

SIX LESSER KNOWN JAPANESE VEGETABLE OILS

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This paper records the results of our studies on the seed oils from *Clerodendron tricotomum*, *Euonymus japonica*, *Mallotus japonicus*, *Hamamelis japonica*, *Pittosporum tobira* and *Phytolacca americana*. Of these oils, oil from *C. tricotomum* has been previously studied.¹⁾ Quite recently, kamala oil obtained from *Mallotus philippinensis*, which is kindred to *M. japonicus*, has been studied intensely since a new acid named kamlolenic acid (18-hydroxy-9, 11, 13-octadecatrienoic acid)²⁾ was separated as a chief component of fatty acids. Some characteristics of the oil obtained from *Phytolacca acinosa*,³⁾ which is closely related to *P. americana*, were also reported by a previous author.

1. Materials used for extraction of oil. Growing place, date of harvest, and some data on the yield of oil are shown in Table 1. In the line "material for oil

TABLE 1. List of Material for Oil Extraction

Species	<i>Clerodendron tricotomum</i>	<i>Euonymus japonica</i> Thunb.	<i>Mallotus japonicus</i> Muell. Arg.		<i>Hamamelis japonica</i> Sieb et Zucc.	<i>Pittosporum tobira</i> Ait.	<i>Phytolacca americana</i> L.
Family	Verbenaceae	Calastraceae	Euphorbiaceae		Hamamelidaceae	Pittosporaceae	Phytolaccaceae
Growing place	Higashiyama, Nagoya	Higashiyama, Nagoya	Yokkaichi City		Higashikamogun, Aichi Pref.	Higashiyama, Nagoya	Higashiyama, Nagoya
Date of harvest	Late Nov., 1954	Middle Dec., 1954	(a) Early Sept., 1953	(b) Early Sept., 1954	Autumn, 1954	Late Nov., 1954	Late Oct., 1954
Material for oil extraction	Naturally dried up whole fruit	Dried seed	Seed	Seed	Seed	Dried seed	Dried seed
Wt. of Material for oil extraction (g)	51	178	21.2	294	11.5	—	530
Ether-extract {(g) / {(%)}	12.8 / 25.1	70 / 39.3	9.5 / 44.8	122 / 41.5	1.2 / 10.4	6.0** / —	59 / 11.1
Hexane-soluble oil {(g) / {(%)}	12.5 / 24.5	67 / 37.6	9.2* / 43.4	102 / 34.7	1.2 / 10.4	5.5 / —	57 / 10.8

* Acetone-soluble oil.

** Seeds of *P. tobira* were coated with reddish mucilage and could not be thoroughly dried. Seeds not thoroughly dried were crushed and mixed with anhydrous sodium sulfate prior to the extraction with ether. Their oil content appears to be very small. The oil content of *Pittosporum coriaceum* was reported to be about 3%.⁴⁾

extraction" in Table 1, the term "seed" denotes the raw seed without any treatment and the term "dried seed" denotes the dried material prepared by drying raw seed in an oven at about 80°C. The material for oil extraction was ground prior to the extraction with ether. The hexane-soluble oil was obtained by treating the ether-extract with about tenfold hexane and then removing the insoluble matter. In the case of *M. japonicus* (a), the acetone-soluble oil was obtained by using acetone instead of hexane.

2. Properties of oils. Properties of the hexane-soluble oils (acetone-soluble oil in the case of *M. japonicus* (a)) are shown in Table 2. All iodine values recorded in this paper were determined by the Wijs method. Saturated esters in the methyl esters of fatty acids were determined by permanganate oxidation in acetone. The ether-insoluble bromides from the fatty acids of *E. japonica* and *H. japonica* oils, recrystallized from benzene, melted at 180°–182°C and were identified with hexabromostearic acid by the mixed melting point method. After removal of the ether-insoluble bromides, brominated fatty acids from both oils were treated with hexane, and hexane-insoluble bromides were separated. Recrystallization of the hexane-insoluble bromides from 90% ethanol gave crystalline bromides of m.p. 114°–115°C which were identified with tetrabromostearic acid by the mixed melting point test. Bromination of the fatty acids of *C. tricotomum*, *M. japonicus* (b) and *P. americana* oils gave no ether-insoluble bromides but hexane-insoluble bromides

TABLE 2. Properties of Oils

Oil	<i>C.</i> <i>tricotomum</i>	<i>E.</i> <i>japonica</i>	<i>M. japonicus</i>		<i>H.</i> <i>japonica</i>	<i>P.</i> <i>tobira</i>	<i>P.</i> <i>americana</i>
			(a)	(b)			
Appearance at ordinary temp.	Light yellow liquid with some solid	Reddish orange liquid with a little solid	Light yellow liquid with a little solid	Light yellow liquid with some solid	Light yellow liquid with a little solid	Orange yellow liquid with a little solid	Dark greenish orange liquid with a little solid
d_4^{20}	0.9103	0.9534	0.9358	0.9275	—	0.9272	0.9228
n_D^{20}	1.4663	1.4707	1.4925	1.4862	1.4782	1.4807	1.4737
Acid V.	60.8	1.6	6.4	33.8	8.4	5.3	4.6
Saponif. V.	195.0	264.5	195.5	199.0	190.4	171.5	189.6
Iodine V.	90.5	85.4	121.4	110.0	161.8	87.4	110.3
Unsap. M. (%)	1.03	2.27	0.72	0.63	1.45	15.20	2.48
Fatty acids							
n_D^{20}	1.4572	1.4576	1.4795	1.4731	1.4662	1.4612	1.4626
Neutr. V.	196.8	214.1	—	204.7	203.9	189.8	197.7
Iodine V.	92.7	99.6	—	112.0	167.0	76.1	113.9
Ether-insol. bromide (%)	0	3.1	0	0	11.1	—	0
Saturated esters in the methyl esters of fatty acids (%)	12.8	18.0	—	—	—	—	—
Acetyl V. of the methyl esters of fatty acids	—	3.1	17.9	38.4	—	—	1.2

which, after recrystallization from 90% ethanol, were identified with tetrabromostearic acid by its melting point and mixed melting point 114°-115° C.

3. Fatty acids of *Euonymus japonica* oil. This oil was saponified, and the unsaponifiable matter was removed by extraction of the soap solution with ether. The soap solution was then acidified with hydrochloric acid, and the fatty acids were taken up with ether. After washing the ether solution several times with water, the aqueous washing was still colored yellowish orange and slightly acidic. Washing was repeated until the final washing has become faintly colored. The fatty acids were obtained by distilling ether from the ether solution. Since this oil had S.V. 264.5 and unsaponifiable matter 2.27%, the total fatty acids were expected to have a neutralization value over 280. The fatty acids obtained above, however, had N.V. 214.1, not so high as expected, as shown in Table 2. Hence this oil was considered to contain some water-soluble acids. But the total distillate obtained from this oil by the procedure used for the determination of Reichert-Meissl value required a relatively small amount of alkali for neutralization; 30.2 mg KOH for one g of oil. Accordingly the remarkably high saponification value of this oil is attributable not only to volatile acids but also to non-volatile and water-soluble acids.

The fatty acids (28 g) separated from this oil after removal of the water-soluble acids and unsaponifiable matter were dissolved in 150 cc of acetone, the solution was cooled with ice, and the crystalline solid (*A*, about 3 g) formed was removed. The fatty acids remaining in the acetone solution were recovered and brominated in the usual way. After removal of ether-insoluble and hexane-insoluble bromides, hexane-soluble bromide (about 30 g) was obtained. The hexane-soluble bromide was debrominated with zinc and sulfuric acid in methanol, and the product was saponified. The fatty acid fraction thus obtained was separated into solid fraction (*B*, about 3 g) and liquid fraction by the lead salt ethanol method. The liquid fraction was converted to the lithium salt, and the latter was recrystallized from 50% ethanol. Acidification of the recrystallized lithium salt gave an acid fraction of N.V. 197.9 and I.V. 96.2. On heating this acid with a small amount of selenium, a solid product was obtained. Recrystallization of this solid product from 80% ethanol gave elaidic acid of m.p. 43°-44.5°C, N.V. 198.9 and I.V. 92.4 (calcd., N.V. 198.6 and I.V. 89.8).

The solid acids (*A* and *B*) were separated into several fractions by fractional crystallization, which were considered to consist chiefly of mixtures of palmitic and stearic acids from their neutralization values and melting points; N.V. 200.8 (m.p. 59°-60°C) - N.V. 210.5 (m.p. 55.5°-57°C).

4. Separation of kamlolenic acid from *Mallotus japonicus* oil. The fatty acids from both samples of this oil show the ultraviolet absorption curves (Fig. 1) which have the absorption maxima characteristic to conjugated triene. The methyl esters from this oil have relatively high acetyl values as shown in Table 2. From these facts, this oil, like kamala oil, is expected to contain kamlolenic acid.

The hexane-insoluble oil obtained by treating the ether-extract with hexane was a very viscous oil and turned into a gel after standing for a few days, which had A.V. 7.7, S.V. 201.5, I.V. 115.7 and Unsap. M. 0.14% and was considered to be a polymerization product of the glycerides rich in kamlolenic acid.

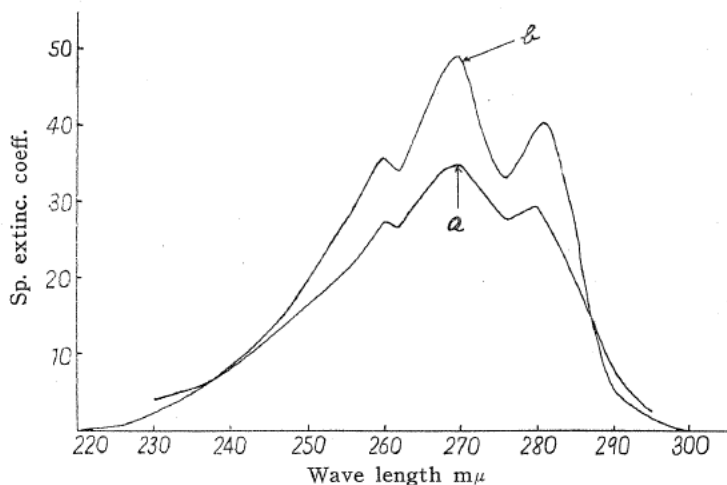


FIG. 1. Absorption curves of the fatty acids of *Mallotus japonicus* oil.

Curve *a* for the fatty acids of acetone-soluble oil.

Curve *b* for the fatty acids of hexane-soluble oil.

For the experiments described below, the fatty acids prepared from the hexane-soluble oil (*b*) were used.

The fatty acids (80 g) were dissolved in 700 cc of acetone, the solution was neutralized with 125 cc of an aqueous solution of lithium hydroxide (concentration, about 5.6%), and then added with 300 cc of acetone. On cooling the solution with ice, the precipitate of lithium salt was filtered. The fatty acid fraction (67 g) from the precipitate had n_D^{20} 1.4681, I.V. 108.5 and $k_{270} = 43.3$, while the fatty acid fraction (12 g) from the filtrate had n_D^{20} 1.4708, I.V. 110.5 and $k_{270} = 50.3$. The fatty acid fraction from the precipitate was dissolved in ethanol and fractionally precipitated in the form of lithium salt by adding a solution of lithium hydroxide in successive portions. The results are shown in Table 3.

TABLE 3. Fractional Precipitation of Lithium Salt

Fatty acid fraction	Yield (g)	Neutr. V.	I.V.	After recrystallization from ethanol	
				Neutr. V.	I.V.
1	6.5	205.6	32.6	212.0	7.4
2	5.2	205.7	54.7	213.7	7.0
3	7.0	204.0	51.2	206.4	20.0
4	2.8	199.6	91.6	—	—
5	5.5	204.0	110.5	—	—
From the final filtrate	34.0	—	—	—	—

As is seen from Table 3, since the fatty acid fractions 1-3 have still noticeable iodine values even after recrystallization from ethanol, they are considered to be contaminated with some solid unsaturated acids. On adding 200 cc of hexane to

the fatty acid fraction from the final filtrate, it dissolved partly in hexane while a considerable amount of crystalline solid together with a small amount of yellowish oily liquid separated from the solution. Ether was added to the mixture until the crystalline solid has completely disappeared. The clear solution was separated from the yellowish oily liquid and cooled with ice, giving about 4 g of crystalline substance which was recognized as α -kamlolenic acid by its m.p. 72°-73°C, N.V. 192.5 and I.V. 178.1 after recrystallization from ether-hexane (α -kamlolenic acid: m.p. 78°-79°C,¹⁾ 72°-75°C;⁵⁾ N.V., calcd., 190.6; I.V., calcd., 258.6. The Wijs method gives an iodine value corresponding to about two-thirds of the calculated value). To the mother liquor of the recrystallization of α -kamlolenic acid was added a bit of iodine, and the solution was allowed to stand over a night. The crystalline substance formed was separated and recognized as β -kamlolenic acid by its m.p. 87°-89°C (β -kamlolenic acid: m.p. 90°-92°C,¹⁾ 85°-87°C⁵⁾).

α - and β -Kamlolenic acids obtained above were united, and the united material was hydrogenated in ethanol in the presence of platinum black. The product, after recrystallization from ether, showed m.p. 98.5°-99°C and N.V. 184.5, and its acetylated product had S.V. 299.8 (hydroxy-octadecanoic acid: m.p. 99°-100°C,²⁾ N.V., calcd., 186.7; S.V. of its acetylated product, calcd., 327.6). The somewhat low saponification value of the acetylated product may possibly be attributable to the difficulty of a complete acetylation of hydroxy-octadecanoic acid due to some side reaction such as self-esterification.

The hydrogenation product obtained above was oxidized with chromic acid in glacial acetic acid. The oxidation product was washed with hexane and then recrystallized from acetone, yielding hexadecamethylene-1,16-dicarboxylic acid in a crude form; m.p. 116.5°-118°C and N.V. 346.9 (m.p. 125°-126°C²⁾ for the pure substance; N.V., calcd., 341.6).

Ultraviolet absorption values for α - and β -kamlolenic acids were measured in methanol. In Table 4, our data are compared with those previously reported. It is noteworthy that the specific extinction coefficients for β -kamlolenic acid obtained by us is considerably higher than the corresponding values by previous authors.

TABLE 4. Ultraviolet Absorption Values for α - and β -Kamlolenic Acids

α -Acid		β -Acid	
Wave length (m μ)	Absorption value	Wave length (m μ)	Absorption value
270	$k=177.8$	268	$k=226.1$
271	$E_{1\text{cm}}^{1\%}=1,750$	269	$E_{1\text{cm}}^{1\%}=1,880$ ⁵⁾
270.5	$E_{1\text{cm}}^{1\%}=1,800$	268	$E_{1\text{cm}}^{1\%}=1,990$ ⁶⁾
271	$k=167.5$	268	$k=186.0$ ⁷⁾
271	$10^{-3} \epsilon=52.0$	268	$10^{-3} \epsilon=60.0$ ⁸⁾

Notes: The specific extinction coefficient for α -acid obtained by us was measured with a sample which had been stored in the form of an ether solution for several days in the dark after its preparation. In a preliminary measurement with a sample of α -acid immediately after its preparation, a very high value, $k_{270}=233.0$, was obtained. Since kamlolenic acid is liable to undergo some changes during its storage, even when stored cautiously, it is not quite excluded that the higher absorption value is the real one. In this respect, the authors are going to make a closer study.

Summary

1. Oils were extracted from the seeds of *Clerodendron tricotomum*, *Euonymus japonica*, *Mallotus japonicus*, *Hamamelis japonica*, *Pittosporum tobira* and *Phytolacca americana*, and some properties of these oils and their fatty acids were determined.

2. Polyethenoid acids of the oils from *C. tricotomum*, *M. japonicus* and *P. americana* contain no linolenic acid but linoleic acid. Polyethenoid acids of the oil from *E. japonica* contain linoleic acid together with a small amount of linolenic acid, while those of the oil from *H. japonica* contain linoleic acid and linolenic acids.

3. The oil from *E. japonica* has a very high saponification value, and appears to contain non-volatile and water-soluble acids besides volatile acids.

4. Kamlolenic acid (18-hydroxy-9,11,13-octadecatrienoic acid) was separated from the fatty acids of the oil from *M. japonicus*. The content of kamlolenic acid in this oil, however, seems to be smaller than in kamala oil.

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