Anal. Calcd. for $C_{22}H_{13}O_3N_2SI$: S, 6.26. Found: S, 5.18.

2-Amino-8-(N-2-quinolyl)-aminothiaxanthone-5-dioxide (IV).—A mixture of 0.32 g. (0.00062 mole) of XVI, 10 ml. of concentrated ammonium hydroxide, and a trace of copper powder was heated fifteen hours at 205° in a sealed tube. Water (90 ml.) was added and the insoluble dark-brown solid filtered off. Upon heating this material three times with 10 ml. of approximately 4 *N* hydrochloric acid, removing insoluble material by filtration, and reprecipitating from the cooled filtrate with ammonium hydroxide three impure brown-yellow fractions were obtained from which 8 mg. (3%) of pure 2-amino-8-(N-2-quinolyl)-aminothiaxanthone-5-dioxide was isolated by fractional extractions with boiling dioxane followed by reprecipitation from the cooled solutions with water.

Anal. Calcd. for $C_{22}H_{15}O_3N_3S$: S, 7.99. Found: S, 7.70.[18]

Summary

2-Amino-8-(N-2-pyridyl)-aminothiaxanthone-5-dioxide, 2-amino-8-(N-2-pyrimidyl)-aminothiaxanthone-5-dioxide and 2-amino-8-(N-2-quinolyl)-aminothiaxanthone-5-dioxide have been synthesized for study as possible new antibacterial agents.

[18] Analysis by Dr. Carl Tiedcke.

BETHLEHEM, PENNA. RECEIVED JUNE 21, 1947

[CONTRIBUTION FROM THE OFFICE OF DERMATOLOGY, INDUSTRIAL HYGIENE DIVISION, BUREAU OF STATE SERVICES, U. S. PUBLIC HEALTH SERVICE]

The Allergenic Principles of Poison Ivy. VII. Absorption Spectra of 3-*n*-Pentadecylcatechol and Related Compounds[1]

BY HOWARD S. MASON

In this study the absorption spectra of 3-*n*-pentadecylcatechol and a group of other substituted catechols, catechol derivatives and *o*-quinones have been determined. The feasibility of direct spectrophotometric assay of poison ivy allergens was also investigated.

Experimental

Unless otherwise noted, all substances examined were analytically pure samples previously described[1].

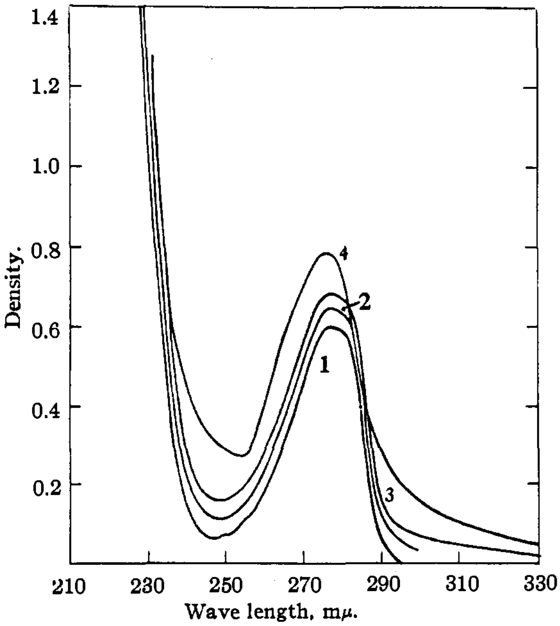

Fig. 1.—Spectrum of 3-*n*-pentadecylcatechol in ethanol. The solution contained 0.102 mg. per ml. The measurements were made at intervals of (1) zero days, (2) fourteen days, (3) thirty days and (4) ninety-one days.

3-*n*-Pentadecyl-*o*-benzoquinone.—This compound was prepared and purified by following the procedure of Willstätter[2] for the preparation of *o*-benzoquinone. It was recrystallized from a mixture of ether and hexane, from which it separated as orange rhomboids sintering and decomposing between 63–67°. The colorless modification could also be obtained by following the procedure of Willstätter and Müller[3] for the preparation of colorless *o*-benzoquinone.

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.8. Found: C, 79.0; H, 11.0.

***o*-Benzoquinone.**—This compound was readily prepared and recrystallized by the procedures of Willstätter[2] and Goldschmidt.[4] The product consisted of bright red crystals melting and decomposing between 60–70°.

3-*n*-Pentadecylcatechol Diphenylmethylene Ether.—This compound was synthesized by a general method already described[1]. It crystallized as white prisms from methanol and melted at 42°.

Anal. Calcd. for $C_{34}H_{44}O_2$: C, 84.3; H, 9.16. Found: C, 84.0; H, 9.14.

Spectral curves were determined with a Beckman quartz spectrophotometer. The solvent used was ethanol unless otherwise specified. The quartz cells employed were 10 mm. in thickness.

Results

Fresh solutions of 3-*n*-pentadecylcatechol in ethanol displayed maximum absorption at 277 mμ, log ε = 3.28. On standing for several months absorption became more intense, the spectral curve shifting to slightly shorter wave lengths (Fig. 1). The effect of solvent upon the rate of this process was determined by following simultaneously the absorption spectra of identical concentrations of 3-*n*-pentadecylcatechol in ethanol, acetone and hexane. Over a period of forty-five days at 21–24° the spectral changes took place most markedly in acetone and least markedly in hexane (Table I).

Crude extracts of poison ivy also displayed

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[1] For the previous paper in this series, see Mason, THIS JOURNAL, 69, 2241 (1947).

[2] Willstätter and Pfannenstiel, *Ber.*, 37, 4744 (1905).

[3] Willstätter and Müller, *ibid.*, 41, 2580 (1908).

[4] Goldschmidt and Graef, *ibid.*, 61, 1858 (1928).

TABLE I

SPECTRAL STABILITY OF SOLUTIONS OF 3-*n*-PENTADECYLCATECHOL

Solvent	Concn. mole/liter	Density at 0 days (mμ)	Density at 45 days (mμ)
Ethanol	0.000156	0.300 (277)	0.384 (277)
Acetone[a]	.000156	.303 (277)	.407 (275)
Hexane[b]	.000156	.326 (273)	.372 (272)

[a] Aliquots of the acetone solution were evaporated in vacuum at room temperature. Spectral curves were determined with ethanolic solutions of the residues. [b] Determination upon hexane solution.

maximum absorption at 277 mμ, and underwent optical transformations upon standing (Fig. 2).

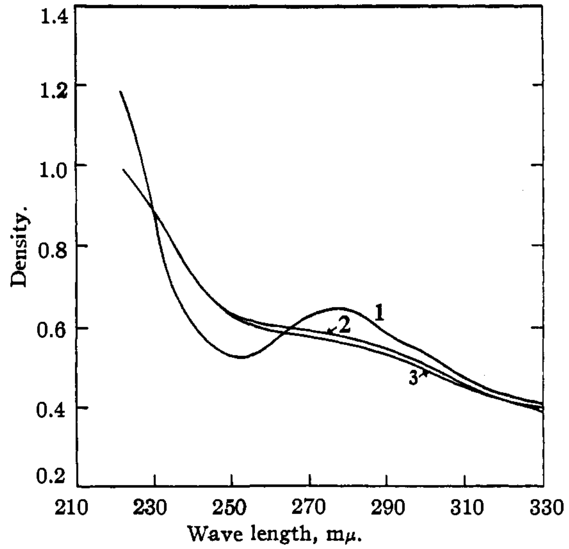

Fig. 2.—Crude poison ivy extract containing 0.0542 mg. of resin per ml. of ethanol at (1) zero days, (2) eighteen days and (3) thirty-two days.

o-Benzoquinone and 3-*n*-pentadecyl-*o*-benzoquinone were unstable in ethanol, chloroform, ether and hexane. The spectral curve of 3-*n*-pentadecyl-*o*-benzoquinone in ethanol (Fig. 3B) developed a maximum at 273 mμ over a period of six days. In hexane solution this substance possessed an initial maximum at 388 mμ, log ε = 3.36 (Fig. 3A). During a period of six days this specific absorption disappeared and only general absorption could be observed. The changing spectral curve of *o*-benzoquinone in ethanol (Fig. 4B) developed a maximum at 282 mμ in twenty-four hours. The chloroform solution displayed an initial maximum at 368 mμ, log ε = 3.23 (Fig. 4A). In three days this shifted to 372 mμ and a new maximum appeared at 273 mμ.

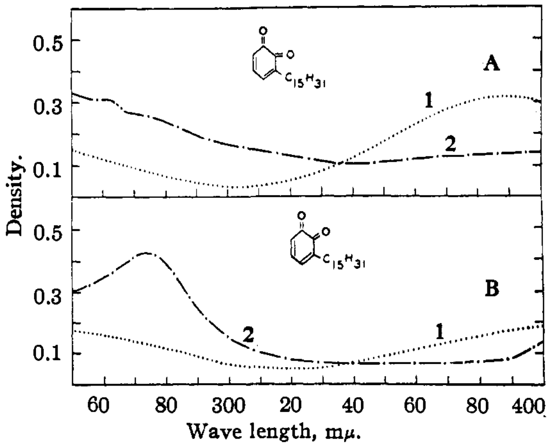

Fig. 3.—A, 3-*n*-pentadecyl-*o*-benzoquinone in hexane, 0.044 mg. per ml. at (1), twenty-five minutes and (2) six days; B, in ethanol, 0.032 mg. per ml. at (1) twenty minutes and (2) six days.

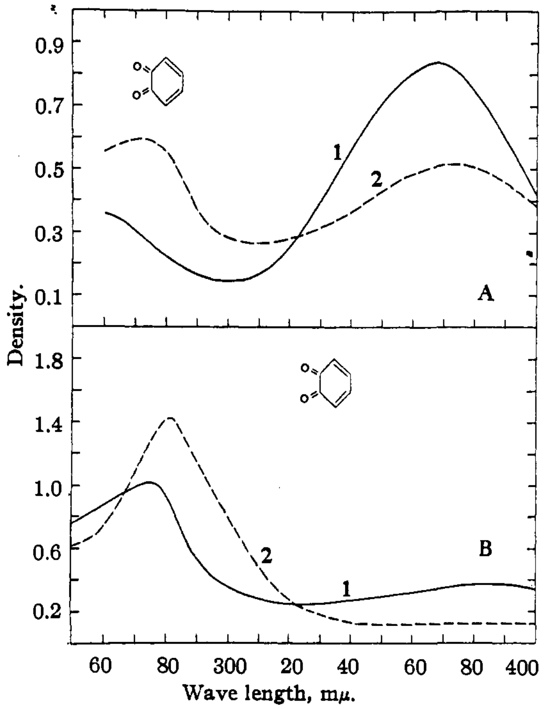

Fig. 4.—A, *o*-benzoquinone in chloroform, 0.053 mg. per ml. at (1) zero days and (2) three days; B, in ethanol, 0.0364 mg. per ml. at (1) twenty minutes and (2) twenty-four hours.

In the following summary of additional spectral curves the principal maxima are given in millimicra and the corresponding log molecular extinction coefficients are enclosed in parentheses.

Catechol	277 (3.36)
3-*n*-Pentadecylcatechol (hexane)	273 (3.32), 280 (3.31)
3-*n*-Propylcatechol	276 (3.35)
4-*t*-Butylcatechol	281 (3.48)
3-Bromocatechol	279.5 (3.41)
Bhilawanol[5]	276.5 (3.32)
Catechol diphenyl	283 (3.68)
methylene ether	279 (3.66), 282 (3.67),
(hexane)	284 (3.70), 290 (3.60)
3-*n*-Pentadecylcatechol diphenylmethylene ether	281 (3.55), 284 (3.55)
3-*n*-Propylcatechol diphenylmethylene ether	281 (3.52)

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(5) Mason, THIS JOURNAL, 67, 418 (1945).

3-Bromocatechol diphenylmethylene ether	287 (3.61)
4-*t*-Butylcatechol diphenylmethylene ether	287 (3.73)
Bhilawanol diphenylmethylene ether[5]	280 (3.60)
2,3-Dimethoxy-*n*-pentadecylbenzene ·	271 (3.18), 277 (3.16)
2,3-Dimethoxy-*n*-pentadecen-1-ylbenzene	271 (3.07), 277 (3.05)

Discussion

Adams and co-workers[6] observed that substitution of alkyl groups in the 4 position of catechol resulted in bathochromic spectral shifts of approximately 5 mμ. This phenomenon has been generalized by Jones[7] as the B-effect, and it has been shown that "the magnitude of the shift depends upon the position of the substituent in the ring system." The absorption spectrum of 4-*t*-butylcatechol, determined in the present study, is consistent with the observation of Adams.[6] However, it has been found that catechol, 3-*n*-propylcatechol, and 3-*n*-pentadecylcatechol display principal absorption (in ethanol) at 277, 276 and 277 mμ, respectively, and that the corresponding diphenylmethylene ethers show principal absorption at 283 281 and 281–284 mμ. The B-effect therefore does not obtain when alkyl groups are attached to the 3 position of catechol.

The increase in intensity of absorption at 277 mμ characteristic of solutions of 3-*n*-pentadecylcatechol and the changes with time in the spectrum of solutions of crude poison ivy extracts limit the applicability of spectrophotometric assay of the poison ivy allergens. However, the results indicate that standard solutions of these allergens are best prepared, from the point of view of chemical stability, in hydrocarbon solvents.

Goldschmidt and Graef[4] have found that, in hexane, *o*-benzoquinone and 4-methyl-*o*-benzoquinone display principal maxima at 363 and 365 mμ, respectively. 3-*n*-Pentadecyl-*o*-benzoquinone shows maximum absorption in the same solvent at 388 mμ. The substitution of an alkyl group in the 3 position of *o*-benzoquinone thus results in a bathochromic shift of unexpected magnitude, suggesting that the α-methylene group may be bonded through hydrogen to the adjacent carbonyl group.[8,9] The major shift of the spectral curves of *o*-benzoquinone and 3-*n*-pentadecyl-*o*-benzoquinone solutions, from initial absorption in the region of 368–388 mμ to final absorption between 273 and 282 mμ indicates that in the solvents investigated benzenoid molecules form from the quinones originally present. In the case of 3-*n*-pentadecyl-*o*-benzoquinone both the position and intensity of the final absorption are consistent with the hypothesis that the changes in the spectrum of aging solutions of 3-*n*-pentadecylcatechol are autoxidative and proceed through the formation of the corresponding *o*-quinone. This in turn is transformed into a benzenoid molecule. In order to characterize this substance attempts at isolation were made using *o*-benzoquinone as a starting material. From ethanolic solutions only catechol and an intractable black polymer were obtained. Upon zinc dust distillation, the polymer yielded biphenyl in small amounts. Some of the absorption in the 273–282 mμ region must therefore be due to the catechols themselves, but no decision with respect to the structures of the remaining solutes can yet be made.

Acknowledgments.—I wish to acknowledge the assistance of Mrs. Dorothy Peterson of the Industrial Hygiene Laboratory, National Institute of Health, in the determination of some of the spectral curves. I am indebted to Mr. Charles A. Kinser for the microchemical analyses.

Summary

1. The spectral curves of 3-*n*-pentadecylcatechol, related substituted catechols, catechol derivatives and *o*-quinones, have been determined.

2. The effects upon absorption spectra of changes in structure and autoxidation of the catechols, and of instability of quinonoid solutes, were observed.

3. The syntheses of 3-*n*-pentadecyl-*o*-benzoquinone and 3-*n*-pentadecylcatechol diphenylmethylene ether are reported.

BETHESDA, MARYLAND RECEIVED JUNE 28, 1947

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(6) Adams, Cain and Wolff, THIS JOURNAL, **62**, 732 (1940).

(7) Jones, *ibid.*, **67**, 2127 (1945).

(8) Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

(9) *Cf.* Marvel, Copley and co-workers, *e. g.*, THIS JOURNAL, **62**, 3109 (1940).