Communications to the Editor

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STRUCTURE OF MENISPORPHINE: A NEW TYPE OF ISOQUINOLINE ALKALOID

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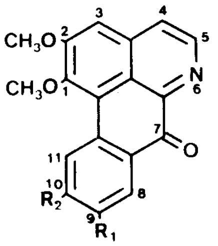
The structure of an unknown yellow base from *Menisperum dauricum* DC. (Menispermaceae) was determined to be 5,6,9-trimethoxy-7*H*-dibenzo[*de, h*]quinolin-7-one (1) by spectral data and total synthesis. It was named menisporphine and the skeletal name "oxoisoaporphine" was proposed for this new type of alkaloid. The biosynthesis route of oxoisoaporphine-type alkaloids in plants is suggested.

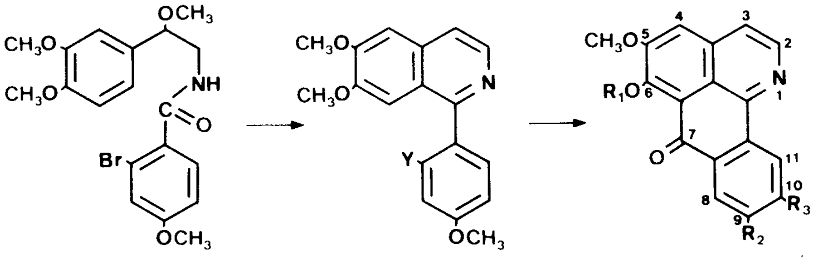
KEYWORDS —— *Menisperum dauricum* DC; Menispermaceae; menisporphine; dibenzo[*de, h*]quinoline; oxoisoaporphine-type alkaloid

A previous paper[1)] reported the isolation of six unknown yellow alkaloids from *Menisperum dauricum* DC. (Menispermaceae). This communication describes the structure of one of them, Base II, and names this new alkaloid menisporphine.

Menisporphine, mp 199.5∿200.5°C, was found to be $C_{19}H_{15}NO_4$ (m.w., 321.32) from its elemental analysis and MS. Its IR spectrum showed a conjugated carbonyl band at 1660 cm^{-1}. The UV spectrum [λ_{max}^{EtOH} nm (log ε): 254 (4.72), 288 (sh, 4.13), 3.19 (3.97), 368 (3.91), 420 (3.97)] indicated a highly conjugated system similar to that of oxoaporphine-type alkaloids.[2)] The ^{1}H NMR spectrum (in $CDCl_3$) showed the presence of *ortho*-coupling protons C_3-H and C_4-H [δ 7.55 (d, *J* = 5.5 Hz), δ 8.65 (d, *J* = 5.5 Hz)] of isoquinoline ring and four aromatic protons [δ 7.40 (s), δ 7.33 (d.d, *J* = 2.5, 9.0 Hz), δ 7.86 (d, *J* = 2.5 Hz), δ 8.79 (d, *J* = 9.0 Hz)] with three methoxyl groups. These data suggested the structure of 1,2,9- or 1,2,10-trimethoxyoxoaporphine [(3) or (4)].[3)] However, further study led to the structure, trimethoxy-7*H*-dibenzo[*de, h*]quinolin-7-one [(1) or (2)], which is the isomer of trimethoxyoxoaporphine-type alkaloids. Two of the substituted positions of the three methoxyl groups were determined to be located at C-5 and C-6 because of the appearance of a C_4-H signal at δ 7.40 as a singlet. The third was found to be located at C-9 or C-10 according to the splitting and coupling constant of signals due to the three residual aromatic protons in the ^{1}H NMR spectrum. The proton at C_{11}-H in this skeleton is expected to appear appreciably downfield due to steric strain from the biphenyl system, as in the case of C_1-H or C_{11}-H in oxoaporphine-type alkaloids. Consequently, the signals at δ 7.33 and δ 8.79 were assigned to the aromatic protons at C-10 and C-11, respectively. The position of the remaining methoxyl group must be C-9. These results suggested that menisporphine is 5,6,9-trimethoxy-7*H*-dibenzo[*de, h*]quinolin-7-one (1). Final evidence for this structure came from the total synthesis of the compound as follows:



(3) R_1=OCH_3, R_2=H
(4) R_1=H, R_2=OCH_3



(5)

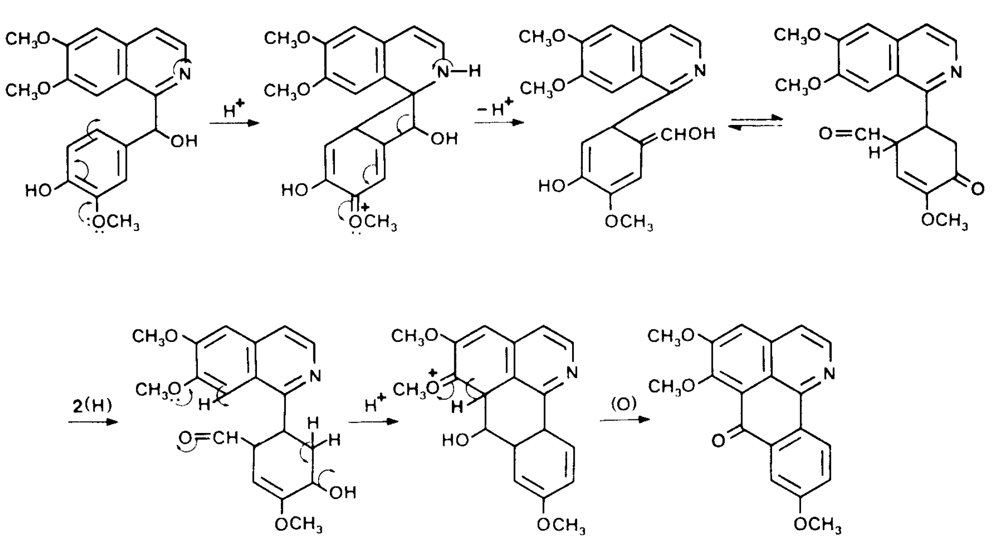
(6) Y=Br
(7) Y=CN
(8) Y=COOH

(9) R_1=R_3=H, R_2=OCH_3
(1) R_1=CH_3, R_2=OCH_3, R_3=H
(2) R_1=CH_3, R_2=H, R_3=OCH_3

Reagents: $(5)\xrightarrow{POCl_3}(6)\xrightarrow{CuCN/DMF}(7)\xrightarrow{KOH}(8)\xrightarrow{PPA}(9)\xrightarrow{CH_3I/Ag_2O}(1)$

The synthetic compound (1) was identified with the natural product, menisporphine by direct comparison of spectra (UV, IR, ^{1}H NMR and MS) and TLC. This new type of alkaloid has an entirely new skeleton (7*H*-dibenzo[*de*, *h*]quinolin-7-one) and we propose to name it "oxoisoaporphine" because of its relation to the isomer of oxoaporphine.

Biogenesis of oxoisoaporphine-type alkaloids in the plants may occur as follows:



The precusor may be a papaverinol derivative. The biogenesis route may involve the formation of isoquinoline derivatives containing a cyclobutane ring from the precusor by intramolecular oxidative coupling, followed by a dienone enol rearrangement with fission of cyclobutane ring.

REFERENCES

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