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Varietal Discrimination of Hop Pellets. II. Comparison Between Fresh and Aged Samples

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ABSTRACT

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The aim of this study was to assess the stability during storage of several compounds previously described for distinguishing hop varieties. Volatile compounds of five aromatic cultivars (Styrie, Saaz, Lublin, Mount Hood, and Hallertau) and six bitter cultivars (Northern Brewer, Nugget, Pride of Ringwood, Northdown, Target, and Challenger), stored at different temperatures, were extracted with a Likens-Nickerson simultaneous solvent extractor. Only compounds remaining stable through aging were kept to build an identification flowchart. Although very typical of fresh aromatic hops, farnesene proved much too unstable to be selected for distinguishing aged samples. 3-Methylbutylisobutyrate, which authenticates all fresh European bitter hops, is also partially destroyed upon storage. On the other hand, bergamotene, α- and β-selinene, methyl geranate, humulene epoxide II, α-amorphene, 2-undecanone, and an unknown compound can be used to distinguish all cultivars whatever the storage temperature. Both the ratios of humulene to humulene + humulene epoxides (I, II, and III) and of bergamotene to farnesene proved good indicators of the freshness status of hop samples.

Keywords: Aroma stability, Bergamotene, Flavor

RESUMEN

Diferenciación varietal de pellets de lúpulo. II. Comparación entre muestras frescas y las mismas después de ser almacenadas

Mediante este estudio nos propusimos evaluar la estabilidad, durante el periodo de almacenaje, de determinados compuestos que con anterioridad se han utilizado para diferenciar variedades de lúpulo. Mediante un extractor simultáneo Likens-Nickerson, se extrajeron los compuestos volátiles de cinco variedades aromáticas (Styrie, Saaz, Lublin, Mount Hood y Hallertau) y de seis variedades amargas (Northern Brewer, Nugget, Pride of Ringwood, Nortdown, Target y Challenger) que habían sido almacenadas a diferentes temperaturas. Se construyó un diagrama de identificación utilizando solamente aquellos compuestos que permanecieron estables durante el periodo de almacenamiento. Aunque el farneseno es un compuesto muy característico del aroma del lúpulo fresco, no fue seleccionado entre los compuestos que diferenciaban a las muestras almacenadas al presentar demasiada inestabilidad. El 3-metilbutilisobutirato, que es un buen marcador para la identificación de las variedades amargas de los lúpulos europeos, también se degrada parcialmente durante el almacenamiento. Por otra parte, el bergamoteno, los α y β-selinenos, el metil geranato, el epóxido II de humuleno, el α-amorfeno, la 2-undecanona y un compuesto desconocido pueden utilizarse para distinguir todas las variedades independientemente de la temperatura de almacenamiento. Los cocientes entre el humuleno y la suma del humuleno con los epóxidos I, II y III del mismo, o entre el bergamoteno y el farneseno, han demostrado ser buenos indicadores de la frescura de las muestras de lúpulo.

Palabras clave: Estabilidad de aroma, Bergamoteno, Sabor

In the first part of this work, Perpète et al (6) showed a way to distinguish fresh hop pellets by analysis of essential oils. An identification flowchart including seven terpenic compounds, four esters, and one methyl ketone was established to discriminate between samples of the 12 cultivars investigated (Fig. 1). An additional advantage of this diagram was to point out common features between the aromatic hops or the various bitter cultivars. As suggested by many authors (2,4,7), dramatic flavor losses can occur during storage, depending on the conditions (temperature, light exposure, natural antioxidants in hops, etc.). Major hydrocarbons like myrcene, β-caryophyllene, and α-humulene could volatilize or be oxidized to epoxides (8). What happens, therefore, to the reliability of the discrimination flowchart when applied to aged hop samples?

In the present work, we analyzed the hop markers after the storage of 11 hop varieties at 20, 0, and –30°C for one year. The results led us to establish a second authentication procedure for

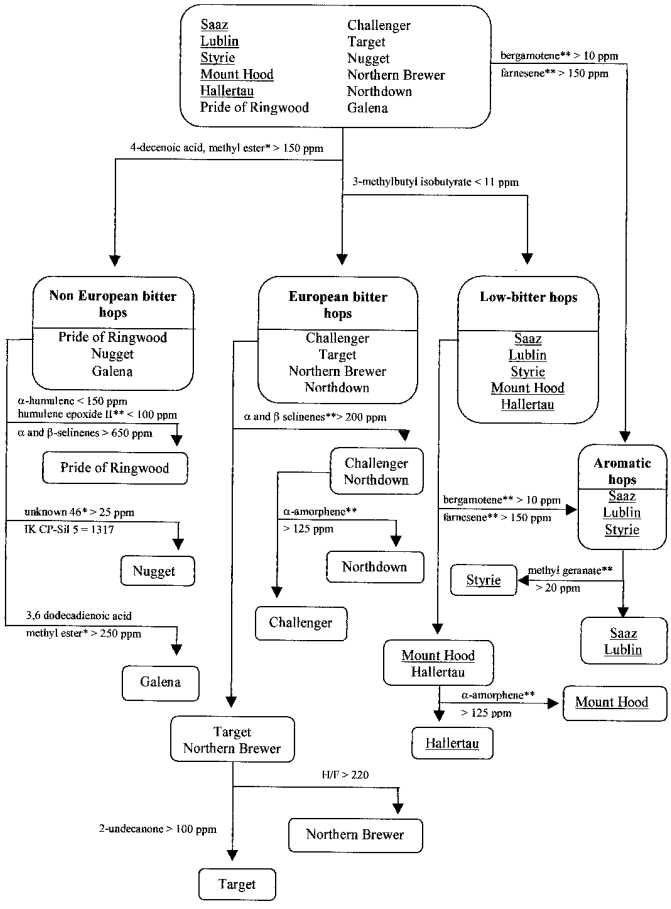

Fig. 1. Flowchart for authenticating 12 fresh hop cultivars (6). * = carvone equivalent for quantification, ** = caryophyllene equivalent for quantification.

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samples of unknown freshness. Understanding the flavor changes occurring at various temperatures should also help the brewer to assess the quality of newly bought samples and their storage conditions. Moreover, some of the stable compounds pointed out in this work could also be found in beers since they probably remain stable through the process.

EXPERIMENTAL

Hop Samples

A total of 11 fresh commercial cultivars were collected. Saaz, Lublin, and Hallertau were in T45 pellet form, while the other cultivars were in T90 pellet form. For better comparison, all our data were calculated for T90 pellet conditioning. Three samples of each cultivar were stored under nitrogen at –30, 0, or 20°C in hermetic dark packaging. The analyses were performed before and at the end of a one-year storage period.

Hop Aroma Analysis

An optimized version (1) of the Likens and Nickerson extraction procedure (3) was used, allowing high recovery of most essential oils (6).

The gas chromatograph-flame ionization detector and gas chromatography-mass spectroscopy analytical conditions were previously described by Perpète et al (6).

RESULTS AND DISCUSSION

According to Perpète et al (6), bergamotene and farnesene are key compounds for discriminating the finest aromatic varieties: Lublin, Saaz, and Styrie. As shown in Figure 2, while the bergamotene concentration is relatively stable through hop aging, the farnesene level drops drastically even when storage is at 0°C. This difference between hop sesquiterpenes probably results from the inability of bergamotene, unlike farnesene and myrcene, to undergo a Diels-Alder reaction (there are no conjugated dienes in

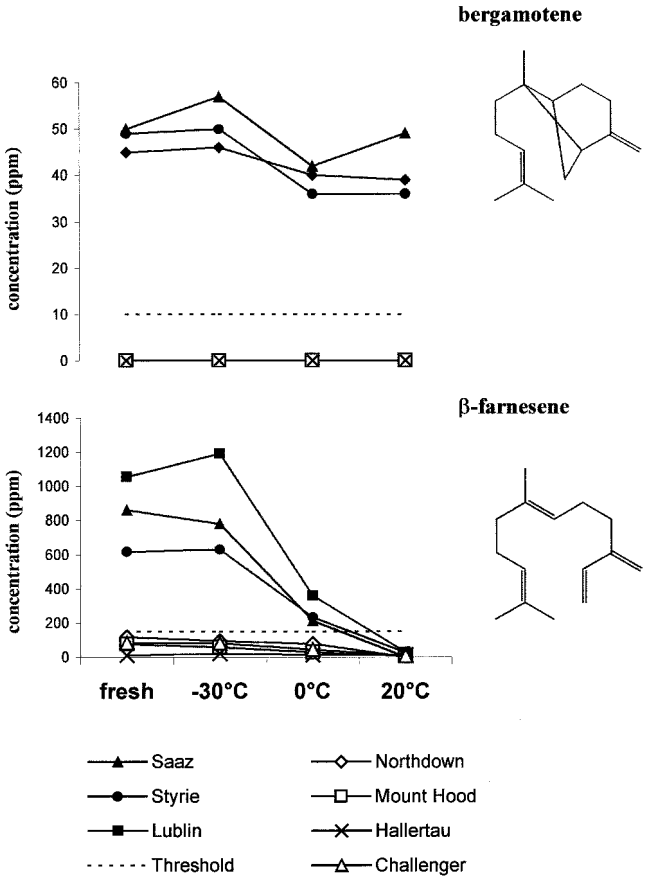

Fig. 2. Evolution of bergamotene and farnesene concentrations according to the storage conditions (–30, 0, or 20°C) in seven hop varieties. The discrimination threshold (dotted line) characterized by Perpète et al (6) allowed us to determine whether the markers were still relevant after storage.

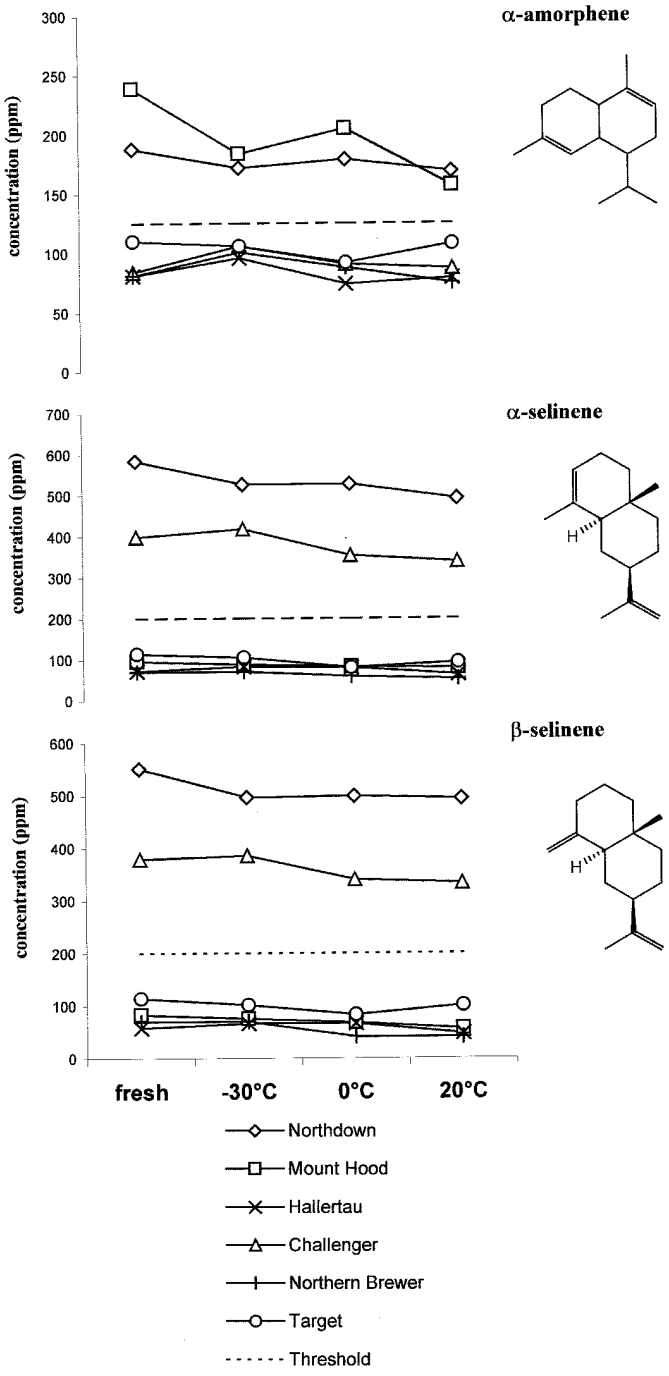

Fig. 3. Evolution of α-amorphene, α-selinene, and β-selinene concentrations according to the storage conditions (–30, 0, or 20°C) in six hop varieties. The discrimination threshold (dotted line) characterized by Perpète et al (6) allowed us to determine whether the markers were still relevant after storage.

bergamotene). From these results, we can assume that the quality of aromatic hops changes drastically during one-year storage in the brewery. Moreover, compounds like farnesene probably are quickly degraded through wort boiling, leading to undetected levels in the final beer.

In keeping with the above observation, three other sesquiterpenes without conjugated dienes (α-amorphene, α-selinene, and β-selinene) proved stable after one year at 0°C (Fig. 3). Thus, even when aged hop samples are compared, an α-amorphene concentration above 125 ppm will differentiate Northdown from Challenger and Mount Hood from Hallertau. Low levels of α-amorphene were also systematically found in other varieties such as Saaz, Lublin, Styrie, and Northern Brewer (6).

Likewise, α and β-selinenes can be kept as very good markers for authenticating the Challenger, Northdown, Nugget, and Pride of Ringwood cultivars, making it possible to distinguish them not only from Target and Northern Brewer as in the first flowchart (6) (Fig. 1), but also from Saaz, Lublin, Styrie or Mount Hood, and Hallertau (all well below 150 ppm). Due to their relative stability, we might assume that significant differences in levels of α- and β-selinenes might also be detected between beers boiled either with low bitter hops (α- or β-selinenes always below 150 ppm) or with Challenger, Northdown, Pride of Ringwood, or Nugget varieties.

Despite the absence of conjugated dienes, humulene turned out to be degraded when stored at 0°C, probably due to oxidation to epoxides (I, II, and III), as depicted in Figure 4. In extreme cases,

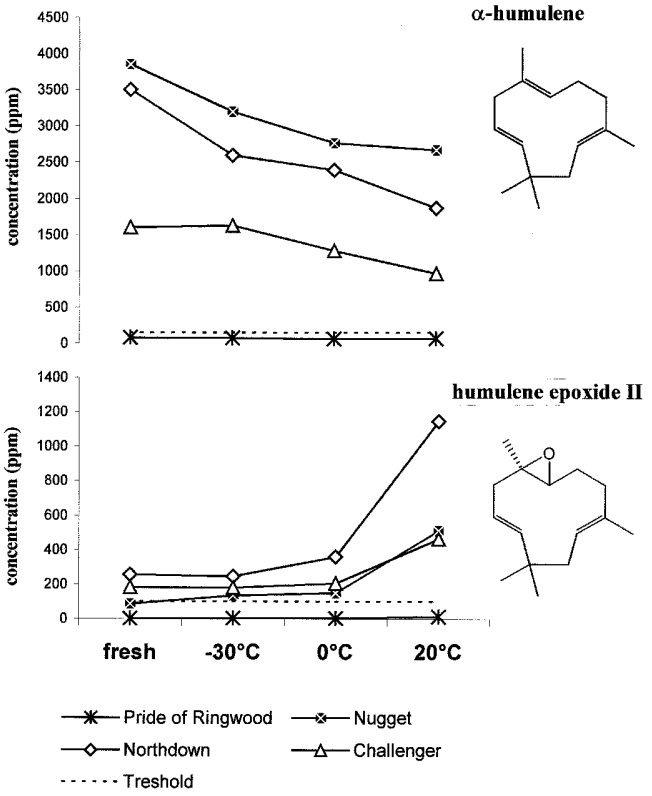

Fig. 4. Evolution of humulene and humulene epoxide II, according to the storage conditions (–30, 0, or 20°C). The discrimination threshold (dotted line) characterized by Perpète et al (6) allowed us to determine whether the markers were still relevant after storage.

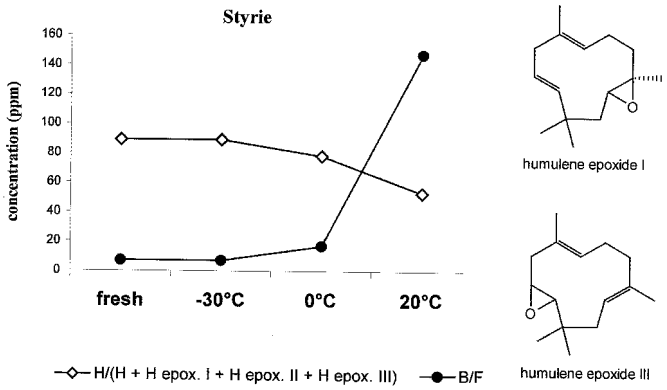

Fig. 5. Behavior of two aromatic-compound ratios for the storage-condition assessment of the Styrie hop variety. H = α-humulene; H epox. = humulene epoxide; B = bergamotene; F = β-farnesene.

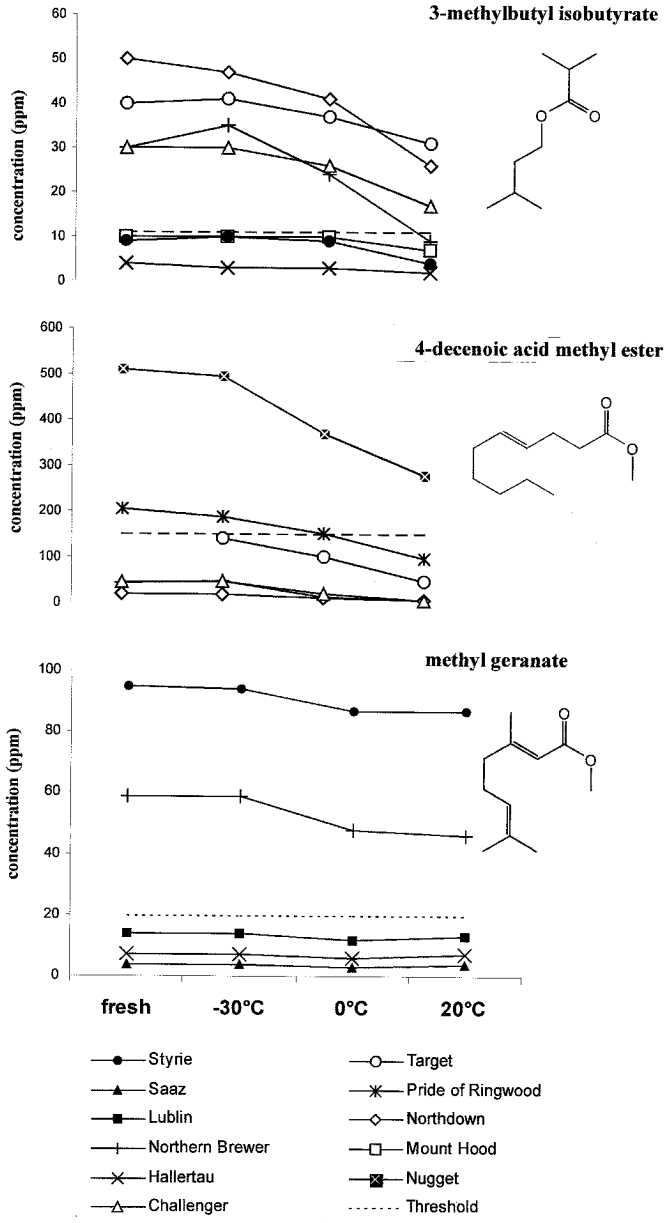

Fig. 6. Evolution of 3-methylbutyl isobutyrate, 4-decenoic acid, methyl ester and methyl geranate concentrations according to the storage conditions (-30°C, 0°C, 20°C) in 10 hop varieties. The discrimination threshold (dotted line) characterized by Perpète et al (6) allowed us to determine whether the markers were still relevant after storage.

we suspect that cultivars other than Pride of Ringwood could be below the 150 ppm proposed in Figure 1. Even in aged Pride of Ringwood samples, however, a very low humulene epoxide II level is always very typical (<30 ppm), in comparison with Challenger, Nugget, and Northdown, three other selinene-rich cultivars.

The bergamotene-farnesene ratio and the humulene-(humulene + epoxides I, II, and III) ratio depend strongly on the storage conditions. These changes occur in all varieties whatever the sample. The case of Styrie is given as an example in Figure 5. On the basis of these results, two quick means of assessing the freshness of hop samples can be proposed. Brewers should require thresholds below 5% for the former ratio (only advisable for aromatic hops [5]) and above 80% for the latter ratio (which is not easy to use for Pride of Ringwood).

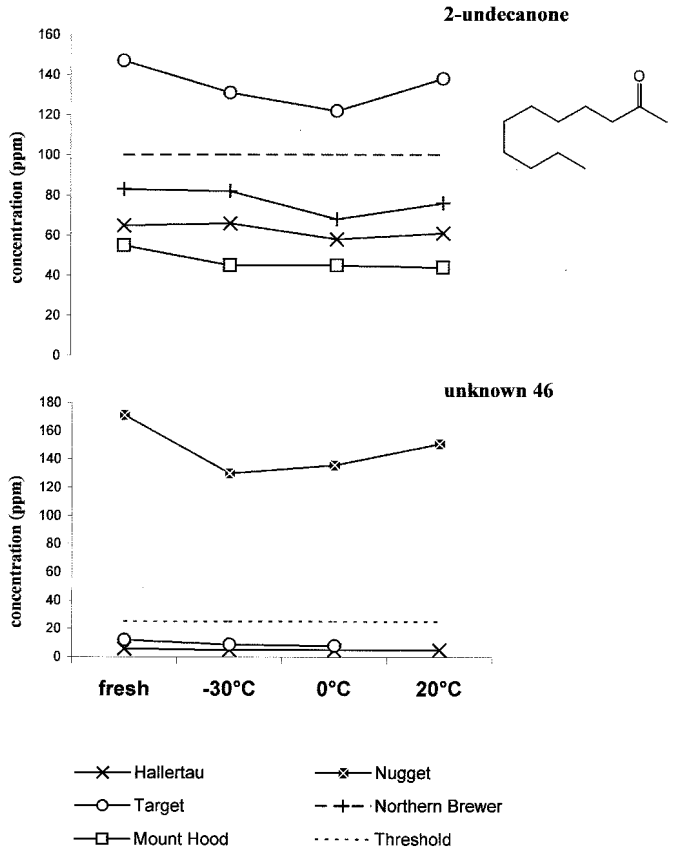

Fig. 7. Evolution of 2-undecanone and unknown 46 concentrations according to the storage conditions (–30, 0, or 20°C) in five hop varieties. The discrimination threshold (dotted line) characterized by Perpète et al (6) allowed us to determine whether the markers were still relevant after storage.

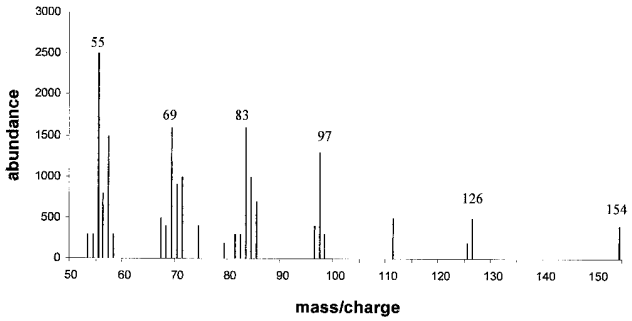

Fig. 8. Mass spectrum of unknown 46.

According to Perpète et al (6), quantification of 4-decenoic acid methyl ester and 3-methylbutyl isobutyrate proves an effective way to distinguish non-European bitter hops from aromatic cultivars. Unfortunately, both compounds turn out to be degraded through hop aging (Fig. 6). Among esters, only methyl geranate appears sufficiently stable to be kept for the second discrimination flowchart.

The levels of methylketone and of unknown compound 46 (Fig. 7) were relatively constant even after one year of storage at 20°C. In the case of 2-undecanone, however, we suspect that degradation occurs in the wort through yeast reduction, giving rise to an organoleptically active alcohol. The mass spectrum of unknown 46 (I_k CP-Sil 5 = 1,317) (Fig. 8) is very similar to the one of menthone (I_k = 1,162). According to the fragmentation, other compounds like carvone (I_k = 1,224), dihydrocarvone (I_k = 1,182), tetrahydrocarvone (I_k = 1,184), terpinene-4-ol (I_k = 1,170), menth-l-en-9-ol (I_k = 1,281), and citronellal (I_k = 1,218) were suspected of being analogs of this compound. However, we couldn't manage to define the exact structure, probably a cyclic monoterpene derivative containing a keto function.

All the stable markers discussed above were taken into account in building the discrimination flowchart shown in Figure 9. Thresholds of 10 ppm bergamotene and 150 ppm selinene are used here to distinguish aromatic hops from two nonaromatic groups. By quantifying only five other compounds (humulene epoxide II, α-amorphene, 2-undecanone, methyl geranate, and an unknown) one can establish the hop cultivar, whatever its freshness. Although not suited, like the former chart, for quickly distin-

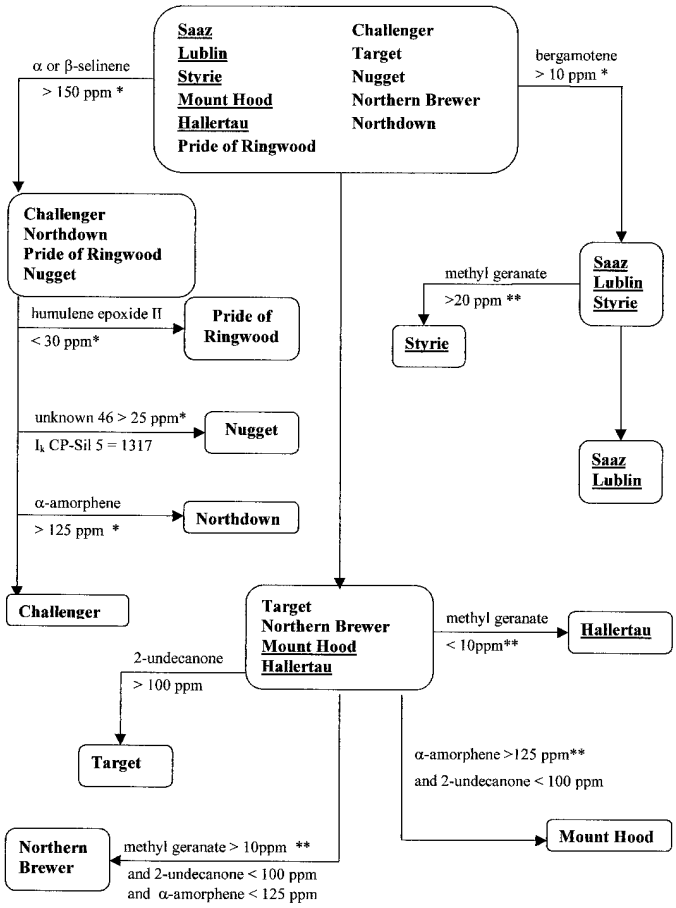

Fig. 9. New flowchart for distinguishing 11 hop cultivars whatever the storage conditions. * = carvone equivalent for quantification, ** = caryophyllene equivalent for quantification.

guishing non-European and European bitter hops from low-bitter hops, this diagram has the advantage of pointing out some stable compounds that could differentiate beers boiled with various hop cultivars.

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