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Study of Effects of Glucoside on Cigarette Smoke Using Pyrolysis-Gas Chromatography-Mass Spectrometry

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Simulated temperature of pyrolysis zone of cigarette burning, used in off-line pyrolysis, glucoside, the significant component existed in tobacco, are pyrolyzed in furnace-type pyrolyzer at 700°C. The volatile and semi-volatile products are trapped with liquid nitrogen bath and the qualitative analysis was carried out by GC-MS. Experimental results had less secondary reactions and better reproducibility.

Key Words: Glucoside, Off-line pyrolysis, Gas chromatography-mass spectrometry.

INTRODUCTION

Cigarette smoke is a complex mixture containing over 4000 known chemical components. In the analysis of smoke, there is often a need to overcome chromatographic and spectroscopic interferences, to prevent ageing of the sample and the need to extract analytes from both vapour and particulate phases. Scan techniques of smoke have been developed to the point where good semi-quantitative data can be obtained for many compounds, but the effect of a single cigarette design change may not be readily discerned when comparing scans of the total smoke.

If smoke scan techniques prove to be too crude for a particular application, then the analytical regime must include specific methods that are targeted to only a limited number of related smoke components at a time. In order to understand the behaviour of tobacco components in the burning cigarette it is important to know whether they transfer intact to the smoke or whether there is any decomposition during transfer.

Pyrolysis gas chromatography-mass spectrometry has been extensively used within the industry in the past to assess the potential effect of individual cigarette components on smoke composition[1–5].

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The pyrolysis techniques commonly used in PGC, the primary rupture of bonds is frequently followed by complex series of competitive reactions between the radicals and the fragment molecules formed and by secondary pyrolysis of the primary products. These secondary reactions complicate the final fragmentation pattern and disturb correlation between the qualitative and quantitative characteristics of the pyrolysis products and the molecular structure of the parent compound. Thus, the results often have poor reproducibility. Consequently, it is of importance to design pyrolysis units in which the possibility of secondary reactions taking place is reduced to a minimum. Furthermore, there is a requirement to establish reliable methods for the analysis and characterization of the pyrolysis products of a single cigarette content.

Two conditions are necessary in order to minimize the extent of secondary reactions: (1) The primary fragments must quickly diffuse into the stream of the carrier gas and be diluted, and (2) The primary fragments must be quickly cooled and stabilized.

In order to carry out pyrolysis close to these conditions, a pyrolysis unit in which a sample material is pyrolyzed by Off-line thermochemolysis combined with GC-MS is designed.

Off-line thermochemolysis combined with GC-MS is a technique that can be focussed upon the effects of combustion from a single material free from interference from the complex mixture of different components present in the smoke. It is, therefore, an ideal analytical technique to apply to a series of related compounds of cigarette. The utility of this technique was examined with glucoside as sample.

EXPERIMENTAL

Commercially available DL-β-glucoside from Kangda component factory, Shanghai, China (99% purity) was used as received. The sample was pyrolyzed directly as a solid. The glucoside sample of 0.9 mg was pyrolyzed using a furnace-type pyrolyzer PYR-2A (Shimadzu, Japan). Pyrolysis tube was heated to 700°C for 1 h to remove any contaminants before use. The interface of the pyroprobe was heated and purged with nitrogen gas. The pyrolysis tube was maintained at 700°C and the connecting piping at 250°C in order to prevent condensation of heavier pyrolysis products. The sample was coated on the sample boat, which was set in the stream of a nitrogen flow of 21 mL/min. Pyrolysis experiments were carried out at the constant temperature 700°C for 2 min. Rapid removal of pyrolysis products from the heated zone is important and this can be accomplished with the aid of a carrier gas flow.

The effluent was passed through a 1.2 m length of 0.53 mm i.d. untreated fused silica tube. Approximately 0.20 m from the exit end of the silica tube, a loop of the tube (about 0.7 m length) was immersed in liquid nitrogen. After pyrolysis, the tube was flushed with nitrogen for 2 min. The tube was then removed from the liquid nitrogen bath (–196°C) and the ends inserted into two sealed GC autosampler vials. One of the vials contained 200 μL of CH_2Cl_2 reagent. After the tube warmed to room temperature, the material trapped in the tube was also dissolved by forcing the liquid through the silica tube from one vial to the other using pressure[21].

TurboMass GC-MS (Perkin-Elmer, USA) was used. A 30 m × 0.25 mm J&W DB-5 fused silica capillary column with 0.25 μm film thickness was used with the following temperature programming: initial oven temperature was 50°C, kept for 5 min; then was raised to 250°C at 10°C/min and kept at 250°C for 5 min. Helium was used as carrier gas with column head pressure at 10 psi. Programming temperature vaporizer (PTV) injector temperature was at 250°C and the amount of injection was 2 μL. The temperature of the G-/MS transfer line was 250°C. The MS was operated at 230°C in the electron impact mode (70 eV), scanning from m/z 33 to 350 in 0.3 s with the 0.2 s interval time of the scan; the voltage of the photoelectric multiplier tube (PMT) was 250 V. The mass spectral identifications were carried out by comparing to the NIST98 (National Institute of Standards and Technology, Gaithersburg, MD) mass spectral library as well as to the Wiley 6.0 (Wiley & Sons, New York, NY) mass spectral library.

RESULTS AND DISCUSSION

"Off-line" pyrolysis conditions

The important considerations in the design of the pyrolysis apparatus were that it should bear the following features: of simple construction; using commercially available parts; using of the furnace-type pyrolyzer that is designed to ensure exact control of pyrolysis temperature by means of semiconductors and can use biggish sample (mg); using liquid N_2 as the cold trapping. Because the balance of smoke components produced from a cigarette must depend upon the range of conditions that exist within the burning zone of the cigarette and the key condition is combustion temperature, which in the cigarette vary from ambient to 900°C and the pyrolysis zone is about 650–750°C, a pyrolysis temperature of 700°C was selected. The positioning of the cold trapping was important because if it were too close to the pyrolysis tube, partial blockage of the flow of gases would have occurred, whereas if it were too far from the tube, higher molecular weight products would not have been trapped and the ratio of dimeric products to monomeric would have decreased.

Mechanism analysis of glucoside pyrolysis products by off-line pyrolysis

The pyrolytic behaviour of common components has been investigated in detail and the principal thermal degradation products have been identified by means of pyrolysis in combination with gas chromatography and mass spectrometry[6–20] (Py-GC-MS).

Glucoside is the significant component that existed in tobaccos[21]. The pyrograms of compounds are shown in Figs. 1 and 2 for the pyrolysis products of glucoside. Table-1 lists GC retention data, mass spectral characteristics and proposed structural assignments for the principal products released from glucoside following pyrolysis.

The pyrolysis of glucoside to give HCN, CO, CO_2, NH_3, H_2 and N_2[12, 22, 23]. The pyrolyses products observed could be explained in terms of an initial benzylic bond cleavage followed by additional competitive paths in which reactive intermediates (phenyl and benzyl radicals) and thermally unstable molecules styrene (**2**) are formed. The ways by which these reactive species produce pyrolysis products have been described previously[24–26].

TABLE-1

PRINCIPAL PRODUCTS RELEASED FROM PYROLYSIS OF GLUCOSIDE

Time	rev	for	Compound	Peak No.	m.w.	m.f.
5.42	995	995	Ethyl benzene	**1**	106	C_8H_{10}
6.28	996	996	Styrene	**2**	104	C_8H_8
8.06	966	896	Benzaldehyde	**3**	106	C_7H_6O
8.64	945	795	Benzonitrile	**4**	103	C_7H_5N
9.99	966	897	1-Propynyl benzene	**5**	116	C_9H_8
10.05	951	905	1H-Indene	**6**	116	C_9H_8
11.86	974	966	Benzene acetonitrile	**7**	117	C_8H_7N
12.69	980	967	Naphthalene	**8**	128	$C_{10}H_8$
13.93	987	982	Isoquinoline	**9**	129	C_9H_7N
14.11	959	921	N-Methyl indole	**10**	131	C_9H_9N
14.48	971	960	1H-Indone	**11**	117	C_8H_7N
15.78	985	976	1,1-Diphene	**12**	154	$C_{12}H_{10}N$
15.84	963	947	3-Methyl-1H-indole	**13**	131	C_9H_9N
16.53	983	970	Diphenyl methane	**14**	168	$C_{13}H_{12}$
16.93	881	725	3-Phenyl pyridine	**15**	155	$C_{11}H_9N$
17.26	936	885	4-Methyl-1,1′-bipheneyl	**16**	168	$C_{13}H_{12}$
17.38	917	877	2-Methyl-1,1′-bipheneyl	**17**	168	$C_{13}H_{12}$
17.82	979	965	Bibenzyl	**18**	182	$C_{14}H_{13}$
18.18	958	945	1,2-Diphenyl propane	**19**	196	$C_{15}H_{16}$
18.60	960	847	9H-Fluorene	**20**	166	$C_{13}H_{10}$
18.87	982	982	4-Methyl fluorene	**21**	180	$C_{14}H_{12}$
19.41	973	968	1,3-Diphenyl propane	**22**	196	$C_{15}H_{16}$
19.98	988	979	9,10-Dihydro phenanthrene	**23**	180	$C_{14}H_{12}$
20.14	986	975	Stilbene	**24**	180	$C_{14}H_{10}$
20.84	972	789	7-Phenylindene	**25**	192	$C_{14}H_{10}$
21.05	991	984	Phenanthrene	**26**	178	$C_{15}H_{15}N$
21.10	937	823	Benzeneethanamin-N-phenylmethylene	**27**	209	$C_{15}H_{12}$
21.14	970	808	Anthracene	**28**	178	$C_{14}H_{10}$
21.87	984	920	1H-Indene-1-(phenylmethylene)	**29**	204	$C_{16}H_{12}$
23.11	987	979	2-Phenyl naphthalene	**30**	204	$C_{16}H_{12}$
25.73	870	737	3,4-Diphenyl pyridine	**31**	231	$C_{17}H_{18}$

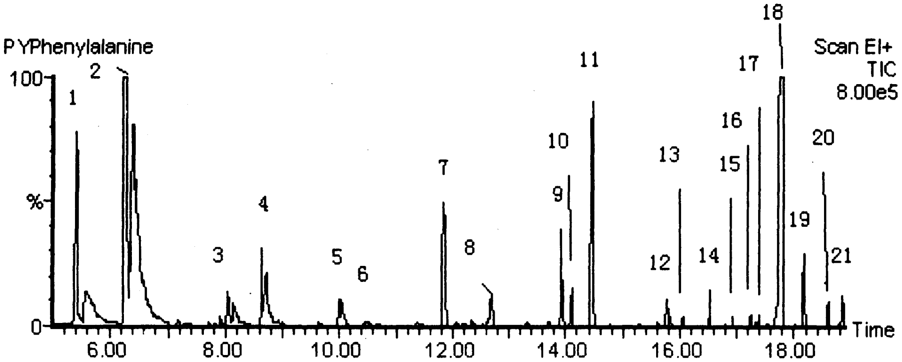

Fig. 1. Pyrogram of compound (1–21)

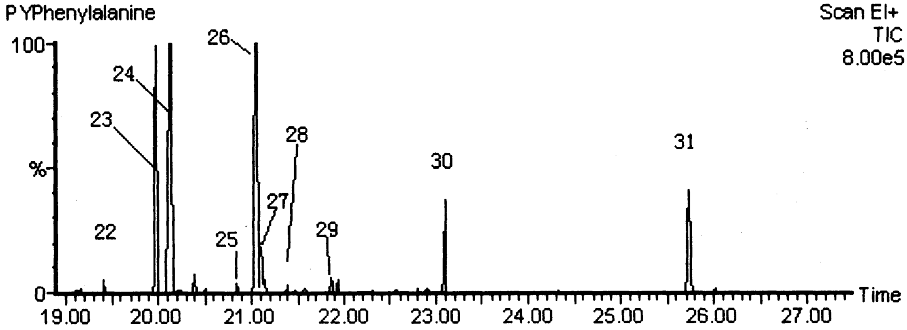

Fig. 2. Pyrogram of compound (22–31)

It is obvious from the products that suitable conditions for oxidation-reduction reactions are established during pyrolysis. Products can be explained as resulting from the following reaction sequences:

Formation of a greater abundance of phenyl, benzyl, methylene ($CH_2=$) methyl (CH_3-) and vinyl, hydrogen radicals is reflected in the increases in yields benzonitrile **(4)**, naphthalene **(8)**, of 1,1′-biphenyl **(12)**, diphenylmethane **(14)**, 1,1′-bipheneyl, 4-methyl **(16)**, 1,1′-bipheneyl, 2-methyl **(17)**, bibenzyl **(18)**, 1,2-diphenylpropane **(19)**, 9H-fluorene **(20)**, 4-methyl-fluorene **(21)**, 1,3-diphenylpropane **(22)**, phenanthrene, 9,10-dihydro **(23)**.

The part of bibenzyl **(18)** from the pyrolytic products may be attributed to the relative ease with which bibenzyl undergoes either cleavage at the carbon-carbon single bond or dehydrogenation to stilbene **(24)**. The yield of phenanthrene **(26)** is in accord with the observations of previous researchers that stilbene may act as a precursor of phenanthrene at 700°C.

At 700°C, styryl radicals may be more abundantly formed and formation from two styryl radicals can explain the formation of 2-phenylnaphthalene (30), especially since the high yield of 2-phenylnaphthalene cannot be accounted for by the reaction of naphthyl radicals and phenyl radicals[27].

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