CHEMISTRY LETTERS, pp. 523-526, 1994.

Dicarboxylic Acids in the Murchison and Yamato-791198 Carbonaceous Chondrites

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Dicarboxylic acids were recovered in the C_2 to C_9 range in concentration about 2000 to 0.1 nmol/g from the Murchison and Yamato-791198 carbonaceous chondrites. The molecular distributions of the saturated straight-chain acids suggest that they approximately show their original compositions when they were formed in the early solar system. Optical isomers of the acids were found to be racemic.

Studies of organic compounds in carbonaceous chondrites have shown various kinds of extraterrestrial compounds and provided useful information to the primordial organic chemistry in the early solar system and chemical evolution on the primitive earth. These studies were reviewed recently.1) However, many questions still remain concerning their origins in the early solar system. Since studies of dicarboxylic acids were a few and were limited to only the Murchison carbonaceous chondrite,2,3) we analyzed dicarboxylic acids not only in the Murchison chondrite (CM2) but also in the Yamato-791198 carbonaceous chondrite (CM2). Our results show a characteristic molecular distribution of the acids common in the two chondrites, in spite of their different places and years of fall, and suggest a formation process of the carbon chains of the acids.

The samples we analyzed were the Murchison specimen (Me 2752, Field Museum of Natural History, Chicago), and the Yamato-791198 specimen (sub-number 22, National Institute of Polar Research, Tokyo). The powdered samples of Murchison (500 mg) and Yamato-791198 (80 mg) were extracted with water by sonication. The extracted solution of Murchison was divided into three parts. One part of the Murchison and the Yamato-791198 extract were dried and treated with 15% wt BF_3/MeOH to make dimethyl esters of dicarboxylic acids. Another aliquot of the Murchison was treated with (*S*)-2-BuOH/2M HCl to prepare the optically active dibutyl esters of the acids. A gas chromatograph coupled to a mass spectrometer (GC-MS) was used for identification and quantification of the acids. The GC was operated with a FFAP Bonded FS-WCOT capillary column (60 m x 0.25 mm i.d.) from 50 to 90 °C at a rate of 10 °C/min and, then, from 90 to 200 °C at a rate of 2 °C/min. The MS was scanned every 1.0 s over m/z 40 to 300 in the electron-impact mode at 70 eV, and over m/z 60 to 300 in the chemical-ionization mode at 200 eV with isobutane as reacting gas.

All glassware was heated at 500 °C at least for 3 h prior to use in order to eliminate any possible organic contaminants. The water was distilled, deionized and redistilled. Methanol and (*S*)-2-BuOH (purity, 99%; Aldrich) were distilled. The 15% wt BF_3/MeOH was prepared by bubbling BF_3 gas into distilled MeOH. Likewise, (*S*)-2-BuOH/2 M HCl was prepared by babbling HCl gas into distilled (*S*)-2-BuOH. All analytical and preparative processes were carried out in a clean room, or when necessary, on a clean bench in the room. A procedural blank was carried out with 0.5 g of pre-ignited sand powder.

Figure 1 shows gas chromatograms of dicarboxylic acids recovered from the Murchison chondrite and

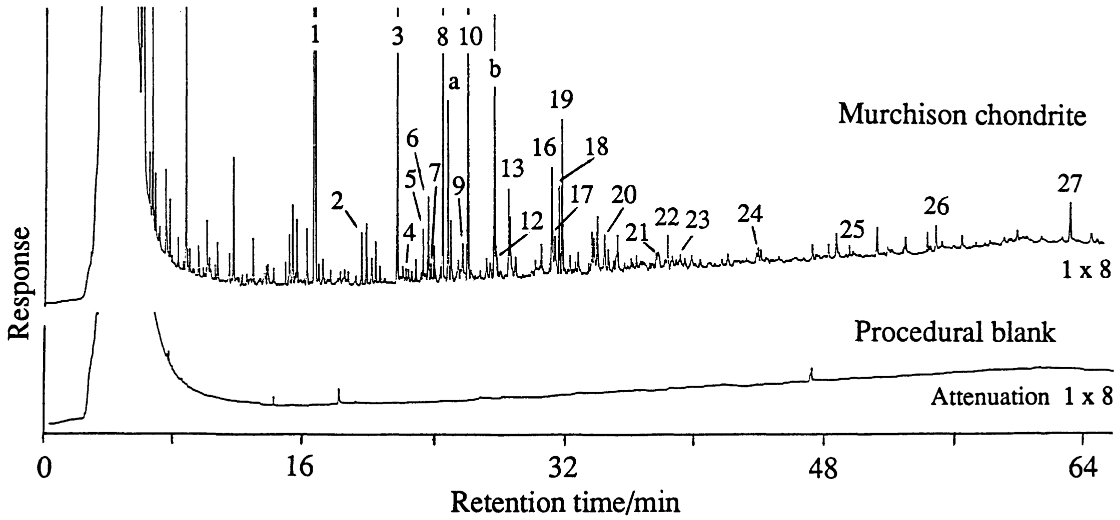

Fig. 1. Gas chromatograms of dimethyl esters of dicarboxylic acids from the Murchison chondrite and the procedural blank. Peak numbers correspond those in Table 1. Peak a 4-oxy-pentanoic acid, b benzoic acid.

the procedural blank. A very similar gas chromatogram to the Murchison chondrite was obtained for the dicarboxylic acids recovered from the Yamato-791198 chondrite. A total of 27 dicarboxylic acids in the C_2 (oxalic acid) to C_9 (azelaic acid) range was identified and the estimated concentrations in the Murchison and Yamato-791198 chondrites are listed in Table 1. However, the presence of phthalic acid in the two chondrites remains questionable, although it was not detected in the procedural blank. The acid and its derivatives are common in plasticizer and are widely spread over the world.

The previous study of the Murchison chondrite2) reported 17 compounds in the range from oxalic acid to azelaic acid. Therefore, our finding increased the number of the acids notably. All structural isomers of the C_4, C_5, and C_6 saturated acids were found except some derivatives of malonic acid. Six of the possible 20 isomers of the C_7 saturated acids were detected. As to the unsaturated acids, two C_4 acids and three C_5 acids were found. In addition to the above identifications, optical isomers from the Murchison chondrite were separated as di-(*S*)-2-butyl esters as shown on the mass fragmentograms in Fig. 2. The (*S*)/(*R*) ratios were found nearly one with 2-methylsuccinic acid, 2-ethylsuccinic acid, 2-methylglutaric acid, and 2-ethylglutaric acid. These observed ratios of nearly one indicate that these acids are racemic in the chondrite.

Our recoveries of oxalic, malonic, and succinic acids from the chondrite were much higher than those by the other study,3) while those of glutaric and adipic acids were quite similar. This is probably due to careful concentration of the solution which contained the dimethyl esters of these acids just before the GC-MS analysis. Our recovery test of the dimethyl esters showed 88% for oxalic acid, 98% for malonic acid, and 102% for succinic acid on the basis of 100% recovery for glutaric acid.

The plots of log concentration versus carbon number of the saturated straight-chain acids give a straight line in the C_2 to C_7 range (except malonic acid with C_3 which is thermally the least stable of all) as shown in Fig. 3. The slopes (-0.63 and -0.73) of the lines indicate that the concentrations decrease to about 24 and 18%, respectively, by each addition of one carbon in the chains. A very similar result was obtained in experiments where dicarboxylic acids were formed from elemental carbon (graphite) and water which were exposed to an arc discharge.4) The result showed a straight line with a slope of -0.72 for the straight-chain

Table 1. Concentrations of dicarboxylic acids in the Murchison and Yamato-791198 (in nmol/g)

No.a)	Compound	Murchison	Yamato-791198
1	Oxalic acid	2100	1900
2	Methylmalonic acid	9.2	3.7
3	Malonic acid	96	20
4	Ethylmalonic acid	2.3	2.3
5	2,2-Dimethylsuccinic acid	8.8	1.4
6	Fumaric acid	< 8.1	< 1.5
7	(meso)-2,3-Dimethylsuccinic acid	1.8	0.39
8	2-Methylsuccinic acid	48	16
9	(DL)-2,3-Dimethylsuccinic acid	5.9	1.0
10	Succinic acid	97	21
11b)	Mesaconic acid	< 1.9	< 0.5
12	(meso)-2,4-Dimethylglutaric acid	n.d.c)	n.d.c)
13	Ethylsuccinic acid	14	3.8
14b)	Maleic acid	1.0	0.3
15b)	Itaconic acid	< 0.4	< 0.1
16	2-Methylglutaric acid	15	3.1
17	3-Methylglutaric acid	4.7	1.2
18	Citraconic acid	19	3.7
19	Glutaric acid	24	6.8
20	Ethylglutaric acid	2.9	n.d.c)
21	2-Methyladipic acid	1.6	0.7
22	Adipic acid	5.8	2.3
23	3-Methyladipic acid	1.9	0.9
24	Pimeric acid	2.0	0.5
25	Suberic acid	1.7	0.3
26	Azelaic acid	3.2	0.3
27	Phthalic acid	3.2	3.2

a) Numbers correspond those shown at the peaks in Fig. 1. b) The compound was identified and quantified by mass fragmentography in the chemical-ionization mode. c) n.d. : not determined.

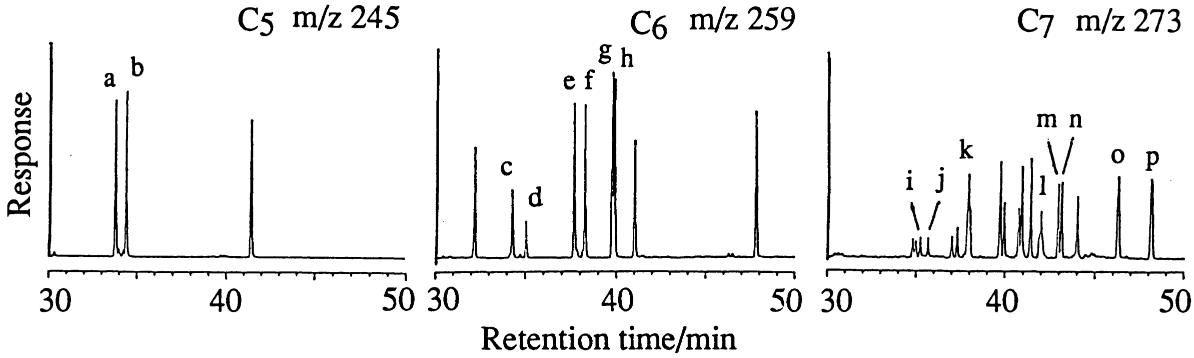

Fig. 2. Mass fragmentograms of di-(*S*)-2-butyl esters of dicarboxylic acids recovered from the Murchison chondrite. Peak a (*S*)-2-methylsuccinic acid, b (*R*)-2-methylsuccinic acid, c and d (D)- and (L)-, and (meso)-2,3-dimethylsuccinic acid, e (*S*)-ethylsuccinic acid, f (*R*)-ethylsuccinic acid, g (*S*)-2-methylglutaric acid, h (*R*)-2-methylglutaric acid, i and j (D)- and (L)-2,4-dimethylglutaric acid, k (meso)-2,4-dimethylglutaric acid, l (D)- and (L)-2,3-dimethylglutaric acid, m (*S*)-2-ethylglutaric acid, n (*R*)-2-ethylglutaric acid, o (*R*)- and (*S*)-2-methyladipic acid, p (*R*)- and (*S*)-3-methyladipic acid.

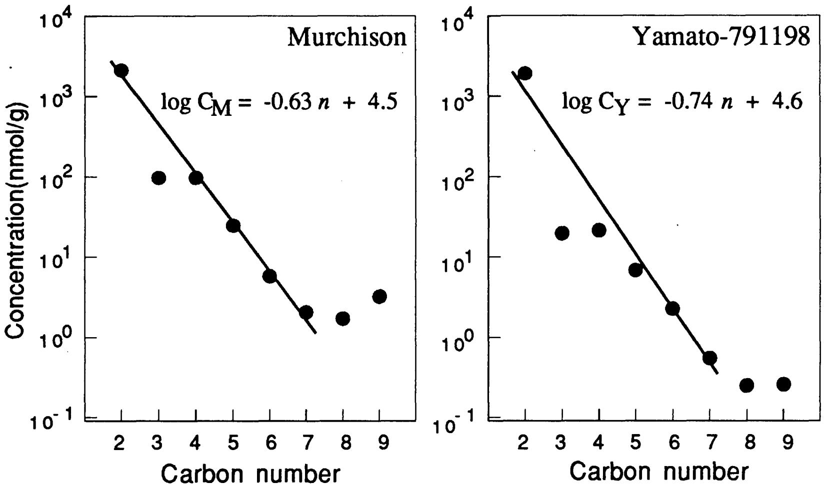

Fig. 3. Concentration versus carbon number of saturated straight-chain dicarboxylic acids in the Murchison and Yamato-791198 chondrites. The equations of the lines were obtained using a least-squares fit. C_M and C_Y are the concentrations (in nmol/g) of dicarboxylic acids in the Murchison and tYamato-791189 chondrites, respectively, and n is the carbon number from 2 to 7 except 3. The coefficients of correlations for the lines are 99.8% for the Murchison and 98.2% for the Yamato-791198 chondrites.

acids (C_2 - C_5) and suggested that they were primary products and that larger molecules were formed from smaller ones in the homologue by a progressive addition of one carbon species. Furthermore, malonic acid was formed in quantity appropriate for the line. On the other hand, the acid in the Murchison and Yamato-791198 chondrites was found in smaller quantity than expected from the line, which is interpreted due to its partial decomposition on the chondrites (or their parent bodies) after its formation. However, it is likely that the decomposition process was mild enough for the other acids to retain their original compositions. A similar straight line with a slope (ca. -0.7) was found in log concentration versus carbon number of the amino acids (C_2 - C_7) recovered from the Murchison chondrite.5)

Our results of the Murchison and Yamato-791198 chondrites supported each other. With the result of the arc discharge study,4) it is suggested that the carbon chain-formations of dicarboxylic acids in the chondrites were taken place by a progressive addition of one carbon species in the early solar system.

This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Area (Intersteller Substance and Its Evolution) No. 05217202 and the Grant-in-Aid for Scientific Research No. 05833002 from the Ministry of Education, Science and Culture, Japan.

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(Received November 24, 1993)