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REVISION OF THE STRUCTURE OF THE LIMONOID PSEUDRELONE B FROM *PSEUDOCEDRELA KOTSCHYII*

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Key Word Index—*Pseudocedrela kotschyii*, Meliaceae, limonoid, pseudrelone B, X-ray crystallography

Abstract—Pseudrelone B has been shown to have an 11–19 oxide ring, not an 11–18 ring as originally proposed

Among the limonoids isolated from *Pseudocedrela kotschyii* [1] one of the most interesting, because of representing a previously unknown type, is pseudrelone B. A structure has been proposed for this compound on the basis of spectroscopic studies, but some features were uncertain In particular, an oxide ring was assigned to the 11α–18 bridging position. The reason for location of the methylene at C-18, rather than C-19, and the remaining methyl group in the other position, was that reduction of the C-17 carbonyl to hydroxyl produced only a very small shift of the methyl group resonance, and a comparatively large shift of the methylene resonance

An X-ray crystal structure determination has now been carried out, showing that pseudrelone B has the structure **1** The original deduction was therefore wrong

The original sample of pseudrelone B was a mixed ester; the selection of the triacetate for X-ray study is an artefact of crystallization

The explanation of the original NMR observations is probably to be found in the conformation of the molecule, because of the puckered ring system the ketonic oxygen at C-17 is closer to C-19 than anticipated

EXPERIMENTAL

A suitable single crystal was selected and irradiated with MoKα ($\lambda=0.7107$A) radiation using an Enraf-Nonius CAD4 diffractometer. Cell parameters were obtained by least squares analysis of the setting angles of 24 reflections in the range $16<\theta<17°$ During the data collection, intensities of three standard reference reflections were monitored every hr and recentring checked every hundred measured reflections Intensities were corrected for Lorentz polarization effects but not for absorption

The structure was solved by direct methods using SHELXS-86 [2] and refined using SHELX-76 [3] In the final refinements, all carbon and oxygen atoms were treated anisotropically and hydrogens isotropically, methyls were treated as rigid groups with a single temperature factor, and the methine, methylene and furan hydrogens were placed in calculated positions again with a single temperature factor In the difference map computed after the final cycle of refinement, electron density max/min was 0.9/−0.4e Å^{-3} No attempt was made to determine the absolute configuration of the molecule on the basis of the X-ray data (This was inferred from the phytochemistry)

The programm PARST [4] was used to obtain molecular parameters and PLUTO (Motherwell, W A S, Programme for Plotting Molecular and Crystal Structures, Cambridge University) to obtain drawings of the structure

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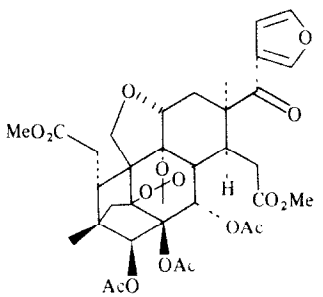

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