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Studies on the Terpenoids and Related Alicyclic Compounds. XXI.[1] Formation and X-Ray Crystal Structure of a Novel Spiro Dimer of 6-Dehydroxysantoninic Acid

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Treatment of 14-bromo-6-dehydroxysantoninic acid (**1a**) with 10% Na_2CO_3–acetone solution gave the lactone dimer (**2**), the spiro dimer (**5**), and a hydroxy compound (**4**), in 17%, 40%, and 21% yields, respectively. The molecular structure of the major product, 6-dehydroxysantoninic acid spiro dimer (**5**), was confirmed by X-ray crystallographic analysis. The mechanism of formation of **5** during the course of this reaction is discussed.

Keywords——sesquiterpene; santonin derivatives; NMR; X-ray analysis; HOMO/LUMO reaction mechanism; dimerization

In a previous paper,[3] we reported the formation of 6-dehydroxysantonin lactone dimer (**2**) as a symmetric lactone during the course of the reaction of 14-bromo-6-dehydroxysantoninic acid (**1a**) with sodium carbonate, for the purpose of synthesizing the trienone carboxylic acid (**3**). In this paper, we report that a novel spiro dimer (**5a**) of 6-dehydroxysantoninic acid is a major product in this reaction. The molecular structure of **5a** was confirmed by X-ray crystallographic analysis.

The 14-bromide (**1a**) was refluxed for 1.5 hr with 10% sodium carbonate in acetone to give the lactone dimer (**2**), mp 310—312°, in 17% yield, as reported previously.[3] The acidic products formed in this reaction, which could not be separated, were converted into methyl ester derivatives by treatment with diazomethane and separated by preparative thin-layer chromatography (TLC) to provide an ester dimer (**5b**), mp 170—171.5°, the hydroxy ester (**4**),[3] and the methyl ester of the starting material (**1a**) in 40%, 21%, and 1% yields, respectively.

The structure of the hydroxy ester was confirmed to be **4**[3] by its nuclear magnetic resonance (NMR) and infrared (IR) spectra, in comparison with those of an authentic specimen which was derived from the lactone dimer (**2**).[3] High-resolution mass spectral analysis of the ester dimer (**5b**) indicated an empirical formula of $C_{32}H_{40}O_6$ (M^+, 520.2792), which suggested the structure to be 6-dehydroxysantoninic acid methyl ester dimer. IR and ultraviolet (UV) spectra of the ester dimer (**5b**) showed absorptions at 1655, 1626, 1600 cm^{-1} and λ_{max}^{EtOH} 232 nm (ε 20700), which indicated the presence of conjugated moieties. In the ^{1}H-NMR spectrum of **5b** four methyl groups appeared at δ 0.91, 1.21, 1.29, and 1.36, two ester methyl signals at δ 3.52 and 3.59, and five olefinic protons at δ 5.25, 5.96, 6.17, 6.61, and 6.77. However, C-4 methyl proton signals were not observed. In the ^{13}C-NMR of **5b**, all 32 carbon signals are seen (see "Experimental").

Hydrolysis of the ester dimer (**5b**) with alkali gave an acid dimer (**5a**) monohydrate, mp 144—146°, $C_{30}H_{34}O_6 \cdot H_2O$. The IR, UV, and ^{1}H-NMR spectra of **5a** were similar to those of the ester dimer (**5b**), and the ^{13}C-NMR of **5a** also showed all 30 carbon signals (see "Experi-

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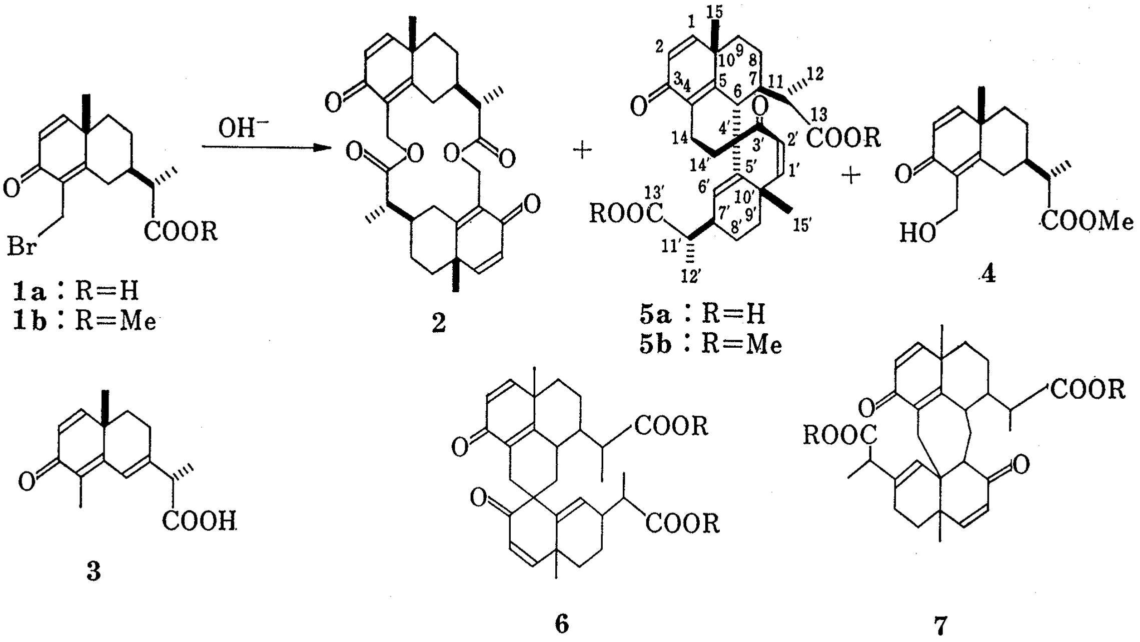

1a : R=H
1b : R=Me

2

5a : R=H
5b : R=Me

4

3

6

7

Chart 1

mental"). The above spectral data for **5a** and **5b** suggested asymmetric structures for these compounds. The possible structures of the dimer include (**5**—**7**), but it could not be decided which structure is correct.

The structure and stereochemistry of 6-dehydroxysantoninic acid dimer (**5a**) monohydrate were determined by X-ray crystallographic analysis. The crystals were grown in aqueous ethanol solution as small colorless prisms elongated along the *c* axis. The lattice parameters and intensity data were measured on a Philips PW 1100 automatic four-circle diffracto-

TABLE Ia. Fractional Atomic Coordinates, $\times 10^4$

Atom	x	y	z
C1	6940(5)	508(6)	2601(12)
C2	6849(6)	−225(6)	2085(13)
C3	6592(5)	−344(6)	503(11)
C4	6326(5)	318(5)	−397(10)
C5	6344(5)	1037(5)	167(10)
C6	6032(5)	1737(5)	−637(10)
C7	5535(5)	2192(5)	501(11)
C8	6033(6)	2460(6)	1837(12)
C9	6333(6)	1753(6)	2720(11)
C10	6756(5)	1202(5)	1673(11)
C11	5120(5)	2890(6)	−211(12)
C12	4499(7)	3091(6)	910(13)
C13	5623(7)	3595(7)	−579(15)
C14	6061(5)	132(6)	−1987(11)
C15	7546(6)	1571(6)	1246(13)
OW	2998(4)	2795(4)	3201(8)
O1	6604(4)	−997(4)	−61(8)
O2	4475(5)	3681(5)	1682(11)
O3	3980(4)	2582(4)	998(9)
C1′	4531(6)	2311(6)	−4200(13)
C2′	5202(6)	2605(6)	−4117(12)
C3′	5813(5)	2247(6)	−3266(11)
C4′	5656(5)	1535(5)	−2222(11)
C5′	4817(5)	1335(5)	−2126(11)

Atom	x	y	z
C 6′	4562(5)	936(5)	−949(11)
C 7′	3753(6)	701(6)	−718(13)
C 8′	3255(6)	878(7)	−2113(15)
C 9′	3499(6)	1649(7)	−2857(15)
C 10′	4305(6)	1550(6)	−3479(12)
C 11′	3722(6)	−190(7)	−388(13)
C 12′	4118(7)	−362(7)	1123(15)
C 13′	2897(8)	−490(8)	−289(17)
C 14′	6090(5)	872(6)	−2995(11)
C 15′	4354(7)	930(7)	−4819(14)
O 1′	6450(4)	2473(4)	−3415(8)
O 2′	3835(6)	−212(7)	2342(12)
O 3′	4777(5)	−672(5)	999(10)

Estimated standard deviations are given in parentheses.

TABLE Ib. Anisotropic Thermal Parameters, ×10^4

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C 1	21(3)	38(4)	113(16)	0(3)	−3(7)	12(7)
C 2	25(4)	39(5)	124(17)	0(4)	−8(7)	16(8)
C 3	19(3)	28(4)	97(14)	1(3)	8(6)	2(7)
C 4	17(3)	27(3)	71(13)	0(3)	−4(5)	2(6)
C 5	17(3)	23(3)	62(12)	−1(3)	1(5)	2(6)
C 6	20(3)	25(3)	63(13)	1(3)	−1(6)	−1(6)
C 7	24(3)	25(3)	74(13)	5(3)	3(6)	−6(6)
C 8	38(4)	37(4)	83(15)	4(4)	−2(7)	−23(8)
C 9	34(4)	30(4)	85(14)	5(3)	3(7)	−9(7)
C 10	22(3)	26(3)	79(13)	−1(3)	−13(6)	2(6)
C 11	28(3)	26(4)	93(15)	8(3)	4(6)	−12(7)
C 12	39(4)	33(4)	101(16)	8(4)	−11(8)	−14(7)
C 13	41(5)	36(5)	160(21)	−1(4)	17(9)	4(9)
C 14	25(3)	30(4)	74(14)	4(3)	−4(6)	−2(7)
C 15	20(3)	39(4)	129(17)	−8(3)	−12(7)	8(8)
OW	32(3)	38(3)	147(12)	−2(2)	0(5)	−17(5)
O 1	33(3)	26(2)	107(11)	4(2)	4(5)	7(5)
O 2	44(3)	46(4)	225(17)	5(3)	17(7)	−48(7)
O 3	35(3)	40(3)	176(13)	1(3)	10(6)	−21(6)
C 1′	35(4)	39(4)	107(16)	5(4)	0(7)	5(8)
C 2′	32(4)	33(4)	111(16)	2(4)	−2(7)	11(8)
C 3′	26(3)	35(4)	74(13)	−1(3)	3(6)	−6(7)
C 4′	21(3)	22(3)	68(13)	1(3)	−4(6)	4(6)
C 5′	21(3)	20(3)	89(14)	3(3)	−4(6)	−11(6)
C 6′	24(3)	19(3)	90(14)	−1(3)	4(6)	−3(6)
C 7′	22(3)	34(4)	145(18)	−3(3)	1(7)	7(8)
C 8′	28(4)	54(6)	158(21)	0(4)	−15(8)	19(10)
C 9′	22(4)	46(5)	190(22)	2(4)	−11(8)	22(10)
C 10′	28(4)	29(4)	81(14)	−1(3)	−3(7)	2(6)
C 11′	31(4)	41(5)	119(17)	−9(4)	−4(8)	7(8)
C 12′	46(5)	38(5)	150(21)	−5(5)	24(9)	2(9)
C 13′	43(5)	67(7)	224(27)	−27(5)	−6(11)	24(13)
C 14′	28(3)	26(4)	69(14)	6(3)	−2(6)	−13(6)
C 15′	50(5)	40(5)	96(17)	−3(4)	−15(9)	−18(8)
O 1′	28(3)	38(3)	109(10)	−4(2)	6(5)	7(5)
O 2′	69(5)	109(7)	161(17)	25(5)	1(9)	7(10)
O 3′	40(3)	46(4)	179(15)	5(3)	1(6)	4(7)

Estimated standard deviations are given in parentheses. Temperature factors are of the form: $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Table II. Bond Lengths (Å) and Bond Angles (°) of 6-Dehydroxysantoninic Acid Dimer (**5a**) Monohydrate

Atom 1	Atom 2	Length	Atom 1	Atom 2	Length
C 1	– C 2	1.363(15)	C 14	– C 14′	1.563(14)
C 1	– C 10	1.493(14)	C 1′	– C 2′	1.313(16)
C 2	– C 3	1.473(15)	C 1′	– C 10′	1.522(15)
C 3	– C 4	1.476(13)	C 2′	– C 3′	1.466(15)
C 3	– O 1	1.238(12)	C 3′	– C 4′	1.566(14)
C 4	– C 5	1.347(13)	C 3′	– O 1′	1.219(12)
C 4	– C 14	1.505(13)	C 4′	– C 5′	1.552(13)
C 5	– C 6	1.515(13)	C 4′	– C 14′	1.549(13)
C 5	– C 10	1.538(13)	C 5′	– C 6′	1.324(13)
C 6	– C 7	1.555(13)	C 5′	– C 10′	1.545(14)
C 6	– C 4′	1.582(13)	C 6′	– C 7′	1.526(14)
C 7	– C 8	1.545(14)	C 7′	– C 8′	1.544(17)
C 7	– C 11	1.556(13)	C 7′	– C 11′	1.579(16)
C 8	– C 9	1.549(15)	C 8′	– C 9′	1.554(18)
C 9	– C 10	1.530(14)	C 9′	– C 10′	1.558(15)
C 10	– C 15	1.605(14)	C 10′	– C 15′	1.597(16)
C 11	– C 12	1.527(15)	C 11′	– C 12′	1.531(17)
C 11	– C 13	1.559(15)	C 11′	– C 13′	1.577(18)
C 12	– O 2	1.230(14)	C 12′	– O 2′	1.210(16)
C 12	– O 3	1.290(14)	C 12′	– O 3′	1.307(15)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C 2	– C 1	– C 10	123.4(9)	C 3′	– C 2′	– C 1′	123.5(10)
C 3	– C 2	– C 1	118.8(9)	C 4′	– C 3′	– C 2′	119.8(8)
C 4	– C 3	– C 2	119.5(8)	C 4′	– C 3′	– O 1′	119.2(9)
C 4	– C 3	– O 1	120.6(9)	C 2′	– C 3′	– O 1′	120.9(9)
C 2	– C 3	– O 1	119.9(9)	C 5′	– C 4′	– C 6	114.8(7)
C 5	– C 4	– C 3	121.5(8)	C 5′	– C 4′	– C 3′	112.6(7)
C 5	– C 4	– C 14	123.1(8)	C 5′	– C 4′	– C 14′	110.3(7)
C 3	– C 4	– C 14	115.3(8)	C 6	– C 4′	– C 3′	104.9(7)
C 6	– C 5	– C 4	124.7(8)	C 6	– C 4′	– C 14′	109.4(7)
C 6	– C 5	– C 10	115.2(7)	C 3′	– C 4′	– C 14′	104.1(7)
C 4	– C 5	– C 10	120.0(8)	C 6′	– C 5′	– C 4′	119.7(8)
C 7	– C 6	– C 5	109.0(7)	C 6′	– C 5′	– C 10′	121.1(8)
C 7	– C 6	– C 4′	115.3(7)	C 4′	– C 5′	– C 10′	119.0(8)
C 5	– C 6	– C 4′	112.7(7)	C 7′	– C 6′	– C 5′	125.0(9)
C 8	– C 7	– C 6	107.7(8)	C 8′	– C 7′	– C 6′	113.2(9)
C 8	– C 7	– C 11	110.2(8)	C 8′	– C 7′	– C 11′	108.7(9)
C 6	– C 7	– C 11	114.7(8)	C 6′	– C 7′	– C 11′	108.7(8)
C 9	– C 8	– C 7	109.9(8)	C 9′	– C 8′	– C 7′	109.9(10)
C 10	– C 9	– C 8	111.9(8)	C 10′	– C 9′	– C 8′	108.3(9)
C 15	– C 10	– C 1	104.7(8)	C 15′	– C 10′	– C 1′	105.7(8)
C 15	– C 10	– C 5	107.6(7)	C 15′	– C 10′	– C 5′	111.4(8)
C 15	– C 10	– C 9	109.2(8)	C 15′	– C 10′	– C 9′	112.5(9)
C 1	– C 10	– C 5	114.9(8)	C 1′	– C 10′	– C 5′	111.6(8)
C 1	– C 10	– C 9	107.1(8)	C 1′	– C 10′	– C 9′	107.3(9)
C 5	– C 10	– C 9	113.0(8)	C 5′	– C 10′	– C 9′	108.3(8)
C 12	– C 11	– C 7	105.9(8)	C 12′	– C 11′	– C 7′	109.5(9)
C 12	– C 11	– C 13	112.1(9)	C 12′	– C 11′	– C 13′	109.0(10)
C 7	– C 11	– C 13	114.8(8)	C 7′	– C 11′	– C 13′	111.6(9)
O 2	– C 12	– C 11	124.7(10)	O 2′	– C 12′	– C 11′	121.5(12)
O 2	– C 12	– O 3	121.1(10)	O 2′	– C 12′	– O 3′	122.9(12)
C 11	– C 12	– O 3	114.2(9)	C 11′	– C 12′	– O 3′	115.6(10)
C 14′	– C 14	– C 4	109.4(5)	C 14	– C 14′	– C 4′	110.6(8)
C 2′	– C 1′	– C 10′	124.2(10)				

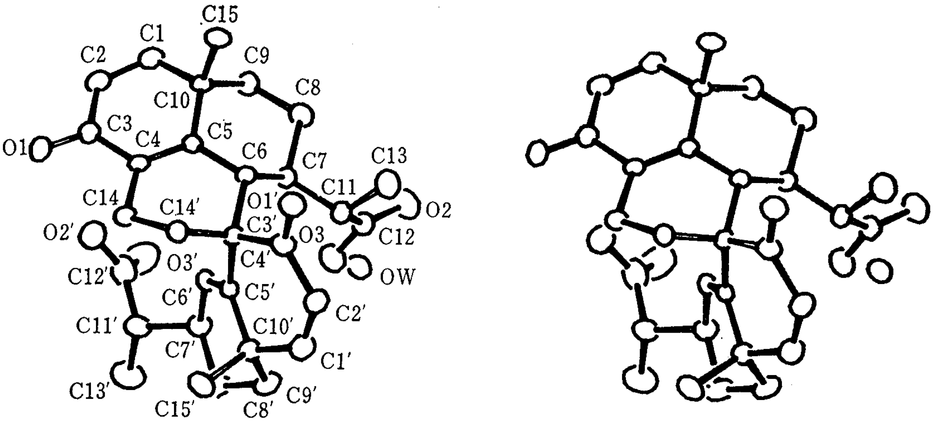

Fig. 1. Stereoscopic View (ORTEP) of 6-Dehydroxysantoninic Acid Dimer (**5a**) Monohydrate

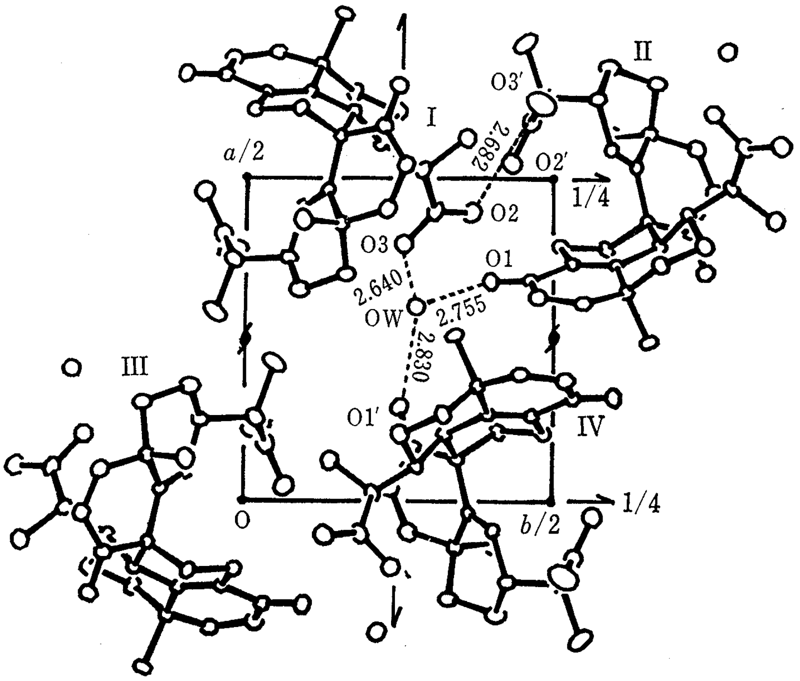

Fig. 2. Projection of the Crystal Structure of **5a** along the *c* Axis

Hydrogen bonds are shown by dotted lines. The symmetry operations are, I: x,y,z, II: $1-x,1/2+y,1/2-z$, III: $1/2-x,-y,1/2+z$, IV: $-1/2+x,1/2-y,-z$.

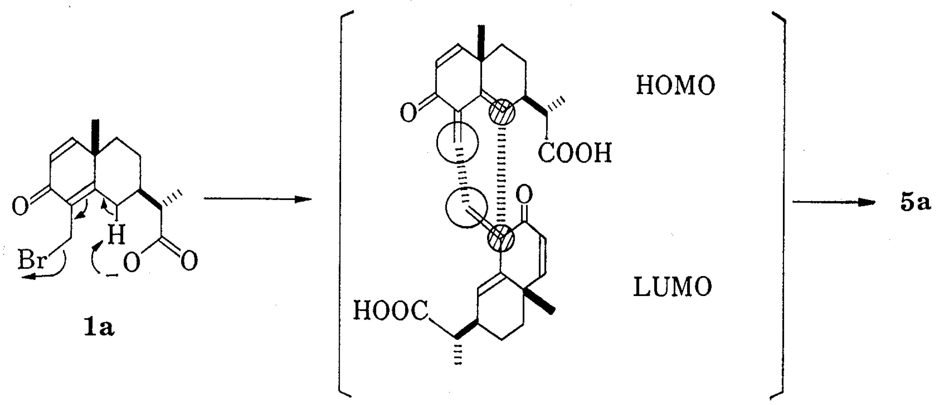

Chart 2

meter using the θ-2θ scan method with CuKα radiation monochromated by means of a graphite plate. The crystal data for **5a** monohydrate, $C_{30}H_{34}O_6 \cdot H_2O$, Mol. Wt. 508.6, are as follows: orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell of dimensions $a=17.990(5)$, $b=17.414(5)$, $c=8.747(3)$ Å, $U=2740.3$ Å. The intensities of 1820 independent reflections were obtained above the 2σ(I) level out of 3134 theoretically possible ones in the 2θ range of 6°—156°. The crystal structure was solved by the direct method using MULTAN⁴⁾ and was refined by the block diagonal least-squares procedure. The final R value was 0.084 for 37 heavier atoms with anisotropic temperature factors. No attempt was made to locate hydrogen atoms. The finals positional and thermal parameters are given in Table I. Bond distances and bond angles of **5a** are shown in Table II. A stereoscopic view of **5a** is illustrated in Fig. 1 in the form of an ORTEP⁵⁾ drawing. The two molecules are bound together through hydrogen bonds which link O(2) to O(3′) (2.682 Å) and O(3) to O(1) *via* water of crystallization [O(3)....O(w), 2.640 Å and O(w)....O(1), 2.755 Å]. Another hydrogen bond binds O(w) to O(1′) of the third molecule [O(3)....O(1′), 2.830 Å]. The crystal structure of **5a** is illustrated in Fig. 2.

The mechanism of formation of the acid spiro dimer (**5a**) from **1a** by the action of sodium carbonate is proposed in Chart 2. The trienone initially formed as an intermediate underwent facile Diels–Alder cycloaddition between the HOMO of 2-Z(electron withdrawing)-substituted diene and the LUMO of 2-Z-substituted olefin, as shown in Chart 2, to give the dimer (**5a**) regioselectively.⁶⁾

On the other hand, treatment of the ester (**1b**) with sodium carbonate under the conditions described for **1a** gave the hydroxyester (**4**) in 26% yield, and 55% of **1b** was recovered. In the case of **1b**, the formation of the trienone in the initial step does not occur because of the difficulty of deprotonation of C-6H, so the ester dimer (**5b**) could not be formed.

Experimental

All melting points were determined on a Yamato micromelting point apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were measured at 100 MHz and 25.0 MHz, respectively, on a JEOL FX-100 Fourier transform NMR spectrometer. IR spectra were measured with a Hitachi Perkin-Elmer 225 and a Hitachi 215 grating spectrophotometer. UV spectra were measured as solutions in ethanol with a Hitachi 323 spectrophotometer. Mass spectra (MS) were recorded on a Hitachi RMU-7M double-focusing mass spectrometer at 70 eV, using direct insertion. High-resolution mass spectral data were determined with a Hitachi datalyzer 002 system connected on-line with the mass spectrometer. Specific rotations were measured with a Jasco DIP-SL digital polarimeter.

Wako silica gel C-200 (200 mesh) containing 2% fluorescence reagent 254 was used in column chromatography. Preparative thin-layer chromatography (TLC) was carried out using Merck silica gel HF_{254}.

Treatment of the 14-Bromide (1a) with Na_2CO_3——(i) 10% Na_2CO_3 (5 ml) was added to a solution of the 14-bromide (**1a**) (297 mg) in acetone (12 ml). This solution was heated under reflux for 1.5 hr. The mixture was concentrated, diluted with 10% Na_2CO_3, and extracted with EtOAc. The EtOAc extracts were washed with H_2O and dried. Removal of the solvent by evaporation gave the lactone dimer (**2**) (38 mg; 17% yield) as pale yellow crystals. Recrystallization from EtOH gave **2** as colorless needles, mp 310—312°. The IR, UV, and NMR spectra of **2** were identical with those of an authentic specimen (**2**) reported previously by us.³⁾

(ii) The above alkaline layer was acidified with 10% HCl and extracted with EtOAc. The extracts were washed with H_2O and dried. Removal of the solvent gave a pale yellow viscous oil. The crude oil was esterified by treatment with excess ethereal diazomethane. The crude products were purified by silica gel preparative TLC, developing with hexane: EtOAc (2: 1) to afford three bands.

Band 1 gave the 14-bromide ester (**1b**) (3.2 mg; 1% yield) and recrystallization from EtOAc gave colorless prisms, mp 89—90°. *Anal.* Calcd for $C_{16}H_{21}BrO_3$: C, 56.31; H, 6.21; Br, 23.41. Found: C, 56.83; H, 6.42; Br, 22.78. $[\alpha]_D^{25°}$ −123.7° (c, 1.09, $CHCl_3$); UV: λ_{max}^{EtOH} 240 nm (ε 12330); IR cm^{-1}: 1725, 1650, 1623, 1598; NMR δ: 1.24 (3H, d, $J=7$ Hz, 11-CH_3), 1.26 (3H, s, 10-CH_3), 2.16 (1H, t, $J=12$ Hz, 6β-CH_3), 2.53 (1H, quintet, $J=7$ Hz, 11-H), 2.83 (1H, bd, $J=12$ Hz, 6α-H), 3.72 (3H, s, $COOCH_3$), 4.22 (1H, d, $J=10$ Hz, 1-H);

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MS *m*/*z* (% Rel. int.); 342, 340 $[M]^{+\cdot}$ (1), 327 (1), 325 (1), 261 $[M-Br]^+$ (70), 260 $[M-HBr]^+$ (35), 173 (100).

Band 2 gave the dimer (**5b**), as pale yellow crystals (96 mg; 40.5% yield), mp 163—168°. Recrystallization from hexane–EtOAc gave **5b**, mp 170—171.5°, as colorless prisms. *Anal.* Calcd for $C_{32}H_{40}O_6$: C, 73.82; H, 7.74. Mol. Wt. 520.2822. Found: C, 74.10; H, 7.64. $[M]^{+\cdot}$, 520.2792. $[\alpha]_D^{25°}$ +84.6° (c, 2.0, $CHCl_3$); UV λ_{max}^{EtOH} nm (ε): 232 (20700), 270 (9760); IR cm^{-1}: 1723, 1655, 1626, 1600; ^{1}H-NMR δ: 0.91, 1.21 (each 3H, d, *J*=7 Hz, 11-, 11′-CH_3), 1.29, 1.30 (each 3H, s, 10-, 10′-CH_3), 3.52, 3.59 (each 3H, s, $COOCH_3$), 5.25 (1H, bd, *J*=3 Hz, 6′-H), 5.96 (1H, d, *J*=10 Hz, 2′-H), 6.17 (1H, d, *J*=10 Hz, 1′-H); ^{13}C-NMR δ: 201.1 (1C, s, C-3′), 184.5 (1C, s, C-3), 175.8 (1C, s, C-13), 175.6 (1C, s, C-13′), 161.0 (1C, s, C-5), 157.3 (1C, d, C-1′), 156.6 (1C, d, C-1), 135.6 (1C, s, C-4), 133.4 (1C, s, C-5′), 129.9 (1C, d, C-6′), 125.4 (1C, d, C-2), 124.6 (1C, d, C-2′), 54.0 (1C, s, C-4′), 51.7 (1C, q, C-16), 51.7 (1C, q, C-16′), 44.6 (1C, d, C-11), 44.2 (1C, d, C-11′), 40.7 (1C, s, C-10), 39.9 (1C, d, C-6), 39.5 (1C, d, C-7), 38.5 (1C, t, C-14), 36.8 (1C, d, C-7′), 35.7 (1C, s, C-10′), 35.5 (1C, t, C-8), 33.9 (1C, t, C-8′), 30.4 (1C, q, C-12), 26.2 (1C, q, C-12′), 21.6 (1C, t, C-9), 21.3 (1C, t, C-9′), 18.3 (1C, t, C-14′), 14.6 (1C, q, C-15), 9.5 (1C, q, C-15′); MS *m*/*z* (% Rel. int.): 520 (M^+, 100), 505 (25), 489 (12), 433 (87), 273 ($[M/2]^+$, 28), 259 (32).

Band 3 gave a hydroxy ester (**4**; 21% yield) as a pale yellow oil. The IR, UV, NMR, and mass spectra of **4** were identical with those of an authentic specimen reported previously.$^{3)}$

6-Dehydroxysantoninic Acid Spiro Dimer (5a)——The ester dimer (**5b**; 100 mg) was dissolved in a solution of KOH (100 mg) in 80% methanol (4 ml). The whole solution was stirred at 70° for 1 hr. After removal of the solvent, the residue was acidified with 10% HCl and then extracted with EtOAc. The extract was washed with water, sat. $NaHCO_3$, and water, then dried. Removal of the solvent afforded 86 mg (91% yield) of colorless crystals. Recrystallization from 40% ethanol afforded the acid dimer (**5a**) monohydrate as colorless needles, mp 144—146°. *Anal.* Calcd for $C_{30}H_{34}O_6 \cdot H_2O$: C, 70.57; H, 7.50. Found: C, 70.41; H, 7.58. $[\alpha]_D^{20°}$ +55.8° (c, 0.2, EtOH); UV λ_{max}^{EtOH} nm (ε): 232 (14100), 272 (shoulder); IR cm^{-1}: 1738, 1700, 1654, 1605. ^{1}H-NMR δ: 0.92, 1.08 (each 3H, d, *J*=7 Hz; 11-, 11′-CH_3), 1.30, 1.36 (each 3H, s, 10- 10′-CH_3), 3.64 (1H, d, *J*=12 Hz; 6-H), 5.28 (1H, d, *J*=3 Hz, 6′-H), 5.98, 6.19, 6.62, 6.74 (each 1H, d, *J*=10 Hz, 2′-, 2-, 1-, 1′-H, respectively); ^{13}C-NMR δ: 11.86 (1C, q, C-15′), 14.79 (1C, q, C-15), 19.73 (1C, t, C-14′), 21.02 (1C, t, C-9′), 22.25 (1C, t, C-9), 26.48 (1C, q, C-12′), 30.76 (1C, q, C-12), 34.99 (1C, t, C-8′), 35.70 (1C, t, C-8), 36.93 (1C, s, C-10′), 37.67 (1C, d, C-7′), 39.98 (1C, t, C-14), 40.86 (1C, d, C-11′), 42.68 (1C, d, C-11), 43.09 (1C, s, C-10), 46.50 (1C, d, C-11), 48.08 (1C, d, C-11′), 55.07 (1C, s, C-4′), 124.41 (1C, d, C-2′), 124.82 (1C, d, C-2), 133.09 (1C, d, C-6′), 133.33 (1C, d, C-5′), 135.09 (1C, s, C-4), 161.98 (1C, d, C-1), 163.27 (1C, d, C-1′), 168.67 (1C, s, C-5), 184.70 (1C, s, C-13′), 185.46 (1C, s, C-13), 188.73 (1C, s, C-3), 206.72 (1C, s, C-3′).

Treatment of the 14-Bromide (1b) with Na_2CO_3——Using the procedure described for **1a**, 10% Na_2CO_3 (2.3 ml) was added to a solution of 14-bromide ester (**1b**) (150 mg) in acetone (6 ml). The solution was heated under reflux for 3 hr. After work-up, the crude products were separated by preparative TLC to give Bands 1—3.

Band 1 gave the 14-bromide ester (**1b**), mp 85—86°, as colorless crystals (82.4 mg; 55% recovered). The IR and NMR spectra were identical with those of the starting material.

Band 2 gave a lactone dimer (**2**) (2.2 mg; 2% yield) as crystals, mp 310—312°. The IR and NMR spectra of **2** were identical with those of the lactone dimer (**2**).$^{3)}$

Band 3 gave a hydroxy ester (**4**) (31.5 mg; 26% yield) as an oil. The NMR spectrum of **4** was identical with that of an authentic specimen of **4**.$^{3)}$

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