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SPECTROSCOPIC STUDIES OF ACID-RESISTANT RESIDUES OF CARBONACEOUS CHONDRITES

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Abstract: Mass and IR spectra have been obtained of the acid-resistant residues resulting from HCl and HF treatments of ALH-77307 (C3). ^{13}C NMR spectra of the residues obtained by partial mineral dissolution with acid treatments of Yamato-791717 (C3) and Allende (C3) have been recorded under CP-MAS conditions. These spectral data were compatible with the polycyclic aromatic structure proposed for the major carbonaceous matter in carbonaceous chondrites by the authors.

1. Introduction

Carbonaceous chondrites are recognized as a distinct meteorite class on the basis of several well-established criteria (MASON, 1963). Although there are some meteorites containing as much or more carbon, the carbonaceous chondrites are unique with respect to their contents of carbon in the form of organic compounds. The major component of the organic compounds is contained in the form of an insoluble high molecular material and depending on carbonaceous chondrite type, this insoluble material may account for from about 70 percent to essentially all of the meteoritic carbon (HAYES, 1967; HAN *et al.*, 1969).

Although various methods have been applied to the characterization of the insoluble organic high molecular compound (SCHULZ and ELOFSON, 1965; HAYES and BIEMANN, 1968; SIMMONDS *et al.*, 1969; GREEN *et al.*, 1971; BREGER *et al.*, 1972; LEVY *et al.*, 1973; BANDURSKI and NAGY, 1976; HAYATSU *et al.*, 1977, 1980; HOLZER and ORÓ, 1979; WHITTAKER *et al.*, 1980; SMITH and BUSECK, 1981, 1982; CRONIN *et al.*, 1987), its structure is not well understood, because completely satisfactory methods for characterizing irregular carbon-containing structures in the solid state have not been available. Nevertheless, elucidation of the structure is essential to understanding primordial carbon chemistry as well as the origin and chemical history of the carbonaceous chondrites. Because the findings of enrichment of ^{13}C (SWART *et al.*, 1983; MING *et al.*, 1988, MING and ANDERS, 1988a, b) and deuterium (ROBERT and EPSTEIN, 1982) in certain fractions of this carbon and the ability of the carbon as the host phase for isotopically anomalous noble gases (LEWIS *et al.*, 1975; OTT *et al.*, 1981; MING *et al.*, 1988; MING and ANDERS, 1988a, b) raised the possibility of an extrasolar origin for at least part of the carbonaceous matter (LEWIS *et al.*, 1975; OTT *et al.*, 1981; ROBERT and EPSTEIN, 1982; MING and ANDERS, 1988b). We have proposed a model of general structure for the solvent-unextractable carbonaceous matter in carbonaceous chondrites

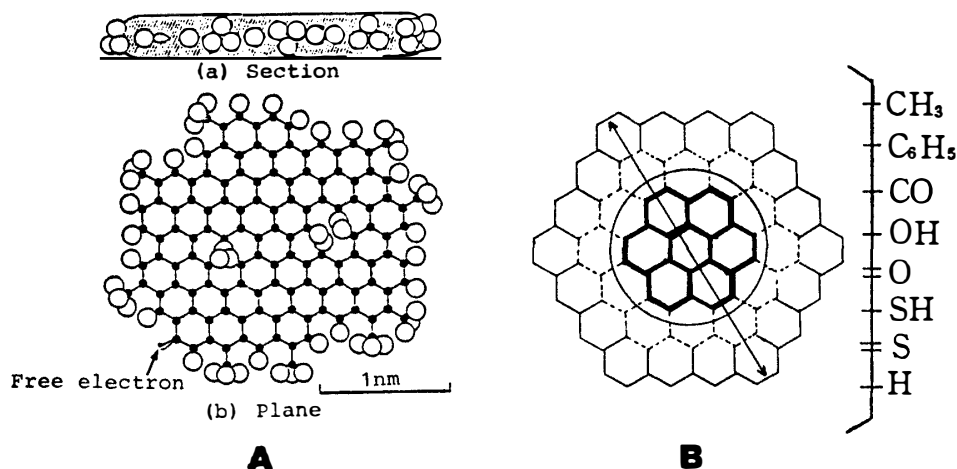


Fig. 1. *A*: The model proposed for the structure of organic polymer in carbonaceous chondrites. The size of molecule changes according to the meteorite. *B*: The simplified structure of *A* in order to calculate the molecular size. Two-carbon units from the circumference (the carbons outside the circle and connected with dot lines to the center unit) are presumed to be lost on pyrolysis. The estimated length from a corner to the opposite corner (indicated by an arrow) is ca. 6 nm for the organic polymer of Murchison and ca. 12 nm for that of Belgica-7904. The contribution of the functional groups other than hydrogen and phenyl groups as edge defects is not significant.

(Fig. 1) based on the results of pyrolytic studies (MURAE *et al.*, 1987). A different model having a similar structure to terrestrial geopolymers has been proposed for organic polymer isolated from Murchison by HAYATSU *et al.* (1983).

Recent developments in spectroscopic instrumentation have made it possible to obtain mass spectra of nonvolatile high molecular organic compounds without decomposition, IR spectra of black fine powder with considerable intensity, and natural abundance ^{13}C NMR spectra of solid samples with sufficient resolution. In this paper, we report preliminary examinations of the acid-resistant organic polymers of carbonaceous chondrites by mass spectra obtained using a time of flight mass spectrometer (TOF-MS) equipped with a laser ionization system (LI), IR spectra obtained using a FT-IR spectrometer equipped with an attachment for diffuse reflection (DR), and ^{13}C NMR spectra obtained using a spectrometer equipped with a probe for magic-angle spinning (MAS) and high-power decoupling under cross-polarization (CP) conditions.

2. Experimental

Mass spectra were determined with a Shimadzu LAMS-50K time of flight mass spectrometer (TOF-MS) equipped with the N_2 laser pulse (337 nm) ionization system. The powdered samples were held on the surface of a copper-sampling block using a glycerol matrix as a binder. The laser irradiation was repeated 200 times and the laser-irradiation spot on the sampling block was moved frequently using a TV monitor to avoid the irradiation on the empty surface during the data accumulation.

IR spectra were recorded with a Horiba FT-300 FT-IR spectrometer equipped with an attachment for diffuse reflection using a micro-sample cup of 1 mm diameter.

^{13}C NMR spectra were obtained at 125.76 MHz with a Bruker AM-500 spec-

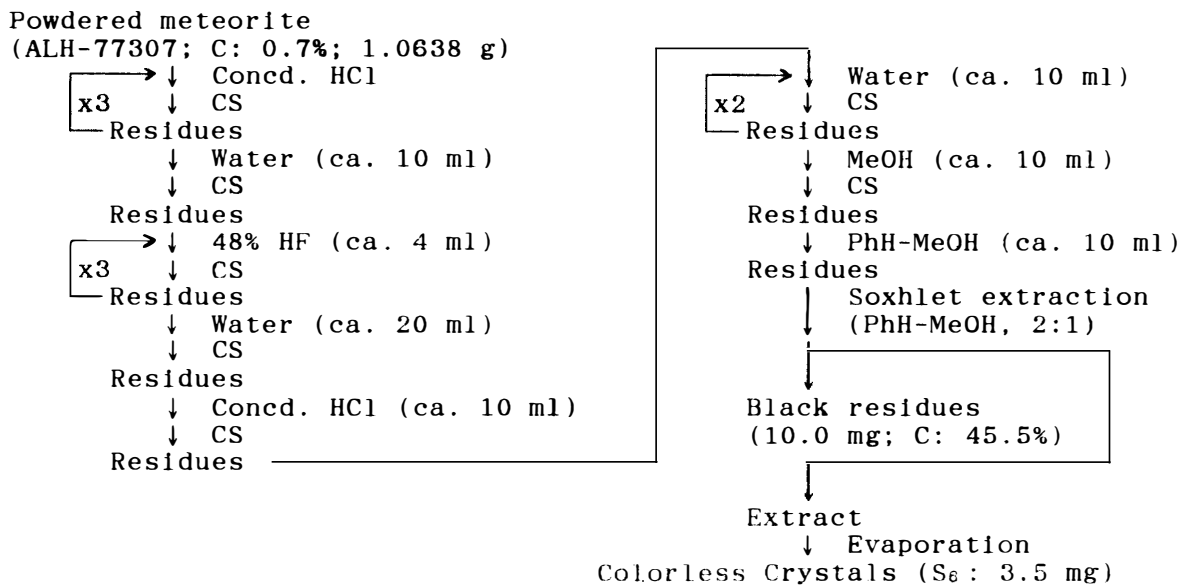


Fig. 2. Preparation of the acid-resistant residues from ALH-77037. CS: centrifugal separation.

trometer with CP-MAS probe. Samples were loaded in bullet rotors and spun at 4.0 kHz. The spectra were acquired with spectral width 41666 Hz; acquisition time, 26 ms with decoupler on at the Hartman-Hahn match level; pulse repetition time, 4 s.

The acid-resistant residues from ALH-77307 were prepared by acid treatments as shown in Fig. 2. The powdered meteorite was extracted with a 2:1 mixture of benzene and methanol and then subjected to the acid treatments; soak in 20% HCl at room temperature and centrifugal separation of the residues (repeated three times); washing with water and centrifugal separation; repetition of digestion with 48% HF and centrifugal separation (three times); washing with water; digestion with 20% HCl; and then washing with water and centrifugal separation. The residues obtained by the acid treatments were enriched with elemental sulfur, which was removed by extraction with a 2:1 mixture of benzene and methanol using a Soxhlet extractor. By this procedure a 1.0 g sample (C: 0.74%) gave 10 mg of the residues (C: 45.5%). Yield: 60% of total meteorite carbon.

Allende (11.5 g, C: 0.23%) was treated by the similar methods to those mentioned above for ALH-77307 and the sample was ultrasonicated during the digestion with acids and the extraction with organic solvents (the Soxhlet apparatus was not used) to yield 2.57 g of acid-resistant residues (C: 0.93%). Yield: 90% of total meteorite carbon. The residues were soaked in 20% HCl for 2 weeks at room temperature and filtered to give residues which were soaked further in 20% HCl for 15 weeks and 6 weeks at room temperature, and then washed with a 3:1 mixture of benzene and methanol to give 302 mg of acid-resistant residues (C: 7.57%). Yield: 86% of total meteorite carbon.

By almost the same treatments as those of Allende, Y-791717 (51.3 g, C: 0.16%) yielded 8.30 g of the acid-resistant residues (C: 0.95%). Yield: 96% of total meteorite carbon. The residues were soaked in 20% HCl for 2 weeks at room temperature and filtered to give residues which were soaked further in 20% HCl for 15 weeks and 6

weeks to give 2.1 g of acid-resistant residues (C: 3.08%). Yield: 78% of total meteorite carbon.

3. Results and Discussion

In Fig. 3 are shown the mass spectra of the acid-resistant residues from ALH-77307. The spectra were recorded at low, medium and high mass unit regions independently. Although it is difficult to differentiate the fragment ions from the molecular ions in the mass spectra obtained by the TOF mass spectrometer, the molecular ions are usually predominant and the relative intensity of the fragment ions to the molecular ions can be reduced by lowering the laser-irradiation power. The peaks observed in the low mass unit region with high intensity were due to Na^+ (m/z 23),

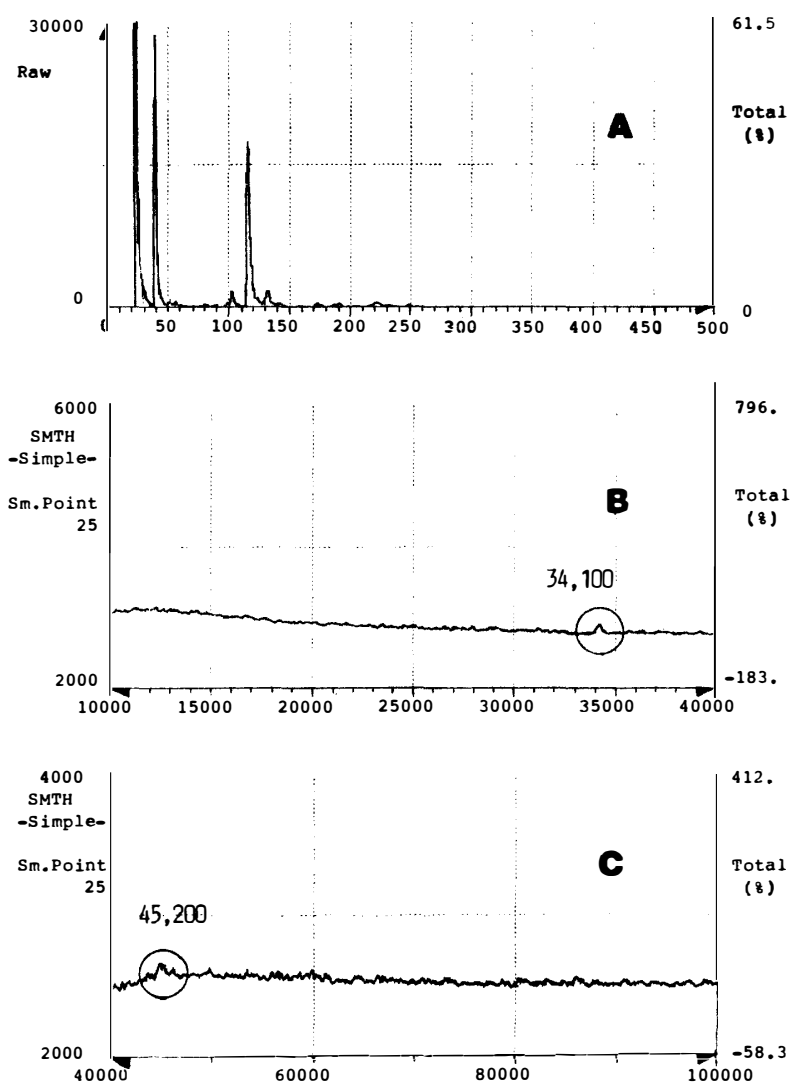


Fig. 3. Laser ionization TOF-Mass spectra of the acid-resistant residues from ALH-77307. A: mass range (MR): m/z 0–500, accumulation times (AT): 200, ionization laser power (ILP): 85; B: MR: m/z 10000–40000, AT: 200, ILP: 85; C: MR: m/z 40000–100000, AT: 200, ILP: 107.

K^+ (m/z 39), and their cluster ions with the matrix glycerol (m/z 115 and 131) (Fig. 3A). And except these peaks, no remarkable ion was detected in that region. This fact means that the organic residues do not have the structure which causes fragmentation on irradiation of the laser at that power.

In the high mass unit region were observed two weak peaks at m/z *ca.* 34100 and *ca.* 45200 (Fig. 3B, C). These peaks were not detected in the spectra of the acid-untreated sample of ALH-77307. Therefore these peaks are supposed to be due to the organic material enriched by acid treatments. Although reproducibility of the spectrum is not confirmed yet, if these peaks are corresponding to the molecular ions of the organic residues, then the residue might contain two types of polymers. And these molecular weights roughly correspond to two and three units of the Murchison polymer, respectively, whose composition $C_{100}H_{70}N_{2.5}S_2O_{12}$ has been estimated by HAYATSU *et al.* (1983). On the other hand, according to the structure (Fig. 1) proposed by the authors (MURAE *et al.*, 1987), the molecular ions indicate that the residues contain two type of polymers whose structure resembles each other except their molecular sizes. The length from a corner to the opposite corner of the smaller molecule is *ca.* 10.4 nm and that of the larger one is *ca.* 11.9 nm provided that the molecules had regular hexagonal structures. The dimensions of the molecules estimated by the mass spectra as above are within the range of the molecular sizes estimated for the organic polymer in Y-74662 (C2) (8 nm) and Belgica-7904 (C2) (12 nm) using the ratio of the amount of the lost carbon by pyrolysis to the amount of the carbon originally contained in the meteorites. This calculation was done on the assumption that they have regular hexagonal structures and a two-carbon unit from the circumference was lost on pyrolysis as the edge defects give rise to benzene-like pyrolysis products (MURAE *et al.*, 1989).

Figure 4 shows the diffuse reflection IR spectrum of the above-mentioned acid-resistant residues from ALH-77307. Some characteristic absorptions for aromatic hydrocarbons (BELLAMY, 1958) were observed at 3070, 1580, 1490, 810, and 720 cm^{-1} . The absorption at 3070 cm^{-1} was assigned to $=C-H$ stretching vibrations, the absorptions at 1580 and 1490 cm^{-1} were assigned to $C=C$ skeletal stretching vibrations whose

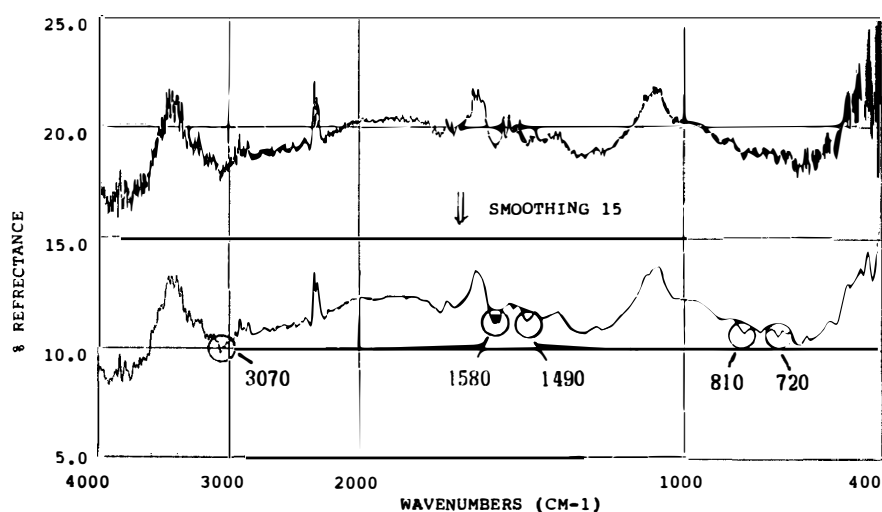


Fig. 4. Diffuse reflection FT-IR spectra of the acid-resistant residues from ALH-77307. Sample cup: 1 mm; resolution: 4 cm^{-1} ; number of scans: 300.

absorption intensities were enhanced by conjugation of the ring with other double bonds, and the absorptions at 810 and 720 cm^{-1} were assigned to out-of-plane C-H deformation vibrations of isolated ring hydrogen atom (BELLAMY, 1958). No remarkable absorption due to other functional groups was observed in the IR spectrum (Fig. 4). This is compatible with the structure proposed by the authors (Fig. 1) and suggests that the remaining edge defects after the acid treatments are mainly composed of aromatic hydrocarbons. The intensities of absorptions in the spectrum are weak as a whole compared with the amount of sample and this is interpretable with the presence of the large condensed aromatic network which shows no specific IR absorption band. This result is compatible with that obtained by the mass spectrometry.

In Fig. 5 are shown high-power decoupled CP-MAS ^{13}C NMR spectra of the acid-resistant residues from the Allende and Y-791717 meteorites and of coronene which is the compound bearing the smallest basic unit of the structure proposed by the authors for the organic polymer in carbonaceous chondrites. The amount of the above-mentioned residues from ALH-77307 was too small for CP-MAS ^{13}C NMR measurement. The spectra of the residues from Allende and Y-791717 showed two major peaks centered at 60 and 150 ppm. The absorption around 150 ppm is attributable to sp^2 -hybridized carbon of olefinic and/or aromatic groups (MACIEL *et al.*, 1979; MIKNIS *et al.*, 1979; ZILM *et al.*, 1981).

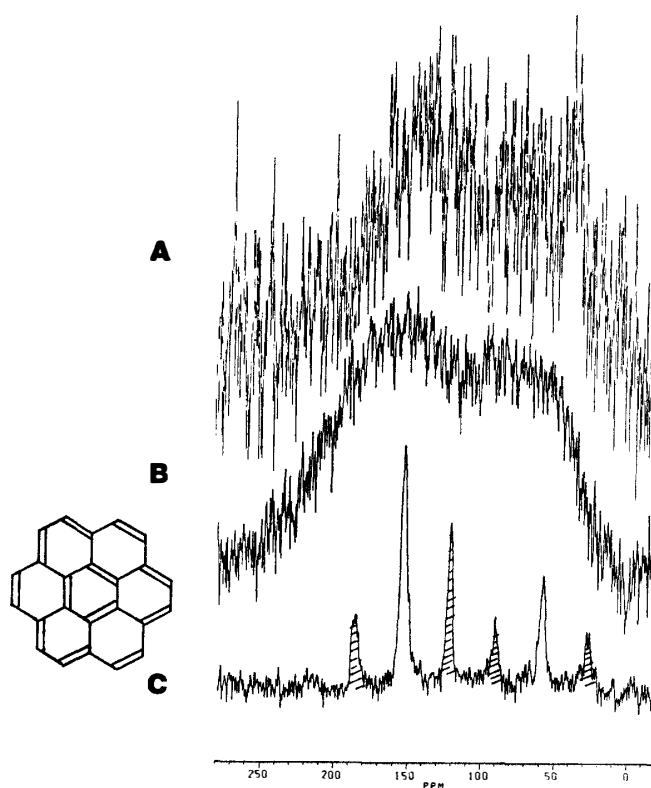


Fig. 5. ^{13}C CP-MAS NMR spectra of the acid-resistant residues from Allende and Y-791717, and commercial coronene. A: Allende (C: 7.57%) 17200 scans; B: Y-791717 (C: 3.08%) 38500 scans; C: coronene (Tokyo Kasei Kogyo: no further purification) 100 mg in 200 mg of NaCl, 2800 scans. The hatched peaks in the spectrum of coronene are spinning sidebands.

The peaks are very broad and the width of the line may indicate structural complexity of the samples. The width of the peaks may also be partially caused by paramagnetic broadening due to the presence of free electrons in the meteoritic insoluble carbon (CRONIN *et al.*, 1987) and also by the appearance of many spinning side bands under standard conditions for CP-MAS ^{13}C NMR of our instrument (125.76 MHz: four intense spinning side bands of the carbonyl carbon of glycine standard sample are usually observed). Although we used CP-MAS conditions, these spectra resembled the ^{13}C single pulse excitation NMR spectra more than the ^{13}C CP-MAS NMR spectra reported by CRONIN *et al.* (1987) for the insoluble carbon of the Orgueil and Allende carbonaceous chondrites. This is probably due to the differences of the sample preparations. The CP-MAS ^{13}C NMR spectral intensities are not representative of the total carbon in the sample and tend to underestimate sp^2 -hybridized carbon because of its common occurrence in "invisible", proton-poor domains. The structure proposed by the authors (Fig. 1) contains large polycyclic aromatic ring structure in which most of carbon atoms are located at considerable distance from protons, and their slow cross-polarization rates will tend to diminish the contribution of these carbon atoms to the spectrum.

The absorptions around 50 ppm are usually attributable to sp^3 -hybridized carbon of alkyl groups. However, the spectrum of coronene which has no alkyl group also showed an absorption at 58 ppm along with an absorption at 152 ppm. Although the assignment of the upper-field absorptions in the CP-MAS NMR spectrum of coronene is under way, the similarity of the spectra among coronene and the acid-resistant residues from Orgueil (C1) (CRONIN *et al.*, 1987), Murchison (C2) (CRONIN *et al.*, 1987), Allende (C3) and Y-791717 (C3) indicates that the structure proposed by the authors (Fig. 1) is common for acid-resistant residues from carbonaceous chondrites. The ^{13}C NMR spectra also suggest that most of carbon in the acid-resistant residues is contained in the aromatic structure and the amount of carbon which constructs three-dimensional network such as methylene chains and ether linkages is under limit of detection. This fact is compatible with the absence of the absorption bands due to the alkyl groups in the IR spectrum.

4. Conclusion

Laser ionization TOF-MS spectra of the acid-resistant residues from ALH-77307 were obtained to indicate the probable presence of two types of the high molecular compounds having molecular weight of *ca.* 34100 atom unit and *ca.* 45200 atom unit, respectively. Diffuse reflection FT-IR spectrum of the above-mentioned residues from ALH-77307 was obtained to show the presence of aromatic hydrocarbons as the only detectable chromophore. ^{13}C CP-MAS NMR spectra of the acid-resistant residues from Allende and Y-791717 were obtained to suggest the presence of aromatic and/or olefinic carbons as the major detectable ones. These results suggest that large polycyclic condensed aromatic rings are an important feature of the structure of the acid-resistant residues from the carbonaceous chondrites. The molecular model proposed by the authors can interpret these results as well as the results of pyrolytic studies and many other studies on the organic polymers in carbonaceous

chondrites.

Acknowledgments

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