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^{13}C AND PROTON NMR STUDIES RELATED TO
THE PREBIOTIC ORIGIN OF MOLECULAR ASYMMETRY

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¹³C and Proton NMR Studies Related to the Prebiotic Origin of Molecular Asymmetry

Optical selectivity is one of life's most distinctive characteristics. Outside of biology, weak interactions can also distinguish between left and right handedness.¹ It is therefore attractive to invoke the parity violation in weak interactions as the explanation of the origin of asymmetry in living systems.^{2,3} The experimental difficulties are numerous^{4,5} and in some cases negative results were obtained.⁶⁻¹⁰

In other experiments, however, a stereoselective response of the optical isomers was found when they were bombarded by β -rays^{10,11}, or by spin polarised positrons¹² or electrons.¹³ Recently, there has been reported a preferential crystallisation of the "unnatural" L(-)-sodium ammonium tartrate from a saturated solution of the racemate in the presence of ³²P beta particles.¹⁴ In order to observe the suggested interactions between the betas and the optically active molecules, we have recently made proton-NMR (PMR) and ¹³C-NMR measurements on tartaric acid solutions containing beta-decaying isotopes. These measurements have led to the interesting results that are reported here.

The D- and L-tartaric acids were purchased from Aldrich Chemical Co. and recrystallised several times before use.¹⁵ The optical purity of the isomers was checked by their specific rotations (except for the sign of rotation, these were identical within 0.01°) and circular dichroism spectra (mirror images of each other). The carrier-free radioactive isotopes used as beta and/or positron sources were New England Nuclear or ICN products. The solvent (D₂O) and isotope solutions were mixed and treated with a

Chelex-100 ion exchange resin prior to sample preparation to remove the paramagnetic ion impurities.¹⁶ Rigorous precautions were also taken to clean the NMR tubes from possible paramagnetic as well as optically active impurities. The probes were degassed and sealed before the NMR measurements.

PMR spectra of 0.2 M solutions were recorded on a Varian HR-220 instrument. Two Varian XL-100 spectrometers, both capable of Fourier transform operation, were used in the ¹³C-NMR study; the probes contained 3 M D- or L-tartaric acid. All the ¹³C NMR spectra were broadband ¹H noise decoupled. The 90° resonance frequency pulses had a repeat time of 60 seconds, and the results of several scans were averaged. The integrated peak areas were taken as a measure of resonance intensity.

Tartaric acid has a single peak in its PMR spectrum. No difference was found in the position or intensity of this peak between irradiated and control samples, nor was any difference observed among the optical isomers. This result is certainly expected since the hydrogen atoms are not centres of asymmetry.

However, the hydroxyl-containing carbons of tartaric acid are centres of asymmetry, and the ¹³C-NMR spectra indeed reveal differences. There are two peaks in the tartaric acid spectrum, corresponding to the two -CHOH and the two -COOH groups respectively. In the ¹³C-NMR experiments the ratios of the two maxima (-CHOH/-COOH) of the individual samples were compared to eliminate possible errors in weighings, alterations of sample tubes, etc. The data were expressed as differences in the peak area ratio values between the unirradiated controls and the irradiated samples, i.e., $(L_{\text{control}} - L_{\text{irrad}}) = \Delta$.

Fig. 1 summarizes the results obtained with several beta decaying isotopes, and under different conditions.

No difference between the -CHOH/-COOH ratios of the control and

irradiated samples of the same optical isomer is expected unless a change in the relative peak intensities occurs due to the presence of the radioactivity in the irradiated probes. The beta-emitting isotopes give a lower peak ratio when compared to that of the unirradiated controls. In the presence of different beta decaying isotopes the effect varies in magnitude, but a change in sign can be seen only when the positron emitting ^{22}Na is the source of radioactivity.

The data indicate that the effect accumulates in time (see 4a and 4b) and that it may depend on the radioactive concentration of the probes. In all experiments the response of the "unnatural" L(-)-tartaric acid is more pronounced. The experimental uncertainty was 5.4%, which corresponds to ± 0.025 in the values of Fig. 1. No chemical shift was observed.

We suggest that stereoselective decomposition takes place in the samples containing the beta isotopes. Radiolytic, and perhaps chiral, products influence the relative intensities of the ^{13}C -NMR signals. Under the circumstances of our experiments, however, no detectable decomposition product(s) were observed in the NMR spectra. On the other hand, a slight yellowing was observable in samples that received the largest radiation doses. Further research is being carried out to determine the cause of these results.

The results are in good agreement with the previously observed preferential crystallisation¹⁴ and indicate that during chemical evolution the parity violation in beta decay could indeed be the asymmetric agent to select a single isomer from the racemic mixture present on the prebiotic Earth.

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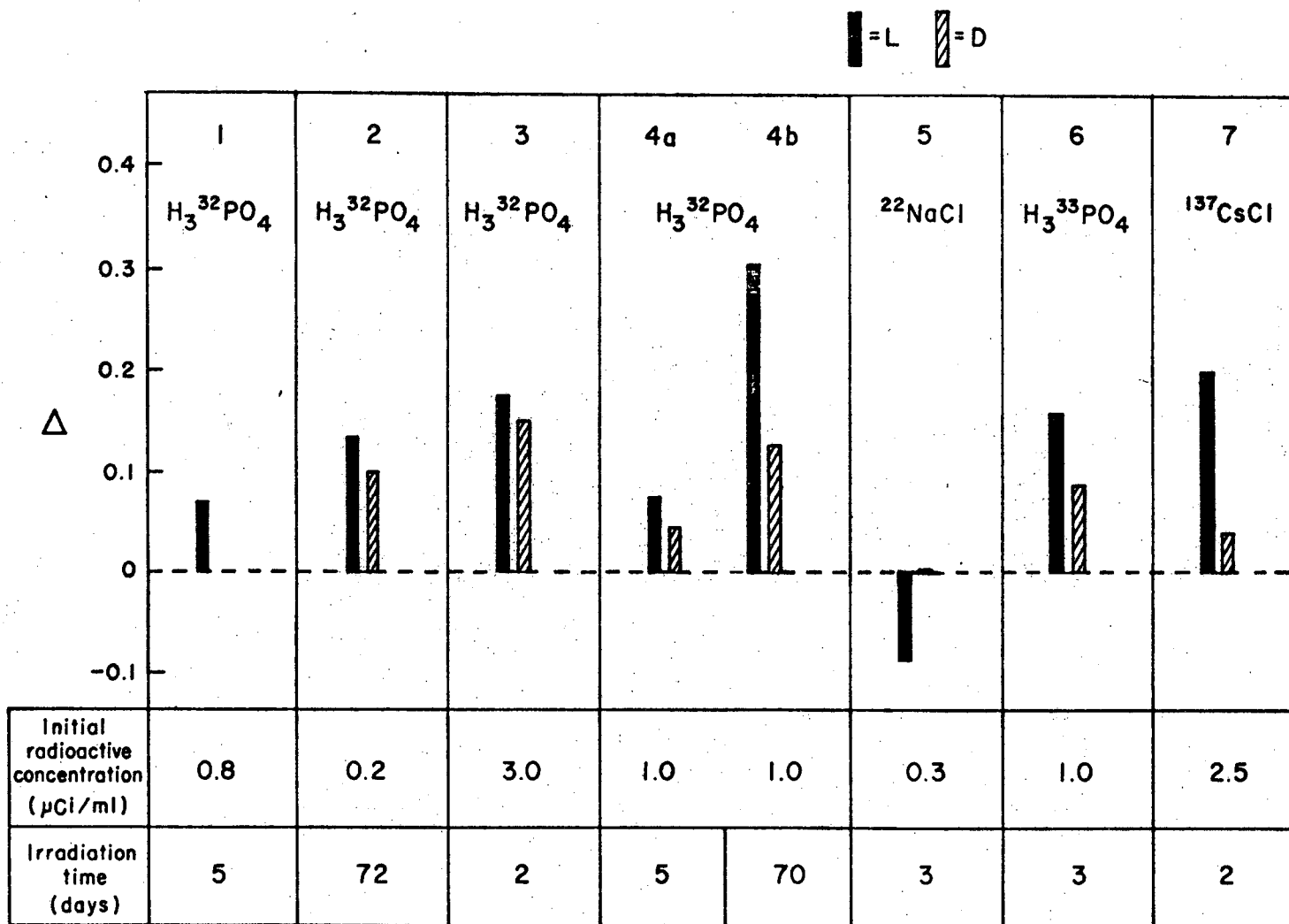


Fig. 1. Effects of Radionuclides on the $-CHOH/COOH$ ^{13}C -NMR peak ratios of irradiated L- and D-tartaric acids compared with unirradiated controls. Δ (the abscissa) equals, for example, L (control)- L (irrad).

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