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THE STRUCTURE OF LUMILUTEOSKYRIN, A PHOTOREACTION PRODUCT OF LUTEOSKYRIN

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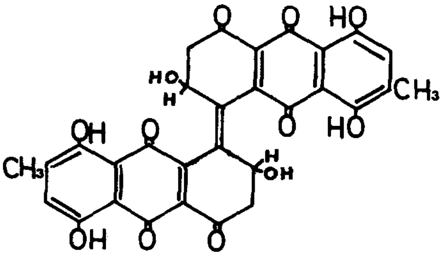
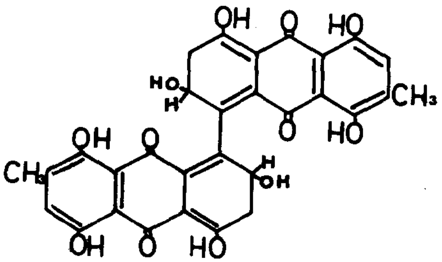
Lumiluteoskyrin, $C_{30}H_{20}O_{12}$, dark reddish purple crystals, m.p.> 360°, was obtained from luteoskyrin, $C_{30}H_{22}O_{12}$, yellow crystals, m.p.>360°, isolated from <u>Penicillium islandicum</u> Sopp, on exposing its acetonic solution under sunlight. In 1961 (1) a structural formula was forwarded for lumiluteoskyrin(I) on the basis of the old structural formula of luteoskyrin (II) (2).


(I)


(II)

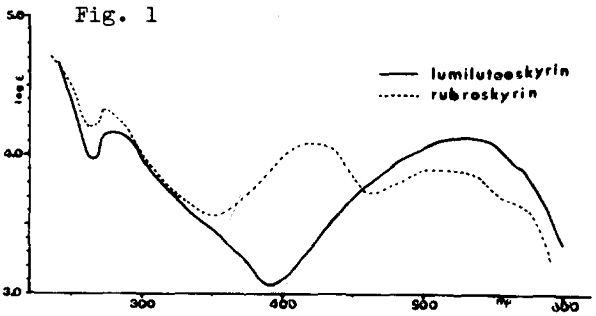


Fig. 1

Recently the structure of luteoskyrin was established as being V (3). It has led us to reëxamine the structure of lumiluteoskyrin. The UV absorption curve of lumiluteoskyrin resembles very closely that of dihydrocatenarin (Quinone B) (III) (4)*and

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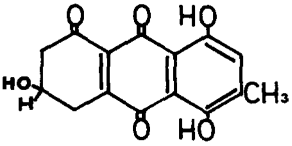
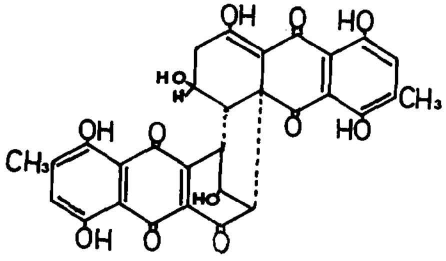
* λ $_{max}$(EtOH) 495, 530 infl., and 570 infl. mμ (log at 495 mμ ca. 3.6) (4)



(III)

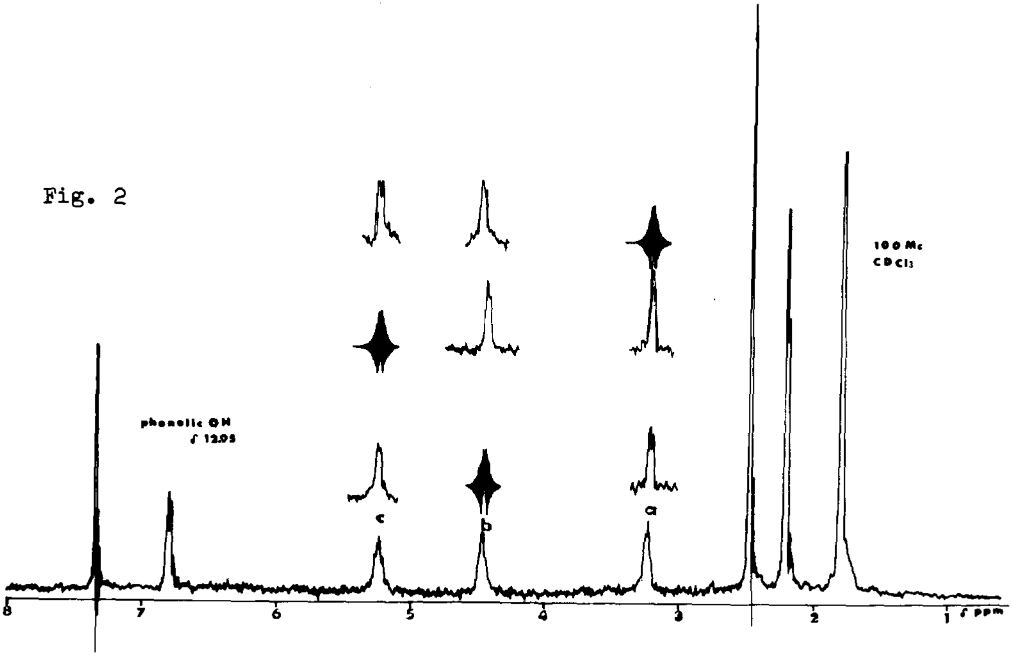


(IV)

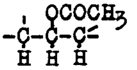
partly that of rubroskyrin (IV) (3). The blue colouration of lumiluteoskyrin and dihydrocatenarin with magnesium acetate suggests a resemblance of the quinonic structure of both compounds. The IR absorptions (KBr)of lumiluteoskyrin which reveal the existence of αβ-unsaturated C=O (1693 cm^{-1}) and chelated C=O (1614 cm^{-1}) correspond to those of rubroskyrin at 1697 cm^{-1} and 1608 cm^{-1}, respectively.

Lumiluteoskyrin tetraacetate, $C_{30}H_{16}O_8(OCOCH_3)$, m.p. > 360°, $/\alpha/_D$ + 178° (dioxane), was obtained on acetylation of lumiluteoskyrin with acetic anhydride and p-toluenesulphonic acid at room temperature. Deacetylation of the tetraacetate was performed readily by warming it with alkali in recovering lumiluteoskyrin.

Fig. 2

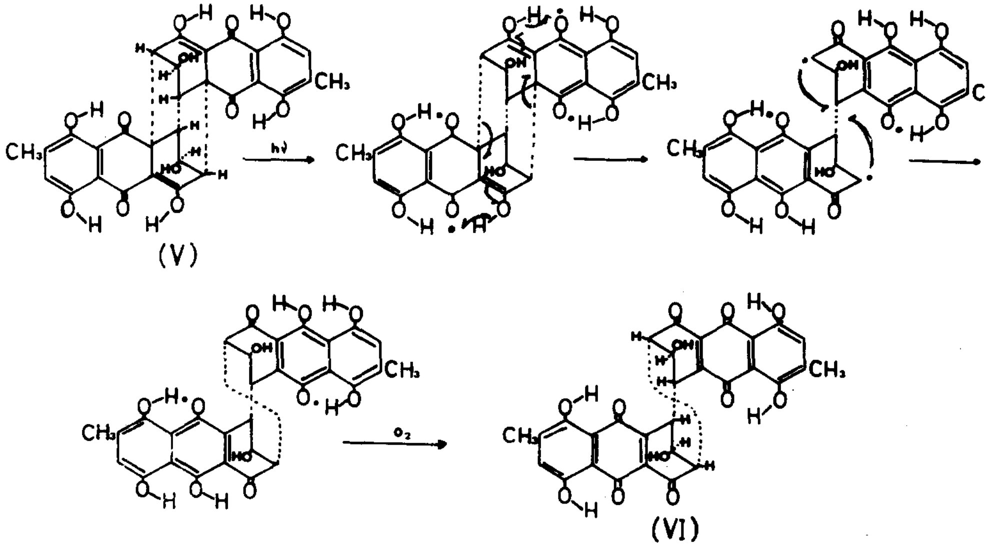


The following signals are given in the NMR spectrum of lumiluteoskyrin tetraacetate: δ(ppm) 1.79 OCOC$\underline{H}_3$, 2.20 arom. C$\underline{H}_3$ (doublet, J = 1 c/s), 2.46 OCOC$\underline{H}_3$, 3.25 (a) H, 4.45 (b) H, 5.23 (c) H, 6.79 arm.H (doublet, J = 1 c/s) and 12.95 phenolic O$\underline{H}$. All the signals are equivalent in the monomeric halves of the dimeric structure of lumiluteoskyrin tetraacetate. The signal (c) is assigned to a proton attached to the carbon atom bearing acetoxyl. The decoupling experiment (J_{ac} = 2.5 c/s, J_{bc} = 3 c/s, J_{ab} = 1 c/s) showed the following disposition of protons, in which a long range coupling between signals, a and b, was observed:



$$-\underset{H}{\overset{|}{C}}-\underset{H}{\overset{OCOCH_3}{C}}-\underset{H}{C}=$$

The structure of lumiluteoskyrin has finally been established to be VI, which would be formed from luteoskyrin (V) by the following mechanism of photochemical reaction:



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