[Chem. Pharm. Bull. 22(1) 115—122 (1974)]

UDC 547.9.04 : 547.384.04 : 541.14

Usnic Acid. XI.[1] The Photolysis of Dihydrousnic- and Methyldihydrousnic-acids

Kōtaro Takahashi, Masako Takani, and Akiko Fukumoto

Faculty of Pharmaceutical Sciences, University of Kanazawa[2]

(Received May 11, 1973)

The structures of the photolysis products of dihydro- and methyldihydro-usnic acids were studied and the mechanism of the photolysis was discussed.

In the previous papers,[1,3] the reaction mechanism of the formation of 7-acetyl-3,5-dimethyl-6-hydroxycoumaran-2-one from dihydrousnic acid (I) by the pyrolysis was discussed, in which the 1,5-suprafacial sigmatropic transformation[4] or the Jacobson and the retro-Jacobson rearrangements were involved. There have been other reports on remarkable differences between usnic acid and I in the chemical degradation reactions, but scarcely any in the photo-reaction. It was reported[5] that on irradiation with ultraviolet (UV) light in the presence of a suitable nucleophile, *ortho*-type cyclohexanedienones underwent smooth fission to acids, but *d*-usnic acid in dioxane gave only racemic isomer. This paper deals with the photolysis of I and methyldihydrousnic acid (II) in methanol, ethanol and dioxane, respectively.

The Photolysis of I in Methanol

I in methanol was irradiated with UV light at —18° in the presence of benzophenone as a sensitizer to afford yellow prisms (III), $C_{19}H_{18}O_6$, mp 194°, faint yellow needles (IV), $C_{19}H_{18}O_6$, mp 218—220°, yellow prisms (V), $C_{19}H_{18}O_6$, mp 174—176° and 1,1-diphenylethane-1,2-diol (VI).[6] III, IV and V gave yellow green, blue green and dark green colorlations with $FeCl_3$, respectively. The UV spectra of III, IV and V resemble that of the methylation product (VII)[7] of usnic acid, suggesting that they are structurally related to VII. III and V show the infrared (IR) band (cm^{-1}) at 1640 (chelated C=O), respectively, but IV does not show such a band and shows a band at 1665 (α,β-unsatd. C=O). But they do not show the characteristic broad band (1550—1500) of the triketone group of I or usnic acid. III and V exhibit the nuclear magnetic resonance (NMR) signals (δ-value) of a OH group at 9.33 and 9.40, respectively, as I does at 9.51,[8] while IV exhibits a signal at 5.89. These spectral evidences indicate that III and V have a OH group at C_9 and a C=O group at C_1, which are chelated, and IV does not have such a chelated OH group. III, IV and V give rise to fragment ions on the mass spectra (MS), such as *m/e* 313 (M^+—29 (CHO)), *m/e* 29 (CHO), respectively, indicating that III, IV and V have a furan ring which has α-proton, respectively. So the NMR signals of III, IV and V could be assigned to each group,[9] as shown in Table I, taking into consideration those of I and VII and the evidences mentioned below: The C=O

---

[1] Part X: K. Takahashi and M. Takani, *Chem. Pharm. Bull.* (Tokyo), 20, 1230 (1972).
[2] Location: *Takaramachi, Kanazawa.*
[3] K. Takahashi and M. Takani, *Chem. Pharm. Bull.* (Tokyo), 19, 2079 (1971).
[4] R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH Weinheim/Bergstr., 1970, p. 114.
[5] D.H. Barton and G. Quinkert, *J. Chem. Soc.*, **1960**, 2.
[6] H. Goth, P. Cerutti and H. Schmid, *Helv. Chim. Acta.*, **48**, 1395 (1965).
[7] L. Bertilson and C.A. Wachmeister, *Acta. Chim. Scand.*, **22**, 3081 (1968).
[8] K. Takahashi and M. Takani, *Chem. Pharm. Bull.* (Tokyo), **19**, 2072 (1971).
[9] J.P. Kutney, H.W. Hansen, and G. Vijakumaran Nair, *Tetrahedron*, **27**, 3323 (1971).

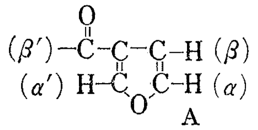
Table I. The NMR Data (δ-value, J in Hz)

	Ang-CH_3	Ar-CH_3	CH_3 of furan α	 β	 α'	$COCH_3$	>CH-C$\underline{H}_2$-
III	1.70(s)3H	2.08(s)3H			2.61(d)3H (J=0.6)	2.58(s)3H	3.13(q)2H (J=4.5, 1.2)
IV	1.86(s)3H	2.06(s)3H		2.20(d)3H (J=1.8)		2.56(s)3H	3.03(q)2H (J=4.5, 1.2)
V	1.72(s)3H	2.04(s)3H		2.18(d)3H (J=1.2)		2.55(s)3H	3.40(d)2H (J=4.2)
X	1.68(s)3H	2.06(s)3H	2.28(s)3H		2.58(s)6H		3.00(q)2H (J=4.8, 1.2)
XI	1.89(s)3H	2.09(s)3H	2.24(s)3H	2.14(s)3H		2.59(s)3H	3.05(q)2H (J=4.2, 1.2)
XII	1.71(s)3H	2.06(s)3H			2.56(s)6H		
VII	1.74(s)3H	2.08(s)3H		2.26(d)3H (J=1.3)		2.68(s)3H	
I	1.67(s)3H	2.01(s)3H				2.54(s)3H 2.56(s)3H	3.10(d)2H (J=4.8)

	>C$\underline{H}$-CH_2-	>CH-CH=	>C=CH-	Furan-H	Ar-H	OH non-chelated	 chelated
III	4.96(t)1H (J=4.5)			7.21(m)1H			9.33(s)1H 13.32(s)1H
IV	4.91(t)1H (J=4.5)			7.15(m)1H		5.89(s)1H	13.41(s)1H
V	5.02(t)1H (J=4.2)			7.18(m)1H			9.40(s)1H 13.30(s)1H
X	4.92(t)1H (J=4.8)						9.56(s)1H 13.35(s)1H
XI	4.90(t)1H (J=4.2)					6.19(s)1H	13.40(s)1H
XII		5.30, 5.37 (d)1H 5.48, 5.55 (d)1H			7.38, 7.34 (s) (s) 10H		10.07(s)1H 13.34(s)1H
VII			6.26(s)1H	7.25(q)1H (J=1.3)			11.07(s)1H 13.43(s)1H
I	4.82(t)1H (J=4.8)						9.51(s)1H 13.70(s)1H 18.70(s)1H

abbreviation: s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet

group at the β'-position of the furan ring such as A causes the deshielding effects[10] on α'-proton (0.70 ppm) and β-proton (0.48 ppm), significantly, but on α-proton (0.05 ppm), scarcely, providing[11] that α-proton of furan resonates at 7.40 and β-proton at 6.30. So the signals at 7.21 of III, at 7.15 of IV and 7.18 of V could be assigned to the α-proton of furan ring, respectively. Similarly, the C=O group at the β'-position could be assumed to cause the deshielding effects on α, α' and β-methyl groups, but the effects are probably smaller than those on α, α' and β-protons due to the longer distance. So the signal of III at 2.61 could be



A

---

[10] C. Kaneko, T. Tsuchiya, and M. Ishikawa, *Chem. Pharm. Bull.* (Tokyo), **11**, 271 (1958).
[11] E.J. Corey, G. Slomp, Sukdev, S. Tobinaga, and E.R. Glazier, *J. Am. Chem. Soc.*, **80**, 1204 (1958).

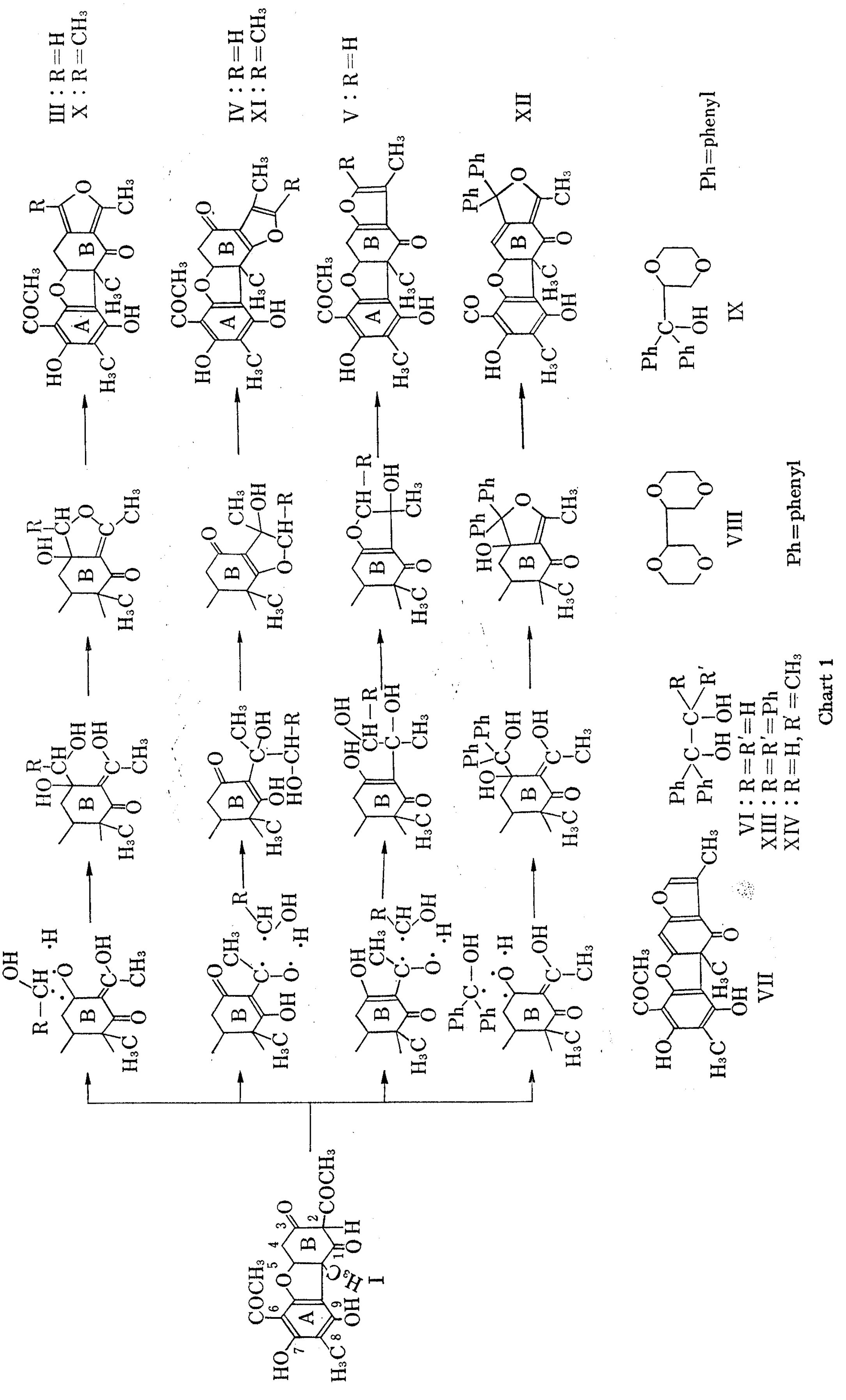

I
III : R=H
X : R=CH$_3$
IV : R=H
XI : R=CH$_3$
V : R=H
XII
VII
VI : R=R'=H
XIII : R=R'=Ph
XIV : R=H, R'=CH$_3$
VIII
IX
Ph=phenyl
Ph=phenyl

Chart 1

assigned to α′-methyl protons of furan ring and the signals of IV at 2.20 and of V at 2.18 could be assigned to β-methyl protons of furan ring, providing[12] that α-methyl protons of α-methyl furan resonates at 2.18 and β-methyl protons of β-methyl furan at 1.95. The deshielding effects of β′-carbonyl group on α′ and β-methyl protons of furan are calculated to be 0.43 ppm, and 0.25, 0.23 ppm, respectively. These spectral evidences indicate that III, IV and V could be formulated as shown in Chart 1 and might be produced by the photochemical addition of methanol to the ring B of I. Analyses of MS also support the proposed structures of III, IV and V, as shown in Chart 2. I was photolysed with benzophenone in dioxane–methanol (45: 1) at room temperature to afford only 2,2′-bidioxane (VIII)[13] and α,α-diphenyl-1,4-dioxane-2-methanol (IX),[14] and was photolysed with benzophenone in methanol at room temperature to afford III, IV, V and methylresacetophenone.

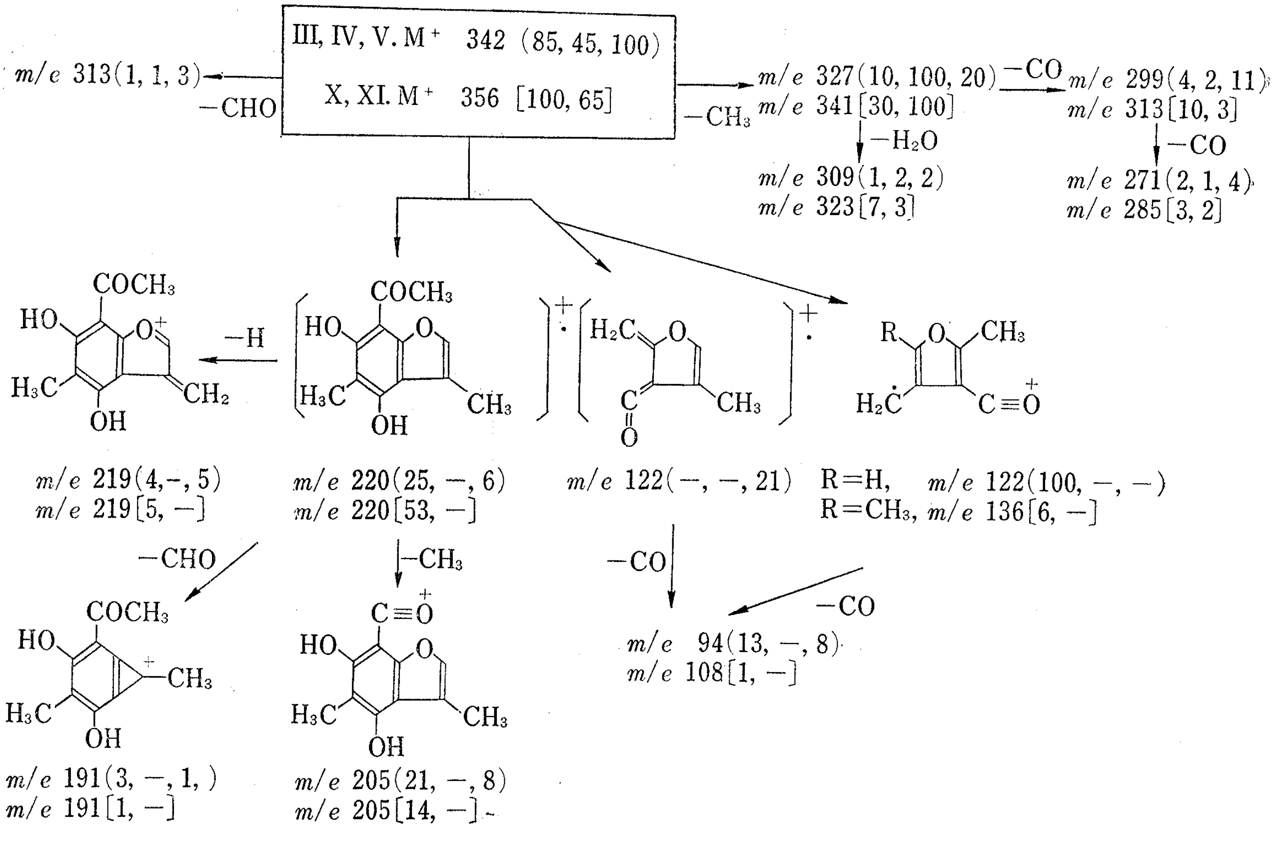


Chart 2. The Fragmentations of III, IV, V, X, and XI

The figures in round and square brackets are the relative intensities of the fragment ions of III, IV, V and X, XI, respectively. - in bracket shows very low intensity.

The Photolysis of I in Ethanol

The result mentioned above suggests that I might give methyl homologs of III, IV and V by the irradiation in ethanol. So I was photolysed under the same condition in ethanol to afford faint yellow needles (X), $C_{20}H_{20}O_6$, mp 175°, faint yellow needles (XI), $C_{20}H_{20}O_6$, mp 206—208°, yellow plates (XII), $C_{31}H_{26}O_6$, mp 222—223° and benzopinacol[14] (XIII), 1,1-diphenylpropane-1,2-diol[15] (XIV). X, XI and XII gave green colorations with $FeCl_3$, respectively. The UV of X resembles that of III, indicating that X is structurally related

---

12) S. Rodmar, S. Foresen, B. Gestblom, S. Gronowitz, and R.A. Hoffman, *Acta, Chim. Scand.*, **19**, 485 (1965).

13) G. Sosnovsky, *Tetrahedron*, **21**, 871 (1965).

14) W. Droste, H.D. Scharf, and F. Korte, *Ann.* **724**, 71 (1969).

15) K.A. Thare and I.G. Vasi, *Chem. Abstr.*, **55**, 24551 i (1961).

to III. X shows IR band (cm^{-1}) at 1635 (chelated C=O), but not a band of triketone group. X exhibits the NMR signals at nearly equal δ-values as III, except a signal of a proton of furan ring of III at 7.21 and a methyl signal of X at 2.28 (Table I). The signal at 2.28 could be assigned to α-methyl protons and the signal at 2.58 to α'-methyl protons, as mentioned above. The deshielding effect of the β'-carbonyl group on α-methyl protons of furan is calculated to be 0.10 ppm and the effect on α'-methyl protons is calculated to be 0.40 ppm. X exhibits also the signal of a chelated OH group at 9.56 as III and I. These spectral evidences indicate that X is methyl homologue of III and could be formulated as shown in Chart 1. The UV of XI is virtually similar to that of IV. XI exhibits IR bands (cm^{-1}) at 3450 (OH), 1660 (α,β-unsatd. C=O), 1630 (chelated Ar-COCH$_3$), but not a band of triketone group as IV. XI exhibits the NMR signals at nearly equal δ-values to those of IV, except a methyl signal at 2.24 of XI and a signal of a proton of furan ring at 7.15 of IV. (Table I). The signal at 2.24 and 2.14 of XI could be assigned to α-methyl- and β-methyl protons, respectively. The deshielding effect of the β'-carbonyl group on α-methyl protons of furan is calculated to be 0.06 ppm and that on β-methyl protons to be 0.19 ppm. XI shows also the signal of a non-chelated OH group at 6.19 as IV. These spectral evidences indicate that XI is a methyl homologue of IV and could be formulated as shown in Chart 1. XII exhibits IR band (cm^{-1}) at 1640 (chelated C=O), but not a band of triketone group, and exhibits the NMR signals of an ang-CH$_3$, an Ar-CH$_3$, a CH$_3$ (2.56), an Ar-COCH$_3$, two chelated OH, $>$CH–CH= and characteristically ten aromatic protons, as shown in Table I. The rather low field methyl signal (2.56) could be assigned to α'-methyl protons, which are probably situated as are those of III and X. These spectral evidences indicate that XII could be formulated as shown in Chart 1. XII might be produced by the photochemical addition of benzophenone to I. The MS of X, XI and XII could be analysed as shown in Chart 2 and Chart 3. The mechanism of the formation of III, IV and V from I in methanol and of X, XI and XII from I in ethanol could be explained as shown in Chart 1, in which the excited triplet state (n—π^*) of one of the C=O

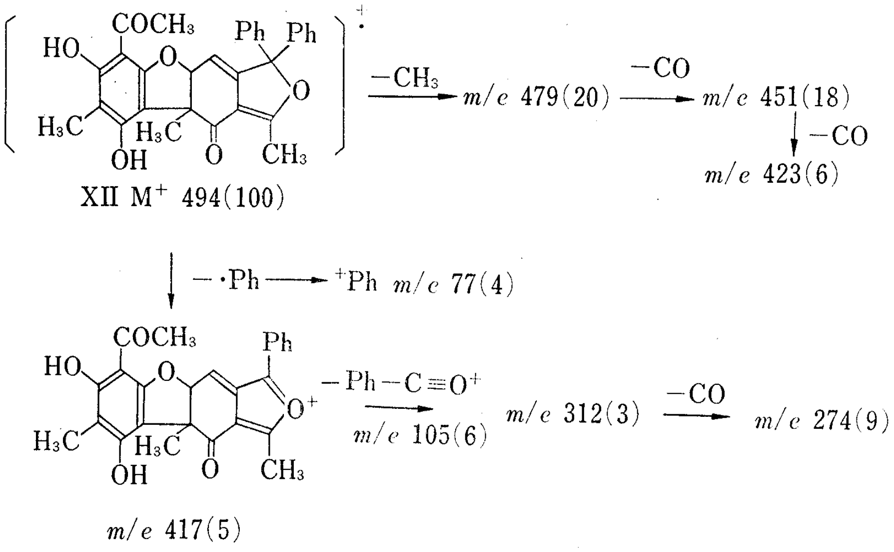
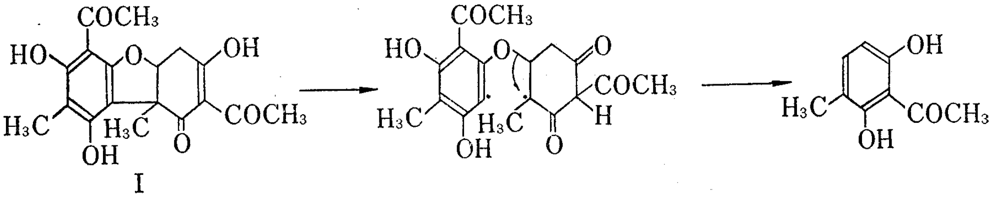


Chart 3. The Fragmentation of XII

The figures in round brackets are the intensities.



I

Chart 4

groups of I and the photochemical addition to it of the solvent might be involved, analogously[6] as in the formation of VI, XIII and XIV from benzophenone. The mechanism of the formation of methylresacetophenone from I could be explained as shown in Chart 4, but further investigation should be performed.

The Photolysis of Methyldihydrousnic Acid (II)

II in dioxane at room temperature, or in methanol at room temperature or at −18° in the presence of benzophenone was photolysed to give IX and colorless needles (XV), $C_{13}H_{14}O_4$, mp 120—121°. But no photochemical addition product has not been obtained. Probably the non-aromatic ring A of II might have caused some effects on the stability of the ring B to the photolysis. XV gave red coloration with $FeCl_3$ and exhibits the IR bands (cm^{-1}) at 1650 ($\alpha\beta$, $\alpha'\beta'$-unsatd. C=O), 1530—1570 (triketone), and the NMR signals at 1.47, 1.59 (6H, gem-dimethyl), 2.25, 2.28 (3H, methyl), 2.62, 2.77 (3H, $COCH_3$), 7.18 (m, 1H, an α-proton of furan ring), 18.46, 18.58 (1H, chelated enol OH), but XV in CF_3COOD exhibits the NMR signals of a gem-dimethyl group at 1.62 and a $COCH_3$ group at 2.82 as singlet, respectively, indicating that XV has a triketone group and is present in two types of enol forms in respect to the location of the hydrogen bond in $CDCl_3$ solution. XV was oxidised with hydrogen peroxide to afford colorless prisms (XVI), $C_{10}H_{12}O_5$, mp 190—192° (decomp.), which gave colorless needles of dimethyl ester (XVII), $C_{12}H_{16}O_5$, mp 35.5° with diazomethane. XVII exhibits the NMR signals at 1.59 (s, 6H, gem-dimethyl), 2.16 (d, 3H, methyl, J=1.5 Hz),[12] 3.71 (s, 3H, $COOCH_3$), 3.84 (s, 3H, $COOCH_3$) and 7.06 (m, 1H, α-proton of furan ring). These spectral evidences, taking consideration the structure of II, indicate that XVII, XVI and consequently XV could be formulated as shown in Chart 5. The mechanism of the formation of XV from II could be explained as shown in Chart 5.

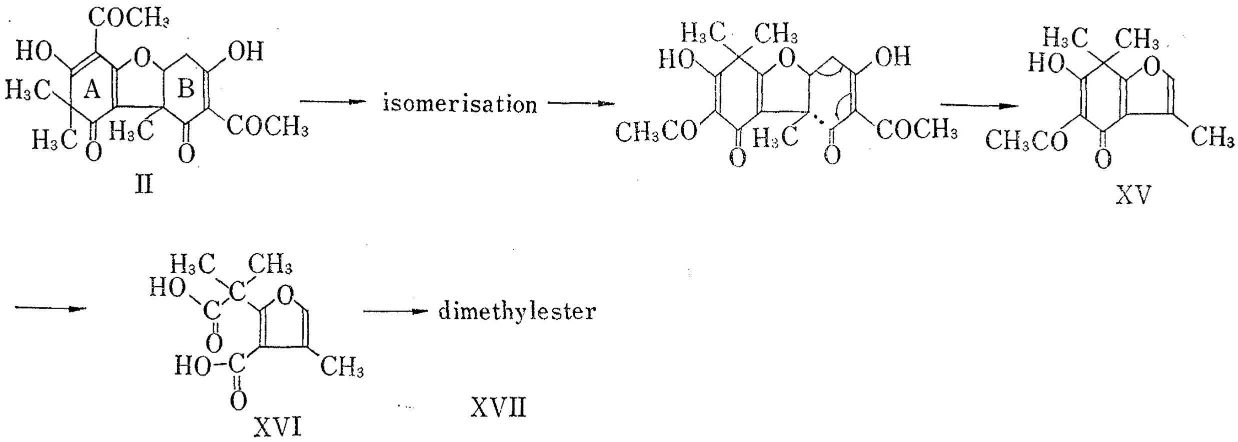
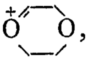


Chart 5

Experimental

The following instruments were used for the physical data. Melting point: Yanagimoto Micro-Melting Apparatus (a hot-stage type); UV spectra: Hitachi EPS-2U recording spectrometer in ethanol; IR spectra: Nippon Bunko IR-G spectrometer in KBr; NMR spectra: JNM-C-60-H high resolution instrument at 60 MHz in $CDCl_3$ with $(CH_3)_4Si$ as internal reference; Mass spectra: JNM-OISG mass spectrometer; Optical rotation: Nippon Bunko Automatic Polarimeter DIP-SL at 589 nm, not otherwise stated.

Irradiation of I in Methanol at −18°——Two grams of I and 0.1 g of benzophenone in 400 ml of methanol was irradiated for 13.5 hr at −18° under nitrogen in a pyrex flask by a high pressure mercury lamp (Halos type PIH-300). The methanolic solution from five runs was evaporated *in vacuo* to about 50 ml to afford 4.5 g of powder (P), which consisted of I mainly, and a brown methanolic solution. The methanolic solution gave 5.8 g of brown resinous substance, which was chromatographed over 400 g of Kieselgel with benzene–AcOEt (10: 1). A fraction of *Rf* 0.54 gave yellow prisms (III) of mp 194° from methanol. Yield: 50 mg. UV λ_{max} nm (log. ε): 229 (4.34, sh), 286.5 (4.37), 335 (3.66). IR ν_{max} (cm^{-1}): 1640 (chelated C=O), 1280, 1080 (-C-O-C-),[16] 860, 765 (ν_{CH} of furan ring).[16] *Anal.* Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found. C, 66.98; H, 5.36. A fraction of *Rf* 0.29 gave yellow prisms (IV) of mp 218—220° from methanol. Yield: 340 mg. UV λ_{max} nm (log. ε): 230 (4.19, sh), 287.5 (4.20), 334 (3.94). IR ν_{max} (cm^{-1}): 3250 (OH), 1665 ($\alpha\beta$-unsatd. C=O), 1630 (chelated $COCH_3$), 1290, 1250, 1085 (-C-O-C-), 865, 764 (ν_{CH} of furan ring). *Anal.* Found: C, 66.47; H, 5.29. A fraction of *Rf* 0.2 gave colorless needles (VI) of mp 120° from benzene. (lit.[6] mp 120—121°). Yield: 72 mg. NMR (δ ppm, at 78°): 2.35 (br, 2H, two OH), 4.17 (s, 2H, $-CH_2-$), 7.35 (m, 10H, Ar-H). IR (cm^{-1}): 3370, 3015, 2945, 1597, 1490, 1445, 1382, 1360, 1211, 1103, 1070, 1045, 951, 909, 881, 762, 702. Mass Spectrum (*m/e*, relative intensity): 214 (M^+, 3), 196 ($M^+ - H_2O$, 4), 184 (61), 183 ($^{ph}_{ph}{>}C{=}\overset{+}{O}H$, 75), 165 (51), 152 (24), 106 (38), 105 ($ph\text{-}C{\equiv}O^+$, 84), 91 (32), 78 (38), 77 (ph^+, 100), 76 (23), 51 (59), 39 (14), 31 (10). *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found. C, 78.89; H, 6.52. The powder (P) of 4.5 g, mentioned above, was chromatographed over Kieselgel (200 g) with benzene–AcOEt (10: 1) to give 500 mg of powder of *Rf ca.* 0.6, which was almost free from I. This was again chromatographed over Kieselgel (25 g) with benzene–AcOEt (50: 1) to give faint yellow powder, which was chromatographed over Kieselgel with benzene–AcOEt (100: 1) to give faint yellow plates (V) of mp 174—176° from methanol. Yield: 28 mg. *Rf*: 0.61 (benzene–AcOEt=10: 1). UV λ_{max} nm (log. ε): 230 (4.28, sh), 285 (4.28), 339 (3.60). IR ν_{max} (cm^{-1}): 1640 (chelated C=O), 1280, 1085 (-C-O-C-),[16] 865, 765 (ν_{CH} of furan ring). *Anal.* Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found. C, 67.06; H, 5.75.

Irradiation of I in Dioxane–Methanol at Room Temperature——I (4.4 g) and benzophenone (0.1 g) in dioxane–methanol (450 ml+10 ml) was irradiated for 19 hr at room temp. under the same condition mentioned above. The solution from 4 runs was concentrated to give 12.6 g of I and resinous substance (3.7 g), the latter of which was chromatographed over Kieselgel (190 g) with benzene–AcOEt (10: 1). The fraction of *Rf* 0.4 gave colorless needles (IX) of mp 163° from CCl_4, which was proved to be identical with α,α-diphenyl-1,4-dioxane-2-methanol,[14] obtained by the photolysis of II in dioxane by mixed fusion and IR. The fraction of *Rf* 0.1 gave colorless needles of 2,2′-bidioxane (VIII)[13] of mp 154—155° from ethanol. Yield: 85 mg. IR ν_{max} (cm^{-1}): 2955, 2910, 1460, 1363, 1333, 1304, 1279, 1230, 1125, 1064, 995, 901, 880, 689. NMR (δ, ppm): 3.36, 3.49, 3.66, 3.70, 3.82, 3.96 (a multiplet). Mass Spectrum (*m/e*, relative intensity): 174 (M^+, 69), 159 (5), 156 (5), 143 (66), 130 (69), 115 (24), 112 (52), 101 (26), 99 (58), 87 (, 94), 86 (100), 73 (68), 59 (80), 57 (59), 45 (66), 43 (68), 31 (67), 29 (45). *Anal.* Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.95; H, 8.04.

Irradiation of I in Methanol at Room Temperature——I (5 g) and benzophenone (250 mg) in methanol was irradiated for 10 hr at room temp. The methanolic solution was concentrated to 30 ml to afford yellow powder (P) (4 g), which was filtered off. The methanolic filtrate from 10 runs was evaporated to give resinous substance (8.8 g), which was chromatographed over Kieselgel (150 g) with benzene–AcOEt (10: 1). The eluate (30 ml each) was separated into two portions: Portion A from No. 7 to 9 and portion B from No. 10 to 13. Portion A (450 mg) was chromatographed over Kieselgel (45 g) with benzene–AcOEt (20: 1). The fractions (10 ml each) from No. 6 to 8 gave 18 mg of yellow prisms (III) of mp 194° from methanol. (mixed fusion and IR). *Anal.* Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.60; H, 5.52. The fractions from No. 14 to 23 gave yellow needles (90 mg) of mp 141°, which was proved to be identical with methylresacetophenone by mixed fusion and IR. *Anal.* Calcd. for $C_9H_8O_3$: C, 65.05; H, 6.07. Found: C, 65.34; H, 6.13. Portion B (840 mg) was rechromatographed over Kieselgel (40 g) with benzene–AcOEt (10: 1). The fractions (10 ml each) from No. 13 to 27 gave colorless needles (IV) (480 mg) of mp 218° from benzene. (mixed fusion and IR). *Anal.* Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.91; H, 5.30. The other fractions were collected to give resinous substance (3 g), which was rechromatographed over silicic acid (100 g) with benzene–AcOEt (10:1). The fractions (10 g each) from No. 50 to 90 gave colorless needles (VI) (67 mg) of mp 121° from benzene (mixed fusion and IR). The yellow powder (P), mentioned above, was chromatographed over Kieselgel (150 g) with benzene–AcOEt (10: 1). The fractions (10 g each) from No 16 to 20 (39 mg) was again chromatographed over Kieselgel with benzene–AcOEt to give yellow prisms (V) (20 mg) of mp 174—176° from methanol (mixed fusion and IR). *Anal.* Found: C, 67.16; H, 5.27. The fractions from No. 21 to 22, 4.3 g of I was recovered.

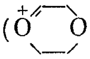
Irradiation of I in Ethanol at −18°——I (2 g) and benzophenone (0.4 g) in ethanol (400 ml) was irradiated for 10 hr at −18° under the similar condition. The ethanolic solution from 15 runs was evaporated to give resinous substance (18 g) and I (13.3 g). The former was chromatographed over Kieselgel (300 g) with benzene–AcOEt (20: 1). The eluate (100 ml each) was separated into three portions: portion A from No 2, portion B from No 3 to 5 and portion C from No 6 to 50. Portion A (87 mg) was chromatographed over Kieselgel (45 g) with benzene–AcOEt (100: 1). The fractions (5 g each) from No 14 to 21 gave colorless needles (XIII) of mp 184—185° from methanol (lit.[14] mp 187°). Yield: 20 mg. IR[17] ν_{max} (cm^{-1}): 3550, 1595, 1445, 1040, 1025, 755, 695. *Anal.* Calcd. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.43; H, 6.07. Portion B

---

[16] L.H. Briggs and L.D. Colebrook, *J. Chem. Soc.*, **1960**, 2458.

[17] IR card, 1960, IX, No 449. Infrared Committee of Japan, published by Nankodo Co., Ltd, Tokyo, Japan.

(960 mg) was chromatographed over Kieselgel (120 g) with benzene–AcOEt (30:1). The fractions (10 g each) from No. 1 to 33 was again chromatographed over Kieselgel (60 g) with benzene–AcOEt (100: 1). The fractions (5 g each) from No. 31 to 48 gave yellow plates (XII) of mp 222—223° from methanol–benzene. Yield: 30 mg. UV λ_{max} nm (log. ε): 285 (4.35), 342 (4.13). IR (cm^{-1}) 1640 (chelated C=O), 1275, 1090 (-C-O-C-). *Anal.* Calcd. for $C_{31}H_{26}O_6$: C, 75.29; H, 5.30. Found: C, 75.51; H, 5.48. The fractions from No. 34 to 45, obtained from the first chromatogram of the portion B, gave faint yellow needles (X) of mp 175° from methanol. Yield: 40 mg. UV λ_{max} nm (log. ε): 235 (4.26), 287.5 (4.31), 340 (3.76, sh). IR ν_{max} (cm^{-1}): 1635 (chelated C=O), 1280,1090 (-C-O-C-). *Anal.* Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.18: H, 5.70. Portion C (6.6 g) was crystallised from methanol to give 4 g of I. The mother liquor was evaporated to give 2.6 g of powder, which was chromatographed over Kieselgel (250 g) with benzene–AcOEt (30: 1). The fractions (10 g each) from No. 320 to 420 gave 600 mg of powder, which was again chromatographed over Kieselgel (120 g) with benzene–AcOEt (10: 1). The fractions (10 g each) from No. 46 to 52 gave faint yellow needles (XI) of mp 206—208° from methanol. Yield: 60 mg. UV λ_{max} nm (log. ε): 234 (4.26, sh), 289 (4.30), 335 (3.71). IR ν_{max} (cm^{-1}): 3450 (OH), 1660 ($\alpha\beta$-unsatd. C=O), 1630 (chelated C=O), 1275, 1085 (-C-O-C-). *Anal.* Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.52; H, 5.65. The fractions from No. 53 to 80 gave colorless plates (XIV) of mp 96° from methanol. Yield: 180 mg. $[\alpha]^{21°}=0.00$ ($c=1.07$, EtOH). (lit.[15]) mp 94°, $[\alpha]^{28°}=-97.16°$). NMR (δ, ppm) 1.13 (d, 3H, $J=6.0$ Hz, $C\underline{H}_3$-CH-), 2.35 (br, 2H, OH), 4.78 (q, 1H, CH_3-C$\underline{H}$-, $J=6.0$ Hz), 7.34 (m, 10H, Ar-H). IR ν_{max} (cm^{-1}): 3550, 3450, 1600, 1495, 1450, 1060, 990, 900, 770, 750, 700. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.22; H, 7.13.

Irradiation of II in Dioxane at Room Temperature——II (6 g) and benzophenone (0.2 g) in dioxane (300 ml) was irradiated for 10 hr at room temp. under the similar condition. The dioxane solution from five runs was evaporated to give resinous substance, from which II (12 g) was recovered by crystallisation from methanol. The methanolic liquor was evaporated to give resinous substance, which was chromatographed over Kieselgel (200 g) with benzene–AcOEt (10: 1). The eluate was separated into two portions: Portion A of *Rf* 0.9—0.7 and portion B of *Rf* 0.6—0.4. Portion A was chromatographed over Kieselgel with benzene–AcOEt (10: 1). The fraction of *Rf* 0.78 gave colorless needles (XV) of mp 120—121° from methanol. Yield: 1.24 g. UV λ_{max} nm (log. ε): 217 (4.21), 269 (3.94), 321 (3.71, sh). Mass Spectrum (*m/e*, relative intensity): 234 (M$^+$, 16), 219 (5), 201 (2), 150 (2), 135 (4), 123 (100), 122 (34), 107 (4), 93 (13), 91 (29), 79 (23), 77 (31), 43 (27). *Anal.* Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.45; H, 6.27. Portion B was chromatographed over Kieselgel with benzene–AcOEt (20: 1). The fraction of *Rf* 0.3 gave colorless needles (IX)[14] of mp 163—164° from *n*-hexane. Yield: 75 mg. UV λ_{max} nm (log. ε): 259.5 (3.12), 220.8 (4.06, sh). IR ν_{max} (cm^{-1}): 3360, 3050, 2965, 2900, 2850, 1596, 1493, 1120, 1060, 872, 760, 742, 700, 690, 635. NMR (δ, ppm): 3.12 (br, 1H, OH), 4.05—3.92 (m, 6H), 4.60 (q, 1H, $J=10.2$ Hz and 3.6 Hz), 7.77—7.29 (m, 10H, Ar-H). Mass Spectrum (*m/e*, relative intensity): 270 (M$^+$, 3), 252 (1), 208 (28), 183 ($\begin{matrix}\text{ph}\\\text{ph}\end{matrix}\!>\!C{=}\overset{+}{O}H$, 100), 182 (5), 167 (2), 165 (3), 152 (2), 105 (ph-$C{\equiv}\overset{+}{O}$, 42), 88 (8), 87 (, 2), 77 (ph$^+$, 14), 45 (4), 44 (5). *Anal.* Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.19; H, 6.72.

Irradiation of II in Methanol at Room Temperature——II (7 g) in methanol (700 ml) was irradiated for 12.5 hr without benzophenone at room temp. and then treated mentioned above to give colorlesss needles (XV) of mp 120.5° (mixed fusion). Yield: 427 mg. *Anal.* Found: C, 66.58; H, 6.08.

Irradiation of II in Methanol at −18°——II (19.5 g) and benzophenone in methanol (180 ml) was irradiated for 8 hr at −18° and then treated mentioned above to give colorless needles (XV) (62 mg) of mp 121° (mixed fusion). *Rf*: 0.68 (benzene–AcOEt=20: 1).

Hydrogen Peroxide Oxidation of XV——To a solution of XV (0.7 g) in 5% KOH (42 ml), 14 ml of 3% H_2O_2 was added three times at an interval of 30 min under stirring and then 1.3 ml of 33% H_2O_2 was added four times at an interval of 1 hr at 80°. The solution was acidified with dil. HCl and salted out with NaCl and extracted with AcOEt. After evaporation of the solvent, colorless prisms (XVI) of mp 190—192° were obtained from AcOEt. Yield: 117 mg. IR ν_{max} (cm^{-1}): 1725, 1705, 1675 (two COOH groups, probably monomeric and dimeric). Mass Spectrum (*m/e*, relative intensity): 212 (M$^+$, 11), 194 (4), 168 (M$^+$ $-CO_2$, 100), 167 (M$^+$ −COOH, 44), 153 (168 $-CH_3$, 95), 150 (168 $-H_2O$, 31), 139 (168 −CHO, 3), 135 (153 $-H_2O$, 17), 123 (168 −COOH, 27), 122 (18), 93 (9), 91 (14), 79 (14), 77 (26). *Anal.* Calcd. for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.85; H, 5.78.

Methylation of XVI——XVI (80 mg) in methanol was methylated with diazomethane to give colorless needles (XVII) of mp 35.5°. IR ν_{max} (cm^{-1}): 1740, 1704 (two methyl ester). *Anal.* Calcd. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.59; H, 6.78.

Acknowledgement The authors express their deep graditude to Dr. Y. Asahina, Emeritus Professor of University of Tokyo, for his encouragement throughout this work. Thanks are also due to Miss M. Kinoshita for technical assistance and to Mr. H. Ogata, Wako Junyaku Co., Ltd. for usnic acid and to Mr. Y. Itatani, Miss. S. Toyoshima for elemental analyses and NMR measurement and to Miss T. Tsuji for mass spectrum measurement.