

FORMATION OF FREE 3-MCPD DURING BARBECUEING OF MEAT

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Abstract – Grilled steaks were analyzed in respect to their contents of free 3-monochloropropane-1,2-diol (3-MCPD) using a newly developed analytical method consisting of pressurized liquid extraction (PLE), derivatization using phenylboronic acid, and GC/MS detection. Charcoal, gas, and an electric grill were used for grilling collars. Further parameters investigated were the pre-treatment of meat (untreated, salted, marinated with an oil marinade or an emulsion marinade), the use of aluminium grill trays, and a lid. For grilled steaks, contents of 3-MCPD in the range of <1 to 365 µg/kg (median: 16 µg/kg) were detected. The highest contamination was found for a steak pre-treated with an oil marinade, which was grilled on a charcoal grill with a closed lid. Consuming such a steak will exhaust the tolerable daily intake (TDI) of 2 µg/kg body weight for 3-MCPD to about 25%.

Key Words – 3-monochloropropane-1,2-diol, grilling methods, minimization strategies

I. INTRODUCTION

3-Monochloropropane-1,2-diol (3-MCPD), the best known member of the group of chloropropanols is a representative of heat-induced contaminants. The Scientific Committee on Food (SCF) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) defined a tolerable daily intake (TDI) of 2 µg/kg body weight (SCF, 2001).

For acid-hydrolyzed vegetable proteins (HVP) and soy sauce, maximum levels of 20 µg/kg for free 3-MCPD were established in Commission Regulation (EU) No 1881/2006. In order to ascertain if further maximum levels for other food groups need to be constituted, the EU member states are invited to analyze other food groups concerning their levels of 3-MCPD.

It has been known for many years now that grilling meat and meat products releases harmful

substances such as polycyclic aromatic hydrocarbons (PAH), heterocyclic aromatic amines, and N-nitrosamines (by heating of cured meat products). In addition to these well known contaminants, 3-MCPD can also be generated while grilling meat (Crews et al., 2001). It was found that while charcoal was smoldering, 3-MCPD was released only after vegetable oil was added to the combustion material (CVUA Stuttgart, 2006).

The aim of this study was to analyze the contents of free 3-MCPD in grilled meat, using charcoal, gas, and an electric grill (in a total of 38 grilling experiments). Other test parameters were the pre-treatment of meat (unsalted, salted, marinated with oil or emulsion marinade) and the use of an aluminum grill tray or a lid for charcoal grilling.

II. MATERIALS AND METHODS

The steaks (thickness: 13 mm) for two grilling experiments came from the same pork neck. For the 38 grilling experiments, a charcoal grill (One-Touch Premium; 57 cm), a gas grill (Typ Q 220 Premium), and an electric grill (TYP Q 140) from Weber-Stephen were used. For the marinated steaks, 8 g oil marinade “Würzöl Magic” and 10 g emulsion marinade “Marinox® Pink Pepper” from Raps were added per 100 g of meat, respectively, then, mixed and stored at 4 °C for 3-4 days. For the salted steaks, 1.1 g salt was added to 100 g meat and stored at 4 °C for 24 hours. After grilling, the same amount of salt relating to the weight of the raw material was added to the unsalted steaks. Six steaks were used for each grilling experiment. For the grilling experiments using an aluminium grill tray the six steaks were evenly distributed to the two grill trays. One grilling experiment was performed with 12 instead of six steaks (oil marinade: 6; emulsion marinade: 6).

The temperature sensor on the grill grate was fixed at the level for meat. For experiments with a grill tray, the sensor was fixed in the aluminium grill tray. Before charcoal grilling, about 80 briquettes of beech wood were lighted in a chimney starter. After 30-40 min the glowing charcoal was transferred to the charcoal grill and the grill grate was positioned. After reaching a constant temperature, the steaks were placed on the grill grate. For the grilling experiments using a lid the grilling process started after a constant temperature was reached under the cover. Only for turning the steaks was the lid opened for a short time.

The gas and electric grill were adjusted to the highest output. After a constant temperature had been reached, the steaks were put on the grill grate. During the grilling process the meat was turned over two or three times. The endpoint of grilling came after a uniform cooking level had been reached, resulting in different cooking times (between 5 and 21 min).

For the determination of 3-MCPD in grilled meat, a new analytical method, consisting of pressurized liquid extraction (PLE), derivatization with phenylboronic acid (PBA), and a subsequent analysis by gas chromatography in combination with high resolution mass spectrometry (GC/HRMS) was used.

III. RESULTS AND DISCUSSION

Considering all the grilling experiments without differentiating between the types of grills used or the pre-treatment of meat, no correlations between the mean temperatures on the level of the grill grate and the contents of 3-MCPD were ascertained. High temperatures above 300 °C indeed resulted in high contents of 3-MCPD above 250 µg/kg (grilling with a lid). However, at comparable temperatures, also lower contents of 3-MCPD in the range of 50 µg/kg were detectable. On the other hand, in two grilling experiments at lower mean temperatures in the range of 200 °C, also high contents of 3-MCPD above 100 µg/kg (grilling of 12 steaks) were observed. These findings suggest that the formation of 3-MCPD in the grilling process is a multivariate problem.

A direct comparison of the first and the second grilling experiments for steaks grilled with charcoal showed that, for most of the value pairs,

increasing temperatures were accompanied by higher contents of 3-MCPD and, consequently, a positive correlation was observed (Fig. 1).

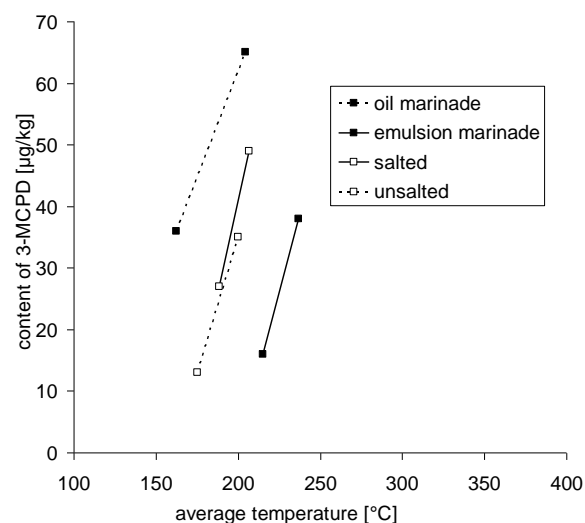


Figure 1 Contents of 3-MCPD [µg/kg] and average temperature [°C] for charcoal grilling

The contents of 3-MCPD in steaks prepared on electric, gas, and charcoal grill are shown in Tab. 1.

Table 1 Contents of 3-MCPD [µg/kg] in steaks prepared on electric, gas, and charcoal grill

	electric	gas	charcoal	charcoal/ grill tray
oil	4/5	49/36	36/65	47/46
marinade				
emulsion	8/11	45/54	16/38	30/14
marinade				
salted	16/<1	9/3	27/49	10/3
unsalted	<1/<1	11/<1	13/35	<1/7

Steaks prepared on an electric grill showed contents between < 1 µg/kg and 16 µg/kg. For steaks that had been salted after grilling, 3-MCPD was not detectable in either one of the two grilling sessions. The use of the oil- and the emulsion marinade as pre-treatment resulted in slightly higher 3-MCPD contents. In salted steaks, 3-MCPD contents of 16 µg/kg were detected in the first grilling session whereas in the second grilling session 3-MCPD was not detectable at all. Consequently, the risk of a contamination with 3-MCPD using an electric grill seems to be higher for salted steaks than for marinated steaks.

In gas grilled steaks the 3-MCPD contents were in the range of < 1 to 54 µg/kg. For marinated steaks,

significantly higher contents of 3-MCPD were detected than in salted or unsalted steaks. Between the two types of marinades, no significant differences regarding the formation of 3-MCPD were observed.

In comparison to steaks prepared on an electric grill, the marinated steaks prepared on a gas grill showed significantly higher contents of 3-MCPD whereas for salted steaks, contents of the same order of magnitude were observed.

The heating times for the marinated steaks for both types of grills were comparable. In addition, the electric grill and the gas grill did not show any differences concerning the mean temperatures at the level of the grill grate. However, as the distance between the grill grate and the heating coil on the electric grill (4 cm) was smaller than between the gas flame and the grill grate of the gas grill (6 cm), differences in the temperature of the heating medium were to be expected. This presumption was confirmed by temperature measurements of the gas flame ($> 850\text{ }^{\circ}\text{C}$) and at the heating coil (about $650\text{ }^{\circ}\text{C}$). Consequently, a correlation between the increase in the 3-MCPD level in marinated steaks prepared on a gas grill and the higher temperature of the heating medium seems to exist. A possible connection between the temperature of the heating medium and the 3-MCPD level of the grilled meat might be due to a formation of 3-MCPD from the salty and fatty marinade dropping into the gas flame. Afterwards, the 3-MCPD that had formed in the gas flame may most likely be transported particle-bound from the gas flame to the steak by the air.

The analyzed contents of 3-MCPD in charcoal-grilled steaks without using an aluminum grill tray were in the range of 13 to $65\text{ }\mu\text{g/kg}$. It was not possible to draw conclusions concerning any significant differences between the different methods of preparation due to the large variation in the analytical data.

For the gas-grilled steaks which were pre-treated with the oil marinade the contents of 3-MCPD were in the same range as observed for the charcoal-grilled steaks. In contrast, the use of the emulsion marinade seemed to result in lower 3-MCPD contents when using the charcoal grill as compared to the gas grill. However, it should be noted that the cooking loss for steaks pre-treated with the emulsion marinade was significantly higher for gas grilling (37-40%) than for charcoal

grilling (23%). Therefore, a similar formation of 3-MCPD resulted in different contents related to the wet weight. Steaks salted before grilling showed significantly higher levels of 3-MCPD using a charcoal grill compared to using a gas or electric grill. A comparable observation was made for unsalted steaks.

The higher contamination of salted and unsalted charcoal-grilled steaks compared to gas-grilled steaks applying comparable heating times might be due to the higher temperatures at the level of the grill grate. The increase in the temperature possibly leads to an increased formation of 3-MCPD on the surface of the grilled meat.

The contamination of marinated steaks may be caused by the marinade dropping on the glowing charcoal. However, higher levels of 3-MCPD would be expected for charcoal-grilled steaks compared to gas-grilled steaks. This was assumed as higher temperatures on the level of the grill grate for grilling with charcoal compared to grilling with gas were observed. The data obtained did not confirm this expectation which may be related to the shorter heating times using the charcoal grill compared to the gas grill.

The contents of 3-MCPD in charcoal-grilled steaks using an aluminium grill tray were in the range of $< 1\text{ }\mu\text{g/kg}$ to $47\text{ }\mu\text{g/kg}$. For salted and unsalted steaks, a reduction in the 3-MCPD level for using a grill tray was observed. This minimization was probably caused by a reduction in the meat juice dropping onto the glowing charcoal. On the other hand, the lower contents of 3-MCPD may be due to lower temperatures on the surface of the grilled meat. The 3-MCPD level of marinated steaks was in the same order of magnitude as it was observed for charcoal-grilled steaks without using an aluminium grill tray. Consequently, using a grill tray did not lead to a significantly reduced level of 3-MCPD in marinated steaks. Concerning the formation of 3-MCPD in this context, a reduced amount of marinade dropping onto the glowing charcoal was possibly compensated by the heating time being extended from 8 to 21 minutes.

Furthermore, charcoal-grilled marinated steaks were prepared with a closed lid. For steaks pre-treated with an oil marinade, high contents of 3-MCPD in the range of 282 to $365\text{ }\mu\text{g/kg}$ were detected. Although the use of a lid reduced the heating time from 8 to 5 minutes (oil marinade, charcoal grill without a grill tray), the 3-MCPD

level was about six times higher. Grilling steaks with an emulsion marinade and a closed lid resulted in 3-MCPD contents of 51 and 54 µg/kg. These values were only twice as high as observed for the comparable grilling experiment with an open lid. Grilling with a closed lid led to higher contents of 3-MCPD in the grilled meat compared to grilling with an open lid. A reason for this may be, on the one hand, an increase in the temperature at the level of the grill tray increasing the formation of 3-MCPD on the surface of the grilled meat. On the other hand, an unimpaired smoke outlet was not possible and, consequently, an increased deposit on the grilled meat of 3-MCPD containing smoke is conceivable.

Simultaneously grilling twelve instead of six steaks pre-treated with different marinades also led to high levels of 3-MCPD. For steaks pre-treated with an oil marinade, 327 µg 3-MCPD/kg were detected; for the steaks pre-treated with an emulsion marinade, 98 µg/kg were analysed. Consequently, a better utilization of the grill grate seemed to result in higher levels of 3-MCPD.

IV. CONCLUSION

The grilling experiments showed very different 3-MCPD levels depending on the pre-treatment of meat and the performance of the grill experiment. For grilling with a charcoal or a gas grill the risk of the 3-MCPD formation seems to be higher than for using an electric grill. The use of a lid in order to lower the heating times does not seem to be a reasonable approach for reducing 3-MCPD.

In order to establish strategies for a minimization of the formation of 3-MCPD during the grilling process, considerably more comprehensive and systematic grilling experiments need to be performed.

Regarding the uptake of 3-MCPD by the consumption of grilled meat, in the worst case, steaks with a 3-MCPD content of 365 µg/kg would be consumed. The consumption of such a steak (95g) would result in an uptake of 35 µg 3-MCPD. Therefore, a person weighing 70 kg would exhaust the TDI to 25%. Since the consumption of two steaks is not unusual, an exhaustion of the TDI of 50% is conceivable. It should be further noted that, so far, only the uptake of free 3-MCPD has been considered. However, 3-MCPD fatty acid

esters can also be formed during the grilling process (CVUA Stuttgart, 2011).

The contents of 3-MCPD esters in the samples of grilled collar were analyzed at MRI Detmold (Matthäus et al., 2011). It was observed that a maximum of about 900 µg 3-MCPD esters /kg fat (average fat content of 17%) were formed during the grilling process. The highest contents of bound 3-MCPD were detected in collar grilled with charcoal equaling the formation of the free 3-MCPD observed. The use of an aluminum grill tray resulted in decreasing the contents of 3-MCPD esters for all types of pre-treatment while this effect was not determined for the free 3-MCPD in marinated collar. A strict correlation between any of the contents of free and bound 3-MCPD in grilled collar cannot be concluded. For further systematic grilling experiments the formation of free 3-MCPD and 3-MCPD esters should be considered.

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