

Comparison of the volatile sulfur compounds in onion oil to those in fresh onion juice

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Abstract

The characteristic aroma of fresh onion (*Allium cepa* L.) is formed enzymatically. [1] When the onions are chopped, the cells release enzymes (alliinases), which transform isoalliin into the highly reactive 1-propenyl sulfenic acid. [2,3] The latter compound can condense with itself to form thiosulfinate (pathway I). Thiosulfinate can react with free thiols to form relatively stable compounds such as disulfides. Alternatively, the enzyme lachrymatory factor synthase (LFS) can convert 1-propenyl sulfenic acid into *syn*-propanethial-S-oxide, the lachrymatory compound in onions (pathway II). [4] It is known that, in water, *syn*-propanethial-S-oxide can decompose to form propanal and hydrogen sulfide. These decomposition products can further react with other volatiles present in onion juice, to form new molecules that contribute to the aroma of fresh onion. [5] Propanal and hydrogen sulfide can readily generate a number of high impact flavor compounds. These molecules possess a powerful fresh onion character, but their analytical characterization is often challenging. This is due to their reactivity towards other molecules present in onion juice, their thermal lability in water and their low concentration in the matrix. A pathway was proposed for the formation of the major sulfur compounds in onion juice.

Objective

The goal of this work was to compare the different types of volatile sulfur compounds in fresh onion juice to those in onion oil. Onion oil can be prepared simply by steam distillation of ground onions in water. The obtained oil contains the volatiles sulfur compounds and can be analyzed directly by GC-MS. The identification of the volatile sulfur compounds in onion juice, however, required a special approach. In *Allium* analysis by GC, cool injection techniques are preferred, because hot injection may result in artifacts. [1,6,7,8] On-column injections have limited sample load ability and may bring non-volatile plant material in the extract onto the column. In this research, it was attempted to overcome these limitations by applying a thiol enrichment step, followed by analysis under mild conditions using an Agilent multimode inlet.

Approach and results

Onion oil. Yellow onions were peeled, chopped and added to water. The mixture was steam distilled under atmospheric pressure. The oil layer was separated from the distillate, dried over magnesium sulfate, filtered and injected directly on an Agilent 5977 single-quadrupole GC/MS system in electron ionization mode. Figure 1 depicts the gas chromatogram of the onion oil. Mass spectral identification was achieved using in-house and commercial libraries. Structure assignment and relative percentages of the seven major signals in the matrix are presented in Table 1.

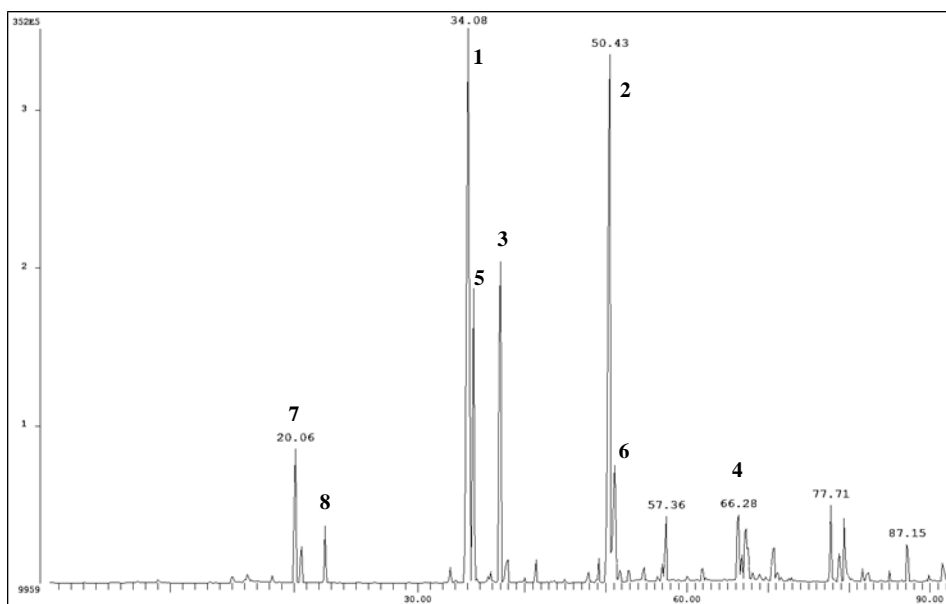


Figure 1: Gas chromatogram of onion oil.

Table 1: Predominant Sulfur Compounds in Onion Oil

#	Compound	Relative percentage
1	dipropyl disulfane	21.8 %
2	dipropyl trisulfane	17.1 %
3	methyl propyl trisulfane	10.1 %
4	dipropyl tetrasulfane	5.8 %
5	<i>trans</i> -1-propenyl propyl disulfane	5.8 %
6	1-propenyl propyl trisulfane	4.8 %
7	<i>cis</i> -1-propenyl methyl disulfane	3.0 %
8	dimethyl trisulfane	1.2 %

Numbers match the signals in the chromatogram.

Onion juice. Yellow onions were peeled, cut and processed with a commercial juicer. The juice was collected and allowed to stand for 30 minutes prior to extraction. During this period, enzymatic reactions and subsequent chemical reactions could take place, by which the compounds of interest were formed. The juice was extracted with methylene chloride, followed by partial evaporation of the solvent. The residue was passed through a mercuric agarose gel which was eluted with methylene chloride / dithiothreitol. [9,10] Prior to the actual analysis, a multimode inlet, operating in the vent mode, was used to evaporate the solvent to further concentrate the sample in the GC inlet liner at low temperature. Only the (semi-)volatile compounds were swept onto the column under mild thermal conditions (150 °C). Analysis was done on an Agilent 5977 single-quadrupole GC/MS system in electron ionization mode. Figure 2 depicts the gas chromatogram of the thiol enriched onion juice extract. Mass spectral identification was achieved using in-house and commercial libraries, as well as synthesized or purchased reference standards. Structure assignment and relative percentages of the seven major signals in the matrix are presented in Table 2.

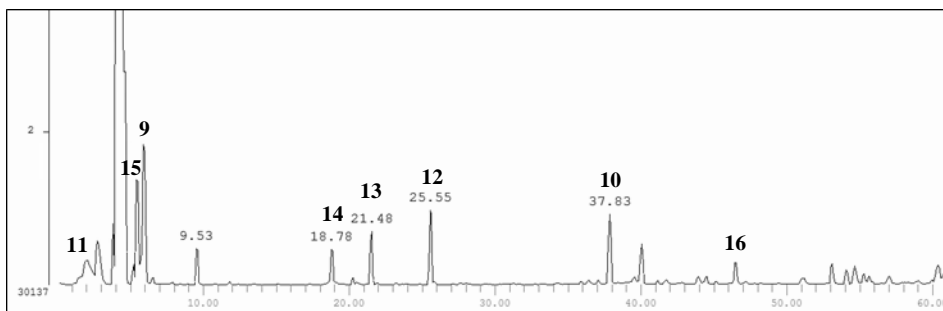


Figure 2: Gas chromatogram of the thiol enriched onion juice extract

Table 2: Predominant Sulfur Compounds in Raw Onion Juice [11]

#	Compound	Relative percentage
9	Propanethiol	21.5 %
10	1-propylsulfanyl-1-propanethiol	15.7 %
11	Methanethiol	15.3 %
12	1-methylsulfanyl-1-propanethiol	12.0 %
13	1,2-propanedithiol	10.1 %
14	1,1-propanedithiol	7.1 %
15	Allylthiol	3.6 %
16	3-sulfanyl-2-methylpentan-1-ol	2.2 %

Numbers match the signals in the chromatogram.

Discussion and conclusion

The sulfur compounds that are found in onion juice are rather different from the sulfur compounds that are found in onion oil. Onion oil has a ‘boiled onion’ aroma and its composition analysis has well been described in literature. It consists mainly of disulfanes, trisulfanes and tetrasulfanes, which are relatively stable end products. These components are formed by reactions of thiosulfinates during boiling in water. Reaction of a thiosulfinate with a free thiol will result in the formation of a disulfane. If a thiosulfinate reacts with hydrogen sulfide, an alkyl hydroper sulfide will be formed as an instable intermediate. Hydroper sulfides can again react with a thiosulfinate to form trisulfane. From the sulfur compounds found in the oil, it can be concluded that by heating in water, 1-propenyl sulfenic acid follows reaction pathway I in Figure 3. Raw onion juice has a ‘fresh onion’ aroma and contains rather different classes of sulfur compounds; disulfanes and trisulfanes are not the major components in the thiol enriched extract of the juice. The major sulfur compounds found in onion juice can be classified in groups: free thiols, thiohemiacetals and aldol condensation products. Figure 3 proposes a potential pathway for their formation. From the sulfur compounds found by analysis of the juice, it can be concluded that in the absence of a boiling step in water, 1-propenyl sulfenic acid follows reaction pathway II in Figure 3.

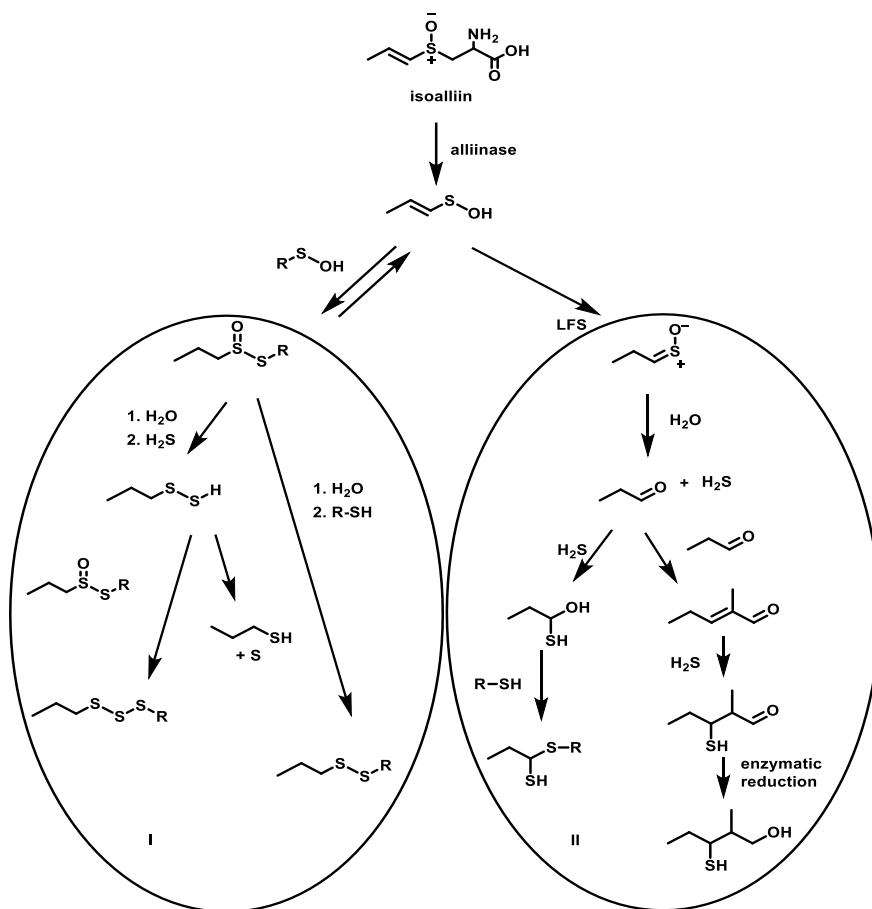


Figure 3: Proposed pathways of 1-propenyl sulfenic acid for the formation of the thiol compounds in onion oil (I) and in fresh onion juice (II)

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