TOBACCO ADDITIVES AND CIGARETTE SMOKE

PART II. ORGANIC, GAS-PHASE PRODUCTS FROM D-GLUCOSE AND SUCROSE

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ABSTRACT

Thirteen gas-phase components of smoke were formed, in part, from uniformly labeled D-glucose-^{14}C and sucrose-^{14}C that had been added to the burley portion of a cigarette blend. The compounds, mainly furans and carbonyls, were isolated and identified by gas-chromatographic and mass-spectrometric techniques, coupled with nondestructive detection of radioactivity. The interaction of the sugars, or products thereof, with nitrogen-containing materials resulted in the formation of labeled acetonitrile.

Although acetone and acetaldehyde were among the products formed in highest radiochemical yields (0.05 to 0.1%), they were greatly diluted by their formation from other precursors. The relative contributions to the smoke from the sugars added were greatest for the furans, intermediate for acetonitrile, and smallest for the carbonyls.

INTRODUCTION

In Part I of this study[1], the transfer of D-glucose-^{14}C, sucrose-^{14}C, and their degradation products from cigarette tobacco to the smoke was reported. The presence was established of 5-(hydroxymethyl)-2-furaldehyde (HMF) and 1,6-anhydro-β-D-glucopyranose in the stub (butt), and of HMF and 5-methyl-2-furaldehyde in the smoke. The gross distributions of the radioactivity in acidic, basic, neutral, and phenolic fractions of the condensed phase of mainstream smoke were given.

The present report describes organic products, comprising less than 0.5% of the total activity, that occur in the gas phase of smoke. Individual radioactive components, detected in a nondestructive, flow ionization chamber, were identified by gas-chromatographic and mass-spectrometric analyses.

RESULTS AND DISCUSSION

The gas-phase components identified, with their calculated radiochemical yields, are listed in Table I. These yields are based on the response in the flow system, and are not corrected for mechanical losses, for interactions of reactive species, or for retention by the condensed phase[2,3]. For example, the values for crotonaldehyde

TABLE I

RADIOCHEMICAL YIELDS

Compound[a]	*Precursor*	
	D-*Glucose*-^{14}C (%)	*Sucrose*-^{14}C (%)
Acetaldehyde	0.05	0.06
Furan	0.01	0.01
Proprionaldehyde	<0.01	<0.01
Acetone	0.08	0.10
Acrolein[b]	<0.01	<0.01
2-Methylfuran	0.02	0.03
2-Butanone	0.02	0.03
Benzene	<0.005	<0.01
3-Buten-2-one	<0.01	<0.01
2,5-Dimethylfuran	0.03	0.07
Acetonitrile	0.03	0.04
2,3-Butanedione	0.01	0.01
Crotonaldehyde	<0.01	<0.01

[a]Listed in order of elution from TEGDME phase. [b]Includes isobutyraldehyde and methyl acetate; see text.

and 2,3-butanedione are probably minimal, due to distribution between the two phases of the smoke. All of the components listed, with the exception of acetonitrile, have been reported as pyrolysis products of carbohydrates[4–6], and had been identified in our own model systems.

The presence of acetonitrile, which was rechromatographed three times, with confirmation by mass spectrometry, is especially noteworthy; it confirms that interactions take place between sugars, or products therefrom, and nitrogenous materials, as predicted by Bradford[7] and Dittmar[8]. The mechanism of formation cannot be established from the data available. However, the pyrolysis of acetamide, possibly formed through intermediate ammonium acetate[9], could readily yield the nitrile. Other possibilities include pyrolyses of intermediates from ammonia–carbonyl reactions, ammonoxidations, or radical scavenging.

Acetone was not completely resolved from acrolein, isobutyraldehyde, and methyl acetate under the conditions and sample loading used, with tetraethyleneglycol dimethyl ether (TEGDME) as the liquid phase. The individual components arising from D-glucose-^{14}*C* were, however, resolved by trapping the acrolein fraction and rechromatographing under the same conditions. The labeled acetone (accounting for 25% of the radioactivity) which had "tailed" into the latter peak was clearly resolved, and the tri-component fraction was trapped again. This fraction was then chromatographed on silicone oil, and the three components, namely, acrolein methyl acetate, and isobutyraldehyde, were resolved, 77% of the activity being found in the acrolein. The comparable fraction from the sucrose-^{14}*C* products was not refractionated; as with D-glucose-^{14}*C*, the radioactivity recorded for labeled acetone was >90% of the combined areas of the two peaks.

Relative specific activities, calculated from the responses of the mass and radiation detection systems are given in Table II. The data show that acetone and, especially, acetaldehyde, although high in absolute activity (see Table I), are diluted by contributions from other precursors, possibly endogeneous carbohydrates.

TABLE II

RELATIVE SPECIFIC ACTIVITIES[a]

D-*Glucose*-^{14}C		*Sucrose*-^{14}C	
2,5-Dimethylfuran	1.00	2-Methylfuran	1.00
2-Methylfuran	0.89	2,5-Dimethylfuran	0.50
Furan	0.54	Acetonitrile	0.50
Acetone	0.53	Furan	0.42
Acetonitrile	0.50	Acetone	0.38
2-Butanone	0.26	2-Butanone	0.28
Acrolein	0.25	3-Buten-2-one	0.21
Acetaldehyde	0.23	2,3-Butanedione	0.20
3-Buten-2-one	0.20	Acetaldehyde	0.14
2,3-Butanedione	0.18	Propionaldehyde	0.11
Propionaldehyde	0.14		

[a] Ratio of detector responses, corrected for carbon contents and given relative to 2,5-dimethylfuran and 2-methylfuran, respectively, as unity.

The intermediate ranking for acetonitrile is especially noteworthy; it is presumably related to the differences in smoking characteristics of cased and uncased burley tobaccos. The contributions to the furans and carbonyls were expected from the results of model pyrolyses and mechanical-smoking experiments conducted with cellulose added to cigarettes[10]. Cigarette paper, smoked in the form of cigarettes, has been shown to give a high yield of carbonyls, especially acrolein and 3-buten-2-one, as compared to normal cigarettes[11]. The other components listed in Table I, but not in Table II, could not be ranked because of low concentration or incomplete resolution, or both.

Although the present information cannot establish reaction mechanisms, the simple furans are probably derived from the reductive degradation of intermediate furaldehydes. Whether the other fragmentation products arise from these initial dehydration products or from intermediate polymers cannot yet be stated. Small accumulations (0.5%) of dehydration intermediates were detected in the unsmoked tobacco of the stubs[1]. During smoking, such products may be transferred to the smoke in subsequent puffs, without further breakdown. To provide the yields of acetone and acetaldehyde detected (0.05 to 0.1%), extensive breakdown would be required. Such products as 2-methyl-5-vinylfuran which, Heyns *et al.*[5] suggested, may be derived from D-glucose polymers in pyrolysis experiments, would not be present in the smoke fraction examined here, and so information on polymer intermediates is lacking. The fact that major differences between the products from D-glucose and sucrose were not detected indicates, however, that comparable mechanisms are involved[12].

EXPERIMENTAL

The cigarettes and procedures for handling the smoke have been described[1]. The mainstream gases, collected on glass wool at the temperature of boiling liquid nitrogen, were transferred through a pre-column, attached to the sample valve of a Cary–Loenco gas chromatograph, and cooled in Dry Ice, which contained 0.95 g of 5% QF-1 on Gas Chrom Z. The effluent gases passed through a bubbler trap containing 40% potassium hydroxide, a conventional combustion furnace containing cupric oxide, and a second potassium hydroxide bubbler. Organic vapors were retained for subsequent analysis. Initially, the gases evolved during thawing provided a gas flow; this was then supplanted by helium at 60 ml/min for 20 min, with a boiling-water bath around the trap. The carbon dioxide, subsequently precipitated from the alkali solution as barium carbonate, was counted for radioactivity, and the result is reported in the mainstream distribution[1].

The organic constituents (of the gas phase) that had been retained by the silicone phase were swept onto the analytical column by helium while the pre-column was heated by means of a boiling-water bath. Chromatography was conducted at 25° in a Teflon column (16 ft × 0.125 in. o.d.) containing 10.65 g of 25% TEGDME on Gas Chrom Z (80–100 mesh) with a helium flow of 78 ml/min. Detection was afforded by thermal conductivity for mass analysis, and by a 250-ml, ion chamber having a vibrating-reed electrometer, for radioactivity. A purge flow of argon at 660 ml/min lowered the response time of the counting system, which was calibrated with toluene-^{14}C or acetone-^{14}C. Peaks corresponding to eluted components were recorded with a two-pen recorder.

Individual compounds were identified by chromatographic-retention data and by mass-spectrometric analyses of trapped fractions. Fractions were rechromatographed on the same phase or in a stainless-steel column (8 ft × 0.125 in. o.d.) containing 1.85 g of 16% Dow–Corning silicone 200 on Gas Chrom Z (80–100 mesh) at 25°, with a helium flow of 20 ml/min. Mass spectra confirmed identities, and, in all cases, radioactivity accompanied the component of interest when it was rechromatographed. The use of liquid nitrogen or liquid nitrogen–isopentane (−155°), or both, facilitated collection by freezing and the removal of argon prior to mass analyses.

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