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Changes in pyruvic acid formation capacity in frozen onion

Dannelse af pyrodruesyre i frosne løg

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Summary

The pungency of frozen onion has been determined by analysis for pyruvic acid using gas chromatography and the spectrophotometric method of *Schwimmer* and *Weston.* About 30 p.c. of the pungency was lost during freezing and further losses occurred during storage at –25°C of the unblanched onion. Onion varieties have different pungency levels. By comparison to raw onions higher amount of frozen onions are required to obtain equal flavour effect in for instance meat products.

An elaborated gas chromatographic method and the spectrophotometric method developed by *Schwimmer* and *Weston* gave similar results.

Key words: *Allium cepa,* onion, pungency, freezing, pyruvic acid.

Resumé

Aromadannelsen hos løg begynder med indvirkning af enzymet alliinase (4.4.1.4) på sulfoxider der er aromaforstadier. Denne proces kan følges ved analyse for de i næste trin dannede aromastoffer, hvoraf især sulfider er vigtige. Det er imidlertid betydeligt lettere at bestemme den mængde pyrodruesyre som frigøres ved den enzymkatalyserede proces. Analyse for pyrodruesyredannelse er blevet anvendt til bestemmelse af dybfrysningens virkning på aromastofdannelse. Allerede under indfrysningen sker der en reduktion i den maksimalt mulige pyrodruesyredannelse, som reduceres yderligere under lagringen.

Nøgleord: Kepaløg, aroma, pyrodruesyre, frysning.

Introduction

The characteristic flavour of raw onion arises when flavour precursors (sulphoxides) and the enzyme alliinase (4.4.1.4) are released by mastication and aroma substance formation processes are initiated (23, 26). Processing of onions by freezing with or without blanching may result in partially or complete loss of enzyme activity and aroma formation ability.

The concentration of aroma compounds in onion and onion products can be determined by use of gas chromatography (2, 4, 5, 10, 16, 18, 21, 25), by spectrophotometric analysis of thiopropanal (8) or by analysis of pyruvic acid. The aroma strength is correlated to the content of pyruvic acid released in the first step of flavour formation (19, 21, 22).

The aim of this paper was to study the effect of freezing on flavour development and to determine flavour strength of frozen onion processed from a number of onion varieties. A further aim was to compare an elaborated gas chromatographic method with the method of *Schwimmer* and *Weston* (21).

Materials and methods

Onions (2.5 kg) of nineteen varieties were peeled manually and sliced (6 mm thick). After thorough mixing of the onion rings two amounts of 500 g were packed in freezing bags and frozen in a freezing cabinet kept at –25°C by supply of CO_2. Four kg raw onions of the varieties 'Hygro' and 'Hyduro' were processed and packed in amounts of 100 g. All the samples were stored at –25°C until analysis.

One sample of 100 g frozen onion was treated in a Waring blender with 100 g of water at 50°C and then kept at 20°C for 30 min untill heating to 90°C in a microwave oven. Another sample was treated with 100 g of water at 50°C and immediately heated to 90°C in the microwave oven. After dilution of 100 g to 250 g and filtration, 1 ml was freeze dried and the content of pyruvic acid was determined by spectrophotometry as 2,4-dinitrophenylhydrazine derivative as described by *Schwimmer* and *Weston* (21). 10 ml of the filtrate were freeze dried and the pyruvic acid content was measured by gas chromatography using malonic acid as internal standard. A Hewlett Packard gas chromatograph (HP 5840) with automatic sampler (HP 7671A) equipped with a stainless steel column (i.d. 1/8 inch) of length 2.5 m and packed with 5 p.c. polyglycolsuccinate on 80/100 mesh diatomite (C-AW-DMCS) was used to analyze for methyl esters. To the freeze dried samples 500 μl malonic acid solution (0.5 g/100 ml), 10 ml methanol, 200 μl concentrated sulfuric acid and 500 μl BF_3-solution were added. After 20 h the methyl esters were extracted by use of 2 ml n-pentane: chloroform (1:3). The column temperature was programmed from 50 to 200°C with 2°C/min for 20 min and then 4°C/min to 200°C and kept for 15 min. Carrier gas flow was 7 ml N_2/min, detector temperature 300°C, injection port temperature 250°C, attenuator 2^7. The sensitivity was 0.1 from start to 25 min and then 1. A linear standard function was found by linear regression on the results from analysis of samples containing 500 μl internal standard solution (0.5 g malonic acid/100 ml water) and 50, 100, 200, 300, 400 or 500 μl of a solution containing 1 g sodium pyruvate in 100 ml of water.

Results

The formation of pyruvic acid was calculated as the difference between the sample with holding time after thawing and the sample heated to 90°C immediately after thawing. The results from determination of pyruvic acid formation in four varieties using both methods of analysis, were in accordance (Table 1).

Pyruvic acid formation in frozen onions stored from 1 week to 3 months decreased during storage (Table 2). Average values for the two methods of analysis are presented. Formation of pyruvic acid was reduced during processing and further during storage of the frozen onions.

The capacity of pyruvic acid formation in frozen onions from 19 varieties stored for 10 months at –25°C were rather different (Table 3).

Table 1. Results from spectrophotometric and gas chromatographic determination of pyruvic acid formation in frozen onions stored for 15 months at –25°C. Three replications.
Resultater fra bestemmelse af pyrodruesyredannelse bestemt ved spektrofotometri og gaskromatografi af dybfrosne løg fremstillet af fire sorter lagret i 15 måneder ved –25°C. Tre gentagelser.

Variety *Sort*	Pyruvic acid mg/100 g *Pyrodruesyre mg/100 g*	
	SPEC.	GLC
'Hygro'	40	34
'Hyduro'	14	12
'Hyblenda'	33	29
'Lucrato'	22	21
LSD	19	11

Table 2. Average formation of pyruvic acid as determined by spectrophotometry and gas chromatography of frozen onion of the variety 'Hygro' stored at -25°C. Six replications.
Gennemsnit af pyrodruesyreanalyse ved spektrofotometri og gaskromatografi af frosne løg fremstillet af sorten 'Hygro' og lagret ved -25°C. Seks gentagelser.

Storage time Months *Lagringstid Måneder*	Pyruvic acid *Pyrodruesyre* mg/100 g *mg/100 g*	Relative *Relativt*
0 (raw)	78	100
0.25	55	71
2	45	58
3	35	45
LSD	12	

Table 3. Pyruvic acid formation in frozen onions of 19 varieties after storage for 10 months at -25°C.
Pyrodruesyredannelse i frosne løg af 19 sorter lagret i 10 måneder ved -25°C.

Variety *Sort*	Pyruvic acid *Pyrodruesyre* mg/100 g *mg/100 g*
'Balstora'	32
'Claudia'	44
'Diskos'	18
'Golden Bear F1'	25
'Hyblenda'	36
'Hyduro'	41
'Hygro'	56
'Hyper'	47
'Hyton'	29
'Karbo'	39
'Lucrato'	42
'Robot'	20
'Rocardo'	40
'SG 95 F1'	47
'Stuart'	50
'Sturon'	23
'Tarzan'	11
'Turbo'	25
'Zirius'	23
LSD	7

Discussion

Onion contains at least three sulphoxides of which S-1-propyl-L-cysteine sulphoxide is present in the highest concentration (9, 14, 26).

The aroma or flavour precursors are split into thiopropanal (the lacrymator), pyruvic acid and ammonia by a very fast alliinase catalyzed step. This is followed by several chemical reactions with formation of alcohols, aldehydes, mercaptans, sulphides (mono-, di-, tri-), thiols, thiophenes and furanones (2, 3, 5, 8, 12, 13, 18, 20, 21, 23, 25). The very volatile lacrymator, mono-, di-, and trisulphides are the most important contributors to onion aroma (3, 4, 5, 6, 8, 17, 18, 27).

Results from determination of pyruvic by gas chromatography was in accordance with the results from determination by the spectrophotometric method (Table 1).

Pyruvic acid determination by the spectrophotometric method of *Schwimmer* and *Weston* (21) has been used to determine the effect of processing on aroma development and pungency of pickled, canned, blanched, frozen and fried onion products (7, 10). The ability to pyruvic acid release was almost lost after canning, pickling and frying. Frozen onion may have an ability to release pyruvic acid (Table 2), (15), but the ability of pyruvic acid formation and the characteristic onion flavour may be very low or completely lost (1, 7, 10, 15, 20). Even freezing for a period of one hour may be very damaging to flavour development. The loss was 29 p.c. one week after freezing increasing to a loss of 55 p.c. three months after freezing (Table 2). The loss could be a result of changes during freezing. The reasons for decreasing aroma formation ability may be complete or partial enzyme destruction, non-enzymic destruction of precursors or partial enzymic hydrolysis of precursors with loss of volatile reaction products (10).

Frozen onions are applied by processing of different meat products. By comparison to raw onions higher amounts of frozen onions are required to obtain equal flavour effect.

As found by (10, 15, 21, 24) onion varieties had different pungency (Table 3). Onion species can be characterised by results from gas chromatography because they have different radicals in the sulphoxides (2, 9).

Onion pungency also depends on the availability of sulphur to the growing plants (10). During bulb formation of growing onions the capability to develop onion flavour increases until the onions are »mature« (15). The increase in the onions can continue during storage (11).

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