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# PHOTO-OXIDATIVE RING CONTRACTION OF DEHYDROROTENONE TO COUMARONO-CHROMONE

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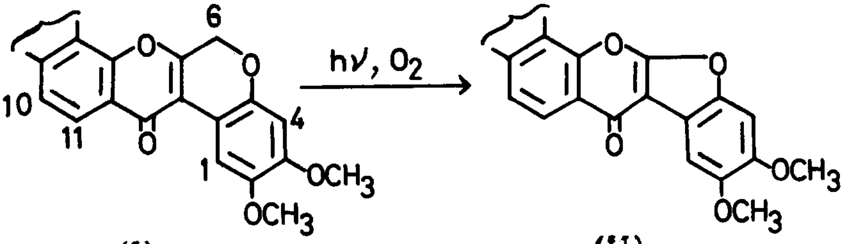
In earlier works$^{1)}$, it was reported that rotenone(IIIa) was converted into dehydrorotenone(Ia) and rotenonone(IVa) under the exposure to air in alcoholic alkaline solution. Recently, Suginome, Yonezawa and Masamune$^{2)}$ indicated that the irradiation of Ia in dioxane-ethanol mixture containing sodium borohydride affords rotenonone(IVa) as the major product. We have found that the irradiation of Ia in pyridine induces an interesting ring contraction besides the usual oxygenation.

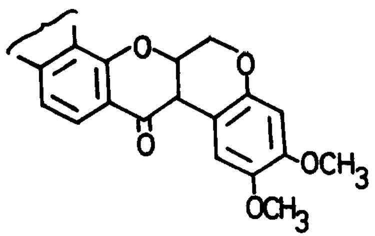
A pyridine solution(2%) of Ia was irradiated with high-pressure mercury lamp at 42° for 3 hr under the bubbling of oxygen. The reaction mixture was cooled overnight and rotenonone(IVa) was isolated in 25% yield. Subsequently, the remaining substances were separated into neutral, phenolic and acidic fractions, and the neutral fraction was subjected to thin-layer and column chromatographic separations. Light brown crystals, which are slightly soluble in organic solvents, were isolated in about 3% yield from the fraction$^{3)}$.

The compound is mp. 251-252°, $M^+$378(mass spectroscopy), Anal. Calcd for $C_{22}H_{18}O_6$: C,69.83; H,4.80. Found: C,69.66; H,4.75 and $[\alpha]_D$ -55°(c=0.17,$CHCl_3$). Ultraviolet maxima in ethanol appeared at 236(ε26,400),259(29,000),289(24,900) and 315(infl)(11,500)nm; infrared(KBr) showed at 1654, 1633,1617 and 1593cm$^{-1}$. On the basis of above data and the following evidences, we formulated the structure of the compound as IIa, being 1,2-dihydro-2-isopropenyl-8,9-dimethoxybenzofurano[2,3-b]furo[2,3-h][1] benzopyran-6-one.



(I)

(II)



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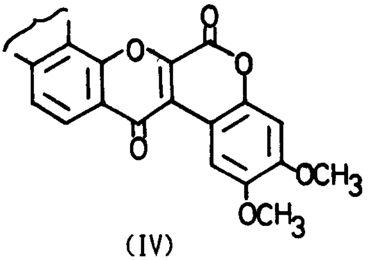

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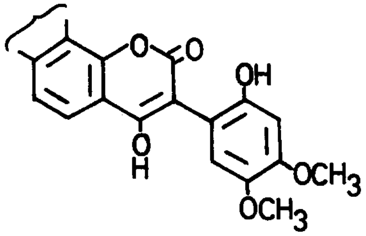

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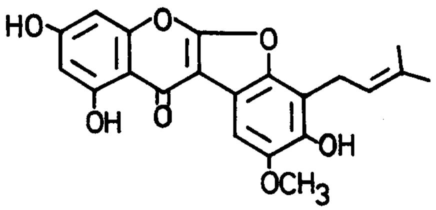
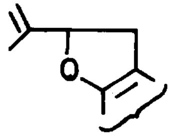
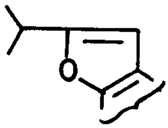


(VI)



a



b

The nmr absorption bands of compound IIa in $(CD_3)_2SO$ at $\tau$ 8.21 and 6.11 belong to a methyl group and to the two methoxyl groups, respectively. Since 2.47 and 2.66 peaks are singlets, they are assigned to the protons of para positions corresponding to those at positions 1 and 4 of dehydrorotenone(Ia), respectively$^{4)}$, and 3.01 and 1.94(doublet, J=8.8$H_z$) peaks are attributed to ortho protons corresponding to those at positions 10 and 11. Ia is known to be converted to the isomer Ib by the treatment with concd.sulfuric acid$^{5)}$. By the similar treatment of compound IIa, we obtained a compound IIb, mp.214-215°, $M^+$378, $[\alpha]_D$ ±0°, Anal. Calcd. for $C_{22}H_{18}O_6$: C,69.83; H,4.80. Found: C,69.63; H,4.74; $\nu_{max}^{KBr}$ 1648,1625 and 1578cm$^{-1}$; $\lambda_{max}^{EtOH}$ 246(ε41,380), 293 (15,400), 302(15,400) and 320(infl)(8,370)nm. The peaks in nmr spectrum of compound IIb in $CDCl_3$ were easily assigned: two methyl protons at $\tau$ 8.61(d, 6H, J=6.9$H_z$); and a methyne proton, coupled to its methyl protons at 6.87(m,1H, J=6.9$H_z$); two methoxyl protons at 6.04 and 6.09(s,6H); a proton of furan ring at 3.30(s,1H); 1 and 4 protons at 2.45(s,1H) and 3.01(s,1H), respectively, and protons in positions 10 and 11 at 2.59 and 1.87(d,2H, J=9.0$H_z$), respectively. From the above results, the compound is an isomer of IIa. Thus, the photoproduct IIa has the structure which was not oxidized either at dihydrofuran ring or isopropenyl moiety in dehydrorotenone(Ia).

The chemical shifts(IIa; $H_1$, $\tau$ 2.47, IIb; $H_1$, 2.45) of the protons in the position 1 of compound IIa and IIb associated with the low field singlets in nmr spectra demonstrate clearly the deshielding effect by the carbonyl function which is analogous to the deshielding shown by the protons in lisetin(VI; $H_1$,$\tau$ 2.42)$^{6)}$ and dehydroisorotenone(Ib; $H_1$,$\tau$ 1.56, lit.$^{7)}$ 1.67). The magnitude of chemical shifts of protons in position 1 of compound IIa and IIb, as compared with VI and Ib, indicated that the compound IIa has the structure whose skeleton is similar to lisetin. Furthermore, in the mass spectrum of compound IIa, a base peak is molecular ion(m/e378) and the peak by the predominant fragmentation is the ion(88%) at m/e363 due to loss of methyl radical from the molecular ion. Among the other peaks whose relative abundances were small, the ions at m/e335 (22%), m/e305(22%) and m/e161(15%) were also assigned. The structure of coumarono-chromone type presented as IIa is consistent with these assignment.

An additional support for the structure of IIa is provided by a chemical evidence that hydrolysis of compound IIb in potassium hydroxide solution gave 4-hydroxy-coumarin(Vb), mp.253-254°. The structure of Vb was elucidated by elemental analysis( Anal. Calcd.for $C_{22}H_{20}O_7$: C,66.66; H,5.09. Found: C,66.55; H,5.03), infrared and ultraviolet spectroscopic data( $\nu_{\text{dioxan}}$ 1720cm$^{-1}$(C=O); $\lambda_{\text{max}}^{\text{EtOH}}$ 238(ε41,900), 253(25,900), 261(25,100) and 326(16,000)nm ).

From the results that compound IIa was photochemically produced from dehydrorotenone(Ia), it was proved that chromeno-chromone is converted to coumarono-chromone by the ring contraction. In the first step of the photo-oxygenation of Ia, secondary hydroperoxides$^{2)}$ at position 6 in Ia would be formed. These hydroperoxides may be predominantly converted to ketone(IVa), otherwise it seems reasonable to assume that β-fission process of the hydroperoxides leads to the formation of IIa.

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## References and Footnotes

(1) S.Takei, S.Miyajima and M.Ohno, Report. Inst.Phys.Chem.Res(Japan), **12**, 527(1933). R.Cahn, R.Phipers and E.Brodaty, J.Soc.Chem.Ind, **64**,33(1945)

(2) H.Suginome, T.Yomezawa and T.Masamune, Tetrahedron Letters, 5079(1968)

(3) The other minor product was detected on the tlc. The structure of this compound is under investigation.

(4) For ease of comparison of the chemical shifts of corresponding protons, the formulae of compound IIa,b have been numbered to correspond with the usual convention for rotenone.

(5) A.Butenandt and F.Hildebrandt, Ann., **477**, 245(1930)

(6) C.P.Falshaw, W.D.Ollis, J.A.Moore and K.Magnus. Tetrahedron,Suppl.(NO.7) 333(1966)

(7) L.Crombie and J.W.Lown, J.Chem.Soc., **1962**, 775