APPENDIX 6

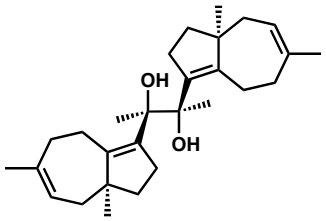
X-Ray Crystallography Reports Relevant to Chapter 3:

Unified Approach to Daucane and Sphenolobane

Bicyclo[5.3.0]decane core: Enantioselective Synthesis of

Four Daucane Sesquiterpenes and Related Molecules

A6.1 CRYSTAL STRUCTURE ANALYSIS OF 262



Compound **262**

(NBB04)

Contents

Table A6.1. Crystal data.

Table A6.2. Atomic coordinates.

Table A6.3. Full bond distances and angles.

Table A6.4. Anisotropic displacement parameters.

Table A6.5. Hydrogen coordinates and isotropic displacement parameters.

Table A6.6. Hydrogen bond distances and angles.

*Figure A6.1. Diol **262**.*

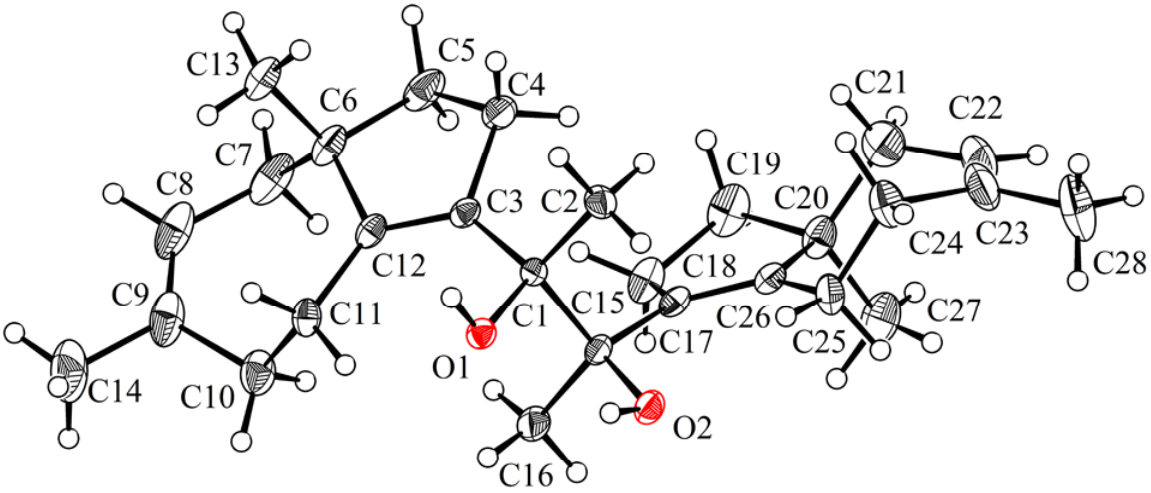


Table A6.1. Crystal data and structure analysis details for diol ***262****.*

Empirical formula	C28 H42 O2
Formula weight	410.61
Crystallization solvent	CH_2Cl_2/hexanes
Crystal shape	blade
Crystal color	colourless
Crystal size	0.09 x 0.25 x 0.48 mm

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker APEX-II CCD	
Wavelength	0.71073 ≈ MoK	
Data collection temperature	100 K	
Theta range for 9010 reflections used in lattice determination	2.71 to 27.56∞	
Unit cell dimensions	a = 9.7419(3) ≈ b = 10.9851(4) ≈ c = 23.6134(8) ≈	α= 90∞ β= 90∞ γ = 90∞
Volume	2527.01(15) $≈^3$	
Z	4	
Crystal system	orthorhombic	
Space group	P 21 21 21 (# 19)	
Density (calculated)	1.079 g/cm^3	
F(000)	904	
Theta range for data collection	2.0 to 37.4∞	
Completeness to theta = 25.000∞	100.0%	
Index ranges	-14 ≤ h ≤ 16, -17 ≤ k ≤ 17, -37 ≤ l ≤ 40	
Data collection scan type	and scans	
Reflections collected	61255	
Independent reflections	11770 [R_{int}= 0.0700]	
Reflections > 2σ(I)	8166	
Average σ(I)/(net I)	0.0702	
Absorption coefficient	0.06 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9369	

Table A6.1 (cont.)

Structure Solution and Refinement

Primary solution method	dual
Secondary solution method	?
Hydrogen placement	difmap
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11770 / 0 / 439
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.53
Final R indices [$I>2\sigma(I)$, 8166 reflections]	R1 = 0.0571, wR2 = 0.0678
R indices (all data)	R1 = 0.1007, wR2 = 0.0719
Type of weighting scheme used	calc
Weighting scheme used	
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	0.4(4)
Extinction coefficient	0
Largest diff. peak and hole	0.35 and -0.31 e$\approx^{-3}$

Programs Used

Cell refinement	SAINT V8.18C (Bruker-AXS, 2007)
Data collection	APEX2_2012.4-3 (Bruker-AXS, 2007)
Data reduction	SAINT V8.18C (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2012 (Sheldrick, 2012)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Table A6.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for diol ***262****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
O(1)	7807(1)	6932(1)	5090(1)	17(1)
O(2)	5443(1)	7868(1)	5280(1)	21(1)
C(1)	7808(1)	7750(1)	5565(1)	15(1)
C(2)	8110(2)	9030(1)	5338(1)	21(1)
C(3)	8843(1)	7404(1)	6018(1)	17(1)
C(4)	9476(2)	8399(1)	6383(1)	26(1)
C(5)	10151(2)	7684(2)	6859(1)	32(1)
C(6)	10488(1)	6435(1)	6606(1)	24(1)
C(7)	10388(2)	5445(2)	7068(1)	35(1)
C(8)	10753(2)	4178(2)	6892(1)	37(1)
C(9)	10009(2)	3526(2)	6538(1)	36(1)
C(10)	8761(2)	4065(2)	6255(1)	30(1)
C(11)	9140(2)	5120(1)	5853(1)	21(1)
C(12)	9400(1)	6320(1)	6138(1)	17(1)
C(13)	11929(2)	6439(2)	6345(1)	29(1)
C(14)	10366(3)	2243(2)	6373(1)	53(1)
C(15)	6276(1)	7657(1)	5776(1)	16(1)
C(16)	5932(2)	6374(1)	5986(1)	25(1)
C(17)	5928(1)	8596(1)	6225(1)	17(1)
C(18)	6114(2)	8266(1)	6844(1)	27(1)
C(19)	6028(2)	9496(2)	7140(1)	35(1)
C(20)	5128(1)	10286(1)	6756(1)	26(1)
C(21)	5581(2)	11630(2)	6799(1)	37(1)
C(22)	4725(2)	12522(2)	6476(1)	42(1)
C(23)	4670(2)	12550(1)	5919(1)	38(1)
C(24)	5474(2)	11644(1)	5572(1)	31(1)
C(25)	4939(2)	10347(1)	5641(1)	24(1)
C(26)	5380(1)	9708(1)	6175(1)	18(1)
C(27)	3610(2)	10146(2)	6918(1)	39(1)
C(28)	3765(3)	13405(2)	5594(1)	58(1)

Table A6.3. Bond lengths [Å] and angles [°] for diol ***262***.

O(1)-H(1)	0.805(16)	C(19)-H(19A)	0.965(18)
O(1)-C(1)	1.4370(15)	C(19)-H(19B)	1.018(17)
O(2)-H(2)	0.785(18)	C(19)-C(20)	1.532(2)
O(2)-C(15)	1.4447(16)	C(20)-C(21)	1.544(2)
C(1)-C(2)	1.5345(18)	C(20)-C(26)	1.5297(19)
C(1)-C(3)	1.5172(18)	C(20)-C(27)	1.536(2)
C(1)-C(15)	1.5763(18)	C(21)-H(21A)	0.977(16)
C(2)-H(2A)	0.985(16)	C(21)-H(21B)	0.985(19)
C(2)-H(2B)	0.971(14)	C(21)-C(22)	1.496(3)
C(2)-H(2C)	0.961(15)	C(22)-H(22)	0.912(16)
C(3)-C(4)	1.5230(18)	C(22)-C(23)	1.317(2)
C(3)-C(12)	1.3393(17)	C(23)-C(24)	1.508(2)
C(4)-H(4A)	0.989(15)	C(23)-C(28)	1.500(3)
C(4)-H(4B)	1.009(16)	C(24)-H(24A)	1.005(18)
C(4)-C(5)	1.521(2)	C(24)-H(24B)	0.989(17)
C(5)-H(5A)	1.017(17)	C(24)-C(25)	1.526(2)
C(5)-H(5B)	0.992(16)	C(25)-H(25A)	0.956(14)
C(5)-C(6)	1.532(2)	C(25)-H(25B)	1.020(16)
C(6)-C(7)	1.543(2)	C(25)-C(26)	1.5056(19)
C(6)-C(12)	1.5371(19)	C(27)-H(27A)	1.034(18)
C(6)-C(13)	1.534(2)	C(27)-H(27B)	0.963(19)
C(7)-H(7A)	1.008(15)	C(27)-H(27C)	0.952(18)
C(7)-H(7B)	0.975(16)	C(28)-H(28A)	0.96(2)
C(7)-C(8)	1.496(2)	C(28)-H(28B)	0.97(2)
C(8)-H(8)	0.989(16)	C(28)-H(28C)	1.03(2)
C(8)-C(9)	1.318(2)		
C(9)-C(10)	1.508(2)	C(1)-O(1)-H(1)	106.8(11)
C(9)-C(14)	1.503(3)	C(15)-O(2)-H(2)	104.6(14)
C(10)-H(10A)	0.978(15)	O(1)-C(1)-C(2)	107.47(11)
C(10)-H(10B)	0.962(16)	O(1)-C(1)-C(3)	113.13(10)
C(10)-C(11)	1.544(2)	O(1)-C(1)-C(15)	101.87(10)
C(11)-H(11A)	0.969(14)	C(2)-C(1)-C(15)	110.59(11)
C(11)-H(11B)	0.999(13)	C(3)-C(1)-C(2)	110.41(11)
C(11)-C(12)	1.5015(19)	C(3)-C(1)-C(15)	112.98(10)
C(13)-H(13A)	0.948(16)	C(1)-C(2)-H(2A)	107.8(9)
C(13)-H(13B)	0.955(16)	C(1)-C(2)-H(2B)	111.5(8)
C(13)-H(13C)	0.997(17)	C(1)-C(2)-H(2C)	108.5(8)
C(14)-H(14A)	1.013(19)	H(2A)-C(2)-H(2B)	109.6(12)
C(14)-H(14B)	0.99(2)	H(2A)-C(2)-H(2C)	111.1(12)
C(14)-H(14C)	0.96(2)	H(2B)-C(2)-H(2C)	108.4(11)
C(15)-C(16)	1.5310(19)	C(1)-C(3)-C(4)	119.21(11)
C(15)-C(17)	1.5181(19)	C(12)-C(3)-C(1)	129.90(11)
C(16)-H(16A)	1.011(16)	C(12)-C(3)-C(4)	110.74(11)
C(16)-H(16B)	0.986(15)	C(3)-C(4)-H(4A)	111.0(9)
C(16)-H(16C)	0.969(15)	C(3)-C(4)-H(4B)	109.0(9)
C(17)-C(18)	1.5160(19)	H(4A)-C(4)-H(4B)	109.5(12)
C(17)-C(26)	1.3383(17)	C(5)-C(4)-C(3)	102.85(12)
C(18)-H(18A)	0.987(15)	C(5)-C(4)-H(4A)	112.8(9)
C(18)-H(18B)	0.984(16)	C(5)-C(4)-H(4B)	111.5(9)
C(18)-C(19)	1.524(2)	C(4)-C(5)-H(5A)	113.1(9)

Table A6.3 (cont.)

C(4)-C(5)-H(5B)	108.3(9)	O(2)-C(15)-C(16)	106.67(11)
C(4)-C(5)-C(6)	105.53(12)	O(2)-C(15)-C(17)	109.40(10)
H(5A)-C(5)-H(5B)	109.5(13)	C(16)-C(15)-C(1)	111.65(10)
C(6)-C(5)-H(5A)	112.6(9)	C(17)-C(15)-C(1)	112.85(10)
C(6)-C(5)-H(5B)	107.7(8)	C(17)-C(15)-C(16)	110.57(11)
C(5)-C(6)-C(7)	110.03(12)	C(15)-C(16)-H(16A)	107.9(8)
C(5)-C(6)-C(12)	101.88(11)	C(15)-C(16)-H(16B)	112.2(9)
C(5)-C(6)-C(13)	110.53(14)	C(15)-C(16)-H(16C)	108.1(9)
C(12)-C(6)-C(7)	114.03(13)	H(16A)-C(16)-H(16B)	109.2(12)
C(13)-C(6)-C(7)	110.13(12)	H(16A)-C(16)-H(16C)	109.2(13)
C(13)-C(6)-C(12)	109.99(12)	H(16B)-C(16)-H(16C)	110.2(13)
C(6)-C(7)-H(7A)	107.2(8)	C(18)-C(17)-C(15)	118.92(11)
C(6)-C(7)-H(7B)	105.2(9)	C(26)-C(17)-C(15)	130.37(12)
H(7A)-C(7)-H(7B)	106.7(12)	C(26)-C(17)-C(18)	110.58(12)
C(8)-C(7)-C(6)	116.39(13)	C(17)-C(18)-H(18A)	114.0(9)
C(8)-C(7)-H(7A)	109.7(8)	C(17)-C(18)-H(18B)	109.2(9)
C(8)-C(7)-H(7B)	111.2(9)	C(17)-C(18)-C(19)	102.90(12)
C(7)-C(8)-H(8)	117.3(9)	H(18A)-C(18)-H(18B)	105.4(12)
C(9)-C(8)-C(7)	123.48(16)	C(19)-C(18)-H(18A)	112.9(9)
C(9)-C(8)-H(8)	119.1(9)	C(19)-C(18)-H(18B)	112.6(8)
C(8)-C(9)-C(10)	120.73(15)	C(18)-C(19)-H(19A)	112.8(10)
C(8)-C(9)-C(14)	123.12(17)	C(18)-C(19)-H(19B)	107.9(10)
C(14)-C(9)-C(10)	116.11(18)	C(18)-C(19)-C(20)	105.16(13)
C(9)-C(10)-H(10A)	110.7(8)	H(19A)-C(19)-H(19B)	108.5(14)
C(9)-C(10)-H(10B)	110.0(9)	C(20)-C(19)-H(19A)	111.8(10)
C(9)-C(10)-C(11)	111.99(13)	C(20)-C(19)-H(19B)	110.5(10)
H(10A)-C(10)-H(10B)	103.8(13)	C(19)-C(20)-C(21)	109.76(13)
C(11)-C(10)-H(10A)	109.9(9)	C(19)-C(20)-C(27)	110.28(14)
C(11)-C(10)-H(10B)	110.1(9)	C(26)-C(20)-C(19)	101.77(11)
C(10)-C(11)-H(11A)	108.6(8)	C(26)-C(20)-C(21)	114.20(12)
C(10)-C(11)-H(11B)	107.2(8)	C(26)-C(20)-C(27)	109.69(13)
H(11A)-C(11)-H(11B)	107.9(11)	C(27)-C(20)-C(21)	110.79(13)
C(12)-C(11)-C(10)	115.05(13)	C(20)-C(21)-H(21A)	107.1(9)
C(12)-C(11)-H(11A)	109.8(8)	C(20)-C(21)-H(21B)	105.3(10)
C(12)-C(11)-H(11B)	108.1(8)	H(21A)-C(21)-H(21B)	104.7(14)
C(3)-C(12)-C(6)	111.04(12)	C(22)-C(21)-C(20)	115.65(14)
C(3)-C(12)-C(11)	128.09(12)	C(22)-C(21)-H(21A)	112.5(9)
C(11)-C(12)-C(6)	120.75(11)	C(22)-C(21)-H(21B)	110.7(10)
C(6)-C(13)-H(13A)	111.1(10)	C(21)-C(22)-H(22)	118.4(11)
C(6)-C(13)-H(13B)	110.5(9)	C(23)-C(22)-C(21)	123.13(16)
C(6)-C(13)-H(13C)	111.6(9)	C(23)-C(22)-H(22)	118.4(11)
H(13A)-C(13)-H(13B)	109.9(13)	C(22)-C(23)-C(24)	120.46(16)
H(13A)-C(13)-H(13C)	105.9(12)	C(22)-C(23)-C(28)	123.33(18)
H(13B)-C(13)-H(13C)	107.7(12)	C(28)-C(23)-C(24)	116.10(17)
C(9)-C(14)-H(14A)	110.7(10)	C(23)-C(24)-H(24A)	109.3(10)
C(9)-C(14)-H(14B)	110.9(11)	C(23)-C(24)-H(24B)	109.6(10)
C(9)-C(14)-H(14C)	111.9(12)	C(23)-C(24)-C(25)	112.35(14)
H(14A)-C(14)-H(14B)	105.5(15)	H(24A)-C(24)-H(24B)	104.7(14)
H(14A)-C(14)-H(14C)	107.3(15)	C(25)-C(24)-H(24A)	112.1(10)
H(14B)-C(14)-H(14C)	110.3(16)	C(25)-C(24)-H(24B)	108.4(9)
O(2)-C(15)-C(1)	105.36(10)	C(24)-C(25)-H(25A)	109.1(8)

Table A6.3 (cont.)

		C(20)-C(27)-H(27C)	111.4(10)
C(24)-C(25)-H(25B)	107.3(8)	H(27A)-C(27)-H(27B)	109.9(15)
H(25A)-C(25)-H(25B)	105.6(13)	H(27A)-C(27)-H(27C)	108.5(15)
C(26)-C(25)-C(24)	115.28(13)	H(27B)-C(27)-H(27C)	104.9(15)
C(26)-C(25)-H(25A)	108.5(8)	C(23)-C(28)-H(28A)	109.4(14)
C(26)-C(25)-H(25B)	110.6(9)	C(23)-C(28)-H(28B)	106.8(11)
C(17)-C(26)-C(20)	111.30(11)	C(23)-C(28)-H(28C)	109.9(10)
C(17)-C(26)-C(25)	127.83(12)	H(28A)-C(28)-H(28B)	111.7(16)
C(25)-C(26)-C(20)	120.72(11)	H(28A)-C(28)-H(28C)	110.4(17)
C(20)-C(27)-H(27A)	112.1(10)	H(28B)-C(28)-H(28C)	108.6(16)
C(20)-C(27)-H(27B)	109.8(11)		

Table A6.4. Anisotropic displacement parameters ($Å^2$ x 10^4) for diol ***262****. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	148(5)	184(5)	165(5)	-13(4)	16(4)	7(4)
O(2)	170(5)	245(5)	208(5)	-55(4)	-40(4)	47(4)
C(1)	133(6)	143(6)	169(6)	-7(5)	9(5)	4(5)
C(2)	201(8)	170(7)	251(8)	14(6)	48(7)	-10(6)
C(3)	123(6)	219(7)	161(6)	-31(5)	18(5)	7(5)
C(4)	186(7)	299(8)	292(8)	-123(6)	-23(6)	25(7)
C(5)	210(8)	520(10)	242(8)	-139(7)	-71(7)	72(8)
C(6)	167(7)	396(8)	164(7)	-14(6)	-15(6)	79(7)
C(7)	234(9)	631(12)	173(7)	81(7)	-1(7)	102(8)
C(8)	284(9)	541(11)	288(9)	234(8)	46(8)	158(8)
C(9)	337(9)	365(9)	366(9)	216(8)	109(8)	137(8)
C(10)	289(9)	277(8)	330(9)	98(7)	26(8)	55(7)
C(11)	226(8)	205(7)	187(7)	34(6)	-11(6)	61(6)
C(12)	130(6)	261(7)	131(6)	2(5)	21(5)	34(5)
C(13)	182(8)	415(10)	264(8)	0(8)	-20(6)	79(7)
C(14)	528(13)	376(11)	696(16)	219(10)	35(12)	193(10)
C(15)	119(6)	178(6)	194(7)	26(5)	-3(5)	16(5)
C(16)	157(8)	215(8)	391(9)	55(7)	63(7)	-13(6)
C(17)	114(6)	236(7)	160(6)	30(5)	14(5)	3(5)
C(18)	240(8)	375(9)	186(7)	84(6)	36(6)	79(7)
C(19)	361(10)	525(11)	153(7)	-13(7)	-4(7)	130(9)
C(20)	235(8)	346(8)	183(7)	-45(6)	24(6)	89(7)
C(21)	397(10)	425(10)	284(9)	-176(8)	-9(8)	63(8)
C(22)	486(11)	288(9)	487(11)	-176(8)	3(10)	115(8)
C(23)	470(11)	200(8)	466(11)	-64(7)	-14(9)	82(7)
C(24)	408(10)	235(8)	289(9)	31(6)	16(8)	68(7)
C(25)	297(9)	216(7)	203(7)	-30(6)	-45(6)	100(7)
C(26)	133(6)	244(7)	159(6)	-15(5)	-12(5)	14(6)
C(27)	309(10)	506(12)	366(11)	-18(9)	117(8)	128(9)
C(28)	779(17)	299(10)	669(16)	27(11)	5(14)	248(12)

Table A6.5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$ x 10^3) for diol ***262***.

	x	y	z	U_{iso}
H(1)	854(2)	700(1)	494(1)	29(5)
H(2)	584(2)	754(2)	503(1)	43(6)
H(2A)	745(2)	920(1)	503(1)	28(4)
H(2B)	802(1)	964(1)	563(1)	21(4)
H(2C)	904(2)	905(1)	520(1)	19(4)
H(4A)	877(2)	897(1)	652(1)	28(4)
H(4B)	1018(2)	886(1)	615(1)	30(4)
H(5A)	1099(2)	811(1)	702(1)	45(5)
H(5B)	946(2)	756(1)	716(1)	30(4)
H(7A)	942(2)	546(1)	722(1)	26(4)
H(7B)	1098(2)	573(1)	737(1)	34(5)
H(8)	1163(2)	384(1)	704(1)	36(4)
H(10A)	825(2)	344(1)	605(1)	25(4)
H(10B)	812(2)	434(1)	654(1)	28(4)
H(11A)	842(1)	521(1)	557(1)	18(4)
H(11B)	1000(1)	488(1)	565(1)	15(3)
H(13A)	1210(2)	570(1)	615(1)	30(4)
H(13B)	1204(2)	712(1)	610(1)	29(4)
H(13C)	1266(2)	650(1)	664(1)	36(5)
H(14A)	959(2)	167(2)	647(1)	59(6)
H(14B)	1049(2)	217(2)	596(1)	54(6)
H(14C)	1117(2)	196(2)	657(1)	61(6)
H(16A)	611(2)	579(1)	566(1)	29(4)
H(16B)	649(2)	614(1)	632(1)	25(4)
H(16C)	496(2)	635(1)	608(1)	31(4)
H(18A)	698(2)	783(1)	692(1)	29(4)
H(18B)	538(2)	771(1)	696(1)	26(4)
H(19A)	566(2)	944(1)	752(1)	45(5)
H(19B)	700(2)	984(2)	716(1)	44(5)
H(21A)	655(2)	1166(1)	669(1)	26(4)
H(21B)	557(2)	1182(2)	721(1)	49(5)
H(22)	418(2)	1304(1)	668(1)	40(5)
H(24A)	648(2)	1171(2)	567(1)	44(5)
H(24B)	542(2)	1187(1)	517(1)	40(5)
H(25A)	522(1)	987(1)	532(1)	21(4)
H(25B)	389(2)	1038(1)	562(1)	37(5)
H(27A)	332(2)	924(2)	694(1)	56(6)
H(27B)	344(2)	1055(2)	727(1)	52(6)
H(27C)	303(2)	1054(2)	665(1)	40(5)
H(28A)	328(2)	1393(2)	586(1)	79(7)
H(28B)	436(2)	1386(2)	534(1)	50(6)
H(28C)	307(2)	1292(2)	535(1)	58(6)

Table A6.6. Hydrogen bonds for diol ***262*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.805(16)	1.927(17)	2.7217(14)	169.1(16)
O(2)-H(2)...O(1)	0.785(18)	2.035(17)	2.5617(14)	124.4(17)