Volatile Phenols of Cigar Smoke

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Introduction

Several recent publications (Hoffmann and Wynder, 1961; Crouse *et al.*, 1963; Spears, 1963) have been concerned with the phenolic constituents in cigarette smoke; however, no comparable study has been made on cigar smoke. The present report describes the isolation and identification of certain phenolic compounds in cigar smoke condensate and the amounts of such compounds therein.

Experimental

Preparation of Smoke Condensate. The smoking conditions, collection system, and cigars (perfectos with domestic filler) have been described previously (Schepartz 1959, 1960; Schmeltz and Schlotzhauer, 1961).

Isolation of Weak Acids. **Figure 1** illustrates the isolation of the weakly acidic fraction. The smoke traps were successively washed with ether (250 ml) and aqueous 0.5% sodium hydroxide (50 ml) after which the ether (A) was extracted with 160 ml of 0.5% sodium hydroxide (4 x 40 ml); all alkaline solutions were combined (B) and washed with ether (C) (4 x 40 ml) to remove any non-acidic contaminants. Ether (C) was, in turn, washed with 20 ml of 0.5% sodium hydroxide which was combined with alkaline extract (D) to give alkaline solution (E); (E) was then adjusted to pH 6.1 with 0.5% sulfuric acid at 0°C followed by extraction with ether (4 x 40 ml) which resulted in an aqueous solution (F) and an ether extract (G). Ether (G) was dried over anhydrous sodium sulfate and concentrated to 1.0 ml *in vacuo* (50 mm.) at 0° to 10°C. The concentrate (H) was then analyzed by gas chromatography.

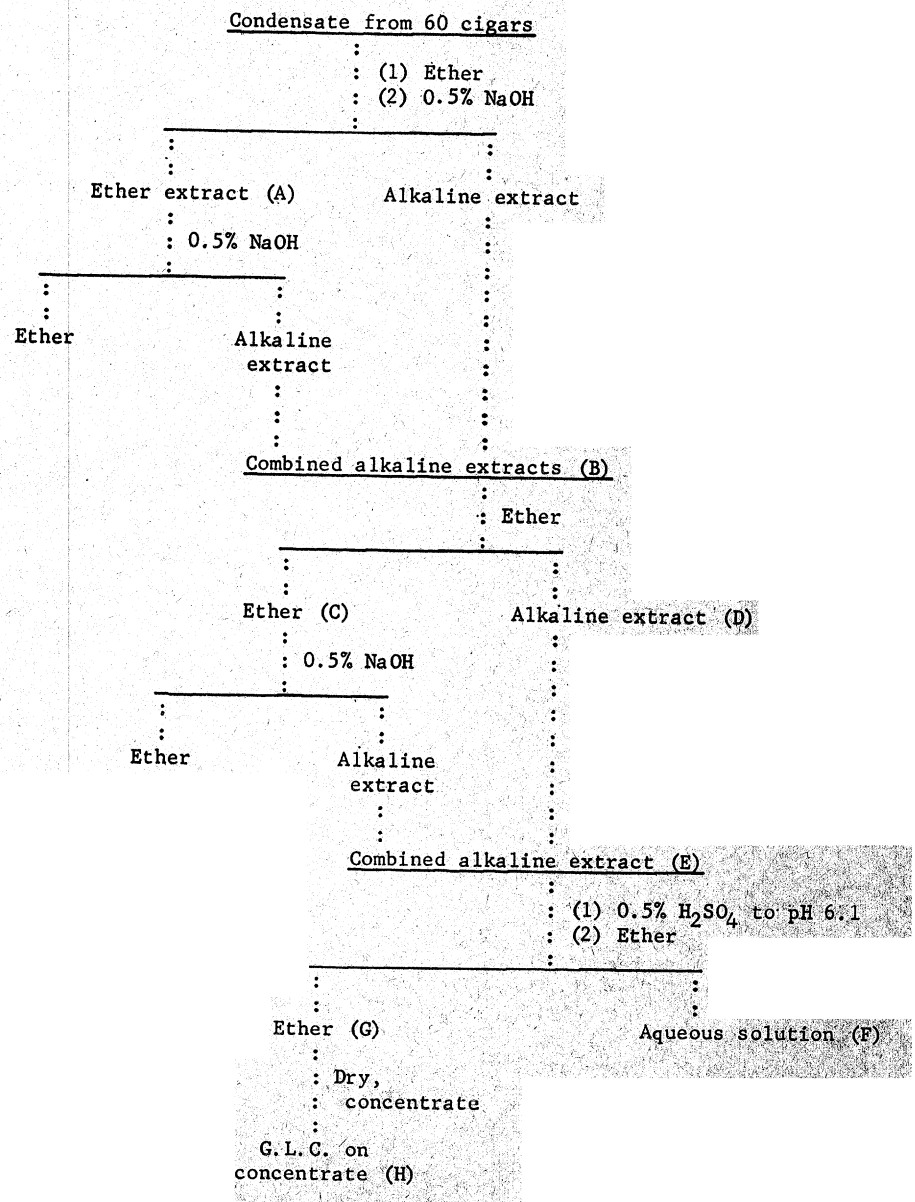

Figure 1. Isolation of weakly acidic substances from cigar smoke condensate.

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Gas Chromatography. An Aerograph[5] Model A-350 with a thermal conductivity cell was used in the analysis. Initial chromatography was done on a column (5 ft x 0.25 in) of 15% di-n-octyl sebacate coated on Gas Chrom P (60-80 mesh). A typical chromatogram obtained with a 1 mv. full scale recorder is shown in **Figure 2.** Further chromatography was carried out on a column (5 ft x 0.25 in) of 20% Carbowax 20M coated on 60-80 mesh Chromosorb W (flow rate, 60 ml helium-min; column temperature, 240°C) and on a column (5 ft x 0.25 in) of 20% Silicone SE-30 on Chromosorb W (flow rate, 60 ml helium/min; column temperature, 200°C). Quantitative evaluations were done on the di-n-octyl sebacate column by comparing peak areas (determined by triangulation) with area concentration curves of the corresponding knowns. Co-chromatography with authentic compounds was performed on all columns. For further identification, ultraviolet spectral comparisons of known and collected eluates of the major gas chromatographic peaks were made.

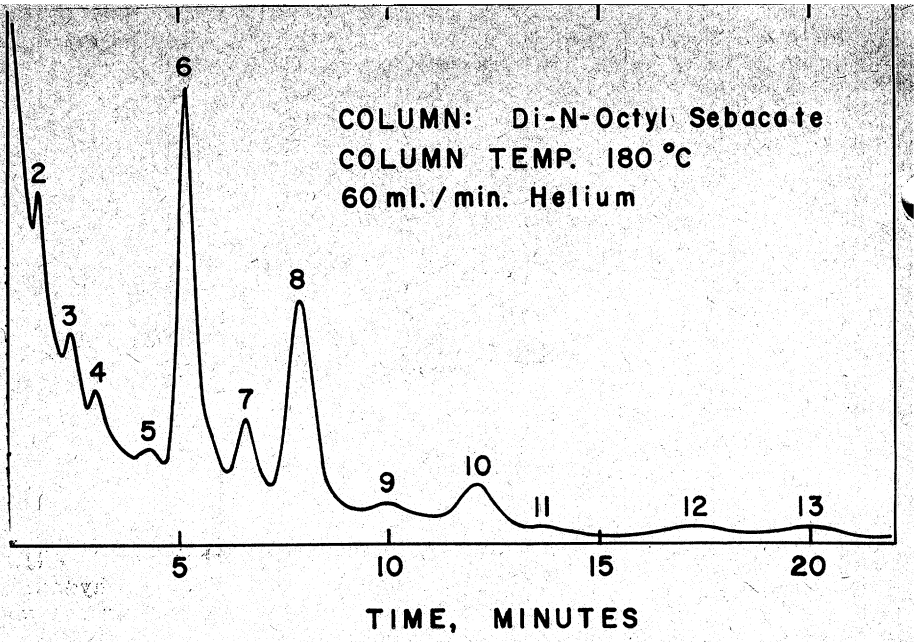

Figure 2. Chromatogram of phenols of cigar smoke. (See Table I for peak identities.)

Results and Discussion

Two main problems were observed initially in attempting to isolate quantitatively the weak acids from the smoke condensate; (a) losses of phenols from the aqueous basic solution during the ether washing step to remove interfering nonacidic contaminants, and (b) considerable losses of the free phenols (boiling points >140°C) during concentration of the final ether extract containing the weakly acidic substances. Similar losses have been reported recently by Stedman and Miller (1963) for weakly concentrated ethereal solutions of homologous esters, including high boiling compounds. The first problem was overcome by using alternate ether and basic washes as shown in **Figure 1.** The second problem was eliminated by removal of the ether *in vacuo* (50 mm.) at 0°C. Using these techniques recoveries of phenols in control experiments were in the order of 85-95% whereas previous experiments in which these precautions were not followed gave recoveries of 25-50%. Further purification by steam distillation of the acid fraction was also studied; however, the chromatogram of the steam volatile material was identical to that of a sample not steam distilled. The coefficient of variation was 5.7% for solutions of pure phenols and 12% for phenols in smoke condensates.

Table 1 lists the qualitative and quantitative findings obtained. Similar levels were obtained with a second brand of cigar which, however, was not as intensively investigated. The levels (μg per cigar) of phenols obtained were within the range of values reported by other workers for cigarette smoke (μg per cigarette). However, on the basis of μg per g of tobacco smoked, cigar smoke contained less phenol than the smoke from unfiltered cigarettes.

In addition to the phenols shown in **Table 1,** two carboxylic acids, palmitic and myristic acid, were found in the weakly acidic frac-

Table 1. Phenols of cigar smoke.

Peak No.	Compound	Amount (μg/cigar)*
1	Ether	—
2	Unknown from ether**	—
3	" " "	—
4	" " "	—
5	Unknown	Trace
6	Phenol	110
7	o-Cresol	12
8	m-Cresol, p-Cresol	90
9	2,5-Xylenol, 2,4-Xylenol	17
10	3,5-Xylenol, m-Ethylphenol, p-Ethylphenol	28
11	3,4-Xylenol	Trace
12	Unknown	"
13	"	"

* *Average of three runs. Average weight of cigars was 7 g and 67% of length of cigar was smoked.*

** *Chromatograms of ether blanks showed peaks corresponding to peaks 2, 3, and 4.*

[5] *Mention of a specific commercial product does not constitute an endorsement by the United States Department of Agriculture over similar items not named.*

tion; identification was made by co-chromatography on a Carbowax 20M column and by comparison of the infrared spectra of collected gas chromatographic effluents with authentic samples. A previously unidentified smoke component, 3-pyridinol, was also found in the weakly acidic fraction (Schmeltz and Stedman, 1962) but could not be isolated by the procedure outlined in **Figure 1.** The removal of 3-pyridinol from alkaline extract E **(Figure 1)** with ether required pH adjustment of the extract by saturation with carbon dioxide (final pH, 6.7) rather than by addition of sulfuric acid to pH 6.1. The difference is undoubtedly a reflection of the amphoteric nature of 3-pyridinol.

Although several trimethylphenols have been reported present in cigarette smoke (Hoffmann and Wynder, 1961; Spears, 1963; Crouse et al., 1963) no evidence was obtained for their presence in cigar smoke.

Summary

The major volatile phenolic components from two commercial cigars condensates were isolated and their amounts per cigar were estimated. The following compounds were found in the weakly acidic fraction; phenol; o-, m- and/or p-cresol; 2,4- and/or 2,5-xylenol; 3,4-xylenol; 3,5-xylenol and/or m- and/or p-ethylphenol; 3-pyridinol; myristic acid; and palmitic acid. The levels (μg per cigar) of the phenols were generally similar to those reported for cigarette smoke (μg per cigarette); however, on the basis of μg per g of tobacco smoke, the smoke of these cigars contained less phenol than the reported amounts in smoke from unfiltered cigarettes.

Acknowledgment

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