

## X-RAY CRYSTAL STRUCTURE OF A NEW DITERPENE, GANERVOSIN A

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We have isolated a new diterpene, ganervosin A [**1**], from *Rabdosia nervosa* Hemsl. (Labiatae) collected in the mountainous Wen Xian district of south Gansu Province. Comparison of its ir,  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr data with the known diterpene, odonicin [**2**] (1,2), suggested a similar structure. The accurate molecular weight 448.2111 given by ms showed the composition  $\text{C}_{24}\text{H}_{32}\text{O}_8$  (calcd 448.2098). Acylation of **1** by the normal method gave a compound iden-

tified as odonicin [**2**], indicating that dehydration occurred under acylation conditions; however, the position of the hydroxyl group in ring A was undetermined. The present X-ray analysis was taken to determine the complete structure of ganervosin A.

An ORTEP view of ganervosin A is depicted in Figure 1. The configuration and conformation of this compound may be described as follows. Ring A has a twist boat conformation and is fused in

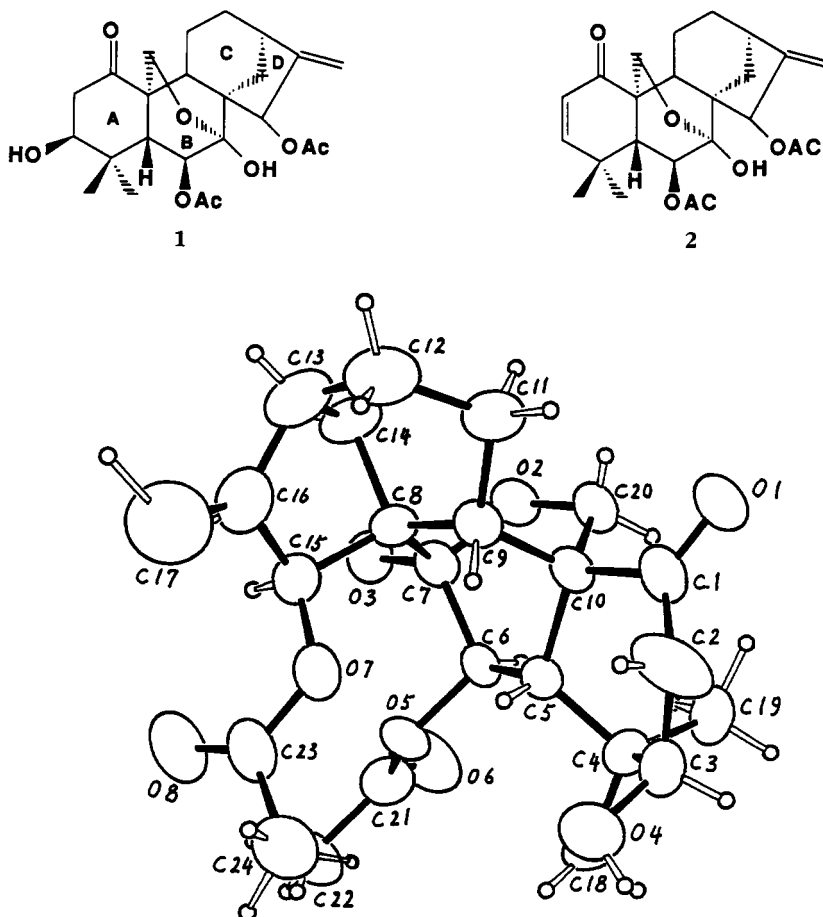


FIGURE 1. The molecule of ganervosin A [**1**] showing the atom labeling scheme.

the *trans* configuration with ring B, which has a boat conformation. The dihedral angle between rings A and B is  $29.7^\circ$ . Ring C, which also has a boat conformation, is *cis*-fused to ring B with a dihedral angle of  $148.9^\circ$ . The five-membered ring D, which takes an envelope conformation, is nearly perpendicular to ring C (dihedral angle  $96.5^\circ$ ). The fifth ring, which contains an Et<sub>2</sub>O bond, is perpendicular to ring B (dihedral angle  $90.4^\circ$ ).

### EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—The ir spectra in KBr were recorded on a 5DX-FTIR spectrometer, <sup>1</sup>H and <sup>13</sup>C nmr on a Varian FT-80 nmr spectrometer in Me<sub>2</sub>CO-*d*<sub>6</sub> and C<sub>5</sub>D<sub>5</sub>N using TMS as internal standard, and mass spectra on a ZAB-HS instrument.

PLANT MATERIAL.—*R. nervosa* was collected in August 1986, in the Wen Xian district, south Gansu Province. A voucher specimen is preserved in the Organic Analysis Laboratory of the Chemistry Department, Lanzhou University.

ISOLATION OF GANERVOSIN A.—The air-dried, powdered stems and leaves of *R. nervosa* (3.9 kg) were extracted with Et<sub>2</sub>O for 5 days. When the Et<sub>2</sub>O extract was concentrated, a crystal was precipitated. After filtration and recrystallization, compound **1** was obtained (yield 2.32 g).

CHARACTERIZATION OF **1**.—Crystallized from Me<sub>2</sub>CO in colorless, pyramidal crystals, mp 224–226°; ir (KBr)  $\nu$  max 3521, 3400, 1750, 1740, 1723, 1695, 1379, 1266, 1236, 1067, 1050, 902 cm<sup>-1</sup>; ms *m/z* [M]<sup>+</sup> 448, 430, 406, 388, 370, 346, 328, 303, 261, 243, 229, 215, 199, 182, 163, 145, 128, 117, 105, 91 (100%); <sup>1</sup>H nmr (Me<sub>2</sub>CO-*d*<sub>6</sub>)  $\delta$  5.59 (1H, t, *J* = 1.8 Hz, H-15), 5.20 (1H, d, *J* = 10 Hz, H-6), 5.07 and 4.87 (1H for each, m, 2H-17), 4.22 and 3.91

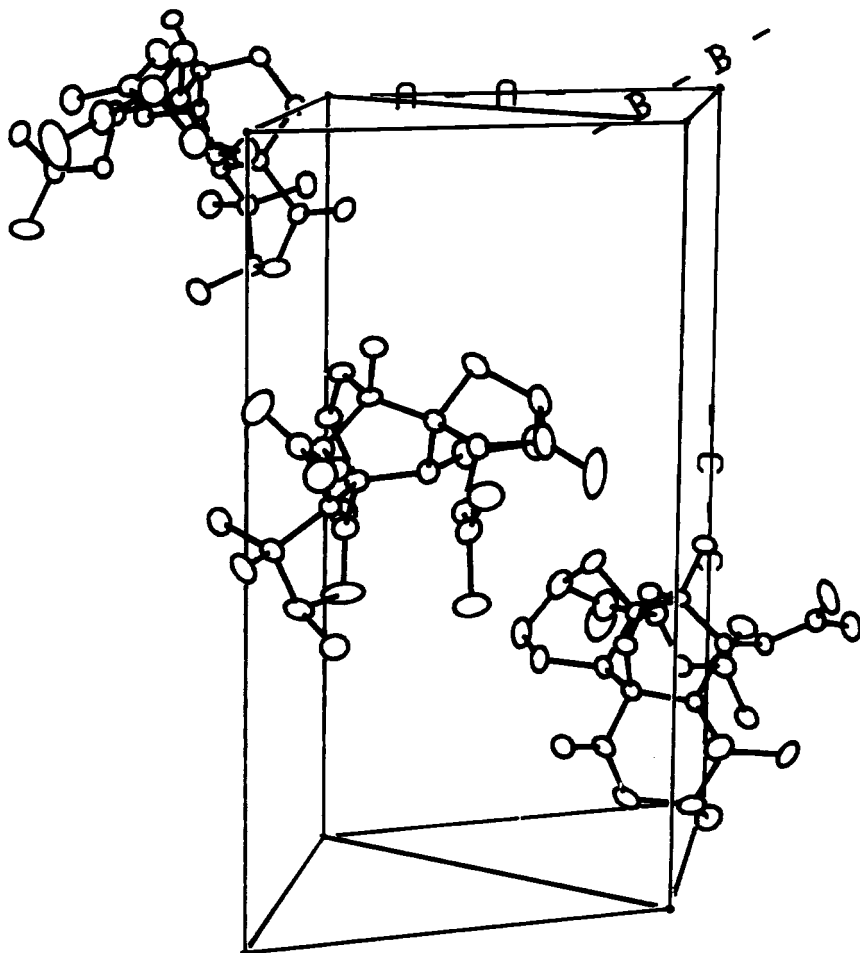


FIGURE 2. View of the packing arrangement of ganervosin A [**1**] in the crystal.

TABLE 1. Atomic Coordinates for Nonhydrogen Atoms (ESDs in Parentheses).

Atom	x	y	z	B(Å <sup>2</sup> )
O-1	0.2900(5)	0.1975(5)	0.800	4.9(1)
O-2	0.0867(4)	0.2365(4)	0.6108(3)	3.5(1)
O-3	-0.0387(5)	0.3471(5)	0.5650(3)	3.7(1)
O-4	-0.0719(6)	0.2566(5)	0.9210(3)	5.5(1)
O-5	-0.2010(4)	0.2891(4)	0.6963(4)	3.22(9)
O-6	-0.3691(5)	0.1200(6)	0.6208(3)	6.5(2)
O-7	0.0332(4)	0.5690(4)	0.7504(3)	3.5(1)
O-8	-0.1192(6)	0.6485(6)	0.7118(3)	6.1(1)
C-1	0.1923(7)	0.2279(7)	0.8086(4)	3.8(1)
C-2	0.1343(8)	0.236(1)	0.8805(5)	7.2(1)
C-3	-0.0365(8)	0.1538(7)	0.8869(4)	4.7(2)
C-4	-0.1182(7)	0.0999(7)	0.8121(4)	3.7(2)
C-5	-0.0319(6)	0.2341(6)	0.7597(4)	2.7(1)
C-6	-0.1028(6)	0.2294(6)	0.6849(4)	2.8(1)
C-7	0.0206(6)	0.3257(6)	0.6299(3)	3.0(1)
C-8	0.1444(6)	0.4730(7)	0.6602(4)	3.1(1)
C-9	0.2192(6)	0.4437(6)	0.7287(4)	3.2(1)
C-10	0.1310(6)	0.2720(6)	0.7422(4)	3.0(1)
C-11	0.3884(7)	0.5119(9)	0.7190(5)	4.9(2)
C-12	0.4567(9)	0.685(1)	0.7010(6)	6.4(3)
C-13	0.3442(9)	0.6363(8)	0.9746(6)	6.0(2)
C-14	0.2620(8)	0.5585(8)	0.5990(5)	5.1(2)
C-15	0.1014(7)	0.5917(7)	0.6789(4)	3.7(2)
C-16	0.2491(9)	0.7375(8)	0.6775(6)	6.1(3)
C-17	0.590(1)	0.727(1)	0.043(1)	11.8(4)
C-18	-0.1165(9)	-0.0438(7)	0.7877(5)	5.0(2)
C-19	-0.2810(8)	0.0615(9)	0.8185(5)	5.1(2)
C-20	0.1393(6)	0.1923(7)	0.6724(4)	3.5(1)
C-21	-0.3335(7)	0.2198(8)	0.6616(4)	4.0(2)
C-22	-0.4239(8)	0.292(1)	0.6819(6)	5.9(2)
C-23	-0.0751(7)	0.6012(7)	0.7589(4)	4.2(2)
C-24	0.7058(9)	0.138(1)	0.1689(5)	6.4(3)

(1H for each, AB q,  $J = 10$  Hz, 2H-20), 3.75 (1H, t,  $J = 3.5$  Hz, H-3), 3.23 (1H, d,  $J = 10$  Hz, H-5), 2.80 (2H, s, disappeared in D<sub>2</sub>O, 3-OH, 6-OH), 2.67 (2H, d,  $J = 3.5$  Hz, H-2), 2.24 and 1.99 (3H for each, s, 2Me-OAc), 1.01 and 0.95 (3H for each, s, 2Me-18, 19); <sup>13</sup>C nmr (C<sub>5</sub>D<sub>5</sub>N)  $\delta$  210.5 (s, C-1), 47.0 (t, C-2), 76.0<sup>a</sup> (d, C-3), 38.0 (s, C-4), 47.7 (d, C-5), 74.5<sup>a</sup> (d, C-6), 96.5 (s, C-7), 52.7 (s, C-8), 42.0 (d, C-9), 49.7 (s, C-10), 17.5 (t, C-11), 32.0 (t, C-12), 35.5 (d, C-13), 26.5 (t, C-14), 76.0<sup>a</sup> (d, C-15), 158.5 (s, C-16), 109.5 (t, C-17), 21.0 (q, C-18), 24.0 (q, C-19), 65.5 (t, C-20), 170.3<sup>b</sup> (s, C-21), 21.4<sup>c</sup> (q, C-22), 170.1<sup>b</sup> (s, C-23), 21.6<sup>c</sup> (q, C-24). Chemical shifts denoted by the same superscript letter can be interchanged.

CONVERSION OF **1** TO **2**.—Compound **1** (120 mg) was dissolved in 2 ml Ac<sub>2</sub>O and pyridine and let stand for 24 h at room temperature. Evaporation of solvent left a residue that was recrystallized from EtOH to yield **2** as colorless needles (95 mg). The spectroscopic data and physical con-

stants were identical with those of authentic **2** (2).

DETERMINATION OF THE CRYSTAL STRUCTURE.<sup>1</sup>—Crystal data.—C<sub>24</sub>H<sub>32</sub>O<sub>8</sub>;  $m/z$  [M]<sup>+</sup> 448.2111. Space group: P<sub>3</sub><sub>2</sub> (no. 145) trigonal system with hexagonal cell parameters  $a = b = 10.400(3)$ ,  $c = 18.186(4)$  Å,  $V = 1703(1)$  Å<sup>3</sup>,  $D_c(Z = 3) = 1.313$  g cm<sup>-3</sup>,  $F(000) = 720$ ,  $\mu(\text{Mo-K}\alpha) = 0.916$  cm<sup>-1</sup>.

The laue group of this crystal diffraction is  $\bar{3}$ . Systematic absences singled out both P<sub>3</sub><sub>1</sub> and P<sub>3</sub><sub>2</sub> possible space groups; the asymmetric unit contains only one molecule.

<sup>1</sup>Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.

The integrated intensities were measured on an Enraf-Nonius CAD-4 diffractometer, with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) at the  $\theta$  range from  $2^\circ$  to  $25^\circ$ . Standard reflections measured at regular intervals showed no significant change in intensity. A total number of 3284 reflections was collected, of which 2164 were unique and 1869 were observed with  $I \geq 3.0\sigma$ . The net intensities were corrected for Lorentz and polarization factor and also for absorption. The corrected structure amplitudes were placed on an approximately absolute scale by Wilson statistics ( $K = 0.022$ ,  $B = 3.970$ ).

On a PDP 11/44 computer, the 260 normalized structure factors ( $E > 1.452$ ) were put into the MULTAN 82 program. Origin fixed reflections and enantiomorph were selected by the program, but the starting sets were selected by the user on the principle of optimal selection (3). Twenty-nine of the atoms appeared on the E map corresponding to the best figure of merit, and the remaining three nonhydrogen atoms were revealed in a difference Fourier map based on this

model. Full-matrix least-squares refinement of the 32 atoms, three cycles isotropically and two cycles anisotropically, reduced the  $R$  factor to 0.074. All 32 H atoms were found in the difference Fourier maps computed at this point. Anisotropic refinement of skeletal atoms without refinement of H atoms resulted in a final  $R$  of 0.052 for 1869 data points. The final positional parameters are given in Table 1. The packing arrangement of ganervosin A in the crystal is shown in Figure 2.

#### LITERATURE CITED

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