

Structure of a Diterpene *ent*-Labdane Xyloside

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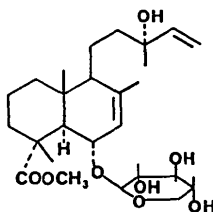
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(Received 22 May 1986; accepted 17 November 1986)

Abstract. Methyl (4*R*,5*R*,6*S*,9*R*,10*R*,13*S*)-6,13-dihydroxyabd-7,14-dien-18-oate 6-*O*- β -D-xyloside, C₂₆H₄₂O₈, $M_r = 482.62$, orthorhombic, $P2_12_12_1$, $a = 13.718(3)$, $b = 24.909(3)$, $c = 7.5655(4)$ Å, $V = 2585.2(5)$ Å³, $Z = 4$, $D_m(\text{floatation}) = 1.231$, $D_x = 1.239$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 7.05$ cm⁻¹, $F(000) = 1048$, $T = 300$ K, $R = 0.041$ for 1948 unique reflections and Friedel pairs. The absolute configuration was determined and is consistent with the known stereochemistry of the β -D-xylose residue. The six-membered ring of the sugar moiety exhibits an almost ideal chair conformation while the cyclohexane ring is a flattened chair and the cyclohexene ring is intermediate between 1,2-diplanar and half-chair. There is an extensive network of hydrogen bonds.

Introduction. In the course of a chemotaxonomic study of the genus *Gutierrezia* (Tribe Astereae, Family Compositae) (Fang, Leidig & Mabry, 1985; Gao, Leidig & Mabry, 1985, 1987; Fang, Mabry & Le-Van, 1986; Gao & Mabry, 1987), diterpene xylosides and arabinosides were isolated from dichloromethane extracts of the aerial parts of *G. sphaerocephala*. From a comparison of the optical rotation of an analogue, the xyloside was initially thought to be an *ent*-labdane. Here we report the diterpene to be the labdane (1) based on an X-ray diffraction investigation.



(1)

Experimental. A colorless prismatic crystal of dimensions $0.38 \times 0.36 \times 0.29$ mm, Nicolet $R3m/\mu$ update of a $P2_1$ diffractometer, data collected in the Wyckoff mode ($4 \leq 2\theta \leq 115^\circ$), graphite-monochromated

Cu $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($48.11 \leq 2\theta \leq 109.21^\circ$), angles measured by a centering routine associated with the diffractometer, systematic absences ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) consistent with space group $P2_12_12_1$, Laue symmetry 222, two monitored reflections (022 , $3\bar{3}1$) showed no significant change in intensities; 2115 independent reflections measured ($0 \leq h \leq 14$, $0 \leq k \leq 27$, $0 \leq l \leq 8$) with 1948 intensities greater than $2.5\sigma(I)$, 1462 Friedel pairs collected, Lorentz-polarization corrections applied, ψ -scan empirical absorption correction (transmission factors 0.235 – 0.267 , $R_{\text{merge}} = 0.017$), direct methods and difference Fourier syntheses revealed the positions of all non-H atoms, block-cascade least-squares refinement with riding model for most H atoms, H atoms involved in hydrogen bonding located in difference Fourier and fixed, final R of 0.041 , $wR = 0.048$, 310 parameters, 3404 reflections, $S = 1.98$, $(\Delta/\sigma)_{\text{max}} = 0.11$, $(\Delta/\sigma)_{\text{av}} = 0.012$, largest peaks in the final difference Fourier map of 0.21 and -0.15 e Å⁻³, $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0.0032F_o^2]^{-1}$; free variable for absolute configuration refined to $0.98(5)$ (Rogers, 1981); all computer programs supplied by Nicolet for DeskTop 30 MicroEclipse and Nova 4 configuration; atomic scattering factors and anomalous-dispersion corrections contained in the program package. Table 1 lists atomic positional parameters and U_{eq} values while Table 2 lists interatomic distances and valence angles.*

Discussion. Fig. 1 is a drawing of the title compound. The absolute configuration is established by the refinement of Friedel pairs and by the known configuration of the β -D-xylose moiety attached at C(6). The six-membered sugar ring exhibits torsion angles of

* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43585 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	4506 (2)	2236 (1)	-2301 (5)	72 (1)
C(2)	4230 (3)	2743 (1)	-3283 (5)	77 (1)
C(3)	3975 (2)	3174 (1)	-1942 (5)	73 (1)
C(4)	4828 (2)	3314 (1)	-699 (4)	56 (1)
C(5)	5230 (2)	2788 (1)	170 (4)	50 (1)
C(6)	6139 (2)	2868 (1)	1259 (4)	51 (1)
O(6)	5991 (1)	3322 (1)	2431 (3)	53 (1)
C(7)	6360 (2)	2366 (1)	2261 (4)	60 (1)
C(8)	6051 (2)	1885 (1)	1794 (4)	61 (1)
C(9)	5439 (2)	1794 (1)	141 (4)	58 (1)
C(10)	5382 (2)	2297 (1)	-1065 (4)	55 (1)
C(11)	5731 (2)	1277 (1)	-872 (4)	62 (1)
C(12)	5032 (3)	808 (1)	-639 (5)	76 (1)
C(13)	5335 (2)	291 (1)	-1564 (5)	74 (1)
O(13)	4549 (3)	-80 (1)	-1425 (6)	163 (2)
C(14)	6172 (4)	57 (1)	-647 (6)	107 (2)
C(15)	6988 (4)	-106 (2)	-1338 (8)	134 (2)
C(16)	5498 (3)	357 (1)	-3508 (5)	79 (1)
C(17)	6234 (3)	1404 (1)	2953 (5)	86 (1)
C(18)	4405 (2)	3674 (1)	745 (4)	57 (1)
O(18)	3779 (2)	3423 (1)	1775 (3)	75 (1)
C(19)	5590 (2)	3639 (1)	-1725 (4)	66 (1)
C(20)	6331 (2)	2347 (1)	-2143 (4)	64 (1)
C(21)	6831 (2)	3566 (1)	3068 (4)	52 (1)
O(21)	7069 (2)	3319 (1)	4688 (3)	62 (1)
C(22)	6622 (2)	4168 (1)	3325 (4)	52 (1)
O(22)	6491 (2)	4420 (1)	1670 (3)	67 (1)
C(23)	7468 (2)	4435 (1)	4261 (4)	52 (1)
O(23)	7211 (1)	4982 (1)	4573 (3)	63 (1)
C(24)	7711 (2)	4143 (1)	5954 (4)	56 (1)
O(24)	8583 (2)	4343 (1)	6734 (3)	69 (1)
C(25)	7886 (2)	3554 (1)	5531 (4)	66 (1)
C(26)	3388 (3)	3731 (2)	3210 (5)	90 (1)
O(27)	4571 (2)	4149 (1)	919 (3)	69 (1)

-53.2 (3) to 60.5 (3) $^\circ$ which are close to the ideal value of 56 $^\circ$ for the chair conformation (Bucourt & Hainaut, 1965). The deviations may result from the extensive hydrogen-bonding network involving the sugar hydroxyl groups. The cyclohexane ring exhibits a slightly more distorted chair conformation with torsion angles of -43.8 (3) to 60.7 (4) $^\circ$. The cyclohexene ring is intermediate between 1,2-diplanar and half-chair (Toromanoff, 1980). The bond lengths and valence angles all fall within the expected ranges. Librational corrections of bond lengths range from 0.001 to 0.008 \AA . Labdanes reported in other structural studies either have no double bond associated with the bicyclic system (e.g. Smith-Verdier, Florencio & Garcia-Blanco, 1978), or an exocyclic double bond at C(8)-C(17) (Manchand, Blount, McCabe & Clardy, 1979).

There is an intramolecular hydrogen bond formed between the sugar hydroxyl O(22) and the carbonyl O(27) atom; O(22)···O(27) = 2.778 (3), O(22)-H = 0.97, H···O(27) = 1.84 \AA and O(22)-H···O(27) = 161.6 $^\circ$. There are three intermolecular hydrogen bonds: O(24)···O(23')(1.5-x, 1-y, 0.5+z) = 2.937 (3), O(24)-H = 1.01, H···O(23') = 1.98 \AA , O(24)-H···O(23') = 158.2 $^\circ$; O(23)···O(22')(1.5-x, 1-y, 0.5+z) = 2.811 (3), O(23)-H = 1.01, H···O(22') = 2.03 \AA , O(23)-H···O(22') = 132.8 $^\circ$;

O(23)···O(13')(1-x, 0.5+y, 0.5-z) = 2.795 (3), O(23)···H' = 2.10, H'-O(13') = 0.96 \AA , O(23)···H'-O(13') = 128.4 $^\circ$.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

C(1)-C(2)	1.513 (5)	C(1)-C(10)	1.530 (4)
C(2)-C(3)	1.518 (5)	C(3)-C(4)	1.542 (4)
C(4)-C(5)	1.568 (4)	C(4)-C(18)	1.527 (4)
C(4)-C(19)	1.532 (4)	C(5)-C(6)	1.507 (4)
C(5)-C(10)	1.553 (4)	C(6)-O(6)	1.451 (3)
C(6)-C(7)	1.495 (4)	O(6)-C(21)	1.389 (3)
C(7)-C(8)	1.318 (4)	C(8)-C(9)	1.524 (4)
C(8)-C(17)	1.506 (4)	C(9)-C(10)	1.552 (4)
C(9)-C(11)	1.551 (4)	C(10)-C(20)	1.542 (4)
C(11)-C(12)	1.522 (4)	C(12)-C(13)	1.524 (4)
C(13)-O(13)	1.424 (4)	C(13)-C(14)	1.463 (5)
C(13)-C(16)	1.497 (5)	C(14)-C(15)	1.301 (8)
C(18)-O(18)	1.318 (4)	C(18)-O(27)	1.211 (3)
O(18)-C(26)	1.434 (5)	C(21)-O(21)	1.409 (3)
O(21)-C(25)	1.539 (3)	O(21)-C(25)	1.416 (4)
C(22)-O(22)	1.412 (3)	C(22)-C(23)	1.513 (4)
C(23)-O(23)	1.427 (3)	C(23)-C(24)	1.510 (4)
C(24)-O(24)	1.423 (3)	C(24)-C(25)	1.522 (4)
C(2)-C(1)-C(10)	114.5 (3)	C(1)-C(2)-C(3)	108.6 (3)
C(2)-C(3)-C(4)	113.1 (3)	C(3)-C(4)-C(5)	109.5 (2)
C(3)-C(4)-C(18)	106.3 (2)	C(5)-C(4)-C(18)	108.9 (2)
C(3)-C(4)-C(19)	109.1 (2)	C(5)-C(4)-C(19)	114.5 (2)
C(18)-C(4)-C(19)	108.2 (2)	C(4)-C(5)-C(6)	114.1 (2)
C(4)-C(5)-C(10)	117.0 (2)	C(6)-C(5)-C(10)	108.8 (2)
C(5)-C(6)-O(6)	108.8 (2)	C(5)-C(6)-C(7)	109.5 (2)
O(6)-C(6)-C(7)	111.8 (2)	C(6)-O(6)-C(21)	115.9 (2)
C(6)-C(7)-C(8)	124.0 (3)	C(7)-C(8)-C(9)	122.2 (2)
C(7)-C(8)-C(17)	120.9 (3)	C(9)-C(8)-C(17)	116.8 (2)
C(8)-C(9)-C(10)	112.9 (2)	C(8)-C(9)-C(11)	112.8 (2)
C(10)-C(9)-C(11)	113.1 (2)	C(1)-C(10)-C(5)	109.9 (2)
C(1)-C(10)-C(9)	108.6 (2)	C(5)-C(10)-C(9)	106.8 (2)
C(1)-C(10)-C(20)	110.3 (2)	C(5)-C(10)-C(20)	111.5 (2)
C(9)-C(10)-C(20)	109.5 (2)	C(9)-C(11)-C(12)	114.6 (3)
C(11)-C(12)-C(13)	115.0 (3)	C(12)-C(13)-O(13)	107.9 (3)
C(12)-C(13)-C(14)	109.4 (3)	O(13)-C(13)-C(14)	107.5 (3)
C(12)-C(13)-C(16)	113.5 (3)	O(13)-C(13)-C(16)	104.9 (3)
C(14)-C(13)-C(16)	113.2 (3)	C(13)-C(14)-C(15)	127.5 (5)
C(4)-C(18)-O(18)	113.1 (2)	C(4)-C(18)-O(27)	125.4 (3)
O(18)-C(18)-O(27)	121.4 (3)	C(18)-O(18)-C(26)	116.0 (2)
O(6)-C(21)-O(21)	107.6 (2)	O(6)-C(21)-C(22)	108.4 (2)
O(21)-C(21)-C(22)	111.0 (2)	C(21)-O(21)-C(25)	113.3 (2)
C(21)-C(22)-O(22)	110.1 (2)	C(21)-C(22)-C(23)	110.2 (2)
O(22)-C(22)-C(23)	108.5 (2)	C(22)-C(23)-O(23)	107.9 (2)
O(22)-C(23)-C(24)	110.8 (2)	O(23)-C(23)-C(24)	112.0 (2)
C(23)-C(24)-O(24)	111.7 (2)	C(23)-C(24)-C(25)	108.7 (2)
O(24)-C(24)-C(25)	107.0 (2)	O(21)-C(25)-C(24)	111.6 (2)

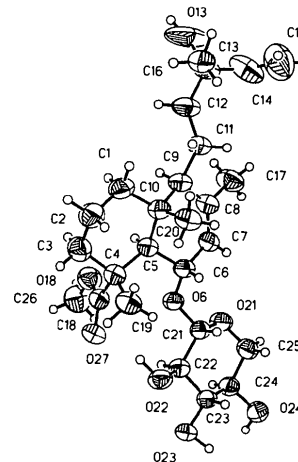


Fig. 1. Thermal-ellipsoid plot of compound (1). Ellipsoids are drawn at the 50% probability level while H atoms are represented by spheres of arbitrary size.

We thank the Robert A. Welch Foundation (P-074 and F-130) and the National Science Foundation (INT8214877 and BSR-8402017) for their financial support.

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Acta Cryst. (1987). **C43**, 756–759

Structure of Adamantanamine Hydrochloride at 143 K

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(Received 8 September 1986; accepted 3 November 1986)

Abstract. Tricyclo[3.3.1.1^{3,7}]decan-1-aminium chloride, C₁₀H₁₅NH₃⁺Cl⁻, *M_r* = 187.71, monoclinic, *C*2/*c*, *a* = 20.549 (10), *b* = 11.138 (5), *c* = 9.658 (6) Å, β = 108.81 (5)°, *V* = 2092.5 Å³ (at 143 K), *Z* = 8, *D_x* = 1.191 Mg m⁻³, λ(Cu *K*α) = 1.54178 Å, μ(Cu *K*α) = 2.847 mm⁻¹, *F*(000) = 816, *R* = 0.065 for 1394 observed reflections. The structure of the high-temperature phase at 143 K has been shown to be ordered. The adamantane skeleton is not affected by the substitution. The molecules are held together by almost linear hydrogen bonds of the type N–H⋯Cl. All three H atoms of the NH₃⁺ group are involved in hydrogen bonds and all Cl atoms form three H bonds. The *d*(N⋯Cl) distances range from 3.163 (5) to 3.219 (5) Å.

Introduction. The occurrence of order–disorder phase transitions in adamantane and its derivatives is well known (Parsonage & Staveley, 1978), and simple substitution, even though the high symmetry of adamantane itself is destroyed, does not always preclude the occurrence of the transitions (Clark, Knox, Mackle & McKervey, 1977). Stronger intermolecular interactions, such as hydrogen bonding, can affect the behaviour. For example, in 1-adamantanol (Amoureux, Bee, Gors, Warin & Baert, 1979) the phase transition occurs at 353 K with a large entropy of 40.6 J K⁻¹ mol⁻¹; thus the phase transition is shifted to a higher temperature than in other adamantyl derivatives, but is

not prevented from occurring. In contrast, adamantyl carboxylic acid shows a transition at 251 K, but with a much smaller entropy change of 8.97 J K⁻¹ mol⁻¹ (Harvey, Gilson & Butler, 1986*a*), and the higher temperature phase is probably ordered.

A study of the adamantanamine hydrochloride salt showed that a sharp phase transition occurs at 124 K (Harvey, Gilson & Butler, 1986*b*) with enthalpy and entropy of transition of 0.32 kJ mol⁻¹ and 2.51 J K⁻¹ mol⁻¹ respectively. This transition is at a lower temperature than for any other adamantane derivative. The room-temperature vibrational spectra show quite narrow vibrational bands which split, usually into two or three components, in the low-temperature phase. In view of these spectral changes, the phase transition is probably first-order even though the enthalpy and entropy changes are small. An activation energy of 33.6 kJ mol⁻¹ obtained from proton spin-lattice relaxation time measurements was assigned to the barrier to rotation of the adamantyl group about its *C*₃ axis.

Thus adamantanamine hydrochloride is a singly substituted derivative that retains the threefold symmetry axis in the parent molecule, but has an ordered high-temperature phase. The same is probably true for the carboxylic acid compound but in this case the molecules exist as dimers. Clearly it is the hydrogen bonding in the amine hydrochloride salt that prevents the order–disorder transition from occurring, and the structure of the high-temperature phase is the subject of