THE DYNAMICS OF VITAMINS C AND E IN BARLEY PRODUCTS DURING MALTING

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Abstract. Barley is a key ingredient in beer production. The aim of the current research was to study the dynamics of vitamin C and vitamin E in flaky and hull-less barley grains during steeping, germinating, and kilning.

The research was accomplished on hull-less barley (two lines – '3528' and '3537') and flaky barley selected in Latvia in 2009 with a germination capacity above 95%. The grains were steeped, germinated and kilned using traditional malt production technology. During research the vitamin content was analysed using standard methods: vitamin C by EN 14130:2003, and vitamin E by AOAC 971.30.

The content of vitamin C increased during steeping in flaky barley grains till 0.23 mg 100 g^{-1}, but in hull-less barley grains: line '3537' till 0.47 mg 100 g^{-1}, and line '3528' till 0.30 mg 100 g^{-1}. During germination vitamin C content in flaky barley increased by 68%, in hull-less barley: line '3528' – by 82%, and line '3537' – by 57%. The content of vitamin C in the analysed malt samples was 0.35-0.38 mg 100 g^{-1}. The content of vitamin E in all barley samples was similar after grain steeping. The content of vitamin E was 3.9 times higher in flaky barley, but in hull-less barley lines: '3528' – 4.1, and '3537' – 4.5 times higher compared with its initial content after germination. After grain kilning, the content of vitamin E decreased in all barley grain samples.

The results show that using some cultivars of hull-less barley for malt production, it is possible to obtain a higher content of vitamins C and E in the end-product.

Key words: barley, hull-less barley, malt, germination, vitamins C and E.

Introduction

Barley (*Hordeum vulgaris L.*) is a common staple in human and animal diets. Part of the grass family, barley grows in over 100 countries and is one of the most popular cereal crops, surpassed only by wheat, corn, and rice. Although barley is fairly adaptable and can be grown in many regions, it is a tender grain, and care must be taken in all stages of its growth and harvest. According to a recent study, eating whole-grain barley can regulate blood sugar (i.e. can reduce blood glucose response to a meal) for up to 10 hours after consumption compared with white or even whole-grain wheat, which has a similar glycemic index. The effect was attributed to colonic fermentation of indigestible carbohydrates (Nilsson et al., 2006).

A large part of the remainder is used for malting, for which barley is the best suited grain. It is a key ingredient in beer and whisky production. Barley has been retained as the primary cereal of choice, not the least, because it retains its husk during threshing and this traditionally forms the filter bed through which the wort is collected in the brewery (Bamforth, 2006). Within the barley malting process, the enzymes activity increases and as a result starch degradation occurs and fermentable sugars are synthesized. Additionally there is a synthesis of the enzymes which degrade the cell walls and much of the protein in the starchy endosperm, thereby softening the grain and making it more millable (Bamforth, 2006).

Barley and malt are rich in substances that are growth factors for yeasts and vitamins for humans. Barley used in malt production should contain high amounts of extract substances (at least 80.0%) and low amounts of proteins (not more than 11.5%).

In the food industry, hull-less barley (*Hordeum vulgaris L.*) is acknowledged as more valuable and more economical, compared with covered barley. The hull-less barley has an elevated ß-glucans content. Soluble dietary fiber, mainly ß-glucans, provides the formation of viscosity; as a result, digestion, cholesterol and fat absorption are decreased (Bhatty, 1999; Belicka and Bleidere, 2005). Selected hull-less barley varieties are able to pass flaky barley criteria: moreover, the amount of extract substances in hull-less barley is higher by 4-5% compared to malting barley.

Vitamin C (ascorbic acid) is a well-known antioxidant. The main function of vitamin C as a radical producer is to provide the regenerating system for tocopherol (Dewick, 2006). Ascorbic acid can act as a synergist with tocopherol by regenerating or restoring their antioxidant properties. (Niki, 1987). Ascorbic acid and its esterified derivatives may also function as oxygen scavengers. Vitamin C declines in the heating process (Pokorny, 2001).

Vitamin E is also a major biological antioxidant, it quenches free radicals and acts as a terminator of lipid peroxidation, particularly in membranes that contain highly unsaturated fatty acids. Barley is one of the best sources of raw food material, containing a high concentration of tocols. A higher content of natural antioxidant tocopherol and tocotrienols, as well as vitamin E, was established in barley grain, compared with wheat and rye grain (Shewry, 1993).

Germinated grains have already been used in food since ancient times because germination is one of the processing methods for increasing the grain nutritive value. The gross chemical changes observed during malting are the net result of the degradation of reserve substances, the interconversion of materials in the living tissues, the flux of materials to the embryo, and their incorporation into the growing tissues, the synthesis of new materials and the losses occasioned by leaching during steeping, oxidation to carbon dioxide and water, and the separation of the rootlets (Briggs et al., 1981). The content of vitamin E increases and vitamin C synthesizes during the grain germination. It leads to the hypothesis that the amount of C and E vitamins in hull-less barley varieties is significantly higher compared to traditional barley.

Germination of grains and external modification are stopped by kilning. Analysing the sources of literature, it can be concluded that more attention has been paid to the efforts of not destroying the enzymes during kilning of the prepared malt for beer production, and less attention has been paid to saving the content of vitamins.

After analysing the scientific data from the literature, the aim of the current research was to study changes in vitamins C and E in flaky and hull-less barley grains during barley steeping, germinating, and kilning.

Materials and Methods

The research was carried out on hull-less barley (two lines '3528' and '3537') and flaky barley (one line 'Rolands') grains, which were selected in Latvia in 2009, with germination capacity above 95%. The following technology was used for malt production from the tested grains: washing and steeping of grains (H_2O t=17±2 °C) till moisture content in grains reached 38 - 40%. Then the grains were put in germination trays where a wet laboratory paper was extended, and then the grains were covered with the same wet paper. The grains were kept for 6 days at 18-20 °C for germination. The changes in the concentration of vitamins C and E were monitored over the germination period. An 8 hour kilning of the germinated grains was carried out in a laboratory kiln. Grains in a small layer were put on sieves in a chamber with controlled hot air circulation at the temperature from +50 °C to +105 °C till a constant moisture content was achieved in the grains (5±1%).

The content of vitamin C was determined by the standard method EN 14130:2003 "Foodstuffs – Determination of vitamin C by HLPC".

The analyses of vitamin E content were carried out by using the AOAC Official Method 971.30 "α-Tocopherol and α-Tocopheryl Acetate in Foods and Feeds" standard colorimetric method (1971-1972). The term "vitamin E" is the generic descriptor for all tocol and tocotrienol derivatives that exibit qualitatively the biological activity of α-tocopherol (Ball, 2006). The figures are created by using MS Excel programme.

Results and Discussion

Cereals are considered only moderate sources of vitamin E, providing 0.6–2.3 mg kg^{-1} of α-tocopherol. Since cereals contain great amount of tocotrienols with very low vitamin E activity, they are more valuable as sources of tocotrienols and tocopherols than vitamin E (She et al., 2000).

The dynamics of vitamin E was analysed during the current research in several barley cultivators starting form non-processed barley to ready malt. It was found that the content of vitamin E in non-processed flaky and hull-less barley was similar. The content of vitamin in two types of hull-less barley grains was identical: 4.03 mg 100 g^{-1}. The content of vitamin E in flaky barley was lower by 0.27 mg 100 g^{-1} compared with hull-less barley grains, which mainly could be explained by the individuality of the barley cultivar. The volume of the endosperm of hull-less barley grain is larger than that of flaky barley. It is known that the endosperm contains many nutritional compounds of grains, such as albumens, vitamins (including vitamin E), carbohydrates, mineral substances, and others.

During grain steeping process, the increase in vitamin E content in flaky and hull-less barley grain types '3528' and '3537' was similar: the content of vitamin increased 1.7 (6.5 mg 100 g^{-1}), 1.8 (7.37 mg 100 g^{-1}), and 2.0 (8.17 mg 100^{-1}) times respectively compared with the initial vitamin content in non-processed grains. Such changes could be explained by the beginning of a biochemical reaction in the grains.

The results of our experiments prove that more intensive synthesis of vitamin E was detected in grains after 2 days of germination. The content of vitamin E increased in flaky barley grains 1.75 times, and in two hull-less barley grain lines - 1.60 times (Fig. 1) compared with the vitamin E content in steeped grains, which indicates intensive growing processes as a result of chemical and biochemical reactions. Increases in vitamin E were detected also after 4 days of germination. After finishing the germination process on the 6^{th}, day the content of vitamin E in flaky barley was 3.9 times (14.8 mg 100 g^{-1}), in hull-less barley grain line '3528' – 4.1 times (16.56 mg 100 g^{-1}), and in hull-less barley grain line '3537' – 4.5 times (18.27 mg 100 g^{-1}) higher compared with the initial vitamin E content in non-processed grains. Such increases could be explained with the modulation of the plant growth. Therefore it is possible to foresee that more suitable for malt production will be hull-less barley grain line '3537', because the content of vitamin E in germinated hull-less barley grains was the highest (Fig. 1).

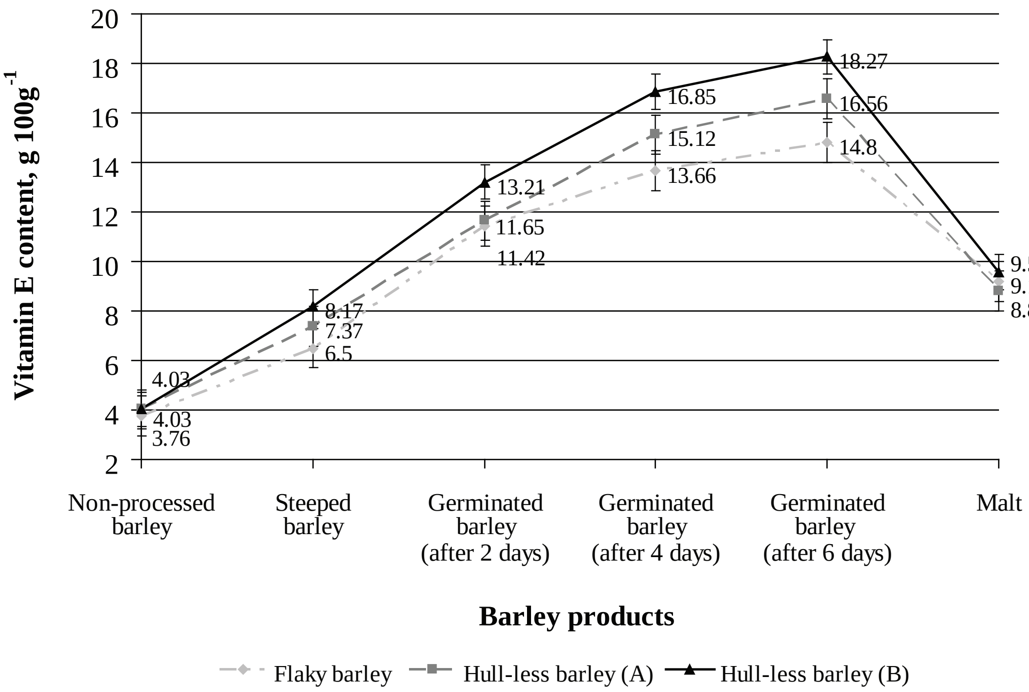

Figure 1. The dynamics of vitamin E content (in dry matter) in barley products.

After grain kilning at temperatures of +50 °C to +105 °C in a time period of 8 h, the content of vitamin E decreased in all barley grain samples: in flaky barley grains 1.6 times (to 9.19 mg 100 g^{-1}), and in hull-less barley grains 1.9 times. The content of vitamin E in hull-less barley grain was (in line '3528' - to 8.82 mg 100 g^{-1}, in line '3537' – to 9.57 mg 100 g^{-1}). The scientific literature data indicate the possible vitamin E resistance to elevated processing temperatures, but the results of our research prove that decreases in vitamin E in grains during processing can be influenced by an elevated processing temperature and the presence of oxygen. Therefore more suitable for malt production is hull-less barley grain line '3537', where the content of vitamin E after kilning was 0.75 mg 100 g^{-1} higher than in hull-less barley grain line '3528', and 0.38 mg 100 g^{-1} higher than in flaky barley grains.

The scientific literature data prove that the content of vitamin C is not detected in grains. Vitamin C synthesizes during grain germination. In our research, the dynamics of vitamin C was analysed in several barley products. In non-processed flaky barley and hull-less barley grain line '3528' it was not detected. In the dry matter of non-processed hull-less barley grain line '3537', vitamin C was detected at the amount of 0.19 mg 100 g^{-1} (Fig. 2), which could be explained by possible germination process beginning in the grains during storage.

The results suggest that, vitamin C synthesis begins during grain steeping for 24±1 h in water ambiance. It can be explained by the increase of moisture content in grains, which is a positive factor for enzymes activation, therefore the synthesis process of vitamin C starts. In addition, the vitamin C synthesise occur during the grain activation time (Rakcejeva and Skudra, 2006). The content of vitamin C was synthesized during the steeping process in flaky barley grains till 0.23 mg 100 g^{-1}, in hull-less barley grain line '3537' till 0.47 mg 100 g^{-1}, and in hull-less barley grain line '3528' till 0.30 mg 100 g^{-1} in dry matter, compared with the vitamin C content in non-processed grains. Therefore more intensive synthesis of vitamin C was found in hull-less barley grains from line '3537'.

Further germination caused a progressive increase in vitamin C in all barley samples after 2 and 4 days. This finding is in agreement with a well-known fact that biosynthesis of vitamin C in grains takes place during germination and seems to be directly involved in the modulation of plant growth, including the early stage of embryo germination (Plaza et al., 2003). After 4 days of germination, maximal vitamin C content increases were found in the tested grain samples (Fig. 2). During the research it was found that vitamin C content in flaky barley increased by 68%, in hull-less barley line '3528' – by 82%, and in hull-less barley line '3537' – by 57%, respectively, after germination for 96 h at 20±2 °C in the dark.

The content of ascorbic acid decreased in all samples of barley grains (Fig. 2) after germination for 6 days, possibly because the grains started to use vitamin C for providing the life processes and for the same growth and development. Therefore, after germination for 6 days, the content of the ascorbic acid in all grain samples was very similar - 0.5 mg 100 g^{-1} in dry matter.

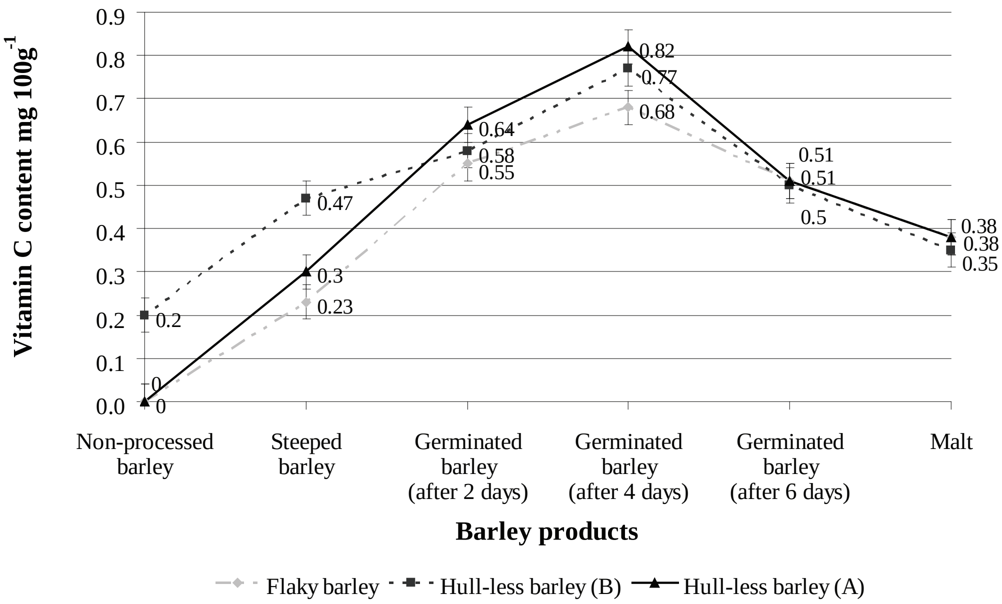

Figure 2. The dynamics of vitamin C content (in dry matter) in barley products.

Ascorbic acid decreases during grain drying at elevated temperatures in the air and oxygen ambiance are not avoided. Decreases in vitamin C in all grain samples were similar – 1.3 times lower compared with its content in grains germinated for 6 days. The content of vitamin C in dried grain samples was 0.35–0.38 mg 100 g^{-1}. The obtained data prove that vitamin C is not resistant to light, temperature and oxygen (Ball, 2006).

Conclusions

1. The content of vitamin C increased in flaky barley grains during steeping till 0.23 mg 100 g^{-1}, in hull-less barley grain line '3537' till 0.47 mg 100 g^{-1}, and in hull-less barley grain line '3528' till 0.30 mg 100 g^{-1}.
2. Grain germination caused a progressive increase in vitamin C content in all barley samples: in flaky barley by 68%, in hull-less barley line '3528' – by 82%, and in hull-less barley line '3537' – by 57%.
3. The content of vitamin C in dried grain samples decreased during kilning and was 0.35 – 0.38 mg 100 g^{-1}.
4. After grain steeping, the content of vitamin E in flaky barley and hull-less barley grain line '3528' and '3537' was similar.
5. The amount of vitamin E in flaky barley was 3.9 times, in hull-less barley grain line '3528' – 4.1 times and in hull-less barley grain line '3537' – 4.5 times higher compared with its initial vitamin E content in grains after germination.
6. After grain kilning, the content of vitamin E decreased in all barley grain samples: in flaky barley grains 1.6 times (to 9.19 mg 100 g^{-1}), and in hull-less barley grains 1.9 times.
7. The obtained results show that use of hull-less barley line '3537' in malt production allows to obtain by 0.38 mg 100 g^{-1} higher content of vitamin E in the end products compared to use of flaky barley grains.

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