Studies on the Terpenoids and Related Alicyclic Compounds. IV.[1] Dimerization of 14-Bromo-6-dehydroxysantoninic Acid

Koji Yamakawa* and Kiyoshi Nishitani

Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan

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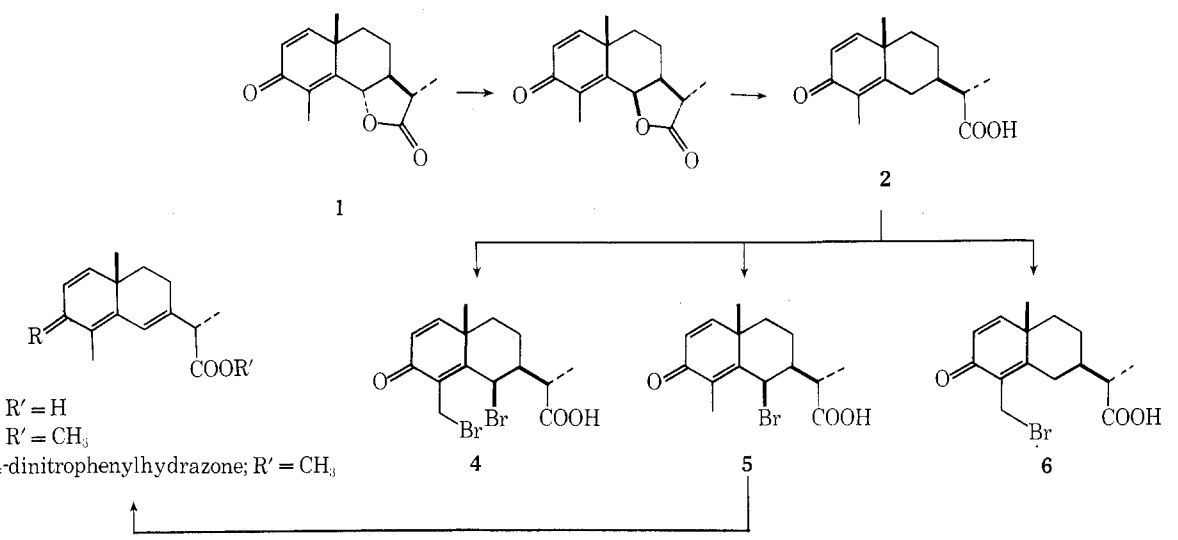
Previous studies in this laboratory have reported the transformation of α- and γ-tetrahydrosantonin into 5α- and 5β-2-oxosantanolide, respectively.[2] The original objective of the investigation outlined in this paper was the introduction of oxygenated functions at the C-8 position in the santan skeleton for the transformation of santan-6,12-olide into santan-8,12-olide.

For the above purpose, the preparation of trienonecarboxylic acid (**3**) from 6-dehydroxysantoninic acid (**2**) by bromination–dehydrobromination was investigated (Scheme I). This paper reports the formation of a novel 6-dehydroxysantonin dimer (**7**) during the course of this reaction.

Scheme I

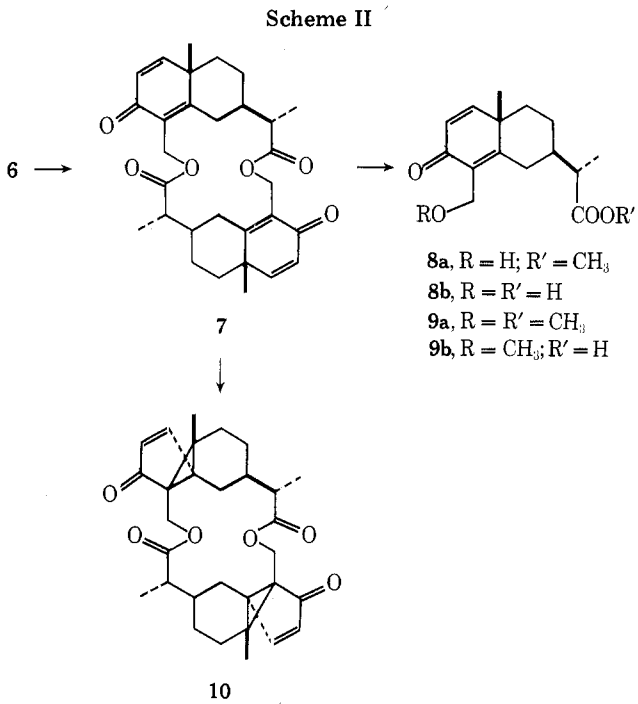


Miki[3] already reported that bromination of (±)-dienonecarboxylic acid (**2**) with *N*-bromosuccinimide in carbon tetrachloride gave a noncrystalline bromide, which was treated with 20% sodium carbonate in acetone and isolated without purification to give (±)-6-deoxysantoninic acid (**3**). Now, bromination of (−)-**2**, prepared from (−)-α-santonin (**1**),[4] was effected using *N*-bromosuccinimide in a carbon tetrachloride solution which was warmed at 40–45 °C until decoloration took place. After work-up, the residue was chromatographed on silica gel and purified by recrystallization. Fraction 1 gave a viscous oil, 6β,14-dibromide **4**, whose structure was determined by ir, uv, and NMR data. The NMR spectrum of **4** showed absorption at δ 5.67 for the C-6 H and at δ 4.05 and 4.07 (AB-type doublets) for the C-14 methylene protons. Fraction 2 gave a crystalline product, mp 97–98 °C, whose structure was shown to be the 6β-bromide **5** by spectral data. The NMR spectrum of **5** indicated a peak at δ 5.61 (broad singlet, $W_{1/2}$ = 5 Hz) for the C-6 H. A viscous oily product, the 14-bromide **6**, was isolated from fraction 3. Its structure was established by means of its mass spectrum, molecular ions $[M]^+$ 326 and 328, and ir and uv spectral data. The NMR spectrum of **6** showed signals at δ 4.22 and 4.48 (AB-type doublets) for the C-14 methylene protons.

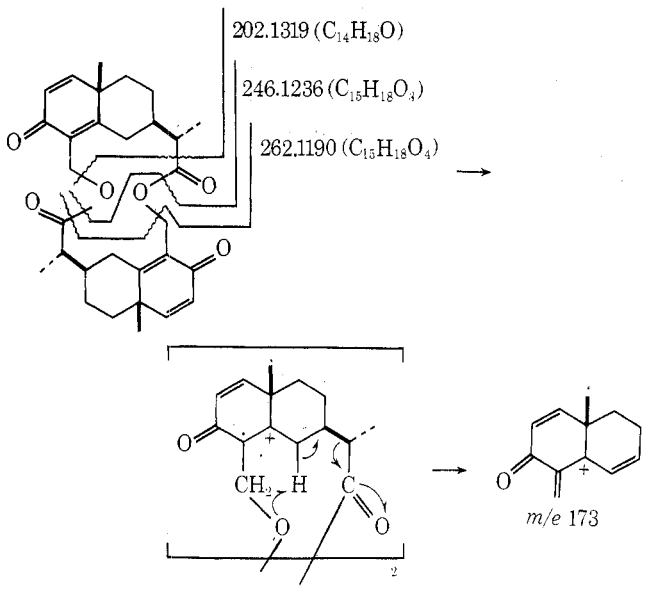
The 6β-bromide **5** was refluxed for 30 min with a 10% sodium carbonate in acetone solution. Work-up of the reaction mixture gave a pale-yellow, viscous oil, 3-oxo-1,4,6-trienic acid (**3a**), in 91% yield. The uv spectrum of **3a** gave λ_{max} (EtOH) 232 and 316 nm (ϵ 12 860 and 12 830) characteristic of a triene chromophore.

The 14-bromide **6** was treated with 10% sodium carbonate in acetone solution as described above for the 6β-bromide **5**. After work-up, the residue was recrystallized to give colorless needles, mp 310–312 °C. High-resolution mass spectral analysis of these crystals indicated an empirical formula of $C_{30}H_{36}O_6$, which suggested the structure to be the 6-dehydroxysantonin dimer (**7**) (Scheme II). The ir and uv spectrum of **7** revealed a cross dienone moiety, 1662, 1630, and 1610 cm^{-1} and λ_{max} (EtOH) 243 nm (ϵ 27 700). In the NMR spectrum of **7**, C-10 and C-11 methyl protons appeared at δ 1.31 (singlet) and 1.18 (doublet), respectively, and AB-type doublet protons were indicated at δ 4.90 and 5.00 for the C-14 methylene group.

Scheme II



Scheme III. Mass Fragmentation Pattern for the 6-Dehydroxysantonin Dimer (7)



The mass fragmentation peaks of **7**, assigned by high-resolution measurement, also supported the dimeric structure **7**. The dimer **7** presumably undergoes fission of the bond connecting the two lactone centers to give the half-molecular ion of **7** at *m/e* 246 corresponding to $C_{15}H_{18}O_3$. Double elimination of the lactone of the dimer **7** occurs in a similar fashion as santonin shown by Budzikiewicz et al.[5] and illustrated in Scheme III. This gave the base peak of the spectrum at *m/e* 173 (*m/e* 246 − 73 ion). The dimer **7** also gave two ions at *m/e* 262 and 202 corresponding to $C_{15}H_{18}O_4$ and $C_{14}H_{18}O$, respectively. The ions at *m/e* 262 and 202 may be explained by cleavage of the C(12)–O and C(14)–O and C(11)–C(12) and C(14)–O bonds, respectively.

Hydrolysis of the dimer **7** with an alkaline methanolic solution gave a mixture of hydroxy keto acid **8b** and methoxy keto acid **9b**, which were converted to the corresponding hydroxy ester **8a** and the methoxy ester **9a**. The structures of **8a** and **9a** were confirmed by their NMR and mass spectra.

The photolysis of santonin under several conditions has been studied extensively by many workers.[6-12] Lumisantonin has been isolated as the initial photolytic rearrangement product of (−)-α-santonin. A solution of dimer **7** in dioxane was irradiated with a mercury lamp (300 nm) at room temperature. A lumisantonin type dimer (**10**) was isolated as colorless prisms, mp 310–312 °C. The structure of the lumisantonin type dimer **10** was confirmed by high-resolution mass spectroscopy for molecular ion $C_{30}H_{36}O_6$ (observed 492.2506) and half-molecular ion $C_{15}H_{18}O_3$ (observed 246.1227). The ir, uv, and NMR spectra of **10** showed λ_{max} (EtOH) 234 nm (ε 9200), ν_{CO} 1700 cm^{-1}, and C-1,1′ and C-2,2′ olefinic protons at δ 7.35 (d, *J* = 5) and 5.95 (d, *J* = 5 Hz), respectively, which also confirmed the presence of a lumisantonin type moiety.[8,13]

Experimental Section

All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra are for solution in $CDCl_3$ and they were measured with a JEOL JNM-4H-100 spectrometer at 100 MHz using Me_4Si as the internal standard. Ir spectra were measured with a Hitachi Perkin-Elmer Model 225 grating spectrophotometer. Uv spectra were measured for solution in ethanol with a Hitachi Model 323 spectrophotometer. Mass spectra were recorded on a Hitachi RMU-7M double-focusing mass spectrometer at 70 eV, by using direct insertion. High-resolution mass spectral data were determined with a Hitachi datalyzer 002 connected on line with the mass spectrometer. Specific rotations were measured for solution in chloroform with a Jasco DIP-SL digital polarimeter.

Gas–liquid phase chromatographic analyses were determined on a Shimadzu gas chromatograph, Model GC-3AF, equipped with a hydrogen flame detector, using a 1% SE-30 on Chromosorb W column. Wako silica gel C-200 (200 mesh) containing 2% fluorescence reagent 254 was used in column chromatography. Preparative thin layer chromatography was carried out using Merck silica gel HF_{254}.

6-Dehydroxysantoninic Acid (2). According to the procedure described by Piers et al.,[4] (−)-6-*epi*-α-santonin was reduced with zinc dust in methanol and glacial acetic acid. 6-Dehydroxysantoninic acid (**2**) obtained in 84% yield, had mp 101–102°; MS *m/e* (rel intensity) 248 $[M]^+$ (66), 230 $[M - H_2O]^+$ (37), 202 (22), 187 (25), 175 (100), 174 (80); $[\alpha]^{21}D$ −71° (*c* 0.6, $CHCl_3$); uv λ_{max} (EtOH) 241 nm (ε 9740); ir (KBr) ν 3200, 1740, 1660, and 1620 cm^{-1}; NMR δ 1.21 (s, 3, C-10 CH_3), 1.26 (d, *J* = 7 Hz, 3, C-11 CH_3), 1.88 (s, 3, C-4 CH_3), 6.27 (d, *J* = 10 Hz, 1, C-2 H), 6.74 (d, *J* = 10 Hz, 1, C-1 H).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.26; H, 8.11.

Bromination of the Keto Acid 2. A. To a solution of the keto acid **2** (800 mg, 3.2 mmol) in 120 ml of carbon tetrachloride was added *N*-bromosuccinimide (800 mg, 4.5 mmol). The reaction mixture was warmed to 40–45 °C under daylight for 6 h until decoloration took place. The reaction mixture was cooled and filtered. After the filtrate had been washed with water and dried, the solvent was removed under reduced pressure to give a pale-brown, viscous oil (1.14 g). The crude product was chromatographed on a silica gel column. Elution with *n*-hexane–ethyl acetate (5:1) gave three fractions. Fraction 1 gave 107 mg of a viscous oil, the 6β,14-dibromide **4**: MS *m/e* (rel intensity) 324, 322 $[M - (H_2 + HBr)]^+$ (17), 279, 277 $[M - (H_2 + HBr + COOH)]^+$ (13), 258 (35), 244 $[M - 2HBr]^+$ (100), 213 (39), 199 (95); $[\alpha]^{21}D$ −269° (*c* 0.8, $CHCl_3$); uv λ_{max} (EtOH) 255 nm (ε 10 810); ir ($CHCl_3$) ν 3500–2500 (broad), 1713, 1663, 1630, and 1610 cm^{-1}; NMR δ 1.34 (d, *J* , 7 Hz, 3, C-11 CH_3), 1.57 (s, 3, C-10 CH_3), 2.80 (m, 1, C-11 H), 4.05 (d, *J* = 10 Hz, 1, C-14 H_a), 4.70 (d, *J* = 10 Hz, 1, C-14 H_b), 5.67 ($W_{1/2}$ = 5 Hz, 1, C-6 H), 6.32 (d, *J* = 10 Hz, 1, C-2 H), 6.75 (d, *J* = 10 Hz, 1, C-1 H), 10.10 (1, COOH).

Fraction 2 gave 530 mg of a viscous oil which was a mixture of 6β,14-dibromide **4** and 6β-bromide **5** (5:4) as evidenced by NMR spectrometry.

Fraction 3 gave 160 mg of a viscous oil, the 14-bromide **6**: MS *m/e* (rel intensity) 328, 326 $[M]^+$ (3), 313, 311 (3), 282, 280 $[M - HCOOH]^+$ (2), 247 $[M - Br]^+$ (72), 246 $[M - HBr]^+$ (44), 201 $[M - (HBr + COOH)]^+$ (18), 174 (35), 173 (100); $[\alpha]^{21}D$ − 93° (*c* 0.7, $CHCl_3$); uv λ_{max} (EtOH) 241 nm (ε 10 000); ir ($CHCl_3$) ν 3500–2500 (broad), 1706, 1660, and 1625 cm^{-1}; NMR δ 1.24 (s, 3, C-10 CH_3), 1.28 (d, *J* = 6 Hz, 3, C-11 CH_3), 4.22 (d, *J* = 9 Hz, 1, C-14 H_a), 4.48 (d, *J* = 9 Hz, 1, C-14 H_b), 6.31 (d, *J* = 10 Hz, 1, C-2 H), 6.78 (d, *J* = 10 Hz, 1, C-1 H), 10.40 (1, COOH).

B. To a solution of the keto acid **2** (4.0 g, 16 mmol) in 400 ml of carbon tetrachloride was added 427 mg (2.4 mmol) of *N*-bromosuccinimide. The reaction mixture was warmed at 40–45 °C under daylight for 2 h. The reaction products (5.6 g) were separated in the same manner as described above. Fraction 1 gave 273 mg of the dibromide **4**.

Fraction 2 gave 1.73 g of 6β-bromide **5**, mp 91–93 °C. Recrystallization from *n*-hexane and ethyl acetate mixture gave colorless prisms: mp 97–98 °C; MS *m/e* (rel intensity) 326, 324 $[M - H_2]^+$ (1.7), 281, 279 $[M - COOH]^+$ (0.8), 246 $[M - HBr]^+$ (41), 244 (17), 201 $[M - (HBr + COOH)]^+$ (32), 174 (36), 173 (100); $[\alpha]^{21}D$ −194° (*c* 0.36, $CHCl_3$); uv λ_{max} (EtOH) 251 nm (ε 11 450); ir (KBr) ν 3400–3500 (broad), 1730, 1650, and 1618 cm^{-1}; NMR δ 1.35 (d, *J* = 7 Hz, 3, C-11 CH_3), 1.53 (s, 3, C-10 CH_3), 1.97 (s, 3, C-4 CH_3), 5.61 (broad s, $W_{1/2}$ = 5 Hz, 1, C-6 H) 6.26 and 6.70 (d, *J* = 10 Hz, 1 each, C-2 and C-1 H).

Anal. Calcd for $C_{15}H_{19}O_3Br$: C, 55.06; H, 5.85; Br, 24.42. Found: C, 54.64; H, 5.90; Br, 25.01.

Fraction 3 gave 1.52 g of a mixture of the 14-bromide **6** and the starting material **2** (1:1) as evidenced by NMR spectrometry.

Dehydrobromination of the 6β-Bromide 5. To a solution of the 6β-bromide **5** (600 mg) in 20 ml of acetone was added 8 ml of 10% sodium carbonate. The resulting solution was heated at the reflux temperature for 30 min. The reaction mixture was concentrated, treated with 10% sodium carbonate, and then extracted with ethyl acetate. The aqueous layer was acidified with hydrochloric acid and the mixture was extracted with ethyl acetate. After the extracts had been washed with water and dried, the ethyl

acetate was removed under reduced pressure, giving 410 mg (91%) of a pale-yellow, viscous oil, 3-oxo-1,4,6-trienic acid (**3a**). This crude trienoic acid (**3a**) was not purified further, but exhibited the following expected spectral properties: uv λ_{max} (EtOH) 232 nm (ϵ 12 860) and 316 (12 880); ir (film) ν 3500–2500 (broad), 1730, 1650, and 1600 cm^{-1}; NMR δ 1.16 (s, 3, C-10 CH_3), 1.41 (d, J = 7 Hz, 3, C-11 CH_3), 1.95 (s, 3, C-4 CH_3), 3.35 (q, J = 7 Hz, 1, C-11 H), 6.32 (d, J = 10 Hz, 1, C-2 H), 6.80 (d, J = 10 Hz, 1, C-1 H), 6.61 (broad s, 1, C-6 H), and 8.50 (1, COOH).

3a was esterified by treatment with excess etheral diazomethane. The crude product was purified by silica gel column chromatography, affording triene keto ester **3b** as a pale-yellow oil: bp 157–159 °C (7 mm); MS *m/e* (rel intensity) 260 $[M]^+$ (58), 245 $[M - CH_3]^+$ (28), 201 $[M - COOCH_3]^+$ (45), 185 (50), 173 (100); $[\alpha]^{21}D$ +273° (*c* 6.6, $CHCl_3$); uv λ_{max} (EtOH) 235 nm (ϵ 12 050), 310 (12 260); ir (film) ν 1735, 1655, 1615 cm^{-1}; NMR δ 1.16 (s, 3, C-10 CH_3), 1.38 (d, J = 7 Hz, 3, C-11 CH_3), 1.93 (s, 3, C-4 CH_3), 3.31 (q, J = 7 Hz, 1, C-11 H), 3.68 (s, 3, $COOCH_3$), 6.22 (d, J = 10 Hz, 1, C-2 H), 6.73 (d, J = 10 Hz, 1, C-1 H), 6.54 (broad s, $W_{1/2}$ = 4 Hz, 1, C-6 H).

The 2,4-dinitrophenylhydrazone of **3b** was obtained as deep-red plates (**3c**), mp 188–190 °C (from ethanol).

Anal. Calcd for $C_{22}H_{24}O_6N_4$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.76; H, 5.57; N, 12.77.

Treatment of 14-Bromide 6 with Sodium Carbonate. To a solution of 14-bromide **6** (400 mg) in acetone (20 ml) was added 10% sodium carbonate (8 ml). The solution was heated to reflux temperature for 1 h. The reaction mixture was concentrated and diluted with 10% sodium carbonate, and the extracted with ethyl acetate. The extracts were washed with water and dried. Evaporation of the solvent gave 60 mg (12%) of pale-yellow crystals. Recrystallization from ethanol or benzene gave colorless needles: mp 310–312 °C; mass spectrum $[M]^+$ 492.2506 (calcd for $C_{30}H_{36}O_6$, 492.2509), *m/e* (rel intensity) 492 $[M]^+$ (14), 477 $[M - CH_3]^+$ (95), 464 $[M - CO]^+$ (5), 262 (27), 246 $[M/2]^+$ (20), 202 (21), 173 (100); $[\alpha]^{21}D$ −214° (*c* 0.4, $CHCl_3$); uv λ_{max} (EtOH) 243 nm (ϵ 27 700); ir (KBr) ν 1725, 1662, 1630, 1610 cm^{-1}; NMR δ 1.18 (d, J = 7 Hz, 6, C-11,11′ CH_3), 1.31 (s, 6, C-10,10′ CH_3), 4.90 (d, J = 12 Hz, 2, C-14,14′ H_a), 5.00 (d, J = 12 Hz, 2, C-14,14′ H_b), 6.28 (d, J = 12 Hz, 2, C-2,2′ H), 6.78 (d, J = 10 Hz, 2, C-1,1′ H).

Anal. Calcd for $C_{30}H_{36}O_6$: C, 73.14; H, 7.37. Found: C, 73.14; H, 7.50.

Hydrolysis of the Dimer 7. The dimer **7** (40 mg) was dissolved in a solution of potassium hydroxide (500 mg) in methanol (5 ml). The solution was stirred at room temperature for 5 h. The reaction mixture was acidified with hydrochloric acid and then extracted with ethyl acetate. The extracts were washed with water, saturated sodium bicarbonate, and water and dried. Evaporation of the solvent afforded 16 mg of pale-yellow oil. The oily product was a mixture of the hydroxy keto ester **8a** and the methoxy keto ester **9a**, which were identified by means of NMR spectroscopy.

The aqueous solution was acidified and extracted with ethyl acetate. The extracts were washed with water and dried and the solvent evaporated to give 28 mg of pale-yellow oil. The acidic oil, which was a mixture of hydroxycarboxylic acid **8b** and methoxycarboxylic acid **9b**, was not purified further but was treated with ethereal diazomethane. The products and proceeding neutral oil (16 mg) were combined. The viscous oil thus obtained was purified by preparative TLC (solvent hexane–acetone, 1:1).

Band 1 gave 17 mg of the methoxy keto ester **9a** as a pale-yellow oil: MS *m/e* (rel intensity) 292 $[M]^+$ (4), 277 $[M - CH_3]^+$ (31), 260 $[M - CH_3OH]^+$ (16), 201 $[M - (CH_3OH + COOCH_3)]^+$ (19), 173 (100); $[\alpha]^{21}D$ −78° (*c* 0.8, $CHCl_3$); uv λ_{max} (EtOH) 242 nm (ϵ 11 100); ir (film) ν 1735, 1660, 1630 cm^{-1}; NMR δ 1.20 (d, J = 7 Hz, 3, C-11 CH_3), 1.24 (s, 3, C-10 CH_3), 3.32 (s, 3, C-14 OCH_3), 3.70 (s, 3, $COOCH_3$), 4.25 (d, J = 10 Hz, 1, C-14 H_a), 4.29 (d, J = 10 Hz, 1, C-14 H_b), 6.25 (d, J = 10 Hz, 1, C-2 H), 6.72 (d, J = 10 Hz, 1, C-1 H).

Band 2 gave 15 mg of the hydroxy keto ester **8a** as a pale-yellow oil: MS *m/e* (rel intensity) 278 $[M]^+$ (2), 260 $[M - H_2O]^+$ (19), 201 $[M - (H_2O + COOCH_3)]^+$ (19), 173 (100); $[\alpha]^{21}D$ −52° (*c* 3.6, $CHCl_3$); uv λ_{max} (EtOH) 242 nm (ϵ 11 400); ir (film) ν 3440, 1730, 1660, 1625 cm^{-1}; NMR δ 1.21 (d, J = 7 Hz, 3, C-11 CH_3), 1.25 (s, 3, C-10 CH_3), 2.80 (1, OH), 3.70 (s, 3, $COOCH_3$), 4.46 (s, 2, C-14 CH_2), 6.25 (d, J = 10 Hz, 1, C-2 H), 6.80 (d, J = 10 Hz, 1, C-1 H).

Photolysis of the Dimer 7. A solution of 70 mg of **7** in 14 ml of dried dioxane was irradiated in a quartz probe at room temperature with a Rayonet preparative reactor RPR-208 (RUL-3000 Å). The solvent was removed in vacuo and the residue was subjected to preparative TLC (benzene–ethyl acetate, 1:1), which yielded 10 mg of colorless prisms, mp 261–262 °C (**10**). Recrystallization from ethanol gave colorless prisms: mp 263–265 °C, mass spectrum $[M]^+$ 492.2503 (calcd for $C_{30}H_{36}O_6$, 492.2509), *m/e* (rel intensity) 492 $[M]^+$ (1), 246 $[M/2]^+$ (20), 202 (12), 173 (81), 145 (70), 105 (55), 91 (100); uv λ_{max} (EtOH) 234 nm (ϵ 9200); ir (KBr) ν 1730, 1700 cm^{-1}; NMR δ 1.07 (s, 6, C-10,10′ CH_3), 1.08 (d, J = 7 Hz, 6, C-11,11′ CH_3), 4.10 (d, J = 12 Hz, 2, C-14,14′ H_a), 4.85 (d, J = 12 Hz, C-14,14′ H_b), 5.95 (d, J = 5 Hz, 2, C-2,2′ H), 7.35 (d, J = 5 Hz, 2, C-1,1′ H).

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Registry No.—**2,** 17974-84-4; **3a,** 57901-33-4; **3b,** 57901-34-5; **3c,** 57901-35-6; **4,** 57901-36-7; **5,** 57901-37-8; **6,** 57901-38-9; **7,** 57901-39-0; **8a,** 57901-40-3; **9a,** 57901-41-4; **10,** 57901-42-5; (−)-6-epi-α-santonin, 1618-78-6; *N*-bromosuccinimide, 128-08-5.

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Electrochemical Oxidation of Halomicin B to Rifamycin S

A. K. Ganguly,* P. Kabasakalian, S. Kalliney, O. Sarre, S. Szmulewicz, and A. Westcott

Chemical Research Department, Schering Corporation, Bloomfield, New Jersey 07003

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In an earlier communication[1] we have disclosed the structure of halomicin B (**1**). Elucidation of the structure of halomicin groups of antibiotics involves their conversion to a rifamycin S derivative and a substituted pyrrolidine base. Thus, the structural elucidation of halomicin B (**1**) involved its conversion into rifamycin S (**2**)[2] and a basic component (**3**).[1] In connection with the above-mentioned work, we have studied electrochemical oxidation of this group of antibiotics. It was conceived that halomicin B on electrochemical oxidation will lose two electrons easily and will be converted into a cationic species (**4**) which upon work-up will hydrolyze spontaneously into rifamycin S (**2**) and compound **3**. A similar cation (**4**) could also be produced from **1** in two steps: losing the first electron will yield a cation radical which could be trapped by a nucleophile (inter- or intramolecularly) into a radical followed by the loss of a second electron to the cation (**4**). The controlled potential[3] electrochemical oxidation of halomicin B was carried out in