On the Structure of Actinidine and Matatabilactone, the Effective Components of Actinidia polygama

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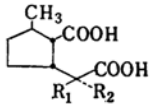
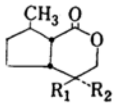
(Received February 10, 1959)

Deep interest has been held in Japan in *Actinidia polygama* Miq., a plant especially liked by the Felidae animals. The authors isolated two substances that excite cats from the leaves and gall of this plant. One is a base, named actinidine, $C_{10}H_{13}N$, b.p. 100~103°C/9 mm., $[\alpha]^{11}_{D}$ $-7.2°$ (c 17.54, chloroform) (picrate: m.p. 143°C; *Anal.* Found: C, 51.45; H, 4.09; N, 14.97. Calcd. for $C_{16}H_{16}O_7N_4$: C, 51.06; H, 4.29; N, 14.89%), and the other, a neutral substance, named matatabilactone, $C_{10}H_{16}O_2$, b.p. 106~109°C/2 mm., $[\alpha]^{28}_{D}$ $+31.9°$ (c 1.82, chloroform) (3,5-dinitrobenzoate of the methyl ester of the corresponding hydroxy acid: m.p. 78~79°C; *Anal.* Found: C, 54.88; H, 5.77; N, 7.09. Calcd. for $C_{18}H_{22}O_8N_2$: C, 54.82; H, 5.62; N, 7.10%).

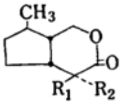
Permanganate oxidation of the hydroxy acid, obtained by alkali hydrolysis of matatabilactone, afforded two isomeric dicarboxylic acids, $C_{10}H_{16}O_4$, of m.p. 84~85°C, $[\alpha]^{13}_{D}+32.5°$ (c 0.63. chloroform), (*Anal.* Found: C, 60.32; H, 8.08. Calcd.: C, 59.98; H, 8.05%), and of m.p. 117~118°C, $[\alpha]^{12}_{D}$ $+15.6°$ (c 0.93, chloroform), (*Anal.* Found: C, 60.32; H, 8.08.), which were found, through the good offices of Dr. McElvain, to be respectively identical with nepetalinic acids[1,2] of m.p. 85°C (Ia*) and of m.p. 117°C (Ib), obtained from nepetalactone by him.**



Ia $R_1=CH_3, R_2=H$
Ib $R_1=H, R_2=CH_3$



IIa $R_1=CH_3, R_2=H$
IIb $R_1=H, R_2=CH_3$



IIIa $R_1=CH_3, R_2=H$
IIIb $R_1=H, R_2=CH_3$

It follows, therefore, that the structure of matatabilactone may be represented by either II or III. In the inrared spectrum of matatabilactone, the value of $\nu_{C=O}$ (5.76 μ in carbon tetrachloride) differs from that[3] of isoiridomyrmecin[4] (iridolactone)[3,5,6](IIIa) and of iridomyrmecin[3,5-9] (IIIb), but is very similar to that of the dihydro derivative of nepetalactone*. Thus, matatabilactone is II, i.e. dihydronepetalactone[10]. Examination are now

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* Heavy dots represent that the substituents are situated above the plane of the cyclopentane ring.

** Through mixed fusion test and comparison of infrared absorption spectra.

[1] S. M. McElvain, R. D. Bright and P. R. Johnson, *J. Am. Chem. Soc.*, **63**, 1558 (1941).

[2] S. M. McElvain and E. J. Eisenbraun, ibid., **77**, 1599 (1955).

*) A private communication from Dr. S. M. McElvain.

[3] G. W. K. Cavill, D. L. Ford and H. D. Locksley, *Autralian J. Chem.*, **9**, 288 (1956).

[4] S. M. McElvain and E. J. Eisenbraun, *J. Org. Chem.*, **22**, 976 (1957).

[5] G. W. K. Cavill, D. L. Ford and H. D. Locksley, *Chem. & Ind.* (London), **1956**, 465.

[6] G. W. K. Cavill and H. D. Locksley, *Australian J. Chem.*, **10**, 352 (1957).

[7] M. Pavan, *Ricerca Sci.*, **19**, 1011 (1959) (*Chem. Abstr.*, **45**, 7309 (1951)); ibid **20**, 1853 (1950) (*Chem. Abstr.*, **45**, 5869 (1951)).

[8] M. Pavan, *Chimica e industria* (Milan), **37**, 625, 714 (1955) (*Chem. Abstr.*, **49**. 16333, (1955); **50**, 13311 (1956)).

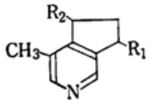
[9] R. Fusco, R. Trave and A. Vercellone, ibid., **37**, 251, 958 (1955) (*Chem. Abstr.*, **50**, 6737 (1956)).

[10] J. Meinwald, *J. Am. Chem. Soc.*, **76**, 4571 (1954).

being made to see whether this lactone is a mixture of IIa and IIb or not.

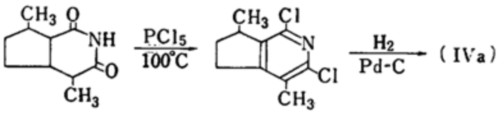
Actinidine was assumed to be a pyridine base from its color reaction (violet to 2,4-dinitrochlorobenzene and alkali) and from ultraviolet and infrared absorption spectra, $\lambda_{\max}$ 262 mμ (ethanol) (ε=2,400) and $\nu_{C=N}$ 6.30 μ (liquid). Several pyridine derivatives were actually isolated as the permanganate-oxidation products. One melting at 255°C with decomposition (*Anal.* Found: C, 53.19; H, 4.24; N, 8.00. Calcd. for $C_8H_7O_4N$: C, 53.04; H, 3.90; N, 7.73%), was found to be identical with 5-methylpyridine-3,4-dicarboxylic acid obtained by similar oxidation of 4-methylisoquinoline. Consideration of the natures of other oxidation products, a hydroxy compound, m.p. 132~133°C (*Anal.* Found: C, 73.11; H, 8.23; N, 8.48. Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03; N, 8.58%) and a lactone, m.p. 92.5~93°C (*Anal.* Found: C, 66.33; H, 5.61; N, 8.28. Calcd. for $C_9H_9O_2N$: C, 66.24; H, 5.56; N, 8.58%), suggests formula IVa for actinidine.

The alternative formula IVb is excluded by the fact that a ketone, m.p. 47~49°C, $\nu_{C=O}$ 5.85 μ (liquid), (*Anal.* Found: C, 74.42; H, 6.92; N, 8.49. Calcd. for $C_{10}H_{11}ON$: C, 74.51; H, 6.88; N, 8.69%), was derived from actinidine-*N*-oxide, m. p. 123.5~124.5°C (*Anal.* Found: C, 73.94; H, 8.04; N, 8.45. Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03; N, 8.58%) through rearrangement, hydrolysis and oxidation.



IVa $R_1=CH_3, R_2=H$
IVb $R_1=H, R_2=CH_3$

The structure IVa is closely related to that of II. Actually, actinidine was synthesized from nepetalinic acid imide as shown below.



It is very interesting to note that a monoterpene and an alkaloid having the same carbon skeleton following the isoprene rule have been found in one and the same plant.

The authors wish to express their sincere gratitude to Dr. S. M. McElvain for the identification of their samples with his nepetalinic acids.

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