Copyrolysis of Carbohydrates and Sulfur Compounds. 1. Formation of Thioacetic Acid and Its Decomposition to Carbonyl Sulfide

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Evidence is presented that in the copyrolysis of carbohydrates and inorganic sulfur compounds, carbonyl sulfide is formed from the decomposition of thioacetic acid. This acid is proposed as an intermediate from the reaction of ketene and hydrogen sulfide. Ketene is a decomposition product of carbohydrates, and hydrogen sulfide is derived from the reaction of sulfur and alkanes. The alkanes result from the degradation of the carbohydrates. This mechanism is reinforced by experiments involving the copyrolysis of glycolaldehyde, an efficient ketene generator, and inorganic sulfur compounds.

In view of the need for a better understanding of the thermal interactions of carbohydrate and inorganic sulfur compounds, we have undertaken a study of these two groups of compounds in a copyrolysis system. Our goal was to gain an overview of product–precursor relationships and to understand the formation mechanisms of certain products such as carbonyl sulfide (COS) and H_2S. All of these compounds have significance in food, agricultural, and environmental consideration.

Both carbohydrate and sulfur compounds are abundant in nature. Their frequent concurrence either in the composition of natural products or in industrial processes and their interactions under various conditions are of interest.

The chemistry of wood pulping (a process in which exogenous sulfur compounds such as sulfurous acid and its magnesium and sodium salts, ammonium bisulfite, and aqueous SO_2 are admixed with wood) has been extensively studied by numerous workers (Hägglund, 1923; Mikawa, 1951, 1952, 1954; Leopold, 1950, 1951, 1952, 1954). The primary emphasis in these studies was on solution chemistry.

The chemistry of pyrolytic reactions of carbohydrates with exogenous or endogenous sulfur compounds, on the other hand, has received less attention. Some inorganic sulfur compounds have been used in small amounts as catalysts to study the mechanisms of thermal decomposition of carbohydrates (Houminer et al., 1969; Shafizadeh and Lai, 1972).

Recently, Shibamoto and Russell (1976, 1977) published their studies on the simulation of meat aroma from a model system consisting of sugar(s), ammonia, and hydrogen sulfide. Their interest was mainly on the formation of heterocyclic compounds. However, product–precursor relationships still await elucidation. In a study on the synthetic applications of levoglucosenone, Shafizadeh et al. (1978) demonstrated the addition reaction of thiol groups to the carbohydrate moiety.

In spite of efforts mentioned above, the mechanisms of thermal interactions involving carbohydrates and sulfur compounds are still not completely understood and warrant further investigation.

MATERIALS AND METHODS

Reagents. Commercially available reagents were obtained and used as received. They consisted of the following: chondroitin sulfate (99% pure, ICN Pharmaceuticals); D(+)-dextrose and D(+)-galactose (Nutritional Biological Corp.); D(+)-mannose (Fisher Scientific Co.); sulfur precipitated, purified (Mallinckrodt); potassium bisulfate, sodium bisulfite, sodium sulfate, sodium bi-

sulfite, cupric sulfate, nickel sulfate, ferrous sulfate, aniline, and calcium hydride (Fisher Scientific Co.); glycolaldehyde (Aldrich Chemical Co., Inc.).

Pyrolysis. Pyrolyses were carried out in helium (100 psi, flow rate 80 mL/min) in a pyrolysis–gas chromatographic system similar to the one described earlier (Johnson and Kang, 1971).

Gas Chromatography. A Perkin-Elmer Model 900 gas chromatograph equipped with a liquid nitrogen cryogenic oven, a flame ionization detector, and a thermal conductivity detector was used. Helium carrier gas was maintained at 80 mL/min. The split ratio of effluent between the flame ionization and thermal conductivity detectors was 1:10. The operating conditions were as follows. The temperature of the injection port was 80 °C and that of the detectors was 250 °C, and the pressures of gases for the flame ionization detector were 12 and 30 psi for hydrogen and air, respectively.

Selected samples were subjected to pyrolysis/GC/MS by using a Bendix Model 2200 gas chromatograph mated to a Finnigan Model 3300 mass spectrometer via a glass, single-stage, molecular jet separator. Mass spectral data were recorded, stored, and processed by using a Finnigan 6110 data acquisition system. Background-subtracted spectra were identified by comparison with a compilation of reference mass spectra.

Methods. A 5.0×10^{-5} mol amount of sample was pyrolyzed to observe the thermal behavior of an individual compound. In copyrolysis studies, the same quantity of a carbohydrate plus an equimolar amount of sulfur compound was weighed into and mixed in a porcelain boat. The sample was pyrolyzed for 90 s, and the pyrolysate was carried onto a 20 ft × 1/8 in. stainless steel column packed with Porapak Q (80/100 mesh). Initially the column was cooled to –70 °C. After the elution of carbon monoxide, the column temperature was raised to 0 °C, held at 0 °C for 10 min, and then programmed at 8 °C/min to 240 °C. This temperature was maintained until the end of the experiment. Identification of individual components in the pyrolysate was accomplished by experiments with GC/MS using the same analytical columns and by retention times using authentic reference samples.

Samples to be analyzed by GC/MS were pyrolyzed in a manner similar to that described above, and the volatile pyrolysates were condensed at the front of the chromatographic column by cooling the column with a regulated liquid nitrogen supply. The pyrolysates from all experiments except sugar plus sulfur were separated by using a 10 ft × 1/8 in. o.d. stainless steel column packed with 3% OV-17 on Chromosorb W (80/100 mesh). Pyrolytic products from sugar plus sulfur experiments were analyzed by using a 20 ft × 1/8 in. o.d. Porapak Q column. The initial temperature was –150 °C. After a 5-min delay from

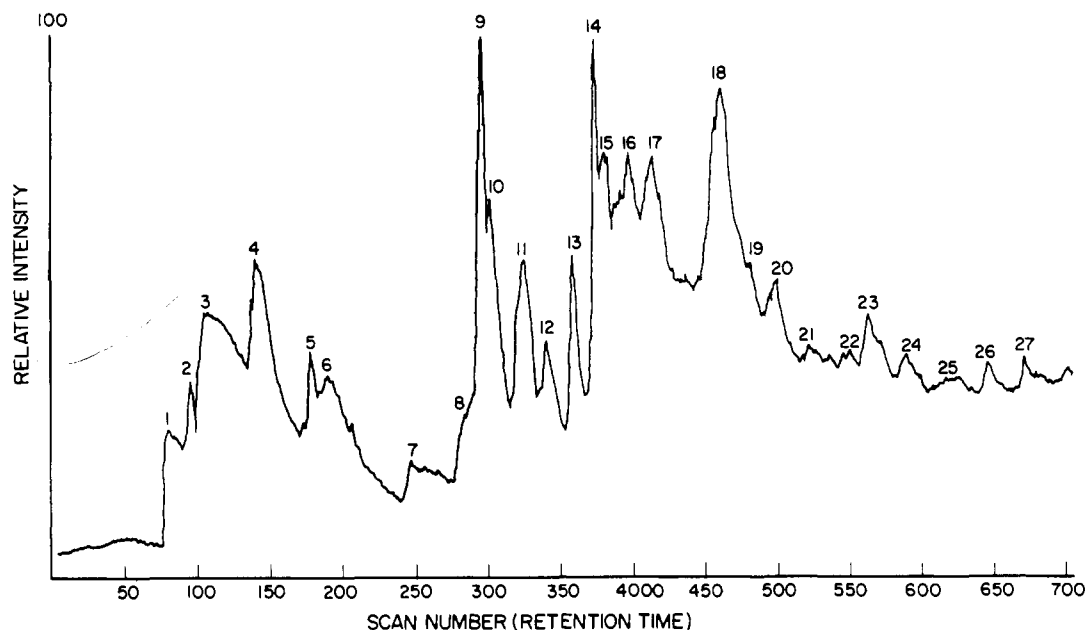Philip Morris U.S.A., Research Center, Richmond, Virginia 23261.

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Figure 1. GC/MS chromatogram of products from 700 °C pyrolysis of chondroitin sulfate.

Table I. Products from 700 °C Pyrolysis of Chondroitin Sulfate

peak no.	identification
1	ethene
2	ethane
3	carbon dioxide
4	propene + propane
5	butene(s) + carbonyl sulfide
6	ketene + minor amounts of butenes and butynes
7	hydrogen cyanide + furan + methyl mercaptan + dimethyl disulfide + cyclopentadiene
8	acetaldehyde + a methylcyclopentene
9	acetone + acrolein + propionaldehyde + acetonitrile
10	methyl furan + acrylonitrile
11	butanone + butenone + benzene + a methylcyclopentadiene + propionitrile
12	dimethylfuran
13	toluene + methacrylonitrile + vinylfuran
14	pyrrole + butyronitrile
15	pyridine + possible isovaleronitrile
16	ethylbenzene + acetic acid
17	methylpyrrole(s) + methylpyridine(s) + styrene
18	acetamide + minor amounts of 2-vinylpyridine, N-methylacetamide, and dimethylpyridine
19	benzofuran
20	indene + phenol + benzonitrile
21	phenyl acetate + an isopropenylpyridine + o- or m-cresol
22	p-cresol + methylindene(s)
23	2-pyridyl acetate or hydroxypyridine + naphthalene
24	methylbenzonitrile(s)
25	a methylnaphthalene + quinoline or isoquinoline + a cyanomethylpyridine or a methoxyaniline
26	methylquinoline or methylisoquinoline + indole + possibly a dihydoxybenzene
27	resorcinol monoacetate + methylindole(s)

Table II. Products from 700 °C Copyrolyis of D(+)-Mannose and KHSO$_4$

peak no.	identification
1	ethene + ethane
2	carbon dioxide
3	propene
4	isobutene + carbonyl sulfide + hydrogen sulfide
5	sulfur dioxide + a trace of ketene
6	furan
7	acetaldehyde
8	a methylfuran + methanol + acetone + acrolein
9	butanone + butenone + minor amounts of benzene and a methylfuran
10	dimethylfuran
11	3-methyl-3-butenone
12	toluene
13	ethylbenzene + xylene(s) + o- or m-cresol
14	furfural + minor amounts of styrene and phenylacetylene
15	methylethylfuran + methylacetylfuran + methylethylbenzene
16	methylethylfuran + o-ethylphenol
17	benzaldehyde
18	indene + trimethylfuran + 5-methyl-2-furfural
19	β-angelica lactone + $M_r = 112$
20	a vinylbenzaldehyde
21	naphthalene + ethylindene
22	a methylnaphthalene + trimethylindan
23	a methylnaphthalene
24	5-(hydroxymethyl)-2-furfural

the onset of pyrolysis, the column temperature was increased at 10 °C/min to 100 °C. At 100 °C the temperature program rate was decreased to 5 °C/min until the upper limit of 240 °C was reached.

RESULTS AND DISCUSSION

Copyrolysis of Carbohydrates with Endogenous or Exogenous Sulfur. Chondroitin sulfate is a mucopoly-saccharide (molecular weight estimated at 50 000) with N-acetylchondrosine as a repeating unit and with one sulfate group per disaccharide unit. This molecule was pyrolyzed to see what sulfur compounds were produced through the thermal interaction between the endogenous sulfur and the rest of the molecule (Figure 1 and Table I).

A comparison of the product distribution was made with that from the copyrolysis of D(+)-mannose and KHSO$_4$ (Figure 2 and Table II). Some differences were observed which can be attributed to the presence of the nitrogen-containing moiety on the chondroitin sulfate system and its interaction (Noller, 1965) with the fragmentation products normally found in sugar pyrolysis (Shafizadeh and Lai, 1972; Houminer et al., 1969). However, both
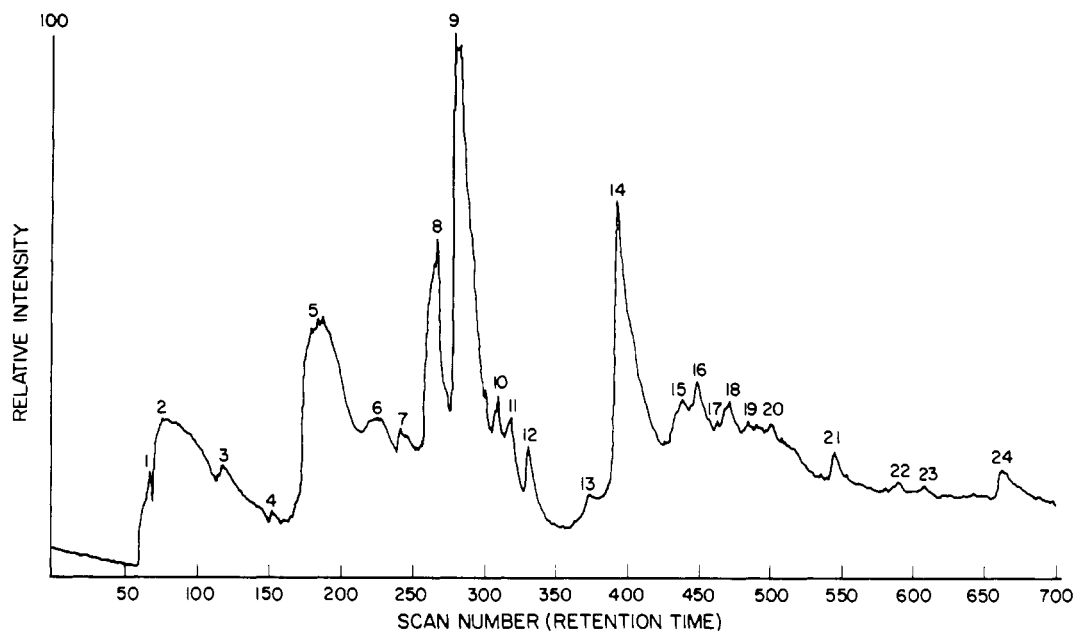
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Figure 2. GC/MS chromatogram of products from 700 °C copyrolysis of D(+)-mannose and KHSO₄.

Table III. Yields[a] of Carbonyl Sulfide from Copyrolyses of D(+)-Glucose and Bisulfates or Sulfates

sulfur salt	900 °C	600 °C
NaHSO₄	76	74
Na₂SO₄	18	12
K₂SO₄	12	11
CuSO₄·6H₂O	12	11
NiSO₄	12	8
FeSO₄	12	10

[a] Yields are indicated by millimeters of peak height.

Table IV. Yields[a] of Selected Products from 600 °C Copyrolyses of Sugars and NaHSO₃

products in pyrolysate	D(+)-glucose	D(+)-mannose	D(+)-galactose
methane	160	114	80
ethane	52	62	56
ethene/ethane	2.9	1.4	1.3
COS	89	76	59

[a] Yields are indicated by millimeters of peak height.

systems produce carbonyl sulfide.

Copyrolyses of Sugars with Various Sulfur Compounds. *Pyrolysis of Sulfur Compounds Only.* When pyrolyzed alone, all the inorganic sulfur compounds in this study yield only SO₂, some H₂O, and a corallike residue. It seems unlikely that the reactive intermediate during copyrolysis of inorganic sulfur compounds and sugars is SO₂. A gas-phase reaction mechanism has recently been elucidated by Yue et al. (1976) for the conversion of SO₂ to H₂SO₄. The initiation of this reaction is believed to

involve the oxidation of SO₂ by the hydroxyl radical in the presence of a third body as expressed by

$$\cdot OH + SO_2 + M \longrightarrow H_2SO_3 + M$$
$$\downarrow$$
$$H_2SO_4$$
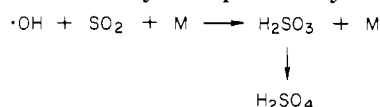
With the postulation of sulfuric acid formation in the copyrolysis system with carbohydrates and the presence of H₂O, the formation of organosulfur compounds becomes better rationalized. This is possible since sulfuric acid can act as an oxidizing agent to oxidize many compounds in the system and, in so doing, undergoes reduction to SO₂, HSO₃⁻, SO₃²⁻, and H₂S (Nebergall et al., 1972).

Bisulfates and Sulfates. D(+)-Glucose was copyrolyzed with various bisulfates and sulfates at 600 and 900 °C to determine their relative efficiency in forming carbonyl sulfide (Table III). Again, no qualitative differences in product formation are observed. Quantitatively, however, bisulfates appear to be more efficient than the sulfates in forming COS.

Bisulfites. A set of monohexoses, i.e., D(+)-glucose, D(+)-mannose, and D(+)-galactose, was copyrolyzed with NaHSO₃. Data in Table IV indicate that the bisulfite is more efficient than the bisulfates and sulfates in COS yield from glucose. For this set of sugars, the yields of COS vary in the following order: D(+)-glucose > D(+)-mannose > D(+)-galactose.

Elemental Sulfur. Because the oxidation of sulfides, the redution of sulfites, and sulfates, or even the reaction between SO₂ and CO (Stagy et al., 1969) gives elemental sulfur, it was studied in our copyrolysis system. Results obtained (Table V) indicate that of the compounds stud-

Table V. Yields[a] of Selected Products from the Copyrolyses of Sugars and Sulfur

products in pyrolysate	600 °C			700 °C		
	D(+)-glucose	D(+)-mannose	D(+)-galactose	D(+)-glucose	D(+)-mannose	D(+)-galactose
methane	480	384	224	350	318	212
ethene	224	248	144	464	488	440
ethane	88	108	156	138	148	168
ethene/ethane	2.5	2.3	0.9	3.4	3.2	2.6
COS	320	217	172	488	432	376

[a] Yields are indicated by millimeters of peak height.

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Table VI. Products from the Copyrolysis[a] of Glycolaldehyde (1 × 10⁻⁴ mol) and H₂S (5 mL at 1 atm Pressure)

| product	yields[b]					
	150 °C	325 °C	450 °C	500 °C	550 °C	600 °C
CO	0	7	16	128	672	1024
CH₄	0	0	0	4	36	35
CO₂	0	7	9	13	60	70
CH₂CH₂	0	0	0	2	6	9
CH₃CH₃	0	0	0	1	5	6
H₂O, H₂S	400	448	470	512	572	928
COS	0	0	0	0	5	25
CH₂O	0	2	12	15	26	38
CH₃CHO	0	0	0	28	102	170
CH₃COCH₃	0	0	0	3	16	10
CH₃COOH	0	0	0	3	12	10
CH₃COSH	464	248	216	168	142	60

[a] To minimize the decomposition of thioacetic acid, the GC injection port temperature was set at 100 °C.
[b] Yields are indicated by millimeters of peak height.

Table VII. Products from the Copyrolysis of Glycoaldehyde (1 × 10⁻⁴ mol) and Sulfur (1 × 10⁻⁴ mol)

product	yields[a]				
	150 °C	300 °C	325 °C	500 °C	700 °C
CO	0	1	7	184	2259
CH₄	0	0	0	1	208
CO₂	5	5	18	26	108
CH₂CH₂	0	0	0	1	36
CH₃CH₃	0	0	0	0.5	14
H₂O, H₂S	140	192	304	560	1200
COS	0	7	8	26	344
CH₂O	0	1	2	10	0
CH₃CHO	0	0	1	13	576
CH₃COCH₃	2	2	3	2	6
CH₃COOH	0	0	0	4	32
CH₃COSH	360	288	276	108	38

[a] Yields are indicated by millimeters of peak height.

Table VIII. Comparison of Selected Products from the 700 °C Copyrolysis of D(+)-Glucose and NaHSO₃

products	yields[a]		
	1:1 D(+)-glucose/ NaHSO₃	1:4 D(+)-glucose/ NaHSO₃	1:1 D(+)-glucose/ NaHSO₃ (quenched with aniline)
COS	144	328	96
CO	1056	1472	1056
ethene	320	144	128
ethane	125	12	88
ethene/ethane	2.6	12	1.5

[a] Yields are indicated by millimeters of peak height.

ied, sulfur is by far the most efficient in COS production. At pyrolytic temperatures of 600–700 °C free radicals are formed. The alkyl radicals from the thermolysis of sugars can react with one another, dimerize in a termination reaction, or react with sulfur, a free radical scavenger. The latter provides a satisfactory explanation for the formation of the alkyl sulfides. Furthermore, as evidenced by the ethene/ethane ratios in Table V, the sulfur–alkane reaction may also take place in which H₂S is formed together with an alkene (Pryor, 1962).

$$CH_3CH_3 + S \rightarrow H_2S + CH_2{=}CH_2$$
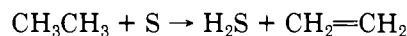
Now we shall address ourselves to the intermediates from the sugars that participate in the formation of sulfur-containing organic compounds. In a previous study on the thermolysis of carbohydrates (Kang et al., 1976), the presence of ketene and its importance in product distribution were noted. Our present study shows that the COS yields from a set of sugar isomers vary in the same order as their ketene yields: namely, D(+)-glucose > D-(+)-mannose > D(+)-galactose. This strongly suggests that in the copyrolysis systems, the reaction of H₂S with ketene from sugars to form thioacetic acid is important in COS production in order to account for the observed differences. This is similar to the reaction of ketene with H₂S in the liquid state (Wilsmore and Chick, 1908).

$$H_2S + CH_2{=}C{=}O \rightleftharpoons CH_3COSH \rightarrow S{=}C{=}O + CH_4$$
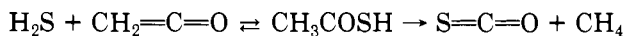
Further substantiation for the above postulate is obtained by the order of methane yields (Tables IV and V): D-(+)-glucose > D(+)-mannose > D(+)-galactose.

Thioacetic acid was pyrolyzed at 700 °C to test its role as an intermediate. GC/MS analysis (Figure 3) shows that this compound indeed produces essentially only COS and methane. The elution of methane was observed but not recorded, and ketene was observed in trace amounts.

Copyrolyses of Glycolaldehyde with Sulfur Compounds. Since sugars are postulated to thermally decompose to ketene from structures formally related to glycolaldehyde, this molecule was copyrolyzed with various sulfur compounds.

Hydrogen Sulfide. The proposed reaction to form COS via thioacetic acid directly involves hydrogen sulfide. Table VI shows the distribution of products from the copyrolysis of glycolaldehyde and hydrogen sulfide. The facility of formation of thioacetic acid, the postulated intermediate to carbonyl sulfide, is strikingly demonstrated in this set of experiments. By the detection of thioacetic

acid, we have demonstrated the feasibility of our postulated reaction scheme. Evidence is presented below that illustrates that sulfur compounds having more positive oxidation numbers also can form COS via conversion to H₂S and reaction with ketene.

Elemental Sulfur. Table VII shows the distribution of products from the copyrolysis of glycolaldehyde and sulfur. Thioacetic acid is formed at a relatively low temperature, and its yield decreases as the pyrolysis temperature increases. In these experiments the yield of COS is not noticeable at 150 °C, but increases as the pyrolysis temperature increases. The yields of methane follow the same trend as those of carbonyl sulfide.

It is not surprising that the low-temperature yield of COS is negligible since no easily accessible source of hydrogen is available to reduce the sulfur to hydrogen sulfide. Calcium hydride was added to glycolaldehyde and sulfur to obtain a greater yield of hydrogen. This ternary mixture was then pyrolyzed at 300 °C. A fivefold increase of COS was found as compared with the copyrolysis without the added hydrogen source (COS yield of 34 vs. 7 mm peak height). This result supports the postulate of the participation of H₂S in the production of carbonyl sulfide.

Sulfites. The yields of carbonyl sulfide from the copyrolyses of glycolaldehyde and sodium bisulfite at 300, 450, and 600 °C were 7, 13, and 40 mm peak height, respectively. These results are consistent with those from the copyrolysis of sugars and the same sulfur compound as shown in Table IV. With a fourfold increase of the sulfur compound in the copyrolysis system at 700 °C, an increase in the yield of carbonyl sulfide was demonstrated (Table VIII). Furthermore, the ethene/ethane ratio was found to have increased also, providing further evidence for the sulfur–alkane reaction discussed earlier.
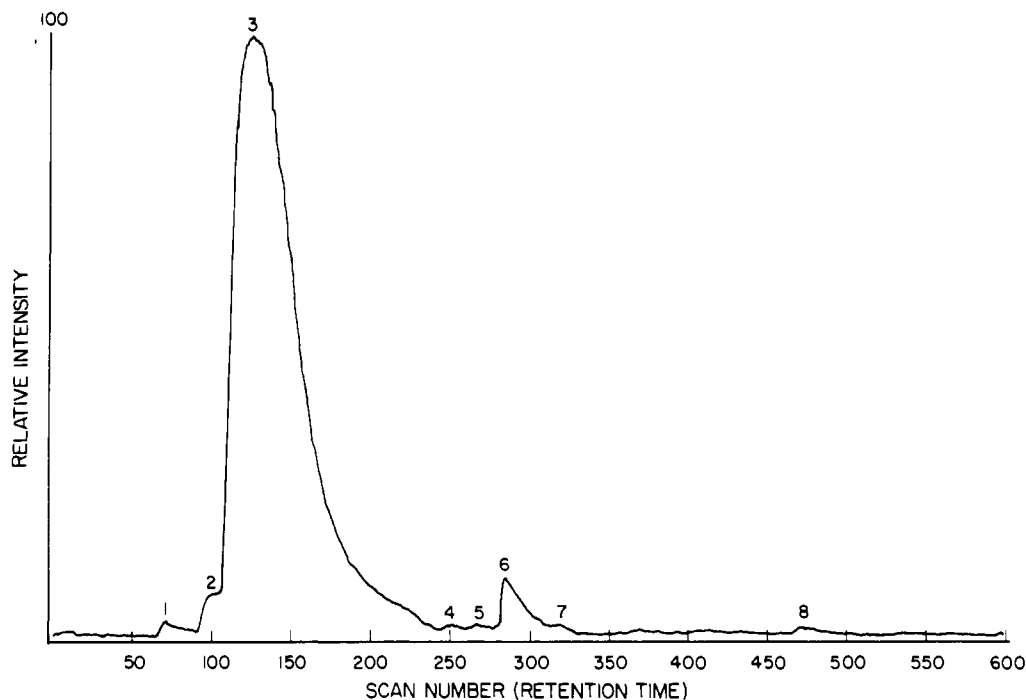
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Figure 3. GC/MS chromatogram of products from 700 °C copyrolysis of thioacetic acid. Peak identity: (1) ethene + ethane, (2) carbon dioxide, (3) carbonyl sulfide + a trace of ketene, (4) methyl mercaptan, (5) sulfur dioxide, (6) carbon disulfide, (7) ethylene oxide, and (8) dithiomethyl acetate or dithioacetol. (Methane was observed but not recorded.)

Table IX. Carbon Monoxide Yields[a] from Monohexoses

sugar	600 °C	700 °C	800 °C
D(+)-glucose	836	840	838
D(+)-mannose	836	840	842
D(+)-galactose	1272	1274	1280

[a] Yields are indicated by millimeters of peak height.

Comments on the Reaction of CO Plus S to Form COS. Of some concern to us was the complete failure of the known formation of carbonyl sulfide from the reaction of carbon monoxide and sulfur (Glemser, 1963) to predict product distribution in our studies. Table IX shows that D(+)-galactose should have produced the most COS and no difference should be found between D(+)-glucose and D(+)-mannose. In fact, D(+)-galactose yielded the least COS of the three sugars with D(+)-glucose producing the most COS (Tables IV and V). This failure of the carbon monoxide and sulfur reaction to predict product distribution can be taken as an independent reason for looking to ketene as a distribution determinant.

A possible explanation of this phenomenon is the breakdown of COS to carbon monoxide and sulfur above 300 °C (Glemser, 1963). We have noted in our work that carbon monoxide yields are not significant at temperatures that favor the carbon monoxide–sulfur reaction. Thus, the high-temperature release of carbon monoxide would tend to keep this pathway insignificant in terms of product distribution. Of special note is the increased COS yield with temperature (Table V) and the lack of carbon monoxide temperature dependency over the same range (Table IX). The temperature dependency of COS yield can, however, be inferred from our previous ketene studies (Kang et al., 1976).

Other experiments further emphasize the significance of ketene in COS formation. The first experiment involves the copyrolysis of glycolaldehyde and sulfur, with and without added calcium hydride. Since the pyrolysis of glycolaldehyde at 300 °C yields practically no carbon monoxide (Tables VI and VII), the formation of COS can not be attributed to the reaction of carbon monoxide and

sulfur. The fivefold increase of COS with the addition of calcium hydride reported above obviously was due to the increased availability of hydrogen, and of hydrogen sulfide subsequently.

The second experiment involves decreasing ketene, one of the reactants, by introducing a competitive reaction which should consume ketene but should not affect carbon monoxide. The D(+)-glucose plus NaHSO₃ copyrolysis system was altered by introducing aniline since the reaction of ketene with amines proceeds rapidly (Lacey, 1960). The last column in Table VIII shows that, when compared to the same copyrolysis system without aniline (column 2), the yields of COS were indeed lowered. This result is significant because the carbon monoxide yields remain the same.

Though we cannot assess quantitatively what contribution, if any, the carbon monoxide–sulfur reaction makes in these studies, the product-determining role of ketene seems unmistakably clear. The most logical route to carbonyl sulfide would be addition by hydrogen sulfide across the carbon–carbon double bond of ketene and the subsequent decomposition of the thioacetic acid generated to give the COS and methane.

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Tobacco Ionones: Dehydration of α-Ionol

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A number of ionone-related compounds are important tobacco flavor and aroma constituents. The acid-catalyzed dehydration and subsequent rearrangements of 1,3,3-trimethyl-2-(3-hydroxybutenyl)-cyclohexene (α-ionol), an ionone derivative, have been investigated. When subjected to treatment with mild acid, α-ionol yielded megastigma-4,7(*E*),9-triene as the major product and 2,2,6,7-tetramethyl-bicyclo[4.3.0]nona-7,9-diene and 3-(2,6,6-trimethyl-2-cyclohexenyl)-2-*trans*-propenal as other products. It was found that megastigma-4,7(*E*),9-triene yielded the 2,2,6,7-tetramethylbicyclo[4.3.0]nona-7,9-diene constituent by an unusual ring-closure reaction. Further, 3-(2,6,6-trimethyl-2-cyclohexenyl)-2-*trans*-propenal, a C-12 oxygenated compound which displayed a strong floral–musty fragrance and had not been reported in the literature previously, could be formed by aerial oxidation of megastigma-4,7-(*E*),9-triene.

Numerous research findings during the past several years which dealt with the flavoring isoprenoids in tobacco and smoke condensate have strongly suggested that many of those isoprenoids may have derived from the carotenoid metabolites or their degradation products (Stedman, 1968; Roberts and Rohde, 1972; Demole and Berthet, 1972; Kimland et al., 1973; Tso, 1974). While biochemical degradation processes of such constituents are possible in burley tobacco leaf during senescence and curing, many other secondary degradation reactions such as further oxidation–reduction, rearrangement, and possibly dehydration may occur. The ionones, which possess unique flavoring properties, have been isolated from tobacco and other plants (Demole and Berthet, 1972; Kimland et al., 1972; Schumacher and Vestal, 1974; Enzell, 1977; Davis, 1977). It has been reported that β-ionone and its related compounds were formed from the carotenoid precursors (e.g., β-carotene) by chemical transformation such as photooxygenation reactions (Isoe et al., 1969, 1972). Other structurally related tobacco constituents which have been reported as flavoring components of burley tobacco were megastigma-4,7(*E*),9-trien-3-one (Figure 1, I), megastigma-4,6(*Z*),8(*Z*)-trien-3-one (Figure 1, II), megastigma-4,6-(*Z*),8(*E*)-trien-3-one (Figure 1, III), megastigma-4,6(*E*),8-(*E*)-trien-3-one (Figure 1, IV), and megastigma-4,6(*E*),8-(*E*)-trien-3-one megastigma-4,6(*E*)8(*E*)-trien-3-one (Figure 1, V) (Roberts and Rohde, 1972; Demole and Enggist, 1974). It has been suggested that these compounds were derived from the dehydration of (9*R*)-9-hydroxy-4,7(*E*)-megastigmadien-3-one (3-oxo-α-ionol, Figure 1, VI) (Aasen et al., 1973, 1974). The objective of the present investigation was to examine the dehydration and rearrangement products of α-ionol in an effort to determine if it would yield megastigmatrienes.

METHODS

Chemicals. α-Ionone (Figure 2, VII) was obtained from Aldrich Chemical Co., Milwaukee, WI, and purified by distillation using a spinning band column. α-Ionol was synthesized from this purified product by sodium borohydride reduction (Corey et al., 1972). Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Spectra. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer. Proton NMR spectra were obtained in $CDCl_3$ solution with a Varian T60A spectrometer and carbon-13 spectra with a Varian CFT-20 spectrometer. UV spectral data were collected with a Shimadzu Model MPS-50L spectrophotometer. Mass spectra were obtained with a Finnigan Model 3300 GC/MS spectrometer operating at 70 eV.

Dehydration Reaction. This reaction was accomplished by treating α-ionol (5.0 g) with 5% *p*-toluenesulfonic acid in refluxing benzene (60 mL) for 30 min. The products were separated on a silicic acid column by serial elution using hexane and hexane–ether (9:1). The analytical samples were purified by using a preparative gas chromatograph (Varian Model 37111 equipped with a 12-port valve and a thermal conductivity detector) and a stainless steel column (12 × 1/8 in. i.d.) packed with 5% XE-60. The operating conditions were as follows: injector at 200 °C, detector at 210 °C, and temperature programming the column oven after a 5-min isothermal hold at 95 °C to 190 °C at 3 °C/min.

RESULTS AND DISCUSSION

The reaction of 1,3,3-trimethyl-2-(3-hydroxybutenyl)-cyclohexene (α-ionol, Figure 2, VIII) with 5% *p*-toluenesulfonic acid in refluxing benzene yielded a mixture of three compounds, megastigma-4,7(*E*),9-triene (Figure 2,

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