Differences in the composition of vocable compounds in fresh and dried mixed heat supply of white rolled cabbage

Oleksandra Niemirich, Nataliia Frolova, Ihor Ustymenko, Andrii Havrysh

National University of Food Technologies, Kyiv, Ukraine

Keywords:

Cabbage
Drying
Chromatography
Volatile compound
Composition

Article history:

Received 25.02.2020
Received in revised form 16.06.2020
Accepted 27.12.2020

Corresponding author:

Oleksandra Niemirich
E-mail: niemirichav@ukr.net

DOI: 10.24263/2304-974X-2020-9-4-11

Abstract

Introduction. The work aims to study the chromatographic profiles of volatile compounds in fresh and dried mixed heat white cabbage with the definition of differences in qualitative and quantitative composition.

Materials and methods. Chromato-mass spectrometry (GC/TOF-MS) methods were used to study the profiles of volatile substances in fresh and dried mixed heat-fed vegetables, in particular, Amager white cabbage, with differences in qualitative and quantitative composition. Fresh white cabbage was chosen as a control.

Results and discussion. During chromatographic studies of volatile aromatic compounds of fresh and dried white cabbage, 20 volatile substances were identified. Both samples contain the following components: 4H-pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-(2.61 and 2.11%), guanosine (1.07 and 0,48%), oxirane, tetradecyl (1.71 and 0.90%), tetradecanal (2.89 and 2.72%), 2-pentadecanone (3.2 and 3.00%), 2-nonadecanone (3, 01 and 2.84%), formamide, N-methyl-N-4-[1- (pyrrolidinyl)-2-butynyl] (3.12 and 2.92%), n-hexadecanoic acid (5.8 and 5.76%), cis-acetic acid (4.43 and 4.44%), oleic acid (3.94 and 4.02%), oleic acid amide (3.12 and 3.2%), 1,2-benzene dicarboxylic acid diisoctyl ether (5.28 and 5.22%), 6-methyl-octadecane (1.96 and 1.16%), 2,6,10-trimethyltetradecane (2.69 and 1.84%), heptacosan (34.16 and 32.15%), 2-hexadecanol (2.25 and 1.76%), 1,2-epoxyhexadecane (11.11 and 10.65%), nonacosanone-15 (3, 83 and 3.45%).

Drying of raw cabbage by drying with mixed heat transfer did not cause a change in the qualitative composition, however, caused a decrease in the amount of volatile aromatic substances.

Decrease in content, % of components: heptacosane, (34,15→32,16), 1,2-epoxyhexadecane (11,11→10,659), octadecenamide (3,12 → 3,02), n-Hexadecanoic acid (5,80→ 5.76) to some extent eliminates the bitter note of raw cabbage, greasy taste, softens its aromatic sensations.

Conclusions. Comparison of volatile substances between fresh and dried samples of cabbage allows us to claim the preservation of valuable biological substances of fresh cabbage after drying with mixed heat and to spread this method of processing cabbage with maximum use of its useful properties.

Introduction

The aroma of dried vegetable raw materials is one of the determining factors of the level of quality because evaporating from the raw material, moisture takes with it volatile components, resulting in some loss of taste and aroma [1, 2]. To obtain high-quality food products using dried vegetable food products obtained by drying with mixed heat, in particular common vegetables – white cabbage, it was advisable to study the complex of its flavoring substances.

The conversion of volatile aromatic compounds of cabbage during heat treatment has been studied to a greater extent at the technological stage of blanching [3, 4] and traditional drying methods – convective, conductive, etc. Drying with mixed heat supply is currently promising and economical among the methods that provide heated air as a drying agent [5, 6]. We did not find studies comparing the profiles of volatile compounds of samples of fresh and dried cabbage with mixed heat, which led to the relevance of the chosen direction of research.

The study aimed to study the chromatographic profiles of volatile compounds in fresh and dried mixed heat of white cabbage with the determination of differences in qualitative and quantitative composition.

Materials and methods

Samples and their preparation

Fresh white Amager cabbage was used for the study. After removing the outer leaves, the cabbage heads were cut into 2 mm thick strips with a shredder. Part of the shredded cabbage (5 kg) was mixed and the juice was squeezed from the pulp. Another portion of cabbage (5 kg) was dried by the method of mixed heat and ground to a powder.

The hardware implementation of drying with mixed heat supply is a chamber measuring 2.0 × 1.0 × 1.5 m, having double walls of sheet steel with a thickness of 10^{-3} m, between which there is a thermal insulator.

The camera is mounted on a frame that serves as a base for the fan and air nozzles. The bottom of the chamber is uninsulated. In the upper part of the chamber, there is a hatch for loading and unloading of products; fan, pipes, heater, and working chamber.

The fan motor is outside the camera. The airflow from the fan is directed to the heater, then through the rotary nozzles to the working chamber and the fan inlet, ie the airflow is recirculated in the chamber [7].

Samples of raw cabbage and dried by drying with mixed heat were distributed in portions of 1 g in glass vials, sealed to prevent loss of volatile compounds.

Qualitative and quantitative analysis of volatile substances

A combination of capillary gas chromatography and mass spectrometry (GC / TOF-MS) was used to measure the concentration of cabbage volatile substances in samples of fresh cabbage and dried cabbage [8].

Separation of the components was performed using a standard chromatographic capillary column from PerkinElmer with active phase "Elite-5MS". The diameter of the column was 250 μm and the length was 30 m. Helium was used as a carrier gas, the flow of which was 20 ml/min. The temperature regime is shown in table 1.

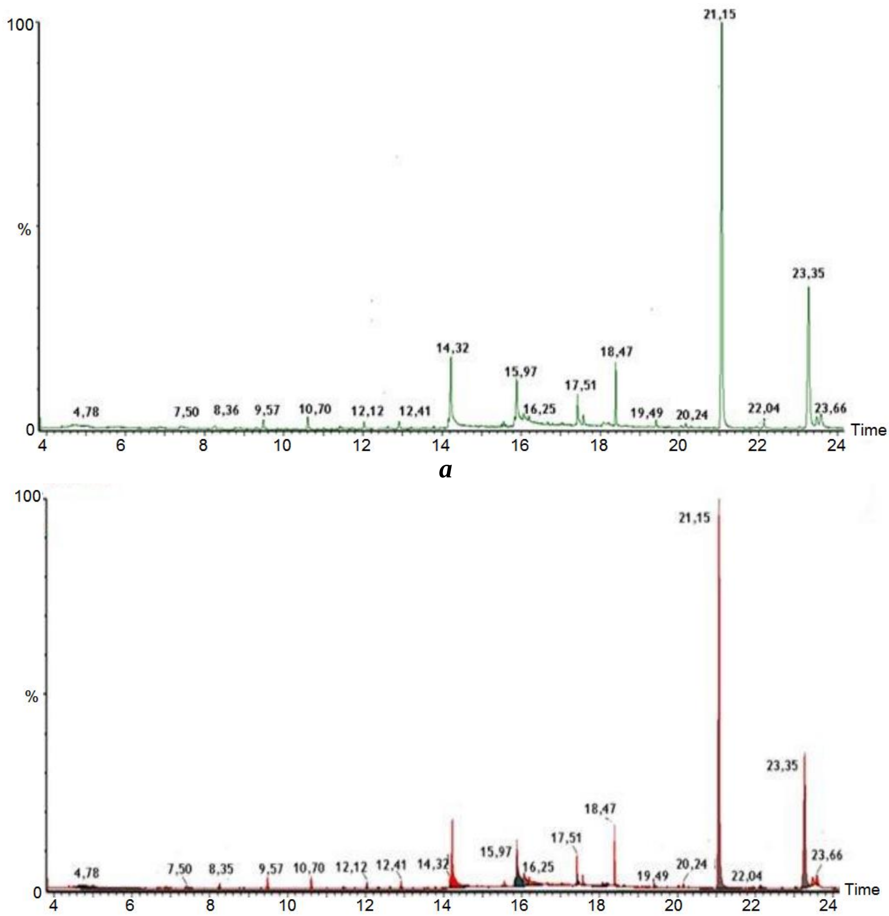
Table 1

Temperature mode of chromatogram registration

Temperature mode	Speed of temperature change, °C / min	Final temperature, °C	Retention time, min.
Initial	0.0	80.0	1.00
1	2.0	130.0	0.00
2	5.0	240.0	4.50
3	20.0	280.0	3.00

Individual retention signals were recorded, in particular, the retention time Rt, which indicates the location of each component on the chromatogram. The paper takes into account to a greater extent compounds with high truth,% with a signal-to-noise ratio (S/ N> 250).

As a result of the experiment, chromatograms of experimental samples of cabbage were obtained (Figure 1).



b

Figure 1. Chromatograms of experimental samples of Amager cabbage:
a – fresh, b – dried by mixed heat dissipation

Calculation of the quantitative content of the components of the experimental samples

Conducted by the method of internal normalization with statistical data processing of three parallel experiments [9]. The mass fraction of the investigated components m_R,% was calculated as the ratio of the peak area of the component SR to the total area of all components. For the final result, we used the mean value with the calculation of the standard deviation S. The level of probability with a confidence level p = 0.95 did not exceed α = 0.05, the critical Student's criterion = 5.47. Average values were chosen as the result.

The registration of mass spectrometers was carried out in the mode of ionization of molecules by electron impact with an electron energy of 70 eV using the El + mode. The scan time of the mass spectra was 0.2 s, with a pause between scans of 0.01 s. The number of scans per averaged mass spectrum was 106. The ions of the studied molecules were fixed in the mass range of 45÷450 m / z. The residual pressure in the ionization chamber was ~ $2.6{\times}10^{-6}$ Pa. The temperature of the ion source was 300 °C. the Input temperature of the analyzer was 280 °C.

Results and discussion

The quantitative and qualitative composition of volatile components in samples of fresh and dried cabbage

The identified components and their quantitative content of substances are listed in Table 2.

Table 2

Quantitative and qualitative composition of volatile components in samples of fresh and dried cabbage

№	t_R, min	Name of components	CAS#, formula	Characteristic	m_R, % in samples of cabbage	
					Fresh	Dried
1	04:78	4H-Pyran-4-one,2,3-dihydro-3,5-dihydroxy-6- methyl	28564-83-2 $C_6H_8O_4$	Ketone. Makes a sweet aroma [18]	2,61	2,11
2	07:50	Guanosine	118-00-3 $C_{10}H_{13}N_5O_5$	Purine nucleoside. Makes a characteristic pungent aroma [18]	1,07	0,48
3	08:35	Oxirane tetradecyl	7320-37-8 $C_{16}H_{32}O$	Saturated three-membered heterocycle. Characteristic pungent odor [2]	1,71	0,90

Table 2 (*Continue*)

№	**t_R, min**	**Name of components**	**CAS#, formula**	**Characteristic**	**m_R, % in samples of cabbage**	
					Fresh	**Dried**
					2,89	2,72
5	10:70	2-Pentadecanone	2345-28-0 $C_{15}H_{30}O$	Ketone. Weak pleasant smell [2]	3,2	3,00
6	11:51	Octadecanoic acid	57-11-4 $C_{18}H_{36}O_2$	Fatty acid. Included in the lipid composition of vegetable wax. Introduces a viscous aroma [18]	1,82	1,06
7	12:12	2-Nonadecanone	629-66-3 $C_{19}H_{38}O$	Oxygen hydrocarbons – ketone. Weak "green" aroma [18]	3,01	2,84
8	12:41	Formamide, N-methyl-N-4-[1-(pyrrolid inyl)-2-butynyl]	18327-40-7 $C_{10}H_{16}N_{2O}$	Heterocyclic diazo compound. Has a weak specific odor [19]	3,12	2,92
9	14:32	n-Hexadecanoic acid	57-10-3 $C_{16}H_{32}O_2$	Saturated fatty acid of the direct chain [18]	5,80	5,76
10	15:60	9,12-Octadecadienoic acid	60-33-3 $C_{18}H_{32}O_2$	Double unsaturated fatty acid, which is widely found in plant glycosides with a pleasant specific odor [18]	2,04	1,83
11	15:97	cis-Vaccenic acid	506-17-2 $C_{18}H_{34}O_2$	Cis-isomer of vaccine acid, part of phospholipids. Is an omega-7 fatty acid [18,2]	4,43	4,44
12	16:25	Oleic Acid	112-80-1 $C_{18}H_{34}O_2$	Belongs to monounsaturated fatty acids. It belongs to the group of omega-9 unsaturated fatty acids. With a mild odor [2]	3,94	4,02

Table 2 (*Continue*)

№	t_R, min	Name of components	CAS#, formula	Characteristic	m_R, % in samples of cabbage	
					Fresh	**Fresh**
13	17:51	9-Octadecenamide	334156 $C_{18}H_{35}NO$	Fatty amide of oleic acid. Plant metabolite [17]	3,12	3,02
14	18:47	1,2-Benzenedicarboxylic acid diisooctyl ester	27554-26-3 $C_{24}H_{38}O_4$	Terpenoid, a derivative of phthalic acid, a complex ethereal odor [18,2]	5,28	5,22
15	19:49	Octadecane, 6-methyl-	10544-96-4 $C_{19}H_40$	Isoprenoid alkane (isoprene). Volatile compound of cabbage, which gives a characteristic fresh aroma [18]	1,92	1,16
16	20:24	Tetradecane, 2,6,10-trimethyl	14905-56-7 $C_{17}H_{36}$	Isoprenoid alkane (isoprene) gives a characteristic fresh aroma [2]	2,69	1,84
17	21:15	Heptacosane	593-49-7 $C_{27}H_{56}$	Saturated hydrocarbon, alkane [17]	34,16	32,15
18	22:04	2-Hexadecanol	14852-31-4 $C_{16}H_{34}O$	Alcohol of high molecular weight, is a part of esters of wax [17]	2,25	1,76
19	23:35	1,2-Epoxyhexadecane	7320-37-8 $C_{16}H_{32}O$	Saturated heterocycle with a weak bitter tone of aroma [18]	11,11	10,65
20	23:66	15-Nonacosanone	2764-73-0 $C_{29}H_{58}O$	Ketone. Component of vegetable wax, covering a thin layer of cabbage leaves. Slight smell of mown hay [2]	3,83	3,45

As a result of the conducted researches in the spectrum of volatile substances of samples of fresh and dried cabbage 20 compounds were identified. Both samples contain the following components: 4H-pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-(2.61 and 2.11%), guanosine (1.07 and 0, 48%), oxirane, tetradecyl (1.71 and 0.90%), tetradecanal (2.89 and 2.72%), 2-pentadecanone (3.2 and 3.00%), 2-nonadecanone (3,01 and 2.84%), formamide, N-methyl-N-4-[1-(pyrrolidinyl)-2-butynyl] (3.12 and 2.92%), n-hexadecanoic acid (5.8 and 5.76%), cis-acetic acid (4.43 and 4.44%), oleic acid (3.94 and 4.02%), oleic acid amide (3.12 and 3.2%), 1, 2-benzene dicarboxylic acid diisoctyl ether (5.28 and 5.22%), 6-methyl-octadecane (1.96 and 1.16%), 2,6,10-trimethyltetradecane (2.69 and 1.84%)), heptacosan (34.16 and 32.15%), 2-hexadecanol (2.25 and 1.76%), 1,2-epoxyhexadecane (11.11 and 10.65%), nonacosanone-15 (3, 83 and 3.45%).

The spectrum of volatile substances is characterized by a wide range of chemical compounds. These are oxygen-containing and esterified compounds, saturated heterocycles, diazo compounds, terpenoids, isoprenoid alkanes.

At the same time, isoprenoid alkanes are among the most typical and biogenic components. This group includes several dozen hydrocarbons, a characteristic feature of the structure of which is the location of methyl groups in the linear carbon backbone in positions up to = 2, k + 4, k + 8, k + 12 [10].

Some compounds are part of vegetable wax [11, 12]. They are a complex, multicomponent mixture of relatively simple hydrocarbons (primarily alkanes), wax esters, as well as fatty acids, alcohols, and ketones.

To some extent, this composition of volatile compounds is associated with their sensory properties. Some of the identified components, in particular, high molecular weight alkanes and their oxygen-containing derivatives, can contribute to "Bitter", "Fresh", "Cabbage", "Fatty" and other notes of cabbage flavor [13, 14].

Also, a significant number of compounds from the volatile substances of cabbage, including bioactive isoprene, nitriles, aldehydes, and alcohols, phospholipids (cis-vaccenic acid), show functional properties [15].

Comparative characteristics of changes in volatile substances in cabbage samples

Comparing the differences in changes in volatile substances in the test samples, we can state the following:

1. The test samples do not differ in qualitative composition, however, have the different quantitative composition of components.
2. It should be noted that the drying of raw cabbage by drying with mixed heat transfer caused a decrease in volatile aromatic substances in the test samples.
3. Both samples have the same dominant components, in particular, heptacosane (34.15 and 32.16%), 1,2-Epoxyhexadecane (11.11 and 10.65%). Heptacosane is a volatile waxy substance with a pungent odor, is part of beeswax [16, 17]. 1,2-epoxyhexadecane is a waxy substance with an ethereal odor, n-hexadecanoic acid is a saturated fatty acid of the direct chain, found everywhere in nature in many plants [18, 19].
4. It can be noted that the decrease in the content, wt% of components: №17 – heptacosane, (34,15 → 32,16), №19 – 1,2-epoxyhexadecane (11,11 → 10,659), №13 – octadecenamide 3.12 → 3.02), №9 – n-Hexadecanoic acid (5.80 → 5.76) eliminates the bitter note of raw cabbage, greasy taste, softens its aromatic sensations.
5. In dried cabbage there was no decrease in the variety and a significant percentage of oxygen-containing compounds. All analyzed samples of cabbage contained ketones, aldehydes (15-Nonacosanone, 2-Pentadecanone, tetradecanal), which introduce aromas of "green tone", in particular, 15-Nonacosanone with a hint of cut hay.

Conclusions

1. Chromato-mass spectrometry (GC / TOF-MS) methods were used to study the profiles of volatile substances in fresh and dried mixed heat-fed vegetables, in particular, amager white cabbage to determine differences in qualitative and quantitative composition.
2. 20 volatile substances were identified, including oxygen-containing and esterified compounds, saturated heterocycles, diazo compounds, terpenoids, isoprenoid alkanes.
3. Comparison of volatile substances between fresh and dried samples of cabbage allows asserting the preservation of valuable biological substances of fresh cabbage after drying with mixed heat supply and to spread this method of processing cabbage with maximum use of its useful properties.

   Therefore, changes in the number of phases and thermodynamic potentials of vegetable raw materials during mixed heat drying have led to minimal changes in functional volatile chemical compounds and maximum changes in substances that cause a bitter taste.

   Thus, the goal of work on studying the qualitative and quantitative composition of volatile substances in samples of fresh and dried white cabbage was achieved, which confirmed the economical conditions of drying with mixed heat.

References

1. Barbieri S., Elustondo M., Urbicain, M. (2004), Retention of aroma compounds in basil dried with low pressure superheated steam, *Journal of Food Engineering*, 65(1), pp. 109–115.
2. Fukuda T., Okazaki K. Shinano T. (2013), Aroma characteristic and volatile profiling of carrot varieties and quantitative role of terpenoid compounds for carrot sensory attributes, *Journal of Food Science*, 78, pp. 1800–1806.
3. Roy M.K. (2009), Steam processed broccoli (Brassica oleracea) has higher antioxidant activity in chemical and cellular assay systems, *Food Chemistry*, 114.1, pp. 263–269.
4. Amin. I., Lee W. Y. (2005), Effect of different blanching times on antioxidant properties in selected cruciferous vegetables, *Journal of the Science Food and Agriculture*, 85, pp. 2314–2320.
5. Eurola M. (2003), Blanching and long-term freezing affect various bioactive compounds of vegetables in different ways, Journal of the Science Food and Agriculture, 83, pp. 1389–1402.
6. Aires A. (2015), Brassica composition and food processing, *Processing and Impact on Active components in Food. Academic Press*, 17–25.
7. Pohozhykh M. I. Pak A. O., Mishchenko T. V, Zherebkin M. V. (2011), Vnutrishni chynnyky protsesu hidrotermichnoi obrobky krup z vykorystanniam pryntsypiv ZTP sushinnia, *Vostochno-Evropeiskyi zhurnal peredovykh tekhnolohyi*, 5(3), 60–64.
8. Wiklund S. (2008), Vizualization of metabolic data based on GC/TOF-MS for identifiable bio-analysis for the support of OPLS classroom models, Analytical Chemistry, 80(1), pp. 115–122.
9. de Winter J.C.F. (2013), Using the Student's t-test with extremely small sample sizes, *Practical Assessment, Research, and Evaluation*, 18, Article 10.
10. Hecht S.S. (2000), Inhibition of carcinogenesis by isothiocyanates, *Drug Metab. Rev.*, 32, pp. 395–411.
11. Bogdanov S. (2004), Quality standards of bee pollen and beeswax, *Apiacta*, 39, pp. 334–341.

12. Jiménez J.J., Bernal J.L, Aumente S, del Nozal M.J., Martín M.T., J Bernal J. (2004), Quality assurance of commercial beeswax. Part I. Gas chromatography-electron impact ionization mass spectrometry of hydrocarbons and monoesters, *Journal of chromatography,* 1024(1–2), pp. 147–154.
13. Wieczorek Martyna N. (2018), Bitter taste of Brassica vegetables: The role of genetic factors, receptors, isothiocyanates, glucosinolates, and flavor context, *Critical reviews in food science and nutrition*, 58(18), pp. 3130–3140.
14. Podsędek A. (2007), Natural antioxidants and antioxidant capacity of Brassica vegetables: A review. *LWT-Food Science and Technology*, 40(1), pp. 1–11.
15. Wieczorek N., Jeleń H. (2019), Volatile Compounds of Selected Raw and Cooked Brassica Vegetables, Molecules, 24(3), pp. 391.
16. Bogdanov S., Münstedt K. (2009), Bee products and their potential use in modern medicine, *JAAS*, 1, pp. 57–63.
17. Maia M., Nunes F. M. (2013), Authentication of beeswax (Apis mellifera) by high-temperature gas chromatography and chemometric analysis, *Food Chemistry*, 136, pp. 961–968.
18. Ma X.,Li X., Zhang J.,Lei J.,Li W.,Wang G. (2020), Analysis of the Volatile Components in Selaginella doederleinii by Headspace Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry, *Molecules*, 25, pp. 1–14.
19. Muttevi Hyagreva Kumar, Prabhu K., Mudiganti Ram Krishna Rao, Shanthi B., Kavimani M., Shruti Dinakar, Lakshmi Sundaram R., Vijayalakshmi N., Sampad Shil, Eladi Kera Thailam (2019), Gas chromatography/mass spectrometry analysis of one Ayurvedic skin oil, *Drug Invention Today*, 11(10), pp. 2675–2678.