Crystal structure of (1*R*,2*S*,5*S*,6*R*,7*R*)-6-(4-bromobenzenesulfonyloxy)-methyl-2,7-dimethyl-tricyclo[5.2.2.0^{1,5}]undec-8-ene, C₂₀H₂₅BrO₃S

A. Kirfel^{*I}, H. Euler^I, C. Valder^{II}, M. Neugebauer^{II}, M. Meier^{III} and N. A. Braun^{III}^I Universität Bonn, Mineralogisch-Petrologisches Institut, Poppelsdorfer Schloss, D-53115 Bonn, Germany^{II} Universität Bonn, Pharmazeutisches Institut, Kreuzbergweg 26, D-53115 Bonn, Germany^{III} DRAGOCO Gerberding & Co. AG, Corporate Research Division, D-37601 Holzminden, Germany

Received July 16, 2002; accepted and available on-line November 7, 2002; CCDC-No. 1267/905

Abstract

C₂₀H₂₅BrO₃S, monoclinic, *P*12₁1 (No. 4), *a* = 9.981(3) Å, *b* = 10.765(3) Å, *c* = 9.565(3) Å, β = 91.04(1)°, *V* = 1027.6 Å³, *Z* = 2, *R*_g(*F*) = 0.046, *wR*_{ref}(*F*²) = 0.091, *T* = 295 K.

Source of material

The title compound was formed by reduction of the corresponding (1*R*,2*S*,5*S*,6*R*,7*R*)-2,7-dimethyl-tricyclo[5.2.2.0^{1,5}]undec-8-en-6-carbaldehyde (**I**) with LiAlH₄ in Et₂O followed by esterification of the crude alcohol with 4-bromobenzenesulfonyl chloride, triethylamine and a catalytic amount of 4-dimethylaminopyridine in CH₂Cl₂. Enantiopure nor-sesquiterpene **I**, a minor constituent (0.4%) of *Santalum spicatum* (R. Br.) A. DC. (Santalaceae), was isolated from Western Australian sandalwood oil [1]. Aldehyde **I** (= nor-helifolen-12-al) is a new natural product possessing the rare tricyclo[5.2.2.0^{1,5}]undecane skeleton [2].

Experimental details

The treatment of the two methyl groups (C12, C13) is according to the recommendation of SHELX97 manual. The AFIX instructions 33 was applied to the hydrogen atoms 'riding' upon the carrier atom (i.e. no e.s.d.'s for *x*, *y*, *z*), but the *U*_{iso}'s were free to refine. The high *U*_{iso} obtained for several H atoms can be explained by the already large *U*_{iso} of the carrier atoms.

Discussion

All intramolecular bond lengths are normal. The molecules are mainly held together by Van der Waals forces and weak intermolecular electrostatic interactions between O2...H₂O (2.522 Å) and O3...Br (3.248 Å), respectively. Both distances are slightly

shorter than the corresponding sums of the associated Van der Waals radii. Without implying chemical interaction, the packing scheme is characterized by chains of Br atoms running along [010] with *d*(Br...Br) = 6.013 Å, and by the Br...S axis, which is approximately pointing towards the next Br viewed along the [100] direction.

Table 1. Data collection and handling.

Crystal:	colorless prisma, size 0.15 × 0.22 × 0.28 mm
Wavelength:	Mo K _α radiation (0.71069 Å)
μ:	21.17 cm ⁻¹ ?
Diffractionmeter, scan mode:	Rigaku AFC-6R, ω
2θ _{max} :	45.08°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	4262, 2084
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 1468
<i>N</i> (<i>param</i>) _{refined} :	250
Programs:	SHELXS-97 [3], SHELXL-97 [4], DIAMOND [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(2)	2a	-0.3852	0.6529	-0.5813	0.12(4)
H(31)	2a	-0.4839	0.6995	-0.3823	0.20(7)
H(32)	2a	-0.4361	0.5768	-0.3068	0.06(3)
H(41)	2a	-0.3100	0.7979	-0.2923	0.12(4)
H(42)	2a	-0.2600	0.6742	-0.2204	0.08(3)
H(5)	2a	-0.1900	0.7696	-0.4807	0.04(2)
H(6)	2a	0.0126	0.7703	-0.4129	0.05(2)
H(8)	2a	0.0042	0.4052	-0.3326	0.10(4)
H(91)	2a	-0.2226	0.4113	-0.3766	0.02(2)
H(101)	2a	-0.1557	0.5020	-0.6810	0.08(3)
H(102)	2a	-0.1597	0.6477	-0.6860	0.08(3)
H(111)	2a	0.0490	0.6562	-0.6328	0.05(3)
H(112)	2a	0.0547	0.5105	-0.6364	0.08(3)
H(121)	2a	-0.3973	0.4292	-0.6220	0.12(4)
H(122)	2a	-0.5305	0.5024	-0.5970	0.3(1)
H(123)	2a	-0.4641	0.4255	-0.4750	0.4(2)
H(131)	2a	0.2093	0.4951	-0.3515	0.3(1)
H(132)	2a	0.2166	0.6404	-0.3434	0.27(9)
H(133)	2a	0.2377	0.5728	-0.4864	0.18(7)
H(141)	2a	-0.0546	0.6385	-0.1677	0.06(2)
H(142)	2a	0.0907	0.6895	-0.1940	0.07(3)
H(16)	2a	0.1782	1.0275	-0.0421	0.02(2)
H(17)	2a	0.4080	1.0161	-0.0080	0.09(3)
H(19)	2a	0.3753	0.6762	0.1495	0.12(4)
H(20)	2a	0.1472	0.6832	0.1029	0.06(3)

* Correspondence author (e-mail: Kirfel@uni-bonn.de)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Br(1)	2a	0.59858(9)	0.8435 ^a	0.0970(1)	0.0657(6)	0.194(1)	0.160(1)	−0.001(1)	−0.0072(6)	−0.036(1)
S(1)	2a	−0.0336(2)	0.8534(3)	−0.0074(2)	0.062(1)	0.044(1)	0.049(1)	−0.003(2)	0.0019(9)	−0.002(2)
O(1)	2a	−0.0457(4)	0.8261(5)	−0.1681(4)	0.090(3)	0.030(4)	0.046(3)	0.010(3)	−0.014(2)	−0.003(3)
O(2)	2a	−0.0842(6)	0.9774(6)	0.0062(5)	0.085(4)	0.035(4)	0.065(4)	0.014(3)	−0.007(3)	−0.015(3)
O(3)	2a	−0.0917(5)	0.7553(5)	0.0701(5)	0.063(4)	0.063(4)	0.046(3)	−0.010(3)	0.007(3)	−0.003(3)
C(1)	2a	−0.218(1)	0.5784(9)	−0.4969(9)	0.092(8)	0.065(7)	0.052(6)	−0.011(7)	0.000(6)	0.000(6)
C(2)	2a	−0.367(1)	0.589(1)	−0.511(1)	0.12(1)	0.092(9)	0.081(8)	−0.015(8)	−0.038(7)	−0.013(9)
C(3)	2a	−0.409(1)	0.643(1)	−0.369(1)	0.093(8)	0.075(8)	0.11(1)	0.004(8)	−0.008(7)	−0.012(8)
C(4)	2a	−0.2883(9)	0.7113(9)	−0.309(1)	0.087(7)	0.074(8)	0.080(8)	0.014(6)	−0.007(6)	−0.001(6)
C(5)	2a	−0.1784(9)	0.7002(7)	−0.4152(8)	0.089(7)	0.032(5)	0.048(6)	−0.002(5)	−0.007(5)	0.010(5)
C(6)	2a	−0.0306(9)	0.6977(8)	−0.3713(8)	0.089(7)	0.033(6)	0.045(6)	−0.002(6)	0.001(5)	−0.001(5)
C(7)	2a	0.037(1)	0.579(1)	−0.4324(9)	0.093(8)	0.053(7)	0.053(6)	−0.003(7)	0.024(5)	−0.025(6)
C(8)	2a	−0.037(1)	0.470(1)	−0.3810(9)	0.106(8)	0.045(7)	0.049(6)	0.014(7)	0.013(6)	−0.015(6)
C(9)	2a	−0.166(1)	0.4726(9)	−0.4094(9)	0.111(9)	0.034(6)	0.062(6)	−0.017(7)	0.018(6)	−0.005(5)
C(10)	2a	−0.136(1)	0.577(1)	−0.628(1)	0.19(1)	0.056(7)	0.041(7)	−0.008(9)	−0.003(8)	−0.004(6)
C(11)	2a	0.011(1)	0.581(1)	−0.594(1)	0.17(1)	0.060(8)	0.059(8)	0.01(1)	0.042(9)	−0.008(7)
C(12)	2a	−0.447(2)	0.476(2)	−0.555(2)	0.14(1)	0.16(1)	0.15(1)	−0.02(1)	−0.01(1)	−0.08(1)
C(13)	2a	0.190(1)	0.571(1)	−0.400(2)	0.078(9)	0.10(1)	0.15(1)	0.012(8)	0.030(8)	−0.03(1)
C(14)	2a	−0.0038(9)	0.7024(7)	−0.2146(8)	0.092(8)	0.031(5)	0.053(6)	0.005(5)	−0.010(5)	−0.001(4)
C(15)	2a	0.1400(6)	0.856(1)	0.0258(7)	0.058(4)	0.037(5)	0.040(5)	−0.010(7)	0.004(4)	−0.021(6)
C(16)	2a	0.217(1)	0.9556(9)	−0.0060(8)	0.092(8)	0.039(7)	0.050(6)	−0.014(7)	0.002(6)	0.003(5)
C(17)	2a	0.354(1)	0.949(1)	0.0159(9)	0.073(8)	0.070(9)	0.063(7)	−0.023(7)	0.028(6)	−0.022(6)
C(18)	2a	0.4111(8)	0.845(2)	0.0724(9)	0.089(6)	0.087(8)	0.064(6)	−0.00(1)	−0.002(5)	−0.011(8)
C(19)	2a	0.336(1)	0.746(1)	0.108(1)	0.075(8)	0.083(9)	0.081(8)	0.021(7)	−0.005(6)	0.015(7)
C(20)	2a	0.200(1)	0.752(1)	0.0821(8)	0.074(8)	0.044(6)	0.072(7)	−0.006(6)	0.002(6)	−0.005(6)

a: arbitrarily fixed for definition of origin.

References

1. Valder, C.; Neugebauer, M.; Meier, M.; Kohlenberg, B.; Hammerschmidt, F.-J.; Braun, N. A.: Western Australian sandalwood oil – new constituents of *Santalum spicatum* (R. Br.) A. DC. (Santalaceae). *J. Essent. Oil Res.* **14** (2002), submitted.
2. Weyerstahl, P.; Marschall, H.; Eckhardt, A.; Christiansen, C.: Constituents of commercial Brazilian lantana oil. *Flav. Fragr. J.* **14** (1999) 15–28.
3. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
5. Brandenburg, K.: Diamond Version 2.1. Visual Crystal Structure Information System, Crystal Impact, Postfach 1251, D-53002 Bonn, Germany 1996–1999.