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Assessing protopectin transformation potential of plant tissue using a zoned criterion space

Vladimir V. Kondratenko[1],*, Tatyana Yu. Kondratenko[1], Andrey N. Petrov[1], Georgy A. Belozerov[2]

[1] Russian Research Institute of Canning Technology – branch of Gorbatov Federal Research Center for Food Systems at Russian Academy of Sciences, Vidnoye, Russia

[2] Russian Scientific Research Institute of Refrigeration Industry – branch of Gorbatov Federal Research Center for Food Systems at Russian Academy of Sciences, Moscow, Russia

* e-mail: nauka@vniitek.ru

Abstract:
Introduction. The existing diversity of plant raw materials and products predetermine the prospects of studying their potential as sources of pectin substances. However all current classifications are either fragmented or inconsistent.
Study objects and methods. Our theoretical ivestigation aimed to develop an adequate classification for all taxa of plant origin, as well as their tissues and derivatives as pectin-containing materials. We developed criteria for assessing transformation potential of the protopectin complex based on the mass fractions of biologically active non-uronide components, native water-soluble pectin, the protopectin complex, and pectin substances. Individual boundary conditions were based on individual pectin potential, protopectin fragmentation potential, and pectin isolation potential.
Results and discussion. Based on the boundary conditions, we defined an universal criterion space that included a set of points *M* in the coordinates expressed by three main criteria. According to individual boundary conditions, the criterion space was divided, or zoned, into four domains corresponding to protopectin fragmentation potential. They were characterized by: 1) lack of pectin potential, 2) ineffective protopectin fragmentation, 3) ineffective isolation of fragmentation products, and 4) effective isolation. Finally, we developed a generalized algorithm to determine the location of points $M[\mu_1, \mu_2, \mu_3]$ in the zoned criterion space, characterizing the plant tissue.
Conclusion. Our approach can be used to assess any plant tissue for its protopectin transformation potential, which determines the technological influence on its pectin potential. This approach is universal, i.e., applicable to both plant tissue and its derivatives.

Keywords: Protopectin complex, potential, transformation, evaluation system, criterion space

INTRODUCTION

Food technology is currently striving to maximize the potential of raw materials and use new, non-traditional sources of essential nutraceuticals and food components with biological (antioxidants, enterosorbents, etc.) and/or technological (thickeners, stabilizers, etc.) functional activity [1, 2]. The most promising way to achieve that is a biotechnological approach that makes use of both living cultures of microorganisms and isolated enzyme systems. When using isolated enzyme systems, this approach involves a multiple stage fragmentation of a native supramolecular complex of plant and/or animal cell walls into target components with a wide range of physicochemical and/or technological properties [3–5].

One of the methods within this approach is to activate the potential of a multicomponent polymer matrix of cell walls and intercellular spaces. This method has a limited use in processing agricultural raw materials. It mainly consists in partial or complete

degradation (depolymerization) of its individual components to change the consistency or transparency of the final product, or to clear it of degradation products and improve its sensory characteristics. Most certainly, a targeted use of this polymer matrix is complicated by its highly heterogeneous components, a system of bonds between them, and highly entangled polymer chains [6]. Moreover, the heterogeneity of individual matrix components is a serious obstacle to controlling their properties during extraction [7, 8].

Pectin substances are among major carbohydrate biopolymers that have a wide variety of functional and technological characteristics [9, 10]. In a plant cell, they are represented by two main fractions – native water-soluble pectin and a native water-insoluble protopectin complex. The last one is the most valuable for transformation due to its molecular structure and composition [9].

The structure of cell walls in almost all terrestrial plants makes them a potentially good resource for the industrial production of pectin [6, 11, 12]. However, it is difficult to implement. Since the protopectin complex is a branched supramolecular structure incorporated into the cell wall, its transformation is mainly fragmentation into water-soluble polymers (soluble pectin). In addition, mass fractions of pectin substances and the protopectin complex may depend on the type, grade, and purpose of raw materials, their structure and phase of development, soil and weather conditions for their vegetation, as well as localization, duration and storage conditions, processing intensity, etc. [10, 13]. In this regard, the choice of a plant as a pectin-containing material should be determined by the purpose of its use.

Raw materials can be classified according to the size of their pectin potential – "high", "medium," and "small" ("low", "insignificant") [9, 10, 14]. The only fundamental approach to pectin production was offered by Donchenko in [15] and supplemented by Rodionova *et al*. in [19, 20] (works [16–18] are actualy based on [15]). Although this approach is rather fragmented, it can be used as a basis for developing a universal system that takes into account the native pectin potential of plant tissue.

The protopectin complex is a key object whose fragmentation enables us to use the biomass of a plant material as a source of pectin substances. Due to the presence of certain plant organisms, mainly a natively soluble fraction of pectin, biomass can be attributed to potential sources of pectin. On the other hand, the biomass of certain taxonomic elements may contain a small amount of pectin, which makes its use ineffective.

Therefore, we found it relevant to develop a clear-cut classification of plant bio-resources into groups to determine the prospects of their use as pectin-containing raw materials.

In this regard, we aimed to develop a system of criteria for assessing the transformation potential of native complexes of plant carbohydrate biopolymers exemplified by pectin. To achieve this aim, we set the following objectives:

– working out criteria to assess the transformation potential of native plant biopolymers and the concept of their applicability, and

– developing a system of boundary conditions and an universal algorithm for classifying plant materials according to the transformation potential of their native pectin components.

STUDY OBJECTS AND METHODS

According to existing data, all plant materials can be classified into four main groups, namely:

– bio-resources with sufficient potential for protopectin fragmentation and subsequent isolation of its products as independent substances;

– bio-resources with sufficient potential for protopectin fragmentation, but with insufficient potential for isolation of its products;

– bio-resources with insufficient potential for protopectin fragmentation, but with sufficient potential for natively soluble pectin;

– bio-resources with no pectin potential.

On the one hand, this differentiation involves unifying plant characteristics and reducing them to certain generalized values. On the other hand, it involves dividing the domain of generalized values into four fixed zones. As we know, a universal tool for unifying an arbitrary set of source factors is a range of anonymized criteria reducible to a certain system with the use of boundary conditions [21, 22]. Thus, we can apply a criteria-based approach to fulfilling our objectives.

To be able to scale the criteria to determine clear boundary conditions, we used Harrington's individual desirability function in its canonical form [23]:

$$d_i = e^{-e^{-(b_{i0}+b_{i1}\cdot\varphi_i)}} \qquad (1)$$

where d_i is the dimensionless value of Harrington's individual desirability function; b_{i0} is the constant; b_{i1} is the coefficient; and φ_i is the dimensionless operator of Harrington's individual desirability function.

We introduced the first and second individual criteria for protopectin fragmentation potential among the main criteria to assess the native pectin potential.

Let us begin with the first criterion. According to [7, 8], the presence of pectin in the tissue or a certain amount of protopectin in the cell wall matrix is not sufficient for assessing the native pectin potential of plant tissue. The tissues of many plant organisms also contain a significant amount of organic and mineral components with valuable vitamins and antioxidant activity, pronounced aroma, micro- and macronutrient values, etc. [17]. They are also highly sensitive to active technological impact factors. During protopectin fragmentation, organic and mineral components can enter into uncontrolled interactions, resulting in a partial or complete loss of their biological potential. Therefore,

when assessing the native pectin potential, we should take into account the presence of these biologically active components among other significant factors.

Thus, we decided a complex operator as an independent variable, taking into account mass fractions of protopectin and biologically active components in the tissue:

$$\varphi_1 = \frac{\omega_{pp}}{\sum_{i=1}^{\lambda} \omega_i + \omega_{pp}} \qquad (2)$$

where ω_{pp} is the mass fraction of protopectin, mg in 100 g; ω_i is the mass fraction of the i-th biologically active component, mg/100 g; and λ is the number of biologically active components in the tissue ($\lambda \in N$).

To apply this operator in practice, we transformed it as follows:

$$\varphi_1 = \frac{1}{\dfrac{\sum_{i=1}^{\lambda} \omega_i}{\omega_{pp}} + 1} = \frac{1}{\mu_1 + 1} \qquad (3)$$

where

$$\mu_1 = \frac{\sum_{i=1}^{\lambda} \omega_i}{\omega_{pp}} \qquad (4)$$

Thus μ_1 is the first dimensionless individual criterion of protopectin fragmentation potential.

As we can see, with all possible values of ω_{pp} and $\sum_{i=1}^{\lambda} \omega_i$, this criterion has the following range of definition:

$$\mu_1 \in [0; \infty) \qquad (5)$$

In this case, Harrington's individual desirability function can be expressed as:

$$d_1 = e^{-e^{-(b_{10}+b_{11}\cdot\varphi_1)}} = e^{-e^{-\left(b_{10}+\frac{b_{11}}{\mu_1+1}\right)}} \qquad (6)$$

where d_1 is the dependent dimensionless variable; b_{10} is the empirical dimensionless constant; and b_{11} is the empirical dimensionless coefficient.

To determine the numerical values of b_{10} and b_{11}, we had to set the primary relations between the pairs $\{\mu_{11}; d_{11}\}$ and $\{\mu_{12}; d_{12}\}$, for which we proceeded from the following considerations.

If an i-th biologically active component has a specific measure of value p_i, the total measure of value for all biologically active components under consideration is:

$$v_{bac} = \sum_{i=1}^{\lambda} m_i \cdot p_i = \frac{m}{100} \cdot \sum_{i=1}^{\lambda} \omega_i \cdot p_i \qquad (7)$$

where v_{bac} is the total measure of value for all biologically active components, units; m_i is the mass of the i-th component, mg/100 g of plant tissue; m is the tissue mass, mg; p_i is the specific measure of value of the i-th component, units/mg; and ω_i is the mass fraction of the i-th component in the plant tissue, %.

If specific measures of value for the components are expressed through some average specific measure of value

$$p_{av} = \frac{\sum_{i=1}^{\lambda} m_i \cdot p_i}{\sum_{i=1}^{\lambda} m_i} \qquad (8)$$

then formula (7) looks as follows:

$$v_{bac} = \frac{m}{100} \cdot \sum_{i=1}^{\lambda} \omega_i \cdot p_{av} = \frac{m \cdot p_{av}}{100} \cdot \sum_{i=1}^{\lambda} \omega_i \qquad (9)$$

from which

$$\sum_{i=1}^{\lambda} \omega_i = \frac{v_{bac} \cdot 100}{p_{av} \cdot m} \qquad (10)$$

If we apply similar considerations to protopectin, then:

$$v_{pp} = m_{pp} \cdot p_{pp} = \frac{m \cdot \omega_{pp}}{100} \cdot p_{pp} \qquad (11)$$

where v_{pp} is the total measure of protopectin value, units; m_{pp} if the mass of protopectin in the tissue, mg; p_{pp} is the specific measure of protopectin value, units/mg; and ω_{pp} is the mass fraction of the i-th component in the plant tissue, %.

From Eq. (11), it follows that

$$\omega_{pp} = \frac{v_{pp} \cdot 100}{p_{pp} \cdot m} \qquad (12)$$

Thus, formula (4) can be presented as:

$$\mu_1 = \frac{v_{bac} \cdot p_{pp}}{v_{pp} \cdot p_{av}} \qquad (13)$$

Grouping similar values on its sides, formula (13) can be transformed as:

$$\frac{v_{bac}}{v_{pp}} = \frac{\mu_1 \cdot p_{av}}{p_{pp}} \qquad (14)$$

Respectively, if $\dfrac{v_{bac}}{v_{pp}} > 1$, protopectin fragmentation makes no sense, even with its significant amount in the tissue. Therefore, a prerequisite for protopectin fragmentation is:

$$\mu_1 \leq \frac{p_{pp}}{p_{av}} \qquad (15)$$

If p_{av} is expressed as $\overline{p}_{av}$ – in fractions of p_{pp}, – then condition (15) looks as follows:

$$\mu_1 \leq \overline{p}_{av}^{-1} \qquad (16)$$

When calculating $\overline{p}_{av}$, it is advisable to use $\overline{p}_i$ rather than p_i, its value reduced to p_{pp}:

$$\overline{p}_{av} = \frac{p_{av}}{p_{pp}} = \frac{\sum_{i=1}^{\lambda} m_i \cdot \overline{p}_i}{\sum_{i=1}^{\lambda} m_i} \qquad (17)$$

Theoretically, $\overline{p}_i$ can be determined using several approaches. However, we believe that the most appropriate approach is based on a daily human need for individual nutrients. This approach is least opportunistic (compared to the financial approach) and subjective (compared to direct expert assessments). Naturally, daily

Table 1 Specific measures of value for biologically active components and pectin in 100 g of plant tissue

Component	Recommended daily requirement, units	Estimated daily requirement		Specific measure of value, mg^{-1}	
		mg	mg/kg	p_i	$\bar{p}_i$
1	2	3	4	5	6
Protein, g			800.00[III]		
Amino acids, mg/kg[III]					
– essential amino acids:					
histidine			14	0.071428571	2.198
isoleucine			19	0.052631579	1.619
leucine			42	0.023809524	0.733
lysine			38	0.026315789	0.81
methionine			13.16[I]	0.075987842	2.338
phenylalanine + tyrosine			27	0.037037037	1.14
threonine			16	0.0625	1.923
tryptophan			4	0.25	7.692
valine			19	0.052631579	1.619
cysteine			5.84[I]	0.171232877	5.269
– non-essential amino acids			514.15[II]	0.001944958	0.06
– other amino acids			87.85[IV]	0.011383039	0.35
Lipids, g[V]	69.9	69 900	1 075.38		
– saturated fatty acids	21.2	21 200	326.15	0.003066074	0.094
– monounsaturated fatty acids	25.4	25 400	390.77	0.00255905	0.079
– polyunsaturated fatty acids	23.3	23 300	358.46	0.002789712	0.086
Digestible carbohydrates, g[VI]	275	275 000	4 230.77	0.000236364	0.007
Pectin, g[VII]	2	2 000	30.77	0.0325 [X]	1
Minerals[VIII]					
– Ca, mg	1 000	1 000	15.38462	0.064999981	2
– Mg, mg	400	400	6.15385	0.162499898	5
– K, mg	2 500	2 500	38.46154	0.025999999	0.8
– Na, mg	1 300	1 300	20	0.05	1.538
– P, mg	800	800	12.30769	0.081250015	2.5
– Cl, mg	2 300	2 300	35.38462	0.028260866	0.87
– Fe, mg	14.4	14.4	0.22154	4.513857543	138.888
– Zn, mg	12	12	0.18462	5.416531253	166.663
– J, µg	150	0.15	0.00231	432.9004329	13 320.013
– Cu, mg	1	1	0.01538	65.01950585	2 000.6
– Mn, mg	2	2	0.03077	32.49918752	999.975
– Se, µg	63	0.063	0.00097	1 030.927835	31 720.856
– Cr, µg	50	0.05	0.00077	1 298.701299	39 960.04
– Mo, µg	70	0.07	0.00108	925.9259259	28 490.028
– Co, µg	10	0.01	0.00015	6 666.666667	205 128.205
– Si, mg	30	30	0.46154	2.166659444	66.666
– F, mg	4	4	0.06154	16.24959376	499.988
Vitamins and provitamin [IX]					
– water soluble					
ascorbic acid (vitamin C), mg	90	90	1.38462	0.722219815	22.222
thiamine (vitamin B$_1$), mg	1.5	1.5	0.02308	43.32755633	1 333.156
riboflavin (vitamin B$_2$), mg	1.8	1.8	0.02769	36.11412062	1 111.204
vitamin B$_6$, mg	2	2	0.03077	32.49918752	999.975
vitamin B$_{12}$, µg	3	0.003	0.00005	20000	615 384.615
niacin, mg	20	20	0.30769	3.250024375	100.001
pantothenic acid, mg	5	5	0.07692	13.00052002	400.016
biotin, µg	50	0.05	0.00077	1298.701299	39 960.04
folic acid and folates, µg	400	0.4	0.00615	162.601626	5 003.127
– fat soluble					
carotenoids, mg	5	5	0.07692	13.00052002	400.016
vitamin D, µg	10	0.01	0.00015	6 666.666667	205 128.205

Continuation of the table 1

1	2	3	4	5	6
vitamin E, mg	15	15	0.23077	4.333318889	133.333
vitamin K, µg	120	0.12	0.00185	540.5405405	16 632.017
– pseudo-vitamins					
inositol, mg	500	500	7.69231	0.129999961	4
L-carnitine, mg	300	300	4.61538	0.216666883	6.667
coenzyme Q10 (ubiquinone), mg	30	30	0.46154	2.166659444	66.666
lipoic acid, mg	30	30	0.46154	2.166659444	66.666
vitamin U, mg	20	20	0.30769	3.250024375	100.001
orotic acid (B13), mg	30	30	0.46154	2.166659444	66.666
paraminobenzoic acid, mg	100	100	1.53846	0.65000065	20
choline, mg	500	500	7.69231	0.129999961	4
Flavonoids, mg[VIII]	250	250	3.84615	0.26000026	8

I – according to [24] and the ratio in [25]
II – according to the ratio between essential and non-essential amino acids in [25]
III – according to the recommended dietary allowance in [24]
IV – the value is a difference between the daily requirement for protein and the sum of essential and non-essential amino acids
V – according to [24] and [26], based on a daily energy requirement of 2000 kcal
VI – according to [27] and [28]
VII – according to [18]
VIII – according to [28]
IX – according to [28] and [29, 30]
X – the value corresponds to p_{ps}

requirements for certain components depend on our knowledge of biochemical processes in the human body, as well as on the constantly changing environmental situation in the world [24]. However, these factors should not significantly affect $\overline{p}_{av}$.

The value of $\overline{p}_{av}$ was calculated in several stages.

At the *first* stage, we determined daily requirements for each of the biologically active components (u_i) and pectin (u_{ps}) based on a daily energy requirement of 2000 kcal and an average body weight of 65 kg. The differences in daily requirements for men and women were averaged. For comparability, all the values were presented in mg/kg of body weight.

At the *second* stage, we calculated specific measures of value for biologically active components (p_i) and pectin (p_{ps}):

$$p_i = u_i^{-1} \qquad (18)$$
$$p_{ps} = u_{ps}^{-1} \qquad (19)$$

The specific measures of value for pectin p_{ps} and protopectin p_{pp} were numerically identical since protopectin is only valuable for the human body in the form of its fragmentation products. To simplify, we assumed that processing resulted in all protopectin fragmented in a targeted manner (i.e., into fragments that could be identified as pectin).

At the *third* stage, we determined specific measures of value in the fractions of the specific measure of pectin values $\overline{p}_i$.

The calculation results are shown in Table 1.

At the *fourth* stage, we calculated the value of $\overline{p}_{av}^{-1}$ (Table 2). Based on the data in [31], we determined the content of biologically active components in 100 g of tissue for 21 types of plant materials from the classification presented in [16]. For each type of raw

material, formula (17) was used to calculate the values of $\overline{p}_{av\,(j)}$ and $\overline{p}_{av\,(j)}^{-1}$, where $j \in$ N.

Some assumptions were made in the calculations. For example, the mass fractions of the components which were not available in the database were assumed as equal to zero [31]. The amount of carotenoids was calculated based on the biological potential of each type of raw material as $m_{car} = m_{\beta-car} + \frac{1}{2} \cdot \sum_{i=1}^{n} m_{i\,(o.c)}$, where $m_{\beta-car}$ is the mass fraction of β-carotene, mg/100 g; $\sum_{i=1}^{n} m_{i\,(o.c)}$ is the sum of mass fractions of other carotenoids, mg/100 g [24]. The amount of tocopherols was also calculated taking into account the biological potential of each type of raw material as $m_{tok} = m_{\alpha-toc} + \frac{1}{10} \cdot m_{\gamma-toc}$, where $m_{\alpha-toc}$ and $m_{\gamma-toc}$ are the mass fractions of α- and γ-tocopherols, respectively; mg/100 g [24]. To determine the sum of the remaining amino acids, we subtracted the mass fractions of essential and non-essential amino acids from the mass fraction of protein.

The calculation results are shown in Table 2.

Since $\overline{p}_{av(j)}^{-1}$ values were significantly different for different types of raw materials, we calculated the average $\overline{p}_{av(av)}^{-1}$ and the margin of error Δ to determine boundary values (μ_{11} and μ_{12}):

$$\overline{p}_{av\,(av)}^{-1} = \frac{\sum_{j=1}^{\zeta} \overline{p}_{av\,(j)}^{-1}}{\zeta} \qquad (20)$$

$$\Delta = t_{(\alpha;\,\zeta-1)} \cdot \sqrt{\frac{\sum_{j=1}^{\zeta} \left(\overline{p}_{av\,(j)}^{-1} - \overline{p}_{av\,(av)}^{-1} \right)^2}{\zeta \cdot (\zeta-1)}} \qquad (21)$$

where ζ is the number of raw material types; $t_{(\alpha;\,\zeta-1)}$ is Student's t-test; and α is the probability of error (0.05).

Based on the above, the value of μ_{11} for the first pair $\{\mu_{11}; d_{11}\}$ was calculated as:

Table 2 Weighted average reduced measures of raw materials value in non-uronide biologically active components

Raw materials	$\overline{p}_{av(j)}$	$\overline{p}^{-1}_{av(j)}$	Raw materials			$\overline{p}_{av(j)}$	$\overline{p}^{-1}_{av(j)}$
Carrot	0.8282	1.207	Persimmon			0.0887	11.274
Beetroot	0.4156	2.406	Grapefruit			0.2355	4.246
Watermelon	0.2860	3.497	Lemon	with skin		0.6618	1,511
Pumpkin	0.6578	1.520		without skin		0.3057	3,271
Melon	0.1749	5.718	Orange			0.2729	3.664
Apples	0.0783	12.771	Tangerine			0.1691	5.914
Quince	0.0993	10.070	Currants	red		0.2654	3,768
Pears	0.0889	11.249		black		0.4389	2,278
Figs	0.1137	8.795	Cranberry			0.3147	3.178
Pomegranate	0.1671	5.984	Gooseberry			0.2935	3.407
Grapes	0.1057	9.461	Feijoa			0.2074	4.822

$$\mu_{11} = \overline{p}^{-1}_{av(av)} - \Delta \qquad (22)$$

The value of μ_{12} for the second pair $\{\mu_{12}; d_{12}\}$ was calculated as the second order of μ_{11}:

$$\mu_{12} = \left(\overline{p}^{-1}_{av(av)} - \Delta\right)^2 \qquad (23)$$

The critical (boundary) values of μ_1 were based on the analysis of Harrington's desirability function, using μ_{11} and μ_{12} as reference values. Since they are preset, the calculated values were rounded to the nearest whole number.

Despite the rigor of expression (16), its right-hand side is an empirical value based on the chemical composition of a finite number of plant raw materials and, therefore, it cannot be considered *a priori*. To make up for this feature, we further determined the critical values of μ_1 on the basis of Harrington's desirability function, using μ_{11} and μ_{12} as reference values.

Since a smaller reference value corresponded to a larger value of Harrington's individual desirability function, we defined a condition $Cond_{d_1}$ that determined the individual form of the function as:

$$Cond_{d_1} = \left[\frac{d_{11}}{\mu_{11}} :\Leftrightarrow \frac{0.60}{3}; \frac{d_{12}}{\mu_{12}} :\Leftrightarrow \frac{0.40}{10}\right] \qquad (24)$$

Based on $Cond_{d_1}$, we calculated the values of the constant and the coefficient: $b_{10} = -0.246$; $b_{11} = 3.673$.

The critical values of the first criterion for the protopectin fragmentation potential at the points with standard critical values of the desirability function can be calculated using Eq. (6) with the variable μ_1:

$$\mu_1[D_i] = -1 - \frac{b_{11}}{b_{10} + \ln\left[-\ln\left(d_{1i}\right)\right]} \qquad (25)$$

where $\mu_1[D_i]$ is the value of the criterion μ_1 at the critical
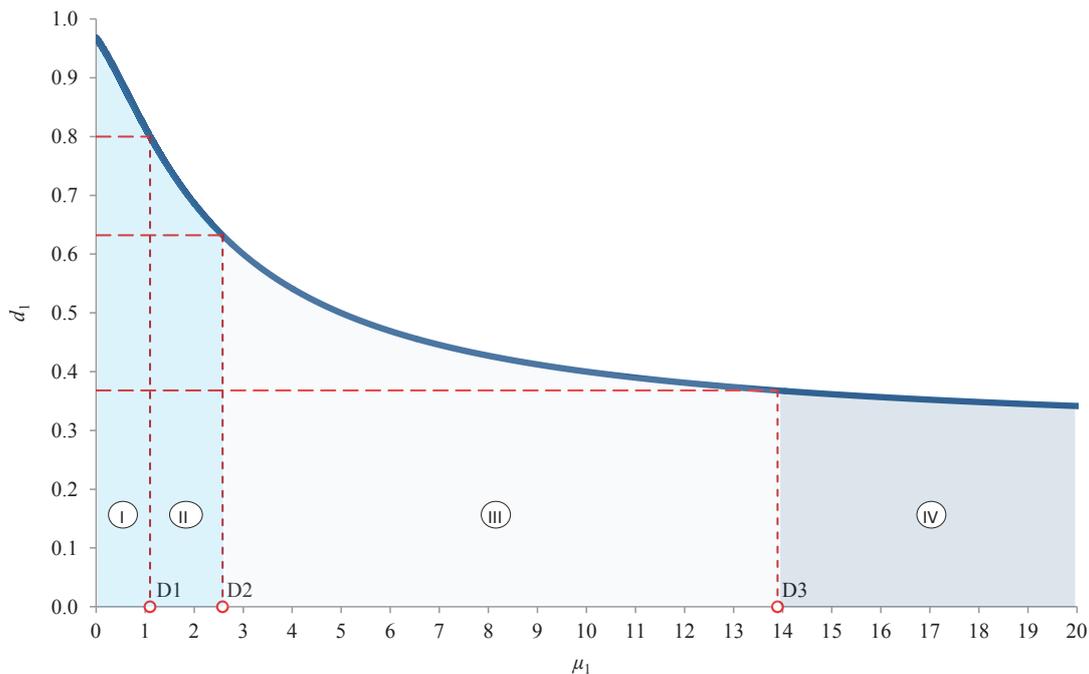
Figure 1 Graphic interpretation of Harrington's individual desirability function given condition $Cond_{d_1}$ and variable μ_1

point D_i of Harrington's individual desirability function determined by Eq. (6) and corresponding to d_{1i}; and d_{1i} is the standard i-th critical (canonical) value d_1 of Harrington's individual desirability function.

The graphic interpretation of Harrington's individual desirability function corresponding to the condition $Cond_{d_1}$ is given in Fig. 1. For each value of d_{1i}, we determined the corresponding values of $\mu_1[D_i]$.

As we can see, the μ_1 range of definition includes four domains separated by the critical values of $\mu_1[D_i]$, where $i = 1, 2, 3$. By definition, domain IV includes those μ_1 values at which the fragmentation of the protopectin complex makes no sense due to a low value of the individual function of desirability.

Domain III covers those μ_1 values at which the individual desirability function is large enough for protopectin fragmentation to make sense, but insufficiently large to neglect non-uronide bioactive components and isolate the products of fragmentation.

In domains I and II, the individual desirability function is so large that the content of non-uronide bioactive components in plant tissue can be completely ignored.

Based on the physical meaning of the boundary conditions for μ_1, we established two individual boundary conditions that partially determined the native pectin potential of plant tissue.

Boundary condition I:
− $\mu_1 > \mu_1[D_3]$ means the absence of the first individual potential for protopectin fragmentation;
− $\mu_1 \leq \mu_1[D_3]$ means the presence of the first individual potential for protopectin fragmentation.

Boundary condition II:
− $\mu_1[D_3] \geq \mu_1 > \mu_1[D_2]$ means the absence of the first individual potential for isolation of protopectin fragmentation products;

− $\mu_1 \leq \mu_1[D_2]$ means the presence of the first individual potential for isolation of protopectin fragmentation products.

Next, we determined the structure and properties of the second dimensionless individual criterion for the protopectin fragmentation potential.

The second independent variable was a complex operator based on the mass fraction of protopectin in the tissue:

$$\varphi_2 = \frac{\omega_{pp}}{100} = \mu_2 \qquad (26)$$

where φ_2 is the dimensionless operator of Harrington's individual desirability function; and μ_2 is the second dimensionless individual criterion for the protopectin fragmentation potential.

Harrington's individual desirability function was expressed as:

$$d_2 = e^{-e^{-(b_{20}+b_{21}\cdot\varphi_2)}} = e^{-e^{-(b_{20}+b_{21}\cdot\mu_2)}} \qquad (27)$$

Thus, the condition $Cond_{d_2}$ that determined the individual function was set as:

$$Cond_{d_2} = \left[\frac{d_{21}}{\mu_{21}} :\Leftrightarrow \frac{0.35}{0.001}; \frac{d_{22}}{\mu_{22}} :\Leftrightarrow \frac{0.65}{0.05}\right] \qquad (28)$$

Based on $Cond_{d_2}$, we calculated the values of the constant and the coefficient: $b_{20} = -6.68\times10^{-2}$ and $b_{21} = 18.179$. The critical values of the μ_2 criterion were calculated as:

$$\mu_2[D_i] = -\frac{b_{20} + \ln\left[-\ln\left(d_{2i}\right)\right]}{b_{21}} \qquad (29)$$

where $\mu_2[D_i]$ is the value of μ_2 at the critical point D_i of Harrington's individual desirability function calculated by Eq. (6) and corresponding to d_{2i}; d_{2i} is the standard i-th critical (canonical) value d_2 of Harrington's individual desirability function.
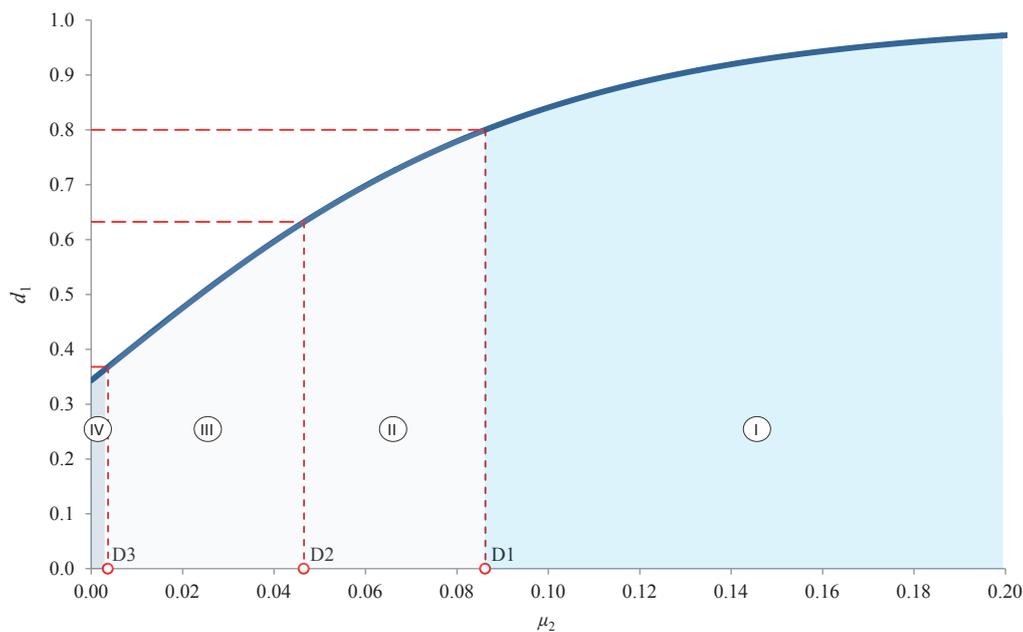
Figure 2 Graphic interpretation of Harrington's individual desirability function given condition $Cond_{d_2}$ and variable μ_2

The graphic interpretation of Harrington's individual desirability function corresponding to the condition $Cond_{d_2}$ is presented in Fig. 2. For each value of d_{2i}, we calculated the corresponding values of $\mu_2[D_i]$.

Just like with μ_1, the μ_2 range of definition includes four domains separated by the critical values of $\mu_2[D_i]$, where $i = 1, 2, 3$.

By definition, domain IV covers those values of μ_2 at which the fragmentation of the protopectin complex makes no sense. This led us to formulate the third individual boundary condition:

– $\mu_2 < \mu_2[D_3]$ means the absence of the second individual potential for protopectin fragmentation;

– $\mu_2 \geq \mu_2[D_3]$ means the presence of the second individual potential for protopectin fragmentation.

We should note that fragmentation potentials I and II are categorical, i.e., if one of them is absent, the total fragmentation potential is absent as well.

Domains I, II, and III include such values of μ_2 that ensure not only protopectin fragmentation, but also the isolation of fragmentation products. Based on the canonical reference values of the individual desirability function, we formulated the fourth boundary condition:

– $\mu_2[D_3] \leq \mu_2 < \mu_2[D_1]$ means the absence of the second individual potential for isolation of protopectin fragmentation products;

– $\mu_2 \geq \mu_2[D_1]$ means the presence of the second individual potential for isolation of protopectin fragmentation products.

Similar to the first and the second fragmentation potentials, the individual isolation potentials are categorical.

The third independent variable was a complex operator based on the mass fraction of pectin substances in the tissue:

$$\varphi_3 = \frac{\omega_{ps}}{100} = \mu_3 \qquad (30)$$

where φ_3 is the dimensionless operator of Harrington's individual desirability function; ω_{ps} is the total amount of pectin substances, %; and μ_3 is the third dimensionless individual criterion for the protopectin fragmentation potential.

In this case, the condition $Cond_{d_3}$ that determined the individual function was calculated as:

$$Cond_{d_3} = \left[\frac{d_{31}}{\mu_{31}} :\Leftrightarrow \frac{0.40}{0.01}; \frac{d_{32}}{\mu_{32}} :\Leftrightarrow \frac{0.65}{0.07} \right] \qquad (31)$$

Based on expression (31), we calculated the constant and the coefficient as $b_{30} = -3.8367 \times 10^{-2}$ and $b_{31} = 12.5788$, respectively, and the critical boundaries of μ_3, as:

$$\mu_3[D_i] = -\frac{b_{30} + \ln\left[-\ln\left(d_{3i}\right)\right]}{b_{31}} \qquad (32)$$

where $\mu_3[D_i]$ is the value of μ_3 at the critical point D_i of Harrington's individual desirability function calculated by (6) and corresponding to d_{3i}; and d_{3i} is the standard i-th critical (canonical) value d_3 of Harrington's individual desirability function.

Figure 3 shows the graphic interpretation of Harrington's individual desirability function given $Cond_{d_3}$. For each value of d_{3i}, we calculated the corresponding values of $\mu_3[D_i]$.

Here, we can clearly see domain IV with no pectin potential in the plant tissue.

As a result, we formulated the fifth individual boundary condition:

– $\mu_3 < \mu_3[D_3]$ means the absence of pectin potential;

– $\mu_3 \geq \mu_3[D_3]$ means the presence of pectin potential.

Thus, the pectin potential is categorical.

The fourth independent variable was a complex operator based on the ratio of the mass fractions of protopectin and pectin substances in the tissue:

$$\varphi_4 = \frac{\omega_{pp}}{\omega_{ps}} = \frac{1}{\mu_4 + 1} \qquad (33)$$

where φ_4 is the dimensionless operator of Harrington's individual desirability function; ω_{sp} is the mass fraction of natively soluble pectin substances, %; and μ_4 is the third dimensionless individual criterion for the protopectin fragmentation potential calculated as:

$$\mu_4 = \frac{\omega_{sp}}{\omega_{pp}} \qquad (34)$$

Then, the condition $Cond_{d_4}$, which determined the individual function, was calculated as:

$$Cond_{d_4} = \left[\frac{d_{41}}{\mu_{41}} :\Leftrightarrow \frac{0.65}{2.50}; \frac{d_{42}}{\mu_{42}} :\Leftrightarrow \frac{0.80}{1.25} \right] \qquad (35)$$

Based on expression (35), we calculated the constant and the coefficient ($b_{40} = -0.3419$, $b_{41} = 4.1441$).

Based on $Cond_{d_4}$, the critical boundaries of μ_4 were calculated as:

$$\mu_4[D_i] = -1 - \frac{b_{41}}{b_{40} + \ln\left[-\ln\left(d_{4i}\right)\right]} \qquad (36)$$

where $\mu_4[D_i]$ is the value of μ_4 at the critical point D_i of Harrington's individual desirability function calculated by (6) and corresponding to d_{4i}; and d_{4i} is the standard i-th critical (canonical) value d_4 of Harrington's individual desirability function.

Figure 4 shows the graphic interpretation of Harrington's individual desirability function given $Cond_{d_4}$, with d_{4i} values corresponding to $\mu_4[D_i]$ values.

Based on the logical content of d_{4i} and the numerical values of $\mu_4[D_i]$, the range of definition can be divided into four domains that determine the fragmentation potential of the protopectin complex and the isolation potential of fragmentation products.

According to Fig. 4, domain IV covers those values μ_4 at which the mass fraction of water-soluble pectin exceeds that of the protopectin complex so much that there is practically no reason for its individual fragmentation. Thus, we determined the sixth boundary condition as follows:

– $\mu_4 > \mu_4[D_3]$ means the absence of the third individual potential for protopectin fragmentation;

– $\mu_4 \leq \mu_4[D_3]$ means the presence of the third individual potential for protopectin fragmentation.
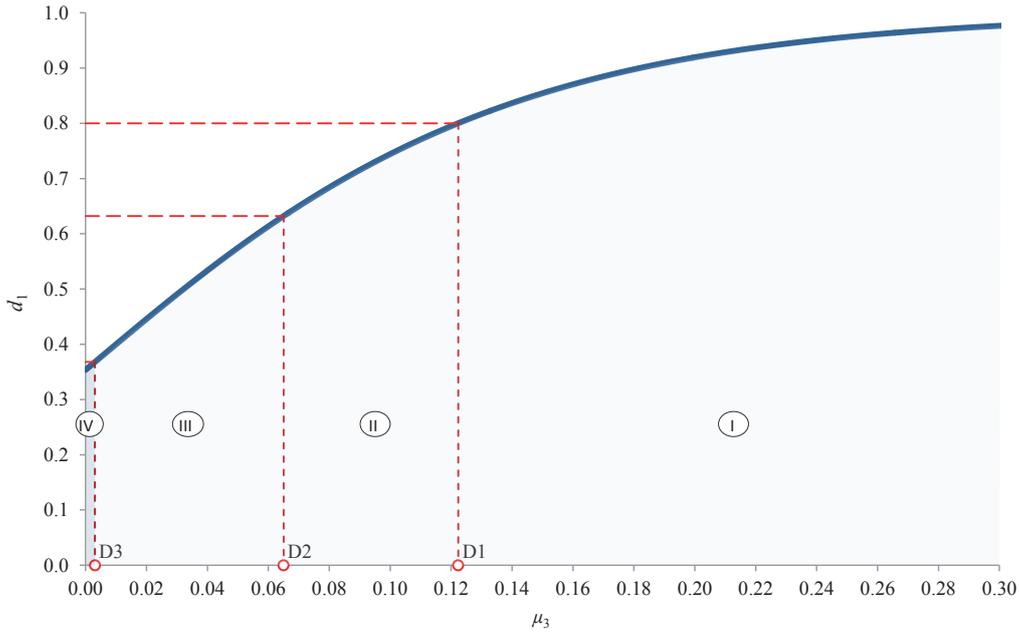
Figure 3 Graphic interpretation of Harrington's individual desirability function given condition $Cond_{d_3}$ and variable μ_3
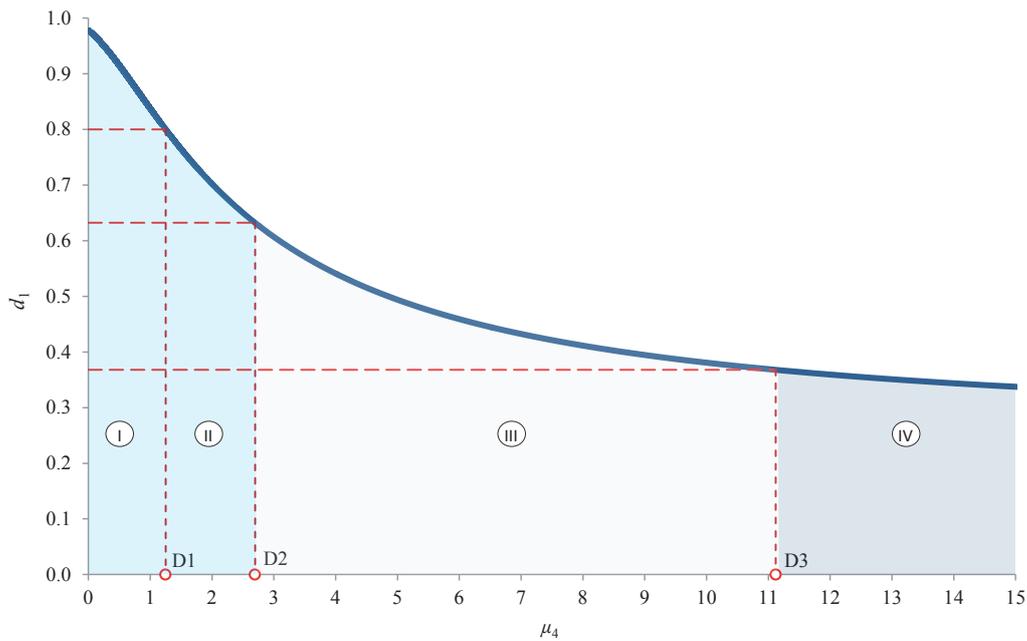
Figure 4 Graphic interpretation of Harrington's individual desirability function given condition $Cond_{d_4}$ and variable μ_4

Following the same pattern, we determined the seventh boundary condition (VII), namely:

– $\mu_4[D_2] < \mu_4 \leq \mu_4[D_3]$ means the absence of the third individual potential for isolation of protopectin fragmentation products;

– $\mu_4 \leq \mu_4[D_1]$ means the presence of the third individual potential for isolation of protopectin fragmentation products.

In addition, boundary conditions VI and VII are based on:

$$\mu_4 \leq \mu_4[D_i] \qquad (37)$$

where $i = 3$ for condition VI and, $i = 2$ for condition VII.

However, μ_4 can be expressed as:

$$\mu_4 = \frac{\omega_{sp}}{\omega_{pp}} = \frac{\omega_{ps} - \omega_{pp}}{\omega_{pp}} = \frac{\mu_3 - \mu_2}{\mu_2} \qquad (38)$$

Then, given the presence of the third individual fragmentation potential:

$$\mu_3 \leq \mu_2 \cdot (\mu_4[D_i] + 1) \qquad (39)$$

Thus, the third individual potentials of fragmentation and isolation are relative since they are involved in the formation of respective total potentials indirectly,

through expressions in which they act as one of the variables.

If we assume that there is a certain criterion space with coordinates μ_1, μ_2 and μ_3, the pectin potential of any plant material can be clearly determined as a geometrical location of the point $M[\mu_1, \mu_2, \mu_3]$ corresponding to the material under analysis.

Based on the *a priori* assumption that

$$\omega_{ps} + \sum\nolimits_{i=1}^{\lambda} \omega_i \leq 100 \qquad (40)$$

we can establish the eighth boundary condition (VIII): the top boundary of the range of definition for all possible values of $M[\mu_1, \mu_2, \mu_3]$ is determined by the following basic proposition:

$$\mu_{3(top)} = 1 - \mu_1 \cdot \mu_2 \qquad (41)$$

In addition, since a part cannot be larger than a whole, it is also true that:

$$\omega_{pp} \leq \omega_{ps} \qquad (42)$$

which leads to the following condition:

$$\mu_3 \geq \mu_2 \qquad (43)$$

i.e., the bottom boundary of the range of definition for all possible values of $M[\mu_1, \mu_2, \mu_3]$ is determined by the second basic proposition:

$$\mu_{3(bot)} = \mu_2 \qquad (44)$$

The last formula is an expression of boundary condition IX.

RESULTS AND DISCUSSION

Thus, according to boundary conditions VIII and IX, a set (A) of all points $M[\mu_1, \mu_2, \mu_3]$ can be defined as

$$M[\mu_1, \mu_2, \mu_3] \in [\mu_{3(bot)}, \mu_{3(top)}]\big|_{\mu_1 \geq 0;\, \mu_2 \geq 0;\, \mu_3 \geq 0}, \quad (45)$$

graphically presented in Fig. 5.

The logic of assessing plant bioresources for the presence of pectin substances determines general boundary conditions for defining a set of points $M[\mu_1, \mu_2, \mu_3]$ as the following hierarchy: "individual pectin potential → individual fragmentation potential of the protopectin complex → individual isolation potential of protopectin fragmentation products". Thus, the entire set of points $M[\mu_1, \mu_2, \mu_3]$ can be divided into four subsets:

– subset A_1 characterized by the absence of a common pectin potential in all the elements;

– subset A_2 where $A_2 \cap A_1 = \varnothing$ and all the elements have a common pectin potential, but lack a common potential for protopectin fragmentation;

– subset A_3 where $A_3 \cap A_2 = \varnothing$ and all the elements have common pectin and protopectin fragmentation potentials, but lack a common isolation potential for fragmentation products; and

– subset A_4 where $A_4 \cap A_3 = \varnothing$ and all elements have common pectin and protopectin fragmentation

potentials, as well as isolation potential for fragmentation products.

By definition, the following is true for all the subsets:

$$A_1 \cap A_2 \cap A_3 \cap A_4 = \varnothing \qquad (46)$$

Based on the above, the existence of A_1 corresponds to:

$$\mu_2 \leq \mu_3 < \mu_3[D_3] \qquad (47)$$

The area of definition for all A_1 elements is partially presented in Fig. 6.

The existence of subset A_2 corresponds to:

$$1 - \mu_1 \cdot \mu_2 \geq \mu_3 \geq$$
$$\geq \begin{cases} \begin{cases} \mu_2 \cdot (\mu_4[D_3]+1), & \mu_2 \geq \mu_2[D_3] \\ \mu_3[D_3], & \mu_2 < \mu_2[D_3] \end{cases} \bigg| \mu_1 \leq \mu_1[D_3] \\ \begin{cases} \mu_2, & \mu_2 \geq \mu_3[D_3] \\ \mu_3[D_3], & \mu_2 < \mu_3[D_3] \end{cases} \bigg| \mu_1 > \mu_1[D_3] \end{cases} \qquad (48)$$

Figure 7 shows a partial area of definition for all A_2 elements.

The existence of A_3 corresponds to:

$$\begin{cases} 1 - \mu_1 \cdot \mu_2 & \bigg| \mu_1 \leq \mu_1[D_3] \\ \mu_2 \cdot (\mu_4[D_3]+1) & \bigg| \mu_2 \geq \mu_2[D_3] \end{cases} > \mu_3 \geq$$
$$\geq \begin{cases} \mu_2 \cdot (\mu_4[D_2]+1) & \bigg| \begin{matrix} \mu_1 \leq \mu_1[D_2] \\ \mu_2 \geq \mu_2[D_1] \end{matrix} \\ \mu_2 & \bigg| \begin{matrix} \mu_1[D_3] \geq \mu_1 > \mu_1[D_2] \\ \mu_2[D_3] \leq \mu_2 < \mu_2[D_1] \end{matrix} \end{cases} \qquad (49)$$

Figure 8 presents the area of definition for all A_3 elements.

The existence of subset A_4 corresponds to:

$$\begin{cases} \begin{cases} 1 - \mu_1 \cdot \mu_2 \\ \mu_2 \cdot (\mu_4[D_2]+1) \end{cases} > \mu_3 \geq \mu_2 \end{cases} \bigg| \begin{matrix} \mu_1 \leq \mu_1[D_2] \\ \mu_2 \geq \mu_2[D_1] \end{matrix} \qquad (50)$$

The area of definition for all A_4 elements is presented in Fig. 9.

Thus, the specific value $M[\mu_1, \mu_2, \mu_3]$ that shows its belonging to one of the subsets A_i (where $i = 1, 2, 3, 4$) in the zoned criterion space clearly determines the plant tissue's overall potential for protopectin fragmentation.

Our approach to classifying plants as pectin-containing materials, which is based on a system of criteria and a zoned criterion space, has clear advantages over existing methods due to its objectivity determined by the boundary conditions.

However, when analyzing this approach, we can easily see that the μ_{j1} and μ_{j2} values corresponding to d_{j1} and d_{j2} in the conditions $Cond_{d_j}\big|_{j=2,3,4}$ were set *a priori*, based on general assumptions regarding the degree of acceptability of certain μ_j values within Harrington's individual desirability functions in accordance with the boundary (canonical) values of d. Yet, the conditions $Cond_{d_j}\big|_{j=2,3,4}$ determine the coefficients and constants, and, consequently, individual desirability
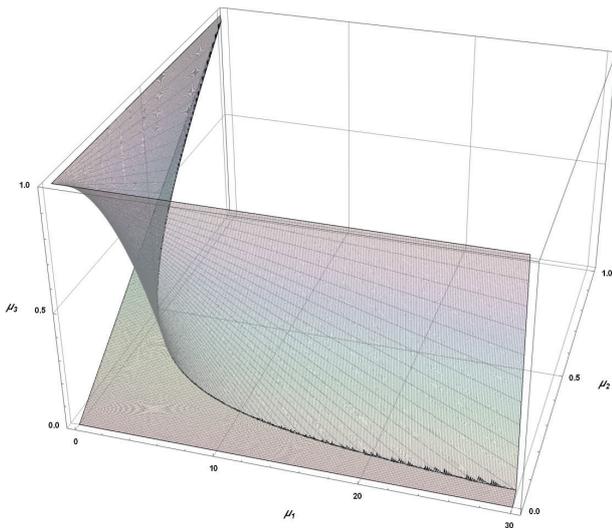
Figure 5 Definition area of the criterion space
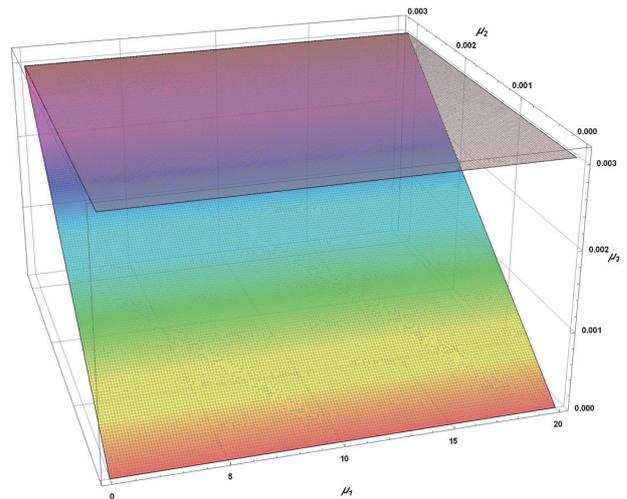
Figure 6 Partial definition area for subset A$_1$
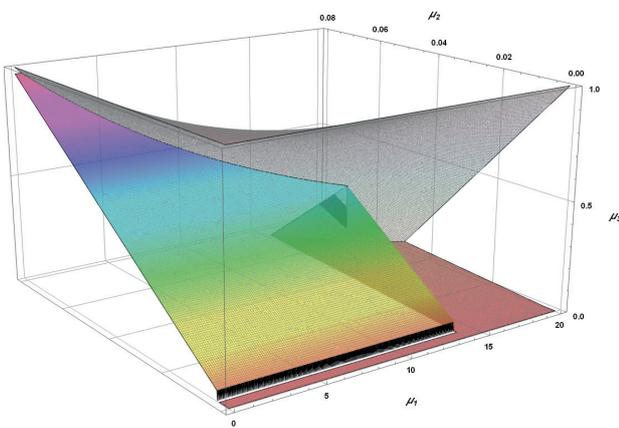
Figure 7 Partial definition area for subset A_2
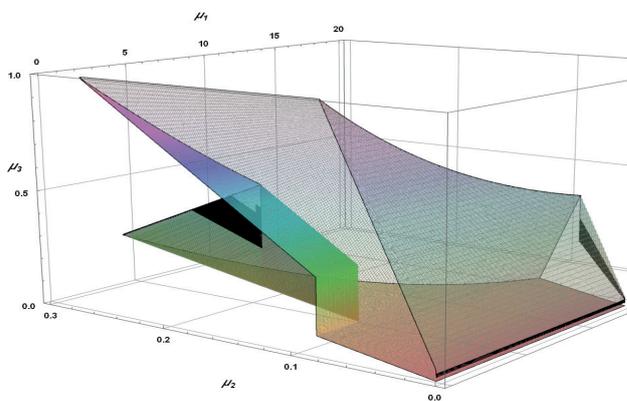
Figure 8 Partial definition area for subset A_3

functions, as well as numerical values of $\mu_j[D_i]$. Therefore, at this stage, our approach has a general, conceptual form requiring further research.

Based on the results, we developed a generalized algorithm to determine the geometric location of plant tissue in the zoned criterion space, or $M[\mu_1, \mu_2, \mu_3]$ belonging to one of the subsets (Fig. 10). We can use this algorithm to assess any plant tissue's potential for transformation of the protopectin complex, which determines the influence of any technological impact on its pectin potential.

The approach that we used to determine the criterion space and boundary conditions for its zoning explicitly suggests that this algorithm is universal for classifying plant tissue or its derivatives as pectin-containing materials. Thus, the algorithm is applicable to any type of plant material for which the μ_1, μ_2 and μ_3 criteria can be numerically expressed.

CONCLUSION

To sum up, our investigation showed the following results.
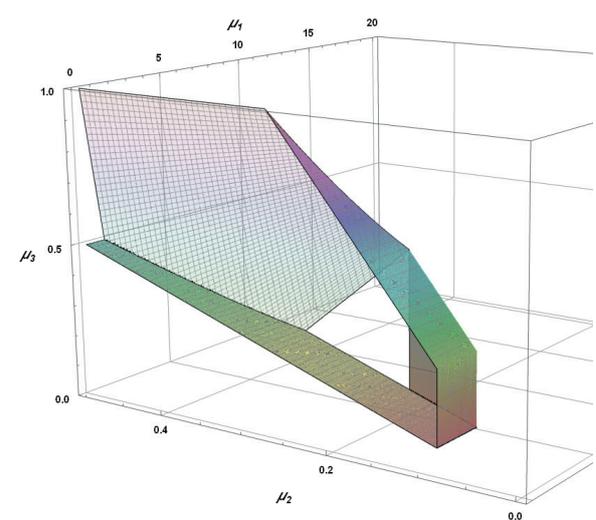
Figure 9 Partial definition area for subset A_4

1. We developed a system of criteria to assess the transformation potential of the protopectin complex in plant tissue. This system is based on the geometrical
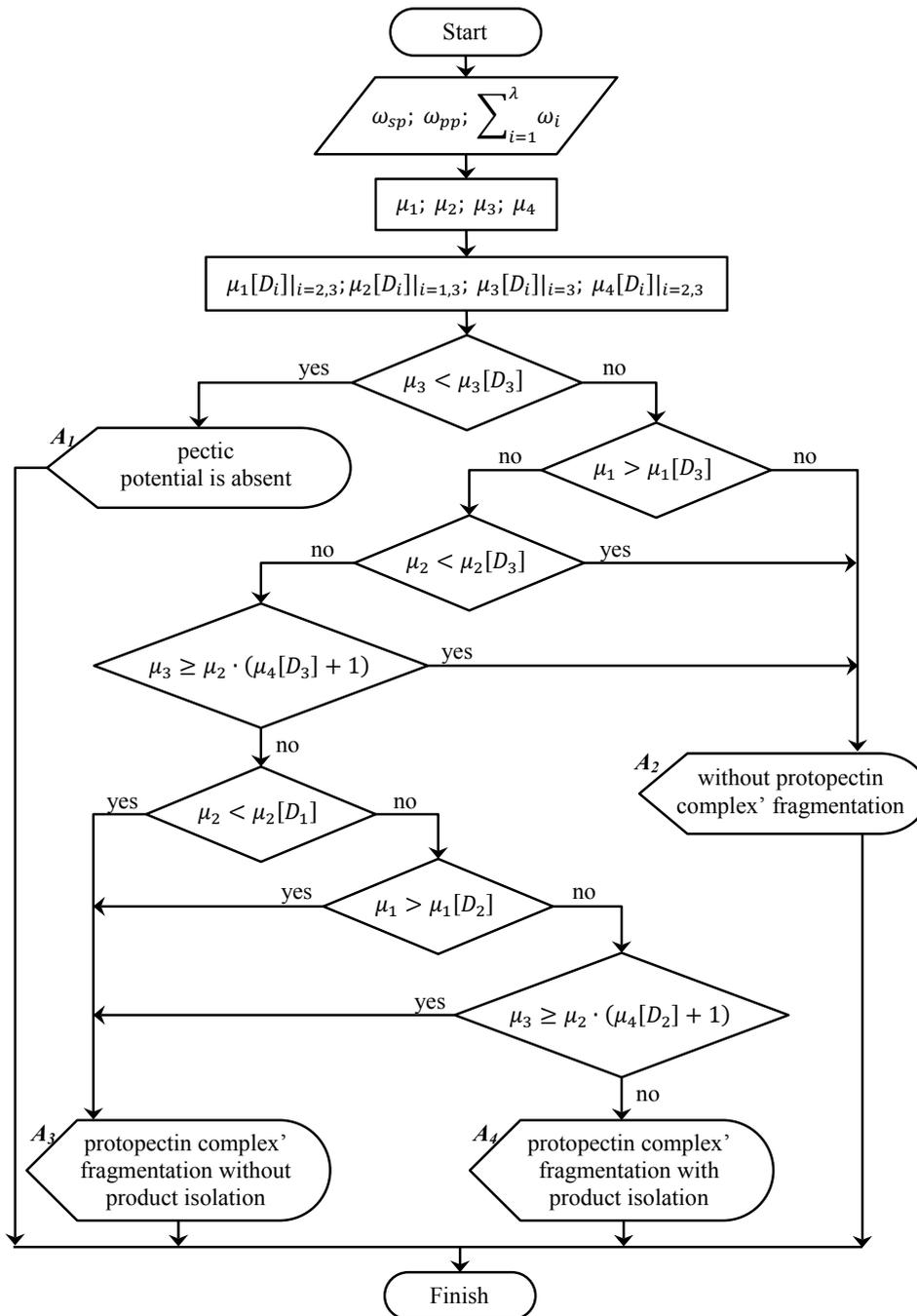
Figure 10 Algorithm for plant tissue classification according to protopectin fragmentation potential based on the geometric location in the zoned criterion space

location of $M[\mu_1, \mu_2, \mu_3]$ – the point that corresponds to the material under analysis – in a zoned criterion space with coordinates in the form of dimensionless individual criteria for protopectin fragmentation potential.

2. The dimensionless individual criteria for protopectin fragmentation potential included the ratio between the mass fractions of biologically active components and protopectin in plant tissue, the mass fraction of the protopectin complex expressed in

unit fractions, and the mass fraction of total pectin substances expressed in unit fractions.

3. We established nine individual boundary conditions, individual pectin potential, two individual fragmentation potentials, and three individual isolation potentials for pectin substances, which altogether determine a system of zoning the criterion space.

4. The boundary conditions in the definition area for a set of points $M[\mu_1, \mu_2, \mu_3]$ had the following hierarchy: individual pectin potential → individual

fragmentation potential of the protopectin complex → individual isolation potential of protopectin fragmentation products.

5. We developed an algorithm to classify plant tissues according to protopectin fragmentation potential based on the geometric location in the zoned criterion space.

CONTRIBUTION

All the authors were equally involved in writing the manuscript and are equally responsible for plagiarism.

CONFLICT OF INTEREST

The authors state that there is no conflict of interest.

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ORCID IDs
Vladimir V. Kondratenko https://orcid.org/0000-0002-0913-5644
Tatyana Y. Kondratenko https://orcid.org/0000-0001-8237-0774
Andrey N. Petrov https://orcid.org/0000-0001-9879-482X
Georgy A. Belozerov https://orcid.org/0000-0002-8152-146X