lated as described previously. A mixture of the salt and that obtained in a preceding experiment melted at 229–231°.

The ether solution yielded an oil (0.371 g.) which could not be induced to crystallize.

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The Alkaloids of *Liriodendron tulipifera* L. The Structure and Synthesis of the Unnamed Yellow Alkaloid and the Isolation of *d*-Glaucine

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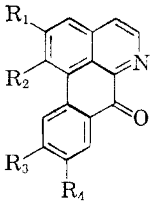
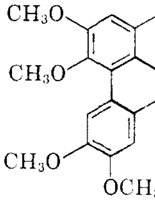
Buchanan and Dickey[1] have traced the color of the heartwood of the yellow poplar (*Liriodendron tulipifera* L.) to two yellow alkaloids, liriodenine and an unnamed base. Although liriodenine was degraded to benzo[*g*]quinoline-5,10-dione, the authors were unable to propose a satisfactory structure for the alkaloid. We have shown[2] that liriodenine must be I from the data which had been presented and biogenetic considerations. This conclusion was substantiated by synthesis.

In the same paper we suggested that the second unnamed base should be a tetramethoxy analogue of liriodenine and by synthesis it is now shown to be II. Nitropapaveraldine[3] prepared either by a total synthesis or in two steps from papaverine, was reduced to the amine and its diazonium derivative subjected to Pschorr cyclization conditions. The resulting 1,2,9,10-tetramethoxydibenz[*de*,*g*]quinoline-7-one (II) had physical properties identical in all respects with those recorded by Buchanan and Dickey[1] for the unnamed yellow base.





III

I. $R_1R_2 = OCH_2O$; $R_3 = R_4 = H$ III.

II. $R_1 = R_2 = R_3 = R_4 = OCH_3$

It was our opinion that these yellow bases could have been derived oxidatively from co-occurring aporphines—*e.g.* roemerine or glaucine or their nor compounds. As a corollary we would expect compounds like I and II to be of wide occurrence as minor alkaloids in Magnoliaceous plants.

A sample of yellow poplar heartwood was worked up for alkaloid in a manner essentially the same as previously described.[1] Chromatography of the crude material resulted in the isolation of *d*-glaucine (III) as a major component of the mixture. The isolation of this aporphine can be considered to support but not to prove our hypothesis for the origin of the yellow bases.

EXPERIMENTAL

All melting points are uncorrected. The alumina used for chromatography was Woelm neutral activity III.

Nitropapaveraldine. 1,2′-Nitro-4′,5′-dimethoxybenzyl-6,7-dimethoxy-3,4-dihydroisoquinoline[4] (0.5 g.) in acetic acid was heated with chromic oxide (0.5 g.) until an exothermic reaction began. After the solution had cooled, it was diluted with water and extracted with methylene chloride. The solution was concentrated to dryness and the residue in methylene chloride was filtered through a plug of alumina to furnish 1,2′-nitro-4,5-dimethoxybenzoyl-6,7-dimethoxy-3,4-dihydroisoquinoline (250 mg.), m.p. 168–172° from methylene chloride–methanol.

Anal. Calcd. for $C_{20}H_{20}O_7N_2$: C, 60.0; H, 5.0. Found: C, 60.3; H, 5.0.

The above benzoyl derivative (100 mg.) was boiled in methanol containing several drops of 2*N* potassium hydroxide for 15 min. After the solution had cooled the resulting nitropapaveraldine (40 mg.) m.p. 207° dec. was filtered off.

Anal. Calcd. for $C_{20}H_{18}O_7N_2$: C, 60.3; H, 4.6. Found: C, 60.2; H, 4.5.

1,2,9,10-Tetramethoxydibenz[*de,g*]*quinoline-7-one.* Nitropapaveraldine (567 mg.) suspended in ethanol was shaken overnight in an atmosphere of hydrogen in the presence of Raney nickel. The catalyst was filtered off and the ethanol removed *in vacuo* after the addition of a few drops of hydrochloric acid. The resultant hydrochloride (524 mg.) in dilute sulfuric acid (5 ml.) and methanol (5 ml.) was diazotized then heated on a steam bath for 0.5 hr. After dilution with water, treatment with base and extraction with chloroform, the crude product (355 mg.) was chromatographed using chloroform as an eluant. From the slower running eluate (187 mg.) the desired product (II) was obtained (86 mg.), m.p. 227–229° after crystallization from chloroform and then methanol; $\lambda_{max}^{C_2H_5OH}$ 242 mμ (ε 33,000, 272 (34,000), 355 (9,770) and a plateau at 376–382 (8,010). The infrared spectrum (potassium bromide disc) checked with the published curve[1] of the unnamed yellow base in all thirty-four peaks and shoulders of the fingerprint region.

Isolation of d-glaucine. Yellow poplar heartwood (8.26 kg.) was extracted three times with benzene:alcohol (10:1). The combined extracts were concentrated *in vacuo* to about 2 l. A precipitate was filtered off, then the solution was extracted, after the addition of benzene (1 l.), twice with 0.5% tartaric acid (each 600 ml.). The acid extracts were washed with benzene, made basic, and the precipitate extracted into methylene chloride. This was dried, and its concentrate passed over alumina (40 cm. × 4.5 cm. diam. column) to yield a pale tan eluate (26.07 g.) and a yellow eluate (9 g.). Rechromatography of the first fraction furnished a colorless oil (22.9 g.) a portion (5 g.) of which gave *d*-glaucine hydrochloride (2.8 g.) upon treatment with dilute acid. It had m.p. 245–246° dec. from either water or methanol.

Anal. Calcd. for $C_{21}H_{25}O_4N \cdot HCl \cdot H_2O$: C, 61.7; H, 7.0. $C_{21}H_{25}O_4N \cdot HCl . 0.25H_2O$: C, 63.7; H, 6.8; OCH_3, 31.4.

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Found (dried room temperature *in vacuo*): C, 61.6; H, 7.5; dried at 80° *in vacuo:* C, 63.6; H, 7.4; OCH_3, 32.0, 32.1.

The free base regenerated from the hydrochloride crystallized with difficulty from methylene chloride–hexane only after most of the solvent had evaporated, m.p. 122°, $[\alpha]_D$ 120° (chloroform)[5], $\lambda_{max}^{C_2H_5OH}$ 218 (37,800), 280–282 (15,100), and 302 (14,400).

Anal. Calcd. for $C_{21}H_{23}O_4N$: C, 71.0; H, 7.1. Found: C, 70.6; H, 7.3.

Acknowledgment. We are grateful to Dr. E. Schlittler for his continued interest and encouragement and to Mr. E. Solook, Developmental Research, for carrying out the extraction for us. We are indebted to Hofmann La Roche Inc. for the gift of the papaverine used in this work.

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Some Properties and Reactions of Phenylacetoxysilanes

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Although a number of papers,[2–9] have appeared on organoacetoxysilanes, few have dealt with phenylacetoxysilanes.

In the present paper, the authors wish to report on some properties and reactions of both diphenyldiacetoxysilane and phenyltriacetoxysilane.

Each acetoxysilane was obtained as an acicular crystal at room temperature; concentrated solutions of these acetoxysilanes were found to have a marked tendency of supercooling.

The x-ray powder pattern data and the infrared spectra data for the purified sample are also given.

Diphenyldiacetoxysilane undergoes reactions with diphenyldichlorosilane and with dipotassiumdiphenylsilanolate producing diphenylpolysiloxane. Stoichiometry supports the following equations;

TABLE I

X-RAY POWDER PATTERN DATA[a] AND INFRARED SPECTRA DATA OF ACETOXYSILANES IN CARBON TETRACHLORIDE

d, kx	I/I_0	Positions of Band, Cm.$^{-1}$	Int.	Assignment[10,11]
		$(C_6H_5)_2Si(OCOCH_3)_2$		
7.38	1.00	1750	S	C═O
5.99	0.09	1730	M	
5.19	0.50	1600	W	
4.90	0.05	1540	W	
4.62	0.31	1440	M	Si-Phenyl
4.44	0.03	1380	M	CH_3—C
4.23	0.25	1300	W	
3.92	0.25	1250	S	C—O—
3.68	0.03	1220	S	C—O—
3.47	0.03	1190	W	
3.28	0.15	1135	M	Si-Phenyl
3.12	0.02	1125	M	Si-Phenyl
2.99	0.03	1050	W	
2.88	0.06	1020	M	Si—O—C
2.68	0.05	995	W	
2.51	0.03	940	M	Monosubstituted benzene
2.44	0.03	695	M	
2.38	0.05			
2.25	0.03			
2.11	0.06			
2.73	0.09			
		$C_6H_5Si(OCOCH_3)_3$		
5.95	0.11	1750	S	C═O
5.57	0.11	1720	M	
5.19	0.11	1590	W	
4.40	0.10	1540	W	
4.19	0.20	1440	M	Si-Phenyl
4.11	0.10	1375	M	CH_3—C
3.85	0.30	1295	W	
3.68	0.10	1260	M	C—O—
3.55	0.20	1210	S	
3.44	1.00	1135	M	Si-Phenyl
3.34	0.21	1110	W	
2.90	0.26	1045	W	
2.76	0.25	1015	M	Si—O—C
2.72	0.10	995	W	
		940	M	
		690	W	Monosubstituted benzene

[a] Cu Kα radiation filtered by Ni was used to obtain the powder diffraction data; d = interplanar spacing; I/I_0 = relative intensity.

$$(C_6H_5)_2Si(OCOCH_3)_2 + (C_6H_5)_2SiCl_2 \longrightarrow {}^2/_3[(C_6H_5)_2SiO]_3 + 2CH_3COCl$$ and

$$(C_6H_5)_2Si(OCOCH_3)_2 + (C_6H_5)_2Si(OK)_2 \longrightarrow {}^2/_3[(C_6H_5)_2SiO]_3 + 2CH_3COOK$$

The reaction with gaseous ammonia was also investigated and corresponding silanols were obtained in each case.

EXPERIMENTAL

Preparation and some properties of diphenyldiacetoxysilane and Phenyltriacetoxysilane. Diphenyldiacetoxysilane was prepared by the method of Schuyten, by the reaction of

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