changes in bacterial morphology, a sensitive and reproducible assay can still be obtained. Note the difference between the milk and the serum dose–response curves for penicillin (Figures 3 and 4). The effect of sample turbidity may be reduced by using a higher dilution ratio.

The four drugs studied may be assayed quite effectively in serum. Assay organisms tend to exhibit initially slow growth in 100% serum. This problem is overcome by the initial 1:1 dilution with BHI broth. Urine samples involve the simplest preparation and also provide the most sensitive DLS assay. However, the correlation of antibiotic residue levels in urine and tissue has not yet been fully studied. Bile samples yield sensitivities similar to those in serum.

An important feature of the DLS method is the simplicity of the various sample preparations. Because of the relatively large final dilution, sample cleanup time is minimized and effectively eliminated. As will be described in later papers, even tissue specimens are easily prepared with negligible sample cleanup labor.

The high speed and high sensitivity obtained with the single test organism *S. aureus* SS41 suggest its immediate use as a negative screening organism to be used routinely on large numbers of samples. The inherent speed and simplicity of the DLS assay will permit the early realization of fully automated systems with throughputs of hundreds of samples per hour. Work now in progress suggests that by using several test organisms with varied sensitivity, a particular drug can be assayed in the presence of other drugs. The basic techniques developed here are applicable to tissue samples and to a wide range of drugs. The potential applications of the new DLS assay method are limited only by the genetic possibilities of bacteria. Some bacterial strains with specific nutritional requirements can be used for vitamin assays, etc., while other organisms exhibit high sensitivity to toxins ranging from pesticides to heavy metals. The DLS assay technique promises to become an important tool for many parts of the food industry.

ACKNOWLEDGMENT

We wish to acknowledge the able laboratory work of Mark Scher, Frank Cordeiro, and Roger Kahn. We wish to thank E. R. Squibb and Sons for samples of penicillin-G (lot 4J626) and neomycin sulfate (lot 5C781), Lederle Laboratories for samples of chlortetracycline (lot 7670B-95-1), and Norwich Pharmaceutical for samples of furaltadone (lot Nf-260 S-3144 RN41992).

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Received for review January 29, 1976. Accepted May 26, 1976. This study was supported by the U.S. Food and Drug Administration under Contract No. 223-75-7004.

Pyrolysis of Some Sulfur-Containing Amino Acids at 850 °C

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The pyrolysis of cysteine, cystine, homocystine, methionine, methionine sulfone, and methionine sulfoxide at 850 °C in a nitrogen atmosphere produces pyrolysates whose composition is qualitatively similar to those obtained from non-sulfur-containing amino acids except for a few organosulfur compounds. Most of the sulfur in the amino acids listed above is converted to carbon disulfide, carbon oxysulfide, or to derivatives of these compounds.

The pyrolysis of protein (Higman et al., 1970; Smith et al., 1974) and amino acids (Higman et al., 1970; Patterson et al., 1969, 1971, 1973) has been shown to give pyrolysates with qualitative similarities but with quantitative differences. These quantitative differences were suggested to arise from variations in reactive intermediate concentrations which in turn are related to the structure of the substance pyrolyzed. Because sulfur or sulfur derivatives are known to combine with carbon species to form stable heterocyclic systems and to function as dehydrogenation agents (Vadekar and Pasternak, 1970; Plattner

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Table I. Relative Yields of Gases Compared to Carbon Dioxide[a]

	CO	CH_4	C_2H_4	C_2H_6
Methionine	3.0	1.1	1.4	0.10
Cysteine	0.40	0.44	0.17	0.03
Cystine	0.06	0.14	0.05	0.003
Homocystine	0.16	0.26	0.14	0.02
Methionine sulfone	0.17	0.44	0.26	0.05

[a] C_2H_2, CS_2, COS, and HCN were detected in gases produced during pyrolysis of all the amino acids. SO_2 was observed in the methionine sulfone gases only. Peak area ratios (CO_2 = 1) uncorrected for detector response differences.

Table II. Yields[a] of Carbon Dioxide and Ammonia

	CO_2	NH_3
Methionine	9.7	0.41
Cysteine	16.7	0.08
Cystine	22.3	0.10
Homocystine	88.9	0.24
Methionine sulfone	42.7	0.19

[a] Reported in grams of gas per mole of substance pyrolyzed.

and Armstrong, 1948) it might be anticipated that the sulfur in sulfur-containing amino acids would have some influence on the composition of the pyrolysates formed from these substances. In a continuation of our studies on the effect of structural variation in amino acids on the composition of the pyrolysates, we have pyrolyzed the sulfur-containing amino acids, methionine, cysteine, cystine, homocystine, methionine sulfone, and methione sulfoxide at 850 °C in a nitrogen atmosphere with the thought that these sulfur-containing amino acids may give more polynuclear aromatic hydrocarbons than those of nonsulfur amino acids.

EXPERIMENTAL SECTION

Materials. DL-Methionine, DL-homocystine, L-cystine, L-cysteine (Nutritional Biochemicals, Cleveland, Ohio), methionine sulfone [DL-2-amino-4-(methylsulfonyl)butyric acid], and methionine sulfoxide [DL-2-amino-4-(methylsulfinyl)butyric acid] (Eastman Organic Chemicals, Rochester, N.Y.) were used as received.

Methods. Ultraviolet spectra were measured in cyclohexane using a Perkin-Elmer Model 202 spectrophotometer, and infrared spectra were measured in chloroform or carbon tetrachloride using a Beckman IR-8 spectrophotometer equipped with a mirror beam condenser. GLPC retention times were measured and separations of the pyrolysate constituents were carried out on a F&M Model 810 gas chromatograph.

Pyrolyses. The pyrolyses were carried out in the apparatus previously described (Patterson et al., 1968) using 10 ml of Berl saddles, a nitrogen flow of 100 ml/min, and a rotating screw device for the introduction of samples into the pyrolysis tube.

The liquid products were collected in two traps, each of which was cooled in a dry ice–chloroform–carbon tetrachloride mixture. Gases which were not condensed by these traps were examined by infrared spectroscopy using a 100-mm gas cell. Identifications were based upon comparisons of the absorption bands observed with those reported in the literature (Pierson et al., 1956) and with those obtained from authentic samples.

Quantitative gas analyses were carried out in separate experiments in which the compounds under investigation were pyrolyzed under the conditions previously described. The gases were directed through a series of traps without cooling. Carbon dioxide and hydrogen cyanide were absorbed in 2 M KOH and ammonia in 3.5 M H_2SO_4. The amounts of hydrogen cyanide were not determined because of the interference by sulfur compounds in the KOH trap. Carbonate was precipitated with barium nitrate solution and determined gravimetrically. The ammonia collected in the sulfuric acid trap was distilled into boric acid solution after basification and titrated potentiometrically with hydrochloric acid. The amounts of carbon monoxide and light hydrocarbon gases relative to carbon dioxide were determined by gas chromatography using a 4 ft × 0.25 in. silica gel (100–120 mesh) column at 25 °C. The results are reported as ratios of areas (CO_2 = 1) without correction for thermal conductivity detector response differences (Table I). Quantitative gas analyses (CO_2 and NH_3) are reported in Table II.

The pyrolysate was heated in a water bath at 100 °C and the gases evolved were analyzed by infrared spectroscopy.

In the cysteine, homocystine, and methionine experiments, a brown solid deposited on the condenser walls and an orange-yellow solid collected in the receiver. When the brown solid was heated to 150 °C it decomposed to give gases which were identified by their ir spectra as carbon dioxide, carbon oxysulfide, ammonia, and hydrogen cyanide. Mass spectral analysis of the solid was consistent with a mixture of salts consisting mainly of ammonium carbonate or bicarbonate, ammonium carbamate, ammonium thiocarbamate, and ammonium cyanide.

The gases obtained on decomposition of the orange-yellow solid were identified (ir analysis) as carbon disulfide, carbon oxysulfide, carbon dioxide, and ammonia. The mass spectrum of this solid was consistent with a mixture of ammonium thiocarbamate, ammonium dithiocarbamate, ammonium carbamate, and ammonium carbonate.

When the pyrolysate from cystine was heated to 100 °C a black, fluffy solid was obtained. Thermal decomposition of this solid at 150 °C gave the following gases, identified by their infrared spectra: carbon disulfide, ammonia, hydrogen cyanide, and carbon oxysulfide.

The residue obtained after the 100 °C heating of the pyrolysate was extracted with ether and the ether-soluble material was separated into acidic, neutral, and basic fractions by extraction with successive portions of 5% HCl and 5% NaOH, each saturated with NaCl. Phenols were separated from carboxylic acids using the appropriate pH adjustment (pH 6.5). The compounds pyrolyzed along with the amounts of the major fractions obtained are reported in Table III.

Table III. Weight[a] of Pyrolysate Constituent per Mole of Amino Acid Pyrolyzed

	Methionine								Methionine sulfoxide	
Constituent	N_2	Air	Cysteine	Cystine	Alanine	Serine	Homocystine	Methionine sulfone	N_2	Air
Neutrals	2.92	1.54	1.25	5.35	0.26	1.42	5.40	2.10	1.32	2.01
Bases	0.91	0.63	0.65	5.83	0.14	1.32	4.51	0.59	3.96	3.02
Acids	0.18		0.03	0.09	0.02	0.26				
Phenols	0.18		0.26	0.18	0.03	0.28	0.72	0.10	1.06	1.01

[a] Reported in grams of constituent produced per mole of substance pyrolyzed.

Table IV. Relative Concentrations of Components[a] Produced in the Pyrolysis of Methionine, Cysteine, Cystine, Homocystine, 2-Amino-4-(methylsulfonyl)butyric Acid, and 2-Amino-4-(methylsulfinyl)butyric Acid

Component	Methionine		Cysteine	Cystine	Homocystine	Methionine sulfone	Methionine sulfoxide	
	N_2	Air					N_2	Air
Acenaphthalene			0.01	0.16	0.08			
Benzene		0.02	0.08					
Benzonitrile	0.07	0.08	0.11	1.41	0.65	0.52	0.13	0.43
2,3-Benzoquinoline	0.02		0.01	0.03	0.08	0.01	0.11	0.02
3,4-Benzoquinoline	0.05		0.01	0.01	0.17	0.01	0.07	0.02
Biphenyl	0.03	0.01	0.01	0.01				
2-Cyanopyridine			0.01	0.05	0.25	0.01	0.03	0.01
3-Cyanopyridine			0.01	0.13	0.64	0.18	0.42	0.28
4-Cyanopyridine			0.01	0.05	0.15	0.02	0.07	
3-Cyano-5-methylpyridine			0.01	0.02	0.39	0.05	0.18	0.09
Fluoranthene	0.03							
Fluorene	0.05	0.03	0.01	0.01	0.08			
Indole	0.21		0.19	0.44	0.47		0.16	0.14
Isoquinoline	0.06		0.15	0.01	0.13	0.07	0.56	0.22
4,5-Methylenephenanthrene	0.01	0.01						
1-Methylnaphthalene	0.11	0.06	0.16	0.01	1.07			
2-Methylnaphthalene	0.18	0.13	0.07	0.13	0.71	0.13	0.03	0.07
4-Methylquinoline			0.03	0.05	0.09	0.01	0.06	0.02
6-Methylquinoline	0.04		0.02	0.09	0.15	0.03	0.17	0.07
o-Methylstyrene		0.01		0.04				
m-Methylstyrene		0.01	0.07	0.20				
β-Methylstyrene		0.05	0.06	0.25				
Naphthalene	0.92	0.54	0.13	0.70	0.39	0.38	0.16	0.40
1-Naphthonitrile	0.05	0.05	0.03	0.34	0.30	0.10	0.26	0.21
2-Naphthonitrile	0.01	0.02	0.01	0.06	0.05	0.05	0.09	0.06
Phenanthrene	0.18	0.06	0.01	0.06	0.08	0.01	0.08	0.06
4-Phenylpyridine	0.02							
2-Picoline			0.01	1.84		0.03	0.10	0.07
3-Picoline	0.01			1.03	0.14	0.22	0.55	0.40
Pyrene	0.02	0.01						
Pyridine	0.01			0.89	0.04	0.19	0.20	0.14
Quinoline	0.16		0.12	0.34	0.52	0.10	0.77	0.31
Quinaldine	0.04		0.01	0.03	0.19	0.01	0.02	0.01
trans-Stilbene	0.01			0.01				
Styrene	0.01	0.02						0.02
Thianaphthene	0.13	0.06	0.04	0.04				
Toluene		0.02						
o-Toluidine	0.01				0.15			
m-Toluidine	0.01				0.17			
o-Toluonitrile	0.03				0.10	0.10		
m-Toluonitrile	0.08		0.06					
2-Vinylnaphthalene	0.01	0.03	0.01			0.10		

[a] Reported in grams of component produced per mole of substance pyrolyzed.

Separation and Identification of Components. Components of the neutral and basic fractions were separated by GLPC using a 25 ft × 0.375 in. 20% Apiezon L column (Anakrom 50/60 U) heated at 92 °C for 8 min and then programmed at 2 °C/min to 275 °C. The final temperature was maintained for an extended period to ensure elution of high-boiling components. Identifications of components are based on comparisons of GLPC retention times, ultraviolet spectra, and infrared spectra with those obtained from authentic samples. Estimations of relative abundances of constituents are based on area percent values obtained from GLPC. The results are listed in Table IV.

RESULTS AND DISCUSSION

The low-temperature pyrolysis (270–300 °C (30 mm pressure)) of representative sulfur-containing amino acids (Fujimaki et al., 1969) resulted largely in the formation of the expected pyrodegradation products arising from the cleavage of various bonds in the molecule. Thus, the pyrolysis of L-cystine and L-cysteine gave ethylamine, mercaptoethylamine, ammonia, hydrogen sulfide, acetaldehyde, ammonium carbonate, and alanine. Some pyrosynthesis occurred as indicated by the formation of isoleucine and methionine as well as some nitrogen and sulfur heterocyclic compounds (thiophenes, pyridines) (Kato et al., 1973). The thiophenes were found in the cysteine pyrolysate but not in the cystine pyrolysate.

Under the more severe high-temperature pyrolytic conditions (850 °C, nitrogen atmosphere) reported here, both pyrodegradation and pyrosynthesis appear to be far more extensive and a complex product mixture is obtained from methionine, cysteine, cystine, homocystine, methionine sulfone, and methionine sulfoxide. The pyrolysates were qualitatively similar to those obtained from nonsulfur amino acids (Patterson et al., 1969, 1973) and contained the usual aromatic hydrocarbons, nitriles, and nitrogen heterocycles (see Table IV). Just one sulfur heterocyclic substance, thianaphthene, was detected in the pyrolysates of methionine, cystine, and cysteine—none of the thiophenes or thiazoles previously reported (Kato et al., 1973) were found. The only other sulfur-bearing substances identified were the simple volatile compounds carbon disulfide and carbon oxysulfide (or their derivatives). These results suggest that the amino acids, including the sulfur-containing amino acids, undergo degradation into common intermediates of two-, three- (Hurd et al., 1962), and four-carbon (Badger, 1965) types which subsequently recombine to form aromatic systems. The intermediacy of the three-atom species (trimethine or

azatrimethine) appears to be of particular importance in the pyrolysis of the sulfur amino acids reported herein. The number of contiguous carbon atoms (exclusive of the carboxyl carbon) in the amino acid can be correlated with the nature of the reactive species produced on pyrodegradation and thence with the aromatic products obtained from pyrogenesis. Sulfur amino acids with three contiguous carbon atoms (methionine, homocystine) undergo decomposition to produce both the trimethine (1) and azatrimethine (2) intermediates which then react by

$$\underset{1}{:CH-CH=CH\cdot} \qquad \underset{2}{:N-CH=CH\cdot}$$

combination with one another or with other reactive intermediates to form aromatic hydrocarbons and nitrogen heterocycles. In these three-carbon systems, it might be expected that aromatic hydrocarbons as typified by naphthalene and methylnaphthalenes would be substantial or major products of reaction. On the other hand, amino acids with two contiguous carbon atoms (cystine) would decompose to form the azamethine species which on subsequent recombination would produce predominantly aromatic nitrogen heterocycles (indole, pyridines, quinolines) and nitriles (see Table IV). Introduction of oxidized sulfur functions in the three-carbon amino acids facilitates cleavage at the β,γ bond to produce the aromatic nitrogen heterocyclic products via the azatrimethine intermediate. The sulfoxide group is particularly effective in initiating this type of cleavage (Tables III and IV).

A comparison of the yields of aromatic substances indicates that sulfide, disulfide, sulfoxide, and sulfone functional groups are more effective than the thiol (mercapto) group in the pyrogenesis of aromatic compounds. Replacement of the thiol group with a disulfide (compare cysteine with cystine, Table III) results in substantial increases in the yields of neutral and basic products while replacement of a sulfide by a disulfide group (compare methionine with homocystine) results in increases in base yields. In comparisons of yields from compounds containing the disulfide group, values in the table should be divided by two.

The extent to which the thiol group affects the nature of the pyrolysate was evidenced by a comparison of pyrolysate constituents obtained from cysteine with those from alanine and serine (Patterson and Smith, 1967) (Table III). Both the thiol and hydroxyl groups enhance the formation of neutrals, bases, and phenols relative to alanine. This observation is consistent with the idea that aromatic pyrolysate constituents arise primarily by the combination of reactive intermediates (trimethines, radicals, carbenes, etc.) produced via cleavage and elimination reactions and that functional groups in the β position facilitate the formation of these labile species. Some variations in the behavior of the thiol and hydroxyl groups were observed. The thiol group was not effective in promoting carboxylic acid formation (relative to that obtained from alanine) while the hydroxyl group was. Phenol production, on the other hand, was enhanced by both the thiol and hydroxyl groups. These results imply that carboxylic acid formation is related in some way to the total oxygen content of the pyrolysand while phenol production is not.

Extensive quantities of gas were produced during the pyrolyses. These consisted of carbon monoxide, carbon dioxide, carbon disulfide, carbon oxysulfide, hydrogen cyanide, ammonia, methane, ethane, ethylene, and acetylene. The yields of carbon dioxide and ammonia are reported in Table II. The yields of carbon dioxide, which in some instances are greater than theoretical, do not reflect the quantity of carbon dioxide generated in the pyrolysis because of the hydrolysis of carbon disulfide and carbon oxysulfide by the trapping media (Bruss et al., 1957; Folkins, 1949). Yields of carbon monoxide and light hydrocarbon gases relative to carbon dioxide are listed in Table I.

The volatile sulfur compounds, carbon disulfide and carbon oxysulfide, probably arise from the interaction of the reactive carbon species (radicals, carbene, trimethine) along with carbon monoxide with sulfur radicals or H_2S in ways similar to commercial production methods (Folkins, 1949). Since thiophene is not observed in these pyrolysates and because of the relative high stability of thiophene under the pyrolytic conditions used [60% recovery of thiophene at 850 °C (Wynberg and Bantjes, 1959); 78% recovery at 800 °C (Hurd et al., 1962); 17% recovery at 825 °C (Hurd et al., 1962)] it is likely that sulfur, sulfur radical, or sulfur derivatives interact with the active carbon species (to form carbon disulfide) before the formation of thiophene occurs to any appreciable extent.

Sulfones are known to generate SO_2 on pyrolysis (Leonard, 1962). When methionine sulfone was pyrolyzed, it gave sulfur dioxide as one of the products. It was thought that methionine and methionine sulfoxide might also give sulfur dioxide if they were pyrolyzed in air. Our results indicate that this is not the case.

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Received for review March 1, 1976. Accepted May 10, 1976. This study was carried out under Contract No. 12-14-100-9575(73) with the Agricultural Research Service, U.S. Department of Agriculture, administered by Athens, Ga. Area, Richard B. Russell Agriculture Research Center, Athens, Ga. 30604.