

# Comparison of quality parameters of Czech and foreign hop varieties

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## ABSTRACT

Market varieties of hops are classified to several groups according to their use in the brewing industry – aroma, bitter (dual-purpose), high-alpha ones. Saaz and other genetically related varieties form a separate group among the aromatic hops. The group called fine aroma hops has a low content of  $\alpha$ -bitter acids (3–4% w/w), its content of  $\beta$ -bitter acids is in the range of 4–7% w/w and cohumulone ratio in the interval of 23–26% rel. The composition of hop oils is characterised by the content of  $\beta$ -farnesene in the range of 15–20% rel. and *trans*- $\alpha$ -bergamotene at the amount of ca. 1% rel. Most market varieties of hops are of hybrid origin. It holds true about the Czech varieties Sládek, Bor, Premiant and Agnus. The content of  $\alpha$ -bitter acids in bitter varieties is in the range of 7–10% w/w while the content of  $\alpha$ -bitter acids in high-alpha hops is higher than 10% w/w.

**Keywords:** hop varieties; hop resins; hop oils;  $\alpha$ -bitter acids;  $\beta$ -bitter acids

The number of registered hop varieties increases all the time. The assortment of cultivated hops conforms to changes in brewing technology and to economics of production process. Market varieties of hops are classified to the groups according to their use in the brewing industry parallelly with increasing knowledge of the composition of hop resins and other secondary metabolites (Forster and Schmidt 1993, Maier 1995). An up-to-date classification scheme was worked out by Vent and Vent (1999). According to this scheme hop varieties are sorted into four groups – fine aroma, aroma, bitter (dual-purpose) and high-alpha ones. Several varieties with different use in the brewing industry are usually grown in the countries with developed hop industry. The only variety, Saaz fine aroma hops, was grown in the Czech Republic until the mid-90ies. A turnover came in the second half of the 90ies. Hybrid varieties of Czech origin Bor, Sládek, Premiant and Agnus started to be cultivated on a large scale. A part of Saaz variety is preserved in their genetic constitution (Nesvadba 2001, Krofta and Nesvadba 2002). Currently, the Czech hop industry offers breweries a large assortment of market varieties of hops including high-alpha hops. The objective of this paper is to compare selected quality parameters of Czech and foreign hop varieties of the same brewing use.

## MATERIAL AND METHODS

Qualitative characteristics of hop varieties were determined by analyses of hop resins and hop oils. Hop resins were analysed by HPLC method according to EBC 7.7 and by modified Wöllmer's method (EBC 7.5). Both methods are based on the extraction of hop resins in a two-phase diethyl ether-methanol system.  $\alpha$ -Bitter acids and  $\beta$ -bitter acids were separated directly from the diethyl ether phase on HPLC column Nucleosil RP C<sub>18</sub> (Macherey Nagel, Germany), 5  $\mu$ m, 250  $\times$  4.0 mm. The column temperature was 40°C. The mobile phase consisted of a mixture

of methanol-water-phosphoric acid (850:190:5 v/v/v), flow 0.8 ml/min. The analyses were performed on Shimadzu LC-10A liquid chromatograph with diode array detector at a wavelength of 314 nm. Contents of total, soft, hard resins and  $\beta$ -fraction were determined gravimetrically from the ether phase after removal of waxes by freezing. The content of  $\alpha$ -acids was expressed as lead conductance value (LCV) determined by conductometric titration. Hop oils were isolated from hops by steam distillation (Wright and Connery 1951, Green and Osborne 1993) with 100 g of raw hops. Hop oils were analysed by gas chromatography (GC Varian 3400 + mass detector Finnigan ITD 800). An analytical capillary column DB5 (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m) was temperature programmed at the range of 60–250°C. Carrier gas was helium, flow rate 1.0 ml/min. Concentrated oil (0.1  $\mu$ l) was injected in split mode 1:50.

## RESULTS AND DISCUSSION

### Aroma hops

The category of aroma varieties comprises two subgroups of hops. The first consists of fine aroma hops, original landraces from Central Europe named according to the region of their cultivation. Saaz, Tett nang and Spalter belong to this group. The second group contains hybrid aroma varieties. Sládek is a representative of this group in the assortment of Czech hops. Spalter Select, Hersbrucker, Mount Hood, Willamette, Cascade, Sterling, Golding, Celeia are the most notable foreign hybrid aroma varieties. Composition of hop resins of Czech aroma varieties is summarised in Table 1, composition of hop resins of foreign aroma hops in Table 2. The composition of hop resins in Czech varieties is expressed in form of typical intervals as a result of long-term evaluation of a high number of samples. The composition of hop resins in foreign hops is given by individual samples in the

Table 1. Typical composition of hop resins of Czech aroma varieties

| Component                      | Saaz      | Sládek    |
|--------------------------------|-----------|-----------|
| Total resins (% w/w)           | 13–17     | 17–24     |
| $\alpha$ -bitter acids (% w/w) | 3.0–4.5   | 4.0–8.0   |
| $\beta$ -bitter acids (% w/w)  | 4.5–6.5   | 3.5–8.0   |
| $\alpha/\beta$ ratio           | 0.60–0.80 | 0.70–1.30 |
| $\beta$ -fraction (% w/w)      | 8.0–10.0  | 8.0–12.0  |
| Hard resins (% w/w)            | 1.0–2.0   | 1.5–2.5   |
| Cohumulone (% rel.)            | 23–26     | 25–31     |
| Colupulone (% rel.)            | 39–43     | 45–51     |

period 1995–2002. All samples were obtained from the country of origin. Traditional Central-European fine aroma hops (Saaz, Tettnang, Spalter) have a similar composition of hop resins owing to genetic affinity. The content of  $\alpha$ -bitter acids is mostly in the range of 3–4% w/w and is lower than the content of  $\beta$ -bitter acids. The ratio of  $\alpha/\beta$  bitter acids lower than 1.0 is typical of these hops. Cohumulone ratio is predominantly in the range of 23–26% rel., colupulone ratio in the range of 39–43% rel. The English variety Fuggle is a landrace too (Seefelder 2000). Its composition of bitter acids is different from the composition of Central-European fine aroma hops. The content

Table 2. Composition of hop resins of world aroma varieties

| Variety        | Country of origin | Year | HPLC analysis of bitter acids (EBC 7.7) |                           |                      |                        |                        |
|----------------|-------------------|------|---|---------------------------|----------------------|------------------------|------------------------|
|                |                   |      | $\alpha$ -acids<br>(% w/w)              | $\beta$ -acids<br>(% w/w) | ratio $\alpha/\beta$ | cohumulone<br>(% rel.) | colupulone<br>(% rel.) |
| Tettnang       | Germany           | 1995 | 3.2                                     | 4.6                       | 0.69                 | 26.5                   | 43.7                   |
| Spalter        | Germany           | 1995 | 3.2                                     | 4.8                       | 0.67                 | 26.4                   | 42.7                   |
| Spalter Select | Germany           | 1995 | 4.4                                     | 4.0                       | 1.10                 | 23.1                   | 43.6                   |
|                | Germany           | 1996 | 6.4                                     | 6.0                       | 1.07                 | 24.5                   | 43.9                   |
| Fuggle         | Germany           | 1998 | 5.0                                     | 4.1                       | 1.22                 | 24.3                   | 43.9                   |
|                | Germany           | 2000 | 6.4                                     | 5.0                       | 1.28                 | 24.8                   | 46.0                   |
|                | England           | 1995 | 4.5                                     | 2.1                       | 2.14                 | 28.0                   | 49.0                   |
|                | England           | 1996 | 4.8                                     | 2.7                       | 1.78                 | 30.1                   | 52.6                   |
| Willamette     | England           | 1998 | 6.7                                     | 3.1                       | 2.16                 | 27.1                   | 49.8                   |
|                | England           | 2000 | 6.8                                     | 3.1                       | 2.19                 | 29.5                   | 53.9                   |
|                | USA               | 1995 | 4.0                                     | 2.7                       | 1.48                 | 33.7                   | 55.6                   |
|                | USA               | 1998 | 4.9                                     | 4.3                       | 1.14                 | 29.0                   | 51.5                   |
| Sterling       | USA               | 2000 | 4.7                                     | 3.2                       | 1.47                 | 27.3                   | 55.9                   |
|                | USA               | 2002 | 5.2                                     | 3.8                       | 1.37                 | 32.7                   | 54.0                   |
|                | USA               | 1999 | 6.9                                     | 5.7                       | 1.21                 | 21.9                   | 45.2                   |
|                | USA               | 2001 | 7.1                                     | 4.5                       | 1.58                 | 22.2                   | 43.6                   |
| Mount Hood     | USA               | 2002 | 6.4                                     | 5.0                       | 1.28                 | 21.1                   | 41.5                   |
|                | USA               | 1995 | 5.1                                     | 6.0                       | 0.85                 | 21.0                   | 43.9                   |
|                | USA               | 1998 | 4.1                                     | 5.7                       | 0.72                 | 21.3                   | 42.2                   |
|                | USA               | 2000 | 4.9                                     | 5.1                       | 0.96                 | 19.5                   | 37.7                   |
| Santiam        | USA               | 2002 | 5.6                                     | 5.9                       | 0.95                 | 21.9                   | 43.4                   |
|                | USA               | 1998 | 5.3                                     | 7.8                       | 0.68                 | 19.9                   | 36.3                   |

| Variety        | Country of origin | Year | Analysis of hop resins (EBC 7.5) |                 |                |                              |                 |
|----------------|-------------------|------|----------------------------------|-----------------|----------------|------------------------------|-----------------|
|                |                   |      | total<br>(% w/w)                 | soft<br>(% w/w) | LCV<br>(% w/w) | $\beta$ -fraction<br>(% w/w) | hard<br>(% w/w) |
| Tettnang       | Germany           | 1995 | 13.5                             | 12.0            | 3.8            | 8.1                          | 1.5             |
| Spalter        | Germany           | 1995 | 14.6                             | 13.1            | 3.9            | 9.2                          | 1.5             |
| Spalter Select | Germany           | 1995 | 15.8                             | 14.1            | 5.0            | 9.1                          | 1.7             |
|                | Germany           | 1998 | 17.0                             | 15.3            | 6.2            | 9.1                          | 1.7             |
| Fuggle         | England           | 1995 | 13.3                             | 11.7            | 4.9            | 6.7                          | 1.6             |
|                | England           | 1998 | 16.7                             | 14.9            | 7.6            | 7.3                          | 1.8             |
| Willamette     | USA               | 2002 | 16.7                             | 15.4            | 7.2            | 8.2                          | 1.2             |
|                | USA               | 1995 | 15.0                             | 13.5            | 5.0            | 8.5                          | 1.5             |
|                | USA               | 1998 | 16.6                             | 14.6            | 4.8            | 9.8                          | 2.0             |
| Mount Hood     | USA               | 2002 | 15.9                             | 14.3            | 6.1            | 7.2                          | 1.6             |
|                | USA               | 1995 | 17.9                             | 16.3            | 5.7            | 10.7                         | 1.6             |
|                | USA               | 1998 | 16.6                             | 14.6            | 4.8            | 9.8                          | 2.0             |
| Santiam        | USA               | 2002 | 20.5                             | 18.4            | 6.6            | 11.8                         | 2.1             |
|                | USA               | 1998 | 20.1                             | 18.3            | 5.8            | 12.5                         | 1.8             |

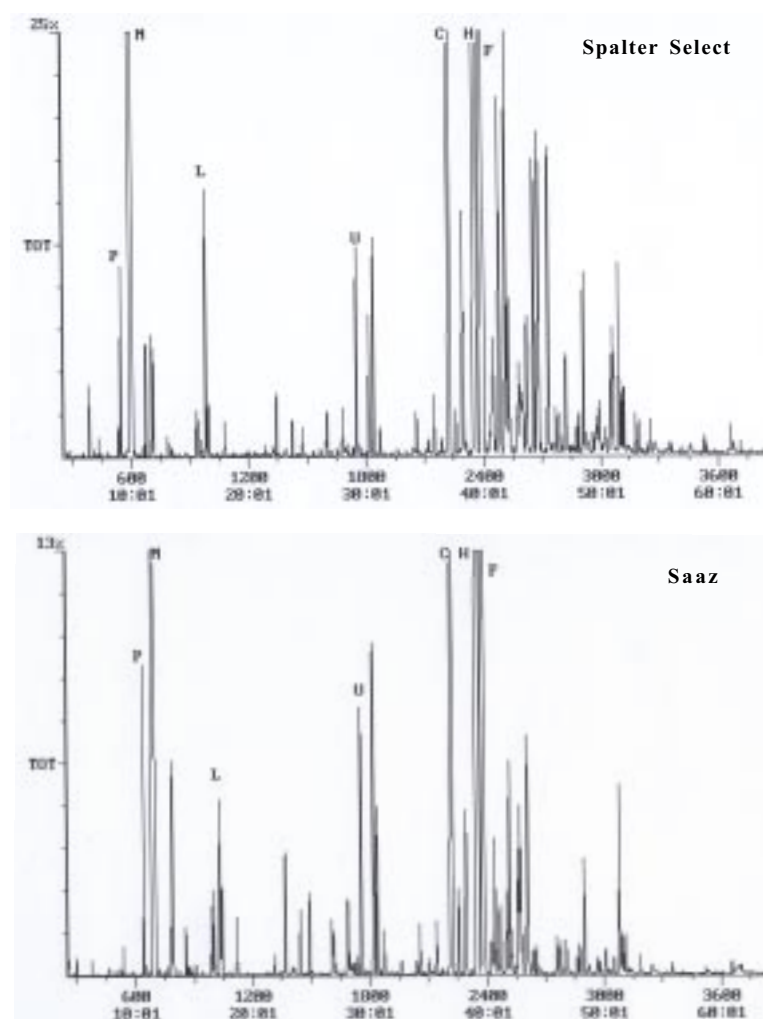


Figure 1. Gas chromatograms of hop oil analyses of aroma varieties Saaz and Spalter Select, GC Varian 3400 + detector Finnigan ITD 800, column DB5, 30 m × 0.25 mm × 0.25 µm, helium 1.0 ml/min, split injection 1:50

P =  $\beta$ -pinene, M = myrcene, L = linalool, U = 2-undecanone, C =  $\beta$ -caryophyllene, H =  $\alpha$ -humulene, F =  $\beta$ -farnesene

of  $\alpha$ -bitter acids in Fuggle hops exceeds twice the content of  $\beta$ -bitter acids. Cohumulone ratio is about 30% rel. Owing to a low content of  $\beta$ -bitter acids and  $\beta$ -fraction the amount of total resins is not higher than 17% w/w. All other world varieties in Table 2 are of hybrid origin.

Spalter Select variety originated from the crossing of Hallertauer, Saaz, Northern Brewer varieties and wild

hops whose provenance is not specified (Neve 1991, Seefelder et al. 2000). Hybrid origin reflects a higher content of  $\alpha$ -bitter acids and  $\alpha/\beta$ -acids ratio ( $> 1.0$ ). The US variety Sterling was registered in 1999. It is a diploid seedling with marked proportion of Saaz variety (female component), Cascade and Brewers' Gold varieties (male component) (Kenny – personal communication). Other US hops Willamette, Mount Hood and Santiam are also hybrids because no original aroma variety exists in the USA. The effort of US breeders to translate excellent brewing properties of European fine aroma hops (Saaz) to the gene pool of American varieties is evident (Hauhold et al. 1988). In spite of different genetic origin, all aroma hops, landraces and hybrids are characterised by a relatively low content of  $\alpha$ -bitter acids that does not usually exceed the limit of 6–7% w/w. Cohumulone ratio is rarely higher than 30% rel. The content of  $\beta$ -bitter acids is in the range of 2–8% w/w. Aroma hops are usually used in breweries at the last portion of hopping to tune the final sensory profile of beers.

Table 3. Typical composition of hop resins of Czech bitter varieties

| Component                      | Bor      | Premiant |
|--------------------------------|----------|----------|
| Total resins (% w/w)           | 18–25    | 19–25    |
| $\alpha$ -bitter acids (% w/w) | 6.5–11   | 7–11     |
| $\beta$ -bitter acids (% w/w)  | 3.5–6    | 3.5–6.0  |
| $\beta$ -fraction (% w/w)      | 8.0–12.0 | 8.0–11.0 |
| Hard resins (% w/w)            | 1.5–2.0  | 1.5–2.0  |
| Cohumulone (% rel.)            | 22–27    | 18–23    |
| Colupulone (% rel.)            | 43–48    | 39–44    |

Table 4. Composition of hop resins of world bitter (dual-purpose) varieties

| Variety         | Country of origin | Year | HPLC analysis of bitter acids (EBC 7.7) |                           |                      |                        |                        |
|-----------------|-------------------|------|---|---------------------------|----------------------|------------------------|------------------------|
|                 |                   |      | $\alpha$ -acids<br>(% w/w)              | $\beta$ -acids<br>(% w/w) | ratio $\alpha/\beta$ | cohumulone<br>(% rel.) | colupulone<br>(% rel.) |
| Perle           | Germany           | 1995 | 8.6                                     | 3.7                       | 2.32                 | 28.9                   | 53.0                   |
|                 | Germany           | 1997 | 10.0                                    | 4.8                       | 2.08                 | 29.6                   | 50.8                   |
|                 | Germany           | 1998 | 9.4                                     | 4.9                       | 1.92                 | 28.8                   | 49.9                   |
|                 | Germany           | 2000 | 8.8                                     | 4.8                       | 1.83                 | 29.6                   | 51.3                   |
|                 | Germany           | 2001 | 8.1                                     | 5.1                       | 1.59                 | 28.8                   | 49.8                   |
|                 | Germany           | 2002 | 6.8                                     | 5.5                       | 1.24                 | 28.6                   | 50.4                   |
|                 | USA               | 2001 | 7.5                                     | 3.8                       | 1.97                 | 28.1                   | 52.0                   |
|                 | USA               | 2002 | 6.4                                     | 3.7                       | 1.73                 | 27.3                   | 50.2                   |
| Northern Brewer | Germany           | 1995 | 7.8                                     | 4.6                       | 1.70                 | 28.7                   | 51.1                   |
|                 | Germany           | 2001 | 11.1                                    | 5.3                       | 2.09                 | 27.9                   | 50.6                   |
| Brewers' Gold   | Germany           | 1998 | 8.0                                     | 4.2                       | 1.90                 | 37.7                   | 62.5                   |
| Challenger      | England           | 1995 | 9.4                                     | 4.9                       | 1.92                 | 22.6                   | 46.2                   |
| Northdown       | England           | 1998 | 10.1                                    | 5.6                       | 1.80                 | 27.0                   | 50.9                   |
| Aurora          | Slovenia          | 2001 | 9.0                                     | 4.9                       | 1.84                 | 21.8                   | 44.0                   |
|                 | Slovenia          | 2002 | 9.9                                     | 4.8                       | 2.06                 | 22.4                   | 51.6                   |
| Marynka         | Poland            | 2000 | 7.3                                     | 4.2                       | 1.74                 | 21.4                   | 47.2                   |
|                 | Poland            | 2002 | 7.4                                     | 4.3                       | 1.72                 | 25.1                   | 51.2                   |

| Variety         | Country of origin | Year | Analysis of hop resins (EBC 7.5) |                 |                |                              |                 |
|-----------------|-------------------|------|----------------------------------|-----------------|----------------|------------------------------|-----------------|
|                 |                   |      | total<br>(% w/w)                 | soft<br>(% w/w) | LCV<br>(% w/w) | $\beta$ -fraction<br>(% w/w) | hard<br>(% w/w) |
| Perle           | Germany           | 1995 | 21.9                             | 19.8            | 9.3            | 10.5                         | 2.1             |
| Perle           | USA               | 2002 | 17.3                             | 16.2            | 7.2            | 9.0                          | 1.1             |
| Northern Brewer | Germany           | 1995 | 21.1                             | 18.3            | 8.6            | 9.7                          | 2.8             |
| Brewers' Gold   | Germany           | 1998 | 20.9                             | 18.7            | 9.2            | 9.5                          | 2.2             |

### Content and composition of hop oils in Central-European fine aroma hops

The composition of hop oils of traditional Central-European fine aroma hops (Saaz, Tettnang, Spalter, Lubelski)

substantially differs from that of the majority of other market varieties of hops. Hop oil content is low, not exceeding 1.0% w/w. Year to year and local differences in hop oil content are typical (0.4–1.0% w/w). The oxygen fraction of hop oils contains low or trace amounts of fat-

Table 5. Content of selected hop oil components in Czech bitter varieties Bor and Premiant

| Component                    | Parameter               | Bor       | Premiant  |
|------------------------------|-------------------------|-----------|-----------|
| <i>Trans</i> -ocimene        | mean value (%)          | 0.92      | 0.46      |
|                              | confidence interval (%) | 0.77–1.07 | 0.39–0.52 |
|                              | experimental values (%) | 0.57–1.31 | 0.21–0.63 |
| Linalool                     | mean value (%)          | 0.28      | 0.65      |
|                              | confidence interval (%) | 0.25–0.30 | 0.50–0.79 |
|                              | experimental values (%) | 0.12–0.35 | 0.26–1.13 |
| Methyl octanoate             | mean value (%)          | 0.35      | 0.21      |
|                              | confidence interval (%) | 0.27–0.43 | 0.15–0.27 |
|                              | experimental values (%) | 0.12–0.49 | 0.11–0.36 |
| Methyl 3,6-dodecadienoate    | mean value (%)          | 0.16      | 0.46      |
|                              | confidence interval (%) | 0.13–0.19 | 0.39–0.54 |
|                              | experimental values (%) | 0.07–0.23 | 0.30–0.72 |
| <i>Trans</i> -farnesol       | mean value (%)          | 0.03      | 0.26      |
|                              | confidence interval (%) | 0.0–0.06  | 0.16–0.35 |
|                              | experimental values (%) | 0.0–0.07  | 0.06–0.50 |
| Ratio humulene/caryophyllene | mean value (%)          | 3.00      | 3.08      |
|                              | confidence interval (%) | 2.76–3.24 | 2.91–3.24 |
|                              | experimental values (%) | 2.42–3.72 | 2.67–3.59 |

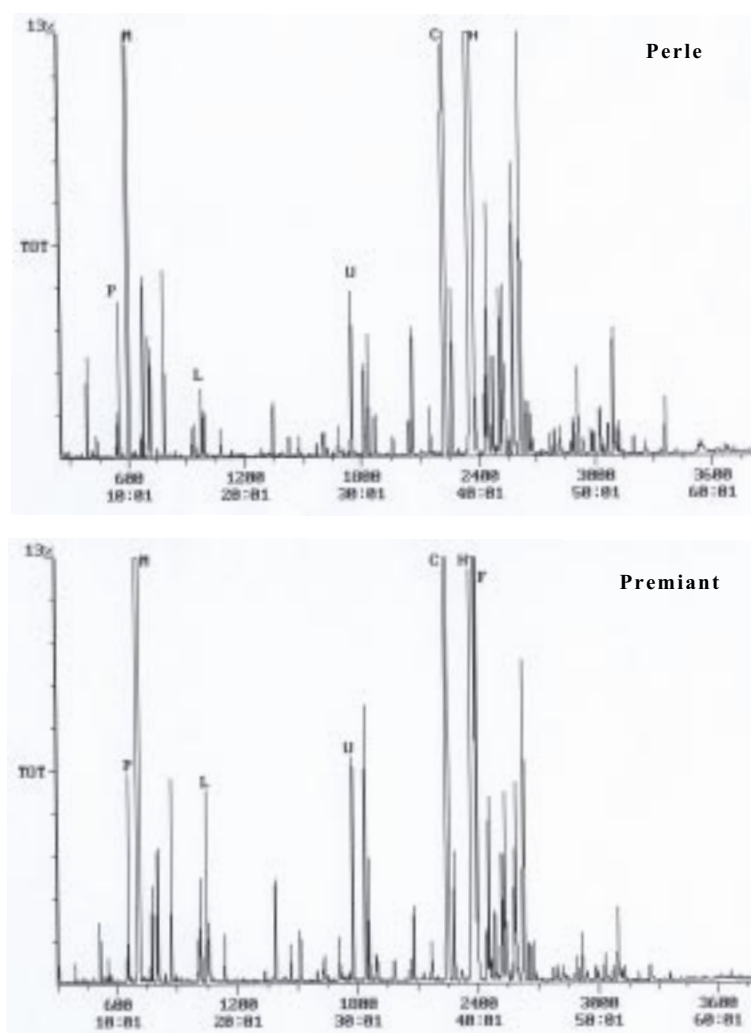


Figure 2. Gas chromatograms of hop oil analyses of bitter (dual-purpose) varieties Perle and Premiant, GC Varian 3400 + detector Finnigan ITD 800, column DB5, 30 m × 0.25 mm × 0.25 μm, helium 1.0 ml/min, split injection 1:50

P = β-pinene, M = myrcene, L = linalool, U = 2-undecanone, C = β-caryophyllene, H = α-humulene, F = β-farnesene

ty acid esters: 2-methylbutylacetate, methylhexanoate, isobutylisobutyrate, 2-methylbutylpropanoate, 2-methylbutylisobutyrate and 3-methylbutylisobutyrate. Secondary alcohols are typical components of hop oils of Saaz and other genetically related varieties. These compounds

are present in minority amounts. The content of 2-nonanol is maximally 0.20%, the amounts of 2-decanol and 2-undecanol are much lower. Substantial differences between fine aroma hops and most of other varieties exist in the composition of terpenic fraction. Besides β-caryophyllene (5–10% rel.) and α-humulene (15–25% rel.), acyclic sesquiterpene β-farnesene is found in hop oils of fine aroma varieties as a majority component at the amount of 14–20%. Together with myrcene these terpenes form 70–80% of total mass of hop oils. *Trans*-α-bergamotene and β-bisabolene belong to other typical sesquiterpenes in fine aroma hops. Figure 1 shows the chromatograms of hop oil analyses of aroma varieties Saaz and Spalter Select.

### Bitter (dual-purpose) hops

All bitter (dual-purpose) hops are of hybrid origin with the content of α-bitter acids in the range of 7–10% w/w.

Table 6. Typical composition of hop resins of the Czech variety Agnus

| Component             | Interval  |
|-----------------------|-----------|
| Total resins (%w/w)   | 27–32     |
| α-bitter acids (%w/w) | 10–15     |
| β-bitter acids (%w/w) | 5–8       |
| β-fraction (%w/w)     | 11–14     |
| α/β ratio             | 1.90–2.60 |
| Hard resins (% w/w)   | 2–3       |
| Cohumulone (% rel.)   | 29–38     |
| Colupulone (% rel.)   | 51–59     |

Table 7. Content and composition of bitter acids of world high- $\alpha$  varieties

| Variety  | Country of origin | Year | Bitter acids (EBC 7.7)     |                           |                      |                        |                        |
|----------|-------------------|------|----------------------------|---------------------------|----------------------|------------------------|------------------------|
|          |                   |      | $\alpha$ -acids<br>(% w/w) | $\beta$ -acids<br>(% w/w) | ratio $\alpha/\beta$ | cohumulone<br>(% rel.) | colupulone<br>(% rel.) |
| Columbus | USA               | 1998 | 14.5                       | 4.5                       | 3.22                 | 29.4                   | 54.1                   |
| Columbus | USA               | 1999 | 14.6                       | 5.0                       | 2.92                 | 29.1                   | 53.6                   |
| Columbus | USA               | 2000 | 14.6                       | 5.1                       | 2.86                 | 30.8                   | 53.9                   |
| Columbus | USA               | 2002 | 13.7                       | 4.6                       | 2.98                 | 33.0                   | 56.9                   |
| Tillicum | USA               | 1998 | 14.7                       | 10.7                      | 1.37                 | 36.4                   | 61.1                   |
| Nugget   | USA               | 1998 | 14.7                       | 4.9                       | 3.00                 | 23.6                   | 49.4                   |
| Nugget   | USA               | 2000 | 12.2                       | 4.6                       | 2.65                 | 19.9                   | 51.2                   |
| Nugget   | USA               | 2002 | 10.7                       | 4.0                       | 2.67                 | 23.3                   | 48.6                   |
| Horizon  | USA               | 1999 | 12.1                       | 6.6                       | 1.83                 | 17.5                   | 40.5                   |
| Magnum   | Germany           | 1998 | 16.1                       | 7.6                       | 2.12                 | 24.1                   | 43.1                   |
| Magnum   | Germany           | 1999 | 13.7                       | 8.1                       | 1.69                 | 28.5                   | 45.9                   |
| Magnum   | Germany           | 2000 | 15.0                       | 6.4                       | 2.34                 | 25.7                   | 46.2                   |
| Magnum   | Germany           | 2002 | 15.1                       | 8.2                       | 1.84                 | 27.9                   | 46.1                   |
| Nugget   | Germany           | 1998 | 12.7                       | 5.0                       | 2.54                 | 27.4                   | 52.0                   |
| Nugget   | Germany           | 1999 | 10.3                       | 5.3                       | 1.94                 | 30.5                   | 54.3                   |
| Nugget   | Germany           | 2000 | 15.1                       | 5.2                       | 2.90                 | 25.8                   | 50.1                   |
| Taurus   | Germany           | 1998 | 14.6                       | 4.7                       | 3.11                 | 21.5                   | 41.1                   |
| Taurus   | Germany           | 2000 | 14.9                       | 5.0                       | 2.98                 | 22.4                   | 44.5                   |
| Taurus   | Germany           | 2002 | 17.5                       | 5.9                       | 2.97                 | 24.6                   | 47.4                   |
| Merkur   | Germany           | 2000 | 16.2                       | 6.4                       | 2.53                 | 19.7                   | 44.0                   |
| Merkur   | Germany           | 2002 | 14.3                       | 7.3                       | 1.96                 | 17.8                   | 42.1                   |
| Target   | England           | 1998 | 10.9                       | 5.0                       | 2.18                 | 36.3                   | 59.2                   |
| Target   | England           | 2000 | 13.1                       | 5.9                       | 2.22                 | 35.0                   | 58.0                   |
| Admiral  | England           | 1999 | 14.5                       | 7.1                       | 2.04                 | 36.0                   | 58.3                   |

Owing to the higher content of  $\alpha$ -bitter acids and favourable hop aroma bitter hops are used in the brewing industry on a large scale. The Czech varieties Bor and Premiant belong to this category of hops. Perle, Northern Brewer, Brewers' Gold, Aurora, Marynka, Challenger are typical representatives of world bitter varieties. Composition of hop resins of Czech bitter varieties is summarised in Table 3, composition of hop resins of foreign bitter hops in Table 4. The composition of hop resins in Czech varieties is expressed in form of typical intervals as a result of long-term evaluation of a high number of samples. The composition of hop resins in foreign hops is given by individual samples in the period 1995–2002. All samples were obtained from the country of origin.

Data in Table 4 show that the composition of bitter acids and other hop resin components of Czech and foreign hop varieties is similar in many traits. This finding has genetic coherence in the origin of individual varieties. The content of total resins in foreign hop varieties presented in Table 4 is about 20% w/w, the ratio of  $\beta$ -fraction and total resin content is 0.45–0.55. Content of  $\alpha$ -bitter acids is in the interval of 7–11% w/w. Content of  $\beta$ -bitter acids is substantially lower in comparison with that of  $\alpha$ -bitter acids, therefore their mutual ratio is in the range of 1.21–2.32. Analytical data from six crops of Perle variety document the level of year-to-year fluctuations in the content of  $\alpha$ -bitter acids in the range of 6.4–10.0% w/w.

The co-analogue ratio is relatively stable and is not influenced by cultivation in the climatic conditions of Oregon and Washington. The cohumulone ratio in world varieties does not exceed 30% rel., the colupulone ratio 53%. The English variety Brewer's Gold extremely differs from this scheme with cohumulone ratio 37.7% rel. and colupulone ratio 62.5% rel. This variety was bred by Salmon as early as in 1934 (Neve 1991). It originated by open pollination of wild American hops and at the time of registration it belonged to the first hops with  $\alpha$ -acid content close to 10% w/w. It was the starting material for breeding another notable world hop varieties such as Galena, Nugget, Olympic, Northern Brewer, etc. (Seefelder et al. 2000). The Northern Brewer variety participates by various proportions in the common genetic constitution of many bitter (dual-purpose) and aroma hop varieties. Besides the Czech varieties Bor and Sládek it features the genetic origin of the varieties Aurora, Perle, Northdown, Challenger, Spalter Select, Hallertauer and others (Seefelder et al. 2000).

The content of hop oils in bitter varieties is in the range of 1.0–2.0% w/w and is twice to three times higher in comparison with fine aroma hops Saaz, Spalter and Tettnang. Myrcene,  $\beta$ -caryophyllene and  $\alpha$ -humulene are the main components of hop oils.  $\beta$ -Farnesene at the amount higher than 10% is found only in some bitter hops such as Polish varieties Marynka and Izabela or Slovenian

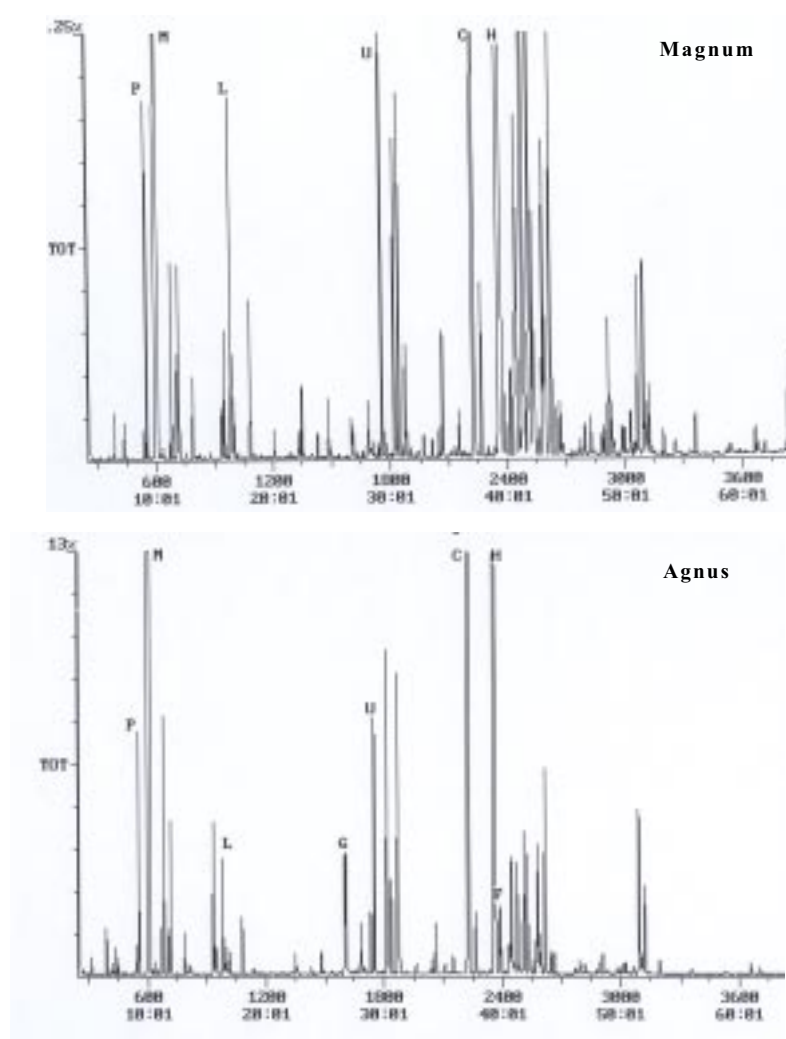


Figure 3. Gas chromatograms of hop oil analyses of high- $\alpha$  varieties Magnum and Agnes, GC Varian 3400 + detector Finnigan ITD 800, column DB5, 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m, helium 1.0 ml/min, split injection 1:50

P =  $\beta$ -pinene, M = myrcene, L = linalool, G = geraniol, U = 2-undecanone, C =  $\beta$ -caryophyllene, H =  $\alpha$ -humulene, F =  $\beta$ -farnesene

variety Aurora. It is very difficult to distinguish the Czech hop varieties Bor and Premiant exclusively on the basis of hop oil composition. Most components are present at comparable concentrations. Bor variety is characterised by a high content of *trans*-ocimene that is twofold compared to Premiant variety (Table 5). Figure 2 shows the chromatograms of hop oil analyses of bitter varieties Premiant and Perle from the crop 2001.

### High- $\alpha$ varieties

Hops with the content of  $\alpha$ -bitter acids higher than 10% w/w belong to the group of high- $\alpha$  hops. Magnum, Taurus, Merkur, Columbus, Nugget and Target are the best known world varieties of this category. These varieties are used in breweries predominantly in the form of hop extracts. The Czech variety Agnus, registered in 2001, belongs to this category too. Its composition of hop resins is summarised in Table 6. The values charac-

teristic of the content and composition of bitter acids in world high- $\alpha$  hops from the USA, England and Germany are given in Table 7.

The highest content of  $\alpha$ -bitter acids in world high- $\alpha$  varieties exceeds the limit of 15% w/w. The content of  $\beta$ -bitter acids is always lower compared to the content of  $\alpha$ -bitter acids, therefore their mutual ratio is lower than 1.0. Cohumulone and colupulone ratios are in relatively wide ranges of 17–36% rel. and 41–61% rel., respectively. The wide range is given by different genetic origins of individual varieties. Some hops (Magnum, Taurus) exceed the limit of 30% w/w in the content of total resins. Owing to the high content of  $\beta$ -bitter acids and  $\beta$ -fraction the Czech variety Agnus also reaches this limit in spite of the content of  $\alpha$ -bitter acids being lower by 10–15% compared with the best world varieties.

The content of hop oils in high- $\alpha$  hops is in the range of 1.5–3.0% w/w prevalently. Identification of high- $\alpha$  varieties on the basis of hop oil composition is very difficult. Figure 3 shows the chromatograms of hop oil

analyses of high-alpha varieties Agnus and Magnum from the crop 2000. The composition of hop oils in the Czech variety Agnus is characterised by a high content of geraniol (0.60–1.00%), methylgeranate (1.50–2.00%) and detectable amount of geranylacetate (0.05–0.10%). The oxygen fraction is rich in esters, many are present in a homologous series. It holds true about the group of fatty acid methyl esters with linear chain in the order of hexanoate to dodecanoate. The high content of  $\alpha$ -selinene and  $\beta$ -selinene in the range of about 10% is a typical trait of hop oil composition in the German variety Taurus. The US variety Columbus differs by a high content of geranylacetate in the range of 0.5–1.0%. In spite of these differences the identification of high-alpha varieties merely on the basis of hop oil composition is not reliable.

## CONCLUSIONS

All aroma hops, landraces and hybrid varieties are characterised by a relatively low content of  $\alpha$ -bitter acids that does not usually exceed the limit of 5–7 w/w. Cohumulone ratio is rarely higher than 30% rel. and hop oil content lower than 1.0% w/w.

The composition of hop oils in traditional Central-European fine aroma hops (Saaz, Tettnang) is characterised by a low content of fatty acid esters, by the presence of secondary alcohol fraction (2-nonanol) and by a high content of  $\beta$ -farnesene (15–20%) and *trans*- $\alpha$ -bergamotene (1%).

All bitter (dual-purpose) hops are of hybrid origin with the content of  $\alpha$ -bitter acids in the interval of 7–10% w/w. The Czech varieties Bor and Premiant belong to this category. The English variety Brewer's Gold is the first variety of this group bred in 1934. It forms the genetic basis

of many current bitter hops. The content of hop oils in bitter hops is in the range of 1.0–2.0% w/w.

Content of  $\alpha$ -bitter acids in high-alpha hops is higher than 10% w/w, content of total resins is at the level of 30% w/w. Content of hop oils is predominantly in the range of 1.5–3.0% w/w.

In spite of many differences in the hop oil composition of world hop varieties their identification merely on the basis of hop oil composition is not reliable.

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## ABSTRAKT

### Porovnání kvalitativních znaků českých a zahraničních odrůd chmele

Tržní odrůdy chmele se na základě pivovarského použití rozdělují do několika skupin – na aromatické, hořké neboli dual purpose a vysokoobsažné. Mezi aromatickými odrůdami tvoří samostatnou skupinu Žatecký poloraný červenák a další geneticky příbuzné odrůdy. Jde o původní krajové populace. Je pro ně charakteristický nízký obsah  $\alpha$ -hořkých kyselin (3 až 4 % hm.), obsah  $\beta$ -hořkých kyselin v rozmezí 4 až 7 % hm. a zastoupení kohumulonu v intervalu 23 až 26 % rel. Složení chmelových silic se vyznačuje především obsahem  $\beta$ -farnesenu v rozmezí 15 až 20 % rel. a *trans*- $\alpha$ -bergamotenu v množství cca 1 % rel. Většina tržních odrůd chmele je hybridního původu. Platí to i o českých odrůdách Sládek, Bor, Premiant a Agnus. Hořké odrůdy mají obsah  $\alpha$ -hořkých kyselin v rozmezí 7 až 10 % rel., obsah  $\alpha$ -hořkých kyselin ve vysokobsažných odrůdách je vyšší než 10 % hm.

**Klíčová slova:** odrůdy chmele; chmelové pryskyřice; chmelové silice;  $\alpha$ -hořké kyseliny;  $\beta$ -hořké kyseliny

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