Communications to the Editor

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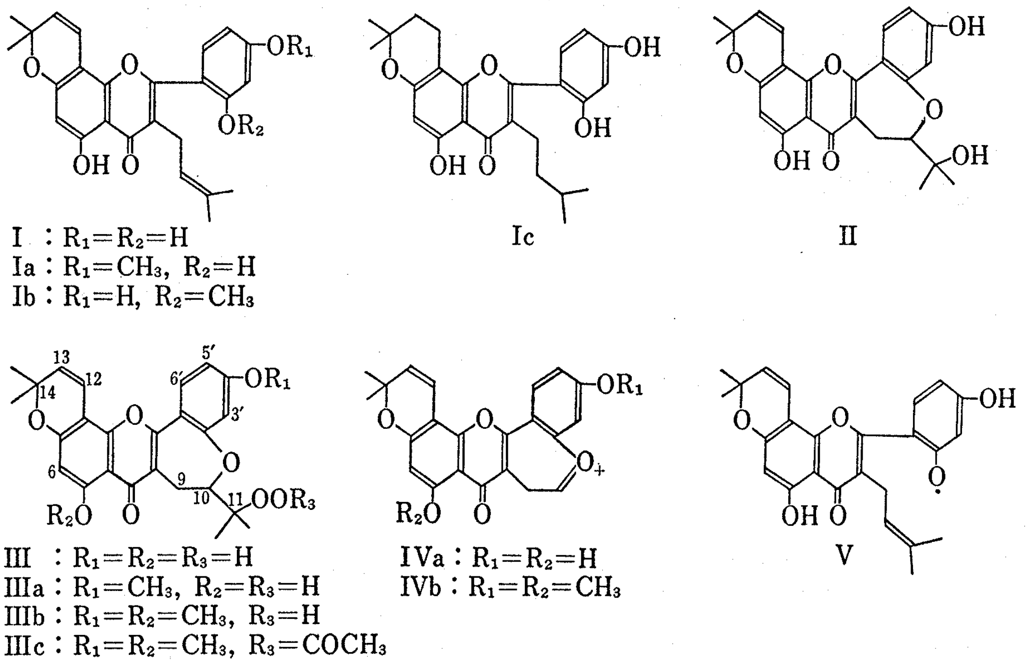
Photo-oxidative Cyclization of Morusin

When a solution of morusin (I) in $CHCl_3$ or benzene was exposed to bright sunshine, or irradiated with a high-pressure mercury lamp, morusin hydroperoxide (III) was obtained in a high yield. The reduction of III gave compound A (II) which had been isolated from the root bark of *Morus alba* L. The reaction mechanism of the photooxidation was discussed based on the several experimental results.

Keywords——photooxidation; morusin; *Morus alba* L.; hydroperoxide; phenoxy radical; dihydrooxepin ring

In the previous communication,[1] the authors reported the structure determination of three new flavone derivatives, morusin (I), compound A (II), and cyclomorusin, obtained from the root bark of *Morus alba* L. We now report the formation of morusin hydroperoxide (III) on photooxidation of morusin (I).

When a solution of I in $CHCl_3$ was exposed to bright sunshine for 7 hr, or irradiated with a high-pressure mercury lamp (40 W) for 5 hr, morusin hydroperoxide (III) was obtained in *ca.* 80% yield. This reaction did not occur in the dark and was dependent on the solvent, proceeding in $CHCl_3$ or benzene solution, but in MeOH, EtOH or *tert*-BuOH solution the starting material being recovered unchanged. III shows the following data: $C_{25}H_{24}O_8$,[2] mp 204—206° (yellow needles from MeOH), positive reaction on $FeCl_3$, Mg–HCl, and Zn–HCl test, negative on Gibbs test, UV absorption λ_{max}^{EtOH} nm (log ε): 280 (4.46), 335 (4.42); IR absorption ν_{max}^{Nujol} cm^{-1}: 3320, 1660, 1635, 1540; proton magnetic resonance (δ in pyridine-d_5) shows the AMX pattern,



I : $R_1=R_2=H$
Ia : $R_1=CH_3$, $R_2=H$
Ib : $R_1=H$, $R_2=CH_3$

Ic

II

III : $R_1=R_2=R_3=H$
IIIa : $R_1=CH_3$, $R_2=R_3=H$
IIIb : $R_1=R_2=CH_3$, $R_3=H$
IIIc : $R_1=R_2=CH_3$, $R_3=COCH_3$

IVa : $R_1=R_2=H$
IVb : $R_1=R_2=CH_3$

V

$$\mathrm{I} \xrightarrow[O_2]{h\nu} \mathrm{III} \longrightarrow \mathrm{II}$$

Chart 1

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[1] T. Nomura, T. Fukai, S. Yamada, and M. Katayanagi, *Chem. Pharm. Bull.* (Tokyo), 24, 2898 (1976).

[2] Elemental analysis of the compound gave a satisfactory result.

such as 2.89 (dd, $J=10$ and 18 Hz, C_9–H), 3.90 (dd, $J=2$ and 18 Hz, C_9–H), 4.76 (dd, $J=2$ and 10 Hz, C_{10}–H); mass spectrum *m/e*: 452 (M^+), 436 (M^+–O), 421 (M^+–O–CH_3), 377 (M^+–$C_3H_7O_2$, IVa), 203 (formed from the ion at 421 by a reverse Diels-Alder reaction).[3,4] From these data, III can be regarded as a flavone containing a dihydrooxepin ring.[1,5,6]

When III was reduced by $NaBH_4$, Ph_2S, Ph_3P, or $(CH_3)_3N$, in MeOH, compound A (II) was obtained in *ca.* 80% yield. The following data indicate the presence of two phenolic hydroxyls and a hydroperoxide group in III. Treatment of III with ethereal CH_2N_2 in MeOH gave the monomethylate[2] (IIIa), $C_{26}H_{26}O_8$ (M^+ 466), mp 187—190°, IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3280, positive on $FeCl_3$ test, and the dimethylate (IIIb),[7] $C_{27}H_{28}O_8$ (M^+ 480), mp 228—230°, IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3300, negative on $FeCl_3$ test. Treatment of IIIb with Ac_2O in pyridine yielded the dimethyl ether monoacetate (IIIc), $C_{29}H_{30}O_9$ (M^+ 522), mp 150—152°; IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 1780 (–OO–$COCH_3$),[8] mass spectrum *m/e*: 405 (base peak, M^+–$C_5H_9O_3$, IVb).[3,4] From these results, the structure of morusin hydroperoxide is deduced to be III. Considering the result of photooxidation, it is probable that compound A (II) is an artifact which was formed from morusin (I) *via* hydroperoxide (III) during isolation.

III was also obtained in the dark in the presence of diphenyl picryl hydrazyl (DPPH)[9] or MnO_2,[10] and the yield of III was 20% and 35%, respectively. When the $CHCl_3$ solution of Ia[11] was treated with DPPH in the dark, the formation of IIIa was detected by TLC. These findings suggest that phenoxy radical (V) is presumably intermediate of this oxidation. On the other hand, the photooxidation of I was inhibited by the addition of 2,6-di-*tert*-butyl cresol, a free radical inhibitor. This photooxidation did not occur in tetrahydro morusin (Ic)[1] and 2′-O-methyl morusin (Ib).[11] However irradiation of 4′-O-methyl morusin (Ia)[11] gave the hydroperoxide (IIIa). These result indicate that both of the free hydroxyl group at $C_{2'}$ and the isolated double bond are required for this photooxidation. The present findings probably suggest that the photooxidation proceeds *via* V as an intermediate. Further studies are now in progress to elucidate the mechanism of the photooxidation of morusin.

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11) Ia and Ib were obtained by the treatment of I in ispropanol with ethereal CH_2N_2. Ia, $C_{26}H_{26}O_6$ (M^+ 434), mp 162—164°, Gibbs test (+), Ib, $C_{26}H_{26}O_6$ (M^+ 434), mp 198—199°, Gibbs test (−).