level that expresses the number of enterprises;

- But on the average of the enterprises turnover there is an increasing trend for both comparison base – to the previous year and to year 2007. It can be mentioned the situation of the reduction of the turnover total in 2009 that influenced the indicators levels in the coming years.

Synthetically, it can be signalized the quantitative aspect linked to the enterprises number decrease (in the last year of analysis is half compared to the first year), together with the qualitative aspect of the level of turnover which is witnessing a decline in total (but in a slower rhythm), along with an increase in the average turnover per enterprise.

c. The tobacco processing enterprises and their results in the activity.

The employment and the earnings from tobacco products in Romania, analyzed in the period 2007-2012, is a continuation of the overall analysis. Regarding this problem, the data shown in Table 4 highlights the indicators level in absolute and relative data, the following aspects:

Table 4. The employees and the earnings from tobacco production in Romania

Specification	UM	2007	2008	2009	2010	2011	2012	Average/ rhythm	Standard deviation	Coefficient of variation (%)
Actual employees	Number	1,818	1,648	1,616	1,514	1,568	1,632.8	115.2	7.1
	Compared to the previous year		0.91	0.98	0.94	1.04		-3.63	x	x
	% Compared to 2007	100	90.64	88.88	83.27	86.24	-	x	x	x
Average no. of employees	Number	1,818	1,618	1,591	1,520	1,458	1,601.0	136.5	8.5
	Compared to the previous year		0.89	0.98	0.96	0.96		-5.37	x	x
	% Compared to 2007	100	88.99	87.51	83.60	80.19	-	x	x	x
Monthly average net nominal earnings (total economy)	lei per month	1,042	1,309	1,361	1,391	1,470	1,541	1,352.3	172.7	12.8
	previous year		1.26	1.04	1.02	1.06	1.05	8.14	x	x
	% Compared to 2007	100	125.62	130.61	133.49	141.07	147.88	x	x	x
of which: in tobacco production	lei per month	2,136	2,623	2,852	3,224	3,581	3,721	3,022.8	602.5	19.9
	% Compared to the national economy	204.99	200.38	209.55	231.77	243.60	241.46			

Compared to the previous year		1.23	1.09	1.13	1.11	1.04	11.74	x	X
% Compared to 2007	100	122.79	133.52	150.93	167.65	174.20	x	x	x

Source: Statistical Yearbook of Romania, INS, 2013 SMEs in the Romanian economy, INS, Romania, 2010-2013 [9]

- The number of employees and its average number are in an annual decrease, which is marked both by comparison to the previous year, but also compared to 2007. Since the decreases oscillations in the annual variation are low and the variation expressed by the coefficient of variation falls within a low variation (less than 10%), the values were of 7.1% and 8.5%;

- The earnings from the tobacco products, expressed in lei / month, play an increase in the annual dynamics. This increase is significant in comparison to the national level as well as to previous year and to comparison with the base year 2007. The upward trend analyzed through the expression from the calculation of the coefficient of variation of 19.9% , fall into a middle variation (between 10-20%).

It follows that even if the workforce used for tobacco products has an annual trend of decrease, the net nominal earnings per month recorded significant annual increases.

d. Consumption, foreign trade and tobacco subsidies in Romania

The foreign trade policy is a form of the relations that can be evidenced by import and export. It may be mentioned that Romania consumes approx. 40,000 tons of tobacco per year and produce up to 2,000 tons, which means that all Romanian tobacco cope the market competitiveness [5] .

The tobacco consumption in Romania, (restored in 2004) is appreciated by a national level of tobacco consumers at 62.1%, which can be evidenced by the structural situation, on the following criteria [7] :

- On gender, representation is: male 75.4% , female 48.7%;
- The age group (years), which can play the following structure: 15-24 → 61.8%, 25-34→ 70.5%, 35-44 → 65.0%, 45-54 → 62.7 % , 55-64→ 44.2%;
- The educational level: primary studies 33.3%, 45.4% for incomplete secondary studies, secondary studies 65.8% and 76.0% for higher studies;
- The socio-economic level is given by: low income 58.5%, average income 67.6%, and high income 82.0%;
- The residence: rural 53.9%, small urban 67.5%, high urban 68.5%;

- The territorial form can be presented by region as follows: 62.9% Moldova, Muntenia 54.6%, 54.9% Oltenia, Dobrogea 53.6%, 68.2% Transylvania, Banat-Crişana-Maramureş 63.8%, Bucharest 73.0%.

However an analysis at the national level for the external trade for the tobacco products rise the question of imports and exports of raw and processed tobacco. In *Table 5* is shown the situation for 2007-2012, which finally summarize the foreign trade balance for this product. You can find the following:

- The Export of raw and processed tobacco. The dynamics of 2007-2012, recorded a growth trend, analyzed in terms of value (expressed in thousand euros) and compared (in%) from the previous year and from the year 2007. Analyzing the oscillations of annual rates we found very high variations, the significance of the coefficient of variation was of 36.5%, which signifies a high variation (over 20%);

Table 5. Comet outside for tobacco products in Romania

Specification	UM	2007	2008	2009	2010	2011	2012	Average / rhythm	Standard deviation	Variation Coefficient (%)
Export (raw and processed tobacco)	million euros	139	265	368	386	460	474	348.7	127.1	36.5
	% to previous year		1.91	1.39	1.05	1.19	1.03	27.81	x	x
	% Compared to 2007	100	190.6	264.74	277.69	330.93	341.00	x	x	x
Import (raw and processed tobacco)	million euros	156	176	190	157	229	260	194.7	41.8	21.5
	% to previous year		1.13	1.08	0.83	1.46	1.14	10.76	x	x
	% Compared to 2007	100	112.8	121.7	100.6	146.7	166.6	x	x	x
Foreign Trade Balance	million euros	-17	91	179	230	241	217	156.8	101.1	64.5
	% to previous year		-5.35	1.97	1.28	1.05	0.90	-266.4	x	x
	% Compared to 2007	100	-535.2	1052.9	1352.9	1417.6	1276.4	x	x	x

Source: SMEs in the Romanian economy, INS, Romania, 2010-2013 [9]

-The import is represented also by increases rendered as value and percentage, but it is recorded a lower level of the annual fluctuations. The coefficient of variation is of 21.5%, which falls into a high variation representation (over 20%);

- The foreign trade balance with raw and processed tobacco, is positive for

the period 2008-2012.

It may be mentioned that at this favorable trend we have significant oscillations that are played by a very high value of the coefficient of variation (64.5%).

The common market organizations, as organizational forms (attributional-functional) are considered as a tool of the OCP, that the structure of the main food includes direct aid to tobacco, covering about 10% of Community agricultural production.

For Romania, the subsidies development in recent years (2007-2013) for the tobacco crop, shown in *Table 5*, highlights the rhythms of these subsidies, which in particular it may be mentioned the following:

Table 5. The tobacco subsidies evolution in Romania (the national budget funding source PNDC)

The subsidy type	UM	2007	2008	2011	2012	2013	Average / rhythm	Standard deviation (million euro)	Coef. Var.(%)
Total subsidies	thousand euros	1,710	3,917	1,719	1,312	2,589	1,279	49.4
	% to the previous year	-	2.29	69	76	-5.15	x	x
	% Compared to 2007	100	229.06	100.52	76.72	-			
Subsidies per hectare (PNDC 4)	euro / ha	2,000.0	2,000.0	1,167.6	1,200.0	1,300.0	1,760	554	31.49
	% to the previous year	-	<i>One</i>	<i>0.44</i>	<i>1.03</i>	<i>One</i>	-6.93	x	x
	% Compared to 2007	100	100	58.38	60	65			

Source: APIA data [8]

- For total subsidies for the tobacco crop we can see an annual variation rhythm at which the average for the period is of 2,589 million Euro. The oscillations by calculating the coefficient of variation falls within the high variation (over 20%), which is given by the level of 49.4%;

- The analysis of the subsidies per hectare for the period under review reflects a decrease in the annual oscillations within the coefficient of variation at the level of 31.49% (which is a high variation represented by the values above 20%).

So in case of payment by the FEADR and the national budget and for tobacco culture there were increases in funds allocated and annual variations noting that the variation coefficient values are assigned to the large group. Note that after the EU accession of Romania, the restructuring process and the alignment with the other countries agriculture progressed slowly, without visible consequences in

terms of structural and functional compatibility of the tobacco chain.

The insufficient adaptation of the policies to this branch, was due to reduced capacity for the absorption of both policies, viewed in terms of increasing structural and functional compatibility and also in financial terms (absorption of funds for rural development). To all, it can be added the adaptability form still inadequate of the Romanian supply of tobacco products on the European market.

Conclusions

The study carried out by an interdisciplinary approach highlights existing events and limits regarding the activities of the tobacco market in Romania being evidenced the commercial purpose, adapting the production possibilities to the consumers' needs or desires. These can be rendered synthetic by socio-economic conclusions.

(1). In Romania there is an annual consumption of tobacco products by approx. 40,000 tons annually, and this consumption level, according to a presumptive presentations can be played by a structure of the form: predominance of men (75.4%), the age groups 25-34 (70.5%), the people with higher education (76.0%), those with a high average level of education (82.0%) , for people in the residence which is in higher urban areas (68.5%), the territorial predominance is for Bucharest Region (73.0%).

(2). The results focused on the tobacco chain policy (production → processing → consumption) within the areas and yields tobacco crop structural form, which for Romania we found an annual oscillating level for surfaces and productions. The grants for the tobacco culture record an annual decrease, with an annual variation rhythm, the rate oscillations signifies a great variation.

(3). Regarding the number of the processing enterprise, it can be seen a sharp drop of their number, tendency manifested also on turnover. For this indicator the coefficient of variation falls at a high level of variation, along with an increase in turnover on the enterprise.

(4). The number of employment and the average number of the employees are in an annual decrease, but the earnings for the manufacture of tobacco products, play an increase. It is signaled the existence of oscillations, a trend emerged from the calculation of the coefficient of variation falling into a middle variation (10-20%).

(5). The foreign trade as value and percentage for raw tobacco and processed plays the following aspects: the export register a growth trend, manifesting fluctuations of annual levels for which the significance of the variation coefficient is high ; the import is represented by increases, but the annual oscillations rhythms are recorded at a low level , employing a large variation

representation; the foreign trade balance is positive manifesting a favorable trend, and also the existence of significant oscillations that are played by very high value of the coefficient of variation.

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REVIEW REGARDING THE CONTENTS IN POLYPHENOLS AND THE NUTRITIONAL VALUE OF PLANTS FROM ROMANIA'S SPONTANEOUS FLORA

Dan SCHIOPU¹, Stefan BLANCIOTI²

Abstract.

After polyphenols are defined, the benefits they bring to the body are presented and a few examples of polyphenols are given, polyphenol food sources are listed. It is subsequently mentioned that synthetic polyphenols are used in the food industry as additives with antioxidant properties. Because it was found that they negatively affect health efforts are made to replace them with polyphenols extracted from plants. They can be found in every flower making plant, being spread in all vegetative organs but also in flowers and fruits. Furthermore, research outcomes regarding the contents in antioxidants are presented, as well as the nutritive value of certain plants from our country and examples are given of plants from the spontaneous flora the colours of which indicate high contents of anthocyanin in flowers and fruits and flavonoids in flowers.

Keywords: meat industry, myoglobin, natural preservatives, polyphenols, scavenging activity

1. Introduction

Polyphenols are substances characterised by the presence of various classes of phenols, associated to different structures more or less elaborated. Chemically speaking, they are found under the shape of hydrogen, carbon or several groups of hydroxyl atom cyclic structures. Examples could include quercitrine, resveratrol, coumarines, and tannins. (Fig. 1)

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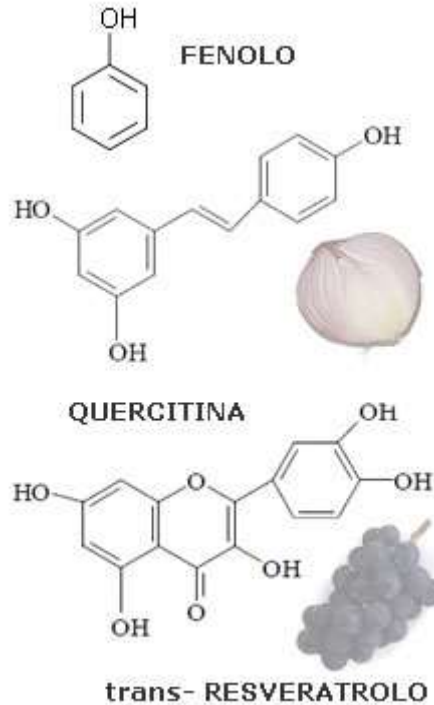


Fig.1. Examples of polyphenols.

[(37) <http://www.my-personaltrainer.it/integratori/polifenoli.html>]

Advantages for the body

- Helps in therapies aiming the prevention of tumour formations;
- Succeed in preventing hepatic pathologies;
- Protect the bodies against cardiovascular diseases;
- Successfully prevent inflammatory processes;
- Actively participate to the stimulation of the immunity system;
- Contribute to the acceleration of hair growth.

Polyphenols are known for their antioxidant, anti-inflammatory, anti-bacterial, anti-tumour and anti-atherogenic action (limiting the fat deposition on the blood vessel walls). [36] Simple phenols belong to phenolic acids, for ex.: coumarines and benzoic acids. Their condensation can result in polymers such as lignin.

Tannins include condensed tannins (also known as proanthocyanidins, because by hydrolysis with strong acids they result in anthocyanidine) and hydrolysable tannins. There are heterogeneous polymers which contain phenolic acids (for ex. Gallic acid) and simple sugars.

Flavonoids (in Greek "flavus"= yellow): represent the largest group of natural phenols and they all have as reference structure 2 phenyl-benzo[a]pyrene, a flavanol. Structural variations from the hexane ring allow the subdivision of flavonoids in various families: flavanols, flavones, isoflavones, anthocyanins etc.

Of natural flavones we mention: *Luteolin* 5,7,3',4'-tetrahydroxyflavone, is found in wild Reseda (*Reseda lutea*). *Apigenine* 5,7, 4'-trihydroxyflavone is found in chamomile (*Matricaria chamomilla*). (15).

Quercetine, 3,5,7,3',4'-pentahydroxyflavone, a flavanol-derivative, is found, among others, in hop (*Humulus lupulus*) but also in some species of oak (*Quercus* sp.) [3].

From *Quercus robur* wood *vescalagin* was isolated, an ellagitannin.

From nutshells *juglanin* was isolated, from chestnut wood (*Castanea vesca* Gaertn. sin. *C. vulgaris* Lam. sin. *C. sativa* Gard.) Another ellagitannin was extracted, called *castalagin*. Rich in condensed tannins are also the bark and wood of pine spruce (*Picea excelsa* Lam.), birch (*Betula* type), willow (*Salix fragilis* L.), acacia (*Robinnia pseudoacacia* L.) [(4) p. 1187].-1193). -(n.n. Acacia is cultivated but it also spontaneously multiplied).

Rich in tannin is also the alder (common alder) tree bark (*Alnus glutinosa* Gaertn.).

Rutina, 3-rhamnno-glycoside of quercetin, is found in buckwheat (*Fagopyrum esculentum*) (n.n. we conclude that also in wild buckwheat – *Fagopyrum sagittatum*) and rue (*Ruta graveolens*)

Morin, 3,5,7,2',4'-pentahydroxyflavone, isomer with quercetin, isolated from "yellow wood" (*Morus tinctoria*) [15].

- *Arnica* type includes approximately 18 species spread in Europe, Asia, America de Nord. *Arnica montana*.L. (*Arnica*) which can be found in our country contains Gallic acid, tanning matters. [28 p.504]

Food sources of polyphenols. There are 3 classes of polyphenols: the flavonoids, tannins and phenolic acids. In a regular diet, polyphenols represent most of the antioxidants, especially in fruits and green goods. They are abundantly present in:

- Fruits, especially the ones with red-violet pigmentation, considered as the most popular source of flavonoids and tannins: berries, plums and cherries, but also melons apples, grapes and pears;

- vegetables, beetroot, eggplants, onion, celery, parsley, cabbage, broccoli, peas, beans (important sources of flavonoids);
- whole grains: oats, rye (both of them sources of phenolic acids), soya (rich in flavonoids);
- aromatic plants: oregano, rosemary, salvia, sesame;
- dry fruits: almonds, peanuts, nuts, ground nuts;
- red wine, rich in tannin and flavonoids, especially in resveratrol;
- coffee and chocolate, with a high concentration of phenolic acids;
- green tea and olive oil; [37]

The company Adams Vision from the USA [38] trades a food supplement containing trans-resveratrol, extracted from *Polygonum cuspidatum*.

The European Food Safety Authority (EFSA) reassessed the synthetic antioxidants BHA (E 320) and BHT (E 321) used as additives in food industry and found that, despite the doses used are believed as safe, sometimes they can have negative effects upon people's health: aggravate symptoms of patients suffering from chronic rash, they are cytotoxic and genotoxic, induce apoptosis, have an estrogenic effect, increase the risk for stomach cancer, etc.[33, 34 cited by17]. Plant-extracted polyphenols, especially flavonoids, because of their antioxidant activity, can be efficient replacers of synthetic antioxidants and, in addition, they exert beneficial effects on consumer's health. Despite the fact that they raise the price of food and hinder their characterisation, plant-extracted polyphenols give more value to foods, keep blood vessels healthy and the immunity system as well, and have antibacterial and antifungal properties [35 cited by 17].

Polyphenols represent a group of substances spread in every flower-making plant, being distributed in each vegetative organ, but also in flowers and fruits. They are considered as secondary metabolites involved in the chemical defense systems plants have against pests, as well as in the performance of plant-to-plant interference. From the structural point of view, polyphenols contain at least one aromatic nucleus and one or several hydroxyl groups, engrafted on aromatic nuclei together with other substituents. The studies carried out proved that polyphenols exert important biological properties, having antioxidant, anti-cancerigenous, anti-inflammatory, antibacterial and antiatherogenic effects (limiting the fat deposition on the blood vessel walls).

In the famous magazine European Journal of Clinical Nutrition, Perez Jimenez and col. (2010) published the list of the 100 richest foods in polyphenols. This list includes: clove, mint, star anise, cocoa powder, oregano, beet seeds, sage, rosemary, black olives, capers, green olives, basil, gooseberries, strawberries, ginger, black grapes, red onion, mere, spinach, green tea, broccoli, asparagus,

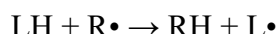
nectarines, anchovies, salad, carrots etc.

Nationally and internationally performed studies proved that medicine plants are also highly rich in polyphenols with a remarkable antioxidant activity. Thus, harvest mite fruits have high contents of phenolic acids, proanthocyanidins and catechins [1 cited by 17], hips contain phenolic acids and flavonoids [18 cited by 17], and sea-buckthorn fruits contain flavonoids [9 cited by 17].

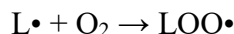
Thanks to the remarkable antioxidant activity and to beneficial effects polyphenols exert on the human body, researchers are interested in the extraction of polyphenols from plants and subproducts of food industry for the purpose of using them as preservatives in the food industry.

In meat there are three major oxidative processes affecting the taste, smell and colour of the means and food products obtained from meat, namely the oxidation of membrane lipids, oxidation of proteins and oxidation of the conjugated protein - myoglobin. The oxidation of lipids from meat, also known as lipid peroxidation, is an undesired chemical process because the resulted peroxides decompose and form toxic carbonic compounds with an unpleasant smell (they give to the meat the characteristic smell of rankness). Moreover, lipid oxidation can also initiate other unwanted chemical processes such as myoglobin and protein oxidation of, affecting the quality of the meat and meat products. Myoglobin oxidation (red-coloured pigment) with met myoglobin (brown-coloured pigment) is responsible for the change of the colour of the meat and the protein oxidation is responsible for various biochemical changes, protein fragmentation or aggregation and the decrease of their solvability [14].

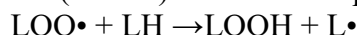
Lipid oxidation. Lipids' stability to oxidation depends on the balance existing between anti- and pro-oxidants, including on the concentration of polyunsaturated fatty acids. In the cell membranes meat has high contents of polyunsaturated fatty acids likely to oxidation chain reactions, hard to control, initiated by free radicals. The initiation of oxidation takes place by pulling out a hydrogen atom from a methylene grouping of the lipid molecule (LH), under the action of a free radical (R•):



The number of lipid radicals (L•) increases with the number of bis-allylic carbon atoms, namely with the degree of fatty unsaturation. The polyunsaturated radical L• undertakes an intermolecular electronic rearrangement forming a conjugated diene, capable of reacting with molecular oxygen and forming the peroxy radical (LOO•):



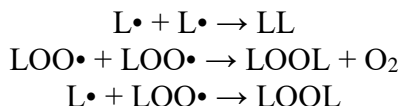
In the propagation phase, LOO• pulls out a hydrogen atom from another lipid molecule and forms a peroxide (LOOH) and another lipid radical L•:



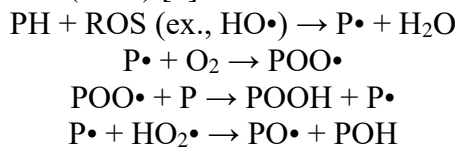
Resulted lipid peroxides are considered primary products of lipid peroxidation

because at high temperatures or in the presence of transitional metal ions they decompose in secondary volatile or non-volatile products such as carbonyl compounds, alcohols, alkanes, furans which determine the change in smell and taste of foods products.

The reaction chain is concluded with the union of two radicals existing in the reaction environment:



Protein oxidation occurs, just as lipid oxidation, by a chain radical mechanism, but much more complex if taken into consideration the large number of oxidation products formed. Pulling out a hydrogen atom by a reactive oxygen species (ROS) from a protein (PH) generates a carbon-centred protein radical (P•) consecutively converted into peroxy radical (POO•), in the presence of oxygen and in alkyl peroxide (POOH), by pulling out a hydrogen atom from another molecule. Further reactions with the hydroperoxy radical (HO₂•) generate an alkoxy radical (PO•) and its hydroxyl derivatives (POH) [7]:

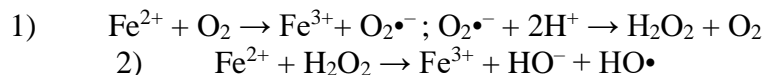


Myofibril proteins are likely to oxidate, the most sensitive of all being the myozine, followed by troponin T. Of amino acids, cysteine, tyrosine, phenylalanine, tryptophan, histidine, proline, arginine, methionine and lysine were characterised as being sensitive to free radical attack.

The nature of the resulted reaction products depends on the primary structure of polypeptide catenary. Radicals coming from arginine, lysine and proline are oxidated at carbonilic radicals and the ones coming from cysteine and methionine take part to the formation of crossed covalent connections or to the formation of sulphur derivatives.

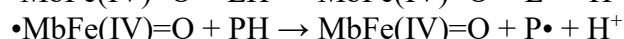
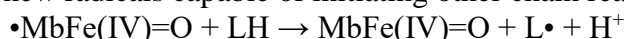
In conclusion, the most significant chemical changes occurring with muscular proteins because of oxidation are: *The formation of protein carbonyl, loss of thiol functional groupings and crossed tying of proteins.*

Myoglobin oxidation. Oxidation of feros-oxymyoglobin (Fe²⁺) to feric-metmyoglobin (Fe³⁺) is responsible for the discoloration of meat while stored. The oxidation of the ion Fe²⁺ from the oxymyoglobin occurs as a consequence of two reactions:



Not only myoglobin oxidation affects the colour of the meat but also the stability

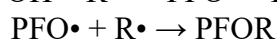
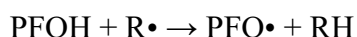
of lipids and proteins from meat, metmyoglobin being pro-oxidant in these two processes. When antioxidant enzymes (reducers) from muscles are exhausted as a result of sacrifice, metmyoglobin accumulated in the meat will react with the hydrogen peroxide and will form the species of myoglobin hypervalente perpherilmyoglobin ($\bullet\text{MbFe(IV)=O}$) and ferrimyoglobin (MbFe(IV)=O). In order for the radical $\bullet\text{MbFe(IV)=O}$, which is extremely reactive, to stabilize it will pull out a hydrogen atom from another lipid or protein molecule and it will determine the formation of new radicals capable of initiating other chain reactions:



Recent studies proved that ferrimyoglobin can also initiate the protein oxidation reaction, for ex., myosin oxidation ([Baron and Andersen, 2002]).

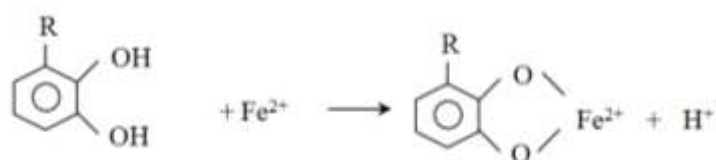
The protective effect of polyphenols over lipids and proteins is mediated by the following mechanisms: 1) polyphenols remove the species of oxygen and nitrogen free radicals; 2) polyphenols inhibit the formation of oxygen and nitrogen free radicals with the inhibition of certain enzymes and the chelating of ions corresponding to traditional metals involved in the production of free radicals; 3) polyphenols regulate or protect antioxidant defense [5].

- 4) Polyphenols (PFOH) work as hydrogen donors, being capable of annihilating free radicals ($\text{R}\bullet$) and interrupt the reaction chain. The resulted phenoxyl radicals ($\text{PFO}\bullet$) have low reactivity and cannot initiate another reaction chain. In some cases, phenoxyl radicals can combine with other radicals they interfere with, working as terminators of the reaction chain:



The capacity of polyphenols to annihilate free radicals depends on the number of hydroxyl grouping (phenolic acids) and the structure if the polycyclic system (flavonoids).

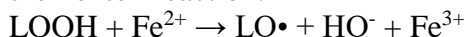
- 5) Polyphenols which have in their structure two neighbouring hydroxyl groupings (for ex., gallates and catecholates) can form with ions Fe^{2+} , Cu^{2+} or Cu^+ inactive complexes:



Chelating ions Fe^{2+} , Cu^{2+} and Cu^+ is highly important as these ions generate free radicals in the Fenton reaction:



Davies and Slater (1987) believe that the ion Fe^{2+} has the ability to decompose lipid peroxides (LOOH) according to a mechanism similar to the decomposition of oxygenated water in the Fenton reaction:



Radical $\text{LO}\cdot$ has the ability to extract hydrogen from another fatty acid or LOOH molecule, generating other chain reactions. The $\text{LO}\cdot$ radical's ability to extract hydrogen atoms from the mentioned molecules was proved based on the reduction potential of $\text{LO}\cdot$ (+1,6 V) and based on the Gibbs (ΔG°) free energy exchanges in hydrogen's reaction with the bis-allyl carbon of propene (-23kcal/mole) and LOOH (-14 kcal/mole).

To the meat industry, polyphenols' property of chelating the Fe^{2+} ions is very important because meat can be easily contaminated with these ions from knives and metal pots. This contamination accelerates oxidative processes both regarding lipids and proteins. In conclusion, adding plant-extract polyphenols in the products obtained from meat inhibit lipid and protein oxidation because of their ability to annihilate free radicals and chelating transitional metal ions. The antioxidant activity of polyphenols is explained by their capacity to inhibit certain enzymes directly involved in the oxidative processes (lipooxygenases, cyclooxygenases, myeloperoxidases, NADPH oxidases, xantinoxidases), generating reactive oxygen species, and even organic peroxides (8), as well as the activity of certain enzymes indirectly involved in the oxidative processes (for ex., phospholipases A₂) [11].

- 6) Polyphenols stimulate the activity of antioxidant enzymes superoxid dismutase (SOD) and catalases (CAT) [32].

2. Material and method

In works [12] and [13] the method and materials used are broadly described and, as such, they will only be mentioned again very briefly when needed, so as not to affect the cursive understanding of the text. Work [10] was not published. In order to identify plants from our country's spontaneous flora which contain polyphenols, in what quantities and conditions, Israel-Roming Florentina et al. [10, 2014] carried out certain determinations in the laboratory, on ramsin (*Allium ursinum* L.), celandine (*Ficaria verna* Huds. sin. *Ranunculus Ficaria* L.) and dandelion plants (*Taraxacum officinale* Weber.), which were picked before blooming, mid-March, from two different places: Băneasa forest and Tulcea forest. As a reference plant greenhouse-cultivated salad was used (*Lactuca sativa*), purchased from a market in Bucharest.

Table 1 lists information on the analysed samples.

Table 1

Information on the analysed samples
(ISRAEL -ROMING Florentina ș.a., 2014)

Sample	Sample code	Origin	Cropping period	Development stage when cropped	Used part
Ramsin	LT	Tulcea forest	14.03.2014	before blooming	young leaves
Ramsin	LB	Băneasa forest	13.03.2014	before blooming	young leaves
Celandine	UT	Tulcea forest	13.03.2014	before blooming	young leaves
Celandine	UB	Băneasa forest	14.03.2014	before blooming	young leaves
Dandelion	PT	Tulcea forest	20.03.2014	before blooming	young leaves
Dandelion	PT	Băneasa forest	20.03.2014	before blooming	young leaves
Salad	S	Bucharest Market (greenhouse)	20.03.2014	maturity	leaves

Table 2 shows the outcomes of the analyses carried out on the plants mentioned in the previous table regarding the polyphenol contents and Table 3 - the contents in ascorbic acid.

Table 2
Overall polyphenol contents
(ISRAEL -ROMING Florentina and collaborators, [10])

Sample	mg GAE/g su.*	mg GAE/g su.
LT	2,41	22,12
LB	2,12	19,57
UT	2,34	19,61
UB	2,80	21,78
PT	1,14	8,58
PT	0,94	7,00
S	0,41	6,55

- su = stove dried substance at 105° C
- GAE = Gallic acid equivalent.

Table 3 Ascorbic acid contents
(ISRAEL -ROMING Florentina and collaborators, [10])

Sample	mg/g sp	mg/gsu
LT	0,66	6,06
LB	0,80	7,41
UT	0,76	6,36
UB	0,90	7,06
PT	0,23	1,76
PT	0,13	0,98
S	0,04	0,69

It can be noticed the high nutritive value of plants in the spontaneous flora by their antioxidant content.

A comparative study on the antioxidant content in some bacca fruit from six species - raspberries (*Rubus idaeus* L.), blackberries (*Rubus fruticosus* L.), strawberries (*Fragaria ananassa*), field ash (*Aronia melanocarpa*), blackcurrants (*Ribes nigrum* L.), sea-buckthorn (*Hippophaë Rhamnoides* L.) was carried out by Luță Gabriela and collaborators [12]. The overall polyphenol content is showed in table 4.

Table 4. Overall polyphenol content of some bacca fruit (Gabriela LUȚĂ and collaborators [12])

Species	Overall polyphenol content – GAE mg/100g	Standard deviation	Relative standard deviation %
Field ash	7791,6	695,5	8,93
Raspberries	1728,6	75,3	4,36
Blackberries	3340,2	134,2	4,02
Strawberries	4501,1	207,6	4,61
Blackcurrants	6339,1	312,8	4,93
Sea buckthorn	2890,6	119,6	4,14

Regarding the anthocyanin level, the highest content was found in blackcurrants and the lowest - in strawberries (table 5). After the Chernobîl accident, Bulgaria exported in Ukraine blackcurrant juice.

Table 5 Anthocyanin content of some bacca fruit Gabriela LUȚĂ and collaborators [12]

Species	Anthocyanin cianidine-3 Glucosidal equivalent	Standard deviation	Relative standard deviation %
Field ash	386,,2	7,4	1,92
Raspberries	109,0	12,0	11,01
Blackberries	266,9	21,3	7,98
Strawberries	91,3	3,4	3,72
Blackcurrants	520,0	14,1	2,71

These analyses do not include sea-buckthorn because the colour of sea-buckthorn leaves is yellow. The standard deviation has values which may vary up to three times, probably because frozen fruit were analysed.

The overall flavonoid content was high in each sample taken (table 6)

Table 6. The overall flavonoid content of some bacca fruit
(Gabriela LUȚĂ and collaborators [12])

Species	The overall flavonoid content quercetin equivalent–mg/100g	Standard deviation	Relative standard deviation %
Field ash	1793,3	23,2	1,29
Raspberries	536,6	25,7	4,79
Blackberries	591,2	11,0	1,86
Strawberries	662,8	31,7	4,78
Blackcurrants	1288,4	58,3	4,52
Sea buckthorn	1379,9	45,1	3,27

The highest flavonoid content was found with the field ash. A comparative analysis reveal field ash and sea-buckthorn as the richest sources of phenolic antioxidants for the bacca fruit studied.

The authors conclude that, by the high content of phenolic compounds found, the analysed bacca fruit are an excellent source of natural antioxidants with a beneficial medical potential.

According to some authors, the overall phenol content in sea-buckthorn depends on the cropping and varies between 828,7-1099,6 mg/100g [16, 31].

Gabriela Luță and collaborators [13] also made estimations regarding the overall antioxidant content (phenols and ascorbic acid) and their scavenging activity (antioxidant activity), from raspberry (*Rubus idaeus* L.), strawberry (*Fragaria ananassa*) and sea-buckthorn (*Hippophaë Rhamnoides* L.) samples coming from the market. The determinations were made by using fresh fruit. The results are showed in image 2. It highlights the fact that sea-buckthorn fruit are the richest in polyphenols and ascorbic acid and have the most intense scavenging activity, and raspberry fruit have the lowest scavenging capacity, requiring the highest concentration in antioxidants of the sample (512,76 µg/ml, respectively 727,63µg/ml) in order to remove 50% of the free radical DPPH.

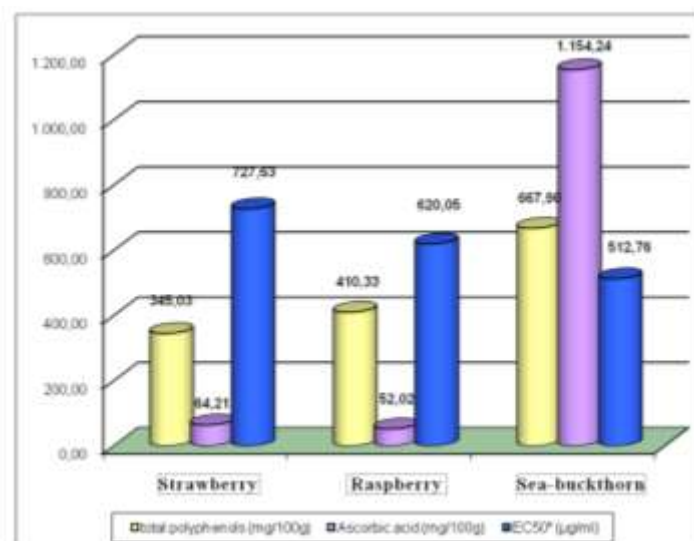


Fig. 2. The antioxidant content and scavenging activity from the analysed fruit (LUȚĂ Gabriela and collaborators [13]).

* Free radical scavenging activity (overall antioxidant capacity) was determined (expressed) by using the stable free radical diphenylpicrylhydrazyl (DPPH). EC₅₀ is the sample's concentration in antioxidants, necessary so as to remove 50% of the free radical DPPH.

Furthermore, examples are given of plants from our country's spontaneous flora the colours of which indicate high content of anthocyanin in flowers and fruit and flavonoids in flowers (some were previously mentioned).

Anthocyanin containing plants (with pink, red, purple, blue coloured flowers)

- Genus *Corydalis* Vent. (stagger weed) [22 p. 84-95]: *C. solida* L.- violet-red flowers.
- Genus *Arctium* L. [28 p. 622-631] includes 5 species spread in Europe and Asia. They have red flowers, thus they contain anthocyanin. Ex. *A. tomentosum*. (burdock).
- Genus *Agrostemma* L. [21 p. 123-127] *A. Githago* L. (corn cockle)
- Genus *Ajuga* L. (bugleweed) [27 p. 86-97] : *A. genevesis* L..
- Genus *Melandrium* Röhl. [21 p. 186- 198]: *M. Rubrum* (Weig.) red campion.
- Genus *Dianthus* L. (carnation, dianthus). In [21 p. 217-290] 42 species and various hybrids are described: *D. Armeria* L. – red corolla; *D. trifasciculatus* Kit. – red petals;
- Genus *Carduus* L. [28 p. 631-672] includes over 120 species, of which in *Flora* 17 species are described.

Species from genus *Carduus* contain anthocyanin (mauve, pink, red, purple coloured leaves).

C. nutans L. (sin. *C. ortocephalus* Schur.) (thistle). Red flowers.

- Genus *Cirsium* Adans. [28 p. 672-743] includes approximately 120 species (after another 200 species) and various hybrids.

Most of the species in genus *Cirsium* contain anthocyanin (pink, purple coloured leaves).

In [28] 31 species are described. We will list the first 9.

- *C. arvense* L. (bull thistle). Light red and violet flowers

- *C. lanceolatum* L. (Saint Mary's thistle, burr). Red flowers

- *C. furiens* Gris et Sch. (sin. *C. transsilvanicum* Schur Enum., sin. *C. ferox* Baumg., *C. ciliatum* Auct., etc.) Saint Mary's thistle – light red or white-pink flowers.

- *C. albidum* Velen. (sin. *C. Albidum* ssp. *poycroum* Petrak) red flowers.

- *C. bulgaricum* DC. (sin. *C. odontolepis* Boiss.) – red flowers.

- *C. sintenisii* Freyn. (sin. *C. Boissieri* Freyn et Bornm. Sin. *C. Sintenisii* ssp. *galaticum* Freyn l.c.) – pink flowers.

- *C. ciliatum* (Murr) - red flowers.

- *C. serulatum* M.B. (sin. *Cnicus serrulatus* M.B.) – red flowers.

- *C. eriophorum* (L.) (sin. *Cnicus eriophorus* Baumg) – red purple flowers.

- Genus *Onopordon* L. [28 p.748-751] includes 30 species.. red flowers.

- *Onopordon acanthium* L.(sin. *Cousinia bulgarica* Koch.) (thistle, big butcher's broom).

- Genus *Papaver* L. [22 p. 64-83]: *P. Rhoas* L. (corn poppy), *P. dubium* L. (wild poppy).

- Genus *Centaurea* L. (buggieweed, knotweed, cornflower) includes over 400 species). In Flora RPR [28 p. 785-951] 69 species and various hybrids are described. Most of the species have flowers with anthocyanin (blue, black-purple, red, pink or sometimes white). However there are species with yellow flowers.

- *C. cyanus* L. (sin. *Cyanus segetum* Baumg.) (bluebottle, buggieweed). Disk flowers mauve, the marginal radiant ones are blue, rarely white or pink.

- Genus *Vicia* L. [24 p. 349-402] (vetch) includes approximately 150 species. *V. villosa* Roth., *V. cracca* L., *V. sativa* L.

- *C. orientalis* L. (sin. *Cyanus orientalis* Baumg.). Yellowish flowers.

- Genus *Medicago* L. (lucerne) [24 p. 118-136]. Blue-violet flower species are *M. sativa* L. (lucerne) and *M. varia* Martyn.

- Genus *Rhododendron* L. (rhododendron) [26 p. 121-122] *R. kotschyi* Simk.

- Genus *Trifolium* L. (clover). [24 p. 145-220].. *T. pratense* L. (red clover).

- Genus *Viola* L. [22 p. 553- 625] includes approximately 500 species spread all over the globe. Ex. *V. ambigua* W. Et K. (sin. *V. campestre* M.B.) dark violet petals.

- *V. tricolor* L. (pansy) – usually has dark violet flowers, rarely light violet, yellow or violet-blue.

Genera and species the fruit of which contain anthocyanin

- Genus *Berberis* L. [22 p. 28-32]: *B. vulgaris* L. (barberry) vermillion fruit.
- Genus *Fragaria* L. (strawberries, wild strawberries) [23 p. 580-595].. Ex. *F. vesca* L. (forest wild strawberries). Red-carmine receptacle flowers.
- Genus *Phytolacca* L. [20 p. 607-612] includes an overall number of 26 species of which in our country only 2 can be found: *P. esculenta* Van Houtte. and *P. americana* L. Fruit are bacca, of dark-red colour and are used to colour the wine.
- Genus *Crataegus* L. (hawthorn) [23 p. 256-271] : *C. monogyna* Jacq. (hawthorn, dahlia).
- Genus *Punus* L. (plum, myrobalan plum) [23 p. 835-847]: *P. spinosa* L. (porumbar). Rimy blackish blue flowers.
- Genus *Cerasus* Adans. (sweet cherry, sour cherry) [23 p. 847-861] : *C. avium* (L.) Mnch. (sin. *Prunus avium* L., sin. *Prunus Cerasus* var. *Avium* L) (sweet cherry).
- Genus *Ribes* L. [23 p. 136] : *R. rubrum* L. (red currant); *R. nigrum* L. (blackcurrant).
- Genus *Rosa* L. (brier, eglantine, rose) [23 p. 708-835].). Ex. : *R. canina* L. (brier).
- Genus *Rubus* L. (blackberries, brambles, raspberries, [23 p. 276-580]. 101 species and various hybrids are described. Ex. : *R. caesius* L. (stubble bramble), *R. idaeus* L. (raspberry).
- Genus *Ruscus* L. [39 p. 379-683]: *Ruscus aculeatus* L. (bur).

Flavonoid containing plants (the have yellow coloured flowers)

- Genus *Abutilon* Adans.(abutilon, corchorus) [25 p. 29-30]: *A. theophrastii* Medik.; corchorus, abutilon.
- Genus *Adonis* L. [21 p. 653-661]: *A. vernalis* L. (adonis).
- Genus *Chelidonium* L. [22 p. 62-63]: *C. majus* L. (common celandine).
- Genus *Crocus* L. includes two species with yellow flowers: *C. chrysanthus* Herb. and *C. moesiacus* Ker-Gawl. [30 p. 450-454]).
- Genus *Lotus* L. (bird's-foot trefoil). [24 p. 230-236]. *Lotus corniculatus* L.(small bird's-foot trefoil).
- Genus *Melilotus* (L.) Adans. [24 p. 136-145]. Includes two species with yellow flowers: *M. officinalis* (L.) Medik (melilot) and *M. arenarius*. Greek.
- Genus *Medicago* L. (lucerne) [24 p. 118-136] mentioned at the blue-violet flower species. The yellow flower species include *M. lupulina* L. (small clover), *M. falcata* L. (yellow lucerne, trefoil) etc.

- Genus *Onobrychis* Adans. (esparcet) [24 p. 338-346]. *O. viciifolia* (esparcet).
- Genus *Papaver* L. [22 p. 64-83]: *P. pyrenaicum* L., *P. Agemone* L.
- Genus *Ranunculus* L. (crawfoot) [21 p. 561-627]. Ex.: *R. Lingua*. L., *R. sardous* Cr., *R. Bulbom* L.
- Genus *Nuphar* Sm. (water lily) [22 p. 38-39]. *N. luteum* (L.) yellor (water lily).
- Genus *Reseda* L. [22 p. 501-509]: *R. Luteola* L. (reseda); *R. lutea* L. (weld).
- Genus *Rorippa* Scop. [22 p. 215-250]: *R. pyrenaica* (L.) Rchb. (marigold); *R. islandica* (Oed.) Borb. (urnip); *R. austriaca* Cr. (marigold).
- Genus *Sinapis* L. [22 p. 467-473]: *S. arvensis* L. (sin. *S. campestris* Schurr.) (charlock, canola).
- Genus *Rapistrum* Crantz. (barilla) [22 p. 481- 486]: *R. perenne* (L.) All.; (sin. *Bunias Erucago* Landoz. (white barilla).
- Genus *Taraxacum* Wigg. [29 p. 109-126]: *T. officinale* Weber. (dandelion).

Conclusions

Based on the data showed the following important conclusions can be reached:

(1) – Upon determinations made in spring, by their antioxidant content, some plants from the spontaneous flora - ramson (*Allium ursinum*) and celandine (*Ficaria verna* sin. *Ranunculus ficaria*) – have a much higher nutritional value compared to greenhouse salad.

(2) – With regard to the level of anthocyanin, the largest content was found in blackcurrants and the lowest – in strawberries.

(3) – Among the plants from our country's spontaneous flora there are species with a very high polyphenol content; in this respect field ash (*Aronia melanocarpa*) and sea-buckthorn (*Hippophaë rhamnoides*) fruit are noticed. (Overall polyphenol content – 7791,6 GAE mg/100g, respectively 2890,6 GAE mg/100g)

(4) – Comparative research in strawberry, raspberry and sea-buckthorn fruit highlighted that sea-buckthorn fruit are the richest in polyphenols and ascorbic acid and have the most intense scavenging activity (require an antioxidant concentration of the sample of only 512,76 µg/ml in order to remove 50% of the free radical DPPH), and raspberry fruit have the lowest scavenging activity and require the highest antioxidant concentration of the sample (727,63µg/ml) in order to remove 50% of the free radical DPPH.

(5) – Research is necessary on the polyphenol content of more and more species from the spontaneous flora in order to highlight other species useful in the food industry, as well.

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