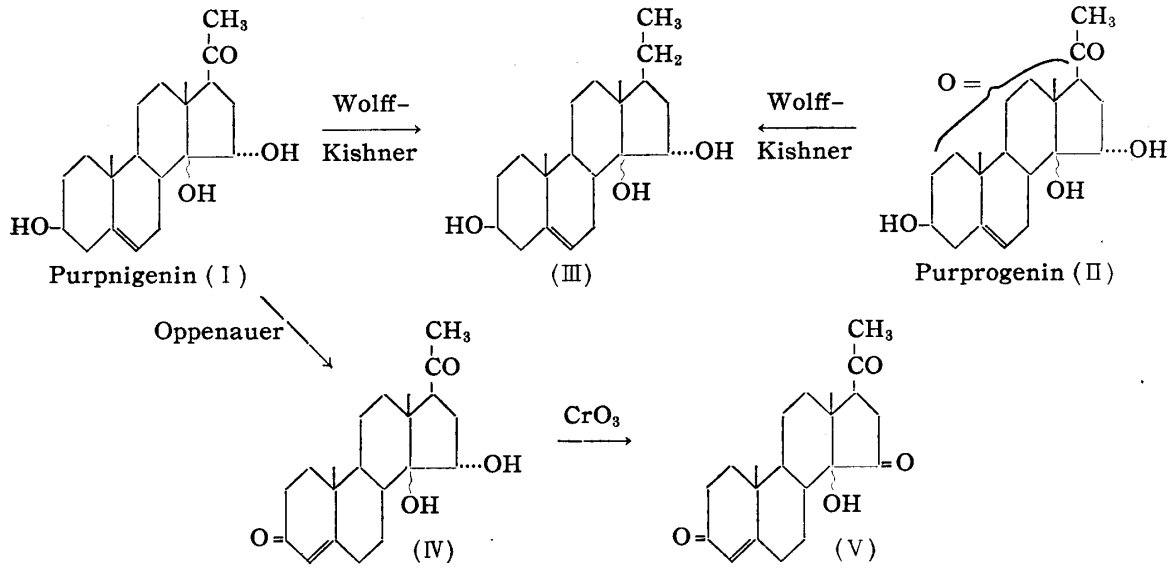
232~235°, $[\alpha]_D^{21}$ +117.8°(UV λ_{max}^{EtOH} 241 mμ (log ε 4.16); IR $\lambda_{max}^{CHCl_3}$ μ : 3.01, 5.72, 5.90, 6.01, 6.18), which contained a five-membered ring ketone. Since its ultraviolet spectrum and color reaction precluded the presence of a β-diketone, it was highly probable that the newly produced ketone occupies the 15-position, and both purpnigenin and purprogenin contain a 14,15-glycol group. Orientation of the 15-hydroxyl group was inferred to be α, in view of the acetate formation, but that of the 14-hydroxyl group is still to be clarified.

From these results it seems to be appropriate to assign tentative formulae (I) and (II), respectively, to purpnigenin and purprogenin.



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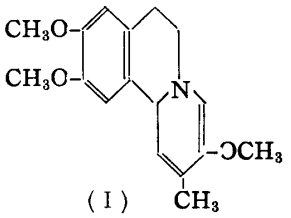
Synthesis of *rac*-Tetrahydrorotundine

The writers have been engaged in the synthesis of rotundine, a main alkaloid of *Stephania rotunda* LOUREIRO, to which the structure of 2-methyl-3,9,10-trimethoxy-6,7-dihydro-11b*H*-benzo[*a*]quinolizine (I) had been forwarded by H. Kondo and Matsuno.[1] Sugasawa and Mizukami[2] recently synthesized *rac*-dihydrorotundine. The corresponding 1,2,3,4-tetrahydro derivative (IX) appeared to be a suitable intermediate for this synthesis, in which case partial dehydrogenation of 1,2,3,4-positions would be possible.

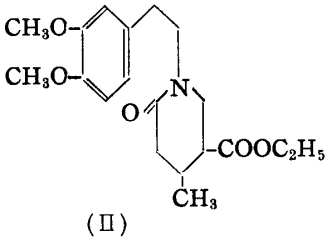
Various procedures for this synthesis were examined and the ring-closure of N-substituted pyridone was tried but only the N-substituted 2-chloropyridinium salt, which

1) H. Kondo, T. Matsuno : Yakugaku Zasshi, **64A**, 28(1944); **64B**, 113, 274(1944).
2) S. Sugasawa, K. Mizukami : This Bulletin, **6**, 539(1958). cf. K. Mizukami : *Ibid.*, **6**, 312(1958).

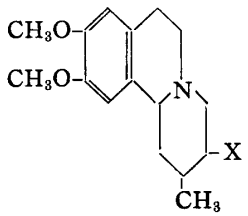
easily converted to the corresponding 2-pyridone by the action of sodium hydroxide, was obtained.[3] Accordingly, the ethyl ester (III) was prepared by ring closure of the piperidone (II), which was obtained by condensation of 3,4-dimethoxyphenethyl bromide and 4-methyl-5-ethoxycarbonyl-2-piperidone[4] in the presence of sodium hydride. In this case, the reductive condensation of diethyl α-cyano-β-methylglutarate with homoveratrylamine was also tried according to the procedure of Preobrazhenskii[5] but the objective compound (II) was not obtained as the main product.[6]



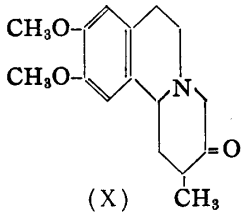
(I)



(II)



(III) $X=COOC_2H_5$
(IV) $X=CONHNH_2$
(V) $X=NHCOOCH_2C_6H_5$
(VI) $X=NH_2$
(VII) $X=OH$
(VIII) $X=OSO_2CH_3$
(IX) $X=OCH_3$



(X)

The Curtius degradation was then applied to the preparation of the amino derivative (VI), m.p. 302~303° (decomp.) (*Anal.* Calcd. for $C_{16}H_{24}O_2N_2 \cdot 2HCl \cdot \frac{1}{2}H_2O$: C, 53.63; H, 7.51; N, 7.82. Found : C, 53.25; H, 7.67; N, 7.99), via the hydrazide (IV), m.p. 220~221° (*Anal.* Calcd. for $C_{17}H_{25}O_3N_3 \cdot \frac{1}{2}H_2O$: C, 62.17; H, 7.98; N, 12.80. Found : C, 61.68; H, 7.73; N, 13.33), and benzylurethan (V), m.p. 207~208° (*Anal.* Calcd. for $C_{24}H_{30}O_4N_2$: C, 70.22; H, 7.37; N, 6.82. Found : C, 69.70; H, 7.19; N, 7.28). The amino derivative (VI) was then diazotized with sodium nitrite in acetic acid according to Akiya's method[7] and the objective hydroxyl compound (VII) was obtained as a viscous oily substance, which was purified as its methiodide of m.p. 223~225° (*Anal.* Calcd. for $C_{16}H_{23}O_3N \cdot CH_3I \cdot 1\frac{1}{2}H_2O$: C, 45.74; H, 6.50; N, 3.14. Found : C, 45.77; H, 6.48; N, 4.80). In order to prove the presence of a hydroxyl group in (VII), its methanesulfonate (VIII), m.p. 255~257° (decomp.) (*Anal.* Calcd. for $C_{17}H_{25}O_5NS \cdot CH_3I \cdot H_2O$: C, 41.99; H, 5.83. Found : C, 41.99; H, 6.04), was prepared. This hydroxyl compound (VII) was then methylated with diazomethane in the presence of fluoroboric acid in chloroform[8] and this methyl ether (IX) was found to be a methiodide, m.p. 240~241° (*Anal.* Calcd. for $C_{17}H_{25}O_3N \cdot CH_3I \cdot \frac{1}{2}H_2O$: C, 48.87; H, 6.56; N, 3.17. Found : C, 48.56; H, 6.29; N, 3.34).

3) *a*) S. Sugasawa, S. Akaboshi, Y. Ban : *Ibid.*, **7**, 236(1959). *b*) Y. Ban, *et al.* : *Ibid.*, **7**, 609(1959). *c*) T. Kametani, Y. Nomura : *Ibid.*, 8(1960), to be published. *d*) T. Kametani, Y. Nomura, K. Fukumoto : Yakugaku Kenkyu, **31**, 673(1959).
4) T. Kametani, Y. Nomura : Yakugaku Kenkyu, **31**, 678(1959).
5) R. P. Evstigneeva, R. S. Livshits, L. I. Zakharkin, M. S. Bainova, N. A. Preobrazhenskii : Doklady Akad. Nauk S. S. S. R., **75**, No. 4, 539(1950) (C. A., **45**, 7577(1951)).
6) T. Kametani, Y. Nomura : Unpublished data.
7) S. Akiya, T. Osawa : This Bulletin, **7**, 277(1959).
8) M. Neeman, M. C. Casero, J. D. Robert, W. S. Johnson : Tetrahedron, **6**, 36(1959).

In order to prove the structure of diazotization product (Ⅷ), it was oxidized with pyridine–chromic acid complex. The objective cyclic ketone (X) was thereby obtained as a crystalline methiodide of m.p. 234~236° (decomp.), identical with the melting point reported in the literature.[2] It was therefore found that the substance (IX) had a six-membered ring.

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February 11, 1960.