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CONTRIBUTION OF SMOKE COMPOUNDS TO SENSORY, BACTERIOSTATIC AND ANTIOXIDATIVE EFFECTS IN SMOKED FOODS

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INTRODUCTION

Smoking as one of the preservation methods for food has its centuries-old history. However, in modern food technology the smoke-curing or smoke flavouring process has changed its main purpose and should be considered primarily as a flavouring operation.

In this lecture attention will be focused mainly on the sensory effects of smoke compounds and methods for their measurement, with only a brief review of bacteriostatic and antioxidative aspects.

CONTRIBUTION TO SENSORY EFFECTS

Wood smoke formed by pyrolysis of wood constituents is a very complex aggregate. Up to now, more than 300 substances have been isolated and identified (14) - many of them have also been quantitatively determined. All of them - or at least, their great part - can be considered as potential contributors to the flavouring effect in smoked products. According to recent knowledge phenols are mainly responsible for developing the typical, desirable aroma of smoked goods (9, 12, 13, 22, 23, 27), especially those phenols of medium boiling point (12, 27). Among these, quaiacol and eugenol are believed by some authors (12, 30), to play a leading role; others mention also siringol and 2,6-dimethoxy-methylphenol as important contributors of smoky flavour (25, 5, 18). Carbonyls and acidic compounds are supposed to play a minor role (12, 13). However, only very few experimental data are available confirming the above opinions (12, 37).

The "dual approach" to the problem

The difficulty of studying this problem is similar to that of investigations in other areas of flavour research. As is well known, the flavouring effect depends not only on the presence or absence of a certain compound (or compounds), but also on its concentration and interaction with accompanying substances in the smoke and/or in the smoked product (33). Moreover, no informative data can be obtained by instrumental analysis only simply because flavour is a psychophysiological phenomenon which cannot be investigated apart from human senses (2, 32). In studying the contribution of smoked compounds to sensory effects, the "dual approach", as was stressed by Prof. Tilgner is necessary in order to obtain informative results (33). This means that instrumental or chemical investigations must be accompanied by psychometric or sensory ones. The last means qualitative and quantitative characteristics of sensory responses to the large number of wood smoke components.

Correlation of instrumental and sensory data can provide meaningful information about important aroma and flavour contributors, as was successfully done in the other field of flavour research (29).

Since the methodological problems of GC and GC-MS analysis of smoke flavour compounds were presented in detail in the separate lecture (14), and paper submitted for the Symposium (30), more attention will be given here to psychometric (sensory) analysis of smoke and smoke compounds.

Three-dimensional characteristics of sensory phenomena and their measurements

The modern approach to studying odour or flavour properties of wood smoke and smoke flavourings and their single compounds, as well as smoked products, should take into consideration their three-dimensional characteristics: a) the quality, or the type of odour (or flavour), b) its intensity, and c) the hedonic response to the odour (or flavour), which means its characteristics expressed in the categories of liking or disliking. All above listed sensory "dimensions" are of course closely interrelated. The formula of theoretical relation between the intensity and hedonic response of odour has been proposed by Tilgner and Miler (36).

The determination of each of the above sensory characteristics requires a thorough, uniform preparation of samples and application of special analytical procedure followed by the statistical elaboration of experimental data.

In the preparation of samples for sensory testing, the diluting medium is of great importance. Threshold concentrations of smoke compounds and fractions determined in water can be up to 50 times lower than those determined in lard (38). Uniform and absolutely odourless testing glasses, and of temperature control, are other factors influencing sensory results (38).

Type of odour. For the characterisation of the type or quality of odour flavour for single smoke compounds or smoke fractions, the method of modified descriptive analysis can be applied, as shown in one of the papers submitted for the Symposium concerning the quality - intensity characteristics of Polish smoke flavouring and its fractions (3). It shall be noticed here, that qualitative characteristics change with changes of sample concentrations, which demonstrates the strong quality - intensity dependences.

Intensity. The intensity of odour sensation is obviously related to the concentration of the stimulus - in this case to the concentration of volatiles in the smoke sample, or the concentration of a single volatile substance when analysed separately. This relationship has been described using the Weber-Fechner formula for multicomponent mixtures, which can be of help in predicting the over-all sensory intensity of smoke odour for particular concentrations of separate phenolic fractions (3).

The absolute and difference thresholds are commonly used "units" for sensory characteristics of the odour intensity of smoke compounds and smoke fractions. It has been observed by analysing Polish smoke flavouring, that among three analysed phenolic fractions of different boiling points the highest intensity (lowest Th value) was shown by the fraction of the boiling point within the range up to 120^{o}C (3).

Th values are of great importance in combined instrumental - sensory investigation contribution of the smoke compounds to the smoky aroma and flavour, because the sensory effectiveness of a given smoke component cannot be expressed by its amount in ppm or ppb. A meaningful expression must be related to the threshold value.

The ratio of the amount of a substance in a given mixture determined by GC to the Th value of the substance has been taken as a measure of its sensory effectiveness and its contribution to the over-all aroma. The above ratio, called "coefficient of relative sensory importance", has been introduced and is quite commonly used in flavour research (32). Thus, a small amount of a compound of very low Th value can make more contribution to the over-all sensory impression than a great amount of a substance of very high Th value (32, 37).

According to the above, the large quantities of some volatiles found in wood smoke, smoke flavourings or smoked products do not necessarily mean their major contribution to an overall smoky aroma, as was suggested by Potthast (30).

The detailed study of threshold values Th_{abs} and Th_{diff} of the Polish smoke flavouring and its three phenolic fractions allowed analysis of experimental data in the light of the relationship of stimulus concentration and intensity of sensory response described by Weber-Fechner law. As a result, concentration - intensity curves were obtained for three smoke flavouring fractions and their contribution to the overall odour intensity was determined (3).

Hedonic. The third "dimension" of the sensory characteristics of the smoke and its components is a hedonic note. As has been observed, the hedonic note depends highly on the intensity of odour (24). The shape of hedonic-intensity curves is distinctive for a given compound or fraction. On the basis of the above relations the changes in hedonic note with a change of the intensity can be predicted. Mixing of two or more compounds or fractions caused not only changes in the intensity, but also in hedonic response to the smoky odour (24). A good agreement of experimental data with those calculated from the Tilgner and Miler formula (36) showed that the hedonic effect of mixing can also be predicted, which may be of practical importance in the production of smoke flavouring of predicted and desirable sensory characteristics.

The discussed studies show, that although the problem of the contribution of smoke compounds to the sensory effect is a very complex one, some steps have been made in preparing a background for the "flavourogy era" (33), which should assist in the wider use of fully engineered foods, among them also smoked products.

Conclusions

The above remarks on sensory aspects of smoke-curing and smoke flavouring of foods can be summarized as follows:

1. To learn the contribution of smoke compounds to sensory effect in smoked food, the "dual approach" of parallel instrumental and psychophysical (sensory) analysis is necessary. The correlation of these two can give an answer to the general question.

2. In the psychophysical approach such phenomenon as three-dimensional characteristics of odour and flavour (type, intensity, hedonic) and their interrelation should be considered and analysed in the light of known theoretical psychophysical laws.

3. A number of data from instrumental analysis and few results from psychophysical evaluation of smoke compounds have been collected now. Further extensive research in this field is needed.

CONTRIBUTION TO BACTERIOSTATIC AND ANTIOXIDATIVE EFFECTS

Although the sensory effect of smoking and applying smoke flavourings is of primary interest, two other effects, the bacteriostatic and antioxidative ones will also be considered.

It has to be remembered, that smoke compounds are multifunctional agents - they act simultaneously as flavourings, bacteriostatic and antioxidative factors. Thus, the concentrations in which they exhibit bacteriostatic and antioxidation properties are practically limited to the level at which they are acceptable for their flavouring effect.

Bacteriostatic effect

The bacteriostatic effect of smoking had been already observed by Shewan in 1949 on fish products. The growth rate of bacterial population during storage was compared in non-smoked and smoked fish, being much slower in the latter (31).

Many studies made since that time have given more information about the compounds and fractions exhibiting the strongest antibacterial effect. They are reviewed elsewhere (19).

It has been stated that phenolic fraction possess the highest inhibiting ability. Within this fraction, phenols of lower boiling point are more active (15, 16, 28). The other fractions, e.g. terpenes, show no antibacterial effect. What is more, there are some indications that the terpene fraction is not only bacteriostatically inactive, but it is acting as an antagonist to the phenolic fraction, lowering its bactericidal effect (28).

Phenols inhibit the growth of bacterial population by the prolongation of the lag phase, proportionally to their concentration in the body or in the products (4, 28), whereas the growth rate in the exponential phase remains unchanged - unless the concentration of phenols is very high (4, 15, 28).

Very interesting results have been obtained by Olsen in model tests using staphylococcus aureus as a testing strain (28). He has observed that addition of smoke flavouring containing predominant phenolic fraction in the concentration of 45 ppm results in similar effect on the prolongation of the lag phase to a reduction of the storage temperature from 20^{o}C to 10^{o}C. This observation may be of great practical importance. The inhibiting influence of the wood smoke and smoke flavourings on various type of microflora appeared to be very selective: high inhibiting effect on micrococcus was observed, whereas staphulococcus and lactobacillus were quite insensitive on the same concentration of smoke flavourings (28). The selective influence may change the natural environmental balance of common saprophytic microflora present in the products, resulting in an unexpected growth of these types of microflora, which normally is depressed by other accompanying types.

The yeast and mold microflora show a relatively high resistance to the inhibiting influence of smoke-curing and smoke flavouring additive at concentrations up to 60 ppm (4, 17).

As would be expected, smoke flavourings because of the higher concentration of phenols show generally higher bacteriostatic activity compared with the traditional smoke-curing process. The bacteriostatic effect of the two-stage generated wood was compared with that of smoke flavouring in the same concentration, processed according to a Polish patent (26). The last exhibited much stronger bacteriostatic effect, as was observed recently by Chomiak *et al.* (8).

Antioxidative effect

Since most foods to which the smoke-curing process is applied are fat-containing products, the antioxidative activity of smoke components must be considered as an important factor prolonging their shelf-life.

The phenomenon of antioxidative activity (a.a.) of the wood smoke has been observed as early as in 1933 by Lea in his classical experiments on smoked and unsmoked bacon (21). Further investigations showed, that again phenolic fraction is mainly responsible for a.a. effect - whereas other fractions, e.g. hydrocarbons, organic bases may even demonstrate opposite, pro-oxidative activity (11).

Among phenols those of higher boiling points had the more pronounced inhibiting effect on peroxide formation (11). The numerous earlier investigations concerning smoke constituents have been reviewed elsewhere (16, 19).

In the last ten years further remarkable progress has been made in learning the a.a. properties of the wood smoke, smoke flavourings and their single components (7, 20, 34) as well as in the analytical methodology of their determination (6, 7). The problem of the influence of smoke generation parameters on the composition of the wood smoke and its a.a. activity was an object of extensive investigation by Tilgner and Daun (34, 35). It has been observed, that the dispersed phase of the smoke generated over a range of the parameters pyrolysis and oxidation temperature and air supply demonstrates a strong a.a. effect - whereas the vapour phase has very low or no a.a. properties. The oxidation temperature in the two-stage generator seems to be a critical factor: the increase of oxidation temperature up to 400^{o}C was accompanied by a decrease of a.a. activity, parallel with the decreased ratio of phenolic fraction in the smoke (35).

Smoke flavourings as wood smoke condensates with purposely elevated ratio of phenolic fraction, achieved by removing ballast substances, are generally recognised as possessing high a.a. effectiveness (28, 7, 6). Like any other antioxidant, this effectiveness rises with the concentration of smoke flavouring. On the other hand it is known that some antioxidants can demonstrate a pro-oxidative effect when occurring in very high concentrations (1).

The question arose how will the phenols act in the commercial preparations of Polish smoke flavouring, which is prepared as 2% and 10% solutions in lard. The results of the study are presented in the paper of Chomiak and Goryn submitted to the Symposium (6). The authors have observed that within the investigated range of SF concentrations in the lard, only antioxidative effect was demonstrated. The a.a. activity showed curvilinear changes with the concentration, similar to the behaviour of BHA (6).

Concerning methodological questions, the authors noticed that the data expressed as protective indices depend strongly on the applied testing technique and on the quality grade of fat used as diluting agent. The last could be explained by assuming that the lards contain different amounts of naturally occurring antioxidants; no reasonable explanation can as yet be given for the first observation.

Other important methodological remarks were made by Tilgner and Daun, who observed that there is a possibility of destructive changes in the smoke composition during fractionation and analytical procedure when improper methods are used (35).

Conclusions

The following conclusions can be drawn concerning bacteriostatic and antioxidative effects of smoke-curing:

1. Wood smoke and smoke flavourings demonstrate some bacteriostatic and antioxidative effects in smoked foods. It is generally agreed, that for the same concentration of smoke compounds in the product, above effects are more pronounced when smoke flavourings are applied.

2. The phenolic fraction is mainly (or entirely) responsible for both effects. Within the fraction, separate chemical individuals demonstrate differentiated activity, related to their chemical structure and physical properties.

3. Since phenols present in the smoke are multifunctional agents - flavouring, bacteriostatic and antioxidative - the concentrations in which they show bacteriostatic and antioxidative properties are practically limited to the level at which they are acceptable for their flavouring effect.

FINAL REMARKS

This short review shows that smoke compounds cause many various effects in smoked products, among which flavouring must be considered a primary one. The flavouring effect is an extremely complex phenomenon; its investigation requires parallel instrumental and psychometric approaches in order to obtain meaningful results, helping to produce smoked foods of uniformly high consumer quality.

It is a great joint responsibility of food scientists and food technologists to produce smoked food which is not only absolutely safe from the toxicological point of view, but also fully acceptable by the consumers as a food giving psychological satisfaction and joy in eating.

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