The Lipids of Tea

By TOYOMASA ANAN

Tea Technology Division, National Research Institute of Tea (Kanaya, Haibara, Shizuoka, 428 Japan)

Lipid is a compound with biochemical and food-chemical importance. Particularly, it is known that the lipid changes by heating or oxidation etc. during the course of processing and storage of foods, resulting in loss of amino acids¹⁰, browning⁸, and formation of bitter taste compounds¹⁴ or volatile compounds⁶, and these changes exert effects on food quality related mainly to food flavor. Therefore, it is necessary to examine tea lipids from that point of view.

With regard to the tea lipids, results of chemical analysis of seed lipid¹³⁾, polar lipid of leaves¹¹⁾, sterol of leaves⁹⁾, etc. as well as formation of flavor compounds from fatty acids during manufacturing black tea^{7,12)}, and changes of lipids during the storage of black tea¹⁵⁾ have been reported so far. As the author and his co-workers have clarified the kinds of lipids and fatty acids contained in tea shoots¹⁾, and examined differences in lipid contents caused by different growing conditions of tea shoots¹⁾, and changes of lipids occurring during manufacture and storage of green tea^{4,5)}, the results of these studies will be presented briefly.

Lipid composition of tea shoots and green tea

Analysis of lipids and fatty acids of tea shoots and green tea made it clear that those of tea shoots and green tea have the same composition. Namely, the lipids included neutral lipids such as triglyceride (TG), diglyceride (DG), free fatty acids (FFA), sterol ester (SE) and sterol (S), glycolipids such as monogalactosyl diglyceride (MGDG), digalactosyl diglyceride (DGDG), sterol glycoside (SG), and cerebroside (CE), sulfoglycolipids such as sulfoquinovosyl diglyceride (SQDG), and phospholipids such as phosphatidyl choline (PC), phosphatidyl ethanolamine (PE), phosphatidyl glycerol (PG), and phosphatidyl inositol (PI). The component fatty acids were palmitic acid (C_{16:0}), palmitoleic acid (C_{16:1}), stearic acid (C_{18:0}), oleic acid (C_{16:1}), linoleic acid (C_{18:2}), linolenic acid (C_{18:1}), etc.. In addition, a small amount of lauric acid (C_{12:0}), myristic acid (C_{14:0}), etc. was detected.

Differences in lipid content caused by different growth conditions of tea shoots

Tea quality differs considerably by different growth conditions of tea shoots, the material for producing tea. In case of green tea of Japan, the first crop, harvested in spring, is better in quality than the second and third crops harvested in the summer season, and, even with the same crop, tender shoots harvested early give better quality than hardened shoots harvested later. Therefore, relationship between lipid contents and different growth conditions of the shoots was examined. Samples used were shoots plucked at an early, a middle, and a late stage in each of the first crop season and the second crop season. Differences in content of major lipids were as shown in Table 1^{1} .

Total lipid content in the shoots plucked at a middle stage of the first crop season was 4.26% on dry weight basis, and glycolipids, phospholipids and neutral lipids accounted for 50, 30, and 20% of it, respectively. As to each

T-11 -1		First crop		S	econd crop	1
Lipid class	Early	Middle	Late	Early	Middle	Late
Total lipids	3.68	4.26	3.84	3.40	3.85	3.79
Total neutral lipids	0.73	0.78	0.86	0.74	0.92	0.97
Triglyceride	0.16	0.19	0.16	0.14	0.17	0.19
Sterol	0.32	0.36	0.41	0.32	0.43	0.41
Total glycolipids	1.60	2.17	2.13	1.75	2.06	2.23
Monogalactosyl diglyceride	0.59	0.82	0.85	0.66	0.77	0.85
Digalactosyl diglyceride	0.70	1.04	1.08	0.81	0.96	1.12
Total phospholipids	1.35	1.31	0.85	0.91	0.87	0.59
Phosphatidyl choline	0.66	0.72	0.51	0.50	0.47	0.34
Phosphatidyl glycerol	0.15	0.15	0.11	0.07	0.07	0.06

Table 1. Changes of lipid content in tea shoots during growth (% on dry weight basis)

Table 2. Changes of fatty acid content in tea shoots during growth (% on dry weight basis)

Zatta azila		First crop			Second crop		
ratty acids	Early	Middle	Late	Early	Middle	Late	
Total	2.05	3.40	3.23	2.13	3.39	3.23	
C16:0	0.53	0.82	0.71	0.56	0.76	0.72	
C16:1	0.01	0.02	0.03	0.01	0.03	0.03	
C18:0	0.04	0.07	0.07	0.05	0.08	0.10	
C18:1	0.15	0.31	0.24	0.15	0.30	0.27	
C18:2	0.49	0.86	0.70	0.56	0.81	0.64	
C18:3	0.83	1.32	1.48	0.80	1.41	1.47	

lipid class, it was shown that the majority of glycolipid was MGDG and DGDG, that of phospholipid was PC, and that of neutral lipid was S and TG. Although the total lipid content did not show an appreciable difference with different crop seasons, content of each lipid group was changed: more amount of phospholipid in the first crop season and slightly more amount of glycolipid and neutral lipid in the second crop season. The total lipid content changed with growth stages of shoots similarly for two crop seasons: it increased in an early half of the growth stage and then decreased to some extent in the later half. As to each lipid group, glycolipids increased in the early half, and remained almost without change, but phospholipids decreased slightly in the early half and considerably in the later half, while neutral lipids increased slightly with the growth of shoots. As to individual lipids, MGDG and DGDG increased, while each of phospholipids decreased.

Changes in fatty acids are shown in Table 2^{11} . The total fatty acid content of shoots plucked at the middle stage of the first crop season was 3.40% on dry weight basis: 40, 25, and 25% of which were C_{18:3}, C_{16:0} and C_{18:2}, respectively. Fatty acids which constitute major lipids were examined with a result that C_{16:0} accounted for more than 50% of each of the neutral lipids, while MGDG and DGDG of glycolipid contained a particularly large amount of C_{18:3}, and each of phospholipids contained a plenty of C_{16:0} and C_{18:2}. C_{16:0} was found specific to PG.

The total fatty acid content changed not much with crop seasons, and its change with the growth stage was similar for both crop seasons. Namely, the contents of the total fatty acid as well as $C_{16:0}$ and $C_{16:2}$ increased considerably in the early half of shoot growth, followed by slight decrease in the later half, while $C_{18:3}$ increased slightly in the later half

22.33	Content (% of dry weight)				
Lipid class	S-1	S-2	S-3	S-4*	
Total lipids	4,46	3.86	3.01	2.69	
Total neutral lipids	0.75	0.83	0.72	0.75	
Triglyceride + Free fatty acids	0.08	0.08	0.09	0.07	
Sterol + Diglyceride	0.36	0.37	0.31	0.31	
Total glycolipids	2.19	1.78	1.26	1.08	
Monogalactosyl diglyceride	0.81	0.71	0.60	0.48	
Digalactosyl diglyceride	0.57	0.44	0.30	0.27	
Sulfoquinovosyl diglyceride	0.57	0.43	0.22	0.19	
Total phospholipids	1.52	1.25	1.03	0.86	
Phosphatidyl choline	1.07	0.90	0.76	0.63	
Phosphatidyl glycerol	0.16	0.15	0.12	0.07	
Phosphatidyl ethanolamine	0.16	0.10	0.08	0.07	

Table 3. Changes of lipid content during manufacture of green tea

* S-1; Fresh tea shoots, S-2; Crude green tea, S-3; Green tea prepared by heating at 130°C for 30 min, S-4; Green tea prepared by heating at 170°C for 30 min.

after a considerable increase in the early half of shoot growth.

Changes of lipids during manufacturing green tea

It has been known that hexanal and trans-2-hexenal are formed from C18:2 and C18:3 in the manufacturing process of black tea^{7,12}, but the present author examined changes of lipids during the manufacturing of green tea. In the green tea manufacture in Japan, at first the crude green tea is produced, and then treated by Hiire (firing: heating at a definite condition) aiming at giving a specific taste and flavor by heating, and a good storableness. The crude green tea is also heated at a higher temperature to produce Hojicha (roasted green tea) which possesses stronger flavor and taste by heating. To examine changes of lipids in these processes, 4 different samples were used, i.e. fresh shoot (S-1), crude green tea (S-2), crude green tea heated at 130°C for 30 min (S-3 which corresponds to green tea after Hiire), and that heated at 170°C for 30 min (S-4, which corresponds to roasted green tea). Changes in content of major lipids are given in Table 32). As compared with S-1, the total lipid content of S-2 was decreased to 85%, that of S-3 to 70%, and S-4 to 60%. As to each lipid group, glycolipid and phospholipid decreased considerably, while neutral lipid was relatively stable. As to individual lipids, it was observed that DGDG and PC decreased in parallel to the decrease of the total lipid content, but MGDG and SQDG decreased more remarkably. Particularly, SQDG showed the greatest decrease; S-2 was 75%, and S-3 and S-4 were only $35\sim40\%$ of that of S-1.

Changes in fatty acid content are shown in Table 4^{3}). The total fatty acid content of S-2 was decreased to 80% of that of S-1, and that of S-3 and S-4 was 70% of S-1. As the content of individual fatty acids decreased in parallel to the total fatty acid content, the composition ratio of them was kept almost unchanged.

To make clear the changes of fatty acid component by lipid groups, the lipids were subjected to silicic acid column chromatography to separate them into chloroform fraction (CH fraction) containing neutral lipids, aceton fraction (AC fraction) containing glycolipid except SQDG, and methanol fraction (ME fraction) containing phospholipids and SQDG. The results showed that the CH fraction hardly changed in content during the manufacturing, while the AC and ME fractions decreased, particularly the ME fraction

Fatty acids		Content (% fof dry weight)				
	S-1	S-2	S-3	S-4*		
Total	4.03	3.31	2.80	2.98		
C16:0	0.86	0.69	0.57	0.62		
C16:1	0.04	0.03	0.03	0.03		
C18:0	0.06	0.05	0.04	0.04		
C18:1	0.32	0.26	0.22	0.25		
C18:2	0.87	0.71	0.59	0.63		
C18:3	1.88	1.57	1.35	1.41		

Table 4. Changes of fatty acid content during manufacture of green tea

* S-1, S-2, S-3, S-4; The same as shown in Table 3.

to more or less greater extent.

Changes of lipids during the storage of green tea

It was reported¹⁵⁾ with black tea that contents of lipids and $C_{16:0}$, among the fatty acids, increased during storage. Content of lipids in green tea stored at 25°C for 0, 3, 6 and 18 months was examined. The result with major lipids is shown in Table 5⁴⁾. The total lipid content was decreased by 10% after 3 months of storage, and by 20% after 6 months, but only a little by further storage. Of the lipid groups, glycolipids showed the greatest decrease amounting to 15% after 3 months and 30% after 6 months, while both neutral lipids and phospholipids decreased by 10% and 15% after 3 and 6 months of storage, respectively. As to individual lipids, MGDG, DGDG, SQDG, and PC showed remarkable decreases, particularly SQDG showed the greatest decrease: 25% and 50% decrease after 3 and 6 months, respectively.

Changes of fatty acid content are given in Table 6^{5}). The total fatty acid content decreased by 10% and 15% after 3 and 6 months, respectively, followed by a small decrease by further storage. Changes of fatty acid content in each of the CH, AC, and ME fractions were of the same extent as the change of the total fatty acid before the fractionation.

As described above, changes of lipids in growing shoots, and those during the manufacturing and storage of green tea were

field sleep	Content (% of dry weight)			
Lipid class	А	В	С	D*
Total lipids	3.96	3.52	3.07	3.03
Total neutral lipids	0.78	0.71	0.66	0.65
Triglyceride + Free fatty acids	0.10	0.07	0.08	0.08
Sterol + Diglyceride	0.41	0.39	0.36	0.33
Total glycolipids	1.76	1.50	1.24	1.20
Monogalactosyl diglyceride	0.60	0.52	0.42	0.41
Digalactosyl diglyceride	0.79	0.66	0.54	0.53
Sulfoquinovosyl diglyceride	0.21	0.15	0.12	0.11
Total phospholipids	1.42	1.31	1.17	1.18
Phosphatidyl choline	0.90	0.81	0.73	0.74
Phosphatidyl glycerol	0.28	0.28	0.24	0.26
Phosphatidyl ethanolamine	0.20	0.19	0.16	0.15
* Storage period at 25°C: A: 0 month	R. 3 months	C: 6 m	onthe D 18	monthe

Table 5. Changes of lipid content during storage of green tea

Fatty acide	Content (% of dry weight)				
Fatty acids	Α	В	С	D*	
Total	3.14	2.84	2.61	2.61	
C16:0	0.64	0.58	0.55	0.53	
C16:1	0.02	0.02	0.02	0.02	
C18:0	0.05	0.05	0.04	0.04	
C18:1	0.24	0.22	0.21	0.20	
C18:2	0.67	0.61	0.57	0.56	
C18:3	1.52	1.36	1.22	1.26	

Table 6. Changes of fatty acid content during storage of green tea

* A, B, C, D; The same as shown in Table 5.

studied. Further problems such as effects on tea quality like flavor, etc. have to be studied in the future.

References

- Anan, T. & Nakagawa, M.: Studies on the lipids of tea leaves. I. Changes in lipid content and fatty acid composition of tea leaves during growing period of the first and second flushes. J. Jpn. Soc. Food Sci. Technol., 24, 305-310 (1977) [In Japanese with English summary].
- Anan, T. et al.: Changes in lipid content during manufacture of green tea (Studies on the lipids of tea leaves, Part II). (Under contribution to J. Jpn. Soc. Food Sci. Technol.) [In Japanese with English summary].
- Anan, T. et al.: Changes of fatty acid content during manufacture of green tea. (Under contribution to J. Jpn. Soc. Food Sci. Technol.) [In Japanese with English summary].
- Anan, T. et al.: Changes in lipid content during storage of green tea. (Under contribution to *Tea Res. J.*) [In Japanese with English summary].
- 5) Anan, T. et al.: Changes in the content of fatty acids during storage of green tea. (Under contribution to *Study of Tea*) [In Japanese with English summary].
- Forss, D. A.: Role of lipids in flavors. J. Agr. Food Chem., 17, 681-685 (1969).
- Gonzalez, J. G., Coggon, P. & Sanderson, G. W.: Biochemistry of tea fermentation;

Formation of t-2-hexenal from linolenic acid. J. Food Sci., 37, 797-798 (1972).

- Homma, S. et al.: Studies on the browning of Kori-tofu. Part II. Changes of the ether extractable fraction of Kori-tofu during browning process. Agr. Biol. Chem., 33, 876– 883 (1969).
- Khanna, I., Seshadri, R. & Seshadri, T. R.: Sterol and lipid components of green *Thea* Sinensis. Phytochemistry, 13, 199-202 (1974).
- 10) Lien, Y. C. & Nawar, W. W.: Thermal interaction of amino acids and triglycerides. Valine and tricaproin. J. Food Sci., 39, 917-919 (1974).
- Roberts, G. R.: Polar lipid composition of the leaves and seeds from the tea plant (*Camellia sinensis L.*). J. Sci. Food Agr., 25, 473-475 (1974).
- 12) Saijyo, R. & Takeo, T.: The importance of linoleic acid and linolenic acid as precursors of hexanal and trans-2-hexenal in black tea. *Plant & Cell Physiol.*, 13, 991–998 (1972).
- 13) Sengupta, C., Sengupta, A. & Ghosh, A.: Triglyceride composition of tea seed oil. J. Sci. Food Agr., 27, 1115-1122 (1976).
- 14) Sessa, D.J., Warner, K. & Honig, D.H.: Soybean phosphatidylcholine develops bitter taste on autoxidation. J. Food Sci., 39, 69-72 (1974).
- 15) Stagg, G.V.: Chemical changes occurring during the storage of black tea. J. Sci. Food Agr., 25, 1015-1034 (1974).

(Received for publication, July, 2, 1982)