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Glucosinolate Derivatives in Stored Fermented Cabbage

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The research focused on the glucosinolate (GLS) breakdown products formed during the fermentation of cabbage. A relationship between the contents of degradation products in fermented cabbage and native GLS in raw cabbage was investigated. The effect of fermented cabbage storage on the contents of individual compounds was also assayed. Ascorbigen formed from one of the degradation products of glucobrassicin (indole GLS) was found to be a dominating compound in fermented cabbage. Irrespective of the time of fermented cabbage storage, the content of ascorbigen reached ~14 μmol/100 g. Neither the content of isothiocyanates, the major degradation products of aliphatic GLS, nor that of cyanides exceeded 2.5 μM. Storage of cabbage caused periodical increases and decreases in the contents of cyanides and consequent declines in the contents of isothiocyanates. The highest relative contents (expressed as a percentage of the native GLS content) of degradation products—ranging from >70 to 96%—were reported for the products of glucoraphanin degradation, whereas the lowest—<5%—were reported for the products of sinigrin degradation.

KEYWORDS: Cabbage; fermented cabbage; glucosinolates; glucosinolate breakdown products

INTRODUCTION

Epidemiological data indicate that a high intake of cruciferous vegetables, including cabbage, broccoli, Brussels sprouts, and cauliflower, lowers the incidence of various forms of cancer in humans (*1*). The anticarcinogenic activity of cruciferous vegetables is linked with the presence of glucosinolates (GLS). By means of enzymatic and nonenzymatic transformations GLS release a number of biologically active products.

The products of enzymatic degradation of aliphatic and aralkyl GLS are corresponding isothiocyanates and cyanides or, as in the case of 5-vinyloxazolidine-2-thione, a product of spontaneous of cyclization, isothiocyanate (*2*). The direct products of indole GLS hydrolysis are also corresponding isothiocyanates and cyanides, which undergo further changes or reactions. In the case of glucobrassicin, these processes result in the formation of a number of compounds, including indole-3-carbinol and products of its oligomerization (3,3′-diindolylmethane, indolo[3,2-*b*]carbazole) and ascorbigens (reaction products: indole-3-carbinol with vitamin C), as well as indole-3-acetonitrile and indole-3-acetic acid (*3*, *4*). The direction of GLS degradation is determined by environmental pH (*5*, *6*) as well as by the presence of Fe^{2+} ions (*7*) and epithiospecific protein (*8*).

It was found that direct or secondary degradation products of glucobrassicin (one of indole GLS, dominating in cruciferous vegetables), such as indole-3-acetonitrile, indole-3-carbinol, 3,3′-diindolylmethane, ascorbigen, and indolo[3,2-*b*]carbazole, were likely to act as anticarcinogens by decreased carcinogen activation through the inhibition of phase I enzymes, increased detoxification by induction of the phase II enzymes that affect the xenobiotic transformations, inhibition of tumor cell growth, and stimulation of apoptosis (*9*−*14*).

Some indole products of GLS are claimed to demonstrate breast cancer-preventing actions, due to their affinity and ability to bind with estrogen receptors. Such an activity has been displayed by 3,3′-diindolylmethane (*15*), indole-3-carbinol (*15*, *16*), and indolo[3,2-*b*]carbazole (*17*), which is formed from ascorbigen or indole-3-carbinol in a strongly acidic environment (upon the activity of gastric juice) (*18*).

Unfortunately, under some conditions, indole compounds have been reported to demonstrate mutagenic (*19*) and carcinogenic activities (*11*, *20*).

The impact of phases I and II of cellular detoxication on enzymatic activity has also been observed in the case of isothiocyanates released from aralkyl and aliphatic GLS such as glucotropaeolin, gluconasturtiin, glucoraphanin, glucoiberin, gluconapin, and sinigrin (*9*−*14*).

Cruciferous vegetables are not always consumed fresh. They are often subjected to technological and culinary processing, namely, freezing, cutting, blanching, and cooking, which in turn result in a partial decomposition of GLS in the final product. It should be emphasized, however, that depending on the type and conditions of processing, GLS undergo either enzymatic hydrolysis or thermal degradation (*2*).

Due to dietary habits, fermentation of vegetables, mainly of white cabbage, has been limited only to some parts of the world.

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Fermented cabbage is very popular in Germany and Poland; however, it is also consumed in the United States, Canada, and Russia. Fermentation of cabbage is performed directly after the harvest of cabbage. Fermented cabbage is consumed throughout the winter period, as a properly performed process guarantees good quality of the product during storage. The effect of fermentation on GLS degradation products is poorly recognized. Literature data referring to that matter are fragmentary and usually deal with selected products or even single compounds. Daxenbichler et al. reported the presence of thiocyanate ions released during the hydrolysis of indole GLS and cyanate being a degradation product of glucoiberin—alkyl GLS. Both of these compounds were determined 1, 2, and 3 or 17, 19, and 28 weeks after fermentation, depending on cabbage variety (*21*). On the other hand, the research of Aleksandrova et al. focused on such products of indole GLS degradation as indole-3-carbinol, indole-3-acetonitrile, and ascorbigen, ascorbigen dimer, and ascorbigen trimer, which are the products of ascorbic acid reaction with 1, 2, and 3 molecules of indole-3-carbinol, respectively (*22*). Tolonen et al. determined the contents of isothiocyanates and cyanates released from sinigrin and glucoraphanin and single breakdown products of glucoiberin, gluconapin, progoitrin, and glucobrassicin (*23*). The extracts obtained from fermented cabbage were also investigated for their biological properties. As shown by the results of research carried out by Ju et al., the extracts obtained from fermented cabbage might play a role in altering the development and growth of estrogen-dependent cancers (*20*).

The aim of the presented study was to assess the effect of fermentation and storage of fermented cabbage on GLS breakdown products as well as to determine a quantitative relationship between GLS degradation products in fermented cabbage and native GLS in raw material.

MATERIALS AND METHODS

Fermentation. Commercial white cabbage was used for fermentation. After removal of outer leaves, cabbage heads were cut in a shredder into ~2 mm thick strips. From the shredded cabbage were taken five samples to determine the initial content of GLS. Next, 3% NaCl was added to the remaining cabbage, and, after mixing, the whole was transferred to three traditional stoneware pots to run three independent fermentations. Beginning from day 3 up to the end of the effervescent fermentation phase, cabbage was pricked to remove releasing fermentation gases. After 7 days, intensive emission of gases and juice typical of the effervescent fermentation phase stopped, the excess of the formed juice was removed, and cabbage was transferred into Weck jars (volume of ~900 mL). The jars were filled, by strongly pressing down, to 2 cm from their upper edges and kept until analyses at a temperature of ~5 °C. The contents of breakdown products were analyzed jointly for cabbage and juice after 2, 5, 8, 11, 14, and 17 weeks of storage. The beginning of storage was the moment of at which cabbage was put into jars. Cabbage stored for 2 weeks was additionally determined for the content of GLS to confirm their total degradation. Juice obtained from samples of fermented cabbage and that stored from 2 to 17 weeks was determined for pH values using a Radiometer PHM85 (Copenhagen, Denmark) pH-meter.

Standards. Indole-3-carbinol and indole-3-acetonitrile were purchased from Merck (Darmstadt, Germany). Benzyl isothiocyanate, allyl isothiocyanate, and allyl cyanide were obtained from Fluka Chemie (Buchs, Switzerland).

Synthesis of Ascorbigen. Ascorbigen was synthesized from indol-3-ylmethanol and ascorbic acid according to the procedure of Kiss and Neukom (*24*). Reactions were run at room temperature, pH 4, and a substrate molar ratio of 1:1. After duplicate extraction with diethyl ether, the reaction mixture was re-extracted with ethyl acetate. The ethyl acetate extract was dried over anhydrous sodium sulfate and evaporated in vacuo. Chromatographic purity (HPLC) of the compound obtained reached 99.6%.

Analysis of GLS. Individual GLS were analyzed by HPLC following enzymatic desulfatation according to the *Official Journal of European Communities* (*25*) as described earlier by Ciska et al. (*26*).

Analysis of GLS Breakdown Products. *GC-MS Analysis.* The breakdown products of the GLS were analyzed according to the method of Chiang et al. (*27*) with slight modifications. Briefly, duplicate 50 g samples of fermented cabbage were homogenized with 50 mL of distilled water in an Ultra Turrax homogenizer (Janke & Kunkel). The homogenate was extracted three times with 50 mL of methylene chloride. Benzyl isothiocyanate was added just before the first extraction as an internal standard. The combined organic layers were dried over anhydrous sodium sulfate and filtered through a PTFE filter (0.22 μm). Next, the filtrate was concentrated to the volume of ~8 mL on a rotary evaporator, under reduced pressure and a temperature of 30 °C. The concentrate was transferred into a measuring flask and filled with dichloromethane to 10 mL.

The analysis of degradation products was performed on a Hewlett-Packard 5972 mass selective detector coupled with an HP 5890 gas chromatograph and data station containing the Wiley 275 library of spectra. The compounds were separated in a capillary column HP-5MS (30 m × 0.25 mm, film thickness = 0.25 μm). The carrier gas was helium (1.5 mL/min). Samples (2 μL) were injected in the splitless mode. The oven temperature was initially set at 30 °C for 5 min, then increased to 200 °C (5 °C/min), and held for 5 min. Injector and detector temperatures were 210 and 230 °C, respectively. Mass spectra were obtained by electron impact ionization (EI) over the range of *m*/*e* 50−550. The ion source temperature was 250 °C, and the electronic impact energy was 70 eV.

Identifications of but-3-enyl isothiocyanate, 5-vinyloxazolidine-2-thione, and 2-phenylethyl isothiocyanate were carried out by comparing mass spectra with the Wiley 275 library and those of allyl isothiocyanate and allyl cyanide by comparison with mass spectra of standards. The other compounds were identified by comparing their mass spectra with those reported by other authors: mass spectrum of 1-cyano-2,3-epithiopropane, Springett and Adams (*28*) and Kyung et al. (*29*); mass spectra of 3-(methylsulfinyl)propyl isothiocyanate, 1-cyano-3-(methylsulfinyl)propane, and 1-cyano-3-(methylthio)propane, Spenser and Daxenbichler (*30*); mass spectrum of 3-(methylthio)propyl isothiocyanate, Buttery et al. (*31*); and mass spectra of 4-(methylsulfinyl)butyl isothiocyanate and 1-cyano-4-(methylsulfinyl)butane, Kore et al. (*32*) and Chiang et al. (*27*).

The contents of individual compounds were calculated using the arbitrary response factor of 1.00.

HPLC Analysis. The analysis of the products of indole GLS breakdown involved three degradation products of glucobrassicin dominating in cabbage: ascorbigen, indole-3-carbinol, and indole-3-acetonitrile. The analysis was carried out according to that of Aleksandrova et al. (*22*) with slight modifications. Briefly, duplicate 50 g samples of fermented cabbage were homogenized with 5 g of NaCl using an Ultra Turrax homogenizer (Janke & Kunkel). Next, the samples were extracted two times with 50 mL of acetone. The acetone extracts were combined and, after filtration, concentrated to the volume of ~30 mL. The concentrate was extracted two times with 20 mL of ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, filtered through a PTFE filter (0.22 μm), and evaporated in vacuo to dryness. The residue was dissolved in acetonitrile and made up to 10 mL with mobile phase.

The HPLC analysis was run with a Shimadzu system. The compounds were separated from 20 μL samples in an ODS-2 3 Micron column (150 × 4.6 mm). The chromatogram was developed at a flow rate of 1.3 mL/min by eluting in a gradient of 10% acetonitrile in 0.1 M ammonium acetate buffer (pH 5.7) (A) and 80% acetonitrile in 0.1 M ammonium acetate buffer (pH 5.7) (B) as follows: linear gradient of 100% A−100% B for 25 min, isocratic 100% B for 5 min, linear gradient of 100% B−100% A for 5 min, equilibrate for 5 min. Detection was performed at λ = 280 nm.

RESULTS AND DISCUSSION

The contents of individual GLS initially present in cabbage used for fermentation are presented in **Table 1**. Because GLS

Table 1. Contents of Individual GLS in Shredded Cabbage Used for Fermentation

GLS	content[a] (μmol/100 g of FW)
sinigrin	24.21 ± 0.11
gluconapin	1.40 ± 0.35
glucoibervirin	1.23 ± 0.01
glucoiberin	31.49 ± 2.13
glucoraphanin	1.21 ± 0.05
progoitrin	4.12 ± 0.15
gluconasturtiin	tr[b]
glucobrassicin	31.95 ± 3.76
4-hydroxyglucobrassicin	0.44 ± 0.01
4-methoxyglucobrassicin	1.98 ± 0.23
neoglucobrassicin	0.76 ± 0.13

[a] Values are means ± SD ($n = 5$). [b] Trace, <0.05 μmol/dm.

Table 2. Degradation Products of Individual GLS Identified in Fermented Cabbage

code	degradation product	GLS
Ia	allyl isothiocyanate	sinigrin
Ib	allyl cyanide	
Ic	1-cyano-2,3-epithiopropane	
II	but-3-enyl isothiocyanate	gluconapin
IIIa	3-(methylthio)propyl isothiocyanate	glucoibervirin
IIIb	1-cyano-3-(methylthio)propane	
IVa	3-(methylsulfinyl)propyl isothiocyanate	glucoiberin
IVb	1-cyano-3-(methylsulfinyl)propane	
Va	4-(methylsulfinyl)butyl isothiocyanate	glucoraphanin
Vb	1-cyano-4-(methylsulfinyl)butane	
VI	5-vinyloxazolidine-2-thione	progoitrin
VII	2-phenylethyl isothiocyanate	gluconasturtiin
VIIIa	ascorbigen	glucobrassicin
VIIIb	indole-3-carbinol	
VIIIc	indole-3-acetonitrile	

were determined in shredded cabbage, it should be kept in mind that certain amounts of GLS might have been hydrolyzed by native myrosinase as a result of cell damage. Only three of all of the GLS compounds were dominating, namely, glucoiberin and sinigrin in the group of aliphatic GLS and glucobrassicin in the group of indole GLS. The summary content of these three compounds constituted ~90% of total GLS. The contents of individual GLS present in cabbage are consistent with the results reported in previous studies (*26*, *33*, *34*). In both fermented and 2-weeks-stored cabbage even trace amounts of GLS were not observed.

Fermented cabbage was characterized with good taste and aroma and an appropriate color and hardness of strips. Juice pH values of stored fermented cabbage ranging from 3.4 to 3.6 also point to a proper course of fermentation.

Fermented cabbage was found to contain 15 products of GLS degradation (**Table 2**). Three of them were the indolyl compounds likely to be formed during the hydrolysis of glucobrassicin, namely, indole-3-carbinol (1.5 μmol/100 g), indole-3-acetonitrile (0.1 μmol/100 g), and ascorbigen (14 μmol/100 g), and all of them were stable during the storage time (**Table 3**). Moreover, the last one was a dominating derivative of all GLS degradation products identified. Similar contents of the above compounds were found in commercially fermented cabbage by Aleksandrova et al. (*22*). Indole-3-carbinol in 124-h-fermented cabbage, in traces, was found also by Toleonen et al. (*23*).

Individual aliphatic GLS were hydrolyzed to corresponding isothiocyanates and cyanides (**Table 2**). Single products of

Table 3. Content (Micromoles per 100 g of FW) of GLS Degradation Products in Fermented Cabbage Stored for 2–17 Weeks

time (weeks)	degradation products													
	Ia	Ib	Ic	II	IIIa	IIIb	IVa	IVb	Va	Vb	VI	VII	VIIIa	VIIIb	VIIIc
2	1.22 ± 0.25[a]	0.51 ± 0.11	0.05 ± 0.02	0.17 ± 0.09	0.43 ± 0.13	0.24 ± 0.13	2.22 ± 0.55	0.24 ± 0.16	1.07 ± 0.31	0.06 ± 0.03	0.20 ± 0.06	tr	13.80 ± 0.48	1.53 ± 0.06	0.11 ± 0.02
5	1.03 ± 0.22	0.33 ± 0.20	tr[b]	0.29 ± 0.06	0.38 ± 0.11	0.45 ± 0.14	2.04 ± 0.48	0.09 ± 0.06	1.15 ± 0.45	tr	0.15 ± 0.05	tr	13.90 ± 0.29	1.55 ± 0.05	0.10 ± 0.02
8	1.13 ± 0.15	0.32 ± 0.11	tr	0.22 ± 0.07	0.27 ± 0.07	0.47 ± 0.14	1.94 ± 0.63	0.06 ± 0.05	1.03 ± 0.26	tr	0.02 ± 0.01	nd[c]	13.90 ± 0.80	1.44 ± 0.09	0.12 ± 0.05
11	0.93 ± 0.31	0.45 ± 0.17	nd	0.19 ± 0.07	0.20 ± 0.10	0.49 ± 0.18	1.39 ± 0.74	0.12 ± 0.05	0.89 ± 0.52	tr	0.06 ± 0.03	nd	14.20 ± 0.79	1.59 ± 0.06	0.11 ± 0.02
14	0.75 ± 0.29	0.39 ± 0.18	nd	0.14 ± 0.04	0.09 ± 0.06	0.47 ± 0.20	1.51 ± 0.47	0.19 ± 0.07	1.16 ± 0.22	tr	0.04 ± 0.02	nd	14.20 ± 0.30	1.62 ± 0.06	0.11 ± 0.04
17	0.60 ± 0.18	0.47 ± 0.22	nd	0.13 ± 0.08	0.04 ± 0.02	0.46 ± 0.13	1.57 ± 0.76	0.22 ± 0.09	0.90 ± 0.33	nd	0.06 ± 0.02	nd	13.30 ± 0.55	1.51 ± 0.07	0.12 ± 0.03

[a] Values are means ± SD ($n = 3$). [b] Trace, mean of three samples <0.02 μmol/100 g. [c] Not detected.

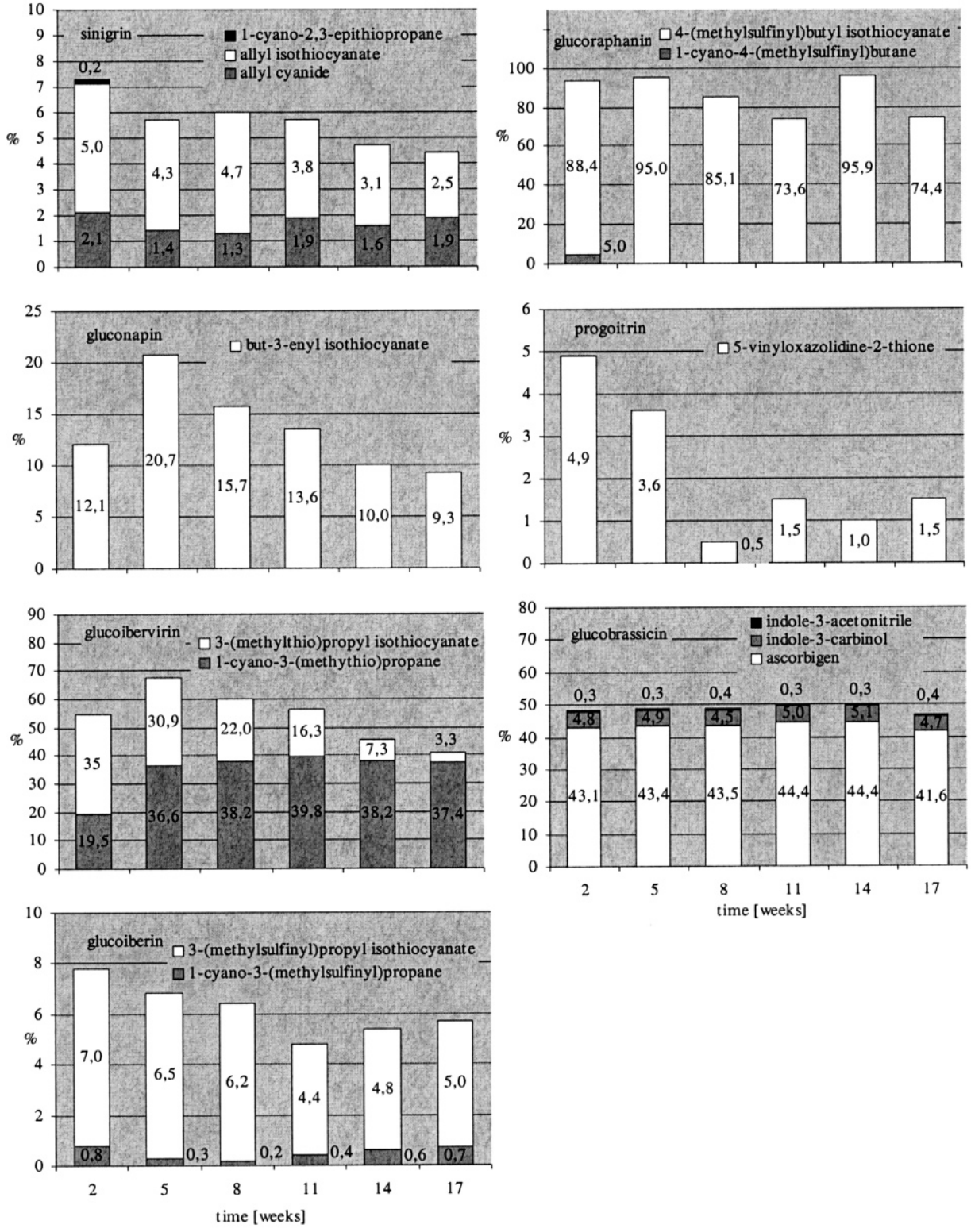

Figure 1. Relative contents of degradation products of individual GLS in fermented cabbage stored for 2–17 weeks, expressed as percentage of parent GLS content in raw cabbage.

breakdown were found in the case of progoitrin, gluconapin, and aralkyl GLS—gluconasturtiin. Progoitrin was represented by 5-vinyloxazolidine-2-thione, a product of isothiocyanate cyclization.

The presence of isothiocyanates and cyanides derived from sinigrin and glucoraphanin, isothiocyanates from glucoiberin, and gluconapin as well as 5-vinyloxazolidine-2-thione in the fermented cabbage confirms the results of research by Toleonen et al. (*23*). Daxenbichler et al. (*21*) also identified 1-cyano-3-(methylsulfinyl)propane—the second product of glucoiberin hydrolysis also found by us. Moreover, in our investigation a new product of GLS degradation was found: small amounts of 1-cyano-2,3-epithiopropane—a derivative of sinigrin—and two compounds derived from the hydrolysis of glucoibervirin as well as phenylethyl isothiocyanate whose precursor was gluconasturtiin.

The contents of aliphatic GLS degradation products in fermented cabbage stored for 2 weeks ranged from 0.05 to 2.22 μmol/100 g for 1-cyano-2,3-epithiopropane and 3-(methylsulfinyl)propyl isothiocyanate, respectively (**Table 3**). Except glucoibervirin, the major and/or sole products of aliphatic GLS were isothiocyanates. Their content was at least twice as high as that of cyanates derived from the same parent GLS. Whereas in the case of the products of glucoibervirin degradation in cabbage stored from 5 to 17 weeks, the content of 1-cyano-3-(methylthio)propane was higher from that of a corresponding isothiocyanate.

Similar results referring to the proportion between isothiocyanates and respective cyanates released from sinigrin and glucoraphanin in cabbage fermented for 5 days were reported by Toleonen et al. (*23*). Gil and MacLeod (*5*), in their earlier model research into the dependence of sinigrin degradation direction from environmental pH, showed that in an environment with pH 4−5 isothiocyanate is the major degradation product of that GLS, whereas cyanate is a predominating product at pH values below 3.7. Usually higher contents of respective isothiocyanates than of cyanates or the presence of sole isothiocyanates may be explained by a relatively high pH at the beginning of the fermentation process. Confirmation of this hypothesis would require monitoring the pH values and contents of GLS and products of their degradation as early as in the initial phase of the fermentation process. In addition, the effect of pH on the direction of GLS degradation will depend on the chemical structure of GLS. Hence, in the case of hydrolysis of individual GLS, proportions between isothiocyanates and cyanates may differ from those reported by Gil and MacLeod for sinigrin (*5*).

During the storage of cabbage, the contents of isothiocyanates were gradually decreasing. Losses in their contents reported between the 2nd and 17th weeks of storage ranged from 1.07 to 0.90 μmol (15% loss) and from 0.43 to 0.04 μmol (90% loss) for 4-(methylsulfinyl)butyl isothiocyanate and 3-(methylthio)-propyl isothiocyanate, respectively. No clear tendency was observed in the case of cyanates: the content of 1-cyano-3-(methylthio)propane increased 2-fold between the 2nd and 5th weeks, whereas those of allyl cyanide and 1-cyano-3-(methylsulfinyl)propane first decreased to finally become higher. As a result of these changes, the contents of both of these compounds after 2 and 17 weeks of storage were alike. Different tendencies and rates of changes in the contents of GLS degradation products during the storage of cabbage may result from diverse chemical and microbiological stabilities of individual compounds. Divergent results of changes in the content of 1-cyano-3-(methylsulfinyl)propane upon storage of fermented cabbage were obtained by Daxenbichler et al. (*21*). In one of the three experiments, the content of 1-cyano-3-(methylsulfinyl)propane between the 2nd and 19th weeks of cabbage storage increased. In the second experiment, it decreased between the 1st and 7th weeks, and in the third experiment it was comparable between the 2nd and 17th weeks of storage.

Taking into account the contents of GLS in raw cabbage, a relatively small amount of products formed from dominating aliphatic GLS as well as a relatively high content of compounds released from glucoraphanin and glucoibervirin, whose contribution in the total GLS was low, are worth emphasising (**Tables 1** and **3**). Depending on the time of storage of the cabbage, relative contents of major breakdown products of sinigrin and glucoiberin in fermented cabbage, expressed as a percentage of parent GLS content in raw material, ranged as little as from 2.5 to 5% and from 4 to 7% for allyl isothiocyanate and 3-(methylsulfinyl)propyl isothiocyanate, respectively (**Figure 1**). The relative content of ascorbigen synthesized from indole-3-carbinol, formed after the hydrolysis of glucobrassicin—a dominating indole GLS in raw cabbage hydrolysis, was considerably higher and reached >40%. A low relative content of degradation products released from some aliphatic GLS may result from their chemical and microbiological instability and, additionally, in the case of sinigrin and gluconapin, may be linked with exceptional volatility of their degradation products. The losses of volatile compounds could occur as early as during cabbage fermentation, which was accompanied by intensive release of fermentation gases. However, one may not exclude the losses caused upon analytical procedure connected with the extraction of volatile compounds from fermented cabbage.

In contrast to low contents of 3-(methylsulfinyl)propyl isothiocyanate, the content of its homologue 4-(methylsulfinyl)-butyl isothiocyanate, derived from glucoraphanin, ranged from 70 to >90%. Such a high relative content of butyl isothiocyanate in fermented cabbage may point to the high stability and/or low chemical reactivity of that compound. Thus, it may be assumed that the content of degradation products in fermented cabbage does not depend only on the content of native GLS in raw cabbage, but may substantially depend on such physicochemical properties as volatility, stability, and reactivity in an acidic environment and microbiological stability as well.

Taking into consideration the results obtained, it may be concluded that ascorbigen, acknowledged as having a beneficial impact on human health, is the major product of GLS degradation in fermented cabbage. Taking into account low volatility, potential microbiological, chemical stability, and the fact that, irrespective of white cabbage variety, glucobrassicin always belongs to a group of predominating GLS (together with sinigrin and glucoiberin), it may be assumed that ascorbigen will always be a main product of GLS degradation in fermented cabbage. A high relative content of 4-(methylsulfinyl)butyl (known as sulforaphane), expressed as the percentage of parent glucoraphanin in raw cabbage, despite small amounts of glucoraphanin in white cabbage, makes fermented cabbage an additional source of that beneficial compound in a human diet. What is more, at a lower availability of fresh vegetables in the winter period, fermented cabbage may be an ultimate source of these compounds in a diet, as their content during the storage of cabbage remains practically unchanged. An additional advantage of fermented cabbage as a dietary component is a low relative content of especially toxic 5-vinyloxazolidine-2-thione.

It is obvious that absolute contents of particular products of GLS degradation in fermented cabbage depend on the contents of native GLS of the raw material. Therefore, from the nutritional point of view, fermentation of GLS-rich cabbage is favorable and highly advised.

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