The Composition of the Oil Obtained from the Seeds of Alpinia speciosa K. Schumann

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1. Introduction

The oil obtained from the seeds of ***Alpinia speciosa K.*** S***chum.*** (Japanese name Getto) was first examined by ***Kafuku*** and his co-workers[1], and ***Kimura***[2].

The data recorded in the ***Kafuku***'s paper were only its general properties [d_4^{16} 0.9454, $(n)_D^{16}$ 1.4732, S.V. 181.73, I.V. (Wijs method) 83.57, A.V. 33.03, unsaponifiable matter 14.51%], and ***Kimura's*** report was limited to the contents of the essential oil and fatty oil extracted from the seeds of Getto were 0.7% and 8.5%, respectively.

Since it seems that the studies on the subjects of Getto have not been carried out yet, the author made a research on the component of the fatty acids contained in the seeds of Getto. The author found by the gas chromatography that the fatty oil of Getto consists of lauric acid (C_{12}), myristic acid (C_{14}), palmitic acid (C_{16}), palmitoleic acid($C_{16}^{1=}$), stearic acid(C_{18}), oleic acid($C_{18}^{1=}$), and linol eic acid($_{18}^{2=}$), and the main components of them were palmitic acid and oleic acid.

The seeds of Getto were assumed to contain two unsaturated C_{16} and C_{20} fatty acids with one double bond (palmitoleic acid and eicosenic acid) and a saturated C_{20} fatty acid(arachidic acid) in addition to fatty acids mentioned above. This is guessed from the relation between the number of carbon atoms and the logarithm of the retention volumes of fatty acids as will be mentioned in the later section.

The interesting fact here is that the fatty oil of Getto contains fatty acids extending from C_{12} to C_{20}, some of which may be peculiar fatty acids, namely, palmitoleic acid($C_{16}^{1=}$), arachidic acid(C_{20}), and eicosenic acid($C_{20}^{1=}$).

2. Experimental

2—1 Extraction of Raw Oil

Raw material, the seeds of Getto, was collected at the southern parts of Okinawa late in October. The colour of the seed is black. The black seeds are wrapped in waxy membrane in the red shells.

The red shells containing the seeds of Getto were dried in the sun and then were removed.

The black seeds in the shells were dried naturally again and the waxy mambrane was removed. The seeds of 100 grains weighed 3.1 g., and a shell contains seeds from 20 to over 30 pieces. The seeds, freed from membrane, were crushed to pieces with a crusher and were extracted with cold n-hexane for 7 days, and the extraction from the same seeds was repeated three times. The n-hexane was evaporated off and the remaining oil was dried over sodium sulfate, yielding raw oil (yield: 11.04%).

The raw oil obtained (this will hereafter be referred to as A) was darkish brown and its general properties are as follows :

specific gravity	d_4^{25}	0.9445
A. V.		11.4
S. V.		224.5
I. V. (Hanus' method)		73
unsaponifiable matter		16.73%

2—2 Preparations of Samples

2—2—1 Separation of Fatty Acids and Unsaponifiable Matter

Sample oil A, 348 g, was saponified with 2 N alcoholic potash solution. The unsaponifiable matter was washed with water and extracted with ether eight times. Then the ether was assembled and evaporated off after drying over sodium sulfate, yielding an unsaponifiable matter (57g.). The soap which did not extract with ether and washings of unsaponifiable matter, with HCl added, were separated into two parts. The upper part is fatty acids (this will hereafter be referred to as B), which were dried over sodium sulfate, yielding B, 261 g. Since the lower part contains fatty acids dissolved in water, it was extracted with ether after drying over sodium sulfate and put together with the B mentioned above.

The fatty acids B, which were obtained from A by removing unsaponifiable matter, have come to solidify.

2—2—2 Separation of Solid and Liquid Fatty Acids

Free fatty acids B, 135 g, were separated into solid and liquid fatty acids byTwitchell's method[3]. (The former will hereafter be referred to as C and the latter D). The C and D gave a yield of 80 g. and 54 g., respectively.

The lead salts of solid fatty acids C were separated naturally into two parts after allowing to stand for several days. (The one will hereafter be referred to as C_1 and the other C_2).

The yields of C_1 and C_2 were 35.3 g. and 44.7 g, and the colours of them were darkish brown and yellowish brown, respectively.

2—3 Gas Chromatograph

2—3—1 Column Conditions

Instrument : Hitachi KGL—2 type (owned by Tokyo Factory of Nikka Yushi Co., LTD.)

Column : 20%(w/w) polyethylene glycol adipate deposited in a conventional manner on Celite 545 and packed under vibration into a 2 m long, 4 mm diameter stainless tube.

Gas : Helium

Flow Rate : Sample A, 25 ml/min.
Sample B—D, 40 ml/min.

Temperature : 200°C

Sample Size : 1 μl∼2 μl at sensitivity 1

2—3—2 Esterification

The samples A was esterificated with 3 % sodium hydroxide-methanol solution and the samples B, C_1, C_2, and D were esterificated with 1.5 % (wt.) sulphuric acid-methanol solution by a common method, respectively. These methyl esters, which were dried after washing with water, were gas chromatographed.

2—3—3 Gas Chromatogram

Each gas chromatogram of A, B, C_1, C_2, and D is shown in Fig. 1—5. Sample A differs from another samples in the retention time, since its flow rate of He gas was dropped. The gas chromatogram of soy bean oil is also shown in Fig. 6 for comparing with those of A, B, C_1,C_2, and D.

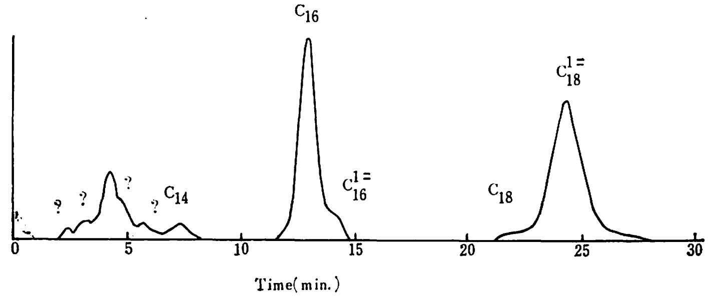

Fig. 1 Gas chromatogram of A, where :
A : Raw oil extracted from the seeds of Getto

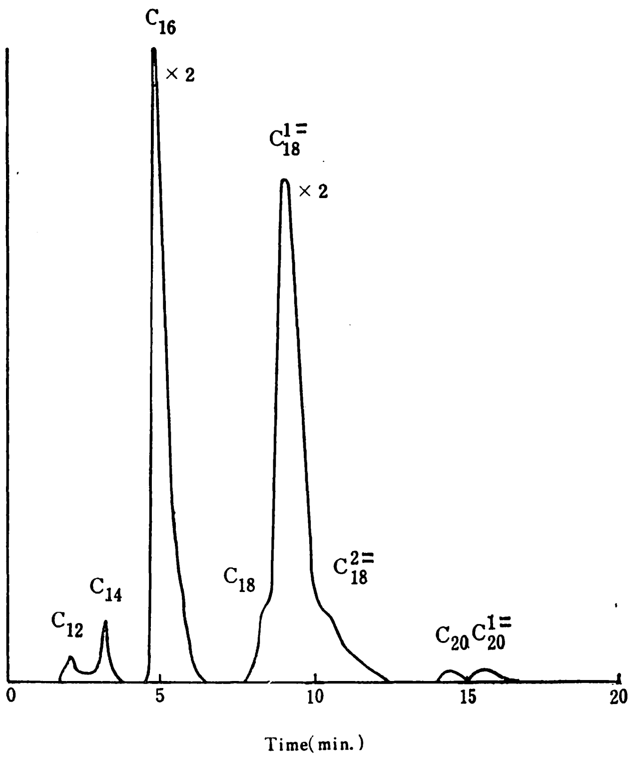

Fig. 2 Gas chromatogram of B, where :
B : Fatty acids separated from A

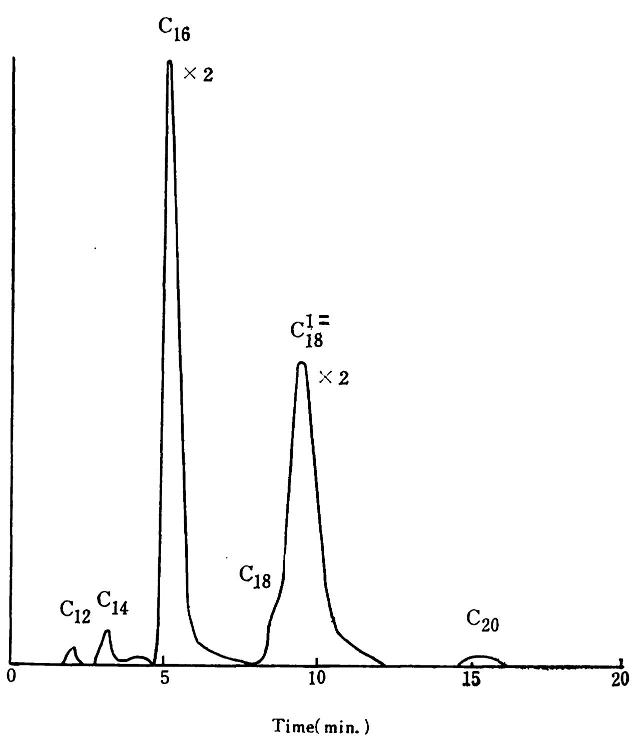

Fig. 3 Gas chromatogram of C_1, where :
C_1 : Solid fatty acids (1) sseparated from B

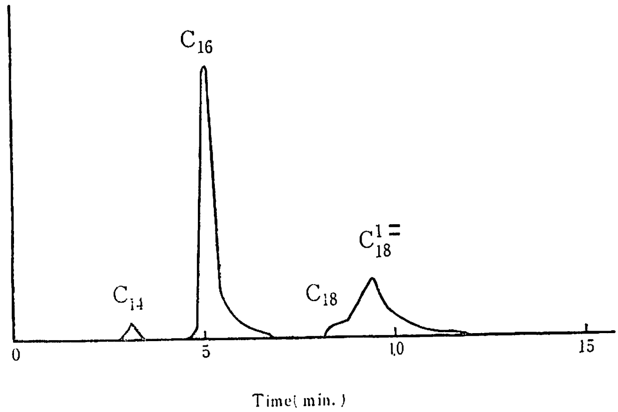

Fig. 4 Gas chromatogram of C_2, where :
C_2 : Solid fatty acids (2) separated from B

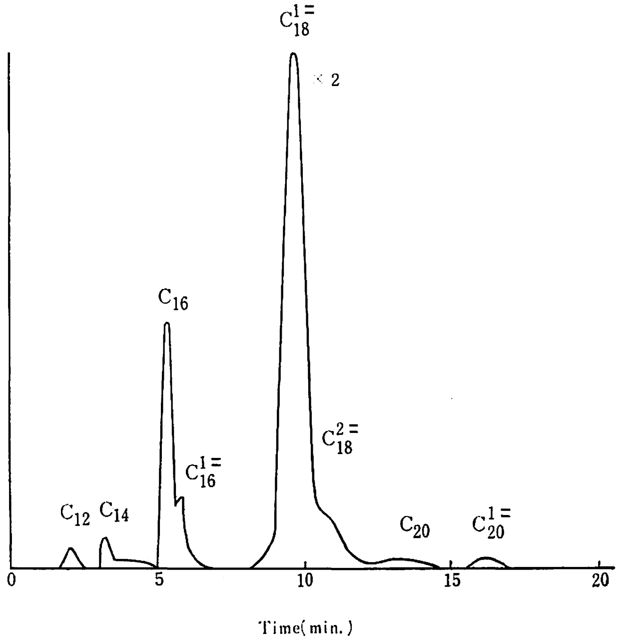

Fig. 5 Gas chromatogram of D, where :
D : Liquid fatty acids separated from B

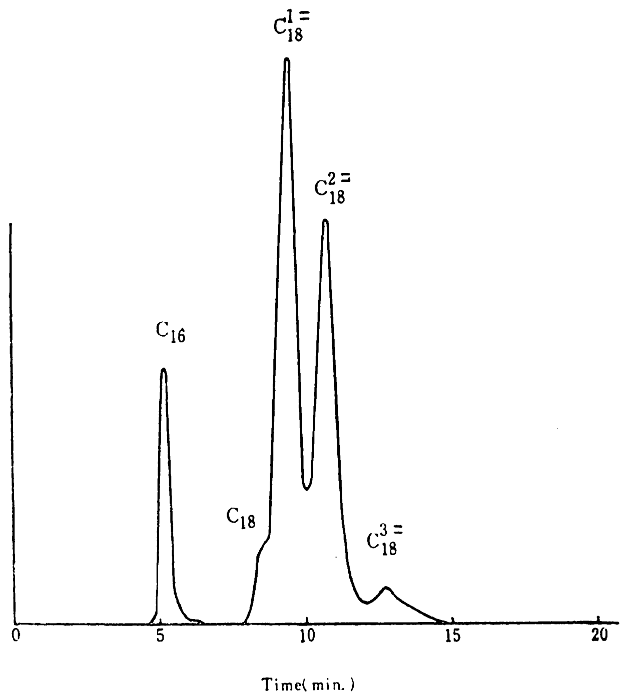

Fig. 6 Gas chromatogram of Soy Bean Oil

3. Results and Discussion

3-1 Relative Retention Volumes of Methyl Esters of Fatty Acids

Retention time and retention volume of methyl ester of each fatty acid relative to that of methyl esters of palmitic acid are shown in Table 1. And logarithm of each retention volume of fatty acids multiplied by 10 is also shown in Table 1.

	Retention Time (min.)	Relative Retention Volume, V_R	log (V_R X 10)
Lauric acid	2.0	0.38	0.58
Myristic acid	3.2	0.62	0.79
Palmitic acid	5.2	1.00	1.00
Palmitoleic acid	5.6	1.08	1.03
Stearic acid	8.5	1.63	1.21
Oleic acid	9.6	1.85	1.27
Linoleic acid	10.8	2.08	1.32
Arachidic acid	13.2	2.54	1.40
Eicosenic acid	16.1	3.10	1.49

Table 1 Gas chromatographed Data of methyl esters of fatty acids

The graph showing the relation betewen the number of carbon atoms of the homologous series of fatty acid methyl esters and the logarithm of their relative retention volumes is almost a straight line as shown in Fig. 7.

The last one or two unknown peaks in the gas chromatograms of samples B, C_1, and D are assumed to be a saturated C_{20} fatty acid (arachidic acid) and an unsaturated C_{20} fatty acid with one double bond, because of the fact that, for the homelogous series of fatty acid methyl esters, a plot of the logarithm of the retention volume against the number of carbon atoms assumed to be 20 falls almost on the straight line.

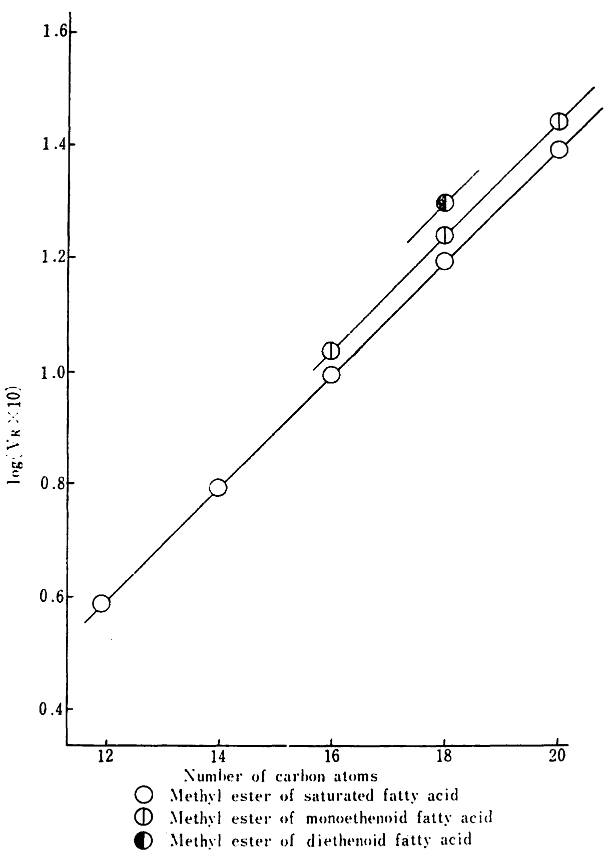

Fig. 7 Relation between the number of carbon atoms of the homologous series of fatty acid methyl esters and logarithm of their relative retention volumes (V_R)

3—2 **Components of Fatty Acids**

Most of the fatty acids contained in the seeds of Getto were confirmed by comparing with those of soy bean oil used as standard fatty acids in the gas chromatography.

Samples A (raw oil) and B (fatty acids obtained from A by removing unsaponifiable matters) contain myristic acid, palmitic aɔid, stearic acid and oleic acid as components common to the two samples, respectively.

It was tried to raise the sensitivity of gas chromatography of sample A by dropping the flow rate of He gas. In consequence, it was found that the sample A contained five unknown lower members of fatty acids, one of which may be lauric acid (C_{12}) by the reason that sample B contained it as shown in Table 2.

The last two unknown peaks of sample B in the gas chromatography may be arachidic acid (C_{20}) and eicosenic acid ($C_{20}^{1=}$) by the reason mentioned previously.

As regards to sample C_1 (solid fatty acid (1)) and C_2 (solid fatty acid (2)), C_1 contains lauric acid, myristic acid, palmitic acid, oleic acid and stearic acid. In addition to these acids, C_1 may also contain arachidic acid.

C_2 contains all the components contained in C_1 except lauric acid and arachidic acid.

Sample D (liquid fatty acid) contains lauric acid, myristic acid, palmitic acid, oleic acid, and linoleic acid. Moreover, judging from its retention times, the sample D is assumed to contain palmitoleic acid ($C_{16}^{1=}$), arachidic acid(C_{20}), and eicosenic acid ($C_{20}^{1=}$). This is shown also by the fact that the relation between the number of carbon atoms and logarithm of each retention time of their methyl esters showed almost linear correlation as mentioned previously.

The contents of each component of samples A, B, C_1, C_2, and D are shown on Table 2.

Sample	?	Lauric acid	Myristic acid	Palmitic acid	Palmitoleic acid	Stearic acid	Oleic acid	Linoleic acid	Arachidic acid	Eicosenic acid
A	19.25		2.3	32.7	3.0	1.45	41.3			
B		0.72	1.1	40.0		2.75	50.0	4.23	1.20*	
C_1		0.52	1.16	50.2		2.5	44.3		1.32	
C_2			2.45	69.4		3.39	24.76			
D		0.79	0.83	10.9	3.5		77.1	5.3	0.64	0.94

Table 2. Contents, %, of Fatty acids of samples A, B, C_1, C_2, and D, where:

A : Raw oil extracted from the Seeds of Getto

B : Fatty acids separated from A

C_1 : Solid fatty acids (1) separated from B

C_2 : Solid fatty acids (2) separated from B

D : Liquid fatty acids separated from B

* : Sum of % of both arachidic acid and eicosenic acid

The main components of them are palmitic acid and oleic acid, which each of the B to D contain no less than 90 %.

It is interesting that the oil extracted from the seeds of Getto consists of fatty acids ranging from C_{12} to C_{20}, some of which may be curious fatty acids, palmitoleic acid, arachidic acid, and eicosenic acid.

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References

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