

Pyrolysis of Chlorogenic Acid and Rutin[†]

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Chlorogenic acid and rutin, major polyphenols in tobacco, were pyrolysed with a furnace type pyrolyser connected directly to a gas chromatograph and 22 compounds (including catechol, benzoic acid, 4-vinylcatechol and quinic acid γ -lactone) from chlorogenic acid and 24 compounds [including catechol, 5-methyl-2-furaldehyde, 4-methylcatechol and 1,6-anhydroglucopyranose (levoglucosan)] from rutin have been identified as pyrolysis products. The gas chromatograph was also replaced by a capillary cold trap which allowed collection of the pyrolysis products prior to a quantitative determination using an internal standard. Comparison of the pyrolysis products produced from chlorogenic acid or rutin with those derived from tobacco and analysis of the pyrolysis products from a mixture of tobacco and chlorogenic acid or rutin indicated that fairly large proportions of catechol, 4-vinylcatechol and quinic acid γ -lactone produced by the pyrolysis of tobacco may originate from endogenous chlorogenic acid.

Frequent studies on the pyrolysis products of tobacco components have been made to establish precursor-product relationships between the tobacco constituents and cigarette smoke components.¹⁻⁸⁾ We have investigated the volatile pyrolysis products of cellulose⁹⁾ in order to gain a better understanding of the relationship between cellulose and cigarette smoke components. Although the pyrolysis of polyphenols such as chlorogenic acid, rutin and quercetin, which are thought to influence the quality of tobacco,¹⁰⁻¹²⁾ has been made in the past,¹³⁾ only a few pyrolysis products have been identified and none quantitatively estimated.

In this paper we report on the qualitative analysis of the pyrolysis products of chlorogenic acid and rutin by pyrolysis-gas chromatography. Some of the major compounds in the collected pyrolysate were also quantified. The relationships between the pyrolysis products derived from chlorogenic acid or rutin and tobacco are discussed.

EXPERIMENTAL

Sample. The tobacco sample used in this study was a flue-cured tobacco (powdered and passed through a sieve of 80 mesh) produced at Okayama Tobacco Experiment Station in 1980. Chlorogenic acid was purchased from Tokyo Kasei Kogyo Co. Ltd. and rutin from Nakarai Chemicals Ltd.

Pyrolysis. Samples (0.2~0.6 mg) in a platinum boat were pyrolysed with a furnace-type pyrolyser (Shimadzu PYR-2A) at 500°C for 40 sec in an atmosphere of helium gas (flow rate 50 ml/min).

Analysis of pyrolysis products. For identification, the volatile pyrolysis products were introduced directly on to a gas chromatograph from the pyrolyser (direct method). Quantitative determination, however, was done after trapping the pyrolysis products in a capillary U trap cooled by dry ice-acetone (trap method, Fig. 1). Soon after the pyrolysis products were trapped, 5 μ l of pyridine containing 1,3-butylene glycol as an internal standard and 40 μ l of trimethylsilylation reagent, BSTFA, were added to the U trap. The well mixed sample solution was then transferred into a 1 ml vial and heated at 80°C for 30 min before gas chromatographic analysis.

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