

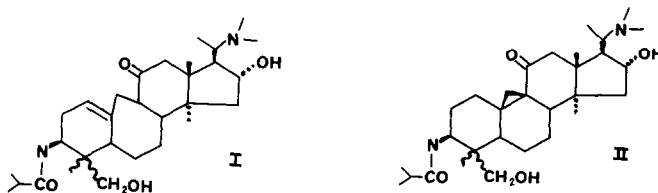
THE CONFIGURATION at C-4 of STEROIDAL ALKALOIDS FROM BUXUS :
A X-RAY STRUCTURE DETERMINATION

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In a previous article ⁽¹⁾, G Lukacs et al have used ¹³C n m r data to revise the configuration at C-4 of several steroidal alkaloids isolated ^(2, 3, 4) from various species of Buxus. To confirm their results, they gave us a sample of (I), a ν, δ unsaturated derivative of the N-3-isobutyryl cycloobuxidine F (II), obtained by heating the latter to 180°C in glycol ⁽⁵⁾



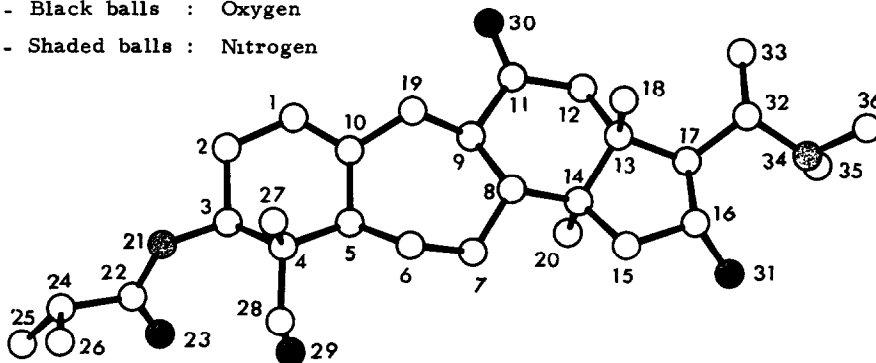
Good crystals of (I), grown from an acetone : water solution, are orthorhombic prisms. The space group is $P 2_1 2_1 2_1$, with 4 molecules in the cell, whose dimensions are : $a = 10\ 627$, $b = 15\ 862$, $c = 17\ 740$ Å. Of 3074 data, collected with a Philips PW 1100 diffractometer, 2649 were above the background ($3\ \sigma$). The structure was solved by direct methods ⁽⁶⁾ and refined by the full-matrix least-squares method, to a conventional R-value of 0.037. One molecule of water and all the hydrogen atoms were located by difference syntheses and refined.

As shown in the figure, the hydroxymethyl group is actually α . Furthermore, it is linked with the neighbouring carbonyl oxygen through an intramolecular hydrogen bond of 2.77 Å. Another intramolecular hydrogen bond can exist between the hydroxyl group at C-16 and its neighbouring nitrogen atom: the O-N distance is 2.91 Å and the angle is 135° , similar to that found in the dimethylglyoxime structure ⁽⁷⁾. Using the sign convention of Klyne and Prelog ⁽⁸⁾, the torsional angles of the cycles are

Ring A (half-chair)	1	-13°	2	40°	3	-60°	4	51°	5	-26°	10	5°	1		
Ring B (twist-chair)	5	-78°	6	83°	7	-61°	8	65°	9	-85°	19	54°	10	19°	5
Ring C (chair)	8	57°	14	-66°	13	57°	12	-43°	11	35°	9	-41°	8		
Ring D (envelope)	14	-32°	15	6°	16	22°	17	-42°	13	46°	14				

(The conformations given in brackets are of course schematic ones)

- Black balls : Oxygen
- Shaded balls : Nitrogen



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