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STRUCTURE OF (-)FLAVOSKYRIN, A COLOURING MATTER OF PENICILLIUM ISLANDICUM SOPP NRRL 1175

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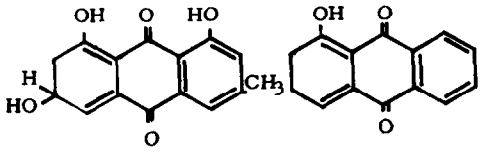
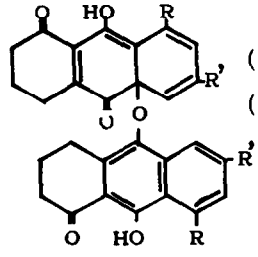
(-)Flavoskyrin, m.p. 215°(decomp.), $[\alpha]_D$ - 295°(dioxane), a yellow colouring matter of Penicillium islandicum Sopp NRRL 1175 (1) was supposed to be a monomeric modified anthraquinone for which a structural formula (Ia) was proposed (2) referring Zahn and Koch's compound (IIa) (3) as the model.



(Ia)

(IIa)



(IIb) R=R'=H

(IIc) R = OH
R'= CH_3

As the structure of rugulosin which was elucidated formerly as being a 1,1'-dimer of flavoskyrin was revised recently, the structures of flavoskyrin (Ia) and the model compound (IIa) have become unplausible. The reactions proposed by Zahn and Koch (3) and the structures of the homologous compounds derived by the same process have been reexamined as described in the preceding report (4) to revise the structure of IIa as being formulated by a dimeric structure (IIb).

It has now been found that by the action of pyridine , (-)flavoskyrin is converted into (-)rugulosin (III) which has recently been isolated from Penicillium islandicum Sopp NRRL 1175, and Myrothecium verrucaria (Alb.et Schw.)Ditmer ex Fr. (5), while on treatment with thionyl chloride in pyridine (-)flavoskyrin is transformed into (+)dianhydrorugulosin (=dichrysophanol(8,8'))(IV).

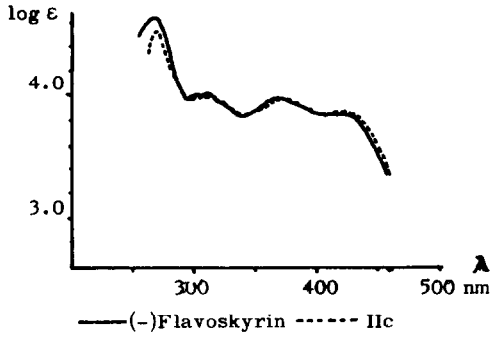
Referring the dimeric structures of the model compounds and the above-mentioned findings in the chemical properties of (-)flavoskyrin, it has been suggested that (-)flavoskyrin is not a monomer but a dimeric modified anthraquinone whose molecular formula, $C_{30}H_{24}O_{10}$, has been supported by the mass spectrum, m/e 526 (M $-H_2O$), 506 (M - H_2 - $2H_2O$).

The UV absorption spectral curve of (-)flavoskyrin is almost superimposable on that of the model compound (IIc) (4) prepared from chrysophanol to indicate that flavoskyrin possesses the same chromophore with it. The n.m.r. spectrum of (-)flavoskyrin indicated that it is an unequivalent dimer showing signals of 2 methyls, 2 olefinic and 2 aromatic ring protons, and 4 enolic or phenolic hydroxyls. The multiplets of $-CH_2-$ coupled with the multiplet of the proton attached to the carbon atom bearing a hydroxyl revealed the position of the C-C linkage connecting two monomeric moieties at 1 and 1'.

Table I. The N.m.r. Spectrum of (-)Flavoskyrin (in d_8 Dioxane) δ ppm

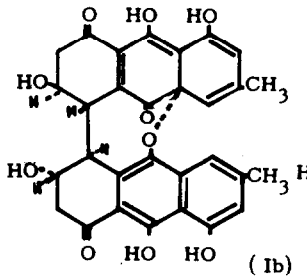
CH_3	1.96	2.10
$-CH_2-CH-$	2.5∿3.0 (m)	
$-CH_2-C(H)$	4.06 (m)	4.30 (m)
$-CH_2-C(OH)$	4.60 (d)	4.90 (d)
Arom. H	6.55	6.96
Olefinic H	6.13	6.31
Phenolic OH	9.50	15.76
Enolic OH	11.21	14.13

Fig. 1

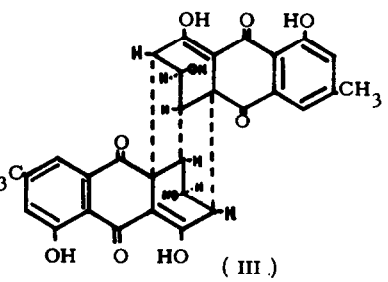


Considering the n.m.r. and UV spectral evidences (-)flavoskyrin must be formulated as (Ib).

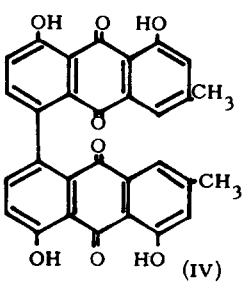
The IR spectral absorption at 1715 cm^{-1} is assigned to the carbonyl at $C_{(9)}$ which is twisted by the effect of the neighbouring quarternary carbon atom as shown in the model compounds (IIb ,c) (4).



(Ib)



(III)



(IV)

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