THE EFFECT OF FREEZING-DRYING, CLOUDINESS AND CONCENTRATION ON THE KEEPING QUALITY OF VARIOUS BLACK-CURRANT PRODUCTS

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Received August 10, 1964

In studying the various possibilities of storing the surplus of berry crops so that the yearly variations may be levelled off, it is worthwhile to consider whether new methods could be devised capable of keeping the quality of the material at as high a level as possible. Freezing, already applied to a considerable extent, appears to be a good method, although it presupposes the treatment and storage of the material at low temperature which is an expensive matter. Another method which may be adopted, and is a rather new one, is that of freezing-drying; in comparison with freezing, this has the advantage that the storage of the product may be effected at ordinary room temperature, provided that the packing is sufficiently waterproof. Although the initial cost is high, this method might still be of advantage; storage costs are low because no refrigeration is necessary, and the low weight reduces transport costs. However, it must be ensured that the quality of the freeze-dried products is well preserved. In literature (cf. 9, 10, 18) it is said that in general freeze-dried fruit and berry products are of high quality. To check whether this is also the case with black-currant material, which has so far not been the subject of much investigation, experiments were required to determine how, inter alia, ascorbic acid, colour and aroma would be preserved in this instance; these criteria are the most important ones in the assessment of quality.

Today, berry crops are most commonly preserved in the form of juice. The storage of single strength juice requires extensive storage space, and therefore concentration of the juice becomes of interest (cf. 4). Attempts at concentration have not been successful in all respects. KIESER et al. (11) report that juice concentrates of black-currant are of good quality, provided that they are stored in the frozen state at —23°C, and that the volatile aroma substances are recovered and returned. In contrast, if the concentrates are stored at room temperature, or

at 0°C, browning reactions occur whereby the organoleptic properties and particularly the colour suffer. It thus seems that concentration is not particularly favourable as a method of preservation, as frozen storage is recommended. In addition, aroma losses occur. Theoretically, it can be assumed that the more the juice is concentrated, the greater is the tendency for harmful browning reactions to take place, in view of the increase in concentration of the components. In principle, drying is a process of concentration, where removal of the water is effected to such an extent that the amount remaining becomes a limiting factor for the reactions mentioned. Thus in dried products the browning reactions are prevented, if the amount of water is kept sufficiently low (cf. 6). In this connexion, interest is attached to comparison of the loss of quality in single strength juice with that of concentrate and freeze-dried product.

The third factor which may influence the keeping quality is the presence of cloud. In some cases, it has been assumed (e.g. 21) that cloudiness may protect ascorbic acid against oxidation. Moreover, ROVESTI (23) has suggested that cloudiness is important for the stability of aroma. Consequently, experiments were performed for comparison of the keeping quality of cloudy and clarified juice stored as such, and also in the freeze-dried state.

On the basis of the above, the effects of freezing-drying, cloudiness and concentration were studied in the following combinations:

1) Whole berries
   a) Frozen starting material
   b) Freeze-dried berries
   c) Freeze-dried crushed berries
2) Cloudy juice
   a) Cloudy press juice, pasteurized
   b) » freeze-dried
3) Clarified juice
   a) Single strength juice, pasteurized
   b) Juice concentrated 3 times, pasteurized
   c) Freeze-dried juice.

Material. Frozen material was used throughout. Small and unripe berries were discarded from an ample lot, and the remainder used for the experiment. Part of the material selected in this way was further stored as a frozen control sample.

Methods

Preparation of the samples. In the freezing-drying of whole berries, it has been found by JOYCE (cf. 12) that the waxy materials at the surface greatly hamper the drying process. Consequently the author passed the pre-frozen material through an abrasive potato peeler to puncture the rather tough skin (cf. also 5). In the present experiments, such equipment was not available, but the berries were pricked with a needle in the mentioned purpose. The second type comprised crushed berries, so treated in the thawed state, and refrozen afterwards. For the freezing-drying

of both these samples and the cloudy and clarified juice, laboratory scale Leybold G 07 apparatus was employed. The process was rather slow: the size of the samples was usually 100 g, and e.g. in the case of whole berries the drying lasted for 45 hours.

Cloudy press juice was prepared by thawing the berries without the addition of water, homogenizing them with an electric mixer, and pressing the juice through etamine. The juice was bottled in 100 ml bottles and pasteurized.

Of this cloudy press juice, one part was treated with pectinase (Rapid Panzym), and then centrifuged. Samples of the juice were bottled and pasteurized as singlestrength juice. A part of the juice was concentrated in vacuum at low temperature to give a third of the original volume; this sample was also pasteurized.

Storage of the samples. Frozen sample was kept at the usual storage temperature (—20°C). Freeze-dried samples were stored at room temperature (approximately 18°C) in darkness. The bottles were closed either with rubber stoppers, or bakelite stoppers tightened with plastic sealing. The bottles were provided with tubes containing calcium oxide as a desiccant to prevent the products becoming moist. This at the same time ensured that the drying could be completed subsequently. DESROSIER (6, p. 158) mentions that if the residual moisture is reduced below 1 per cent, browning reactions are greatly retarded. This may be achieved with in-package desiccants. Samples of the cloudy and clarified juice, as well as the concentrate, were kept in a refrigerator (+ 4°C) and other samples at room temperature.

In all, the storage time was 8 months. Analyses were carried out initially, after 4 ½ months, and at the end of the storage.

Analytical methods to characterize the quality. The following methods were used (cf. 13, 14, 15, 16); vitamin C was assayed by the method of ROBINSON & STOTZ (22), the correction for reductones being used (formalin correction); the method was slightly modified in accordance with ERKAMA (8). The results are given as total and corrected ascorbic acid. The colour was measured at the absorption maximum (ordinarily at 520 mμ); in addition, the form of the absorption curve was checked between 320—800 mμ, to find out whether the maximum of the anthocyanins had disappeared, and signs of browning reactions were observable (see 11). The aroma number was measured in accordance with the BRUNNER & SENN method (3). For organoleptic appraisal, the colour, smell and taste were evaluated according to the scheme of KOCH (ref. 2, p. 356). Details of preparation of the samples for this evaluation are reported separately in each series.

To ensure that the samples for analysis were as comparable as possible, the concentrate was before analysis diluted to the original volume. Similarly, the weights of the freeze-dried samples were recorded initially and at each storage phase studied. The samples were reconstituted with water to the original weight as accurately as possible. In some cases, in addition, the dry matter was determined by direct drying at 100°C to constant weight, or the dilutions of the samples were checked by refractometrical measurement of the soluble solids and by titration of the acid content by electrometric means, with pH 8.2 as the end point (19).

Results

Whole berries

A check of the weights of the freeze-dried samples gave the following results, expressed as percentages of the original weight:

	Whole berries	Crushed berries
At the start	22.9	22.7
Storage for 4 ½ months	21.2	22.2
» » 8 »	21.2	22.1

It can be seen that there had occurred no moistening of the samples during storage but that instead more moisture had been lost through the agency of the in-package desiccant. However, it is possible that the weighings of the freeze-dried preparations were not wholly accurate, as these products are very hygroscopic. Dry matter assay of the original crushed berries gave a figure of 23.2 per cent, and thus some small losses may have taken place in the freezing-drying process, or in packing. Regeneration of the freeze-dried samples might thus imply some slight inaccuracy. To check this point, acid titration of the regenerates was carried out.

Regeneration of the freeze-dried samples after storage for 4 ½ months was as follows:

Whole berries, 10.426 g → 48, g, corresponding to approximately 49 g of the original frozen sample.

Crushed berries, 9.75 g → 45 g, corresponding to approximately 44 g of the original frozen sample.

After storage for 8 months the regeneration was as follows:

Whole berries, 10.7932 g → 50 g, corresponding to approximately 51 g of the frozen sample.

Crushed berries, 9.7137 → 45 g, corresponding to approximately 44 g of the original frozen berries.

To check the dilutions, acid titrations of the regenerates were carried out. A sample of 1 g was taken, and the acidity calculated as ml of 0.1 n NaOH/100 g of the original frozen berries. The following results were obtained:

	pH		Acidity	
	4 ½ months	8 months	4 ½ months	8 months
Frozen starting material	3.44	3.49	495	515
Freeze-dried whole berries	3.30	3.55	480	475
» » crushed »	3.42	3.55	486	481

It can be seen that the changes which took place in the acidity values were very small. In the frozen starting material, a small increase was noted, whereas in the freeze-dried samples there was a slight decrease. However, this check demonstrates that the dilutions are well comparable, and that no significant changes in acidity occur during processing and storage.

Ascorbic acid. First, there should be considered the effect of the freezing-drying process on the ascorbic acid content, i.e. the changes which take place during the preparation of the samples. The values have been calculated as mg of ascorbic acid in 100 g of the original sample.

	Whole berries		Crushed berries	
	Original	Freeze-dried	Original	Freeze-dried
Total ascorbic acid	147.5	130.3	112.5	161.9
Corrected »	93.8	58.7	76.5	54.6
Percentage of C corr.	63.6	45.1	68.0	33.7
Retention of total ascorbic acid, per cent		88.3		144
Retention of corrected ascorbic acid, per cent		62.6		71.3

The crushing of berries accordingly causes a loss of both total and corrected ascorbic acid. Also, freezing-drying causes losses in whole berries, although they are small. In crushed berries, freezing-drying decreases the value of the corrected ascorbic acid, whereas the total ascorbic acid increases. This suggests that freezing-drying augments the amount of »reductones».

Secondly, ascorbic acid changes during storage are considered. Here, the values have similarly been calculated as mg ascorbic acid in 100 g of samples regenerated to the original strength.

Total ascorbic acid	Initial value	4 ½ months	8 months
Frozen berries	147.5	136	84
Freeze-dried whole berries	130.8	121.5	98.2
» crushed berries	161.8	141	96.1
Corrected ascorbic acid			
Frozen berries	93.8	94	72
Freeze-dried whole berries	58.7	78.4	72.7
» crushed berries	54.5	47.0	57.3
Percentage of C corrected			
Frozen berries	63.6	69.1	85.7
Freeze-dried whole berries	45.1	64.5	74
» crushed berries	33.7	33.3	59

The values of total ascorbic acid thus decreased in all samples during storage. The stability was best in whole freeze-dried berries, where retention amounted to 75.4 per cent of the original. The content of corrected ascorbic acid changed less in freeze-dried samples than in the frozen control. In consequence, the stability of ascorbic acid was good in freeze-dried products, being even better than in the frozen sample. As regards the absolute amounts in freeze-dried samples, the crushed berries contained less ascorbic acid than did the whole berries. Consequently, the freeze-drying of whole berries seems more advantageous than that of crushed berries.

Colour. The measurements were made only after storage for 4 ½ and 8 months, with the values for the frozen sample being taken as control. The dilution was 1 g of the berries or the regenerate, which was after homogenization made up to 50 ml

and centrifuged. In all cases, there was obtained a typical absorption curve of anthocyanins, although prolonged storage lowered its level. In the table below, the values at the absorption maximum have been corrected taking into account the concentration of the regenerate as compared with the original frozen berries.

Storage for	4 ½ months	8 months
Frozen berries	498	394
Freeze-dried whole berries	466	462
» crushed berries	585	482

In the frozen berries, accordingly, the colour strength diminished somewhat during storage. In freeze-dried whole berries, the colour remained unchanged being stronger than in the frozen sample. In freeze-dried crushed berries, the colour was initially stronger than in the other samples. Although it decreased during storage, it was still after storage for 8 months stronger than in both the other samples. Thus the retention of colour in the freeze-dried samples was excellent.

Aroma. The analysis was carried out only after storage for 8 months. Samples of 10 g were taken from the frozen berries and regenerates. The values are given as ml 0.1 n $K_2Cr_2O_7$/100 g of the sample.

	Aroma number
Frozen berries	68.5
Freeze-dried whole berries	57.0
» crushed berries	15.3

The freezing-drying thus brought about a loss of volatile reducing substances, which was particularly evident in the crushed berries.

Organoleptic evalution. This examination was made only after storage for 4 ½ months, since the amount of the remaining samples was not sufficient after storage for 8 months. All the samples were presented in the homogenized state. No sugar was added. As the acidities of the samples were very similar, no adjustment was made in this respect. The evalution comprised appraisal of the colour, smell and taste, the scores being 0—2, 0—4 and 0—10 respectively. The sum of points is thus 16 maximum. The values are given as uncorrected averages. The number of panel members was 7.

	Frozen	Freeze-dried	
	berries	whole berries	crushed berries
Colour	1.8	2.0	1.7
Smell	3.7	1.6	2.2
Taste	8.0	4.9	4.6
Sum of points	13.5	8.5	8.5

This established that the frozen berries were far superior to the freeze-dried products in respect to organoleptic properties. The only advantage of freezing-drying noted here was the superior stability of colour in the whole berries. Incidentally, similar results have been obtained in other unpublished experiments

made in our laboratory, where black-currants were crushed in the frozen state before freezing-drying. It seems that the use of a vacuum in freezing-drying removes from the products a part of the most typical aroma components of the black-currant, as the aroma of the freeze-dried samples was described as »hay-like» and not typical of this berry.

In conclusion, in the freezing-drying of whole or crushed black-currants ascorbic acid, and colour in particular, are very well preserved, but considerable aroma losses occur. This method thus needs modification to give products of good quality also in the latter respect, as primary importance should be attached to measures designed to prevent such aroma losses.

Cloudy juices

The weights of the freeze-dried cloudy juice were checked as above; the findings have been expressed as percentages of the original weight.

Initial value	21.2
Storage for 4 ½ months ..	20.2
» 8 » ..	20.0

As could be expected, the weights were somewhat lower than those of the crushed berries. Here, as was the case with whole and crushed berries, a further loss of moisture took place during storage. Dry-matter assay of the original cloudy juice gave the result 19.4 per cent. Regeneration of the freeze-dried sample to the original amount again involved an element of uncertainty, and thus a check was made on the regeneration by means of acid titration.

Regeneration was as follows:

After 4 ½ months, 19 g → 89.1 g (= 81.8 ml)

After 8 months, 18.67 g → 88 g (= 84 ml); this dilution corresponded to 18.9 g of the previous sample, and as a result the regenerations were almost identical.

A check on the acidity values gave the following results:

	pH		Acidity	
	4 ½ months	8 months	4 ½ months	8 months
Juice stored at + 4°C	3.40	3.51	628	653
» » + 18°C	3.40	3.51	643	655
Freeze-dried juice	3.30	3.56	630	560

Apparently the acidity was reduced in the freeze-dried sample, and somewhat increased in the other samples during storage.

Dry matter, assayed refractometrically. As an additional check of the regeneration, the strength of the regenerate was also estimated by dry matter content, although this method is not wholly reliable as regards cloudy and strongly coloured juice. The results are presented in the table below, expressed as percentages of the soluble solids.

	4 ½ months	8 months
Freeze-dried juice	18.8	19.4
Juice stored at + 4°C	16.4	17.4
+ 18°C	16.4	16.9

The values increased to some extent during storage. In freeze-dried juice, the values were sligthly higher than those for the other samples, in contrast to the corresponding acidity values. The difference in dry matter varied between 111.5 and 114.8 per cent for freeze-dried juice, if the other juices were taken as 100 per cent. Moreover, the colour in the freeze-dried juice was stronger than in the other samples, which might have influenced the refractometer reading. Similarly, the assay might have been affected by the amount and fineness of the cloud. Estimation of the amount of cloud was accordingly arrived at by centrifugation.

Amount of cloud. For this assay, there was taken 5 ml of juice or regenerate. The samples were centrifuged until the cloud was clearly separated; the sediments were then washed to remove disturbing colour, and the amount was measured by volume. The following results were obtained:

	4 ½ months	8 months
Freeze-dried juice	3.3 ml	3.2 ml
Juice stored at + 4°C	2.1 ml	2.2 ml
» + 18°C	2.2 ml	2.0 ml

It can be observed that in the freeze-dried sample the amount of cloud was regularly greater than in the other samples. The pectin might partly disintegrate in the juices stored in liquid form if the pectic enzymes were not completely inactivated during pasteurization, or precipitation might occur and render the cloud less voluminous. The separation of cloud was clearly discernible in these samples, making the appearance of the juices rather unpleasant.

Ascorbic acid. First of all, there was considered the stability of ascorbic acid during the preparation of the samples. In pressing, 1000 g of homogenate yielded 750 ml of cloudy juice. The ascorbic acid content at this phase was found to be as follows:

	Total ascorbic acid, mg	Corrected ascorbic acid, mg
in 1000 g homogenate	1125	765
in 750 ml cloudy juice	1180	765

Accordingly, no losses of ascorbic acid occur on pressing cloudy juice from the homogenate, although it is true that losses are experienced in preparation of the homogenate from the original frozen berries. In addition, pasteurization is effected before storage, and its effect has not been studied separately.

The stability of ascorbic acid during freezing-drying can be seen from the following calculation. The ascorbic acid content in cloudy juice was 157.5 mg total, and 102 mg corrected ascorbic acid/100 g. Now, 100 g cloudy juice yielded 21.05 g freeze-dried product. In the latter, the amounts were 816 mg total, and 384 mg

corrected ascorbig acid/100 g, which means, in 21.05 g of freeze-dried product, 171.8 mg total and 80.8 mg corrected ascorbic acid. Thus, the total ascorbic acid increased, but the corrected ascorbic acid decreased somewhat as a result of freezing-drying, the former value being 110 %, the latter 81.9 % from the original.

The stability of ascorbic acid during storage is presented in the table below. The values are given in mg calculated per 100 g of original or regenerated sample.

	Initial value	4 ½ months	8 months
Total ascorbic acid			
Juice stored at + 4°C	157.5	148	116
» + 18°C	157.5	120	110
Freeze-dried juice	171.8	166	146
Corrected ascorbic acid			
Juice stored at + 4°C	102	78	34
» + 18°C	102	46	38
Freeze-dried juice	80.8	108	98
Percentage of C corrected			
Juice stored at + 4°C	64.8	52.7	29.3
» + 18°C	64.8	38.3	34.5
Freeze-dried juice	47.1	65.1	67.1

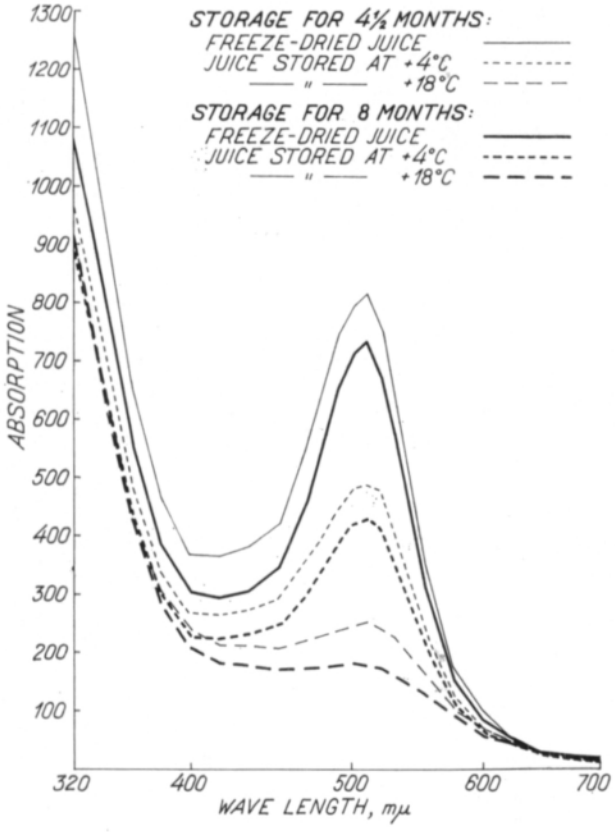

Fig. 1. Stability of colour in cloudy black-currant juices during storage.

These values indicate that the retention of ascorbic acid was better in the freeze-dried sample than in the other samples, both the total and in particular the corrected ascorbic acid displaying this tendency. Furthermore, the high percentage of corrected ascorbic acid of the total is a sign of good retention.

Colour. Measurements were made after storage for 4 ½, and 8 months. The dilution was 1 ml of juice or regenerate to 50 ml final volume. Absorption curves of the centrifuged dilutions are given in Fig. 1, and it can be observed that the colour was strongest in the freeze-dried sample, and better in the juice stored at + 4°C than that at + 18°C. In all samples storage caused a lowering of absorption, as the values at maximum demonstrate:

	4 ½ months	8 months
Freeze-dried juice	816	735
Juicestored at + 4°C	489	428
» + 18°C	251	176

As regards colour, freeze-drying is evidently the most advantageous method, and for the cloudy juices the effect of temperature is important: the higher the storage temperature, the more the anthocyanins are destroyed. This is well in accord with earlier experience.

Aroma. The analysis was carried out only after storage for 8 months. Samples of 10 ml were taken from the juices or the regenerate. The values are given in ml of 0.1 n $K_2Cr_2O_7$/100 ml of the sample.

	Aroma number
Freeze-dried juice	17
Juice stored at + 4°C	48
» + 18°C	59

In this series, as in the preceding one, the aroma of the freeze-dried sample was considerably decreased. For storage at + 18°C, the aroma number was higher than at + 4°C. As a higher temperature exerts an unfavourable effect on quality, it seems evident that the aroma number alone does not provide a reliable picture of the quality of the aroma. Storage at room temperature may cause the formation of reducing substances, which have an undesirable effect on the aroma (cf. also 4). Similar substances are present in fermented juices.

Organoleptic evaluation. The main analysis was carried out after 4 ½ months; after 8 months, the material was sufficient for a limited check only. For taste-testing, the samples from the juices and regenerate were prepared as follows: 25 ml of juice or regenerate + 15 g sugar → 100 ml of final dilution. Colour and smell were evaluated from the samples as such. The scores and the means of expressing the values are similar to those in the preceding series. The number of panel members was 8 after 4 ½ months, and 4 after 8 months.

After 4 ½ months, the results were as follows:

	Freeze-dried juice	Juice stored at + 4°C	Juice stored at + 18°C
Colour	1.9	1.8	0.9
Smell	1.3	3.6	3.3
Taste	5.2	8.8	6.3
Sum of points	8.4	14.2	10.4

As regards colour, freeze-dried juice is superior to the others. In contrast, in smell and taste, the effect of freeze-drying is disadvantageous, the typical character of black-currant having been lost. Storage at + 18°C is clearly less favourable than that at + 4°C.

In the check evalution after 8 months, the results were almost the same. The sample stored at + 4°C proved to be the best, particularly as concerns smell and taste, although by contrast the colour was deteriorated somewhat. Storage at + 18°C had lowered the quality considerably, and in consequence this sample was rated at a lower level than the freeze-dried sample, although complete agreement among the panel members was not achieved.

In conclusion, the results of this series agree very well with those of the preceding one. Ascorbic acid and colour were well preserved in the freeze-dried sample, but aroma losses had occurred. Also, storage of the juice at room temperature proved to be rather injurious to the quality. The stability of the cloud in these juices was poor both in the cold and at room temperature. In this respect, freeze-drying gives better results.

Clarified juices

A complete analysis was made only after 4 ½ months, as after storage for 8 months only clarified juice kept at + 4°C was available.

The weight of 100 g of juice after freezing-drying was 17 g. After storage, the checking of weight was not reliable, as the powder was firmly attached to the walls of the container. As a consequence, regeneration to the original strength was approximate, its reliability being checked by means of acidity and dry matter assays. The dry matter content of the original clarified juice was 16.1 per cent.

A check of the acidity values gave the following results:

	pH		Acidity	
	4 ½ months	8 months	4 ½ months	8 months
Juice stored at + 4°C	3.30	3.32	610	650
» + 18°C	3.29		600	
Concentrate stored at + 4°C	3.30		610	
» + 18°C	3.29		610	
Freeze-dried juice	3.28		580	

Dry matter, assayed refractometrically. The results have been expressed as percentages of the soluble solids. The regeneration of freeze-dried juice was the same as in the above check.

	4 ½ months	8 months
Juice stored at + 4°C	15.8 %	17.4 %
» + 18°C	16.3 »	
Concentrate stored at + 4°C	15.8 »	
» + 18°C	16.4 »	
Freeze-dried juice	16.1 »	

It can be concluded that the acidities and dry matter content of the samples after regeneration were very much alike.

Ascorbic acid. First of all, consideration is given to the stability of ascorbic acid in the preparation phase. A comparison of the clarified juice with the cloudy juice, of which the former was prepared, shows that on the average 100 ml of cloudy juice yields 66.4 ml of clarified juice. The ascorbic acid content in 100 ml of cloudy juice is 157.5 mg of total and 102 mg of corrected ascorbic acid. Correspondingly, 66.4 ml of clarified juice contains 89.0 mg of total and 55.8 mg corrected ascorbic acid. Retention is thus 56.5 per cent for total and 54.7 per cent for corrected ascorbic acid. Evidently the clarification brought about a loss of ascorbic acid.

Comparison between the clarified juice and the concentrate (3×) made from it shows that in 100 ml of clarified juice there is 134 mg of total ascorbic acid and 84 mg of corrected ascorbic acid, whereas in 100 ml of the concentrate there is 383 mg of total, and 258 mg of corrected ascorbic acid. The retention is thus 95.3 per cent for total, and 102 per cent for corrected ascorbic acid. The stability of ascorbic acid in the concentration phase is accordingly good.

In freezing-drying, 100 g (= 95.6 ml) of clarified juice resulted in 17 g of freeze-dried product. The ascorbic acid content in 100 g of the juice is 128.1 mg of total, and 80.3 mg of corrected ascorbic acid. In 17 g of the freeze-dried product, the content is 129.2 mg of total, and 95.2 mg of corrected ascorbic acid. The retention of the former is 101 per cent and that of the latter 119 per cent which can be regarded as very good.

Following this, examination of the stability of ascorbic acid during storage is due. The values have been calculated in mg per 100 ml of original or regenerated juice.

	Initial value	4 ½ months	8 months
Total ascorbic acid			
Juice stored at + 4°C	134	91	42
» + 18°C	134	73	
Concentrate stored at + 4°C	128	69	
» + 18°C	128	72	
Freeze-dried juice	135	106	
Corrected ascorbic acid			
Juice stored at + 4°C	84	48	0
» + 18°C	84	28	
Concentrate stored at + 4°C	86	25	
» + 18°C	86	32	
Freeze-dried juice	100	52	
Percentage of C corrected			
Juice stored at + 4°C	62.7	52.8	0
» + 18°C	62.7	38.4	
Concentrate stored at + 4°C	67.4	35.6	
» + 18°C	67.4	44.4	
Freeze-dried juice	73.7	60.3	

From these values, it can be discerned that after storage for 4 ½ months, the retention was best in freeze-dried juice for both total and corrected ascorbic acid, although even in this case losses occurred. Juice stored at + 4°C came next in order, whereas the differences between the other samples were small. After storage for 8 months the corrected ascorbic acid was completely lost from the juice kept at + 4°C. Freeze-drying again proved favourable as regards the keeping of ascorbic acid.

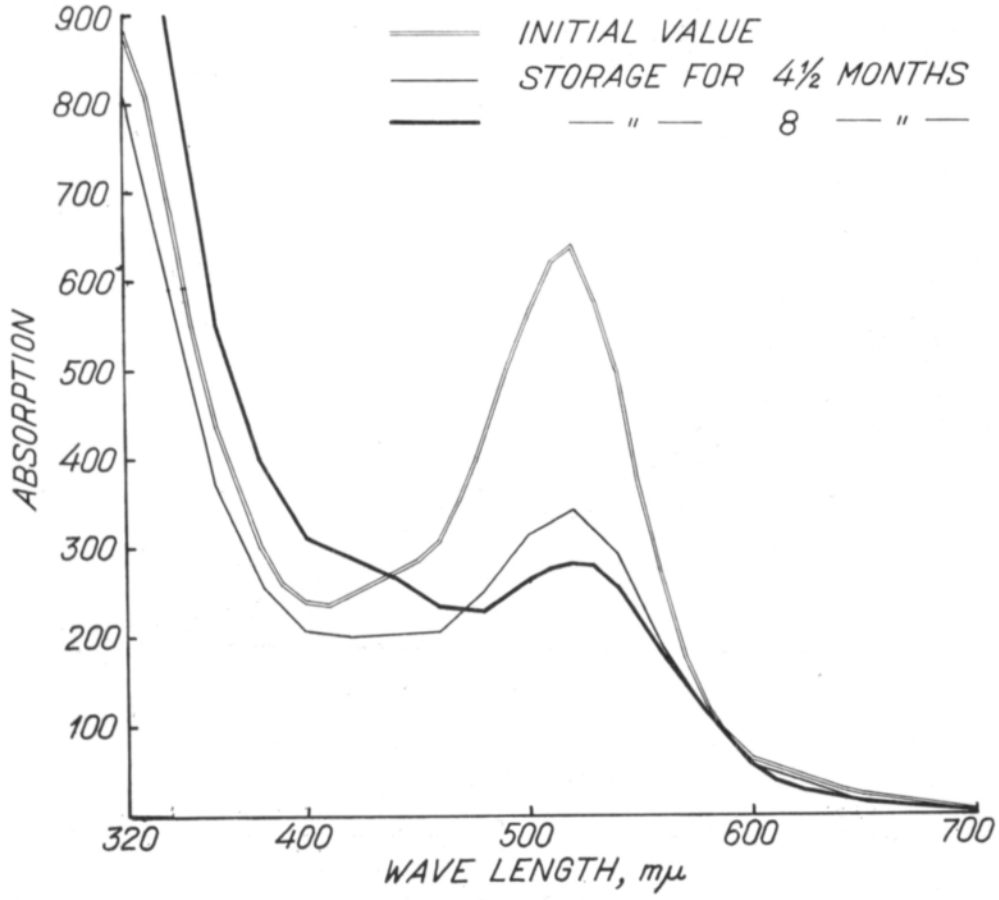

Fig. 2. Strength of colour in clarified black-currant juice during storage at + 4°C.

Colour. Measurements were made with the original juice initially, from all samples after 4 ½ months, and from juice stored at + 4°C after 8 months. Dilution corresponded to the preceding series; no centrifugation was necessary. The results are shown in Fig. 2 and 3, of which the former illustrates the absorption curves of the single strength juice kept at + 4°C after various periods of storage. Progressive weakening of the colour took place, but even after 8 months the maximum of anthocyanins was observable. The latter figure makes a comparison of the absorption curves of the different samples after storage for 4 ½ months. The freeze-dried

sample was clearly the best, and the juice stored at + 4°C next; the others were almost similar to each other, the maximum having nearly disappeared. Thus the conclusion is that once again freeze-drying is favourable for colour stability. Storage in the cold is better than that at room temperature, and concentration does not seem to be beneficial.

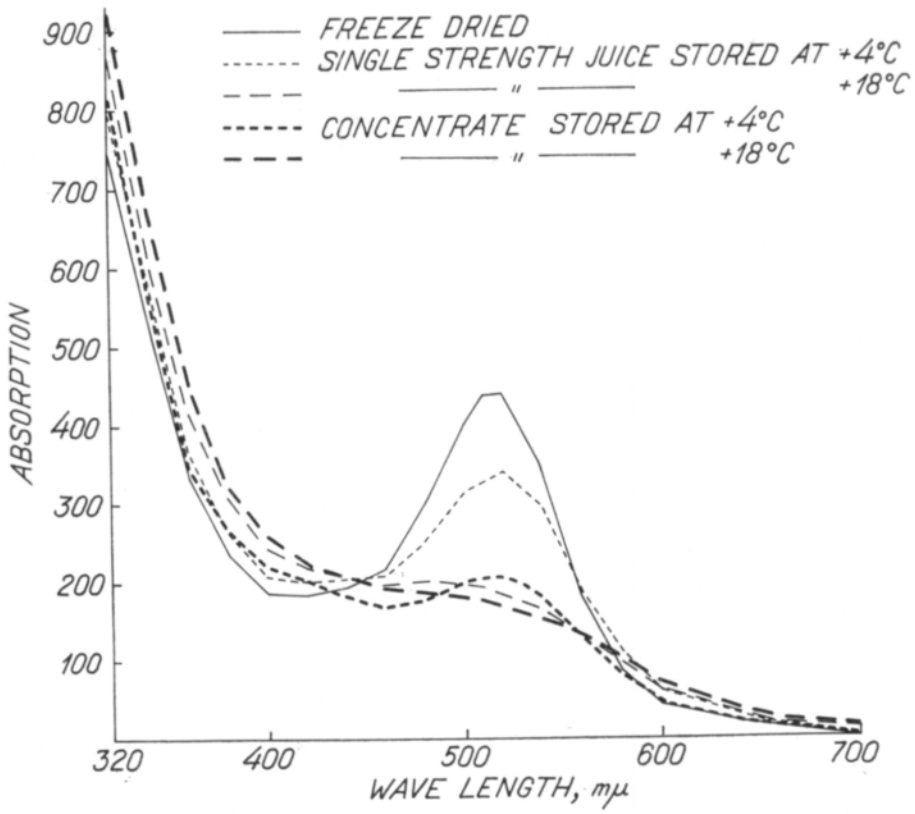

Fig. 3. Strength of colour in derivatives of clarified black-currant juice in various conditions after storage for 4 ½ months.

Aroma. The analysis was carried out as in the preceding series, only the juice kept at + 4°C for 8 months being studied. The amount of sample was 10 ml, and the value is given as ml of 0.1 n $K_2Cr_2O_7$/100 ml of sample.

The aroma number obtained was 78.

In comparison with the other aroma numbers arrived at in these experiments, this value seems somewhat high (corresponding cloudy juice 48, frozen berries 68.5). The explanation is not self-evident. It might be that the aroma components in black-currants are water-soluble, and that cloudiness constitutes a diluting factor. It is also possible that the presence of cloud renders the distillation of aroma components more difficult. The enzyme treatment employed in the production of the clarified juice may increase the aroma number. However, the difference is not very great, and thus there need not be present any effect of fermentation or related changes.

Organoleptic evaluation. This check was made only after storage for 4 ½ months. The preparation of the samples was similar to that for the cloudy juices, as well as scores and expression of the values. The number of panel members was 7.

	Juice stored at		Concentrate stored at		Freeze-dried
	+ 4°C	+ 18°C	+ 4°C	+ 18°C	juice
Colour	2	1.0	1.8	1.1	2
Smell	3.9	0.9	2.1	1.7	2.1
Taste	9.1	3.1	5.6	5.0	8.3
Sum of points ..	15.0	5.0	9.5	7.8	13.4

As regards colour, the freeze-dried sample was the best. The effect of refrigerated storage was also favourable. Both storage at room temperature and the concentrating process were unfavourable in their effects on the smell. Freeze-drying lessened the aroma, although the effect was not very pronounced. In the opinion of the panel members, the aroma remaining was perhaps more terpene-like than in the ordinary juice. With respect to taste, storage at room temperature and the concentrating process were unfavourable. By contrast, freeze-dried juice proved nearly equal to the juice stored at + 4°C.

In conclusion, these results agree with those in both of the preceding series as concerns the good stability of ascorbic acid and colour in freezing-drying. Furthermore, the aroma was comparatively well preserved, as appraised by organoleptic evaluation. As for the concentrate, the ascorbic acid stability was not so good, and colour deteriorated considerably. Furthermore, the organoleptic properties suffered.

Discussion

In what follows, consideration is given to the possibilities of each method studied, and comparisons made with information contained in literature.

First of all, a comparison of cloudy and clarified juice may provide some information on the keeping of quality in both instances. As regards ascorbic acid, the cloud may exert a slight protective effect, but this is not of great significance. Fig. 4 presents a comparison of the ascorbic acid values of both these juices during storage. The initial values are higher in the cloudy juice, and the decline of ascorbic acid, although approximately parallel, is somewhat steeper in the clarified juice. It is difficult to draw clear conclusions with respect to aroma. The aroma number is higher in the clarified than in the cloudy juice, but this may be because in the assay method the cloud hampers the distillation of the aroma compounds. In the organoleptic evaluation, the juices were awarded approximately equivalent points, but as the juices were not directly compared one with the other, comparison of the values may not be wholly reliable. In the cloudy juice, the poor stability of the cloud was an unfavourable feature, with particular effect upon the appearance. This drawback was not present to the same degree in the freeze-dried sample, but

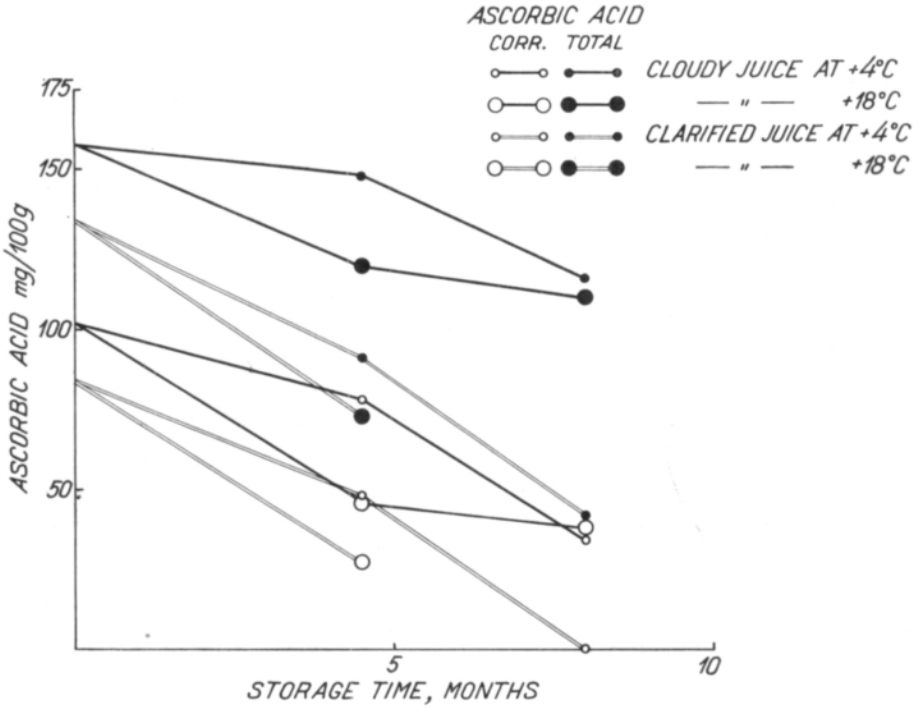

Fig. 4. Comparison of stability of ascorbic acid during storage in cloudy and clarified black-currant juice.

here aroma losses occurred instead. Thus the findings give but little support to the opinion that cloudy juices are of improved quality, although it cannot be claimed that the subject has as yet been thoroughly investigated or finally settled.

The results concerning the juice concentrate are also not so encouraging. Compared with the single strength juice, the concentrate showed a more rapid loss of ascorbic acid, a deterioration of colour, and weakening of the organoleptic properties. This is in agreement with the observations made by KIESER et al. (11), and POLLARD et al. (20), at similar storage temperatures: although the production of good quality concentrates is feasible, the quality is preserved only when the storage is effected in the frozen state. However, the new results of CHARLEY (4) deserve mention in this connection. He stored 6:1 black-currant juice concentrate at 0 ± 1°C, and reports that if the stripped volatiles were returned, the reconstituted juice was practically indistinguishable from the original. It also seems, according to investigations performed in our laboratory, that the juice concentrates produced in Yougoslavia, where aroma recovery was effected, are very good in quality (cf. e.g. 25, 26). There thus exists some discrepancy between the results concerning the possibilities of using the method of concentration succesfully. Theoretically, it is to be assumed that during prolonged storage, in any case the colour of the concentrate suffers when anthocyanins are destroyed and browning reactions take place, and simultaneously there occur a loss of ascorbic acid and deterioration of the organoleptic properties, limiting the storage stability.

As regards freezing-drying, four different preparations were taken into consideration in these experiments: whole berries, crushed berries, cloudy juice and clarified juice. In every case, the results were in agreement in that they clearly demonstrated the excellence of the method with respect to the retention of ascorbic acid and colour. This was to be expected, as sufficient lowering of the water content prevents anthocyanin losses, browning reactions and the oxidation of ascorbic acid. In this respect, freezing-drying thus provides a better and more easily stored product than does concentration (cf. 11). In contrast, freezing-drying was less favourable as concerns taste and aroma, as can be observed from the organoleptic assessments and aroma numbers. In this respect, freeze-dried clear juice proved to be superior to the other freeze-dried products. In any event, it seems obvious that suitable methods for aroma recovery are essential for the production of first class preparations.

In the current experiments, the freeze-dried products were compared with the original frozen berries or juice, but not with corresponding preparations produced by other drying methods. It is not known whether ordinary drying methods have been used for black-currant, although they have been applied to bilberries, which are very mild in taste. To the extent that trials have been made in the drying of juice, the results have not been encouraging. In the case of black-currant, the drying of the berries may be hampered by the thick skin. Moreover, the high acidity may result in a dried product too strong in taste. In considering the conditions of freeze-drying, there is generally the danger that the berries, being brittle, may crumble during packing, storage, etc. This danger is not very serious as regards black-currant, which is comparatively small and tough. If before freezing-drying the berries are subjected to an abrasive treatment, such as the application of a potato peeler to speed up the drying, this brings about partial detachment of the skin, which is probably unfavourable for the appearance. A corresponding effect may be obtained by pricking the berries; the appearance then suffers less. For this purpose, there is available equipment on an industrial scale (cf. 1).

In the present studies, no particular attention was directed to the rehydration ability of the freeze-dried samples. In literature (e.g. 18, p. 157), the opinion is expressed that in fruits and berries rehydration is in general somewhat incomplete. It may be mentioned that in parallel experiments made in our laboratory, the rehydration of freeze-dried black-currants was rapid when the speed of drying was similar to that applied in the present series. The amount of moisture remaining in the dry products was not assayed separately, but from the dry matter analyses and final weights it may be calculated at between 3 and 5 per cent or perhaps less. The moisture content has importance insofar as if it is very low, it may cause a diminution of rehydration power and enhance oxidative changes (cf. 24). Again, if the residual moisture content is high, the chemical and microbiological stability is impaired. In the present experiments, where an attempt was made to reduce the residual moisture as much as possible, neither of the meni oned harmful changes was observed.

The decisive factor as regards the quality of the freeze-dried products is thus the changes which take place in the taste and aroma. In black-currant, it is probable

that the most important of these changes is the loss of volatile aroma compounds. On the other hand in black-currant it is probable that less importance is attached to such difficulties as the changes in structure and appearance than obtains with strawberry and raspberry. COTSON & SMITH (5) mention that on reconstitution these berries are more like stewed fruit than fresh fruit in appearance. In black-currant, the aroma losses are considerable to judge from the aroma numbers of the products, although no direct assay has been made of the volatile fraction. Therefore, to obtain first class products by freezing-drying, aroma recovery should be connected with the process. A similar opinion was expressed by DUPAIGNE as early as in 1956 (7), in a review of the possibilities of freezing-drying. In some other methods for the manufacture of fruit-juice powder, the procedure was first of all to isolate the aroma compounds in concentrated form, and add them to the powder in the final stage; this was the case in climbing film evaporation and foam-mat drying (cf. 17). Such a procedure would further increase the already high cost of the freezing-drying method. It might be that the recent »Birs-method» possessed greater advantages. In this method, the juice is dried with cold air in accordance with the reverse-flow principle; a special feature is the »washing-zone» in the upper part of the drying tower, which to a considerable degree prevents aroma losses (17).

Summary

Experiments have been made in the development of various new black-currant products, such as cloudy juice, juice concentrate and various freeze-dried preparations, along with a study of the effect of these different methods of preparation on the initial quality and storage properties. The quality was assessed from the stability of ascorbic acid and colour, the aroma number, and organoleptic evaluation. Storage lasted up to 8 months.

It was established that the cloudiness exercised a slight protective effect on ascorbic acid. However, the instability of the cloud meant that the appearance of the cloudy juice was less attractive than that of the clear juice. No well-founded advantage of the cloudy juice could be demonstrated.

Concentration proved less suitable, as there occurred harmful changes in ascorbic acid, colour and organoleptic properties.

The freezing-drying method was excellent with respect to ascorbic acid and colour. In contrast, considerable losses in aroma occurred, with consequent weakening of the organoleptic properties. This method would be of advantage only in combination with aroma recovery, and solution of the financial problems involved.

The results are discussed in the light of relevant literature.

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SELOSTUS:

PAKKASKUIVAUKSEN, SAMEUDEN JA KONSENTROIMISEN VAIKUTUS LAADUN SÄILYMISEEN ERÄILLÄ MUSTAHERUKKATUOTTEILLA

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Uusien mustaherukkatuotteiden kehittämiseksi valmistettiin kokeilutarkoituksessa sameaa ja kirkasta mustaherukkamehua, mehukonsentraattia kirkkaasta mehusta sekä pakkaskuivattua kirkasta ja sameaa mehua sekä murskattuja ja kokonaisia marjoja. Tarkoituksena oli selvittää näiden valmistusmenetelmien vaikutusta tuotteiden laatuun sekä laadun säilymiseen. Laadun karakterisoimiseen käytettiin askorbiinihappopitoisuuden ja värinvoimakkuuden määrittämistä, aromilukua sekä organoleptistä arvostelua. Säilytysaika oli 8 kuukautta.

Voitiin todeta, että sameudella oli vähäinen askorbiinihappoa suojeleva vaikutus. Kuitenkin sameuden laskeutuminen aiheutti sen, että samea mehu jäi ulkonäöltään kirkasta mehua huonommaksi. Samealla mehulla ei voitu osoittaa mitään ratkaisevaa etua kirkkaaseen mehuun verrattuna.

Konsentrointi osoittautui epäedulliseksi, aiheuttaen haitallisia muutoksia askorbiinihappopitoisuudessa, värissä ja makuominaisuuksissa.

Pakkaskuivausmenetelmä oli erinomainen, mitä tulee askorbiinihapon ja värin säilymiseen. Sensijaan aromissa tapahtui huomattavia häviöitä, joka aiheutti makuominaisuuksien huononemista. Tämä menetelmä voidaan saada edulliseksi vain sillä edellytyksellä, että aromin talteenoton avulla estetään mainitut muutokset. Lisäksi taloudelliset kysymykset on saatava ratkaistuiksi edullisella tavalla.

Tuloksia on pyritty vertailemaan uusimpaan alan kirjallisuuteen.

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