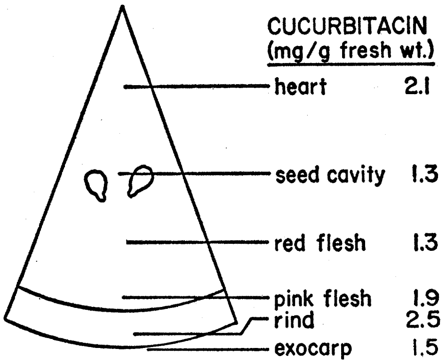

Fig. 2. Concentration (milligrams per gram, fresh weight) of cucurbitacin in different areas of fruit of a bitter watermelon.

Relative attractiveness of fruit samples is shown in Table 1. Bitter fruits had a much greater attractiveness for cucumber beetles than the nonbitter ones. After an exposure of only 15 minutes in one experiment the number of beetles on bitter samples was almost four times greater than the number on nonbitter samples. When exposure time was increased to 24 hours in a second experiment, the number of beetles on bitter samples was more than ten times the number on the nonbitter. Differences in the number of honey bees and yellow jacket wasps were also significant, but their response was opposite to that of cucumber beetles, that is, they exhibited greater preference for the nonbitter samples. The absence of yellow jackets from all 30 bitter samples, although not conclusive evidence for repellency, might suggest that the bitter samples are repellent to these insects. Cucumber beetles feeding on the cut surfaces of bitter fruit collected in the area adjacent to the exocarp (Fig. 1); this was the area of the fruit that contained the highest concentration of cucurbitacin (Fig. 2).

A quantitative relation was indicated in the feeding response of cucumber beetles to seedlings with different concentrations of cucurbitacin. Damage to cotyledons was also correlated with the concentration of cucurbitacin in the seedling (Table 2), as was the part of the seedling most damaged by the beetles. It was evident from the studies of damage to seedlings that the extent of the damage to cotyledons was greater than to hypocotyls. Our analysis, as well as that of others (*4*), of different plant parts from a number of commercial varieties showed that cotyledons and roots were high and hypocotyls low in cucurbitacin.

The average number of defecations and feeding punctures per sample on paper wrappings from water-, chloroform-, and pentane-soluble fractions of a bitter fruit extract in agar was 19.7, 45.4, and 3.3, respectively, which places the attractant primarily in the chloroform-soluble fraction. Chemical studies of these bitter compounds have shown them to be slightly soluble in water, highly soluble in chloroform, and highly insoluble in pentane (*1*). Moreover, cucumber beetles fed on dry filter paper in areas where chloroform solutions of purified cucurbitacins had been streaked. Cucurbitacin B was most heavily fed on, followed by cucurbitacins E and D. There was no evidence of feeding on cucurbitacin I. The positive response to several purified cucurbitacins definitely establishes them as specific feeding attractants for the spotted cucumber beetles, since induction of feeding on inert materials is considered conclusive evidence for a specific feeding attractant (*5*). Differences in chemical structure may explain the unattractiveness of cucurbitacin I.

Evidence that the toxic and repellent cucurbitacins are attractive to a limited group of insects has important implications in the evolution of the Cucurbitaceae. It may now be possible to study much more thoroughly the interactions of protective mechanisms of the plant against insect attack and the insect's adaptive responses. These results may also be important in the breeding of insect-resistant plants.

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High-Temperature Synthesis of Aromatic Hydrocarbons from Methane

Abstract. *Arenes of 1, 2, 3, 4 and more rings have been synthesized in a flow system by passing methane through silica gel at 1000°C. Yields of 4.8 to 7.2 percent have been obtained per single pass. As determined by combined gas chromatography–mass spectrometry, the major compound synthesized that are of less than 5 rings are benzene, naphthalene, acenaphthylene, phenanthrene, fluoranthene, and pyrene. Under certain conditions (presence of ammonia and water), small amounts of aliphatic hydrocarbons are also synthesized. Even-carbon-numbered hydrocarbons (aromatic as well as aliphatic) predominate, to the extent that about 97 percent of the total weight of the analyzed arenes have even numbers of carbon atoms.*

It is known that methane is one of the most abundant organic molecules in the solar system, being an important component of comets and the Jovian planets (*1*). It is also known that high temperatures are likely to be generated by the collision of either comets or large meteorites with planets (*2*) and that methane at high temperatures is converted to aromatic hydrocarbons (*3*). Because of the possible significance of these observations to organic cosmochemistry (*4*), we have studied in some detail the products formed from methane at temperatures of about 1000°C. The availability of a new gas chromatographic–mass spectrometric technique (*5*) has permitted us to carry out a qualitative and quantitative analysis of the reaction products with simplicity and accuracy not possible heretofore.

The experimental procedure can be summarized as follows: A Vycor tube (20 cm in length by 0.4 cm I.D., or 10 by 0.6 cm I.D.) filled with 100- to 200-mesh silica gel was heated at 1000°C in an electric furnace. Methane gas (Matheson, C.P.) was allowed to flow for 5 (or 10) hours at 0.2 cm^3/sec (measured at about 25°C). A total of 3.6 (or 7.2) liters of methane gas was consumed in each experiment. In some experiments, the methane was mixed with water and ammonia or bubbled through 1*N* ammonium hydroxide at 25°C, as it had been done before for the synthesis of amino acids (*6*). The products formed were collected in a "cold-finger" glass tube or trap which was cooled with ice water. A yellow to brownish-black material condensed on the walls of the trap and some white crystals deposited on the top part of the collecting tube.

The product in the trap was taken up in 5 ml of *n*-heptane, transferred to a silica gel column (1 by 16 cm), and separated into three fractions by successive elution with *n*-heptane, benzene, and methanol. Only the benzene eluates expected to contain aromatic hydrocarbons were analyzed in some detail. Analyses of the *n*-heptane eluate which could possibly contain aliphatic hydrocarbons were also performed. Gas-liquid chromatography and combined gas chromatography–mass spectrometry done with an LKB 9000 gas chromatograph–mass spectrometer were used in these analyses. Stainless steel capillary columns (30 to 210 m long, 0.25 to 0.75 mm inside diameter) coated with Polysev, or other stationary phases (SF-96 and G-60) were used (*7*). The mass spectral data were obtained at 70 ev. Proper solvent blanks and control runs were analyzed in an identical manner. In one experiment a second "cold-finger" trap was connected in series with the first and cooled in dry ice–acetone and used in order to condense the more volatile hydrocarbons which were directly analyzed without previous fractionation. Additional details and references on the fractionation and analytical procedures have been described elsewhere (see *8* and *9*).

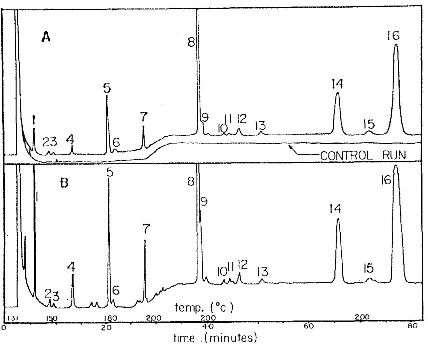

Fig. 1. Gas chromatograms of aromatic hydrocarbons synthesized at 1000°C (*A*) from methane and (*B*) from methane bubbled through 1*N* ammonium hydroxide. The reaction was carried out in a Vycor tube 20 cm long by 0.4 cm inside diameter, filled with silica gel as catalyst. The analysis was performed in a 75 m long by 0.75 mm inside diameter stainless steel capillary column coated with Polysev (*7*). An F and M model 810 gas chromatograph with flame ionization detector, linear temperature programming, and nitrogen as carrier gas were used for this purpose. A control run made by passing methane through the silica gel at room temperature and doing everything else in a manner identical to the actual experiment showed that no detectable amounts of aromatic hydrocarbons were formed.

Figure 1 shows two chromatograms of the benzene eluate fraction corresponding to two typical experiments. It can be seen that aromatic hydrocarbons are formed when either pure methane (*A*) or methane with ammonia and water (*B*) was passed through silica gel at 1000°C. No significant differences between these two runs were observed except in the relative amounts of naphthalene and other volatile components. By looking at the chromatographic analysis of a control run which included all components and operational procedures except heating (Fig. 1), one can see that the contribution of aromatic hydrocarbons by contamination was negligible. The average contamination of several runs was less than 1×10^{-6} g, which is five orders of magnitude lower than the actual yield (see below).

Table 1 lists the hydrocarbons identified by their retention times, using the above-listed three different chromatographic columns and their individual mass spectra. Figure 2 gives the mass spectra of compound No. 14 and of standard fluoranthene. Good mass spectra for the other 15 hydrocarbons were also obtained. The separation of pairs of isomers, such as fluoranthene and pyrene, and anthracene and phenanthrene, was accomplished with four different stationary phases, including the above three. Infrared analysis of the white crystals which deposited in relatively large amounts in the upper part of the cold trap showed that they were essentially pure naphthalene. Gas chromatographic analysis in three different columns of the more volatile hydrocarbons collected in the experiment in which a second cold trap was used demonstrated the presence in substantial amounts of benzene, toluene, styrene, and minor quantities of ethylbenzene, xylenes (*o*−, *m*−, and *p*−) and two other unknown components (*10*).

The yield of aromatic hydrocarbons in two experiments was at least 7.2 percent (long tube) and 4.8 percent (short tube), on the basis of the methane used in one single pass, which is equivalent to 0.15 g and 0.10 g, respectively. The actual total yield was no doubt higher, since some of the naphthalene and some of the mononuclear aromatic hydrocarbons were probably lost by evaporation during recovery, transfer, and other phases of the analytical procedure.

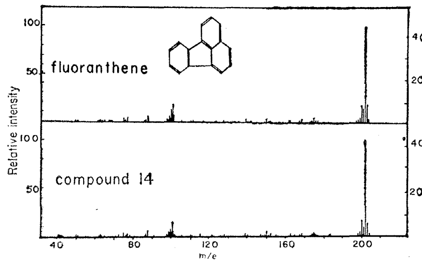

Fig. 2. Mass spectrum of one of the aromatic hydrocarbons (fluoroanthene) obtained at 70 ev with the LKB 9000 gas chromatograph–mass spectrometer. Good mass spectra of the other major components emerging from the gas chromatograph were also obtained.

The product did also contain aromatic hydrocarbons of higher molecular weight, as indicated by the yellow to brownish color of the condensed material. The detection of these aromatic hydrocarbons was limited by their solubility and volatility in rela-

Table 1. Aromatic hydrocarbons synthesized from methane at 1000°C, with silica gel used as catalyst. The corresponding chromatogram is shown in Fig. 1*A*. In this first experiment naphthalene and the more volatile hydrocarbons were not recovered quantitatively. A total yield of at least 7.2 percent (0.15 g) was obtained in this experiment. The amounts of the individual hydrocarbons are given relative to phenanthrene. Relative values smaller than 1×10^{-2} are designated as trace.

Aromatic hydrocarbon	Relative amounts
1. Naphthalene	4.6×10^{-2}
2. 2-Methylnaphthalene	Trace
3. 1-Methylnaphthalene	Trace
4. Biphenyl	3.3×10^{-2}
5. Acenaphthylene	2.6×10^{-1}
6. Acenaphthalene	Trace
7. Fluorene	5.1×10^{-2}
8. Phenanthrene	1.0
9. Anthracene	5.0×10^{-2}
10. 4-Methylphenanthrene	Trace
11. 2-Methylphenanthrene	Trace
12. 4 H-Cyclopenta [def] phenanthrene	4.0×10^{-2}
13. Vinylphenanthrene	Trace
14. Fluoranthene	4.5×10^{-1}
15. 4,5-Benzacenaphthylene	Trace
16. Pyrene	1.39

tion to the technique used. Analysis by ultraviolet spectrophotometry of the compounds separated by adsorption silica-gel chromatography indicated the presence of arenes with five or more rings (*10*).

In addition to what has been described thus far, the following pertinent observations were also made. These are concerned mainly with the ordered nature of the synthesized hydrocarbons (aliphatic and aromatic) and with the possible bearing which the above results may have on the origin of the hydrocarbons detected in carbonaceous chondrites (*8, 9*).

The amounts of aliphatic hydrocarbons detected in the experiments in which only methane was used were no larger than those of the control runs. However, small amounts were formed, about 8×10^{-5} g, when ammonia and water were present as reactants together with methane. Interestingly enough, the prevailing compounds from the *n*-heptane eluate in the range C_{18} to C_{24} were found to correspond to even-carbon-numbered aliphatic hydrocarbons with the retention times of olefins. Of course, this is not surprising when one considers that ethylene and acetylene are known to be formed from methane (*3*) and that condensation of ethylene can be expected to lead to the formation of even-carbon-numbered olefins or cyclic aliphatic hydrocarbons. The distribution of aliphatic hydrocarbons below C_{18} showed a certain resemblance to that found in carbonaceous chondrites and to the products of certain Fischer-Tropsch processes (*11*). It should be added that an analysis of the hydrocarbons synthesized by the action of ionizing radiation on methane, as described by Davis and Libby (*12*), showed also a predominance of even-carbon-numbered olefins.

A more striking observation concerning the prevalence of compounds with even numbers of carbon atoms was made on examination of the aromatic hydrocarbons. In fact, about 97 percent of the total amount of aromatic hydrocarbons synthesized in the experiment represented in Fig. 1A (see also Table 1) is made of compounds with even numbers of carbon atoms. As implied above, this may result in part from the fact that at the high temperatures used, acetylene and other C_2 species are thermodynamically more stable than methane and other C_1 species. Therefore, the products formed will have an empirical carbon-skeleton formula, $(C_2)_n$. A complete understanding of such "ordered" synthetic processes will have to await a detailed study of the intermediates formed and the reaction mechanisms involved in the "pyrolysis" of methane and other hydrocarbons at different temperatures. Work along these lines has been carried out by Badger and co-workers (*13*) and more recently in our laboratory (*14*).

It is also of interest to try to make a correlation of the aromatic hydrocarbons obtained in these experiments with the aromatic hydrocarbons detected in carbonaceous chondrites. At present, however, there seems to be insufficient data on the latter to be able to establish meaningful correlations. Preliminary results in our laboratory (*15*) have revealed significant qualitative and quantitative variations in the aromatic hydrocarbons from different types and samples of carbonaceous chondrites. Similar variations have been observed in the aliphatic hydrocarbons of the same meteorites (*8*). Therefore, until most of the carbonaceous chondrites have been analyzed for aromatic hydrocarbons, it would seem premature to attempt any correlations.

We conclude by saying that since methane, or radicals presumably formed from methane, have been detected in comets and in Jupiter and other Jovian planets, it is possible that aromatic hydrocarbons and other organic compounds have been formed as a result of collisions of comets with planets or satellites such as the moon and collisions of large meteorites with planets containing reducing atmospheres. Furthermore, it is also possible that the formation of these compounds is occurring presently in localized areas of Jupiter where the necessary thermal energy is available, as indicated by the emission of large radiation outbursts from different parts of this massive planet (*16*), and in a more general way in the upper layers of the Jovian atmosphere where the corpuscular and noncorpuscular ionizing radiation from the solar wind is absorbed by methane (*17*).

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18. We thank H. B. Skewes for carrying out some of the early experiments and D. W. Nooner for analyzing the aliphatic hydrocarbon fraction of some of these experiments. We thank Prof. W. F. Libby for a sample of the product obtained by irradiation of methane. This work was supported in part by research grants NsG-257 and NGR-44-005-020 from NASA.

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