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THE MOLECULAR STRUCTURE OF DAUCYL D,L-ALANINATE HYDROBROMIDE

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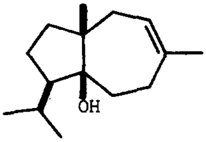
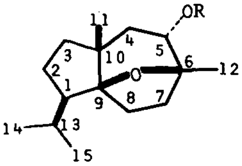
In 1962, the first proposal was made regarding the stereochemistry of carotol(I), daucol(II), and daucene(III), three chemically interrelated compounds from *Daucus carota*, the common carrot; a *trans* ring juncture was suggested for carotol.[1] Two years later, configurations at all three asymmetric centers were proposed as shown in I-III, with a *cis* ring juncture for carotol(I).[2] We have now verified the relative configurations shown in I-III *via* an X-ray study on a crystal of daucyl D,L-alaninate hydrobromide(IV).

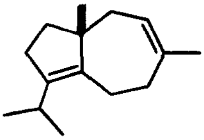


I



II R = H

IV $R = (CO)CH(CH_3)\overset{\oplus}{N}H_3\ \ Br^{\ominus}$



III

This derivative was synthesized from daucol(II) and phthaloyl-L-alaninyl chloride with heating at 80° in dimethylformamide for 1 hr, a treatment which unfortunately caused epimerization α to the carbonyl group.[3] After removal of the phthaloyl group with hydrazine, the beautifully crystalline hydrobromide, mp 234-5°, was formed. Oscillation and Weissenberg photographs indicated the space group to be $P2_1$ with cell dimensions a = 25.03(3), b = 10.63(3), and c = 7.25(3)Å, and β = 90.02(2)°. These data, coupled with a result of 1.28 g/cm^3 for the crystal density, indicated the asymmetric unit to contain two molecules of the derivative, warning that epimerization might have occurred. However, since this was the only heavy atom derivative known for daucol(II), and since the presence of *two* bromines in the asymmetric unit would eliminate the "ghost" molecule problem which usually plagues this space group, it was decided to proceed with the crystal structure analysis of this derivative.

Intensity data was collected around the b and c axes using a Supper automatic diffractometer, and was interlayer scaled by least squares to give 1183 independent observed reflections; large temperature factors in the y direction resulted in the loss of the majority of the reflections with high b orders. The bromines were readily located on a 3-dimensional sharpened Patterson map, and refinement of their coordinates gave an R of 45. With considerable difficulty, all of the atoms in one molecule were located in the first Fourier map, and in a Fourier including this molecule, the second molecule was located. R, 34 at this point, was lowered only to 31 by isotropic refinement. However, anisotropic refinement permitted the temperature factors in the y direction to increase considerably, and lowered R to 13.7. The resulting coordinates are shown in Table I.[4]

Table I. Fractional Coordinates with Estimated Standard Deviations

	Upper Molecule			Lower Molecule		
	x/a	y/b	z/c	x/a	y/b	z/c
Br	.0130(2)	-.2505	.442(1)	.1232(2)	-.871(2)	.080(1)
O-1	.231(1)	-388(4)	.160(3)	.362(1)	-.734(5)	.342(4)
O-2	.097(1)	-.371(5)	-.012(5)	.234(1)	-.821(3)	.500(3)
O-3	.089(1)	-.517(4)	-.259(4)	.200(1)	-.684(3)	.695(3)
N	-.012(1)	-.462(7)	-.242(4)	.106(1)	-.743(5)	.693(4)
C-1	.304(1)	-.245(7)	.071(5)	.450(1)	-.808(6)	.473(6)
C-2	.315(2)	-.173(6)	-.104(7)	.458(1)	-.837(8)	.677(6)
C-3	.259(2)	-.148(5)	-.198(5)	.406(2)	-.878(7)	.771(6)
C-4	.174(1)	-.271(5)	-.139(5)	.314(2)	-.854(9)	.679(6)
C-5	.158(1)	-.378(5)	-.031(7)	.288(1)	-.752(8)	.526(8)
C-6	.179(1)	-.392(6)	.182(6)	.308(1)	-.800(7)	.318(6)
C-7	.167(1)	-.270(5)	.265(5)	.314(2)	-.926(6)	.284(8)
C-8	.217(2)	-.177(5)	.200(5)	.371(2)	-.956(6)	.376(6)
C-9	.250(2)	-.281(5)	.085(6)	.386(1)	-.832(8)	.454(6)
C-10	.236(1)	-.276(6)	-.135(5)	.372(1)	-.794(5)	.666(5)
C-11	.259(1)	-.375(7)	-.217(5)	.380(2)	-.647(6)	.713(6)
C-12	.162(1)	-.496(5)	.302(6)	.286(1)	-.698(8)	.177(6)
C-13	.343(1)	-.343(6)	.115(5)	.476(1)	-.713(11)	.394(5)
C-14	.341(2)	-.384(7)	.319(6)	.469(1)	-.694(10)	.170(6)
C-15	.398(1)	-.310(6)	.061(7)	.536(1)	-.737(11)	.428(8)
C-16	.067(4)	-.459(9)	-.109(11)	.187(2)	-.775(6)	.589(5)
C-17	.012(2)	-.412(8)	-.069(9)	.139(1)	-.827(12)	.561(8)
C-18	.002(2)	-.561(6)	-.065(8)	.143(2)	-.983(9)	.574(7)

As can be seen in Fig. 1, which shows the two molecules in an asymmetric unit, the X-ray results fully confirm the relative configurations forwarded in 1964 by Levisalles and Rudler.[2] No attempt was made to determine the absolute configuration crystallographically, but the verification of the other structural features increases the likelihood that the absolute configurations shown, based on the circular dichroism studies of the French workers,[2] are correct.

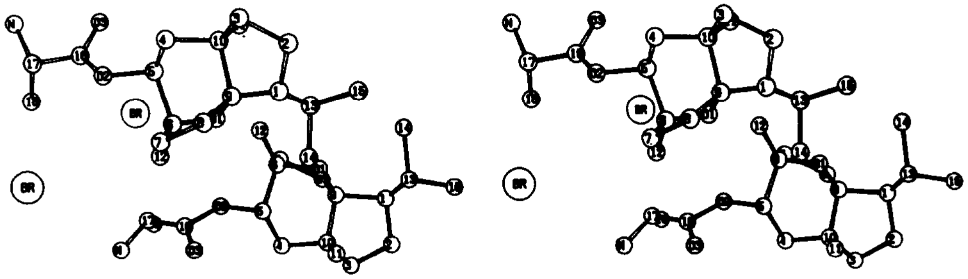


Fig. 1. Left and Right Eye Stereo Views of an Asymmetric Unit, Looking Down the b Axis with the a Axis Horizontal and the c Axis Vertical.

The nitrogens can readily be distinguished from the alanyl methyl carbons by the hydrogen bonding which they undergo (both nitrogens also give larger peaks than these carbons, but this seems a much less reliable basis on which to choose); the nitrogen in the upper molecule in the Figure is hydrogen bonded to three bromide ions, and the other nitrogen to two bromide ions and the carbonyl oxygen of the upper molecule. The structure is layered, with alternate sheets of polar groups and non-polar groups in the yz plane.

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References

1. M. Souček, Coll. Czech. Chem. Comm., 27, 2925 (1962).
2. J. Levisalles and H. Rudler, Bull. Soc. Chim. France, 8, 2020 (1964).
3. See the following paper for a discussion of the use of this type of derivative.
4. Reflection data can be obtained from the Ph.D. thesis of C.D.G., University of Arizona, 1967; R was 19.6 at the time this thesis was written.