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CARBON-13 CHEMICAL SHIFTS IN TRICYCLO[6.3.0.$0^{3,7}$]UNDECANES (LINEARLY FUSED TRICYCLOPENTANOIDS)

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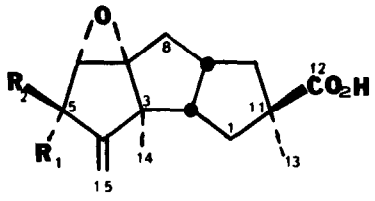
The preceding paper describes some of our work directed toward the development of the diyl trapping reaction (DTR) as an efficient synthetic route to linearly fused tricyclopentanoid systems.[1] Because of the interest expressed in these systems by numerous workers[2] and because of the paucity of CMR data, we thought it reasonable to publish the results of our analysis of the CMR data of a variety of functionalized tricyclopentanoids. This work should be of benefit to other researchers dealing with this same class of compounds.

ASSIGNMENTS

The assignments are based upon four factors: (1) chemical shifts (relative to the central line of $CDCl_3$ at 1538 Hz downfield from TMS); (2) established α, β, and γ effects;[3] (3) off-resonance proton decoupling experiments; and (4) analogy with the assignments made in simpler systems[3]--especially the bicyclo(3.3.0)octanes of Whitesell.[4] Throughout, we have attempted to maintain consistency with the existing literature as well as internal consistency within the collection of data.

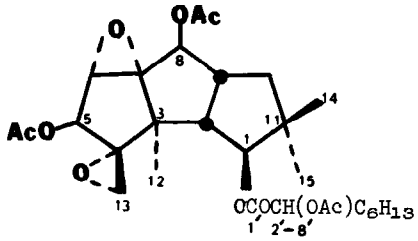
In the discussion which follows, attention will be directed toward the analysis of tricyclopentanoid 3. Assignments for the other compounds were made in a similar fashion; the pertinent data can be found in Table I.

The CMR spectrum of 3, which was shown by PMR and chemical methods to possess the cis, anti stereochemistry shown,[1] displayed the required thirteen signals; an off-resonance decoupling experiment afforded three singlets, four doublets, four triplets and two quartets. The singlet resonances were readily assigned as belong to C_{10} (C=O, 220.4), C_7 (vinyl, 161.8), and C_8 (40.9). (Note the numbering system shown in Table I.) Of the four doublets, that at 116.0 was assigned to the vinyl carbon C_6. Three pieces of information were used to assign the three remaining doublets to the ring-junction carbons C_2, C_3, and C_9. First, Whitesell has shown that a bridgehead carbon adjacent to a carbonyl in a bicyclo(3.3.0)octane system experiences a deshielding effect of 9 ppm (+9) relative to the saturated hydrocarbon, whereas a bridgehead carbon β to the carbonyl experiences a shielding effect of 2.1 ppm (-2.1).[4] Second, Whitesell has also shown that an allylic bridgehead carbon in a (3.3.0) system is deshielded by 9.3 ppm (+9.3).[4] These two facts in conjunction with the well-established β-methyl deshielding effect,[3] allowed us to assign C_2 (46.9, β to carbonyl), C_3 (55.2, allylic), and C_9 (66.3, α to carbonyl and β to two CH_3 groups). The methylene carbons C_1 (26.8, β to carbonyl; c.f. the β-C of cyclopentanone at 22.3), C_4 (32.7), C_5 (36.1), and C_{11} (39.6, α to carbonyl; c.f. the α-C of cyclopentanone at 37) were assigned on the basis of established α and β effects.[3] Finally, the remaining two quartets of 24.1 and 28.1 obviously correspond to the geminal carbons C_{12} and C_{13}.



1a, R_1 = H, R_2 = OH

1b, R_1 = R_2 = O



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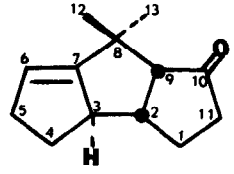

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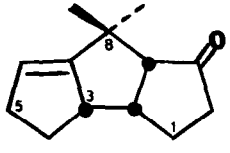

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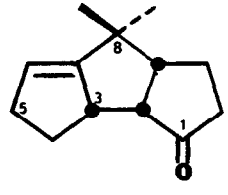

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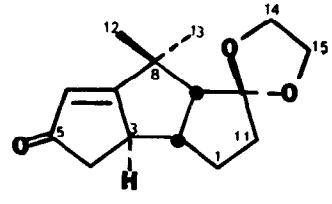

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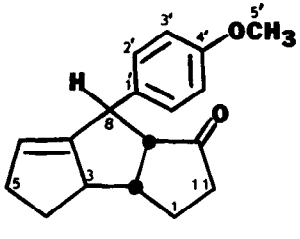

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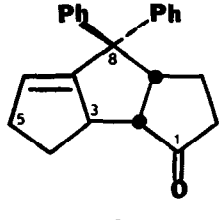

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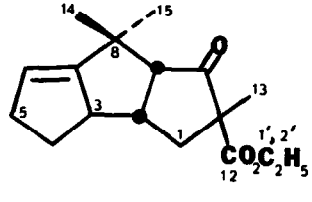

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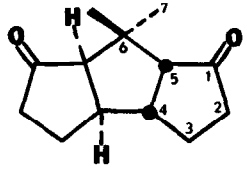

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TABLE I. SUMMARY OF CMR DATA FOR TRICYCLOPENDANOIDS 1-10.[a]

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_1'	C_2'	C_3'	C_4'	C_5'
1a[b]	36.6	48.5	48.5	158.3	74.0	63.7	75.4	30.0	39.2	46.3	53.2	183.7	24.2	17.0	111.8					
1b[b]	36.9	49.6	46.4	152.8	197.8	60.9	76.5	29.8	39.3	46.1	53.3	183.8	24.2	17.4	120.5					
2[c,e]	80.8	51.0	47.1	64.5	71.7	60.9	73.5	72.7	41.3	37.6	43.9	13.1	44.9	26.5	21.4	170.0	72.4	31.3	25.2	28.8
3	26.8	46.9	55.3	32.7	36.1	116.0	161.8	40.2	64.5	220.4	39.6	28.1*	24.1*							
4	24.9	41.9	51.8	31.9	37.0	117.3	160.0	39.4	66.8	221.4	38.4	25.0*	22.3*							
5	221.2	56.0	50.0*	31.8	35.3	119.2	158.4	40.5	49.8*	24.4	40.0	27.3*	20.1*							
6	27.0	45.0	49.9	43.4	210.4	120.3	198.6	41.3	60.3	118.0	35.5	28.1*	22.5*	64.9*	62.9*					
7	23.4	46.8	55.6	31.1	35.3	120.4	156.8	45.3	65.2	220.8	37.0					135.9	128.6	113.5	157.8	54.9
8[f]	220.0	62.5	47.2	27.7	34.8	‡	158.0	60.0	55.3	34.8[d]	40.3									
9	44.4	43.3	55.2	34.3	35.4	116.7	161.9	40.5	64.6	215.3	60.6	172.3	18.9	26.6*	23.8*	61.2	13.9			
10	219.3	39.5	28.1	48.9	63.4	47.6	27.5													

*: Assignments may be reversed.

‡: Chemical shift is not known; buried under aromatics.

a: The chemical shifts for compounds 1a and 1b are relative to TMS while those for the other compounds are relative to $CDCl_3$.

b: Note reference 2i.

c: Note reference 2j.

d: This carbon has been deshielded by the C_8 phenyl groups (cf, C_1 of compounds 3, 4 and 7 as well as C_{10} of compound 5).

e: $C_6' = 31.5$, $C_7' = 22.5$, $C_8' = 14.0$, $\underline{CH_3}CO(20.5, 20.5, 20.9)CH_3\underline{CO}$ (170.0, 170.5, 170.8).

f: aromatics = 125-130, 143-146

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1. R. D. Little, A. Bukhari and M. G. Venegas, Tetrahedron Lett., this issue (1978).

2. See inter alia (a) H. Hashimoto, K. Tsuzuki, F. Sakan, H. Shirahama, and T. Matsumoto, ibid., 3745 (1974); (b) P. T. Lansbury, N. Y. Wang and J. E. Rhodes, ibid., 2053 (1972); (c) T. Takeuchi, S. Takahashi, H. Iinuma and H. Umezawa, J. Antibiotics, 24, 631 (1971); (d) K. Hayano, Y. Ohfune, H. Shirahama and T. Matsumoto, Tetrahedron Lett., 1991 (1978); (e) T. Gebreysus, C. M. Beechan, C. Djerassi, and M. Kaisin, ibid., 1671 (1978); (f) K-I. Hirao, S. Unno and H. Miura, Chem. Pharm. Bull., 25 (12), 3354 (1977); (g) J. S. H. Kueh, M. Mellos, and G. Pattenden, J.C.S., Chem. Comm., 5 (1978); (h) P. E. Eaton, C. Giordano, G. Schloemer and U. Vogel, J. Org. Chem., 41, 2238 (1976); (i) G. Mellows and T. C. Feline, J.C.S., Chem. Comm., 63 (1972); (j) M. Tanabe and K. T. Suzuki, Tetrahedron Lett., 2271 (1974).

3. J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, pp.57, 67 and 84.

4. J. K. Whitesell and R. S. Mathews, J. Org. Chem., 42, 3878 (1977).

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