

Pyrolysis of caffeic acid, a tobacco leaf constituent

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In the course of a study of the pyrolytic behaviour of various acids present in tobacco¹ and of the pyrolysis of cinnamic acid and cinnamic acid derivatives,^{2,3} we pyrolysed 3,4-dihydroxy-cinnamic (caffeic) acid. Free caffeic acid has been reported in trace amounts in tobacco leaf^{4,5} as well as in main-stream cigarette smoke.⁶ Generally, caffeic acid is considered to exist in tobacco leaf primarily as a component of chlorogenic⁷ and neochlorogenic acids.⁸ Chlorogenic acid is a major component of the polyphenolic fraction of tobacco leaf⁷ and has been reported to occur in concentrations of 2.3–7.7 per cent.⁹ Chlorogenic acid pyrolysis by dry distillation at a reported melt temperature of 600°C has been found to yield catechol, 4-methylcatechol, 4-ethylcatechol, benzoic acid and quinide.¹⁰ Pyrolysis of rutin and quercetin yielded a similar list of products with catechol as the major one.¹⁰ Catechol has been reported in cigarette smoke in concentrations of 0.1 to 0.5 per cent.¹¹ Although tailing has been noted in the g.l.c. separation and identification of catechol on SE-30 columns,^{12,13} we encountered no difficulties.

Caffeic acid was pyrolysed under nitrogen (60 ml/min) at a temperature of 700±10°C in a Vycor* tube packed with quartz chips. A Lindberg Hevi-Duty Furnace maintained the temperature. Following its condensation in a series of cooled (Dry Ice-acetone) traps, the pyrolysate was fractionated into ether-soluble neutrals, phenols and acids. Each of the fractions was dried, concentrated (in ether) and analysed by g.l.c. on a Varian-Aerograph Model 202 Gas Chromatograph equipped with dual detectors and dual stainless steel columns (5 ft × 0.25 in OD) packed with 20 per cent SE-30 on Chromosorb W. The various fractions were analysed by programming the column-oven temperature at a rate of 6°C/min to a final temperature of 250°C which was maintained for about 1h to ensure complete elution of high-boiling materials. Starting temperatures for the programmed runs were 70°, 100° and 175°C for neutrals, phenols and acids (as trimethylsilyl esters¹⁴), respectively. Other g.l.c. conditions were: detector and injector temperature, 260°C; helium flow rate, 60 ml./min. All peak identifications were made by comparing the ultraviolet and infrared absorption spectra of collected peak effluents with known compounds, and confirmed by co-injection studies. The components in each fraction are listed in the Table. Pyrolysis of 3g of

* Mention of trade or Company names is for identification only and does not imply endorsement by the Department.

Table
Products of caffeic acid pyrolysis, 700°C, (N₂)

Fraction	Compound	Mole per cent yield ^a
Acid ^b	Salicylic acid ^c	0.31
	1,3-Phthalic acid ^c	0.26
	Caffeic acid (recovered)	—
Phenols ^d	Phenol	3.42
	<i>o</i> -Cresol	1.30
	<i>p</i> - and/or <i>m</i> -Cresol	1.27
	<i>p</i> -Ethylphenol	0.64
	Catechol	31.60 ^f
Neutrals ^e	Toluene	0.64
	Ethylbenzene	0.40
	Styrene	0.68
	<i>p</i> -Methylstyrene	0.36
	Indene	0.53
	Naphthalene	0.24
	<i>c</i> -Stilbene	0.10
	Fluorene	0.06
	Phenanthrene	0.03
4,5-Methylenephenanthrene	0.02	

^a Yields were calculated on the basis of reacted caffeic acid.

^b 63.74 per cent of the g.l.c. peaks of the acid fraction were identified. All unidentified peaks had relative areas of less than 2 per cent. The major peak (44 per cent) was catechol.

^c Only co-injection data was available.

^d 96.6 per cent of the peaks were identified.

^e 65.7 per cent of the peaks were identified. Unidentified peaks were mixed, with relative areas of 3 per cent or less.

^f Includes catechol found in acid fraction.

caffeic acid gave 0.1g of acids, 0.7g of phenols and 0.1g of neutrals. Analysis of carbonaceous ash (0.24g) gave C, 87.98; H, 2.76; O, 5.80 per cent.

Catechol was the major pyrolysis product (yield, 31.6 per cent). Little caffeic acid (0.02g) was recovered from the pyrolysis of 3g. The major components of the neutral fraction were toluene, ethylbenzene, styrene, indene, *p*-methylstyrene and naphthalene. These products were also found previously in the pyrolysis of cinnamic acid,^{2,3} although caffeic acid pyrolysis yielded a much smaller neutral fraction (3 per cent versus 20 per cent by weight). Unlike cinnamic acid pyrolysis where styrene, *t*-stilbene and toluene were the major components of the neutrals, caffeic acid pyrolysis resulted in no major products.

A free radical pyrolytic pathway would result in the types of products found here. Free radical mechanisms have been implicated in the high temperature pyrolysis of a large variety of compounds.¹⁵ The primary product, catechol, could result from the simple homolytic fission of the molecule.

This study indicates that caffeic acid, or a structure containing the caffeic acid moiety, could be the major precursor for catechol formation in tobacco pyrolysis. There was little evidence for the formation of a substituted stilbene, although *t*-stilbene was a major product of cinnamic acid pyrolysis.^{2,3} From the appearance of the pyrolysate there is some indication that a polyphenolic type of polymer may have been formed during pyrolysis. Since the polyphenols in tobacco are known to be very important in taste and quality,⁷ it is possible that these polymeric products of caffeic acid or a caffeic acid type of structure may be quite important in that respect.

Further work is in progress on the pyrolyses of chlorogenic acid and other tobacco polyphenolic compounds.

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