

**Drunkard** : Will I ever, ever get home again?

**Polya** : You can't miss, just keep going and stay out of 3D!

From Gerold Adam and Max Delbrück. Reduction in dimensionality of biological diffusion processes, in Structural Chemistry and Molecular Biology, (Edns) N Davidson and A Rich, W H Freeman, San Francisco, 1968.

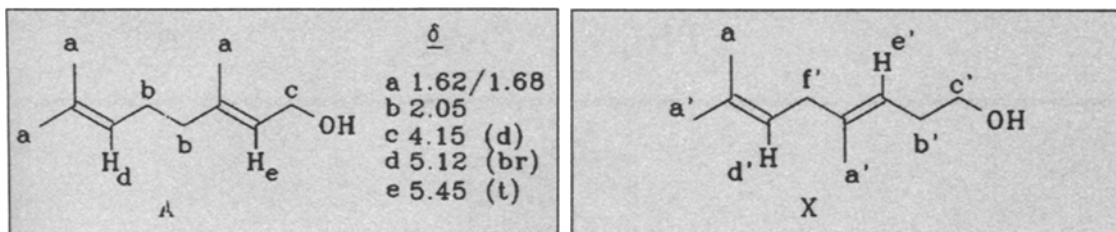
what happens. Given *any* point, however far away from the origin, the probability that the particle will eventually reach that point is 1. Or, putting it another way, the chance that it *never* reaches the chosen point is 0. Indeed, with probability 1 it returns infinitely often to the point. The motion is smeared into 'uniform' fluctuations over the whole line.

So, if you are lost in a 1-dimensional desert, and go East or West by repeatedly tossing a coin, you will eventually reach any point you wish. But there's a price to pay: it takes a very long time. In fact the time is so long that the *average* time between successive returns to the same point is infinite. If you perform a similar random walk, but now move in the plane, with probabilities 1/4 of going East, West, North, or South, the results are very similar. If you are lost in a 2-dimensional desert, you still expect to reach every point eventually by moving at random in each of the four directions. What about three dimensions? Now you can go up and down as well, with all transition probabilities being 1/6. In 1921 George Pólya proved that the results are very different: there is a non-zero probability (about 0.65) that you *never* reach your chosen position, however long you walk.

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### ! Distinguishing Isomers by NMR Analysis

Our readers may recall that in the January, 1996 issue of *Resonance* NR Krishnaswamy discussed in detail how the structure of a natural product may be determined through a combination of chemical and spectroscopic methods. In particular, the use of  $^1\text{H-NMR}$  spectral analysis for the assignment of the structure of geraniol (A) was illustrated (page 60, *Scheme 2*). S V Eswaran (St. Stephen's College, New Delhi) has asked if the NMR data provided are consistent with any other structure (for example, X). This is an interesting question. It is highly desirable to show that the spectral data support the proposed structure and at the same time are inconsistent with alternative structures.



Even though structure X satisfies the general conclusions suggested by the NMR analysis such as the presence of three methyl groups, two olefinic hydrogens etc., the precise position of the NMR signals ( $\delta$  values) and the multiplicities are very different for these two isomeric molecules. Specifically, the  $\text{CH}_2\text{OH}$  signal in compound X would appear as a triplet, and not as a doublet as is observed. Similarly, signal  $c'$  would be expected to be upfield when compared with  $c$  (since  $c$  is allylic and next to the OH group). Signal  $f'$  would also be expected to be more downfield than  $b$  (as it is doubly allylic) and would appear as a doublet.

This discussion in fact illustrates that even two closely related structures can often be distinguished by NMR spectroscopy, through a careful analysis of the positions ( $\delta$  values) and the multiplicities (singlet, doublet etc.). [There are further complications possible here because of the presence of the OH group, but we have assumed that the OH hydrogen is NOT coupled to the hydrogens on the neighbouring carbon atom. We have also ignored long range (allylic) couplings].

There were a few errors in the  $\delta$  values reported for geraniol in the original article. The corrected values are shown here. However, these errors do not affect the general conclusions. There was, on the other hand, a more serious typographical mixup of the names of geraniol/geranial and nerol/neral towards the end of this article. This sentence should read: "However, upon oxidation, both geraniol and nerol give a mixture of aldehydes (citral) which is an inseparable mixture of geranial and neral". We regret the confusion caused by these errors.