The importance of the crop year for evaluating hop products

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Issue

Hops and hop products, as far as they are produced within the European Union, are marketed according to the criteria of variety, growing region and crop year. The certification regulations of the EU assure that hop products can be traced back to the raw hops used and that they are classified correctly according to the aforementioned criteria.

The development of hop products minimized the use of raw hops in breweries mainly due to the considerably improved storability of e.g. pellets and extract. Although this stability is proved in many publications, the crop year is still of great importance when purchasing hop products. The work reported here investigates the question of the importance of the crop year for evaluating hop products.

Methods for describing the ageing degree of hop products

Up to the 1960's breweries used raw hops. As far as possible, the hops were stored cold at about 0°C after preparation (additional kilning and sulphuring). There was no protection against oxidation. Thus, hops could only be used for two years without a drastic loss in brewing value. The brewer had to increase the hopping rate once or twice a year in order to balance the losses in bitter value caused by oxidation.

Oxidation processes do not occur with hop products when the packaging excludes air. Furthermore, changes of measurable values occur during storage which make a cold storage reasonable. Essential facts can be found in the EBC-Manual "Hops and Hop Products" (1). Although hop products are protected against oxidation, experts recommend a cold storage. Thus, only if hop products are packaged and stored properly they are considerably more stable than raw hops.

Inasmuch as the crop year of the raw hops is known, the degree of oxidation, which depends on the moment of processing, is not. A hop product therefore cannot be "fresher" than the raw hops used. For obtaining reliable information methods for describing the degree of ageing even of the hop products are useful.

The following methods for example are suitable for analysing the respective valuable constituents:

- ♦ Ageing of the bitter substances
  - Gravimetric determination of hard resins according to Wöllmer from the difference of total resins and soft resins (HR-fraction) according to Mebak (2):
    This method is suitable for describing the ageing degree of raw hops, pellets and partly ethanol extracts, but not for CO_2-extracts, since hard resins are not extracted with CO_2. The analyses are comprehensive and not reproducible in a satifactory way. Inexperienced laboratories often obtain results that are not very useful.

  - Analysis of the Hop Storage Index (HSI) according to ASBC (3):
    The spectrophotometric method also requires careful operation and much practice. Within trained laboratories, however, results are obtained which are comparable without problems and which are useful for hops and pellets. For CO_2-extracts similar observations apply as for the hard resin fraction. Also in this case the HSI fails inevitably.

  - HPLC methods:
    The high performance liquid chromatography (HPLC) according to EBC (4) shows the α and ß-contents. In the front area of the chromatogram besides xanthohumol, peaks are visible which can be described as polar bitter components with ageing character (5). At the moment, the working team Hop Analysis (AHA) and the European Brewery Convention (EBC) try to develop instructions of analysis which allow an ageing characterisation of a sample in the scope of the HPLC method. In one laboratory with only one HPLC system rather useful information can be obtained by invalidating the relation between the peak areas of the polar bitter substances and the peak areas of the α- and ß-acids. Presently there are considerable differences between several laboratories. Besides, the same applies to CO_2-extracts as to hard resins and the HSI. Since CO_2 does not dissolve the ageing components of the bitter substances, what can also be seen positively from the aspect of quality, these components cannot be detected as hard resins or polar ageing peaks in CO_2-Extracts.

- Ageing of the aroma substances
    - Relationship between oxygen fraction and hydrocarbon fraction of the hop oil:
      The hop oil water steam distillate of a sample is separated by column chromatography into a fraction of pure hydrocarbons (mono-, sesqui- and diterpenes) and a fraction of components containing oxygen. The amount of the oxygen fraction in relation to the hydrocarbon fraction is an indicator for proceeding oxidation. A corresponding characteristic, however, is subject to considerable variations and is only little reproducible.

    - Expoxide fraction of sesquiterpenes (6):
      The gas chromatography of the aroma components allows a quantitative determination of oxidised sesquiterpenes (e.g. caryophyllene epoxide and humulene epoxide I and II), the contents of which in relation to the non-oxidised sesquiterpenes ß-caryophyllene and humulene informs on the oxidation degree of important hop oil components. The advantage of an "epoxide figure" is that it provides good assertions on ageing for CO_2-extracts as well.

    - Humulenol value (7):
      Also the humulene-2-ol-proportion, f.i. in relation to the humulene, is an ageing indicator determined by the gas chromatography, which is applicable for CO_2-extracts as well.

- Ageing of the polyphenols
    - Polymerisation index of polyphenols (PI):
      The unselective analysis of the total polyphenols and the determination of the low molecular anthocyanogenes according to Harris and Riquetts allows the calculation of the ageing index as a relation of both values, also called polymerisation index (8).

    - Flavanol and proanthocyanidine fractions:
      The HPLC allows the determination of individual low-molecular polyphenols (9). In this case flavanols (catechin and epicatechin) as well as proanthocyanidines are especially prone to oxidation. The lower the proportion is in a sample in relation to another more stable substance group of the polyphenols (e.g. the flavanongylcosides), the more the oxidation of the polyphenols has progressed. However, so far there have not been any analytical activities in analysis circles like AHA or EBC. Since pure

resin extracts do not contain polyphenols, assertions regarding ageing can only be made for hops and pellets.

Besides the determination of the α– and ß-acids by means of HPLC following methods of analysis were applied for the observations made:

- The proportion of hard resins in % relative from the total resin
- The Hop Storage Index according to ASBC
- The expoxide fraction of ß-caryophyllene and humulene in relation to the non-oxidised sesquiterpenes

Possible quality losses on the way from raw hops to hop products

At first, it is reasonable to bear in mind all possibilities of quality losses by ageing of constituents of hops or hop products. In the following sectors losses may occur in the course of manufacturing a hop product:

- ♦ Quality of kilning and conditioning at the hop grower.
- ♦ Kind of storage of a hop lot until processing to a hop product.
- ♦ Quality parameters during processing to a hop product.
- ♦ Transport of the hop product from the producer to the brewer.
- ♦ Kind and duration of storage of a hop product at the producer respectively brewer.

Some investigations provide information especially on the losses of α-acids during the individual phases. The following numerical examples are being considered as preliminary only:

1. Kilning and conditioning of hops

   A gentle operating at low kilning temperatures (< 65°C) and an unsatisfactory conditioning with circulating air results in at least 10 % relative lower α-acid losses compared with procedures which apply for example kilning temperatures of more than 70°C and conditioning with moistened air (10).

2. Storage of hops until processing

   This point is of special importance. There are considerable differences in the quality of warehouses. The optimum method is storing the raw hops immediately after harvesting in a cold storage. Due to capacity reasons, however, this method is not being practised consequently. Mostly hop lots are being brought into hop halls or external warehouses. While big hop halls offer a good protection against weather influences, external warehouses are different. Since much space is needed, warehouses are tolerated which have a negative influence on the hop quality. Comprehensive investigations (10) demonstrate the effects of different kinds of storage on the quality characteristics of hops. Table 1 shows the changes in measured values resulting from an average of 12 hop varieties according to the kind of storage (6 months storage time):

A quote in a paper reads as follows: "The quality reductions are considerable in normal unrefrigerated warehouses. Finally, they depend on which protection exists against temperature and moisture absorption. Unsatisfactory external warehouses are especially critical, since hops can absorb moisture at high atmospheric humidity. This has a negative influence on the storage stability. Quality losses can be limited effectively only in refrigerated warehouses."

During the time of storage of raw hops until processing considerable ageing processes take place, which inevitably are reflected in the resulting hop products. There are the following two factors:

- During cold storage the hop quality is maintained to a large degree until processing. The moment of processing is not so important. The quality is not affected essentially whether the hops are pelletised or extracted in October/November or March. Cold storage minimizes the influence on the storage time of hops considerably.

- During an unrefrigerated storage, however, the storage time has much influence. Hops, which are processed early in October/November, are "fresher" than those, which are processed late (March/April). Consequently, the same applies to the hop product. In an inferior warehouse, the factor of storage time has a corresponding negative effect.

An early processing of hops stored in normal warehouses or alternatively a proper cold storage result in a qualitatively "fresh" hop product.

3. Quality parameters during the manufacturing to hop products

Processing plants are very much interested in treating α-acids gently because of efficiency reasons. An indicator for differences between various processing plants may be the pelletizing process. An especially gentle pelletizing at 50°C does not cause any evident α-acid losses against a pelletizing at more than 60°C (1).

Special extraction procedures as practised nowadays using carbon dioxide as solvent are so gentle that specific damage according to the procedure applied (sub- or super-critical) or processing plant can hardly be quantified.

4. Kind and duration of storing a hop product

   There are many publications on this topic. For comparing a cold storage (0 to 5°C) with a storage at ambient temperature (15 to 20°C), the following α-acid losses may be used as reference points (values in % relative) after one year storage:

	Cold storage	**Normal storage**
Pellets	abt. 5 – 7 %	abt. 15 – 20 %
CO_2-Extract	abt. 1 – 2 %	abt. 3 - 5 %

5. Transport of the hop product

   The EBC-Manual (1) contains corresponding information. A temporary warm transport phase (e.g. 30°C) during a few weeks causes considerable damage. An overseas transport taking place at moderate temperatures of maximum 25°C causes α-acid losses in the range of about 5 % relative. A transport at temperatures of around 40°C, which unfortunately cannot be excluded, causes α-acid losses of about 20 % relative.

In table 2 the approximate damaging potentials of the α-acids are added in % relative for pellets after summarising all individual facts.

As shown in table 3 more favourable figures result for extracts since they have a better storage stability than pellets.

It is interesting to note which dominance the storage conditions of raw hops occupy in the quality chain. In a model, unsatisfactory hop storage conditions can be combined with optimum conditions, which are compared with the other extreme (good hop storage conditions, remaining conditions unsatisfactory). The comparison in table 4 does not consider transport conditions.

Even optimum conditions in all other ranges cannot compensate for improper hop storage.

The influence of the crop year

In this paragraph the factor crop year is added to the figures investigated so far. Often additional quantities of hop products are stockpiled during favourable market situations, the consumption of which often takes at least one year or more. The ageing, which has to be taken into account, has to be considered under the aspect of other possible quality reductions.

For this purpose following range of test was chosen: Firstly a big homogene hop lot of the variety Hallertau Perle crop 1997 was divided into three parts. Two weeks after harvesting two parts were stored in a cold storage at an average temperature of 3 - 4°C and one part in a normal external warehouse. One part from the cold storage was processed at the beginning of October to enriched pellets and to CO_2-extract. The second part remained in the cold storage. The two thirds of the lot from the external warehouse and the cold storage were also processed after a total storage time of six months at the end of March to lupulin enriched pellets with an α-acid content of 10 weight-% and to CO_2-extract. The respective three pellets and extracts designated as "fresh" (processing in October from the cold storage), "cold" (processing in March from the cold storage) and "normal" (processing in March from the external storage) were stored for a total of 12 months at an average temperature of 3°C.

Analyses were made from the three parts of hops ("fresh", "cold", "normal") and from the resulting products, which were analysed again after one year of cold storage according to the characteristics α- and ß-acids (HPLC EBC 7.7), conductometric value according to EBC 7.5, hard resin fraction, Hop Storage Index (ASBC Hops 15) and expoxide fraction of the sequiterpenes:

$$100\,\% \; * \; \frac{\text{epoxides of ß-caryophyllene} \; + \; \text{humulene}}{\text{ß-caryophyllene} \; + \; \text{humulene}}$$

Table 5 shows the results of analysis of the three partial lots of raw hops. The values obtained clearly demonstrate the progressed ageing of the "normal" hop lot.

Table 6 shows the results of the three pellet lots standardised to 10 % α-acids immediately after processing and after one year of storage time. All ageing characteristics of the pellets firstly reflect the raw hops used. The obtained figures range within the accuracy of analysis. One year of storage of all pellets causes following changes:

- α-acids decrease moderately.

- ß-acids remain stable.
- Indicators, which would demonstrate an oxidative ageing (hard resin and epoxide fractions), remain logically stable.
- Only the HSI increases slightly since the value reflects among others the formation of iso-α-acids.

The reactions of α- and ß-acids during inert storage are briefly described in the EBC-Manual (1). Detailed information can be found in the literature references (11) and (12). Since part of the α-acid reductions in the stored pellets can be explained by the formation of iso-α-acids, the losses are minimised. This fact is also reflected in the conductometric value, which includes besides α-acids also commonly formed iso-α-acids and some ageing components. Thus, it is subject to slighter decreases.

When making a qualitative evaluation according to the ageing criteria, following clear rank order results:

- "fresh" directly after production and tightly followed by "fresh" after one year storage time are first
- followed in short distance by "cold" after production and immediately by "cold" after one year storage time.
- In considerable distance ranges in the last place "normal" after production and after one year of storage time.

It becomes obvious that the storage of pellets for one year in a cold storage does not affect typical ageing indicators and consequently qualitatively relevant changes do not occur. The destiny of hops before processing, however, is clearly reflected in the ageing indicators. The degree of ageing of raw hops thus is qualitatively absolutely dominant. In other words: A one year old cold stored product from fresh or cold stored hops can be qualitatively considerably better than a product from a later crop from normal stored hops. The characteristic "crop" consequently does not solely represent a quality criteria. The ageing indicators are more important for describing the degree of freshness of hop pellets and especially of the raw hops used.

As already mentioned, the reduction of α-acids does not experience equivalent losses in quality since non-oxidative reactions, like isomerisation, of α-acids take place. At the time of selling this fact can be taken qualitatively into account when evaluating the α-acids.

Table 7 shows the corresponding figures for the three CO_2-extracts. With regard to the ageing indicators, only the epoxide fraction is able to reflect the quality of the raw hops used. Also in this case, the “normal” storage stands out negatively. Negligible differences exist between “fresh” and “cold”. The extracts stored cold for one year do not at all differ from the extracts immediately after production, which proves the good storage stability of CO_2 pure resin extracts, a fact which was published already several times.

Thus, the assertions made for pellets are still more valid for extracts. The crop year itself is not predicative for the quality of an extract. Only the application of a suitable ageing indicator like the epoxide fraction is useful. Also with regard to the quality of the extract, the clear assertion can be made that the preceding treatment of the raw hops (how long and under which conditions they were stored) is of dominant importance. The age of the extract can be neglected when storing it under suitable cold conditions.

In the following illustrations 1 to 3 some ageing indicators are compared. The condition of the hops stands out against the storage of the products. While the ageing characteristics react very sensitively on the storage quality of the hops, a proper (i.e. inert and cold) storage does not have any influence.

Outlook

Principal considerations and investigations demonstrate that the quality of the raw hops used is decisive for the quality of a hop product. Mistakes, which were made before processing by a too long and improper storage, affect pellets and extracts. Optimum results are obtained when hops are stored cold immediately after harvesting. The moment of processing then loses importance.

Suitable methods of analysis for describing ageing indicators help to find out the “degree of freshness” in hop products respectively the quality of raw hops and consequently also of the hop product itself. Since the ageing indicators of hop products do not change considerably during cold storage in an absolutely oxygen protected environment the characteristic of the crop year loses importance. Thus, a three year old pellet or a five year old CO_2-extract each made from fresh or cold stored hops can be of considerable better quality than a product of the current crop year made from hops which were stored “normal” for 7 months. Consequently, the crop year of a hop product is a little predicative value with regard to quality.

Many breweries take this fact into account when stockpiling products out of crop years of good quality and favourable prices and using them up in the following years. The hop industry fulfils reluctantly and to a limited degree only the task of balancing crop year fluctuations because problems occur when marketing merchandise of previous crop years. Without any clear and practical reasons breweries mostly prefer the latest crop even though they often receive a strongly aged product. They unwillingly purchase products of preceding crop years and only if price reductions are granted.

As already mentioned the prejudice against previous crop years should give way an objective evaluation by means of analytical ageing indicators. So, the brewer would receive a better product and the hop industry could fulfil better the task of balancing crop fluctuations. Furthermore there would be an incentive to improve the storage conditions of hops in order to be able to control more effectively the "fresh character" of hops and the resulting products. If hop products are marketed increasingly according to ageing indicators, the crop year inevitably loses importance.

For the hop grower an evaluation independent of the crop year would have the advantage that an oversupply would not automatically cause a drastic price reduction.

In any case the hop industry is responsible that hop products are being described with reproducible ageing characteristics.

Summary

According to the EU regulation, hop products are classified according to crop year, growing region and variety. Without any clear reasons breweries mostly prefer the latest crop year since they expect a fresher product compared to previous crop years. Investigations, however, demonstrate that the ageing degree of a hop product is exclusively determined by the ageing degree of the raw hops used, which primarily depends on the duration and especially on the quality of the hop storage. An early processing immediately after harvesting or a cold storage of the raw hops result in considerably fresher hop products with more favourable values as regards the ageing indicators compared with a later processing of normal stored hops.

Consequently, in hop products, the degree of freshness and the quality of the raw hops used can be described by analytical ageing indicators, since these indicators do not change during cold and oxygen protected storage of hop products. Thus, a several year-old product made from fresh or cold stored hops can be of considerably better quality than a comparable product of the current crop year which was made from hops which were stored in a normal unrefrigerated storage for half a year. Thus, the crop year of a hop product is little predicative as regards its quality respectively its degree of freshness.

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Table 1: Average changes in measured values (in % rel.) during 6 months storage

	Unsatisfactory store up to 30°C	Good store up to 20°C	Cold store abt. 3°C
α-acid reduction in % rel (EBC 7.4)	42	31	8
α-acid reduction in % rel (EBC 7.7)	49	39	10
Increase of Hop Storage Index in % rel. (ASBC)	120	93	23

Table 2: Various damaging potentials of a **-acids in pellets in % rel.**

	Good conditions		Unsatisfactory conditions	
	Damage in % rel.	Remaining value in % rel.	Damage in % rel.	Remaining value in % rel.
Kilning and conditioning	5	95	15	85
Storage of raw hops	8	87	40	51
Product manufacturing	2	86	5	48
Pellet storage for 1 year	6	81	16	41
Oversea transport	5	76	20	33

Table 3: Various damaging potentials of a **-acids in extracts in % rel.**

	Good conditions		Unsatisfactory conditions	
	Damage in % rel.	Remaining value in % rel.	Damage in % rel.	Remaining value in % rel.
Kilning and conditioning	5	95	15	85
Storage of raw hops	8	87	40	51
Product manufacturing	2	86	5	48
Pellet storage for 1 year	2	84	5	46
Oversea transport	0	84	3	45

Table 4: Possible combinations of damaging potentials of the a -acids in % rel. for pellets and extracts

	Pellets		Extract	
	Damage in % rel.	Remain. value in % rel.	Damage in % rel.	Remain. value in % rel.
Hop storage good, other parameters unsatisfactory	38	62	29	71
Hop storage unsatisfactory, other parameters good	47	53	45	55

Table 5: Analysis data of the 3 raw hop partial lots

"fresh" = cold storage beginning of October
"cold" = cold storage beginning of March
"normal" = external storage beginning of March

	α-acids (weight-%)	β-acids (weight-%)	conductometric value (weight-%)	HR-fract. (% rel.)	HSI	epoxide fract. (% rel.)
"fresh"	7.2	4.1	7.6	8	0.26	1.0
"cold"	6.6	3.8	7.2	10	0.28	3.0
"normal"	5.4	3.0	6.4	21	0.45	8.5

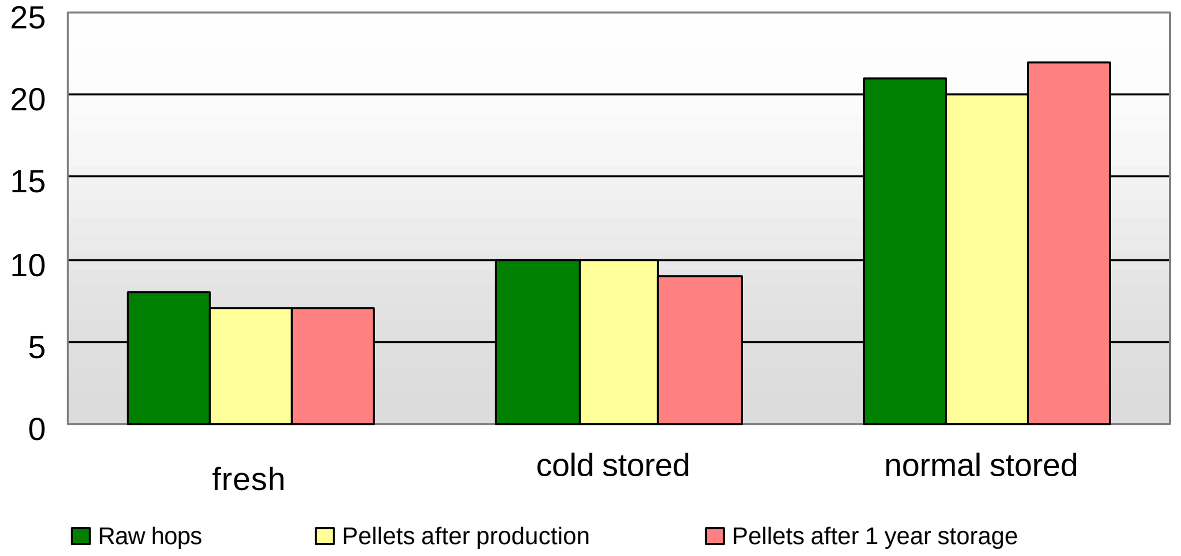
Table 6: Analysis data of the 3 pellet lots immediately after production and after 1 year storage at 3°C

	α-acids (weight-%)	β-acids (weight-%)	conductometric vaue (weight-%)	HR-fraction (% rel.)	HSI	epoxide fraction (% rel.)
"fresh" after production	10.0	5.6	10.5	7	0.25	1.0
"fresh" after 1 year	9.4	5.5	10.1	7	0.26	1.5
"cold" after production	10.0	5.7	10.6	10	0.28	3.0
"cold" after 1 year	9.5	5.8	10.2	9	0.30	3.0
"normal" after production	10.0	5.7	11.2	20	0.43	9.0
"normal" after 1 year	9.4	5.4	10.7	22	0.46	8.0

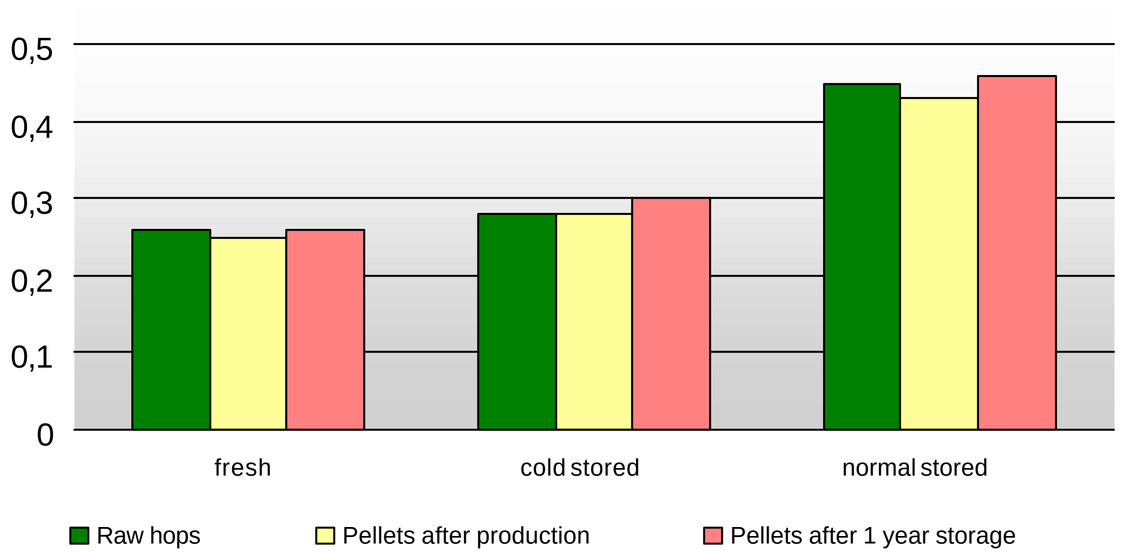
Table 7: Analysis data of the 3 extract lots immediately after production and after 1 year storage at 3°C

	α-acids (weight-%)	β-acids (weight-%)	conductometric value (weight-%)	HR-fraction (% rel.)	HSI	epoxide fraction (% rel.)
"fresh" after production	48.0	27.6	49.4	5.0	0.21	1.0
"fresh" after 1 year	47.8	27.8	49.6	4.8	0.22	1.5
"cold" after production	46.7	26.5	48.0	5.3	0.22	2.5
"cold" after 1 year	46.8	26.3	47.7	5.5	0.24	3.0
"normal" after production	43.7	24.2	45.3	5.7	0.23	9.0
"normal" after 1 year	43.3	24.0	45.5	5.4	0.24	8.5

Ill. 1: Ageing indicator "hard resin fraction" of fresh, cold stored and normal stored hops and pellets made from these hops



Ill. 2: Ageing indicator "Hop Storage Index" of fresh, cold stored and normal stored hops and pellets made from these hops



Ill. 3: Ageing indicator epoxide fraction of fresh, cold stored and normal stored hops and pellets and extracts made from these hops