Table I. Absorption of Immunoprecipitable ^{131}I *via* Portal Vein and Lymphatics after Intraintestinal Administration of ^{131}I-EWL 2 mg/kg in Rats

Absorption	EWL eq μg	% of dose
Amount *via* portal vein (A)	10.61±2.40	1.99±0.41
Amount *via* lymphatics (B)	0.37±0.18	0.07±0.04
Amount *via* both routes (A+B)	10.98±2.45	2.06±0.43
Percentage of lymphatics [100×(B)/(A+B)]	3.24±1.69	

Each value is represented as mean with S.E. of 4 experiments.

Table I indicates that the main route in intestinal absorption of ^{131}I–EWL is the portal vein, not lymphatics. This result seems to be in accordance with the results of heparin[1d] and insulin.[1e] However, as compared with the result that 36% of the total amount of elastase absorbed was *via* lymphatics,[1c] the percentage of lymphatics absorption of ^{131}I–EWL is extremely small. Thus, further studies on the relationship between the physicochemical properties of macromolecules and the absorption rate *via* lymphatics will be necessary. In addition, whether or not the immunoprecipitable and protein-bound ^{131}I in serum and lymph originates from intact ^{131}I–EWL administered remains to be investigated.

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Department of Drug Metabolism,
Section of Experimental
Therapeutics Research,
Research & Development Division,
Eisai Co., Ltd.,
4-6-10 Koishikawa Bunkyo-ku Tokyo

Teruaki Yuzuriha
Kouichi Katayama
Takeshi Fujita

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Wave Length Dependent Photolysis of Phenanthrene Oxide

Though the chemistry of monocyclic arene oxides has been investigated,[1] studies on polycyclic arene oxides are very poor.[2] The evidece, however, is growing that arene oxides are the active carcinogens formed from polycyclic aromatic hydrocarbons.[3] The stereochemistry of polycyclic arene oxides is dreamy: the epoxide ring is nearly perpendicular to the aromatic ring(s) from investigation by a Dreiding Model. This may cause an extensive conjugation between the pi-bonds and the C–O sigma-bonds.[4] These situations prompted us to investigate the chemical behaviour of compounds of this kind. In this communication

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[1] J.W. Daly, D.M. Jerina and B. Witkop, *Experientia*, **15**, 1129 (1972).

[2] D.M. Jerina and D.R. Boyd, *Tetrahedron letters*, **1970**, 457; M.S. Newman and S. Blum, *J. Am. Chem. Soc.*, **86**, 5559 (1964).

[3] for example, J.K. Selkirk, H. Huberman and C. Heiderberger, *Biochem. Biophys. Res. Commun.*, **43**, 1010 (1971).

[4] T.G. Traylor, W. Hanstein, H.J. Berwin, N.A. Clinton and R.S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971).

we wish to report that an interesting wave length dependent photochemistry of 9,10-dihydro-9,10-epoxyphenanthrene (**1**).2)

Irradiation of the epoxide (**1**) in methylene chloride with a high pressure mercury lamp or a monochrometer5) (300—350 nm) gave 9-phenanthrol (**2**, 50%),6) phenanthrene (**3**, 11%) and an oxepine (**4**, 0.5%, *vide infra.*) The very similar reaction as above was observed by irradiation of very short wave ultraviolet (UV) light. Irradiation of **1** in methylene chloride by the monochrometer (207—235 nm) gave 9-phenanthrol (**2**, 56%), phenanthrene (**3**, 0.2%), the oxepine (**4**, 3%) and fluorene (**5**, 0.2%).

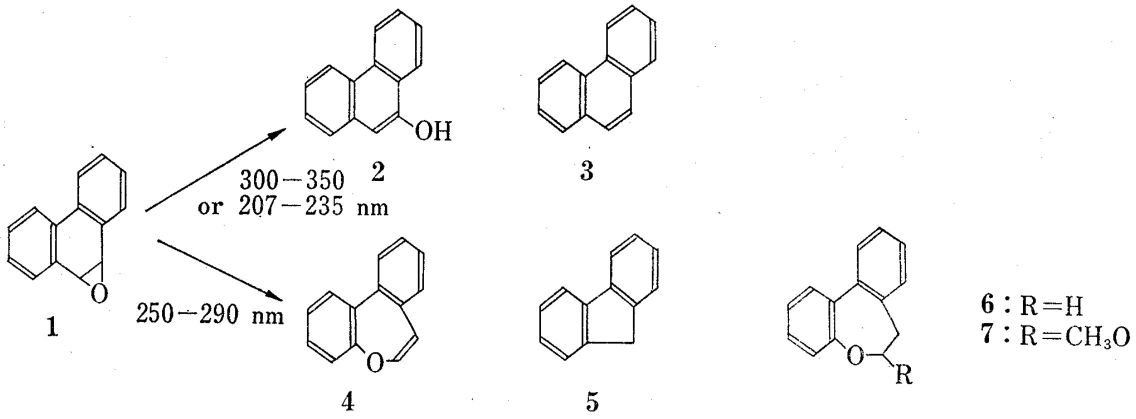

Fig. 1

TABLE I. Wave Length Dependence of Products

Wave length nm	2	3	4	5%
300—350	50	11	0.5	0
250—290	8	0	20—30	3
207—235	56	0.2	3	0.2

On the other hand, irradiation of **1** in methylene chloride with a low pressure mercury lamp gave dibenzo[*b*,*d*]oxepine (**4**, 20—30%) as the major monomeric product, which was reported7) after the completion of the present result, 9-phenanthrol (**3**, 8%), fluorene (**5**, 3%), and a dimer (about 25%), but no phenanthrene was observed. The compound **4** was isolated by a silica gel column chromatography, and easily crystallised from methanol to give prisms, mp 47—47.5°, UV λ_{max}^{EtOH} nm (ε): 237 (37700), 274—276 (5700). The nuclear magnetic resonance (NMR) spectra of **4** (in $CDCl_3$, $\delta=5.98$ ($J=6$), $\delta=6.85$ ($J=6$) for the olefinic hydrogens) and of a hydrogenation product, **6**, mp 114—115°, (in $CDCl_3$, two triplets at $\delta=4.59$ and at $\delta=2.82$, $J=6.5$) support the structure **4**. Such a localized double bond of **4** has been expected by a molecular orbital calculation for the compound.8) The oxepine could be isolated by the photolysis in benzene or *n*-hexane, but in methanol a hemiacetal methyl ether (**7**) was formed in 40% yield, instead. The methyl ether was purified by a column chromatography and a

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5) Concave Radiating Monochrometer, JASCO-CRM-FA.

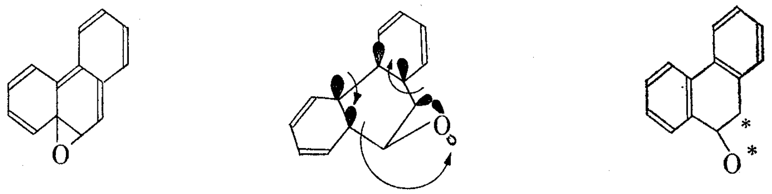
6) All the new compounds were analised and their molecular weight were determined by a mass spectrometer. Yields are dependent on concentration and reaction time. Yields shown were determined by gas chromatography after disappearance of the starting epoxide on thin-layer chromatography (0.1% solution.) **1** is thermally stable under the TLC conditions.

7) N.E. Breghtwell and G.W. Griffin, *Chem. Commun.*, **1973**, 37.

8) M.J.S. Dewar, *Tetrahedron*, **26**, 4269 (1970).

molecular distillation (120° (bath)/0.1 mmHg), mp 54—55°, NMR ($CDCl_3$) δ: 5.30 (1H, q, $J=8$ and 5.5), 3.62 (OCH_3), and 2.80 (2H, $J_{AB}=14$, $J_{AX}=8$, $J_{BX}=5.5$).

These experiments which were summarised in the Table demonstrates that the epoxide (**1**) does undergo photochemical rearrangements in three different modes according as the three regions of irradiated wave length. Two different excitations give the same major product, 9-phenanthrol, and the other excitation gives other products in a completely different way.



8 9 10

Fig. 2

The formation of the oxepine is reasonably explained by an electrocyclic ring opening of a rearranged epoxide (**8**),⁹⁾ which is a thermal reaction and gains a big aromatic stability. Two routes to the intervening epoxide (**8**) are possible as discussed by Griffin⁷⁾. If the rearrangement is concerted, a [1,5]sigmatropic reaction with inversion of the reaction center (oxygen) (see Fig. 2, **9**) is photochemically allowed. It is possible to speculate a nonconcerted process involving the photochemical cleavage of the C–O bond which gives a diradical or a dipole (**10**, * shows an unpaired electron or a charge.) They may attack the aromatic ring thermally to form the epoxide (**8**), though such a process sacrifies two aromatic rings. Among these two mechanisms leading to the epoxide (**8**), the concerted mechanism looks more attractive because the overlap shown in **9** is favorable by the σ-π conjugation,⁴⁾ and in turn the photochemical rearrangement to 9-phenanthrol seems to involve the cleavage of the C–O bond (*via* **10**). The formation of fluorene is compaired with the photolysis of steroidal epoxyketones,¹⁰⁾ and that of phenanthrene could be discussed in connection with the interesting fate of oxygen atom.¹¹⁾

Faculty of pharmaceutical Sciences
University of Tokyo
Hongo, Bunkyo-ku, Tokyo

Koichi Shudo
Toshihiko Okamoto

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9) E. Vogel and H. Gunster, *Angew. Chem.*, **79**, 684 (1967).

10) D. Bauer, T. Iizuka, K. Shaffner and O. Jeger, *Helv. Chim.*, **55**, 852 (1972).

11) Methylene instead of oxygen atom, see, D.B. Richardson, L.R. Durett, J.M. Martin, W.E. Putnum, S.C. Slaymaker and I. Davoretdky, *J. Am. Chem. Soc.*, **87**, 2763 (1965).