

STRUCTURES OF PACHYSANDIOL-B AND PACHYSONOL, NEW TRITERPENES FROM  
PACHYSANDRA TERMINALIS SIEB. ET ZUCC. (II): NEW CONFORMATION OF  
FRIEDELIN TYPE TRITERPENE DERIVED BY THE X-RAY ANALYSIS

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(Received in Japan 6 October 1972; received in UK for publication 21 November 1972)

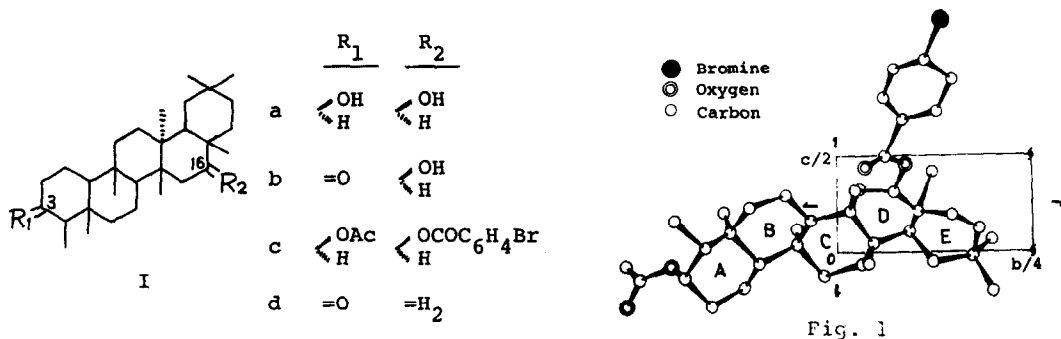
In the preceding communication<sup>1)</sup>, structures of pachysandiol-B and pachysonol were reported as the friedelin type triterpenes Ia and Ib except for the configuration at C-16. Now the structures including stereochemistry were confirmed by the X-ray analysis of 3-O-acetyl-16-O-p-bromobenzoylpachysandiol-B (Ic).

Single crystals of Ic were obtained from CH<sub>2</sub>Cl<sub>2</sub>-MeOH solution, mp 264-266°, C<sub>39</sub>H<sub>57</sub>O<sub>4</sub>Br, D<sub>obs</sub>=1.210. The unit-cell which contains four molecules of Ic, is orthorhombic (space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) with parameters a=15.58, b=30.88, c=7.40 Å.

Intensities of 1765 reflections from equi-inclination Weissenberg photographs of this crystal taken along the c- and a-axes with CuKα radiation were estimated visually. The structure was solved by the heavy atom method and refined by the block diagonal least squares methods to an R-factor of 15.2 %. The absolute configuration was determined from the comparison of Bijvoet pairs.

The perspective view of the molecule so derived is shown in Fig. 1. It confirmed the molecular structure of 3-O-acetyl-16-O-p-bromobenzoylpachysandiol-B as Ic in which the hydroxyl group at C-16 is in β-configuration and the other part of the molecule is the one predicted from the chemical and spectroscopic studies. It should be noted that five six-membered rings A, B, C, D, and E in this molecule are in the chair-chair-chair-boat-boat conformation. This is different from the manner in the structure of friedelin (Id) which was predicted by Corey and Ursprung<sup>2)</sup> as all-chair conformation based upon the 2-D X-ray analysis of friedelan-3α-ol chloroacetate.

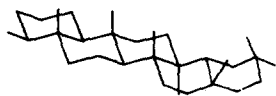
By the consideration of the molecular models and the calculation of inter-



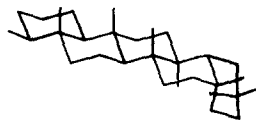
atomic distances based upon the X-ray structure, it was found that the available conformations for five rings of friedelin type triterpene are restricted to two conformations, named S and F, if rings A, B, and C are in chair form. The one is a chair-chair-chair-boat-boat conformation appeared in the structure of Ic depicted above and the other is an all-chair conformation where E-ring is intermediate between chair and boat, probably corresponding to that appeared in friedelin.

The dihedral angles between H(C-16) and H(C-15),  $\text{H}(\text{C}-16)-\text{C}(16)-\text{C}(15)-\text{H}(\text{C}-15)$   $\alpha=29.8^\circ$  and  $\text{H}(\text{C}-16)-\text{C}(16)-\text{C}(15)-\text{H}(\text{C}-15\beta)=146.2^\circ$ , are in good agreement with the values  $32^\circ$  and  $143^\circ$  calculated from the J-value of H(C-16), 9.0 Hz, in the NMR spectrum of Ic in  $\text{CDCl}_3$  using the Abraham's equation<sup>3)</sup>. It means the molecule in solution keeps the same conformation as in the crystal at least in D-ring.

The NMR spectra<sup>1)</sup> of the related derivatives of pachysandiol-B show that two stable conformations, S and F, are actually existing: the S conformation is kept in all the compounds having a  $16\beta$ -substituent, while the F conformation is kept in the  $16$ -epimeric derivatives. Detail will be published elsewhere.



S (stretched form)



F (folded form)

#### REFERENCES

- 1) T. Kikuchi, M. Takayama, T. Toyoda, M. Arimoto, and M. Niwa, Tetrahedron Letters, 1535 (1971).
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- 3) R. J. Abraham and J. S. E. Holker, J. Chem. Soc., 806 (1963).