218. Michiya Kimura, Masahiko Tohma, and Itsuo Yoshizawa*1:
Constituents of Convallaria. II*2 Structure of Convallagenin-B.

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Convallagenin-B (Ⅲ) from the flowers of Convallaria keiskei Max., Japanese lily of the valley, has been elucidated as 25l,5β-spirostan-1β,3β,4β,5β-tetrol, that represents the first instance of the 25l-tetrahydroxy steroidal sapogenin.

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In a previous paper of this series,*1 the authors reported three new steroidal saponins, convallasaponin-A, -B, and -C, isolated from the flowers of Convallaria keiskei Max., Japanese lily of the valley (SUZURAN) and two new sapogenins, convallagenin-A and -B, together with the known isorhodeasapogenin (I)*5 as their aglycones. The structure of convallagenin-A (Ⅱ) was regarded as 25l,5β-spirostan-1β,3β,5β-triol.*5 The present paper deals with a study on the structure of convallagenin-B (Ⅲ), C38H63O10, m.p. 277~278°, [α]D -42.7°, which was elucidated as 25l,5β-spirostan-1β,3β,4β,5β-tetrol from the following evidence.

![Chart 1](image)

Convalagenin-A and -B showed close similarity in physical properties and chemical behaviors as mentioned previously.*1 Comparison of the intensities of the characteristic infrared absorption bands at 920 and 897 cm⁻¹,*1,2 and the doublet signal for the 27-methyl group at δ 8.98 in lower field than that of the 18-methyl group (δ 9.15) in the nuclear magnetic resonance (NMR) spectrum,*5 revealed that Ⅲ was likely to be in the 25l-series as has been clearly indicated in Ⅱ.*5 The NMR data of both sapogenins and their derivatives as summarized in Table I, suggested further that Ⅲ may contain one secondary hydroxyl group in addition to those of Ⅱ, according to the additivity principle of the substituents effect on the angular methyl group shift.*6 In contrast to Ⅱ, the sapogenin (Ⅲ) was found to consume two-oxygen-equivalents of periodic acid, giving

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*1 Nishi-6-chome, Kita-12-jo, Sapporo (木村道也, 藤岡貞彌, 吉沢達雄).
*2 Part Ⅱ: This Bulletin, 15, 1204 (1967).
2) H. Nawa: Yakugaku Zasshi, 73, 1192 (1953); This Bulletin, 6, 255 (1958).
Table I. Chemical Shifts of 18- and 19-Methyl Groups in Pyridine

<table>
<thead>
<tr>
<th></th>
<th>19-CH₃ (τ)</th>
<th>Diff. (p.p.m.)</th>
<th>18-CH₃ (τ)</th>
<th>Diff. (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Convallagenin-B ( atrocities)</td>
<td>8.41</td>
<td>−0.67</td>
<td>9.15</td>
<td>0.00</td>
</tr>
<tr>
<td>-diacetate (V)</td>
<td>8.40</td>
<td>−0.68</td>
<td>9.14</td>
<td>−0.01</td>
</tr>
<tr>
<td>-triacetate (IV)</td>
<td>8.72</td>
<td>−0.36</td>
<td>9.15</td>
<td>0.00</td>
</tr>
<tr>
<td>-1-one (VII)</td>
<td>8.43</td>
<td>−0.65</td>
<td>9.16</td>
<td>+0.01</td>
</tr>
<tr>
<td>-A-triacetate (VI)</td>
<td>8.81</td>
<td>−0.27</td>
<td>9.14</td>
<td>−0.01</td>
</tr>
<tr>
<td>Convallagenin-A and its derivatives (the)</td>
<td>8.41</td>
<td>−0.67</td>
<td>9.14</td>
<td>−0.01</td>
</tr>
<tr>
<td>1β-OH 3β-OH 5β-OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-OH -OAc -OH</td>
<td>8.46</td>
<td>−0.62</td>
<td>9.13</td>
<td>−0.02</td>
</tr>
<tr>
<td>-OAc -OAc -OH</td>
<td>8.78</td>
<td>−0.30</td>
<td>9.17</td>
<td>+0.02</td>
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<tr>
<td>-CO -OAc -OH</td>
<td>8.47</td>
<td>−0.61</td>
<td>9.15</td>
<td>0.00</td>
</tr>
<tr>
<td>-OAc -OAc -A⁴</td>
<td>8.82</td>
<td>−0.26</td>
<td>9.14</td>
<td>−0.01</td>
</tr>
<tr>
<td>5β-Spirostanet (the)</td>
<td>9.08</td>
<td></td>
<td>9.15</td>
<td></td>
</tr>
</tbody>
</table>

a) Difference in chemical shifts of the angular methyl group between the sapeogenin derivatives and 5β-spirostanet.

b) Reference 3.

c) Reference 6c.

formic acid from the reaction mixture; that indicated II may contain a glycerol structure in the molecule, so that the additional hydroxyl group might be located at C-2 or C-4 in II.

The triacetate (V), m.p. 227~230°, derived from III was readily dehydrated with thionylchloride in pyridine to give an enolacetate (VI), which showed the characteristic bands at 1759 cm⁻¹ in the infrared and at τ 7.88 in the NMR spectra, together with another acetoxyl band. Therefore, the tertiary hydroxyl group adjacent to an acetoxyl one which was seemed to be at C-4, participated in dehydration. The diacetate (V), m.p. 217~219°, derived from III, on the other hand, was oxidized with chromium trioxide in acetone to give a ketone (VII; 1709 cm⁻¹) having a tertiary hydroxyl group (3580 cm⁻¹). The compound (VII) afforded an α,β-unsaturated ketone (VIII), λmax: 220 μm (log ε: 3.92), νmax: 1677 cm⁻¹, by the treatment with an alkaline alumina. Infrared spectrum of VII still indicated the presence of a hydroxyl (3540 cm⁻¹) as well as a normal acetoxyl group (1723 cm⁻¹) and its NMR spectrum also showed the expected olefinic bands of AB type at τ 3.55 (C-3) and τ 3.95 (C-2), both having the coupling constant J=10.2 c.p.s. as shown in Fig. 1. The further splitting of these signals may be considered due to long range spin–spin couplings with the allylic C-4α-proton.⁷ These findings appeared to be in good accordance with the above observation on the enolacetate (VI) and II was regarded as a 1,3,4,5-tetrol; the reactions mentioned above may thus be represented in Chart 2. Selective oxidation of III by molecular oxygen using platinum oxide was carried out further to obtain the 3-ketone (X; 1722 cm⁻¹) which was then readily dehydrated in methanolic potassium hydroxide at room temperature. The dehydration product was regarded as a diosphenol (X) from the following evidences: it gave a

positive ferric chloride color test; its infrared spectrum suggested the presence of a hydroxyl (3420 cm\(^{-1}\)) as well as an \(\alpha,\beta\)-unsaturated ketone group (1652 and 1605 cm\(^{-1}\)); its ultraviolet spectrum in ethanol showed an anomalous curve which shifted to the longer wave length region by adding one drop of \(1N\) sodium hydroxide solution, as shown in Fig. 2. The acetate (X) of X showed the absorption bands at 244 m\(\mu\); (log \(\varepsilon\): 4.10) in the ultraviolet spectrum as shown in the same Figure and at 1757, 1660 as well as 1614 cm\(^{-1}\) in the infrared spectrum corresponding to the enol ester of 1,4-dien-3-one,\(^8\) without normal acetoxy band. The NMR spectra of these compounds showed the clearly resolved doublet signals due to the olefinic protons conjugated with carbonyl group as shown in Fig. 3, so that the substituent presented at C-4, not at C-2. Thus, III was reasonably regarded as a 1,3,4,5-tetrahydroxyxasapogenin.

The negative Cotton effects observed on the optical rotatory dispersion (ORD) curves of the 3- (X) and the 1-ketone (VII) (\(\alpha = -46.2\) and \(-116.7\), respectively) were consistent with the A\(\!\!/\!\!/B\!\!\!\!/\!\!\!\!/\!\!\!\!/cis\) fusion similarly to the ketones of convallagenin-A,\(^9\) so that the tertiary hydroxyl group at C-5 was required \(\beta\)-configuration. The diacetate (V) gave a carbonate (XII; 1740, 1106 cm\(^{-1}\)) without any hydroxyl group by the treatment with phosgene in pyridine, suggesting that the 1-hydroxyl group may form the 1,3-diaxial configuration with the 5\(\beta\)-hydroxyl group and may necessarily have the \(\beta\)-orientation. The orthoester (XIII) of XIII still showed the hydroxyl band at 3580 cm\(^{-1}\) in the infrared spectrum and afforded a monoacetate (XIV; 1732 cm\(^{-1}\)). The ketone (XV) derived from XIII by chromium trioxide in acetone revealed an anomalous data not attributable to the six-membered ketone in ultraviolet

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\(^8\) K. Sasaki: This Bulletin, 9, 684 (1961).
(320 mν, ε : 38.5) as well as infrared spectrum (1745 cm⁻¹), and in ORD curve⁹ (traugh: 341 mν, peak : 303 mν, a = −39.5), due to the 1,3-dioxane ring in the orthoester; further information should be required for the plausible explanation. These findings were likely to be similar to the observation on the kitigenin derivatives by Sasaki,⁹ suggesting that XII was the 1,3,5- rather than 1,4,5-ester and that these original hydroxyl groups were of the β-configurations. By refluxing in anhydrous acetone and 2,2-dimethoxypropane with p-toluensulfonic acid, on the other hand, convallagenin-B (III) formed a monoacetonide (XVI) which gave only a monoacetate (XVII; 1720 cm⁻¹) even by the drastic acetylation and a ketone (XVIII; 1706 cm⁻¹) by the chromium trioxide oxidation in pyridine, showing also the tertiary hydroxyl bands at 3500 and 3550 cm⁻¹ in the infrared spectra, respectively. The ORD curve of XVIII gave a negative Cotton effect (a = −86.3) in accordance with the 1-ketone, but not with the 3- (a = −27) or 4-ketone (a = +3)⁶. These results indicated that XVI was derived from the cis-vicinal diol at C-3 and C-4 in the original sapogenin (III), so that the hydroxyl group at C-4 was also orientated to the β-side.

All of the hydroxyl groups in III were thus considered to have β-configuration and this was confirmed in connection with convallagenin-A (II) further as described below. The NMR spectrum of anhydroconvallagenin-A diacetate (XIX) obtained previously,⁹ showed a sharp singlet band at τ 4.70, which was in good agreement with the value found in Δ⁴-cholesteneacetate, but was different in both shape and position from those given by the olefinic 6-proton (τ 4.32) in rusgocenin diacetate (XX),¹⁰ so that the double

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bond in XIX seemed to be located at C-4. Osmium tetroxide oxidation of XIX gave a mixture which was found to contain two products besides the starting material by thin-layer chromatography. After the energetic extraction of XIX, the residual mixture was acetylated and chromatographed on alumina to give a triacetate, m.p. 227\(^\circ\)C to 230\(^\circ\)C, as the main product which was saponified to a free tetrol, m.p. 275\(^\circ\)C to 279\(^\circ\)C, with methanolic potassium hydroxide. These compounds were identified with convallagenin–B (III) and its triacetate (IV) through the melting points on admixture with authentic specimens, infrared spectral comparison and Rf values on thin-layer chromatography.

Consequently, convallagenin–B (III) may reasonably be defined as 25\(\alpha\),5\(\beta\)-spirostan-1\(\beta\),3\(\beta\),4\(\beta\),5\(\beta\)-tetrrol which is the first tetrahydroxy steroidal sapogenin possessing the 25\(\alpha\)-configuration and which can be regarded as a 25\(\alpha\)-isomer of kitigenin isolated from Reineckia carnea Kunth by Takeda and coworkers.\(^{5,11}\) The constitution of convallasaponin–B has also been established as convallagenin–B-\(\alpha\)-l-arabopyranoside in which the sugar moiety combined unusually with a tertiary hydroxyl group at C-5 of III and the details will be presented in the forthcoming paper.

**Experimental**

Melting points were determined on a micro hot-stage and are uncorrected. Ultraviolet spectra were recorded with a Hitachi EPS-2U and infrared spectra with a Koken-DS-301 Spectrophotometer. Optical rotatory dispersion curves were measured with a Nihon Bunko ORD-UV-5 Recording Spectropolarimeter. Nuclear magnetic resonance spectra were recorded on a Japan Electron Optics Lab. JNM-3H-60 Spectrometer by using 5\% solutions containing (CH\(\_\)\(_2\))\(_2\)Si as an internal reference.

**Convallagenin–B Diacetate (V)**—A mixture of III (1.85 g.), pyridine (40 ml.) and Ac\(_2\)O (20 ml.) was allowed to stand for 15 hr. at 1\(\sim\)3\(^\circ\)C, with the subsequent treatment in the usual way to give a crude acetate (1.96 g.) showing two spots on thin-layer chromatography using CHCl\(_3\)-Me\(_2\)CO (9:1) as solvent. The product was chromatographed on alumina (60 g.), elution with \(n\)-hexane-benzene (3:2) afforded the triacetate (IV; 83 mg.), m.p. 227\(\sim\)230\(^\circ\)C, as reported previously.\(^{3}\) Further elution with \(n\)-hexane-benzene (1:4) gave the diacetate (V; 1.73 g.) which was recrystallized from Me\(_2\)CO as colorless needles, m.p. 217\(\sim\)219\(^\circ\)C, [\(\alpha\)]\(_{D}\)\(^{20}\) = -44.7\(\circ\) (c = 0.525; CHCl\(_3\)), IR\(_{\text{max}}\) cm\(^{-1}\): 3460 (OH, broad), 1742 (OAc), 980, 922\(\sim\)988, 855 (25\(\alpha\)-spiroketal). Anal. Calcd. for C\(_{37}\)H\(_{40}\)O\(_4\): C, 67.85; H, 8.82. Found: C, 67.84; H, 8.76.

**Dehydration of Triacetate (IV)**—To a solution of IV (75 mg.) in pyridine (2 ml.), SOCl\(_2\) (0.1 ml.) was added dropwise under ice cooling. After the mixture was allowed to stand at room temperature for 1 hr.,

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sufficient amounts of ice were added and the product was extracted with ether. The extract was washed with N HCl, 10% Na2CO3 and water, dried over anhydrous Na2SO4 and evaporated. Recrystallization of the residue from MeOH gave an enolacate (VI) as colorless plates (46 mg, m. p. 202–206°, positive reaction for tetranitromethane, IRvmax cm⁻¹: 1739 (enolacete, shoulder), 1735 (OAc), NMR (δ in CDCl3): 7.88 (enolate-H), 7.95 (OAc-H). Anal. Calcd. for C6H4O2: C 69.20; H 8.45. Found : C, 68.88; H, 8.25.

Oxidation of Diacetate (V) — To a stirred solution of V (439 mg) in acetone (20 ml) was added dropwise 0.35 ml of CrO3-H2SO4 solution* (containing 93.5 mg of CrO3, 1.25 equiv.) under ice cooling. After 10 min., the reaction mixture was diluted with water and extracted with ether. The extract was washed with 5% NaHCO3 and water, dried over anhydrous Na2SO4 and evaporated. Recrystallization of the residue from MeOH gave the 1-ketone (VI) as prisms (386 mg), m. p. 215–216°, ORD: [α]320° +855° (c=9, CHCl3), [α]320° -172.9° (c=106.8°, a=-116.9° (c=0.395); MeOH, temp. 26°), IRvmax cm⁻¹: 3580 (OH), 1741 (OAc), 1709 (C=O). Anal. Calcd. for C6H4O2: C 68.10; H, 8.48. Found : C, 67.74; H, 8.35.

Elimination of Acetic Acid from 1-Ketone (VI) — A solution of VI (172 mg) in benzene (10 ml) was stirred with Al2O3 (Brockman, 1.5 g) for 15 hr. at room temperature. After filtration and evaporation, recrystallization from MeOH–CHCl3 (4:1) gave the 4a,1-one (VII) as colorless needles (151 mg), m. p. 255–259°, [α]310° -10.9° (c=1.00, CHCl3). UV Vλmax nm: 220 μ (log ε 3.92), IRVmax cm⁻¹: 3540 (OH), 1723 (OAc), 1677 (α,β-unsaturated ketone). Anal. Calcd. for C6H10O2: C 71.57; H, 8.70. Found : C, 71.60; H, 8.74.

Selective Oxidation of Convolvulain–B (III) — A suspension of PrO2-H2O (65 mg) in a mixture of H2O (5 ml) and AcOH (1 ml) was stirred magnetically in an atmosphere of H2 until the reduction to metallic Pt was completed, and the solvent was decanted off. A solution of VII (74 mg) in 20 ml of AcOEt-acetone (1:1) was added and the mixture was stirred in an atmosphere of O2 for 20 hr. until the uptake of O2 ceased. After the catalyst was removed by filtration, the evaporation under reduced pressure gave the residual material (72 mg) which was recrystallized from acetone to give the 3-ketone (K) as colorless needles, m. p. 214–216°, IRVmax cm⁻¹: 3340 (OH), 1723 (C=O), ORD: [α]310° +337°, [α]310° 0°, [α]310° -30.9°, a=-46.2° (c=0.264, MeOH, temp. 26°). Anal. Calcd. for C6H10O2: C 70.10; H, 9.15. Found : C, 70.10; H, 9.08.

Convolvulain–B Diophenol (X) — To a solution of K (127 mg) in MeOH (30 ml), 1.5% KOH-MeOH solution (3 ml) was added, showing yellow color. After 30 min., the reaction mixture was diluted with water, neutralized with 2N HCl, and extracted with ether. Ether layer was washed with water, dried over anhydrous Na2SO4, and evaporated to dryness in vacuo. Crystallization of the residue from MeOH-CHCl3 furnished 102 mg of the diophenol (X) as colorless needles, m. p. 172–173°, [α]320° -30.1° (c=0.665, CHCl3), positive reaction for FeCl3 test, UV (Fig. 2) λmax nm: 212 (log ε 3.95), 243 (log ε: 3.71), 305 (log ε: 3.51) and IRmax nm 370 (log ε: 3.37), IRvmax cm⁻¹: 3420 (OH), 1652 (C=O), 1605 (C=H), NMR (Fig. 3). Anal. Calcd. for C6H10O2: C 76.82; H, 9.88. Found : C, 75.89; H, 8.66.

Acetation of X: A solution of X (57 mg) in a mixture of pyridine (1 ml) and AcO (0.5 ml) was heated on a steam bath for 2 hr. After treatment in the usual way, the product was recrystallized from MeOH-CHCl3 to give the acetate (X) as colorless needles (51 mg), m. p. 244–246°, [α]320° -80.0° (c=0.425, CHCl3). UV (Fig. 2) λmax nm: 244 μ (log ε: 4.10), IRVmax cm⁻¹: 1757 (enolacetate), 1689 (C=O), 1614 (C–C). NMR (Fig. 3). Anal. Calcd. for C6H10O2: C 74.32; H, 8.60. Found : C, 74.21; H, 8.54.

Periodate Oxidation of III — A solution of III (14.5 mg) in 15 ml of dioxane-ETOH (2:1). NaIO4 (39.4 mg) in 1% AcOH (15 ml) was added and the mixture was allowed to stand for 2 hr. at room temperature. The consumption of periodate was iodometrically determined as 2.02 moles per mole of III.

b) Formic acid was detected from the periodate oxidation products by the method of Frieden and Fuerst.13

Treatment of V with Phosgene — A 10% COCl2-toluene solution (7 ml) was added dropwise to a mixture of V (43 mg), alcohol-free CHCl3 (7 ml), and pyridine (4 ml) under cooling at -15°. The reaction mixture was allowed to stand at room temperature for 20 hr. After decomposing an excess of COCl2 with ice, water and ether were added. The organic layer was washed successively with 2N HCl, 5% NaHCO3, and evaporated to dryness in vacuo. The residue (38 mg) was chromatographed on alumina (1.2 g) to give an amorphous material (23 mg), regarded as the carbonate (XI). IRVmax cm⁻¹: 1470, 1006.

Convolvulain–B Orthoester (XII) — In warm MeOH (50 ml) was dissolved III (114 mg). After cooling, 28.8% HCl-MeOH (2 ml) and ethyl orthoformate (3 ml) was added and the mixture was stirred at room temperature for 20 hr. Evaporation of the solvent in vacuo gave the residue (133 mg) which was crystallized from MeOH to give the orthoester (XII) as colorless plates (95 mg), m. p. 233–234°, [α]320° -47.2° (c=0.725, CHCl3), IRVmax cm⁻¹: 3580 (OH, sharp), 1148, 998, 981 (RO3C=O), NMR (δ in CDCl3): 4.43 (orthoester-H). Anal. Calcd. for C6H10O2: C 70.85; H, 8.92. Found : C, 70.90; H, 8.81.

*3 A solution of CrO3 (6.7 g) in conc. H2SO4 (5.3 ml) was diluted with water to a volume of 25 ml and it was used as a standard solution (CrO3=268 mg/ml); cf. C. Djerassi, R.R. Engel, A. Bowers : J. Org. Chem., 21, 1547 (1966).

Acetylation of XIX: A solution of XIX (51 mg.) in a mixture of pyridine (0.5 ml.) and Ac₂O (0.5 ml.) was allowed to stand at room temperature for 40 hr. After treatment in the usual way, the product was recrystallized from MeOH-CHCl₃ (4:1) to give the acetate (XXIV) as colorless needles (46 mg.), m.p. 276°-277°(c=0.800, CHCl₃), IRυ_{max}^{cm^{-1}}: 1732 (OAc), 1135, 998, 987 (RO₂C=O), NMR (τ in CDCl₃): 4.35 (orthoester-CH₃). Anal. Calcd. for C₂₅H₂₆O₈: C, 69.74; H, 8.58. Found: C, 69.86; H, 8.54.

Oxidation of XIX: To a stirred solution of XIX (57 mg.) in Me₂CO (10 ml.) was added dropwise CrO₃- H₂SO₄ solution# (0.046 ml.) under cooling at 0°-2°. After 20 min., the reaction mixture was diluted with water and extracted with ether. The organic layer was washed with 5% NaHCO₃ and water, dried over anhydrous Na₂SO₄, and evaporated in vacuo. Recrystallization of the residue (48 mg.) from MeOH-CHCl₃ (4:1) gave the ketone (XXV) as needles, m.p. 241°-244° (decomp.), UVυ_{max}^{nm} : 320 mp (ε : 38.5), IRυ_{max}^{cm^{-1}}: 1745 (C=O), 1135, 1000, 999 (RO₂C=O), ORD: peak [α]_390 -190°, trough [α]_589 -647°, [α]_999 -69.3°, a = -79.5 (c=0.263, MeOH, temp. 25°). Anal. Calcd. for C₂₅H₂₄O₃: C, 71.16; H, 8.53. Found: C, 71.17; H, 8.47.

**Convalleagin-B Acetone (XVI)**——A mixture of III (79 mg.), Me₂CO (30 ml.), 2,2-dimethoxypropane (10 ml.), and p-toluensulfonic acid (84 mg.) was refluxed for 18 hr. The solution was neutralized with 10% Na₂CO₃ and concentrated under reduced pressure. The product was extracted with ether and the extract was washed with water, then dried over anhydrous Na₂SO₄. After removal of the solvent, crystallization of the residue from MeOH-CHCl₃ (4:1) gave the anhydride (XVI) as colorless prisms (50 mg.), m.p. 227°-230°, IRυ_{max}^{cm^{-1}}: 3420 cm⁻¹ (OH), 3630 (sharp), 3480 (broad) cm⁻¹. Anal. Calcd. for C₂₅H₂₄O₃: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.42.

Acetylation of XVI: A solution of XVI (48 mg.) in a mixture of pyridine (0.5 ml.) and Ac₂O (0.5 ml.) was allowed to stand for 18 hr. at room temperature. Thin-layer chromatography of the reaction mixture using CHCl₃-Me₂CO (9:1) as solvent gave a spot of the acetate (XVII) together with a larger one of the starting material. After heating on a steam bath for 5 hr., a spot of XVII diminished away. Treatment in the usual way gave the product (45 mg.) which was recrystallized from MeOH to give the acetate (XVII) as colorless needles, m.p. 191°-193°, IRυ_{max}^{cm^{-1}}: 3500 (OH), 1720 (OAc). Anal. Calcd. for C₂₅H₂₆O₈: C, 70.30; H, 9.22. Found: C, 70.48; H, 9.24.

Oxidation of XVI: A solution of XVI (173 mg.) in pyridine (4 ml.) was added at 0° to the CrO₃ (170 mg.)-pyridine (2 ml.) complex and the mixture was stirred at room temperature for 16 hr. The solution was poured on to crushed ice and the mixture was extracted with ether. The organic layer was washed with water, dried over anhydrous Na₂SO₄, and evaporated. The residue (110 mg.) was crystallized from MeOH-CHCl₃ to give the ketone (XVII) as colorless plates (87 mg.), m.p. 211°-213°, IRυ_{max}^{cm^{-1}}: 3550 (OH), 1706 (C=O), ORD: peak [α]_390 +257°, [α]_2390 0°, trough [α]_999 -1448°, [α]_999 -46.9°, a = 86.3 (c=0.265, MeOH, temp. 23°). Anal. Calcd. for C₂₅H₂₄O₃: C, 71.68; H, 9.22. Found: C, 71.50; H, 8.94.

**Preparation of III from Anhydroconvalleagin-A Diacetate (XIX)**——To a solution of XIX (270 mg.) in anhydrous ether (15 ml.) was added pyridine (0.3 ml.) and a solution of OsO₄ (261 mg.) in anhydrous ether (5 ml.). After stirring at room temperature for 6 days, the mixture was refluxed for 3.5 hr. with Na₂SO₄, 7H₂O (2 g.) in EtOH (7 ml.) and H₂O (15 ml.). The solid material formed was collected by filtration and washed with warm CHCl₃. A combined solution of filtrate and washings was evaporated in vacuo, the product was dissolved in CH₂Cl₂, washed with water, dried, and evaporated (184 mg.). Thin-layer chromatography of the residue suggested the presence of X of XXI together with the products. After removing of XIX (68 mg.) from the residue with n-hexane, the insoluble fraction (108 mg.) was directly acetylated by heating for 3.5 hr. on a steam bath with Ac₂O (0.5 ml.) and pyridine (1 ml.). The product (110 mg.) was chromatographed on alumina (3.3 g.) and the n-hexane-benzene (3:2) fraction gave convalleagin-B triacetate (XIX) as colorless needles (51 mg.), m.p. 227°-230°, which was identified with the authentic specimen by a mixed melting point determination, thin-layer chromatography, and infrared spectroscopy. With 1.5% methanolic KOH solution (10 ml.) under reflux for 1 hr., N (23 mg.) was saponified. Crystallization of the product from MeOH-CHCl₃ gave the expected convalleagin-B (III) as colorless plates (17 mg.), m.p. 275°-279°, which was identical in all respects with the specimen of III.

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