and for valuable advices and Dr. K. Kuriyama of the same Laboratory for optical rotatory dispersion (ORD) measurements and helpful discussions. They are also indebted to Dr. T. Shingu of this Faculty and Dr. K. Tori of Shionogi & Co., Ltd. for the NMR measurements and kind discussions, Dr. K. Miyajima and collaborators for determination of infrared spectra in KBr disc, and Dr. K. Konobu and his collaborators for microanalyses.

[Chem. Pharm. Bull. 15(2) 207～213 (1967)]

UDC 581.19 : 582.761 : 547.94

28. **Tohru Kikuchi and Shoichiro Uyeo**: Pachysandra Alkaloids. Ⅲ.*1 Structures of Pachysandrine-B, -C, and -D.*2

(*Faculty of Pharmaceutical Sciences, Kyoto University**3)

Structures of pachysandrine-B, -C, and -D isolated from *Pachysandra terminalis* Sieb. et Zucc., a Buxaceous plant, were investigated and their structures were proved to be Ⅲa, Ⅱ, and Ⅴa, respectively.

(Received May 27, 1966)

In the preceding paper,*1 we discussed the constitution of pachysandrine-A, one of the major alkaloids of *Pachysandra terminalis* Sieb. et Zucc. (Japanese name: Fukkiso), and gave the complete structure (Ⅰ) to this alkaloid.

In the present paper, structure elucidation of three closely related alkaloids isolated from the same plant, for which we proposed the name pachysandrine-B, -C, and -D, will be discussed herewith.

Of these alkaloids, pachysandrine-C (Ⅱ), m.p. 214～215°, $[\alpha]_D$ −38° ($CHCl_3$), was first isolated in a very poor yield*4 from the N-methylated product of strong base fraction obtained by alkaline hydrolysis of the mother liquor of weakly basic alkaloid fraction. Later, this alkaloid was discovered in the strongly basic alkaloid fraction of the plant.[1] This alkaloid was analysed for $C_{24}H_{44}ON_2$ and was found to be identical with 3α-methylamino-4α-hydroxy-20α-dimethylamino-5α-pregnane (Ⅱ),*1 which had been derived from pachysandrine-A (Ⅰ), by direct comparison (mixed m.p. and IR in KBr).

Pachysandrine-B (Ⅲa), m.p. 187～189°, $[\alpha]_D$ +93° ($CHCl_3$), was analysed for $C_{31}H_{52}O_3N_2$ and revealed the infrared bands*5 for an O-acetyl (1730 and 1240 cm^{-1}) and a conjugated tertiary amide (1650 and 1610 cm^{-1}) (Fig. 1). As shown in Fig. 2, the NMR spectrum*6 of this alkaloid revealed the presence of one olefinic proton (4.23τ, 1H, multiplet), the grouping CH-CH(O-Ac)-CH (4.75τ, quartet, J 4 and 6 c.p.s.), one amide N-methyl (7.08τ, 3H), one N-dimethyl (7.83τ, 6H), one O-acetyl (7.97τ, 3H), one isopropylidene (8.12 and 8.17τ, 6H, two doublets, J about 1 c.p.s.),*7 two tertiary C-methyls (8.94 and 9.33τ, 6H), and one secondary C-methyl (9.14τ, 3H, doublet, J 7 c.p.s.) in the molecule.

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*1 Part Ⅱ. M. Tomita, S. Uyeo, Jr., T. Kikuchi: This Bulletin, **15**, 193 (1967).

*2 Preliminary communications of this work appeared in Tetrahedron Letters, No. 18, 1053 (1964); *Ibid.*, No. 27, 1817 (1964).

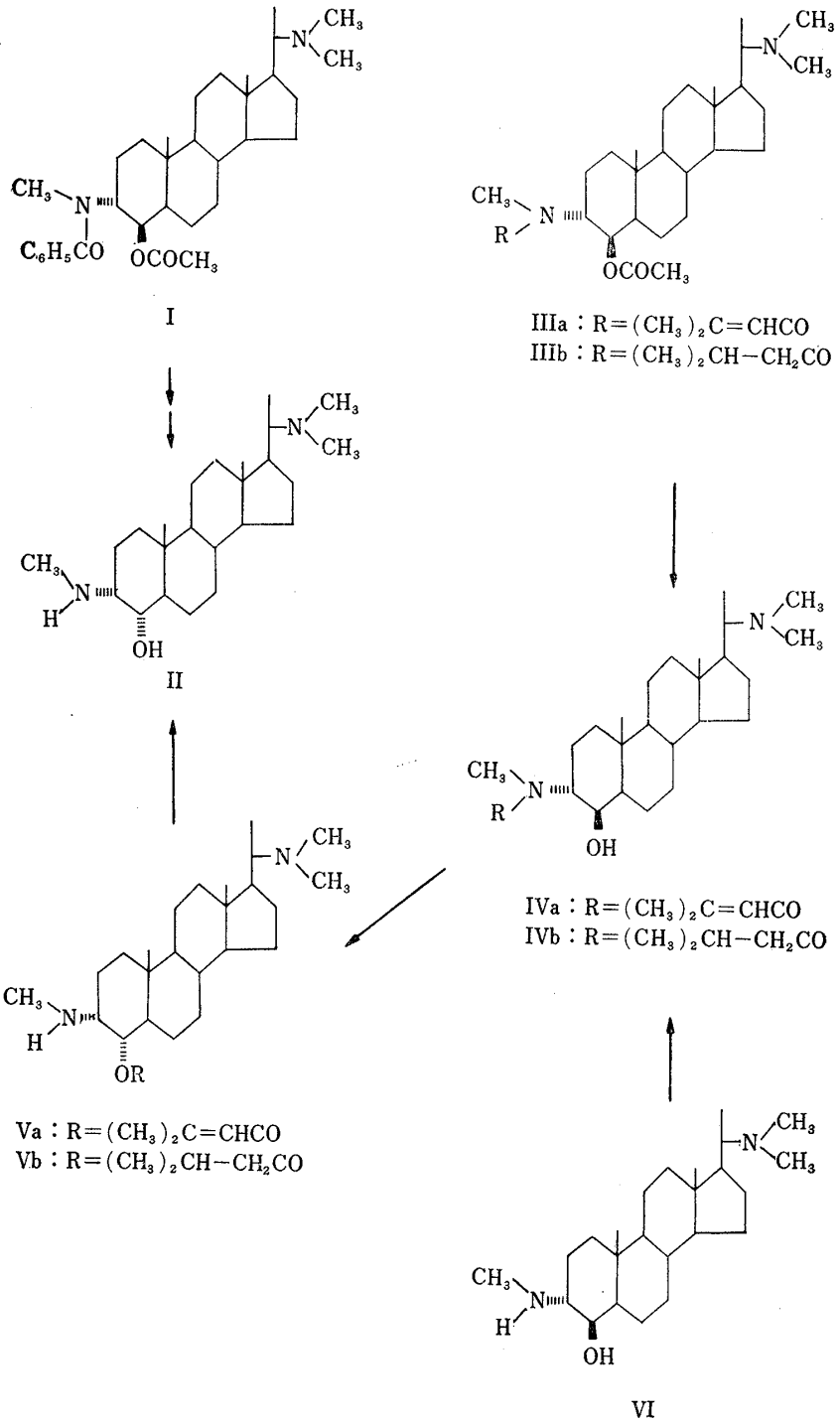
*3 Yoshida-shimoadachi-cho, Sakyo-ku, Kyoto (菊池 徹, 上尾庄一郎).

*4 This was because major part of pachysandrine-C had been transformed to the oxazolidine compound by formalin-formic acid procedure and only small amount of the unreacted material was obtained.

*5 Infrared spectra were taken in chloroform solutions unless otherwise specified. For identification of compounds, spectra were measured on a Koken DS-301 Spectrometer in KBr discs.

*6 All the NMR spectra were determined on a Varian Associates A-60 High-Resolution NMR Spectrometer in deuterated chloroform and chemical shifts are reported in τ scale using tetramethylsilane as the internal reference.

1) Part Ⅰ. M. Tomita, T. Kikuchi, S. Uyeo, Jr., T. Nishinaga, M. Yasunishi (née Ando), A. Yamamoto: Yakugaku Zasshi, **87**, 198 (1967).



I

IIIa : R=$(CH_3)_2C=CHCO$
IIIb : R=$(CH_3)_2CH-CH_2CO$

II

IVa : R=$(CH_3)_2C=CHCO$
IVb : R=$(CH_3)_2CH-CH_2CO$

Va : R=$(CH_3)_2C=CHCO$
Vb : R=$(CH_3)_2CH-CH_2CO$

VI

Catalytic hydrogenation of pachysandrine-B gave a dihydro compound (IIIb), $C_{31}H_{54}O_3N_2$, m.p. 184~186°, showing an infrared band for a saturated tertiary amide (1630 cm^{-1}). Its NMR spectrum was characterized by the disappearance of the olefinic proton and two allylic methyl signals and the appearance of new signals at 9.00 and 9.10τ attributable to two secondary C-methyl groups.

Upon basic hydrolysis, pachysandrine-B (IIIa) and dihydropachysandrine-B (IIIb) gave rise to the corresponding O-desacyl compounds (IVa), $C_{29}H_{50}O_2N_2$, m.p. 184~185°, $[\alpha]_D$ +

*7 A possible alternative structure CH_3-CH=C(CH_3)-CO- can be eliminated because the olefinic proton in this case resonates usually at 3.0~4.0 τ region.

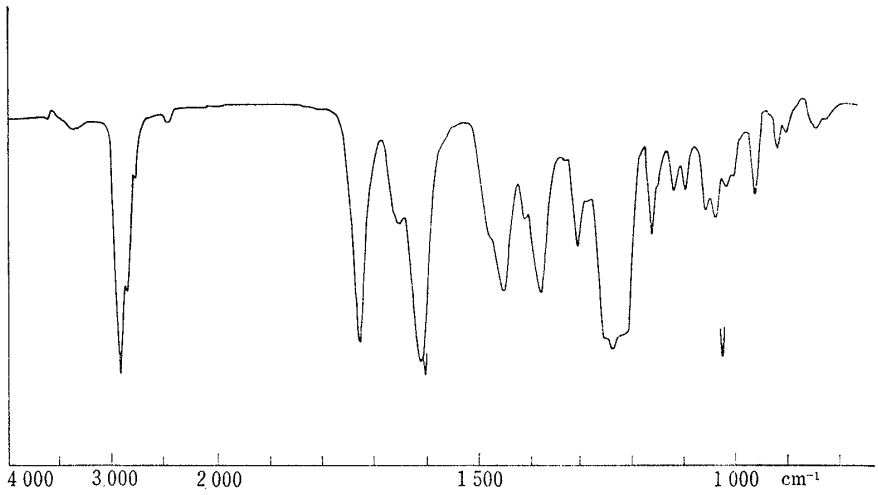


Fig. 1. Infrared Spectrum of Pachysandrine-B (Ⅲa)

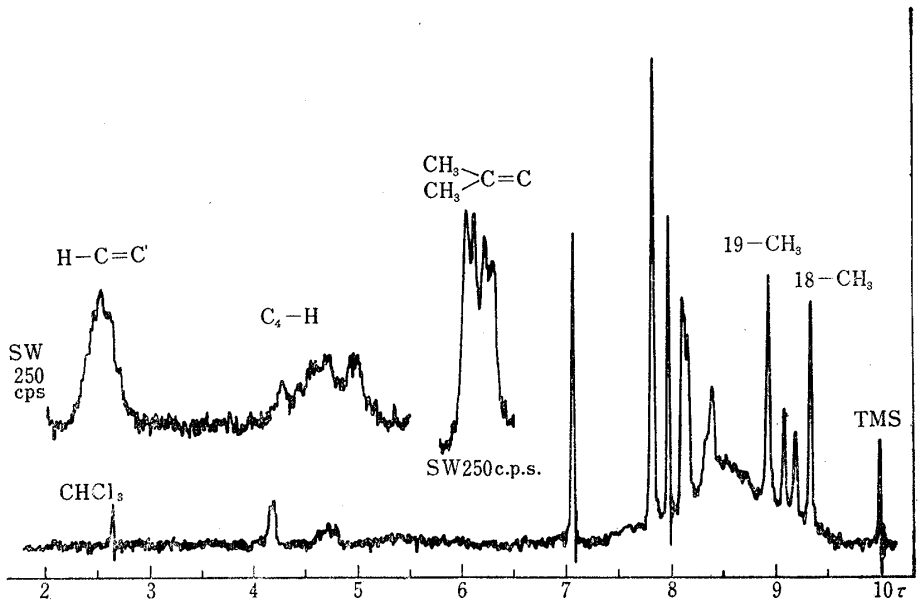


Fig. 2. NMR Spectrum of Pachysandrine-B (Ⅲa)

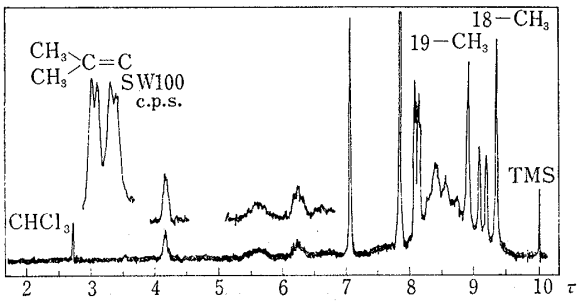


Fig. 3. NMR Spectrum of O-desacyl-pachysandrine-B (Ⅳa)

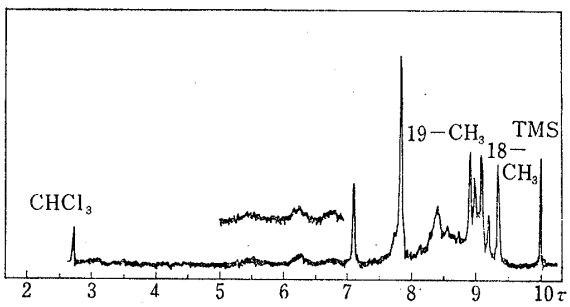


Fig. 4. NMR Spectrum of O-desacyl-dihydropachysandrine-B (Ⅳb)

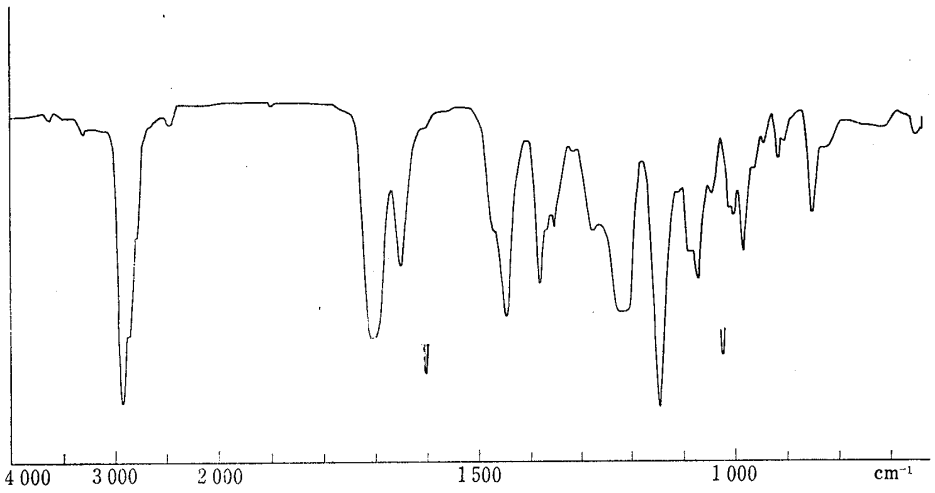


Fig. 5. Infrared Spectrum of Pachysandrine-D (Va)

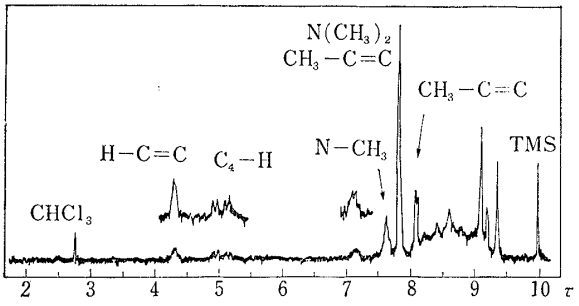


Fig. 6. NMR Spectrum of Pachysandrine-D (Va)

127° ($CHCl_3$), and (Ⅳb), $C_{29}H_{52}O_2N_2$, m.p. 204°, $[\alpha]_D$ +125° ($CHCl_3$), respectively. Their infrared spectra evidently demonstrated each amide band, whereas NMR spectra did not give signals for the acetyl groups as illustrated in Fig. 3 and 4. Furthermore, both compounds regenerated the corresponding parent alkaloids, Ⅲa and Ⅲb, upon acetylation with acetic anhydride in pyridine. It follows that pachysandrine-B should have an O-acetyl group and probably a $(CH_3)_2C=CHCO-N(CH_3)$-grouping.*7

The above O-desacyl compounds, Ⅳa and Ⅳb, resisted further basic hydrolysis under vigorous conditions. However, treatment of O-desacylpachysandrine-B (Ⅳa) with concentrated hydrochloric acid and acetic acid in a sealed tube led to an ester,*8 which might be formed by the acyl migration with inversion of configuration.[2] The subsequent alkaline hydrolysis yielded an amino-alcohol (Ⅱ), m.p. 214~215°, $[\alpha]_D$ −39° ($CHCl_3$). The latter was found to be identical with pachysandrine-C (Ⅱ) in every respect. Ⅱ was also obtained by the reaction of O-desacylpachysandrine-B (Ⅳa) with phosphorous oxychloride*1 followed by acidic hydrolysis.

The comparison of NMR spectra of O-desacylpachysandrine-B (Ⅳa) and its dihydro compound (Ⅳb) (Fig. 3 and 4) with that of pachysandrine-C (Ⅱ) revealed the remarkable paramagnetic shift (17 c.p.s.) of the 19-methyl signals in the former compounds, that is the diagnostic of 1,3-diaxial relationship between the 4-hydroxyl group and the 19-methyl group.[3] This observation therefore provides a support for the epimerization at 4-position during the acidic hydrolysis. Accordingly, the structure of pachysandrine-B must be 3α-methylamino-4β-acetoxy-20α-dimethylamino-5α-pregnane-3-carboxamide.

The acid moiety of the 3-carboxamide group was believed to be β,β-dimethylacrylic acid on the basis of spectroscopic data as described previously. This was verified by

*8 This ester, m.p. 201~204°, was first considered to be Va. However, the compound is not identical with pachysandrine-D (Va) and showed a saturated ester band at 1725 cm^{-1} in the infrared spectrum. Hence, it might be a hydrated ester. We did not examine further because of its poor yield and difficulty of purification.

2) M. S. Newman : "Steric Effects in Organic Chemistry," 293 (1956), John Wiley & Sons, Inc., New York.
3) Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto, K. Tsuda : This Bulletin, **10**, 338 (1962).

the result of ozonolysis of pachysandrine-B, whereby obtained acetone and formaldehyde as their 2,4-dinitrophenylhydrazones.

A confirmative proof was provided by the treatment of 3α-methylamino-4β-hydroxy-20α-dimethylamino-5α-pregnane (Ⅵ),*1 derived from pachysandrine-A (Ⅰ), with β,β-dimethylacrylyl chloride in pyridine. Mild alkaline hydrolysis of the condensation product gave O-desacylpachysandrine-B (Ⅳa), m.p. 186~187°, $[\alpha]_D$ +128° ($CHCl_3$). The identity was confirmed by mixed melting point determination and infrared (KBr) comparison, and thus established the structure of pachysandrine-B to be Ⅲa.

Now we will discuss the structure of the third alkaloid, pachysandrine-D (Va), m.p. 184~185°, $[\alpha]_D$ +2° ($CHCl_3$), which is a minor alkaloid isolated from the strongly basic alkaloid fraction of the plant.[1] Elemental analyses of this alkaloid afforded results in agreement with the empirical formula $C_{29}H_{50}O_2N_2$ and the infrared spectrum exhibited characteristic bands at 1705 and 1655 cm^{-1} which could be ascribed to an α,β-unsaturated ester (Fig. 5).

The basic structure and stereochemistry of the alkaloid (Va) was indicated by the mild alkaline hydrolysis, which yielded pachysandrine-C (Ⅱ), $C_{24}H_{44}ON_2$, m.p. 214~215°, $[\alpha]_D$ −40° ($CHCl_3$), identified by mixed melting point determination and infrared (KBr) comparison with the authentic sample.

Upon catalytic hydrogenation over platinum oxide, pachysandrine-D (Va) gave a dihydro compound (Vb), $C_{29}H_{52}O_2N_2$, m.p. 181~182°, $[\alpha]_D$ −8° ($CHCl_3$), whose infrared spectrum showed a saturated ester band at 1725 cm^{-1}.

The NMR spectrum of pachysandrine-D (Va) is reproduced in Fig. 6. It exhibited signals for an olefinic proton (4.30τ, multiplet), an N-methyl (7.62τ, broad peak*9 corresponding with 3H), and an allylic C-methyl group (8.10τ, doublet, J about 1 c.p.s.) along with signals due to one secondary C-methyl and two tertiary C-methyl groups. An intense singlet at 7.85τ, corresponding with nine protons, was able to be assigned to an N-dimethyl and an allylic C-methyl group on the basis of comparison with the spectrum of dihydropachysandrine-D (Vb), which gave a singlet due to the N-dimethyl group at 7.85τ and a doublet at 9.05τ (J 6.5 c.p.s.) arising from two, newly formed, secondary C-methyls. It should also be mentioned that a quartet at 5.05τ (J 4 and 11 c.p.s.), which was ascribed to the C_4-hydrogen geminal to the ester group, reflected itself the assigned 3α,4α-configuration.[4]

These observations together with the relation to pachysandrine-B (Ⅳa) led us to suppose that pachysandrine-D should be pachysandrine-C O-β,β-dimethylacrylate (Va). It was then expected that the compound Va would be synthesized by the acyl migration reaction[2] of O-desacylpachysandrine-B (Ⅳa). In view of the unsuccessful reaction with Ⅳa as described previously, we then attempted the transformation of O-desacyldihydropachysandrine-B (Ⅳb) to the compound Vb. Treatment of Ⅳb with concentrated hydrochloric acid in acetic acid gave rise to an ester (Vb), $C_{29}H_{52}O_2N_2$, m.p. 181~182°, $[\alpha]_D$ −6° ($CHCl_3$), which was found to be identical with dihydropachysandrine-D in every respect.

The structure of pachysandrine-D is accordingly assigned to Va.

Experimental*10

Dihydropachysandrine-B (IIIb)——A solution of pachysandrine-B (Ⅲa) (200 mg.) in EtOH (25 ml.) was shaken with hydrogen in the presence of $PtO_2 \cdot 2H_2O$ (70 mg.) at room temperature and atmospheric pressure

*9 A reason of this broadening may be the restricted rotation due to the interaction of the $NHCH_3$ group with the ester grouping located in close proximity.

*10 All the melting points were measured on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. All the optical rotations were taken in chloroform solutions.

4) M. Karplus : J. Chem. Phys., **30**, 11 (1959); *Idem* : J. Am. Chem. Soc., **85**, 2870 (1963); M. Karplus, D. H. Anderson : J. Chem. Phys., **30**, 6 (1959).

until the hydrogen uptake ceased. Catalyst was then removed by filtration and the filtrate was evaporated under reduced pressure. Alumina chromatography of the residue in CH_2Cl_2 and elution with the same solvent afforded the crystalline dihydro compound (IIIb) (195 mg.). Recrystallization from acetone-CH_2Cl_2 gave needles, m.p. 184~186°, $[\alpha]_D^{20}$ +78°(c=1.0). *Anal.* Calcd. for $C_{31}H_{54}O_3N_2$: C, 74.05; H, 10.83; N, 5.57. Found : C, 73.81; H, 11.02; N, 5.48. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1730, 1240 (O-Ac), 1630 (N-COR). NMR τ : 4.76 (1H, broad, CH-OAc), 7.11 (3H, RCON-CH_3), 7.85 (6H, N-$(CH_3)_2$), 8.00 (3H, O-Ac), 8.94, 9.35 (6H, two tert. CH_3), 9.05 (6H, doublet, J 6 c.p.s.; $(CH_3)_2CH$-), and 9.15 (3H, one sec. CH_3).

O-Desacylpachysandrine-B (IVa)——A solution of pachysandrine-B (IIIa) (75 mg.) in 5% KOH-EtOH (10 ml.) was refluxed for 3 hr. Solvent was removed under reduced pressure and the residue was diluted with water and extracted with CH_2Cl_2. The extract was washed successively with 3% HCl and dil. Na_2CO_3, dried over K_2CO_3, and vaporated. Recrystallization of the crystalline residue (55 mg.) from acetone gave O-desacyl-pachysandrine-B (IVa) (46 mg.) in colorless prisms, m.p. 184~185°, $[\alpha]_D^{19}$ +127° (c=1.12). *Anal.* Calcd. for $C_{29}H_{50}O_2N_2$: C, 75.93; H, 10.99; N, 6.11. Found : C, 75.70; H, 10.86; N, 6.06. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3350 (OH), 1655 (C=C), and 1595 (conj. amide). NMR τ : 4.15 (1H, multiplet, olefinic proton), 5.60 (1H, broad, RCON-CH), 6.25 (1H, triplet, J 5 c.p.s.; CH-OH), 7.07 (3H, RCON-CH_3) ,7.85 (6H, N-$(CH_3)_2$), 8.10, 8.17 (6H, two doublets, J 1 c.p.s.; $(CH_3)_2C$=C), 8.91, 9.35 (6H, two tert. CH_3), and 9.15 (3H, doublet, J 6 c.p.s.; sec. CH_3).

Acetylation of O-Desacylpachysandrine-B——The base (IVa) (300 mg.) was dissolved in pyridine (1.5 ml.) and acetic anhydride (0.7 ml.) and the solution was allowed to stand at room temperature overnight. The product, isolated by usual working up, was recrystallized from acetone to afford the O-acetate (IIIa) (260 mg.), m.p. 185~187°, which was identified with pachysandrine-B (IIIa) by mixed m.p. determination and IR (KBr) comparison. $[\alpha]_D^{17}$ +86°(c=1.0). *Anal.* Calcd. for $C_{31}H_{52}O_3N_2$: C, 74.35; H, 10.47; N, 5.59. Found : C, 74.09; H, 10.34; N, 5.45.

O-Desacyldihydropachysandrine-B (IVb). i) By Hydrogenation of O-Desacylpachysandrine-B (IVa)——The compound (IVa) (100 mg.) in EtOH (20 ml.) was hydrogenated over $PtO_2 \cdot 2H_2O$ (55 mg.) until the hydrogen uptake ceased (H_2 : 10 ml.). Usual working up and recrystallization of the product from acetone gave colorless needles (87 mg.), m.p. 204°, $[\alpha]_D^{19}$ +125°(c=1.12). *Anal.* Calcd. for $C_{29}H_{52}O_2N_2$: C, 75.60; H, 11.38; N, 6.08. Found : C, 75.62; H, 11.26; N, 6.16. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1615 (N-COR). NMR τ : 5.50 (1H, broad, RCON-CH), 6.25 (1H, broad, CH-OH), 7.09 (3H, RCON-CH_3), 7.84 (6H, N-$(CH_3)_2$), 8.91, 9.35 (6H, two tert. CH_3), 9.03 (6H, doublet, J 6 c.p.s.; $(CH_3)_2CH$-), and 9.15 (3H, doublet J 6 c.p.s.; sec. CH_3).

Acetylation of this compound (IVb) with acetic anhydride in pyridine gave an O-acetate, m.p. 184~185°, whose IR spectrum ($CHCl_3$) is superimposable upon that of dihydropachysandrine-B (IIIb).

ii) By Alkaline Hydrolysis of Dihydropachysandrine-B (IIIb)——The alkaloid (IIIb) (67 mg.) was hydrolysed by refluxing with 10% KOH-EtOH (10 ml.). The product obtained (63 mg.) was recrystallized from acetone to give IVb, m.p. 204°. Identity was confirmed by direct comparison with the sample described at i).

Acid Treatment of O-Desacylpachysandrine-B (IVa) and the Subsequent Alkaline Hydrolysis (Formation of Pachysandrine-C (II))——A mixture of O-desacylpachysandrine-B (IVa) (100 mg.), acetic acid (2 ml.), and conc. HCl (2 ml.) in a sealed tube was heated at 100° for 4 hr. The reaction mixture was poured into ice-water, made basic with NH_4OH, and extracted with CH_2Cl_2. The extract was dried over K_2CO_3 and evaporated to leave a crystalline mass, which showed an ester band but no amide band in the IR spectrum. Several recrystallizations from acetone gave a small amount of crystals, m.p. 201~204°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1725. Further investigation of this substance was not achieved yet.

The above crude product was dissolved in 10% KOH-EtOH (5 ml.) and the solution was refluxed for 3 hr. The product, obtained in the usual working up, was recrystallized from acetone to give colorless prisms (30 mg.), m.p. 214~215°, $[\alpha]_D^{19}$ −39° (c=1.0), which were identified with an authentic sample of pachysandrine-C (II) by mixed m.p. determination and IR (KBr) comparison.

Reaction of O-Desacylpachysandrine-B (IVa) with Phosphorous Oxychloride and the Subsequent Acid Hydrolysis——To a solution of the compound (IVa) (300 mg.) in pyridine (3 ml.) was added $POCl_3$ (1 ml.) at room temperature and the mixture was kept overnight. Solvent and the excess reagent were removed by evaporation *in vacuo* and the residue was dissolved in CH_2Cl_2 and extracted with 3% HCl. The aqueous phase was then made basic with NH_4OH, extracted again with CH_2Cl_2, and evaporated. The residue was dissolved in 15% HCl and refluxed for 5 hr. for hydrolysis. After washing with ether, the reaction mixture was made basic with NH_4OH, extracted with CH_2Cl_2, dried over K_2CO_3, and evaporated to give a crystalline residue (200 mg.). Recrystallization of the residue from acetone-CH_2Cl_2 gave pachysandrine-C (II), m.p. 210~212°. Identity was established by direct comparison with an authentic sample.

Ozonolysis of Pachysandrine-B (IIIa)——Ozonized oxygen was passed through a chilled solution of pachysandrine-B (IIIa) (250 mg.) in CH_2Cl_2 (15 ml.) (dry ice-acetone bath) until pale green color appeared. After the solvent was removed by distillation *in vacuo* at room temperature, the residue was steam-distilled and volatile carbonyl compounds were trapped in a solution of 2,4-dinitrophenylhydrazine in H_2SO_4-EtOH to precipitate a yellow solid. This was collected by suction and dissolved in CH_2Cl_2, dried over anhydrous $MgSO_4$, and evaporated to give a crystalline residue (20 mg.) which showed two spots on thin-layer chromatogram (T. L. C. : Silica gel G acc. to Stahl-$CHCl_3$). This was chromatographed on silicic acid (Mallinckrodt, 3 g.) from benzene and the earlier fractions, showing single spot on T. L. C., were combined and evaporated. Recrystallization of the eluate from EtOH gave yellow prisms, m.p. 165~167°, which were identified with

an authentic sample of formaldehyde-2,4-dinitrophenylhydrazone by mixed m.p. and IR (nujol) comparison. Further elution with the same solvent gave fractions corresponding to the other spot on T. L. C. The substance obtained from these fractions was recrystallized from EtOH to give acetone-2,4-dinitrophenylhyrazone as yellow prisms, m.p. 124~127°. No melting point depression was observed upon admixture with an authentic sample and their IR (KBr) spectra are superimposable.

Synthesis of O-Desacylpachysandrine-B (IVa)——A mixture of 3α-methylamino-4β-hydroxy-20α-dimethylamino-5α-pregnane (O,N-desacylpachysandrine-A) (45 mg.), β,β-dimethylacrylyl chloride (0.3 ml.), and dry pyridine (1.5 ml.) was allowed to stand overnight at room temperature. After dilution with dil. NaOH, the product was taken up in ether and the etherial solution was shaken with 3% HCl. The aqueous phase was made basic with NH_4OH and extracted with CH_2Cl_2, dried over K_2CO_3, and evaporated. The residue (O,N-diacyl compound) was then hydrolysed by refluxing with 5% NaOH-MeOH (10 ml.) for 2 hr. Solvent was evaporated under reduced pressure and the product (25 mg.), recovered with CH_2Cl_2 and water, was crystallized from acetone to give colorless prisms (14 mg.), melting at 184~186°. Further recrystallizations from the same solvent afforded a pure sample (IVa), m.p. 186~187°, $[\alpha]_D^{10}$ +128°(c=0.90), which was found to be identical with O-desacylpachysandrine-B by mixed m.p. determination and IR (KBr) comparison.

Hydrolysis of Pachysandrine-D (Va)——A solution of pachysandrine-D (Va) (150 mg.) in 5% NaOH-MeOH (15 ml.) was refluxed for 4 hr. The solvent was evaporated under reduced pressure, water was added to the residue, and the product was extracted with CH_2Cl_2. Washing of the extract with water, drying, and evaporation gave a crystalline residue (70 mg.) which was recrystallized from acetone-CH_2Cl_2 to give the O-desacyl compound (II) (53 mg.), m.p. 214~215°, $[\alpha]_D^{10}$ −40°(c=1.2). This compound was identified with pachysandrine-C (3α-methylamino-4α-hydroxy-20α-dimethylamino-5α-pregnane) (II) by mixed m.p. and IR (KBr) comparison. *Anal.* Calcd. for $C_{24}H_{44}ON_2$: C, 76.54; H, 11.78. Found : C, 76.24; H, 11.52.

Catalytic Hydrogenation of Pachysandrine-D (Va)——The alkaloid (Va) (100 mg.) was hydrogenated in MeOH (20 ml.) over pre-reduced platinum oxide (40 mg.) at room temperature and atmospheric pressure. Ten ml. of hydrogen was absorbed within 1 hr. The product, obtained by the usual working up, was recrystallized from acetone to give the dihydro compound (Vb) (60 mg.), m.p. 175~180°. Further recrystallizations gave colorless needles, m.p. 181~182°, $[\alpha]_D^{10}$ −8°(c=1.5). *Anal.* Calcd. for $C_{29}H_{52}O_2N_2$: C, 75.60; H, 11.38. Found : C, 75.50; H, 11.25. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1725 (OCOR). NMR τ : 5.05 (1H, quartet, J 4 and 11 c.p.s.; CH-OCOR), 7.17 (1H, broad, NH-CH), 7.65 (3H, N-CH_3), 7.85 (6H, N-$(CH_3)_2$), 9.12, 9.37 (6H, two tert. CH_3), 9.05 (6H, doublet, J 6.5 c.p.s.; $(CH_3)_2$CH-), and 9.17 (3H, doublet, J 6 c.p.s.; sec. CH_3).

Transformation of O-Desacyldihydropachysandrine-B (IVb) to Dihydropachysandrine-D (Vb)——A mixture of the compound (IVb) (100 mg.), conc. HCl (2.5 ml.), and acetic acid (2.5 ml.) in a sealed tube was heated for 4 hr. at 100°. After dilution with water and washing with CH_2Cl_2, the solution was basified with NH_4OH and extracted with CH_2Cl_2, dried over K_2CO_3, and evaporated. The residue was dissolved in CH_2Cl_2 and chromatographed on alumina (1×3 cm.). Elution with CH_2Cl_2 and crystallization from acetone yielded the O-acyl compound (Vb) in colorless needles (60 mg.) melting at 179~181°. Analytical sample, prepared by further recrystallizations from acetone, showed m.p. 181~182°, $[\alpha]_D^{10}$ −6°(c=1.14). This was proved to be identical with dihydropachysandrine-D (Vb) by mixed m.p. determination and IR (KBr) comparison. *Anal.* Calcd. for $C_{29}H_{52}O_2N_2$: C, 75.60; H, 11.38. Found : C, 75.73; H, 11.36.

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