

Yb(1) — NH <sub>2</sub> :	2 NH <sub>2</sub> (1): 2,43	2 NH <sub>2</sub> (3): 2,43	2 NH <sub>2</sub> (4): 2,28	(3)
Yb(2) — NH <sub>2</sub> :	2 NH <sub>2</sub> (1): 2,37	2 NH <sub>2</sub> (2): 2,28	2 NH <sub>2</sub> (3): 2,44	(3)
Na(1) — NH <sub>2</sub> :	2 NH <sub>2</sub> (2): 2,57	2 NH <sub>2</sub> (3): 2,96	2 NH <sub>2</sub> (4): 2,56	(5)
Na(2) — NH <sub>2</sub> :	2 NH <sub>2</sub> (2): 2,52	2 NH <sub>2</sub> (3): 2,80	2 NH <sub>2</sub> (4): 2,52	(5)

Tab. 2. Yb- und Na—NH<sub>2</sub>-Abstände (in Å).

Im Gitter des Na[Yb(NH<sub>2</sub>)<sub>4</sub>] läßt sich die Amidionenordnung von einer kubisch dichten Packung durch starke Deformation ableiten; in Richtung [210] ergibt sich die Schichtenfolge ABC.

Die Yb- und Na—NH<sub>2</sub>-Abstände (in Å) sind in Tab. 2 angegeben. Ytterbium befindet sich in schwach deformierten Oktaederlücken. Die Na<sup>+</sup>-Ionen sind in sehr stark deformierten Oktaederlücken; eine der Oktaederkanten ist so weit entfernt, daß man besser von einer stark deformierten Tetraederlücke spricht.

In den Amidionen-Ebenen senkrecht [100] liegt jeweils in  $\sim n/8$  mit  $n=0$  bis 8 folgende Kationenverteilung vor: leer, 1 Yb + 2 Na, 2 Yb, 1 Yb + 2 Na, leer, 1 Yb + 2 Na, 2 Yb, 1 Yb + 2 Na, leer. Die kürzesten Yb—Yb-Abstände (3,70 Å) sind zwischen den mit Ytterbium besetzten, benachbarten Schichten; über nicht

besetzte Schichten hinweg betragen sie 6,27 Å. In dem Na[Yb(NH<sub>2</sub>)<sub>4</sub>] erkennt man demnach einen Übergang zur Schichtung, während beim Na<sub>3</sub>[Y(NH<sub>2</sub>)<sub>6</sub>] eine weitgehend gleichmäßige Verteilung der Kationen vorliegt.

An der Struktur des Na[Yb(NH<sub>2</sub>)<sub>4</sub>] werden noch weitere Rechnungen durchgeführt. Insgesamt liegen über 4000 Meßdaten vor. Hiermit soll versucht werden, die Temperaturfaktoren anisotrop zu verfeinern und eventuell den Wasserstoff am Amidion zu lokalisieren.

Die Strukturberechnungen wurden im Rechenzentrum der Universität Kiel durchgeführt. Der Deutschen Forschungsgemeinschaft danken wir für die großzügige Förderung dieser Untersuchung.

### Effect of Adenosine-(3',5')-monophosphate on the Inhibition of Dark Repair by Caffeine

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(Z. Naturforsch. 26 b, 166—167 [1971]; eingegangen am 10. Oktober 1970,  
revidiert am 7. Dezember 1970)

Photochemical lesions in DNA, produced on irradiation of bacterial cells with u.v. light<sup>1</sup>, can be repaired by two processes, photoreactivation and dark reactivation. The dark reactivation includes excision repair and recombination repair. The excision repair part of the dark reactivation is known to be inhibited by caffeine<sup>2-4</sup>.

The dark reactivation enables one to explain the molecular basis of the so-called excision repair systems<sup>5,6</sup>, by which the pyrimidine dimers as such and also the neighbouring nucleotides in the DNA are enzymatically removed. The points of attack here are the phosphodiester bonds in the DNA. It is known that in the mammalian system caffeine inhibits phosphodiesterase<sup>7</sup>, which hydrolyses adenosine-(3',5')-monophosphate (cAMP) to AMP. This tempted us to

examine the role of cAMP in the inhibition by caffeine of the dark-recovery phenomenon of u.v.-irradiated *E. coli* 15T<sup>-</sup>.

### Experimental

Adenosine-(3',5')-monophosphate was purchased from Boehringer Mannheim GmbH. Other chemicals used in this work were of reagent grade and were obtained from Merck, or from Difco Laboratories, Detroit (Michigan), USA. *E. coli* 15T<sup>-</sup>, from the collection of this institute, was maintained on Bacto-agar (2.5%) containing 0.5% NaCl and 1.5% nutrient broth, as well as on glucose-salts synthetic medium supplemented with thymine for smooth colony growth.

*E. coli* 15T<sup>-</sup> was grown at 37°C for 20 hrs in steam sterilised glucose-salts medium containing 2 µg/ml of thymine. At appropriate times cells were spun down at 4°C and suspended in 0.14% saline at 10<sup>7</sup> cells/ml. 5 ml of this suspension were irradiated with a Hanau UV lamp (Quarzlampen Gesellschaft, Hanau, Type NN 30/89, main output at 253.7 nm). After irradiation suitable aliquots were diluted with saline after each u.v. dose and plated on Bacto-agar. Caffeine (100 µg/ml) was incorporated in Bacto agar (2.0%) containing 0.5% NaCl and 0.8% nutrient broth, and 100 µg/ml of cAMP was instilled just before plating the irradiated

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<sup>1</sup> A. WACKER, Progr. in nucleic acid research **1**, 369 [1963].

<sup>2</sup> E. M. WITKIN, X. Int. Cong. Genetics **I**, 280 [1958].

<sup>3</sup> E. M. WITKIN and E. L. FARQUHARSON, Mutation as a cellular process, P. 36, J. & A. Churchill Ltd., London 1969.

<sup>4</sup> M. LIEB, Z. Vererbungslehre **92**, 416 [1961].

<sup>5</sup> R. B. SETLOW and W. L. CARRIER, Proc. nat. Acad. Sci. USA **51**, 226 [1964].

<sup>6</sup> R. P. BOYCE and P. HOWARD-FLANDERS, Proc. nat. Acad. Sci. USA **51**, 293 [1964].

<sup>7</sup> G. A. ROBINSON, R. W. BUTCHER, and E. W. SUTHERLAND, Ann. Rev. Biochemistry **37**, 149 [1968].

suspension. After incubation at 37 °C overnight, cell counts were made to calculate the percentage survivors as shown in the Figure.

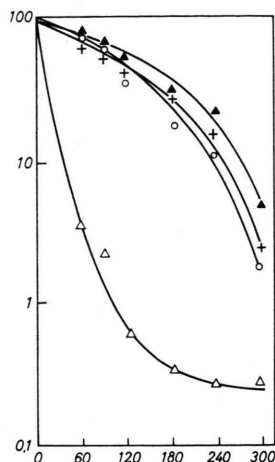


Fig. 1. Dark repair of u.v.-inactivated *E. coli* 15T<sup>-</sup> in the presence of caffeine and cAMP. Survival of *E. coli* 15T<sup>-</sup> in the presence of caffeine ( $\Delta$ - $\Delta$ ), cAMP (o-o), caffeine and cAMP ( $\blacktriangle$ - $\blacktriangle$ ) and the control (+-+). Ordinate: Percent survival; Abscissa: UV-dose (ergs/mm<sup>2</sup>).

As shown in the Fig. 1, caffeine strongly inhibits the excision repair part of the dark reactivation in *E. coli* 15T<sup>-</sup> at the u.v. doses used. This inhibition can be reversed by cAMP. It is to be noted that in the presence of cAMP alone, the dark-reactivation directs no significant influence in the survival rates.

Recently it was reported that, in vivo<sup>8</sup> as well as in vitro<sup>9</sup>, caffeine depresses the excision of pyrimidine dimers, presumably by binding to the excision enzyme involved in dark repair. The reversal with cAMP of the inhibition by caffeine in our experiments indicates that both compounds compete with the phosphodiesterase-like enzymes necessary for the removal of u.v. photo-products, whereby cAMP binds to the enzyme with a greater affinity than caffeine.

<sup>8</sup> A. S. SIDEROPOULOS and D. M. SHANKEL, *J. Bacteriol.* **96**, 198 [1968].

<sup>9</sup> K. SHIMADA and Y. TAKAGI, *Biochim. biophysica Acta* [Amsterdam] **145**, 763 [1968].

### Photochemistry and Photobiology of 5-Ethyl- and 5-Propyldeoxyuridine

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(*Z. Naturforsch.* **26 b**, 167-168 [1971]; eingegangen am 22. Oktober 1970)

Thymine-, 5-ethyluracil- and 5-propyluracildeoxyriboside, irradiated with ultraviolet light (254 m $\mu$ ) in a frozen aqueous solution undergo a photochemical

change which can be followed by extinction measurements at 266 m $\mu$  (Table 1). As follows from these results the absorption of thymine-deoxyriboside as well as that of 5-ethyluracildeoxyriboside increases on re-irradiation (254 m $\mu$ ) in water, showing that dimerization<sup>1</sup> has taken place. However, the magnitudes of their dimerization are different. For example, at the same ultraviolet-light dose, the dimerization of thymine-deoxyriboside goes to an extent of 30% (80-50) while that of 5-ethyluracildeoxyriboside to to 6% (77-71) only. The inability of 5-propyluracildeoxyriboside to dimerize shows that it reacts in a different manner which still remains to be studied.

Compound	Test solution before irradiation	Absorption at 266 m $\mu$ in per cent				
		After irradiation in ice	After reirradiation in water			
UV Dose [ergs/mm <sup>2</sup> · 10 <sup>-5</sup> ]	—	2	0.2	0.4	1.2	2.4
Thymine-deoxyriboside	100	50	60	66	73	80
5-Ethyluracildeoxyriboside	100	71	76	77	76	60
5-n-Propyluracildeoxyriboside	100	73	73	72	64	49

Table 1. Relative change in absorption of thymine-, 5-ethyluracil- and 5-propyluracil-deoxyriboside after irradiation with ultraviolet light (254 m $\mu$ ). Lamp: Low-pressure mercury lamp, NN 30/89 Quarzlampengesellschaft Hanau, Germany. Concentration: 10<sup>-4</sup> M. Synthesis: 5-ethyluracil- and 5-propyluracil-deoxyriboside were synthesized by the method described by HOFFER et al.<sup>8</sup>

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<sup>1</sup> R. BEUKERS and W. BERENDS, *Biochim. biophysica Acta* [Amsterdam] **41**, 550 [1960].