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Acta Cryst. (1992). C**48**, 1246–1248

Structure of [1*R*-(*endo,anti*)]-3-Bromo-1,7-dimethyl-7-vinylbicyclo[2.2.1]heptan-2-one

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(*Received* 14 *June* 1991; *accepted* 11 *November* 1991)

Abstract. $C_{11}H_{15}BrO$ (1), $M_r = 243.14$, orthorhombic, $P2_12_12_1$, $a = 7.413$ (1), $b = 9.943$ (1), $c = 14.779$ (2) Å, $V = 1089.3$ (5) Å^3, $Z = 4$, $D_x = 1.483$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 36.38$ cm^{-1}, $F(000) = 496$, $T = 298$ K, final $R = 0.0459$ for 974 reflections [$F_o > 3\sigma(F_o)$]. This vinyl compound, synthesized from commercially available D(+)-3-bromocamphor-π-sulfonic acid, shows clearly that the π substituent is *anti* configured to the carbonyl group, which is in contrast to the description in several chemical supply catalogues and articles in the literature.

Introduction. A method for the determination of the enantiomeric purity of chiral compounds is complexation gas chromatography (Schurig, 1986) using chiral metal–β-diketonate complexes as stationary phases. Usually the β-diketone ligand is trifluoroacetyl- or heptafluorobutyryl-1*R*-camphor. To determine which factors influence the chiral recognition of these stationary phases, we decided to modify the camphor framework. In this regard, the D(+)-α-bromocamphor-π-sulfonic acid ammonium salt, listed in the *Aldrich Handbook of Fine Chemicals* 1990–1991, or the (+)-3-bromocamphor-8-sulfonic acid monohydrate, listed in the *Merck–Schuchardt Manual* 1989, seemed to be suitable starting materials, allowing us to modify the space required for potentially coordinated substrates during the separation of enantiomers. However, only the variation of the π substituent *syn* relative to the carbonyl group should influence this distinctly. ^{13}C NMR spectra of the vinyl derivative (1) revealed some doubt as to the orientation of the π substituent.

Experimental. Compound (1) was synthesized by chlorination of the sulfonic acid ammonium salt with PCl_5 and subsequent addition of diazomethane/triethylamine followed by elimination of N_2 and SO_2 (Laderer, 1990). Colourless needle-like crystals of (1) were obtained after vacuum distillation (5 Pa) and sublimation of the distillate. A single crystal of approximate dimensions 0.1 × 0.1 × 1.5 mm was used for the data collection. Lattice constants were determined from 88 reflections having $2\theta > 25°$ on a Stoe Stadi-4 diffractometer. 1581 reflections were measured with the scan mode ω–θ = 1:1 (hkl, $\bar{h}\bar{k}l$, $0 \le h \le 8$, $0 \le k \le 11$, $0 \le l \le 17$, $3 \le 2\theta \le 50°$). Three

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. $U_{iso} = 0.06$ for all H atoms.

	x	y	z	U_{eq}
C1	−0.260 (2)	0.0014 (6)	−0.0219 (4)	0.041 (5)
C2	−0.219 (1)	−0.1481 (6)	−0.0201 (4)	0.039 (4)
O	−0.2330 (8)	−0.2234 (4)	0.0430 (2)	0.053 (4)
C3	−0.1646 (9)	−0.1859 (5)	−0.1157 (4)	0.044 (3)
Br	−0.2706 (2)	−0.3504 (1)	−0.1581 (1)	0.0793 (6)
C4	−0.2061 (1)	−0.0569 (7)	−0.1674 (5)	0.046 (5)
C5	−0.4115 (9)	−0.0374 (8)	−0.1673 (5)	0.067 (6)
C6	−0.4464 (9)	−0.0091 (9)	−0.0685 (5)	0.065 (8)
C7	−0.139 (1)	0.0490 (7)	−0.1006 (5)	0.044 (5)
C8	−0.176 (1)	0.1953 (6)	−0.1273 (4)	0.050 (6)
C9	0.0616 (8)	0.0449 (7)	−0.0779 (5)	0.057 (6)
C10	−0.245 (2)	0.0679 (6)	0.0701 (3)	0.078 (5)
C11	−0.197 (2)	0.2438 (7)	−0.2063 (5)	0.074 (6)
H111	−0.21 (1)	0.336 (4)	−0.216 (3)	
H112	−0.180 (9)	0.190 (5)	−0.254 (3)	

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

C1—C2	1.518 (7)	C4—C5	1.535 (9)
C1—C6	1.545 (9)	C4—C7	1.527 (8)
C1—C7	1.545 (8)	C5—C6	1.554 (8)
C1—C10	1.515 (5)	C7—C8	1.532 (7)
C2—C3	1.515 (6)	C7—C9	1.523 (8)
C2—O	1.200 (5)	C8—C11	1.272 (7)
C3—C4	1.514 (7)	C11—H111	0.933 (4)
C3—Br	1.929 (5)	C11—H112	0.90 (4)

C10—C1—C2	113.4 (5)	C5—C4—C7	103.7 (7)
C7—C1—C2	101.3 (5)	C6—C5—C4	101.7 (6)
C7—C1—C10	119.8 (6)	C5—C6—C1	104.8 (5)
C6—C1—C2	103.6 (6)	C9—C7—C1	113.2 (6)
C6—C1—C10	116.5 (7)	C8—C7—C1	112.3 (5)
C6—C1—C7	99.8 (5)	C8—C7—C9	105.0 (6)
O—C2—C3	126.7 (5)	C4—C7—C1	94.9 (5)
C1—C2—C3	105.9 (4)	C4—C7—C9	116.2 (6)
C1—C2—O	127.4 (5)	C4—C7—C8	115.4 (5)
C2—C3—Br	113.5 (4)	C11—C8—C7	128.1 (6)
C4—C3—Br	118.1 (4)	H111—C11—C8	120 (3)
C4—C3—C2	102.3 (4)	H112—C11—C8	119 (4)
C7—C4—C3	100.8 (5)	H112—C11—H111	119 (5)
C5—C4—C3	107.9 (6)		

standard reflections measured every hour showed a slow decomposition of the crystal leading to a decrease of their intensities to 70% (rescaling with the averaged reciprocal loss of intensity). The data were corrected for Lorentz and polarization effects and a numerical absorption correction, minimum and maximum transmission factors 0.59 and 0.71, was applied, leading to 974 unique reflections with $F_o > 3\sigma(F_o)$ (unique data set, 213 unobserved). The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1986). Refinement on F with anisotropic parameters and H atoms in geometrically calculated positions (C—H = 0.96 Å, except the H atoms at C11) (*SHELX*76; Sheldrick, 1976), converged at $R = 0.0459$, $wR = 0.0272$, $w = 1.7/\sigma(F_o)^2$. Anomalous-dispersion effects ($\Delta R = 0.012$), f' and f'' values taken from Cromer & Liberman (1970). Maximum shift/e.s.d. in final cycle < 0.1, extinction correction as in *SHELX*76 (1.4×10^{-3}), 132 parameters, maximum residual electron density 0.63 e Å^{-3}. Scattering factors as supplied by *SHELX*76. Diagrams were drawn with *SHELXTL-Plus* (Sheldrick, 1987). Table 1 contains atomic parameters. Bond distances and angles are given in Table 2. Fig. 1 shows the molecular structure of (1) and Fig. 2 contains a stereoscopic view of the unit cell (viewed along [001]).*

Discussion. The crystal structure determination confirmed the *anti* configuration of the vinyl group and the carbonyl group (Fig. 1) and will help to prevent the use of the wrong formula (Wedekind & Strüsser, 1923) of 3-bromocamphor-π-sulfonic acid in future.

Bond distances and angles show no anomalies and vary in the usual range. The torsion angle of the C9—C7—C8—C11 fragment is 102.8°; this arrangement prevents hydrogen contacts of the vinyl group with those attached to C9 and to C6 and C5.

The effective packing of the molecules can be described by an approximately coplanar arrangement of fourfold pseudo-equatorially substituted cyclopentane moieties in the (011) plane with the ethylidene bridge below this plane and the C9 methyl group above it.

* 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 54851 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

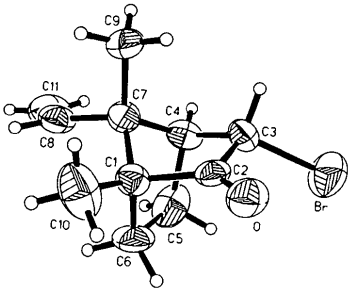

Fig. 1. Molecular structure of (1).

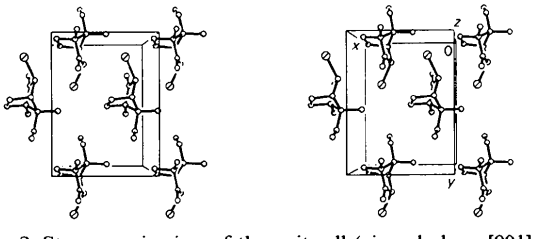

Fig. 2. Stereoscopic view of the unit cell (viewed along [001]).

We are grateful to E. M. Peters for plotting Figs. 1 and 2 and to the Deutsche Forschungsgemeinschaft for financial support.

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Acta Cryst. (1992). C**48**, 1248–1252

Structures of Some New D-Secoestrone Derivatives

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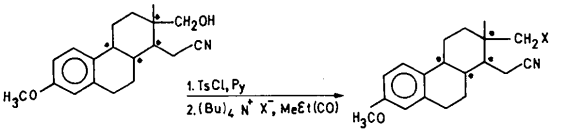
(*Received* 20 *March* 1991; *accepted* 25 *November* 1991)

Abstract. $C_{19}H_{24}NOX$ (X = Cl, Br, I; the three compounds are isostructural), monoclinic, $P2_1$, $Z = 2$, λ(Mo $K\alpha$) = 0.71069 Å. 17-Chloro-3-methoxy-16,-17-secoestra-1,3,5(10)-triene-16-nitrile (1), M_r = 371.860, $a = 7.768$ (2), $b = 14.590$ (5), c = 7.647 (2) Å, $\beta = 96.16$ (3)°, $V = 861.7$ (6) Å^3, D_x = 1.225 g cm^{-3}, $\mu = 1.83$ cm^{-1}, $F(000) = 340$, T_c = 391–392 K, $R = 0.040$ for 1098 observed reflections. 17-Bromo-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile (2), $M_r = 362.316$, $a = 7.774$ (2), b = 14.615 (7), $c = 7.719$ (3) Å, $\beta = 96.50$ (2)°, V = 871.4 (9) Å^3, $D_x = 1.380$ g cm^{-3}, $\mu = 22.89$ cm^{-1}, $F(000) = 376$, T_c = 402–403 K, $R = 0.035$ for 1136 observed reflections. 17-Iodo-3-methoxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile (3), M_r = 409.311, $a = 7.832$ (3), $b = 14.668$ (8), c = 7.872 (3) Å, $\beta = 97.05$ (2)°, $V = 897$ (1) Å^3, D_x = 1.514 g cm^{-3}, $\mu = 16.49$ cm^{-1}, $F(000) = 412$, T_c = 407–408 K, $R = 0.049$ for 1659 observed reflections. These three new D-secoestrone derivatives have been synthesized and submitted to a biological screening of their possible antiestrogenic activities.

Introduction. In an earlier paper (Petrović, Pejanović, Miljković & Hranisavljević, 1990) we proved that some newly synthesized D-secoestrone derivatives completely lack estrogen activity. Though this fact was already established for some other D-seco- and D-heteroestrone derivatives (Baran, 1967), there is no evidence in the literature about their structure–biological activity relationship. On the other hand, for some natural estrogen derivatives such relationships have been firmly established (Segaloff, Gabbard, Flores, Borne, Baker, Duax, Strong & Rohrer, 1980).

Therefore we have undertaken X-ray structure determinations of selected D-secoestrone derivatives, with an aim to explain their biological behaviour. The D-secoestrone derivatives tested were obtained according to the scheme below (Petrović *et al.*, 1990).



(1) X = Cl
(2) X = Br
(3) X = I

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