Tetrahedron Letters No. 9, pp 731 - 734, 1972. Pergamon Press. Printed in Great Britain.

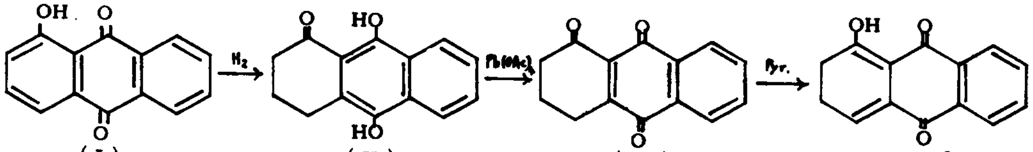
DIMERISATION OF 3,4-DIHYDRO-1,9,10(2H)ANTHRACENETRIONE DERIVATIVES

Shujiro Seo, Ushio Sankawa and Shoji Shibata

Faculty of Pharmaceutical Sciences, University of Tokyo . Japan

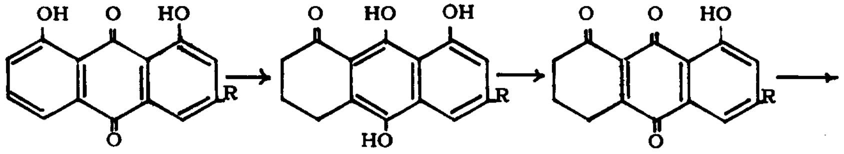
(Received in Japan 14 January 1972; received in UK for publication 27 January 1972)

Recent revision of the structures of luteoskyrin, rubroskyrin and rugulosin (1,2,3) prompted us to reexamine the chemical conversion of 3,4-dihydro-1,9,10(2H)anthracenetrione (III) into a non-quinonic compound (IV) which was formulated as (IV') by Zahn and Koch (4) and referred as the model compound in our earlier studies on the above-mentioned mould pigments (5).



(I) (II) (III) (IV')

Starting from chrysazin (V a) (5) and chrysophanol (V b) a series of homologous compounds (VI a,b VII a,b and VIII a,b) have been prepared.



VIII a R = H
or
VIII b R = CH_3

(V) a R = H, b R = CH_3 (VI) a R = H, b R = CH_3 (VII) a R = H, b R = CH_3

The quinonic compound (VII b), $C_{15}H_{12}O_4$, orange red crystals ,m.p. 196°,IR $\nu_{KBr}^{cm^{-1}}$ C=O 1695, 1663. 1625, is very unstable as like as its homologous compound (VII a) (5) converting into a non-quinonic compound (VIII b), m.p. 212°, on standing the solution at room temperature. The conversion is promoted by the addition of a drop of pyridine in the chloroform solution of VII b.

The compounds (IV), (VIII a) and (VIII b) showed in their IR spectra a carbonyl absorption band in higher frequency region along with a chelated carbonyl absorption. The UV spectra of the compounds (VIII a) and (VIII b) revealed the presence of the same chromophore in their molecules.

Contrary to the previous presentations (4,5), it has now become quite clear that these compounds

(IV, VIIIa and VIIIb) must be dimeric compounds as being shown by the mass spectra (Table I).

Table I The Mass and Infrared Spectra of the Compounds (IV),(VIIIa) and (VIIIb)

Compounds	m/e						ν C=O (cm^{-1})	
	M^+			$\frac{1}{2}M+1$	$\frac{1}{2}M-1$			
IV	454	452	450	228	226	224	1717	1625
VIII a	486	484	482	244	242	240	1717	1623
VIII b				258	256	254	1715	1618

The n.m.r. spectrum of the compound (VIII b) gave singlet signals of 2 methyls, 2 olefinic and 2 aromatic proton signals to reveal a dimeric structure consisting of unequivalent moieties, though the dimeric molecular ion peak was not observed in the mass spectrum.

The UV spectrum of VIII b gave absorption maxima at 270, 306, 315, 330, 372, 417 and 434 nm, almost all of which except 372 nm were also given by the hydroquinone-type compound (VI b).

Therefore, VIII b would involve the structure of VI b as a monomeric moiety (Fig.1).

As the n.m.r. signal of $C_{(9)}$-OH at δ 7.48 given by VI b was not observed in the spectrum of VIII b , the oxygen atom at $C_{(9)}$ of VIII b must participate to form the linkage connecting two monomeric moieties.

Fig. 1

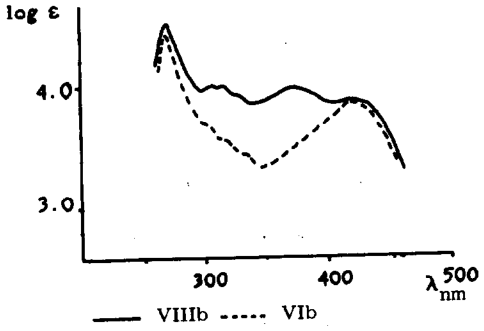


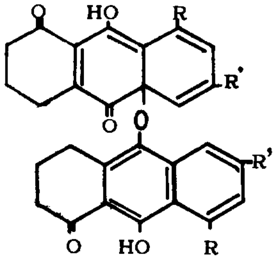
Table II The n.m.r. Spectra (δ (ppm)) of the Compounds (VIII b) and (VIb)

	VIII b (in $CDCl_3$)	VI b (in $(CD_3)_2CO$)
CH_3	2.04, 2.14	2.42
$-CH_2-$	2.0~3.0 (m)	2.6~3.1 (m)
Arom. H	6.61, 6.98	6.69, 7.47
Olefinic H	6.25, 6.40	
Phenolic and enolic H	9.65, 15.81 11.35, 14.49	7.48, 9.81, 16.09

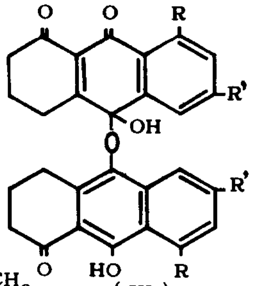
The higher shift of the n.m.r. signals which was shown in VIII b in comparison with the correponding signals of VI b would be resulted by the anisotropic effect of the monomeric halves.

Consequently the dimeric compounds could be formulated as (IV), (VIII a) and (VIII b), respectively. The IR absorption band at 1717 or 1715 cm^{-1} of these compounds would reasonably account for the carbonyl which is twisted by the effect of adjacent quarternary carbon atom splitting the enone resonance system (7,8).

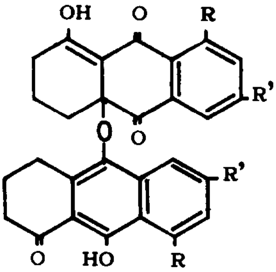
The alternative structures, (IX) and (X), for the dimers could be ruled out by the following reasons: Absence of ketal hydroxyl signal,and appearance of ring proton signals in the higher field of the n.m.r. spectrum than those expected for the aromatic protons of X ; the carbonyl on the hydrogenated 6-membered ring fused to the aromatic system should give the IR absorption at lower frequency than 1715 cm^{-1}; the negative evidence in the UV and IR spectra for the existence of the chromophore of rugulosin (2) which must exist in X ; the n.m.r. spectrum of aromatic protons differs from that of rugulosin.



(IV)R=R'=H;(VIIIa)R=OH R'=H;(VIIIb)R=OH R'=CH$_3$

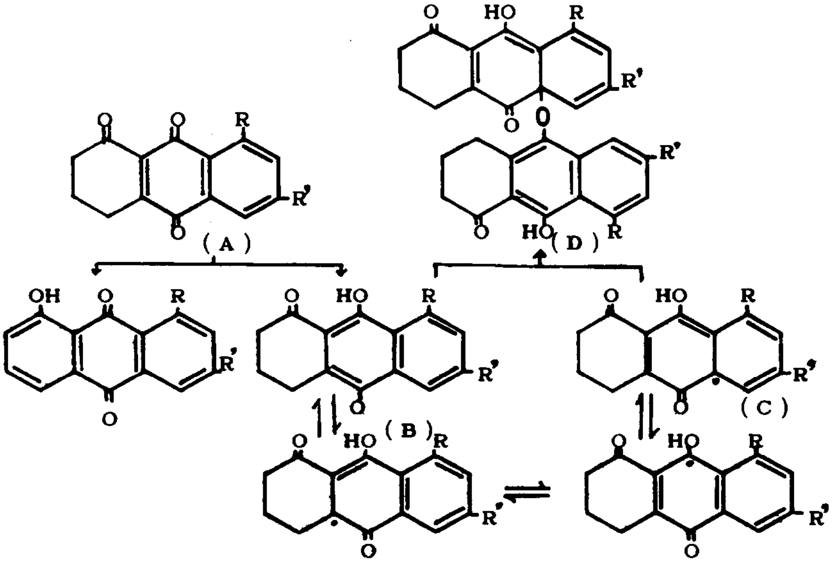


(IX)



(X)

As the corresponding anthraquinones are formed in the case of dimerisation of the quinones,III, VII a and VII b , it would be reasonable to assume the formation of 2 moles of semiquinone (B) with 1 mole of anthraquinone from 3 moles of the hydrogenated quinone (A). Among the various radical forms C would be coupled with B to form the dimer D.



Acknowledgements: The authors wish to thank Ministry of Education and Hoansha for grants.

REFERENCES

1) S. Shibata, Y. Ogihara, N. Kobayashi and S. Seo , Tetrahedron Letters , 3178 (1968).

2) U. Sankawa, S. Seo, N. Kobayashi, Y. Ogihara and S. Shibata, Tetrahedron Letters , 5557 (1968).

3) N. Kobayashi, Y. Iitaka and S. Shibata, Acta Cryst. (B) 26 , 188 (1970).

4) K. Zahn and H. Koch, Ber.deutsch.chem.Ges. , 71 , 172 (1938).

5) S. Shibata, T. Murakami, I. Kitagawa and T. Kishi, Pharm.Bull.(Tokyo) , 4 , 111 (1956).

6) S. Shibata, T. Murakami and M. Takido, Pharm.Bull. (Tokyo) , 4 303 (1956).

7) F.M. Dean, J. Stannton, and W.B. Whalley, J. Chem.Soc. , 3004 (1959).

8) E.J. Haws, J.S.E. Holker, A. Kelley and A.D.G. Powell and A. Robertson, J.Chem.Soc. , 5598 (1959).