THE STRUCTURE OF MAGNOCOCLINE, A NOVEL BENZYLISOQUINOLINE ALKALOID FROM *MAGNOLIA COCO* (LOUR.) DC.

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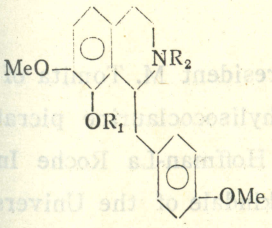
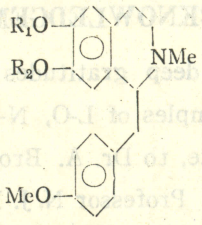
As reported in the previous paper[1] we have isolated three alkaloids: oxoushinsunine, salicifoline and magnoflorine from the stem of *Magnolia coco* (LOUR.) DC. Further investigation on the same part of this plant led to the isolation of a small amount of a new crystalline alkaloid which we proposed the name magnococline, together with two known alkaloids, stepharine and anolobine. The present communication deals with the structural elucidation of this new alkaloid.

Magnococline (I) was crystallized from acetone as leaflet plates, mp. 181-182° $[\alpha]_D$ −38° ($CHCl_3$), showed the molecular ion peak at *m/e* 299 in the mass spectrum ($C_{18}H_{17}O_3N$, M.W. 299). The UV spectrum gives absorption maxima at 227 (4.30), 279 (3.59) and 284 *nm* (log ε 3.52) and the IR spectrum at 3340 (secondary amino group), 1610, 1588, 1515 and 1495 (phenyl) and 1280 and 1250 cm^{-1} (OCH_3 and OH). The pattern of the UV spectrum is similar to that of benzylisoquinoline alkaloid, N-norarmepavine.[11]

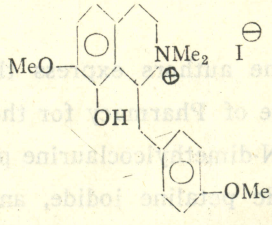
The NMR spectrum (CF_3COOH) of magnococline gives signals of six protons singlet of two *O*-methyl peak at 6.01 τ, six methylene protons at 6.25-6.90 τ, a hydroxyl proton centered at 4.9 τ, and six aromatic protons at 2.5-3.2 τ. There is no signal attributable to the N-methyl group and the methoxyl group is almost free from the deshielding effect of the benzyl-benzene ring.



(I) R_1, R_2=H
(II) R_1=H, R_2=CH_3
(III) R_1, R_2=$COCH_3$



(IV) R_1=H, R_2=CH_3
(V) R_1=CH_3, R_2=H



(VI)

Acetylation of magnococline (I) with acetic anhydride and pyridine gave an oily diacetate (III). The IR spectrum showed the presence of —N·$COCH_3$ at

1650 cm^{-1} and —O·$COCH_3$ at 1770 cm^{-1}. Treatment of magnococline with formalin in methanol and subsequent reduction with $NaBH_4$ gave N-methylmagnococline (II), a yellowish oil, which was characterized as picrate, yellow needles, mp. 166-170°. The IR spectra and tlc of II were not identical with L-O, N-dimethylisococlaurine (IV) picrate[2] or dl-O, N-dimethylcoclaurine (V) picrate[3]. Thus the two oxygen function in isoquinoline nucleus should not attach at the usual C_{6-7} position as the most of the benzylisoquinoline alkaloids isolated from the natural source. The NMR spectrum ($CDCl_3$) of II showed at 7.69 τ (3H, N—CH_3), 6.29, 6.18 τ (3H each, singlet, two O—CH_3), 4.26 τ (1H, broad, OH). The N—CH_3 signal at 7.69 τ is higher by 0.1 *ppm* than that of normal C_{6-7} substituted benzyltetrahydroisoquinoline[4] due to the shielding effect. In addition, both magnococline (I) and N-methylmagnococline (II) were positive with Gibb's reagent and negative with Feigal and Millon tests suggested that magnococline is a novel benzylisoquinoline alkaloid having an unusual C_{7-8} dioxygenation pattern, most likely substituted at C_7—OCH_3 and C_8—OH respectively. From these chemical and spectral properties, structure I was assigned for magnococline, and this was supported by mass spectrum. The mass spectrum shows the weak molecular ion peak at *m/e* 299, the base peak at *m/e* 178, and the other intense peaks at *m/e* 163, 162, 134, 121, 91 and 65. This fragmentation pattern has been shown to be characteristic to the benzylisoquinoline alkaloids[5,6] having the benzyl-benzene ring with a methoxyl group. The evidence for structure was adduced from the experimental results which follow.

Upon being treated with methyliodide in methanol, N-methylmagnococline (II) yielded a yellowish oily N-methyliodide compound (VI). The IR spectrum was superimposable with that of racemic petaline iodide[7] (VI). Its *l*-form was isolated originally from *Lenotice Leontapetalum* L.[8] and was elucidated[9,10] to have the structure VI. The identity was also confirmed by the tlc on silica gel G with $CHCl_3$—MeOH (4:1) as the mobile phase. Consequently, the structure of magnococline is N, N-norpetaline represented by the formula I.

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