The Constituents of the Flower Oil of Lily of the Valley[1)]

By Seiji WAKAYAMA and Satoshi NAMBA

(Received March 4, 1965)

The absolute oil of lily of the valley (*Convallaria keisukei Miq.*), which it is known, can not be obtained by steam distillation, has not well been investigated.[2)]

The extraction of the flower (100 kg.) with hexane afforded a yellowish-colored concrete (0.26% of the flower) which was then a digested with methanol.

The methanol-insoluble wax (0.13%) was found to contain palmitone triacontanol, wax with a m. p. of 68—69°C and nonacosane by the comparison of the infrared spectra with those of authentic specimens, by comparing the melting points of the derivatives, and by the elementary analyses.

The methanol-soluble part afforded a pale brown-colored essential oil (0.13%) on the removal of the methanol. About a half weight of the essential oil was a mixture of aliphatic acids; this mixture was collected by the treatment of the oil with sodium carbonate and was found to be composed of acetic, caproic, palmitic, stearic and linoleic acids.

The oil obtained on the removal of the acids had the properties of AV 6.3, EV 90.3, and HV 89.3 and gave no distillate under the diminished pressure of 2 mmHg. The essential oil (5.571 g.)

1) Presented at the 8th Symposium on the Chemistry of Terpenes and Essential Oils, Sendai, September, 1964.

2) E. Guenther, "The Essential Oils," Vol. VI, Van Nostrand Company, New York (1952), p. 75; S. Sabetay, *Chem. Abstr.*, **44**, 5537c (1950).

was subjected to separation by chromatography on alumina* (300 g.). The elutions were made with hexane, hexane-benzene (1 : 1), benzene and benzene-ethanol successively. Some fractions eluted with hexane gave a mixture of esters of aliphatic acids which was one of the major components of the oil (20—25%). It should be noted that these esters have afforded, on saponification, a mixture of fresh, lily-like scented alcohols, although the esters themselves smell faintly like the essence. The chromatography of the mixture of the alcohols on alumina with benzene resulted in the isolation of citronellol, nerol and cinnamyl alcohol. Those alcohols were identified on the basis of both the comparison of the infrared spectra with those of the respective authentic samples and the transformation into the derivatives; citronellol was converted into the silver salt of the acid phthalate[3] (m. p. 124.5—125°C); nerol, into the tetrabromide[4], (m. p. 115—117°C) and the allophanate[4] (m. p. 98.5—99.5°C), and cinnamyl alcohol, into the 3,5-dinitrobenzoate (m. p. 124.2—124.8°C). The acidic constituent consisted mainly of stearic acid.

Some fractions eluted with hexane-benzene afforded a mixture of esters. On saponification, it gave as an acidic component only phthalic acid, which melted at 213°C with decomposition into the anhydride (m. p. 130—131°C). The acid was also identified by derivation into the phenacyl ester (m. p. 152—152.7°C).

Fractions eluted with benzene emitted a lily-like scent, and the infrared spectra suggested that they were a mixture of citronellol and nerol. Rechromatography on alumina with benzene led to the isolation of those alcohols, which were identified as has been mentioned above.

Finally, cinnamyl alcohol was isolated by elution with benzene containing 1% ethanol, followed by rechromatography on alumina with benzene.

In summary citronellol, nerol and cinnamyl alcohol are the principal fragrant constituents of "lily of the valley," and they are present in the plant as both free alcohols and stearates.

Investigations of the other constituents are now in progress.

Chemical Laboratory
Hokkaido Gakugei University
Sapporo

* Brockmann Grade II alumina.

3) E. Funakubo, "Yūki Kagōbutsu Kakuninhō," Vol. I, Yōkendō, Tokyo (1954), p. 147; H. Meyer, "Nachweis und Bestimung organischer Verbindungen," J. Springer, Berlin (1933), s. 39.

4) E. Guenther, "The Essential Oils," Vol. II, Van Nostrand Company, New York (1957), p. 175.