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Deamination of 8-Amino-1,2,3,4-tetrahydro-6,7-dimethoxy-1-(4-methoxybenzyl)-2-methylisoquinoline

We have already reported[1] that deamination of 8-amino-1-benzyl-1,2,3,4-tetrahydro-6,7-dimethoxy-2-methylisoquinoline (I) by hypophosphorous acid combined with a diazotization step give two compounds, one of which is a deamination product, 1-benzyl-1,2,3,4-tetrahydro-6,7-dimethoxy-2-methylisoquinoline (Ic), and the other is an intramolecular cyclization product, *dl*-nuciferin (Ia).

Now we wish to report that the deamination of 8-amino-1,2,3,4-tetrahydro-6,7-dimethoxy-1-(4-methoxybenzyl)-2-methylisoquinoline (II) with sodium nitrite and 5% sulfuric acid solution at 5° followed by reduction of the resulting diazonium salt with hyposphophorous acid give three compounds.

The product was chromatographed on silica gel eluted with chloroform to be separated into three components, which were respectively identified with authentic samples by the infrared and nuclear magnetic resonance spectral comparisons.

The first eluted component was one of the intramolecular cyclization product, *dl*-1,2,10-trimethoxyaporphine (IIa), the second was the other cyclization product, *dl*-pronuciferin (IIb), which had a spiro-dienone system, and the third was a deamination product, 1,2,3,4-tetrahydro-6,7-dimethoxy-1-(4-methoxybenzyl)-2-methylisoquinoline (IIc).

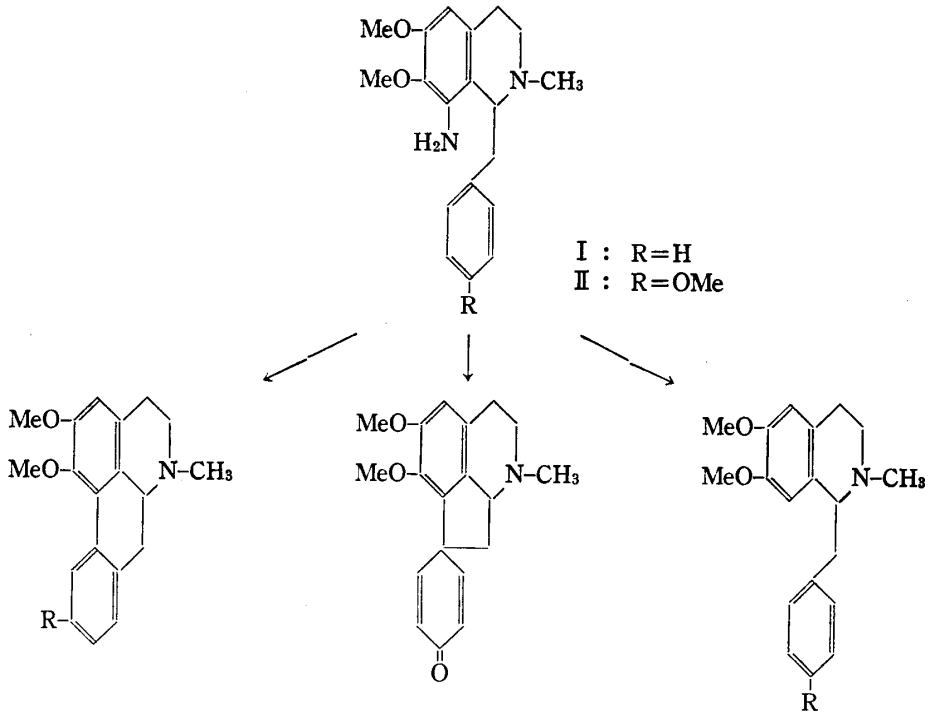

Chart 1

Hey, *et al.*[2] first reported the synthesis of the spiro-dienone system by thermal decomposition of the diazonium sulfate of the corresponding amino compound in an aqueous solution,

1) This work was presented at the 88th Annual Meeting of the Pharmacuetical Society of Japan, Tokyo, April 1968; S. Ishiwata and K. Itakura, *Chem. Pharm. Bull.* (Tokyo), submitted.
2) D.H. Hey, J.A. Leonard, T.M. Moynehan, and C.W. Rees, *J. Chem. Soc.*, **1961**, 232.

and recently, Kametani, *et al.*[3] and Battersby, *et al.*[4] also reported the synthesis of the spiro-dienone system under the same conditions following that of Hey, *et al.* However, there has been no report that the deamination of 8-aminoisoquinoline gives the spiro-dienone system, proaporphine.

Further investigation on the deamination of 8-aminoisoquinolines is in progress in this laboratory.

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3) T. Kametani, K. Fukumoto, and T. Sugahara, *Tetrahedron Letters*, **52**, 5459 (1968).
4) A.R. Battersby, A.K. Bhatnagar, P. Hackett, C.W. Thornber, and J. Stauton, *Chem. Commun.*, **1968**, 1214.

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Structures of New Flavonoids, Sophoradin and Sophoranone, from *Sophora subprostrata*

During the course of our studies on the constituents of the root of *Sophora subprostrata* CHUN et T. CHEN (Chinese Drug: Shan-Dou-Gen (山豆根)), two new flavonoids, sophoradin (I) and sophoranone (VIII), (both named by us), have been isolated from the ether-soluble fraction of the methanol extract.

In this communication, we wish to report the structures of these flavonoids.

Sophoradin (I) was obtained as yellow needles; mp 161°; $C_{30}H_{36}O_4$; $FeCl_3$ (+); UV λ_{max}^{EtOH} mμ (log ε): 380 (4.60), $\lambda_{max}^{EtOH\text{-}NaOEt}$ mμ (log ε): 480 (4.70); IR (KBr) cm^{-1}: 3400, 3200 (OH), 1635 (conjugated CO), 1610 (aromatic C=C), 1380 ($-CH_3$).

The UV spectrum suggested the presence of chalcone nucleus in I,[1a] which was also supported by the formation of a dihydrochalcone derivative (II) (octahydrosophoradin), mp 102°, $C_{30}H_{44}O_4$; UV λ_{max}^{EtOH} mμ (log ε): 288 (4.22); IR (KBr) cm^{-1}: 3500(OH), 1630 (conjugated CO), 1610, 1600 (aromatic C=C), 1385, 1375 ($-CH_3$), by catalytic hydrogenation.

On acetylations, I and II gave each of the triacetates, III[2]; $FeCl_3$ (—); NMR[3]: 7.70 (6H, s., –OAc×2), 7.75 (3H, s., –OAc), and IV[2]; $FeCl_3$ (—); NMR: 7.72 (9H, s., –OAc×3).

The NMR spectrum of I shows the presence of three γ,γ-dimethylallyl groups: 8.20 (18H, s., $-C{=}C\langle^{CH_3}_{CH_3}\times 6$), 4.70 (3H, br. t., J=6 cps, $-CH_2-\underline{C}H{=}C\langle\times 3$), 6.65 (6H, br. d., J=6 cps, $Ar-\underline{C}H_2-CH{=}C\langle\times 3$). Furthermore, these signals in I disappeared in II, while a sharp doublet

1) *a*) L. Jurd, "The Chemistry of Flavonoid Compounds," T.A. Geissman, ed., Pergamon Press, London, 1962, pp. 141—147; *b*) W.A. Whalley, *ibid.*, pp. 441—467.
2) The product was failed to be crystallized, but its purity was certified by thin-layer chromatography.
3) All NMR spectra were taken at 60 Mcps in $CDCl_3$ with TMS as an internal standard. Chemical shifts were given in τ values. Abbreviations: s.; singlet, d.; doublet, t.; triplet, m.; multiplet, br.; broad.