学位論文内容の要旨

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学 位 論 文 題 目

Study on the Characteristic Oxidative Stability of Plant and Seaweed Lipids: Application to Halal Alternative Ingredients

（植物および海藻脂質の特徴的な安定性に関する研究：ハラル食品素材の開発を目指して）

Different chemical mechanisms are responsible for the oxidation of fats and oils during processing, storage, and cooking. Two types of oxygen, atmospheric triplet oxygen and singlet oxygen, can react with fats and oils. Triplet oxygen, having a radical character, reacts with radicals and causes autoxidation. The non-radical electrophilic singlet oxygen does not require radicals to react with; it directly reacts with the double bonds of unsaturated fats and oils with high electron densities, which is called type II photosensitized oxidation.

Plant leaves contain up to 7 % of lipid per dry weight. Major constituents which made up these lipids are monogalactosyl diacylglycerol (MGDG), digalactosyl diacylglycerol (DGDG) and sulfoquinovosyl diacylglycerol (SQDG). These constituents, collectively called Glyceroglycolipids (GL), made up the photosynthetic membrane (chloroplast; in the layers of the thylakoids) of higher plants, algae and bacteria. The fatty acid composition of each of these GLs have been proven to have unusually high in polyunsaturated fatty acid (PUFA) namely; α-Linolenic acid (18:3n-3) as the main fatty acid. In seaweeds, the main fatty acid composition comprise of Stearidonic acid (SA,18:4n-3), Arachidonic acid (AA, 20:4n-6) and Eicosapentanoic acid (EPA, 20:5n-3). All these PUFA are easily oxidized as they are structured in the chloroplast. Continual exposure to oxidative stress with involving in the absorbtion of light energy would surely exhaust the fatty acid through oxidation. However, instead of it being oxidized, the opposite response was found to happen. Protective mechanisms underlining this contradictory response are still being research upon.

On the same note, oxidation decreases consumer acceptability of foods by producing low-molecular-weight off-flavor compounds, as well as by destroying essential nutrients, and it produces toxic compounds and dimers or polymers of lipids and proteins. Oxidation of foods can be minimized by removing prooxidants such as free fatty acids, metals, and oxidized compounds, and by protecting foods from light.

The major objectives, as listed in **Chapter 1**, of the present study were:-

a) To determine and evaluate the lipid class, fatty acids and bis-allylic content
b) To establish and compare oxidative stability between Glyceroglycolipids (GL) and Triacylglycerol (TAG)
c) To analyze volatile compounds formed throughout the oxidation process

d) To assess the efficacy of Glyceroglycolipids (GL) with other compounds as a source of potential for halal ingredients in food

Chapter 2 reviews some background of the underlying studies pertaining to cell membranes, photosynthesis, thylakoids, chloroplast, glyceroglycolipids, oxidation and a brief understanding of the global 'Halal' scenario and basic of between Kosher and 'Halal' diet.

Chapter 3 is on the oxidative stability of glyceroglycolipids (GLs) namely monogalactosyl diacylglycerol (MGDG) and digalactosyl diacylglycerol (DGDG) from Spinach and Akamoku including Linseed triacylglycerol (TAG) were compared after being oxidized at 50 ^{o}C under the dark, in the first setting of oxidation analysis. Results from the analysis of oxygen consumption and the effect of polyunsaturated fatty acid (PUFA) composition, demonstrated that the Spinach DGDG had the highest oxidative stability followed by Akamoku DGDG, Akamoku MGDG, Spinach MGDG and Linseed TAG. The results however, were in dispute with the expected average number of bis-allylic positions of each GLs and TAG. DGDG constituents of GLs from both Spinach and Akamoku were more stable than their MGDG constituents. It was predicted that the stereochemistry configuration and assembly of the molecules might be most probably the main reason of the high in stability.

Chapter 4 utilizes the static headspace methods which is found to be an effective method in volatile analysis. This analysis was done in accordance to the same type of sample with was investigated in the previous chapter, chapter 3. Since the analysis involved 2 constituents of GL; both Spinach and Akamoku MGDG and DGDG, although in the previous chapter shows that DGDG is more stable as compared to the MGDG constituents, the volatiles formed in this chapter was in contrary much higher in the DGDG. All samples was especially analysed for the 5 major volatiles; 1) acrolein, 2) propanal, 3) pentane, 4) 1-penten-3-ol, 5) hexanal. Some distinct features was highlighted as all constituents of GL revealed to be very low and much reduced amount of acrolein as compared to Linseed TAG. Also especially in DGDG, some un-identified compounds were found which to be predicted as either impurities that might cause the sample to form a high amount of hexanal or this could either form as a result of the reaction of sugar breakdown (sugar moieties of GL) throughout the incubation. Overlapping peaks between acetone and propanal was also observed for all GL samples but a clear separation was observed in Linseed TAG. Volatile compounds was managed to be quantified but yet with many incomprehensible involve with the much complexity that DGDG is having.

Chapter 5 deals with a second setting of oxidation analysis, 6 types of lipids (only with Spinach MGDG and Linseed TAG with some samples mixed to medium chain fatty acid (MCT) in varying concentrations were compared under the same condition mentioned. Oxidative stability were compared with regard to bulk oil system and during the presence of spread and mixed molecules. Spinach MGDG with MCT 92 wt % managed to delay the oxidation process the most, followed by Spinach with MCT 67 wt %. Same goes to samples of Linseed TAG when added with MCT 92 % managed to delay oxidation process the most, followed by Linseed TAG when added with MCT 67 %. Oxidative stability of both GL and TAG in mix samples were shown to be much more stable as compared separately to their bulk oils system. By understanding the physical nature of how bulk oil influence lipid oxidation reactions, more effective ways in applying existing antioxidant ingredients and to new development of antioxidant technologies could be achieved.

Chapter 6 was also done in accordance to the setting of oxidation analysis from the previous chapter; Chapter 5. With still using the static headspace method in volatile analysis. Analysis involved only one constituents of GL; Spinach MGDG (variation of mixed samples with MCT and Linseed TAG (also in the same mix ratio). The volatiles formed in this chapter was in accordance to the oxidative stability; where Linseed TAG was found to have much volatiles forming. All samples was again analysed for the 5 major volatiles; 1) acrolein, 2) propanal, 3) pentane, 4) 1-penten-3-ol, 5) hexanal. All samples variation of Spinach MGDG retained its distinct features by having low and much reduced amount of acrolein as compared to Linseed TAG. Overlapping peaks between acetone and propanal was still observed for all Spinach MGDG samples and again a clear separation was observed in Linseed TAG. Volatile compounds was managed to be quantified with much ease unlike the complexity involved with DGDG. Another unique behavior of MGDG when mixed with considerable amount of MCT, was there could probably be some aggregates depending on the dilution factor (ratio) between them.

Chapter 7 finally access the effect of α-tocopherol in different concentration to the oxidative stability of both Spinach MGDG and DGDG and Linseed TAG. 9 samples was prepared; 3 variation mixed from Spinach MGDG, 3 variation mixed from Spinach DGDG and 3 variation mixed from Linseed TAG. 3 sets of result were evaluated as both GLs and the TAG have different response on the efficacy of α-tocopherol being an antioxidant and prooxidant. With having a low amount of α-tocopherol mixed to Spinach DGDG, resulted in elevated oxidative stability. On the other hand, with more α-tocopherol mixed to it, they exert antagonistic effect. Spinach MGDG slightly differ in the response. While both less and more amount of α-tocopherol mixed resulted in synergistic effect, the sample containing the least α-tocopherol has the most stability among this particular constituents. Last but not least, both much and less α-tocopherol when mixed with Linseed TAG, showed a higher in oxidative stability and it favors much α-tocopherol in order to exert the stability.