The configuration at C-7 and C-10 has also to be considered, because the oxide bridge may not retain the original configuration during the conversion from α-kessyl ketone (Ⅱ) to β-kessyl ketone (Ⅲ). Although the nuclear magnetic resonance signals of the C-10 methyl groups in Ⅲ, Ⅳ, Ⅷ, and Ⅶ suggest a close steric proximity to the C-2 oxygen functions, inspection of Dreiding models reveals that no difinite conclusion can be drawn concerning the configuration of the C-10 methyl group (*i.e.*, the oxide bridge) due to the flexible nature of the molecules. Further studies on this point are now being pursued.

A possible mechanism for the transformation of α-kessyl ketone (Ⅱ) into β-kessyl ketone (Ⅲ) is outlined in Chart 2.

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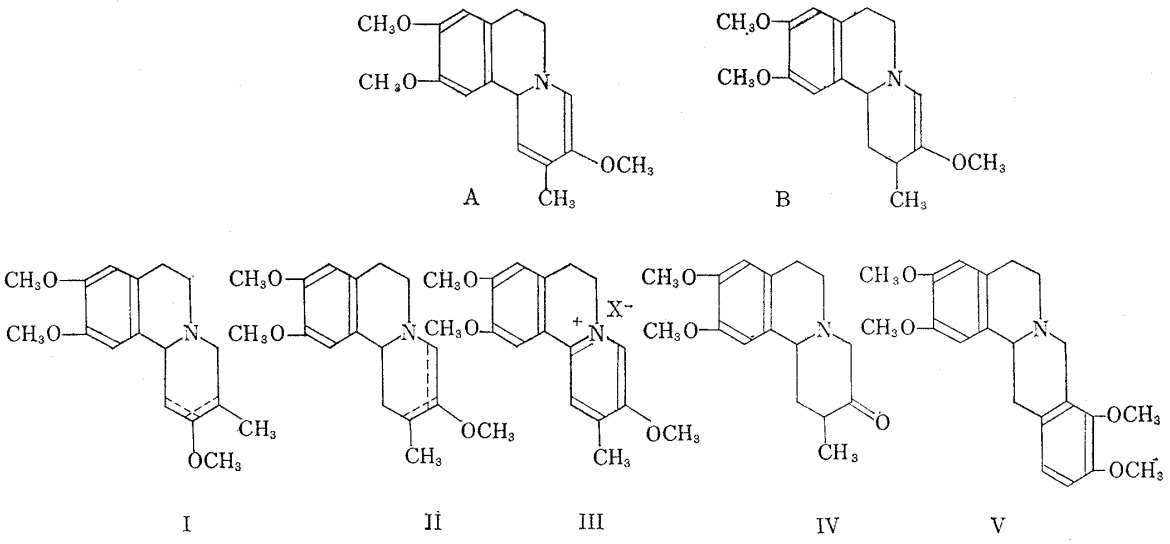
On the Structure of So-called Rotundine

Rotundine was originally isolated in 1944 by Kondo and Matsuno[1] from the rhizome of *Stephania rotunda* Loureio indigenous to Indo-China, and the structure (A) was assigned to this alkaloid and (B) to dihydrorotundine, which was claimed to have been obtained by them through catalytic hydrogenation of the former.

Later, for the purpose of providing synthetical support for these structures, Sugasawa and Mizukami[2] synthesized *rac*-dihydroisorotundine (I) and *rac*-dihydrorotundine (Ⅱ), and then, one of the present authors (M. K.)[3] studied behaviour of Ⅱ. By treating Ⅱ with $Hg(OAc)_2$ he obtained (Ⅲ, X=Cl), which, on being reduced catalytically, furnished two partially reduced isomeric compounds of *rac*-dihydrorotundine type. Both of them, however, were found not to be identical with and behaved differently from Matsuno's dihydrorotundine (B); *i.e.*, they smoothly gave the ketone (Ⅳ) when treated with dil. hydrochloric acid, whereas (B) was quite stable to hydrochloric acid. Moreover, the compound (Ⅲ, X=Cl) did not coincide with dehydrorotundinium chloride prepared from (B).

The structure of rotundine as proposed by Matsuno thus appears to be improbable and its reappraisal became necessary. Though our efforts to obtain *S. rotunda* ended

1) H. Kondo, T. Matsuno : Yakugaku Zasshi, **64B**, 113 (1944).
2) S. Sugasawa, K. Mizukami : This Bulletin, **6**, 313, 359 (1958).
3) M. Kawanishi : *Ibid.*, **10**, 191 (1962).



fruitless, fortunately we happened to gain information that *Stephania glabra* indigenous to India is identical with *S. rotunda*. Therefore, tubers of *S. glabra*[*1] were used as a source material in place of *S. rotunda* in this investigation.

From the air-dried powdered tubers an alkaloid was isolated in a crystalline form in a yield of 0.5%. The evidence of the identity of this base with *l*-rotundine was provided from the physical and chemical data of the former given below, which also stand in close similarity with those of *l*-tetrahydropalmatine (V).[*2]

$[\alpha]_D^{26}$ −276° (c=1.56, EtOH); mol. wt. 343 (Rast method); *Anal.* Found : C, 70.65; H, 6.95; N, 3.88; OCH_3, 33.80. UV λ_{max}^{EtOH} mμ (log ε) : 282 (3.64); IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 2760 (Bohlmann's *trans*-quinolizidine band); Rf : 0.68 (Thin-layer chromatography on aluminum oxide G, $CHCl_3$); HCl salt m.p. 222~223° (decomp.); methiodide m.p. 248~250° (decomp.); The dehydrogenated (with $Hg(OAc)_2$) product as chloride m.p. 205~206° (decomp.), as iodide m.p. 233~235° (decomp).

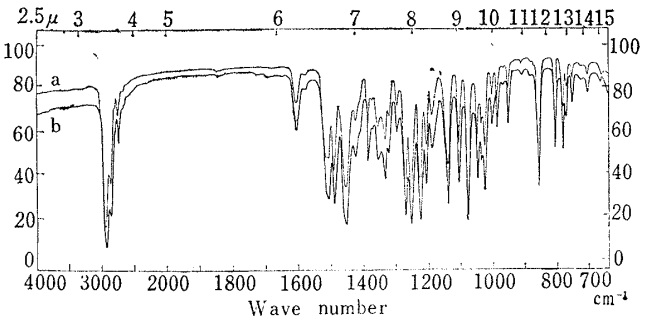


Fig. 1. Infrared Spectra (in $CHCl_3$)

a) synthetic *rac*-tetrahydropalmatine
b) *rac*-rotundine

Hence, our base was first dehydrogenated with $Hg(OAc)_2$ and then catalytically reduced to furnish *rac*-derivative of the original base. The product was found to be identical by direct comparision (mixed melting point and infrared spectra (Fig. 1)) with *rac*-tetrahydropalmatine synthesized by the authentic procedure, making it possible to draw a deduction that *l*-rotundine is in reality *l*-tetrahydropalmatine.

Therefore, the authors would like to propose to erase the name rotundine from the literature and thus the existence of benzo[*a*]quinolizine type of alkaloid in Stephania species has been made invalid.

Full details will appear in the forthcoming Chem. pharm. Bull.

*1 Purchased from United Chemical & Allied Products 10, Clive Row, Calcutta-1, India. The authors are grateful to Dr. Otto Isaac, Germany, for this valuable information on the source material.

*2 This compound was first isolated from *Stephania glabra* by G. R. Chaudhry, S. Siddqui, V. N. Sharma & M. L. Dhar (J. Sci. Ind. Research., **9B**, 79 (1950); *Ibid.* **11B**, 337 (1952)).

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