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Principal Component and Linear Discriminant Analyses of Free Amino Acids and Biogenic Amines in Hungarian Wines

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Principal component analysis (PCA) and linear discriminant analysis (LDA) were used to classify 187 Hungarian white and red wines according to wine-making technology, geographic origin (wine-making region), grape variety, and year of vintage based on free amino acid and biogenic amine contents. Determination of free amino acids and biogenic amines was accomplished by ion-exchange chromatography. Six principal components accounted for >77% of the total variance in the data. The plots of component loadings showed significant groupings of free amino acids and biogenic amines. The component scores grouped according to wines made by different wine-making technologies. Using LDA the variables with a major discriminant capacity were determined. Almost complete classification (94.7%) was achieved concerning both white and red wines and wines made by different wine-making technologies. The results of differentiation between white wines according to geographic origin, grape variety, and year of vintage were 70.8, 62.4, and 73.5%, respectively. The same numbers for red wines according to geographic origin, grape variety, and year of vintage were 64.9, 71.6, and 82.4%, respectively.

KEYWORDS: Wine; free amino acids; biogenic amines; chemometrics; principal component analysis; linear discriminant analysis

INTRODUCTION

Nitrogen in amino acids represents 30−40% of the total wine nitrogen. Amino acids, present in grape must, are used as nutrients for yeast and bacterial growth as they are consumed as a nitrogen source during fermentation (*1*, *2*). Amounts of amino acids depend on the grape variety, region, year of vintage, and different wine-making technologies (*3*).

Biogenic amines are present in grape must and are also formed during fermentation with decarboxylation of free amino acids (*4*). The polyamines (agmatine, spermine, and spermidine) are beneficial for health, but consumption of foods and beverages rich in some amines (histamine, tyramine, putrescine, and cadaverine) may cause inconvenient symptoms, such as nausea, sweating, and respiratory distress (*5*). The interaction between ethanol and amines seems to be synergetic; hence, their study in wines has great importance.

Different chemometric procedures have already been applied to establish wine authenticity and criteria for differentiation (*6*, *7*).

Vasconcelos et al. (*8*) studied the free amino acid composition of four white and four red wine varieties from Portugal over a seven year period. All of the varieties were grown in the same vineyard, and the wines were made under identical conditions. The data were treated by cluster analysis (CA), principal component analysis (PCA), and discriminant analysis (DA). The red and white wines were distinguished using these techniques, and the free amino acid compositions of wines were correlated to the corresponding grape varieties.

Etiévant et al. (*9*) analyzed French red wines from three regions and six varieties for amino acids, ethanolamine, total nitrogen content, and aromatic alcohols. PCA demonstrated that the concentration of most amino acids was mainly affected by the technology used in wine production. According to varieties the wines were divided only into two groups. There were clear differences between wines according to the latitude of the production area.

Soufleros et al. (*1*) studied Greek white wines from seven grape varieties, six geographic regions, and three vintages for their amino acids. Using DA the amino acid profiles have been useful in the classification of wines according to variety, geographic origin, and vintage, too.

In another study, Soufleros et al. (*10*) used PCA to classify French wines of four various regions according to their sort and origin by analysis of amino acids, biogenic amines, volatile compounds, and organic acids. Liquor wines, which were made from botrytized grapes, formed a separate group.

Csomós et al. (*11*) distinguished Hungarian red and white wines from the same geographic origin and vintage using

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CA and PCA on the basis of biogenic amines and polyphenols. Variables not necessary for classification were determined. Patterns for red and white wine groupings were observed.

The aim of the present work was to apply chemometric techniques to classify Hungarian white and red wines according to wine-making technology, geographic origin (wine-making region), grape variety, and year of vintage on the basis of free amino acid and biogenic amine contents. Moreover, we hope to determine which compounds (free amino acids and biogenic amines) are responsible for an appropriate classification.

MATERIALS AND METHODS

Wine Samples. Altogether 187 Hungarian wines (113 white and 74 red wines) were investigated. The wines represented four groups according to wine-making technology: quality white wines ($N = 101$), white liquor wines ($N = 12$), quality red wines ($N = 71$), and red wines with barrique aging ($N = 3$). White wines originated from 18 wine-making regions [Ászár-Neszmély = 1, Badacsony = 2, Balatonfüred-Csopak = 3, Balaton-North = 4, Bükkalja = 5, Balaton-South = 6, Eger = 7, Etyek-Buda = 8, Kunság = 9, Mátraalja = 10, Mecsekalja = 11, Pannonhalma-Sokoróalja = 12, Somló = 13, Szekszárd = 14, Tokajhegyalja = 15, Tokajhegyalja (liquor wines) = 16, Tolna = 17, Villány = 18]; 19 varieties (5-butts Aszú = 1, 6-butts Aszú = 2, Szamorodni = 3, Chardonnay = 4, Furmint = 5, Hárslevelű = 6, Irsai Olivér = 7, Királyleányka = 8, Leányka = 9, Muscat Ottonel = 10, Olaszrizling = 11, Pinot Blanc = 12, Rajnai Rizling = 13, Rizlingszilváni = 14, Sárgamuskotály = 15, Sauvignon Blanc = 16, Szürkebarát = 17, Tramini = 18, Zöldveltelini = 19); and 9 years of vintage (1993, 1994, 1996, 1997, 1998, 1999, 2000, 2001, 2002), whereas red wines originated from 10 wine-making regions (Csongrád, = 1 Balaton-South = 2, Eger = 3, Hajós-Baja = 4, Kunság = 5, Mátraalja = 6, Sopron = 7, Szekszárd = 8, Tolna = 9, Villány = 10), 9 varieties (Bikavér = 1, Cabernet Franc = 2, Cabernet Sauvignon = 3, Kadarka = 4, Kékfrankos = 5, Kékoportó = 6, Merlot = 7, Pinot Noir = 8, Zweigelt = 9); and 6 years of vintage (1994, 1997, 1999, 2000, 2001, 2002).

Sample Preparation. Free amino acids after a 0.45 μm membrane filtration and dilution 2 times were directly determined by an amino acid analyzer. For the determination of biogenic amines, from 15 to 20 cm^3 of the samples the water was evaporated at 80 °C. The evaporated samples were diluted in 1.5−5 cm^3 of sodium citrate buffer. The samples were subjected to a 2 min centrifugation at 8000 rpm and, finally, they were analyzed by the amino acid analyzer.

Chromatographic Conditions. Determination of free amino acids and biogenic amines was accomplished by ion-exchange chromatography. Separation of free amino acids was solved with two amino acid analyzers: LC 3000 (Biotronik) and AAA 400 (Ingos). Chromatography of biogenic amines was performed with the AAA 400 instrument. Both free amino acids and biogenic amines were separated by stepwise gradient elution using sodium/potassium citrate buffer systems. Post-column derivatization with ninhydrin reagent and spectrophotometric measurement at 570 and 440 nm was used for determination of free amino acids and biogenic amines (*12*).

Principal Component Analysis. PCA is a projection method, and dimension reduction of the data can be achieved using a smaller number of principal components than original variables. The principal components are often called underlying components, and their values are the scores. The principal components are, in fact, linear combinations of the original variables. The linear coefficients of the inverse relation of linear combinations are called the component loadings, that is, the correlation coefficients between the original variables and the principal components. PCA is an unsupervised method of pattern recognition in the sense that no grouping of the data has to be known before the analysis. Still, the data structure can be revealed easily and class membership is easy to assign.

The principal components are uncorrelated and account for the total variance of the original variables. The first principal component (PC1) accounts for the maximum of the total variance, the second (PC2) is uncorrelated with the first one and accounts for the maximum of the residual variance, and so on, until the total variance is accounted for. For practical reasons, it is sufficient to retain only those components that account for a large percentage of the total variance.

In summary, PCA decomposes the original matrix into multiplication of loading (amino acids and biogenic amines) and score (wine sorts) matrices. PCA will show which kinds of amino acids and biogenic amines (and which sorts of wines) are similar to each other, that is, carry comparable information, and which one is unique. The algorithm of PCA can be found in standard chemometric articles and textbooks (*13*, *14*).

Linear Discriminant Analysis (LDA). LDA is perhaps the most frequently used pattern recognition technique. LDA is supervised; that is, the class membership has to be known for the analysis. LDA, similarly to PCA, can be considered as a dimension reduction method. For feature reduction, we need to determine a smaller dimension hyperplane on which the points will be projected from the higher dimension space. Whereas PCA selects a direction that retains maximal structure in a lower dimension among the data, LDA selects a direction that achieves maximum separation among the given classes. The latent variable obtained in this way is a linear combination of the original variables. This function is called the canonical variate, and its values are the roots. If we have k classes, $k - 1$ canonical variates can be determined. In the method of LDA a linear function of the variables is to be sought, which maximizes the ratio of between-class variance and minimizes the ratio of within-class variance. Finally, a percentage of correct classification is given. A variant of this method is the stepwise discriminant analysis that permits the variables with a major discriminant capacity to be selected. The description of the LDA algorithm can be found in references *14*−*16*.

RESULTS AND DISCUSSION

Principal Component Analysis. The following data set was analyzed: the concentrations of the following 28 components (columns of the input matrix) were ordered as variables (abbreviations in parentheses): 8 biogenic amines [histamine (Him), tyramine (Tym), putrescine (Put), cadaverine (Cad), agmatine (Agm), spermidine (Spd), spermine (Spm), sum of biogenic amines (sum BA)] and 20 amino acids [aspartic acid (Asp), threonine (Thr), serine (Ser), glutamic acid (Glu), proline (Pro), glycine (Gly), alanine (Ala), cysteine (Cys), valine (Val), methionine (Met), isoleucine (Ile), leucine (Leu), tyrosine (Tyr), phenylalanine (Phe), γ-aminobutyric acid (GABA), histidine (His), ornithine (Orn), lysine (Lys), arginine (Arg), sum of amino acids (sum AA)]. The 187 wines were arranged in rows of the input matrix. The variables (columns) were standardized to zero mean and unit variance; that is, column means were subtracted from each matrix entry, and then each entry was divided by standard deviations of columns.

PCA yields six principal components explaining >77% of the total variance in the data. Loading values $>+0.65$ and <-0.65 are marked in boldface type (PC1 and PC2 in **Table 1**). The loadings express how well the new PCs correlate with the old variables. The first PC, which explains 44.8% of the total variance, correlates negatively with all amino acids. The second PC (11.8% of the total variance) correlates positively with biogenic amines Put, sum BA, and amino acid Pro. In the remaining PC3, PC4, PC5, and PC6 none of the variables were decisive. If we consider the high correlations (loading values are $>+0.65$ and <-0.65), two PCs are enough to be retained. A scree plot suggests involving four PCs into the model. As a reasonable compromise four PCs are given in **Table 1**.

Figure 1 shows the first two PC loadings against each other. Three different clusters can be observed in **Figure 1**; they are separated with curves. The first cluster (I) is formed by the majority of amino acids. Agm, Orn, Cys, Tym, sum AA, and Gly belong to the second cluster (II). The third cluster contains five biogenic amines, sum AA, and the amino acid Pro (III).

Table 1. Unrotated Principal Component Loadings for Free Amino Acids and Biogenic Amines[a]

	PC1	PC2	PC3	PC4
Him	–0.1399	0.5606	0.0319	0.4966
Tym	–0.5950	0.3769	–0.4871	0.1521
Put	0.0169	**0.7955**	0.2563	0.1375
Cad	0.0757	0.4113	0.2204	0.0279
Agm	–0.1648	–0.1086	–0.1318	0.4719
Spd	–0.1501	0.6025	0.1408	–0.0289
Spm	–0.0309	0.1839	0.1845	–0.0530
sum BA	–0.4718	**0.7207**	–0.2275	0.4003
Asp	**–0.9197**	–0.0301	–0.1300	0.0257
Thr	**–0.9258**	–0.0811	0.0011	0.0016
Ser	**–0.9480**	–0.0756	0.0545	–0.0199
Glu	**–0.8455**	–0.0874	0.0508	–0.2358
Pro	–0.0167	**0.6679**	0.3722	–0.3381
Gly	**–0.8261**	0.3004	0.0121	–0.2234
Ala	**–0.8970**	–0.0195	–0.0374	–0.2324
Cys	–0.5842	0.2990	–0.2983	–0.1481
Val	**–0.9300**	–0.0458	0.1531	0.0540
Met	**–0.7507**	–0.2277	0.2793	0.1564
Ile	**–0.8820**	–0.2105	0.2178	0.1233
Leu	**–0.7850**	–0.3047	0.2226	0.2420
Tyr	–0.5807	–0.0945	0.5599	–0.1387
Phe	**–0.8217**	–0.2065	0.3496	0.0046
GABA	**–0.7321**	–0.0553	–0.3951	–0.1074
His	**–0.7581**	–0.1742	0.0257	0.1514
Orn	–0.3694	0.1207	–0.3474	–0.5148
Lys	**–0.7648**	–0.0801	–0.0212	0.3863
Arg	**–0.7031**	–0.1237	–0.4666	–0.0360
sum AA	**–0.7712**	0.3821	0.0457	–0.3157
explained variance	12.55	3.29	1.86	1.64
proportion of total variance, %	44.84	11.76	6.64	5.87

[a] PC, principal component; Him, histamine; Tym, tyramine; Put, putrescine; Cad, cadaverine; Agm, agmatine; Spd, spermidine; Spm, spermine; sum BA, sum of biogenic amines; Asp, aspartic acid; Thr, threonine; Ser, serine; Glu, glutamic acid; Pro, proline; Gly, glycine; Ala, alanine; Cys, cysteine; Val, valine; Met, methionine; Ile, isoleucine; Leu, leucine; Tyr, tyrosine; Phe, phenylalanine; GABA, γ-aminobutyric acid; His, histidine; Orn, ornithine; Lys, lysine; Arg, arginine; sum AA, sum of amino acids.

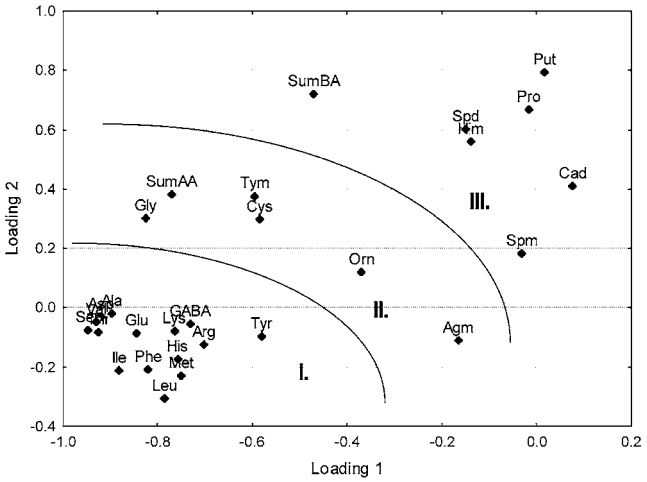

Figure 1. Principal component loadings, loading 1 versus loading 2. Him, histamine; Tym, tyramine; Put, putrescine; Cad, cadaverine; Agm, agmatine; Spd, spermidine; Spm, spermine; SumBA, sum of biogenic amines; Asp, aspartic acid; Thr, threonine; Ser, serine; Glu, glutamic acid; Pro, proline; Gly, glycine; Ala, alanine; Cys, cysteine; Val, valine; Met, methionine; Ile, isoleucine; Leu, leucine; Tyr, tyrosine; Phe, phenylalanine; GABA, γ-aminobutyric acid; His, histidine; Orn, ornithine; Lys, lysine; Arg, arginine; SumAA, sum of amino acids.

Score plots show similarities among the different wine sorts. **Figure 2** shows the first two PC scores against each other.

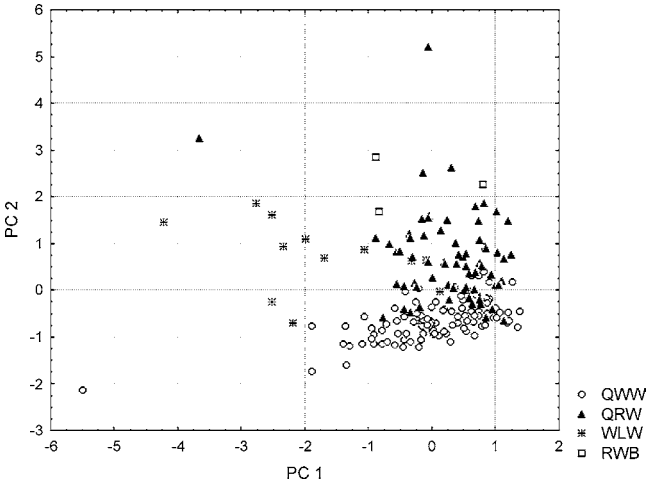

Figure 2. Principal component scores, score 1 versus score 2. QWW, quality white wines; QRW, quality red wines; WLW, white liquor wines; RWB, red wines with barrique aging.

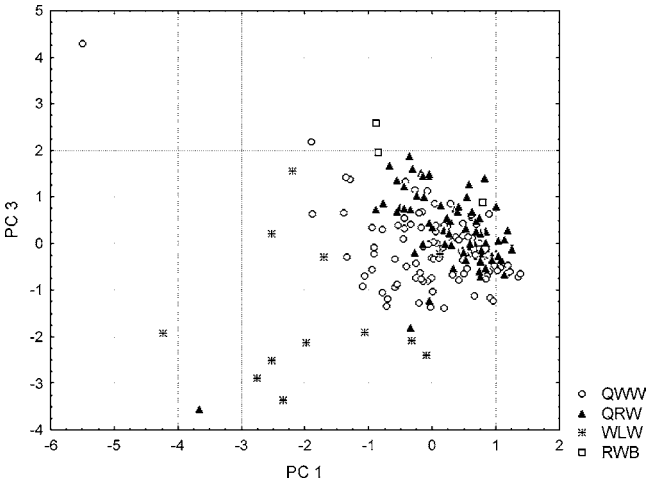

Figure 3. Principal component scores, score 1 versus score 3. QWW, quality white wines; QRW, quality red wines; WLW, white liquor wines; RWB, red wines with barrique aging.

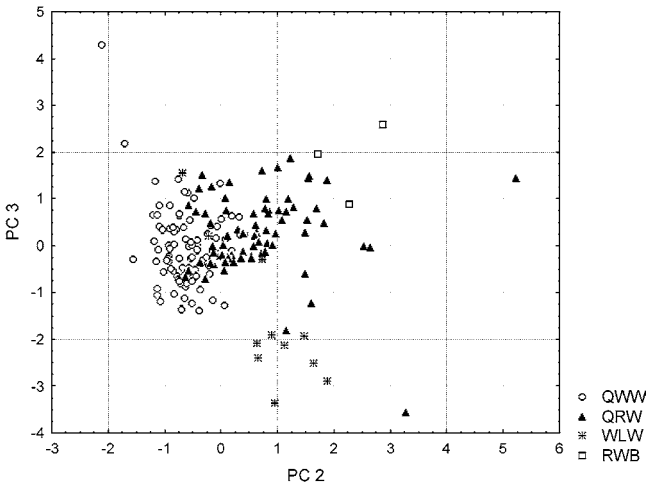

Figure 4. Principal component scores, score 2 versus score 3. QWW, quality white wines; QRW, quality red wines; WLW, white liquor wines; RWB, red wines with barrique aging.

Wines made by different wine-making technologies show good separation. The points for quality red wines are situated above those for quality white wines. Three points of red wines with

Table 2. Percentage of Correctly Classified Wines Using Linear Discriminant Analysis of Wines Made by Different Wine-Making Technologies

observed group[a]	no. of samples	correct classification, %	predicted groups[a]			
			QWW	QRW	WLW	RWB
QWW	101	97.0	98	3	0	0
QRW	71	91.5	6	65	0	0
WLW	12	91.7	1	0	**11**	0
RWB	3	**100.0**	0	0	0	**3**
total	187	**94.7**	105	68	**11**	**3**

[a] QWW, quality white wines; QRW, quality red wines; WLW, white liquor wines; RWB, red wines with barrique aging.

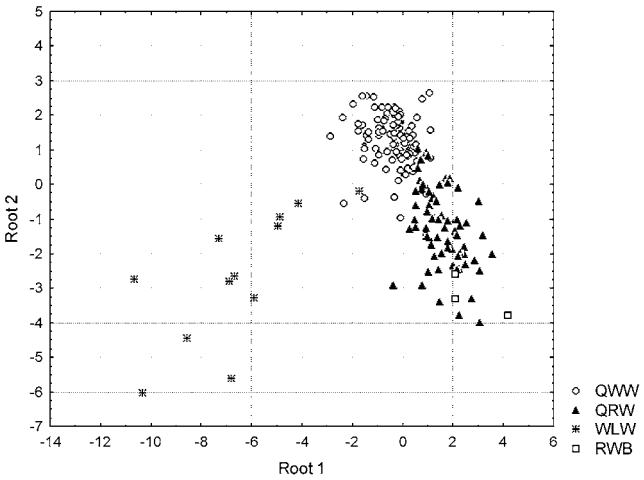

Figure 5. LDA of wines according to wine-making technology, root 1 versus root 2. QWW, quality white wines; QRW, quality red wines; WLW, white liquor wines; RWB, red wines with barrique aging.

barrique aging are situated above the majority of points for red wines. White liquor wines seem to form a separate group on the left of other wines. Both quality white and quality red wines form a comet-like shape.

The distinction between wines made by different wine-making technologies is also shown in **Figures 3** and **4** (PC1 vs PC3 and PC2 vs PC3, respectively). Quality white wines are mixed with quality red wines. The separation of the 12 white liquor wines and 3 red wines with barrique aging is acceptable.

Linear Discriminant Analysis. Stepwise LDA was used for differentiation of different wine sorts using the same data set as for PCA.

Correct classification concerning white and red wines is 94.7%. This classification was achieved using the following 12 variables: Put, Asp, Thr, Ser, Pro, Gly, Ala, Cys, Val, Leu, Tyr, and GABA. The classification of white wines (96.5%) is better than that of red ones (91.9%).

Table 2 shows the classification of wines made by different wine-making technologies. Twenty of the variables, Tym, Put, Cad, Spd, Spm, Asp, Thr, Ser, Glu, Pro, Gly, Ala, Cys, Met, Leu, Tyr, Phe, GABA, Orn, and Lys, showed high discriminant power. The percentage of correctly classified wines with these variables is 94.7%. The classification of the three red wines with barrique aging is correct.

In **Figures 5**, **6**, and **7** the groupings of wines made by different wine-making technologies are shown. In **Figures 5** and **6** (root 1 vs root 2 and root 1 vs root 3, respectively) different wine sorts show an acceptable separation. Although wines made by different wine-making technologies are mixed in **Figure 7** (root 2 vs root 3), red wines with barrique aging form a separate group in this projection.

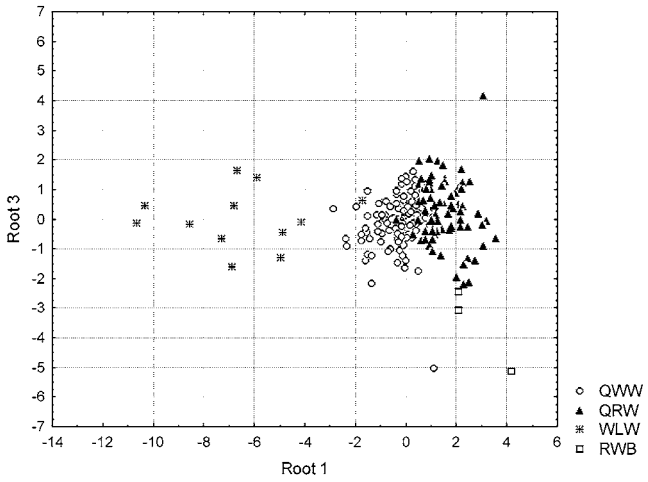

Figure 6. LDA of wines according to wine-making technology, root 1 versus root 3. QWW, quality white wines; QRW, quality red wines; WLW, white liquor wines; RWB, red wines with barrique-aging.

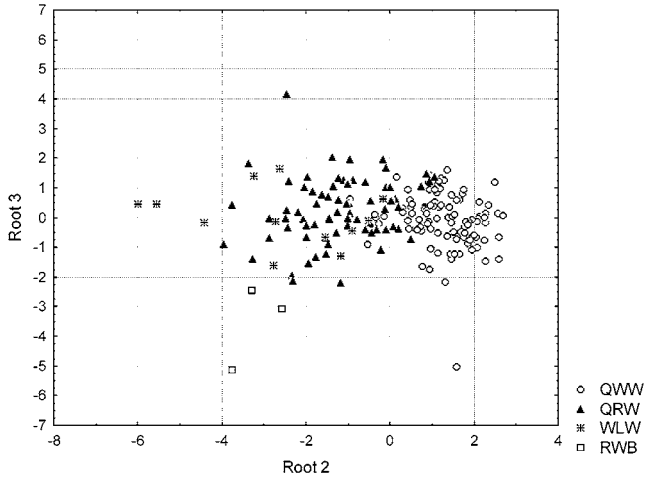

Figure 7. LDA of wines according to wine-making technology, root 2 versus root 3. QWW, quality white wines; QRW, quality red wines; WLW, white liquor wines; RWB, red wines with barrique aging.

Linear Discriminant Analysis II. Stepwise LDA was also used for differentiation of white and red wines according to geographic origin (wine-making region), grape variety, and year of vintage. Red and white wines were handled separately. A 10% significance level was predefined. Those variables were excluded, which surpassed the predefined significance limit. In such a way, a more realistic, but worse classification can be obtained than when using all variables.

Although **Figure 8** shows the best two roots, the groups overlap to a large extent. The mentioned classification can be achieved multidimensionally, for example, using all 14 roots.

The following variables have the highest discrimination power for differentiation of geographic regions (18 white wine groups) at the 10% significance level: Ile, Ala, Leu, Tym, Pro, Tyr, Met, Asp, Glu, Phe, Gly, Thr, GABA, and His (ordering in decreasing significance). The correct classification was 70.8%.

Figure 9 shows overlapping groups, although Tokaj liquor wines are easy to discriminate from other sorts. It is difficult to classify white wines according to varieties (worst classification).

The stepwise forward selection algorithm has selected the following variables for differentiation of white wine varieties (19 white wine groups) at the 10% significance level: Lys, Pro, Leu, Tym, Orn, Him, Ala, Thr, His, Agm, Gly, GABA, Glu, and Ser (ordering in decreasing significance).

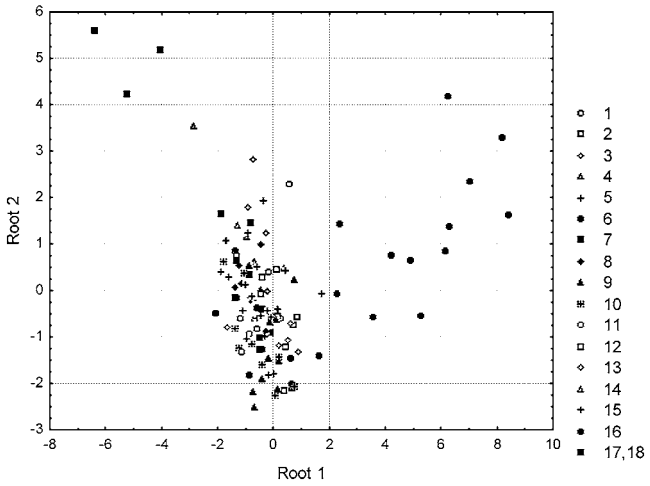

Figure 8. LDA of white wines according to geographic origin, root 1 versus root 2. See text for wine sample numbering.

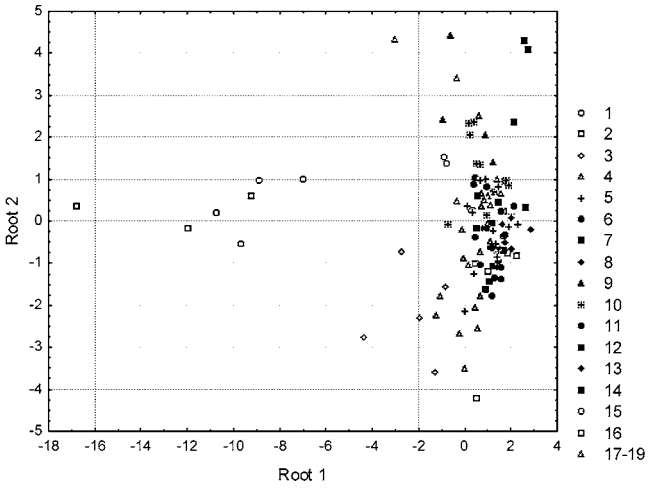

Figure 9. LDA of white wines according to wine varieties, root 1 versus root 2. See text for wine sample numbering.

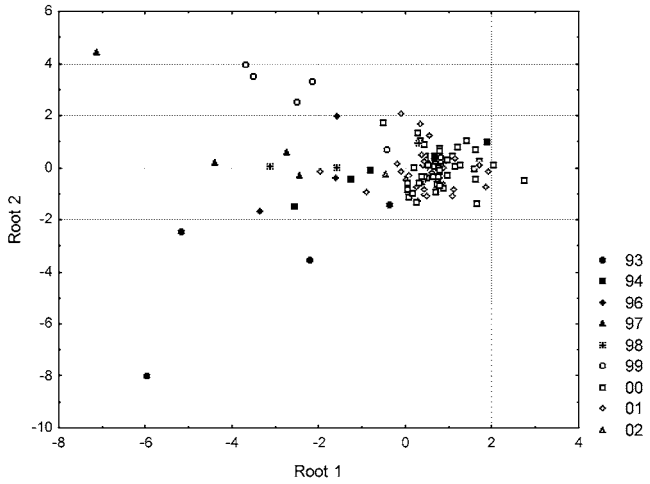

Figure 10. LDA of the year of vintage for white wines, root 1 versus root 2. Years are represented by the last two digits.

Using all roots (14) the correct classification achieved 62.4%.

Figure 10 shows the ambiguity of classification task: for example, year of vintage 1999 can be distinguished from the year 1997 or 1993, whereas years 2001 and 2000 are indistinguishable.

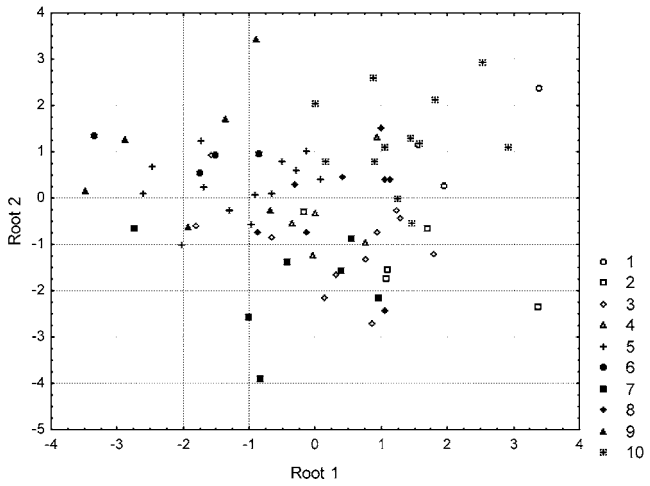

Figure 11. LDA of red wines according to geographic origin, root 1 versus root 2. See text for wine sample numbering.

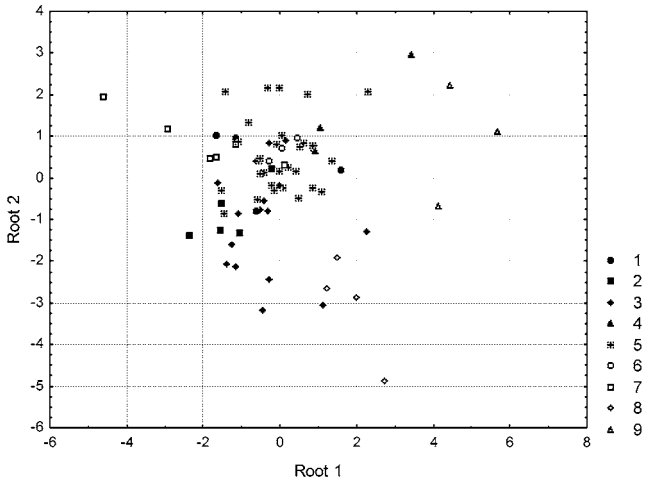

Figure 12. LDA of red wines according to wine varieties, root 1 versus root 2. See text for wine sample numbering.

The stepwise forward selection algorithm has selected the following variables for differentiation of years of vintage (nine white wine groups) at the 10% significance level: Spm, Thr, His, Met, Tyr, Gly, Cys, Leu, Asp, GABA, Spd, Lys, Ala, and Put (ordering in decreasing significance). Using all roots (eight) the correct classification achieved 73.5%.

Although **Figure 11** shows a considerable overlap among the groups of wine-making regions (10 red wine groups), no doubt several discrimination tasks can be solved fully: for example, regions Villány (10) and Sopron (7) are clearly distinguished. Similarly, even geographically close regions can be separated, for example, Hajós-Baja (4) and Kunság (5). Although clouds of the points for Kunság (5) and Villány (10) touch each other, the majority of points are well-separable. A 64.9% separation can be achieved using all roots (nine) combined from the following variables: Orn, Glu, Pro, sum AA, Cys, Tyr, Arg, Gly, Spd, and Ala (in decreasing significance).

The roots having the best discrimination power in the case of red wine varieties are plotted in **Figure 12**. The overlapping is again a typical feature for the points of groups. Nevertheless, several discriminations of groups can immediately be seen: for example, Merlot (7) and Zweigelt (9) are easy to distinguish. Points for Bikavér and Kékfrankos cover the points of other sorts, although five points of Kékfrankos are separated clearly.

The stepwise forward selection algorithm has selected the following variables for differentiation of red wine varieties (nine

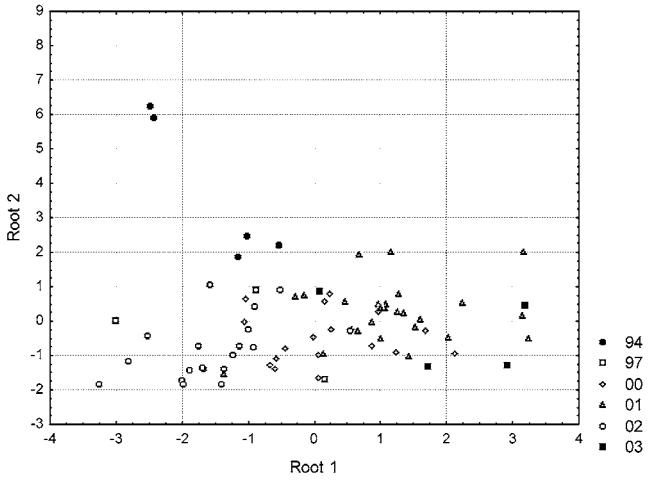

Figure 13. LDA of the year of vintage for red wines, root 1 versus root 2. Years are represented by the last two digits. Points for some years overlap (e.g., 2000 and 2001), whereas points for other years are clearly separated (e.g., 2002 and 1994).

red wine groups) at the 10% significance level: Cad, Orn, Asp, Ala, Ile, Gly, sum AA, Pro, Tym, GABA, and Val (ordering in decreasing significance). Using all roots (eight) the correct classification achieved 71.6%.

Figure 13 shows the best discrimination of years of vintage (six red wine groups). Again, points for some years overlap (e.g., 2000 and 2001), whereas points for other years are clearly separated (e.g., 2002 and 1994). The stepwise forward selection algorithm has selected the following variables for differentiation of years of vintage for six red wine groups at the 10% significance level: His, Spm, Ser, Cys, Thr, Ile, Tym, Sum AA, Leu, Pro, Tyr, Arg, Gly, Lys, Him, and Met (ordering in decreasing significance). Using all roots (five) the correct classification achieved 82.4%

Ala, GABA Gly, His, Leu, and Thr are all important for the classification of white wines (in all aspects: wine-making region, variety, and year of vintage). Similarly, Gly, Pro, and sum AA are important for the classification of red wines.

There is no general trend in classification: the region is better distinguishable for white wines, whereas the varieties and years can be better ordered to red wines.

PCA gives an acceptable differentiation between white and red wines and also between wines made by different wine-making technologies.

Using LDA wine-making technology had a greater effect on classification of wines than geographic origin (wine-making region), grape variety, and year of vintage.

In summary, on the basis of the results of chemometric analyses, free amino acid and biogenic amine contents seem to be useful to differentiate wines according to wine-making technology and, although to a lesser extent, geographic origin, grape variety, and year of vintage, too.

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