

Volatile Acids of Cigar Smoke

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Introduction

Although cigarette smoke has been investigated extensively for the presence of volatile acids, no reports have appeared describing similar studies on cigar smoke. The lower aliphatic acids of cigarette smoke have been isolated and identified by several groups of workers. Recently, Izawa and Kobashi (1958) isolated the lower fatty acids from C_1 to C_5 in addition to β -methylvaleric and benzoic acids; identification was made by preparation of crystalline derivatives. In another study, Buyske and his co-workers (1957) reported the presence in cigarette smoke of the fatty acids from C_1 to C_{10} in addition to benzoic acid, using column and paper chromatographic methods of identification. The latter work included quantitative data.

Since cigar tobacco undergoes a method of processing different from that of cigarette tobacco and since no information is available on the volatile acid composition of cigar smoke, a study of such constituents appeared to be of interest. The present report presents qualitative and quantitative data on the major volatile acids of cigar smoke condensate.

Experimental

Collection of Smoke: Cigars were equilibrated for one week at 68 per cent relative humidity and 25° C. before smoking. They were smoked using the automatic smoking machine and experimental conditions

described earlier (Schepartz, 1959, 1960). The smoke was collected in traps cooled in acetone-dry ice.

Two popular brands of cigars were smoked: a panatella with all-Havana filler and drawn tuck, and a perfecto with a cut filler of blended domestic tobaccos. Usually, 25-30 cigars yielded sufficient smoke condensate for analysis.

Fractionation of the Condensate: The traps containing smoke condensate were washed successively with ether, absolute methanol and 5 per cent sodium hydroxide solution. The ether extract was then extracted with alkali to remove acidic material. The methanolic solution was made alkaline with 5 per cent sodium hydroxide solution and the solvent evaporated in vacuo. The residue was dissolved in water and extracted with ether to remove neutrals and bases. All the alkaline solutions were then pooled.

The combined alkaline solution was concentrated to a volume of 100 ml, acidified to pH 2.0 with phosphoric acid and steam distilled. One and a half liters of steam distillate were collected and titrated potentiometrically to pH 7.0 with 0.1 N sodium hydroxide to estimate the total steam-volatile acidity. After extraction of the resulting neutralized distillate with ether,³ the distillate was evaporated to dryness yielding a brown residue of sodium salts.

Silicic Acid Chromatography: The chromatographic procedure of Buyske *et al.* (1957) was applied to the mixture of sodium salts. However, the silicic acid was unwashed, and the column was larger (2 x 20 cm). The column was prepared by mixing 40 g of silicic acid with 36 ml of 2 M glycine adjusted to pH 2.0 with concentrated hydrochloric acid, concentrating the resulting powder in 200 ml of chloroform and pouring the slurry into the column. A slurry of the

sample and 2 g of silicic acid in 2 ml of glycine solution and 5 ml of chloroform was quantitatively transferred to the column, and the column was successively eluted with 200 ml each of 1, 10 and 25 per cent n-butyl alcohol in chloroform. Finally, an additional 100 ml of the 25 per cent solution was then passed through the column. Ten milliliter fractions were collected and titrated with 0.01 N methanolic sodium hydroxide using bromthymol blue as the indicator. A plot of the elution data indicated two major and two minor peaks (Figure 1). The elution curves for the two brands of cigars were similar to each other and to the data obtained by Buyske *et al.* (1957) for the volatile acids of cigarette smoke. According to these workers, the first peak contains higher homologues of propionic acid and other acids, the second peak is propionic acid, the third peak is acetic acid and the fourth peak is formic acid.

Identification of Acids: The peaks were chromatographed on paper using several different solvent systems:

- (1) 95% ethanol/concentrated ammonia (100:1) (Kennedy and Barker, 1951)
- (2) n-butyl alcohol/water/n-propylamine (100:15:1) (Buyske *et al.*, 1957)
- (3) t-butyl alcohol/n-butanol/concentrated ammonia (1:1:1) (Schwartzman, 1960)
- (4) acetone/water/concentrated ammonia (95:5:1) (Kennedy and Barker, 1951). Spray reagents consisted of a mixture of 50 mg bromphenol blue, 200 mg citric acid, 100 ml absolute ethanol or, in case of the solvent system containing propylamine, of 0.1 per cent ninhydrin in chloroform.

Following the column chromatographic separation, the eluted fractions corresponding to a single peak were pooled, evaporated to dryness,

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³This ether solution contained only a small amount of the steam distillate material, later shown to be phenol in nature.