

STRUCTURES OF PACHYSANDIOL-B AND PACHYSONOL, NEW TRITERPENES FROM
PACHYSANDRA TERMINALIS SIEB. ET ZUCC. (I)

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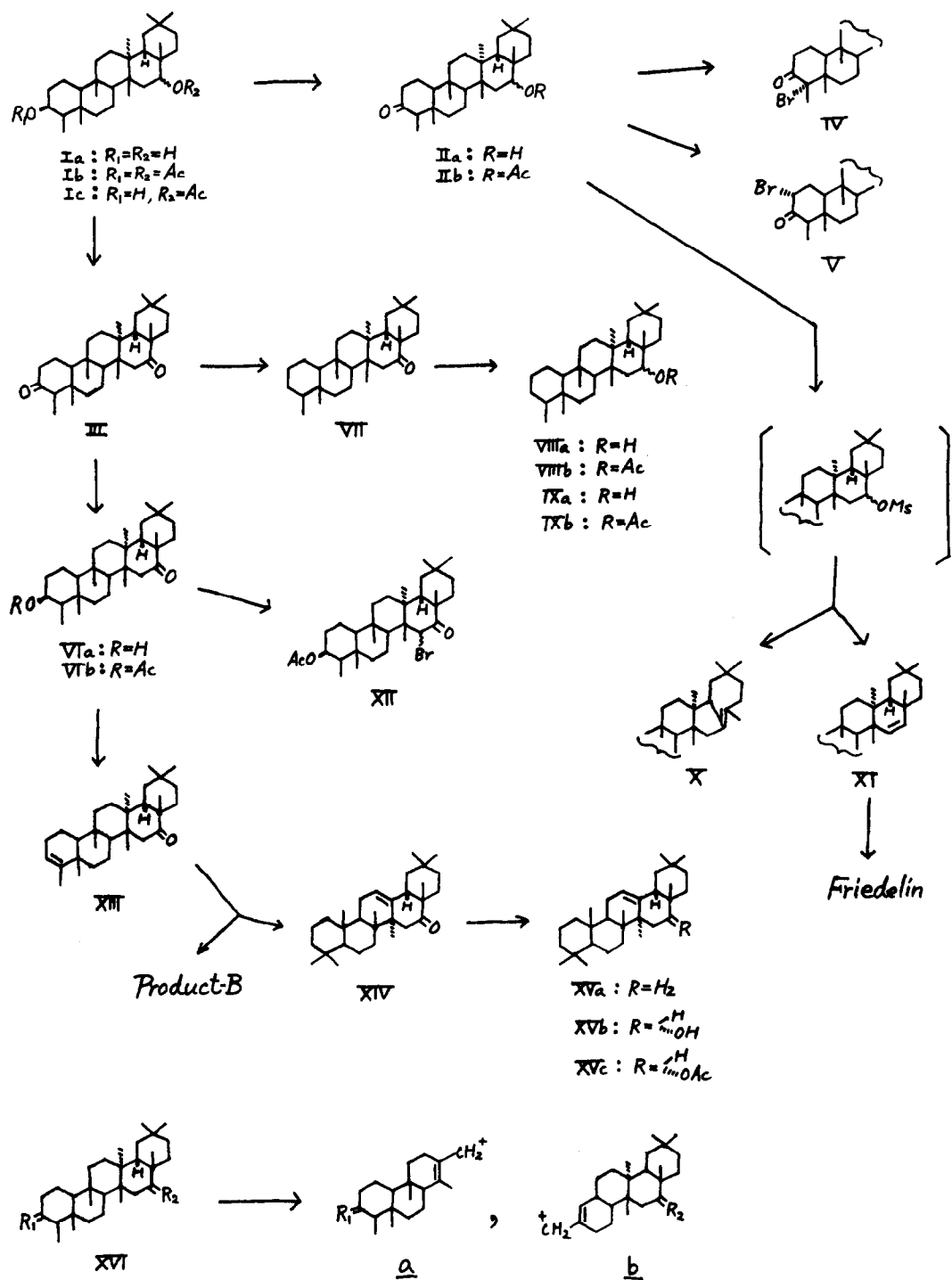
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We have previously reported¹⁾ the isolation and characterization of pachysandiol-B and pachysonol from the neutral fraction of Pachysandra terminalis SIEB. et ZUCC. (Buxaceae) along with many other triterpenes and sterols. In this communication we wish to discuss their structures on the basis of chemical and spectroscopic evidences.

Pachysandiol-B (Ia), $C_{30}H_{52}O_2$, mp 280-282°, $[\alpha]_D +11^\circ (CHCl_3)$, has two hydroxyl groups as indicated by the NMR spectrum²⁾ of its diacetate (Ib) (τ : 4.80 (1H, t., $J=9$ Hz), 5.10 (1H, br., $w^{1/2}=6.5$ Hz), 7.96, 8.00 (each 3H)), while pachysonol (IIa), $C_{30}H_{50}O_2$, mp 278-280°, $[\alpha]_D +7^\circ (CHCl_3)$, has one carbonyl (ν : 1700 cm^{-1})²⁾ and one hydroxyl group. Also the NMR spectra of Ib and pachysonol acetate (IIb) reveal the presence of one sec-CH₃ and seven tert-CH₃ groups. The interrelationship of Ia and IIa was shown as follows: on CrO₃ oxidation, both compounds gave rise to the same diketone (III), $C_{30}H_{48}O_2$, mp 299-300°, ν : 1703 and 1680 cm^{-1} , whereas partial acetylation of Ia gave a mono-acetate (Ic), mp 256-259°, τ : 4.80 (1H, t., $J=9$ Hz, CH-OAc), 6.26 (1H, br., $w^{1/2}=6$ Hz, CH-OH), and 8.01 (3H, Ac), which on CrO₃ oxidation yielded a keto-acetate, mp 233-235°, identified as pachysonol acetate (IIb).

Treatment of IIb with NBS under the IR light³⁾ gave an oily bromo-ketone (IV), ν : 1710 cm^{-1} , τ : 8.30 (3H, s., C(Br)-CH₃), while the reaction of IIb with Br₂-HBr in CHCl₃³⁾ led to an isomeric bromo-ketone (V), ν : 1710 cm^{-1} , τ : 5.61 (1H, t., $J=3$ Hz, CH₂-CH(Br)-CO) and 6.87 (1H, q., $J=6.5$ Hz, CO-CH(CH₃)-C^t-). On the other hand, reduction of the diketone (III) with NaBH₄ afforded mainly an axial keto-alcohol (VIa), mp 275-277°, ν : 3550, 3400, and 1680 cm^{-1} ; τ : 6.26



(1H, m., $W^{1/2}=7$ Hz, CH-OH). Treatment of the latter with POCl_3 gave a dehydrated ketone (XIII), mp $279-280^\circ$, ν : 1680 cm^{-1} , which demonstrates NMR signals for an olefinic proton ($4.84\text{ }\tau$, m.) and a vinyl CH_3 group ($8.40\text{ }\tau$, s.).

These findings suggested that the compounds Ia and IIa are members of friedelin type triterpenes. A support was provided by the ORD curve (in dioxane) of IIb which shows a negative Cotton effect, very similar to that of friedelin.

In order to clarify their skeletal structure we then attempted the Wolff-Kishner (W-K) reduction (Nagata's modification⁴) of the diketone (III). However, the reaction resulted in the formation of a mono-ketone (VII), $\text{C}_{30}\text{H}_{50}\text{O}$, mp $279-280^\circ$, ν : 1680 cm^{-1} , which resisted further reduction. Upon LiAlH_4 reduction, VII gave rise to a mixture of epimeric alcohols (VIIIa and IXa). Separation of each epimer was effected by preparative TLC after acetylation, whereupon acetate-A (VIIIb), mp $216-217^\circ$, τ : 4.78 (1H, t., $J=9$ Hz, CH-OAc) and 8.00 (3H, Ac), and acetate-B (IXb), mp $182-183^\circ$, τ : 4.81 (1H, q., $J=7.5, 8.5$ Hz; CH-OAc) and 7.94 (3H, Ac), were obtained. The alcohol VIIIa (amorphous powder) was also produced by W-K reduction of IIb.

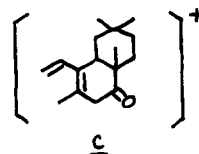
Treatment of VIIIa and IXa with mesyl chloride failed to give the corresponding mesylates, but gave dehydrated products with a rearranged skeleton. Similarly, reaction of IIa with mesyl chloride afforded an unstable oily mesylate, ν : 1170 and 1340 cm^{-1} , which on standing in ether-methanol gave mainly a rearranged, unsaturated ketone (tentatively assigned to X), mp $238-240^\circ$, and a minute amount of another product (XI), mp $234-236^\circ$. Catalytic hydrogenation of the latter (XI) furnished a saturated ketone, mp $255-257^\circ$, whose IR spectrum in KBr is superimposable upon that of friedelin.

Another hydroxyl group common to Ia and IIa was shown to be involved in the partial structure $-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_2-\text{CH}(\text{OH})-\overset{|}{\underset{|}{\text{C}}}-$ from the following NMR evidences: 1) the hydrogen on the hydroxyl-bearing carbon in various derivatives appears as triplet ($J=9$ Hz), 2) the ketol acetate VIb shows a clean AB quartet ($7.63, 7.92\text{ }\tau$; $J=19$ Hz) arising from an active methylene group, 3) the bromo-ketone (XII) derived from VIb reveals a sharp singlet ($5.88\text{ }\tau$) due to a CH-Br hydrogen. In addition, the mass spectra of various derivatives of pachysandiol-B exhibit peaks which would be ascribed to the fragments a and b⁵, suggesting the pre-

sence of an oxygen function in the D- or E-ring. Therefore, the possible position of the hydroxyl group is limited to C₁₅, C₁₆, C₂₁, and C₂₂.

It is well known that the acid-catalyzed rearrangement of friedel-3-ene generates several oleanene derivatives. Thus the treatment of XIII with ZnCl₂ in AcOH⁶⁾ afforded a rearranged product (XIV)⁷⁾, mp 192–193°, ν : 1690 cm⁻¹, and an unidentified product, mp 204–210°, ν : 1680 cm⁻¹. The W-K reduction of XIV gave 18 β H-olean-12-ene (XVa) which was identified with an authentic sample (XVa), kindly provided by Professor Barton.

The mass spectrum of XIV shows a strong peak assignable to the fragment c at m/e 232, thus excluding the possibility of C₁₅-disposition of the carbonyl group⁵⁾. Reduction of XIV with NaBH₄ yielded an alcohol (XVb) as a sole product, whose NMR spectrum indicates the hydroxyl group is axial (6.25 τ , $W^{1/2}$ =9 Hz, CH-OH). The signal for the C₁₄-CH₃ group in XVb appears at considerably low field (8.62 τ) and the corresponding signal in the acetate (XVc) shifted to 8.72 τ . This observation is indicative of the 1,3-diaxial relationship between the C₁₄-CH₃ and the newly formed hydroxyl group, hence the presence of 16 α -hydroxyl in XVb.



On the basis of foregoing observations the structure of pachysandiol-B and pachysonol should be assigned to Ia and IIa, respectively. The stereochemistry of the 16-hydroxyl group will be presented in the succeeding paper.

REFERENCES and FOOTNOTE

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- 3) V. V. Kane and R. Stevenson, Tetrahedron, **15**, 223 (1961).
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- 7) The compound XIV has been reported by O. Jegar et al. (Helv. Chim. Acta, **40**, 2390 (1957)), but direct comparison could not be achieved.