

ANOMALOUS ENANTIOMER RATIOS IN METEORITIC SUGAR DERIVATIVES

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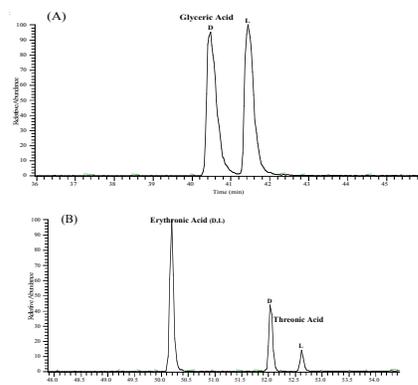
Introduction: Carbonaceous meteorites contain a diverse suite of soluble organic compounds. Studies of these compounds allow a critical look at the Solar System's earliest organic chemistry. In addition, these compounds were delivered to the early Earth in asteroids and possibly comets and therefore were likely to have been very important in the origin and/or evolution of life. The Murchison and Murray meteorites are the best-characterized carbonaceous meteorites with respect to organic chemistry. Among the classes of organic compounds found in these meteorites are amino acids, amides, carboxylic acids, hydroxy acids, sulfonic acids, phosphonic acids, purines and pyrimidines [1-3]. The study of carbonaceous meteorites and their organic content is also important in understanding the nature of the interstellar (i.e., widespread) chemical processes that may lead to the formation of compounds of importance in the origin(s) of life. To date, these compounds provide the only record available for the laboratory study of (a range) of organic chemical processes in interstellar space and our early Solar System. We have identified several chiral sugar derivatives in carbonaceous meteorites [4]: this presentation focuses on chiral sugar acids

Chiral molecules, such as ribose in RNA, are special molecules in biochemistry - they are composed of non-superimposable mirror-images (enantiomers) and are said to be "chiral". Such molecules are important on Earth because biological polymers (proteins, nucleic acids, etc.) are composed of only one (the D or L) of an enantiomer pair, i.e., they are homochiral. However in laboratory syntheses as well as in natural abiotic (non-biological) processes, such as those expected to have operated on the parent-body of the meteorites, equal amounts of D and L enantiomers of compounds should be synthesized. As far as we know, enantiomers have nearly equal energies of formation. 50:50 ratios are the norm with the vast majority of meteoritic compounds. However, some of the more unusual amino acids contain slightly more of one enantiomer (the L) than the other [5]. The origins of such enrichments are still subject to debate, however, the findings may have major implications for the origins of homochirality on Earth, i.e., could the enrichments in meteorites have led to homochirality on Earth? This project seeks to determine the enantiomer ratios of meteoritic sugar acids and implications (if any) for critical pre-biotic chemistry.

Analytical techniques: We have examined standards of all three-carbon (3-C) to six-carbon (6-C) straight-chained sugar acids by derivatization and gas chromatography-mass spectrometry (GC-MS) (Cooper G., 2009 Submitted for publication). Where needed, D and/or L sugar acid enantiomers were prepared by bromine oxidation of the corresponding sugar. Carboxylic groups were derivatized to their isopropyl ester/O-trifluoroacetyl (ISP-TFA), ethyl ester/O-trifluoroacetyl (Et-TFA), or isopropyl ester/O-pentafluoropropionic (ISP-PFA) derivatives. An Agilent 5973 inert Mass Selective Detector interfaced to an Agilent 6890N quadrupole mass spectrometer fitted with a Varian (Chrompack) Chirasil Dex-CB column (25m x 0.25) for GC separations. The GC injector temperature was 200°C and the

helium flow rate was constant at 30 cc/min. MS detector conditions: injector - 200°C; quadrupole MS temp. -150°C; carrier gas - helium; transfer line - 200°C; electron voltage - 70eV. GC conditions: initial oven temp. 45°C - heat at 3°C/min to 70°C, hold for 30 min - heat at 3°C/min. to 200°C.

Results: Chromatograms A and B, below, are representative of multiple runs from the Murchison meteorite.

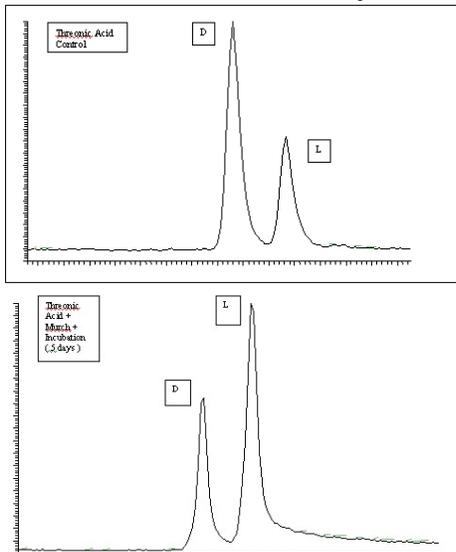


It can be seen that glyceric acid (A) has an approximately 50:50 ratio of D to L enantiomers as expected of a non-biological mechanism of synthesis. In several other samples glyceric acid is also racemic. Also racemic (in the same sample/same run) are 4-C deoxy sugar acids (not shown): 2-methyl glyceric acid, 2,4-dihydroxybutyric acid; 2,3-dihydroxybutyric acid; and 3,4-dihydroxybutyric acid.

It is also seen that threonic acid, (B), is apparently not racemic. We have also achieved enantiomer separation of erythronic acid (not shown) - it too appears to have significant D enantiomer excess. In other samples of Murchison and one of GRA 95229 (a relatively uncontaminated carbonaceous meteorite) threonic acid has nearly the same D enrichment. Isotopic measurements of individual enantiomers (in progress) will determine the extent (if any) of Earthly contamination. However, of the compounds shown above, glyceric acid is the most widely distributed in biological systems (predominately as the D enantiomer) and would appear to be the most likely candidate to have some fraction present as a result of contamination. However, as shown, it is consistently racemic (or nearly so) and an early ¹³C analysis (combined D and L - unpub. data) shows it be of extraterrestrial origins. Enantiomer analysis of the five-carbon mono-sugar acids, ribonic, arabinonic, xylonic, and lyxonic acids also show large D excesses. It is worth noting that all four of the possible straight-chained five-carbon sugar acids are present, including the rare lyxonic acid, and their abundances are in equilibrium proportions [10]. Lyxonic acid is the corresponding acid of the sugar lyxose, which is rare in biological systems again inferring that a significant portion of these compounds is indigenous to the meteorites. In addition, when lyxose or lyxonic acid is found in living systems it is often the L enantiomer that is present, e.g., as an

oxidation product of L-ascorbic acid (vitamin C). The same is true for some other sugar acids [6-9].

We also attempted to characterize the results of preferential consumption of one enantiomer of a pair by microorganisms. Preliminary experiments on sugar acids tend to show that microorganism(s) do consume, at least initially, one enantiomer over the other. The following chromatograms show the first results using DL-threonic acids (others acids show similar results). In this experiment the D enantiomer was made the most abundant for identification purposes. The top chromatogram is the control sample containing only D and L threonic acid and water; the bottom is after addition of a small amount of Murchison powder and incubation at 37°C for 5 days. The results clearly show preferential consumption of the D enantiomer. If these and repeat analysis can be extended to the meteorites it would indicate that the above enrichment in D-threonic acid was not the result of microbial consumption of this enantiomer. Further results of these and 6-C acids will be presented.



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