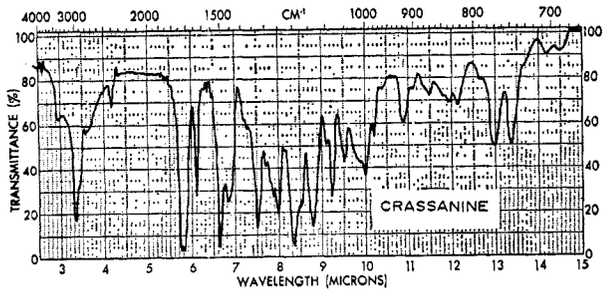


Figure 2.

A number of indole alkaloids have been converted into their oxindole analogs.[11,12] Preliminary attempts to adapt the procedures described in the literature to the transformation of conopharyngine into crassanine have not been successful to date. We plan to continue this investigation when additional supplies of conopharyngine can be obtained.

### Experimental Section

**Plant Material and Crude Tertiary Bases.**—Although *T. crassa* is native to Africa rather than to the South Pacific, the material used in this investigation was collected near the botanical garden in Tahiti in December 1964, by Mr. George Uhe of the Department of Botany, University of Auckland, New Zealand. A voucher specimen (no. 718) has been preserved in Mr. Uhe's personal herbarium. We gratefully acknowledge Mr. Uhe's assistance in collecting and identifying this plant.

The dried and ground plant material (23.75 lb of bark, leaves, twigs, and fruit) was extracted with alcohol in the usual manner. The concentrated extract was refluxed for about 1 hr with ethyl acetate containing 5% concentrated aqueous ammonia. After it had cooled, the ethyl acetate was decanted, and the residue was reextracted until it was free of alkaloids (Mayer's test). The tertiary bases were removed from the combined ethyl acetate extracts by extraction with 5% aqueous $H_2SO_4$. The acid extract was washed with benzene and made basic with ammonia, and the alkaloids were extracted with chloroform to give 26.5 g of crude tertiary bases after solvent evaporation.

**Separation and Characterization of the Tertiary Bases.**—A major aliquot (21.4 g) of the crude tertiary bases was dissolved in chloroform (50 ml) and benzene (200 ml) was added. The resulting precipitate (8.0 g) was removed by filtration; it was not further investigated. The filtrate was shaken successively with the following aqueous phases to give, after the usual work-up, the weights of alkaloidal material recorded: (a) 1% NaOH, 0.1 g; (b) pH 5 McIlvain buffer, 0.8 g; (c) pH 4 McIlvain buffer, 2.2 g; and (d) 3.5% HCl, 9.2 g. Additional work described in this paper was carried out with the major 3.5% HCl fraction; thin layer chromatography of the only other major fraction (pH 4) indicated the absence of additional major constituents.

The pH 3.5 fraction (9.2 g) appeared by tlc ($CHCl_3$–$CH_3OH$ on silica gel H) to consist of two major constituents of similar $R_f$, and one minor constituent. The less polar compound was partially separated by repeated chromatography on alumina (neutral, grade II), the columns being eluted with benzene, followed by benzene–chloroform mixtures. When the pure benzene fractions were evaporated and crystallized from ether, they afforded conopharyngine (1, 4.48 g), mp 133–136° (lit.[1] mp 141–143°). This material was identical (ir and uv spectra) with an authentic sample kindly supplied by Dr. U. Renner (Geigy, A. G., Basel).

On concentration, some of the benzene–chloroform fractions deposited crystals (0.070 g) of the minor base, crassanine (9). Crassanine crystallized from chloroform as colorless plates, mp 190–191°. The physical data for crassanine were as follows: $[\alpha]^{26}D$ +21.4 (*c* 0.013, EtOH); $\lambda_{max}$, mμ (log ε), 210 (4.37), 275 (3.68), and 302 (3.55); $\nu_{max}^{CHCl_3}$ 1739 and 1701 $cm^{-1}$; nmr, δ 9.30 (NH, singlet), 6.50 and 7.01 (aromatic singlets, 1 H each), 3.83 (aromatic $OCH_3$, singlet, 6 H), and 3.47 (ester $OCH_3$, singlet, 3 H). See Figure 1 for the mass spectrum of 9. Infrared spectral data is given in Figure 2.

The more polar major, alkaloid was the principal constituent of the benzene–chloroform fractions. This material, 20-hydroxyconopharyngine (2), was obtained in pure form as follows: a sample of crude 2 (0.0988 g) was dissolved in dry pyridine (1.6 ml) and treated with an excess of benzyl chloroformate, work-up in the usual manner, followed by crystallization from methanol, afforded 20-carbobenzoxyconopharyngine (3, 0.0396 g), mp 193°.

*Anal.* Calcd for $C_{31}H_{36}N_2O_7$: C, 67.87; H, 6.61. Found: C, 68.14, 67.98; H, 6.92, 6.79.

Hydrogenolysis of ester 3 in methanol in the presence of 5% palladium–charcoal gave pure 20-hydroxyconopharyngine (2) as an amorphous glass, tlc of which showed only one clear spot.

The physical data for 20-hydroxyconopharyngine were as follows: $[\alpha]^{26}D$ −36.4 (*c* 1.62, $CHCl_3$); $\lambda_{max}$, mμ (log ε), 226 (4.42) and 304 (3.93); $\nu_{max}^{CHCl_3}$, 3521, 1730, and 1639 $cm^{-1}$; nmr, δ 6.71 and 6.83 (aromatic singlets, 1 H each), 3.86 (aromatic $OCH_3$, 3 H), 3.78 (aromatic $OCH_3$, 3 H) 3.70 (ester $OCH_3$, 3 H) 1.12 δ ($CH_3$-CH(OH)-, doublet, $J$ = 6). The mass spectrum showed significant peaks at 414 ($M^+$), 396, 370, 369, 312, 274, 268, 255, 254, 214, 190, 152, 140, 122, 108, and 94.

**Degradation of 20-Hydroxyconopharyngine (2) to Ibogaline (5).**—Purified base 2 (0.227 g) was hydrolyzed by heating with 20% KOH in methanol. After methanol was removed, the resulting salt was made strongly acid with aqueous HCl and heated on the steam bath for 1 hr to effect decarboxylation. Basification of the solution afforded the amorphous 20-hydroxyibogaline (6, 0.164 g), which was treated with tosyl chloride in pyridine. A portion (0.025 g) of the resulting crude quaternary tosylate (7, 0.063 g) was reduced with $LiAlH_4$ in refluxing tetrahydrofuran to give, after work-up and crystallization, ibogaline (5, 0.003 g), mp 138–142°. This material was identical (mixture melting point and ir spectra) with material prepared from conopharyngine by hydrolysis and decarboxylation.[2]

**Registry No.**—2, 16790-93-5; 3, 16790-91-3; 9, 16790-92-4.

(11) N. Finch and W. I. Taylor, *J. Amer. Chem. Soc.*, **84**, 3871 (1962).
(12) J. Shavel and H. Zinnes, *ibid.*, **84**, 1320 (1962).

## 3-Hydroxy- and Alkoxyaryl Derivatives of 1,2-Dithiolium Salts

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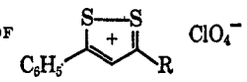
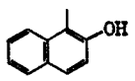
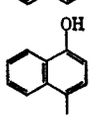
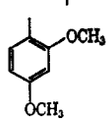
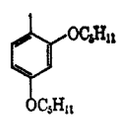
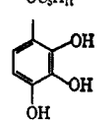
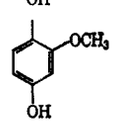
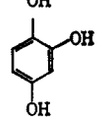
Certain 1,2-dithiolium salts have been shown to undergo substitution reactions at the 3 position of the dithiolium ring with nucleophiles such as amines, hydrazines, and the anions of active methylene compounds.[1]

It has now been found that 3-chloro-5-phenyl-1,2-dithiolium perchlorate (1) reacts with relatively unreactive nucleophiles such as hydroxy- and alkoxy-substituted aromatic compounds to give 3-aryl-1,2-dithiolium salts. Benzene derivatives which contain one hydroxy, alkoxy, or thioalkyl group fail to yield aryldithiolium salts when allowed to react with 1. However, the corresponding *meta*-disubstituted benzene derivatives readily react with 1, and naphthalene derivatives containing only one hydroxy group give aryldithiolium salts. These results are similar to many other substitution reactions of strong electrophiles with benzene and naphthalene derivatives of this type.[2]

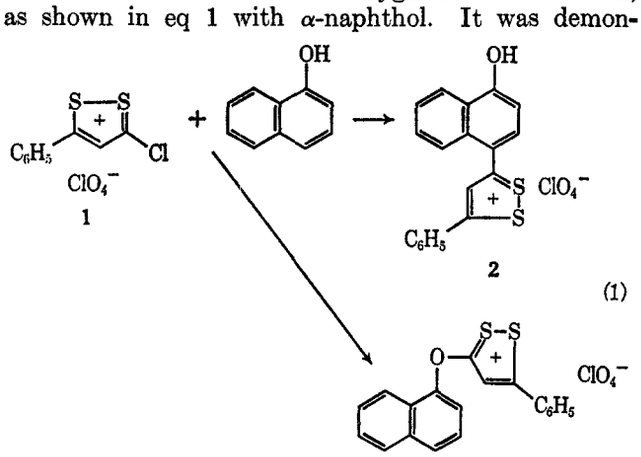
(1) P. S. Landis, *Chem. Rev.*, **65**, 237 (1965).
(2) *Cf.* M. R. DeMaheas, *Bull. Soc. Chim. Fr.*, 1989 (1962).

TABLE I

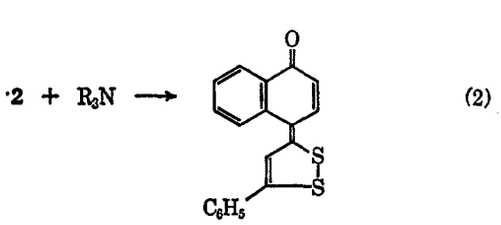
3-ARYL DERIVATIVES OF 

| R | Mp, °C | Yield, % | Empirical formula (registry no.) | Anal, % Calcd C | Calcd H | Calcd N | Found C | Found H | Found N |
|---|---|---|---|---|---|---|---|---|---|
|  | 180–181 | 60 | $C_{19}H_{13}ClO_5S_2$ (16915-98-3) | 54.2 | 3.1 | 15.2 | 53.9 | 3.1 | 14.8 |
|  | 279–280 | 63 | $C_{19}H_{13}ClO_5S_2$ | 54.2 | 3.1 | 15.2 | 54.0 | 3.2 | 14.9 |
|  | 230 | 72 | $C_{17}H_{15}ClO_6S_2$ (16915-99-4) | 49.4 | 3.6 | 15.5 | 49.6 | 3.6 | 15.3 |
|  | 162 | 38 | $C_{25}H_{31}ClO_6S_2$ (16957-25-8) | 57.0 | 5.9 | 12.2 | 56.7 | 6.0 | 12.1 |
|  | 239–240 | 64 | $C_{15}H_{11}ClO_7S_2$ (16916-00-0) | 44.8 | 2.7 | 15.8 | 44.7 | 3.0 | 15.7 |
|  | 231–232 | 61 | $C_{16}H_{13}ClO_6S_2$ (16916-01-1) | 46.9 | 3.2 | 15.6 | 47.2 | 3.6 | 15.9 |
|  | 250–251 | 58 | $C_{15}H_{11}ClO_6S_2$ (16916-02-2) | 46.7 | 2.9 | 16.6 | 46.4 | 3.2 | 16.4 |

In the cases in which hydroxy derivatives of benzene and naphthalene were employed, there is a possibility that **1** has reacted at either an oxygen or a carbon atom, as shown in eq 1 with $\alpha$-naphthol. It was demonstrated that substitution occurs at the carbon atom to yield **2**, since the product shows a strong absorption in the hydroxy region of the infrared spectrum, and treatment of **2** with base results in the formation of the dye **3** (eq 2).



(1)



(2)

## Experimental Section

**3-Chloro-5-phenyl-1,2-dithiolium Perchlorate** (1).—A mixture of 15 g (0.077 mol) of 5-phenyl-1,2-dithiol-3-one[3] and 40 ml of phosphorous oxychloride was heated on the steam bath for 1 hr. After cooling, the mixture was diluted with two volumes of ether and the solid collected and washed with ether. The hygroscopic solid was dissolved in acetone and 5 ml of 70% perchloric acid was added to the solution; after chilling the solid which separated was collected and recrystallized from acetone to yield 18 g of product, mp 177–178°.

*Anal.* Calcd for $C_9H_6Cl_2O_4S$: C, 34.6; H, 1.9; Cl, 22.4. Found: C, 34.9; H, 2.1; Cl, 22.7.

The 3-aryl-1,2-dithiolium salts listed in Table I were prepared by the following general procedure.

A mixture of 3.1 g (0.01 mol) of **1**, 0.015 mol of the hydroxy- or alkoxyaryl derivative, and 25 ml of acetic acid was refluxed for 3 hr and cooled to room temperature, and the solid was collected and recrystallized. Acetonitrile was a satisfactory recrystallization solvent for all of the compounds listed in Table I.

**Treatment of 2 with Base.**—A solution of 1 g of **2**, 1 ml of triethylamine, and 75 ml of acetonitrile was stirred for 1 hr and chilled, and the dark solid was collected and recrystallized from acetonitrile to yield 0.6 g of **3**, mp 145–146°.

*Anal.* Calcd for $C_{19}H_{12}OS_2$: C, 71.2; H, 3.7; S, 20.0. Found: C, 71.1; H, 3.5; S, 20.2.

The absorption spectrum of **3** (in acetonitrile) showed the following absorption maxima recorded as m$\mu$ ($\epsilon \times 10^3$): 243 (19.9); 305 (15.0); 380 (3.2); 517 (26.6). The maxima recorded for **2** were 228 (30.4); ~245 (11.4); 355 (13.5); 490 (15.0).

**Registry No.**—**1**, 5541-12-8; **2**, 16960-02-4; **3**, 16915-97-2.

(3) E. Klingsberg, *J. Amer. Chem. Soc.*, **83**, 2937 (1961).