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PROMORPHINANE AND HASUBANANE ALKALOIDS OF *STEPHANIA SUBEROSA*

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Key Word Index—*Stephania suberosa*; Menispermaceae; promorphinane hasubanane alkaloid; stephaphylline; delavaine; nordelavaine; stephanubine.

Abstract—A new promorphinane alkaloid stephaphylline and two new hasubanane alkaloids, nordelavaine and stephanubine, have been isolated along with the known hasubanane, delavaine, from *Stephania suberosa*. Their structures and stereochemistry have been established from chemical and detailed NMR (^{1}H, ^{13}C and NOEDS) spectral studies.

INTRODUCTION

As a part of our phytochemical investigations we were interested in studying the alkaloid content of the roots of the vine *Stephania suberosa* Forman (Menispermaceae), native to Thailand, and commonly used in that country for medicinal purposes under the local name 'Borapet Pungchang' [1]. The basic fraction was found to contain a number of protoberberine [2] and bisbenzylisoquinoline alkaloids [3]. Further chemical investigation has led to the isolation of a new promorphinane, stephaphylline (**1**), and two new hasubananes, nordelavaine (**5**) and stephanubine (**10**), along with the known hasubanane, delavaine (**3**). This paper is concerned with the chemical and spectral characterization of these new hasubanane and promorphinane alkaloids differing in the orientation of the enone chromophore.

RESULTS AND DISCUSSION

The novel promorphinane alkaloid isolated from the plant was stephaphylline (**1**), $C_{21}H_{27}O_5N$. Its UV and IR spectra indicated the presence of a conjugated carbonyl function. The ^{1}H NMR (360 MHz) spectral assignments, summarized in formula **1**, were supported by extensive homo-decoupling experiments. Signals for four methoxyls, two *para* oriented aromatic protons, an N-Me, a CH_2CH_2N group and a set of isolated nonequivalent aliphatic methylene protons were clearly visible. The spectrum also displayed a signal at δ3.66 (*m*) for a methine proton linked to nitrogen. This proton is coupled to a methine proton (δ2.63, *d*, J = 3.3 Hz) as well as to one of the protons of another set of nonequivalent methylene protons resonating at δ2.78 (1H, *dd*, J = 18.4 Hz and 5.7 Hz). The ^{13}C spectrum of stephaphylline (Table 1) was also in conformity with structure **1**.

The T-shaped geometry of stephaphylline (**1**) was established from detailed NOEDS experiments. The decisive factor was the observation of reciprocal NOE (7% either way) between H-14 resonating at δ2.63 (*d*) and the axial proton on C-15 resonating at δ1.92 (*ddd*). The promorphinane structure **1** for stephaphylline received further support from its mass spectrum which exhibited an intense peak at *m/z* 315 (52%) for the loss of 58 mu comprising the portion $[-CH_2CH_2NMe+H]^+$.

Sodium borohydride reduction of stephaphylline (**1**) afforded quite reluctantly a tetrahydro derivative **2**, conceivably formed by the approach of the hydride from the more exposed flat face of the T-shaped molecule. The 360 MHz ^{1}H resonance assignments of the reduction product, summarized by formula **2**, followed from homo decoupling experiments. The hydroxy-methine proton in **2** resonating at δ4.18 (*br d*) had a fairly large coupling constant (10.9 Hz) with the hydroxyl proton (sharp doublet at δ2.89) disappearing upon addition of D_2O with a concommitant collapse of the signal at δ4.18 to a *br* singlet. It was further observed that irradiation of the signal at δ4.18 (*br d*) influenced the signal at δ3.22 (1H, *t*, J = 2.9 Hz) as well as that at 2.89 (1H, *d*, J = 10.9 Hz). Again, irradiation of the signal at δ1.87 (*br s*) collapsed the signal at δ4.18 (*br d*) to a double doublet and also affected the signal at δ3.18 (*m*), while irradiation of the δ3.18 (*m*) region influenced the δ3.32 (*m*) signal. Conversely, irradiation of the δ3.32 (*m*) resonance collapsed the resonance at δ2.91 (*d*) concommitant with sharpening of the δ3.18 (*m*) resonance. Furthermore, irradiation of the δ2.90 region influenced the δ4.18 (*br d*) resonance as well as that of the δ3.32 (*m*) signal. A set of non-equivalent methylene protons (double doublets at δ3.06 and 1.42, J_{gem} = 15.4 Hz) is further coupled to a neighbouring equatorial proton. It thus becomes apparent that this proton whose resonance is obscured by the methoxyl resonance at δ3.86 is likely to be coupled to the axial proton resonating at δ3.22 (1H, *t*, J = 2.9 Hz). The absence of coupling of the hydroxymethine proton (δ4.18, *br d*) with the methylene protons (δ3.06 and 1.42) at C-5 in **2** thus ruled out the presence of a $-CH_2CO-$ function in stephaphylline (**1**). The decoupling experiments also led to the conclusion that the multiplets (1H each) at δ2.46, 2.11, 1.68 and 1.40 in **2** were coupled to each other and are thus related with the $-CH_2CH_2N<$ portion of a chair-shaped ring.

The first hasubanane alkaloid we isolated was sub-

sequently found to be delavaine (3) [4]. We report here for the first time its detailed NMR analysis and some interesting chemical studies. The ^{1}H spectrum (360 MHz) is summarized in formula 3. ^{13}C NMR, homonuclear decoupling and NOE experiments indicated that five aliphatic methylenes (other than OCH_2O) are present as two CH_2CH_2 units and an isolated CH_2 one. The NOE experiments further demonstrated that the isolated methylene (resonating somewhat downfield at δ3.04 and 2.60 as doublets, 1H each, J = 15.9 Hz) is proximate to the aromatic proton resonating at δ6.68. Catalytic reduction of the aforesaid alkaloid using platinum dioxide and subsequent purification of the product by TLC unexpectedly afforded 4 which was probably generated *in situ* during purification by the loss of methanol from the dihydrodelavaine formed. The ^{1}H NMR spectrum of 4 displayed only one methoxyl signal at δ3.65 and an olefinic proton singlet at δ5.63 establishing that the conjugated carbonyl was next to the isolated methylene as shown in 3.

The first new hasubanane alkaloid was *N*-nordelavaine (5), $C_{19}H_{21}O_5N$. Its UV and IR spectra indicated the presence of conjugated CO and NH functions. The ^{1}H NMR spectrum (360 MHz), summarized around formula 5, showed signals for the presence of an OCH_2O and two OCH_3 functions as well as two aromatic protons which are *para* oriented. A set of isolated nonequivalent methylene protons (doublets at δ2.92 and 2.58, 1H each, J = 16.5 Hz) was also discernible. In addition there were signals for two CH_2CH_2 groups. The ^{13}C NMR spectrum of nordelavaine (5) bore a striking similarity to that of the congener alkaloid delavaine, except that the N-CH_3 group was missing and that the methylene carbon signals at δ51.2 and 22.5 present in the spectrum of 3 were somewhat displaced to δ42.1 and 27.0, respectively, in the spectrum of 5. Finally, we had resort to NOEDS experiments to arrive at the structure for nordelavaine except for the actual disposition of the carbonyl and the isolated methylene groups.

Consonent with the presence of a secondary amine function nordelavaine (5) formed an *N*-acetyl derivative 6. Again, treatment of 5 with methanal–formic acid furnished the congener alkaloid delavaine (3). However, when treated with $NaCNBH_3$ and formalin, 5 afforded 3 together with the allyl alcohols 7 and 8. The alcohols 7 and 8 were also obtained when delavaine (3) was reduced with sodium borohydride. The hydroxymethine proton in 7 appeared as a broad triplet at δ4.27 ($J \approx$ 4.0 Hz) and in 8 as a broad doublet of doublets at δ4.00 ($J \approx$ 8.7 Hz and 5.6 Hz), both signals sharpening on addition of D_2O. These observations thus indicated that the hydroxymethine protons in 7 and 8 (and thus the carbonyl in 5) had a methylene neighbour. Allyl alcohol 7 or 8, or a mixture, underwent smooth rearrangement to the enone 9 upon treatment with dilute HBr. The ^{1}H NMR spectrum of 9 showed the presence of only one OCH_3 signal at δ3.59 and an olefinic proton signal at δ5.63 as a triplet (J = 4.9 Hz). The formation of the enone 9 thus further supported the presence of a CH_2CO function in both delavaine (3) and nordelavaine (5). In the mass spectrometer delavaine (3), as well as nordelavaine (5), suffered facile loss of the ethyleneamine side chain which led to the generation of a number of common ion fragments in their spectra.

The second new hasubanane alkaloid isolated from Borapet was stephanubine (10), $C_{20}H_{25}O_5N$. The UV and IR spectra indicated the presence of a conjugated CO and NH functions. The ^{1}H NMR spectrum (360 MHz) was very similar to that of nordelavaine (5) except for the presence of additional OCH_3 signals at δ3.84 and 3.85 instead of an OCH_2O signal. The $[M]^+$ peak, as expected, was 16 mu higher than that of nordelavaine (5) and this difference was manifested in most of the ion peaks which were formed from the ion derived by the initial loss of the ethyleneamine unit.

^{13}C resonance assignments of stephaphylline (1) followed from consideration of carbon resonance reported for tridictyophylline (11) [5] where the OH group led to upfield shifts for the C-5 and C-15 resonances by *ca* 4.9–5.0 ppm relative to 1. A redesignated signal assignment of tridictyophylline is given in Table 1. ^{13}C resonance assignments of delavaine and nordelavaine (Table 1) followed from mutual correlation and consideration of stephaphylline resonances. The orientation of the enone chromophore in 1, 3, 5 and 10 is striking. The biogenetic equivalent of stephaphylline (1) undergoes *in vivo* enzymic oxidation to a tridictyophylline analogue which is transformed in the plant cell to hasubananes similar to those reported herein.

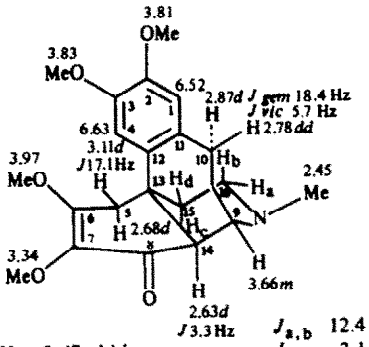
EXPERIMENTAL

UV and CD spectra were recorded in MeOH, IR spectra and rotations in $CHCl_3$. NMR spectra were usually measured in $CDCl_3$. Multiplicities of ^{13}C NMR signals (50 MHz) were determined by SFORD and GASPE techniques. TLC purification of reaction product/s was done on silica gel using $CHCl_3$–MeOH–NH_3 (90–10–tr). R_f values of compounds quoted are for solvent systems used in the purification step.

Isolation. Air-dried powdered tuberous roots (1.8 kg) were extd with EtOH at room temp. The solvent was evapd and the residue (200 g) treated with 5% HOAc. The mixt. was filtered, the extract was basified (NH_4OH) and extd with $CHCl_3$ to give an alkaloidal fraction (22 g). This was chromatographed on a column prepd using 1.3 kg silica gel (70–200 mesh) in $CHCl_3$. Elution was first with $CHCl_3$, and then with $CHCl_3$ containing increasing amounts of MeOH. Alkaloidal mixtures obtained with $CHCl_3$–MeOH (49:1) and $CHCl_3$–MeOH (19:1) eluates were further purified by TLC on silica gel using $CHCl_3$–MeOH–NH_4OH (95:5:0.5). The following alkaloids were obtained roughly in the order of their elution from the column: delavaine (3), 108 mg; nordelavaine (5), 42 mg; stephanubine (10), 6 mg; stephaphylline (1), 18 mg.

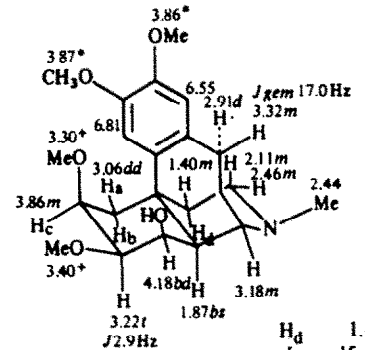
Delavaine (3). Stout crystals from MeOH; mp 151° (lit. [4] 149–150°); $[\alpha]_D^{25}$ −270° (*c* 0.25) (lit. [4] $[\alpha]_D^{25}$ −240°); λ_{max} 207, 241, 270, 292 (sh) nm (log ε 4.06, 3.72, 4.01, 3.89); ν_{max} 1480, 1500, 1585, 1658 (sh), 1665 cm^{-1}; MS *m/z* (%) 357 $[M]^+$ (48), 299 (98), 298 (43), 268 (10), 242 (26), 229 (26), 228 (14), 227 (15), 59 (100); CD $\Delta\varepsilon$ (nm) + 5 (311), −4 (271), −4 (233); NOEDS H-1 $\overset{3}{\rightleftharpoons}$ H-10β, H-4 $\overset{5}{\rightarrow}$ H$_a$-5, H-4 $\overset{6}{\rightleftharpoons}$ H$_b$-5, H$_a$-5 $\overset{24}{\rightleftharpoons}$ H$_b$-5, H-4 $\overset{3}{\rightleftharpoons}$ H$_c$-15, H$_a$-5 $\overset{3}{\rightarrow}$ H$_d$-15, H$_c$-15 $\overset{5}{\rightarrow}$ H$_e$-16, MeO-7 $\overset{7}{\rightleftharpoons}$ MeO-8; R_f 0.50.

Nordelavaine (5). Amorphous; $[\alpha]_D^{25}$ − 187° (*c* 0.61); λ_{max} 210, 239, 268 nm (log ε 4.00, 3.69, 3.97); ν_{max} 1480, 1500, 1605, 1660, 3350 cm^{-1}; MS *m/z* (%) 343 $[M]^+$ (10), 315 (5), 300 (21), 299 (100), 298 (10), 269 (8), 268 (26), 267 (20), 239 (12), 45 (44); CD $\Delta\varepsilon$ (nm) − 10 (262), + 2 (231); R_f 0.32; NOEDS H-4 $\overset{8}{\rightleftharpoons}$ H$_a$-5, H$_a$-5 $\overset{24}{\rightleftharpoons}$ H$_b$-5, H-4 $\overset{11}{\rightleftharpoons}$ H$_c$-15, H$_c$-15 $\overset{10}{\rightleftharpoons}$ H$_e$-16, H$_d$-15 $\overset{5}{\rightleftharpoons}$ H$_f$-16, H-1 $\overset{6}{\rightleftharpoons}$ H-10β, H-10α $\overset{25}{\rightleftharpoons}$ H-10β, H-10β $\overset{7}{\rightleftharpoons}$ H-9α, H-9α $\overset{17}{\rightleftharpoons}$ H-9β, MeO-7 $\overset{8}{\rightleftharpoons}$ MeO-8.



H_a	2.47 *ddd*	$J_{a,b}$	12.4 Hz
H_b	2.10 *ddd*	$J_{a,c}$	3.1 Hz
H_c	1.92 *ddd*	$J_{a,d}$	2.1 Hz
H_d	1.53 *ddd*	$J_{b,c}$	12.4 Hz
		$J_{b,d}$	4.8 Hz
		$J_{c,d}$	12.1 Hz

1



H_d	1.68 *m*
$J_{a,b}$	15.4 Hz
$J_{a,c}$	3.4 Hz
$J_{d,c}$	2.5 Hz

2

Stephanubine (**10**). Amorphous; $[\alpha]_D^{25}$ −170° (*c* 0.22); λ_{max} 232, 271 nm (log ε 3.65, 3.93); ν_{max} 1505, 1605, 1660, 3350 cm^{-1}; ^1H NMR δ2.63 (1H, *d*, *J* = 16.5 Hz, H-5β), 2.99 (1H, *d*, *J* = 16.5 Hz, H-5α), 3.70 (3H, *s*, C-7 OCH_3), 3.84 and 3.85 (3H each, *s*, C-2 OCH_3 and C-3 OCH_3), 4.16 (3H, *s*, C-8 OCH_3), 6.54 (1H, *s*, H-1), 6.68 (1H, *s*, H-4); MS *m/z* (%) 359 $[M]^+$ (12), 316 (22), 315 (100), 314 (10), 285 (7), 284 (21), 283 (15), 254 (8), 45 (16); CD Δε (nm) −11 (261) +6 (228); R_f 0.26.

Stephaphylline (**1**). Needles from $CHCl_3$–hexane; mp 197°; $[\alpha]_D^{25}$ +77.3° (*c* 0.35); λ_{max} 227 sh, 274 nm (log ε 4.08, 4.12); ν_{max} 1445, 1460, 1505, 1610, 1658 cm^{-1}; MS *m/z* (%) 373.1891 $[M]^+$ ($C_{21}H_{27}O_5N$, 84), 358.1620 ($C_{20}H_{24}O_5N$, 100), 342.1668 ($C_{20}H_{24}O_4N$, 12), 330.1673 ($C_{19}H_{24}O_4N$, 5), 315.1218 ($C_{18}H_{19}O_3$, 52), 299.1037 ($C_{17}H_{15}O_3$, 12); CD Δε (nm) +14 (295), −27 (269), +5 (221); R_f 0.22; NOEDS H-1 $\overset{1}{\underset{25}{\rightleftharpoons}}$ MeO-2, H-1 $\overset{3}{\underset{8}{\rightleftharpoons}}$ H-10α, H-1 $\overset{2}{\underset{8}{\rightleftharpoons}}$ H-10β, H-10α $\overset{9}{\underset{3}{\rightleftharpoons}}$ H-9, H-10β $\overset{10}{\underset{6}{\rightleftharpoons}}$ H-9, H-10α $\overset{8}{\leftarrow}$ N-CH_3, H_{ax}-16 $\overset{18}{\leftarrow}$ N-CH_3, N-CH_3 $\overset{14}{\rightarrow}$ H-9, H-9 $\overset{11}{\underset{10}{\rightleftharpoons}}$ H-14, H-14 $\overset{7}{\underset{7}{\rightleftharpoons}}$ H_{ax}-15, H_{ax}-15 $\overset{6}{\underset{5}{\rightleftharpoons}}$ H_{eq}-16, H_{ax}-15 $\overset{25}{\underset{23}{\rightleftharpoons}}$ H_{eq}-15, H_{eq}-15 $\overset{3}{\underset{5}{\rightleftharpoons}}$ H_{ax}-16, H_{ax}-16 $\overset{24}{\underset{21}{\rightleftharpoons}}$ H_{eq}-16, MeO-3 $\overset{13}{\underset{14}{\rightleftharpoons}}$ H-4, H-4 $\overset{13}{\underset{15}{\rightleftharpoons}}$ H-5β, H-4 $\overset{-4}{\underset{-5}{\rightleftharpoons}}$ H-5α, H-5β $\overset{14}{\underset{13}{\rightleftharpoons}}$ H-5β, MeO-6 $\overset{6}{\underset{5}{\rightleftharpoons}}$ MeO-7.

Reduction of stephaphylline (**1**). Stephaphylline (10 mg) in MeOH (6 ml) was treated with $NaBH_4$ (100 mg) in portions at 0° and then kept for 48 hr. Usual work-up afforded a mixture of unreacted stephaphylline and reduction product **2** which were sepd by TLC. Compound **2** (3 mg), R_f 0.59, exhibited MS peaks at *m/z* (%) 377 $[M]^+$ (100), 362 (9), 346 (23), 318 (10), 288 (5), 274 (16), 256 (19), 244 (9), 226 (19), 213 (5), 201 (13), 192 (10), 59 (89).

Table 1. ^{13}C NMR signal assignments of stephaphylline (**1**), delavaine (**3**), nordelavaine (**5**) and tridictyophylline (**11**)

	1*	3*	5*	11†
C-1	110.9	107.8	108.0	107.2 (110.5)
C-2	147.5[c]	145.8[c]	145.8[c]	148.1
C-3	147.7[c]	146.2[c]	146.5[c]	148.1
C-4	106.6	107.0	107.0	110.5 (107.2)
C-5	39.5[d]	37.2	37.5	34.6
C-6	160.8	193.3	193.1	135.0 (161.9)
C-7	136.3	137.8	136.5	161.9 (135.0)
C-8	193.4	164.7	165.2	
C-9	53.5[e]	48.3	48.0	60.3 (57.6)
C-10	23.3	25.7	25.4	29.6
C-11	129.4[f]	127.9	127.9	129.4
C-12	130.7[f]	135.1	135.1	129.4
C-13	37.2	48.2	46.7	40.5
C-14	52.7[e]	67.0	66.2	66.7
C-15	39.6[d]	22.5	27.0	34.6
C-16	46.4	51.2	42.1	45.8
N-Me	42.7	36.0		42.6
C(2)–OMe	56.0[g]			55.8
C(3)–OMe	55.7[g]			55.8
C(6)–OMe	58.7			58.7
C(7)–OMe	60.5	60.4	60.5	57.6 (60.3)
C(8)–OMe		60.4	61.2	
OCH_2O		100.6	100.7	

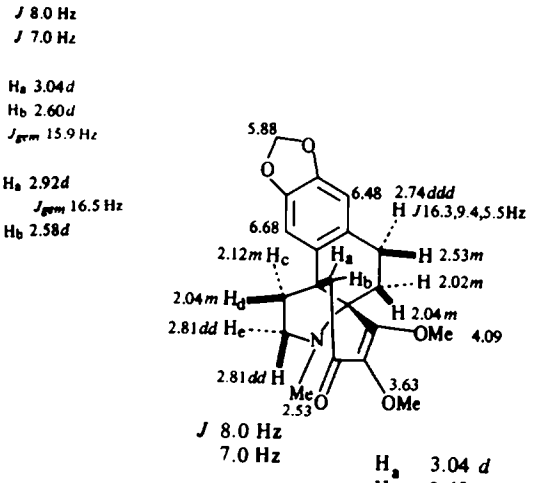
* In $CDCl_3$; $\delta_{TMS} = \delta_{CDCl_3} + 77.0$ ppm.
† Values in parentheses represent revised assignments.
c,d,e,f,g Values with the same supercript are interchangeable.

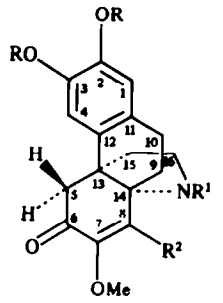
Hydrogenation of delavaine. Delavine (**3**) (10 mg) was hydrogenated in EtOH soln using PtO_2 (5 mg) for *ca* 2 hr. Catalyst was removed by filtration. Removal of solvent and purification of the residue by TLC on silica gel using C_6H_6–MeOH–NH_3 (85:15:tr) furnished **4** (6 mg), R_f 0.59; ν_{max} 1665 cm^{-1}; ^1H NMR δ2.43 (3H, *s*, N-CH_3), 2.64 (1H, *d*, *J* = 16.5 Hz, H-5β), 3.02 (1H, *d*, *J* = 16.5 Hz, H-5α), 3.65 (3H, *s*, C-7 OCH_3), 5.63 (1H, *s*, H-8), 5.88 and 5.89 (1H each, *d*, *J* = 1.4 Hz, OCH_2O), 6.51 (1H, *s*, H-1), 6.68 (1H, *s*, H-4); MS *m/z* (%) 327 $[M]^+$ (8), 312 (3), 284 (17), 268 (33), 256 (3), 242 (10), 227 (8), 211 (4), 59 (100).

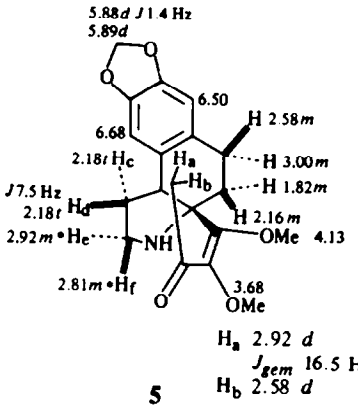
N-Acetylnordelavaine (**6**). Nordelavaine (3 mg) treated with pyridine (0.3 ml) and Ac_2O (0.2 ml) was allowed to stand at room temp for 16 hr. MeOH was then added and the solvents removed in a stream of N_2. Purification of the residue by TLC gave *N*-acetylnordelavaine (**6**), ^1H NMR δ2.01 (3H, *s*, $NCOCH_3$), 2.63 (1H, *d*, *J* = 17.4 Hz, H-5β), 2.85 (1H, *d*, *J* = 17.4 Hz, H-5α), 3.68 (3H, *s*, C-7 OCH_3), 4.10 (3H, *s*, C-8 OCH_3), 5.92 (2H, *s*, OCH_2O), 6.52 (1H, *s*, H-1), 6.66 (1H, *s*, H-4).

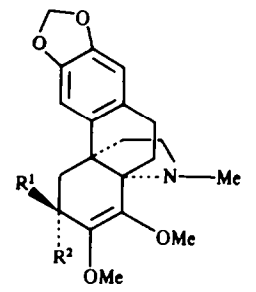
N-methylation of nordelavaine. Nordelavaine (5 mg) was refluxed with 90% HCO_2H (1 ml) and 37% formalin (2 ml) for *ca* 12 hr. Diln with H_2O, subsequent basification with NH_4OH and extn with $CHCl_3$ gave a residue (~ 5 mg) which upon purification by TLC yielded a product identical with natural delavaine (**3**) in all respects.

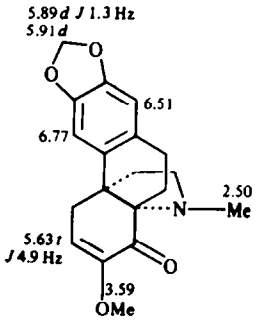
Action of formalin and $NaCNBH_3$ on nordelavaine (**5**). Nordelavaine (10 mg) in MeCN (2 ml) was stirred with 37% formalin (0.4 ml) and $NaCNBH_3$ (50 mg) for *ca* 12 hr. Occasionally a few drops of a soln of HOAc in MeCN (1 ml) were

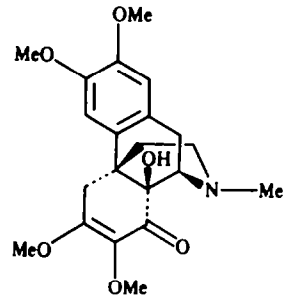












added to maintain neutrality. The solvent was removed under red. press. The residue was treated with H_2O, basified with NH_4OH and extd with $CHCl_3$. The residue from the $CHCl_3$ layer was purified by TLC to afford delavaine (3) along with allyl alcohols 7 (1 mg), R_f 0.67; amorphous; $[\alpha]_D^{25} - 108°$ (*c* 0.30); ν_{max} 3440 cm^{-1}; ^1H NMR (C_6D_6) δ 2.46 (3H, *s*, N-CH_3) 3.40 (3H, *s*, C-7 OCH_3), 3.65 (3H, *s*, C-8 OCH_3), 4.27 (1H, *br t*, $J \approx 4.0$ Hz, H-6), 6.15 (2H, *s*, OCH_2O), 6.37 (1H, *s*, H-1), 6.74 (1H, *s*, H-4); MS *m/z* (%) 359 $[M]^+$ (13), 344 (3), 328 (6), 301 (9), 300 (18), 283 (12), 229 (12), 60 (13), 59 (100) and **8** (2 mg), R_f 0.51; amorphous; $[\alpha]_D^{25} - 41°$ (*c* 0.36); ν_{max} 3350 cm^{-1}; ^1H NMR (C_6D_6) δ 2.45 (3H, *s*, N-CH_3), 3.19 (3H, *s*, C-7 OCH_3), 3.66 (3H, *s*, C-8 OCH_3), 4.00 (1H, *dd*, $J \approx 8.7$ Hz and 5.6 Hz, H-6), 6.15 (2H, *s*, OCH_2O), 6.45 (1H, *s*, H-1), 6.77 (1H, *s*, H-4); MS *m/z* (%) 359 $[M]^+$ (21), 344 (11), 328

(6), 300 (11), 284 (21), 283 (48), 282 (7), 268 (8), 252 (5), 241 (9), 229 (29), 228 (14), 59 (100).

Reduction of delavaine (3). Delavaine (30 mg) in MeOH (5 ml) was treated with $NaBH_4$ (100 mg) in portions at 0° and then kept at −5° overnight. Usual work-up afforded a residue which on prep. TLC gave allyl alcohols 7 (8 mg) and 8 (17 mg).

Rearrangement of allyl alcohols 7 and 8. Allyl alcohol 8 (5 mg) was stirred with a soln of 48% HBr (1 ml) and H_2O (2 ml) at room temp. for 3 hr. The soln was basified with NH_4OH and extd with $CHCl_3$. Final purification of the residue by TLC afforded the rearranged product 9 (~ 3 mg), R_f 0.81. The enone 9 was also obtained when 7 or a mixture of 7 and 8 was similarly treated.

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