The Separation of the Main Constituents of Hiba Oil by Nitromethane Extraction

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Thujaplicin is a valuable terpenoid compound used industrially in a very small amount as a constituent of Thujopsis dolabrata. On the contrary, thujopsene is quantitatively the main constituent. Katsura et al.[1] showed in 1959 that thujaplicin can be isolated by the phosphoric acid treatment of an acidic oil which has been extracted with alkali.

Judging from the results reported by one of the present authors,[2] it is probable that terpene hydrocarbons are insoluble and that terpenoids, except for *l*-menthol and a few other compounds, are soluble in nitromethane. In this paper, the authors will propose a nitromethane method for the separation of the constituents of Hiba oil. It has been found that thujaplicin, can be isolated as a soluble part of the solvent, while thujopsene remains in the insoluble part. Therefore, a nitromethane-*n*-hexane system has been developed for the same separating purpose, because thujaplicin is insoluble and thujopsene is soluble in *n*-hexane, in contrast to nitromethane.

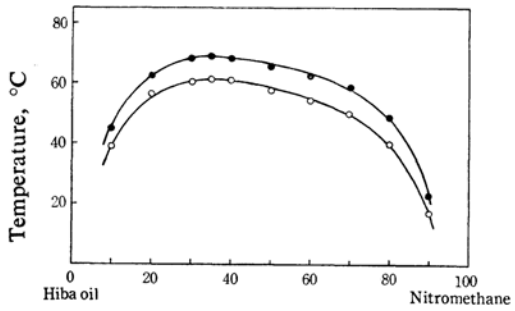

Fig. 1. The Hiba oil - nitromethane system.
○ Natural oil, ● Rectified oil

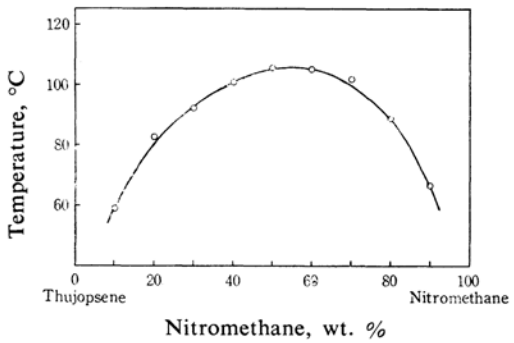

Fig. 2. The thujopsene-nitromethane system.

The mutual solubility curves between Hiba oil, thujopsene and nitromethane are shown in Figs. 1 and 2. The consolute temperature and the corresponding composition for these systems may be recorded as follows:

System	Consolute temperature °C	Composition	
		Oil wt. %	Nitromethane wt. %
Hiba oil - nitromethane	61.0	35	65
Rectified oil - nitromethane	68.3	37	63
Thujopsene - nitromethane	105.8	53	47

The distribution of β-thujaplicin and thujopsene in the nitromethane - *n*-hexane system is shown in Tables I and II.

The extraction of an imitation oil (contents : β-thujaplicin 4.98%, thujopsene 95.02%) with the nitromethane - *n*-hexane system was carried out in order to confirm this separating

1) S. Katsura and A. Komatsu, Japanese Pat. 3794 (1959).
2) M. Ito, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **59**, 981 (1956); ibid., **60**, 375 (1957).

Table I. Distribution of β-thujaplicin between nitromethane and *n*-hexane

Temp., °C	Distribution of: Nitromethane layer, wt. %	*n*-Hexane layer, wt. %
30	89.11	10.20
0	90.91	8.21
−10	93.40	5.41

Table II. Distribution of thujopsene between nitromethane and *n*-hexane

Temp., °C	Distribution of: Nitromethane layer, wt. %	*n*-Hexane layer, wt. %
30	3.74	95.43
0	1.86	97.47
−10	1.20	98.37

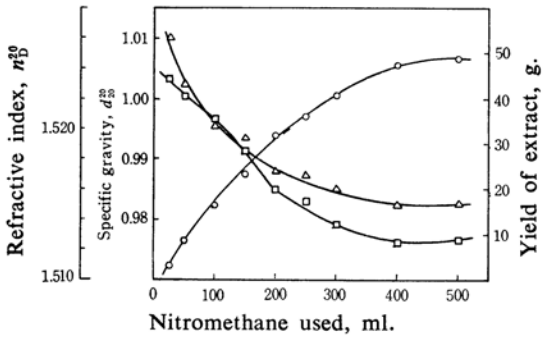

Fig. 3. Extraction of the Hiba oil by nitromethane.
○ Yield of extract, △ Specific gravity, □ Refractive index

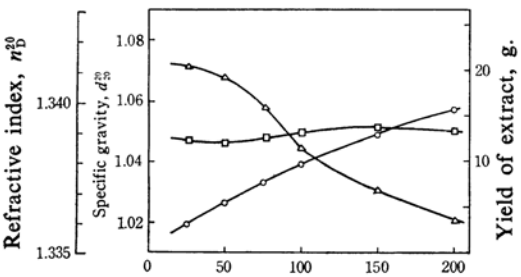

Fig. 4. Extraction of the Hiba oil by nitromethane - *n*-hexane system.
○ Yield of extract, △ Specific gravity, □ Refractive index

method. The crude thujaplicin and thujopsene were recovered quantitatively.

Subsequently, the nitromethane treatment and the nitromethane - *n*-hexane treatment of Hiba oil were carried out. The results are shown in Figs. 3 and 4. The results of the extractions were checked by the measurement of the specific gravity and the refractive index.

The residual oil in the nitromethane extraction and the *n*-hexane layer in the nitromethane - *n*-hexane system treatment was distilled under reduced pressure and rectified through a fractionating column (the number of the theoretical plate, 80) at 10 mmHg. The recovered thujopsene is of good quality.

Experimental

Hiba Oil.—This was obtained by the steam-distillation from sawdust of Thujopsis dolabrata Sieb.; d_{20}^{20} 0.9594, n_D^{20} 1.5117.

Rectified Hiba Oil.—This was obtained by the steam-distillation of the above natural oil; d_{20}^{20} 0.9485, n_D^{20} 1.4955.

Thujopsene.—This was isolated from Hiba oil by the nitromethane method and then rectified; b. p. 119—120°C/10 mmHg, d_{20}^{20} 0.9362, n_D^{20} 1.5033, $[\alpha]_D^{20}$ −93.68.

The Distribution of β-Thujaplicin and Thujopsene in the Nitromethane - *n*-Hexane System.—A sample was distributed in nitromethane - *n*-hexane in a separating funnel which had been dipped into a thermostat. The solvent in each layer was evaporated, and the residual solute was weighed.

The Extraction of an Imitation Oil with the Nitromethane - *n*-Hexane System.—The nitromethane - *n*-hexane system (20 ml. of each) was added to the imitation oil (20 g.) and left to stand at −20°C overnight. The nitromethane layer was separated and evaporated. The crude thujaplicin was recovered in about a 100% yield. When it was then recrystallized from petroleum ether, its yield amounted to 70.3%. Also, thujopsene was recovered quantitatively from the *n*-hexane layer.

The Nitromethane Treatment of Hiba Oil.—Hiba oil (100 g.) was extracted with a definite volume of nitromethane at 20°C.

The Nitromethane - *n*-Hexane System Treatment of Hiba Oil.—A definite volume of nitromethane was added to a mixture of Hiba oil (100 g.) and *n*-hexane (100 ml.) in a separating funnel at 20°C. After the mixture had been shaken, the nitromethane layer was separated and then evaporated.

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