ON NIGAKI OIL.

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"Nigaki" (literally, "bitter tree"), *Picrasma quassioides Benn.* (*Simarubaceae*), is a shrub or tree grown in hills and fields, and has yellowish-green blossoms from May to July; the fruits are of the size of a pea. The plant has an intense bitter taste, and the bitter substance in the ligneous parts is used as a stomachic, and the decoction sap as an insecticide. The plant is distributed in Japan and China, and also in the Himalaya; in Chôsen (Corea) it is found in almost all mountaineous districts.

No mention of nigaki oil is found in the literature. The oils from the *Simarubaceae* mentioned in the literature have mostly been obtained from tropical plants. It is interesting to note that tariri fat obtained from the genus *Picramnia* belonging to the *Simarubaceae* has been reported to contain a peculiar acid called "tariric acid." The acid melts at 50.5°C., has the formula $C_{18}H_{32}O_2$, and is thus an isomer of linolic acid; but the acid contains a triple bond, its constitutional formula being $CH_3.(CH_2)_{10}.C\vdots C.(CH_2)_4.COOH$, and resembles in this respect to stearolic acid.⁽¹⁾

In our study of nigaki oil, a particular attention has been directed as to the occurrence of tariric acid in the oil, but with negative result. On the other hand we have confirmed that the oil contains a large proportion of petroselinic acid, an isomer of oleic acid.

Experimental Part.

(1) General Properties of Nigaki Oil. The nigaki fruits used for this experiment were procured from Chûsei-Nandô, Chôsen. They were of a nearly spherical form, and had rumples on the rinds. Most of them had a brown colour, while the others were brownish-yellow or brownish-green. As the fruit shell rather easy to be stripped off, it was not difficult to separate it from the kernel. The kernels were dark yellow and had brown spots. The weight of 50 c.c. of the fruits was 230 gr., and 610 fruits weighed 50 gr. The ratio of the shell to the kernel was about 45 : 55. On analysis the following figures were obtained:

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(1) Arnaud, *Bull. Soc. Chim.*, 1892, (3), 7, 233.

	Moisture	Oil
Shell	7.49%	38.36%
Kernel	5.96%	46.57%

From 2240 gr. of the fruits, 660 gr. of the oil were obtained by pressing.

There are three kinds of nigaki oil, viz., obtained (1) from the whole fruit, (2) from the fruit shell, and (3) from the kernel. The nigaki oil mentioned in this paper represents the oil obtained from the whole fruit as mentioned above, but the other two oils have also been prepared and their properties examined.

Nigaki oil was a brownish-yellow, viscous liquid at the room temperature of 26°C., and deposited a large amount of crystalline solid in winter. It had a bitter taste and an unpleasant odour. Its characteristics, etc., were determined as follows:

d_4^{20}	0.9322	Iodine value (Wijs)	76.7
n_D^{20}	1.4712	Reichert-Meissl value	1.21
Acid value	19.0	Acetyl value	28.70
Saponification value	200.5	Unsaponifiable matter	1.48%

On cooling to 0°C., the oil did not solidified in an hour, but at –20°C. it solidified to a salve-like mass, which regained its mobility at 15°C.

The fatty acids had a brownish-yellow colour, and consisted of liquid and solid substances at 26°C. They showed the neutralisation value 207.0 and the iodine value 79.5. By the lead-salt-ether method, 76.7% of liquid and 23.3% (by difference) of solid acids were obtained; they had the following properties:(2)

	Melt. pt.	Neutr. v.	Iodine v.	n_D^{20}
Solid acids	57.5–58°C.	219.6	14.0	—
Liquid acids	—	200.6	93.8	1.4613

On bromination the liquid (unsaturated) acids produced a small amount of precipitate in petroleum ether solution; in ether only a very small amount of precipitate was formed.

(2) Examination of the Composition of the Fatty Acids. The oil was heated with an equal weight of methyl alcohol containing 2.5% of hydrogen chloride on a water bath for about 12 hours. The fractional

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(2) This experiment was performed in summer season. At lower temperature (ca. 10°C.) lead petroselinate is sparingly soluble in ether. As petroselinic acid is solid at the ordinary temperature, the designation of "liquid" acids would be incorrect, and is used here only conventionally.

distillation of 500 gr. of the methyl esters thus prepared under 15 mm. pressure gave the following result:

	Yield		Appearance	Saponif. value	Iodine value	n_D^{20}
	gr.	%				
(1) Until 180°	5.9	1.2	Pale yellow liquid	265.8	45.0	1.4420
(2) 180–190°	5.5	1.1	,,	258.2	48.3	1.4444
(3) 190–200°	16.4	3.3	,,	230.1	55.6	1.4469
(4) 200–210°	155.0	31.0	Light orange-yellow liquid	199.8	68.0	1.4493
(5) 210–215°	215.9	43.2	,,	193.5	85.1	1.4519
(6) 215–216°	35.8	7.2	,,	192.4	93.3	1.4540
(7) Residue	ca. 65	ca. 13	Dark brown viscous liquid	—	—	—

The distillation nearly ceased at 216°C. The comparatively large amount of the residue was probably due to somewhat incomplete esterification, and possibly also to the presence of some high boiling compounds in the shell oil.

The above result showed that the chief constituents are the esters of C_{18} acids boiling between 200–216°C. under 15 mm. pressure, which amounted to more than 80%.

On saponifying the fractions (1), (2), and (3), the fatty acids were separated into solid and liquid parts by the lead-salt-ether or lead-salt-alcohol method. From the solid acids palmitic acid was identified. From the fraction (1), an acid of the neutralisation value of 282 was obtained, which appeared to be impure lauric acid. Although not isolated, myristic acid was likely to be present. Of the liquid (unsaturated) acids, the presence of the lower acids (C_{12} to C_{16}) was not ascertained, but those from the fraction (3) consisted of C_{18} acid (probably petroselinic acid).

The fractions (4), (5), and (6) were used for the identification of C_{18} acids. As a preliminary test, a mixture of the corresponding amounts of (5) and (6) was re-fractionated under 15 mm. pressure, and the fatty acids obtained from the fraction boiling at 212–214°C. were treated by the lead-salt-ether method. After the separation of the solid acids (chiefly palmitic), the unsaturated acids were changed into lithium salts and dissolved in 80% alcohol. The salt deposited on cooling was decomposed with hydrochloric acid, and free acid separated. The acid had the neutralisation value 199 and the iodine value 87. As it was liquid in summer season, the presence of tariric acid, a solid of comparatively high melting point, seemed to be excluded. At first we considered the substance to be ordinary oleic acid, but by the elaidin test, an acid of m.p. 50°C. was obtained. Also the original substance solidified to a crystalline mass at a lower temperature. So we were convinced that the substance consists of a solid octadecenoic acid.

To prepare a larger amount of the acid, the fractions (4)-(6) and the residue (re-esterified) were mixed and fractionated. The fraction 206–212°C. (14–15 mm.) was similarly treated as above, and the crude octadecenoic acid recrystallised from dilute acetone by ice-cooling, and finally the admixed saturated acids were removed as far as possible by means of magnesium acetate. The acid thus purified formed a crystalline mass, melted at 29–29.5°C., and had the neutralisation value 199.7 and the iodine value 86.0 (calc. for $C_{18}H_{34}O_2$, neutr. value 198.8, iodine value 89.9). Judged from the iodine value, it still contained a small proportion of saturated acids. On hydrogenation the acid was changed into stearic acid. By the elaidin reaction, an elaidic acid of m.p. 53°C. was produced. The hydroxy-acid obtained by Hazura's method melted at 121–121.5°C. From these results, the octadecenoic acid appeared to be petroselinic acid.

A small amount of a liquid octadecenoic acid was found to accompany petroselinic acid; it probably consisted of oleic acid.

In the above experiment, the free acids obtained from the filtrate of the lithium salts in alcohol had the iodine value 114. On bromination they gave insoluble precipitates in petroleum-ether and ether solutions; so linolic and linolenic acids were likely to be present. The presence of the latter was highly probable by the melting point (178°C.) of the ether-insoluble bromide.

(3) **Confirmation of Petroselinic Acid.** Although the octadecenoic acid described above appeared in all probability to be petroselinic acid, its constitution has been confirmed by the oxidation method with potassium permanganate.(3)

20 Gr. of the methyl ester of the acid were dissolved in 200 c.c. of acetone and oxidised with 80 gr. of potassium permanganate. On dissolving the precipitated manganese oxide with sodium bisulphite and dilute sulphuric acid, the product was repeatedly extracted with ether (total 3000 c.c.). The ether solution was concentrated and treated with 20% aqueous solution of sodium carbonate to dissolve out acidic compounds. On evaporating off the ether, 4.6 gr. of the "neutral" substance were obtained. It formed a crystalline mass, and had the saponification

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(3) E. F. Armstrong and T. P. Hilditch, *J. Soc. Chem. Ind.*, **44** (1925), 45T.

value 244, the acid value 134, and the iodine value 15. So it contained, besides neutral substance, still an appreciable amount of acidic product. The latter on isolation was found to consist chiefly of white crystals, which melted at 35°C. and had the neutralisation value 279.6. It was recognised to be impure lauric acid.

The soda extract was saponified with caustic potash and on acidifying shaken with ether. The residue obtained on evaporating off the ether was then treated with petroleum ether, and separated into the soluble and insoluble parts in it.

(1) Petroleum Ether Soluble Part. Yield 10.2 gr.; white crystals with a marked odour of lower fatty acids; neutralisation value 304.4. 9 Gr. of this substance were fractionated under 15 mm. pressure as follows:

		Yield (gr.)	Appearance	Neutr. v.
(a)	Until 170°C	0.2	Colourless liquid	—
(b)	170–180°C.	6.3	White crystals	308.1
(c)	180–185°C.	1.5	,, ,,	309.6
(d)	Residue	0.5	Pale orange-yellow crystals	—

The boiling point of the chief fraction (b) corresponded to those of lauric acid. The high neutralisation value was due to admixed lower acids formed by the secondary reactions. On recrystallising the mixture of (b) and (c) from 70% alcohol by ice-cooling, 4 gr. of the refined substance were obtained. It was white crystals of m.p. 40°C. and had the neutralisation value 283.6. No depression of melting point was observed by the mixed test with lauric acid (Kahlbaum). So the substance was confirmed to be lauric acid $C_{12}H_{24}O_2$ (m.p. 43.6°C., neutr. v. 280.3).

The acids contained in the mother liquor were converted into barium salts and deposited from hot alcohol. The analysis of the salts gave Ba 26.89% (calc. for $(C_{12}H_{23}O_2)_2Ba$, Ba 25.64%) and showed that they consisted mainly of barium laurate.

(2) Petroleum Ether Insoluble Part. Yield 4.9 gr.; white crystals; neutr. value 755.9. On recrystallisation from acetic ether, first crop, 2.3 gr., m.p. 150.5–151°C., neutr. value 772.8; second crop, 0.6 gr., m.p. 148–148.5°C., neutr. value 773.1. So they were recognised to be adipic acid $C_6H_{10}O_4$ (m.p. 151°C., neutr. value 768.2).

The above experiments have shown that the oxidation products of the octadecenoic acid from nigaki oil are lauric and adipic acids, so that its constitution corresponds to those of petroselinic acid as follows:

$$CH_3.(CH_2)_{10}.CH:CH.(CH_2)_4.COOH.$$

Petroselinic acid was discovered by E. Vongerichten and A. Köhler⁽⁴⁾ from the seed oil of parsley, *Petroselinum sativum.* The content of the acid in the mixed fatty acids of the oil has been stated to be about 76%. Further the acid occurs in the seed oil of *Hedera helix* (up to 62%).⁽⁵⁾

We have found petroselinic acid in the oil of a tree quite different from the above two plants.

(4) **Nigaki Shell and Kernel Oils.** Besides the nigaki oil mention-above, we have examined the shell and kernel oils separately.

The shell oil was a brownish-yellow liquid mixed with solid constituents at 20°C.; it became clear on warming to 29°C. It had a bitter taste.

The kernel oil was a yellow liquid at 20°C.; at the room temperature of 13°C., it mostly solidified to a white crystalline mass. The oil had also a bitter taste.

	Shell oil	Kernel oil
Sp. gr.	d_4^{30} 0.9580	d_4^{15} 0.9217
Ref. index	d_D^{30} 1.4710	n_D^{20} 1.4705
Acid value	44.5	4.8
Saponif. value	219.7	190.4
Iodine value (Wijs)	50.6	93.9

The shell oil had a high saponification value and a low iodine value; it appeared to contain chiefly the comparatively lower saturated acids (mainly palmitic). Whether the oil contains petroselinic acid or not, has not yet been ascertained.

The kernel oil contained petroselinic acid as the chief constituent. The ether solution of the lead salts of the fatty acids of the oil gave a large amount of precipitate at 10°C., which did not wholly dissolve at 15°C. The precipitate consisted mostly of lead petroselinate. The liquid acids isolated from the ether-soluble lead salts at 15°C. had the iodine value 104, a fact indicating the occurrence of the higher unsaturated acids (linolic and linolenic) in the oil.

Summary.

(1) The properties and composition of the nigaki oil (a mixture of the shell and kernel oils) obtained from the whole fruit of "nigaki," *Picrasma quassioides Benn.*, have been examined.

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(4) *Ber.* **42** (1909), 1638.

(5) Grün-Halden, „Analyse der Fette u. Wachse", II, 324.

(2) As the chief constituent of the fatty acids of the oil, the occurrence of petroselinic acid, $C_{18}H_{34}O_2$ ($\Delta^{6:7}$ octadecenoic acid), has been ascertained.

(3) As the other constituent, palmitic acid has been identified from the saturated acids; lauric acid appears also to be present. Of the unsaturated acids, oleic, linolic, and linolenic acids are likely to be present.

(4) The shell and kernel oils have also been examined separately. The former contains an appreciable proportion of saturated acids, while the latter has been found to contain petroselinic acid as the chief constituent.

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