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White precipitate in red table beets

Hvidt bundfald i syltede rødbeder

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Summary

White precipitate often occurs in red table beets containing a considerable percentage of calcium oxalate.

The theoretical solubility of calcium oxalate in solutions containing acetic acid, NaCl and sucrose was experimentally confirmed. Calcium oxalate solubility increases by lowering the pH value and by addition of NaCl, because of the salt effect. Complete removal of the precipitate by varying the pH value or addition of salt may be disastrous to the flavour of the red beet products.

Further experiments are necessary to evaluate the effect of varied pH-value by addition of H_3PO_4 and to evaluate the flavour change when NaCl is added.

Selection for a lower content of oxalic acid is suggested because of a considerable variation in the content of oxalic acid in the beet roots.

Key words: *Beta vulgaris,* calcium oxalate, red beets.

Resumé

Det hvide bundfald, som ofte findes i syltede rødbeder, indeholder meget calciumoxalat.

Der blev udført forsøg med opløseligheden af calciumoxalat i opløsninger, som indeholdt eddikesyre, NaCl og sucrose. Opløseligheden øges med faldende pH og med stigende saltindhold. Yderligere forsøg bør gennemføres for at afgøre, om den nødvendige ændring af pH og tilførsel af salt kan accepteres.

Forædling ved selektion for lavere oxalsyreindhold kan muligvis gennemføres med et godt resultat. Der blev konstateret stor variation i de enkelte rødbeders indhold af oxalsyre.

Nøgleord: *Beta vulgaris,* oxalsyre, rødbeder.

Introduction

In Danish products of red table beets a white precipitate often appears at the bottom of the glasses. The white precipitate blemishes the product and consumer complaints are received because of this defect. By microscopic analysis the precipitate was detected to consist of crystals that were soluble in sulphuric acid.

Red beets contain at least 50 mg of free oxalic acid (1, 2, 5) and enough calcium (3, 6) to precipitate oxalic acid completely. This leads to the hypothesis expressing that white precipitate consists of calcium oxalate.

The aim of this project was to confirm the above mentioned hypothesis and to give proposals for a remedy for the defect of this product.

Materials and methods

Ten glasses (580 cm^3) of red table beets of eighteen different products were analyzed for the content of oxalic acid in the precipitate.

All the slices were removed carefully and most of the brine was taken away. The white pricipitate from all the glasses was suspended in distilled water. After centrifugation the supernatants were removed and the precipitates were vaccuum-dried (20 mm Hg, 30°C, 18 h). The acids (free or as salts) in the dry precipitate were esterified by addition of 10 microliter sulphuric acid, 1 ml BF_3MEOH and 1 ml benzoic acid solution (20 mg/20 ml MEOH) as internal standard. After 18 h the solution was transferred to a separation funnel with 2 ml MEOH. Fifteen ml distilled water, 1 g NaCl and 2 ml pentane-chloroform (1:3) were added for extraction of the esters to the pentane-chloroform phase which was used for a GLC-analysis as described in Table 1. A standard function was prepared using solutions with 10–50 mg oxalic acid and benzoic acid as internal standard.

The cooking and packing of red beets were carried out as described earlier (4).

The solubility product of calcium oxalate ($CaOxH_2O$) and the dissociation constants (25°C) of oxalic acid (OxH_2) were found in Handbook of Chemistry and Physics (7). The equilibrium constants (j = activity constant) may be represented by:

$$K_0 = (Ca^{++})(Ox^{--})j^2 = 2.57\cdot10^{-9} \quad 1)$$
$$K_1 = (OxH)(H^+)/(OxH_2) = 5.9\cdot10^{-2}) \quad 2)$$
$$K_2 = (Ox^{-})(H^+)/(OxH) = 6.4\cdot10^{-5}) \quad 3)$$

Soluted Ca^{++} may be expressed by:

$$(Ca^{++}) = (Ox^{--}) + (OxH^{-}) + (OxH_2) \quad 4)$$

Equation (1) was solved by use of equatin (2,3,4):

$$(Ox^{-}) = \frac{K_O}{j(1+(H^+)/K_2 + (H^+)(H^+)/K_1K_2)} \quad 5)$$

Table 1. Gas chromatographic equipment and analyses parameters.
Gaskromatografisk udstyr og analyseparametre.

Gas chromatograph	PYE UNICAM 64
Integrater	Hewlett Packard 3370 B
Recorder	Philips PM 8100
Column	Stainless steel 5 m, 1/8 inch i.d.
Column packing	80/100 mesh diatomite CT, 10 p.c. CW 20M
Injection temperature	250°C
Column temperature	50–150°C, 6°C/min
Carrier gas flow	40 ml N_2/min
Detector	FID
Detector temperature	350°C
Air flow	300 ml/min
Hydrogen flow	30 ml/min
Slope	0.1 mV/min
Sample size	10 μl

Using the above equations, the theoretical solubilities of OxH_2, $Ca(OxH)_2$, CaOx and the total amount of dissolved $CaOxH_2O$ were calculated.

The solubility of calcium oxalate was determined using a fully factorial experiment with different concentrations of sucrose, NaCl and acetic acid (Table 2). The dissolved amount of calcium was determined by atomic absorption spectrophotometry.

By use of multiple linear regression the soluble $CaOxH_2O$ (Z) was expressed as a function of pH(X), %NaCl(y) at each level of sugar:

$$Z = b_0 + b_1x + b_2y + b_3xy + b_4x^2 + b_5y^2 + b_6x^3 + b_7y^3 \quad 6)$$

Table 2. Levels of sucrose, NaCl and acetic acid in the factorial experimental design for determination of the solubility of calciumoxalate.
Koncentrationer af sucrose, NaCl og eddikesyre i den faktorielle forsøgsplan, der blev anvendt ved bestemmelse af opløseligheden af calciumoxalat.

	W/W p.c. *Vægtprocent*
Sucrose *Sukrose*	0; 5; 10; 15; 20;
NaCl *NaCl*	0.25; 0.5; 1.0; 2.0;
	Mole/l *Mol/l*
Acetic acid *Eddikesyre*	0.0005; 0.001; 0.005; 0.01; 0.05; 0.1; 0.5

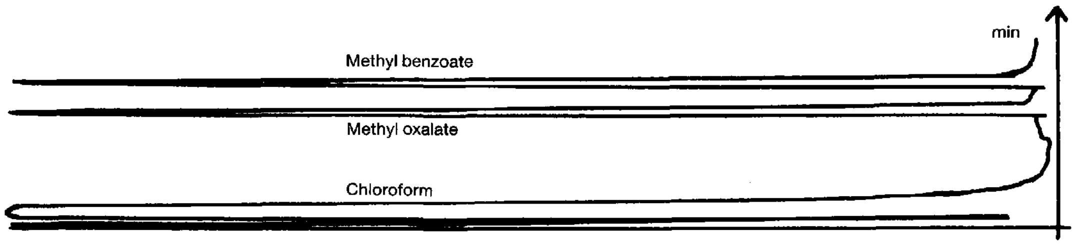

Fig. 1. Gas chromatogram for methyl esters.
Gaskromatogram for methylestere.

Because it could be an advantage to decrease the pH value without addition of acetic acid, an experiment was carried out to determine the necessary amount of H_3PO_4 to obtain a change of the pH value of 0.1 unit. For this experiment red table beets of three brands were used.

Results

The methyl esters separated by gas chromatography (Fig. 1) were identified by mass spectrometry.

On an average, the red table beets contained 44 mg precipitate per 100 g of cooked beets of which 9 mg was $CaOxH_2O$. The amount of precipitate ranged from 11 to 89 mg or 2 to 22 mg per 1000 g of cooked beets. On average the brine contained 15 mg $CaOxH_2O$ per 1000 g with a range of 2 to 39 mg, per 1000 g.

When decreasing the pH value the solubility of $CaOxH_2O$ increases especially because the concentration of Ca $(OxH)_2$ increases (Fig. 2).

The experimental determined solubility of $CaOxH_2O$ was in excellent accordance with the theoretical values (Fig. 3).

There was found a salt effect of NaCl on the solubility of calcium oxalate (Fig 4 and 5). Addition of sugar lowered the solubility of the $CaOxH_2O$ but the effect was small.

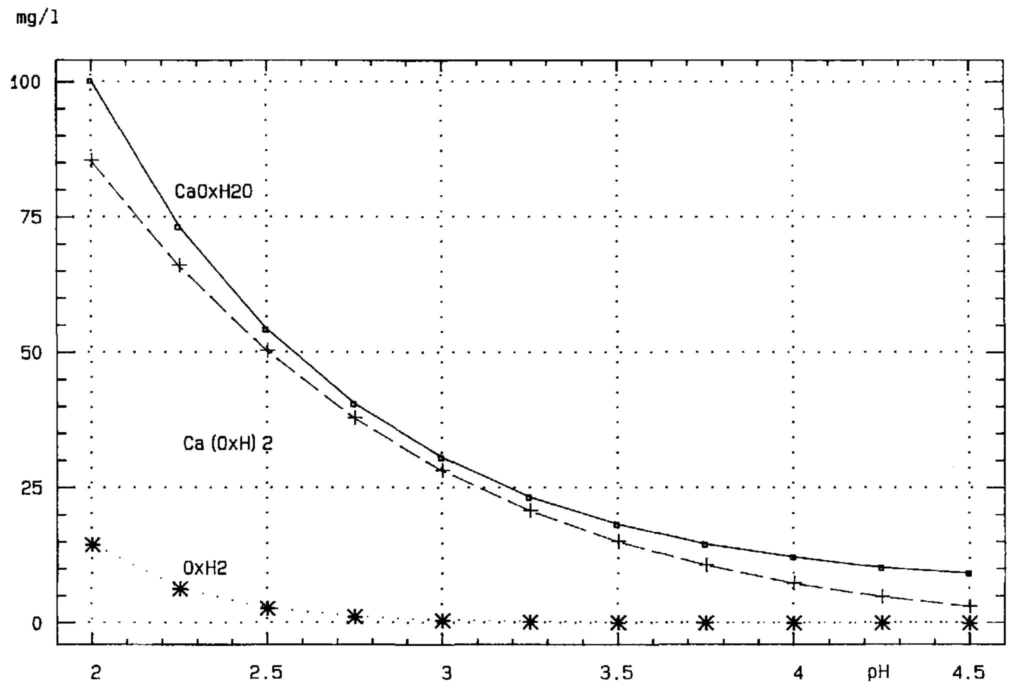

Fig. 2. Theoretical concentration of $CaOxH_2O$, $Ca(OxH)_2$ and OxH_2.
Beregnede koncentrationer af $CaOxH_2O$, $Ca(OxH)_2$ og OxH_2.

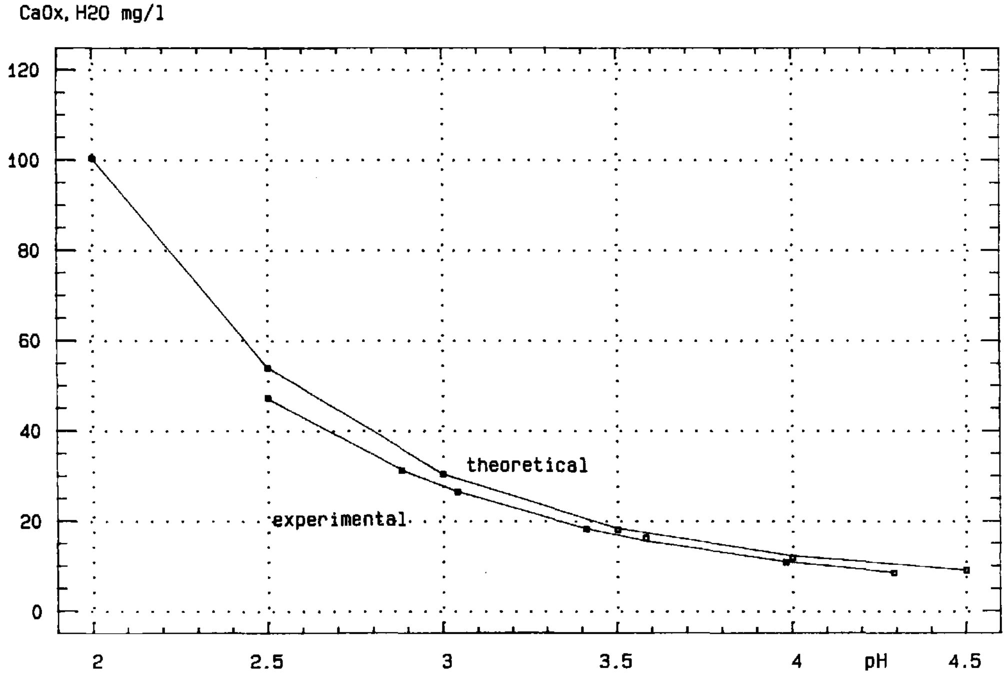

Fig. 3. Calculated and experimental determined solubility of $CaOxH_2O$ in acetic acid solutions without NaCl and sucrose.

Beregnet og eksperimentelt bestemt opløselighed af $CaOxH_2O$ i eddikesyreopløsninger uden NaCl og sucrose.

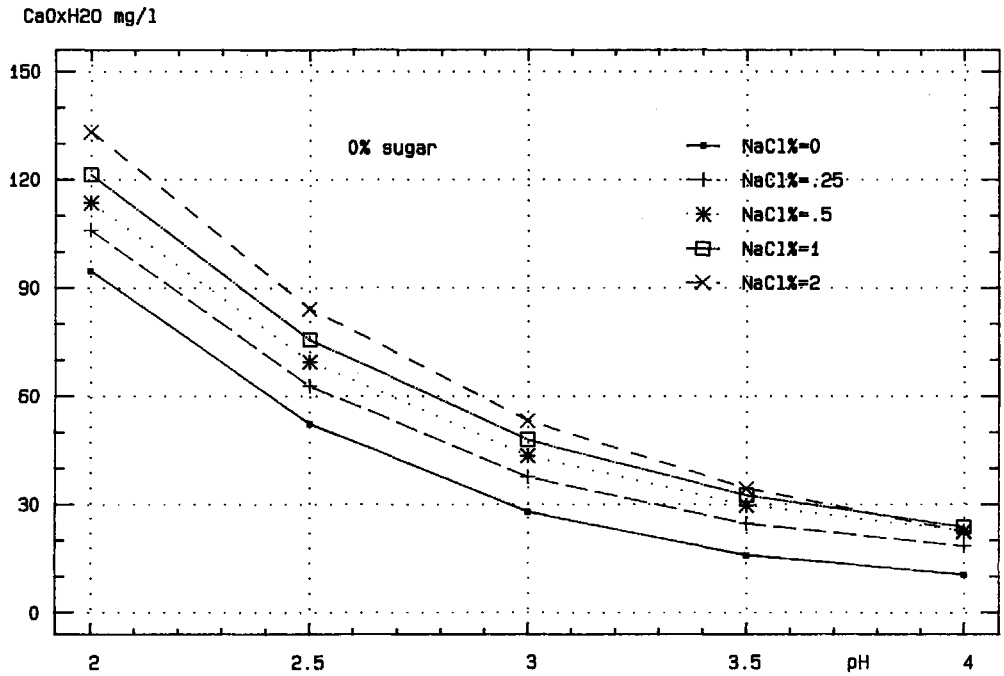

Fig. 4. Results from experimental determination of the solubility of calcium oxalate at different values of pH and concentrations of NaCl (without sugar).

Resultater fra eksperimentel bestemmelse af opløseligheden af calciumoxalat ved forskellige natriumkloridkoncentrationer og pH (uden sukker).

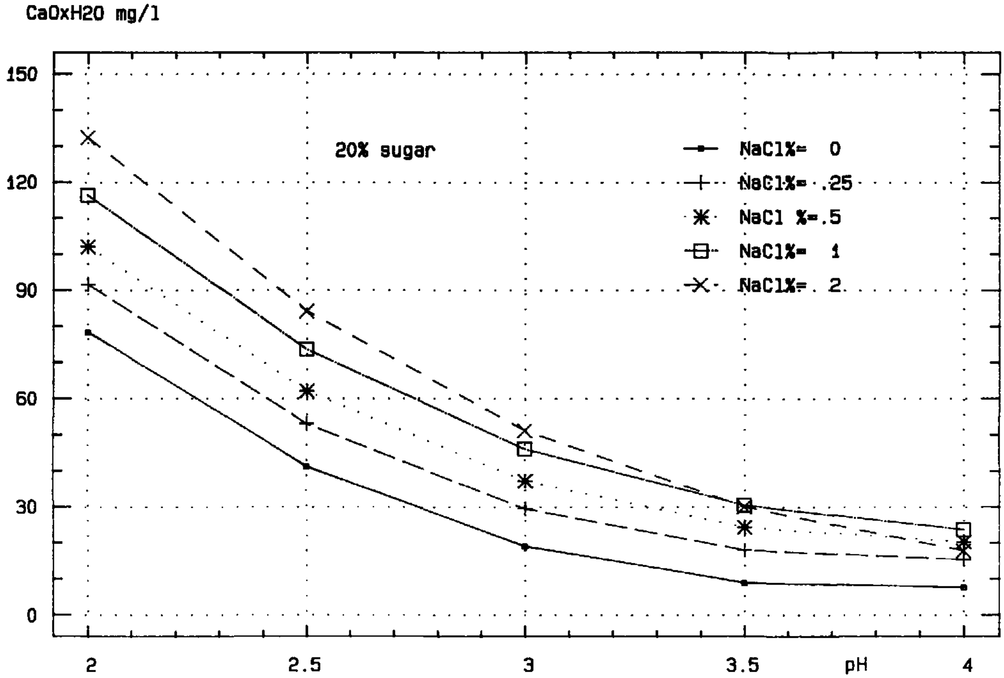

Fig. 5. Results from experimental determination of the solubility of calcium oxalate at different values of pH and concentrations of NaCl (20 p.c. sugar).
Resultater fra eksperimentel bestemmelse af opløseligheden af calciumoxalat ved forskellige natriumkloridkoncentrationer og pH (20 pct. sukker).

To obtain a change of 0.1 pH unit it was necessary to use 0.4 g H_3PO_4 per kg of the product.

The solubility of $CaOxH_2O$ can be calculated from the constants (b_0) and the regression coefficients (b_1) (Table 3).

The content of oxalic acid in 36 red beets ranged from 96 to 246 mg/100 g with an average of 162 mg/100 g and a standard deviation of 31 mg/100.

Discussion and conclusion

The white precipitate in glasses of red table beets contains considerable amounts of calcium oxalate. By addition of NaCl to obtain a salt effect (decreasing activity coefficient) or by lowering the pH value by increasing the acid concentration less precipitate was visually detectable. This was confirmed by theoretical considerations and experimental determination of calcium oxalate solubility.

NaCl is normally not used in the brine for the processing of red table beets. And a low pH value obtained by increasing the concentration of acetic acid can increase the acetic acid flavour too much. Another possibility is to lower the pH by addition of phosphoric acid. At the normal level of 20% sugar and pH 4 the solubility of $CaOxH_2O$ is about 10 mg/l. At a concentration of 20 p.c. sugar and 0.5 p.c. NaCl was the following relationship found (r = 0.984):

$$\log_e (CaOxH_2O) = 6{,}29 - 0{,}89\,(pH) \qquad 7)$$

The solubility is 37 mg/l at pH 3 or enough to dissolve the maximum of the white precipitate found in different brands of red table beets. Further experiments are necessary to evaluate the effect on the flavour of the red table beet products.

The content of oxalic acid in four cylindrical varieties varied from 69 to 92 mg/100 g (4). Because of a considerable variation of oxalic acid concentration in the individual red beets it may be possible to reduce the oxalic acid content by selection within a variety.

Table 3. Results from linearization of the solubility of $CaOxH_2$ as a function of pH at different levels of sugar and NaCl.

Resultater fra lineær regression for opløselighed af $CaOxH_2O$ som funktion af pH ved forskellige concentrationer NaCl og sucrose.

Sucrose p.c. *Sukker pct.*	Salt p.c. *Salt pct.*	Constant (b_0) *Konstant (b_0)*	Slope (b_i) *Hældning (b_i)*	Corr. coeff. *Korr. koeff.*
0	0	6.22	– 0.96	0.999
	0.25	6.16	– 0.82	0.997
	0.5	6.30	– 0.83	0.999
	1.0	6.45	– 0.85	0.991
	2.0	6.43	– 0.82	0.993
5	0	6.23	– 1.01	0.995
	0.25	6.27	– 0.91	0.997
	0.5	6.00	– 0.79	0.992
	1.0	6.05	– 0.76	0.987
	2.0	6.30	– 0.80	0.987
10	0	5.91	– 0.95	0.997
	0.25	5.52	– 0.68	0.984
	0.5	5.68	– 0.69	0.987
	1.0	6.06	– 0.78	0.993
	2.0	6.17	– 0.80	0.989
15	0	5.63	– 0.83	0.991
	0.25	6.18	– 0.85	0.992
	0.5	6.21	– 0.82	0.992
	1.0	6.42	– 0.84	0.982
	2.0	6.54	– 0.85	0.981
20	0	5.42	– 0.81	0.995
	0.25	6.04	– 0.84	0.987
	0.5	6.29	– 0.89	0.984
	1.0	6.81	– 0.98	0.987
	2.0	6.51	– 0.87	0.980

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