БИОХИМИЯ И ФИЗИОЛОГИЯ РАСТЕНИЙ

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RESEARCHING THE CONNATURAL MONOTERPENIC HYDROCARBONS BIOSYNTHESIS DYNAMICS APPLYING THE KINETIC MODEL AND THE STATE SPACE MODEL

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To investigate in succession the dynamics of monoterpenic hydrocarbons biosynthesis in plants of genus Artemisia the algorithm, which connects the intermediates analysis of results after each stage processes and the comparison of theoretical conclusions with new experimental data is developed in this article.

It is proved that the uniform kinetic model of chemical essential compounds transformations in a stream from the glucose, mevalonate and isoprene to monoterpenes developed by authors is universal kinetics model in order to explain the connatural biosynthesis of monoterpenes in any ethereous carrier plants.

There are founded some kinetic (by specific velocities of biochemical stages of metamorphosis) and a balance sheet (by rations between ring closure degrees) relations during the monoterpenes connatural biosynthesis corresponding to the vegetative phases.

The state space model (SSM) for open nonlinear biochemical system is compounded. In this model macroscopic metamorphosis of essential substances is introduced as the sequence of vector's micro-alterations (or a velocity of the modification of a system's biochemical composition) in a orthogonal system of co-ordinates. At the application of the model to substantiate with the theory of a kinetic chemo-systematics, which becomes clear correlations between plants-producers is offered.

The biochemical substantiation of individual distinctive indications between plants of genus *Artemisia* for seven types is introduced, such as: *A.abrotanum, A.annua, A.dracunculus, A.glauca, A.scoparia (two chemostrains)* and *A.taurica.* The mathematical model of molecular-and-phylogenetic exposition of the relationship in a flora based on the example of genus *Artemisia* is compounded.

The influence of environmental factors on kinetic parameters of monoterpenes biosynthesis in plants of the genus *A.scoparia* from different regions of their growth by means of comparative graph-analytic and matrix analyses of their accumulation dynamics in plants by own results of the experiment and the literary data with the made by authors modeling calculations is proved.

The possibility to combine the systematization of plants based on morph-anatomic principles and chemo-regular principles based on the kinetic particularities of monoterpenes biosynthesis during the chemo-phases in vegetative taxons is shown.

Keywords: *Artemisia; biosynthesis kinetics; monoterpenes; the state space; chemo-taxonomy*

Introduction

Essential oils from the plants of genus *Artemisia* are applicable in various branches of perfumery, pharmaceutical and food-processing industry. Practical value of oils is defined by essential components and rations of their content.

Valuable components in these oils are various representatives of monoterpenic compounds (Polansky et al., 2007; Khodakov, Kotikov, 2008; 2009; Khodakov et al., 2009; Loloiko et al., 2011; Danilenko et al., 2012; Guliev et al., 2015; Buzuk, 2016; Muchametchanova et al., 2017; Zhigzhitzhapova et al., 2018). Numerous researches in the field of their biosynthesis in plants are confined only by a detection of concrete predominant substances, which are useful for any taxon-carrier in practical purposes. And, the application of cluster analysis or a method of general components using statistical packages of computing

programs allows to become clear only a membership of this or that vegetative type to chemotype on the basis of the received experimental data (Zhigzhitzhapova et al., 2018).

Now there was a necessity to dilate researches with incorporation of all monoterpenic components in plants due to detect kinetic particularities of their biosynthesis in order to offer references to some practical application, such as:

a) detecting the time to gather plants for extraction from them essential oil with target properties;

b) predicting some biochemical particularities during the vegetation of plants at planning of their cultivation for industrial needs;

c) solving direct and inverse problems of formal chemical kinetics in the branch of connatural biosynthesis having the purpose to connect these particularities of kinetics with a concrete vegetative taxon.

The direct problem here consists in the mathematical description of a combined multistage biochemical reaction regularities, in which each stage is characterized by its characteristic kinetic constant and by initial conditions determined for all process.

The inverse problem in narrow sense consists in that within the limits of the offered biochemical process founded on experimental data about it and on the character of its some stages to estimate constants of velocities at each stage of this process. In a wide sense the inverse problem can be formulated as a reconstruction of the schema for complex process founded on the data about its separate stages and on the knowledge about the kinetics of process as a whole.

In the article (Panitchev et al., 2001) one offered to use a model of linear space (LS) for handling and generalizing experimental data received in chemical kinetics. Employing the LS permits to carry out and effectively to solve a series of principal and important problems such as: a) to systematize permissible states of system and to establish the mutual connection between them in the form of the state equations; b) to describe processes of evolution by means of operators and the evolution equations; c) to introduce obvious geometrical manners, for example: trajectories, surfaces, diversities, etc. One indicates a possibility of a model LS to introduce the new theoretical concepts, which allow revealing and describing the mechanism and regularities of processes by two types such as: a) input or output of substances through open system bounds; b) chemical transformations inside the system. However, in that the closed systems are characterized only by their chemical composition.

In articles of authors (Khodakov, Ustimenko, 2017; Ustimenko, Khodakov, 2018) it is detailed the research of monoterpenes biosynthesis in plants as uniform biochemical process, and estimations of general stages were presented. The process of investigations includes the consecutive solution of direct and inverse problems of chemical kinetics.

In the present paper one present the algorithm to research the monoterpenic hydrocarbons biosynthesis dynamics in plants of genus *Artemisia* using the intermediate analysis of results, obtained in the each stage as well as the comparison of theoretical conclusions to new experimental data by (Zhigzhitzhapova et al., 2018).

The base of research is the generalized kinetic model of their biosynthesis presented in author's article (Khodakov, Ustimenko, 2017), which adequacy to experimental data has been shown by us in the article (Ustimenko, Khodakov, 2018).

The purpose of this paper is to substantiate and to unify the mechanism of monoterpenes biosynthesis using an individualization of its kinetic parameters for everyone vegetative taxon, that is based on the comparison of experimental data for some types of genus *Artemisia* with the modeling calculations received for them, which together permits to find regularities of kinetic chemotaxonomy.

To achieve the purpose following problems were solved, such as:

a) to find a correlation between solutions of direct and inverse problems in the kinetics concerning with a biosynthesis of monoterpenic hydrocarbons;

b) to develop an algorithm for researching the connatural biosynthesis of monoterpenic hydrocarbons dynamics with the account of experimental data concerning the component composition of essential oils in plants of genus *Artemisia*;

c) determining the prospects to apply the developed algorithm of the research in branches of chemical kinetics, an ecology, plant growing and other branches of agriculture;

г) finding a possibility to combine the systematization of plants by mortho-anatomic principles and by chemosystematics basing on kinetic particularities of the monoterpenes biosynthesis according to pheno-phases in vegetative taxons.

Objects and research methods

Objects of researches are dynamics of a monoterpenes productivity in ethereous carrier plants and corresponding kinetic model of the monoterpenes biosynthesis, which is the continuation of researches spent by us and presented in articles (Khodakov, Ustimenko, 2017; Ustimenko, Khodakov, 2018). It reflects a dynamics of qualitative and quantitative changes of the compose of monoterpene hydrocarbons in the essential oil, extracted from plants of genus *Artemisia* during all phases of the vegetation, which are obtained by means of the chromate-mass spectroscopic device Agilent Technologies 6890 together the mass-spectrometer 5973 and database of NIST 02 (Khodakov, Kotikov, 2008; 2009; Khodakov et al., 2009).

The research methods – relative graphical-and-analytical and matrix analyses of data for seven types of plants by the genus *Artemisia,* in which one employs as experimental as modeling rated data for a dynamics of monoterpenic components accumulation in corresponding essential oils during all phases of the vegetation. Also, one used the Fisher's method to determine an adequacy of the created kinetic model to obtained experimental data. Incorporated mass fractions of monoterpenic components in the plants essential oil were distributed by us according to the degree of its ring formation (acyclic, mono- and bicyclic), and after that they were reduced accordingly to their general amount, – they are named further as normalized mass fractions.

Corresponding modeling calculations are based on the kinetic scheme (fig. 1) and on the numerical decision of kinetic equations by the kind (1)–(3) and the equations of (4) (Khodakov, Ustimenko, 2017; Ustimenko, Khodakov, 2018):

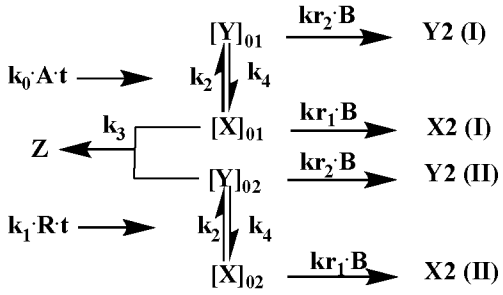


Fig. 1 The basic model, which explains the reproduction of monoterpenes X2, Y2, Z in plants of the genus *Artemisia, where it is named by:* X2 – alicyclic; Y2 – monocyclic; Z – bicyclic; X – carbocation of dimethyl-allyl; Y – carbocation of isopentyl; A – glucose; R – mevalonate; B – isoprene; k_i, kr_i – kinetic constants of corresponding processes (Ustimenko, Khodakov, 2018)

$$\frac{dX2}{dt} \cong \frac{kr_1 \cdot (B - X2)}{1 + \frac{kr_1 \cdot (B - X2)}{k_2}} \cdot [X] \cong \frac{k_2 \cdot kr_1 (B - X2)}{k_2 + kr_1 \cdot (B - X2)} \cdot \{\frac{k_0 \cdot A + k_1 \cdot R}{k_{24} + 1} \cdot t - Z\} \quad (1)$$

$$\frac{dY2}{dt} \cong k_{24} \cdot \frac{kr_2 \cdot (B - Y2)}{1 + \frac{kr_2 \cdot (B - Y2)}{k_4}} \cdot [X] \cong \frac{k_2 \cdot kr_2 (B - Y2)}{k_4 + kr_2 \cdot (B - Y2)} \cdot \{\frac{k_0 \cdot A + k_1 \cdot R}{k_{24} + 1} \cdot t - Z\}$$

$$\frac{dZ}{dt} \cong k_3 \cdot (\frac{k_0 \cdot A \cdot t}{k_{24} + 1} - Z) \cdot (\frac{k_1 \cdot R \cdot t}{k_{24} + 1} - Z)$$

where $[X]_{01} + [X]_{02} \equiv [X]$ (2)

$[Y]_{01} + [Y]_{02} \equiv [Y]$

$$k_{24} = \frac{k_2}{k_4}$$

The residual content of monoterpenes in samples of plants by modeling calculations was defined by the equations (3) according to articles (Khodakov, Ustimenko, 2017; Ustimenko, Khodakov, 2018):

$$X2_i(res.) \equiv X2_i - v_X \cdot t_i \quad (3)$$

$$Y2_i(res.) \equiv Y2_i - v_Y \cdot t_i$$

$$Z_i(res.) \equiv Z_i - v_Z \cdot t_i$$

where $X2_i$, $Y2_i$, Z_i – numerical solutions of the equations system (1); v_X, v_Y, v_Z are velocities of dispersion of monoterpenic hydrocarbons in the surroundings, accordingly; t_i – the dimensionless time in terms of the season first phase (I) of the vegetation.

Mass fractions in the residual content of monoterpenic hydrocarbons types (wX_i, wY_i, wZ_i) in samples of plants (or normalized mass fractions according to the condition, such as $wX_i + wY_i + wZ_i = 1$) as by experimental data (in the composition of the essential oil) as by modeling calculations (in plants) were defined with the help of the equations (4) (Khodakov, Ustimenko, 2017):

$$w_{X_i}(res.) \equiv \frac{X_i(res.)}{X_i(res.) + Y_i(res.) + Z_i(res.)} \quad (4)$$

$$w_{Y_i}(res.) \equiv \frac{Y_i(res.)}{X_i(res.) + Y_i(res.) + Z_i(res.)}$$

$$w_{Z_i}(res.) \equiv \frac{Z_i(res.)}{X_i(res.) + Y_i(res.) + Z_i(res.)}$$

It is expedient to present normalized mass fractions as vectors in the tridimensional system of orthogonal co-ordinates. As a result, it is possible to calculate its modules as the vector modules of normalized mass fractions of monoterpenic components $|\vec{w}|$ in plants (the vectors of a productivities) by the equations (5)–(7) using the representation in the matrix form by equations (6) of solutions for the nonlinear kinetic equations (1). The initial conditions for the kinetic equations (1) – (3) are reduced in table 1.

$$|\vec{w}| = \sqrt{w_x^2(res.) + w_y^2(res.) + w_z^2(res.)} \quad (5)$$

$$\vec{X}2(res.) = \overrightarrow{(V_x - v_x)} \cdot \vec{t}$$

$$\vec{Y}2(res.) = \overrightarrow{(V_Y - v_Y)} \cdot \vec{t} \quad (6)$$

$$\vec{Z}(res.) = \overrightarrow{(V_z - v_z)} \cdot \vec{t}$$

where $V_X \cong \frac{k_2 \cdot kr_1 (B - X2)}{k_2 + kr_1 \cdot (B - X2)} \cdot \{\frac{k_0 \cdot A + k_1 \cdot R}{k_{24} + 1} \cdot t - Z\}$ (7)

$$V_Y \cong \frac{k_2 \cdot kr_2 (B - Y2)}{k_4 + kr_2 \cdot (B - Y2)} \cdot \{\frac{k_0 \cdot A + k_1 \cdot R}{k_{24} + 1} \cdot t - Z\}$$

$$V_Z \cong k_3 \cdot (\frac{k_0 \cdot A \cdot t}{k_{24} + 1} - Z) \cdot (\frac{k_1 \cdot R \cdot t}{k_{24} + 1} - Z)$$

are instantaneous velocities of monoterpenes reproduction in plants.

We carried out the relative analysis for the monoterpenes accumulation dynamics in plants *A.scoparia* using values of kinetic parameters of monoterpenes biosynthesis as applied to data of our experiments, and also according to the literary data from other region of the growth (Zhigzhitzhapova et al., 2018) (tab. 1 – the column 8).

To obtain more information about the influence of kinetic parameters of monoterpenes biosynthesis in plants at each stage on their biochemical differences one founded the state space model (SSM) according to the article (Ustimenko, Khodakov, 2018), on which it is possible to present any macroscopic metamorphosis as the series of a vector's micro-displacements. The curve outlined in SSM by the vector head of composition may has name as a metamorphosis trajectory. We generated that experimental points for each plant investigated issuing from theoretical positions of chemical kinetics. It has given the possibility to check up an adequacy of the used theoretical suppositions in a solution of target problems.

Table 1

Initial conditions for the kinetic equations (1) – (3) and the corresponding kinetic parametres to coordinate the courses of modelling curves (as graphical solutions of the equations) with the experimental data (Ustimenko, Khodakov, 2018) the column 7 and (Zhigzhitzhapova et al., 2018) the column 8

Parameters in the kinetic equations		Vegetative types of the genus *Artemisia*					
	A. abrotanum	*A. annua*	*A. dracunculus*	*A. glauca*	*A. taurica*	*A. scoparia*	*A. scoparia*
1	3	3	4	5	6	7	8
Initial conditions							
$X2_0$	0	0,00125	0,500	0,0075	0,025	0,0065	0,020
$Y2_0$	0,075	0,0002	0,450	0,7250	0,215	0,025	0,350
Z_0	0,0125	0,00125	0,885	0,250	0,375	0,0075	0,250
t_o	0,125	$1{,}25 \cdot 10^{-4}$	0,045	0	0	0	0
Content of initial substances by the glucose unit (g/g)							
A (glucose)	1	1	1	1	1	1	1
R (mevalonate)	0,75	0,85	0,85	0.75	0,75	0,85	0,85
B (isoprene)	1,75	0,125	0,125	0.95	0,65	0,125	0,125
Kinetic constants							
k_0	1,500	1,725	0,512	1,50	1,50	5,25	5,25
k_1	0,2512	0,212	6,85	0,7512	0,7512	0,112	0,112
k_2	7,500	1,25	3,375	6,125	6,125	8,500	8,500
k_3	20,00	3,00	1,750	0,250	0,500	25,85	0,85
k_4	1,500	10,375	8,500	1,500	1,500	4,375	4,375
kr_1	0,025	0,225	0,850	0,025	0,200	0,785	0,785
kr_2	0,125	0,250	0,150	6,950	0,175	0,025	0,025
k_{24}	5,000	0,120	0,397	4.083	4,083	1,943	1,943
Velocities of monoterpenes dispersion in environment according to the equation (3), t^{-1}							
v_X	$5{,}6 \cdot 10^{-4}$	0,0015	0	0,0055	0,001	0,030	0,050
v_Y	0,120	0	0,045	0,0005	0,100	0,010	0,0125
v_Z	0,0012	0,002	0,125	0,025	$7{,}5 \cdot 10^{-4}$	0,005	0,015

In generally, trajectories of the chemical transformation had the complicated curvilinear form, which depended on a series of chemotypical and ecological factors. The individuality of these trajectories has allowed to use kinetic and parametrical characteristics in the SSM permitted to compare the stages of a biochemical processes during the connatural monoterpenes biosynthesis and to classify the taxons.

Results and discussion

Throughout the previous researches, we made the recalculations of the productivity for plants by the genus *Artemisia* on the normalized mass fractions, obtained from the experimental data (tab. 2). The presented values are the base to fix the modeling kinetic dependences of monoterpenes biosynthesis in studied types of plants. The multiplication of each normalized mass fraction on the unit vector leads to the vector of its productivity.

Table 2

Normalized mass fractions and the productivities of monoterpenes in the essential oil made by plants of the genus *Artemisia* during the vegetation seasons according to the experimental data (Ustimenko, Khodakov, 2018)

Types of a degree of the monoterpenes cyclization	Normalized mass fractions of monoterpenes during the vegetation seasons			
	I	II	III	IV
1	3	4	5	6
A.abrotanum				
Acyclic (**X2**)	0,00	0,01	0,01	0,01
Monocyclic (**Y2**)	0,53	0,25	0,33	0,35
Bicyclic (**Z**)	0,47	0,74	0,66	0,64
The vector modules of a productivity $\lvert\vec{\mathbf{w}}\rvert$	0,708	0,781	0,738	0,730
A.annua				
Acyclic (**X2**)	0,40	0,58	0,68	0,56
Monocyclic (**Y2**)	0,11	0,16	0,06	0,19
Bicyclic (**Z**)	0,49	0,26	0,26	0,25
The vector modules of a productivity $\lvert\vec{\mathbf{w}}\rvert$	0,642	0,655	0,730	0,642
A.dracunculus				
Acyclic (**X2**)	0,32	0,35	0,19	0,23
Monocyclic (**Y2**)	0,13	0,12	0,35	0,22
Bicyclic (**Z**)	0,55	0,53	0,46	0,55
The vector modules of a productivity $\lvert\vec{\mathbf{w}}\rvert$	0,650	0,646	0,608	0,635
A.glauca				
Acyclic (**X2**)	0,00	0,01	0,01	0,00
Monocyclic (**Y2**)	0,79	0,61	0,71	0,84
Bicyclic (**Z**)	0,20	0,38	0,28	0,16
The vector modules of a productivity $\lvert\vec{\mathbf{w}}\rvert$	0,815	0,719	0,763	0,855
A.taurica				
Acyclic (**X2**)	0,00	0,00	0,01	0,03
Monocyclic (**Y2**)	0,13	0,09	0,07	0,06
Bicyclic (**Z**)	0,87	0,91	0,92	0,91
The vector modules of a productivity $\lvert\vec{\mathbf{w}}\rvert$	0,880	0,914	0,923	0,912
A.scoparia				
Acyclic (**X2**)	0,28	0,16	0,32	0,31
Monocyclic (**Y2**)	0,42	0,32	0,20	0,13
Bicyclic (**Z**)	0,30	0,52	0,48	0,56
The vector modules of a productivity $\lvert\vec{\mathbf{w}}\rvert$	0,587	0,631	0,611	0,653

To establish an influence of ecological factors on parameters of the monoterpenes biosynthesis in other region of the growth, the data from the article (Zhigzhitzhapova et al., 2018) have been rearranged by us, and they were tabulated in table 3.

Table 3

Recalculations of experimental data about the composition of essential oil, made by plants of the genus *Artemisia scoparia* from other region (Zhigzhitzhapova et al., 2018), on the normalized mass fractions according to their degrees of the cyclization

Degree of the monoterpenes cyclization	Content of monoterpenes in the vegetation seasons			
	Vegetation beginning	Budding	Blooming	Fructification
Sum mass fractions of monoterpenes in the essential oil by the degree of its cyclization, %				
Acyclic	19,23	3,92	0,74	6,16
Monocyclic	16,77	13,51	1,51	9,26
Bicyclic	12,3	7,98	0,87	6,92
Sum	48,3	25,41	3,12	22,34
Normalized mass fractions of the monoterpenes				
Acyclic	0,398	0,154	0,237	0,276
Monocyclic	0,347	0,532	0,484	0,415
Bicyclic	0,255	0,314	0,279	0,310
The vector modules of a productivity $\left\|\vec{\mathbf{w}}\right\|$	0,586	0,637	0,607	0,587

Graphic dynamics dependences of the monoterpenes biosynthesis, placed in the table 4, are the solutions of the differential equations (1)–(3) included three variables. Points on a drawing indicate the experimental values, which in an optimum variant should coincide with modelling curves or the received curves should come nearer to them as much as possible.

1. In the first column of table 4 one combined experimental data of accumulation acyclic, mono- and bicyclic monoterpenes in the oils (normalized mass fractions) in the plants of the genus *Artemisia* and results of a solution for the kinetic equations (1)–(4), – there are designated by arrows: **1** – for monoterpenes-Z w_z(res.); **2** – for monoterpenes-Y2 w_y(res.); **3** – for monoterpenes-X2 w_x(res.). Points on curves (the first column of this table) one designates corresponding experimental values of normalized mass fractions of monoterpenes hydrocarbons by the data of table 4.

2. By arrows (the second column of this table) one shows vectors of a plants productivity (for normalized mass fractions). On unit vectors in a three-dimensional frame one puts aside normalized mass fractions for third degrees of the monoterpenes cyclization, and for each phase of vegetation one indicates the eigenvector of a productivity in three-dimensional space. Thus, genesis of plants vegetation is characterized by rotation of this vector, i.e. the extremities of the vector describe a world line.

3. By points on curves (the second and third columns of this table) one places corresponding values of vectors of a monoterpenes distribution in the oil, and also the vector module of normalized mass fractions, calculated according to the equation (5).

In the third column of this table one combined the dynamics changes of the vectors length (or the module) constructed as by our received experimental data (points) as by results of mathematical modeling (lines) for each plant, – the high convergence of both dynamics changes is observed.

Table 4

Kinetics characteristics of the dynamics changes in the composition of the essential oils and its vector representations for the plants of genus *Artemisia* by the works (Ustimenko, Khodakov, 2018; Zhigzhitzhapova et al., 2018)

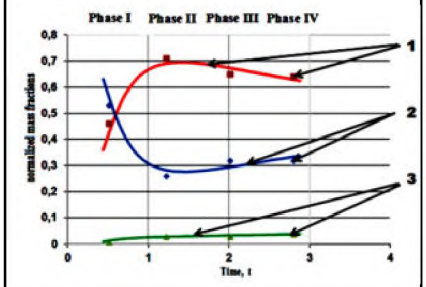
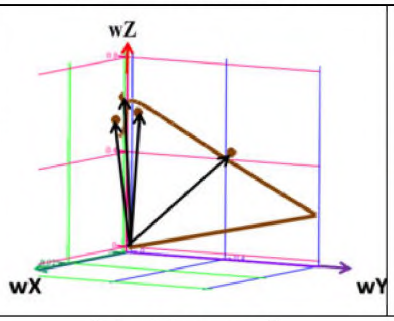
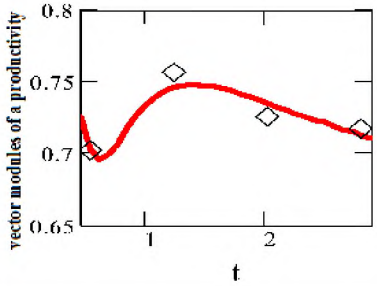
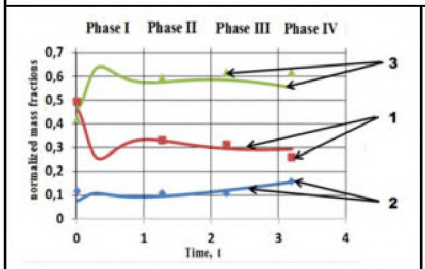
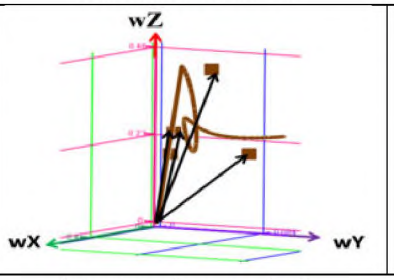
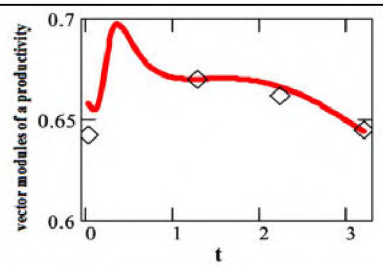
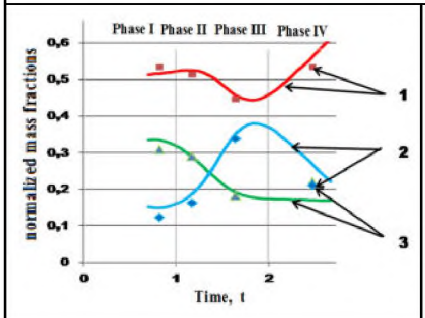
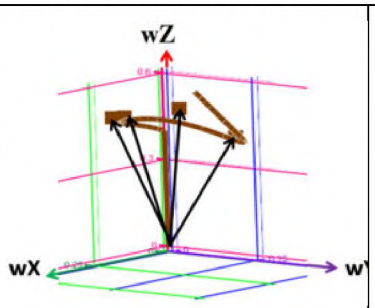
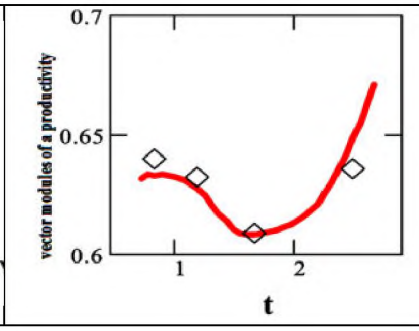
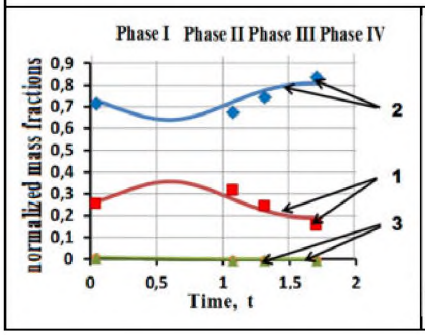
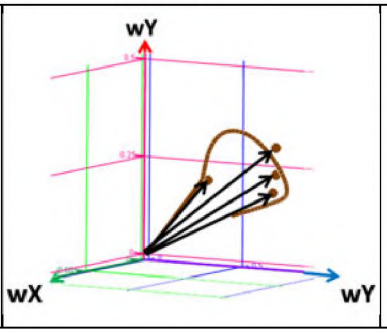
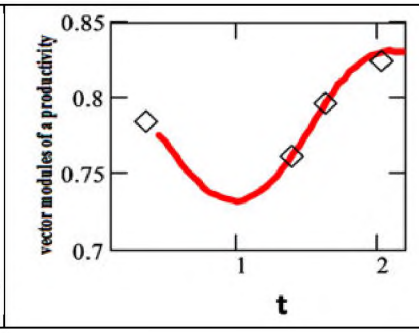
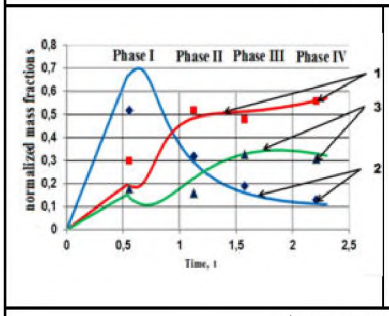
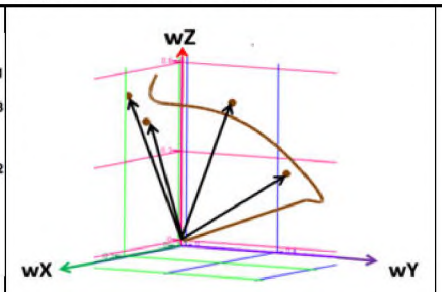
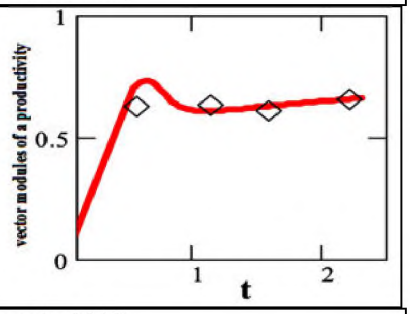
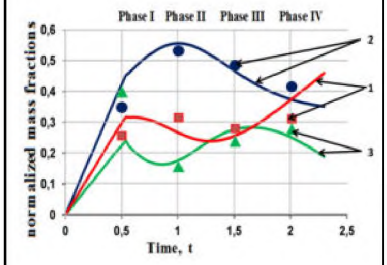
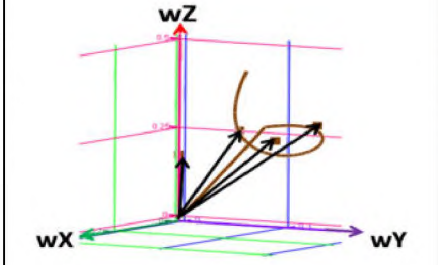
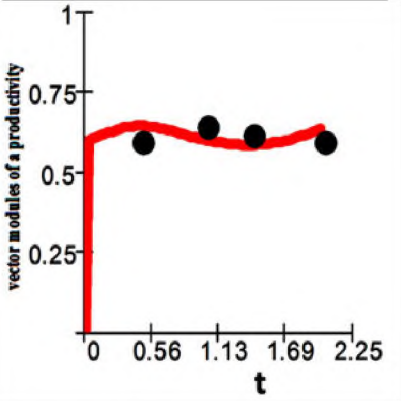
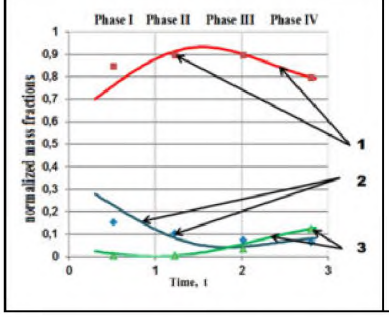
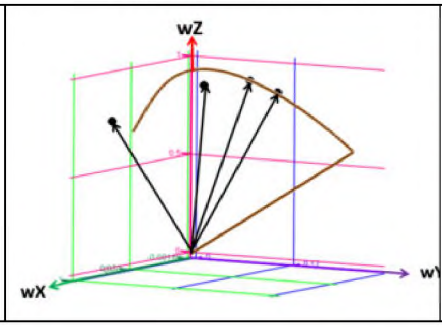
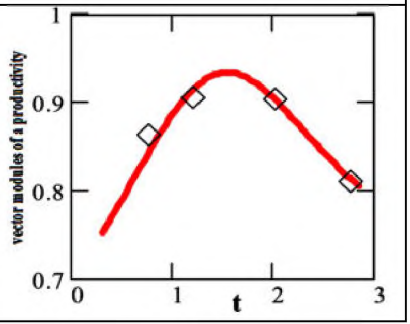
Hodographs of the monoterpenes content in the essential oil according to the degree of the cyclization in plants of the genus *Artemisia*	The vector head track of an monoterpenes efficiency in the essential oil during vegetation phases, by the equations (4)	Hodograph of the vector module of the monoterpenes productivity in the essential oil (points are correlated with vegetation phases), – by the equation (5)
1	**2**	**3**
Artemisia abrotanum L.		
		
Artemisia annua L.		
		
Artemisia dracunculus L.		
		
Artemisia glauca Pall. ex Willd		
		

Table 4 terminal

1	2	3
Artemisia scoparia Waldst.et Kit (Ustimenko, Khodakov, 2018)		
		
Artemisia scoparia Waldst.et Kit (Zhigzhitzhapova et al., 2018)		
		
Artemisia taurica Willd		
		

Data of tables 1–4 has allowed to establish the scalar values of a time-vector (**t ***) in the time-units in accordance with the first phase of the vegetation season by the comparison of corresponding co-ordinates on the graphs (tab. 4, a column 1) and they was corrected at the numerical solution of the equations (1)–(3) with (4).

Table 4 is a part of the SSM as the series of graphical trajectories for the biochemical transformations in plants, which make geometrically an image of the evolution operator (or a vector of the displacement) for the chemical transformations into a time by the vector's format; – that contains (by the compressed appearance) the information about the kinetics of chemical transformation.

As in the presented article the additional experimental data for the plant *Artemisia scoparia* reduced by us from the article (Zhigzhitzhapova et al., 2018) were used, there was a necessity to check on an adequacy the hodographs lines (regression lines) (tab. 4 – column 1) to the data in table 1 (column 8) and in table 3 to the experimental data, reduced in the same place in the form of points, according to the procedure of regressive analysis described in the article (Ustimenko, Khodakov, 2018). In our article according to the article (Ustimenko, Khodakov, 2018) is obtained that "the regression calculated on four phases of vegetation is

adequate to the experiment if Fisher's rated criterion does not exceed its table value at the chosen level of a confidence probability (P) with corresponding degree of freedoms (f_{ad} and $f_{repr.}$):

$$F = \frac{s^2(ad.)}{s^2(repr.)} \leq F_{1\text{-}P}(f_{ad.}, f_{repr.}) \qquad (8)$$

where $F_{1\text{-}P}$ (f_{ad}, $f_{repr.}$) = 9,55 – table value of Fisher's criterion for P = 0,05 and numbers of degree of freedoms f_{ad} = 2) and $f_{repr.}$ = 3".

For the data for the plant *A.scoparia* from the article (Zhigzhitzhapova et al., 2018) one obtains values of criterion F, which are smaller than the table value of Fisher's criterion, namely (for tab. 4, column 1):

– Fisher's criterion for a line of a regression 3 at acyclic (monoterpenes-**X2**) according to the formula (8) is equal 7,99;

– that for a line of a regression 2 at monocyclic (monoterpenes-**Y2**) according to the formula (8) is equal 1,39;

– that for a line of a regression 1 at bicyclic (monoterpenes-**Z**) according to the equation (8) is equal 2,83.

Thus, the constructed graphic model to the monoterpenes biosynthesis in plant *A.scoparia* from the article (Zhigzhitzhapova et al., 2018) is adequate to experimental data.

To research the regularities of monoterpenes biosynthesis in the offered modeling schema (fig. 1) we evolve two key paths of their formation, which are carried out through the equilibrium dynamics between carbocations of dimethylallyl (**X**) and of isopentyl (**Y**). And, their equilibrium concentrations can are stable on various ways of the reproduction, namely, on non-mevalonate way producing the equilibrium concentrations $[X]_{01}$, $[Y]_{01}$ (from **A**) and also on mevalonate way (from **R**) producing the equilibrium concentrations $[X]_{02}$, $[Y]_{02}$ with kinetic constants k_0 and k_1 correspondingly. The dynamic equilibrium is characterized by constants k_2 and k_4, and their interrelation shows a direction of its displacement. "Equilibrium" carbocations **X** and **Y** as intermediate and highly active compounds are in turn sources of all monoterpenic hydrocarbons from attaching an isoprene. As a result, monoterpenes **X2** and **Y2** with kinetic constants kr_1 and kr_2 are formed accordingly, and compositions of carbocations **X** and **Y** in one stage by various ways of the biosynthesis leads to monoterpenes **Z** with a kinetic constant k_3.

We detected the contribution of each kinetic constant in the uniform modeling schema of monoterpenes biosynthesis for investigated plants of genus *Artemisia* (fig. 1) by construction of individual factor planes (fig. 2) according to table 2.

Figure 2 discloses interrelations between kinetic stages of connatural monoterpenes biosynthesis in investigated plants according to their velocities at each stage according to the schema (fig. 1). As a result the individual biosynthetic particularities, concerning each plant, are observed and that can be afterwards the base for their allocation as a quality of the chemo-taxonomic indications along with phenological indications.

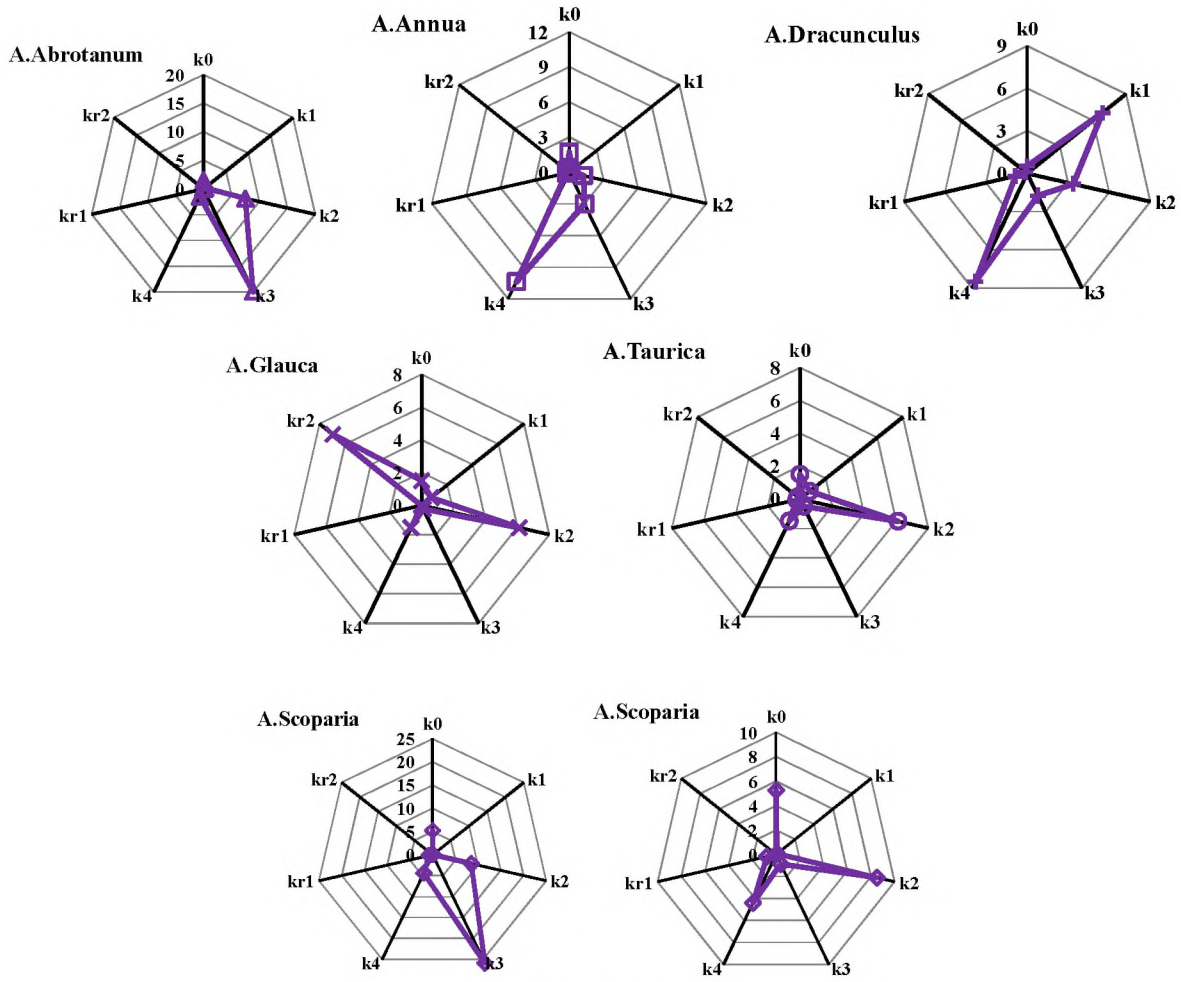
For example, during the comparison of the most high-speed stages in connatural monoterpenes biosynthesis we observed in the experiment the presence of conforming ring structures of monoterpenic hydrocarbons, i.e. the figure 2 shows the presence of dominating and defining the high-speed stages in connatural monoterpenes biosynthesis.

Individual particularities of vegetative types are reduced in the figure 2 as the comparison of the most high-speed stages in connatural monoterpenes biosynthesis, namely:

– for a group of perennial plants, such as *Artemisia abrotanum, A.scoparia, A.taurica, A.glauca* and *A.dracunculus* the dynamic equilibrium state is characterized by an interrelation between values of constants k_2, k_4 where the constant k_2 exceeds the value of k_4, that leads to the accumulation of carbocations **Y**;

– for an annual plant *A.annua* the inverse interrelation of these value with accumulation of carbocations **X** is observed;

– for plants such as *A.abrotanum*, *A.annua*, *A.taurica* and *A.glauca* equilibrium concentrations between carbocations **X** and **Y** are supported by two ways (non-mevalonate from **A** and mevalonate from **R**) at the same level, that follows from the affinity of values of constants $\mathbf{k_0}$ and $\mathbf{k_1}$.



(a) (b)

Fig. 2 Factor planes of kinetic constants as graphic images for the velocities distribution of common monoterpenes biosynthesis according to the schema (fig. 1): (a) – for the model by (Ustimenko, Khodakov, 2018); (b) - for the model by (Zhigzhitzhapova et al., 2018)

In the plant *A.abrotanum* one observes a high speed of bicyclic monoterpenes biosynthesis (terpenes-Z) from the carbocation of dimethyl-allyl $[X]_{01}$ and from the carbocation of isopentyl $[Y]_{02}$ by different equilibrium ways (high value k_3), and at the same time a reversible transferring of the carbocation of dimethyl-allyl X to the carbocation of isopentyl **Y** is realysed and displased to the direction of the last ($\mathbf{k_2}$ **is** hardly more than $\mathbf{k_4}$).

In the plant *A.annua* – the reversible transferring of the carbocations of dimethylallyl **X** to the carbocations of isopentyl **Y** is displased move essentially in a direction of the first (significant prevalence of value $\mathbf{k_4}$ over $\mathbf{k_2}$), and, at the same time, this plant is the annual plant, in which one observes initial values of monoterpenes concentration ($\mathbf{X2_0}$, $\mathbf{Y2_0}$ and $\mathbf{Z_0}$) as final products of biochemical reactions more lower, than in the other investigated types,.

In the plant *A.dracunculus* for maintenance of equilibrium concentrations between carbocations **X** and **Y** one observes the prevalence of mevalonate way of biosynthesis from **A**

over non-mevalonate way from **R** (significant prevalence of value k_1 over k_0). The quick stage of metamorphosis of a mevalonate to the carbocations of isopentyl **Y** (high value k_1) dominates at the essential values of k_2 and k_4 with high value of k_4 accompanying with the displasement of reversible transferring aside the carbocations of dimethylallyl **X**.

In the plant *A.glauca* – the reversible transferring between the carbocations of dimethyl-allyl **X** and the carbocations of isopentyl **Y** is displaced move essentially inside the last (significant prevalence of k_2 over k_4), with which an isoprene **B** quickly makes further a series of monocyclic terpenes (high value of the constant kr_2).

In the plant *A.taurica* – **the** reversible transferring between the carbocations of dimethyl-allyl **X** and the carbocations of isopentyl **Y** is displaced move essentially inside the last (essential prevalence of k_2 over k_4).

In the plant *A.scoparia* for maintenance of equilibrium concentrations between carbocations **X** and **Y** one observes the prevalence of non-mevalonate way of the biosynthesis over mevalonate way of biosynthesis (prevalence of value k_0 over k_1).

1. In the chemo-type of plants *A.scoparia* (Ustimenko, Khodakov, 2018) performances of biosynthesis are affinitive to *A.abrotanum* with those differences only, that the constant k_0 is more great and, hence, the velocity of metamorphosis of glucose **A** to carbocations of isopentyl **Y** is above also, but the difference between values of constants k_2 and k_4 is less, consequently the displacement of reversible transferring of the carbocations of dimethyl-allyl **X** to the carbocations of isopentyl **Y** is slow, and it is inside the last. One observes the stage with high speed of bicyclic monoterpenes production (significant value of k_3).

2. In the chemo-type of plants *A.scoparia* (Zhigzhitzhapova et al., 2018) one observes the high-speed enough stage during the production of acyclic (monoterpenes-**X2**) and monocyclic (monoterpenes-**Y2**) from a glucose **A** accompanied by a quick establishment of equilibrium biosynthesis of monocyclic monoterpenes and by the displacement of that inside direction the carbocations of isopentyl **Y**.

Graphic performances of biosynthesis *A.scoparia* according to (Ustimenko, Khodakov, 2018) and (Zhigzhitzhapova et al., 2018) coincide practically, but in the latter case there is extremely low value of a constant k_3, i.e. the stage of production of bicyclic monoterpenes (monoterpenes-**Z**) is essentially retarded.

Remaining irreciprocal stages of monoterpenes biosynthesis in all plants are retarded and they define a velocity of all process.

Data of table 4 permit to estimate the dynamics of modifications of the vector modules for a productivity (for non-normalized mass fractions,) during vegetative phases in vectorial and matrix forms according to foundations of the kinetics in the article (Ustimenko, Khodakov, 2018), i.e.:

$$\begin{bmatrix} X2_i \\ Y2_i \\ Z_i \end{bmatrix} = \begin{bmatrix} \overline{\overline{V_x(t_i) - v_x}} \\ \overline{\overline{V_y(t_i) - v_y}} \\ \overline{\overline{V_z(t_i) - v_z}} \end{bmatrix} \square [t_i] \qquad (9)$$

where $\overline{\overline{V_x(t_i) - v_x}}$ $\overline{\overline{V_y(t_i) - v_y}}$ $\overline{\overline{V_z(t_i) - v_z}}$ – average velocities of modeling monoterpenes accumulation in a plant (average velocities of productivity).

For the equation (9) it is possible to make a corresponding functional:

$$\left\| \begin{bmatrix} X2_i \\ Y2_i \\ Z_i \end{bmatrix} \right\| = F[X2(t), Y2(t), Z(t), t] \qquad (10)$$

where the vector module of a productivity is represented by «an evolution operator» according to the article (Panitchev et al., 2001), and the functional can be presented in a form with the divided functions (11):

$$\mathbf{F[X2(t), Y2(t), Z(t), t] = N \cdot \sqrt{X2_i^2 + Y2_i^2 + Z_i^2} \cdot f(t)} \quad (11)$$

where N – dimension factor.

Function **f(t)** – presents a connection between a motion of the curve of the corresponding graphic in the column 3 (tab. 4) and the co-ordinates of the productivity vector (for non-normalized mass fractions). Therefore, the graphic image of this operator should be corresponding to the graphic presented in the table 4 (a column 3).

Transferring to this productivity vector (for non-normalized mass fractions) it is necessary to consider the modifications of fractions at the time (during a vital ability of the plant) and the computation of their values according to equations (4), (5), namely:

$$\mathbf{\sqrt{X2_i^2 + Y2_i^2 + Z_i^2} = \sqrt{wX_i^2 + wY_i^2 + wZ_i^2} \cdot (X2_i + Y2_i + Z_i)} \quad (12)$$

Disclosing the functional represents a complicated mathematical problem. However, from the received equality it is possible previously to conclude, that a series of vectors modules, which are disposed in a left side of the equations (10,12), is reduced to their equating with the unique function, named by the functional and has being in a right side of the equation (10). Biological sense of this equation is in that a series of theoretical and experimental data about the monoterpenes components in ours investigations for representative types of the genus *Artemisia* results from the solutions of this unique functional.

The solution of this functional can lead to a series of values of non-normalized mass fractions, which represent three functions describing an accumulation in plants of three types of hydrocarbon's structures depended on a time (tab. 4), and the form of these dependences is defined by a series of the kinetic constants (tab. 1).

Discrete solutions at the same time are the kinetic characteristics of monoterpenes biosynthesis for each concrete vegetative type, and series of such discrete decisions correspond to the molecular-and-phylogenetic tree (fig. 3).

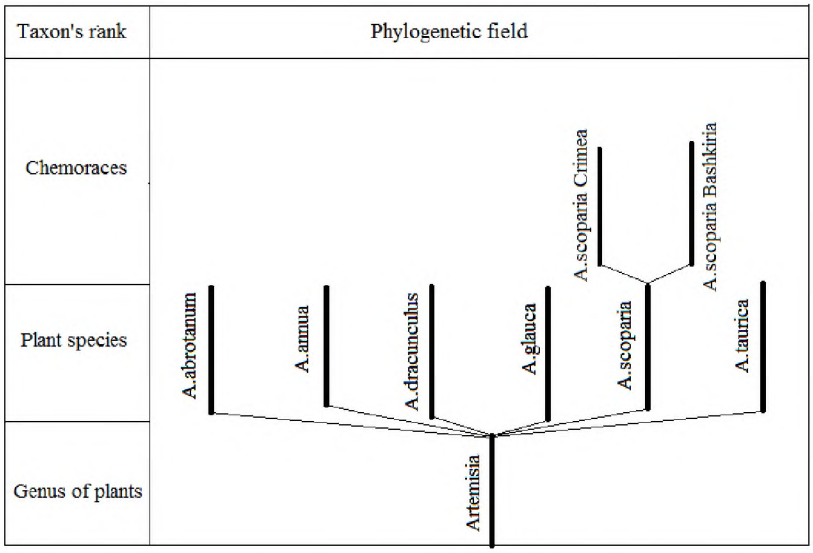


Fig. 3 Molecular-and-phylogenetic tree of a relayionship between the taxons of the genus *Artemisia*

To do an obviousness we generated a phylogenetic field (fig. 3), on which the mathematical description of the biochemical indications segmentation is presented, also, each rank of the taxon is reflected by characteristic biochemical performance. For a vegetative genus it is a functional (the

equation 10), for the vegetative types – the forms of solutions of the functional as the changes in a time of the length of a radius-vector, which are presented in table 4 (the column 3). For the chemo-races – the form of the rotated radius-vector in the three-dimensional orthogonal space, extremity of which forms a world line (table 4, the column 2), or there are three hodographs for everyone taxon (table 4, the column 1). As a result, it is possible to assume that the chemo-races was appeared after the hybridization of the investigated plants together with the regional flora, when which have taken place a natural selection in the regional conditions where the gained biochemical indications were genetically fixed are.

Conclusions

1. One proposed the method to characterize the vegetative types using the graphic images of their productivity with the account of an interrelation between groups of monoterpenic hydrocarbons and the method to define the kinetic constants of the connatural processes of their biosynthesis according to the developed kinetic model.

2. One proposed the universal kinetic model of connatural monoterpenes biosynthesis in the ethereous carrier plants, which should be used to forecast the dynamics of monoterpenes biosynthesis in the various vegetative seasons of plants.

3. One presents the biochemical reason of the individual distinctive indications of some representatives plants of the genus *Artemisia* presented by *A.abrotanum, A.annua (an annotinous plant), A.dracunculus, A.glauca, A.scoparia (two chemo-races from Crimea* and *Bashkiria)* and *A.taurica* has.

4. Specific particularities of monoterpenes biosynthesis dynamics in the investigated kinds of the genus *Artemisia* correspond to their position on the molecular-and-phylogenetic tree, and the researches can be expanded up to finding-out of affine relationships in flora.

5. One compounded the mathematical model of molecular-and-phylogenetic description for a relationship in flora on an example of genus *Artemisia*.

6. The state space model (SSM) for open nonlinear biochemical system, which expends the descriptive possibilities of known model coincided for the closed linear chemical system (LS) is presented.

7. One demonstrated a possibility to combine the systematization of plants based on the morph-anatomic principles and chemo-regular principles based on the kinetic description of monoterpenes biosynthesis during the chemo-phases in vegetative taxons.

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Устименко В.Н., Ходаков Г.В. Исследование динамики природного биосинтеза монотерпеновых углеводородов с применением кинетической модели и модели пространства состояний // Plant Biology and Horticulture: theory, innovation. 2019. № 2(151). P. 94-108.

В работе разработан алгоритм последовательного исследования особенностей биосинтеза монотерпеновых углеводородов в растениях рода *Artemisia* с промежуточным анализом результатов каждого этапа и сопоставлением теоретических выводов с новыми экспериментальными данными.

Доказано, что разработанная авторами единая кинетическая модель химических превращений базисных веществ (глюкозы, мевалоната и изопрена) до монотерпенов в потоке является универсальной для описания кинетики природного биосинтеза монотерпенов любых эфироносных растений.

Выявлены кинетические (по удельным скоростям биохимических стадий превращений) и балансовые (по соотношениям степеней циклизации) особенности природного биосинтеза монотерпенов по фазам вегетации.

Составлена модель пространства состояний (ПС) для открытой нелинейной биохимической системы. В этой модели макроскопические превращения базисных веществ представлены в виде последовательности микросдвигов вектора (скорости изменения биохимического состава системы) в ортогональной системе координат. Предложено использование модели для теоретического обоснования кинетической хемосистематики, которая выясняет взаимосвязи между растениями-продуцентами.

Представлено биохимическое обоснование индивидуальных различительных признаков растений рода *Artemisia* для шести видов: *A.abrotanum, A.annua, A.dracunculus, A.glauca, A.scoparia (две хеморасы) и A.taurica.*. Составлена математическая модель молекулярно-филогенетического описания родства в растительном мире на примере рода *Artemisia.*

Установлено влияние экологических факторов на кинетические параметры биосинтеза монотерпенов *A.scoparia* с разных регионов произрастания за счет сравнительного графоаналитического и матричного анализов динамики их накопления в растениях по результатам собственного эксперимента и литературным данным с проведенными авторами модельными расчётами.

Показана возможность совмещения систематики растений на морфо-анатомических принципах и хемосистематических на основании кинетических особенностей биосинтеза монотерпенов по фенофазам в растительных таксонах.

Ключевые слова: *Artemisia; кинетика биосинтеза; монотерпены; пространство состояний; хемотаксономия.*