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Three new dihydro- β -agarofuran sesquiterpenes from the seeds of *Maytenus boaria*

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A brief notes on AIM Analysis

AIM (an acronym for the "Atoms In Molecules" theory, Bader, 1990) interprets chemical bonding in terms of shared (covalent bonds) or closed-shell (H-bonding, ionic bonding, van der Waals, etc.) interactions. The relevant parameters used to characterize the attractive bonding character of short contacts are the electron density ($\rho(r)$), its gradient vector ($\nabla\rho(r)$), its Laplacian ($\nabla^2\rho(r)$), the kinetic, potential and total energy densities in the region of the BCP ($G(r)$, $V(r)$, $E(r)$).

In some seminal papers on the subject (Bader, 1990, 2009) the author discloses two fundamental concepts on which the theory is based: viz., the "Bonding Path" (BP), a line linking atomic nuclei along which the charge density has a maximum with respect to any lateral shift and the "Bond Critical Point" (BCP), an eventual minimum along these lines which provide an indicator of interatomic interaction. In addition, the sign and magnitude of $\rho(r)$, $\nabla^2\rho(r)$ at the BCP characterizes the interaction type. The interactions are considered as "shared" when $\nabla^2\rho(r) < 0$ (viz., electronic charge concentrated at the BCP) or of the "closed-shell" type when $\nabla^2\rho(r) > 0$ (viz., electronic charge drifted away from the interatomic surface, towards the nuclei). In this latter case, $\rho(r)$ is relatively low in value, and the fact that $\nabla^2\rho(r) > 0$, a result of the (positive) curvature of $\rho(r)$ along the interaction line or bond path (BP) due to the exclusion principle forcing a relative depletion of charge in the atomic surface. AIM has been a matter of debate on theoretical grounds (viz., Haaland *et al.*, 2004; Poater *et al.*, 2006; Krapp & Frenking, 2007 vs. Bader, 2009) and still goes on being a controversial issue (Dunitz, 2015 vs. Thakur *et al.*, 2015; Lecomte *et al.*, 2015). Even if now accepted as an extremely valuable tool, some critical viewpoints concerning the application of the method when "absolute" AIM

values are analyzed have been raised (Spackman, 2015); nevertheless, its use for "relative" comparisons (as in the present approach) is steadily gaining generalized acceptability (Wang *et al.*, 2016, etc.)

References

- Bader, R. F. W. (1990). In *Atoms in Molecules: a Quantum Theory*. Oxford University Press.
- Bader, R. F. W. (2009). *J. Phys. Chem. A*, 113, 10391--10396.
- Dunitz, J. D. (2015). *IUCrJ*, 2, 157--158.
- Haaland, A., Shorokhov, D. J. & Tverdova, N. V. (2004). *Chem. Eur. J.*, 10, 4416--4421.
- Krapp, A. & Frenking, G. (2007). *Chem. Eur. J.*, 13, 8256--8270.
- Lecomte, C., Espinosa, E. & Matta, Ch. F. (2015). *IUCrJ*, 2, 161--163.
- Poater, J., Solá, M. & Bickelhaupt, F. M. (2006). *Chem. Eur. J.*, 12, 2902-2905.
- Thakur, T. S., Dubey, R. & Desiraju, G. R. (2015). *IUCrJ*, 2, 159--160.
- Spackman, M. (2015). *Cryst. Growth Des.* 15, 5624--5628.
- Wang, G., Chen, Z., Xu, Z., Wang, J., Yang, Y., Cai, T., Shi, J. & Zhu, W. (2016). *J. Phys. Chem. B*, 120, 610--620.
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Table ST1

*¹H and ¹³C NMR data in CD₂Cl₂. Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz.*

(Compounds III and IV at 600 MHz and compound II at 500 MHz.)

Structure II					
pos.	¹³ C	¹ H	COSY	HMBC	NOESY
1	72.7	5.19 (dd, 12.0, 4.1)	2 β	9 (w), 10, 15, 1C	2 β , 9, 3B, 5B
2	23.3	1.48 (m, β) 1.84 (m)	1		1
3	39.1	1.65 (m, α) 1.83 (m)			8 (w), 9 (w)
4	70.7	-			
4-OH	-	2.84 (br q, 1.1)	14	4, 5, 14	
5	92.4	-			
6	76.0	6.09 (s)		5, 7 (w), 8, 10, 11, 1A	7, 8 (w), 9, 12, 14
7	56.0	2.47 (br d, 3.2)	8		6, 8, 12, 13 (w)
8	74.4	4.33 (dd, 5.8, 3.0)	7, 8-OH	6, 10	3 α (w), 6 (w), 7, 9, 13
8-OH	-	2.70 (d, 3.3)	8	7, 8, 9	
9	79.3	4.85 (br s)		5, 7, 8, 10, 1B	1, 3 α (w), 6, 8
10	50.6				
11	83.5	-			
12	30.2	1.53 (s)		7, 11, 13	6, 7, 13, 3A
13	25.4	1.44 (s)		7, 11, 12	7 (w), 8, 12, 3B
14	23.9	1.32 (br s)	4-OH	3, 4, 5	3 α , 6, 15, 3A (w), 5A (w)
15	19.8	1.51 (s)		1, 5, 9, 10	14
1A	162.4				

2A	119.8				
3A	110.0 ^a	6.81 (dd, 1.9, 0.8)		2A, 4A, 5A	12, 14 (w)
4A	144.3 ^b	7.45 (m)			
5A	149.4	8.16 (dd, 1.6, 0.7)		3A, 2A, 4A	14 (w)
1B	162.1				
2B	118.8	-			
3B	109.9 ^a	6.73 (dd, 1.9, 0.8)		2B, 5B, 4B	1, 13
4B	144.2 ^b	7.45 (m)			
5B	149.1	8.02 (dd, 1.5, 0.8)		2B, 3B, 4B	1
1C	170.2				
2C	19.8	1.69 (s)		1C	

^{a,b} or reversed

Structure III					
	pos.	¹³ C	¹ H	HMBC	NOESY
	1	72.7	5.23 (1H, dd, 12.1, 4.0)	2 (w), 3 (w), 10, 15, OC(O)Me	2", 4", 2 α /3 α , 9
	2	23.6	1.46 (1H, m) α : 1.85 (1H, m)		1?
	3	39.1	1.66 (1H, m) α : 1.85 (1H, m)	2, 4, 5	1?
	4	70.8	-		
	5	91.7	-		
	6	80.1	5.52 (1H, br s)	5, 7, 8, 10, 11, 6-OC(O)	4 (w), 7, 8 β , 14, 15
	7	49.2	2.31 (1H, t, 3.1)		6, 8 α , 8 β
	8	32.0	α : 2.20 (1H, dd, 16.3, 3.1) 2.49 (1H, ddd, 16.4, 7.1, 3.5)	6, 7, 9, 10 6, 7, 11	7, 9, 12 6, 7, 9
	9	72.7	4.96 (1H, d, 6.6)	5, 8, 10, 15, 9-OC(O)	1, 8 α , 8 β , 15
	10	51.5	-		

11	84.5	-		
12	25.8	1.50 (3H, s)	11, 13	8
13	29.7	1.51 (3H, s)	11, 12	
14	23.9	1.31 (3H, s)	3, 4, 5	2', 4' (w), 6
15	19.7	1.38 (3H, s)	1, 5, 9, 10	6, 9
AcO	170.2	-		
	20.9	1.72 (3H, s)	1-OC(O)	
9- OC(O)Fu	162.0	-		
	148.7	8.02 (1H, dd, 1.6, 0.8, H-2'')		1
	119.4	-		1
	110.0	6.74 (1H, dd, 1.9, 0.8, H-4'')		
	144.0	7.45 (1H, t, 1.7, H-5'')		
6- OC(O)Fu	162.4	-		
	149.4	8.18 (1H, dd, 1.6, 0.7, H-2')		14
	119.8	-		14
	109.9	6.83 (1H, dd, 1.9, 0.8, H-4')		
	144.3	7.47 (1H, t, 1.7, H-5')		
6-Bz				

Structure IV				
pos.	¹³ C	¹ H	HMBC	NOESY
1	72.7	5.25 (1H, dd, 12.1, 3.9)	10, 15	2" (w), 4" (w), 2α/3α, 9
2	23.7	1.49 (1H, m) α: 1.87 (1H, m)		1?
3	39.1	1.68 (1H, dt, 12.8, 3.2) α: 1.87 (1H, m)		1?
4	70.8	-		
5	91.7	-		
6	80.8	5.62 (1H, br s)	5 (w), 8, 10, 11, 6-OC(O)	8β, 7, 9, 13, 14, 15
7	49.2	2.34 (1H, t, 3.1)	8, 9	6, 8β, 8α, 13
8	32.1	α: 2.22 (1H, dd, 16.3, 3.1) 2.54 (1H, ddd, 16.3, 7.0, 3.5)	6, 7, 9, 10 6,7,11	7, 9, 12 6, 7, 9
9	72.7	4.98 (1H, d, 6.7)	5, 7, 10, 8, 15, 9-OC(O)	1, 6, 8α, 8β, 15
10	51.6	-		
11	84.5	-		
12	25.8	1.50 (3H, s)	11, 13	8α
13	29.7	1.52 (3H, s)	11, 12	6, 7, <i>o</i> -Ph
14	23.9	1.33 (3H, s)	3, 4, 5	6
15	19.7	1.40 (3H, s)	1, 5, 9, 10	6, 9
AcO	170.2 20.9	- 1.72 (3H, s)	1-OC(O)	
9-OC(O)Fu	162.0 148.7 119.4 110.0 144.0	- 8.03 (1H, dd, 1.5, 0.7) - 6.75 (1H, dd, 1.9, 0.7) 7.46 (1H, t, 1.7)		

6- OC(O)Fu				
6-Bz	166.1 130.4 130.3 128.8 133.5	- - 8.21 (2H, dd, 8.3, 1.3, <i>o</i> -H) 7.48 (2H, t, 7.7, <i>m</i> -H) 7.59 (1H, tt, 7.5, 1.2, <i>p</i> -H)	OC(O)Ph, <i>p</i> -Ph, <i>o</i> -Ph	13