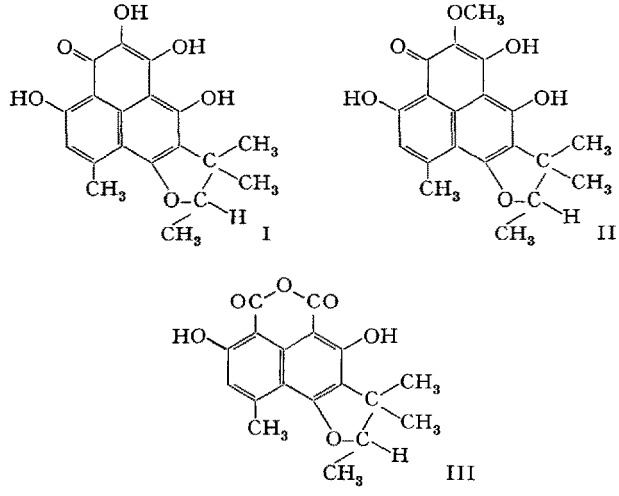
Photolytic Decomposition of Perinaphthenone Derivatives

During studies on the separation by thin-layer chromatography of the perinaphthenone pigments produced in cultures of *Penicillium herquei*[1] it was observed that solutions of atrovenetin (I), after storage, gave an additional zone which was attributed to the naphthalic anhydride (III), formed by slow photochemical decomposition of the pigment. This reaction has been investigated in greater detail using both atrovenetin and deoxyherqueinone[2] (II) and the identity of the product conclusively established.



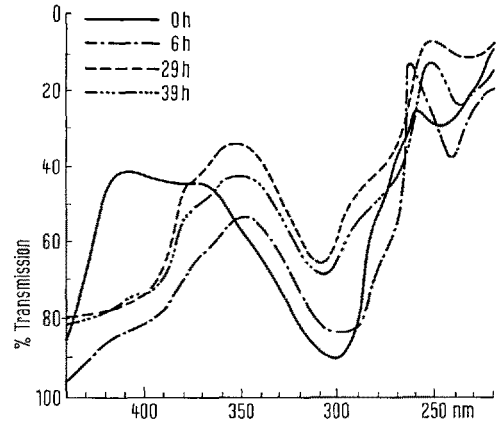
Quartz cuvettes containing 4 mg/ml of atrovenetin or deoxyherqueinone in methanol benzene or dioxane were irradiated in air with light from a 350 W mercury arc lamp. Changes in the solutions were followed at intervals by examining the absorption spectra, antibacterial activity[3] and behaviour when chromatographed on thin-layer plates of polyamide irrigated with chloroform-methanol-water (5:15:1). Within 3 h the solutions had changed in colour from yellow to green; samples taken at 4 h showed a second zone (yellow changing slowly to green) at Rf 0.60 on thin-layer chromatography, and at 30 h an intense blue fluorescent zone, Rf 0.56 was first observed. With increasing time of exposure the antibacterial activity of the solutions decreased steadily and at 36 h could no longer be detected. Concomittant changes also occurred in the absorption spectra (Figure). On prolonged exposure the green colour of the solutions was discharged and colourless crystals could be seen in cuvettes which had contained deoxyherqueinone. Irradiation was discontinued at approximately 72 h when no further changes occurred in either the absorption spectrum or the behaviour of the reaction mixture on thin-layer chromatograms.

While the nature of the solvent used appeared to have little effect on the course of the reaction, the rate was fastest in dioxane. Addition of benzophenone, acetophenone or eosin in small amounts as sensitizers did not noticeably alter the rate. The reaction products were separated by chromatography on columns of silica gel. Benzene eluted an intense blue-fluorescent zone from irradiated solutions of both atrovenetin and deoxyherqueinone. In each instance these zones yielded a substance crystallizing from benzene as colourless needles m.p. 251–252°. (Found: C, 66.16; H, 4.68%. $C_{17}H_{16}O_6$ requires C, 65.85; H, 4.89%).

This was indistinguishable (m.p., mixed m.p., UV- and IR-spectra) from the naphthalic anhydride (III) obtained by oxidation of atrovenetin[4] and subsequently isolated from cultures of *P. herquei*[5].

From the irradiation of atrovenetin a number of minor fractions were obtained (Table). The characterization of these products was rendered difficult because of their photosensitivity. When irradiation of deoxyherqueinone was interrupted after several hours in an attempt to isolate intermediates, an amorphous deep-green coloured substance could be separated by column chromatography. This material had the same Rf value as deoxyherqueinone upon thin-layer chromatography (Table) and on further irradiation yielded the naphthalic anhydride (III). Attempts to fractionate the material on long columns of silica gel gave zones varying in colour from deep-green to blue. When these were eluted and the solutions evaporated, the products obtained were found to have IR-spectra indistinguishable from that of deoxyherqueinone. It appears likely that the highly coloured intermediates are present in trace amounts only and are superimposed during column chromatography on a streaked zone of deoxyherqueinone.

The effect of variations in the perinaphthenone structure on the reaction was investigated. All of the substances tabulated in the Table were decomposed photolytically under the conditions used for atrovenetin and deoxyherqueinone (irradiation in dioxane solution with light from a mercury arc lamp). The course of the reaction was followed by periodic examination of the absorption spectra and thin-layer chromatographic properties of the reaction mixtures. When none of the starting material remained the reaction mixture was fractionated by chromatography on columns of silica gel eluted successively with petroleum ether, benzene and chloroform, or where only small quantities of reactants were available, by preparative thin-layer chromatography. The Rf values and some spectral characteristics of the principal products detected in each reaction are recorded in the Table. In



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Thin-layer chromatographic behaviour and spectral properties of some perinaphthenones and products obtained after irradiation

Compound irradiated	Product		
	Rf	$\lambda\lambda_{max}$ (nm)	ν_{max} (1600–1800 cm^{-1})
Perinaphthenone Rf 0.26[a], $\lambda\lambda_{max}$ 385, 360, 315, 255, 248; $\lambda\lambda_{min}$ 372, 325, 275, 230 nm; ν_{max} 1650, 1630, 1600 cm^{-1}	0.10[a]	380 (infl.) 360, 320 (infl.) 250, (λ_{min} 280)	1770, 1740, 1650, 1620
2-Hydroxyperinaphthenone Rf 0.61; $\lambda\lambda_{max}$ 420, 365, 330, 315, 230; $\lambda\lambda_{min}$ 385, 355, 300 nm; ν_{max} 1620 cm^{-1}	–	328, 300, 230 ($\lambda\lambda_{min}$ 322, 270)	1760–1740 (broad)
6-Hydroxyperinaphthenone Rf 0.63; $\lambda\lambda_{max}$ 450, 355, 312, 262, 235; $\lambda\lambda_{min}$ 368, 330, 242, 225 nm; ν_{max} 1640 cm^{-1}	0.76	380, 325	1740, 1640
2,4-Dihydroxyperinaphthenone Rf 0.37; $\lambda\lambda_{max}$ 440, 328, 315, 275, 268; $\lambda\lambda_{min}$ 390, 345, 295, 235 nm, ν_{max} 1645, 1615 cm^{-1}	0.64	355, 310, 280 ($\lambda\lambda_{min}$ 325, 288, 275)	1720 (broad), 1640, 1600
Xanthoherquein $\lambda\lambda_{max}$ 390, 280 (infl.) 218; $\lambda\lambda_{min}$ 305 nm; ν_{max} 1640 cm^{-1}	–	240	1730, 1640
Atrovenetin Rf 0.00; $\lambda\lambda_{max}$ 425, 380, 280 (infl.) 260; $\lambda\lambda_{min}$ 405, 310 nm; ν_{max} 1620, 1580 cm^{-1}	0.45	355, 290, 220 ($\lambda\lambda_{min}$ 325, 265)	1750, 1620
	0.56	375 (infl.) 355, 295 (infl.) 255 ($\lambda\lambda_{min}$ 325, 265)	1722, 1678, 1635, 1622
	0.56	340, 258, 220 ($\lambda\lambda_{min}$ 290, 238)	1650, 1620
	0.01	340, 260 ($\lambda\lambda_{min}$ 290, 238)	1640, 1620
Atrovenetin triacetate	–	370, 336, 255	1790, 1750, 1680
Deoxyherqueinone Rf 0.04; $\lambda\lambda_{max}$ 415, 370 (infl.) 280 (infl.) 265 (infl.); λ_{min} 300 nm; ν_{max} 1618, 1605 cm^{-1}	0.56	375 (infl.), 355, 295 (infl.) 255 ($\lambda\lambda_{min}$ 310, 237)	1722, 1678, 1637, 1622
Atrovenetin-9-methyl ether Rf 0.68; $\lambda\lambda_{max}$ 405 (infl.) 390, 370 (infl.) 280 (infl.) 263; $\lambda\lambda_{min}$ 305 nm; ν_{max} 1650, 1600 cm^{-1}	0.60	385, 367, 350, 297, 255 ($\lambda\lambda_{min}$ 378, 360, 310, 288, 235)	1760, 1658, 1630, 1600
Deoxyherqueinone monomethyl ether Rf 0.68; $\lambda\lambda_{max}$ 415, 275 (infl.); $\lambda\lambda_{min}$ 390, 300 nm	0.60	410 (infl.), 380, 340 (infl.) 255 ($\lambda\lambda_{min}$ 310, 240)	1765, 1720, 1675, 1630
	0.79	–	1620
Haemocorin[6] Rf 1.0; $\lambda\lambda_{max}$ 445, 370, 355, 278, 225	0.24	375, 340, 255 (infl.)	1735, 1650, 1600

[a] Rf value on thin-layer chromatography using silica gel with benzene as solvent. All other Rf values were measured using polyamide and the solvent mixture: chloroform-methanol-water (5:15:1).

each instance an intensely fluorescent product which, from its characteristic UV- and IR-absorption maxima, is believed to be the appropriate naphthalic anhydride, was produced.

It is evident that hydroxyl substituents are not required for photolytic decomposition of the perinaphthenone system. 3-Hydroxyperinaphthenone did not react but 2, 3-dihydroxy derivatives such as xanthoherquein and atrovenetin were oxidized. Methylation of this system, as in atrovenetin trimethyl ether[5] prevented the reaction. Atrovenetin triacetate, on the other hand, was decomposed to a product which corresponded in properties with a naphthalic anhydride monoacetate (cf. the corresponding diacetate described by BARTON et al.[4]). Deacetylation of this substance with alcoholic hydrochloric acid gave the expected naphthalic anhydride (III)[7].

Zusammenfassung. Atrovenetin und Desoxyherqueinon liefern beim photolytischen Abbau dasselbe Naphtalsäureanhydrid. Es handelt sich um eine allgemeine Reaktionsweise der Perinaphthenone. Atrovenetintrimethyläther zeigt diese Reaktion nicht, das Triacetat liefert Naphtalsäureanhydrid-monoacetat.

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[7] Acknowledgment. Our thanks are due to Prof. R. G. COOKE of the University of Melbourne for supplying samples of natural haemocorin, the 6-hydroxy- and 2,4-dihydroxy derivatives of perinaphthenone.