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Synthetic Studies on Aphidicolane and Stemodane Diterpenes. I. Synthesis of (2′*R**,4a′*S**,8a′*R**)-2′,8a′-Dimethyl-4a′,5′,8′,8a′-tetrahydrospiro[2,5-cyclohexadiene-1,1′(2*H*)-naphthalene]-3′(4′*H*),4,6′(7′*H*)-trione

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The title compound (**8**), a possible intermediate for the synthesis of aphidicolane and stemodane diterpenes, was synthesized by the decomposition of the phenolic α-diazoketone (**9**) in the presence of copper(II) chloride.

Keywords——aphidicolane diterpene; stemodane diterpene; spiro[cyclohexanaphthalene]; conjugate addition; half-chair conformation; steric hindrance; gamma-effect; spiroannelation; diazoketone

Aphidicolin (**1**) is a tetracyclic diterpene-tetraol isolated from the culture filtrate of the mold, *Cephalosporium aphidicola* Petch,[1] and in spite of its simple functionality displays very interesting biological actions, for example antibiotic[2] and antitumor[3] activities. Recently, two analogues, 3-deoxyaphidicolin (**2**) and aphidicolin-17-monoacetate (**3**), were isolated from the culture of *Phoma betae* Frank PS-13, and they markedly inhibited the *in vivo* deoxyribonucleic acid (DNA) synthesis of sea urchin embryos and Hela cells.[4] Stemodane diterpenes—stemodin (**4**),[5] stemodinone (**5**),[5] maritimol (**6**),[6] and 2-deoxystemodinone (**7**)[7]—isolated from *Stemodia maritima* L. possess the same carbon framework as aphidicolane diterpenes. These two families of diterpenes have basic carbon skeletons composed of bicyclo[3.2.1]octane (C/D rings) and *trans*-decalin (A/B rings) systems. In the aphidicolanes, the B/C ring junction is *trans*, but in the stemodanes it is *cis*.

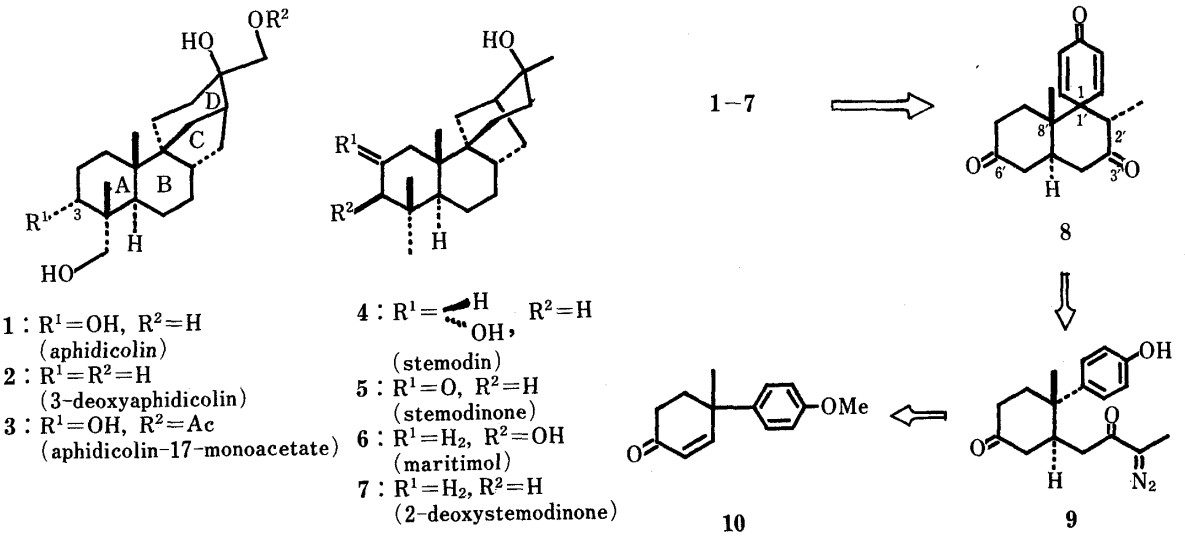

Chart 1

In view of their biological activities and unique tetracyclic skeletons, these diterpenes have been the targets of synthetic studies by many workers.[8] The spirocyclic B/D ring systems of these diterpenes attracted our attention in connection with our studies on the synthesis of spirocyclic natural products, and we therefore addressed ourselves to the synthesis of aphidicolane and stemodane diterpenes.

We settled on the spiro[cyclohexanaphthalene] derivative (**8**) as the initial key intermediate for the synthesis of these diterpenes. The oxygen function at $C_{3'}$ in this compound (**8**) should serve as a tool for the control of the stereochemistry during the elaboration of the C/D ring systems,[9] and for the introduction of a leaving group onto the 2′-methyl group for the construction of the C ring. The synthesis of **8** was expected to be possible by applying the spiroannelation developed in our laboratory.[10] In this paper, we describe the synthesis of the spiro[cyclohexanaphthalene] derivative (**8**) *via* the decomposition of the phenolic α-diazoketone (**9**) derived from the cyclohexenone derivative (**10**).

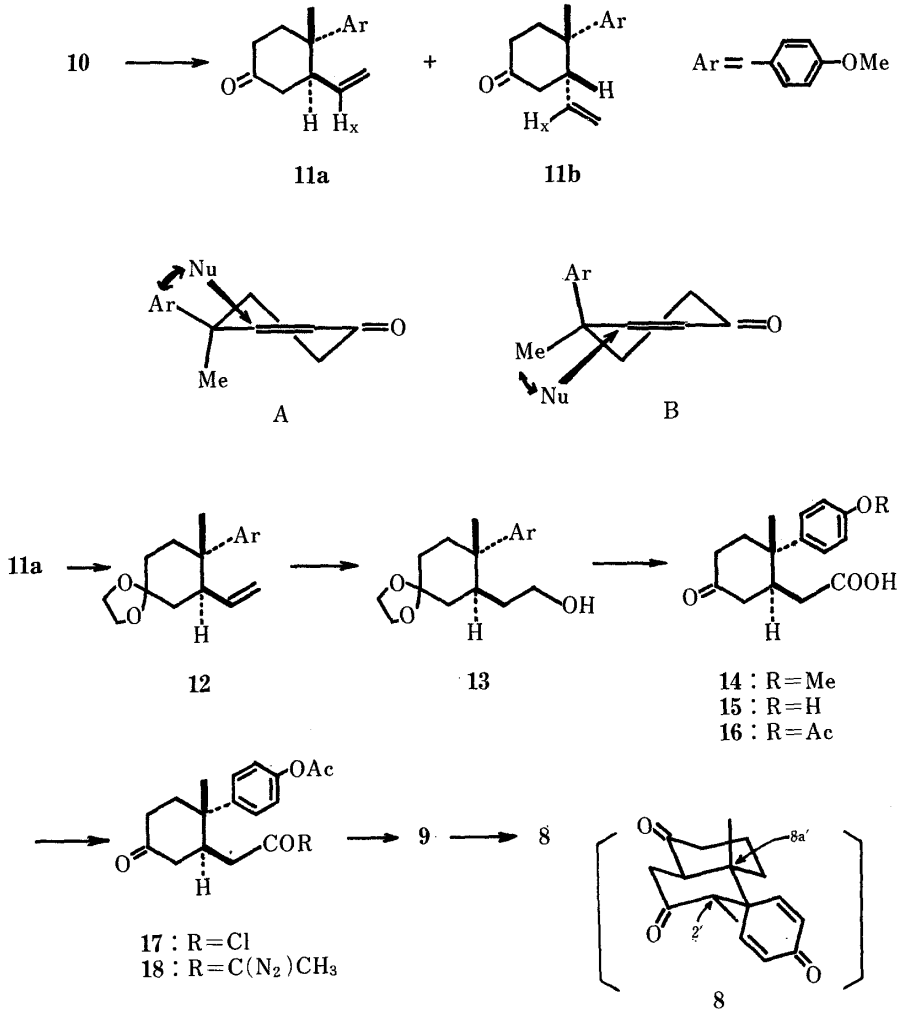

Chart 2

It is known that conjugate 1,4-addition to a 4-monosubstituted cyclohexenone is governed by steric, rather than stereoelectronic, factors to give predominantly the *trans*-isomer as regards the 4-substituent and the incoming nucleophile.[11] In the reaction of 4-aryl-4-methylcyclohexenone (**10**)[12] with vinylmagnesium bromide in the presence of copper(I) bromide–dimethyl sulfide complex,[13] the desired *trans*-isomer (**11a**) should be produced predominantly for the following reasons. The enone (**10**) can adopt two half-chair confor-

mations, A and B. While the attacks of the nucleophile on the top faces of both conformations produce the *cis* product, the attacks on the bottom faces afford the *trans* product. Though the attacks on the top face of A and on the bottom face of B afford a stereoelectronically favorable chair-like enolate anion intermediate, the attacks on the bottom face of A and on the top face of B yield unfavorable boat-like intermediates. The steric hindrance between the incoming nucleophile and the aromatic group is larger than that between the nucleophile and the methyl group, and the steric factor probably plays the most important role in this reaction.

The stereochemistries of the products **11a** and **11b** (64% yield, *ca.* 16:1) were determined by analysis of their proton (^{1}H-) and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra. When the vinylic methine protons (H_X) were irradiated, the C_3-H signal in the major product (**11a**) appeared at δ 3.00 as a multiplet with a half-width, $W_{1/2}$, of 16 Hz, and in the minor product (**11b**) at δ 2.89, $W_{1/2}=5$ Hz. These values show that the vinyl group of **11a** is equatorial while that of **11b** is axial. In the ^{13}C-NMR spectra, the C_4-methyl signal of **11a** (δ 20.8) appears at higher field than that of **11b** (δ 27.6), while C_5 of **11b** is found at higher field (δ 32.5) as compared with that of **11a** (δ 38.4). The upfield shift of the C_4-methyl group in **11a** shows that the C_4-methyl and vinyl groups are in a *gauche* relationship, and the upfield shift of C_5 in **11b** is due to the γ-effect of the axially oriented vinyl group. Accordingly, the major product (**11a**) proved to be the desired compound in which the aromatic and vinyl groups are *trans*.

Compound **11a** was protected in the usual manner to give the ketal (**12**), which was transformed to the hydroxy compound (**13**) by hydroboration and subsequent oxidation in 81% yield from **11a**. Compound **13** was treated with the Jones reagent in acetone to afford the keto-carboxylic acid (**14**) in 76% yield. Demethylation was performed by treatment with hydroiodic acid in acetic acid to give the phenolic compound (**15**) in 13.5% yield (68% yield based on the starting material consumed), a sodium hydroxide solution of which was treated with acetic anhydride to provide the acetate (**16**) in 91% yield. Compound **16** was subjected to reaction with oxalyl chloride in methylene chloride to give the acid chloride (**17**), which afforded the diazoketone (**18**) upon reaction with diazoethane in ether. Compound **18** was hydrolyzed with buffered alkali (aq. Na_2CO_3–$NaHCO_3$) to give the phenolic α-diazoketone (**9**) in quantitative yield from **16**. Addition of a chloroform solution of **9** to a boiling chloroform containing copper (II) chloride gave the spirodienone (**8**) in 10% yield. The angular ($C_{8a'}$-) and secondary ($C_{2'}$-) methyl signals appeared at δ 1.60 and 0.83 in the ^{1}H-NMR spectrum, respectively. These data show that the former is located near the plane of the dienone moiety, *i.e.*, axial, and the latter is situated in the shielding region of the dienone, *i.e.*, equatorial in the B ring. It is evident that compound **8** has the desired structure as depicted in parenthesis in Chart 2.

As described above, though the yield is low at present, we were able to obtain the desired spiro[cyclohexa-1,1′-naphthalene] derivative (**8**). After the introduction of the leaving group onto the $C_{2'}$-methyl group for the construction of the C ring, it should be possible for this compound to be transformed to both the aphidicolane and stemodane skeletons by use of the oxygen function at $C_{3'}$.

Experimental

Both melting and boiling points are uncorrected. Melting points were determined on a Yanagimoto micromelting point apparatus. Ultraviolet (UV) spectra were recorded on a Hitachi 124 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on Hitachi R-22 (90 MHz) and R-900 (22.6 MHz) instruments, respectively, with tetramethylsilane as an internal standard. The following abbreviations for the signal patterns are used: s = singlet, d = doublet, q = quartet, m = multiplet, and br = broad. Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrophotometer. Mass spectra (MS) and high-resolution mass spectra (High MS) were obtained with a JEOL JMS-D300 mass spectrometer. For preparative thin layer chromatography (PTLC) and column chromatography,

Merck Kieselgel PF_{254} and Merck Kieselgel 60 (70—230 mesh) were used, respectively.

(3*R,4*S**)-4-(4-Methoxyphenyl)-4-methyl-3-vinylcyclohexan-1-one (11a)**——A solution of copper(I) bromide–dimethyl sulfide ($CuBr \cdot Me_2S$) (0.4 eq) in Me_2S (2.5 ml) was added dropwise at −78 °C to a solution of vinylmagnesium bromide [prepared from Mg (2.4 g) and vinyl bromide (18.7 g)] in dry tetrahydrofuran (THF) (130 ml). After the mixture had been stirred for 30 min at −78 °C, a solution of 4-(4-methoxyphenyl)-4-methylcyclohex-2-en-1-one (**10**) (5.8 g) in THF (10 ml) was added. After being stirred for 1 h, the reaction mixture was quenched by the addition of satd. NH_4Cl solution, and extracted with benzene. The extract was washed, dried, and evaporated. The residue was purified by column chromatography (*n*-hexane : AcOEt = 10 : 1) to give a mixture of **11a** and **11b** in 67% yield. This mixture was separated on a Lobar column (Merck, Lichroprep Si 60; *n*-hexane : AcOEt = 10 : 1) to provide **11a** (3.8 g) as colorless crystals, mp 69.5—70.5 °C, and **11b** (0.234 g) as colorless crystals, mp 81.0—83.0 °C. **11a**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1640, 920. ^{1}H-NMR ($CDCl_3$) δ: 1.32 (3H, s, C_4-CH_3), 3.00 (1H, m, $W_{1/2}$ = 16 Hz, C_3-H), 3.73 (3H, s, OCH_3), 4.87—5.57 (3H, ABC in ABCM type, olefinic H), 6.78—7.27 (4H, AA′BB′-type aromatic H). ^{13}C-NMR ($CDCl_3$) δ: 20.8 (C_4-CH_3), 37.8 (C_6), 38.4 (C_5), 39.9 (C_4), 42.9 (C_2), 49.0 (C_3), 55.1 (OCH_3), 113.8 ($C_{3'}$ and $C_{5'}$), 116.0 (olefinic C), 126.7 ($C_{2'}$ and $C_{6'}$), 137.8 (olefinic C), 138.9 ($C_{1'}$), 157.7 ($C_{4'}$), 210.4 (C_1). MS *m/z*: 244 (M^+). *Anal.* Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.13; H, 8.44. **11b**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1640, 920. ^{1}H-NMR ($CDCl_3$) δ: 1.52 (3H, s, C_4-CH_3), 2.89 (1H, m, $W_{1/2}$ = 5 Hz, C_3-H), 3.77 (3H, s, OCH_3), 4.85—5.50 (3H, ABC in ABCM type, olefinic H), 6.80—7.22 (4H, AA′BB′-type aromatic H). ^{13}C-NMR ($CDCl_3$) δ: 27.6 (C_4-CH_3), 32.5 (C_5), 37.8 (C_6), 39.1 (C_4), 41.8 (C_2), 49.5 (C_3), 55.1 (OCH_3), 113.6 ($C_{3'}$ and $C_{5'}$), 116.3 (olefinic C), 126.9 ($C_{2'}$ and $C_{6'}$), 138.4 (olefinic C), 138.9 ($C_{1'}$), 157.6 ($C_{4'}$), 210.4 (C_1). MS *m/z*: 244 (M^+). *Anal.* Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.28; H, 8.54.

(3*R,4*S**)-4-(4-Methoxyphenyl)-4-methyl-3-vinylcyclohexan-1-one Ethylene Acetal (12)**——A mixture of **11a** (4.06 g), ethylene glycol (9 ml), *p*-TsOH (50 mg), and benzene was refluxed for 5 h in a flask equipped with a Dean–Stark water separator. After cooling, the mixture was poured into $NaHCO_3$ solution containing crushed ice and extracted with benzene. The extract was washed, dried, and evaporated. The residue was purified by column chromatography (*n*-hexane : AcOEt = 5 : 1) to give **12** (2.93 g) in 60% yield as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1255, 1040, 916. ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, s, C_4-CH_3), 2.78 (1H, m, C_3-H), 3.72 (3H, s, OCH_3), 3.79—3.86 (4H, m, OCH_2CH_2O), 4.69—5.43 (3H, ABC in ABCM type, olefinic H), 6.67—7.20 (4H, AA′BB′-type aromatic H). MS *m/z*: 288 (M^+). *Anal.* Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.00; H, 8.41.

(3*R,4*S**)-3-(2-Hydroxyethyl)-4-(4-methoxyphenyl)-4-methylcyclohexan-1-one Ethylene Acetal (13)**——Diborane generated from sodium borohydride (0.11 g) and $BF_3 \cdot Et_2O$ (0.4 g) in THF (10 ml) was introduced into a THF (15 ml) solution of **12** (138 mg) with dry N_2. After the disappearance of the starting material on TLC, water (2 ml), 3 N NaOH (2 ml) and 30% H_2O_2 (2 ml) were added to the reaction mixture, which was then stirred for 2.5 h at room temperature. The mixture was extracted with ether, and the extract was washed, dried, and evaporated. The residue was purified by PTLC (*n*-hexane : AcOEt = 1 : 1) to give **13** (119 mg) in 81% yield as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610, 3450. ^{1}H-NMR ($CDCl_3$) δ: 1.27 (3H, s, C_4-CH_3), 3.40 (2H, m, $CH_2\underline{CH_2}OH$), 3.76 (3H, s, OCH_3), 3.93 (4H, m, OCH_2CH_2O), 6.76—7.29 (4H, AA′BB′-type aromatic H). MS *m/z*: 306 (M^+). *Anal.* Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.12; H, 8.59.

(3*R,4*S**)-3-(Carboxymethyl-4-(4-methoxyphenyl)-4-methylcyclohexan-1-one (14)**——The Jones reagent was added dropwise under stirring at 0 °C to a solution of **13** (132 mg) in acetone (2 ml) until the color of the reagent persisted for more than 5 min. The stirring was continued for 2 h, and the excess reagent was decomposed by the addition of isopropyl alcohol. The mixture was neutralized with $NaHCO_3$. The precipitates were filtered off, the filtrate was evaporated, and the residue was acidified with HCl then extracted with ether. The extract was washed, dried, and evaporated to give the crude acid, which was purified by PTLC (*n*-hexane : AcOEt = 1 : 1) to afford **14** (90 mg) in 76% yield as colorless crystals, mp 130—132 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500—2300, 1709. ^{1}H-NMR ($CDCl_3$) δ: 1.44 (3H, s, C_4-CH_3), 3.76 (3H, s, OCH_3), 6.81—7.29 (4H, AA′BB′-type aromatic H), 9.50 (1H, br s, COOH). MS *m/z*: 276 (M^+). *Anal.* Calcd for $C_{16}H_{20}O_4$: C, 69.54, H, 7.30. Found: C, 69.44; H, 7.37.

(3*R,4*S**)-3-Carboxymethyl-4-(4-hydroxyphenyl)-4-methylcyclohexan-1-one (15)**——Fifty percent hydroiodic acid (10 ml) was added to a solution of **14** (3.2 g) in acetic acid (12 ml), and the mixture was refluxed for 20 min. The acetic acid and hydroiodic acid were removed under reduced pressure, and the residue was extracted with satd. $NaHCO_3$ solution. The extract was washed with AcOEt, acidified with 10% HCl, and extracted with AcOEt. This extract was washed with water, satd. $Na_2S_2O_3$ solution, and water once again before being dried and evaporated. The residue was purified by column chromatography (*n*-hexane : AcOEt = 1 : 1) to give **15** (410 mg) in 13.5% yield (68% yield based on the starting material consumed) as colorless crystals, mp 197—199 °C, with recovery of the starting material (2.6 g). ^{1}H-NMR (CF_3COOH) δ: 1.57 (3H, s, C_4-CH_3), 6.92—7.37 (4H, AA′BB′-type aromatic H). MS *m/z*: 262 (M^+). *Anal.* Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.30; H, 7.01.

(3*R,4*S**)-4-(4-Acetoxyphenyl)-3-carboxymethyl-4-methylcyclohexane-1-one (16)**——Acetic anhydride (0.08 ml) was added at 0 °C to a solution of **15** (180 mg) in 1 N NaOH (1.5 ml). The mixture was stirred for 1 h at room temperature, acidified with 5% HCl, and extracted with AcOEt. The extract was washed, dried, and evaporated to give the crude product, which was purified by PTLC (*n*-hexane : AcOEt = 1 : 1) to afford **16** (193 mg) in 91% yield as colorless crystals, mp 198—200 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500—2300, 1750, 1715. ^{1}H-NMR ($CDCl_3$) δ: 1.44 (3H, s, C_4-

CH_3), 2.24 (3H, s, $OCOCH_3$), 7.02—7.38 (4H, AA'BB'-type aromatic H). MS *m/z*: 304 (M^+). *Anal.* Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.54; H, 6.87.

(3*R,4*S**)-3-(3-Diazo-2-oxobutyl)-4-(4-hydroxyphenyl)-4-methylcyclohexan-1-one (9)**——Oxalyl chloride (0.63 ml) was added to a solution of **16** (225 mg) in methylene chloride (1.5 ml), and the mixture was stirred for 2 h at room temperature. The solvent and excess reagent were removed under reduced pressure, and dry benzene was added. The benzene solution was evaporated under reduced pressure to give the acid chloride (**17**), which was dissolved in methylene chloride immediately, and the resulting solution was added slowly to ethereal diazoethane over a period of 10 min. The solution was evaporated under reduced pressure to give the diazoketone (**18**), which was stirred for 1 h with Na_2CO_3 (0.8 g), $NaHCO_3$ (0.9 g), water (9 ml), and MeOH (10 ml). After the removal of MeOH under reduced pressure, the mixture was adjusted to pH 7 with oxalic acid, and extracted with benzene. The extract was washed, dried, and evaporated under reduced pressure to give the phenolic α-diazoketone (**9**) (226 mg) as a yellow oil, which was used immediately for the annelation reaction without purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3480, 3320, 2090, 1715, 1610. ^{1}H-NMR ($CDCl_3$) δ: 1.43 (3H, s, C_4-CH_3), 1.85 (3H, s, $C(N_2)CH_3$), 6.74—7.22 (4H, AA'BB'-type aromatic H).

(2'*R,4a'*S**,8a'*R**)-2',8a'-Dimethyl-4a',5',8',8a'-tetrahydrospiro[2,5-cyclohexadiene-1,1'(2*H*)-naphthalene]-3'(4'*H*)-4,6'(7'*H*)-trione (8)**——A solution of the phenolic α-diazoketone (**9**) (116 mg) in chloroform (3 ml) was added dropwise during 1 min to boiling chloroform (80 ml) containing copper (II) chloride (52 mg), and the mixture was refluxed for 2 min. After cooling, the mixture was filtered through a Florisil column. The filtrate was evaporated under reduced pressure, and the residue was purified by PTLC (ether) to give the spiro dienone (**8**) as colorless crystals, mp 161.5—163.0 °C, in 10% yield. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1670, 1630. ^{1}H-NMR ($CDCl_3$) δ: 0.85 (3H, d, J= 7 Hz, $C_{2'}$-CH_3), 1.59 (3H, s, $C_{8a'}$-CH_3), 3.00 (1H, q, J=7 Hz, $C_{2'}$-H), 6.38—6.88 (4H, AA'BB'-type olefinic H). UV λ_{max}^{EtOH} nm (ε): 241 (10800). MS *m/z*: 272 (M^+). High MS *m/z*: 272.139 (M^+, Calcd for $C_{17}H_{20}O_3$: 272.142).

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