Isodelphinine, a New Alkaloid from Aconitum miyabei, Nakai

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Recently a third new alkaloid, sachaconitine, and a fourth probably new alkaloid (I)[1], base D, having the same empirical formula, $C_{33}H_{45}O_9N$, as that of delphinine (II)[2] but different m.p. and $[\alpha]_D$, were isolated from Aconitum *miyabei*, Nakai. As described below, I has the same empirical formula and the same functional groups as II, but differs distinctly from II as shown by the mixed m. p. and infrared spectra. Thus the name isodelphinine was assigned to I. This substance, m. p. 167~168°C, $[\alpha]_D^{20}+20.1°$, gave a perchlorate, m. p. 171~172°C, $[\alpha]_D^{20}-2.38°$. (*Anal.* Found: C, 56.35; H, 4.97; Cl, 4.87. Calcd. for $C_{33}H_{45}O_9N \cdot HClO_4$: C, 56.55; H, 5.19; Cl, 5.06%). The aurichloride crystallized from chloroform-ethanol in prisms, m. p. 228~229°C. (*Anal.* Found: Au, 20.96. Calcd. for $C_{33}H_{45}O_9N \cdot HAuCl_4$: Au, 20.94%). Other salts of I, for example, acid oxalate or hydrochloride, did not crystallize although the corresponding salts of II had been obtained[3] as crystals.

On acetylation with acetyl chloride I gave a monoacetate, m.p. 188~190°C. (*Anal.* Found: C, 65.43; H, 6.81. Calcd. for $C_{35}H_{47}O_{10}N$: C, 65.55; H, 6.76%). Saponification of I gave benzoic acid which was identified with an authentic sample, and acetic acid which was confirmed as silver salt. (*Anal.* Found: Ag, 64.49. Calcd. for $C_2H_3O_2Ag$: Ag, 64.67%). The presence of four methoxyl groups was determined by the micro-Zeizel determination. (*Anal.* Found: OCH_3, 20.11. Calcd. for $C_{29}H_{33}O_5N \cdot 4(OCH_3)$: OCH_3, 20.63%). In the Herzig-Meyer *N*-alkyl determination, I gave methyl iodide which was confirmed as tetramethylammonium iodide. (*Anal.* Found: I, 67.46. Calcd. for $(CH_3)_4 \cdot NI$: I, 67.86%).

Above evidences show that the formula of I may be extended as follows in the same way as that of II:

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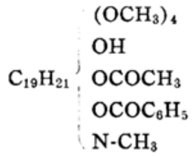
[1] H. Suginome, N. Katsui and G. Hasegawa, This Bulletin, **32**, 604 (1959).

[2] R. H. F. Manske and H. L. Holmes, "The Alkaloids", Vol. IV, Academic Press Inc., New York (1954), p. 275.

[3] T. Walz, *Arch. Pharm.*, **260**, 9 (1922); W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **127**, 301 (1939).



$$C_{19}H_{21}\left\{\begin{array}{l}(OCH_3)_4\\ OH\\ OCOCH_3\\ OCOC_6H_5\\ N\text{-}CH_3\end{array}\right.$$

The infrared spectra of I and II were quite similar except for the region due to ester carbonyl groups : compound I showed two bands at 1720 cm^{-1} and 1702 cm^{-1}, whilst II one band[4] at 1720 cm^{-1}.

On the basis of the same extended formula and the resemblant spectra, it may be reasonable to consider that I possesses a skeletal formula closely related to that of II. Furthermore, the same ring structure has been suggested for several alkaloids[5] of two genera, Aconitum and Delphinium, in which oxygen atoms are similarly located although the substituents are different. And then it may be considered that the substituents of I and II are also similarly located. On the other hand, it is well known[6] that the benzoyl group in II covers a secondary hydroxyl group which is vicinal to a free *tert* hydroxyl group.

If above consideration is correct, a simple explanation of the difference in infrared spectra of I and II may be that the free hydroxyl and the benzoyl group have *trans* orientation in II against *cis* in I.

In the *cis* orientation, an ester carbonyl band displacement[7] to lower frequencies due to hydrogen bonding is considerable. An experiment to clarify the relation of I and II is in progress and will be reported in a later paper.

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[4] Schneider has reported that the spectrum of II showed one band due to two ester groups at 5.78 μ, *Ann.*, **590**, 155 (1954).

[5] R. C. Cookson and M. E. Trevett, *J. Chem. Soc.*, **1956**, 3121; R. Anet, D. W. Clayton and L. Marion, *Can. J. Chem.*, **35**, 397 (1957); F. Sparatore, R. Greenhalgh and L. Marion, *Tetrahedron*, **4**, 157 (1958); O. E. Edwards, L. Marion and K. H. Palmer, *Can. J. Chem.*, **36**, 1097 (1958); E. Ochiai, T. Okamoto and M. Kaneko, *Chem. Pharm. Bull. Japan*, **6**, 730 (1958).

[6] W. A. Jacobs and Y. Sato, *J. Biol. Chem.*, **180**, 479 (1949); K. Wiesner, F. Bickehaupt and Z. Valenta, *Tetrahedron*, **4**, 418 (1958).

[7] R. N. Jones, P. Humphries, F. Herling and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2820 (1952).