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LIRIODENDRONINE, AN OXOAPORPHINE PIGMENT FROM DISCOLORED SAPWOOD OF *LIRIODENDRON TULIPIFERA*[*]

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Key Word Index—*Liriodendron tulipifera*;Magnoliaceae; discolored sapwood; oxoaporphine; liriodendronine; 2-*O*,*N*-dimethylliriodendronine.

Abstract—A new violet oxoaporphine alkaloid. liriodendronine, has been isolated from the discolored sapwood of *Liniodendron tulipifera* and its structure determined by spectroscopic methods and by conversion into a corunnine-type compound, 2-*O*,*N*-dimethylliriodendronine. UV studies demonstrated that the compound exists primarily as a quinone-methide in a neutral medium, a dianion in base, an isoquinolinium ion in weak acid, and as an antiaromatic conjugate acid in conc H_2SO_4.

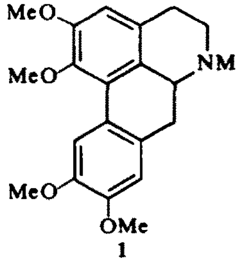
INTRODUCTION

When living trees of *Liriodendron tulipifera* (yellow poplar) are injured, the synthesis of glaucine (1), and related aporphine alkaloids is greatly stimulated [1]. Injured wood of this tree is frequently highly discolored. The colors can range from violet, blue, green, brown and even black [2]. The origin of the discoloration is most likely due to metabolism of aporphine alkaloids by micro-organisms that invade the parenchyma or wood fiber cells after wounding [3]. In this paper, we report the isolation of a new violet oxoaporphine, liriodendronine (2), a major pigment which contributes to the discoloration of injured *L. tulipifera* wood.

RESULTS AND DISCUSSION

Liriodendronine was isolated from an acidic methanol extract of discolored *L. tulipifera* sapwood by adjusting the pH to 1.7 and extracting with diethyl ether. The pigment precipitated on cooling, showing a single spot on TLC, and could not be recrystallized due to its high insolubility in water and neutral organic solvents. Liriodendronine was violet in neutral solvents, red in acid, and blue in base. The pigment was unstable in alkali, turning red in the presence of air. High resolution MS gave the molecular formula $C_{16}H_9NO_3$ (M^+ *m/e* 263.0586) for **2**. The compound was soluble in dilute sodium hydroxide solution but insoluble in dilute sodium bicarbonate solution showing that it was phenolic. In conc sulfuric acid, **2** gave a UV and visible spectrum similar to that of liriodenine (**3**), which indicated that these compounds were closely related [1, 4]. The IR spectrum of **2** showed absorption bands at 1650, 850, 800, and 770 cm^{-1}, characteristic of a conjugated carbonyl, isolated, two adjacent, and 4 adjacent aromatic hydrogens, respectively. The PMR spectrum (CF_3COOD) of **2** comprised only 7 aromatic hydrogens. The one-proton singlet at δ 6.95 corresponded to an isolated aromatic hydrogen (H-3). Decoupling experiments established that two one-proton doublets at δ 8.28 and 9.11 were the M and X parts (H-8 and H-11) of an ABMX spin-system. The AB part (H-10 and H-9) of the spectrum was second order. This established that ring D was unsubstituted. On the basis of this spectroscopic evidence, liriodendronine was assigned the structure **2**.

Treatment of **2** with dimethyl sulfate in alkaline solution gave a dimethyl derivative, 2-*O*, *N*-dimethylliriodendronine (**4**) as dark green needles, mp 275–278° (decomp.). High resolution MS gave a molecular formula $C_{18}H_{13}NO_3$ (M^+ *m/e* 291.0891) for **4**. The intense UV absorption band at λ_{max} 311 nm indicated that it was a zwitterionic oxoaporphine similar in structure to the corunnine-type compounds [1, 6–8]. The carbonyl region of the IR spectrum of **4** was nearly the same as corunnine (**4**). The absorption bands at 1628 and 1581 cm^{-1} corresponded to a carbonyl with the corunnine-type resonance forms **5** and **5a** [6, 7]. The PMR



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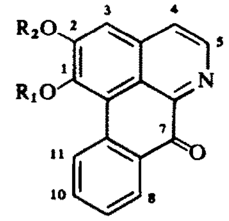
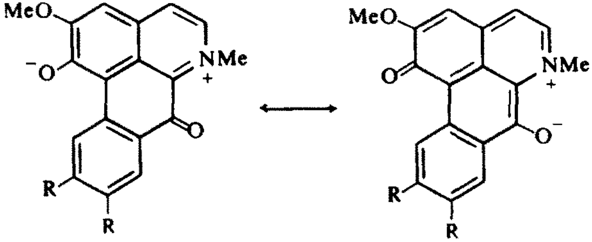


2, $R_1 = R_2 = H$
3, $R_1 = R_2 = -CH_2-$



4, R = H
5, R = OMe

4a, R = H
5a, R = OMe

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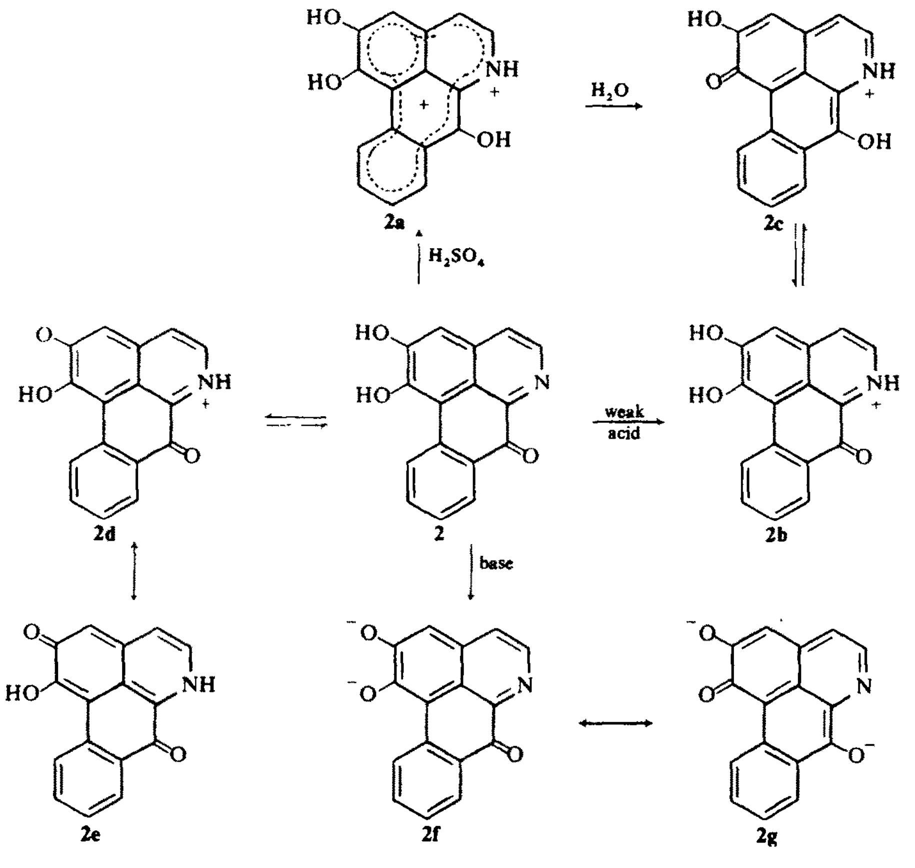
[*] Part 3 in the series 'The Chemistry of *Liriodendron tulipifera*' For Part 2 see ref. [1].

(CF_3COOD) revealed an aromatic N^+-Me group at δ 4.9 and a OMe group at δ 4.36, which were not present before methylation. The spectrum also comprised 7 aromatic hydrogens and was compatible with the structure proposed for the compound. Thus, 2-*O*, *N*-dimethylliriodendronine possesses the corunnine-type resonance forms **4** and **4a**. The identification of the Me derivative **4** proves that liriodendronine must have the structure **2**. 2-*O*,*N*-Dimethylliriodendronine has recently been synthesized by Cava *et al.* [9]. The reported mp of 275–277° is in agreement with that found for **4**.

In conc sulfuric acid, **2** gave a UV spectrum substantially different from that recorded in dilute acidic methanol. When the conc sulfuric acid solution was diluted with water, the spectrum underwent a strong hypsochromic shift and was identical to the spectrum of **2** in weak acid. Oxoaporphines dissolved in conc sulfuric acid give UV spectra similar to strong acid solutions of benzanthrone derivatives, which are known to form antiaromatic conjugate acids [5, 10, 11]. Therefore, when dissolved in conc sulfuric acid, **2** forms the antiaromatic conjugate acid **2a** (Scheme 2). In dilute acid solution, **2** can undergo keto-enol tautomerization, and the isoquinolinium ions **2b** and **2c** are formed. In neutral aqueous solutions, it has been established that 6-hydroxyisoquinoline exists primarily as a quinone-methide in resonance with the zwitterionic form [12]. The strong visible absorption bands in methanol at λ_{max} 543 and 569 nm indicate that **2** exists as the quinnone-methide **2e** in resonance with the zwitterion **2d** in a neutral medium. In base, **2** exists as a dianion with the charge distributed among all 3 oxygens. It is apparent from the resonance forms **2f** and **2g** that the C-2 oxygen has a larger net negative charge than the C-1 and C-7 oxygens. Methylation at the C-2 oxygen yields a resonance stablized anion which can undergo further methylation at the N-6 to give **4**.

EXPERIMENTAL

Isolation of liriodendronine (**2**). The discolored sapwood was obtained from a 31 year old tree of *L. tulipifera* harvested near Benson, NC, U.S.A. The discolored portion was ground to pass a 40 mesh screen. The wood (2060 g) was then preextracted with petrol, steeped in 12 l. of 1% HCl–MeOH for 24 hr at room temp. and then filtered. The wood was treated again with 9 l. of 1% HCl–MeOH and filtered. The extracts were combined and concd to 350 ml. The dark red soln was stirred with 1.2 l. of Et_2O and the solvent was decanted from the tar and extracted with H_2O. The tar was stirred for 30 min with 1 l. hot H_2O. The water-insoluble ppt. was filtered off and washed with 0.5 l. of hot H_2O. The filtrate and washings were combined and adjusted to pH 1.7 with 18 M NH_4OH, whereupon the color changed to cloudy violet. The aq. soln was extracted continuously for 24 hr with 4.8 l. Et_2O. The Et_2O soln was dried, concd to 600 ml, then cooled to 0° for several days to give **2** as violet crystals (350 mg), mp 265–270° (dec). UV: λ_{max}^{MeOH} 260. 297. 543. 569 (*infl*) nm (log ε 4.08, 3.84 [illegible] 24 (*infl*), 526, 634 nm (lo[illegible] N) 253, 261 (*infl*), 278 (*infl*), 477, 602 (*inf*) nm (log ε 4.12, 4.08, 3.88, 3.56, 306); $\lambda_{max}^{H_2SO_4}$ 249, 290, 408, 488 nm (log ε 4.26, 3.88, 3.72, 3.59). IR (KBr) γ_{max} m^{-1}: 3305 (OH), 3220 (NH), 1650 (conj. C═O), 1565, 850 (*iso.* Ar-H), 800 (two adj. Ar-H), 770 (4 adj. Ar-H). PMR (CF_3COOD): δ 9.11 (1H, *d*, J_{AX} = 8.5 Hz, H-11), 8.28 (1H, *d*, J_{BM} = 7.4 Hz, H-8), 7.87 (2H, *m*, H-10, H-5), 7.54 (2H, *m*, H-9, H-4), 6.95 (1H, *s*, H-3). MS: *m/e* (rel. int.), 264 (14), 263 (M^+, 75), 236 (25), 235 (100), 234 (7), 207 (11), 206) (18), 179 (25), 178 (29),



177 (18), 164 (21), 163 (20), 152 (25), 151 (23), 150 (19). High resolution MS: M^+ *m/e* 263.0586 (calc for $C_{16}H_9NO_3$, 263.0582).

2-O, N-*Dimethylliriodendronine* (**4**). Me_2SO_4 (0.09 ml) was added to a stirred soln of **2** (50 mg) in 7.6 ml 0.1 N NaOH under a stream of N_2 at 50°. Stirring was continued for 2hr. The reaction mixture was extracted continuously for 12 hr with $CHCl_3$. The $CHCl_3$ soln was dried and the solvent removed. The green residue was subjected to preparative-TLC on Si gel (C_6H_6–MeOH, 9:1). The dark green crude crystals recovered from the last band were recrystallized from MeOH to give **4** as dark green needles (35 mg), yield 63 %, mp 275–278° (decomp.) (lit. 275–277°) [9]. UV: λ_{max}^{MeOH} and $\lambda_{max}^{NaOMe + MeOH}$ (0.005 N) 247 (*infl*), 311, 420, 585, 602 nm (log ε 4.03, 4.29, 3.46, 3.44, 3.44); $\lambda^{HCl + MeOH}$ (0.005 N) 251, 286, 387, 473 nm (log ε 4.16, 4.16, 3.56, 3.37); $\lambda_{max}^{H_2SO_4}$ 246, 280, 295, 412, 488 nm (log ε 4.36, 416, 4.16, 4.06, 3.74). IR ν_{max}^{KBr} cm^{-1}: 2950, 2920, 2850 (Me), 1628 (conj. C=O), 1585, 1538, 1300, 1255 (C=C—OMe), 1210, 855 (*iso*. Ar-H), 796 (two adj. Ar-H), 765 (4 adj. Ar-H). PMR (CF_3COOD): δ 9.35 (1H, *d*, J_{AX} = 8.6 Hz, H-11), 8.62 (1H, *d*, J_{AB} = 6.8 Hz, H-4 or H-5), 8.52 (1H, *d*, J_{BM} = 7.7 Hz, H-8), 8.43 (1H, *d*, J_{AB} = 6.8 Hz, H-4 or H-5), 8.01 (1H, *m*, J_{AB} = 7.7, J_{AX} = 8.6 Hz, H-10), 7.72 (1H, *t*, $J_{AB} = J_{BM}$ = 7.7 Hz, H-9), 7.6 (1H, *s*, H-3), 4.9 (3H, *s*, N^+-Me), 4.36 (3H, *s*, OMe). MS: *m/e* (rel. int.), 292 (23), 291 (M^+, 100), 290 (35), 277 (24), 276 (93), 263 (16), 262 (58), 261 (12), 249 (14), 220 (19), 219 (58), 218 (27), 190 (20), 177 (22), 176 (27) 163 (21), 151 (26), 150 (20), 149 (23), 136 (20). High resolution MS: M^+ *m/e* 291.0891 (calc for $C_{18}H_{13}NO_3$, 291.0891).

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