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Processing of juice from sour cherry (*Prunus cerasus* L.)

*Saftfremstilling af surkirsebær (*Prunus cerasus *L.)*

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Summary

Several experiments have been carried out to study the effect of unit operations on quality attributes of cherry juice.

Juice processed from the variety 'Stevnsbær' had an excellent flavour.

The soluble solid content of the juice was equal to the concentration in the fruit, but the amount of titratable acid was lower. The yield of anthocyanins is normally fairly high, but treatment with pectolytic enzymes can increase the concentration of anthocyanin in the juice.

The content of benzaldehyde in the juice depends on the extent of kernel crushing, which leads to enzyme catalyzed release of benzaldehyde from the glucoside prunasin. Hydrogen cyanide released by the above mentioned process may occur in a very high concentration if the majority of the cherry kernels are crushed during processing.

The hydrogen cyanide disappears during storage of the juice.

Key words: *Prunus cerasus* L., sour cherries, juice processing, benzaldehyde, anthocyanin, hydrogen cyanide.

Resumé

Der er blevet udført forsøg med henblik på bestemmelse af, hvorledes forarbejdningen af kirsebær til saft påvirker saftens kvalitetsegenskaber.

Sorten 'Stevnsbær', der anbefales til erhvervsplantager, giver saft med en udmærket smag.

Indholdet af opløseligt tørstof i saft er det samme som i råvaren. Derimod er indholdet af titrerbar syre lavere i saften. Nedbrydningen af anthocyaniner ved saftfremstilling er næsten ubetydelig. Ved enzymering med pektolytiske enzymer kan opnås et lidt større farvestofudbytte.

Dannelsen af benzaldehyd er proportional med sønderdelingsgraden for kirsebærstenene. Dette skyldes, at dannelsen af benzaldehyd sker ved enzymatisk katalyseret omsætning af glucosidet prunasin, som især findes i kirsebærkernerne.

Samtidig med dannelsen af benzaldehyd frigøres cyanbrinte, som på grund af giftigheden er et uønsket stof. Under lagring reagerer cyanbrinte med glucose, og der dannes uskadelige ammoniumsalte. Denne proces fremmes ved tilsætning af sukker.

Nøgleord: *Prunus cerasus* L., surkirsebær, saftfremstilling, benzaldehyd, anthocyaniner, cyanbrinte.

Introduction

Sour cherries are procesed to sweetened or unsweetened juice.

The effect of unit operations has been described earlier (1,2,3,4,14) but some of the most important processing steps have not until now been taken into consideration.

The objective of this study is to determine the effect of important unit operations on the quality attributes of cherry juice.

Materials and methods

Samples of sour cherry varieties were picked as described by *Kaack* (9).

The sensory evaluation was carried out by seven trained panelists. Sweetened juices were diluted with water (1:3) and evaluated at six tasting sessions.

Samples of fresh fruit, jam and stewed fruit were prepared for analysis by blending with water (dilution factor = f) in a Waring blender.

Soluble solids were determined by use of a Bausch & Lomb refractometer for analyses of filtrates of the blended samples. Titratable acid was determined by use of a Mettler DL 4 automatic titrator for titration of blended material (5–10 g) to pH 8.1 with 0.1 N NaOH. The content of titratable acid was expressed as citric acid (g/100 g). For each sample three replications of determination of soluble solids and titratable acid were carried out.

Samples for determination of the content of anthocyanin were prepared by dilution of m gram (4–10) blended material or juice with 50 ml distilled water. After 30 minutes q ml were diluted with 10 ml $MeOH/H_2SO_4$ and the absorbance (A) at 530 mm was measured using a spectrophotometer (Shimadzu MPS 2000). The content of anthocyanin (a) was calculated as cyanidin-3-glucoside which has a molecular weight of 445.2 and an extinction coefficient of 29600 (24).

$$a = \frac{445.2\,A\,(t+10)\,50\,f\,100}{29600\,mq}\ \text{mg/100} \qquad 1)$$

The content of cyanide was determined by use of a micro-Kjeldahl distillation apparatus. 25 g juice or blended material were weighed into the distillation flask. 1 ml of concentrated H_2SO_4 and 15 ml of distilled water were added. The distillate was sampled in a 50 ml flask with 1 ml 1N NaOH and 10 ml distilled water. 10 ml of the 50 ml distillate were added to 10 ml of a buffer solution (Radiometer S 3566) and the concentration of cyanide was measured using a specific electrode (Radiometer F 1042) connected to a pH-meter (Radiometer 43) equipped with a reference electrode (Radiometer K 401).

Values from similar measurements of standard solutions with 10^{-5} to 10^{-2} mol/l of cyanide were applied for calculation of a standard function expressing the relation between minus log to the cyanide concentration (pC) as a function of millivolt (MV).

$$pC = 5.7 + 0.01515MV \qquad r = 1.000 \qquad 2)$$

The content of cyanide (CN) was calculated by multiplication with the molecular weight (M = 26) and twice the dilution factor (f) used by blending or dilution of juice before distillation.

$$CN = 10\,(EXP\text{-}pC)\,52\,f \qquad 3)$$

Aroma distillates were prepared from juice or blended samples. 100 g (m) were diluted with m g distilled water and distillate (t gram) were va-

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

HP 7675A head space sampler:	
Sample size	10 ml
Purge gas	37.5 ml N_2/min
Prepurge time	5 minutes
Purge time	30 –
Precolumn	Tenax GC
Precolumn temperature	20°C
Eluting temperature	180°C
Eluting time	5 min
Cleaning temperature	250°C
HP 5840A gas chromatograph:	
Column	5 m, stainless steel, i.d. 1/8 inch
Carrier material	diatomite, C-AW, 80–100 mesh
Stationary phase	10% UCON-LB-1715
Carrier gas	15 ml N_2/min
Column temperature	50–200°C, 4°C/min
Detector temperature	250°C
Paper velocity	3 mm/min
Attenuator	2 exp (10)
Slope sensitivity	3 microvolt/sec
Internal standard	cyclohexanone

cuum evaporated at 40°C in an evaporator with the temperature kept at 12°C with tap water and the distillation flask in a water bath at 70°C.

The content of benzaldehyde in the aroma distillate was determined by head space analysis using a Hewlett Packard gas chromatograph equipped with a purge and trap sampler (Table 1).

Immediately before analysis 0.5 ml solution of cyclohexanone (300 microgram/ml) were added to 10 ml distillate. For preparation of a standard function 0.5 ml solution of cyclohexanone were added to solutions containing 30, 40, 50, 100, 200, 300, 400, and 500 microgram/10 ml of benzaldehyde.

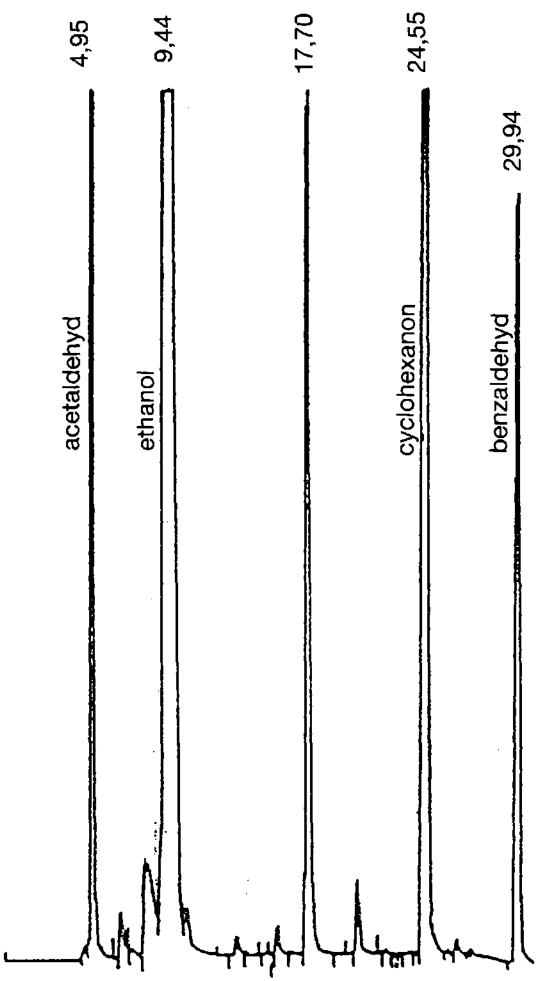

Fig. 1. A gas chromatogram from analysis of juice.
Et gaskromatogram fra analyse af saft.

By use of the amounts of benzaldehyde (c) in 10 ml of standard solutions and the area ratios (F) a standard function was found.

$$c = 73.5\,F \qquad r = 0.999 \qquad 4)$$

The content of benzaldehyde (b) in the samples was calculated using this function and the values of m and t.

$$b = (1000\,ct)/(10\,m) = 100\,ct/m \qquad 5)$$

For determination of the seed content the fruits were blended with water in a Waring blender at low knife speed. The fruit flesh was removed by washing in a sieve and the seeds were dried in the laboratory at 20°C before weighing. The kernels were picked out after gentle crushing of the seeds.

The unit operations of the industrial juice processing are described in Table 2. Throughout one day samples of 5 kg raw fruit, crushed fruit and juice were taken 6 times with 2 hours between each sampling. After blending the samples 250 g were added to glasses with 750 g water at 95°C.

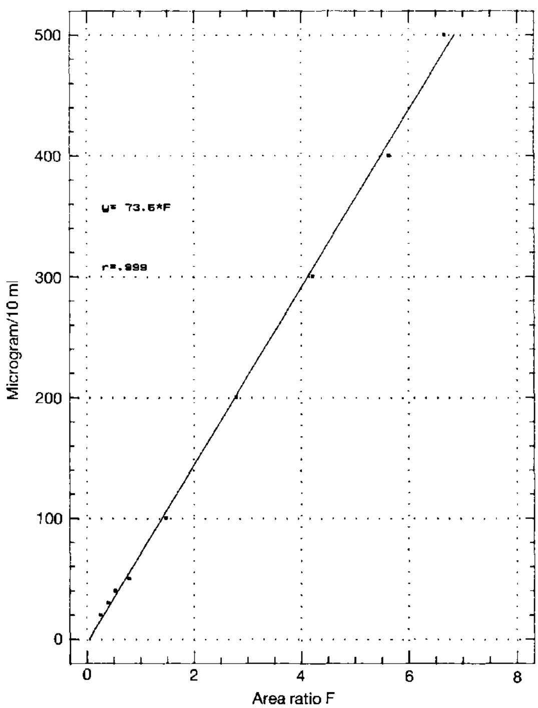

Fig. 2. Standard curve for benzaldehyde analyses.
Standardkurve til benzaldehydanalyser.

Table 2. Unit operations for industrial juice processing.
Enhedsoperationer ved industriel saftfremstilling.

Weighing in batches of 500 kg
Crushing of the fruits
Heating to 90°C for 20 seconds
Cooling to 50°C
Enzyme treatment using pektolase (2 hr, 45°C)
Pressing (200 atu)
Centrifugation
Pasteurization (90°C, 25 sec)
Storage (5°C)

Sodium benzoate and potassium sorbate were added and the glasses were cooled in tap water (12°C).

Processing of juice in the laboratory was carried out by use of a tincture press. Frozen cherries (200–350 g) were thawed overnight in the laboratory and then pressed by gradual increasing the pressure to 100 kg/cm^2 within 30 minutes. The juice yield was determined from the weight of juices and fruits.

To increase the content of benzaldehyde in the juice to a certain level a corresponding amount of seeds were crushed by blending with a Waring blender.

After filtering the juices were sweetened by addition of sugar. The juices were bottled and pasteurized in a water bath at 85°C (15 min). The bottles were cooled in tap water (12°C) and stored at 12°C until analysis.

Results

Sweetened juice processed from four varieties was diluted with water (1:3) and evaluated by seven panelists at six tasting sessions. (Table 3). The juice processed from 'Stevnsbær' and 'Skyggemorel' had the most and least cherry flavour respectively. Juices processed from 'Crisana 2' and 'Fanal' had intermediate intensity of cherry flavour.

Fig. 3 shows the maximum amount of benzaldehyde and cyanide which can be released from the fruit flesh of 'Stevnsbær' harvested over a long period. The ratio between benzaldehyde and cyanide was calculated to be 4.05, which corresponds almost to the theoretical ratio.

Results from analysis of samples from a factory processing juice from 'Stevnsbær' are presented in Table 4. In one day six samples were taken out.

Table 3. Average points for cherry flavour of juice processed from four cherry varieties. 0 = no cherry flavour, 10 = very strong cherry flavour.
Gennemsnitspoint for kirsebærsmag hos saft fremstillet af fire kirsebærsorter. 0 = ingen kirsebærsmag, 10 = meget stærk kirsebærsmag.

Variety *Sort*	Cherry flavour *Kirsebærsmag* points
'Stevnsbær'	6.7
'Crisana 2'	6.1
'Skyggemorel'	4.7
'Fanal'	5.4
LSD	0.6

The content of soluble solids in the juice is equal to the concentration in the juices. A significant lower content of titratable acid, anthocyanin, benzaldehyde and cyanide were found in the juice compared to the concentrations in the fruits.

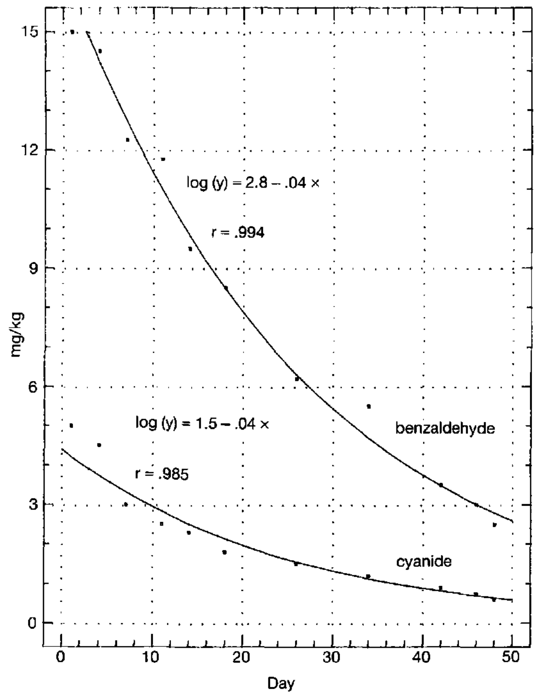

Fig. 3. Benzaldehyde and cyanide released from the flesh of ripening 'Stevnsbær'. Experiment 3. Day 1 27 July.
Benzaldehyd og cyanid dannet i frugtkødet af modnede 'Stevnsbær'. Forsøg 3. Dag 1 27. juli.

Table 4. Results from analyses of samples from a factory processing juice from 'Stevnsbær'.
Resultater fra analyse af prøver fra en fabrik, der fremstillede saft af 'Stevnsbær'.

Product *Produkt*	Soluble solids *Opl. tørstof* g/100 g	Acidity *Titr. syre* g/100 g	Anthocyanin *Anthocyanin* mg/100 g	Benzaldehyde *Benzaldehyd* mg/kg	Cyanide *Cyanid* mg/kg
Raw fruit *Råvare*	21	1.9	204	93	34
Juice *Saft*	21	1.6	181	17	6
LSD	1	0.1	20	5	1

Average values from eight determinations of the content of whole seeds in raw fruits and mash were 12.1 and 2.9 w/w% respectively.

The press cake contained glucosides corresponding to 22 mg/l of benzaldehyde and 4 mg/l of cyanide (CN) which were obtainable by complete release to the juice.

In the laboratory juice was processed from 'Fanal' and 'Stevnsbær'. Average values of soluble solids, titratable acid and anthocyanin in raw fruit and juice are shown in Table 5. The average juice yield was 85 w/w%.

Experimental results from processing of juice from 'Stevnsbær' with and without crushing of the kernels are shown in Table 6. By seed crushing very high levels of benzaldehyde and cyanide were obtained. The average juice yield from four determinations was 81 w/w%.

'Stevnsbær' contained 31 g kernels and the release of benzaldehyde was on average from five determinations 3622 microgram/g with a standard deviation of 250 microgram/g.

Fig. 4 shows the release of benzaldehyde to fruit juice heated to the treatment temperature before addition of the kernels and blending.

The enzyme catalyzed release of benzaldehyde and cyanide may be avoided by heating of the mash to 80°C for a few seconds.

Results from determination of benzaldehyde in the juice processed after maintaining the mash at 40 or 60°C for 2 hours are shown in Fig. 5.

From these results may be concluded that enzyme catalyzed formation of benzaldehyde and cyanide may take place during enzymation. This proces can be avoided by heating of the mash before enzymation.

Table 7 shows the results from determination of benzaldehyde in juice heated to 85°C for up to 80 minutes. Heating had no significant effect.

The results from determination of the content of cyanide and benzaldehyde in juice with different levels of seed crushing, sugar addition and storage are shown in Fig. 6.

The content of benzaldehyde and cyanide increases by increasing stone decomposition. During storage of the juice decreases the content of benzaldehyde and especially the content of cyanide. The decrease of cyanide content increased by addition of sugar.

Results from determination of the loss of benz-

Table 5. Average values from juice processing of 'Fanal' and 'Stevnsbær' in the laboratory.
Gennemsnitsresultater fra saftfremstilling i laboratoriet.

Material *Materiale*	Soluble solids *Opl. tørstof* *g/100 g*	Acidity *Titr. syre* *g/100 g*	Anthocyanin *Anthocyanin* *mg/100 g*
Raw fruit *Råvare*	17.3	2.4	176
Juice *Saft*	17.5	2.3	176
LSD	1	0.1	20

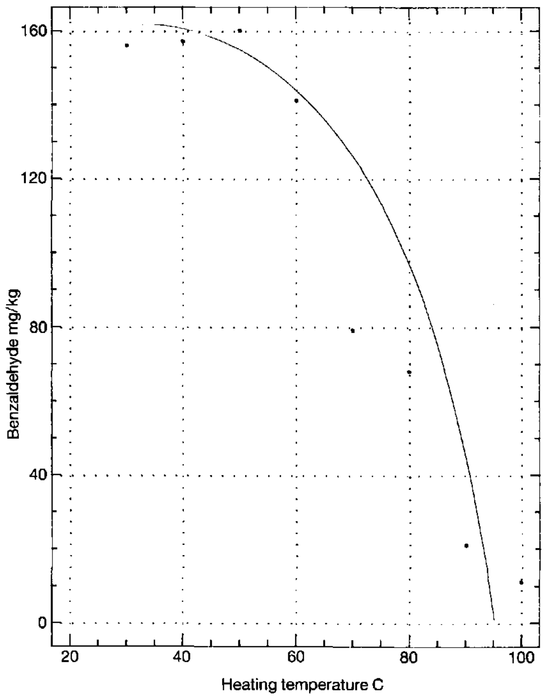

Fig. 4. Content of benzaldehyde in juice heated to the treatment temperature before addition and blending of the seeds (0.7 g seeds, 75 g juice, 750 g water).
Indhold af benzaldehyd i fortyndede prøver af saft opvarmet til behandlingstemperaturen før tilsætning og formaling af frøene (0,7 g frø, 75 g saft, 750 g vand).

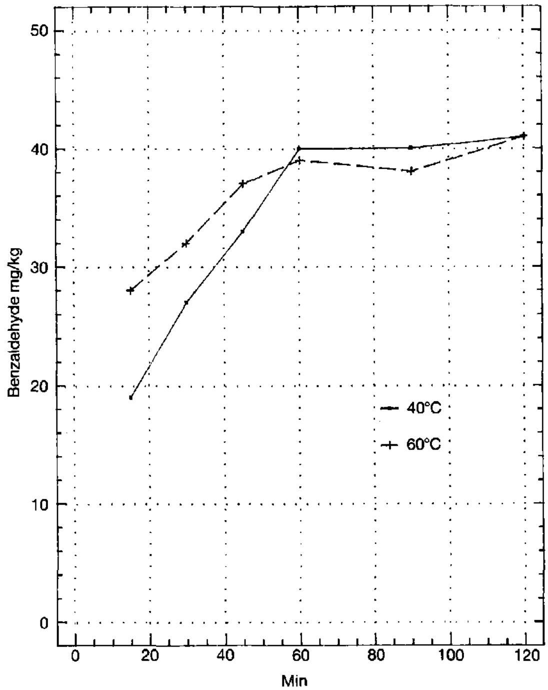

Fig. 5. Content of benzaldehyde in juice processed from 'Stevnsbær' with different holding times for the mash at 40 and 60°C.
Indhold af benzaldehyd i saft fremstillet med varierende holdetider for maischen ved 40 og 60°C.

aldehyde by evaporation from the juice is shown in Fig. 7. After evaporation of 5, 10, 20 and 40% liquid 41, 60, 77 and 91% of the benzaldehyde were removed from the juice.

By evaporation of 1% liquid (four determinations) from the juice 42% of the cyanide was lost.

Discussion

Cherry juice processed from the variety 'Stevnsbær' had the best flavour (Table 3). Because of high yield and good flavour of the juice the variety 'Stevnsbær' is recommended for commercial growing (22). The most valuable is

Table 6. Content of soluble solids, titratable acid, anthocyanin, benzaldehyde and cyanide in juice processed from 'Stevnsbær' without and with complete crushing of the kernels.
Indhold af opløseligt tørstof, titrerbar syre, anthocyanin, benzaldehyd og cyanid i saft fremstillet af 'Stevnsbær' uden og med sønderdeling af kernerne.

Kernels *Kerner*	Soluble solids *Opl. tørstof* g/100 g	Titratable acid *Titrerbar syre* g/100 g	Anthocyanin *Anthocyanin* mg/100 g	Benzaldehyde *Benzaldehyd* mg/kg	Cyanide *Cyanid* mg/kg
–	20.2	1.75	249	6	3
+	20.3	1.78	226	157	46
LSD	2.6	0,16	22	20	3

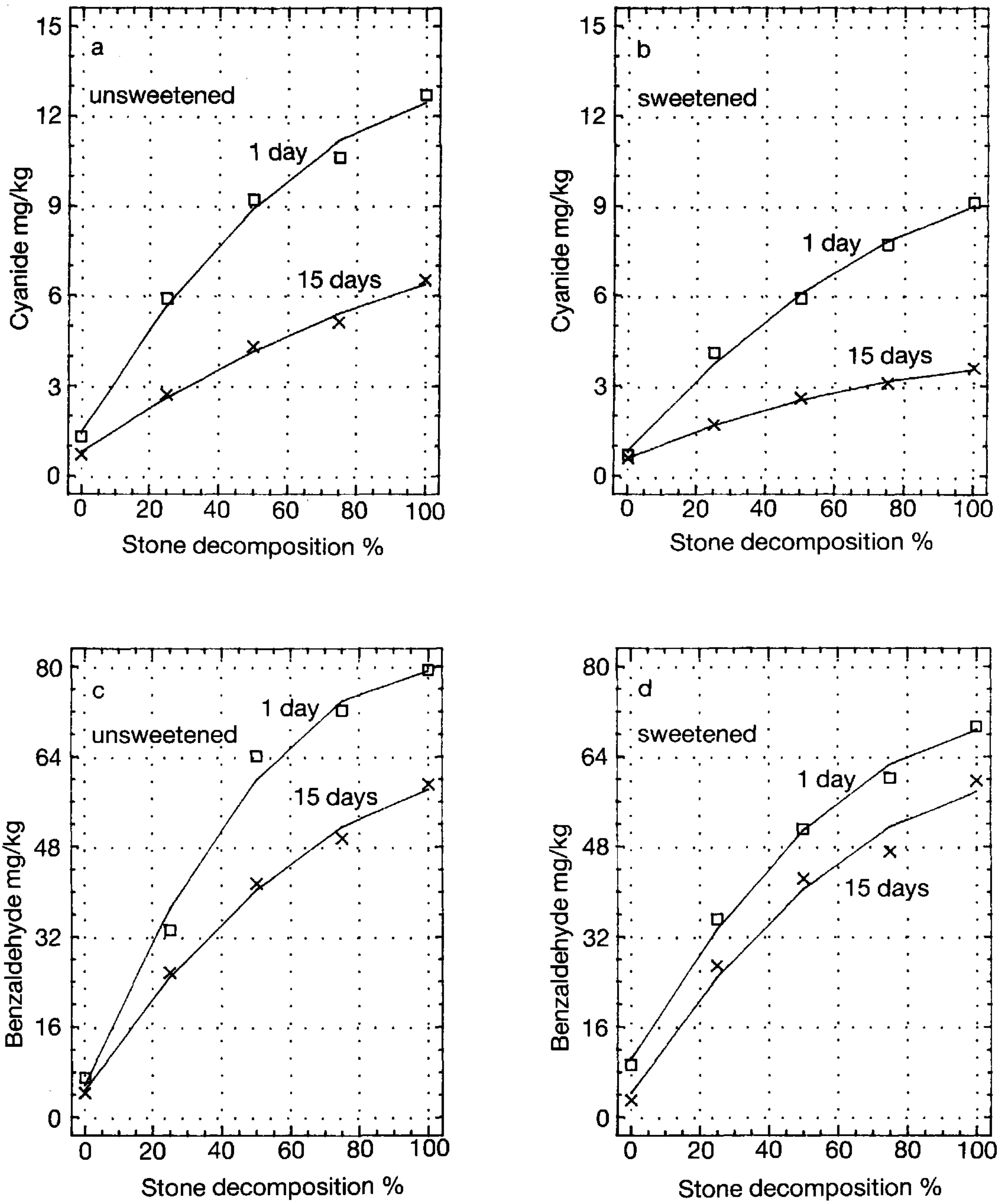

Fig. 6. Content of cyanide and benzaldehyde in unsweetened and sweetened juice processed after different levels of stone crushing and stored at 12°C.

Indhold af cyanid og benzaldehyd i usødet og sødet saft fremstillet ved forskellige niveauer af stensønderdeling og lagret ved 12°C.

Table 7. Content of benzaldehyde in sweeted (40% sucrose) and unsweetened juice of 'Stevnsbær' heated at 85°C. LSD = 4.
Indhold af benzaldehyde i usødet og sødet (40 pct. sucrose) saft af 'Stevnsbær' efter opvarmning ved 85°C. LSD = 4.

Time *Tid* Min	Benzaldehyde mg/kg *Benzaldehyd mg/kg*	
	Unsweeted juice *Usødet saft*	Sweetened juice *Sødet saft*
0	91	87
10	88	85
40	93	90
80	92	91
Average	91	88

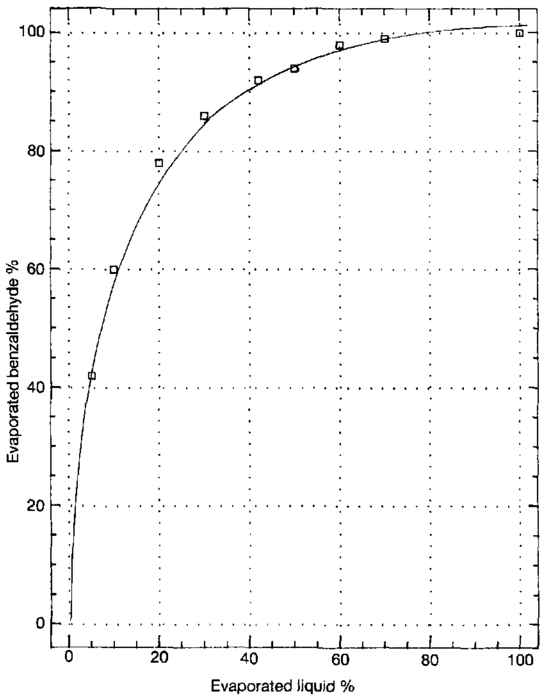

Fig. 7. Benzaldehyde and liquid evaporated from cherry juice.
Benzaldehyd og væske fordampet fra kirsebærsaft.

'Stevnsbær' clone Viki (21). The reason for the high flavour scores is unknown. Aroma substances, sugars, acids, phenolics and other organic compounds in certain optimum mixtures are of importance for the cherry flavour (1,4,5,9, 13,17,18,20). The most abundant aroma substance in cherry juice is benzaldehyde (Fig. 1). A very high concentration of this substance can be obtained by complete stone decomposition. This may give a very strong note of benzaldehyde, which are disliked by the consumers.

Characteristical changes can take place during industrial processing (Table 4). The content of soluble solids in juice and raw fruits is equal, but the concentration of titratable acid and anthocyanins can be lower in the juice. One reason for higher content of titratable acid in raw fruits is hydrolysis of pectins during titration.

Enzyme treatment before pressing increases the content of anthocyanins in the juice but losses may occur because of polyphenol oxidase activity (1,2,7,11,12,15,19,23). Better juice is obtained by heating to 80°C before and after enzyme treatment (2,3,7).

During industrial processing a certain percentage of seeds is crushed. The aim is to obtain enzyme release of the important aroma substance, benzaldehyde from the glucoside prunasin occurring in cherry kernels (6). As mentioned above this may be disliked by the consumers.

Release of benzaldehyde is catalysed by the enzymes amygdalase (3.2.1.21) and hydroxynitril lyase (4.1.2.11).

$$\text{prunasin} \xrightarrow{\text{amygdalase}} \text{glucose} + \text{benzaldehyde cyanohydrin} \qquad 6)$$

$$\text{benzaldehyde cyanohydrin} \xrightarrow{\text{hydroxynitril lyase}} \text{cyanbrinte} + \text{benzaldehyde} \qquad 7)$$

Benzaldehyde is released during the holding time for enzyme treatment (Fig. 5), but the enzyme catalysed process cease by heating to 80°C (Fig. 4).

Heating of juice to the pasteurization temperature had no effect on the concentration of benzaldehyde (Table 7). From this it may be concluded that normal pasteurization has no effect on the benzaldehyde content.

As shown in Tables 4 and 6 the release of benzaldehyde is followed by formation of hydrogen cyanide (8,16). *Stadelman* (16) found 2 mg/l of hydrogen cyanide in juice processed from sour cherries.

According to the above equations and as described earlier (Fig. 3) the theoretical proportion between benzaldehyde and hydrogen cyanide is equal to 4.05. By evaluation of the figures of Table 4 and 6 it is clear that a lower amount of benzaldehyde was released.

The reason can be that the juice contained small particles of kernels containing prunasin.

By addition of sugar to cherry products *Daneschwar* (6) found a decrease in the content of hydrogen cyanide. A similar conclusion may be drawn from the results shown in Fig. 6.

Hydrogen cyanide reacts with glucose to glucose cyanohydrin and further to ammoniumgluconate (10). Because of this the cyanide concentration decrease during storage as shown in Fig. 6.

By evaporation of water during processing benzaldehyde and other aroma substances are lost (Fig. 7). Compared to aroma substances of apples the evaporation rate of benzaldehyde is rather low (9). A loss of 95% of apple aroma substances is obtained by evaporation of 12% water.

According to the results (Fig. 7) 95% loss of benzaldehyde require evaporation of 55% of the water.

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