

## Barbacenic Acid, a Bisnorditerpene with a Novel Skeleton from *Barbacenia flava*

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Barbacenic acid, a bisnorditerpene with a novel skeleton, has been isolated from *Barbacenia flava* Martius ex Schultes f.; its structure and relative configuration were established by X-ray diffraction analysis of its methyl ester.

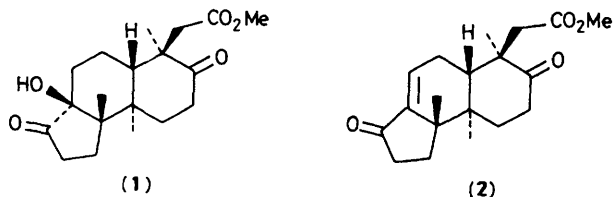
During the course of a continuing phytochemical survey of Brazilian Velloziaceae, we have examined a sample of *Barbacenia flava* Martius ex Schultes f., a species occurring in the Serra do Cipó, State of Minas Gerais, from which a bisnorditerpene with a novel skeleton, designated barbace-nane, was isolated.

The chromatographic behaviour and the i.r. spectrum of the novel substance suggested its acidic nature, which could be confirmed by methylation of the isolated product with diazomethane.

This methylation product, which has been called methyl

barbacenoate (**1**), was used for obtaining the spectral data and for the chemical transformations.

The molecular formula of methyl barbace-noate (**1**), m.p. 137–139 °C,  $[\alpha]_{\text{D}}^{25} + 40^\circ$  (*c* 0.6, CHCl<sub>3</sub>), C<sub>19</sub>H<sub>28</sub>O<sub>5</sub>, was established by high resolution mass spectrometry. The i.r. spectrum showed absorptions for hydroxy (3500 cm<sup>-1</sup>) and carbonyl (1738 and 1704 cm<sup>-1</sup>) groups. The 100 MHz <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed the following clearly resolved signals: four methyl singlets at  $\delta$  0.88, 0.94, 1.20, and 3.58, this last signal being assigned to a methoxycarbonyl group, and two doublets for two geminal protons at  $\delta$  2.46 and 2.86



(*J* 16 Hz). The absence of  $-CHOH$  protons indicated that the hydroxy group is tertiary, which was confirmed by a singlet at  $\delta$  75.8 in the  $^{13}C$  n.m.r. spectrum.<sup>†</sup>

Dehydration of (1) with  $POCl_3$  in pyridine at  $0^\circ C$  afforded the  $\alpha,\beta$ -unsaturated ketone (2)<sup>†</sup> which showed in its u.v. spectrum an absorption  $\lambda(EtOH)$  244 nm ( $\log \epsilon$  3.63) characteristic of a disubstituted enone, indicating that the tertiary hydroxy is  $\alpha$  or  $\beta$  in relation to a carbonyl group.

The  $^1H$  n.m.r. spectrum of enone (2) showed a triplet at  $\delta$  6.60 (1H, *J* 4 Hz) which can be assigned to an olefinic proton linked to the  $\beta$ -carbon atom of an enone moiety coupled to a methylene group.

The fragmentation pattern with losses of 73 and 74 a.m.u. in

<sup>†</sup> (1):  $^{13}C$  n.m.r. (25.2 MHz,  $CDCl_3$ ):  $\delta_C$  16.0 (q), 16.5 (q), 20.3 (t), 23.0 (q), 27.3 (t), 27.9 (t), 29.2 (t), 34.4 (t), 34.9 (t), 38.8 (s), 41.9 (d), 44.1 (t), 48.0 (s), 49.0 (s), 51.6 (q), 75.8 (s), 172.4 (s), 215.5 (s), and 216.7 (s); (2): m.p.  $80-83^\circ C$ ;  $\nu_{max}$  ( $CHCl_3$ ) 2963, 1717, 1702, and  $1602\text{ cm}^{-1}$ ;  $^1H$  n.m.r. (100 MHz,  $CDCl_3$ ):  $\delta$  1.07 (3H,s), 1.15 (3H,s), 2.40 (1H,d,*J* 18 Hz), 2.90 (1H,d,*J* 18 Hz), 3.63 (3H,s), and 6.60 (1H,t,*J* 4 Hz);  $^{13}C$  n.m.r. (25.2 MHz,  $CDCl_3$ ):  $\delta_C$  17.0 (q), 22.8 (q), 23.0 (q), 25.1 (t), 27.0 (t), 29.8 (t), 35.2 (t+s), 35.8 (t), 36.9 (s), 39.1 (d), 42.8 (t), 48.1 (s), 51.5 (q), 129.7 (d), 144.3 (s), 172.1 (s), 206.1 (s), and 214.0 (s).

the mass spectrum of (1) and (2) suggested the presence of a  $-CH_2CO_2Me$  residue.

On the basis of spectral data and with only small quantities of pure sample available, it was not possible to make an unambiguous structure proposal for (1). Therefore it was decided to carry out an X-ray diffraction analysis. Suitable crystals of (1) were obtained by recrystallization from hexane-diethyl ether (9:1).

*Crystal data:* Orthorhombic, space group  $P2_12_12_1$ ,  $a = 20.261$  (3),  $b = 11.207$  (2),  $c = 7.670$  (1) Å,  $U = 1772$  (1) Å<sup>3</sup>,  $Z = 4$ . The intensities of 1401 reflections were collected (Syntex  $P2_1$  diffractometer, radiation  $Cu-K\alpha$ ,  $2\theta$  max =  $114^\circ$ ) of which 1163 were considered as observed [ $I > 2.5\sigma(I)$ ]. The structure was solved using the MULTAN 80 program<sup>1</sup> and refined to  $R = 0.049$  with SHELX.<sup>2†</sup>

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## References

- 1 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, M. M. Woolfson, G. Germain, and J. P. Declercq, MULTAN 80, 1980, A system of Computer Programmes for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. Universities of York, England, and Louvain-la-Neuve, Belgium.
- 2 G. M. Sheldrick, SHELX 76, 1976, Program for Crystal Structure Determination, University of Cambridge, England.

<sup>†</sup> The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.