The Linolenic Acid Content of Peanut Oil

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ABSTRACT AND SUMMARY

Oils prepared from eight peanut cultivars grown in four locations were analyzed for linolenic acid (18:3) content by gas liquid chromatography. Columns packed with either OV 225 or butanediol succinate provided excellent separation of 18:3 from major fatty acids and from trace constituents exhibiting retention times suggestive of 19:0 and 19:1. Average linolenic acid values for cultivars ranged between 0.03 and 0.13 weight percent of total fatty acids.

INTRODUCTION

It is generally recognized that the fatty acid distribution pattern of an oil or fat provides useful evidence of authenticity and in some cases may be used to detect adulteration. The Food and Agriculture Organization/World Health Organization Codex Alimentarius Committee on Fats and Oils has agreed upon a range of values for each fatty acid in ten commercial fats and oils (1). The values specified for arachis (peanut) oil indicate that this oil should contain <1.0% linolenic acid, a maximum value that is high in view of the available evidence.

The content of linolenic acid (18:3) in edible oils is of considerable importance because of its effect on oil flavor and oxidative stability, and the level of this acid in peanut oil has been the subject of conflicting reports. Dam et al. (2) were unable to detect linolenic acid in peanut oil by alkali isomerization. In an investigation of the fatty acid content of several oils by gas liquid chromatography (GLC) on diethylene glycol adipate (DEGA), diethylene glycol succinate (DEGS), and butanediol succinate (BDS) columns, Graig and Murty (3) found eicosenoic (20:1) but not linolenic acid in peanut oil. These workers observed that methyl linolenate has an emergence time coincidental with methyl eicosenoate on DEGS columns and that this liquid phase is therefore unsuitable for the analysis of oils containing both these acids. Iverson et al. (4) fractionated peanut oil methyl esters with urea and confirmed the presence of eicosenoic acid by GLC and chemical techniques but did not detect linolenic acid. Worthington and Holley (5) examined oils from seven genetically diverse peanut cultivars and reported <0.1% (0.02-0.04%) linolenic acid.

In order to unambiguously demonstrate and quantitate linolenic acid in oils that also contain arachidic (20:0) and eicosenoic acid, it is necessary to choose GLC liquid phases with polarity characteristics that permit elution of the C18 series of fatty acid methyl esters prior to elution of the C20 series. Diethylene glycol succinate and other polyester liquid phases of similar polarity are frequently used in the analysis of fatty acid methyl esters but these phases do not adequately separate linolenic from arachidic and eicosenoic acid esters. Thus eicosenoic acid, and less frequently arachidic acid, are sometimes misidentified and reported as linolenic acid in the analysis of peanut oil. A recent paper (6) reported values for eicosenoic and linolenic acid in peanut oil but not for arachidic acid, although arachidic acid was first isolated from arachis oil by Gössman in 1854 (7).

In establishing the identity of fatty acids of seed oils it is also essential that the oils be extracted from mature seed of good quality in the laboratory in which the analyses are to be made. Commercial oils may suffer from contamination during refining and handling.

In addition to genetic factors it is generally recognized that environment, particularly temperature during seed formation, can modify the fatty acid distribution pattern of oil from a given variety of a species, and that in some cases these values may vary considerably with geographic area of production (8). This report presents evidence that authentic peanut oils contain less than ca. 0.15% linolenic acid and that this value is not greatly influenced by geographic area of production.

EXPERIMENTAL METHODS

Seed of known varieties of peanuts were obtained from the three principal areas of production within the U.S. (Georgia, Oklahoma, North Carolina) and from Malawi, Africa. Oils were prepared in the laboratory by Carver press or by extraction with a 2:1 mixture of chloroform and methanol. Methyl esters were prepared by transesterification with 3% sulfuric acid in a 3:1 mixture of methanol and benzene. In some cases recovery tests were made by adding sufficient trilinolenin (99+%, Hormel Institute, Austin, MN) to oil prior to transesterification to give final levels of 0.28 and 0.80% linolenic acid. Methyl esters were separated on 185 x .4 cm glass columns packed with either 10% butanediol succinate (BDS) or 4% OV 225 on 70/80 mesh Chromosorb W (AW) (DMCS). Analyses were performed with a MicroTek 220 gas chromatograph equipped with dual flame ionization detectors. Peak areas were measured with an Infotronics CRS-100 integrator and values are reported as weight percent of total fatty acids. The performance of the system was monitored with Fat and Oil Reference Mixture Number 3 recommended for the analysis of peanut oil (9).

Methyl esters were separated according to degree of unsaturation on silver nitrate thin layer plates prepared by the procedure of Galanos et al. (10) and developed in 85:15 hexane-diethyl ether. The plates were examined under UV light after spraying with the dye solution of Jones et al. (11).

RESULTS AND DISCUSSION

Methyl linolenate is clearly and unambiguously separated from the major fatty acid methyl esters of peanut oil on either OV 225 (Fig. 1) or BDS (Fig. 2) columns. The polarity of OV 225 is such that saturated and monoene esters are not separated but are eluted as a single peak, followed by the diene and triene esters of the same carbon chain length. Methyl linolenate is eluted as a sharp discrete peak that appears to be free of contamination; it is closely followed by a peak of similar size with a retention time indicative of 19:0 and 19:1. On the more polar BDS liquid phase 18:3 is eluted just after 19:1 and the saturated and monoene esters are resolved (Fig. 2) thus permitting quantitation of all major fatty acids. Two additional liquid phases (CHDMS, Carbowax 20M) with McReynolds polarity constants intermediate between those of OV 225 and BDS (12) were also evaluated but these phases did not separate 18:3 from 19:0 and 19:1. Oils from some peanut cultivars contained varying amounts of one or more trace compounds that were incompletely resolved from 18:3 on BDS columns and consequently the values for 18:3 obtained with this liquid phase were frequently higher than those obtained with OV 225 (Table I).

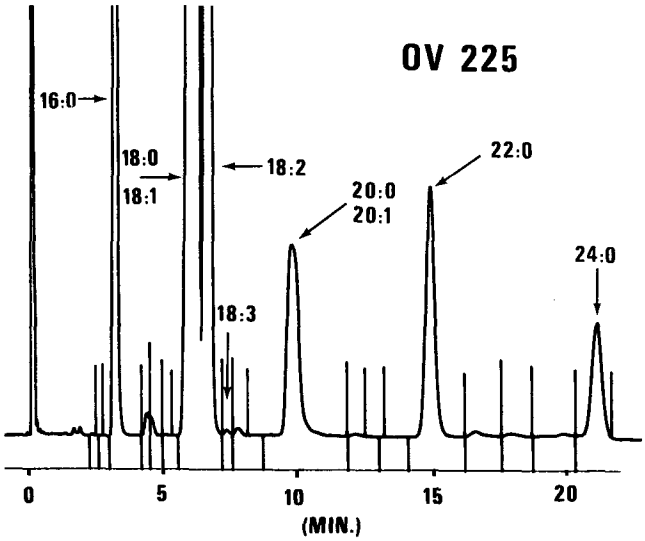

FIG. 1. Elution pattern of peanut oil fatty acid methyl esters on OV 225. Helium flow 100 ml/min. Oven temperature programmed from 180 C at 2 C/min.

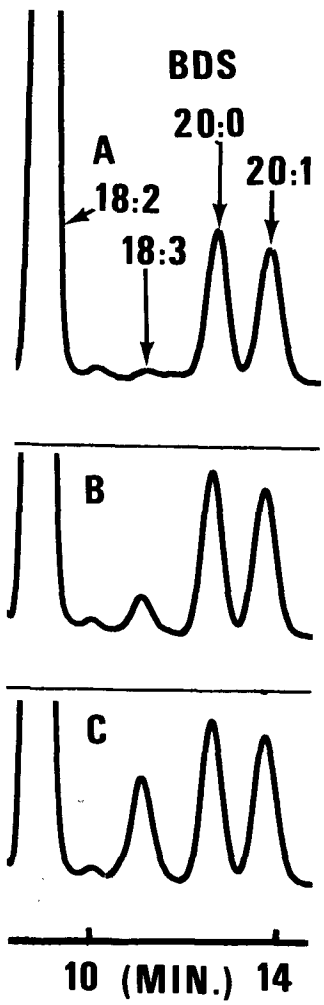

FIG. 2. Elution pattern of methyl linolenate and adjacent fatty acid esters on BDS columns. Esters prepared from peanut oil before (A) and after addition of sufficient trilinolenin to give final concentrations of .28 (B) and .80 (C) weight percent linolenic acid. Helium flow 100 ml/min. Oven temperature 200 C isothermal.

The linolenic acid values found in several varieties of peanuts by area of production are presented in Table I. These values are uniformly low and agree well with values

TABLE I

Linolenic Acid Content of Oils from Peanut Cultivars Grown in Three Production Areas of the U.S. and in Malawi, Africa

		Percent linolenic acid		
		Liquid phase		
Variety	Area of Production	OV 225[a]	BDS[a]	Ave.
'Va Bunch 67'	GA	.03	.04	.04
'F-393-7-1'	GA	.01	.04	.03
'Florunner'	GA	.03	.03	.03
'Argentine'	OK	.05	.04	.05
'Florigiant'	NC	.05	.09	.07
'NC-Fla 14'	NC	.01	.04	.03
'Mani Pintar'	Malawi	.09	.16	.13
'Chalimbana'	Malawi	.04	.08	.06

[a]Weight percent of total fatty acids. Average of two determinations.

reported previously for cultivars grown in one location (5). Linolenic acid is a constituent of peanut oil triglycerides (13), and oils prepared by Carver press and by extraction with the polar solvent system did not differ in linolenic acid content. Linolenic acid values higher than those shown in Table I could be expected in oils derived primarily or entirely from the embryonic axes of peanut seed (13) as these tissues contain somewhat higher levels of linolenic acid (ca. 0.6%).

Some environmental influence may be inferred from the data in Table I in that the highest values for U.S. cultivars were obtained from seed grown in Oklahoma and North Carolina, the more northerly and hence cooler production areas of the U.S. The highest value (0.13%) was found in a cultivar grown in Malawi at an elevation of 3360 ft. This cultivar—'Mani Pintar'—is a long-season spreading type of the Nambyquarae Bunch group of *Arachis hypogaea* subsp. *hypogaea* (14).

When sufficient trilinolenin was added to peanut oil to give levels of .28 and .80% linolenic acid, recoveries of 87 and 101% were obtained on BDS columns and 87 and 88% on OV 225 columns, respectively. The appropriate regions of chromatograms obtained with BDS before and after the addition of trilinolenin are shown in Figure 2. Thin layer argentation of methyl esters prepared from oils with added trilinolenin revealed spots corresponding to methyl linolenate. Similar spots were not observed in other oils, indicating that methyl linolenate was below the limits of detection by the thin layer methods employed.

Low linolenic acid is a characteristic of peanut oil useful in its identification and in the detection of adulteration with other oils containing appreciable levels of this acid. The acceptance of a value of <1.0% linolenic acid would permit the adulteration of peanut oil with 10% or more of soybean oil without exceeding the fatty acid values proposed by the Codex Committee. For example, a mixture of 88 parts peanut oil containing 9.9% palmitic acid, 3.6% stearic acid, 56.6% oleic acid, 26.7% linoleic acid, 0.04% linolenic acid, 1.5% arachidic acid, 1.0% eicosenoic acid, 3.1% behenic acid, and 1.6% lignoceric acid and 12 parts soybean oil containing 11.7% palmitic acid, 4.7% stearic acid, 23.0% oleic acid, 54.2% linoleic acid, and 7.1% linolenic acid, would produce an oil containing 10.0% palmitic acid, 3.8% stearic acid, 52.6% oleic acid, 30.0% linoleic acid, 0.9% linolenic acid, 1.3% arachidic acid, 0.9% eicosenoic acid, 2.7% behenic acid, and 1.4% lignoceric acid. All of these values fall within the ranges proposed by the Codex Committee for peanut oil and thus adulteration would not be detected by GLC. Higher levels of undetectable adulteration would be possible with soybean or other oils containing levels of linolenic acid lower than 7%.

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