SEED OILS FROM SEVEN SPECIES OF JAPANESE PLANTS

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Among the plants grown wild or cultivated in this country, there are many species, the seed oils of which have been but little studied or not yet been studied at all. The authors have intended to analyze the seed oils from fairly widely distributed one of these species for their characteristics and fatty acid composition. The present paper is concerned with seed oils from *Quamoclit angulata, Frangula crenata, Daphniphyllum glaucescens, Cocculus trilobus, Mirabilis jalapa, Polygonum perfoliatum* and *Broussonetia papyrifera.* Previously recorded data on these oils appear to be limited to a report by Tsuchiya[1] for some characteristics of *Mirabilis jalapa* oil.

1. Seeds used for extraction of oil. Regarding the seeds used for extraction of oil in this study, name of the species of parental plant, growing place, date of the harvest of fruit, and yield of seed oil are shown in Table 1. For the separation of seeds from fruits, whole fruits were smashed, a sufficient amount of water was added to smashed material, and the mixture was rubbed until husks, skins and fleshy portion were removed from seeds. Seeds were dried in an oven at about 80°C, and the dried seeds were crushed to fine powders and then extracted with ether. To the ether-extract obtained was added about tenfold hexane, and the insoluble matter was removed. The seed oil was obtained from the hexane solution by distilling off hexane.

TABLE 1. List of Samples

Species	*Quamoclit angulata* Bojer	*Frangula crenata* Miq.	*Daphniphyllum glaucescens* Blume	*Cocculus trilobus* DC.	*Mirabilis jalapa* L.	*Polygonum perfoliatum* L.	*Broussonetia papyrifera* L'Herit
Family	*Convolvulaceae*	*Rhamnaceae*	*Euphorbiaceae*	*Menispermaceae*	*Nyctaginaceae*	*Polygonaceae*	*Moraceae*
Growing place	Higashikamo-gun, Aichi Prefecture	Chikusa-ku, Nagoya	Atsumi-gun, Aichi Pref.	Naga-gun, Mie Pref.	Kita-ku, Nagoya	Kita-ku, Nagoya	Naka-ku, Nagoya
Date of harvest of fruits (1955)	Middle Oct.	Late Sept.	Late Dec.	Middle Nov.	Late Sept.-Middle Oct.	Late Sept.-Early Oct.	Late Oct.-Early Nov.
Wt. of fruits (g)	125	1,350	256	1,200	1,095	490	660
Wt. of dried seeds (g)	106	298	31	149	647	113	58
Average wt. of one dried seed (g)	0.012	0.019	0.050	0.024	0.079	0.018	0.004
Ether-extract (g)	14.5	91.0	13.8	28.0	28.0	3.7	18.4
Ether-extract (%)	13.7	30.5	44.5	18.8	4.3	3.3	31.7
Hexane-sol. oil (seed oil) (g)	13.8	89.6	13.6	27.5	27.6	3.6	18.3
Hexane-sol. oil (seed oil) (%)	13.0	30.1	43.9	18.5	4.3	3.2	31.6

Notes: Percentage yields of ether-extract and hexane-soluble oil were expressed on the basis of dried seeds.

2. Properties of Oil. Characteristics of the seed oils obtained above and of their fatty acids prepared as usual are given in Table 2.

TABLE 2. Properties of Oil

Oil	*Q. angulata*	*F. crenata*	*D. glaucescens*	*C. trilobus*	*M. jalapa*	*P. perfoliatum*	*B. papyrifera*
Appearance at ordinary temp.	Yellowish orange with some solid	Dark reddish orange with some solid	Pale yellowish orange with a little solid	Dark greenish yellow with some solid	Dark yellowish orange with some solid	Dark yellowish orange with some solid	Yellowish orange with a little solid
d_4^{20}	0.9240	0.9185	0.9201	0.9227	0.9106	0.9250	0.9242
n_D^{20}	1.4736	1.4726	1.4709	1.4745	1.4713	1.4737	1.4767
Acid value	3.3	1.3	1.2	3.1	3.1	2.9	2.4
Saponif. value	189.2	189.4	189.6	187.1	181.7	184.6	189.0
Iodine value (Wijs)	115.1	115.8	97.7	127.5	100.9	105.9	145.3
Unsaponifiable matter (%)	2.24	0.84	0.93	1.26	3.76	4.93	2.67
Fatty acids							
Neutralization value	199.6	195.3	194.7	198.5	194.6	195.2	197.7
Iodine value	120.1	122.1	101.4	133.6	107.9	110.2	151.1
Acetyl value	2.0	1.8	4.4	4.1	3.5	19.4	2.6
Ether-insol. bromide(%)	8.0	1.0	0	0	12.0	1.0	0

Notes: Determination of acetyl value was carried out with the methyl esters of fatty acids. Acetyl value for the fatty acids was calculated from the observed data for the methyl esters. *M. jalapa* oil was reported by Tsuchiya[1] to have n_D^{20} 1.4751, acid value 2.3, saponification value 180.5, iodine value 109.2 and unsaponifiable matter 6.03%.

Ether-insoluble bromides from the fatty acids of *Q. angulata* oil, *F. crenata* oil, *M. jalapa* oil and *P. perfoliatum* oil showed the following melting points after recrystallization from benzene: m.p. 181°–182°C, m.p. 180°–181°C, m.p. 180°–181°C and m.p. 179°–180°C, respectively. These melting points were not lowered when admixed with a pure specimen of hexabromostearic acid prepared from linolenic acid. Ether-soluble bromides obtained from these oils after removal of ether-insoluble bromides were treated with hexane to give hexane-insoluble bromides which showed m.p. 113°–114°C (m.p. 114°–115°C in the case of *P. perfoliatum* oil) after recrystallization from 90% ethanol and were identified with the tetrabromostearic acid derived from linoleic acid by the mixed melting point test. Fatty acids from *D. glaucescens* oil, *C. trilobus* oil and *B. papyrifera* oil yielded no ether-insoluble bromides but hexane-insoluble bromides which showed the same m.p. and mixed m.p. 114°–115°C after recrystallization from 90% ethanol.

In order to know whether conjugated unsaturated acids are present in these oils, ultraviolet absorption was measured for each oil in ethanol; the oil itself dissolved in ethanol was used in the case of *P. perfoliatum* oil while the product obtained by saponification of oil with N/5 ethanol-KOH followed by dilution with ethanol was used in the case of other oils. *Q. angulata*, *C. trilobus* and *M. jalapa* oils exhibited no absorption maxima at 233 mμ and at 268 mμ and accordingly these oils were found to contain neither conjugated dienoic acid nor conjugated trienoic acid. *F. crenata*, *D. glaucescens*, *P. perfoliatum* and *B. papyrifera* oils exhibited an absorption peak at 233 mμ. The contents of conjugated dienoic acid[2] in these oils calculated from the specific extinction coefficient at 233 mμ were

found to be 0.78%, 1.95%, 3.96% and 0.73%, respectively (0.80%, 2.00%, 4.19% and 0.76%, respectively, on the basis of total fatty acids). *D. glaucescens* and *P. perfoliatum* oils exhibited also an absorption peak at 268 mμ, indicating the presence of conjugated trienoic acid in these oils, but the content of conjugated trienoic acid calculated from the absorption value was found very small (less than 0.1%) for both oils.

3. Fatty acid composition. The fatty acid composition for each oil was determined as described below.

The fatty acids from *D. glaucescens*, *C. trilobus* and *B. papyrifera* oils, which were found to contain no linolenic acid by bromination test, were analyzed for the content of solid acids by the lead salt ethanol method, and the content of saturated acids was calculated from the content of solid acids by assuming unsaturated acids contained in solid acids to be solely oleic acid. The contents of oleic acid and linoleic acid were then calculated from the iodine value of total fatty acids and the content of saturated acids.

TABLE 3. Fatty Acid Compositions of *D. glaucescens*, *C. trilobus* and *B. papyrifera* Oils

Fatty acids	*D. glaucescens*	*C. trilobus*	*B. papyrifera*
Linoleic acid (%)····	22.7	57.7(57.9)	76.0
Oleic acid (%) ·····	67.1	32.3(31.9)	15.0
Saturated acids (%) ·	10.2	10.0(10.2)	9.0
Solid acids (%)·····	11.3	11.0	9.9
m.p. (°C)·····	46.5-48	53-54	53.5-54
Iodine value ·····	8.6	8.7	8.6

Notes: Figures in parentheses for the fatty acids of *C. trilobus* oil are calculated on the basis of the absorption value, $k_{233}=50.31$, for the alkali-isomerized oil. In the case of *D. glaucescens* oil and *B. papyrifera* oil, linoleic acid includes conjugated dienoic acid preformed in oil, 2.00% and 0.76%, respectively.

TABLE 4. Fatty Acid Compositions of *Q. angulata*, *F. crenata*, *M. jalapa* and *P. perfoliatum* Oils

Fatty acids	*Q. angulata*	*F. crenata*	*M. jalapa*	*P. perfoliatum*
Spec. extinc. coeff. of alkali-isomerized oil				
at 233 mμ·····	44.72	40.87	20.34	34.56
at 268 mμ·····	5.34	1.89	7.10	2.03
Linolenic acid (%) ·····	11.2	3.9	15.1	4.2
Linoleic acid (%)·····	43.7	42.9	13.6	35.7
Oleic acid (%)·····	11.5	37.6	46.9	38.0
Saturated acids (%) ·····	33.6	15.6 (15.2)	24.4 (22.2)	22.1

Notes: In the case of *F. crenata* oil and *P. perfoliatum* oil, linoleic acid includes conjugated dienoic acid preformed in oils; 0.8% and 4.2% respectively. The fatty acids of *P. perfoliatum* oils is considered to contain some hydroxy acid from the relatively high acetyl value (19.4) of fatty acids. Figures in parentheses for saturated acids were calculated from the content of solid acids. Solid acids from *F. crenata* oil: 18.2%, m.p. 48.5°-50°C and iodine value 15.0; solid acids from *M. jalapa* oil: 23.7%, m.p. 52°-52.5°C and iodine value 5.6.

Oils from *Q. angulata*, *F. crenata*, *M. jalapa* and *P. perfoliatum* were isomerized under the condition of 6.5% KOH-ethylene glycol, 180°C and 25 min. with a current of nitrogen, and the ultraviolet absorption values of the alkali-isomerized fatty acids at 233 mμ and 268 mμ were measured. The contents of linoleic acid and linolenic acid in total fatty acids were calculated from the absorption data.[2] The contents of oleic acid and saturated acids were then calculated from the iodine value of total fatty acids and the contents of linoleic acid and linolenic acid.

For the sake of comparison, the fatty acid composition of *C. trilobus* oil was also calculated from the data based on the ultraviolet absorption measurement, and the content of saturated acids in the fatty acids of *F. crenata* oil and *M. jalapa* oil were estimated by the lead salt ethanol method.

The results are shown in Tables 3 and 4.

4. Unsaponifiable matter. Unsaponifiable matter from each oil was a mixture of crystalline solid and viscous liquid. On treating unsaponifiable mater with hot methanol, the insoluble fraction and soluble fraction were separated. Recrystallization of the fraction soluble in hot methanol from methanol or 95% ethanol gave a crystalline substance of m.p.: 132°–134°C for *Q. angulata* oil, 134°–136°C for *F. crenata* oil, 114°–116°C for *D. glaucescens* oil, 128°–130°C for *C. trilobus* oil, 134°–136°C for *M. jalapa* oil, 115°–125°C for *P. perfoliatum* oil and 136°–137°C for *B. papyrifera* oil. The crystalline substance obtained from each oil exhibited the Liebermann-Burchard reaction for sterol. The fraction insoluble in hot methanol, after recrystallization from a comparatively large amount of 95% ethanol or benzene-ethanol, had m.p. 80°–82°C for *Q. angulata* oil, 80°–81°C for *C. trilobus* oil and m.p. 68°–70°C for *B. papyrifera* oil, respectively. The recrystallized material from each oil was found to be negative for the Liebermann-Burchard reaction.

Summary

Seed oils from *Quamoclit angulata*, *Frangula crenata*, *Daphniphyllum glaucescens*, *Cocculus trilobus*, *Mirabilis jalapa*, *Polygonum perfoliatum* and *Broussonetia papyrifera* were analyzed for their characteristics. Linolenic acid was absent in the oils from *D. glaucescens*, *C. trilobus* and *B. papyrifera*, while the other oils contained linolenic acid.

Assuming the component fatty acids other than linolenic acid to be linoleic, oleic and saturated acids, the fatty acid composition for each oil was estimated approximately by applying the determination of solid acids by the lead salt ethanol method and the ultraviolet absorption measurement of alkali-isomerized fatty acids.

References

1) T. Tsuchiya: "Jitsuyo Yushi Binran" p. 716 (1949).
2) "Official and Tentative Methods of the American Oil Chemists' Society" Cd 7-48.