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EFFECT OF MODIFICATION OF APPLE JUICE PRODUCTION TECHNOLOGY ON POLYPHENOLS CONTENT AND SENSORY PROPERTIES

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Key words: polyphenols, apple juice, ascorbic acid, depectinization catehins, leucoanthocyanidins, phenolic acids.

Pulp aeration markedly reduced the content of polyphenol compounds in apple juice. The largest quantities of these compounds were found in juice obtained from depectinized pulp and by a technology involving an addition of ascorbic acid to disintegrated apples. The juice obtained by technologies using pulp aeration or additions of ascorbic acid to disintegrated apples received the lowest organoleptic ratings. Changes in the contents of ferulic, m-coumaric, p-coumaric, caffeic acids and of the flavonols kempherol and quercetin appear to have no effect on the sensory properties of the juice.

INTRODUCTION

The various methods of obtaining apple juice are responsible for considerable differences in its organoleptic or dietetic properties. The juice components fairly susceptible to all kinds of chemical and biochemical transformations include, in addition to aromatic substances and vitamins, also polyphenols. The latter although occurring in relatively small quantities, of the order of 0.05-0.5%, play an important role in the shaping of organoleptic and dietetic properties of various kinds of juices.

The effect polyphenols have on the qualitative properties of apple juice (colour, taste) is one of the reasons for the considerable interest in the possible transformations of these compounds during the processing of apples into juice. The greatest changes and losses of polyphenol substances in apple processing occur during:

— the disintegration of apples,

— the extraction of juice apple pulp,

— the clarification and filtering of juices [8, 15, 23, 27]. In the course of these processes we have to do mainly with enzymatic and nonenzymatic oxidation of polyphenol compounds. The susceptibility of the various polyphenols to oxidation differs considerably. Catechins, leucoanthocyanidins and chlorogenic acid oxidize most readily while, for example, flavonols are relative immune to this process. Certain losses of polyphenols are also due to reactions with, among others, heavy metal ions and proteins, resulting in various different combinations [7, 11, 12, 24].

Recent studies tend to concentrate on the problems of increasing the extraction of polyphenol compounds from apples, and of reducing the losses of these compounds during technological processing. This creates possibilities of far-reaching quantitative and qualitative changes in polyphenols content in apple juice which could lead to the production of juices with desirable organoleptic properties.

OBJECTIVES AND SCOPE OF STUDY

The present studies were prompted by the increasing share of the so called "table" apples in industrial processing. These apples contain considerably less polyphenol substances than the varieties processed heretofore. When the polyphenols content in apples is high, its reduction in the technological process is downright welcome and there is no need for inhibiting polyphenol oxidation or for extracting the forms of these compounds which are localized mainly in the peel.

The goal of the present studies was the determination of the effect of various technological procedures applicable on an industrial scale and used in apple juice production on the quantitative changes in polyphenol compound content.

Experiments were performed for four years on musts obtained from Mc Intosh apples, and for the last two years also on musts from so called "industrial" apples, i.e. mainly from the Landsberska, Boiken, Jonathan and many other Reneta varieties. The following variants of apple juice production technology were used:

1. Addition of ascorbic acid (AA) to disintegrated apples — pulp depectinization — pressing — centrifugation — preservation;
2. Disintegration of apples — pulp depectinization — pressing — centrifugation — preservation;
3. Disintegration of apples — pulp aeration — pressing — centrifugation — preservation;
4. Addition of ascorbic acid (AA) to disintegrated apples — pressing — centrifugation — preservation;
5. Disintegration of apples — pressing — juice depectinization — centrifugation — preservation;

6. Disintegration of apples — pressing — centrifugation — preservation (control technology).

Washed apples were disintegrated and then pressed on a Bucher Guyer type TPZ-7 apparatus. The juice was pressed at ca. 1 MPa pressure. Must yield ranged from about 73 to 80% depending on the initial processing applied. Prior to bottling, the must was centrifuged in a chamber centrifuged in a chamber centrifuge manufactured by VEB(K) Separatorenbau Hainichen (SA). After pouring into 0.33 dm^3 bottles the must was pasteurized. The pasteurization parameters were $\frac{25\text{-}20\text{-}20}{85^{\circ}C}$.

Ascorbic acid (500 mg per kg apple pulp) was added directly after the disintegration of the fruits. Pulp depectinization was performed with enzymatic preparation PT (2 kg per 1000 kg of pulp) at 45°C for 2.5 h. Juice was depectinized for 1.5 h. Pulp was aerated by mechanical mixing of apple pulp for 2.5 h in an open jam evaporator.

The obtained juice were analysed during the first month after production and after six months of storage at room temperature in darkness. The following was determined:

— Total polyphenols by the Folin-Denis colourimetric method with the use of the Folin-Ciocialteu reagent [5, 21]. When ascorbic acid was present in the studied must (technologies 1 and 4), the obtained result was decreased by the magnitude read from a curve representing the dependence between ascorbic acid content in the must and the "increase of the content" of total polyphenols;

— Total catechins by the colourimetric method using the vanilla reagent according to the procedure given by Swain and Hillis [26];

— Total leucoanthocyanidins by the colourimetric method described by Swain and Hillis [26];

— The qualitative and quantitative determination of some polyphenol compounds was done by the method of gas chromatography according to the studies of Coffin and Dupont [3], Schultz and Herrmann [22] and Kataga et al. [9] with our modifications concerning mainly the hydrolysis parameters and chromatographic separation of sililic derivatives of polyphenol substances.

The sililation of polyphenol compounds was done with the sililating mixture TBT-332 produced by the Experimental Plant "Chemipan" in Warsaw. The obtain TSM derivatives of polyphenols were separated on a Pye Unicam Series 104 gas chromatograph. The conditions of chromatographic separation were as follows:

— column = glass, 3 m×4 mm, filled with 3% OV-101 on Gas-Chrom Q 80/100 mesh;

— temperature: programmed 200°C — 4 min; from 200°C to 310°C — 10°C min;

— carrier gas: argon, 40 cm^3/min;

— detector: flame-ionization, 350°C.

The organoleptic evaluation of apple juice was performed by a team of six-seven people. The most important features of the juice, i.e. colour, odour and taste, were graded according to a five-point scale with 1 denoting bad quality, 2 — unsatisfactory quality, 3 — satisfactory, 4 — good and 5 — very good quality.

The results pertaining to the content of m-coumaric, ferulic, caffeic, p-coumaric and chlorogenic acids and of kempherol in the apple must, depending on the applied technological process, the variety of apples, and juice storage, were analysed statistically by the method of three-directional variance analysis [4].

RESULTS AND DISCUSSION

Apple juice obtained in separate stages of research by the same technologies exhibited considerable differences in the content of polyphenol compounds ranging from 40 to 100%. Since in the separate periods of study the changes of the analysed juice components and the results of organoleptic evaluation dependent on the applied technology tended to be similar, we illustrate these variances with results obtained in stage IV of the studies only. The results confirm the reports of other authors [2, 8, 15, 20, 23] indicating that the content of polyphenols in apple juice is severely affected by the technological process, and especially by initial processing. Depending on this initial processing, the differences in total polyphenol content in some of the juice were four- to six-fold (Fig. 1).

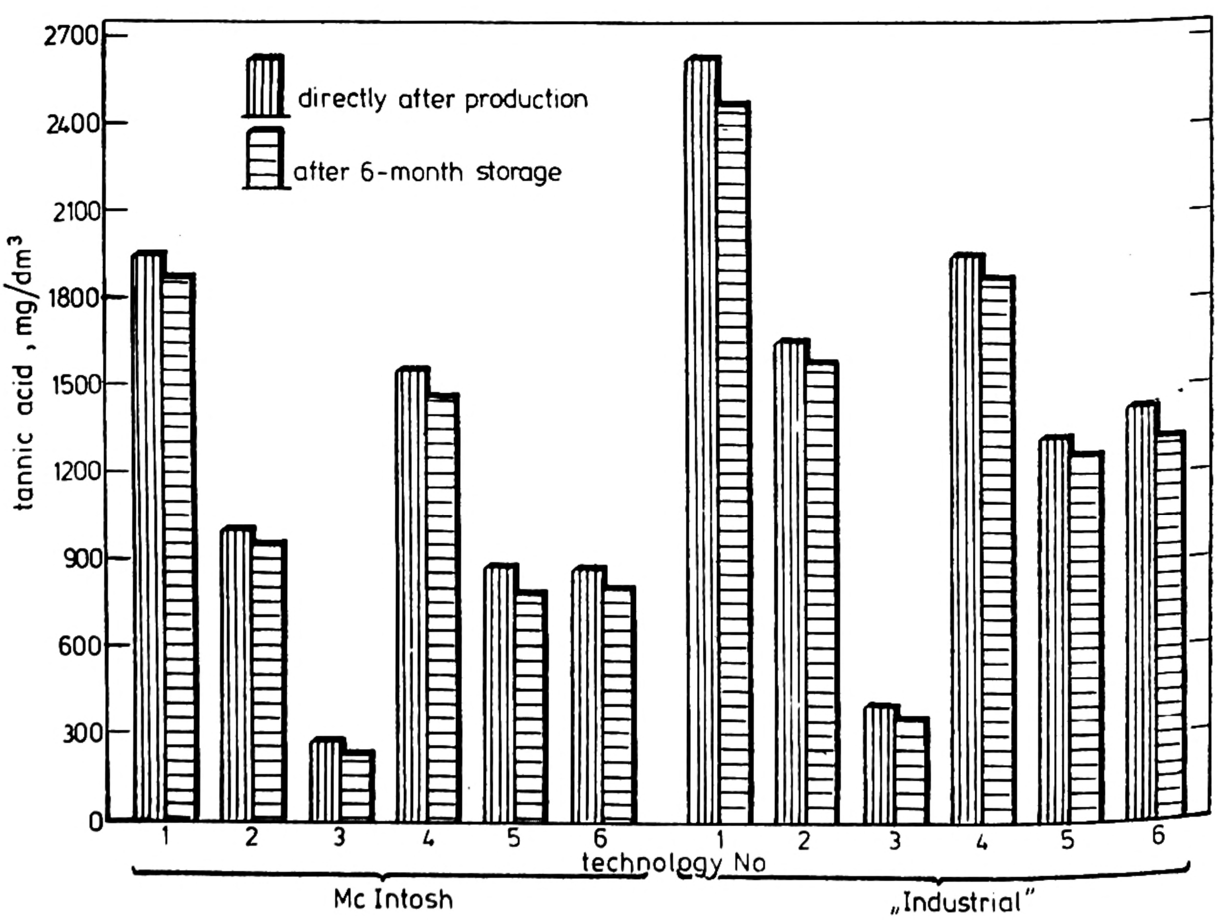

Fig. 1. Total content of polyphenol compounds in apple must depending on the applied technology

This is true mainly of technologies 1 (depectinization of pulp+AA addition) and 4 (AA addition) as compared to technology 3 (pulp aeration).

Comparing the differences in the contents of total polyphenols (Fig. 1) and of leucoanthocyanidins and catechins (Fig. 2) in juice obtained by technologies 1 (AA addition+pulp depectinization), 2 (pulp depectinization), 4 (AA addition) and 6 (control) we can see that if a high content of polyphenol compounds is required it is necessary to apply measures preventing their oxidation and facilitating their extraction, also from the fruit peel.

In our studies we used additions of ascorbic acid to disintegrated apples as an antioxidant and we applied depectinization of pulp to facilitate polyphenol extraction. The role of ascorbic acid added to the apple pulp (500 mg/kg) as an antioxidant consisted mainly in reducing the appearing

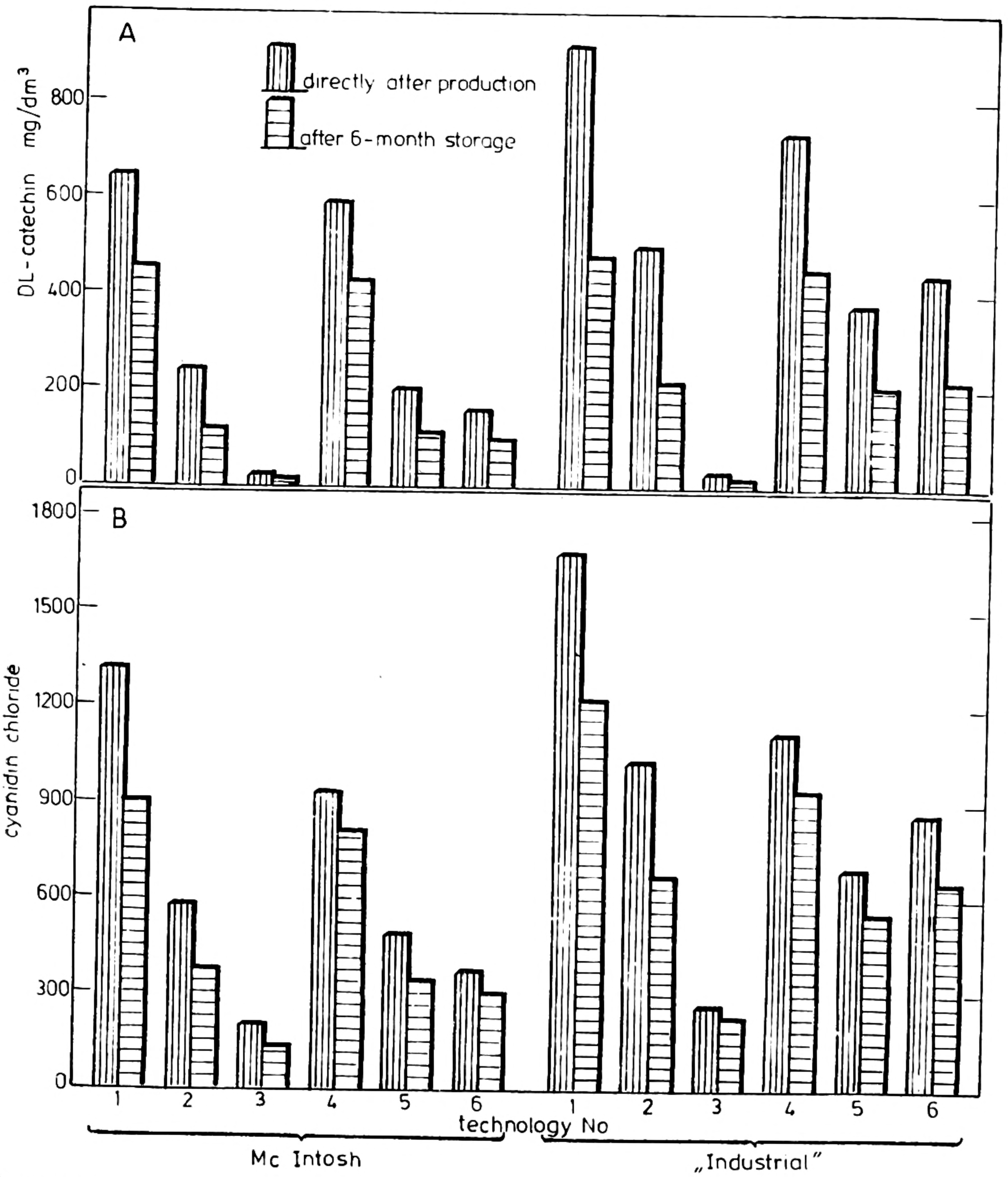

Fig. 2. Total content of catechins (A) and leucoanthocyanidins (B) in apple must depending on the applied technology

quinones to polyphenols, in addition to inhibiting somewhat the activity of o-diphenol oxidase. The outcome is a regeneration of the substrate for o-diphenol oxidase which in turn causes an inhibition of the accumulation of quinones and products of their transformation in the medium.

The content of quercetin and kempherol in the studied musts (Fig. 5) depended mainly on factors permitting their maximum extraction from apple peel where they mostly occur. The studies of Van Buren et al. [2] indicate that it is enough to disintegrate the peel and store the apple pulp for some time before pressing to ensure considerable extraction of flavonol glicosides into the juice.

This, however, has not been fully confirmed in the mentioned work; the results obtained therein suggest that enzymatic processing may contribute to a better extraction of favonol glicosides from the peel. Musts obtained by technology 3 (aeration of the pulp) contained much less quercetin and kempherol than musts obtained with technologies employing pulp depectinization (technologies 1 and 2). Since quercetin and kempherol glicosides are immune to the activity of oxidizing enzymes [24, 25], this factor could not have had a significant bearing on such a considerable drop of the content of these compounds in juice obtained by the technology using pulp aeration.

The divergencies in the evidence concerning the role of pectinolytic enzymes in flavonol glicosides extraction to the juice may have been due to different degrees of peel disintegration. It seems that when the peel is disintegrated in an insufficient degree, the loosening of cell walls caused by depectinization should facilitate the extraction of the mentioned compounds to the must.

Increased extraction of flavonol glicosides to the juice may have also been partly due to the increased temperature in which depectinization was performed. This phenomenon would be related to an increased solubility of these compounds and to the rate of their diffusion from the tissue to the juice at an increased temperature [15]. Pulp depectinization also increased the content of catechins and leucoanthocyanidins in the juice.

It must be stressed that the increase of total polyphenols and of leucoanthocyanidins and catechins due to the depectinization of pulp was lower than the respective increase caused by an addition ascorbic acid to disintegrated apples. Two processes superimpose here. On the one hand, polyphenol compounds pass from the peel and the flesh to the must which raises their content in the latter, and on the other, the extended contact of the must with the solid parts of he fruit containing most of the enzymes (including o-diphenol oxidase [6, 15, 17] leads to a decrease of the content of these compounds, chiefly as a result of the action of oxidizing enzymes. An increase of polyphenols content in the must due to a better extraction of the compounds from the peel cannot make up for the losses caused by the oxidizing enzymes.

The results of polyphenol compounds determination by gas chromatography demonstrate that by applying different technologies of apple juice production it is possible to obtain both quantitative and qualitative changes in the content of polyphenol compounds. This is caused by their uneven distribution throughout the fruit or, as in the case of flavonols, their almost exclusive concentration in some fruit part. The following polyphenolic acids were identified in the studied musts: m-coumaric, p-coumaric, ferulic, caffeic and chlorogenic. Also indentified were shikimic acid and two flavonols: kempherol and quercetin. The identified polyphenol compounds are typical for apples and have been determined by numerous authors [15, 16, 18, 28].

The results indicate that pulp processing had a manifest effect on the content in apple musts of m-coumaric, p-coumaric, ferulic, caffeic, chlorogenic and shikimic acids and of kempherol and quercetin (Fig. 3).

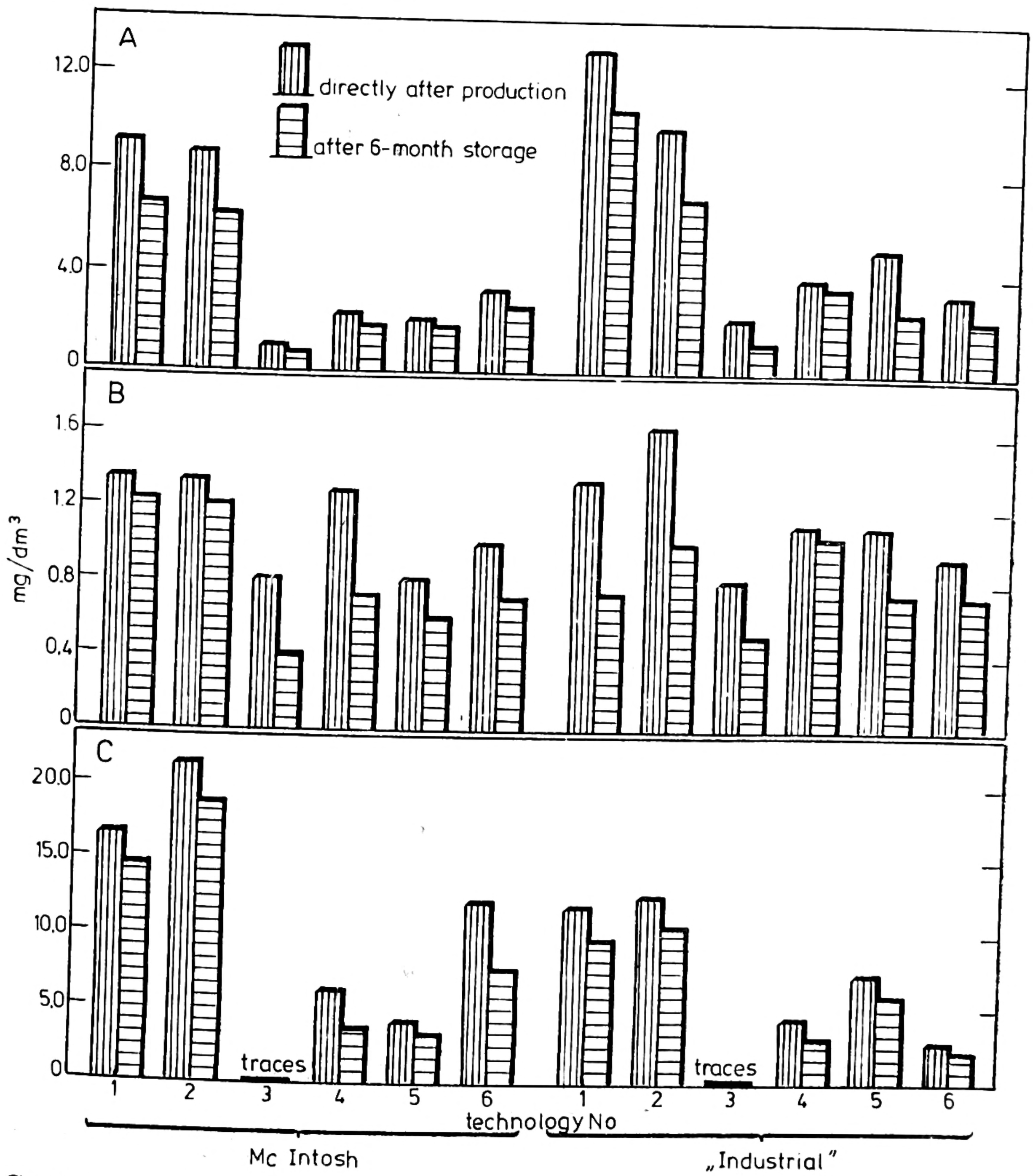

Fig. 3. Contents of ferulic acid (A), m-coumaric acid (B) and p-coumaric acid (C) in apple must depending on the applied technology

Whenever pulp depectinization was applied (technologies 1 and 2) the content of all the mentioned compounds, with the exception of chlorogenic acid (Fig. 4), was decidedly higher than in all other juice produced without depectinization. Pulp aeration (technology 3) had a markedly adverse effect on the content of these compounds in the apple juice.

Since polyphenolic acids derived from cinnamic acid occur in apples mainly as esters [23], the differences in their content in the verious juice may be also caused by the enzymatic hydrolysis of these combinations in the initial processing of the fruit. This would explain the higher contents of p-coumaric, ferulic and especially of caffeic acid in juice obtained by technology 5 (must depectinization) as compared to the content of these compounds in juice obtained with the use of technologies 4 (AA addition to disintegrated apples) and 6 (control).

After six-month storage of apple juice at room temperature the grea-

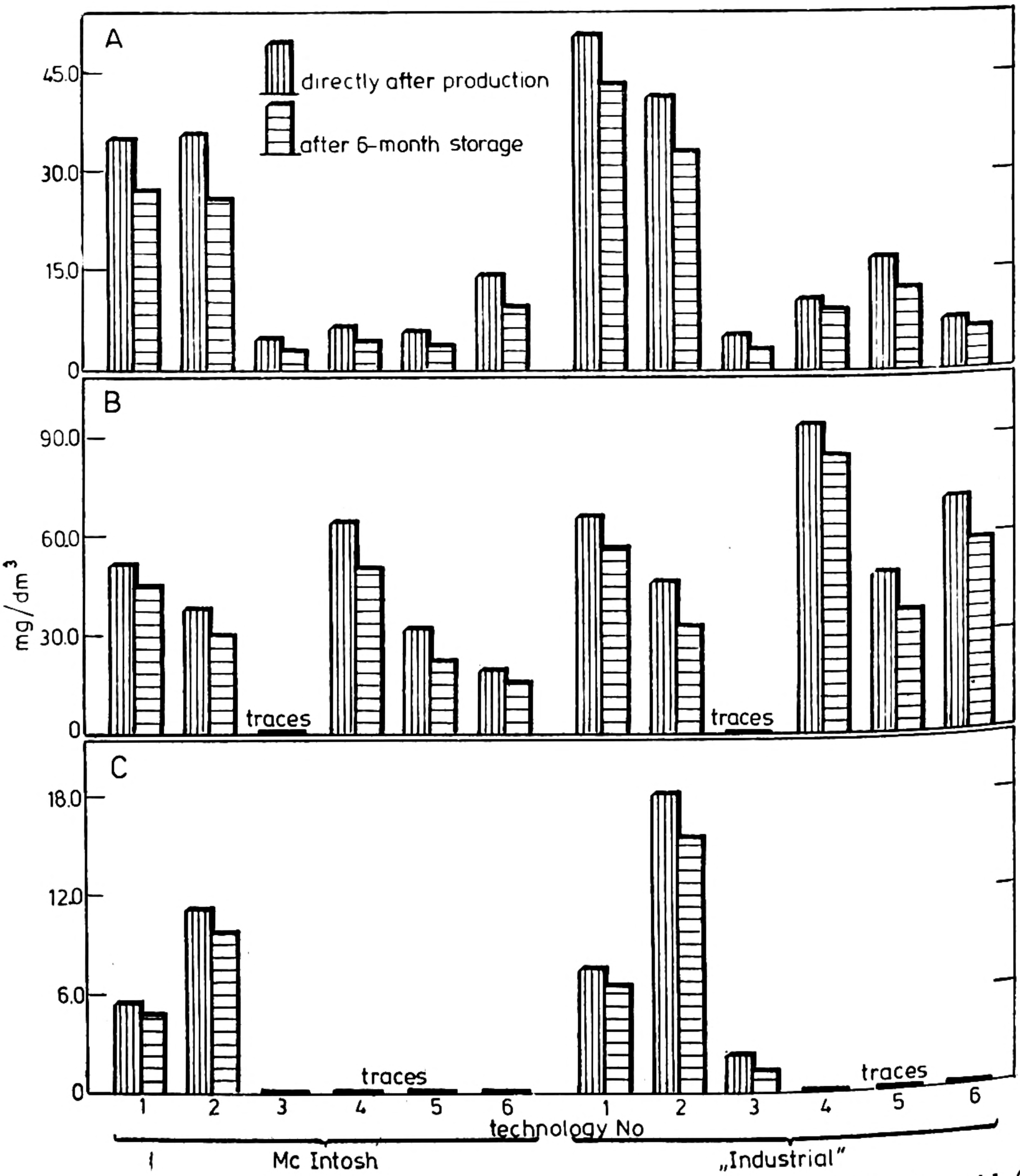

Fig. 4. Contents of caffeic acid (A), chlorogenic acid (B) and shikimic acid (C) in apple must depending on the applied technology

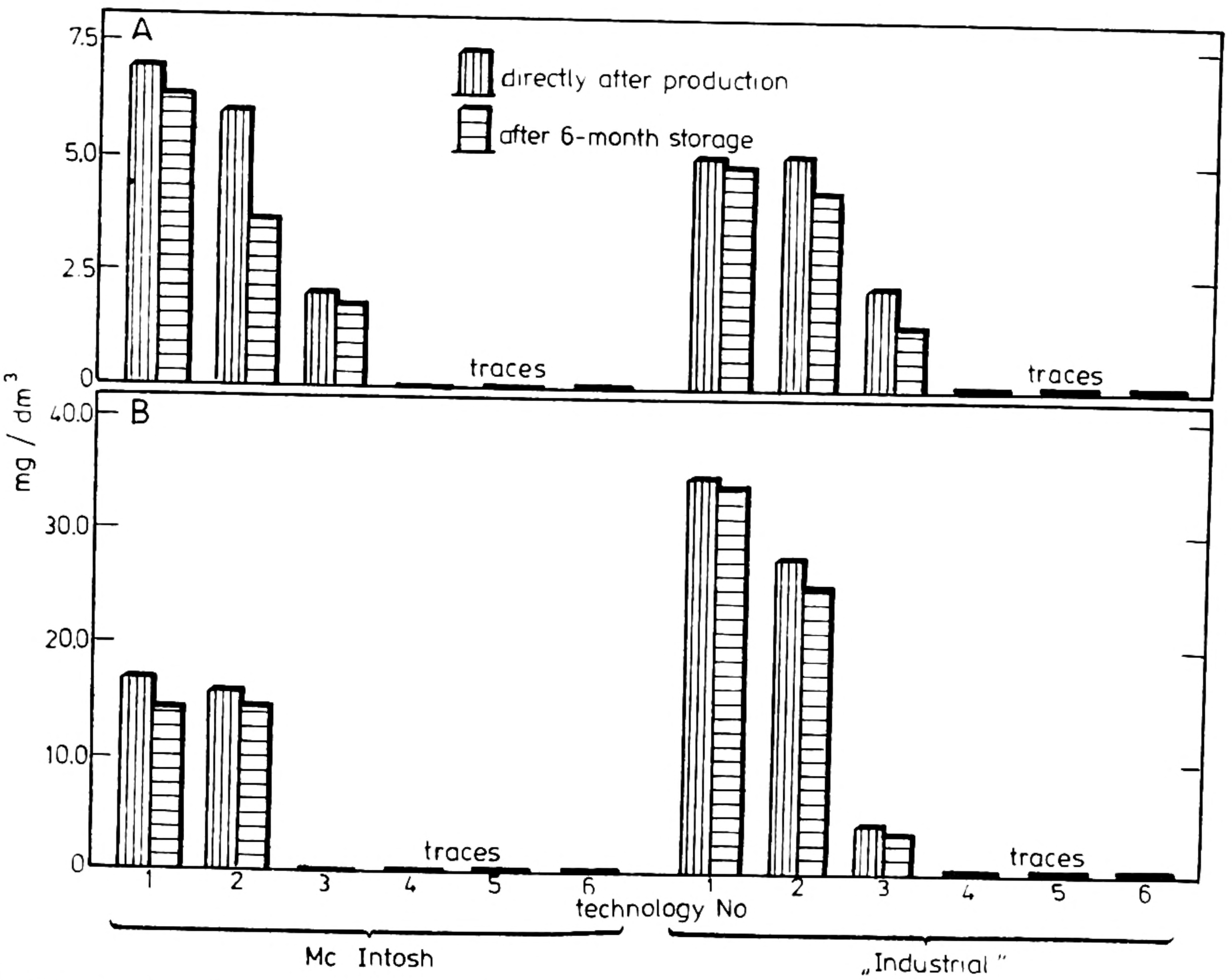

Fig. 5. Contents of kempherol (A) and quercetin (B) in apple must depending on the applied technology

test losses were observed in the case of catechins (30-60%) and leucoanthocyanidins (20-40%) (Fig. 2). The losses of these compounds in stored juice are due to chemical oxidation processes and the accompanying polymerization or condensation of the oxidized compounds [10, 15, 19].

The organoleptic analysis of the investigated apple juice revealed that their quality deteriorates mostly as a result of pulp aeration (technology 3) leading to substantial elimination of polyphenols from the juice and of ascorbic acid additions to disintegrated fruits (technologies 1 and 4) which in turn leads to the retaining of large quantities of these compounds in the juice. The highest marks for colour, ranging from 3.8 to 4.8 points, were given the golden-brown hue of juice produced by technologies 2 (pulp depectinization), 5 (juice depectinization) and 6 (control). The colour of juice obtained by technologies 3 (pulp aeration) and 4 (AA addition) were graded lowest. They were lightly coloured, and the juice produced according to technology 3 had a slight greenish tint; they received 2.0-3.0 points.

The lighter colour of the juice produced by technology 3 (pulp aeration) was due to the removal of a part of the polyphenol compounds from the removal of a part of the polyphenol compounds from the must already during pressing, and mainly during pasteurization of the must (precipitation from the solution). The juice obtained by technology 4 (AA addition) retained their light hue mainly because of the slight degree of exidation and polymerization of polyphenols of the catechin and leucoanthocyanidin groups present in the juice.

As far as the odour of juice is concerned, no differences as drastic as those of colour were found. Graded lowest were musts obtained by technology 3 (pulp aeration). It is worth noting that juice from "industrial" apples were graded lower than those from Mc Intosh apples.

Analysing the content of catechins, the natural dimeric and trimeric forms of which are responsible for bitterness while the polymeric forms account for tartness [1, 13, 14], we may say that the taste of the musts was graded highest when the content of these compounds in the juice ranged from 200 to 400 mg per dm^3. When they were almost completely absent (technology 3) the juice had what is known as an "empty flavour", but was excessively bitter and tart when these compounds were present in large quantities, as in juice produced by technologies 1 (AA addition + + pulp depectinization) and 4 (AA addition).

Table contains the results of organoleptic evaluation of apple juice produced in the fourth stage of study. As regards the individual polyphenols determined in the studied juice by gas chromatography, there was no significant dependence between the content of these compounds and the ratings of the various juice.

Table. Results of organoleptic evaluation of must obtained from Mc Intosh (A) and "industrial" (B) apples

Technology	Colour		Odour		Flavour	
	I	II	I	II	I	II
A						
1 (AA addition + pulp depectinization)	2.5	2.7	3.6	3.3	3.3	3.1
2 (pulp depectinization)	3.9	3.7	3.9	3.8	3.6	3.2
3 (pulp aeration)	2.1	2.0	3.3	3.1	2.4	2.2
4 (AA addition)	1.6	2.4	3.4	3.7	3.2	2.9
5 (must depectinization)	4.8	4.1	3.8	3.5	3.5	3.2
6 (control)	3.9	3.5	4.1	4.0	3.8	3.4
B						
1 (AA addition + pulp depectinization	3.3	3.5	3.5	3.2	2.7	2.5
2 (pulp depectinization)	3.8	3.7	3.8	3.7	3.5	3.3
3 (pulp aeration)	2.0	2.0	3.3	3.3	3.1	2.9
4 (AA addition)	1.9	2.5	3.0	3.4	2.0	2.0
5 (must depectinization)	4.6	4.3	3.8	3.6	3.6	3.5
6 (control)	3.4	3.5	4.1	3.9	3.9	3.8

I — directly after production; II — after six months of storage

CONCLUSIONS

1. Modifications of technology make possible a wide-ranging variation of the polyphenol fraction composition in apple juice.
2. Pulp aeration drastically reduces polyphenols content in apple juice.
3. Pulp depectinization and an addition of ascorbic acid to disintegrated apples markedly increase polyphenols content in apple juice.
4. The content of catechins, leucoanthocyanidins and chlorogenic acid in apple juice depends primarily on the protection of these compounds against oxidation.
5. Changes in the content of shikimic, m-coumaric, p-coumaric, ferulic, caffeic and chlorogenic acids as well as of kempherol and quercetin do not affect the organoleptic properties of apple must as profoundly as do changes in leucoanthocyanidins and catechins content.
6. It seems that the polyphenol compounds present in apple juice affect mainly the colour and taste, playing a slight role in odour "formation".
7. An excessive or insufficient content of polyphenols in apple juice has an adverse effect on its organoleptic features (mainly colour and taste).

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WPŁYW MODYFIKACJI PROCESU TECHNOLOGICZNEGO OTRZYMYWANIA MOSZCZU JABŁKOWEGO NA ZAWARTOŚĆ POLIFENOLI I WŁAŚCIWOŚCI SENSORYCZNE

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S t r e s z c z e n i e

Przeprowadzone badania dotyczyły wpływu: depektynizacji miazgi, depektynizacji moszczu, dodatku kwasu askorbinowego do rozdrabnianych jabłek oraz napowietrzania miazgi jabłkowej na zawartość związków polifenolowych w moszczach jabłkowych. W zależności od zastosowanej technologii moszcze jabłkowe zawierały: polifenoli ogółem (rys. 1) od ok. 300 mg/dm³ do ok. 2600 mg/dm³, katechin ogółem (rys. 2) od ok. 5 mg/dm³ do ok. 900 mg/dm³, leukoantocyjanidyn ogółem (rys. 2) od ok. 180 mg/dm³ do ok. 1700 mg/dm³.

W badanych moszczach metodą chromatografii gazowej określono ilościowo zawartość 7 związków polifenolowych. Stwierdzono występowanie kwasów: ferulowego (rys. 3) od ok. 0,5 mg/dm³ do 12 mg/dm³, m-kumarowego (rys. 3) od ok. 0,8 mg/dm³ do 1,6 mg/dm³, p-kumarowego (rys. 3) od ilości śladowych do ponad 20 mg//dm³, kawowego (rys. 4) od ok. 5 mg/dm³ do ok. 50 mg/dm³, chlorogenowego (rys. 4) od ilości śladowych do ponad 90 mg/dm³ oraz dwóch flawonoli: kemferolu (rys. 5) do ok. 7 mg/dm³ i kwerceryny (rys. 5) do ok. 35 mg/dm³. Występowanie flawonoli stwierdzono przede wszystkim w moszczach otrzymywanych wg technologii stosujących depektynizację miazgi. W moszczach tych stwierdzono również występowanie kwasu szikimowego (rys. 4) w ilości do 18 mg/dm³.

Otrzymywane moszcze jabłkowe poddawano ocenie organoleptycznej (tabela) oceniając barwę, zapach i smak. W zależności od stosowanej technologii produkcji moszcze jabłkowe uzyskiwały od 1,6 do 4,8 punktu za barwę, od 3,0 do 4,1 za zapach i od 2,0 do 3,9 za smak. Najniżej oceniane były moszcze otrzymywane wg technologii stosujących napowietrzanie miazgi lub dodatek kwasu askorbinowego do rozdrabnianych jabłek.

Sześciomiesięczny okres przechowywania moszczów w temperaturze pokojowej nie powodował istotnych zmian w ogólnej zawartości związków polifenolowych. Maksymalne straty nie przekraczały 15%. W przypadku indywidualnych związków polifenolowych straty dochodziły niekiedy do 50%.