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Usnic Acid. VIII.[1] The Dienone-Phenol Rearrangement of 9-O-Acetyltetrahydrodesoxyusnic and Dihydrousnic Acids

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The Dienone–Phenol rearrangement of 9-O-acetyl-tetrahydrodesoxyusnic- (IV), 9-O-acetyldihydrousnic- (VI) and dihydrousnic acids (V) were studied.

It was reported in previous papers of this series that methyldihydrousnic aicd (I) gave, on acetylation with acetic anhydride and conc. H_2SO_4, the acetates of anhydromethyldihydrousnic- (II)[3] and isoanhydromethyldihydrousnic acids (III)[4] as the products followed by the Dienone–Phenol rearrangement. This paper deals with the Dienone–Phenol rearrangement of 9-O-acetyltetrahydrodesoxyusnic- (IV), dihydrousnic- (V) and 9-O-acetyldihydrousnic acids (VI). Asahina, Maeda and Yanagita[5] reported that *d*-diacetylusnic acid was hydrogenated to *l*-diacetyldihydrousnic acid and a compound $C_{22}H_{24}O_8$, mp 194°, $[\alpha]^{30}=27.7°$, which they assumed to be *d*-diacetyltetrahydrodesoxyusnic acid (VII). The present authors prepared the same compound of mp 196°, $[\alpha]^{26.5}=33.8°$ and concluded that it is 9-O-acetyltetrahydrodesoxyusnic acid $C_{20}H_{22}O_7$ (IV) by the following spectral and chemical evidence. A precise molecular weight determination of the compound, mp 196° by the mass spectrometry gave a value (M^+, *m/e* 374.137) in excellent agreement with the formula $C_{20}H_{22}O_7$ (Calcd. *m/e* 374.137). IV was acetylated to diacetate $C_{22}H_{24}O_8$ (VII) of mp 134° and deacetylated to $C_{18}H_{20}O_6$ (VIII) of mp 154°. VIII gave the diacetate $C_{22}H_{24}O_8$ (VII′) of mp 118°, which was deacetylated to VIII. The deacetylated compound of mp 154° could be formulated as either VIII (isotype) or VIII′ (normal type), but it is plausible to assume that IV and VII (normal type), on treatment with conc. H_2SO_4, are deacetylated and isomerized to give VIII (isotype), which yields VII′ (isotype) by acetylation and VII′ (isotype) yields VIII (isotype) by deacetylation with conc. H_2SO_4. VII exhibits the infrared (IR) bands (cm^{-1}) at 1765 (OAc), 1680 ($\alpha\beta$-unsatd. C=O), 1575—1520 (broad, triketon), 1110, 1010 (-C-O-C-) and VII′ at 1765 (OAc), 1675 ($\alpha\beta$-unsatd. C=O), 1575—1520 (broad, triketone), 1105, 1010 (-C-O-C-). IV exhibits IR bands at 3400 (OH), 1740 (OAc), 1670 ($\alpha\beta$-unsatd. C=O), 1632 (chelated C=O), 1550—1535 (broad, triketone), 1115, 1020 (-C-O-C-) and VIII at 3540—3880 (OH), 1670 ($\alpha\beta$-unsatd. C=O), 1632 (chelated C=O), 1550—1520 (broad, triketone), 1110, 1023 (-C-O-C-). The nuclear magnetic resonance (NMR) signals (δ-value) of IV, VII, VII′ and VIII could be assigned as shown in Table I. VII shows OH signals at 18.32 and 18.75 (1H, chelated enol OH), VII′ at 18.24 and 18.70 (1H, chelated enol OH), and IV at 5.34 (s, broad, non-chelated OH), 18.05 and 18.40 (1H, chelated enol OH) and VIII at 4.92 (1H, broad, non-chelated OH), 18.10 (s, 1H, chelated enol OH) and furthermore at 8.58 (s, 1H), which could be assigned to the OH group at C_9. The rather low δ-value (8.58) is probably due to the chelation of the OH group at C_9 with the C=O group at C_1. The NMR spectrum of IV and VII in CF_3COOD shows the signals of the angular-CH_3 and Ar-CH_3 groups as singlets, respectively, suggesting that IV and VII might be present in two types of enol forms in respect of the location of hydrogen

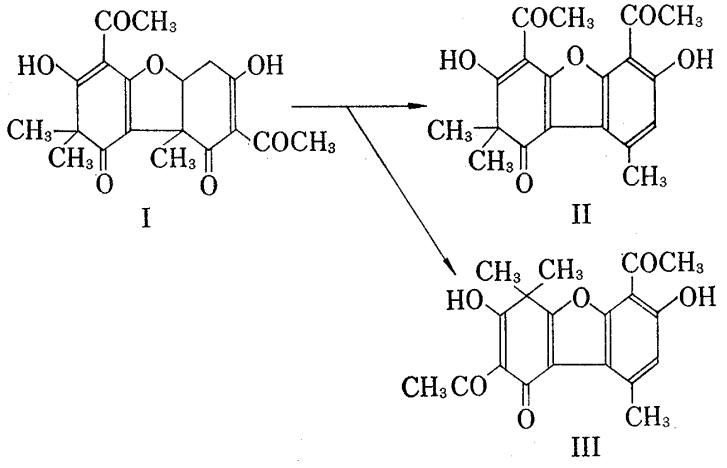
1) Part VII: K. Takahashi and M. Takani, *Chem. Pharm. Bull.* (Tokyo), **18**, 1831 (1970).
2) Location: *Takaramachi, Kanazawa.*
3) K. Takahashi and S. Miyashita, *Chem. Pharm. Bull.* (Tokyo), **11**, 209 (1963).
4) K. Takahashi, S. Miyashita and Y. Ueda, *Chem. Pharm. Bull.* (Tokyo), **11**, 473 (1963).
5) Y. Asahina, S. Maeda and M. Yanagita, *Yakugaku Zasshi*, **58**, 219 (1938); *idem*, *Ber.*, **70**, 1500 (1937).

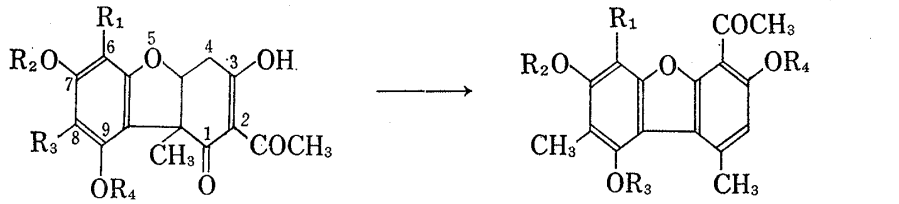
Table I. The NMR Data (δ-Value, 60 Mc)

	$\underline{CH_3}$–CH_2	Ang–CH_3	Ar–CH_3	OAc	$COCH_3$	CH_3–$\underline{CH_2}$[a]	CH–$\underline{CH_2}$	$\underline{CH}$–CH_2	OH non-chelated	OH chelated	OH enol chelated	Solvent
IV	0.85—1.12 (m) 3H	1.63, 1.75 (d) 3H	1.83, 1.89 (d) 3H	2.38,2.43,2.56 6H		2.20— (m) 2H	2.87—3.04 (m) 2H	4.54—4.79 (m) 1H	5.34 (s) 1H		18.05,18.40 (d) 1H	$CDCl_3$
VII	0.93,1.05,1.18 (t) 3H	1.66,1.80,1.82 6H		2.23(s)3H 2.38(s)3H	2.42, 2.58 (d) 3H	2.22— (m) 2H	2.90—3.10 (m) 2H	4.66—4.85 (m) 1H			18.32,18.75 (d) 1H	
VII′	0.92,1.05,1.18 (t) 3H	1.65,1.79,1.82,1.92 6H		2.30(s)3H 2.36(s)3H	2.41, 2.57 (d) 3H	2.20— (m) 2H	2.87—3.05 (m) 2H	4.60—4.84 (m) 1H			18.24,18.70 (d) 1H	
VIII	1.01,1.13,1.26 (t) 3H	1.70, 1.82 (d) 3H	2.13 (s) 3H		2.62 (s) 3H	2.37—2.74 (q) 2H	3.06, 3.14 (d) 2H	4.68,4.76,4.84 (t) 1H	4.92[b] (s)(broad)1H	8.58 (s) 1H	18.10 (s) 1H	
IV	1.00,1.13,1.26 (t) 3H	1.90 (s) 3H	2.07 (s) 3H	2.62 (s) 3H	2.69 (s) 2H	2.48— (m) 2H	3.22—3.33 (m) 2H	4.80—4.90 (m) 1H				CF_3COOD
VII	0.99,1.12,1.24 (t) 3H	1.93 (s) 3H	1.96 (s) 3H	2.53(s)3H 2.61(s)3H	2.69 (s) 3H	2.35— (m) 2H	3.30 (m) 2H	4.90 (m) 1H				
VII′	1.00,1.12,1.25 (t) 3H	1.91,1.95,2.03 6H		2.52(s)3H 2.60(s)3H	2.68 (s) 3H	2.35— (m) 2H	3.29 (m) 2H	4.90 (m) 1H				
VIII	1.02,1.15,1.27 (t) 3H	1.88 (s) 3H	2.21 (s) 3H		2.75 (s) 3H	2.46,2.58— (m) 2H	3.25, 3.33 (d) 2H	4.86,4.93,5.00 (t) 1H				
Diacetyl dihydro usnic acid		1.73, 1.84 (d) 3H	1.82, 1.90 (d) 3H	2.32,2.42,2.45,2.51,2.63 12H			3.04—3.13 (m) 2H	4.86—5.02 (m) 1H			18.60,19.02 (d) 1H	$CDCl_3$
VI		1.68, 1.80 (d) 3H	1.91, 1.93 (d) 3H	2.39,2.42,2.44,2.60 9H			2.96—3.13 (m) 2H	4.75—5.02 (m) 1H		13.30,13.35 (d) 1H	17.75,18.21 (d) 1H	
		1.95 (s) 3H	2.04 (s) 3H	2.65 (s) 3H	2.69(s)3H 2.84(s)3H		3.33—3.44 (m) 2H	5.02—5.14 (m) 1H				CF_3COOD

a) The signal was overlapped with the signals of the OAc and $COCH_3$ groups.
b) The signal was overlapped with the signals of the -$\underline{CH}$-CH_2- groups.
abbreveation: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet

bonds in the ring B in chloroform solution, as VI and diacetyldihydrousnic acid. These spectral and chemical evidences indicate that IV has an acetoxyl group at C_9 and the monoacetate of mp 196° and diacetate of mp 134° could be formulated as IV and VII (usnic acid type[6]), respectively, because the NMR data indicate that these two compounds could not be formulated as any other two iso-type of compounds,[6] respectively. Both VII and VII′ exhibit almost the same ultraviolet (UV), IR and mass spectrum (MS) spectra, but the NMR signals of VII′ are slightly different from those of VII, probably indicating that the diacetate of mp 118° could be formulated as VII′ (isousnic acid type).[6] The MS spectrum of IV could be analysed as follows: IV gave on electron impact, M^+ (*m/e* 374.137, relative intensity 13, formula $C_{20}H_{22}O_7$) and $M^+ - C_2H_2O$ (332.126, 8, $C_{18}H_{20}O_6$), which in turn gave rise to species A (248.105, 27, $C_{14}H_{16}O_4$) and species B (206.096, 100, $C_{12}H_{14}O_3$), respectively, by the retro-Diels–Alder fragmentation of the ring B. Species A and B, which could be considered to be benzofuran structure, gave rise to species (219.103, 16, $C_{13}H_{15}O_5$) and species (177.091, 1, $C_{11}H_{13}O_2$) by the loss of a CHO group, respectively, by the characteristic fragmentation of benzofuran derivatives.[7] Species $M^+ - C_2H_2O$ gave rise to species (289.108, 1, $C_{16}H_{17}O_5$) by the loss of a $COCH_3$ and then species (261.113, 3, $C_{15}H_{17}O_4$) by the loss of a C=O group. Species B gave rise to species (191.068, 22, $C_{11}H_{11}O_3$) by the loss of a CH_3 group. Similarly, V gave rise to species (220.074, 100, $C_{12}H_{12}O_4$) by the retro-Diels–Alder fragmentation of the ring B, which gave rise to species (191.071, 3, $C_{11}H_{11}O_3$) by the loss of a CHO group. These evidences indicate that IV, VII, VII′ and VIII could be formulated as shown in Chart 1. But





IV: R_1=Et, R_2=H, R_3=Me, R_4=Ac
V: R_1=Ac, R_2=R_4=H, R_3=Me
VI: R_1=R_4=Ac, R_2=H, R_3=Me
VII: R_1=Et, R_2=R_4=Ac, R_3=Me
VII′: R_1=Me, R_2=R_4=Ac, R_3=Et
VIII: R_1=Me, R_2=R_4=H, R_3=Et
VIII′: R_1=Et, R_2=R_4=H, R_3=Me

IX: R_1=Et, R_2=R_3=R_4=Ac
X: R_1=Et, R_2=R_3=Ac, R_4=H
XI: R_1=Et, R_2=R_3=R_4=H
XII: R_1=R_2=R_3=R_4=Ac
XIII: R_1=R_3=Ac, R_2=R_4=H
XIV: R_1=R_2=R_3=Ac, R_4=H
XV: R_1=Ac, R_2=R_3=R_4=H

Chart 1

6) S. Shibata and H. Taguchi, *Tetrahedron Letters*, **48**, 4867 (1967).
7) H. Budzikiewics, C. Djerassi and D.H. Williams, "Interpretation of Mass Spectra of Organic Compounds," 1964, p. 231.

there still remain a possibility that the structure of the deacetylated compound of mp 154° might not be the iso-form (VIII) assigned, but its isomeric form (VIII'), because isodihydrousnic acid is readly converted into dihydrousnic acid even by the process of recrystallization.[6]

IV was treated with acetic anhydride and conc. H_2SO_4 to give colorless needles $C_{24}H_{24}O_8$ (IX) of mp 194—195° and colorless needles $C_{22}H_{22}O_7$ (X) of mp 221—222°. Both IX and X were deacetylated to give yellow needles $C_{18}H_{18}O_5$ (XI) of mp 282—283°. IX gave no coloration but X and XI gave green coloration with $FeCl_3$. IX exhibits the IR bands at 1760 (OAc), 1692 (non-chelated Ar-$COCH_3$), 1110, 1055 (-C-O-C-) and 890 (isolated Ar-H) and X at 1770 (OAc), 1645 (chelated Ar-$COCH_3$), 1110, 1058 (-C-O-C-), 875 (isolated Ar-H) and XI at 1630 (chelated Ar-$COCH_3$), 1115, 1043 (-C-O-C-), 890 (isolated Ar-H). But IX, X and XI do not exhibit the characteristic broad band of the triketone group at about 1550—1500. The NMR signals of IX, X and XI could be assigned as shown in Table II.

Table II. The NMR Data (δ-Value, 60 Mc)

	$\underline{CH_3}$-CH_2	OAc	Ar-CH_3	$COCH_3$	CH_3-$\underline{CH_2}$[a]	Ar-H	OH	Solvent
IX	1.15,1.28,1.41 (t) 3H	2.34(s)3H 2.40(s)6H	2.02(s)3H 2.77(s)3H	2.81(s)3H	2.64—3.02 (q)2H	6.86(s)1H		$CDCl_3$
X	1.17,1.29,1.41 (t) 3H	2.42(s)6H	2.03(s)3H 2.70(s)3H	2.94(s)3H	2.65—3.01 (q)2H	6.70(s)1H	13.02(s)1H	$CDCl_3$
XI	1.37,1.45,1.57 (t) 3H		2.77(s)3H 3.17(s)3H	2.90(s)3H	3.05—3.44 (q)2H	6.82(s)1H	—	C_5D_5N
XII		2.36(s)3H 2.39(s)3H 2.46(s)3H	2.09(s)3H 2.78(s)3H	2.82(s)6H		6.89(s)1H		$CDCl_3$
XIII		2.41(s)3H	2.07(s)3H 2.60(s)3H	2.83(s)3H 2.87(s)3H		6.68(s)1H	12.97(s)1H 13.54(s)1H	$CDCl_3$
XIV		2.37(s)3H 2.42(s)3H	2.05(s)3H 2.64(s)3H	2.77(s)3H 2.85(s)3H		6.67(s)1H	13.07(s)1H	$CDCl_3$

a) The signal was overlapped with the signals of the Ar-CH_3 and $COCH_3$ groups.

IX, X and XI do not exhibit NMR signals of angular-CH_3, -CH-CH_2-, and chelated enol OH groups which are observed on the NMR spectrum of IV, but they exhibit signals of two Ar-CH_3 groups and an Ar-H. The rather low δ-value of the aromatic protons of IX (6.86) and X (6.70) and the difference (0.16 ppm) between them might indicate[8] that the ortho position of the aromatic proton of IX and X is substituted by a OAc and a OH groups, respectively. These spectral evidences indicate that IX, X and XI are dibenzofuran derivatives and could be formulated as shown in Chart 1. IX was kept in a mixture of benzene and ethylacetate (15:1, V/V) and Kiesel gel for a few days at room temperature to give X, suggesting that IX was partly deacetylated to give X during the column chromatography for the purification. The reaction mechanism of the formation of IX from IV might be the same as that of the acetylation of I,[3,4] which involves the Dienone–Phenol rearrangement.

Dihydrousnic- (V) and 9-O-acetyldihydrousnic acids (VI) gave, by the acetylation with acetic anhydride and conc. H_2SO_4, colorless needles $C_{24}H_{22}O_9$ (XII) of mp 201—202°, faint yellow needles $C_{20}H_{18}O_7$ (XIII) of mp 211—212° and colorless needles $C_{22}H_{20}O_8$ (XIV) of mp 199—200°. XII, XIII and XIV were deacetylated to $C_{18}H_{16}O_6$ (XV) of mp 291—293°, indicating that XII, XIII and XIV are acetyl derivatives of XV. XII exhibits IR bands at 1760 (OAc), 1685 (non-chelated Ar-$COCH_3$), 1168, 1082 (-C-O-C-), 895 (isolated Ar-H) and XIII at 1770 (OAc), 1645 and 1630 (two chelated Ar-$COCH_3$), 1170, 1080 (-C-O-C-), 890 (isolated Ar-H) and XIV at 1775 (OAc), 1700 (non-chelated Ar-$COCH_3$), 1645 (chelated Ar-$COCH_3$), 1175, 1085 (-C-O-C-), 895 (isolated Ar-H) and XV at 1645 and 1635 (two chelated

8) J.A. Ballantine and C.T. Pillinger, *Tetrahedron*, 23, 1691 (1967).

Ar-$COCH_3$), 1187, 1077 (-C-O-C-), 872 (isolated Ar-H). XII, XIII and XIV do not exhibit the characteristic broad band of triketone group at about 1550—1500. The NMR signals of XII, XIII and XIV could be analyzed as shown in Table II. XII, XIII and XIV do not exhibit the NMR signals of angular-CH_3 and -CH-CH_2-, but exhibit an Ar-H, two Ar-CH_3 groups. The chemical shifts of the aromatic protons of XII (6.89), XIII (6.68) and XIV (6.67) are in rather low δ-values and the difference (0.21 ppm) between the δ-values of the aromatic protons of XII and XIII and that (0.22 ppm) between those of the aromatic protons of XII and XIV are almost equal to the value (0.25 ppm) of the difference between the shielding effects of OAc and OH groups[8] to the protons at their *ortho* position, respectively. The δ-value of the chemical shift (12.97) of one of the two chelated OH groups of XIII is nearly equal to those of the OH signals at C_3 of II, III and X, and the value (13.54) of the chemical shift of the other is also nearly equal to those of the OH signals at C_7 of usnic acid, V and VI. The value (13.07) of the chemical shift of the OH group of XIV is nearly equal to that (12.97) of the OH signal at C_3 of XIII and to that (13.02) of the OH signal at C_3 of X, as shown in Table III. These spectral evidence indicates that XII, XIII, XIV and XV could be formulated as shown in Chart 1. V and VI gave the same compounds XII, XIII and XIV, disproving the formation of isousnic acid type of compound.[6] XII was deacetylated to give XIII and XIV by keeping XII in a mixture of benzene and ethylacetate and Kiesel gel for a few days at room temperature. The reaction mechanism of the formation of XII from dihydrousnic- (V) and 9-O-acetyldihydrousnic acids (VI) might involve the Dienone–Phenol rearrangement. The Dienone–Phenol rearrangement products of IV, V and VI and of I[3,4] were all *m*-cresol type of compounds, but not *p*-cresol type of compounds, probably due to the difficulty of the formation of the highly strained four-membered spiran intermediate.[9]

TABLE III. The NMR Data (δ-Value, 60 Mc) of the OH Groups

	Usnic acid	9-O-Acetyl usnic acid	II	III	V	VI	X	XIII	XIV
C_3	18.8	18.61	12.78	12.73	18.44	17.75 18.21	13.02	12.97	13.07
C_7	13.3	13.21	17.60	18.56 18.88	13.49	13.30 13.35		13.54	
C_9	11.0				9.51				

Experimental

The IR spectra were measured in KBr pellet with a Nippon Bunko DS-402G spectrometer, the UV spectra in EtOH with a Hitachi EPS-2U recording spectrometer, the NMR spectra in $CDCl_3$ with a JNM-C-60-H high resolution NMR instrument at 60 Mc with $(CH_3)_4Si$ as internal reference and the MS spectra with JMS-OlSG mass spectrometer, the ionizing current kept at 200 μA, while the ionizing energy being maintained at 75 eV and the source temperature at 170° (IV), 80° (VII), and 90° (VII'), and the optical rotation at 589 mμ with a Nippon Bunko automatic polarimeter DIP-SL, not otherweise stated.

Hydrogenation of *d*-Diacetylusnic Acid[5]——One gram of *d*-diacetylusnic acid, dissolved in acetic acid (50 ml), was hydrogenated with Pd-black (0.3 g). After six hours shaking, when 200 ml of H_2 was absorbed, the solvent was filtered and the filtrate was poured into water to give precipitate, which was crystallized from methanol to give colorless prisms (IV) of mp 196°. Yield: 0.4 g. $[\alpha]^{26.5}=33.8°$ ($c=1.185$, $CHCl_3$). $FeCl_3$: red brown. UV λ_{max} (mμ, log ε): 210 (4.46, an end absorption), 226 (4.23, sh), 277 (4.12). *Anal.* Calcd. for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.23; H, 5.94. $M^+=374.137$ (Calcd. for $C_{20}H_{22}O_7$: 374.137, Mass spectrometry).

Acetylation of IV——(i) A mixture of 1 g of IV, sodium acetate (1.0 g) and acetic anhydride (10 ml) was warmed at 110° for 3 hr and was treated as usual to give faint yellow needles (VII) of mp 134° from 80%

9) S.M. Bloom, *J.A.C.S.*, **81**, 4728 (1959).

methanol, after purification by chromatography with silicic acid and benzene–ethylacetate (4: 1, v/v). Yield: 270 mg. $[\alpha]^{18}=53.4°$ ($c=1.012$, $CHCl_3$). UV λ_{max}(mμ, log e): 210 (4.45, an end absorption), 226 (4.24, sh), 279 (4.15). Mass Spectrum (m/e, intensity): 416 (19), 374 (24), 332 (16), 290 (30), 248 (90), 219 (10), 206 (100), 191 (13). *Anal.* Calcd. for $C_{22}H_{24}O_8$: C, 63.45; H, 5.81. Found: C, 63.49; H, 5.90.

(ii) A mixture of 2 g of IV, acetic anhydride (10 ml) and pyridine (10 ml) was kept at room temperature for 14 hr and was treated as usual to give faint yellow needles (VII) of mp 134° from 80% methanol, after purification by chromatography mentioned above. Yield: 138 mg. *Anal.* Found: C, 63.60; H, 5.96.

Deacetylation of VII, followed by Acetylation——(i) VII (350 mg) was dissolved in ice cold conc. H_2SO_4 (1 ml) and the solution was kept in cold for 20 min and poured into water to give yellow plates (VIII) of mp 154° from 80% methanol. Yield: 150 mg. *Anal.* Calcd. for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 64.80; H, 6.07.

ii) A mixture of VIII (185 mg), obtained above, acetic anhydride (1.8 ml) and sodium acetate (185 mg) was warmed at 110° for 3 hr and treated as usual to give yellow needles (VII′) of mp 118° from methanol, after purification by chromatography mentioned above. Yield: 20 mg. Mass Spectrum: 416 (21), 374 (24), 332 (15), 290 (30), 248 (96), 219 (9), 206 (100), 191 (9). *Anal.* Calcd. for $C_{22}H_{24}O_8$: C, 63.45; H, 5.81. Found: C, 63.41; H, 5.86.

Deacetylation of IV, followed by Acetylation and Deacetylation——(i) IV (5 g) was dissolved in ice cold conc. H_2SO_4 (20 ml) and after 20 min, the mixture was poured into water to give yellow plates (VIII) of mp 154° from 70% methanol. Yield: 2.0 g. $[\alpha]_D^{18}=57°$ ($c=1.00$, $CHCl_3$). UVλ_{max}(mμ, log e): 210 (4.64, an end absorption), 233 (4.21, sh), 274.5 (4.24). *Anal.* Found: C, 65.03; H, 6.02.

(ii) A mixture of VIII (1 g) obtained above, acetic anhydride (10 ml), sodium acetate (1 g) was warmed at 110° for 3 hr and treated as usual to give faint yellow needles (VII′) of mp 118° from 80% methanol, after purification by chromatography mentioned above. Yield: 170 mg. $[\alpha]^{18}=52.6°$ ($c=1.008$, $CHCl_3$). UV λ_{max} (mμ, log e): 210 (4.43, an end absorption), 226 (4.22, sh), 278.5 (4.12). *Anal.* Found: C, 63.46; H, 5.81.

(iii) VII′ of mp 118° obtained above, was deacetylated to give VIII of mp 154°. *Anal.* Found: C, 65.40; H, 6.08.

Dienone-Phenol Rearrangement of IV——A mixture of IV (3 g), acetic anhydride (30 ml) and four drops of conc. H_2SO_4 was gently refluxed for 4 hr. After cooling, the mixture was poured into water to give resinous powder (3.4 g), which was chromatographed over 300 g of Kiesel gel (column diameter 5 cm) with benzene–ethylacetate (15: 1, v/v). The eluate was separated into portions of 10 g each. The eluate collected from Nos 111 to 159 was evaporated to give colorless needles (X) of mp 221—222° from methanol-benzene. Yield: 67 mg. UV λ_{max} (mμ, log e): 228.5 (4.59), 258.0 (4.41, sh), 271.0 (4.51), 304.0 (3.94, sh), 352.0 (3.75). *Anal.* Calcd. for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.43; H, 5.57. The eluate collected from Nos 270 to 320 was evaporated to give colorless needles (IX) of mp 194—195°. Yield: 362 mg. UV λ_{max} (mμ, log e): 216.5 (4.65), 227.5 (4.63), 252.5 (4.46), 261.5 (4.43), 295.5 (4.06), 326.0 (3.86, sh). *Anal.* Calcd. for $C_{24}H_{24}O_8$: C, 65.44; H, 5.49. Found: C, 65.14; H, 5.40. The eluate collected from Nos 160 to 269 was rechromatographed over 100 g of Kiesel gel (column diameter 3.5 cm) with benzene–ethylacetate (20: 1, v/v) to give X (87 mg) and IX (54 mg) and colorless needles of mp 272—274° (110 mg). The studies on the constitution of the compound are under way.

Deacetylation of X——X (50 mg) was treated with conc. H_2SO_4 (1 ml) to give yellow needles (XI) of mp 284—286° from benzene–methanol. Yield: 20 mg. $FeCl_3$: green. UV λ_{max} (mμ, log e): 228.0 (4.54, sh), 232.6 (4.56), 268.0 (4.50), 282.0 (4.36, sh), 310 (3,74). *Anal.* Calcd. for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 68.93; H, 5.83.

Deacetylation of IX——IX (110 mg) was deacetylated with conc. H_2SO_4 to give yellow needles (XI) of mp 282—283° from benzene–methanol. Yield: 60 mg. *Anal.* Found: C, 68.80; H, 5.78.

Treatment of IX in Benzene-Ethylacetate with Kiesel Gel——IX (1 mg) ($Rf=0.46$) was dissolved in 16 ml of benzene–ethylacetate (15:1, v/v) and 2 g of Kiesel gel was added and the mixture was kept at room temperature for 5 days. The solution showed two spots at $Rf=0.46$ and at $Rf=0.68$ on a thin-layer chromatogram (benzene–ethylacetate=10:1, Kiesel gel), the latter of which was almost equal to that of X ($Rf=0.70$).

The Dienone-Phenol Rearrangement of V——A mixture of V (3 g), acetic anhydride (30 ml) and 3 drops of conc. H_2SO_4 was gently refluxed for 3 hr and after cooling, the mixture was poured into water to give precipitate (3.5 g), which was chromatographed over 200 g of Kiesel gel (column diameter 5 cm) with benzene–ethylacetate (15:1, v/v). The eluate was separated into portions of 10 g each. The eluate from Nos 181 to 430 was evaporated to give 1.05 g of powder, which was rechromatographed over 100 g of Kiesel gel with benzene–ethylacetate (8:1, v/v). The eluate from Nos 24 to 34 gave faint yellow needles (XIII) of mp 211—212° from benzene–methanol. Yield: 38 mg. $FeCl_3$: green. UV λ_{max} (mμ, log e): 218.0 (4.32, sh), 259.0 (4.69), 284.5 (4.37), 359.0 (4.05). *Anal.* Calcd. for $C_{20}H_{18}O_7$: C, 64.86; H, 4.90. Found: C, 64.89; H, 4.95.

The eluate from Nos 58 to 87 gave colorless needles (XIV) of mp 199—200°. Yield: 198 mg. $FeCl_3$: green. UV λ_{max} (mμ, log e): 251.5 (4.53), 282.0 (4.42), 317.0 (4.02). *Anal.* Calcd. for $C_{22}H_{20}O_8$: C, 64.07; H, 4.89. Found: C, 63.84; H, 4.98.

The eluate from Nos 113 to 125 gave colorless needles (XII) of mp 201—202° from benzene–methanol. Yield: 29 mg. $FeCl_3$; negative. UV λ_{max} (mμ, log e): 213.5 (4.59), 239.0 (4.48), 250.0 (4.41, sh), 262.5 (4.33), 306.0 (4.18). *Anal.* Calcd. for $C_{24}H_{22}O_9$: C, 63.43; H, 4.88. Found: C, 63.57; H, 4.67.

Deacetylation of XII——XII (50 mg) was treated with conc. H_2SO_4 (1 ml) to give pale yellow needles (XV) of mp 291—293° from benzene–methanol. Yield: 20 mg. $FeCl_3$: green. UV λ_{max} (mμ, log e): 264.0 (4.64), 295.5 (4.37, sh), 354.0 (4.21). *Anal.* Calcd. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.91; H, 4.86.

Deacetylation of XIII——XIII (20 mg) was deacetylated with conc. H_2SO_4 (0.5 ml) to give pale yellow needles (XV) of mp 291—293°. *Anal.* Found: C, 66.03; H, 4.91.

Deacetylation of XIV——XIV (70 mg) was deacetylated with conc. H_2SO_4 to give XV of mp 291—293°. *Anal.* Found: C, 65.51; H, 4.85.

The Dienone-Phenol Rearrangement of VI——A mixture of VI (2 g), acetic anhydride (20 ml) and 3 drops of conc. H_2SO_4 was refluxed gently for 2 hr and the mixture was poured into ice water to give resinous precipitate (2.2 g), which was chromatographed over 250 g of Kiesel gel with benzene–ethylacetate (15:1, v/v). The eluate was separated into portions of 10 g each. The eluate from Nos 121 to 460 gave 620 mg of powder, which was rechromatographed over 124 g of Kiesel gel with benzene–ethylacetate (8:1, V/V). The eluate was separated into portions of 8 g each and the eluate from Nos 28 to 32 gave pale yellow needles (XIII) of mp 211—212° from benzene–methanol. Yield: 30 mg. *Anal.* Found: C, 64.92; H, 4.91. The eluate from Nos 70 to 76 gave colorless needles (XIV) of mp 199—200°. Yield: 75 mg. *Anal.* Found: C, 64.04; H, 5.25. The eluate from Nos 156 to 160 gave colorless needles (XII) of mp 201—202°. Yield: 20 mg. *Anal.* Found: C, 63.23; H, 4.83.

Treatment of XII in Benzene-Ethylacetate with Kiesel gel——XII (1 mg, Rf=0.33) was dissolved in 16 ml of benzene–ethylacetate (15:1, v/v) and 2 g of Kiesel gel was added and the mixture was kept at room temperature for 5 days. The solution showed two spots on a thin-layer chromatogram at Rf=0.57 and Rf=0.82, which were almost equal to those of XIV (Rf=0.55) and VIII (Rf=0.82), respectively (benzene–ethylacetate=10:1, Kiesel gel).

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