The Aconite Alkaloids. XXV. Selenium Dehydrogenation of Miyaconitinone and Lucidusculine*

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Miyaconitinone[1], $C_{23}H_{27}O_6N$, which has been isolated from *Aconitum miyabei*, Nakai, belongs to the aconine group that may be derived from the fundamental base, $C_{19}H_{29}N$; while lucidusculine[2], $C_{24}H_{35}O_4N$, which has been isolated from *Aconitum lucidusculum*, Nakai, may be derived from the fundamental base, $C_{20}H_{31}N$, similar to atisine. These two aconite alkaloids, belonging to different fundamental bases, were subjected to dehydrogenation by selenium, producing the following results:

$$\text{Miyaconitinone} \rightarrow \begin{cases} C_{21}H_{38}\ \text{(unsure)} \\ \text{phenanthrene} \\ \text{anthracene} \end{cases}$$

$$\text{Lucidusculine} \rightarrow \begin{cases} \text{phenanthrene} \\ \text{3-methylphenanthrene} \\ \text{pimanthrene (unsure)} \end{cases}$$

Hetisine, atisine, napelline and staphisine all yielded neutral fractions consisting of complex mixtures of phenanthrene hydrocarbons, some of which were identified to be phenathrene, 1-methyl-, 1,7-dimethyl-, 1-methyl-6-ethylphenanthrene, 3-methylretene, and $C_{17}H_{16}$ or $C_{18}H_{18}$[3].

The conditions, employed at first, to dehydrogenate miyaconitinone were rather more vigorous than Lowson's procedure, but a good result was not obtained. Only an oily mixture of unsaturated hydrocarbons and a saturated hydrocarbon, which melted at 60° and seemed not to be pure but near to $C_{21}H_{38}$, were obtained.

When miyaconitinone was dehydrogenated under more drastic conditions, e.g., heated in a sealed tube at 300∼320° for 24 hr. and then at 370∼380° for 24 hr., an oily mixture of unsaturated hydrocarbons was yielded. High vacuum distillation of the mixture afforded crystalline hydrocarbons from which pure phenanthrene and anthracene were separated by means of recrystallization. Each of them was determined by observation of ultraviolet absorption spectrum and preparation of quinone and picrate.

Under the same condition, giving phenanthrene and anthracene from miyaconitinone, lucidusculine was dehydrogenated. The main part of mixture of crystalline hydrocarbons was phenanthrene, and two other hydrocarbons were obtained in small quantities. One of them was determined to be a methylphenanthrene by elementary analysis. It melted at 62° and was converted into the picrate, bright yellow needles, m. p. 130°, and into the quinone, orange plates, m. p. 204°. Therefore, it was decided to be a 3-methylphenanthrene[4]. The other hydrocarbon melted at 80° and was converted into the picrate, yellow needles, m. p. 125°, and into the quinone, reddish needles, m. p. 182°. It seemed to be 1,7-dimethylphenanthrene (pimanthrene)[5]. From lucidusculine no anthracene derivative was yielded, but only the derivatives of phenanthrene.

It has not yet been reported that anthracene is obtained from other aconite alkaloids. The authors have been able to obtain anthracene from miyaconitinone. But it may be too early to conclude that the aconite alkaloid, having the fundamental base, $C_{20}H_{31}N$, has a constitution with a skeleton that yields both phenanthrene and anthracene, because miyaconitinone has so many oxygen atoms that it is very unstable to oxidation (cf. Part XXIV) and because it requires a drastic condition for dehydrogenation. It is of interest that some cholestanediols can be converted readily into anthracene ring system[6].

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* Part XXIV, S. Kakimoto, This Bulletin, **32**, 349(1959).

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Experimental

Dehydrogenation of Miyaconitinone. — A mixture of 3 g. of miyaconitinone and 15 g. of selenium was divided into four portions. Each of them was sealed in a hard glass tube and heated at 320° for 35 hr. The reaction mixtures were combined and extracted with ether, and from the extract, basic substances from which no crystalline substance could be isolated, were removed by extraction with dilute hydrochloric acid. After ether was distilled off, the residue was fractionated by high vacuum distillation (over 10^{-3} mm.). Three hundred mg. of first fraction, distilled at 80∼130°, was treated with glacial acetic acid. The insoluble part was recrystallized three times from methanol to give 13 mg. of white leaflets, m. p. 60°. The material has no color reaction with tetranitromethane and may be $C_{21}H_{38}$ or hydrocarbon near $C_{21}H_{38}$.

Anal. Found: C, 85.36; H, 14.38. Mol. Wt. 294 (Rast's method). Calcd. for $C_{21}H_{38}$: C, 86.79; H, 13.21%. Mol. Wt. 290.

When water was added to the solution of unsaturated hydrocarbon in glacial acetic acid, oil was separated. It was distilled to give 230 mg. of oil which was colored by tetranitromethane. It seemed to be a mixture of unsaturated hydrocarbons.

Anal. Found: C, 89.64; H, 7.98%.

Since it was not possible to isolate the pure substance in the above described experiment, more drastic conditions were employed as the following.

A mixture of 20 g. of miyaconitinone and 80 g. of selenium was divided into ten portions. Each of them was heated at 300∼320° for 24 hr., and then at 370∼380° for the same period in a sealed tube. The reaction mixtures were combined and extracted with ether. Ethereal extract was washed with dilute hydrochloric acid, next with dilute sodium bicarbonate solution and then with water. After removal of the ether, the residue was distilled under a high vacuum to give one part of oil and 460 mg. of crystalline part. The latter was fractionally recrystallized from methanol into three parts, i) melted at 90∼100°, ii) melted at 190∼200°, iii) melted at 120∼150°. Recrystallization through picrate and chromatographic separation of crude substance was not effective to obtain pure compounds. The part i thus separated was able to be purified through the picrate which was recrystallized from ethanol, and then the derived free hydrocarbon was recrystallized from methanol again to yield 25 mg. of phenanthrene, m. p. 99∼100°. The substance was characterized by the observation of ultraviolet absorption spectrum and by preparing the picrate, m. p. 144° and phenanthrenequinone, m. p. 205°, which was derived by oxidation with chromic trioxide in glacial acetic acid. These derivatives gave no depression of the melting points on admixture with the corresponding derivatives of pure phenanthrene.

Anal. Found: C, 94.33; H, 5.24. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 80.70; H, 3.66. Calcd. for $C_{14}H_8O_2$: C, 80.69; H, 3.87%. Found: C, 59.37; H, 2.71. Calcd. for $C_{14}H_{10}\cdot C_6H_3O_7N$: C, 58.97; H, 2.80%.

The part ii, mentioned above, was recrystallized from methanol to yield 20 mg. of an anthracene, m. p. 215°. The derived anthraquinone melted at 283°.

Anal. Found: C, 94.35; H, 5.65. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 80.41; H, 3.62. Calcd. for $C_{14}H_8O_2$: C, 80.69; H, 3.87%.

The part iii was found to be a mixture of i and ii. Recrystallization through picrate and chromatographic separation afforded no good result. Therefore, the mixture was oxidized with chromic trioxide in glacial acetic acid. The oxidized substance was dissolved in alcohol and the product was adsorbed on neutral alummina and eluted with benzene; 20 mg. of pure phenanthrenequinone and 15 mg. of anthraquinone could be separated.

Dehydrogenation of Lucidusculine. — The conditions of dehydrogenation were the same as those used for miyaconitinone to obtain phenanthrene and anthracene. Neutral oil in an amount of 1.731 g. was obtained from 20 g. of lucidusculine. From the oil, 426 mg. of crystalline hydrocarbon mixture was separated by high vacuum distillation. The mixture was repeatedly recrystallized from methanol, but only 45 mg. of phenanthrene, m. p. 98°, (its picrate, m. p. 142°, the quinone, m. p. 204°) was isolated and no anthracene could be obtained. Other parts of hydrocarbon mixture were converted into picrate. The recrystallization was repeated again to give phenanthrene picrate and two other picrates. One of them was in the form of bright yellow needles, m. p. 130° and the other of yellow needles, m. p. 125°. From the former, 38 mg. of 3-methylphenanthrene, m. p. 62° was obtained and it was oxidized to the quinone, m. p. 204°. Orange plates.

Anal. Found: C, 93.58; H, 6.06. Calcd. for $C_{15}H_{12}$: C, 93.71; H, 6.26%. Found: C, 80.92; H, 4.79. Calcd. for $C_{15}H_{10}O_2$: C, 81.10; H, 4.54%.

From the latter, 9 mg. of hydrocarbon, m. p. 80° was obtained. Five mg. of this substance was oxidized to quinone which was recrystallized from methanol and melted at 182°. Reddish needles. But its yield was too small to be recrystallized repeatedly for analysis. It seemed to be pimanthrene (1,7-dimethylphenanthrene).

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