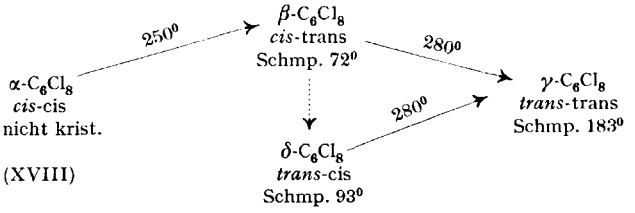
folgende weitere Befunde nahegelegt: α-, β- und δ-C_6Cl_8 werden durch verschiedene Agenzien (Cl_2, Br_2, HNO_3) in das am höchsten schmelzende und am schwersten lösliche γ-Isomere übergeführt. Die Umlagerung ist auch durch Erhitzen allein möglich. Bei etwa 250° wandelt sich α- zunächst in β-C_6Cl_8 um, das dann gleichzeitig mit dem δ-Isomeren bei etwa 280° quantitativ in die γ-Form übergeht.

Diesen Beobachtungen wird die zunächst hypothetische Zuordnung der Isomeren nach Schema XVIII am besten gerecht.



(XVIII)

Alle bisherigen Versuche machen die Existenz atropisomerer Polychlorpolyene höchst wahrscheinlich[1]; ein schlüssiger Beweis für eine Atropisomerie kann aber nur mit physikalischen Prüfmethoden (UV-Absorption, Raman-Spektren, Dipolmomente usw.) erbracht werden.

Diesbezügliche Untersuchungen an den C_6Cl_8-Körpern sind in die Wege geleitet worden.

A. ROEDIG

Chemisches Institut der Universität Würzburg, den 27. März 1948.

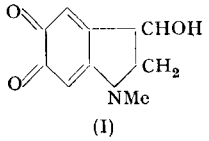
Summary

The synthesis of some unsaturated polychloro compounds, starting from the heptachloropropanes, octachloropropane and hexachloropropane, by means of aluminium in ether is described. For four compounds C_6Cl_8, subject to some conversions, the structure of octachlorohexatriene-(1, 3, 5) has been made probable, and the possibility of a special stereoisomerism is discussed.

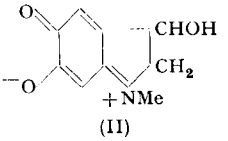
[1] Bei dem kürzlich von H. GERDING und G. W. A. RIJNDERS (Rec. Trav. chim. Pays-Bas *66*, 225 [1947]) ramanspektroskopisch untersuchten Oktachlorpentadien-(1,3) ist trotz behinderter Rotation um die C_2–C_3-Einfachbindung eine Atropisomerie sterisch unmöglich.

The Structure of Adrenochrome and its Reduction Products

Adrenochrome, the red pigment obtained by the oxidation of adrenalin[1], has generally been formulated as the o-quinone (I). It can also, however be formulated as a zwitterion p-quinoneimine (II), this structure differing from (I) only in electron distribution. It seems probable that this zwitterion mesomeric structure does in fact make a large contribution to the resonance hybrid on the basis of the following observations.



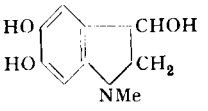
(I)



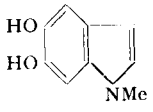
(II)

Adrenochrome is very soluble in water, fairly soluble in alcohol but almost insoluble in benzene and ether: behaviour analogous to that of the aliphatic aminoacids and strongly indicative of a zwitterion structure. It has already been observed that adrenochrome readily formes a monoxime[1] and a mono-semicarbazone. All attempts by the present author to induce reaction with a second molecule of hydroxylamine or semicarbazide have proved unsuccessful, indicating that the molecule probably contains only one true carbonyl group. In general, o-quinones react cleanly with o-phenylenediamine to give phenazine derivatives. Adrenochrome reacts with o-phenylenediamine, but under a wide variety of conditions only ill-defined amorphous products could be obtained and there was no indication of the formation of a phenazine. Adrenochrome is much more intensely coloured than either o-quinone or a quinoneimine salt; however an intensification of absorbtion would be expected in a molecule which was a resonance hybrid of both these structural types.

The reduction of adrenochrome is of particular interest, and moreover, can only be interpreted satisfactorarily on the basis of structure (II). Hitherto it has been supposed that on reduction a leuco-compound (III), re-oxidizable to adrenochrome, is obtained[2]: though this leuco-compound has in fact never been isolated.

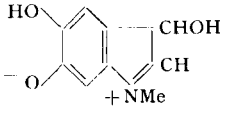


(III)

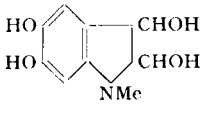


(IV)

It has now been found that reduction with hydrogen – Pd charcoal in aqueous solution at room temperature and atmospheric pressure presents some rather unusual features and does not give rise to (III). Hydrogen absorption ceases when only *one* atom of hydrogen per mol. of adrenochrome has been absorbed, and two products are obtained in approximately equal amounts. One of these is 5:6-dihydroxy-N-methylindole (IV), which can easily be extracted with ether, and crystallizes from light petroleum in colourless needles, m.p. 135–136°. On acetylation it yields the diacetyl derivative m.p. 101° already described[3]. The other product which is not extracted by ether is the zwitterion (V).



(V)



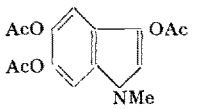
(VI)

This could not be isolated as such owing to the ease with which its solution decomposed on concentration, but on treatment with alkali 2:3:5:6-tetrahydroxy-N-methyldihydroindole (VI) was readily obtained, the change being analogous to the formation of a pseudobase from a quarternary salt. (VI) forms yellow prisms m.p. 228° dec., very sparingly soluble in water giving yellow solution with a strong green fluorescence, particularly marked in ultra-violet light. Acetylation with acetic anhydride-pyridine gave a dehydration product, 3:5:6-triacetoxy-N-methyl indole (VII), m.p. 111°. It was found by GADDUM and SCHILD[4] that dilute alkaline solutions of adrenalin absorb oxygen from the air with the development of a green fluorescence and it is suggested that this phenomenon is due to the formation of (VI) by a similar series of reactions. In any case the contention of UTEVSKY[5] that the fluorescence

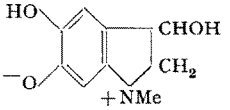
[1] D. E. GREEN and D. RICHTER, Biochem. J. *31*, 596 (1937).

[1] D. E. GREEN and D. RICHTER, Biochem. J. *31*, 596 (1937).
[2] Cf. G. B. WEST, Brit. J. Pharm. Chemotherapy *2*, 121 (1947).
[3] F. BERGEL and A. L. MORRISON, J. Chem. Soc. London, 48 (1943).
[4] J. H. GADDUM and H. SCHILD, J. Physiol. *80*, 9 P (1934).
[5] UTEVSKY, Advances Med. Biol. *18*, 45 (1944).

is due to the formation of (III) seems untenable in the light of the present work.



(VII)



(VIII)

It will be observed that (IV) is a dehydration product of the fully reduced compound (III) and that (V) is isomeric with adrenochrome. As these two products are formed in equal amounts, it is very probable that they arise from a common intermediate by disproportionation: this intermediate can only be the semi-quinone zwitterion (VIII), derived from (II) by the addition of one atom of hydrogen. Evidently the semiquinone disproportionates irreversibly into (IV) and (V) more readly than it can accept another hydrogen atom, so that hydrogen uptake stops at this stage. Exactly similar results were obtained when sodium hydrosulphite was employed as the reducing agent.

Neither (IV) nor (V) can be reconverted to adrenochrome and the reduction under these conditions is thus strictly irreversible. Yet it has been shown[1] that adrenochrome can act as a reversible hydrogen accepter in the aerobic lactic and malic dehydrogenase systems. The present work indicates that (II) and (III) cannot form a redox system owing to the fact the latter immediately undergoes dehydration irreversibly. The most probable alternative interpretation is that the redox system involves *one*-electron transfer between adrenochrome and the semi-quinone: a similar one-electron transfer mechanism for other dehydrogenase systems has been proposed[2].

Fuller details of this work will be published elsewhere.

J. HARLEY-MASON

University Chemical Laboratory, Cambridge, February 10, 1948.

Zusammenfassung

Für das Adrenochrom wird, gestützt auf die physikalischen Eigenschaften und das Verhalten bei der Reduktion, eine Zwitterionenstruktur vorgeschlagen. Zwei Reduktionsprodukte, und zwar 5,6-dihydroxy-N-methylindol und 2,3,5,6-tetrahydroxy-N-methyldihydroindol, konnten isoliert und charakterisiert werden. Die erwartete Reduktionsstufe, *Leuko*-Adrenochrom, konnte *nicht* erhalten werden.

Es wird ein Reduktionsmechanismus in Vorschlag gebracht, bei dem als Zwischenstufe ein Semichinon beteiligt ist. Dieser Zwischenkörper dürfte bei biologischen Oxydationen, die das Adrenochrom betreffen, eine Rolle spielen.

[1] D. E. GREEN and D. RICHTER, Biochem. J. *31*, 596 (1937).

[2] Cf. W. WATERS, Chemistry of Free Radicals (Oxford, 1946), Chapter 12.

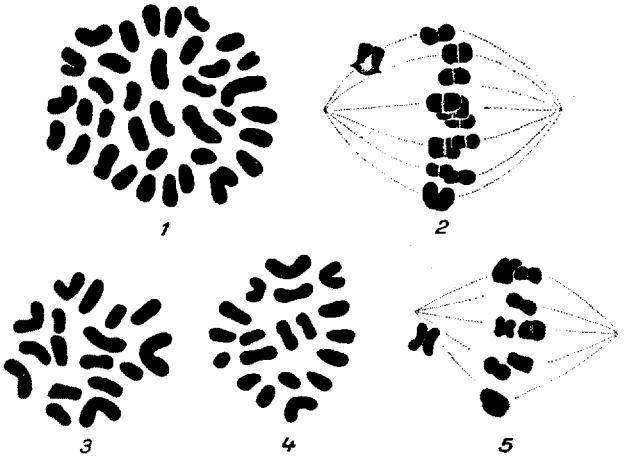
La formule chromosomiale de la race bisexuée de *Pycnoscelus surinamensis* L., comparée à celle de la race parthénogénétique

Pycnoscelus surinamensis est une Blatte probablement originaire de la région indo-malaise d'où elle s'est répandue dans toutes les zones tropicales et équatoriales du globe. En Europe et aux Etats-Unis, où elle a été accidentellement introduite, elle se rencontre dans les serres chaudes. Alors que dans son habitat primitif l'espèce est bisexuée, elle n'est représentée que par des ♀♀ parthénogénétiques en Amérique du Nord et en Europe.

En 1945 j'ai[1] publié une étude complète des conditions chromosomiques dans la race thélytoque, étude qui fut grandement facilitée par l'analyse cytologique d'un ♂ unique apparu dans mon élevage. Après avoir supposé que le nombre diploïde était égal à 40, j'arrivai à la conclusion que la formule correcte était:

$$♀\colon\ 2N = 38\ (36+2X). \qquad ♂\colon\ 2N = 37\ (36+X).$$

En 1945, également, E. SUOMALAINEN[2] publia une brève communication sur le même sujet: n'étant pas parvenu à obtenir des cinèses ovogoniales non plus que les divisions de maturation; n'ayant, d'autre part, eu que des ♀♀ à sa disposition, SUOMALAINEN admit que le nombre $2N$ était égal à 36. Influencé alors par le fait que chez une espèce voisine, *Leucophæa maderæ*,



Pycnoscelus niger BRUN. Fig. 1. – Métaphase spermatogoniale montrant 36 chromosomes. Fig. 2. – Métaphase spermatogoniale, vue de profil avec un 37e chromosome non compris dans la plaque équatoriale. Fig. 3. – Métaphase II avec 17 dyades. Fig. 4. – Métaphase II abec 19 dyades (cas rare, le plus souvent la 19e est en dehors de la plaque qui ne renferme alors que 18 dyades). Fig. 5. – Métaphase II, de profil, montrant la dyade non incorporée.
BOUIN-ALLEN (fig. 1 et 2) ou FLEMMING (fig. 3–5) -FEULGEN.

MORSE (1909) a compté 24 chromosomes, le cytologiste finlandais supposa que *Pycnoscelus* représentait une forme triploïde dérivée d'une race bisexuée dotée probablement de 24 chromosomes. L'incontestable caractère géographique de la parthénogénèse de *Pycnoscelus* serait ainsi confirmé par la polyploïdie de la race thélytoque. Notons, en passant, que SUOMALAINEN a utilisé par ses recherches des insectes qui, comme les miens, provenaient du Jardin botanique et de la Maison des crocodiles de Berlin: la différence entre nos décomptes ne saurait donc être attribuée à une différence raciale.

Dans mon travail de 1945, j'ai également envisagé l'hypothèse de la triploïdie, mais montré que celle-ci était insoutenable puisque le ♂ que j'avais élevé montrait une méiose absolument normale. Je n'en restais pas moins intrigué par la difficulté qu'il y avait à établir avec certitude le nombre $2N$ dans un matériel réputé facile et d'ailleurs très bien fixé.

[1] R. MATTHEY, Rev. suisse Zool. *52*, fasc. suppl. (1945).

[2] E. SUOMALAINEN, Hereditas *31*, 501 (1945).