

✿ Fatty Acid Composition of Lipid Classes in Oils from Peanuts Differing in Variety and Maturity

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ABSTRACT

Oils from three varieties of mature peanuts and from one variety at seven physiological maturity stages were extracted with petroleum ether and fractionated into lipid classes. The fatty acid composition of the whole oils and fractions were then determined. The fractions from the Starr variety generally contained more 16:0 and 18:2 and less 18:1 than those from the Florunner and Florigiant varieties. Long chain fatty acids (C20-C24) were generally more predominant in the *sn*-1,3-diacylglycerol fraction than in other fractions, and only traces of long chain acids were found in the *sn*-1,2(2,3)-diacylglycerol fraction. An unusual compound associated with the *sn*-1,3-diacylglycerol fraction was detected by GLC. Fatty acid compositions of classes in the different maturity stages showed that, generally, the concentration of 18:1 increased and that the concentrations of all other fatty acids decreased with maturity.

INTRODUCTION

Peanut harvests consist of seed differing in physiological maturity, and the overall quality of a harvest is related to the maturity of the bulk of the seed. A previous study (1) demonstrated that the oils from three major commercial varieties of mature peanuts did not differ substantially in

relative weight distributions of lipid classes, but that distribution of lipid classes was affected by peanut maturity. Others have shown that the total fatty acid composition of peanut oil is related to overall quality (2-4). The total fatty acid composition of a large number of peanut varieties has been determined and found to vary with variety (3,5-8), environment (5-8), and maturity (6,9). The various findings mentioned above, therefore, suggest that the fatty acid compositions of the various lipid classes might be different in oils from different varieties of peanuts and from peanuts differing in maturity. Only few studies on the composition of fatty acids in lipid classes have been made. Worthington (9) examined triacylglycerols from cotyledons and embryonic axes of Virginia Bunch 67 peanuts at four different maturities. Senn (10) examined phosphatide and triacylglycerol fractions of peanut oil and found substantially different fatty acid compositions.

As part of an ongoing investigation to identify factors that affect the stability and quality of peanut oil, this report details the fatty acid composition within classes of lipids in peanut oils. The oils were extracted from three major varieties of mature peanuts and from one variety at different stages of physiological maturity.

TABLE I

Fatty Acid Composition of Various Lipid Classes in Petroleum Ether-Extracted Starr, Florunner, and Florigiant Peanut Oil^a

Variety	Lipid class	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
		Mole %							
Starr	TG	14.1	3.3	44.6	32.1	1.5	0.8	2.7	0.9
	FFA	21.0	4.2	40.4	29.9	1.2	0.4	2.2	0.8
	<i>sn</i> -1,3-DG	17.7	3.8	48.2	22.9	1.5	1.2	3.4	1.3
	<i>sn</i> -1,2(2,3)DG	15.5	2.5	48.9	33.1	—	—	—	—
	MG	17.9	2.4	46.5	27.8	0.8	0.8	2.4	1.4
	PL	22.3	3.6	44.8	24.6	0.8	1.0	1.6	1.2
	WO	14.0	2.6	43.9	34.2	1.3	0.8	2.5	0.8
Florunner	TG	11.4	2.3	51.9	28.5	1.2	1.2	2.4	1.2
	FFA	16.9	3.0	45.0	30.1	1.1	1.2	1.9	0.8
	<i>sn</i> -1,3-DG	13.8	2.6	51.5	25.1	1.2	1.6	2.4	1.4
	<i>sn</i> -1,2(2,3)DG	13.6	1.5	48.6	36.3	—	—	—	—
	MG	16.1	3.3	47.9	27.4	0.7	0.6	3.2	0.8
	PL	21.3	3.4	45.1	28.9	—	—	0.7	0.7
	WO	11.0	1.8	51.7	29.9	1.0	1.1	2.4	1.1
Florigiant	TG	11.2 (11.3) ^b	3.5 (2.8)	52.7 (53.9)	26.6 (26.4)	1.5 (1.3)	0.9 (0.8)	2.3 (2.1)	1.2 (1.2)
	FFA	16.1 (19.5)	3.9 (3.8)	46.6 (45.0)	28.2 (26.9)	1.6 (1.3)	1.0 (0.7)	1.9 (1.9)	0.7 (0.8)
	<i>sn</i> -1,3-DG	13.2 (13.9)	3.9 (3.2)	52.1 (53.3)	22.2 (22.6)	2.4 (1.4)	1.7 (1.0)	3.4 (2.6)	1.2 (1.8)
	<i>sn</i> -1,2(2,3)DG	12.6 (12.9)	2.2 (1.7)	48.9 (52.6)	35.8 (32.4)	— (—)	— (—)	0.3 (0.2)	0.3 (0.2)
	MG	16.7 (18.4)	4.4 (3.6)	48.4 (47.1)	26.8 (27.7)	0.8 (—)	— (—)	2.3 (3.6)	0.6 (—)
	PL	22.1 (21.5)	3.8 (2.7)	42.8 (41.0)	29.0 (32.8)	0.4 (—)	— (—)	1.0 (0.4)	0.9 (0.9)
	WO	11.0 (11.2)	2.8 (2.9)	54.3 (53.1)	27.2 (27.4)	1.3 (1.3)	0.9 (0.8)	2.0 (2.1)	0.8 (1.1)

^aAll values are the means of three replicate analyses. TG = triacylglycerol; FFA = free fatty acid; DG = diacylglycerol; MG = monoacylglycerol; PL = polar lipid; WO = whole oil.

^b() = Oil extracted with chloroform/methanol (2:1, v/v).

MATERIALS AND METHODS

Source of materials, physiological maturity stages, lipid extraction techniques, and TLC were as described previously (1), except that butylated hydroxytoluene (0.1% BHT in petroleum ether) was added and/or sprayed (0.02% in petroleum ether) onto TLC plates when applicable to insure minimum autoxidation. Lipid samples eluted as classes from the TLC plates were immediately esterified for gas chromatography. Fatty acids of the various lipid classes were converted to their methyl esters with BF_3 methanol (14% w/v) (Applied Science Laboratories, Inc.), according to Morrison and Smith (11), except that toluene was substituted for benzene in the mixture of methyl alcohol/benzene/ BF_3 methanol (11:4:5). The methyl esters in chloroform were injected into a Hewlett Packard Model 5840A gas chromatograph equipped with a flame ionization detector. The stainless steel (3.17 mm x 1.83 m) column was packed with 5% DEGS-PS on 100/120 Supelcoport (Supelco, Inc.). The carrier gas was helium at 30 ml/min and the column was operated isothermally at 200 C. Fatty acids were identified with appropriate standards, and percentages were determined by digital integration and normalization of peak areas. The accuracy of the system was verified by analysis of National Heart Institute-type fatty acid standard KD.

RESULTS AND DISCUSSION

The fatty acid composition of triacylglycerol, free fatty acid, *sn*-1,3-diacylglycerol, *sn*-1,2(2,3)-diacylglycerol, monoacylglycerol and polar lipid fractions, and of whole, petroleum ether-extracted oil of conventionally harvested Starr, Florunner, and Florigiant varieties are shown in Table I. A comparison of the fatty acids of lipid classes in oil extracted with chloroform/methanol (2:1, v/v) is provided for the Florigiant variety. Florunner and Florigiant varieties were similar in fatty acid composition within classes; however, Starr generally contained higher percentages of 16:0 and lower percentages of 18:1 than either of the others. The fatty acid composition of triacylglycerols approximated that of whole oil as expected since triacylglycerols constituted ca. 97% of the oil by weight (1).

Diacylglycerol fractions differed substantially from other fractions. The *sn*-1,2(2,3)-diacylglycerols contained only trace amounts of the long chain fatty acids (C20-C24). Previous investigations (12-14) on the stereospecific structure of peanut triacylglycerols indicated that long chain fatty acids are confined primarily to the *sn*-3 position. Thus, according to the fatty acid profile, the *sn*-1,2(2,3)-diacylglycerol fraction consisted mostly of *sn*-1,2-diacylglycerol. In direct opposition to the *sn*-1,2(2,3)-diacylglycerol fraction, the *sn*-1,3-diacylglycerol fraction contained proportionally more total long chain fatty acids than any other fraction examined. The fatty acid composition of this fraction also fits the stereospecific pattern of peanut triacylglycerols (12-14), if the long chain acids are in fact at the *sn*-3 position. Although isomerization cannot be completely discounted, the diversity in fatty acid composition of the two diacylglycerol fractions is significant since 1,2-diacylglycerols are generally regarded at the precursors of triacylglycerols.

A second difference between the two diacylglycerol fractions is that the *sn*-1,3-diacylglycerol fraction contained an unusual compound (A), as shown in Figure 1. In fact, no other fraction contained this compound; however, small quantities of a compound with a similar GLC elution time were found in the whole oil. TLC of the methylated *sn*-1,3-diacylglycerol fraction separated the compound from the fatty acid methyl esters, and for this reason percentages of

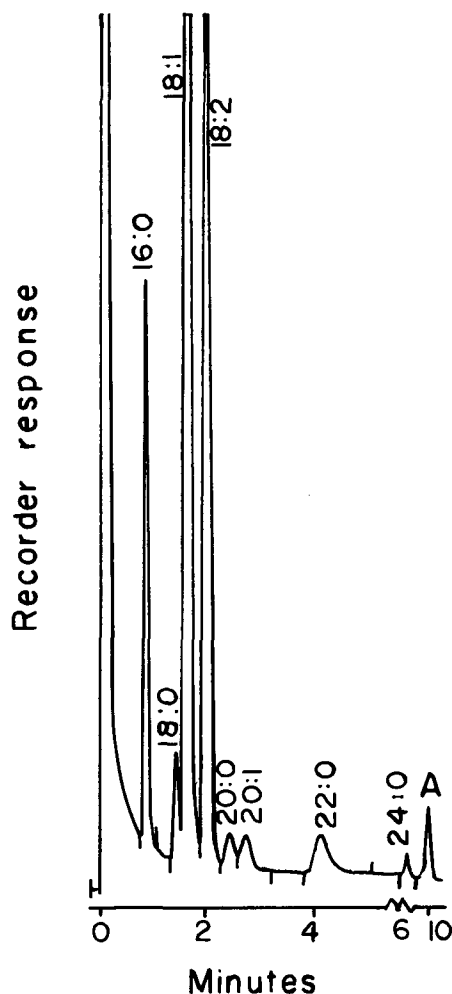


FIG. 1. Gas liquid chromatogram of peanut oil fatty acids and unknown (A) from the methylated *sn*-1,3-diacylglycerol fraction. (3.17 mm x 1.8 m 5% DEGS-PS column operated isothermally at 200 C).

the compound are not included in the tables. Since the compound is found in quantity in only one lipid fraction, it is unlikely that it is an artifact of the methylation procedure. The compound has been isolated in almost 99% purity, as determined by GLC. Identification is in progress and may provide some indication of attachment to the *sn*-1,3-diacylglycerol or cochromatography with it during class separation on TLC. The compound was also present in the *sn*-1,3-diacylglycerol fractions of corn and soybean oils, and, if warranted, a report on the compound will be published later.

The monoacylglycerol fractions of the three varieties were similar, as were the polar lipid fractions. Polar lipids from each variety contained the highest percentages of 16:0 of any fraction examined. Senn (10) reported an average of almost three times as much 16:0 in phospholipids as triacylglycerols in an unidentified Virginia-type peanut oil. The comparison of petroleum ether-extracted and chloroform/methanol-extracted fractions indicates little difference in fatty acid profile, although the more polar solvent extracted quantitatively more of this fraction (4).

Fatty acid compositions of various lipid classes isolated from Florunner peanuts differing in physiological maturity (15) are presented in Tables II-VI. An average harvest of peanuts consists mainly of seed at stages 10, 11, and 12 (increasing distinct brown splotches on internal pericarp), with less amounts of seed at stages

9 (few tan splotches in internal pericarp), and 8-7 (white internal pericarp). At stages below 7, peanuts shrivel to such a degree that they are normally eliminated by conventional harvesting practices. Peanut oil is composed mostly of triacylglycerol; and throughout the maturity stages examined, the fatty acid composition of the triacylglycerol fraction was seldom more than 1% different from that of the whole oil. Changes in the fatty acid composition of triacylglycerols with changes in maturity (Table II) generally followed trends reported in whole oil in other studies (6,9). The concentration of 18:1 increased, whereas the concentrations of nearly all the other fatty acids decreased slightly. As noted previously by Worthington (9), the greatest change other than 18:1 occurred in 22:0.

The trend for the free fatty acid fraction (Table III) was similar to that for the triacylglycerols, but the free fatty acids contained slightly more 18:1 and 20:1 acids and less 22:0. Except for 20:1, the concentrations of long chain fatty acids were generally less than those found in the triacylglycerol fraction.

In the early maturity stages, the *sn*-1,3-diacylglycerol

fraction (Table IV) contained high percentages of long chain fatty acids, except 24:0. These percentages decreased with maturity until at stage 12 they were similar to percentages found in the triacylglycerol fraction. Increases in 18:1 percentage followed a similar trend in all the fractions examined. The unusual compound described earlier in the *sn*-1,3-diacylglycerol fraction appeared to increase with maturity although variation among replications was considerably higher than that for fatty acids in this fraction (data not presented). Of the fractions examined, the *sn*-1,2(2,3)-diacylglycerol fraction (Table V) contained the lowest percentage of long chain acids. The percentage of 18:2 found in this fraction was relatively high when the seeds were immature but decreased as the seed matured. At stage 12, percentage of 18:2 was well below that normally found in the triacylglycerol fraction. The percentage of 18:1 was higher in the *sn*-1,2(2,3)-diacylglycerol fraction from mature seed than in any other fraction. The value of 63.2 mole percent does not agree well with data for Florunner in Table I; however, many factors such as growing year and location, and storage and oil extraction methods may have influenced composition.

TABLE II

Effect of Maturity on Fatty Acid Composition of Triacylglycerol in Florunner Peanut Oil

Maturity stage	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
	Mole %							
6	16.6	2.3	41.7	28.6	1.3	1.8	5.9	1.6
7	14.4	2.0	44.8	28.6	1.4	1.9	5.2	1.5
8	13.0	1.9	45.9	31.1	1.2	1.7	3.5	1.6
9	12.4	2.0	47.7	31.1	1.2	1.4	2.6	1.6
10	12.4	2.0	49.9	29.3	1.1	1.3	2.4	1.7
11	12.6	2.0	50.3	29.2	1.1	1.2	2.3	1.3
12	13.2	2.3	50.7	28.3	1.3	1.1	2.1	1.1

TABLE III

Effect of Maturity on Composition of Free Fatty Acids in Florunner Peanut Oil

Maturity stage	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
	Mole %							
6	17.5	1.9	46.4	29.2	0.7	2.9	1.0	0.4
7	14.3	1.9	55.0	24.1	0.7	2.8	0.7	0.4
8	13.0	2.0	51.8	28.4	0.8	2.5	0.9	0.6
9	12.3	2.0	52.0	29.1	0.9	2.1	0.9	0.6
10	12.7	2.2	52.1	28.2	1.0	1.8	1.2	0.8
11	12.5	2.1	52.6	28.1	1.0	1.8	1.1	0.7
12	13.3	2.5	52.6	27.2	1.1	1.5	1.1	0.6

TABLE IV

Effect of Maturity on Fatty Acid Composition of *sn*-1,3-Diacylglycerols in Florunner Peanut Oil

Maturity stage	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
	Mole %							
6	8.9	3.1	46.1	25.6	2.9	5.6	6.8	0.9
7	10.2	2.1	54.4	24.9	1.4	3.7	2.2	0.9
8	9.7	2.4	52.5	26.4	1.7	4.3	2.2	0.9
9	10.6	1.9	53.4	27.5	1.5	2.9	1.4	0.8
10	11.7	2.1	55.4	25.3	1.0	2.0	1.7	0.9
11	12.4	2.1	54.9	24.7	1.1	2.0	1.8	1.0
12	12.5	2.2	55.4	25.1	1.1	1.6	1.7	1.1

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TABLE V

Effect of Maturity on Fatty Acid Composition of *sn*-1,2(2,3)-Diacylglycerols in Florunner Peanut Oil

Maturity stage	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
	Mole %							
6	18.3	1.6	37.1	39.9	—	1.1	1.1	0.8
7	14.6	1.6	49.1	31.9	0.2	1.2	0.7	0.6
8	14.3	1.7	45.2	37.0	—	0.8	0.4	0.6
9	13.0	1.5	48.2	36.3	—	0.5	0.2	0.3
10	12.9	1.3	58.2	26.8	—	0.3	0.2	0.3
11	13.4	1.3	61.4	23.3	—	0.2	0.3	0.1
12	13.2	1.5	63.2	21.4	0.1	0.2	0.2	0.2

TABLE VI

Effect of Maturity on Fatty Acid Composition of the Polar Lipid Fraction in Florunner Peanut Oil

Maturity stage	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
	Mole %							
6	23.8	2.1	35.3	32.9	0.7	2.3	2.1	0.8
7	17.6	2.0	51.3	23.2	0.9	2.6	1.3	1.0
8	15.3	2.0	51.2	26.5	0.7	2.0	1.3	1.0
9	15.1	1.8	52.7	26.3	0.5	1.9	0.9	0.8
10	15.4	1.8	56.8	23.3	0.6	1.0	0.8	0.7
11	15.9	1.7	58.3	20.6	0.7	1.2	1.0	0.7
12	17.6	2.0	59.3	18.9	0.3	0.7	0.6	0.5

Trends in the fatty acid composition of the monoacylglycerol fraction followed those of other fractions. For stage 12 the fatty acid percentages of the monoacylglycerol fraction were similar to that of the *sn*-1,2(2,3)-diacylglycerol fraction, although slightly higher in long chain acids.

At all stages of maturity, the polar lipid fraction contained a greater percentage of 16:0 than any other fraction; and at stages 11 and 12, contained the lowest percentage of 18:2 found.

These data indicate that composition and quality studies on peanuts in broad maturity groups and harvested lots are actually observations on a composite of several physiologically distinct seed types. Peanut seed size of a given lot of peanuts fits a logistic distribution. This distribution shifts with peanut crop maturity, which indicates a high correlation of seed size with maturity (16). The results of this study imply that quality factors used by the industry can be correlated to seed size and other physiological properties of the peanuts.

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