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Chemical Reactions of Bikaverin

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Methylation of bikaverin (Ib) with diazomethane afforded monomethylbikaverin (Ic). Reductive acetylation of Ia, b, c with acetic anhydride and sodium acetate in the presence of zinc powder gave rise to benzoxanthene derivatives (IIc, d, e), respectively. Ib was hydrolyzed with aqueous sodium hydroxide to give everninic acid (III) and orcinol (IV). However, hydrolysis of Ic with alcoholic potassium hydroxide gave rise to cyclopentenoxanthene derivative (V). Ozonolysis of Ic gave xanthone derivative (XI).

Keywords——bikaverin; 12*H*-benzo[*b*]xanthene; everninic acid; ozonolysis; reductive acetylation

Bikaverin (Ib), a red pigment isolated from cultures of *Fusarium oxysporum* and of *Fusarium oxysporum f. sp. lycopersici* has been studied as a "vacuolation factor" of "ageing factor," affecting the growth of fungi at very low concentration.[2] The structure was determined by the X-ray structure analysis.[3] Recently, Barton, *et al.*[4] reported the total synthesis.

Though considerable literatures have been reported on isolation,[5] production,[6] and biological activities,[7] quite few are available concerning its chemical reactions.[8] In the present paper we wish to report some chemical reactions of bikaverin (Ib).

The reaction of bikaverin (Ib) with methyl iodide in the presence of silver oxide is reported to give monomethylbikaverin (Ic), dimethylbikaverin (Id), and its isomer I′d.

Formation of the dimethyl derivatives suggested the tautomerism of bikaverin between Ib and I′b structures.[8] When diazomethane was used, in our hands, as a methylating agent, the monomethyl derivative (Ic) was obtained as a sole product.

The acetylation of Ib with acetic anhydride at room temperature or in the presence of zinc dust was also reported to give bikaverin diacetate (If and I′f) or bikaverin leucotri- and tetraacetate (IIa and IIb).[8] We reinvestigated the reductive acetylation of Ib in the presence of excess zinc dust, and found that the carbonyl of the B-ring was reduced to give the tetraacetate (IId). Similar reactions were observed in reductive acetylations of norbikaverin (Ia) and monomethylbikaverin (Ic), which afforded compound IIe and IIc, respectively.

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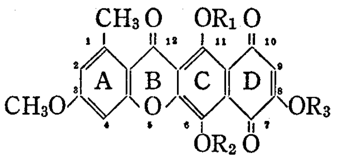
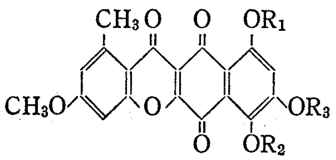
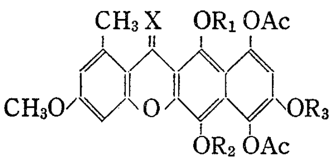


I a : $R_1=R_2=R_3=H$ (norbikaverin)
b : $R_1=R_2=H$, $R_3=CH_3$ (bikaverin)
c : $R_1=H$, $R_2=R_3=CH_3$
d : $R_1=R_2=R_3=CH_3$
e : $R_1=R_3=H$, $R_2=CH_3$
f : $R_1=R_2=Ac$, $R_3=CH_3$



I′ b : $R_1=R_2=H$, $R_3=CH_3$
d : $R_1=R_2=R_3=CH_3$
f : $R_1=R_2=Ac$, $R_3=CH_3$



II a : $R_1=H$, $R_2=Ac$, $R_3=CH_3$, $X=O$
b : $R_1=R_2=Ac$, $R_3=CH_3$, $X=O$
c : $R_1=Ac$, $R_2=R_3=CH_3$, $X=H_2$
d : $R_1=R_2=Ac$, $R_3=CH_3$, $X=H_2$
e : $R_1=R_2=R_3=Ac$, $X=H_2$

Chart 1

Alkaline hydrolysis of bikaverin (Ib) was also investigated to afford norbikaverin (Ia)[8] or orsellinic acid.[9] Heating of Ib with 10% sodium hydroxide gave everninic acid (III) and orcinol (IV) in 8% and 27% yield, respectively. However, refluxing of methylbikaverin (Ic) in an ethanolic potassium hydroxide solution gave yellow needles, $C_{20}H_{16}O_9$ (V), whose structure was assigned as 7,10-dihydroxy-3,6-dimethoxy-1-methyl-9,11-dioxo-7,8,9,11-tetrahydrocyclopenta[*b*]xanthene-7-carboxylic acid on the basis of the spectroscopic data detailed in the experimental section.

Compound V was methylated with diazomethane to give compounds VI and VII. Heating of VII with *p*-toluenesulfonic acid in xylene gave rise to the dehydrated product VIII.

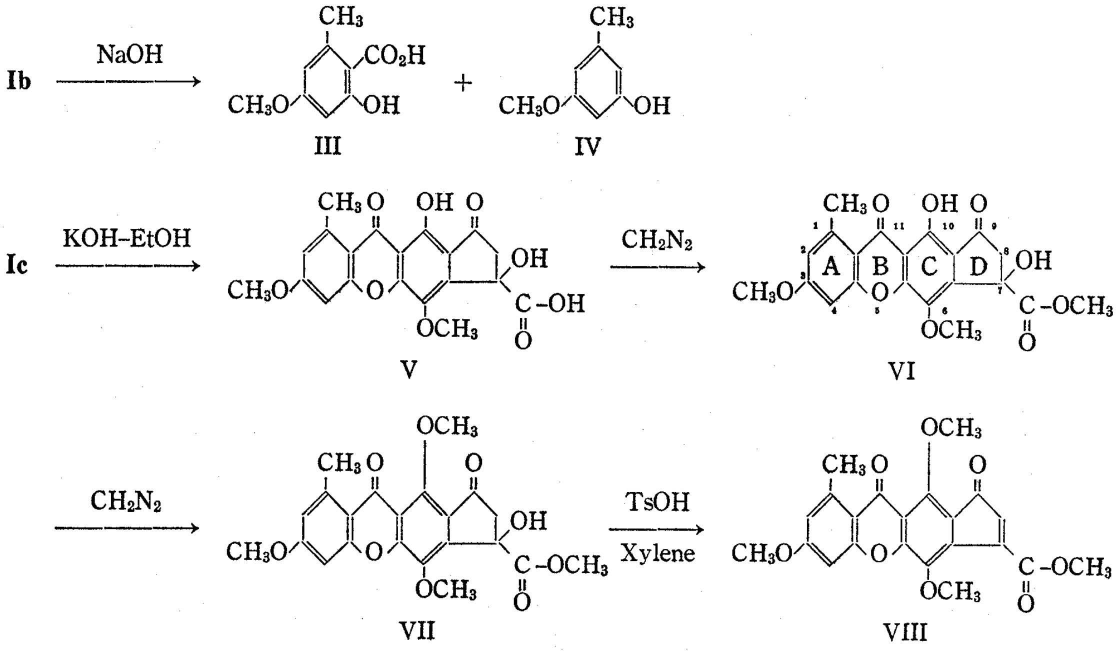


Chart 2

The reason of the formation of everninic acid (III) by the alkaline hydrolysis of bikaverin (Ib) involves the tautomerism of bikaverin (I′b), whose pyrone ring (B-ring) is, on hydrolysis, readily opened to give the acid (III). On the other hand, the D-ring of methylbikaverin (Ic), which exists in the quinone form, is hydrolysed followed by ring contraction to give the product V.

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9) J.W. Cornforth, G. Ryback, P.M. Robinson, and D. Park, *J. Chem. Soc.* (*C*), **1971**, 2786.

Such mechanism had to be considered in view of the reported formation of 2-alkyl-3-hydroxyindanone-3-carboxylic acid (X) from 2-hydroxy-3-alkyl-1,4-naphthoquinone (IX), which is shown in Chart 3.[10] Applying the similar pathway, alkaline hydrolysis of compound Ic would give the demethylated intermediate (Ie) in the first stage. The next stage might well involve the same ring contraction as above to give compound V.

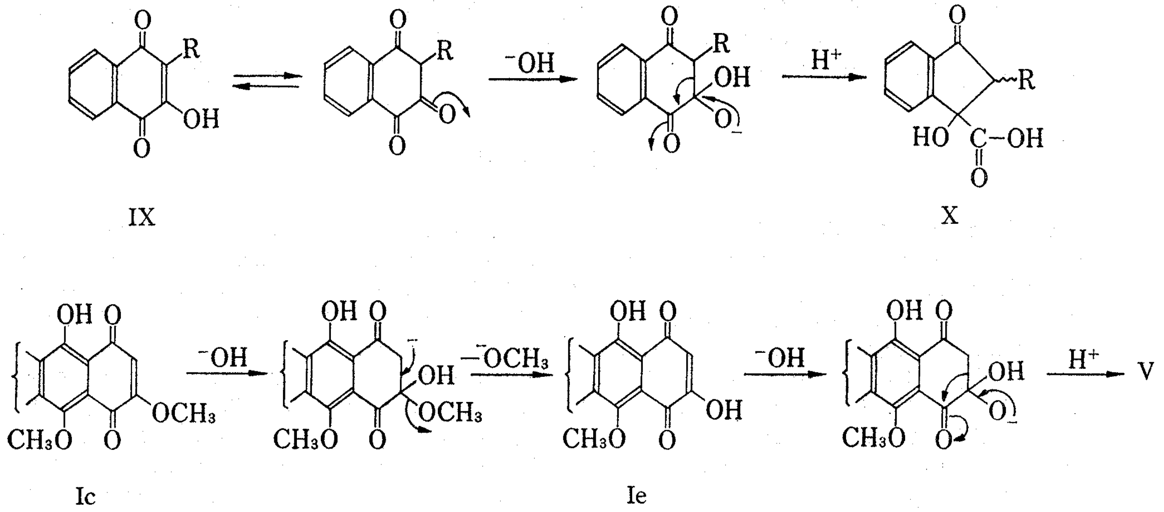

Chart 3

Lastly, ozonolysis of compound Ic was attempted in order to obtain the xanthone derivative. Thus, compound Ic was allowed to react with ozone in chloroform to give 1-hydroxy-3-methoxyoxalyl-4,6-dimethoxy-8-methylxanthone-2-carboxylic acid (XI′) which existed in the ring-chain tautomeric structure, methyl 3,11-dihydroxy-4,7-dimethoxy-9-methyl-1,10-dioxofuro[2,3-*c*]xanthene-3-carboxylate (XI). Namely, as detailed in the experimental

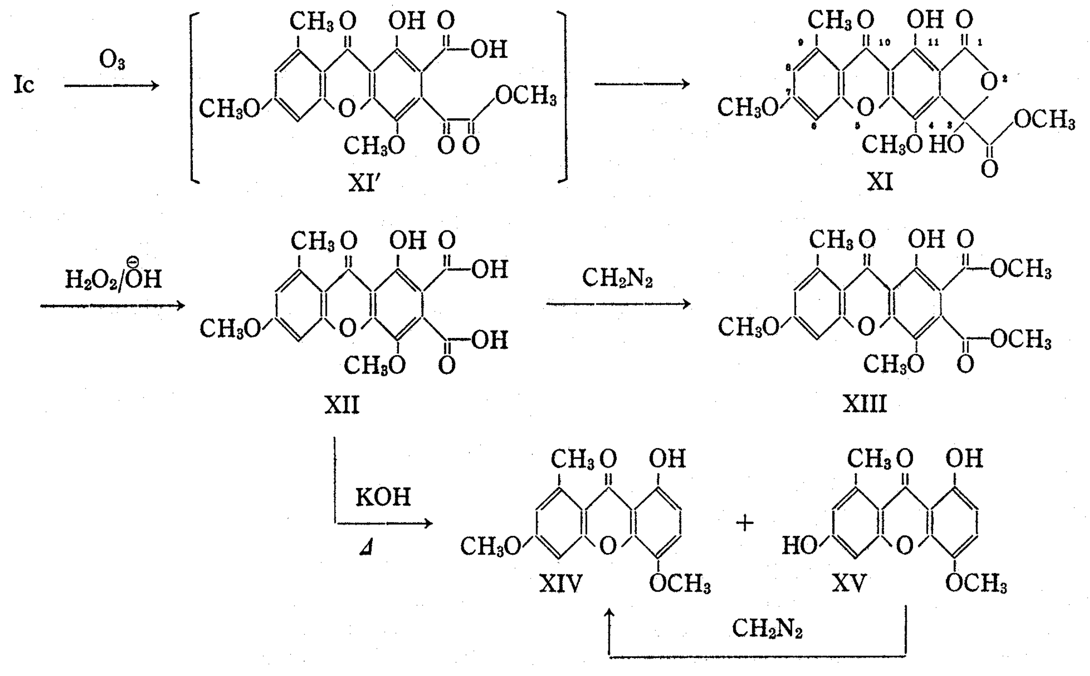

Chart 4

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10) L.F. Fieser, *J. Am. Chem. Soc.*, **70**, 3237 (1948); L.F. Fieser, and A.R. Bader, *J. Am. Chem. Soc.*, **73**, 687 (1951); R.C. Cooke, *Nature*, **162**, 178 (1948); R.C. Cooke and T.C. Somers, *Nature*, **165**, 314 (1950); L.A. Shchkina, A.P. Kandratieva, and M.M. Shemyakin, *J. Gen. Chem. USSR*, **18**, 2121 (1948).

section, the IR spectrum exhibited characteristic peaks due to γ-lactone and ester carbonyl at 1790 cm^{-1} and 1760 cm^{-1}, respectively. Alkaline hydrolysis of compound XI in the presence of hydrogen peroxide gave the xanthonedicarboxylic acid (XII), which was methylated with diazomethane to give the diester (XIII).

Alkali fusion of the diacid (XII) gave the decarboxylated products, 1-hydroxy-4,6-dimethoxy-8-methylxanthone (XIV) and 1,6-dihydroxy-4-methoxy-8-methylxanthone (XV). Compound XIV was identified by the comparison of melting point and spectroscopic data with those of a specimen prepared according to the literature.[11]

Reaction of compound XV with diazomethane gave rise to compound XIV.

Experimental

Bikaverin (Ib) and Norbikaverin (Ia)——A crude red pigment (1 g), isolated from fermentations of *Fusarium solani f. sp. pisi*, was heated at reflux in chloroform (300 ml) for 2 hr. The insoluble substance (250 mg) was filtered off and the filtrate was passed through a column of deactivated silica gel (1 kg) prepared from Wako gel 200 according to the literature.[12] The first elution gave 370 mg of bikaverin (Ib), red needles (from chloroform), mp 320° (dec.), whose spectral data were identical with those of a standard sample. *Anal.* Calcd. for $C_{20}H_{14}O_8 \cdot 1/3CHCl_3$ (Ib): C, 62.59; H, 3.68. Found: C, 62.23; H, 3.92. IR ν_{max}^{KBr} cm^{-1}: 3600—2400. 1655, 1640, 1610. NMR ($CDCl_3$) δ: 2.83 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 6.28 (1H, s, ring-H), 6.64—6.87 (2H, m, ring-H), 12.60 (1H, s, OH), 14.14 (1H, s, OH). MS *m/e*: 382 (M^+).

The second elution gave 40 mg of norbikaverin (Ia), red needles (from chloroform), mp 330° (dec.). *Anal.* Calcd. for $C_{19}H_{12}O_8$ (Ia): C, 61.96; H, 3.29. Found: C, 61.46; H, 3.61. IR ν_{max}^{KBr} cm^{-1}: 3600—2400, 1650, 1610. NMR (CF_3CO_2H) δ: 3.02 (3H, s, CH_3), 4.16 (3H, s, OCH_3), 6.86 (1H, s, ring-H), 7.25—7.35 (2H, m, ring-H). MS *m/e*: 368 (M^+).

Monomethylbikaverin (Ic)——To a solution of Ib (100 mg) in dioxane (120 ml) was added a solution of diazomethane (*ca.* 0.1 g) in ether (8 ml). The mixture was allowed to stand at room temperature for 1 hr, and acetic acid was added to the mixture to decompose excess diazomethane. After evaporation to dryness, the residue was extracted with chloroform. The chloroform solution was submitted to silica gel column chromatography to give orange crystals. Recrystallization from chloroform gave orange needles, mp 307° (dec.). Yield, 45 mg (43%). *Anal.* Calcd. for $C_{21}H_{16}O_8$ (Ic): C, 63.63; H, 4.07. Found: C, 63.65; H, 4.21. IR ν_{max}^{KBr} cm^{-1}: 3600—2000, 1660, 1615, 1600. NMR ($CDCl_3$): 2.85 (3H, s, CH_3), 3.90 (3H, s, OCH_3), 3.95 (3H, s, OCH_3), 4.04 (3H, s, OCH_3), 6.08 (1H, s, ring-H), 6.60—6.80 (2H, m, ring-H), 14.60 (1H, s, OH). MS *m/e*: 396 (M^+).

6,7,10,11-Tetraacetoxy-3,8-dimethoxy-1-methyl-12*H*-benzo[*b*]xanthene (IId)——A mixture of bikaverin (Ib) (80 mg), sodium acetate (0.2 g), zinc dust (1 g) and acetic anhydride (5 ml) was refluxed for 5 hr. Zinc dust was filtered off by suction, and the filtrate was evaporated to dryness *in vacuo*. The residual solid was purified by recrystallization from ethanol and benzene to colorless prisms, mp 208° (dec.). Yield, 15 mg (13%). *Anal.* Calcd. for $C_{28}H_{26}O_{11}$ (IId): C, 62.45; H, 4.87. Found: C, 62.16; H, 4.96. IR ν_{max}^{KBr} cm^{-1}: 1775, 1625, 1600. UV $\lambda_{max}^{95\%\,ethanol}$ nm (log ε): 312 (3.84), 257 (4.64), 240 (4.67). NMR ($CDCl_3$) δ: 2.30 (3H, s, CH_3), 2.42 (6H, s, $2\times CH_3CO$), 2.49 (6H, s, $2\times CH_3CO$), 3.70—3.86 (2H, br, CH_2), 3.81 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 6.41 (2H, br, ring-H), 6.75 (1H, s, ring-H).

7,10,11-Triacetoxy-3,6,8-trimethoxy-1-methyl-12*H*-benzo[*b*]xanthene (IIc)——Methylbikaverin (Ic) (80 mg), together with zinc dust (1 g) and sodium acetate (0.2 g), was refluxed for 5 hr in acetic anhydride (5 ml). The mixture was filtered, and the filtrate was evaporated to dryness *in vacuo*. The residue was purified by recrystallization from ether and benzene to colorless needles, mp 222°. Yield, 20 mg (19%). *Anal.* Calcd. for $C_{27}H_{26}O_{10}$ (IIc): C, 63.52; H, 5.13. Found: C, 63.25; H, 5.25. IR ν_{max}^{KBr} cm^{-1}: 1760, 1620, 1610. UV $\lambda_{max}^{95\%\,ethanol}$ nm (log ε): 320 (3.83), 269 (4.57), 239 (4.60). NMR ($CDCl_3$) δ: 2.28 (3H, s, CH_3), 2.41 (6H s, $2\times CH_3CO$), 2.45 (3H, s, CH_3CO), 3.75—3.83 (2H, br, CH_2), 3.79 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 6.37—6.58 (2H, m, ring-H), 6.80 (1H, s, ring-H). MS *m/e*: 510 (M^+), 468 (M^+-CH_2CO), 426 ($M^+-2\times CH_2CO$), 384 ($M^+-3\times CH_2CO$).

6,7,8,10,11-Pentaacetoxy-3-methoxy-1-methyl-12*H*-benzo[*b*]xanthene (IIe)——Norbikaverin (Ia) (80 mg), together with zinc dust (1 g) and sodium acetate (0.2 g), was refluxed for 5 hr in acetic anhydride (5 ml). The mixture was filtered, and the filtrate was condensed *in vacuo*. The residue was purified by recrystallization from acetone and benzene to colorless needles, mp 244—246°. Yield, 5 mg (4%). IR ν_{max}^{KBr} cm^{-1}: 1775, 1620, 1600. UV $\lambda_{max}^{95\%\,ethanol}$ nm (log ε): 300 (3.99), 242 (4.74). NMR ($CDCl_3$) δ: 2.25 (3H, s, CH_3), 2.27 (3H, s, CH_3CO), 2.38 (6H, s, $2\times CH_3CO$), 2.42 (6H, s, $2\times CH_3CO$), 3.65—3.81 (2H, br, CH_2), 3.76 (3H, s, OCH_3),

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6.39 (1H, br. s, ring-H), 6.45 (1H, br. s, ring-H), 6.98 (1H, s, ring-H). MS *m/e*: 566 (M^+), 524 (M^+-CH_2CO), 482 ($M^+-2\times CH_2CO$), 440 ($M^+-3\times CH_2CO$), 398 ($M^+-4\times CH_2CO$), 356 ($M^+-5\times CH_2CO$).

Alkaline Hydrolysis of Bikaverin (Ib)——A suspension of bikaverin (Ib) (50 mg) in 10% sodium hydroxide (20 ml) was refluxed for 10 hr. The mixture was acidified with conc. hydrochloric acid under ice-cooling and the solution was extracted with chloroform (30 ml × 4). The chloroform solution was evaporated *in vacuo*. The residue (30 mg) was extracted with cold ether. The ether soluble substance was submitted to silica-gel column chromatography. The hexane–ether (10: 1) elution gave a crystalline substance, which was recrystallized from hexane to colorless needles, mp 167° (dec.), whose IR and NMR spectra were identical with those of an authentic sample of everninic acid (III) prepared according to the literature.11) Yield, 2 mg (8%). IR ν_{max}^{KBr} cm^{-1}: 3600—2300, 1620. NMR (CF_3CO_2H): 2.63 (3H, s, CH_3), 3.84 (3H, s, OCH_3), 6.36 (2H, s, ring-H). MS *m/e*: 182 (M^+), 164 (M^+-H_2O).

The hexane mother liquor was evaporated and the residue was purified again by silica gel column chromatography. The hexane–ether (5: 1) elution gave a colorless oil (7 mg), to which petroleum ether was added. The mixture was allowed to stand in a refrigerator overnight to give colorless prisms, mp 61—62°, undepressed on admixture with orcinol (IV), prepared according to the literature.13) Yield, 5 mg (28%). IR ν_{max}^{KBr} cm^{-1}: 3600—3100, 1610, 1600. NMR (CCl_4) δ: 2.20 (3H, s, CH_3), 3.65 (3H, s, OCH_3), 6.01—6.30 (3H, m, ring-H).

7,10-Dihydroxy-3,6-dimethoxy-1-methyl-9,11-dioxo-7,8,9,11-tetrahydrocyclopenta[*b*]xanthene-7-carboxylic Acid (V)——A suspension of Ic (0.15 g) in a 10% solution of potassium hydroxide in 75% ethanol (100 ml) was stirred at room temperature overnight. After refluxing for 5 hr, the mixture was neutralized (pH 4—5) with conc. hydrochloric acid under ice-cooling. After evaporation to dryness *in vacuo*, the residue was purified by recrystallization from acetone to give yellow needles, mp 212° (dec.). Yield, 0.11 g (73%). *Anal.* Calcd. for $C_{20}H_{16}O_9$ (V): C, 60.00; H, 4.03. Found: C, 59.63; H, 4.30. IR ν_{max}^{KBr} cm^{-1}: 3600—2400, 1730 1710, 1630. UV $\lambda_{max}^{95\%\ ethanol}$ nm (log ε): 356 (3.81), 294 (4.41), 261 (4.52). NMR (pyridine-d_5)δ: 2.00 (1H, s, OH), 2.82 (3H, s, CH_3), 3.18—4.78 (2H, ABq, $J=18$ Hz, CH_2), 3.80 (3H, s, OCH_3), 416 (3H, S, OCH_3), 6.78 (1H, d, $J=2$ Hz, ring-H) 6.98 (1H, d, $J=2$ Hz, ring-H). MS *m/e*: 400 (M^+), 356 (M^+-CO_2).

Methyl 7,10-Dihydroxy-3,6-dimethoxy-1-methyl-9,11-dioxo-7,8,9,11-tetrahydrocyclopenta[*b*]xanthene-7-carboxylate (VI)——To a solution of V (40 mg) in dioxane (10 ml) was added a solution of excess diazomethane in ether. After addition of acetic acid (0.5 ml) the mixture was evaporated *in vacuo*. The residue was purified by recrystallization from benzene to yellow needles, mp 264° (dec.). Yield, 30 mg (72%). *Anal.* Calcd. for $C_{21}H_{18}O_9$ (VI): C, 60.87; H, 4.38. Found: C, 60.62; H, 4.50. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600—3200, 1745, 1720, 1640, 1610. UV $\lambda_{max}^{95\%\ ethanol}$ nm (log ε): 357 (3.88), 295 (4.36), 260 (4.55). NMR ($CDCl_3$) δ: 2.83 (3H, s, CH_3), 2.78—3.24 (2H, ABq, $J=18$ Hz, CH_2), 3.78 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 3.98 (3H, s, OCH_3), 4.15 (1H, s, OH), 6.70 (2H, br. s, ring-H), 13.80 (1H, s, OH). MS *m/e*: 414 (M^+), 355 ($M^+-CO_2CH_3$).

Methyl 7-Hydroxy-3,6,10-trimethoxy-1-methyl-9,11-dioxo-7,8,9,11-tetrahydrocyclopenta[*b*]xanthene-7-carboxylate (VII)——To a solution of compound V (20 mg) in dioxane (5 ml) was added a solution of excess diazomethane in ether. After allowing to stand at room temperature for 1 hr, the reaction mixture was evaporated *in vacuo*, and the residue was purified by recrystallization from benzene to pale yellow needles, mp 192°. Yield, 19 mg (92%). *Anal.* Calcd. for $C_{22}H_{20}O_9$ (VII): C, 61.68; H, 4.71. Found: C, 61.91; H, 4.91. IR ν_{max}^{KBr} cm^{-1}: 3600—3100, 1745, 1720, 1655, 1610. UV $\lambda_{max}^{95\%\ ethanol}$ nm (log ε): 335 (3.80), 289 (4.40), 260 (4.45). NMR ($CDCl_3$) δ: 2.82 (3H, s, CH_3), 2.79—3.26 (2H, ABq, $J=18$ Hz, CH_2), 3.78 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 4.02 (3H, s, OCH_3), 4.12 (3H, s, OCH_3), 6.70 (2H, s, ring-H). MS *m/e*: 428 (M^+), 410 (M^+-H_2O), 369 ($M^+-CO_2CH_3$).

Methyl 3,6,10-Trimethoxy-1-methyl-9,11-dioxo-9,11-dihydrocyclopenta[*b*]xanthene-7-carboxylate (VIII)——Compound VII (15 mg) was refluxed in xylene (2 ml) in the presence of a catalytic amount of *p*-toluenesulfonic acid. After 5 hr, the mixture was evaporated *in vacuo*. The residue was purified by silica gel thin-layer chromatography (Merck Kieselgel 60F) using ethyl acetate–benzene (1: 5) as the eluant. Absorption part of *Rf* value 0.25 was collected. Extraction with ethyl acetate and acetone gave a crystalline substance, which was recrystallized from ethyl acetate to pale brown needles, mp 248—250° (dec.). Yield, 7 mg (49%). *Anal.* Calcd. for $C_{22}H_{18}O_8\cdot 1/2H_2O$ (VIII): C, 63.00; H, 4.53. Found: C, 63.14; H, 4.66. IR ν_{max}^{KBr} cm^{-1}: 1740, 1705, 1645, 1615. UV $\lambda_{max}^{95\%\ ethanol}$ nm (log ε): 415 (3.88), 290 (4.23), 261 (4.25), 228 (4.38). NMR ($CDCl_3$) δ: 2.84 (3H, s, CH_3), 3.90 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 4.00 (3H, s, OCH_3), 4.12 (3H, s, OCH_3), 6.20 (1H, s, ring-H), 6.70 (2H, s, ring-H). MS *m/e*: 410 (M^+), 396 (M^+-CH_2), 352 ($M^+-CH_2CO_2$).

Methyl 3,11-Dihydroxy-4,7-dimethoxy-9-methyl-1,10-dioxofuro[2,3-*c*]xanthene-3-carboxylate (XI)——To a solution of compound Ic (0.5 g) in chloroform (200 ml) was bubbled ozone generated by an ozonizer. Bubbling was continued for 15 min until the solution became yellow color. After allowing to stand at room temperature for 30 min, the solution was evaporated to dryness *in vacuo*. The residue was purified by recrystallization from ethyl acetate and ethanol to give pale yellow needles, mp 236° (dec.). Yield, 0.36 g (69%). *Anal.* Calcd. for $C_{20}H_{16}O_{10}$ (XI): C, 57.69; H, 3.87. Found: C, 57.63; H, 3.86. IR ν_{max}^{KBr} cm^{-1}: 3800—2500, 1790, 1760, 1615. UV $\lambda_{max}^{95\%\ ethanol}$ nm (log ε): 357 (3.88), 278 (4.26), 249 (4.51), 243 (4.51). NMR ($CDCl_3$):

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13) F. Henrick and G. Nachtigall, *Ber.*, **36**, 889 (1903).

2.89 (3H, s, CH_3), 3.85 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 4.01 (3H, s, OCH_3), 5.26—5.43 (1H, br.s, OH), 6.72—6.83 (2H, br.s, ring-H), 13.98 (1H, s, OH). MS *m/e*: 416 (M^+), 398 (M^+-H_2O), 357 ($M^+-CO_2CH_3$).

2,3-Dicarboxy-1-hydroxy-4,6-dimethoxy-8-methylxanthone (XII)——Compound XI (40 mg) was added to a mixture of a 10% potassium hydroxide–ethanol solution (2 ml) and 30% hydrogen peroxide (2 ml). The reaction mixture was stirred at room temperature for 30 min. Crystals separated were collected by suction, and dissolved in water (20 ml). The solution was neutralized (pH 4—5) with conc. hydrochloric acid, and the mixture was extracted with ether. The ether solution was evaporated and the residue was purified by recrystallization from dioxane–ether to yellow needles, mp 304—305° (dec.). Yield, 20 mg (57%). IR ν_{max}^{KBr} cm^{-1}: 3800—2300, 1715, 1675, 1640, 1610. NMR (pyridine-d_5) δ: 2.82 (3H, s, CH_3), 3.80 (3H, s, OCH_3), 4.20 (3H, s, OCH_3), 6.76 (1H, d, $J=2$ Hz, ring-H), 7.01 (1H, d, $J=2$ Hz, ring-H). MS *m/e*: 356 (M^+-H_2O), 341 ($M^+-H_2O-CH_3$), 311 ($M^+-H_2O-CO_2H$), 269 ($M^+-CH_3-2\times CO_2H$).

2,3-Dimethoxycarbonyl-1-hydroxy-4,6-dimethoxy-8-methylxathone (XIII)——Compound XII (20 mg) was added to a solution of excess diazomethane in ether. After 5 min, the mixture was evaporated and the residue was purified by recrystallization from ethyl acetate and ether to give yellow needles, mp 186°. Yield, 20 mg (93%). *Anal.* Calcd. for $C_{20}H_{18}O_9$ (XIII): C, 59.70; H, 4.51. Found: C, 59.49; H, 4.39. IR ν_{max}^{KBr} cm^{-1}: 3800—2400, 1735, 1700, 1640, 1620, 1600. UV $\lambda_{max}^{95\%\ ethanol}$ nm (log ε): 360 (3.87), 285 (4.24), 251 (4.46), 245 (4.56). NMR ($CDCl_3$) δ: 2.87 (3H, s, CH_3), 3.92 (3H, s, OCH_3), 3.95 (3H, s, OCH_3), 3.97 (3H, s, OCH_3), 3.99 (3H, s, OCH_3), 6.75 (1H, d, $J=2$ Hz, ring-H), 6.01 (1H, d, $J=2$ Hz, ring-H), 14.02 (1H, s, OH). MS *m/e*: 402 (M^+), 387 (M^+-CH_3), 371 (M^+-OCH_3), 284 ($M^+-2\times CO_2CH_3$).

1-Hydroxy-4,6-dimethoxy-8-methylxanthone (XIV) and 1,6-Dihydroxy-4-methoxy-8-methylxanthone (XV)——Potassium salt of compound XII prepared from compound XII (0.15 g) and potassium hydroxide was placed in a test tube, and heated in an oil bath at 270—280° for 5 min. After cooling, the reaction mixture was acidified with 10% hydrochloric acid. The mixture was extracted with chloroform. The chloroform solution was evaporated, and the residue was purified by silica-gel thin-layer chromatography (Merck Kieselgel 60F) using benzene–ethyl acetate (5:1) as the eluant. Fraction bands at *Rf* 0.70 and 0.39 were collected, and extracted with the mixture of ethyl acetate and acetone (10:1), respectively. The former extraction afforded 1.5 mg of compound XIV, mp 162°, undepressed on admixture with a sample of XIV prepared according to the literature.[11] The latter extraction gave 2 mg (2%) of compound XV, mp 230°. *Anal.* Calcd. for $C_{15}H_{12}O_5$ (XV): C, 66.17; H, 4.44. Found: C, 65.85; H, 4.42. IR ν_{max}^{KBr} cm^{-1}: 3600—2400, 1650, 1610. NMR ($CDCl_3$) δ: 2.82 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 6.55—7.12 (4H, m, ring-H), 12.62 (1H, s, OH). MS *m/e*: 272 (M^+), 257 (M^+-CH_3). Compound XV (2 mg) was added to a solution of diazomethane in ether. After 10 min, the mixture was evaporated to give compound XIV, mp 164°, undepressed on admixture with a sample obtained above.

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