[Chem. Pharm. Bull. 15(11)1713~1719(1967)]

UDC 547.918.02 : 582.59

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

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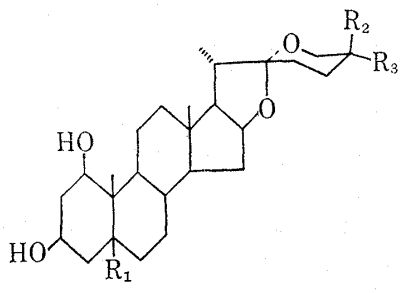
Convallagenin-B (Ⅲ) from the flowers of *Convallaria keisukei* Miq., Japanese lily of the valey, has been elucidated as 25L,5β-spirostan-1β,3β,4β,5β-tetrol, that represents the first instance of the 25L-tetrahydroxy steroidsapogenin.

(Received December 27, 1966)

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 keisukei* Miq., Japanese lily of the valley (SUZURAN) and two new sapogenins, convallagenin-A and -B, together with the known isorhodeasapogenin (I)[2] as their aglycones. The structure of convallagenin-A (Ⅱ) was regarded as 25L,5β-spirostan-1β,3β,5β-triol.[3] The present paper deals with a study on the structure of convallagenin-B (Ⅲ), $C_{27}H_{44}O_6$, m.p. 277~278°, $[\alpha]_D$ −42.7°, which was elucidated as 25L,5β-spirostan-1β,3β,4β,5β-tetrol from the following evidence.



Isorhodeasapogenin (I)
R_1=H
R_2=H
R_3=CH_3

Convallagenin-A (Ⅱ)
R_1=OH
R_2=CH_3
R_3=H

Chart 1.

Convallagenin-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},[1,4] and the doublet signal for the 27-methyl group at τ 8.98 in lower field than that of the 18-methyl group (τ 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.[3] The NMR data of both sapogenins and their derivatives as summerized 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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*2 Part Ⅷ: This Bulletin, **15**, 1204 (1967).

1) M. Kimura, M. Tohma, I. Yoshizawa: This Bulletin, **14**, 50 (1966).
2) H. Nawa: Yakugaku Zasshi, **73**, 1192 (1953); This Bulletin, **6**, 255 (1958).
3) M. Kimura, M. Tohma, I. Yoshizawa: This Bulletin, **15**, 1204 (1967).
4) M.E. Wall, C.R. Eddy, M.L. McClennan, M.E. Klumpp: Anal. Chem., **24**, 1337 (1952); C.R. Eddy, M.E. Wall, M.K. Scott: *Ibid.*, **25**, 266 (1953).
5) J.P. Kutney: Steroids, **2**, 225 (1963).
6) *a*) R.F. Zürcher: Helv. Chim. Acta, **46**, 2054 (1963); *b*) A.I. Cohen, S. Rock: Steroids, **3**, 243 (1964); *c*) K. Tori, K. Aono: Ann. Rept. Shionogi Res. Lab., **14**, 136 (1964).

Table I. Chemical Shifts of 18- and 19-Methyl Groups in Pyridine

	19-CH_3 (τ)	Diff.[a] (p.p.m.)	18-CH_3 (τ)	Diff.[a] (p.p.m.)
Convallagenin-B (Ⅲ)	8.41	−0.67	9.15	0.00
-diacetate (Ⅴ)	8.40	−0.68	9.14	−0.01
-triacetate (Ⅳ)	8.72	−0.36	9.15	0.00
-1-one (Ⅶ)	8.43	−0.65	9.16	+0.01
-Δ^4-triacetate (Ⅵ)	8.81	−0.27	9.14	−0.01
Convallagenin-A and its derivatives[b]				
1β-OH 3β-OH 5β-OH	8.41	−0.67	9.14	−0.01
-OH -OAc -OH	8.46	−0.62	9.13	−0.02
-OAc -OAc -OH	8.78	−0.30	9.17	+0.02
-CO -OAc -OH	8.47	−0.61	9.15	0.00
-OAc -OAc -Δ^4	8.82	−0.26	9.14	−0.01
5β-Spirostane[c]	9.08		9.15	

a) Difference in chemical shifts of the angular methyl group between the sapogenin derivatives and 5β-spirostane.
b) Refference 3). c) Refference 6c).

formic acid from the reaction mixture; that indicated Ⅲ 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 (Ⅳ), 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), λ_{max}: 220 mμ (log ε : 3.92), ν_{max} : 1677 cm^{-1}, by the treatment with an alkaline alumina. Infrared spectrum of Ⅷ 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 Ⅲ 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 (Ⅸ; 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

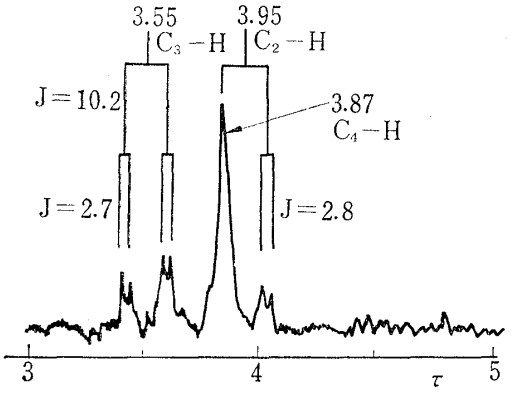

Fig. 1. Nuclear Magnetic Resonance Spectrum of 4-Acetoxy-2-en-1-one (Ⅷ) (in $CDCl_3$)

7) N.S. Bhacca, D.H. Williams : "Applications of NMR Spectroscopy in Organic Chemistry," 110 (1964). Holden-Day, Inc., San Francisco.

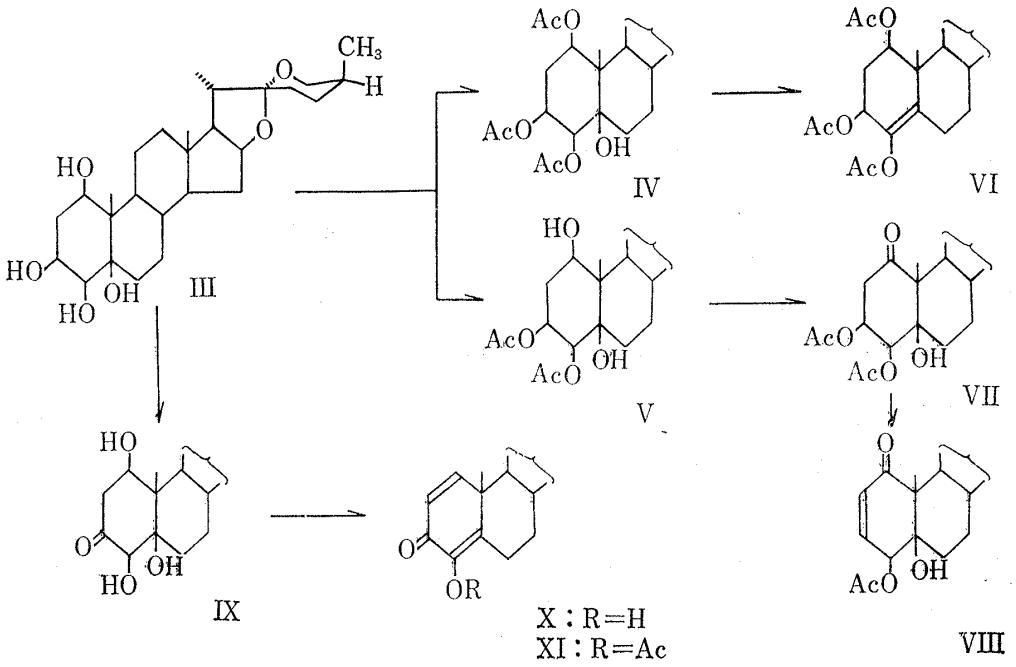

Chart 2.

positive ferric chloride color test; its infrared spectrum suggested the presence of a hydroxyl (3420 cm^{-1}) as well as an α,β-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 1*N* sodium hydroxide solution, as shown in Fig. 2. The acetate (XI) of X showed the absorption bands at 244 mμ : (log ε: 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 acetoxyl 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-tetrahydroxysapogenin.

The negative Cotton effects observed on the optical rotatory dispersion (ORD) curves of the 3- (IX) and the 1-ketone (VII) (a=−46.2 and −116.7, respectively) were consistent with the A/B-*cis* fusion similarly to the ketones of convallagenin-A,[3] so that the tertiary hydroxyl group at C-5 was required β-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 5β-hydroxyl group and may necessarily have the β-orientation. The orthoester (XIII) of III 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

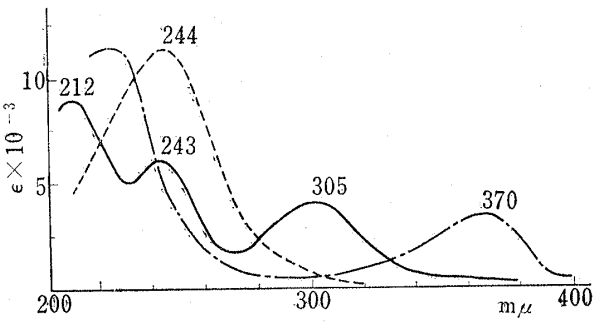

Fig. 2. Ultraviolet Absorption Spectra of the Diosphenol(X) and Its Acetate(XI) (in EtOH)
——— (X) — — — (X)+NaOH ------- (XI)

8) K. Sasaki : This Bulletin, **9**, 684 (1961).

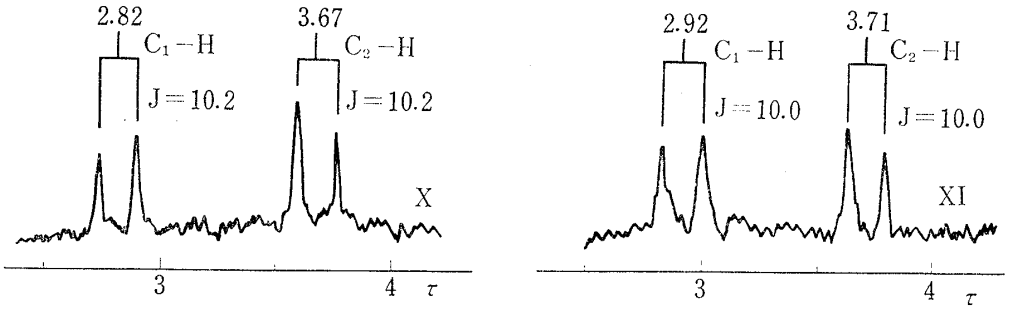

Fig. 3. Nuclear Magnetic Resonance Spectra of the Diosphenol(X) and Its Acetate(XI) (in $CDCl_3$)

(320 mμ, ε : 38.5) as well as infrared spectrum (1745 cm^{-1}), and in ORD curve[9] (traugh: 341 mμ, peak : 303 mμ, 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,[8] suggesting that XIII was the 1,3,5- rather than 1,4,5-ester and that these original hydroxyl groups

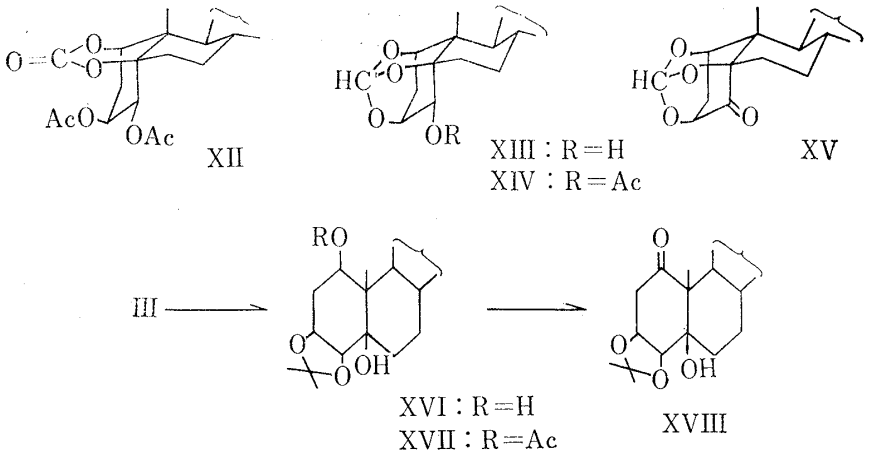

Chart 3.

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).[9] 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,[3] showed a sharp singlet band at τ 4.70, which was in good agreement with the value found in Δ^4-cholestenyl acetate, but was different in both shape and position from those given by the olefinic 6-proton (τ 4.32) in ruscogenin diacetate (XX),[10] so that the double

9) W. Moffitt, R.B. Woodward, A. Moscowitz, W. Klyne, C. Djerassi : J. Am. Chem. Soc., **83**, 4013 (1961).
10) L. Mandell, A.L. Nussbaum, E.P. Oliveto : Tetrahedron Letters, **1960**, 25.

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. 227~230°, as the main product which was saponified to a free tetrol, m.p. 275~279°, 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.

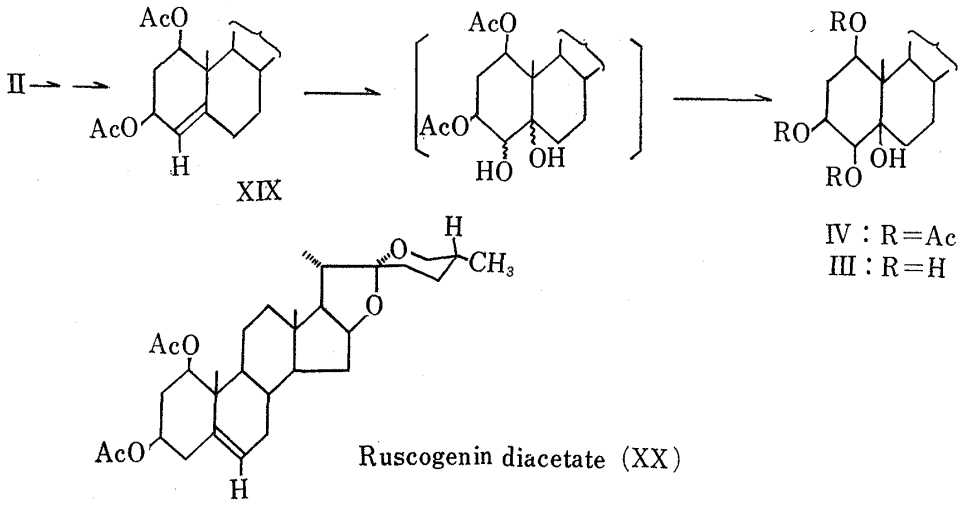

Chart 4.

Consequently, convallagenin-B (Ⅲ) may reasonably be defined as 25L,5β-spirostan-1β,3β,4β,5β-tetrol which is the first tetrahydroxy steroidal sapogenin posessing the 25L-configuration and which can be regarded as a 25L-isomer of kitigenin isolated from *Reineckia carnea* KUNTH. by Takeda and coworkers.[8,11] The constitution of convallasaponin-B has also been established as convallagenin-B-α-L-arabopyranoside in which the sugar moiety combined unusually with a tertiary hydroxyl group at C-5 of Ⅲ[12] 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 Spectopolarimeter. Nuclear magnetic resonance spectra were recorded on a Japan Electron Optics Lab. JNM-3H-60 Spectrometer by using 5% solutions containing $(CH_3)_4Si$ as an internal reference.

Convallagenin-B Diacetate (V)——A mixture of Ⅲ (1.85 g.), pyridine (40 ml.) and Ac_2O (20 ml.) was allowed to stand for 15 hr. at 1~3°, 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_2CO (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. 227~230°, as reported previously.[1] Further elution with *n*-hexane-benzene (1:4) gave the diacetate (V; 1.73 g.) which was recrystallized from Me_2CO as colorless needles, m.p. 217~219°, $[\alpha]_D^{21}$ −44.7° (c=0.525; $CHCl_3$), $IR\nu_{max}^{CHCl_3}$ cm^{-1} : 3460 (OH, broad), 1742 (OAc), 980, 922>898, 855 (25L-spiroketal). *Anal.* Calcd. for $C_{31}H_{48}O_8$: 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.,

11) K. Takeda, T. Okanishi, A. Shimaoka : Yakugaku Zasshi, **75**, 560 (1965); K. Sasaki : This Bulletin, **9**, 693 (1961).
12) I. Yoshizawa, M. Tohma, M. Kimura : *Ibid.*, **15**, 226 (1967).

sufficient amounts of ice were added and the product was extracted with ether. The extract was washed with *N* HCl, 10% Na_2CO_3 and water, dried over anhydrous Na_2SO_4 and evaporated. Recrystallization of the residue from MeOH gave an enolacetate (VI) as colorless plates (46 mg.), m.p. 202~206°, positive reaction for tetranitromethane, $IR\nu_{max}^{Nujol}$ cm^{-1} : 1759 (enolacetate, shoulder), 1735 (OAc). NMR (τ in $CDCl_3$) : 7.88 (enolacetate-H), 7.95 (OAc-H). *Anal.* Calcd. for $C_{33}H_{48}O_8$: 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 CrO_3–H_2SO_4 solution*3 (containing 93.8 mg. of CrO_3, 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% $NaHCO_3$ and water, dried over anhydrous Na_2SO_4 and evaporated. Recrystallizatson of the residue from MeOH gave the 1-ketone (VII) as prisms (366 mg.), m.p. 215~216°, ORD : peak $[\alpha]_{274}$ +853°, $[\alpha]_{293}$ 0°, traugh $[\alpha]_{311}$ −1279°, $[\alpha]_{589}$ −106.6°, a=−116.9 (c=0.395; MeOH, temp. 26°), $IR\nu_{max}^{Nujol}$ cm^{-1} : 3580 (OH), 1741 (OAc), 1709 (C=O). *Anal.* Calcd. for $C_{31}H_{46}O_8$: C, 68.10; H, 8.48. Found : C, 67.74; H, 8.35.

Elimination of Acetic Acid from 1-Ketone (VII)——A solution of VII (172 mg.) in benzene (10 ml.) was stirred with Al_2O_3 (Brockman, 1.5 g.) for 15 hr. at room temperature. After filtration and evaporation, recrystallization from MeOH–$CHCl_3$ (4:1) gave the Δ^2-1-one (VIII) as colorless needles (151 mg.), m.p. 255~256°, $[\alpha]_D^{21}$ −10.0° (c=1.00; $CHCl_3$). UV λ_{max}^{EtOH} : 220 mμ (log ε 3.92). $IR\nu_{max}^{Nujol}$ cm^{-1} : 3540 (OH), 1723 (OAc), 1677 (α,β-unsaturated ketone). *Anal.* Calcd. for $C_{29}H_{42}O_6$: C, 71.57; H, 8.70. Found : C, 71.60; H, 8.74.

Selective Oxidation of Convallagenin-B (III)——A suspention of $PtO_2 \cdot H_2O$ (65 mg.) in a mixture of H_2O (5 ml.) and AcOH (1 ml.) was stirred magnetically in an atmosphere of H_2 until the reduction to metallic Pt was completed, and the solvent was decanted off. A solution of III (74 mg.) in 20 ml. of AcOEt-acetone (1:1) was added and the mixture was stirred in an atmosphere of O_2 for 20 hr. until the uptake of O_2 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 (IX) as colorless needles, m.p. 214~216°. $IR\nu_{max}^{Nujol}$ cm^{-1} : 3340 (OH), 1722 (C=O). ORD : peak $[\alpha]_{264}$ +327°, $[\alpha]_{279}$ 0°, traugh $[\alpha]_{301}$ −669°, $[\alpha]_{589}$ −30.9°, a=−46.2 (c=0.264, MeOH, temp. 26°). *Anal.* Calcd. for $C_{27}H_{42}O_6$: C, 70.10; H, 9.15. Found: C, 70.10; H, 9.08.

Convallagenin-B Diosphenol (X)——To a solution of IX (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 2*N* HCl, and extracted with ether. Ether layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness *in vacuo*. Crystallization of the residue from MeOH–$CHCl_3$ furnished 102 mg. of the diosphenol (X) as colorless needles, m.p. 172~173°, $[\alpha]_D^{21}$ −30.1° (c=0.665, $CHCl_3$), positive reaction for $FeCl_3$ test, UV (Fig. 2) λ_{max}^{EtOH} mμ : 212 (log ε : 3.95), 243 (log ε : 3.71), 305 (log ε : 3.51) and $\lambda_{max}^{EtOH\text{-}NaOH}$: 370 mμ (log ε : 3.37). $IR\nu_{max}^{Nujol}$ cm^{-1} : 3420 (OH), 1652 (C=O), 1605 (C=C), NMR (Fig. 3). *Anal.* Calcd. for $C_{27}H_{38}O_4$: C, 76.02; H, 8.98. Found : C, 75.89; H, 8.66.

Acetylation of X : A solution of X (57 mg.) in a mixture of pyridine (1 ml.) and Ac_2O (0.5 ml.) was heated on a steam bath for 2 hr. After treatment in the usual way, the product was recrystallized from MeOH–$CHCl_3$ to give the acetate (XI) as colorless needles (51 mg.), m.p. 244~246°, $[\alpha]_D^{21}$ −80.0° (c=0.425, $CHCl_3$). UV (Fig. 2) λ_{max}^{EtOH} : 244 mμ (log ε : 4.10). $IR\nu_{max}^{Nujol}$ cm^{-1} : 1757 (enolacetate), 1660 (C=O), 1614 (C=C). NMR (Fig. 3). *Anal.* Calcd. for $C_{29}H_{40}O_5$: C, 74.32; H, 8.60. Found : C, 74.21; H, 8.54.

Periodate Oxidation of III——a) To a solution of III (14.5 mg) in 15 ml. of dioxane-EtOH (2:1), $NaIO_4$ (39.4 mg.) in 1% AcOH (15 ml.) was added and the mixture was allowed to stand for 20 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 Frehden and Fuerst.[13]

Treatment of V with Phosgene——A 10% $COCl_2$-toluene solution (7 ml.) was added dropwise to a mixture of V (43 mg.), alcohol-free $CHCl_3$ (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 $COCl_2$ with ice, water and ether were added. The organic layer was washed successively with 2*N* HCl, 5% $NaHCO_3$ as well as water, dried over anhydrous Na_2SO_4, 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 (XII). IR ν_{max}^{Nujol} cm^{-1} : 1740, 1106.

Convallagenin-B Orthoester (XIII)——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 (XIII) as colorless plates (95 mg.), m.p. 233~234°, $[\alpha]_D^{21}$ −47.2° (c=0.725, $CHCl_3$), $IR\nu_{max}^{Nujol}$ cm^{-1} : 3580 (OH, sharp), 1148, 998, 981 ($(RO)_3C$–), NMR(τ in $CDCl_3$) : 4.43 (orthoester-H). *Anal.* Calcd. for $C_{28}H_{42}O_6$: C, 70.85; H, 8.92. Found : C, 70.90; H, 8.81.

*3 A solution of CrO_3 (6.7 g.) in conc. H_2SO_4 (5.3 ml.) was diluted with water to a volume of 25 ml. and it was used as a standard solution (CrO_3=268 mg./ml.); cf. C. Djerassi, R.R. Engle, A. Bowers : J. Org. Chem., **21**, 1547 (1956).

13) O. Frehden, K. Fuerst : Mikrochem. ver. Mikrochim. Acta, **26**, 36 (1939). cf. F. Feigl : "Spot tests in Organic Analysis," 190 (1960). Elsevier Pub. Co.

Acetylation of XIII: A solution of XIII (51 mg.) in a mixture of pyridine (0.5 ml.) and Ac_2O (0.5 ml.) was allowed to stand for 40 hr. at room temperature. After treatment in the usual way, the product was recrystallized from MeOH–$CHCl_3$ (4:1) to give the acetate (XIV) as colorless needles (46 mg.), m.p. 276~277°, $[\alpha]_D^{21}$ −45.0° (c=0.800, $CHCl_3$), IR$\nu_{max}^{CHCl_3}$ cm^{-1}: 1732 (OAc), 1135, 998, 987 ((RO)$_3$C–), NMR (τ in $CDCl_3$): 4.35 (orthoester-H). *Anal.* Calcd. for $C_{30}H_{44}O_7$: C, 69.74; H, 8.58. Found: C, 69.86; H, 8.54.

Oxidation of XIII: To a stirred solution of XIII (57 mg.) in Me_2CO (10 ml.) was added dropwise CrO_3–H_2SO_4 solution*3 (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% $NaHCO_3$ and water, dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. Recrystallization of the residue (48 mg.) from MeOH–$CHCl_3$ (4:1) gave the ketone (XV) as needles, m.p. 241~244° (decomp.), UVλ_{max}^{EtOH}: 320 mμ (ε: 38.5), IRν_{max}^{Nujol} cm^{-1}: 1745 (C=O), 1135, 1000, 990 ((RO)$_3$C–), ORD: peak $[\alpha]_{303}$ −190°, traugh $[\alpha]_{341}$ −647°, $[\alpha]_{589}$ −69.3°, a=−39.5 (c=0.263, MeOH, temp. 25°). *Anal.* Calcd. for $C_{28}H_{40}O_6$: C, 71.16; H, 8.53. Found: C, 71.17; H, 8.47.

Convallagenin-B Acetonide (XVI)——A mixture of III (79 mg.), Me_2CO (30 ml.), 2,2-dimethoxypropane (10 ml.), and *p*-toluensulfonic acid (84 mg.) was refluxed for 18 hr. The solution was neutralized with 10% Na_2CO_3 and concentrated under reduced pressure. The product was extracted with ether and the extract was washed with water, then dried over anhydrous Na_2SO_4. After removal of the solvent, crystallization of the residue from MeOH–$CHCl_3$ (4:1) gave the acetonide (XVI) as colorless prisms (50 mg.), m.p. 227~230°, IR ν_{max}^{Nujol}: 3420 cm^{-1} (OH), $\nu_{max}^{CHCl_3}$: 3630 (sharp), 3480 (broad) cm^{-1}. *Anal.* Calcd. for $C_{30}H_{48}O_6$: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.42.

Aectylation of XVI: A solution of XVI (48 mg.) in a mixture of pyridine (0.5 ml.) and Ac_2O (0.5 ml.) was allowed to stand for 18 hr. at room temperature. Thin-layer chromatography of the reaction mixture using $CHCl_3$–Me_2CO (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 XVI 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°, IRν_{max}^{Nujol} cm^{-1}: 3500 (OH), 1720 (OAc). *Anal.* Calcd. for $C_{32}H_{50}O_7$: 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 CrO_3 (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 Na_2SO_4 and evaporated. The residue (110 mg.) was crystallized from MeOH–$CHCl_3$ to give the ketone (XVIII) as colorless plates (87 mg.). m.p. 211~213°, IRν_{max}^{Nujol} cm^{-1}: 3550 (OH), 1706 (C=O), ORD: peak $[\alpha]_{268}$ +257°, $[\alpha]_{279}$ 0°, traugh $[\alpha]_{308}$ −1448°, $[\alpha]_{589}$ −46.9°, a=86.3 (c=0.265, MeOH, temp. 23°). *Anal.* Calcd. for $C_{30}H_{46}O_6$: C, 71.68; H, 9.22. Found: C, 71.50; H, 8.94.

Preparation of III from Anhydroconvallagenin-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 OsO_4 (261 mg.) in anhydrous ether (5 ml.). After stirring at room temperature for 6 days, the mixture was refluxed for 3.5 hr. with $Na_2SO_3 \cdot 7H_2O$ (2 g.) in EtOH (7 ml.) and H_2O (15 ml.). The solid material formed was collected by filtration and washed with warm $CHCl_3$. A combined solution of filtrate and washings was evaporated *in vacuo*, the product was dissolved in $CHCl_3$, washed with water, dried, and evaporated (184 mg.). Thin-layer chromatography of the residue suggested the presence of XIX 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 Ac_2O (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 convallagenin-B triacetate (IV) 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., IV (23 mg.) was saponified. Crystallization of the product from MeOH–$CHCl_3$ gave the expected convallagenin-B (III) as colorless plates (17 mg.), m.p. 275~279°, which was identical in all respects with the specimen of III.

The authors express their deep gratitude to Prof. S. Wakayama, Hokkaido Gukugei University and students of Toyoni and Tomioka Junior High School for collecting materials. They are also indebted to Dr. K. Sasaki, Shionogi Research Laboratories, for his valuable advice and to Takeda Chemicals Co., Ltd. for the preparation of crude extracts. Thanks are also due to Mrs. T. Tohma and Miss A. Maeda of the analytical laboratory of this Faculty for elemental analysis and to Mr. S. Shimokawa, Faculty of Engineering, this University, for NMR analysis.