[Chem. Pharm. Bull. 33(7)2772—2777(1985)]

Usnic Acid. XVIII.[1] The Photolyses of Usnic Acid and Its Derivatives. (1)

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(Received October 24, 1984)

The structures of photolysis products of diacetylusnic acid, usnic acid, isoxazolo[4,5-*b*]usnic acid, and isoxazolo[4,5-*a*]usnic acid in the presence of nucleophiles were studied and the mechanisms of the photolyses are discussed.

Keywords——photolysis; diacetylusnic acid; usnic acid; isoxazolo[4,5-*b*]usnic acid; isoxazolo-[5,4-*a*]usnic acid; ^{1}H-NMR; ^{13}C-NMR

In a previous paper of this series, the authors reported on the structural elucidation of the photolysis products of dihydrousnic acid and on the photolysis mechanism, in which the excited triplet state (n–π^*) of one of the C=O groups and photochemical addition of the solvent to it might be involved.[3] 2,4-Cyclohexadienone-type compounds were reported to undergo a facile ring fission to acids or their derivatives on photolysis in the presence of a suitable nucleophile under a nitrogen atmosphere.[4] *l*-Usnic acid, which is a compound of this type, was reported to undergo only racemization in the absence of a nucleophile,[5] indicating that the fate of the ring fission products formed from such 2,4-cyclohexadienones would be recyclization, if a suitable nucleophile is not present in the reaction medium. This paper deals with the photolyses of diacetylusnic acid, usnic acid, isoxazolo[4,5-*b*]usnic acid,[6] and isoxazolo[5,4-*a*]usnic acid,[6] in the presence of nucleophiles under a nitrogen atmosphere.

d-Diacetylusnic acid (Ia) in tetrahydrofuran was irradiated at 0 °C in the presence of water as a nucleophile to afford monoacetyldecarbousnic acid (IIa)[7] and diacetyldecarbousnic acid (IIb).[7] In the presence of ethanol or methanol as a nucleophile, Ia was photolyzed to afford diacetylusnic acid ethoxide (IIIa)[7] or diacetylusnic acid methoxide (IIIb),[8] re-

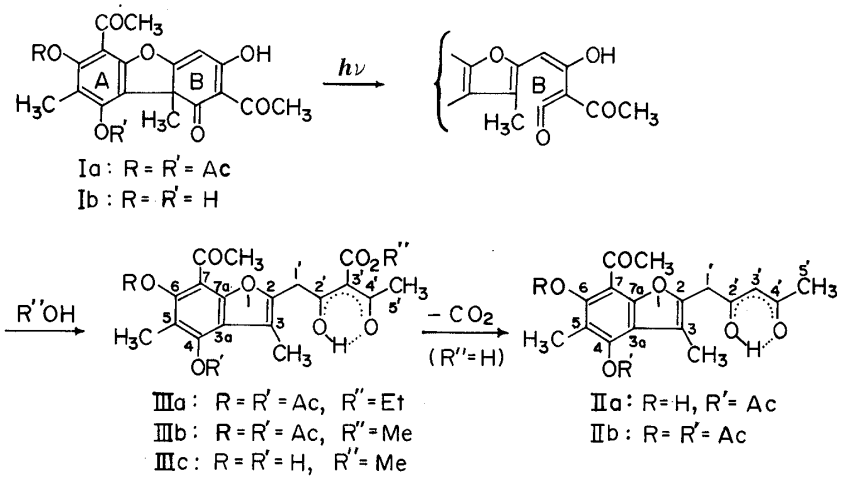

Chart 1

TABLE I. ^{1}H-NMR Spectral Data (δ-Value in $CDCl_3$, 100 MHz, J in Hz)

	C_3-CH_3	C_5-CH_3	C_7-$COCH_3$	$C_{5'}$-H_3	$C_{2'}$-CH_3 ($C_{3'}$-CH_3)	CH_2	OH	Others
IIIb	2.19 **s**, 3H	2.03 s, 3H	2.69 s, 3H	2.39 s, 3H		4.23 s, 2H	17.64 s, 1H	2.35 (s, 3H, OAc) 2.40 (s, 3H, OAc) 3.80 (s, 3H, OMe)
IIIc	2.32 **s**, 3H	2.13 s, 3H	2.74 s, 3H	2.39 s, 3H		4.23 s, 2H	5.56 (s, 1H) 13.74 (s, 1H) 17.66 (s, 1H)	3.82 (s, 3H, OMe)
V	2.40 **s**, 3H	2.13 s, 3H	2.73 s, 3H		(2.45 s, 3H)	4.52 s, 2H	5.52 (s, 1H) 13.73 (s, 1H)	3.90 (s, 3H, OMe)
VIIa	2.39 **s**, 3H	2.14 s, 3H	2.72 s, 3H		2.44 s, 3H	4.47 s, 2H	5.58 (s, 1H) 13.70 (s, 1H)	3.93 (s, 3H, OMe)
VIIb	2.38 **s**, 3H	2.13 s, 3H	2.72 s, 3H		2.44 s, 3H	4.47[a] s, 2H	5.70 (s, 1H) 13.70 (s, 1H)	1.41 (t, 3H, J=7) 4.41[a] (q, 2H, J=7) OEt
VIIc	2.26[b] **s**, 3H	2.03 s, 3H	2.69 s, 3H		2.44[c] s, 3H	4.51[a] s, 2H		2.35 (s, 3H, OAc) 2.41 (s, 3H, OAc) 1.41 (t, 3H, J=7) 4.41[a] (q, 2H, J=7) OEt

These signals *a*) could be considered to be overlapped with each other. The signal *b*) became a sharp signal, when the signal *a*) at 4.51 was irradiated, but the signal *c*) at 2.44 remained unchanged. Abbreviations: s, singlet; t, triplet; q, quartet; **s**, s-like.

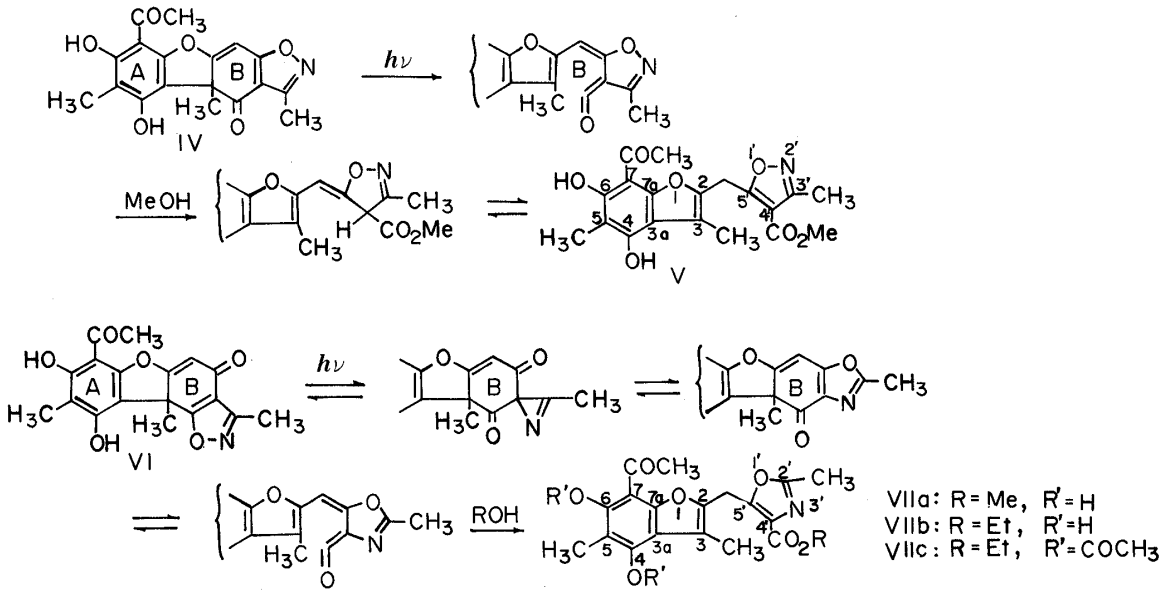

Chart 2

spectively. Similarly, *d*-usnic acid (Ib) in tetrahydrofuran–methanol was photolyzed to afford IIIc, which was decomposed to acetusnetol[7] by 60% acetic acid. The analytical and spectral evidence indicates that IIIc is usnic acid methoxide (Chart 1). The proton and carbon-13 nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra (δ-value, ppm) of IIIc could be interpreted as shown in Tables I and II. The mechanism of the photolysis of these compounds could be explained as shown in Chart 1, involving intermediates of the ketene type and addition of nucleophiles to them.

Isoxazolo[4,5-*b*]usnic acid (IV),[6] a 2,4-cyclohexadienone type of compound, was irradiated in methanol to afford 2-(7-acetyl-4,6-dihydroxy-3,5-dimethylbenzofuranyl)-5′-(4′-

TABLE II. ^{13}C-NMR Spectral Data (δ -Value in $CDCl_3$, 25.15 MHz, J in Hz)

Carbon	Shielding[a]					
	IIIb	IIIc[c]	V[c]	VIIa[c]	VIIb[c]	VIIc
3-$\underline{C}H_3$[b]	8.9 (q, J=128)	9.7 (q, J=128)	9.5 (q, J=128)	9.4 (q, J=128)	9.5 (q, J=128)	8.7 (q, J=127)
5-$\underline{C}H_3$[b]	9.6 (q, J=129)	7.9 (q, J=128)	7.9 (q, J=128)	7.8 (q, J=128)	7.9 (q, J=128)	9.6 (q, J=128)
7-CO$\underline{C}H_3$	32.3 (q, J=128)	30.6 (q, J=128)	30.2 (q, J=128)	30.1 (q, J=128)	30.2 (q, J=128)	32.2 (q, J=128)
3′-$\underline{C}H_3$ (2′-$\underline{C}H_3$)			(11.4 (q, J=130))	13.4 (q, J=130)	13.5 (q, J=130)	13.8 (q, J=130)
2	144.4 (m)	143.3 (m)	142.8 (m)	143.5 (m)	143.8 (m)	144.5 (m)
3	111.7 (m)	113.3 (m)	112.4 (m)	111.6 (m)	112.0 (m)	110.7 (**q**, J=7)
3a	114.8 (s)	111.3 (s)	111.0 (s)	110.9 (s)	111.2 (s)	114.7 (s)
4	145.0 (m)	156.8 (**d**, J=4)	156.9 (**d**, J=5)	156.6 (**d**, J=4)	156.9 (**d**, J=4)	145.1 (m)
5	119.7 (**q**, J=3)	105.1 (**q**, J=6)	105.0 (**q**, J=7)	104.8 (**q**, J=6)	105.1 (**q**, J=6)	119.8 (**q**, J=5)
6	148.3 (m)	162.2 (m)	161.9 (m)	161.5[d] (m)	162.0 (m)	148.8 (m)
7	121.5 (**s**)	101.2 (**d**, J=3)	100.7 (**d**, J=6)	100.5 (**d**, J=3)	101.0 (**d**, J=4)	121.5 (**s**)
7a	151.6 (s)	153.3 (s)	152.8 (s)	152.5 (s)	153.0 (s)	151.5 (s)
1′(2-$\underline{C}H_2$)	35.9 (t, J=132)	35.5 (t, J=131)	23.8 (t, J=133)	22.7 (t, J=132)	22.9 (t, J=132)	23.2 (t, J=133)
2′	194.6[e] (**s**)	195.1[d] (**q**, J=6)		159.5 (**q**, J=7)	159.9 (**q**, J=7)	160.6 (**q**, J=6)
3′	108.4 (**s**)	108.0 (**s**)	159.2 (**q**, J=7)			
4′	194.6[e] (**s**)	195.1[d] (**q**, J=6)	108.4 (**s**)	126.9 (s)	127.5 (**s**)	128.2 (s)
5′	25.4 (q, J=130)	25.1 (q, J=129)	173.0 (**t**, J=6)	153.9 (**t**, J=7)	154.1 (**t**, J=7)	153.4 (**t**, J=8)
7-$\underline{C}OCH_3$	195.4 (**q**, J=6)	200.1 (**q**, J=7)	199.6 (**q**, J=6)	199.2 (**q**, J=6)	199.7 (**q**, J=6)	195.3 (**q**, J=5)
O$\underline{C}OCH_3$	169.3 (**q**, J=6)					169.3 (**q**, J=7)
	168.5 (**q**, J=6)					168.6 (**q**, J=7)
$\underline{C}OOR$	167.0 (**s**)	166.8 (**s**)	161.7 (m)	161.5[d] (m)	161.5 (**s**)	161.9 (**s**)
OCO$\underline{C}H_3$	20.8 (q, J=130)					20.9 (q, J=130)
	20.5 (q, J=130)					20.5 (q, J=130)
O$\underline{C}H_2$					60.6 (t, **q**, J=148, 4)	60.6 (t, **q**, J=148, 4)
$\underline{C}H_3$					14.2 (q, J=127)	14.4 (q, **t**, J=126, 3)
OCH_3	51.8 (q, J=144)	51.7 (q, J=144)	51.6 (q, J=148)	51.5 (q, J=148)		

a) ppm relative to TMS measured with complete decoupling. The letters in parentheses designate the multiplicity of the carbon signal without decoupling. *b*) The multiplicity (q) of each methyl carbon changed to a singlet with off-resonance decoupling by means of the proton selective decoupling technique. *c*) Some DMSO-d_6 was added to dissolve the compound. *d*) These signals could be considered to be overlapping. *e*) Values in any column may be reversed. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; **s**, s-like; **d**, d-like; **t**, t-like; **q**, q-like.

methoxycarbonyl-3′-methylisoxazolyl)methane (V).[6] The mechanism of the photolysis of IV may be similar to that in the case of the photolysis of diacetylusnic acid, as shown in Chart 2.

Isoxazolo[5,4-*a*]usnic acid (VI),[6] a 2,5-cyclohexadienone type of compound, was photolyzed in methanol to afford VIIa. The ultraviolet (UV) spectrum of VIIa resembles that of V. The ^{1}H-NMR spectra of VIIa and V (Table I) are similar, suggesting that VIIa has the same benzofuran structure as V. When the ^{13}C-NMR spectra of VIIa and V (Table II) were compared, it became apparent that VIIa showed almost the same chemical shifts as V, except for the carbon signals due to the heteroaromatic ring and a methyl group. Compound V showed signals of the isoxazole ring carbons[9] at 159.2 (C-3′), 108.4 (C-4′), and 173.0 (C-5′), and the carbon signal of the C-3′ methyl group at 11.4, while VIIa showed carbon signals at 159.5, 126.9, and 153.9 assignable to the heteroaromatic ring. The spectral data suggest that VIIa is an oxazole derivative[10] with a methyl group at C-2′ (13.4). These spectral data suggest that VIIa is 2-(7-acetyl-4,6-dihydroxy-3,5-dimethylbenzofuranyl)-5′-(4′-methoxycarbonyl-2′-methyloxazolyl)methane. Compound VI was also photolyzed in tetrahydrofuran–ethanol to afford VIIb, which gave the diacetate (VIIc) on treatment with acetic anhydride in pyridine.

Compound VIIb could be assumed to be 2-(7-acetyl-4,6-dihydroxy- 3,5-dimethylbenzofuranyl)-5′-(4′-ethoxycarbonyl-2′-methyloxazolyl)methane on the basis of the spectral data (Tables I and II). The mechanism of the photolysis of VI could be explained as follows: firstly, the photo-isomerization[11] of the isoxazole ring to the azirine intermediate takes place and then the intermediate affords VIIa or VIIb *via* the oxazole and the ketene intermediates, as shown in Chart 2. Further studies on the mechanism should be performed to confirm this, however.

Experimental

The following instruments were used for the measurements of physical data. Melting point, Yanagimoto micro melting point appratus (a hot plate type): infrared (IR) spectra (in KBr pellet), Nippon Bunko A-202 spectrometer; UV spectra (in MeOH), Union Giken SM-401 recording spectrometer; ^{1}H-NMR spectra (in $CDCl_3$); JNM-FX-100S instrument at 100 MHz (^{13}C-NMR at 25.15 MHz, in $CDCl_3$) with $(CH_3)_4Si$ as an internal reference; mass spectra (MS), Hitachi M-80 double-focusing spectrometer; optical rotation at 589 nm, Nippon Bunko DIP-181 polarimeter. Thin layer chromatography (TLC) was done on silica gel (Merck), and column chromatography on silica gel (Merck) and silicic acid (Mallinkrodt), unless otherwise stated.

Irradiation of *d*-Diacetylusnic Acid (Ia) in Tetrahydrofuran–H_2O at 0 °C——Ia (890 mg) in tetrahydrofuran–H_2O (590 ml–5 ml) was irradiated for 15 min at 0 °C in a Pyrex flask under a high-pressure mercury lamp (Halos type PIH 300). The solution was evaporated to give a resinous material, which was chromatographed on silica gel (90 g) with chloroform–ethyl acetate (4 : 1). The fraction of *Rf* 0.65 (TLC, chloroform–ethyl acetate = 20 : 1) was crystallized from methanol to afford monoacetyldecarbousnic acid (IIa)[7] as faint yellow needles (100 mg) of mp 126—127 °C. *Anal.* Calcd for $C_{19}H_{20}O_7$: C, 63.33; H, 5.59. Found: C, 63.05; H, 5.46. UV λ_{max} nm (log ε): 239 (4.40), 285 (4.31), 356 (3.73). IR ν_{max} cm^{-1}: 1755 (OAc), 1635 (chelated CO), 1595 (C=C). ^{1}H-NMR (δ-ppm): 2.03 (s, 3H, $C_{5'}$-H_3), 2.09 (s, 3H, C_5-CH_3), 2.19 (s, 3H, C_3-CH_3), 2.42 (s, 3H, OAc), 2.82 (s, 3H, C_7-$COCH_3$), 3.70 (s, 2H, $C_{1'}$-H_2), 5.45 (s, 1H, –CH=), 13.39 (s, 1H, OH), 15.29 (br, 1H, OH). ^{13}C-NMR (δ-ppm, J in Hz): 8.6 (q, J=129, C_5-$\underline{C}H_3$ or C_3-$\underline{C}H_3$), 8.9 (q, J=128, C_3-$\underline{C}H_3$ or C_5-$\underline{C}H_3$), 20.5 (q, J=130, $OCO\underline{C}H_3$), 24.5 (q, J=128, $C_{5'}$), 31.5 (q, J=129, C_7-$CO\underline{C}H_3$), 36.2 (t, J=129, $C_{1'}$), 99.3 (d, J=168, $C_{3'}$), 105.1 (C_5, C_7), 111.7 (C_3), 114.9 (C_{3a}), 145.8 (C_2), 147.7 (C_4), 152.8 (C_{7a}), 161.0 (C_6), 168.4 ($O\underline{C}OCH_3$), 189.9 ($C_{4'}$ or $C_{2'}$), 190.6 ($C_{2'}$ or $C_{4'}$), 202.0 (C_7-$\underline{C}OCH_3$). MS *m/e* (relative intensity): 360 (M^+, 24), 318 (4), 302 (4), 276 (21), 275 (12), 260 (6), 234 (81), 233 (100), 215 (15), 85 (27). The fraction of *Rf* 0.34 (TLC, chloroform–ethyl acetate = 20 : 1) was crystallized from methanol to afford diacetyldecarbousnic acid (IIb)[7] as colorless needles (550 mg) of mp 117 °C. *Anal.* Calcd for $C_{21}H_{22}O_8$: C, 62.68; H, 5.47. Found: C, 62.22; H, 5.73. UV λ_{max} nm (log ε): 237.5 (4.37), 281 (4.28), 315 (3.84, sh). IR ν_{max} cm^{-1}: 1770 (OAc), 1690 (non-chelated Ar-$COCH_3$), 1635 (chelated CO), 1595 (C=C). ^{1}H-NMR (δ-ppm): 2.03 (s, 6H, C_5-CH_3 and $C_{5'}$-H_3), 2.21 (s, 3H, C_3-CH_3), 2.36 (s, 3H, OAc), 2.41 (s, 3H, OAc), 2.71 (s, 3H, C_7-$COCH_3$), 3.72 (s, 2H, $C_{1'}$-H_2), 5.44 (s, 1H, –CH=). ^{13}C-NMR (δ-ppm, J in Hz): 8.8 (q, J=128, C_3-$\underline{C}H_3$), 9.6 (q, J=129, C_5-$\underline{C}H_3$), 20.5 (q, J=130, $OCO\underline{C}H_3$), 20.7 (q, J=130, $OCO\underline{C}H_3$), 24.2 (q, J=128, $C_{5'}$), 32.3 (q, J=129, C_7-$CO\underline{C}H_3$), 36.3 (t, J=129, $C_{1'}$), 99.3 (d, J=167, $C_{3'}$), 111.7 (C_3), 114.8 (C_{3a}), 119.9 (C_5), 121.5 (C_7), 144.4 (C_2), 145.1 (C_4), 148.6 (C_6), 151.6 (C_{7a}), 168.6 ($O\underline{C}OCH_3$), 169.3 ($O\underline{C}OCH_3$), 190.0 ($C_{2'}$ and $C_{4'}$), 195.4 (C_7-$\underline{C}OCH_3$). MS *m/e* (relative intensity): 402 (M^+, 5), 360 (31), 318 (8), 302 (6), 276 (29), 275 (28), 260 (9), 234 (69), 233 (100), 215 (13), 85 (24). IIb was hydrolyzed with 5% alcoholic KOH to afford decarbousnic acid[7] of mp 186 °C (confirmed by mixed fusion and IR comparison). *Anal.* Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 63.72; H, 5.72. ^{13}C-NMR (in $CDCl_3$–DMSO-d_6, δ-ppm, J in Hz): 7.9 (q, J=128, C_5-$\underline{C}H_3$), 9.6 (q, J=128, C_3-$\underline{C}H_3$), 24.0 (q, J=127, $C_{5'}$), 30.5 (q, J=128, C_7-$CO\underline{C}H_3$), 35.8 (t, J=129, $C_{1'}$), 99.3 (d, J=166, $C_{3'}$), 100.9 (C_7), 105.0 (C_5), 111.2 (C_{3a}), 112.9 (C_3), 143.7 (C_2), 153. 0 (C_{7a}), 156.8 (C_4), 162.2 (C_6), 189.2 ($C_{4'}$ or $C_{2'}$), 191.1 ($C_{2'}$ or $C_{4'}$), 199.7 (C_7-$\underline{C}OCH_3$).

Irradiation of Ia in Ethanol at 0°C——Ia (1 g) in ethanol (500 ml) was irradiated for 10 min at 0 °C. The solution was evaporated to give a powder (800 mg), which was recrystallized twice from ethanol to afford diacetylusnic acid ethoxide (IIIa)[7] as colorless needles (488 mg) of mp 98 °C (confirmed by mixed fusion and IR comparison). *Anal.* Calcd for $C_{24}H_{26}O_{10}$: C, 60.75; H, 5.52. Found: C, 60.92; H, 5.55. UV λ_{max} nm (log ε): 237 (4.46), 284 (4.36). IR ν_{max} cm^{-1}: 1765 (OAc), 1715 (CO_2Et), 1685 (non-chelated Ar-$COCH_3$), 1595 (C=C). ^{1}H-NMR (δ-ppm, J in Hz): 1.32 (t, 3H, J=7, $OCH_2C\underline{H}_3$), 2.03 (s, 3H, C_5-CH_3), 2.19 (s, 3H, C_3-CH_3), 2.35 (s, 3H, OAc), 2.39 (s, 3H, $C_{5'}$-H_3), 2.40 (s, 3H, OAc), 2.70 (s, 3H, C_7-$COCH_3$), 4.24 (s, 2H, $C_{1'}$-H_2), 4.28 (q, 2H, J=7, $OC\underline{H}_2CH_3$), 17.58 (s, 1H, OH). ^{13}C-NMR (δ-ppm, J in Hz): 8.9 (q, J=128, C_3-$\underline{C}H_3$), 9.6 (q, J=129, C_5-$\underline{C}H_3$), 14.1 (q, J=127, $OCH_2\underline{C}H_3$), 20.5 (q, J=130, $OCO\underline{C}H_3$), 20.7 (q, J=130, $OCO\underline{C}H_3$), 25.4 (q, J=130, $C_{5'}$), 32.2 (q, J=128, C_7-$CO\underline{C}H_3$), 35.8 (t, J=132, $C_{1'}$), 61.0 (t, J=148, $O\underline{C}H_2CH_3$), 108.4 ($C_{3'}$), 111.7 (C_3), 114.1 (C_{3a}), 119.7 (C_5), 121.5 (C_7), 144.4 (C_2), 145.0 (C_4), 148.3 (C_6), 151.6 (C_{7a}), 166.6 ($\underline{C}O_2Et$), 168.5 ($O\underline{C}OCH_3$), 169.3 ($O\underline{C}OCH_3$), 194.4, 195.1, and 195.6 ($C_{2'}$, $C_{4'}$, and C_7-$\underline{C}OCH_3$). MS *m/e* (relative intensity): 474 (M^+, 5), 432 (11), 428 (5), 386 (20), 344 (10), 302 (36), 276 (48), 275 (63), 260 (32), 234 (59), 233 (100), 215 (8), 157 (28), 129 (6).

Irradiation of Ia in Methanol at 0 °C——Ia (1 g) in methanol (500 ml) was irradiated for 20 min at 0 °C. The solution was evaporated to give a power (800 mg), which was recrystallized from ethanol to afford diacetylusnic acid methoxide (IIIb) as colorless needles (488 mg) of mp 127—128 °C. $FeCl_3$ reaction: violet-brown. *Anal.* Calcd for $C_{23}H_{24}O_{10}$: C, 59.99; H, 5.25. Found: C, 60.10; H, 5.20. UV λ_{max} nm (log ε): 236 (4.45), 283 (4.36). IR ν_{max} cm^{-1}: 1765, 1715, 1695, 1595. MS *m/e* (relative intensity): 460 (M^+, 10), 418 (15), 386 (17), 344 (11), 302 (24), 276 (37), 275 (50), 234 (59), 233 (100), 215 (8), 143 (20).

Irradiation of *d*-Usnic Acid (Ib) in Tetrahydrofuran–Methanol at 0 °C——Ib (1 g) in tetrahydrofuran–methanol (500 ml–50 ml) was irradiated for 7 h at 0 °C. The solution was evaporated to give a resinous material, which was chromatographed on silicic acid (130 g) with benzene–ethyl acetate (10 : 1). The fraction of *Rf* 0.39 (TLC, benzene–ethyl acetate = 20 : 1) was crystallized from methanol to afford IIIc as faint yellow needles (230 mg) of mp 149—150 °C. $FeCl_3$ reaction: violet-brown. *Anal.* Calcd for $C_{19}H_{20}O_8$: C, 60.64; H, 5.36. Found: C, 60.58; H, 5.33. UV λ_{max} nm (log ε): 244 (4.42), 298 (4.34), 350 (3.88). IR ν_{max} cm^{-1}: 3350 (OH), 1690 (CO_2Me), 1620 (chelated CO), 1595 (C=C). MS *m/e* (relative intensity): 376 (M^+, 10), 344 (33), 260 (28), 234 (39), 233 (100), 215 (15), 143 (7). IIIc was hydrolyzed with 60% acetic acid to afford acetusnetol[7] of mp 203 °C (confirmed by mixed fusion and IR comparison).

Irradiation of (+)-Isoxazolo[4,5-*b*]usnic Acid (IV) in Methanol at 0 °C——IV (160 mg) in methanol (500 ml) was irradiated for 2.5 h at 0 °C. The methanolic solution from three runs was evaporated to give a resinous material, which was chromatographed on silica gel with benzene–acetone (20 : 1). The fraction of *Rf* 0.33 (TLC, benzene–acetone = 20 : 1) was crystallized from methanol to give 2-(7-acetyl-4,6-dihydroxy-3,5-dimethylbenzofuranyl)-5′-(4′-methoxycarbonyl-3′-methylisoxazolyl)methane (V)[6] as pale yellow needles (50 mg), mp 228—229 °C (confirmed by mixed fusion, and UV and IR comparisons). *Anal.* Calcd for $C_{19}H_{19}NO_7$: C, 61.12; H, 5.13; N, 3.75. Found: C, 61.11; H, 5.16; N, 3.66. $FeCl_3$ reaction: blue-green. UV λ_{max} nm (log ε): 241 (4.33), 251 (4.23, sh), 302 (4.17), 347 (3.92). IR ν_{max} cm^{-1}: 3350 (OH), 1725 (ester), 1615 (chelated CO), 1510. MS *m/e* (relative intensity): 373 (M^+, 100), 341 (6), 326 (5), 313 (20), 298 (6), 272 (22), 233 (27), 215 (20), 140 (9).

Irradiation of (+)-Isoxazolo[5,4-*a*]usnic Acid (VI) in Methanol at 0 °C——VI (250 mg) in methanol (500 ml) was irradiated for 3 h at 0 °C. The methanolic solution from two runs was evaporated to give a resinous material, which was chromatographed on silica gel with chloroform–acetone (30 : 1). The fraction of *Rf* 0.32 (TLC, chloroform–acetone = 30 : 1) was crystallized from methanol to give VIIa as faint yellow needles (81 mg), mp 255—256 °C. $FeCl_3$ reaction: blue-green. *Anal.* Calcd for $C_{19}H_{19}NO_7$: C, 61.12; H, 5.13; N, 3.75. Found: C, 61.44; H, 5.05; N, 3.68. $[\alpha]_D^{20}$ 0° (c = 0.027, $CHCl_3$). UV λ_{max} nm (log ε): 243 (4.33), 252 (4.26, sh), 304 (4.11), 351 (3.86). IR ν_{max} cm^{-1}: 3450 (OH), 1725 (ester), 1620 (chelated CO), 1585 (C=C). MS *m/e* (relative intensity): 373 (42), 341 (100), 326 (30), 313 (85), 298 (37), 272 (37), 254 (19), 244 (27), 233 (14), 215 (18), 140 (9), 112 (6).

Irradiation of VI in Tetrahydrofuran–Ethanol at 0 °C——VI (830 mg) in tetrahydrofuran–ethanol (500 ml–50 ml) was irradiated for 3 h at 0 °C. The solution was evaporated to give a resinous material, which was solidified by treatment with ethyl acetate to give a powder (418 mg). The powder was chromatographed on silica gel (60 g) with benzene–acetone (10 : 1). The fraction (398 mg) of *Rf* 0.28 (TLC, benzene–acetone = 10 : 1) was crystallized from ethanol to afford VIIb as faint yellow needles (250 mg) of mp 224 °C. $FeCl_3$ reaction: blue-green. *Anal.* Calcd for $C_{20}H_{21}NO_7$: C, 62.01; H, 5.46; N, 3.62. Found: C, 61.99; H, 5.54; N, 3.56. UV λ_{max} nm (log ε): 241 (4.34), 252 (4.25, sh), 302 (4.12), 346 (3.83). IR ν_{max} cm^{-1}: 3300 (OH), 1720 (ester), 1625 (chelated CO), 1590 (C=C). MS *m/e* (relative intensity): 387 (M^+, 44), 341 (100), 326 (38), 313 (90), 298 (29), 272 (40), 254 (17), 244 (18), 233 (11), 215 (13), 126 (17).

Acetylation of VIIb——A mixture of VIIb (50 mg), pyridine (0.5 ml), and acetic anhydride (0.5 ml) was allowed to stand overnight at room temperature and treated as usual to give VIIc as colorless needles (23 mg) of mp 138—139 °C (from ether–petr. ether). *Anal.* Calcd for $C_{24}H_{25}NO_9$: C, 61.14; H, 5.35; N, 2.97. Found: C, 60.97; H, 5.52; N, 2.86. UV λ_{max} nm (log ε): 227.5 (4.36, sh), 234 (4.38), 277.5 (3.96), 312 (3.62, sh). IR ν_{max} cm^{-1}: 1760 (OAc), 1715 (CO_2Et), 1695 (non-chelated Ar-$COCH_3$), 1620, 1595 (C=C). MS *m/e* (relative intensity): 471 (M^+, 23), 429 (12), 425 (22), 383 (100), 341 (43), 326 (13), 313 (49), 298 (10), 272 (12), 254 (5), 244 (6), 233 (5), 126 (12).

Acknowledgement The authors are grateful to Prof. O. Yamauchi for his encouragement. Thanks are due to Mr. Y. Itatani for measuring NMR spectra, to Miss Y. Teranishi and Miss K. Handa for elemental analyses, to Miss T. Ueda and Miss E. Fukui for MS measurement and to Miss Y. Hamashita and Miss Marutani for their technical assistance.

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