opposite direction to the quaternary N side chain ($\tau_2 = -3°$). In (I), the arrangement of the alkyloxy chain over the benzamide moiety allows the H atoms of the terminal C atoms to interact favourably with some of the H atoms of the *B* phenyl ring and with the O atoms of the ester group. This favourable interaction is supported by the lower van der Waals contribution to the total steric energy of this isomer with respect to the second isomer, which shows smaller bending and torsional energy values. On this basis we can assume that the van der Waals interactions involving the alkyloxy side chain are responsible for establishing the overall structure of the cation and its freedom of motion.

References

Allinger, N. L. (1977). *J. Am. Chem. Soc.* **99**, 8127–8134.

Dapporto, P. & Sega, A. (1986). *Acta Cryst.* C**42**, 474–478.

Dapporto, P. & Sega, A. (1987). *Acta Cryst.* C**43**, 1714–1717.

Ghelardoni, M., Pestellini, V., Pisanti, N. & Volterra, G. (1973). *J. Med. Chem.* **16**, 1063–1065.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kashino, S., Ikeda, M. & Haisa, M. (1982). *Acta Cryst.* B**38**, 1868–1870.

Maggi, C. A., Grimaldi, G., Volterra, G. & Meli, A. (1983). *Drugs Exp. Clin. Res.* **9**, 235–242.

Maggi, C. A., Manzini, S. & Meli, A. (1983). *Arch. Int. Pharmacodyn. Ther.* **264**, 305–323.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sega, A., Gaggelli, E. & Valensin, G. (1985). *Magn. Reson. Chem.* **23**, 649–654.

Sega, A., Ghelardoni, M., Pestellini, V., Pogliani, L. & Valensin, G. (1984). *Org. Magn. Reson.* **22**, 649–652.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Valensin, G., Gaggelli, E., Lepri, A. & Sega, A. (1986). *Can. J. Chem.* **64**, 2048–2052.

Valensin, G., Pogliani, L., Ghelardoni, M., Pestellini, V. & Sega, A. (1984). *Can. J. Chem.* **62**, 2131–2135.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

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Structure of a New C_{13}-Norisoprenoid

By Matías L. Rodríguez,* Iván Brito B, A. G. González and Luz N. Almonacid

Instituto Universitario de Bio-Orgánica, Universidad de La Laguna, Carretera de la Esperanza, 2,
38206 *La Laguna, Tenerife, Spain*

and C. Pérez and J. M. Trujillo

Instituto de Productos Naturales y Agrobiología de Canarias, CSIC, Carretera de la Esperanza, 2,
38206 *La Laguna, Tenerife, Spain*

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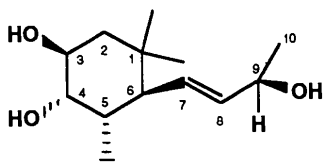
Abstract. (3*S*,4*S*,5*S*,6*S*,9*R*)-3,4-Dihydroxy-5,6-dihydro-β-ionol, $C_{13}H_{24}O_3$, $M_r = 228.3$, monoclinic, $P2_1$, $a = 6.746\ (1)$, $b = 7.712\ (1)$, $c = 12.620\ (10)$ Å, $\beta = 102.86\ (1)°$, $V = 640.1\ (5)$ Å^3, $Z = 2$, $D_x = 1.18$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 6.21$ cm^{-1}, $F(000) = 252$, $T = 298$ K, $R = 0.055$, $wR = 0.058$ for 622 reflections with $I \geq 3\sigma(I)$. The ring adopts a slightly distorted chair conformation, and the side chain is in an extended configuration. The structure is stabilized by two intermolecular O—H···O hydrogen bonds [2.846 (1) and 2.860 (1) Å]. Bond lengths and angles are in the usual range.

Introduction. The compound (I) was isolated from the leaves of *Apollonias barbujana* (Lauraceae) which were collected in the Canary Islands. A large number of the ionone-related compounds have been found mainly in the tobacco leaf (Enzell, Wahlberg & Aasen, 1977; Wahlberg, Eklund, Enzell & Berg, 1987; Ohloff, 1978; Wahlberg & Enzell, 1987), *Vitis vinifera* grapes (Nykänen & Suomalainen, 1983; Marais, 1983) and quince fruit (Winterhalter, Harmsen & Trani, 1991; Ishihara, Tsuneya, Shiota, Shiga & Nakatsu, 1986).



(I)

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* To whom correspondence should be addressed.

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	−0.1982 (9)	−0.5003	−0.6508 (3)	32 (2)
O2	0.0070 (8)	−0.0703 (7)	−0.5691 (3)	28 (2)
O3	−1.0094 (9)	0.2017 (7)	−0.7241 (3)	35 (2)
C1	−0.4152 (13)	−0.1971 (9)	−0.8074 (4)	21 (3)
C2	−0.1972 (13)	−0.2704 (9)	−0.7828 (4)	25 (3)
C3	−0.1067 (12)	−0.3344 (9)	−0.6679 (5)	22 (3)
C4	−0.1433 (13)	−0.2047 (9)	−0.5812 (5)	29 (3)
C5	−0.3649 (12)	−0.1357 (9)	−0.6027 (4)	19 (3)
C6	−0.4316 (13)	−0.0589 (8)	−0.7186 (4)	19 (3)
C7	−0.6367 (12)	0.0220 (10)	−0.7344 (5)	23 (3)
C8	−0.6787 (14)	0.1836 (9)	−0.7695 (5)	28 (3)
C9	−0.8777 (13)	0.2747 (9)	−0.7888 (5)	28 (3)
C10	−0.9875 (16)	0.2717 (14)	−0.9067 (6)	57 (4)
C11	−0.5746 (14)	−0.3414 (10)	−0.8118 (5)	35 (3)
C12	−0.4543 (14)	−0.1108 (10)	−0.9185 (5)	35 (3)
C13	−0.3887 (15)	−0.0054 (11)	−0.5159 (5)	37 (3)

Experimental. The air-dried leaves (2.2 kg) were extracted with MeOH under reflux and the solvent was evaporated *in vacuo* to yield 38 g of extract, which was chromatographed on a silica gel column eluted with *n*-hexane/EtOAc of increasing polarity. The fractions eluted with *n*-hexane/EtOAc 60:40 were combined and, after solvent evaporation, the pure compound (I) (23 mg, 0.001%) was obtained by repeated chromatographies on silica gel; m.p. 435–436 K (acetone/benzene 60:40); $[\alpha]_D^{24\,°C}$ −34.0° (*c* 0.52 g dm^{-3}, MeOH).

A single crystal with dimensions 0.3 × 0.3 × 0.2 mm was used for measurements on a Siemens AED diffractometer, with graphite-monochromated Cu $K\alpha$ radiation, $\omega/2\theta$ scan mode. The lattice constants were obtained from least-squares refinement of 17 reflections in the interval $20 \leq 2\theta \leq 40°$ and two standard reflections monitored every hour showed no significant intensity decay. Of the 888 data measured with $3 \leq 2\theta \leq 121°$, 624 were independent with 622 having $I \geq 3\sigma(I)$ (index range $h = 0 \rightarrow 4$, $k = 0 \rightarrow 8$, $l = -13 \rightarrow 13$) considered observed and used in structure determination and refinement. No absorption correction. The structure was solved by direct methods (*SHELXS86*; Sheldrick, 1986) and refined on F by full-matrix least squares (*XRAY76*; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Some H atoms could be localized in the difference Fourier maps, and others were calculated (*HSEARCH*; Fayos & Martínez-Ripoll, 1980), but all were included with a fixed isotropic contribution ($U = 0.06$ Å^2) and not refined. A weighting scheme $[w = k/|f(F_o)|^2 f(\sin\theta/\lambda)]$ to obtain flat dependence of Δ^2F *vs* F_o and $\sin\theta/\lambda$ was performed (*PESOS*; Martínez-Ripoll & Cano, 1980). Refinement converged to $R = 0.055$, $wR = 0.058$, $S = 2.750$ for 144 refined parameters; overdetermination ratio 4.3; max. shift/e.s.d. 0.022; min. and max. ΔF map excursions −0.220 and 0.188 e Å^{-3} respectively. The absolute configuration was determined as 3(*S*),4(*S*),5(*S*),6(*S*),9(*R*) by comparison of 34 Bijvoet pairs with $F_o \leq 10 \leq (F_o)$, which were in the range $5 \leq F_c \leq 50$ and $0.15 \leq \sin\theta/\lambda \leq 0.4$ Å^{-1} (*CONFAB*; Martínez-Ripoll & Fayos, 1980). The averaged Bijvoet differences are 0.173 for the correct enantiomer *vs* 0.211 for the incorrect enantiomer. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Geometrical calculations were made with *PARST* (Nardelli, 1983).

Discussion. Table 1* gives the final positional and equivalent isotropic thermal parameters for all non-H atoms. The molecular structure for the correct enantiomer of the title compound including the atom-numbering scheme is illustrated in Fig. 1. Bond distances, bond angles and relevant torsion angles are shown in Table 2. The molecular structure of the title compound consists of a six-membered ring with an α-equatorial side chain. The ring exhibits a slightly distorted chair ($^4C_1$) conformation as shown by the ring puckering parameters (Cremer & Pople, 1975): $Q = 0.538$ Å, $\theta = 170.0\,(10)°$ and $\varphi = 104.2\,(6)°$ for the sequence C1, C2, C3, C4, C5, C6, with C1 and C4 displaced −0.608 (11) and 0.660 (10) Å from the best plane through C2, C3, C5 and C6 atoms (max. deviation ±0.04 Å). The hydroxy groups on C3 and C4 have a 1,2-diaxial relationship. The stereochemistry of the double bond is *E*. Average values for distances are C(sp^3)—C(sp^3) = 1.554 (11), C(sp^3)—C(sp^2) = 1.492 (13), C—O =

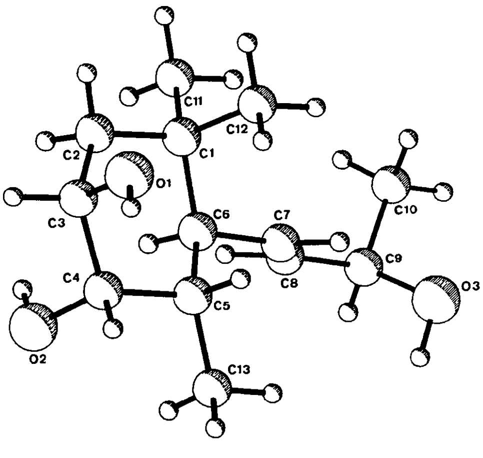

Fig. 1. Molecular structure and atomic numbering for (I).

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* 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 55260 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0522]

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

O1—C3	1.460 (9)	C2—C3	1.528 (9)
O2—C4	1.438 (10)	C3—C4	1.546 (10)
O3—C9	1.452 (11)	C4—C5	1.556 (13)
C1—C2	1.545 (13)	C5—C6	1.553 (9)
C1—C6	1.572 (10)	C5—C13	1.525 (11)
C1—C11	1.544 (12)	C6—C7	1.494 (13)
C1—C12	1.524 (9)	C7—C8	1.335 (11)
C8—C9	1.490 (13)	C9—C10	1.511 (10)
C11—C1—C12	107.9 (7)	O2—C4—C5	113.7 (8)
C6—C1—C12	109.6 (7)	C4—C5—C13	110.6 (7)
C6—C1—C11	111.0 (7)	C4—C5—C6	111.2 (8)
C2—C1—C12	108.0 (8)	C6—C5—C13	111.8 (7)
C2—C1—C11	111.7 (8)	C1—C6—C5	111.2 (6)
C2—C1—C6	108.7 (7)	C5—C6—C7	110.7 (6)
C1—C2—C3	118.2 (8)	C1—C6—C7	113.6 (6)
O1—C3—C2	109.4 (7)	C6—C7—C8	124.0 (10)
C2—C3—C4	111.8 (7)	C7—C8—C9	127.9 (9)
O1—C3—C4	109.0 (7)	O3—C9—C8	111.6 (7)
O2—C4—C3	108.9 (8)	C8—C9—C10	112.5 (8)
C3—C4—C5	113.5 (6)	O3—C9—C10	108.8 (9)
C2—C1—C6—C7	179.4 (9)	O1—C3—C4—O2	157.4 (7)
C12—C1—C6—C5	−172.5 (8)	C2—C3—C4—C5	46.1 (11)
C11—C1—C6—C5	68.5 (10)	O1—C3—C4—C5	−74.9 (10)
C2—C1—C6—C5	−54.7 (10)	C3—C4—C5—C6	−53.7 (10)
C6—C1—C2—C3	50.2 (11)	O2—C4—C5—C6	71.5 (10)
C11—C1—C2—C3	−72.5 (10)	C3—C4—C5—C13	−178.6 (8)
C11—C1—C6—C7	−57.1 (10)	C4—C5—C6—C1	58.3 (10)
C1—C2—C3—O1	74.6 (10)	C13—C5—C6—C1	−177.5 (8)
C1—C2—C3—C4	−46.2 (11)	C6—C7—C8—C9	179.4 (9)

1.450 (10) Å. The valence angles involving tetrahedral and trigonal C atoms have mean values of 111.1 (7) and 126.0 (10)°, respectively. Molecular packing is determined by hydrogen bonds of the O—H···O type involving the hydroxy O atoms in the equivalent positions $-x, y-\frac{1}{2}, -z-1$ [O(1)···O(2) 2.846 (1), H(1)···O(2) 1.972 (1) Å, O(1)—H(1)···O(2) 143.3 (6)°], and $x+1, y, z$ [O(2)···O(3) 2.860 (1), H(2)···O(3) 1.941 (1) Å, O(2)—H(2)···O(3) 150.5 (5)°]. Other contacts are consistent with van der Waals interactions.

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References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Enzell, C. R., Wahlberg, I. & Aasen, A. J. (1977). *Progress in the Chemistry of Organic Products*, Vol. 34, p. 1. New York: Springer-Verlag.

Fayos, J. & Martínez-Ripoll, M. (1980). *HSEARCH*. Instituto Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain.

Ishihara, M., Tsuneya, T., Shiota, H., Shiga, M. & Nakatsu, K. (1986). *J. Org. Chem.* **51**, 491–495.

Marais, J. S. (1983). *Afr. J. Enol. Vitic.* **4**, 49–58.

Martínez-Ripoll, M. & Cano, F. (1980). *PESOS*. Instituto Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain.

Martínez-Ripoll, M. & Fayos, J. (1980). *CONFAB*. Instituto Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Nykänen, L. & Suomalainen, H. (1983). *Aroma of Beer, Wine and Distilled Alcoholic Beverages*. Berlin: Akademie-Verlag.

Ohloff, G. (1978). *Progress in the Chemistry of Organic Natural Products*, Vol. 35, p. 431. New York: Springer-Verlag.

Sheldrick, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Wahlberg, I., Eklund, A.-M., Enzell, C. R. & Berg, J.-E. (1987). *Acta Chem. Scand. Ser. B*, **41**, 455–458.

Wahlberg, I. & Enzell, C. R. (1987). *Nat. Prod. Rep.* **4**, 237–276.

Winterhalter, P., Harmsen, S. & Trani, F. (1991). *Phytochemistry*, **9**, 3021–3025.

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Structure of (2*S*,5*S*)-2-Hydroxymethyl-5-methoxy-*N*-*o*-nitrobenzoylpyrrolidine

By A. Chiaroni, N. Langlois and C. Riche

Institut de Chimie des Substances Naturelles, CNRS, 91198 *Gif-sur-Yvette CEDEX, France*

and G. Snatzke

*Lehrstuhl für Strukturchemie, Ruhr-Universität, D-*4630 *Bochum, Germany*

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Abstract. $C_{13}H_{16}N_2O_5$, $M_r = 280.3$, monoclinic, $P2_1$, $a = 10.307$ (3), $b = 9.364$ (3), $c = 7.394$ (2) Å, $\beta = 104.65$ (2)°, $V = 690.5$ Å^3, $Z = 2$, $D_x = 1.35$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 7.9$ cm^{-1}, $F(000) = 296$, $T = 293$ K, $R = 0.055$ for 1209 observed reflexions. The benzamide group is not planar. The hydroxyl group is engaged in an intramolecular hydrogen bond with the carbonyl of the amido group. A