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

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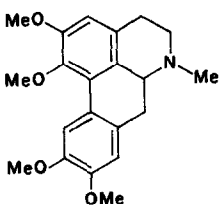
Key Word Index—*Liriodendron tulipifera*; magnoliaceae; yellow poplar; heartwood; aporphine alkaloids; dehydroglaucine; asimilobine; *N*-acetylasimilobine; *N*-acetylnornuciferine; norushinsunine; benzyltetrahydroisoquinoline alkaloids; lignans; (+)-syringaresinol dimethyl ether.

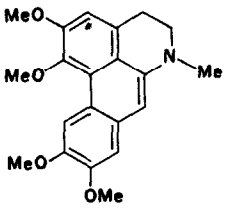
Abstract—The following compounds were isolated from heartwood of *Liriodendron tulipifera*: glaucine, dehydroglaucine, asimilobine, *N*-acetylnornuciferine, norushinsunine, liriodenine, *O*-methylatheroline, (+)-syringaresinol, (+)-syringaresinol dimethyl ether and syringaldehyde. The occurrence of 1-benzyltetrahydroisoquinoline alkaloids also has been indicated by mass spectroscopy. Some characteristic spectral properties of these aporphine alkaloids and their probable biosynthetic pathways are discussed.

INTRODUCTION

In earlier investigations, three aporphine alkaloids have been isolated from the heartwood of *L. tulipifera*—glaucine (**1**), liriodenine (**7**) and *O*-methylatheroline (**8**) [1–3]. An extractable lignan, the di-β-glucoside of (+)-syringaresinol, has also been isolated from the bark of this tree [4]. Thus, *L. tulipifera* is one of the first plant species in which both aporphine alkaloids and lignans have been detected. This could be of chemotoxonomic significance because phenylalanine is a precursor of compounds of both types [5, 6].



(**1**)



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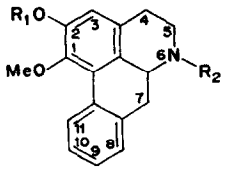
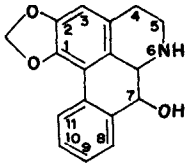
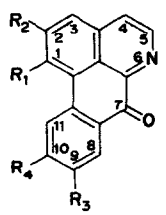


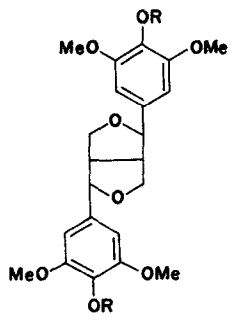
(**3**) $R_1 = R_2 = H$
(**4**) $R_1 = H$; $R_2 = Ac$
(**5**) $R_1 = Me$; $R_2 = Ac$



(**6**)



(**7**) $R_1, R_2 = OCH_2O$; $R_3 = R_4 = H$
(**8**) $R_1 = R_2 = R_3 = R_4 = OMe$



(**9**) R = H
(**10**) R = Me

The purpose of this study was to isolate, characterize, and identify certain of the major extraneous substances present in the normal sapwood and heartwood of *L. tulipifera* trees; our interest also was stimulated by a growing medical interest in aporphine alkaloids—[7] of which this tree could be a readily available source.

RESULTS AND DISCUSSION

Natural products isolated

Sapwood of *L. tulipifera* contained trace amounts of only a single alkaloid—glaucine (**1**). By contrast, a total of 11 compounds were isolated from heartwood of this species: six nonphenolic aporphine alkaloids—glaucine (**1**), dehydroglaucine (**2**), [8] *N*-acetylnornuciferine (**5**), [9] norushinsunine (**6**), [10] liriodenine (**7**), and *O*-methylatheroline (**8**); two phenolic aporphine alkaloids—asimilobine (**3**) [11] and *N*-acetylasimilobine (**4**); two lignans—(+)-syringaresinol (**9**) [12] and its dimethyl ether (**10**); and one simple phenol—syringaldehyde. Four compounds **1**, **5**, **7** and **10** made up the bulk of the acidic methanol extract. Liriodenine (**7**) and *O*-methylatheroline (**8**) are responsible for the yellowish-green color of the

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Table 1. NMR characteristics* of aporphine alkaloids isolated from heartwood of *Liriodendron tulipifera*

Compounds†	Methoxyl C-1	Methoxyl C-2	Methoxyl C-9	Methoxyl C-10	H-3	H-8	H-9	H-10	H-11	Other
Glaucine (1)	6·40	6·17‡	6·15‡	6·12‡	3·43	3·23	—	—	1·88	7·50 N-6 Me
Dehydroglaucine (2)	6·16	6·06‡	6·05‡	6·05‡	3·44	3·04	—	—	0·84	7·02 N-6 Me
										2·95 H-7
Asimilobine (3)	6·48	—	—	—	3·30	2·72	(3H, ABC *m*)		1·66	
N-acetylasimilobine (4)¶	6·09	—	—	—	2·90	2·29	(3H, ABC *m*)		1·24	7·54 N-6 COMe
N-acetylnornuciferine (5)	6·38	6·15	—	—	3·32	2·73	(3H, ABC *m*)		1·51	7·86 N-6 COMe
Norushinsunine (6)	—	—	—	—	3·46	2·83	(3H, ABC *m*)		1·81	6·01 H-6a
										5·48 H-7
										4·11
										3·97 OCH_2O
Liriodenine (7)	—	—	—	—	2·83	1·37	2·36	2·36	1·37	3·66 OCH_2O
										2·23 H-4
										1·06 H-5
O-Methylatheroline (8)	6·01	5·97	5·97	5·97	2·81	1·95	—	—	1·16	2·23 H-4
										1·06 H-5

* All in $CDCl_3$ and in τ values with TMS as internal reference 4 excepted. † See Formulae 1 for structures. ‡ These values may be interchanged. ¶ In DMSO-d_6 with TMS as external reference.

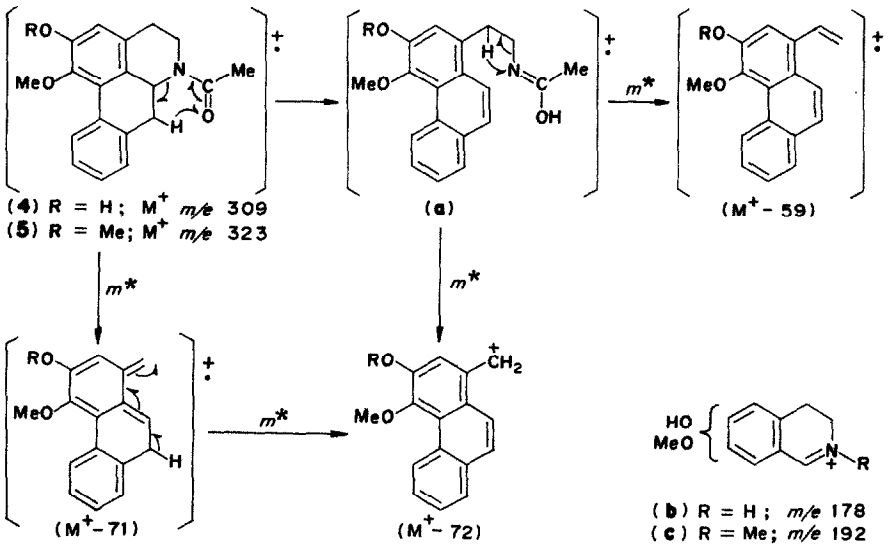
normal heartwood of *L. tulipifera*. *N*-acetyl derivatives of asimilobine and nornuciferine, **4**, and **5**, are the first *N*-acetylaporphine alkaloids isolated from plant sources.

In addition, two other phenolic alkaloids were present in minor amounts. Our attempts to isolate these compounds by preparative TLC were not successful, but mass spectra of the fractions containing these compounds showed an intense ion peak either at *m/e* 178 or *m/e* 192. These peaks are characteristic of ion species **b** and **c** [13, 14]. Thus, at least two alkaloids of the 1-benzyltetrahydroisoquinoline type (**14**) also are present in normal heartwood of *L. tulipifera*.

Spectral properties of aporphine alkaloids

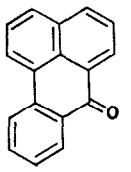
NMR data for compounds **1–9** are given in Table 1. In the NMR spectra of **7** and **8**, H-4 and H-5 constitute an AB system with J_{AB} 5·2 Hz. The four hydrogens on ring D of **7** form an AA'XX' system with H-9 and H-10 as AA' component. By contrast, these hydrogens of **3–6** constitute ABCX system with J_{AX} 8·0 Hz and J_{BX} 2·0 Hz taking H-11 as X component. The C-1 and C-2 methylenedioxyl hydrogens of **6** form a characteristic AB system with J_{AB} 1·6 Hz and $\Delta\tau$ = 0·14 ppm, while N-6 H, H-6a and H-7 form an AMX system with J_{MX} 3·6 Hz; the signal for the N-6 H could not be ascertained because it overlapped with the complex ABCD multiplets of C-4 and C-5 hydrogens.

Among the aporphine alkaloids isolated from heartwood of *L. tulipifera*, **4** and **5** give mass spectra that are not characteristic of either aporphines or noraporphines [14, 15]. The mass spectra of both compounds exhibit a fragmentation pattern dominated by the *N*-acetyl group. A McLafferty rearrangement of molecular ions involving the *N*-carbonyl group produces the intermediate ion **a** which gives (M-59) and (M-72) ion species, respectively, by C-N cleavage with a 1,3 hydrogen transfer and an α-cleavage. An alternative retro-Diels–Alder reaction of molecular ions produces (M-71) ion species which also give (M-72) ion species by loss of hydrogen as indicated by meta-stable ions. Minor ion peaks corresponding to (M-MeCO) are also present in both spectra (Scheme 1).

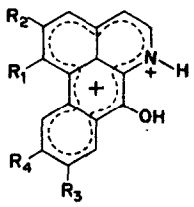


Scheme 1. Fragmentation pattern of *N*-acetyl aporphines.

Oxoaporphines **7** and **8** give very different UV spectra in methanol or chloroform. In cyclohexane, however, they give spectra which are very similar to each other and to the spectrum of benzanthrone (**12**) [16, 17]. In cyclohexane, all three compounds show strong absorption bands at λ_{max} *ca* 377 and 397 nm (log $\epsilon > 4{\cdot}0$). In conc. H_2SO_4, both compounds are purple–blue in color and show absorption bands between 400 and 600 nm; at λ_{max} 412, 503 and 568 (log ϵ 4·27, 3·94 and 3·72) for **7**, and at λ_{max} 455 and 539 nm (log ϵ 4·15 and 4·18) for **8**. When these solutions are diluted with water, strong hypsochromic shifts were observed. Therefore, the 7-oxoaporphines **7** and **8** form conjugated acids of the type **13** in a strong-acid medium, a property similar to the benzanthrone derivatives [16].



(**12**)



(**13**) R_1, R_2 = OCH_2O; R_3 = R_4 = H
or R_1 = R_2 = R_3 = R_4 = OMe

Biosynthetic relationships

Biosynthesis of aporphine alkaloids, lignans and related neolignans could be achieved by the same pathway with bifurcation at the phenylalanine stage—lignans and neolignans being produced from cinnamyl alcohol intermediates and aporphine alkaloids via phenolic 1-benzyltetrahydroisoquinoline intermediates. Dehydrogenative coupling would be required in the synthesis of all these types of compounds. According to Gottlieb [18], this could be accomplished by the same dehydrogenase. Gottlieb has also suggested that the existence of these biosynthetically related classes of compounds in different species can be interpreted as evidence for phylogenic relationships. Arylpropanoids and alkaloids derived from benzylisoquinoline have only rarely been found in the same species although they have been found separately on many occasions. Thus, the co-occurrence of substantial amounts of aporphine alkaloids and lignans in normal heartwood may be a significant exception to this generalization. Co-occurrence of aporphine alkaloids and neolignans, however, has been reported in *Magnolia obovata* (Magnoliaceae) [19–21] and *Litsea turfose* (Lauraceae) [22].

Two biosynthetic pathways have been proposed for transformation of 1-benzyltetrahydroisoquinolines to aporphines—the proaporphine [23] and the neoproaporphine [24] pathway. Since compounds **3**–**6** have no substituents on ring D, these compounds probably are formed from 1-benzyltetrahydroisoquinolines via proaporphine intermediates in *L. tulipifera*—**3**–**5** through a coclaurine-crotonisine pathway and **6** through a coclaurine-anonaine pathway [25]. Oxidation of **6** would yield **7**. Although **6** is stable in the solid state, in chloroform however, it readily undergoes auto-oxidation to give **7** in the presence of light and air. This is compatible with the observation by Cava and Dalton [26] that roemerine gives **7** when air is bubbled through a *t*-butyl solution of this compound.

EXPERIMENTAL

Mps are uncorrected. Preparative TLC was carried out with Si Gel 60 F-254 (Merck) plates. Each compound was identified by a mmp with an authentic sample or by comparison of spectral data with published values.

Extraction and separation of extractives. Heartwood and sapwood of uniform color were obtained from a healthy yellow poplar tree near Zebulon, N. C. The tree was *ca* 30 yr old at the time of felling. The tissue was air-dried, ground to pass a 40-mesh screen, pre-extracted with ligroin to remove waxes and then air-dried again. This sample of heartwood (750 g) was steeped in 4·5 l. 1% HCl–MeOH for 24 hr at room temp. and then filtered. The wet woodmeal was again steeped with 3 l. 1% HCl–MeOH as before. The combined 1% HCl–MeOH solutions were concentrated to about 150 ml at 50° and then dropped slowly into 600 ml Et_2O with stirring. The ether-insoluble mass was filtered off and then stirred for 30 min with 400 ml hot H_2O. The ppt was then filtered off and washed 2× with 100 ml hot H_2O. This ppt. (10·8 g) which consisted mainly of polymeric materials was discarded. The filtrate and washing solutions were combined and extracted continuously with 500 ml Et_2O for 34 hr. The aq. soln was then neutralized and extracted 4× with 200 ml $CHCl_3$. The $CHCl_3$ soln was shaken 4× with 100 ml 1N NaOH, washed 2× with 100 ml H_2O, dried and the solvent evaporated to give a *mixture of nonphenolic alkaloids* (8·9 g). The alkaline soln was then neutralized, extracted with $CHCl_3$(3 × 100 ml). The $CHCl_3$ soln was washed with H_2O, dried, and the solvent evaporated to give a *mixture of phenolic alkaloids* (1·7 *g*).The combined Et_2O solution (neutral and acidic materials) were concentrated to about 300 ml, shaken with 100 ml 1N $NaHCO_3$(× 3), with 100 ml 1 N NaOH(× 4), washed with water, dried, and the solvent evaporated to give a *mixture of neutral substances* (4·8 g). Both alkaline solutions were neutralized and extracted 3× with 100 ml $CHCl_3$. $CHCl_3$ solns were washed with water, dried, and the solvent evaporated to give a *mixture of phenols* (1·1 g) and *of acids* (0·6 g) respectively.

The nonphenolic alkaloid mixture (8·2 g) was dissolved in 50 ml $CHCl_3$, cooled and kept at 0° for 2 days. Crude crystals of **7** were collected and combined with a second crude product obtained later by preparative TLC. The mother-liquor was subjected to preparative TLC using cyclohexane-EtOAc–$NHEt_2$ (7:2:1) to isolate the following compounds: *Dehydroglaucine* (**2**). The brown viscous oil recovered from the first band was rechromatographed on a Si gel plate. The crude product was recrystallized from EtOAc to give slightly brownish rhombic crystals (78 mg), mp 128–131° (Lit. [8] 133–134°). MS: *m/e* (rel. int.) 354 (29), 353 (M^+, 100), 339 (11), 338 (42), 324 (10), 323·6 (*m**). The NMR data (see Table 1) corresponded to those reported by Kiryakov [8].

Glaucine (**1**). The brown solid obtained from the second band was recrystallized from EtOAc to give colorless needles (2·85 g), mp 119–120° (Lit. [1] 122°). MS: *m/e* (rel. int.) 356 (26), 355 (M^+, 100), 354 (83). 341 (9), 340 (50), 325·6 (*m**), 324 (26), 312 (16), 295·7 (*m**), 274·2 (*m**).

Norushinsunine (**6**). The brown solid obtained from the fourth band was recrystallized from $CHCl_3$ to give colorless needles (155 mg), mp 204–206° (Lit. [10] 207°). MS: *m/e* (rel. int.) 282 (27), 281 (M^+, 100), 280 (72), 263 (15), 262 (19), 261 (8), 253 (6), 252 (28), 251 (20), 246·2 (*m**), 225·2 (*m**). The NMR data are shown in Table 1. The IR spectrum was identical with that reported by Yang and coworkers [10].

O-Methylatheroline (**8**). The yellowish–brown solid obtained from the fifth band was recrystallized from $CHCl_3$ to give yellowish–orange needles (86 mg), mp 232–234° (Lit. [3] 233–234°). MS: (rel. int.) 352 (27), 351 (M^+, 100), 337 (6), 336 (28), 321·6 (*m**). UV: λ_{max} in cyclohexane 241, 259, 267, 278, 288, 329 (*sh*), 375, 395 and 473 nm (log ϵ 4·54, 4·46, 4·43, 4·25, 4·13, 3·68, 4·07, 4·11 and 2·73); λ_{max} in conc. H_2SO_4 250, 275 (*sh*), 330, 379, 455 and 539 nm (log ϵ 4·59, 4·34, 3·66, 3·72, 4·15 and 4·18).

Liriodenine (**7**). The yellowish–brown solid obtained from

the sixth band was combined with the first crude product obtained earlier, and recrystallized from $CHCl_3$ to give yellowish-green needles (0·66 g). mp 280–282° (Lit. [3] 282°). MS: *m/e* (rel. int.) 276 (24), 275 (M^+, 100), 248 (5), 247 (18), 246 (10), 232 (*m**). UV: λ_{max} in cyclohexane 244, 259, 261, 268, 278, 335, 377, 398 and 475 nm (log ϵ 4·57, 4·50, 4·48, 4·13, 3·60, 4·10, 4·16 and 2·90); λ_{max} in conc. H_2SO_4 243, 249, 275, 290, 412, 503, 568, and 608 (*sh*) nm (log ϵ 4·49, 4·48, 4·35, 4·28, 4·27, 3·98, 3·72 and 3·65).

The phenolic alkaloid mixture (1·5 g) was subject to preparative TLC in the same manner as the nonphenolic alkaloid mixture to isolate:

Asimilobine (**3**). The brown oil recovered from the second band was rechromatographed on a Si gel plate. The crude product (36 mg) could not be crystallized. TLC indicated the presence of minor impurities. MS: *m/e* (rel. int.) 268 (16), 267 (M^+, 82), 266 (100), 253 (8), 252 (24), 251 (23), 239 (13), 238 (6), 237 (10), 236·8 (*m**), 236 (22). The NMR data (see Table 1) correspond to those reported by Johns and coworkers [11].

The neutral mixture (4·2 g) was dissolved in 30 ml hot MeOH, cooled, and kept at 0° for 12 hr. Crude crystals of **10** were collected and combined with a second crude product obtained later by preparative TLC. The mother-liquor was subjected to preparative TLC using $CHCl_3$–EtOAc (9:1) to isolate the following compounds:

(+)-*Syringaresinol dimethyl ether* (**10**). The crude product obtained from the first band was combined with the first crude product obtained earlier, and recrystallized from MeOH to give colorless plates (0·86 g), mp 116–118° (Lit. [4] 121–123°). NMR ($CDCl_3$): τ 6·93 (2H,*m*, H-β), 6·18 (18H, *s*, OCH_3), 6·07 (2H, *m*, H_AH_B-α), 5·72 (2H, *m*, H_AH_B-α), 5·28 (2H, *d*, *J* 4·8 Hz, H-γ), 3·44 (4H, *s*, ArH). MS: *m/e* (rel. int.) 477 (28), 446 (M^+, 100), 208 (14), 207 (37), 197 (11), 196 (14), 195 (36), 182 (18), 181 (52).

N-*Acetylnornuciferine* (**5**). The crude product obtained from the second band was recrystallized from C_6H_6-cyclohexane to give colorless needles (270 mg), mp 229–231° (Lit. [9] 232–233°). MS: *m/e* (rel. int.) 324 (17), 323 (M^+, 70), 280 (7), 263 (10), 264 (32), 252 (28), 251 (100), 215·8 (*m**). The NMR data (see Table 1) corresponded to those reported by Kupchan and coworkers [9].

The phenolic mixture (1·0 g) was subjected to preparative TLC using C_6H_6–MeOH (9:1) to isolate the following compounds:

Syringaldehyde (**11**). The crude product obtained from the second band was sublimed under reduced pressure to give colorless needle, mp 105–108°. The identity of the compound was established by mmp with an authentic sample (mp 112°). MS: *m/e* (rel. int.) 183 (18), 182 (M^+, 100), 181 (68), 167 (23), 153·3 (*m**), 153 (11), 139 (16), 128·6 (*m**).

N-*Acetylasimilobine* (**4**). The crude product obtained from the third band was recrystallized from $CHCl_3$ to give colorless needles (130 mg), mp 281–283°. IR: 3220 (OH), 1620 (*t*-amide), 1590, 1450, 1415 (Ar-H), 1250 (Ar-OMe), 875 (isolated H), 756 (four adjacent H) cm^{-1}. MS: *m/e* (rel. int.) 310 (22), 309 (M^+, 97), 266 (9), 251 (18), 250 (47), 238 (23), 237 (100), 236 (*m**), 223 (24), 221 (*m**), 209 (*m**), 202·2 (*m**), 183·3 (*m**), 181·8 (*m**). The NMR data are shown in Table 1. On treatment with diazomethane, it gave *N*-acetylnornuciferine (**5**). The identity of the methylated product was established by mmp and comparison of IR spectrum with an authentic sample (mp 229–231°).

(+)-*Syringaresinol* (**9**). The brown oil obtained from the fourth band was rechromatographed on Si gel plate. The crude product was recrystallized with C_6H_6–cyclohexane to give colorless rhombic crystals (36 mg), mp 175–179° (Lit. [4] 186°). NMR ($CDCl_3$): τ 6·97 (2H, *m*, H-β), 6·16 (12H, *s*, OCH_3), 6·11 (2H, *m*, H_AH_B-α), 5·76 (2H, *m*, H_AH_B-α), 5·31 (2H, *d*, *J* 4·8 Hz, H-γ), 4·50 (2H, *br*, OH, exchanged with D_2O), 3·44 (4H, *s*, ArH). MS: *m/e* (ret. int.) 419 (28), 418 (M^+, 100), 388 (8), 387 (7), 280 (20), 251 (8), 235 (10), 234 (10), 226 (9), 221 (9), 210 (19), 193 (28), 182 (43), 181 (71), 168 (20), 167 (66). The IR spectrum was identical with that reported by Dickey and coworkers [4].

The sample of sapwood (1 kg) was treated in the same manner as heartwood to obtain a mixture of alkaloids (0·4 g). Only trace amounts of *glaucine* (**1**) were detected from this fraction by TLC.

Auto-oxidation of norushinsunine (**6**). Air was bubbled through a solution of **6** (20 mg) in 10 ml $CHCl_3$ at room temperature in daylight for 10 hr. The reaction mixture was subjected to preparative TLC in $CHCl_3$-EtOAc (9:1). The band corresponding to *liriodenine* (**7**) was removed, shaken with 200 ml $CHCl_3$ and the UV spectrum measured. Yield for **7**: 12·7%.

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