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Presentation and Determination of Hop (*Humulus lupulus* L.) Cultivars by a Min-Max Model on Composition of Hop Essential Oil

A min-max model of GC data on composition of hop essential oils for presentation and determination of different hop varieties developed on the Institute of Hop Research and Brewing in Žalec by Draga Kralj and coworkers was used to describe the essential oil composition of some commercially interesting German cultivars (Perle, Magnum, Taurus) and some typical modern Slovene cultivars (Celeia, Cerera). The cultivars in question were also compared to the so called European traditional aromatic hops: i.e. the aromatic hops of Bavarian and/or Czech origin together with English Fuggles and Goldings which are considered standard high quality aromatic accessions. The results are commented also for differences in essential oil composition owing to different growing areas. The matching between samples originating from different growing areas is very good: as expected, the composition of the essential oil for a given accession in a given growing area varies little from year to year, is slightly more different for the same accession grown in different growing areas but varies widely (i.e. is characteristically different) for different accessions. The 31-parameter model is a simple and reliable way for cultivar identification and determination. The matching of these parameters for each variety with the parameters for European traditional aromatic hops is also an objective indication of the organoleptically determined aroma score.

BC 12 Hops

(Descriptors: composition of hop essential oil, hop cultivars, min-max model.

Deskriptoren: Zusammensetzung des Hopfenöls, Hopfensorten, Min-Max-Modell).

1 Introduction

1.1 The min-max model (M_{min}-M_{max} system) used

The composition of the essential oil for a given hop (*Humulus lupulus* L.) accession varies very little from year to year, but varies widely (i.e. is characteristically different) for different accessions, this means that the composition of hop essential oil depends very much on the genotype. On the Institute of Hop Research and Brewing in Žalec a method to describe the genetic variability of hops by the differences in the composition of hop essential oil was developed using GC data on hop essential oils of numerous hop accessions (essential oils of more than 100 hop accessions grown mostly in the hop bank in Žalec were analysed several years in succession, about 180 peaks were quantified per chromatogram). The collecting of data and the ways of handling them in order to come the final model (the 31-parameter M_{min}-M_{max} matrix) were presented elsewhere (1, 2). During the last years new data have been added to the data set, making it more and more reliable and useful. None of the newly obtained results caused any significant changes in the already established M_{min}-M_{max} system. Here the model is refered to as a tool used in another practical application, namely in looking for differences in essential oil composition owing to different growing areas and in comparing commercially interesting and/or new cultivars to the so called European traditional aromatic hops: i.e. the aromatic hops of Bavarian and/or Czech origin together with English Fuggles and Goldings which are considered standard high quality aromatic accessions.

1.2 How to read the M_{min}-M_{max} matrix used

The raw GC data obtained by classical chemical methods (1), were best presented by a matrix where each row contained data about a specific sample of the essential oil. In this context a specific sample stands for the essential oil of a given hop sample. In order to evaluate the differences between various samples of the same hop accession several analyses of the same hop accession (cultivar) have to be performed, preferably from different crops, different climatic conditions and grown under as different conditions as possible. So, the variability of the essential oil composition of the same hop accession is evaluated. If the GC data are presented as relative areas, the relative amount of every constituent of the essential oil in such a series is not a single value any more, it becomes an interval indicating the variability of each of these parameters for the accession in question. Using relative areas (relative percentages) to describe the chromatograms can be justified, though strictly chemically speaking it is far from being the best way of presenting such data. In our case, all the peaks (even those "important ones" selected for the M_{min}-M_{max} matrix) were not identified, so absolute values of the concentrations for the compounds in question are not obtainable. Further on, the chromatograms were run without any internal standard, so comparing anything but relative values becomes impossible.

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As the differences between various samples of each accession (with all the variations mentioned above being taken into account) were as a rule minor compared to the differences between various accessions, these data can be considered a characteristic of each accession. And even more than that: the overall M_{min}-M_{max} matrix which includes data on all the samples analysed reveals also information about related accessions and these can be grouped according to their genetic inheritance and even according to their aroma score or other parameters by combining similar chromatograms (meaning similar relevant data from the chromatograms).

So, a discriminating M_{min}-M_{max} matrix has to be prepared for each hop accession and further on as many hop accessions as possible have to be included into the study in order to describe the overall genetic variability of the entire species (*Humulus lupulus* L.). One indication that the data included really cover all the variability is the possibility of including new data without having to change the minimal and maximal values for any of the constituents in the overall M_{min}-M_{max} matrix.

Such an overall M_{min}-M_{max} matrix includes minimal and maximal values for each of the constituents measured, it covers all the accessions analysed and implicitly each individual accession and every possible group of accessions (especially meaningful being those which are linked by common characteristics). Such a M_{min}-M_{max} matrix describing accessions with characteristics clearly defined by other measurements or observations (analyses) can be used to evaluate such characteristics (e. g. aroma) in an independent and objective way (3, 4). They can be used and are currently being used to predict such characteristics by comparing data for new and unknown samples to a partial M_{min}-M_{max} matrix obtained from such a data base.

Taking into consideration that the components selected as important by various standard statistical methods (1) occur in very different concentrations (relative percentages can differ by some orders of magnitude) and that sometimes the ratios between their contents are more important than the contents themselves, we got these data "on the same scale" by expressing the fraction of each essential oil component by an index (X_N) denoting the relative percentage of the component in question relatively to its maximal content in all the accessions studied (2). The presentation of the 31 GC parameters on a chart giving the numbers of the chromatographic peaks on the x-axis and its minimal and maximal indexes (X_N) on the y-axis is referred to as a min-max model of any analysed accession or the min-max model of a group of investigated accessions.

1.3 Using the model for determination and evaluation of hop accessions

The min-max models of various hop varieties as described above can be used for identification and in some aspects also for aroma quality evaluation of hop varieties. The min-max model of each variety is compared to the values obtained for the sample under investigation. Ideally, the values for the relative amounts of each constituent analysed fall within the interval previously determined for the variety. Sometimes different growing conditions (not to mention different picking procedures, sample preparations and other discrepancies) can cause some minor differences, but the pattern remains unmistakable.

Different target groups, sometimes a single variety, sometimes a group of related varieties, are presented as "corridors" on the charts of the min-max model. These "corridors" are wider or narrower depending on the target group in question. On the figures in this paper the narrow ones (the shaded areas) represent the variety under investigation, while the lines max model and min model define the – obviously much wider – "corridor" for the group of European traditional aromatic hops. Each such "corridor" reflects the values of the indexes as they appear in the target group.

2 Materials and Methods

2.1 Chemical analysis of the essential oil

Analytical procedures (preparation of the essential oil and the following capillary GC analysis) have been performed in standard ways, described elsewhere (1). Table 1 gives the components

Table 1 List of the components considered

peak number	rel. % for an index of 100	name of the component
GROUP 1		
108/104*	5.01*	α-humulene/ β-caryophyllene*
108	51.51	α-humulene
127	4.31	
98	1.29	geranyl acetate
83	3.68	methyl-nonyl-ketone
85	4.86	
30	64.91	myrcene
104	23.72	β-caryophyllene
GROUP 2		
56	0.81	methyl octanoate
77	1.63	geraniol
114	4.66	
130	5.05	
128	6.29	
118	16.77	
116	14.95	
GROUP 3		
71	0.58	
110	23.59	farnesene
142	16.21	
174	3.53	
GROUP 4		
113	0.96	
93	0.17	
112	0.71	
131	1.81	
94	0.13	
126	1.56	
88	1.18	
115	9.58	
33	0.69	
40	2.34	
132	7.27	
99	0.55	

*108/104 is the α-humulene/β-caryophyllene ratio considered in the description of the essential oil (1, 2). The first column gives the number of the peak in the chromatogram, the second the relative percentage of each peak which was given an index of 100 and the third the names of some most characteristical components.

2.2 Hop samples analysed

The composition of the essential oils of two German cultivars (Perle and Magnum) grown in Slovenia (where the composition of their essential oils is being followed for some years) was compared with two samples of the same varieties grown in Hallertau. Additionally, the variety Taurus grown in Hallertau is also presented. All the samples from Germany were representative for the 1997 crop.

Essential oil composition of Cerera and Celeia, two modern varieties bred in Slovenia and grown mostly in Slovenian hop growing districts and in Austria are presented. The samples from which their min-max model was obtained were collected in gene bank in Žalec or in near vicinity, the comparative samples were picked in Radlje (another hop growing district in Slovenia with characteristically different climatic conditions). The samples from Radlje were representative for the 1997 crop.

All samples from Germany were given an organoleptical aroma score by the standard method in the Hop Institute in Hüll.

On all the Figures the model of traditionally aromatic hops is also presented. This enables some direct comparison with this group, traditionally praised for excellent aroma quality.

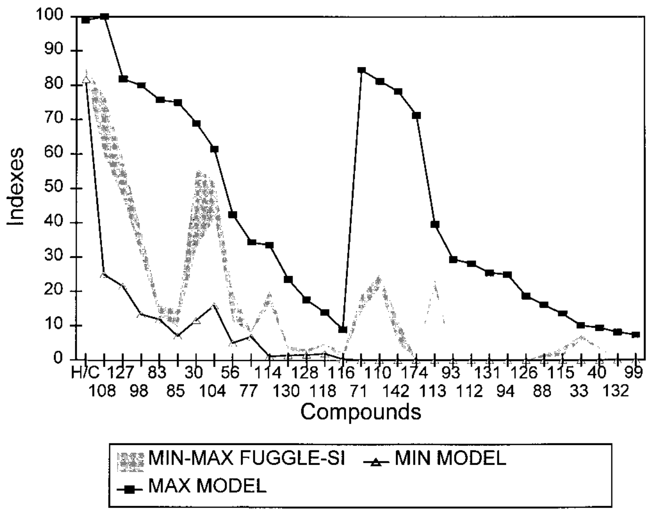

Fig. 1 Min-max model for a typical Fuggle variety (the shaded "corridor" (min-max Fuggle-SI) represents samples grown in Slovenia, analysed some years in succession), in the background min-max model for European traditional aromatic hops (lines min model and max model)

3 Results and Discussion

3.1 The group of European traditional aromatic hops

The so called traditional European aromatic hops: i.e. the aromatic hops of Bavarian and/or Czech origin together with English Fuggles and Goldings were chosen as a reference group, a standard of high quality aromatic accessions. The maximal and minimal values for the chosen 31 parameters (specified in Table 1) for this group are presented on Figure 1. It gives the pattern for the essential oil composition of high quality aromatic hops and data for all the accessions having this quality should fit within these two lines. On Figure 1 this is shown for the example of a typical Fuggle.

3.2 Comparison of the essential oils of cultivars Perle and Magnum grown in Germany and in Slovenia

Figures 2 and 3 represent data on two typical German hop varieties, namely Perle and Magnum. On the background of the

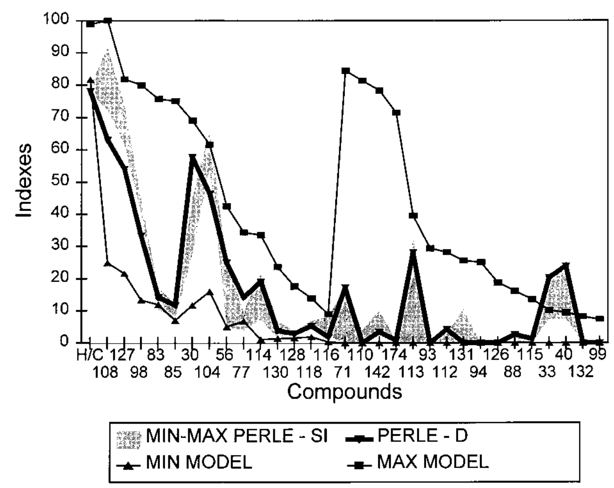

Fig. 2 Min-max model for variety Perle (the shaded "corridor" (min-max Perle-SI) represents samples grown in Slovenia, analysed some years in succession, the strong line (Perle-D) stands for the representative sample of the Hallertau 1997 crop), in the background min-max model for European traditional aromatic hops (lines min model and max model)

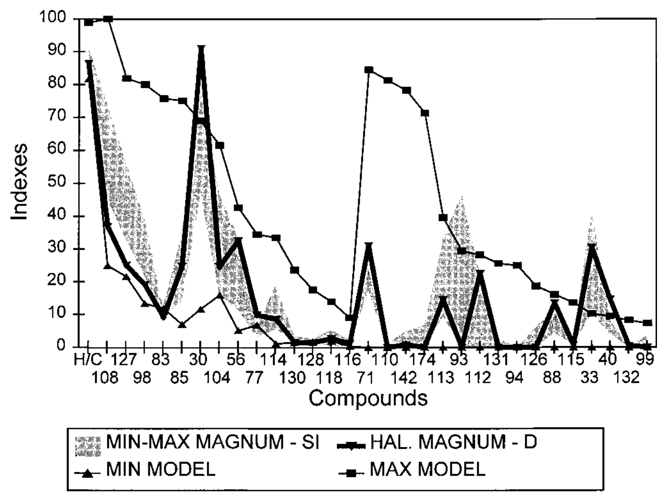

Fig. 3 Min-max model for variety Magnum (the shaded "corridor" (min-max Magnum-SI) represents samples grown in Slovenia, analysed some years in succession, the strong line (Magnum-D) stands for the representative sample of the Hallertau 1997 crop), in the background min-max model for European traditional aromatic hops (lines min model and max model)

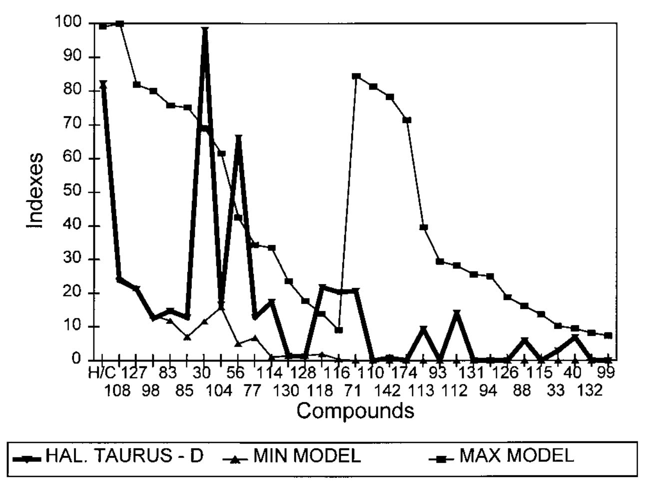

Fig. 4 Min-max model for variety Taurus (the strong line (Taurus-D) stands for the representative sample of the Hallertau 1997 crop), in the background min-max model for European traditional aromatic hops (lines min model and max model)

min-max model of European traditional aromatic hops there is a very narrow min-max model representing the characteristics of hop essential oil for each accession grown in the hop gene bank on the Institute of Hop Research and Brewing in Žalec (Slovenia). It includes results obtained for this variety several years in succession. The strong line on the other hand represents results of a representative sample the 1997 hop crop for each of the two varieties obtained from the Hallertau hop growing district in Germany. The unmistakable pattern for one or the other variety is undoubtedly there, minor differences (especially higher myrcene content for both varieties if grown in Hallertau) can best be explained by different picking time or different drying or storage conditions. Nevertheless, the differences are not very striking and do by no means influence the characteristic pattern of the variety.

Especially the Perle variety fits nearly perfectly into the min-max model for European traditional aromatic hops (only constituents 33 and 40 are found to occur in somewhat higher concentrations than those typical for the accessions chosen to build the European traditional aromatic hop corridor). This is confirmed also by a very high aroma score determined organoleptically for this same sample (24 points).

Differences for the Magnum variety if compared to the same model group are a bit more pronounced (constituents 30, 33 and 40 occur in somewhat higher concentrations than those typical for the accessions chosen to build the European traditional aromatic hop corridor). This speaks also for somewhat lower aroma score (23 points). Also by this method, Magnum is obviously a bitter hop variety with some proprieties qualifying it for a rather good aroma hop variety as well. Details on organoleptical aroma score results and their relations to GC data have been reported elsewhere (3, 4).

3.3 Variety Taurus is rather close to European traditional aromatic hops

Further on, Taurus, another popular German variety, has been presented on the background of the min-max model of the European traditional aromatic hops. Its relatively high aroma score (22 points) qualified it to be compared with the model group and as Figure 4 clearly shows the comparison reveals a close similarity, though the matching is worse as in the cases of Perle and Magnum (constituents 30, 56, 118 and 116 are found to occur in somewhat higher concentrations than those typical for the accessions chosen to build the European traditional aromatic hop corridor). As we had no data on the Taurus variety grown in non German hop growing regions no comparison could be made in this sense.

3.4 Comparison of the essential oils of cultivars Celeia and Cerera grown in Žalec and in Radlje

Figures 5 and 6 show essential oil characteristics for Celeia and Cerera, two modern hop cultivars bred in Slovenia and grown mostly in Slovenia and Austria. The way of presenting data is exactly the same as for Perle and Magnum, KR (Koroška) standing for the hop growing district in Radlje, outside Savinjska dolina. Again the variety pattern is clearly recognisable and once again it has been proven, that the min-max model of the crucial essential oil components proposed in the model described, represents a reliable way for determination of hop varieties.

4 Conclusions

The validity of the min-max model developed on the Institute of Hop Research and Brewing in Žalec has been tested on three representative samples of commercially interesting German cultivars (Perle, Magnum, Taurus) and on two representative samples of modern Slovene cultivars (Celeia, Cerera) grown in Radlje. It was confirmed that the influences of the growing region and/or of different picking, drying and storage conditions are minor compared to the influence of the genetic characteristics of any given cultivar. So, the model can be considered a reliable tool to determine the cultivars. All the samples fit relatively well into the min-max model of traditional European aromatic hops which agrees also with the aroma score determined organoleptically.

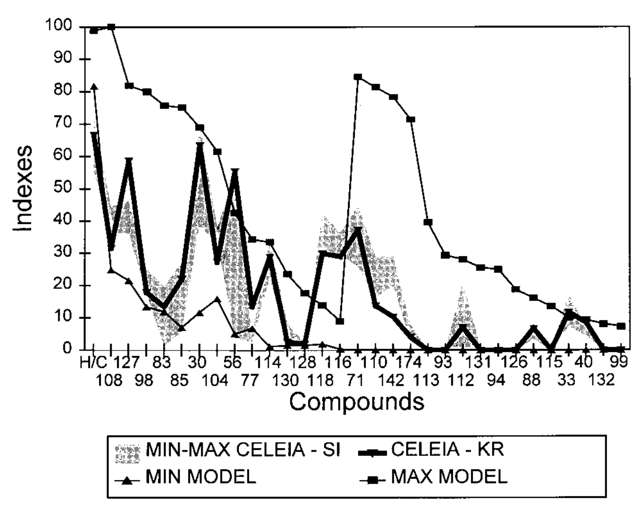

Fig. 5 Min-max model for variety Celeia (the shaded "corridor" (min-max Celeia-SI) represents samples grown near Žalec, analysed some years in succession, the strong line (Celeia-KR) stands for the representative sample of the 1997 crop in Radlje), in the background min-max model for European traditional aromatic hops (lines min model and max model)

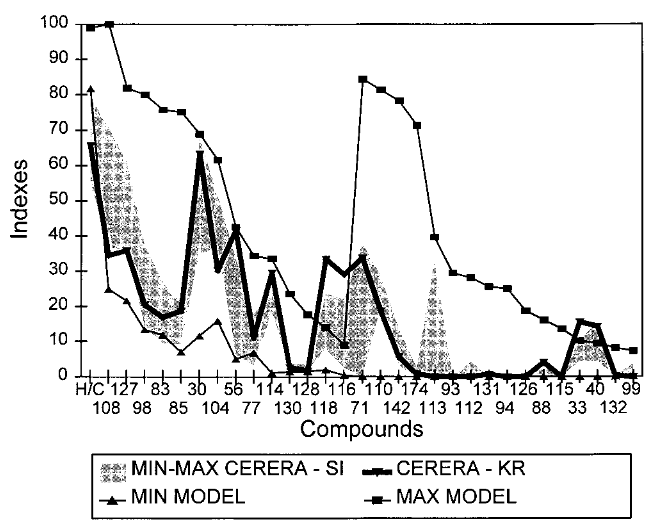

Fig. 6 Min-max model for variety Cerera (the shaded "corridor" (min-max Cerera-SI) represents samples grown near Žalec, analysed some years in succession, the strong line (Cerera-KR) stands for the representative sample of the 1997 crop in Radlje), in the background min-max model for European traditional aromatic hops (lines min model and max model)

Acknowledgements

Authors thank Mr. Bernhard Engelhard and his colleagues of the Bavarian Institute of Hop Research in Hüll for cooperation and hop samples.

Valuable suggestions and encouragements of Dr. Draga Kralj and skilful technical assistance of Mrs. Mira Hrovat as well as funding of Slovenian Ministry of Science and Technology are gratefully acknowledged.

5 Zusammenfassung

Kač, M., und Kovačevič, M.: Darstellung und Identifizierung von Hopfensorten anhand eines Min-Max-Modells der Hopfenöl-Zusammensetzung — Monatsschrift für Brauwissenschaft **53**, Nr. 9/10, 180 –184, 2000

BC 12 Hopfen

Ein Min-Max-Modell der gaschromatographischen Ergebnisse über die Zusammensetzung von Hopfenöl, das am Institut für Hopfenbau und Brauereiwesen in Žalec von Draga Kralj und Mitarbeitern zur Darstellung und Identifizierung von Hopfensorten entwickelt wurde, wird zur Präsentation von einigen kommerziell interessanten deutschen Hopfensorten (Perle, Magnum, Taurus) und einigen typischen modernen slowenischen Hopfensorten (Celeia, Cerera) benutzt. Die erwähnten Hopfensorten werden auch mit den traditionellen europäischen aromatischen Hopfensorten (bayerischer und/oder Saazer Hopfen wie auch englische Fuggles und Goldings), die für ihr edles Hopfenaroma berühmt sind, verglichen. Auch die Einflüsse verschiedener Hopfenanbaugebiete auf die Zusammensetzung des Hopfenöls werden kommentiert. Die Übereinstimmung der Zusammensetzung der Hopfenöle einzelner Hopfensorten aus verschiedenen Hopfenanbaugebieten ist sehr gut. Wie zu erwarten war, sind die Unterschiede in der Zusammensetzung der Hopfenöle einer gegebenen Hopfensorte aus einem bestimmten Hopfenanbaugebiet bei verschiedenen Jahrgängen sehr gering, etwas größer werden sie, wenn dieselbe Hopfensorte aus verschiedenen Hopfenanbaugebieten über einige Jahre hinweg analysiert wird. Die Differenzen werden aber erst charakteristisch, wenn verschiedene Hopfensorten verglichen werden. Das Modell, welches 31 Parameter umfaßt, bietet eine einfache und zuverlässige Möglichkeit zur Identifizierung und Qualitätsbeschreibung von Hopfensorten. Der Vergleich mit den traditionellen europäischen aromatischen Hopfensorten ermöglicht auch eine objektive Indikation des organoleptisch bestimmten Aromas.

Kač, M., et Kovačevič, M.: Représentation et identification de variétés de houblon avec un modèle Min-Max sur la composition d'huiles essentielles du houblon — Monatsschrift für Brauwissenschaft 53, No 9/10, 180 – 184, 2000

BC 12 Houblon

On présente un modèle Min-Max sur les résultats de chromatographie en phase gazeuse concernant les huiles essentielles du houblon effectués à l'Institut de culture du houblon et de la brasserie à Žalec par Draga et collaborateurs. Il a été développé par la représentation et l'identification de variétés de houblon et il est utilisé pour la présentation de quelques variétés de houblon allemand intéressantes (Perle, Magnum, Taurus) ainsi que de quelques variétés de houblon slovènes typiques (Caleia, Cerera). Les variétés de houblon mentionnées ont été comparées aux variétés européennes aromatiques traditionnelles (houblon bavarois et/ ou Saaz ainsi que les anglaises Fuggles et Goldings) qui sont reconnues par leur arôme de houblon noble. On commente également l'influence des differénts lieux de culture sur la composition des huiles essentielles du houblon. La liaison entre la composition des huiles essentielles du houblon de differéntes variétés de houblon de différents lieux de culture de houblon est très bonne. Comme il était attendu, les différences dans la composition des huiles essentielles d'une variété de houblon donnée et d'un lieu de culture de houblon varient peu d'une année à l'autre. La différence s'accroît lorsque la même variété de houblon est cultivée dans différents lieux de culture pendant plusieurs années. Les différences deviennent significatives lorsque l'on compare différentes variétés de houblon. Le modèle qui comprend 31 paramètres présente une possibilité simple et fiable pour l'idendification et la description de la qualité de variétés de houblon. La comparaison avec des variétés de houblon européens traditionnels aromatiques rend possible une identification objective de l'arôme déterminé organoleptiquement.

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(Manuskripteingang 27. 4. 2000)