

Keto-Acids in Carbonaceous Meteorites

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Introduction: The Murchison and Murray meteorites are the best-characterized carbonaceous meteorites with respect to organic chemistry and are generally used as references for organic compounds in extraterrestrial material. Among the classes of organic compounds found in these meteorites are amino acids, carboxylic acids, hydroxy acids, purines, and pyrimidines [1,2]. Such compounds, important in contemporary biochemistry, are thought to have been delivered to the early Earth in asteroids and comets and may have played a role in early life and/or the origin of life. Absent among (today's) critically important biological compounds reported in carbonaceous meteorites are keto acids, i.e., pyruvic acid, acetoacetic acid, and higher homologs. These compounds are key intermediates in such critical processes as glycolysis and the citric acid cycle. In this study several individual meteoritic keto acids were identified by gas chromatography-mass spectrometry (GC-MS) (see figure below). All compounds were identified as their trimethylsilyl (TMS), isopropyl ester (ISP), and tert-butyldimethylsilyl (tBDMS) derivatives. In general, the compounds follow the abiotic synthesis pattern of other known meteorite classes of organic compounds [1,2]: a general decrease in abundance with increasing carbon number within a class of compounds and many, if not all, possible isomers present at a given carbon number. The majority of the shown compounds was positively identified by comparison of their mass spectra to commercially available standards or synthesized standards.

The figure also shows two candidate molecules for unknown six-carbon D-L (enantiomer) pairs observed in Murchison. We have synthesized alpha and beta-methyl levulinic acids and are comparing them to the compounds observed in the meteorites..

Keto acids of the Murchison and Murray meteorites.

Y = Identified

3C		---
4C		Y
5C		Y ---
6C*		Y ? ?
7C**		Y
8C**		Y

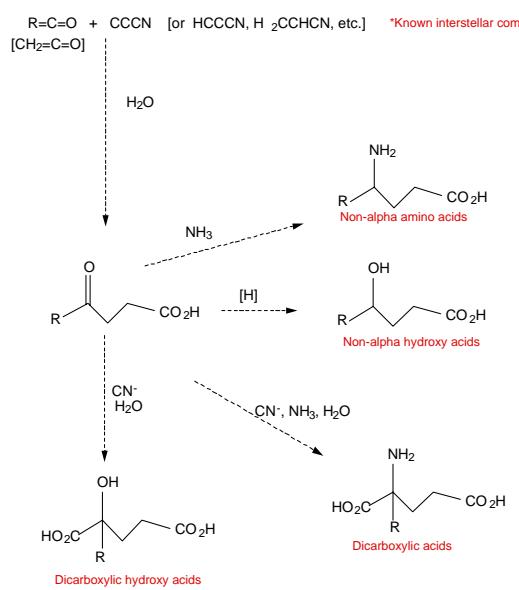
* 4-acetyl butyric acid was identified (mass spectrum) with a standard. Of other tentatively identified 6-C isomers the above two are thought to be present.

** Several isomers (tBDMS derivatives) are present.

Murchison and Murray are similar with respect to the presence of individual acids. We have not observed the first member of the series, pyruvic acid, in either meteorite - this may be due to the known instability of this molecule. The four-carbon homolog (acetoacetic acid), a beta-keto carboxylic acid is also relatively unstable but is definitely present in the meteorites. The relatively long and sometimes harsh GC preparation procedures may also cause losses of pyruvic. LC-MS analysis for pyruvic is in progress.

Below is a possible mode of formation of the meteoritic keto acids from known interstellar compounds. Also shown are possible reactions of the keto acids (using levulinic acid as an example) that may have contributed to the formation of other (known) meteoritic compounds. These reactions could quite possibly have taken place in the meteorite parent-body given the reactivity of ketones and aldehydes towards nucleophiles such as ammonia and cyanide and suggestive evidence of these types of reactions forming amino acids in meteorites [1,2].

A possible mechanism and reaction pathways



If the proposed reactions pathways were significant, isotopic measurements of the keto-acids may show relationships with other classes of meteorite compounds.

References: [1] Botta O. and Bada J. L. (2002) Extraterrestrial organic compounds in meteorites. *Surveys in Geophysics* **23**, 411-465. [2] Sephton M. A. (2002) Organic compounds in carbonaceous meteorites. *Nat. Prod. Rep.*, **19**, 292-311.