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Detection of Irradiation of Fat-containing Foods by On-line LC-GC-MS of Alkylcyclobutanones

Key words: Irradiation, Alkylcyclobutanones, Meat, Cheese, LC-GC-MS-coupling

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Introduction

In some countries, certain foods (e.g. meat, seafood, spices, dried fruits, and vegetables) are legally irradiated. Since such products might be exported into countries, which do not accept such treatment, analytical methods are needed to determine whether or not irradiation has been applied. These methods serve to prevent illegal imports, multiple irradiation of foods and should help to control compliance with labelling regulations.

Two chemical methods, i.e. the determination of volatile compounds (1) and of o-tyrosine, (2) as well as two physical methods, i.e. ESR-spectroscopy (3) and thermoluminescence, (4) are ready for routine analysis.

Irradiation of fat-containing foods forms volatile compounds useful as markers for the detection of irradiation. During irradiation, breaking occurs mainly in the α and ß position with respect to the carbonyl groups resulting in the alkanes$_{Cn-1}$ and alkenes$_{Cn-2:1}$. Also the acyloxygen bond is cleaved and this reaction results in the formation of 2-alkylcyclobutanones and aldehydes, containing the same number of carbon atoms as the parent fatty acid. Methods exist for the analysis of alkanes and alkenes, (5, 6) aldehydes, (5) and alkylcyclobutanones (7). As the previous method for determining alkylcyclobutanones was time-consuming (Soxhlet extraction during 6 hours, Florisil clean-up with 300 ml of solvent), a more rapid and specific method was developed for detecting dodecylcyclobutanone (DCB) formed from palmitic acid and tetradecylcyclobutanone (TCB) from stearic acid. HPLC isolated the alkylcyclobutanones from the raw fat extract. The fraction of interest was transferred on-line to GC. Because of the low concentrations, detection occurred by mass spectrometry (MS), using multiple ion detection (MID) of masses 98 and 112.

Experimental

Extraction of fat

To 30–50 g of homogenized tissue, mixed in a mortar with the same amount of anhydrous sodium sulfate, 100 ml of hexane were added in a 300 ml Erlenmeyer flask. After adding glass beads as boiling aids, the mixture was refluxed for 1 h, then cooled, the hexane decanted and filtered through anhydrous sodium sulfate. The hexane was removed on a rotary evaporator.

LC-GC-MS analysis

A fully automated LC-GC, Dualchrom 3000, was coupled to a MS QMD 1000, both from Carlo Erba/Fisons (Mailand). 20–50 µl of a 10% solution of fat extract in hexane were injected into a 100 x 4.6 mm i.d. LC column packed with silica gel Spherisorb SI (Stagroma, Wallisellen). Pentane/5% methyl-*tert.*-butyl ether (MTBE) at 400 µl/min was the mobile phase. An 800 µl fraction between 5 and 7 min containing the alkylcyclobutanones was transferred to GC through a loop-type interface. The LC-column was backflushed with 5 ml of MTBE immediately after starting the transfer.

A 30 m x 0.25 mm i.d. fused silica column was used, coated with a 0.12 µm film of PS-255 (a methyl polysiloxane from Petrarch Systems). The inlet pressure behind the flow regulator was 1.5 bar (helium), the oven temperature during transfer was 65 °C. The flow regulator delivered a flow of 1.5 ml/min. The vapour exit was closed 15 s after the end of eluent evaporation. Then the temperature was programmed at 5 °C/min from 160 to 220 °C. Finally the column was heated out at 280 °C for 5 min.

The MS was operated in the EI+ mode at 70 eV. The masses observed were m/e 98 and 112 for 0.5 s each with a span of 0.8 amu. The multiplier was at 700 V, the ion source temperature at 200 °C, and the electron current 100 µA.

Results and discussion

Figure 1 shows chromatograms of two cheese samples, one unirradiated and the other irradiated with 3 kGy. The detection limit was 0.05 mg/kg alkylcyclobutanone (8).

Chicken and liquid whole egg samples (nine coded samples of both products) from an interlaboratory test were analyzed with this method and gave similar results to those obtained using the proposed official alkylcyclobutanone methodology (9). The method was also used for the control analysis of 10 samples of Camembert imported from France. None of the latter samples was found to be

irradiated (see table 1). The detection limit is 0.05 mg/kg fat, corresponding to 0.5 kGy.

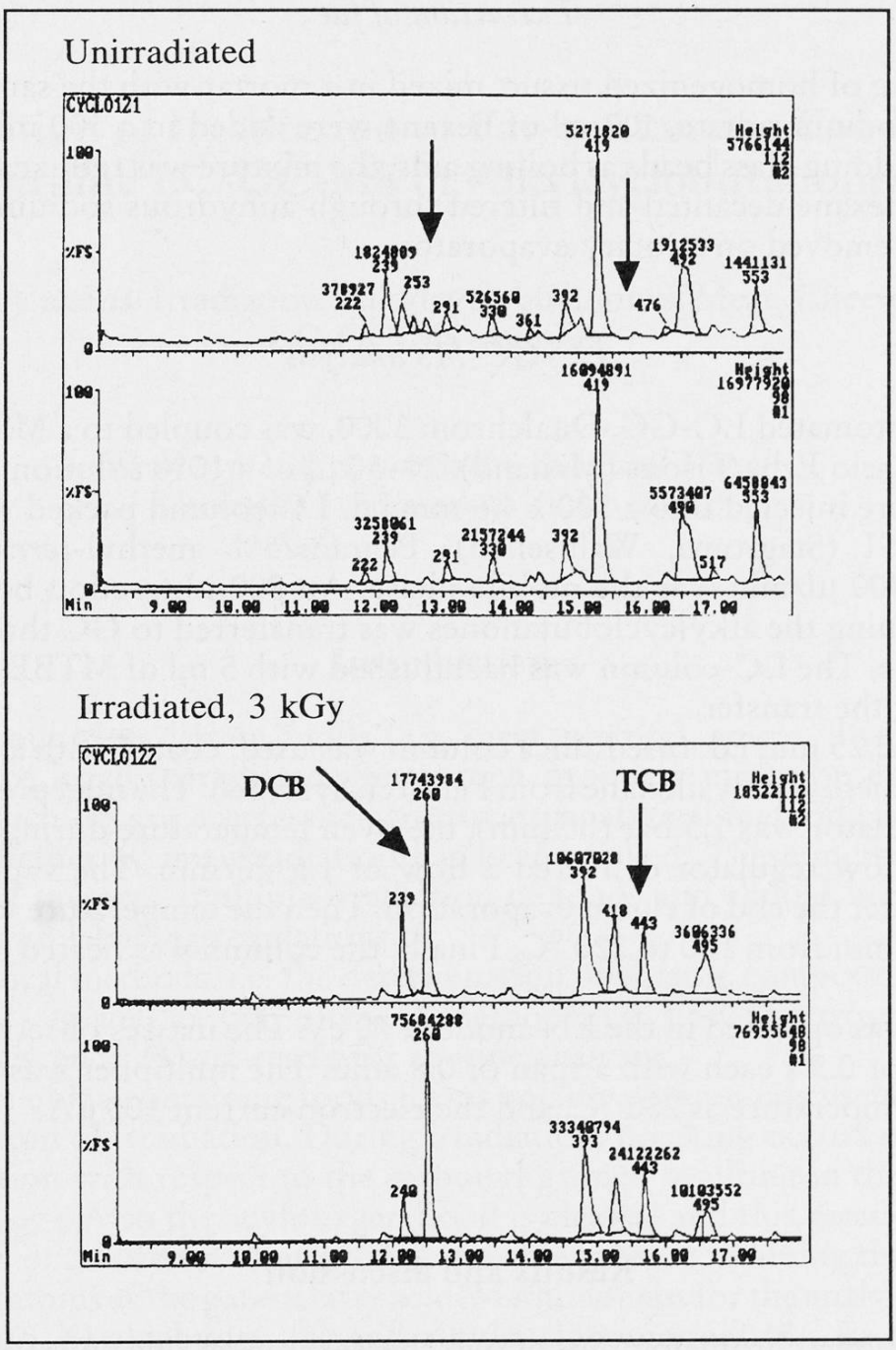

Fig. 1. LC-GC-MS spectra of Camembert

Summary

Alkylcyclobutanones, formed from fatty acids, can be used as markers for the detection of irradiated food. The fat from the food is extracted and injected onto an HPLC column. The fraction containing the alkylcyclobutanones is transferred to GC by concurrent eluent evaporation. The alkylcyclobutanones can then be detected by multiple ion detection (MID)

Table 1. Alkylcyclobutanones found in food in mg kg^{-1} fat

	Unirradiated	1 kGy	3 kGy
Chicken			
DCB	< 0.05	0.2–0.3	0.5–0.8
TCB	< 0.05	0.05–0.07	0.1–0.2
Eggs			
DCB	< 0.05	0.2–0.3	0.6–0.9
TCB	< 0.05	0.06–0.09	0.1–0.2
Cheese			
DCB	< 0.05	–	1.1
TCB	< 0.05	–	0.4

using the masses m/z 98 and 112. With this method doses of irradiation between 0.5 and 5 kGy, which are normally applied to meat and similar products for conservation, can be detected without any problem. The detection limit is 0.05 mg/kg fat, corresponding to 0.5 kGy, analyzing the alkycyclobutanones. The method is simpler, faster and less solvent consuming than previous methods.

Zusammenfassung

Alkylcylcobutanone, die aus Fettsäuren gebildet werden, können als Marker für den Nachweis einer Bestrahlung von Lebensmitteln verwendet werden. Das aus dem Lebensmittel extrahierte Fett wird auf eine HPLC-Säule gegeben und die Fraktion, welche die Alkylcyclobutanone enthält, wird mittels simultaner Eluentabdampfung auf die Gaschromatographiesäule transferiert. Die Alkylcyclobutanone werden durch massenspektrometrische Detektion (MID) der Massen 98 und 112 nachgewiesen.

Mit dieser Methode kann eine Bestrahlung zwischen 0,5 und 5 kGy, wie sie üblicherweise für Fleisch und weitere fetthaltige Produkte zur Anwendung gelangt, problemlos nachgewiesen werden. Die Nachweisgrenze für Alkylcyclobutanone beträgt 0,05 mg/kg Fett, dies entspricht einer Bestrahlungsdosis von 0,5 kGy. Die Methode ist einfacher, schneller und benötigt wesentlich weniger Lösungsmittel als bisher beschriebene Methoden.

Résumé

Les alkylcyclobutanones formés à partir d'acides gras peuvent être utilisés comme «marque» (Marker) pour prouver que les denrées ont été irradiées. La matière grasse qui a été extraite des denrées est injectée sur une colonne HPLC. La fraction qui contient les alkylcyclobutanones est transferrée simultanement par l'évaporation des eluents sur une colonne de chromatographie en phase gazeuse. Les alkylcyclobutanones peuvent être mis en évidence par la détection multiple de ion (DMI) en utilisant les masses 98 et 112.

Des doses d'irradiation entre 0,5 et 5 kGy appliquées lors d'une irradiation de viande et d'autres produits qui contiennent de la graisse, peuvent facilement être détectées par la présente méthode. La limite de détection pour les alkylcyclobutanones s'élève à 0,05 mg/kg

de graisse; ceci correspond à une dose d'irradiation de 0,5 kGy. La méthode est plus simple et plus rapide et elle nécessite beaucoup moins de solvent que les méthodes précédentes.

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