JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

# Principal Component Analysis of Biogenic Amines and Polyphenols in Hungarian Wines

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Biogenic amines, polyphenols, and resveratrol were analyzed quantitatively in 25 different Hungarian wines from the same wine-making region, harvest of 1998. Polyphenols were determined according to a spectrophotometric method, whereas other substrates were analyzed using overpressured-layer chromatography (OPLC). Principal component analyses (PCA) were performed on data matrices consisting of substrates (columns) and different sorts of wines (rows) from the region of Pécs (southern Hungary). It was found that four (unrotated) principal components account for >80% of the total variance in the data. The plots of component loadings showed significant groupings for concentrations of biogenic amines (and polyphenols). Similarly, the component scores grouped according to the different sorts of wines. The loading plots reveal that there is no need to measure all of the variables to achieve the same characterization. It is enough to measure one variable per group. Naturally, this conclusion is valid only within the limits of the present study; wines from other regions may behave differently.

**KEYWORDS: Biogenic amines; polyphenols; resveratrol; chemometrics; wine; multivariate analysis; principal component analysis; pattern recognition**

## INTRODUCTION

Wines are known to contain many biologically active compounds. The amounts and compositions of these compounds depend on the type of grapes and their degree of ripeness and the climate and soil of the viticultural area, as well as vinification techniques.

The biogenic amines usually found in wines are agmatine, spermine, spermidine, putrescine, cadaverine, histamine, and tyramine. Microorganisms produce biogenic amines during fermentation with decarboxylation of free amino acids. Consumption of beverages rich in some biogenic amines (e.g., histamine and tyramine) can lead to headaches, nausea, hot flushes, skin rashes, sweating, respiratory distress, and cardiac and intestinal problems (*1*).

Resveratrol, a prominent representative of polyphenols present in fresh grapes and wines, has a pronounced biological activity. Resveratrol has a cardioprotective effect, because it reduces, for example, the susceptibility of low-density lipoproteins (LDL) to lipid peroxidation (antioxidant effect) and shows a cancer-preventing activity (*2*, *3*).

It is obvious that the composition of wines may be responsible for these biological activities; therefore, the study and characterization of different wine varieties of various origins has great importance.

Different chemometric procedures have been applied to data gained from wines in order to establish criteria for geographical differentiation (*4*).

Tinttunen et al. (*5*) distinguished organic wines from normal wines on the basis of concentrations of phenolic compounds and spectral data. Good differentiation was achieved between organic Burgundy red and normal Burgundy wines. Rebolo et al. (*6*) classified Galician (Spanish) wines on the basis of metals, volatile compounds, and polyphenols. The obtained results indicated a basis for good differentiation between the wines produced in nearby geographical areas. Melssen (*7*) used the amino acid composition to classify four different French wine species. Rae Kim et al. (*8*) characterized four wine brands on the basis of their amino acid profiles, which provided star symbols characteristic to wine brands. Nouadje et al. (*9*) found some correlations between amino acid and biogenic amine quantities during ripening in French red wines. Sivertsen et al. (*10*) classified red wines from France on the basis of both sensory and chemical analyses. A better classification was achieved on the basis of a chemical data set (major acids, alcohols, esters, pH, total phenols, and color). José Benito et al. (*11*) characterized Spanish vinegars obtained from wines according to their chemical composition.

In recent years several studies have dealt with the color properties of red wines. Gómez-Plaza et al. (*12*) classified seven different clones of the same grape variety on the basis of chemical and color characteristics. Cruz Ortiz et al. (*13*) constructed a linear relationship between certain physicochem-

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10.1021/jf011699a CCC: $22.00 
Published on Web 05/18/2002

**Table 1.** Wine Samples for the Pécs Region (Hungary)

| sample | red wine | sample | white wine |
|---|---|---|---|
| R1 | Cabernet Franc | W18 | Olasz Rizling |
| R2 | Cabernet Sauvignon | W19 | Rajnai Rizling |
| R3 | Merlot | W20 | Furmint |
| R4 | Pinot Noir | W21 | Hárslevelü |
| R5 | Kadarka | W22 | Sauvignon Blanc |
| R6 | Kékfrankos | W23 | Chardonnay |
| R7 | Kékoportó | W24 | Cirfandli |
| R8 | Zweigelt | W25 | Zenit |
| R9 | Rubintos | | |
| R10 | Vranac | | |
| R11 | Blauburger | | |
| R12 | Medina | | |
| R13 | Biborkadarka | | |
| R14 | Kármen | | |
| R15 | Alicante Bouschet | | |
| R16 | Turán | | |
| R17 | Titán | | |

ical measurements and sensory evaluation of the color of young red wines. Almela et al. (*14*) classified six red wine varieties on the basis of selected enological and color parameters. Meléndez et al. (*15*) constructed sensitive and specific models for rosé and "claretes" wines on the basis of parameters representing colors. Fernández et al. (*16*) dealt with the modeling and prediction of the color of young red wines.

The aim of our work was to characterize Hungarian wines from the same geographical area on the basis of biologically active compounds. Moreover, we would like to decrease the number of measured quantities while preserving the same level of characterization. Classification of red and white wines was another aim of ours.

This is the first study on the biogenic amine and polyphenol contents of wines using multivariate data analysis techniques.

## EXPERIMENTAL PROCEDURES

**Wine Samples.** Seventeen red and eight white wines from southern Hungary (region of Pécs) of the harvest of 1998 were investigated. The wines are listed in **Table 1**.

**Analytical Methods.** Overpressured-layer chromatography (OPLC) was used for the determination of biogenic amines (*17*). Before analysis, derivatization was carried out with dansyl chloride. Biogenic amines were separated by stepwise gradient elution using a BS 50 personal OPLC chromatograph. The parameters were as follows: stationary phase, HPTLC silica gel 60 $F_{254}$ sorbent layer; mobile phase, eluent A (first step, volume = 11500 $\mu$L), *n*-hexane/*n*-butanol/triethylamine = 90:10:8.1 (v/v), eluent B (second step, volume = 800 $\mu$L), *n*-hexane/*n*-butanol = 80:20 (v/v); development conditions, external pressure = 5.0 MPa, flow rate = 500 $\mu$L/min, rapid volume = 200 $\mu$L, development time = 1576 s, and densitometric evaluation of chromatograms at 300 nm in fluorescent mode.

Total polyphenols were determined by a spectrophotometric method using the Folin−Ciocalteu reagent (*18*).

Resveratrol was analyzed by the OPLC method (*19*). Separation conditions were as follows: stationary phase, TLC silica gel 60 $F_{254}$ sorbent layer; mobile phase, chloroform/methanol = 100:8 (v/v); linear isocratic development, external pressure = 5.0 MPa, flow rate = 250 $\mu$L/min, rapid eluent volume = 450 $\mu$L, eluent volume = 9800 $\mu$L (continuous development), development time = 2370 s. Densitometric evaluation of chromatograms was carried out at 305 nm.

**Cluster Analysis (CA).** CA is used to classify objects into groups. It can be considered to be an alternative to principal component analysis (PCA) (see below). To be able to cluster objects, one must measure their similarity. The dissimilarity between two objects is a distance measure. In the input matrix the rows can be considered as points in the *m*-dimensional space, where *m* is the number of columns. The distance between two points is well-defined; the simplest distance measure is the Euclidean distance. However, numerous clustering algorithms exist as to what is considered to be a distance between two groups. It may be defined as the distance of the two closest points or the two farthest points or the distance of the centroids, etc. Weighted schemes are also reliable alternatives. The most popular is perhaps Ward's method. The definition for distance measures and clustering algorithms can be found in standard chemometric textbooks (*20*, *21*).

**Principal Component Analysis (PCA).** PCA proved to be a powerful tool for pattern recognition, classification, modeling, and other aspects of data evaluation.

Biogenic amines, polyphenols, and resveratrol are taken as variables (columns of the input matrix) and the various wines as mathematical−statistical cases (rows of the matrix).

The columns of these data matrices are intercorrelated; that is, the data are redundant. The method of PCA makes use of intercorrelations starting from the correlation matrix of the variables. It eliminates the redundancy from the data; that is, it reduces the dimensionality of the data by revealing several underlying components.

The underlying components are represented by new variables called principal components. Their values are the component scores. The principal components are, in fact, linear combinations of the original variables and vice versa. 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.

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 a practical problem, it is sufficient to retain only a few components accounting for a large percentage of the total variance.

In summary, PCA decomposes the original matrix into several products of multiplication into loading (biogenic amines) and score (wine sorts) vectors.

PCA will show which kinds of biogenic amines (or polyphenols) (and which sort of wines) are similar to each other, that is, carry comparable information, and which ones are unique. An assumption was made during the analysis, namely, that all biogenic amines and polyphenols express important features of wines of the Pécs region.

The following data set was analyzed: the concentrations of the following biogenic amines (columns of the input matrix) were ordered as variables (abbreviations in parentheses): agmatine (AGM), spermine (SPM), spermidine (SPD), putrescine (PUT), cadaverine (CAD), histamine (HIM), tyramine (TYM), sum of biogenic amines (SBA), resveratrol (RVR), and sum of polyphenols (SPPH). Twenty-five wine sorts were arranged in rows of the input matrix. The notations were R1−R17 for 17 different red wine and W18−W25 for 8 white wine sorts. The mean values of columns were also added to rows (**Table 1**), but this is not influential on the analyses. They show the correctness of calculations, and the wine sorts close to the average can be seen on the dendrogram. The raw data were normalized (scaled) to zero mean and unit variance; that is, column means were subtracted from each data entry, and then the entry was divided by standard deviations of columns.

The algorithm of PCA can be found in standard chemometric articles and textbooks (*20*−*22*).

## RESULTS AND DISCUSSION

A simple CA uses less information (distances only) than PCA. It is interesting to observe what kind of classification can be made on the basis of distances only. Clustering by Ward's method is not able to distinguish red and white wines completely. As can be seen from **Figure 1**, there are several distinct groups ("red wine" group 1, R1, R14, W19, R12, and R15; "white wine" group, W18, W20, W21, W24, W25, W22, and W23; "red wine" group 2, R5, R11, R9, R10, R2, R4, R3, R16, R17, R6, R7, R8, and R13). Unfortunately, W19 is

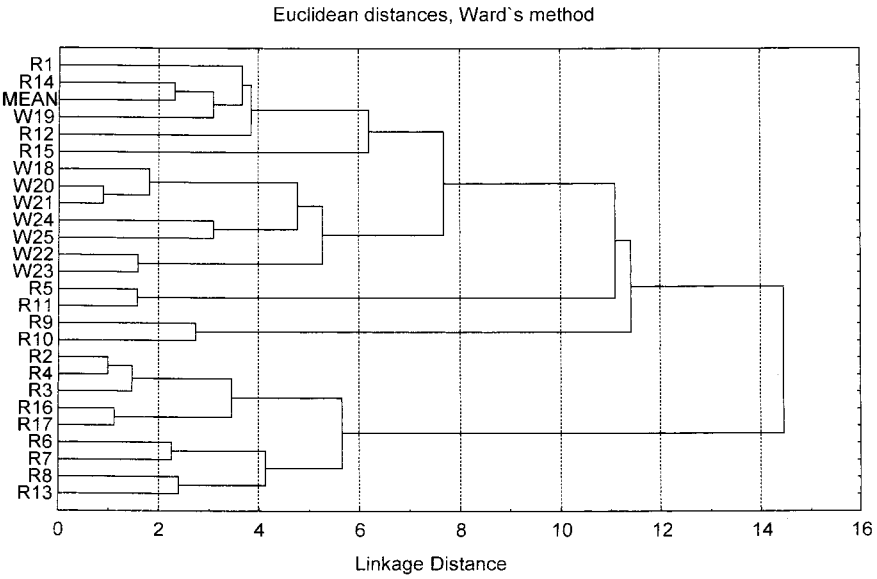


**Figure 1.** Simple cluster analysis of wine samples.

**Table 2.** Results of Principal Component Analysis for Biogenic Amines and Polyphenols: Unrotated Principal Component Loadings

| | PC 1 | PC 2 | PC 3 | PC 4 | PC 5 | PC 6 | PC 7 |
|---|---|---|---|---|---|---|---|
| AGM | –0.253238 | **0.898479** | –0.025651 | 0.323090 | –0.074518 | 0.059401 | –0.118721 |
| SPM | –0.139805 | –0.120646 | **–0.755587** | –0.026630 | –0.546875 | –0.272386 | 0.084833 |
| SPD | **0.834775** | 0.285160 | 0.079420 | –0.243749 | 0.108854 | –0.179975 | –0.066442 |
| PUT | 0.083569 | 0.469120 | –0.658738 | –0.248291 | 0.399332 | –0.104832 | 0.313937 |
| CAD | 0.019899 | –0.381343 | **–0.737110** | 0.117167 | 0.145129 | 0.493024 | –0.081824 |
| HIM | 0.171761 | –0.418431 | –0.165389 | **0.807908** | 0.159456 | –0.218128 | 0.089256 |
| TYM | **–0.722028** | –0.399449 | –0.000934 | –0.057827 | 0.346265 | –0.330214 | –0.187013 |
| SBA | –0.351307 | **0.866655** | –0.182832 | 0.268963 | 0.050933 | –0.028024 | –0.109401 |
| RVR | **0.754836** | –0.022507 | –0.484270 | –0.057885 | 0.032303 | –0.123798 | –0.362064 |
| SPPH | **0.817050** | 0.056189 | 0.269672 | 0.315344 | –0.007735 | 0.010764 | 0.118913 |
| explained variance | 2.699495 | 2.358030 | 1.923167 | 1.071079 | 0.646026 | 0.537024 | 0.331098 |
| proportion of total variance, % | 27.0 | 23.6 | 19.2 | 10.7 | 6.46 | 5.37 | 3.31 16 |

[a] Abbreviations: AGM, agmatine; SPM, spermine; SPD, spermidine; PUT, putrescine; CAD, cadaverine; HIM, histamine; TYM, tyramine; SBA, sum of biogenic amines; RVR, resveratrol; SPPH, sum of polyphenols.

included in the first red wine group. W19 is the white wine closest to the red ones.

PCA yields four principal components explaining >80% total variance in the data. Loading values (i.e., correlation coefficients) >0.7000 (concentration of biogenic amines and polyphenols) are marked throughout **Table 2** in boldface type.

The loadings express how well the new abstract principal components correlate with the old variables. The first new abstract principal component correlates well with SPD, TYM, RVR, and SPPH. TYM correlates with the new PC negatively. This opposite behavior of TYM is not well understood chemically. The second PC correlates with AGM and SBA, the third one with SPM and CAD, and the fourth one with HIM. None of the variables were decisive in the remaining PC5, PC6, and PC7 as shown in **Table 2**.

Loading plots help to explain the similarities and dissimilarities between variables.

**Figure 2** shows the first two PC loadings against each other. As PCA is invariant to the mirroring through the origin, TYM belongs to the first group. The data measured here indicate a significant negative correlation between TYM and SPPH (or RVR). The correlation between SPD and SPPH (or RVR) in relation to the data is unambiguous and significant. The point for RVR is close to that of SPPH because resveratrol comprises a large part of polyphenols. Likewise, SBA and AGM express close resemblance. This is understandable because AGM constitutes the largest portion in the sum of all biogenic amines (SBA).

CAD and HIM can also be considered to be similar variables.

There is no need to measure and evaluate all of the variables to achieve the same characterization in further studies. It is enough to measure one variable per group.

**Figures 3** and **4** illustrate the contribution of original variables to the four principal components retained in the model as bar plots. SPD, TYM, RVR, and SPPH constitute the first PC, whereas PUT is shared between PC2 and PC3. RVR is not negligible in PC3 (**Figure 3**). The remaining variables are decisive in PC2 (AGM and SBA), in PC3 (SPM and CAD), and in PC4 (HIM) (see **Figure 4**).

Red wines differ from white wines mainly because of their RVR and SPPH contents, which derive from the differences in the wine-making process. There is fermentation in the skin of the berries in the case of red wines. This is why these compounds need more time to be solved.

Score plots show similarities among the different wine sorts. Two distinct groups can be observed in **Figure 5** separated with a line. The explained variances can be found on the axes in parentheses.

Red and white wines are well resolved by PCA.

**Figure 5** shows that the first two PCs perform almost a perfect classification (the separation of red and white wines). The wine marked by R1 has low SPD and SPPH contents.

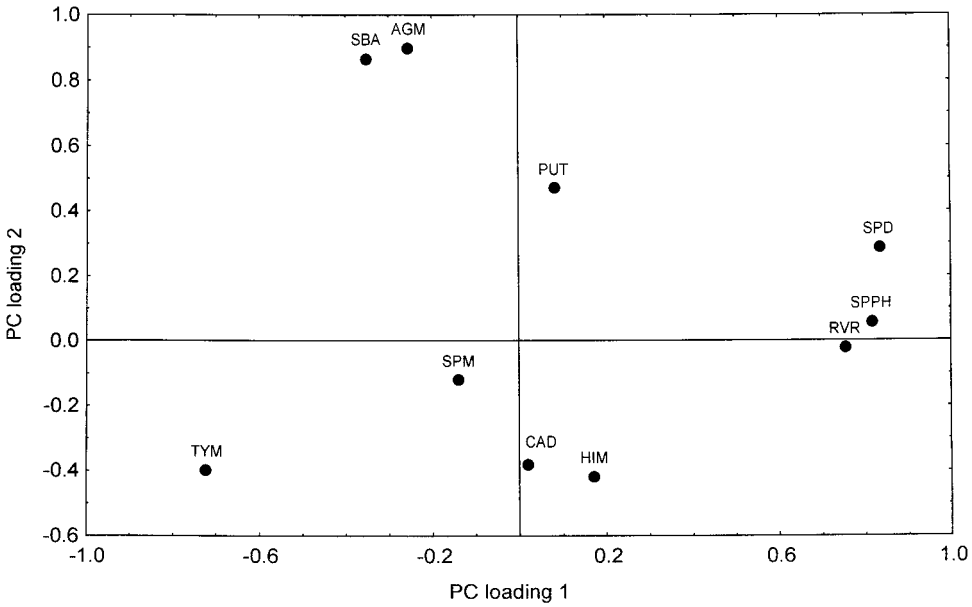


**Figure 2.** Unrotated principal component loadings (similarity of substances), loading 1 versus loading 2.

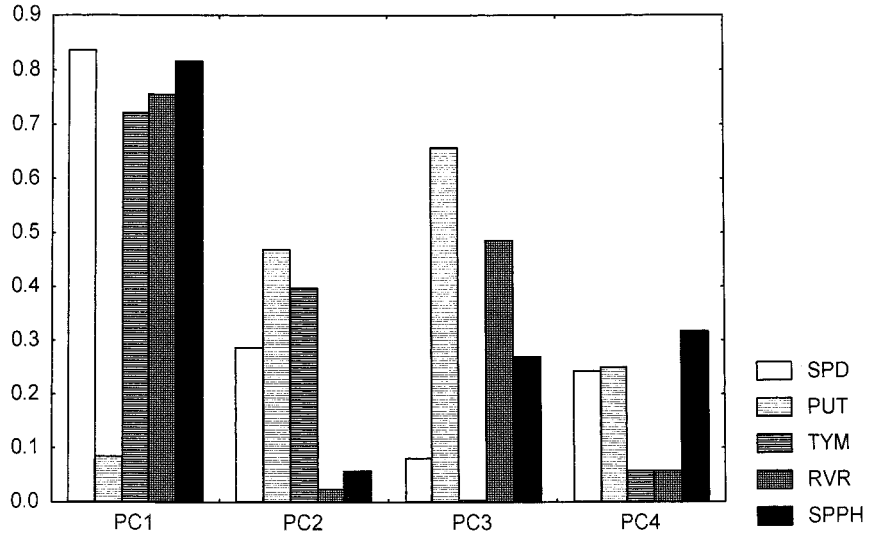


**Figure 3.** Contribution of individual variables (absolute values of loadings) to the four principal components retained in the model.

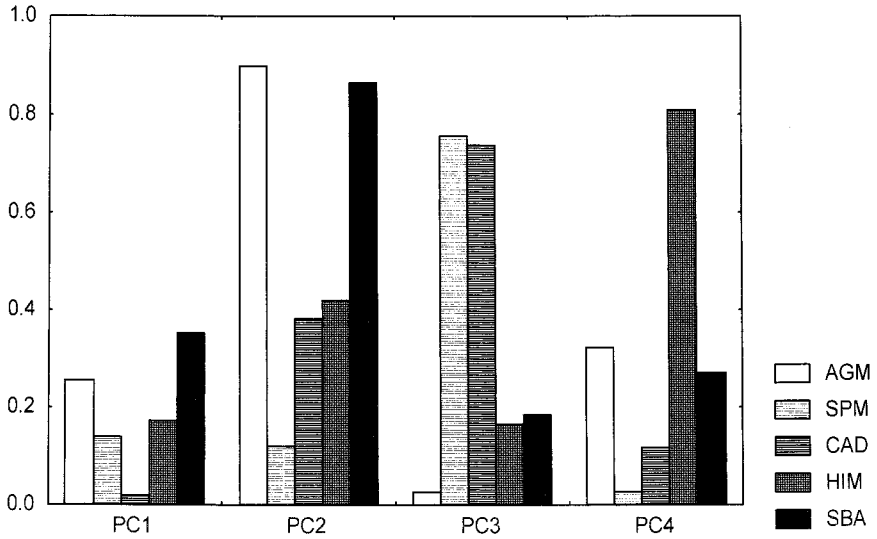


**Figure 4.** Contribution of the remaining variables (absolute values of loadings) to the four principal components retained in the model.

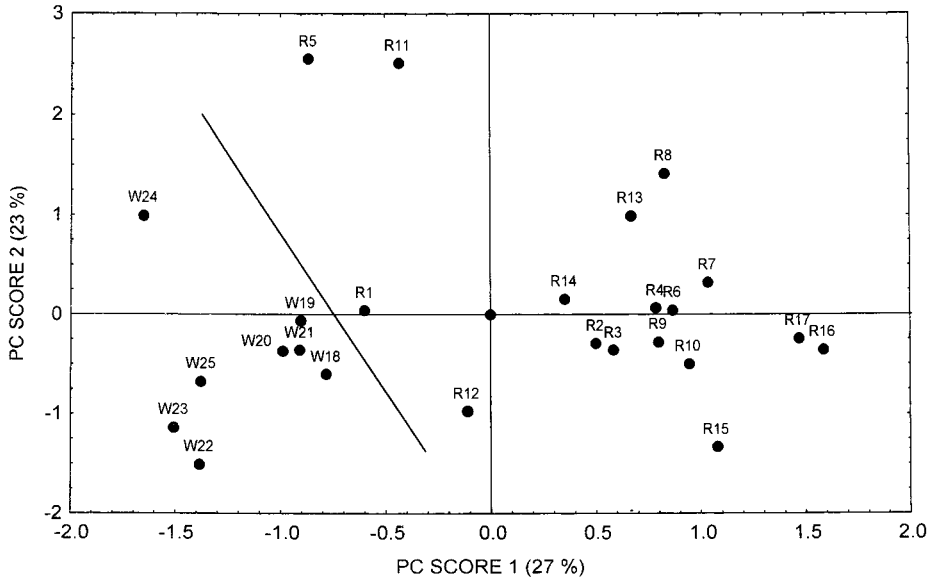


**Figure 5.** Unrotated principal component scores (similarity of wines), score 1 versus score 2. (The explained variances are in parentheses.)

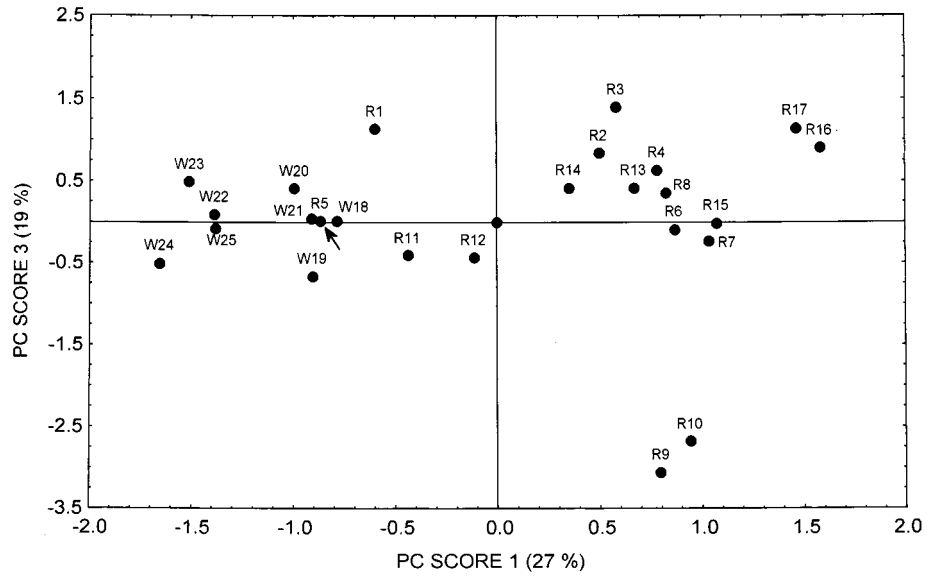


**Figure 6.** Unrotated principal component scores (similarity of wines), score 1 versus score 4. (The explained variances are in parentheses.)

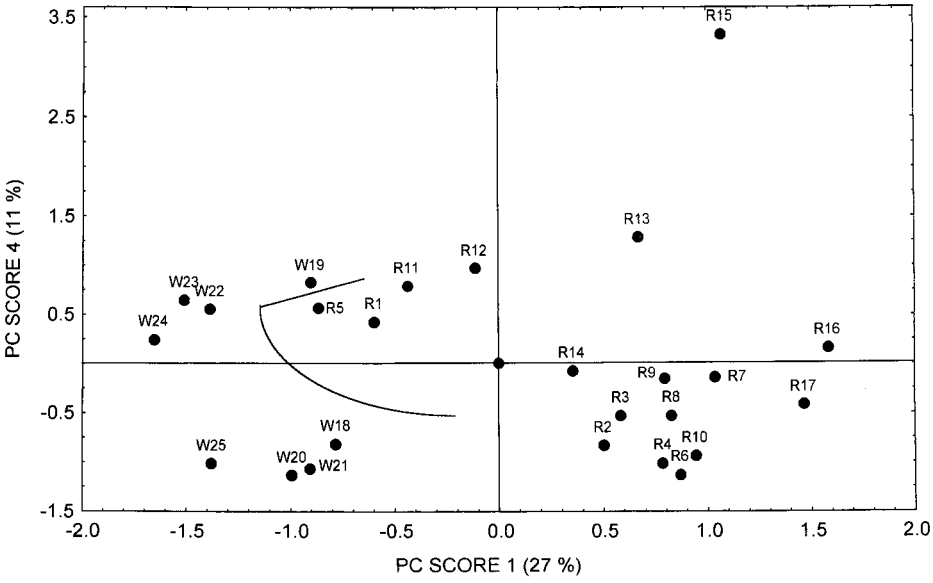


**Figure 7.** Unrotated principal component scores (similarity of wines), score 1 versus score 4. (The explained variances are in parentheses.)

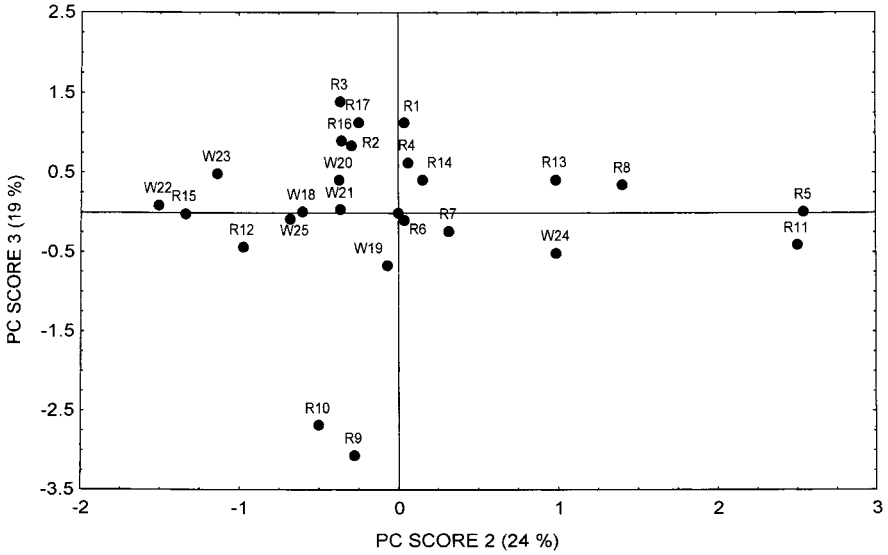


**Figure 8.** Unrotated principal component scores (similarity of wines), score 2 versus score 3. (The explained variances are in parentheses.)

Similarly, its RVR content is relatively low. This can justify the closeness of the R1 point to those of the white wines. The next closeest point to the white wines is the point for R12. It is in the negative area because of its low SPPH and SBA contents. The points in anomalous positions, R5 and R11, are outliers, and they have huge AGM and high SBA contents. There is no RVR and only low SPPH content in the wine marked by R5. W24 stands out among the white wines with its high AGM and SBA contents.

On the second score plot (**Figure 6**) the distinction between red and white wines is almost complete. The only exception is the wine marked by R5.

The lack of RVR and low SPPH content explains this anomaly. The point for R1 gets close to the white wines because of the parameters mentioned above. The "red wine" points closest to "white wine" points are marked by R11 and R12. They have relatively low SPPH contents but get close to the white wines, possibly because of their TYM contents. There are two outliers in this plot: R9 and R10 belong to a separate group because of their high CAD and SPM contents. In other words, PC3 is related to these wines. They form a separate group with Ward's method (cf. **Figure 1**).

Again, the distinction between red and white wines is almost complete in **Figure 7**.

The exception is marked by R5, explained already. The points for R1, R11, and R12 (negative first-score values) have also been explained. The outlier point (R15) is separated from the other red wines because of its very high HIM content. The fourth principal component (score 4) separates the white wines into two groups according to their HIM contents. The "white wine" group (W18, W20, W21, and W25) embraces wines that do not contain any HIM. In the other "white wine" group, only W24 does not contain any HIM. This could put it into the upper group that contains HIM because of its high AGM, SBA, and SPPH contents. The only surprise is W19, which in PCA does not appear to be related to the red wines in its group as compared to cluster analysis (cf. **Figure 1**).

The red wine−white wine distinction has to be given up on the basis of data presented in **Figure 8**, although the principal components embody a large portion of the total variance.

The white and red wines are mixed here. The points for R5 and R11 stand out because of their high AGM and SBA contents. The other two outliers (R9 and R10) do not fit among the majority because of their high SPM and CAD contents.

PCA is able to characterize the wines according to their biogenic amine and polyphenol contents. Different sorts of wines (red and white wines) can be distinguished using PCA. A CA provides similar information; still, not all white wines are classified properly (cf. W19 among the red wines). The loading plots reveal that there is no need to measure all of the variables to achieve the same characterization. It is enough to measure one variable per group. Naturally, this conclusion is valid within the limits of the present study; wines of other regions might behave differently.

## ACKNOWLEDGMENT

We thank Dr. Judit Jakus for reading the manuscript.

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**Received for review December 21, 2001. Revised manuscript received March 4, 2002. Accepted March 11, 2002. This work was supported by the Hungarian Research Foundation (OTKA T 029748).**

JF011699A