# Studies on the Unsaturated Lower Fatty Acids. On the Crystalline Derivatives of the Unsaturated Lower Fatty Acids.

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It is a problem all important to determine the melting points of crystalline derivatives of unsaturated fatty acids, but the work on this line is very imperfect. We have only the data of tiglic,[1] oleic,[2][3][4] erucic,[4] and cetoleic[4] acids. The authors have prepared pure obtusilic,[5] linderic, and tetradecenoic acids from the oil of the nuts of *Lindera obtusiloba*, and determined their physical properties and the melting points of their crystalline derivatives. The tetradecenoic acid of this oil was formerly concluded to be physeteric acid by M. Tsujimoto.[6] The tetradecenoic acid the authors have prepared this time, however, was a solid melting at 18.0–18.5°. From the result of ozonolysis, it has been recognized to be tsuzuic acid.

## Experimental.

The basis of this work was the oil of nuts of "Tohaku" (*Lindera obtusiloba*) as in previous report.[5] It had the following characteristics: $d_4^{20}$ 0.9494, $n_D^{20}$ 1.4701, acid value 28.2, iodine value (Wijs) 77.7, saponification value 236.1.

(1) *Obtusilic Acid.* The oil (3 kg.) was saponified, decomposed, and the mixed fatty acids thus obtained were subjected to fractional distillation under a diminished pressure of 13 mm. A fraction (32.5 g.) up to 153° was taken, and after the removal of the unsaponifiable matter, the fatty acids were converted into methyl esters, and the latter were brominated in ethereal solution cooled with ice. The product of bromination was fractionally distilled under a diminished pressure of 2 mm. The fraction boiling at 149–154°/2 mm. (12 g.) was taken, and after debromination, the obtained methyl ester was saponified. The liberated fatty acid was subjected to a further fractionation, and a fraction (3.2 g.) boiling at 148–150°/13 mm. was collected as decenoic acid. It had the following constants: $d_4^{15}$ 0.9222, $d_4^{20}$ 0.9197, $n_D^{15}$ 1.4519, $n_D^{20}$ 1.4497, mol. ref. 49.76, neutralization value 328.3, iodine value 146.0 (calc. for $C_{10}H_{18}O_2$: mol. ref. 49.47, neutralization value 329.7, iodine value 149.2). This fatty

(1) Lund and Langvad, *J. Am. Chem. Soc.*, **54** (1932), 4107.
(2) Escher, *Helv. Chim. Acta*, **12** (1929), 45.
(3) Drake and Bronitsky, *J. Am. Chem. Soc.*, **52** (1930), 3715.
(4) Kimura, *J. Soc. Chem. Ind., Japan*, **35** (1932), 2213.
(5) Komori and Ueno, this Bulletin, **12** (1937), 226.
(6) *J. Soc. Chem. Ind., Japan*, **27** (1924), 323.

acid was methylated and oxidized with potassium permanganate in acetone solution. In the decomposition product, succinic and caproic acids were detected. This result showed that no isomeric change involving the shifting of an ethylenic linkage had taken place during the process of purification. The obtusilic acid obtained (0.4 g.) was oxidized by Hazura's method (cooled to 0–2° and oxidized with 0.5% $KMnO_4$), but we could not obtain any solid oxidation product. The *p*-bromophenacyl ester of obtusilic acid was prepared according to the method of Y. Kimura.[4] The ester formed lustrous scaly crystals, and had the melting point 43.3°.

(2) **Linderic Acid.** The "Tohaku" oil (5 kg.) was saponified, decomposed, and the mixed fatty acids thus obtained were subjected to fractional distillation under a diminished pressure of 13 mm. The results of the fractional distillation are given in Table 1.

Table 1.

| Fraction | B.p. (°C./13 mm.) | Yield (g.) | $n_D^{20}$ | Saponif. value | Neutr. value | Iodine value |
|---|---|---|---|---|---|---|
| 1 | —160 | 666 | 1.4409 | 268.9 | 238.5 | 77.4 |
| 2 | 160—170 | 1591 | 1.4410 | 272.6 | 259.1 | 90.9 |
| 3 | Residue | 2158 | | | | |

150 g. of fraction 2, after separation of unsaponifiable matter, was subjected to the bromo-ester method of Grün and Janko, and the obtained fraction 178–182°/2 mm. (118 g.), (dibromolinderic acid methyl ester), was debrominated with zink powder and hydrochloric acid in methanol solution. The produced methyl ester was saponified and the liberated fatty acid was subjected to a further fractionation, by which a fraction (29 g.) boiling at 170–172°/13 mm. was collected as linderic acid. The linderic acid had a following properties: $d_4^{15}$ 0.9106, $d_4^{20}$ 0.9081, $n_D^1$ 1.4545, $n_D^{20}$ 1.4529, mol. ref. 58.98, neutralization value 282.1, iodine value 128.4, melting point 1.0–1.3° (calc. for $C_{12}H_{22}O_2$: mol. ref. 58.69, neutralization value 282.0, iodine value 128.1). On oxidizing the linderic acid by Hazura's method, it yielded dihydroxy-lauric acid having the melting point 102°. The cooling curve of this acid is shown in Fig. 1. The melting points of crystalline derivatives were as follows: *p*-phenylphenacyl ester 42.5°, *p*-bromophenacyl ester 47.5°, *S*-benzylthiuronium salt[7] 139.0°.

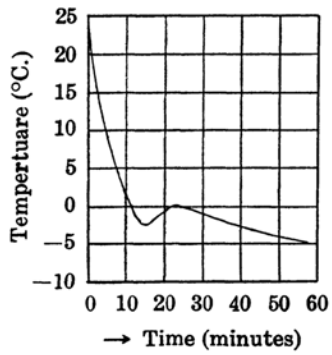


Fig. 1.

(3) **Tetradecenoic Acid.** The residue (1.5 kg.) of the fractional distillation (Table 1), after the removal of the unsaponifiable matter, was converted into methyl ester, and fractionally distilled. The fraction boiling between 145–170°/13 mm. (102 g.) was again fractionated as shown in Table 2.

(7) J. J. Donleavy, *J. Am. Chem. Soc.*, **58** (1936), 1004.

Table 2.

| Fraction | B.p. (°C./13 mm.) | Yield (g.) | $n_D^{20}$ | Saponif. value | Iodine value |
|---|---|---|---|---|---|
| 1 | —145 | 39 | 1.4383 | 255.3 | 63.5 |
| 2 | 145—150 | 12 | 1.4400 | 255.2 | 63.7 |
| 3 | 150—155 | 5 | 1.4414 | 246.6 | 62.9 |
| 4 | 155—160 | 4.5 | 1.4420 | 242.9 | 63.9 |
| 5 | 160—165 | 11.5 | 1.4440 | 234.9 | 64.2 |
| 6 | 165—170 | 5 | 1.4441 | 233.7 | 63.5 |
| 7 | 170—175 | 11 | | 222.6 | |
| | Residue | 13 | | | |

The fatty acids liberated from fraction 5, were separated into unsaturated and saturated acids by the lead salt petroleum ether method. The unsaturated acid portion was fractionally distilled once more, and finally 2.2 g. of the unsaturated acid possessing the following values was obtained: melting point 18.0–18.5°, boiling point 185–188°/13 mm., $d_4^{15}$ 0.9055, $d_4^{20}$ 0.9024, $n_D^{15}$ 1.4575, $n_D^{20}$ 1.4557, mol. ref. 67.83, neutralization value 248.3, iodine value 111.5 (calc. for $C_{14}H_{26}O_2$: mol. ref. 67.93, neutralization value 248.0, iodine value 112.0). The cooling curve of this acid is shown in Fig. 2. 1.3 g. of this fatty acid was subjected to ozonolysis, and from the decomposition product, succinic acid was detected. It is certain, therefore, that the fatty acid is tsuzuic acid. The melting point of *p*-phenylphenacyl ester and *p*-bromophenacyl ester of this acid were respectively 54.5° and 61.3°.

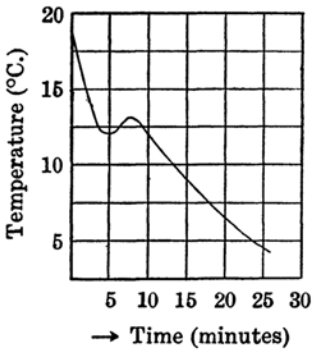


Fig. 2.

## Summary.

(1) It is recognized that the tetradecenoic acid of "Tohaku" oil is tsuzuic acid.

(2) The authors have prepared pure obtusilic, linderic, and tetradecenoic acids from the "Tohaku" oil, and have determined their physical properties and the melting points of their crystalline derivatives.

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