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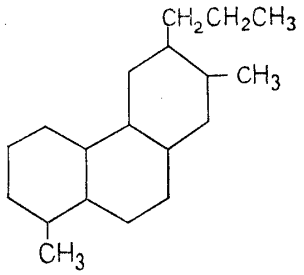
On the Carbon Skeleton of Kobusine

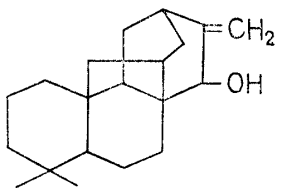
In a previous paper[1] on aconite alkaloid series, catalytic hydrogenation, chromium trioxide oxidation, and acid-catalyzed rearrangement on kobusine, $C_{20}H_{27}O_2N$, were described and it was revealed that the alkaloid possesses an allyl alcohol type of grouping ($CH_2=\overset{|}{C}-\overset{|}{C}-OH$) as do many other C_{20}-aconite and garrya alkaloids. At the same time, another oxygen function was proved to be a secondary hydroxyl group located in a six-membered ring system.

On continuing the research, the writer now carried out a selenium degradation reaction on kobusine itself so as to elucidate the fundamental skeleton of its structure. Three compounds were isolated from the dehydrogenation mixture. One of these, which was obtained from the neutral portion by successive chromatographies on alumina, showed m.p. 84~88° (Kofler) and its ultraviolet absorption spectrum was identical with those of 1,6,7-trialkylphenanthrenes.[2] Trinitrobenzene complex of this compound melted at 150~152°. Judging from these behaviors, this compound seemed to be the same as the alkylphenanthrene from anhydroignavinol[3] and also from hypognavinol,[4] whose structure had been determined as 1,7-dimethyl-6-propylphenanthrene[5] (I). In fact, identification of the alkylphenanthrene from kobusine with (I) was performed by admixture of the phenanthrenes and their trinitrobenzene complexes.

The other two of the dehydrogenation products were aromatic bases, which gave (i) m.p. 115~115.5° (trinitrobenzene complex, m.p. 162~163°); and (ii) m.p. 142~143° (Kofler). Characterization of these bases is being pursued.

(I)





(II)

Now that 1,7-dimethyl-6-propylphenanthrene (I) is established to be one of the chief degradation products, it would be quite probable that kobusine has completely the same carbon skeleton as ignavine[6] and hypognavine,[7] and the formula (II) is proposed for the carbon structure of kobusine, considering in addition to the above-mentioned fact that kobusine belongs to the diterpenoid alkaloid.

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3) E. Ochiai, T. Okamoto, T. Sugasawa, S. Sakai : *Ibid.*, **2**, 388(1954).
4) S. Sakai : Yakugaku Zasshi, **76**, 1054(1956).
5) E. Ochiai, T. Okamoto, S. Hara, S. Sakai, M. Natsume : This Bulletin, **6**, 327(1958).
6) E. Ochiai, T. Okamoto : This Bulletin, **7** (No. 5)(1959), in press.
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