

173.03 (39)°], although it is present with the bulky Phe side chain in close proximity to the Boc group (Benedetti *et al.*, 1980). On the other hand, the value of the torsion angle N(8)–C(9)–C(17)–O(18) between the urethane moiety and the next peptide group is 67.86 (31)°, showing that the Boc derivative occurs in the crystal in a bent conformation.

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## Structure of Spirosta-5,25(27)-diene-3 $\beta$ ,11 $\alpha$ -diol

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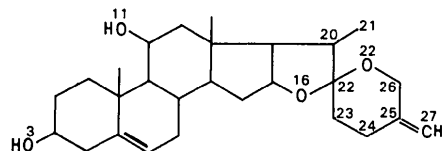
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**Abstract.** C<sub>27</sub>H<sub>40</sub>O<sub>4</sub>,  $M_r = 428.61$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.369$  (1),  $b = 12.240$  (3),  $c = 30.547$  (5) Å,  $V = 2381$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.195$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.73$  cm<sup>-1</sup>,  $F(000) = 936$ ,  $T = 293$  (2) K,  $R = 0.045$  for 1615 unique observed reflections. The compound was isolated from *Helleborus serbicus* Adam 1906 (Ranunculaceae). The rings have the following conformations: *A*, *C* and *F* chair; *B* and *E* intermediate between half chair and envelope; *D* half chair. The molecules are linked by O–H...O hydrogen bonds into chains along the *b* axis. The molecule is very similar to molecule (I) of spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,11 $\alpha$ -triol monohydrate [Kálmán, Argay, Ribár, Živanov-Stakić & Vladimirov (1985). *Acta Cryst.* **C41**, 1645–1647].

**Introduction.** This new steroid sapogenin was isolated from the subterranean organs of the plant *Helleborus serbicus* Adam 1906 (Ranunculaceae) by column chromatography and preparative thin-layer chromatography on silica gel using mobile-phase isopropyl ether–methanol 95:5 (*v/v*) and chloroform–

methanol 95:5. The crystals reached a melt at 496–498 K. The chemical structure (1) proposed from chemical and spectroscopic studies was substantiated by X-ray diffraction.



(1)

**Experimental.** Colourless crystal  $ca$   $0.4 \times 0.6 \times 0.9$  mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation.  $0.0327 \leq \sin\theta/\lambda \leq 0.6606$  Å<sup>-1</sup>,  $\omega$ – $2\theta$  scan,  $h$  0–8,  $k$  0–16,  $l$  0–40. Cell parameters by least-squares fit for 18 centred reflections. Systematic absences:  $h = 2n + 1$  in  $h00$ ,  $k = 2n + 1$  in  $0k0$ ,  $l = 2n + 1$  in  $00l$ . Of 2779 unique reflections, 1615 taken as observed with  $I > 2.5\sigma(I)$ . No absorption correction performed. Three standard

reflections, intensity variation < 2%. Structure solved by *SHELX76* (Sheldrick, 1976) using 458 reflections with  $E > 1.20$  and successive structure-factor, Fourier and difference-Fourier calculations. Full-matrix refinement.  $\sum w(\Delta F)^2$  minimized for 31 heavy atoms (336 parameters). Final  $R = 0.045$ ,  $wR = 0.065$ ,  $w = [\sigma^2(F) + 61.87 \times 10^{-4}(F)^2]^{-1}$ . Residual electron density within  $\pm 0.2 \text{ e } \text{Å}^{-3}$ . Positions of H atoms generated from assumed geometries, remaining H atoms bound to O atoms and C27 found in a difference Fourier map; all H atoms refined isotropically. Max.  $\Delta/\sigma$  for H atoms 0.83. Scattering factors as in *SHELX76*. Calculation on an IBM 43/41 computer.

**Discussion.** Atomic coordinates of non-H atoms are in Table 1. The molecular geometry with atomic numbering is shown in Fig. 1. The bond lengths and angles for non-H atoms are listed in Table 2.\*

Rings *A* and *C* have normal chair conformations while ring *D* assumes a half-chair shape [puckering parameters of Cremer & Pople (1975):  $Q = 0.463$  (5) Å,  $\phi = 202.2$  (6)°; lowest asymmetry factor  $fC_2(C16) = 0.026$  (5) Å (Kálmán, Czugler & Simon, 1982)] with a pseudo  $C_2$  symmetry axis bisecting C13–C14. The flexible *B* ring possesses an intermediate form between envelope and half chair characterized by the puckering parameters  $Q = 0.482$  (5) Å,  $\phi = 194.0$  (6)° and  $\theta = 54.1$  (6)°. Ring *E* fused to ring *D* with a *cis* junction also exhibits an intermediate form

Table 1. Final fractional coordinates for non-H atoms and equivalent isotropic temperature parameters (with *e.s.d.*'s in parentheses)

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

|     | <i>x</i>     | <i>y</i>   | <i>z</i>   | $U_{\text{eq}}$ (Å <sup>2</sup> ) |
|-----|--------------|------------|------------|-----------------------------------|
| C1  | 0.5555 (8)   | 0.3632 (4) | 0.1191 (2) | 0.060 (3)                         |
| C2  | 0.5974 (10)  | 0.3523 (5) | 0.0704 (2) | 0.073 (4)                         |
| C3  | 0.6405 (11)  | 0.2339 (5) | 0.0584 (2) | 0.081 (4)                         |
| C4  | 0.4668 (10)  | 0.1608 (4) | 0.0742 (2) | 0.068 (3)                         |
| C5  | 0.4220 (7)   | 0.1778 (4) | 0.1220 (1) | 0.052 (3)                         |
| C6  | 0.4360 (8)   | 0.0937 (4) | 0.1495 (2) | 0.060 (3)                         |
| C7  | 0.3973 (10)  | 0.1009 (4) | 0.1973 (2) | 0.062 (3)                         |
| C8  | 0.2642 (7)   | 0.2005 (3) | 0.2086 (1) | 0.045 (2)                         |
| C9  | 0.3578 (7)   | 0.3024 (3) | 0.1867 (1) | 0.043 (2)                         |
| C10 | 0.3725 (7)   | 0.2926 (3) | 0.1364 (1) | 0.045 (2)                         |
| C11 | 0.2451 (7)   | 0.4077 (3) | 0.2030 (2) | 0.046 (3)                         |
| C12 | 0.2332 (7)   | 0.4134 (3) | 0.2528 (1) | 0.048 (3)                         |
| C13 | 0.1285 (7)   | 0.3132 (3) | 0.2726 (1) | 0.043 (2)                         |
| C14 | 0.2528 (7)   | 0.2142 (3) | 0.2577 (1) | 0.045 (2)                         |
| C15 | 0.1694 (8)   | 0.1222 (4) | 0.2861 (1) | 0.051 (3)                         |
| C16 | 0.1496 (7)   | 0.1791 (4) | 0.3304 (1) | 0.048 (2)                         |
| C17 | 0.1525 (7)   | 0.3011 (3) | 0.3226 (1) | 0.046 (2)                         |
| C18 | -0.1023 (6)  | 0.3060 (4) | 0.2586 (1) | 0.052 (3)                         |
| C19 | 0.1653 (8)   | 0.3283 (5) | 0.1149 (2) | 0.062 (3)                         |
| C20 | -0.0183 (8)  | 0.3462 (4) | 0.3531 (1) | 0.053 (3)                         |
| C21 | 0.0490 (11)  | 0.4476 (4) | 0.3802 (2) | 0.075 (4)                         |
| C22 | -0.0823 (7)  | 0.2471 (4) | 0.3799 (1) | 0.052 (3)                         |
| C23 | -0.3085 (8)  | 0.2470 (5) | 0.3946 (2) | 0.067 (3)                         |
| C24 | -0.3569 (10) | 0.1534 (5) | 0.4257 (2) | 0.083 (4)                         |
| C25 | -0.1982 (12) | 0.1474 (6) | 0.4615 (2) | 0.094 (5)                         |
| C26 | 0.0185 (10)  | 0.1484 (5) | 0.4432 (2) | 0.074 (4)                         |
| C27 | -0.2340 (21) | 0.0900 (9) | 0.4986 (3) | 0.140 (8)                         |
| O3  | 0.6585 (11)  | 0.2248 (5) | 0.0118 (1) | 0.130 (4)                         |
| O11 | 0.3495 (6)   | 0.5022 (3) | 0.1878 (1) | 0.061 (2)                         |
| O16 | -0.0495 (5)  | 0.1580 (2) | 0.3516 (1) | 0.054 (2)                         |
| O22 | 0.0554 (5)   | 0.2407 (3) | 0.4157 (1) | 0.062 (2)                         |

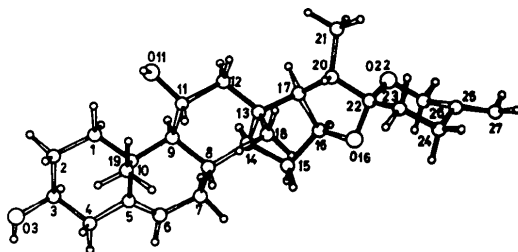


Fig. 1. Perspective view of the molecule with atomic numbering. Numbers are for C unless indicated otherwise. The H atoms are shown but not labelled.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43183 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Cl–C2       | 1.517 (7) | C13–C14     | 1.518 (5) |
| Cl–C10      | 1.545 (6) | C13–C17     | 1.542 (6) |
| C2–C3       | 1.520 (8) | C13–C18     | 1.534 (6) |
| C3–C4       | 1.502 (8) | C14–C15     | 1.517 (6) |
| C3–O3       | 1.433 (6) | C15–C16     | 1.528 (6) |
| C4–C5       | 1.503 (7) | C16–C17     | 1.512 (6) |
| C5–C6       | 1.333 (6) | C16–O16     | 1.448 (5) |
| C5–C10      | 1.506 (6) | O16–C22     | 1.407 (5) |
| C6–C7       | 1.483 (7) | C17–C20     | 1.534 (6) |
| C7–C8       | 1.525 (6) | C20–C21     | 1.552 (6) |
| C8–C9       | 1.535 (6) | C20–C22     | 1.520 (7) |
| C8–C14      | 1.512 (6) | C22–C23     | 1.509 (7) |
| C9–C10      | 1.544 (6) | C22–O22     | 1.404 (5) |
| C9–C11      | 1.557 (6) | O22–C26     | 1.428 (6) |
| C10–C19     | 1.538 (6) | C23–C24     | 1.518 (7) |
| C11–C12     | 1.524 (6) | C24–C25     | 1.492 (9) |
| C11–O11     | 1.413 (5) | C25–C26     | 1.489 (9) |
| C12–C13     | 1.522 (6) | C25–C27     | 1.353 (9) |
| C2–C1–C10   | 114.8 (4) | C17–C13–C18 | 111.5 (4) |
| C1–C2–C3    | 110.6 (4) | C17–C13–C14 | 99.7 (3)  |
| C2–C3–C4    | 111.0 (5) | C18–C13–C14 | 111.7 (4) |
| C2–C3–O3    | 109.1 (5) | C13–C14–C15 | 103.8 (3) |
| O3–C3–C4    | 109.4 (5) | C13–C14–C8  | 114.3 (3) |
| C3–C4–C5    | 111.7 (4) | C8–C14–C15  | 120.1 (3) |
| C4–C5–C10   | 116.9 (4) | C14–C15–C16 | 101.3 (3) |
| C4–C5–C6    | 119.3 (4) | C15–C16–C17 | 108.1 (3) |
| C6–C5–C10   | 123.7 (4) | C15–C16–O16 | 112.9 (4) |
| C5–C6–C7    | 123.9 (5) | O16–C16–C17 | 104.9 (4) |
| C6–C7–C8    | 111.6 (4) | C16–O16–C22 | 105.5 (3) |
| C7–C8–C9    | 109.6 (3) | C16–C17–C20 | 104.6 (4) |
| C7–C8–C14   | 109.8 (3) | C16–C17–C13 | 104.4 (3) |
| C14–C8–C9   | 111.1 (3) | C20–C17–C13 | 119.7 (4) |
| C8–C9–C10   | 113.2 (3) | C17–C20–C21 | 114.6 (4) |
| C8–C9–C11   | 110.7 (3) | C17–C20–C22 | 103.3 (4) |
| C11–C9–C10  | 114.2 (3) | C21–C20–C22 | 115.0 (4) |
| C9–C10–C1   | 110.1 (4) | C20–C22–C23 | 114.7 (4) |
| C9–C10–C5   | 112.1 (3) | C20–C22–O22 | 107.3 (4) |
| C9–C10–C19  | 110.6 (4) | C20–C22–O16 | 104.3 (3) |
| C5–C10–C19  | 108.6 (4) | O23–C22–O16 | 108.9 (4) |
| Cl–C10–C19  | 110.0 (4) | O22–C22–C23 | 111.3 (4) |
| Cl–C10–C5   | 105.3 (4) | O22–C22–O16 | 110.0 (4) |
| C9–C11–O11  | 110.8 (4) | C26–O22–C22 | 113.5 (4) |
| C9–C11–C12  | 112.3 (3) | C22–C23–C24 | 112.4 (5) |
| O11–C11–C12 | 108.5 (2) | C23–C24–C25 | 111.0 (5) |
| C11–C12–C13 | 112.5 (3) | C24–C25–C26 | 110.7 (5) |
| C12–C13–C14 | 107.2 (3) | C24–C25–C27 | 121.1 (8) |
| C12–C13–C17 | 115.4 (3) | C27–C25–C26 | 118.3 (8) |
| C12–C13–C18 | 110.8 (4) | C25–C26–O22 | 112.3 (5) |

between envelope and half chair with the puckering parameters  $Q = 0.382(5) \text{ \AA}$ ,  $\varphi = 263.2(6)^\circ$  and lowest asymmetry factors  $fC_2(C17) = 0.035(5)$  and  $fC_5(O16) = 0.074(6) \text{ \AA}$ . The general features of the molecule resemble those of molecule (I) of spirosta-5,25(27)-diene-1 $\beta$ ,3 $\beta$ ,11 $\alpha$ -triol monohydrate (Kálmán, Argay, Ribár, Živanov-Stakić & Vladimirov, 1985). However, there is one difference, namely the *B* ring of molecule (I) has a pronounced envelope conformation.

There is one hydrogen bond between symmetrically related molecules  $[O(11)-H \cdots O(16)(-x, 0.5 + y, 0.5 - z): O(11) \cdots O(16) \quad 2.956(6), \quad H \cdots O(16)$

$2.18(5) \text{ \AA}$ ,  $\angle O(11)-H \cdots O(16) \quad 173(4)^\circ$ ], which forms a helix about the twofold screw *b* axis.

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## The Structure of 9 $\alpha$ -Acetoxy-8 $\beta$ -[2'-(*N*-morpholino)ethyl]-10 $\beta$ -methyl-*trans*-2-decalone\*

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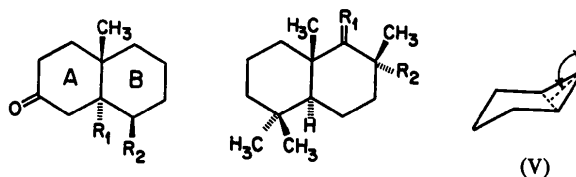
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**Abstract.**  $C_{19}H_{31}NO_4$ ,  $M_r = 337.5$ , monoclinic,  $P2_1/c$ ,  $a = 8.289(8)$ ,  $b = 10.631(1)$ ,  $c = 21.500(2) \text{ \AA}$ ,  $\beta = 94.25(1)^\circ$ ,  $U = 1889.1(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.186 \text{ g cm}^{-3}$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ ,  $\mu(\text{Cu } K\alpha) = 6.6 \text{ cm}^{-1}$ ,  $F(000) = 736$ , room-temperature data collection, final  $R = 0.062$  for 1930 reflections. The decalone skeleton adopts a chair–chair conformation which is essentially undistorted even in the presence of the 1,3-diaxial substituents. The mean torsion angle in ring *A*, the cyclohexanone ring, is  $51.4^\circ$ ; the mean in ring *B* is  $53.4^\circ$ . The *N*-morpholinoethyl substituent is extended with an all-*trans* orientation of bonds C(9)–C(8), C(8)–C(17), C(17)–C(18), C(18)–N(19), N(19)–C(24). The mean distances in the morpholine ring are C–N  $1.458$ , C–C  $1.499$ , and C–O  $1.410 \text{ \AA}$ .

**Introduction.** Reactions in which a proton  $\alpha$  to a carbonyl group is abstracted by a general base are important in the function of many enzymes (Spencer, 1979; Westheimer, 1970; Wood, 1971). In our earlier research (Roberts, Ferran, Gula & Spencer, 1980;

Hupe, Kendall & Spencer, 1973) we focused on elucidating why these biochemical  $\alpha$  proton transfers so often occur *via* iminium ion formation, and concluded that this pathway has an inherent kinetic advantage, at physiological pH, of  $ca 10^5$  compared with direct deprotonation of the carbonyl compound.



- (I)  $R_1 = \text{OCOCH}_3$   
 $R_2 = (\text{CH}_2)_2\text{C}_4\text{H}_8\text{NO}$
- (II)  $R_1 = \text{OCOCH}_3$   
 $R_2 = \text{H}$
- (III)  $R_1 = \beta - (\text{CH}_2)_2\text{OC} - \text{C}_6\text{H}_4 - \text{Br}$ ,  $\alpha - \text{H}$   
 $R_2 = \text{O} \parallel \text{CCH}_3$
- (IV)  $R_1 = \alpha - (\text{CH}_2)_2\text{OH}$ ,  $\beta - \text{H}$   
 $R_2 = \text{OH}$

The current emphasis in our research concerns the geometry of  $\alpha$  proton abstraction. Having the functional groups involved in a reaction localized in the correct positions, rather than free in solution, is generally considered to be an important component of enzymatic catalysis (Jencks, 1969). Accordingly, we have been trying to assess the further contribution to enzymatic rate acceleration of  $\alpha$  proton transfer

\* 4 $\alpha$ -Methyl-8-[2'-(*N*-morpholino)ethyl]-2-oxo-*trans*-decahydro-8 $\alpha$ -naphthyl acetate.

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‡ The word 'alpha' is used to denote the position of carbons relative to the carbonyl group and the symbols  $\alpha$  and  $\beta$  are used to denote substituents underneath and above, respectively, the plane of the decalin ring system.