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STRUCTURE OF THE 2:1 ADDUCT OF DIMETHYL ACETYLENEDICARBOXYLATE AND DEHYDRONUCIFERINE: A NOVEL TANDEM MICHAEL-1,3-DIPOLAR ADDITION REACTION

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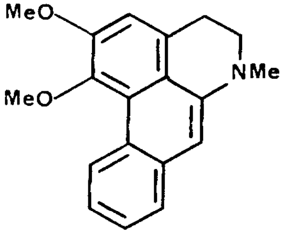
Summary: The structure of a minor 2:1 addition product of dimethyl acetylenedicarboxylate and dehydronuciferine has been shown to be the spiroannelated aporphine 4 by X-ray crystallography. Its formation involves a Michael addition followed in sequence by a proton shift and a 1,3-dipolar addition.

We previously reported the enamine-type Michael addition of dimethyl acetylenedicarboxylate to dehydronuciferine (1), to give the isomeric cis and trans adducts 2 and 3.[1] We now report the isolation of an unusual minor component (<3%) from the reaction mixture. This compound, which was more polar than 2 and 3, crystallized from chloroform as colorless needles, mp 200-201°. Its uv spectrum was similar to that of the aporphine nuciferine. Its nmr spectrum ($CDCl_3$) showed six methoxyls at δ 3.09, 3.54, 3.60, 3.65, 3.75 and 3.88 (3H each), a pattern typical for the D-ring protons of nuciferine, an aromatic singlet (1H) at δ 6.63, an olefinic proton (1H) at δ 5.15, two doublets centered at δ 4.28 and δ 3.51 (1H each, J=13Hz), and a singlet (1H) at δ 4.27. Its mass spectrum gave the molecular composition $C_{31}H_{31}NO_{10}$, indicating the addition of two molecules of dimethyl acetylenedicarboxylate to one molecule of dehydronuciferine. The structure (4) has been determined by X-ray crystallography.



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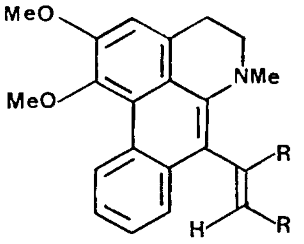

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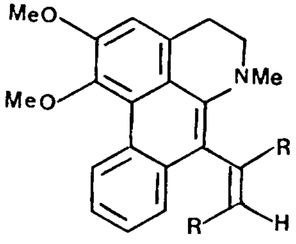
2



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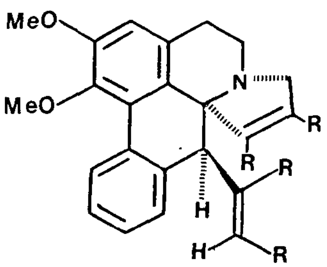
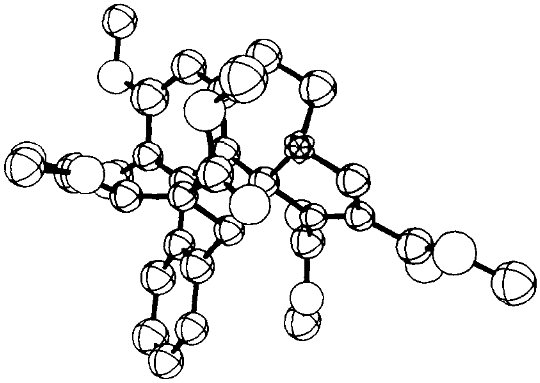


4 R = CO_2Me

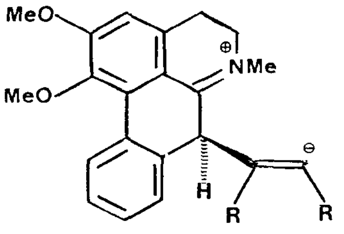


A crystal of dimensions .40mm X .15mm X .12mm was chosen for unit cell determination and intensity data collection. Reflection data were obtained on an Enraf-Nonius CAD4 automated diffractometer using Nickel-filtered Cu-Kα radiation. The unit cell was found to be monoclinic with cell parameters a=10.955(3) Å, b=33.407(10) Å, C=8.070(1) Å, and β=96.06(3)° and the space group was identified as $P2_1/c$ from systematic absences (0k0: k=2n+1; h0l: l=2n+1) with z = 4.

Intensities for 3273 reflections in the range $0^\circ<2\theta<100^\circ$ were measured. Of these, 1611 unique reflections with $I>2.3\sigma(I)$ were used in the structure determination.

The structure was solved by the use of the MULTAN79 program package, which revealed the positions of all 42 non-Hydrogen atoms. Least squares refinement proceeded to R=0.103, but revealed rotational disorder in one of the methoxy groups and one of the ester groups, as reflected in large and asymmetric anisotropic thermal motion. Refinement with this disorder effect taken into account is continuing.

The mechanism of formation of (4) merits some comment. The initial product of addition of DMAD may be formulated as the dipolar species (5). This cis intermediate can then pick up a proton from the neighboring N-methyl group to give another dipolar intermediate, the nitrogen ylid (6), which undergoes a second 1,3-dipolar addition with another molecule of DMAD. The bulky substituent at the C_7-carbon of the aporphine skeleton hinders the attack from the β-side. This mechanism is in accord with our observation that the cis and trans adducts 2 and 3 fail to undergo reaction with a second molecule of DMAD.



R = CO_2Me

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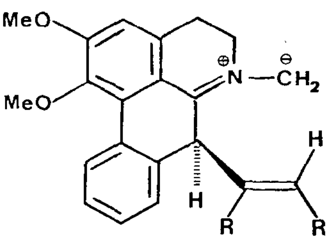

R = CO_2Me

6

Reference

1. M. D. Menachery, J. M. Saa and M. P. Cava, J. Org. Chem. (1981) 46, 2584.

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