Phytochemistry, 1978, Vol. 17, pp 779–782. Pergamon Press. Printed in England

LIGNANS AND APORPHINE ALKALOIDS IN BARK OF *LIRIODENDRON TULIPIFERA**

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(*Revised received* 21 *October* 1977)

Key Word Index—*Liriodendron tulipifera*; Magnoliaceae; bark; lignans; (+)-pinoresinol; (+)-syringaresinol; lirionol; syringic acid methyl ester; noraporphine; *O*-methyl-*N*-noraporphine; *N*-(2-hydroxy-2-phenylethyl)-benzamide.

Abstract—*Lirionol*, a novel tetracyclic lignan, has been isolated from the bark of *Liriodendron tulipifera* and its structure determined by spectroscopic analysis. In addition, syringic acid methyl ester, (+)-pinoresinol, (+)-syringaresinol, *N*-(2-hydroxy-2-phenylethyl)benzamide and 0-methyl-*N*-norlirinine have also been isolated. The structures of lirinine and related compounds isolated from the leaves of this tree-species by Yunusov *et al.* are also discussed.

INTRODUCTION

In previous papers [1–3], we reported the occurrence of aporphine alkaloids and lignans in normal sapwoods, normal heartwood and discolored sapwood of *Liriodendron tulipifera*. The co-occurrence of these two classes of compound in this tree is of chemotaxonomic significance. In earlier investigations, (+)-syringaresinol di-β-glucoside was isolated from the bark of *L. tulipifera* by Dickey [4], while cytotoxic sesquiterpenes including costunolide, tulipinolide, epitulipinolide and γ-liriodenolide were isolated from the root-bark of the tree by Doskotch *et al.* [5–8]. However, no aporphine alkaloids were detected in the bark. In this paper, we report the occurrence of lignans and aporphine alkaloids in the bark of *L. tulipifera*.

RESULTS AND DISCUSSION

Constituents of extractives

Bark of *L. tulipifera* contained *ca* 4% ligroin-extractive and *ca* 8% acidic methanol-extractive. The ligroin-extractive consisted of wax-like substances. The acidic methanol-extractive consisted mostly of basic, neutral and phenolic polymers, and a neutral essential oil with a pleasant smell. The amounts of both lignans and aporphine alkaloids in the latter extractive were insignificant. The following compounds were isolated from the latter extractive: syringic acid Me ester (**1**), (+)-pinoresinol (**2**), (+)-syringaresinol (**3**), lirionol (**4**), *N*-(2-hydroxy-2-phenylethyl)benzamide (**6**), and *O*-methyl-*N*-norlirinine (**8**). *N*-Nornuciferine (**7**) was detected by TLC but was not isolated. In contrast to the woods, none of 1,2-dioxygenated and 1,2,9,10-tetraoxygenated aporphines except for **7** has been detected in the bark. Lirionol is a novel tetracyclic lignan corresponding to a dehydration product of the cyclolignan **5**. The compounds **1**–**4** were also detected in normal heartwood, discolored sapwood and discolored heartwood of this tree species [9].

Identification of the compounds isolated

Lirionol (**4**), $C_{22}H_{24}O_8$ (M^+, *m/e* 416.1468), was soluble in dilute sodium hydroxide solution but insoluble in dilute sodium bicarbonate solution. The compound gave a diacetate with acetic anhydride in sodium hydroxide solution and a triacetate with the same reagent in pyridine. Thus, the compound must have two phenolic OH groups and an aliphatic OH group. The IR spectrum (KBr) of the compound showed absorption bands corresponding to OH (3520 and 3380 cm^{-1}), conjugated carbonyl (1650 cm^{-1}) and isolated aromatic hydrogens (890 and 880 cm^{-1}). In tetrahydrofuran, the carbonyl band shifted to 1670 cm^{-1}, a characteristic similar to the hydrogen-bonded carbonyl group of 4-hydroxyacetophenone derivatives [10]. The UV spectrum of the compound in methanol showed an intense band at λ_{max} 291 nm which underwent an alkali-shift of + 80 nm. In methanol, 4-hydroxy-3,5-dimethoxy-acetophenone absorbs at λ_{max} 298 nm and gives an alkali-shift of +60 nm, while 4-hydroxy-3-methoxyacetophenone absorbs at λ_{max} 275 and 303 nm, and gives an alkali-shift of +68 nm. Both the diacetate and triacetate of **4** absorbed at λ_{max} 272 nm. The acetate of 4-hydroxy-3,5-dimethoxyacetophenone absorbs at λ_{max} 269 nm. Thus, **4** must have a substituted 4-hydroxy-3,5-dimethoxybenzoyl group. The PMR spectra of **4** and its acetates revealed that the compound had 4 aromatic OMe groups, two phenolic OH groups, a primary OH group and two isolated aromatic hydrogens. One of the aromatic hydrogens was deshielded, characteristics of an aromatic hydrogen *ortho* to the carbonyl of a benzoyl group. Furthermore, acetylation of **4** did not produce deshielding of the aromatic hydrogens. This indicates that the aromatic hydrogens are not *ortho* to the phenolic OH groups [11]. Phenolic syringalignans occurring in nature usually have 4-hydroxy-3,5-dimethoxyphenylpropane skeleton derived from sinapyl alcohol. Therefore, **4** must have a 2-substituted 4-hydroxy-3,5-dimethoxybenzoyl group and a 2-substituted 4-hydroxy-3,5-dimeth-

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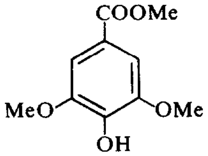
* Part 4 in the series 'The Chemistry of *Liriodendron tulipifera* L.' For Part 3 see ref. [3].



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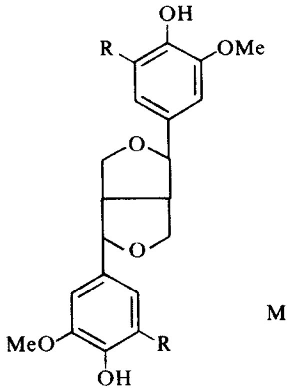
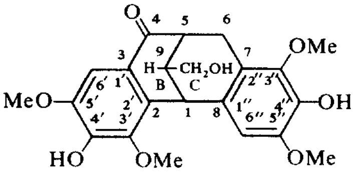


2, R = H
3, R = OMe



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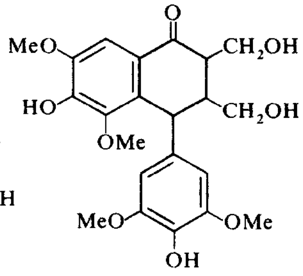

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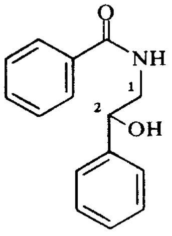

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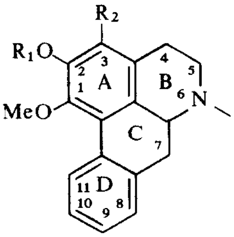
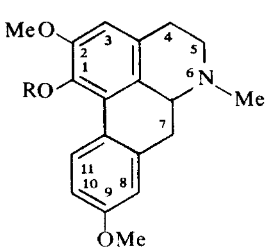


7, R_1 = Me; R_2 = R_3 = H
8, R_1 = Me; R_2 = OMe; R_3 = H
9, R_1 = H; R_2 = OMe; R_3 = Me
10, R_1 = Me; R_2 = OH; R_3 = Me
11, R_1 = R_3 = Me; R_2 = OMe



12, R = H
13, R = Me

oxyphenyl group derived from sinapyl alcohol on the basis of biogenetic considerations. In the PMR spectrum ($CDCl_3$), of the triacetate, the 3-proton multiplet at δ *ca* 3.05 (H-5 and H-6) could be attributable to an ABC spin-system corresponding to an Ar—CH_2—CH(R)—CO—Ar group. Spin-decoupling experiments established that the AB multiplets at δ 4.2 and 4 (C-9, $\underline{CH_2}OAc$) and two one-proton multiplets at δ 2.77 and 4.41 (H-9 and H-1) constituted the ABNX part of an ABMNX spin-system with J_{AB} = 11.6, J_{AN} = 7, J_{BN} = 8, J_{NX} = 3 and J_{MX} = 1.6 Hz. The M part was the H-5 at δ 3.05. This spin-system corresponds to an Ar—CO—CH(R)—CH(CH_2—OAc)—CH—$(Ar)_2$ group, although the N part (H-9) at δ 2.77 is too deshielded to be an aliphatic CH-resonance of the type $R_1(R_2)$—CH—CH_2—OAc. However, the hydrogens of the CH_2-bridge in 3′,6′-dimethoxy-2,3,-benzobicyclo[2,2,1]hept-2,5-diene resonate at δ 2.22 [12]. A bicyclic compound similar to this type with a CH(CH_2—OAc)-bridge could be then expected to have a CH-resonance of about δ 2.5–3 for the bridge hydrogen. This together with the fact that **4** has only two aryl groups indicates, therefore, that the compound has the structure **4**, 4″-dihydroxy-3′,3″,5′,5″-tetramethoxy-2,3:7,8-dibenzobicyclo[3,3,1]non-2,7-dien-4-one. On passing from chloroform-d to benzene-d_6 solution, the resonance of H-9 underwent an ASIS of $\Delta\delta$-0.27 ppm, but the resonances of H-1, H-5 and C-9 CH_2O— were not affected significantly. This indicates that H-9 and H-5 are axial and equatorial with respect to the cyclohexenone ring B, respectively [13, 14]. The long-range coupling between H-1 and H-5 (J = 1.6 Hz) further indicates that H-1 is also equatorial with respect to the ring B [15]. This is in agreement with the coupling constant between H-1 and H-9 (J = 3 Hz) which corresponds to a vicinal equatorial-axial interaction. It is apparent, therefore, that the H-9 is oriented on the side of ring B, and the C-9 CH_2OH group on the side of ring C. However, the absolute configuration of **4** is not settled.

Syringic acid Me ester (**1**), $C_{10}H_{12}O_5$ (M^+, *m/e* 212), gave PMR and MS compatible with the proposed structure. It produced syringic acid upon base-catalysed hydrolysis. Identification of (+)-pinoresinol (**2**) and (+)-syringaresinol (**3**) was made by mmp and comparison of their PMR spectra with authentic samples [1].

N-(2-Hydroxy-2-phenylethyl)benzamide (**6**), $C_{15}H_{15}O_2N$ (M^+, *m/e* 241), gave a PMR spectrum characteristic of a *N*-monoalkylamide [16]. The one-proton multiplet at δ 4.92 (H-2) and two sets of AB multiplets at δ 3.91 and 3.52 (H-1 *cis*) and 3.84 and 3.54 (H-1 *trans*) constituted two separate ABM spin-systems with J_{AB} = 14, J_{AM} = 3.5 and J_{BM} = 7.5 Hz in *ca* equal ratios. The two AB sets integrated for a total of two hydrogens. A broad one-proton signal at δ 6.67 corresponds to an amide NH-resonance. Thus, the compound existed in the *trans* and *cis* forms with respect to the amide C-N bond in a ratio of *ca* 1:1. The aromatic region of the spectrum integrated for 10 hydrogens. A two-proton multiplet at δ 7.72 with J_{AB} = 8 and J_{AM} = 2.4 Hz corresponded to the hydrogens *ortho* to the carbonyl of an unsubstituted benzoyl group. The MS of the compound exhibited intense ions at *m/e* 136, 135 (base peak) 134 and 105 corresponding to Ph—CH(OH)—CH_2NH^+, Ph—CH(OH)—CH=NH^+, Ph—C(OH)=CH—NH^+ and Ph—C≡O^+, respectively. Therefore, the structure **6** for the compound is apparent.

O-Methyl-*N*-norlirinine (**8**), $C_{16}H_{21}O_3N$ (M^+, *m/e* 311), gave PMR and MS characteristic of a *N*-noraporphine [2, 17]. The PMR spectrum was similar to that of *N*-nornuciferine (**7**) [2], except for the absence of a H-3 resonance and the presence of an additional OMe-resonance. The spectrum was also similar to those of lirinine and liridinine isolated from leaves of *L. tulipifera* [18, 19], except for the absence of NMe-resonance and the presence of an additional OMe-resonance. Thus, the structure **3**, 1,2,3,-trimethoxy-*N*-noraporphine, for the compound is apparent.

The structures of lirinine and related compounds

Recently, intensive investigations on aporphine alkaloids from leaves of *L. tulipifera* were carried out by Yunusov *et al.* [18–23]. Among several aporphine alkaloids isolated, lirinine, *O*-methyllirinine and lirinine *N*-oxide were shown to have structures **12**, **13** and *N*-oxide of **12**, respectively, on the basis of spectroscopic analysis and chemical correlation to lirinine by the Russian authors. However, the PMR characteristics of lirinine published by the authors are incompatible with the proposed structure. In the PMR spectrum, the OMe-resonance at δ 3.63 corresponds to that of a C-1 OMe [24]. The aromatic region of the spectrum integrates for 4 hydrogens which constitute a characteristic ABCX spin-system corresponding to 4 adjacent aromatic hydrogens on the ring *D* of an aporphine [1]. This together with the absence of a H-3-resonance around δ 6.5–6.7 [25] shows that lirinine is either 2-hydroxyl-1,3-dimethyoxyaporphine (**9**) or 3-hydroxy-1,2-dimethoxyaporphine (**10**) rather than 1-hydroxy-2,9-dimethoxyaporphine (**12**). Both **9** and **10** also would not undergo a base-catalysed deuterium exchange of phenol as demonstrated by the authors [18]. The structure **9** was proposed for liridinine isolated also from the leaves on the basis of spectroscopic analysis and conversion to liridine by the Russian authors [19]. The PMR spectrum of liridinine is similar to that of lirinine indicating that they are isomers. Thus, liridinine and lirinine are **9** and **10**, respectively, or *vice versa*. Treatment of lirinine with ethereal diazomethane gave *O*-methyllirinine [20]. Therefore, *O*-methyllirinine is 1,2,3-trimethxoyaporphine (**11**) rather than 1,2,9-trimethoxyaporphine (**13**). Reduction of lirinine *N*-oxide with zinc in dilute sulfuric acid gave lirinine [20]. Therefore, lirinine *N*-oxide is the *N*-oxide of **10** or **9** rather than that of **12**.

EXPERIMENTAL

Mps are uncorr. Prep-TLC was carried out on Si gel 60 F-254 (Merck) plates; Me_2CO was used to recover substances from the Si gel. The bark used in this investigation was obtained from a 45-yr-old tree harvested near Zebulon, NC, U.S.A. The discolored sapwood of this trunk was used for previous investigation [2]. The bark was air dried and ground to pass a 40 mesh screen. The bark-meal (1.5 kg) was preextracted with ligroin to remove *wax-like materials* (58 g) and then air-dried again. The bark-meal was then steeped in 9 l. 1% HCl–MeOH at room temp. for 2 days and then filtered off. Wet bark-meal was then treated again with 6 l. 1% HCl–MeOH as before. Combined extracts were concd to *ca* 250 ml and then added slowly to 1 l. Et_2O with stirring. The Et_2O-insoluble mass was collected and stirred for 30 min with 400 ml hot H_2O. The ppt. was filtered off and washed with 2 × 200 ml hot H_2O. This ppt. (78 g) consisted mostly of neutral and phenolic plymeric materials and was not investigated further. The filtrate and washing solns were combined and extracted continuously with 1.5 l. $CHCl_3$ for 2 days. The $CHCl_3$ soln was washed with N $NaHCO_3$, H_2O, dried and the solvent removed to give a *phenol mixture A* (1.5 g). The aq. soln was neutralized, the ppt. produced was centrifuged off and dried to give a *basic polymer mixture* (8.1 g). The supernatant was then extracted continuously with 1.5 l. $CHCl_3$ for 2 days. The $CHCl_3$ soln was dried and the solvent removed to give an *alkaloid mixture* (0.6 g). The Et_2O soln was concd to *ca* 400 ml, shaken with 3 × 100 ml N $NaHCO_3$, then with 4 × 100 ml NaOH, washed with 3 × 100 ml H_2O, dried and the solvent removed to give a *neutral mixture* (23 g) which was not investigated. Both $NaHCO_3$ and NaOH solns were neutralized and extracted with 4 × 100 ml $CHCl_3$, respectively. The $CHCl_3$ solns were washed, dried and the solvent removed to give an *acid mixture* (0.1 g) and a *phenol mixture B* (10.5 g), respectively.

Lirionol (**4**). The *phenol mixture A* was dissolved in 3 ml $CHCl_3$ and kept at 0° for several days. The crude crystals (110 mg) were collected, recrystallized from THF to give colorless rhombics (92 mg), mp 216–225° (decomp) UV: λ_{max} in MeOH 242 and 291 nm (ε 21 400 and 11 000); λ_{max} in 0.05N MeONa–MeOH 262 and 371 nm (ε 12 000 and 21 700). IR (KBr): 3520, 3380 (OH), 3000 (ArH), 2960, 2940, 2910 (OMe), 1650 (conj. CO), 890 and 880 (isolated ArH) cm^{-1}. IR (THF): 3460 (solv. OH) and 1670 (conj. CO) cm^{-1}. PMR (100 MHz, DMSO-d_6, TMS as ref.): δ 2.75 (1H, *m*, H-9), 3.1–3.2 (3H, *m*, H-5, H-6), 3.16 (1H, *dd*, J_{AB} = 11.6, J_{BN} = 8 Hz, C-9 $C\underline{H}_2OH$), 3.34 (1H, *dd*, J_{AB} = 11.6, J_{AN} = 7 Hz, C-9 $C\underline{H}_2OH$), 3.96 (3H, *s*, OMe), 4.04 (3H, *s*, OMe), 4.09 (3H, *s*, OMe), 4.23 (3H, *s*, OMe), 4.7 (1H, *dd*, J_{MX} = 1 6, J_{NX} = 3 Hz, H-1), 7.11 (1H, *s*, H-6″) and 7.5 (1H, *s*, H-6′). MS (70 eV, 190°): *m/e* (rel. int.) 417 (25), 416 (M^+, 100), 386 (11), 357 (14) and 306.4 (*m** 416 → 357). High resolution MS: M^+ *m/e* 416.1468. Calc. for $C_{22}H_{24}O_8$: 416.1469. *Diacetate*. UV: λ_{max} in MeOH 272 and 322, *sh*, nm. IR (CCl_4): 3630 (OH), 1775 (Ar-OAc) and 1682 (conj. CO) cm^{-1}. PMR (100 MHz, $CDCl_3$): δ 2.26 (3H, *s*, Ar-OAc), 2.32 (3H, *s*, Ar-OAc), 2.76 (1H, *m*, H-9) 3.03 (3H, *m*, H-5 and H-6), 3.53 (1H, *dd*, J_{AB} = 11.6, J_{BN} = 8 Hz, C-9 $C\underline{H}_2OH$), 3.66 (1H, *m*, C-9 $C\underline{H}_2OH$, partly hidden), 3.69 (3H, *s*, OMe), 3.73 (3H, *s*, OMe), 3.79 (3H, *s*, OMe), 3.94 (3H, *s*, OMe), 4.53 (1H, *dd*, J_{MX} = 1.6 and J_{NX} = 3 Hz, H-1), 6.85 (1H, *s*, H-6″) and 7.32 (1H, *s*, H-6′). M^+, *m/e* 500. *Triacetate*. UV: λ_{max} in MeOH 272 and 322, *sh*, nm. IR (CCl_4): 1778 (Ar-OAc), 1750 (Ali-OAc) and 1685 (conj. CO) cm^{-1}. PMR (100 MHz, $CDCl_3$): δ 1.99 (3H, *s*, AliOCO), 2.26 (3H, *s*, Ar-OAc), 2.32 (3H, *s*, Ar-OAc), 2.77 (1H, *m*, H-9), 3.05 (3H, *m*, H-5 and H-6), 3.68 (3H, *s*, OMe), 3.72 (3H, *s*, OMe), 3.78 (3H, *s*, OMe), 3.92 (3H, *s*, OMe), 4 (1H, *m*, C-9 $C\underline{H}_2OAc$, partly hidden), 4.2 (1H, *dd*, J_{AB} = 11.6, J_{AN} = 7 Hz, C-9 $C\underline{H}_2OAc$), 4.43 (1H, *dd*, J_{MX} = 1.6, J_{NX} = 3 Hz, H-1), 6.82 (1H, *s*, H-6″) and 7.34 (1H, *s*, H-6′). PMR (100 MHz, C_6D_6): δ 1.64 (3H, *s*, Ali-OAc), 1.85 (6H, *s*, Ar-OAc), 2.5 (1H, *m*, H-9), 2.95–3.1 (3H, *m*, H-5 and H-6), 3.13 (3H, *s*, OMe), 3.42 (3H, s, OMe), 3.45 (3H, *s*, OMe), 3.69 (3H, *s*, OMe), 3.96 (1H, *dd*, J_{AB} = 11.6, J_{BN} = 8 Hz, C-9 $C\underline{H}_2OAc$), 4.16 (1H, *dd*, J_{AB} = 11.6, J_{AN} = 7 Hz, C-9 $C\underline{H}_2OAc$), 4.45 (1H, *dd*, J_{MX} = 1.6, J_{NX} = 3 Hz, H-1), 6.93 (1H, *s*, H-6″) and 7.41 (1H, *s*, OMe). M^+, *m/e* 542.

The mother liquor obtained after removal of **4** was fractionated by prep-TLC using C_6H_6–MeOH (9:1) as solvent to isolate the following compounds: *syringic acid methyl ester* (**1**). The crude crystals obtained from the 1st band was recrystallized from MeOH to give colorless needles (32 mg), mp 85–90°. PMR (100 MHz, $CDCl_3$): δ 3.86 (3H, *s*, COOMe), 3.88 (6H, *s*, OMe), 5.95 (1H, *br*, $ArO\underline{H}$), 7.29 (2H, *s*, ArH adj. to CO). MS (70 eV, 100°): *m/e* (rel. int.) 213 (24), 212 (M^+, 100), 197 (11), 182 (19), 181 (80), 154.5 (*m** 212 → 181). A base-catalysed hydrolysis of **1** gave *syringic acid*, mp 199–203°. Identity of the product was established by mmp with an authentic sample, mp 203–205°. (+)-*Pinoresinol* (**2**). The crude product obtained from the 2nd band was recrystallized from MeOH to give rhombics (25 mg), mp 116–120° (Lit. [26] 120–121°). Identity of the compound was established by mmp with an authentic sample, mp 119–120°, as well as comparison of PMR spectra. (+)-*Syringaresinol* (**3**). The crude product obtained from the 3rd band could not be crystallized, but gave one spot on TLC. Identity of the compound was established by comparison of PMR and TLC data with those of an authentic sample previously isolated [2].

The phenolic mixture B was acetylated with Ac_2O in 3N NaOH soln. The reaction mixture was adjusted to pH 12 and then extracted with $CHCl_3$. The $CHCl_3$ soln was washed with H_2O, dried and the solvent removed. Only *ca* 10% of the original material was recovered as a neutral acetate fraction. This fraction (1.1 g) was subjected to prep-TLC using $CHCl_3$–EtOAc (9:1) as solvent. The crude crystals obtained from the major band was recrystallized from MeOH to give (+)-*pinoresinol diacetate* (180 mg), mp 158–162°. Identity of the compound was established by mmp with an authentic sample, mp 163–165°, as well as comparison of PMR spectra.

The alkaloid mixture was fractionated by prep-TLC using cyclohexane–EtOAc–$NHEt_2$ (7:2:1) as solvent. The following compounds were isolated: N-*(2-Hydroxy-2-phenyethyl) benzamide* (**6**). The crude crystals obtained from the 1st band was recrystallized from MeOH to give rhombics (8 mg), mp 145–150°. PMR (100 MHz, $CDCl_3$): δ 3.45 (0.5H, *dd*, $J_{AB} = 14$, $J_{BM} = 7.5$ Hz, *trans* CH—C$\underline{H}_2$—N—CO), 3.52 (0.5H, *dd*, $J_{AB} = 14$, $J_{BM} = 7.5$ Hz, *cis* CH—C$\underline{H}_2$—N—CO), 3.84 (0.5H, *dd*, $J_{AB} = 14$, $J_{AM} = 3.5$ Hz, *trans* CH—C$\underline{H}_2$—N—CO), 3.91 (0.5H, *dd*, $J_{AB} = 14$, $J_{AM} = 3.5$ Hz, *cis* CH—C$\underline{H}_2$—N—CO), 4.92 (1H, *dd*, $J_{AM} = 3.5$, $J_{BM} = 7.5$ Hz, Ar(HO)—C$\underline{H}$—CH_2), 6.67 (1H, *br*, NH), 7.30–7.45 (8H, *m*, ArH) and 7.72 (2H, *dd*, $J_{AB} = 8$, $J_{AM} = 2.4$ Hz, ArH adj. to CO). MS (70 eV, 140°): *m/e* (rel. int.) 241 (M^+, 0.3), 136 (45), 135 (100), 134 (64, *m** 136 → 135), 106 (11), 105 (70), 77 (94), 76.7 (*m** 241 → 135), 56.5 (*m** 105 → 77). O-*Methyl*-N-*norlirinine* (**8**). The crude product (15 mg) obtained from the 2nd band could not be crystallized, but gave a single spot on TLC. PMR (100 MHz, $CDCl_3$): δ 3.68 (3H, *s*, C-1 OMe), 3.87 (6H, *s*, C-2 and C-3 OMe), 7.3 (3H, ABC *m*, H-8, H-9 and H-10), 8.31 (1H, *dd*, $J_{AM} = 8$, $J_{AN} = 2.2$ Hz, H-11). MS (70 eV, 100°): *m/e* (rel. int.) 213 (24), 311 (M^+, 99), 310 (100) and 296 (35). N-*Nornuciferine* (**7**) was detected in the alkaloid mixture by TLC, but was not isolated.

Acknowledgement—We wish to thank Mrs Margaret C. Bundy of the Department of Chemistry, North Carolina State University for obtaining the PMR spectra.

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