NOTE

Relationship between 3-Methyl-2,4-nonanedione Concentration and Intensity of Light-induced Off-odor in Soy Bean Oil

Takashi Sano1*, Maiko Iwahashi1, Jun Imagi1, Toshiro Sato1, Toshiyuki Yamashita2, Eiichiro Fukusaki1 and Takeshi Bamba2,3*

1 Fundamental Research Laboratory, J-Oil Mills, Inc. (7-41 Daikoku-cho, Tsurumi-ku, Yokohama-city, 230-0053, JAPAN)
2 Department of Biotechnology, Graduate school of Engineering, Osaka University (2-1 Yamadaoka, Suita-city, Osaka, 565-0871, JAPAN)
3 Division of Metabolomics, Research Center for Transomics Medicine, Medical Institute of Bioregulation, Kyushu University (3-1-1 Maidashi, Higashi-ku, Fukuoka-city, 812-8582, JAPAN)

Abstract: A beany and green off-odor is developed in soy bean oil (SBO) under light-induced oxidative conditions. 3-Methyl-2,4-nonanedione (3-MND) was inferred as the compound responsible for the off-odor. In this study, we designed a simple quantification method for 3-MND in SBO, and evaluated the relationship between the 3-MND concentration and the intensity of the off-odor. 3-MND was analyzed by GC/MS with a thermal desorption unit system. By our method, the 3-MND concentration was found to increase with storage days and the SBO content under light exposure, and there was a high correlation between the measured 3-MND concentration and the intensity of the light-induced off-odor in SBO (R = 0.9586).

Key words: 3-methyl-2,4-nonanedione, GC/MS, thermal desorption unit, soy bean oil, light-induced off-odor

1 INTRODUCTION

A beany and green off-odor originates from soy bean oil (SBO) under light-induced oxidative conditions. This phenomenon is peculiar to SBO among plant oils. The off-odor compounds have been speculated to be 2-pentylfuran and 2-pentenylfuran from linoleic acid and linolenic acid, or 3-methyl-2,4-nonanedione (3-MND) from furan fatty acids, but are yet to be identified.

Smouse et al. first identified that 2-pentylfuran, formed from linoleic acid, is an odor compound responsible for the light-induced off-odor in SBO and Ho et al. corroborated this observation. Min et al. proposed that 2-pentylfuran and 2-pentenylfuran are produced from linoleic and linolenic acids, respectively, by singlet-oxygen oxidation, and chlorophyll and light enhance these reactions. However, linoleic acid and linolenic acid are not present in SBO, corn oil, and canola oil in any significant amount. The content of linoleic acid is ~53% and that of linolenic acid is ~7% in SBO. In corn oil, the linoleic acid content is ~57%, and in canola oil, the linolenic acid content is ~10%. Although these values are higher than those in SBO, there is no or little light-induced off-odor generated from corn oil and canola oil. In addition, for hydrogenated SBO that contains reduced linoleic and linolenic acids, there was no reduction in the light-induced off-odor. These studies indicate that 2-pentylfuran and/or 2-pentenylfuran produced from linoleic and/or linolenic acid oxidation are not responsible for the light-induced off-odor.

Grosch et al. suggested that 3-MND was responsible for the off-odor. Using a stable isotope dilution assay, 3-MND concentrations in three samples of SBO stored for 30 days under daylight were quantified as 205, 721, and 1503 ppb. Since these values were above the odor threshold in the oil (23 ppb in Grosch’s study), they identified 3-MND as the compound responsible for the light-induced off-odor in SBO. In addition, they also reported that 3-MND was generated from furan-based fatty acids that exist exclusively in SBO. Kao et al. disagreed with the study because the 3-MND concentration derived from SBO under fluorescent light at 35°C was as high as 0.8 ppb, as analyzed by their dynamic headspace (DHS) analysis; this value was below the odor threshold values reported by...
The intensities of the light-induced off-odor in the samples were evaluated by three expert panels. The off-odor, beany and/or green odor, on the visual analog scale (10 cm). Fresh SBO was used as a negative control. The average distance from 0 to the scored point of the three panels was defined as the intensity of the off-odor.

3 RESULTS

3.1 Relationship among the number of storage days under a fluorescent lamp, 3-MND concentrations, and intensities of the light-induced off-odor in SBO

SBO was bottled into plastic bottles and stored under a fluorescent lamp at 1000 lx (room temperature). The 3-MND concentration was measured after 1, 3, 5, and 7 days (Fig. 1A). The 3-MND concentration in fresh SBO was 23.3 ppb. With light exposure, the 3-MND concentration in the SBO increased during storage, reaching 356.5 ppb after 7 days. The 3-MND concentration in SBO did not increase after 7 days’ storage in the dark.

The intensities of the light-induced off-odor in the samples were evaluated by three expert panels. The off-odor score also increased during storage under the fluorescent lamp (Fig. 1B). Under dark condition, however, the score did not increase even after 7 days’ storage.

3.2 Relationship among the ratio of SBO in canola oil, 3-MND concentrations and intensities of light-induced off-odor for samples stored under a fluorescent lamp

SBO was blended with canola oil at concentrations of
3-Methyl-2,4-nonanedione concentration and intensity of light induced off-odor in soy bean oil

0%, 20%, 50%, 80%, and 100%, and bottled into plastic bottles. These samples were stored under fluorescent lamp at 1000 lx (room temperature) for 7 days. After storage, the 3-MND concentration and intensity of the light-induced off-odor were evaluated. 3-MND concentrations increased with increasing SBO content (Fig. 2A). The light-induced off-odor score also increased in a dose-dependent manner (Fig. 2B).

3.3 Relationship between 3-MND concentration and light-induced off-odor score

The 3-MND concentrations and light-induced off-odor scores from sections 3.2 and 3.3 were plotted (Fig. 3). There was a high correlation between the measured 3-MND concentration and the intensity of the light-induced off-odor in SBO ($R = 0.9586$).

4 DISCUSSION

In this study, we report that the 3-MND concentration in SBO can be quantified using GC/MS coupled with a TDU system. This method only requires weighing the oil samples into micro vials, and no stable isotopes or special pretreatments are needed. By our method, the concentration of 3-MND in SBO was 356.5 ppb after 7 days under light exposure. This value was similar to the result from Grosch’s study$^7$: the average 3-MND concentration of three SBO samples was 810 ppb after storage under daylight for 30 days in their study, which indicates that our method is ap-
appropriately for measuring the 3-MND concentration in oil.

The analytical principle of the TDU used in this study is similar to that of the DHS used by Kao et al. previously, although they could detect almost no 3-MND in SBO. The main difference between the methods is the temperature for the evaporation of 3-MND from SBO. The 3-MND volatilization temperature in this study is 250 °C, whereas it was only 50 °C in their study. We also tried to quantitate the 3-MND concentration in SBO using the DHS system at an evaporation temperature of 100 °C; the value obtained was lower than 5 ppb (data not shown). These results suggest that temperatures >100 °C are needed to evaporate and quantitate the 3-MND generated by light-induced oxidation in SBO. Since the boiling point of 3-MND is 230.6 °C (as calculated by EPI Suite), a temperature higher than 230.6 °C is needed to fully evaporate 3-MND from the oil. Since the TDU system that we used this study could achieve a temperature of 250 °C, the 3-MND could be evaporated from the oil and detected.

The 3-MND concentration in the SBO increased during storage with light exposure, and also increased depending on the SBO content in canola oil. The 3-MND concentration in the SBO did not increase after storage in the dark. These results indicate that 3-MND is certainly generated by light-induced oxidation in SBO. That there was a high correlation between the measured 3-MND concentration and the intensity of the light-induced off-odor in the SBO in this study suggests that measuring the 3-MND concentration using our method could evaluate the intensity of the light-induced off-odor. However, it is still unclear whether 3-MND is the compound responsible for the light-induced off-odor in SBO. Further studies are needed to confirm that 3-MND is responsible for the off-odor.

5 CONCLUSION

To confirm the relationship between the 3-MND concentration and the intensity of the light-induced off-odor in SBO, we designed a simple quantitation method for 3-MND in SBO using GC/MS coupled with TDU. By our method, 3-MND is certainly generated by light-induced oxidation in SBO and there was a high correlation between the 3-MND concentration and the intensity of the light-induced off-odor in SBO.

References