efficacy of phosphatides-gums increases with relative humidity suggests that they could be very effective antioxidants, particularly in intermediate moisture foods. The K_M values (Table V) show that the water washed gums give the oil lower rate constants than BHT at high RH's, and α-T had a slight prooxidant action at the RH's studied. As regulations restrict the use of synthetic antioxidants, phosphatides-gums could be an acceptable natural replacement in some applications for synthetic antioxidants currently in use.

TABLE V

Effects of Antioxidants and Peanut Oil Water Washed Gums on the Monomolecular Rate Constants of Peanut Oil Oxidizing at 40 C

Sample	$K_M \times 10^{-3}$ (meq O_2 /kg/hr) at RH (%)		
	2	47.5	90.5
Refined peanut oil	5.04	4.93	4.54
Refined peanut oil + propyl gallate	1.00	0.91	0.68
Refined peanut oil + butylated hydroxy toluene	2.28	3.60	4.15
Refined peanut oil + α-tocopherol	5.20	–	5.6
Raw peanut oil	2.54	1.83	0.50
Degummed peanut oil	5.42	–	2.98
Degummed peanut oil + peanut oil water washed gums	4.12	–	2.05

Although the mechanism of antioxidant action of phospholipids in oils and fats is attributed to the chelation of trace metal catalysts (7,8), their action still remains unanswered in a system which is free from trace metal catalysts, and no visual browning of the phospholipid occurs. The mechanism of the action of phosphatides and gums and the antioxidant action of individual phospholipids at high RH's need further study.

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Distribution of Major Chemical Constituents and Fatty Acids in Different Regions of Coconut Endosperm

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ABSTRACT

Seven regions of coconut endosperm, comprising four (inner, middle, outer and testa) from the region adjacent to the water cavity to the testa; and three transverse regions from top to bottom, were analyzed for moisture, fat, protein, non-protein nitrogen, soluble sugars, reducing sugars, fiber, total ash and acid insoluble ash. The fat extracted from these regions was analyzed for fatty acid composition and chemical characteristics. A marked gradient in the concentration of major constituents was observed across the endosperm, from the inner region enclosing the water cavity through middle and outer regions and testa, the gradation being more striking for moisture fat and soluble sugars. Fatty acids 6:0 to 12:0 were concentrated in the inner regions, and their contents decreased toward the outer regions with a corresponding increase in the higher acids and unsaturated fatty acids. The chemical characteristics of the fat (Reichert value, Polenske value, iodine value and saponification value) from these regions were found to be compatible with the fatty acid profile. The distribution of the constituents in the transverse regions of the coconut endosperm was fairly uniform.

INTRODUCTION

Coconut palm (*Cocos nucifera* Linn) is the world's principal source of lauric fat. Apart from fat, coconut kernel (endosperm) yields a variety of ingredients for culinary usage. In spite of its economic importance, particularly to the coconut growing countries, information on the chemistry of coconut endosperm is incomplete and often confined to fat because of its commercial importance (1-3). Krishnamurthy et al. (4) reviewed the composition and nutritive value of coconut products in 1958, and since then no comprehensive report has been published on the subject.

Fresh coconut consists of a central water cavity containing coconut water or liquid endosperm surrounded by the white solid endosperm followed by the protective shell and husk. It is generally believed that the chemical constituents are uniformly distributed throughout the coconut endosperm. No concrete evidence exists in the literature to prove the contrary. Earlier attempts by Kartha and coworkers (5-7) revealed only a marginal difference in the quality of the fats extracted from the top, central and bottom regions of the coconut. It is also known that the paring oil (a by-product of desiccated coconut) extracted from the residue comprising testa and a portion of the endosperm adjacent to it, has higher iodine and lower saponification values compared to ordinary coconut oil (8). Recently, Heathcock and Chapman (9) used electron microscopy and observed a marked gradation of cell size, shape and contents between the inner and outer regions of the endosperm. With these exceptions, the idea of quantitative approach to the re-

gional distribution of chemical constituents in the coconut endosperm has escaped the attention of investigators. Considering the economic importance and escalating price of coconut products, a thorough knowledge of the quantitative distribution of the chemical constituents, particularly fat, in the endosperm may help development of tailormade products by fractionation. Therefore, a detailed quantitative study of the distribution of major constituents with special emphasis on fat in seven regions of coconut endosperm, hitherto unknown, is presented in this paper.

MATERIALS AND METHODS

Sample Preparation

Fully matured coconuts (12 mo) were harvested from 10 healthy coconut trees (West Coast Tall variety), one nut from each tree. The nuts were split immediately, and the endosperm was separated from the shell. First, the brown testa was scraped off from the endosperm with care to avoid contamination of the white endosperm. The remaining endosperm was divided into three equal portions based on thickness of the endosperm as indicated in Figure 1. These formed the four regions, namely, inner (region 1), middle (region 2) and outer (region 3) of the white endosperm, and testa (region 4). The respective regions separated from the 10 nuts were pooled together. A second set of 10 nuts was harvested as described above from the same trees. The nuts were separated into three equal parts (regions 5 to 7) based on length from top to bottom as indicated in Figure 1. These three regions were named anterior (region 5), comprising the region surrounding the embryo; posterior (region 7), comprising the region opposite the embryo, and the central region (region 6), comprising the portion between the anterior and posterior regions. A third set of 10 nuts was collected from the same trees as before and used as reference for whole endosperm. The pooled samples of the respective regions and the whole endosperm were blended in a Waring blender and freeze dried.

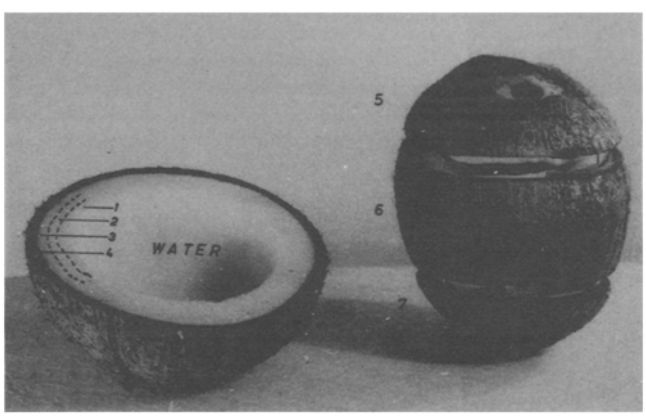

FIG. 1. Regions of coconut endosperm. 1, inner; 2, middle; 3, outer; 4, testa; 5, anterior; 6, central; 7, posterior.

Analytical Methods

Moisture, fat, protein, crude fiber, ash and acid insoluble ash were determined according to AOAC Methods (10). For non-protein nitrogen (NPN) the fat free sample was extracted with 10% TCA, and the supernatant containing NPN was collected by filtration. The filtrate was analyzed for nitrogen content following the micro-kjeldahl method. Total sugars and reducing sugars were estimated by the methods of Roe (11) and Somogyi (12), respectively. The chemical characteristics of oils were determined by AOCS methods (13).

Methyl esters of the fat samples were prepared by transesterification using sodium methoxide. A Hewlett Packard 5840 model gas chromatograph equipped with a flame ionization detector (FID) was used for GLC analysis. A stainless steel column (6 ft long by 1/8 in. i.d.) packed with 10% DEGS on 100-120 chromosorb was used. The injection and detector temperatures were maintained at 250 and 300 C, respectively. Flow rate of the carrier gas (nitrogen) was 20 ml/min. The column temperature was programmed from 100 to 180 C at the rate of 5 C/min. Methyl esters were identified by using authentic standards (Sigma Chemical Co., St. Louis, Missouri), and the peaks were quantitated by digital integration.

RESULTS

Major Constituents

Distribution of major constituents in the fresh coconut endosperm is presented in Table I. The results indicated a marked concentration gradient for all the major constituents across the endosperm from the region surrounding the water cavity to testa (regions 1 to 4). The inner region of the endosperm (region 1) contained the highest amount of moisture, more than three times the moisture content of the outer region (region 3). Fat content of the inner region was 25% that of the outer region, with a marked concentration gradient from region 1 to 3 in increasing order. The testa (region 4) also had a very low level of fat. The protein content showed an increase from region 1 to 3, registering a difference of more than two times between inner and outer

TABLE I

Distribution of Major Chemical Constituents in the Different Regions of Fresh Coconut Endosperm[a]

	Whole endosperm	1 (Inner)	2 (Middle)	3 (Outer)	4 (Testa)	5 (Anterior)	6 (Central)	7 (Posterior)
		% by weight						
Moisture	35.37	61.90	32.60	18.10	29.10	35.10	33.90	33.15
Fat	44.01	15.77	46.36	61.72	19.43	44.15	45.16	44.60
Protein	5.50	2.97	5.28	6.79	4.83	5.45	5.63	5.93
NPN	0.07	0.08	0.07	0.06	0.07	0.07	0.07	0.06
Total soluble sugars	6.57	13.82	6.97	3.47	5.63	6.81	6.94	6.05
Reducing sugars	0.21	1.71	0.12	0.12	0.25	0.25	0.25	0.22
Fiber	3.05	2.88	2.99	2.82	13.28	3.06	3.14	3.49
Total ash	0.77	1.05	0.70	0.57	0.94	0.74	0.79	0.73
Acid insoluble ash	0.05	0.09	0.05	–	0.57	0.05	0.05	0.05

[a]Values are averages of three determinations.

regions. However, non-protein nitrogen did not show appreciable variation. Both total and reducing sugars were found to be concentrated in the inner region; their contents decreased drastically toward the outer region. The amount of total soluble sugars in region 1 was about four times that of the outer region. Reducing sugars were almost entirely concentrated in the inner region. The fiber content was the least variable among all the parameters, showing a fairly uniform distribution except in the testa, which had a very high content. Total ash also recorded a concentration gradient; region 1 had the highest concentration, and it decreased gradually toward region 3. Interestingly, the acid insoluble ash comprised 60% of the total ash in the testa and was totally absent in the adjacent outer region. It should also be noted that the composition of region 2 (middle region) was similar to that of the whole endosperm with respect to all the major constituents. The results of the distribution of major constituents among the transverse regions (regions 5, 6 and 7) showed there was no appreciable difference. Therefore, their composition was almost identical with that of the whole endosperm.

Chemical Characteristics of Coconut Oil

Table II shows the analytical data for coconut oil extracted from the seven regions of coconut endosperm and from the whole endosperm. The results suggest that the different regions, especially regions 1 to 4, varied not only in the quantity of fat they contained (Table I), but in quality also. The chemical characteristics of oil from regions 1 and 2 were almost identical. The iodine value (IV) tended to increase from regions 1 to 4; testa oil (region 4) showed a very high IV value. Saponification value (SV) showed a decrease toward the outer region; testa oil had the lowest value. Both Reichert-Meissl (RM) value and Polenske value (PV) decreased from regions 1 to 4. The testa oil was very distinct in having a very high value for IV and very low values for SV, RM and PV compared to those of the other regions. The chemical characteristics of the oil from regions 5, 6 and 7 did not show any appreciable variations except that region 7 recorded a slightly low IV and slightly higher SV.

Distribution of Fatty Acids

Fatty acid profile of the regions (Table III) highlight the differential distribution of various fatty acids (FA) in the coconut endosperm. Regions 1 and 2 had almost identical FA composition but differed from the whole endosperm in having higher proportion of 6:0, 8:0, 10:0 and 12:0 and lower levels of 14:0, 16:0, 18:1, 18:2 and 20:0. Region 3 showed a greater deviation from the whole endosperm and from regions 1 and 2, with a lower proportion of 6:0 to 12:0 FA and higher levels of 14:0 to 20:0 acids. Testa oil (region 4) composition showed extreme variations from oils of the other regions. It contained very low quantities of 6:0, 8:0, 10:0 and 12:0 and very high amounts of 16:0, 18:1 and 18:2 with respect to whole endosperm and other regions. In general, the lower fatty acids tended to decrease toward the outer region with a corresponding increase of higher fatty acids. Unsaturated FA's also increased toward outer regions. In the transverse regions (regions 5, 6 and 7) no significant variation in the distribution of fatty acids was observed. However, there was a slight tendency in region 7 toward a greater proportion of 8:0 to 12:0 acids. The FA profile of various regions was in agreement with the chemical characteristics of the fat of the corresponding region presented in Table II.

DISCUSSION

The concentration gradient of all the major constituents across the endosperm from inner to outer regions is most striking. Higher content of total soluble sugars, reducing

TABLE II

Chemical Characteristics of Coconut Oil Extracted from Different Regions of Fresh Coconut Endosperm[a]

Chemical characteristic	Whole endosperm	1 (Inner)	2 (Middle)	3 (Outer)	4 (Testa)	5 (Anterior)	6 (Central)	7 (Posterior)
Iodine value	7.7	4.2	4.4	9.8	31.1	7.5	7.3	7.1
Saponification value	249.4	255.9	255.4	249.5	208.4	248.0	248.5	250.9
Reichert-Meissl value	8.3	8.5	8.5	8.1	6.2	8.1	8.2	8.3
Polenske value	12.3	12.4	12.4	10.2	7.9	11.9	12.1	12.1

[a]Values are averages of three determinations.

TABLE III

Regional Distribution of Fatty Acids (area %) in Coconut Endosperm[a]

Fatty acid	Whole endosperm	1 (Inner)	2 (Middle)	3 (Outer)	4 (Testa)	5 (Anterior)	6 (Central)	7 (Posterior)
6:0	0.37	0.60	0.55	0.38	0.13	0.48	0.41	0.48
8:0	8.21	9.16	9.05	7.26	3.90	7.93	7.72	8.61
10:0	5.59	6.05	6.27	5.16	2.71	5.42	5.36	5.83
12:0	47.08	49.59	49.15	43.27	27.55	45.78	46.01	47.72
14:0	19.42	18.87	18.22	19.77	18.47	19.88	20.08	20.00
16:0	7.80	6.48	6.33	9.07	14.45	8.28	8.29	8.04
18:0	4.29	4.88	6.02	6.40	6.64	4.88	4.84	3.27
18:1	4.30	2.81	2.66	4.91	15.60	3.51	3.22	4.11
18:2	1.81	0.93	1.13	2.99	9.44	2.40	2.43	1.88
20:0	1.03	0.63	0.62	0.79	1.11	1.45	1.66	0.08

[a]Values are averages of three determinations.

sugars, ash and moisture in the inner region could be due to the transmigration of these constituents from the coconut water (liquid endosperm) to the inner region that surrounds the water cavity. This is based on the observation that the major constituents of coconut water are soluble sugars with a high proportion of reducing sugars and minerals with a water content of 95% (14). The other constituents, therefore, are reduced proportionately in the inner region. A close scrutiny of the data will reveal that regions 1 and 2 showed a marked quantitative difference in composition of the major components. However, the quality of the most important constituents, i.e. fat from these two regions, was almost identical as shown by the chemical characteristics (Table II) and fatty acid composition (Table III). It is also noteworthy that the fat contents of region 2 and the whole endosperm were similar, but the quality of the fat differed considerably as again revealed by their chemical characteristics and FA compositions. Composition of the transverse regions (regions 5, 6 and 7) was studied to understand if there was any localization of constituents in the region surrounding the embryo. The results indicated no such preferential concentration of any constituents around the embryo.

Earlier studies by Kartha and coworkers (5-7) indicated a qualitative difference in terms of glyceride structure in the transverse regions of coconut endosperm. A selective concentration, though not very appreciable, of saturated acids in the top and bottom regions of the endosperm with slightly lower value for the same at the center was observed by them. Based on their investigations, Sethi and Kartha (7) suggested that upper and lower halves in equal numbers should be collected in the sampling of "copra," and vertical sections of these should be taken for analysis. However, the present study did not show any such significant concentration gradient in the transverse regions. Heathcock and Chapman (9) studied the cell structure of fresh coconut endosperm using light and electron microscopy and demonstrated a marked gradation of cell size, shape and contents between inner and outer endosperm regions. Their study revealed that adjacent to the brown testa (outer region), cells are rigid, compact and lipid filled, while those cells lining the central water-filled cavity (inner region) have thin, easily deformed cell walls and contain little lipid. The values for fat contents of the outer and inner regions of the endosperm reported in this paper, therefore, are compatible with the histochemical observation of Heathcock and Chapman. Apart from these qualitative assessments of the distribution of the constituents in the coconut endosperm, a comprehensive quantitative study has not been reported to this date. The results reported here suggest the possibility of separating coconut endosperm into high- and low-fat fractions. Further studies covering various developmental stages of the endosperm are warranted to explain the physiological significance of the concentration gradient of constituents across endosperm.

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