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Carboxylic Acids in the Yamato-791198 Carbonaceous Chondrites from Antarctica

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Monocarboxylic acids were detected from the Yamato-791198 carbonaceous chondrite(C2). These organic acids include aliphatic and aromatic structures with the most of structural isomers of the C_4, C_5, and C_6 acids. These compounds are abiotic in origin and the products in the early solar system.

Carbonaceous chondrites contain extraterrestrial organic compounds formed in the early solar nebula. During past 15 years, more than 7000 pieces of meteorites have been collected in Antarctica and about 80% of these pieces are preserved in Japan.1) These pieces include about 60 carbonaceous chondrites. We examined one of these chondrites, Yamato-791198, and found that this chondrite was likely the most amino acid-rich chondrite ever analyzed.2) In addition,we found that the terrestrial organic contamination was nil to this carbonaceous chondrite as observed by other Antarctic carbonaceous chondrites.3,4) Accordingly, we extended analysis to carboxylic acids, and found a variety of the organic acids at the levels of one to sub-nmol/g sample. This finding of carboxylic acids is the first for Antarctic carbonaceous chondrites. Only two non-Antarctic carbonaceous chondrites, Murchison and Murray, were analyzed for carboxylic acids previously.5-8)

The sample examined was Yamato-791198.22, a part of Yamato-791198, a C2 chondrite. This sample contains 2.32% carbon and 0.13% nitrogen.2) For carboxylic acids, 0.5 g of the 2.9 g powdered sample prepared previously were extracted with 5 ml of 5% KOH-methanol(w/v) by refluxing in a degassed-sealed glass tube at 80-90 °C for 3 h. To the supernatant recovered after centrifugation were added 10 ml of water. The precipitate was extracted by sonication with 2 ml of methanol and the methanol solution was added to the water solution. The combined solution was extracted with 3 ml of dichloromethane three times and the solution was evaporated near dryness under reduced pressure. To the dried residue were added at ice-water temperature 1.1 ml of 6 mol dm^{-3} HCl to bring the solution pH at about 1. Finally, the acidified solution was extracted with 1 ml of dichloromethane five times for the analysis of carboxylic acids by GC and GC/MS.

Methanol, dichloromethane, water and 6 mol dm^{-3} HCl were doubly distilled and glass ware was heated at 500 °C for at least 3 h prior to use. All analytical and preparative processes described above were carried out with great care in a clean room or, when necessary, on a clean bench set in the clean room. A procedural blank was carried out with 0.5 g of pre-ignited sand powder.

The separation and identification of each carboxylic acid were carried out by a gas chromatograph equipped with FID and a FFAP Chemical Bonded FS-WCOT capillary column(0.25 mm i.d. x 50 m), combined by a mass spectrometer with EI and CI. The gas chromatogram of the Yamato-791198.22 sample is shown in Fig. 1 together with that of the procedural blank. Several peaks appear around the retention times of 10 to 17 min in the procedural blank. However, these peaks were insignificantly small compared with those peaks of the chondrite and they were ignored.

On the chromatogram of Yamato-791198.22 in Fig. 1, a total of 24 peaks were identified by GC/MS. Of these, 23 peaks are monocarboxylic acids of 20 aliphatic (peak No. 6 consists of two compounds) and 3 aromatic carboxylic acids. These aliphatic carboxylic acids include saturated straight and branched-chain structures with acetic acid being the smallest and dodecanoic acid the largest in size. Previous studies found aliphatic carboxylic acids as large as octanoic acid.[5,7] Two structural isomers of C_4 and four isomers of C_5 carboxylic acids were all identified. Of C_6 carboxylic acids, 6 isomers were detected, leaving 2,2-dimethylbutanoic and 3,3-dimethylbutanoic acids unidentified. The identification of these isomers was made by retention times of authentic compounds by GC and MS analyses with EI and CI methods, except 2,3-dimethylbutanoic acid whose authentic compound was not available. However, this compound was identified from the fragmentation pattern by EI and the presence of $(M+1)^+$ at m/e 117.0 by CI.

Only n-aliphatic acids were positively identified from C_7 to C_{12}. Several small peaks of $(M+1)^+$ for the C_7 acids were found on mass chromatograms by CI, indicating that there may be many isomers present. However, probably because of a large number of the isomers, the abundances of these isomers are so small that their identifications become difficult.

Three aromatic carboxylic acids found were benzoic acid, methylbenzoic acid, and phenylacetic acid. The finding of these aromatic carboxylic acids have not been reported for both Antarctic and non-Antarctic carbonaceous chondrites. In addition to these organic acids, phenol(peak No. 15) was also found.

The amounts of carboxylic acids are listed in Table 1. These estimates should be regarded to be approximate, since the treatment with dichloromethane did not extract quantitatively such small molecules as acetic and propionic acids from the acidified solution. With this consideration it seems that the abundances decrease with increase of carbon number of molecules. However, within structural isomers their abundances are at the same order of magnitude. These abundances of isomers indicate that these carboxylic acids(up to C_6) seem to be formed by a random synthesis. On the other hand, the abundances of carboxylic acids with C_7 to C_{12} clearly show the predominance of the straight-chain structure. Formation of these

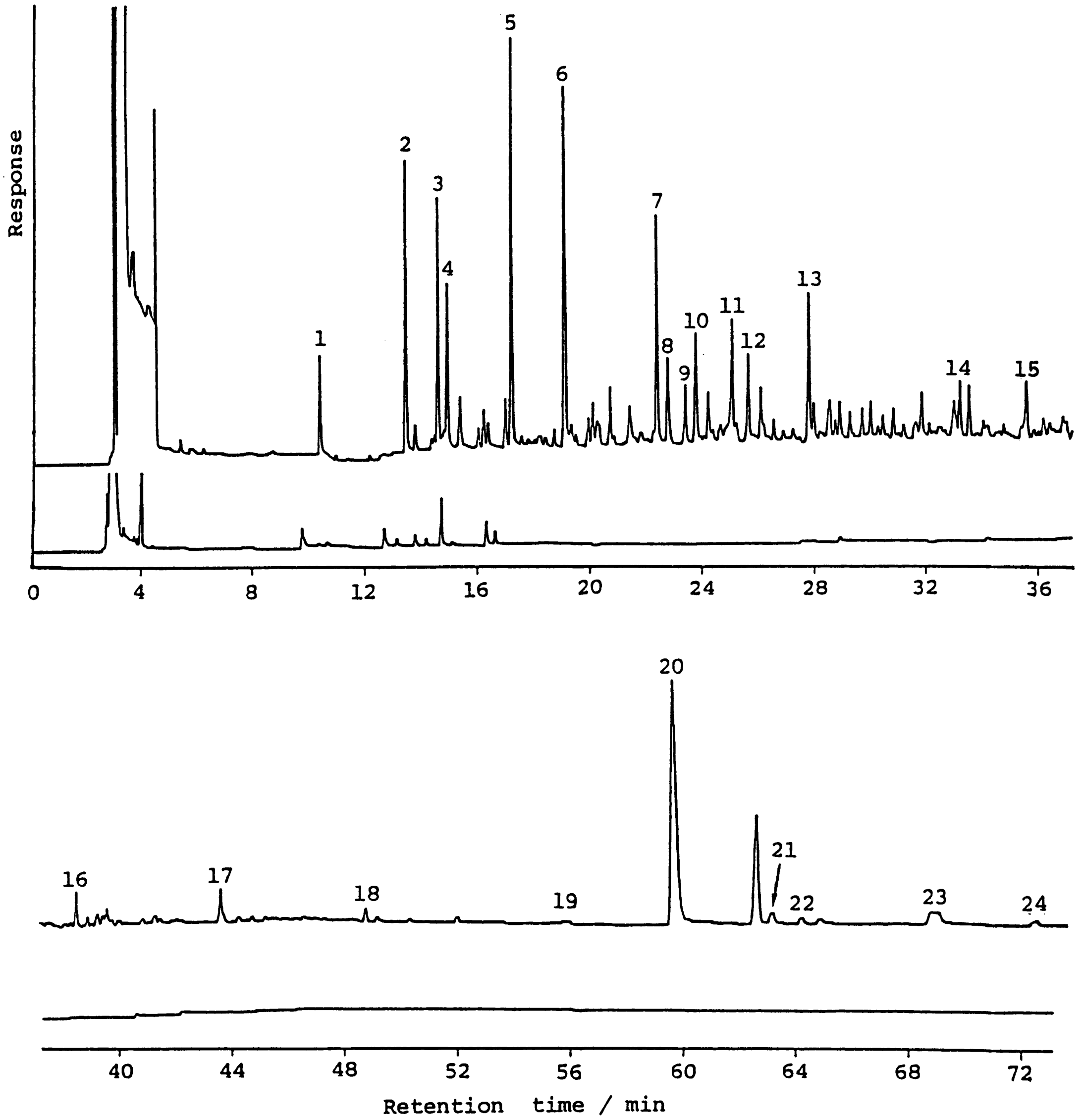

Fig. 1. Gas chromatograms of carboxylic acids in Yamato-791198.22(upper) and the procedural blank(lower). Peak Nos. correspond to Nos. in Table 1.

Table 1. Abundances of carboxylic acids in Yamato-791198.22

No.	Compound	nmol/g	No.	Compound	nmol/g
1	Acetic acid	10.8	13	Hexanoic acid	3.7
2	Propionic acid	14.9	14	Heptanoic acid	1.2
3	2-Methylpropionic acid	8.2	15	Phenol	n.d.
4	2,2-dimethylpropionic acid	4.1	16	Octanoic acid	0.63
5	Butanoic acid	13.6	17	Nonanoic acid	0.82
6	2-Methylbutanoic acid plus		18	Decanoic acid	0.29
	3-Methylbutanoic acid	11.1	19	Undecanoic acid	0.05
7	Pentanoic acid	6.2	20	Benzoic acid	9.1
8	2,3-Dimethylbutanoic acid	2.2	21	*o*-Methylbenzoic acid	0.34
9	2-Ethylbutanoic acid	1.4	22	Dodecanoic acid	0.35
10	2-Methylpentanoic acid	2.8	23	*m*- and *p*-Methylbenzoic acid	0.95
11	3-Methylpentanoic acid	3.4	24	Phenylacetic acid	0.19
12	4-Methylpentanoic acid	2.2			

n.d.:not determined.

acids may be controlled by some heterogeneous catalysts probably on solid surfaces. Benzoic acid is by far the most abundant compared with methylbenzoic acid and phenylacetic acid. Their relative abundances seem to be reasonable, since benzoic acids is known to be formed easily, among the aromatic carboxylic acids, from aromatic compounds by oxidation. These characteristics of the carboxylic acids indicate that they are abiotic in origin and, therefore, indigenous to the chondrite formed in the early solar system.

Carboxylic acids are generally less abundant than those of amino acids for the same carbon-numbered molecules in Yamato-791198. This tendency is particularly notable for small molecules. However, the abundances of amino acids decrease rapidly with increase of carbon number and become approximately the same between hexanoic acid and leucine. No amino acids with carbon number larger than 6 have been detected at the sub-nmol/g level from the chondrite, while carboxylic acids are present up to dodecanoic acid. The amounts of carboxylic acids of Yamato-791198 are about one to two order of magnitudes less than those of Murchison.5,7) Nevertheless, the relative ratios within the carboxylic acids in the two chondrites are somewhat similar. The analytical procedures for the two chondrites are nearly the same and, therefore, these abundances could be correlated each other in further consideration of carboxylic acids in carbonaceous chondrites.

The chemical form of carboxylic acids in carbonaeous chondrites is not well understood. They may exist as free organic acids (or salts) or combined forms in the matrix of the chondrites. Preliminary examination of the chondrite by water extraction did not yield carboxylic acids significantly, suggesting that the presence of the organic acids as free form is minor. The KOH-methanol refluxing seems to have released carboxylic acids from combined forms in the matrix, although we do not exclude completely the possibility of other forms.

Our present analysis focused mainly on aliphatic monocarboxylic acids. Modified analytical procedures are necessary to examine more numbers of aromatic carboxylic acids and the presence of aliphatic carboxylic acids larger than dodecanoic acid as well as dicarboxylic acids. These organic acids are structurally related to amino acids, and therefore, the two groups of organic molecules might have been related in origin in the early nebular processes of the solar system.

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