

X-Ray Crystal and Molecular Structure of Pollinastanol Acetate, a 9,19-Cyclopropane Steroid

By ARNAUD DUCRUIX, CLAUDINE PASCARD-BILLY,* MICHEL DEVYS, MICHEL BARBIER, and EDGAR LEDERER
(*Institut de Chimie des Substances Naturelles, C.N.R.S., 91190-Gif-sur-Yvette, France*)

Summary The structure of pollinastanol acetate has been elucidated by direct method X-ray crystal structure analysis; it is the acetate of 14 α -methyl-9 β ,19-cyclo-5 α -cholestan-3 β -ol (I).

POLLINASTANOL C₂₈H₄₈O m.p. 111—112° has been isolated from the pollen of *Compositae*,¹ from the leaves and rhizomes of the fern *Polypodium vulgare*, and from the roots of the higher plant *Smilax medica*.² The structure of 4,4-desmethylcycloartenol was first proposed in 1964^{1a}; the position of the extra methyl group and the stereochemistry of the molecule was not fully proved but was supported by comparison with the cycloartenol series. Pollinastanol is a possible intermediate in the biosynthesis of cholesterol from

cycloartenol in higher plants and [3-³H]-pollinastanol was incorporated into cholesterol by tobacco leaves.³ 24-Methylene-⁴ and 24-methyl-^{4c} derivatives have also been

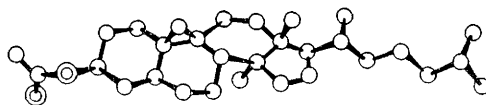
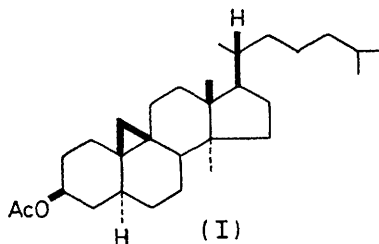


FIGURE. The structure of pollinastanol acetate. Single circles: carbon atoms; double circles: oxygen atoms.

reported. Since some doubts were raised concerning the structure, we have undertaken an X-ray examination of pollinastanol acetate.

For the study, pollinastanol was obtained from pollen of the Compositae *Hypochoeris radicata*^{1b} and the acetate (Ac₂O-pyridine, m.p. 88—90° [α]_D²⁰ = + 25 ± 2° CHCl₃) crystallised by slow evaporation of an ether solution. The crystals are monoclinic, space group *P*2₁; *a* = 13·223, *b* = 7·651, *c* = 27·792 Å, β = 97·49°.



4400 diffraction data were collected on a Philips automatic diffractometer. As there are two molecules per asymmetric unit, the basic structural unit contains 64 atoms, and the structure was solved by direct methods, by application of the Phase Function⁵ developed in our Institute. The *R* final value was 0·12. The two molecules of the asymmetric unit are identical in shape; one of them is shown in the Figure.

Pollinastanol acetate (I) has a 3β-acetoxy-group, a 9β,19-cyclo-structure, 14α,18β,20*R*-methyl substituents, and a 17β-side chain. 5-H is α; 8-H is β.

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¹ (a) M. F. Hügel, M. Barbier, and E. Lederer, *Bull. Soc. chim. France*, 1964, 2012; (b) M. Devys and M. Barbier, *Bull. Soc. Chim. biol.*, 1967, 49, 865.

² M. Devys, A. Alcaide, F. Pinte, and M. Barbier, *Compt. rend.*, 1969, 269, 2033.

³ M. Devys, A. Alcaide, and M. Barbier, *Phytochemistry*, 1969, 8, 1441.

⁴ (a) P. J. Doyle, G. W. Patterson, S. R. Dutky, and M. J. Thomson, *Phytochemistry*, 1972, 11, 1951; (b) F. F. Knapp, D. O. Phillips, L. J. Goad, and T. W. Goodwin, *Phytochemistry*, 1972, 11, 3497; (c) M. Rohmer and R. D. Brandt, *European J. Biochem.*, 1973, 36, 446.

⁵ C. Riche, *Acta Cryst.*, 1973, A29, 133.