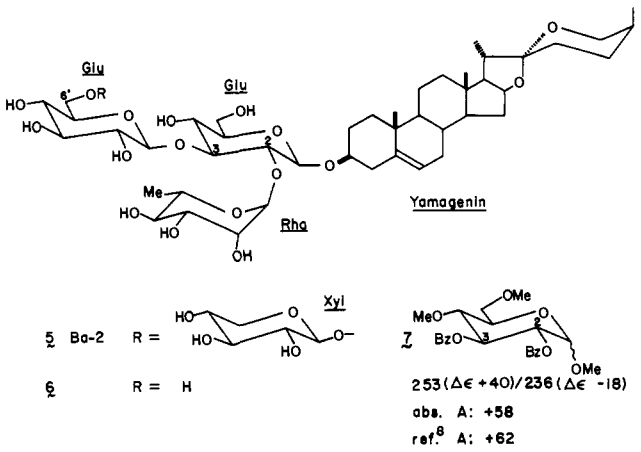
Chart II



by refluxing for 5 h in 8% HCl/MeOH, and *p*-bromobenzoylated after removal of solvent.[14] The two UV-absorbing products **2** (from Glu-2 unit in **1**) and **3** (from Glu-1 unit in **1**) were separated by TLC;[15,16] only the UV-absorbing products need be collected since all terminal units become permethylated methyl glycosides and therefore are "UV transparent".

CI-MS (CH_4 carrier gas)[17] of the two spots showed that they were a mono- and a dibenzoate. The amount of respective benzoates in the UV/CD cells were estimated from the standard UV ϵ values[18] at 244.5 nm without weighing of samples, and from this it was possible to measure the amplitudes of the CD curves.[17] For dibenzoate **3** the A value of the exciton-split CD curve at 253/238 nm was −6, which checks well with the reference value $A = 0$ for 1,3-ee dibenzoates.[8] This establishes that in balanitin-1, one of the glucose unit (Glu-1) is branched at C-2 and C-4 (1,3-ee).

Hydrolysis of Ba-2 (**5**) (5 mg) with $Ac_2O/AcOH/H_2SO_4$ at room temperature for 3 days cleaved the terminal xylose to give 1.2 mg of prosapogenin (**6**) (Chart II). Permethylation of **6**, followed by methanolysis with MeOH/HCl and *p*-bromobenzoylation, gave a single UV visible product which was separated by preparative TLC. CI-MS (CH_4) revealed the product to be a di-*p*-bromobenzoate. The amplitude of +58 of the split CD curve, as deduced from the UV absorbance, leads to a *vic*-ee dibenzoate arrangement, namely, **7**; the glucose is thus branched at C-2 and C-3 to the other sugars.[19]

Since only microgram quantities of material is employed and no reference sample is required, we believe that this method for determining the structure of branching points in oligosaccharides will be useful in structure elucidations of complex saccharides such as those encountered in serum glycoproteins and cell walls.[4] Micromethods for characterization of monosaccharides and determination of glycosidic linkages at nonbranching points in oligosaccharides are currently under development.[20]

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(14) Benzoylation was carried out by adding excess *p*-bromobenzoyl chloride to a solution of the residue in pyridine, keeping the mixture at 60 °C for 12 h, and quenching the reaction with methanol from a microsyringe. The solvent was evaporated after addition of a few drops of benzene (or toluene) to assist in removal of the pyridine.
(15) TLC was run on silica-precoated aluminum sheets (E. Merck, Darmstadt, G.F.R.), MeOH-$CHCl_3$ (2:98). The sensitivity of detecting the UV-absorbing products can be increased by using high-performance LC, μ-Porasil, MeOH-$CHCl_3$ (0.5:99.5).
(16) In the majority of cases, methanolysis of oligosaccharides affords one of the anomeric glycosides as the major product. In the present case, the benzoate **2** and 2,4-dibenzoate **3** only gave one anomeric glycoside as detectable spots. Since the CD data of α- and β-methylglycosides are similar, the anomeric configuration is immaterial for the argument; we have tentatively assumed it to be the α anomer since those are usually the major methanolysis products.
(17) A Finnigan 3300 instrument and a JASCO J-40 spectropolarimeter were employed.
(18) Standard ϵ values of *p*-bromobenzoates (in MeOH): mono, 19 500; di, 38 200; tri, 57 200; tetra, 76 400.[8]
(19) Although no attempts were made, the scale of the reaction can readily be reduced.
(20) Supported by NIH Grant CA 11572.

Amino Acids in the Hydrolysis Products of the Reaction of Carbon Vapor with Ammonia

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The carbon arc is a convenient source of both monoatomic and diatomic carbon which have been observed to undergo a wide variety of fascinating reactions.[1,2] We wish to report that co-condensation of arc generated carbon vapor with ammonia at −196 °C followed by hydrolysis produces amino acids in a reaction which has possible implications in the extraterrestrial synthesis of these compounds.

In a typical experiment, reactants were introduced under high vacuum and codeposited with arc generated carbon vapor on the walls of a reactor at −196 °C.[3] At the conclusion of the reaction, volatile components were removed under vacuum at room temperature and the residue hydrolyzed with 6 N HCl at 60 °C for 24 h. After removal of the solvent, the hydrolysate was heated with acidic *n*-butanol followed by trifluoroacetic anhydride in order to prepare the *N*-trifluoroacetyl *n*-butyl esters of the amino acids.[4] These derivatives were then analyzed by gas chromatography–mass spectrometry (GC–MS).[5] The presence of the primary amino acid products was also confirmed by using a Beckman amino acid analyzer. Reactants employed were (a) ammonia (b) ammonia and water, and (c) a mixture of NH_3, H_2O, and HCN. Table I lists the amino acids formed, along with their yields as determined by GC–MS, using these three sets of reactants. In all experiments, glycine, alanine, β-alanine, *N*-methylglycine, and aspartic acid were produced. When water was added to the reactants, serine was also generated. In each case, the mass spectrum of the amino acid derivative was identical with that of an authentic sample.

This unique reaction represents an example of the formation of amino acids in a system in which carbon vapor is the sole source of carbon.[6] Since arc generated carbon vapor is rich in C_1 and C_2,[1,2] it is likely that carbon enters into initial reactions in the form of one of these intermediates. With this fact in mind, we shall propose a tentative mechanism for the formation of glycine which is the major product.

The reaction of C_1 with NH_3 is expected to generate aminomethylene (**1**) which can either rearrange to methyleneimine (**2**) or lose H_2 to form HCN. Cacace and Wolf[7] have presented

$$C + NH_3 \rightarrow \underset{\mathbf{1}}{H-\ddot{C}-NH_2} \rightarrow HCN + H_2$$

$$\downarrow$$

$$\underset{\mathbf{2}}{H_2C{=}NH} \xrightarrow{HCN} \underset{\mathbf{3}}{NH_2-CH_2-CN} \xrightarrow{H_2O,\ H^+} \text{glycine}$$

evidence for the formation of **2** in the reaction of ^{11}C atoms with anhydrous NH_3. HCN, which was detected among the volatile products of the present reaction (Table 1), could subsequently add to **2** yielding aminoacetonitrile (**3**). The glycine would be generated from **3** in the hydrolytic workup. An examination of

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(5) Leimer, K. R.; Rice, R. H.; Gehrke, C. W. *J. Chromatogr.* **1977**, *141*, 121-144.
(6) Harada and Suzuki (Harada, K.; Suzuki, S. *Nature (London)* **1977**, *266*, 275-276) have reported the formation of amino acids from elemental carbon by contact glow discharge electrolysis in aqueous ammonia.
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Table I. Amino Acids Formed upon Hydrolysis of the Products of the Reaction of Carbon Vapor with Ammonia

amino acid formed	amino acid yield, mmol		
	reaction a[a]	reaction b[b]	reaction c[c]
glycine	6.0×10^{-2}	1.0×10^{-1}	3.0
alanine	1.6×10^{-2}	8.6×10^{-3}	1.8×10^{-1}
β-alanine	2.0×10^{-3}	7.5×10^{-3}	1.7×10^{-1}
N-methylglycine	4.8×10^{-2}	1.1×10^{-2}	2.4×10^{-1}
serine		1.1×10^{-2}	5.9×10^{-2}
aspartic acid	4.4×10^{-5}	2.6×10^{-3}	1.4×10^{-1}

[a] Reactants: carbon (73.7 mmol) and NH_3 (89.1 mmol). Hydrogen cyanide (7.2×10^{-1} mmol) was detected by infrared analysis of the volatile products of this reaction. [b] Reactants: carbon (64.2 mmol), NH_3 (100.7 mmol), and H_2O (55.5 mmol). [c] Reactants: carbon (79.6 mmol), NH_3 (104.2 mmol), H_2O (55.5 mmol), and HCN (31.0 mmol).

the proton NMR spectrum of the products prior to hydrolysis reveals the presence of **3** (1.6×10^{-2} mmol). This mechanism is consistent with the fact that inclusion of HCN among the reactants increases the yield of glycine. The yield of the other amino acids also increases when HCN is added (Table I).

Although evidence regarding the mechanism of formation of the remaining amino acids or their precursors is lacking, it is obvious that a number of reactions must occur subsequent to the initial encounter between carbon and ammonia. These reactions take place in the condensed phase on the walls of a reactor that is immersed in liquid nitrogen.[8] However, this surface is also exposed to thermal and electromagnetic radiation from the carbon arc, and it is reasonable to suppose that various reactive intermediates may be generated and possess mobility under these conditions. These include CH_2, formed by hydrogen abstraction by C_1,[9] and various species formed by the reactions of C_2. The major reaction that has been reported for C_2 is hydrogen abstraction to generate acetylene.[1,10] Skell and Plonka[11] have shown that this reaction involves an intramolecular pathway with vinylidene (**4**) as an intermediate and an intermolecular route involving ethynyl radicals (**5**). If these pathways are operative in

$$C_2 + NH_3 \rightarrow :NH + \underset{\mathbf{4}}{H_2C{=}C:} \rightarrow C_2H_2$$

$$C_2 + NH_3 \rightarrow H_2N\cdot + \underset{\mathbf{5}}{\cdot C{\equiv}CH} \xrightarrow{NH_3} H{-}C{\equiv}C{-}H + \cdot NH_2$$

the reaction of C_2 with ammonia, it is reasonable to assume that such reactive species as **4**, **5**, :NH, and $\cdot NH_2$ are present. Since there are many reactions possible when energetic species such as these are generated in NH_3 containing C_2H_2 and HCN, it is premature to speculate on detailed reaction mechanisms.

It may be that some of the observed amino acids arise not from monomeric precursors but from hydrolysis of a polymeric material produced under the reaction conditions. In particular, the hydrolysis of HCN polymers and oligomers has been shown to generate amino acids.[12] Control experiments demonstrate that HCN is not polymerized when condensed with an excess of NH_3 and warmed to 25 °C. An additional control involved striking the carbon arc in the presence of HCN coated on the reactor walls at −196 °C. Hydrolysis of the residue from this reaction gave only traces of glycine and β-alanine but none of the other amino acids in Table I. However, neither of these controls rule out a polymerization of HCN induced under the reaction conditions. That glycine does not arise solely by hydrolysis of a polymer is demonstrated by the fact that **3**, a monomeric precursor to glycine, is detected prior to hydrolysis. We are currently developing analytical methods that may allow the detection of monomeric precursors of other amino acids.

Although the mechanisms of formation of amino acid precursors in these systems are unclear, the results demonstrate that amino acids can be formed in systems in which carbon vapor is the only source of carbon. It is possible that reactions similar to those reported here may play a role in the formation of extraterrestrial amino acids such as those which have been detected in meteorites[13] and lunar samples.[14] Since ammonia,[15] water,[15] C_1,[16] and C_2[17] have all been detected as extraterrestrial species, the experiments described here may mimic those reactions which occur when interstellar carbon vapor condenses on a cold surface containing solid ammonia and water or in interstellar clouds containing these species.

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Facile Regio- and Stereoselective Total Synthesis of Racemic Aklavinone†

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We have previously described[1] the development of a convergent strategy for the regiospecific construction of the aklavinone (I) skeleton. Aklavinone[2] is the aglycon of aclacinomycin A,[3] which is a highly promising chemotherapeutic agent for the treatment of a wide spectrum of cancers, including acute leukemia,[4] and has been reported to possess lower cardiotoxicity than the existing antineoplastic anthracycline antibiotics, adriamycin and daunomycin.[5] In recent years, its total synthesis has attracted the

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