On the Chemistry of Cigar Smoke: Comparisons between Experimental Little and Large Cigars*

by

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INTRODUCTION

The objective of the study to be described, i. e. to examine the smoke of little and large cigars, represents a part of our continuing effort to determine the parameters influencing smoke composition. Parameters which are likely to play a role are physical design of the cigar, leaf type and composition, and wrapper type (porous vs. non-porous). As in other correlative studies, the goal is to predict smoke composition on the basis of given properties of a smoking product and ultimately to devise a product with modified smoke composition in which undesirable constituents are reduced. This has been achieved to a large extent by various techniques at least for some cigarettes (1 – 6). However, unlike cigarettes, cigars have been the subject of relatively limited study in areas such as smoke composition (7 – 11), effect of leaf type (12), and other factors (13) on such composition, and on similarities and differences between cigars and cigarettes (14 – 16). The present study is an attempt to gain more insight into the composition of cigar smoke and the factors influencing it.

Two basic types of cigars were chosen for this investigation. Some of the physical features of these are given in Table 1. The little cigars were subdivided into two groups, each group being identical except for the wrapper type. The first group was wrapped in conventional cigar wrapper, the second in cigarette paper, thus allowing a demonstration of the effects of wrapper type on smoke composition. One of five different tobaccos was utilized as filler in each cigar fabricated; there were no blends. The filler tobaccos used in the large cigars were cigar scrap cut, those in the little cigars were shredded filler. Overall, then, there were three groups of five cigars each; the first two groups differed mainly in wrapper type; the third group was identical to the first group except for size and presence of binder. Chemical analyses were performed on both

Table 1. Cigar types compared.

Little cigars

85 mm; non-filter; diameter: 8.0 mm; weight: 1.0 g. No binder.

I – With cigar wrapper (RTS)*

II – With cigarette paper

Large cigars

135 mm; non-filter; diameter: 13.0 mm; weight: 7.0 g.

III – With cigar wrapper (RTS) and binder (RTS, Binder Formulation)

Tobaccos

Puerto-Rico, Manila, Colombia, Domingo-Criollo, Pennsylvania.

* RTS = Reconstituted tobacco sheet.

leaf and smoke. The factors and constituents considered in the present report are itemized in Table 2.

The analytical data lead to a search for correlations among the various constituents in both leaf and smoke. At present, even without the aid of computer analysis, the data indicate certain trends among various components, and reveal rather interesting differences between little and large cigars.

Table 2. Analyses.

Leaf constituents	Smoke constituents
Water,	pH
Nicotine,	"Tar":
Nornicotine,	TPM,
Reducing sugars,	Water,
Hexane-solubles,	Nicotine,
Neophytadiene,	Benzo(a)pyrene,
Nitrate.	Volatile phenols,
	Pyridines.
Cigar characteristics	Gas phase:
Draw resistance,	CO, Isoprene,
Burning rate,	CO ₂ , Acetaldehyde,
Puff number.	NH ₃ , Acrolein.

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EXPERIMENTAL

Details of the methods used are presented in the references cited; otherwise, they are given below:

Cigar selection, and determination of average weights (29, 35)

Static burning rate and pressure drop (29)

Total particulate matter (TPM) and smoking conditions (17, 18, 36, 37)

Moisture in TPM (31, 37)

Nicotine in smoke (17, 29, 35, 36)

Volatile phenols (29)

pH of mainstream smoke (20, 21)

Benzo(a)pyrene in smoke [as indicator for yield of PAH (22)]

CO and CO₂ (23)

Moisture in cigar tobaccos (32)

Tobacco (10–20 g) was ground in a blender and placed in a distilling flask, 200 ml xylene was added and the mixture distilled into a Dean-Stark trap. After 8 hours, the volume of water in the Dean-Stark trap was measured.

Ammonia in smoke (24)

Gas phase: isoprene, acrolein and acetaldehyde (15, 16, 25)

Pyridines in smoke (26, 27)

Nornicotine in leaf (30)

Hexane-Extractables and Neophytadiene from Cigar Tobaccos

Cigar tobacco (40–50 g) was extracted by refluxing with n-hexane (250 ml) for 16 hours. The hexane solution was then dried over sodium sulfate and evaporated to dryness. Residue weights were then determined. Neophytadiene was determined by gas chromatography, injecting an aliquot of the hexane solution into a 2 m × 2 mm (i. d.) glass column, 10% UC-W 98 (on Gaschrom Q, 80–100 mesh) at 180°C, with a He flow rate of 55 ml/min; injector and detector were

set at 240°C. Neophytadiene had a retention time of 7.5 minutes.

Leaf Nicotine

Cigar tobacco was ground, and approximately 1 g, accurately weighed, was placed in a distilling flask to which ¹⁴C-nicotine was added as internal standard. Twenty ml of 10% NaOH was also added, and the mixture was steam distilled. The distillate, 500 ml, was trapped in 2N H₂SO₄. The solution was basified and extracted with ether; the ether solution was dried (Na₂SO₄) and concentrated to 1.0 ml. An aliquot was analyzed by gas-liquid chromatography using a 2 m × 0.32 cm stainless steel column packed with 10% UC-W 98 on silylated Chromosorb W (80–100 mesh). The conditions were: column, 150°C; injector, 235°C; FI-detector, 240°C; helium flow, 40 ml/minute. The retention time of nicotine was 6.9 minutes.

RESULTS AND DISCUSSION

Leaf: Levels of various leaf constituents are given in Table 3. Examination of the data shows that Puerto Rico type cigar tobacco, of those listed, contains the highest level of nicotine, and the lowest level of neophytadiene; Colombia cigar tobacco, on the other hand, is lowest in nicotine and highest in neophytadiene. This observation may be a consequence of compositional differences in tobacco varieties and may also be indicative of changes occurring in the leaf during processing (e. g. fermentation) where nicotine levels decrease dramatically relative to other leaf constituents (33). The same relation appears to hold true for the hexane-solubles and nicotine as well; neophytadiene, of course, is part of the hexane-solubles, and levels of these parallel each other. As for the other values, as expected, reducing sugars are low (15, 33) and nitrate is at relatively high levels when compared to cigarette-type tobaccos [except perhaps for Burley and Maryland cigarette tobaccos (3, 33, 34)]. Ranges of values among the different cigar tobaccos, for given constituents, do not show much variation — as often occurs between different tobacco types.

Cigar Characteristics: Prior to smoke analysis, the physical characteristics, i. e. weight, puff number, and pressure drop for the three groups of cigars were

Table 3. Cigar tobaccos: Concentration levels of various constituents* (%).

Type	H ₂ O	Hexane-solubles	Neo-phytadiene	Nicotine	Nor-nicotine	Reducing sugars	NO ₃ **
Puerto-Rico	12.7	4.5	0.46	1.7	0.16	0.45	1.78
Manila	11.7	5.2	0.48	0.9	0.15	0.44	1.27
Colombia	11.6	8.1	0.77	0.6	0.09	0.37	2.53
Domingo-Criollo	10.6	6.3	0.65	1.1	0.19	0.40	1.40
Pennsylvania	13.7	5.1	0.56	1.2	0.08	0.37	1.60

* Dry weightbasis.

** Method of H. Jaclin: Tobacco Science 14 (1970): 28–30; methods for other constituents given in experimental section.

Table 4. Cigar characteristics^a.

Filler	Weight (g)			Puff rate (no./cig.)			Pressure drop (mm H ₂ O)		
	I	II	III	I	II	III	I	II	III
Puerto-Rico	1.1	1.0	6.4	8.9	10.4	68.0	59	45	54
Manila	1.0	1.0	6.8	8.4	9.0	73.0	41	41	54
Colombia	1.1	1.1	6.8	8.6	10.3	69.5	59	53	54
Domingo-Criollo	1.1	1.0	6.8	8.5	9.6	74.0	46	40	61
Pennsylvania	1.0	0.9	6.8	7.9	7.5	66.8	45	27	59
Averages	1.1	1.0	6.7	8.5	9.4	70.3	50	41	56

Key: I: Little cigar, cigar wrapper, II: Little cigar, paper wrapper, III: Large cigar.

a: Burning rates were obtained only for the little cigars, as the large cigars did not stay lit under "free burn" conditions.

For the little cigars, values were (mg/min) 65.1, 67.2, 74.5, 65.6, 79.0 for group I and 48.8, 50.8, 58.4, 48.5, 59.4 for group II.

determined and are given in Table 4. As already noted, the weights of the large cigars are nearly seven times those of the little cigars. Interestingly, the pressure drop, measured as mm H₂O, does not differ significantly among the three groups of cigars. Note that the large cigar has 8 to 9 times the puff number as the little cigar. It should be mentioned that the little cigars were smoked for the most part using standard cigarette conditions, whereas the large cigars were smoked according to the cigar smoking schedule (Table 5). Justification for use of the two different

Table 5. Smoking protocol.

	Cigarette (17, 29, 35)*	Cigar (18)
Puff volume (ml)	35	20
Puff duration (s)	2	1.5
Puff interval (s)	60	40
Butt length (mm)	23	33

* Often referred to as "standard smoking conditions".

smoking protocols lay in the premise of approximating conditions for the smokers of little cigars, which are more like those for cigarette smokers versus conditions for smokers of large cigars. Therefore, when comparing smoke constituents on a per cigar basis,

we try to evaluate smoke levels as the smoker experiences them. However, to equate comparisons on a chemical analytical basis, we also converted the data to quantities per puff, and quantities per liter of smoke.

Smoke Analysis: Considering now the question of smoke composition, we note in Table 6 levels of the principal smoke constituents (i. e. TPM, nicotine and benzo[a]pyrene) delivered by the three groups of cigars. There are two comparisons to be made here — first between the little cigars with different wrappers, and then between the cigars of different sizes. The data for TPM, nicotine, and benzo(a)pyrene (BaP) suggest that a more porous paper (or wrapper) has little, if any, effect on concentration levels of these smoke constituents. It must be realized though that with a more porous wrapper a proportionately smaller volume of the 35 ml puff is drawn through the burning cone of the little cigar than is the case for a little cigar with less porous cigar wrapper. This has at least two effects; namely, the little cigar with cigarette paper burns slower during the actual puffing, thus the combustion is somewhat more complete (less oxygen deficient), and, as a result, smoking a given tobacco column requires more puffs. Both factors, more complete combustion and greater number of puffs, have a compensating effect on the TPM and BaP formation.

Table 6. Smoke* constituents: Little vs. large cigars.

Tobacco	TPM (mg)**			Nicotine (mg)			BaP (ng)		
	I	II	III	I	II	III	I	II	III
	(quantities/cigar)								
Puerto-Rico	41.1	38.9	28.0	2.7	2.9	2.8	61.3	47.8	10.8
Manila	31.6	31.8	36.8	1.4	1.5	1.8	24.1	23.9	36.9
Colombia	33.3	37.6	39.0	0.7	0.8	1.7	36.5	43.5	28.3
Domingo-Criollo	31.4	38.5	36.9	1.6	1.6	2.6	26.9	50.1	17.9
Pennsylvania	29.3	32.5	34.7	1.4	1.3	3.2	18.8	35.8	17.7
Averages	33.3	35.9	35.1	1.6	1.6	2.4	33.5	40.2	22.3

Key: I: Little cigar, cigar wrapper, II: Little cigar, paper wrapper, III: Large cigar.

* Mainstream.

** Federal Trade Commission value for TPM = wet TPM minus water and minus nicotine.

Table 7. Smoke* constituents: Little vs. large cigars.

Tobacco	TPM (mg)**			Nicotine (mg)			BaP (ng)		
	I	II	III	I	II	III	I	II	III
	(quantities/puff)								
Puerto-Rico	4.62	3.74	0.41	0.30	0.27	0.04	6.9	4.6	0.16
Manila	3.76	3.53	0.50	0.17	0.16	0.02	2.9	2.7	0.51
Colombia	3.87	3.65	0.56	0.08	0.08	0.03	4.2	4.3	0.40
Domingo-Criollo	3.68	4.01	0.50	0.19	0.17	0.04	3.2	5.2	0.24
Pennsylvania	3.72	4.33	0.52	0.17	0.17	0.05	2.4	4.8	0.26
Averages	3.93	3.85	0.50	0.18	0.17	0.04	3.9	4.3	0.32
	(quantities/liter)								
Puerto-Rico	132	107	20.5	8.5	7.8	2.1	196	131	7.9
Manila	107	101	25.0	4.9	4.6	1.2	82	76	25.3
Colombia	111	104	28.0	2.3	2.3	1.2	121	121	20.2
Domingo-Criollo	105	115	25.0	5.5	4.8	1.7	90	150	12.1
Pennsylvania	106	124	26.0	4.9	4.9	2.4	68	137	13.2
Averages	112	110	24.9	5.2	4.9	1.7	112	123	15.7

Key: I: Little cigar, cigar wrapper, II: Little cigar, paper wrapper, III: Large cigar.

* Mainstream.

** Federal Trade Commission value for TPM = wet TPM minus water and minus nicotine.

More interesting, perhaps, is the comparison of the large and little cigars. The large cigars weigh nearly seven times more than the little cigars; however, this large weight difference is not reflected in the levels of TPM, nicotine and BaP generated, *inter alia*. In a number of instances, even lower levels of these constituents are generated by the large cigars than by the corresponding little cigars. The data shown are on a per cigar basis (Table 6), and the cigars were smoked by different protocols, as indicated before. However, this alone could not account for the results observed. To gain another perspective, and to perhaps make more appropriate comparisons, the data were converted to a per puff and a per liter of smoke basis. These data, shown in Table 7, emphasize even more the differences between the mainstream smoke of little and large cigars. On a per puff scale, for example,

TPM, nicotine and BaP delivered by the large cigars are, on the average, one-seventh, one-third and about one-tenth that delivered by the little cigars. In reviewing these observations, consideration should be given to the effect of air flow rate over the coal on completeness of combustion as the smoking regimen is changed. Again, as far as the individual smoker is concerned, what is relevant are the quantities of smoke constituents generated per cigar. As noted in Table 6, smokers of little or large cigars "see" approximately the same levels of TPM, nicotine and BaP — the question of inhalation, of course, enters considerations of exposure in this case.

The correlation between nicotine levels in leaf and smoke is especially true for the little cigars, and less so for the large cigars. The transfer rates of nicotine into mainstream smoke are markedly different for the

Table 8. Volatile phenols and pyridines in cigar smoke ($\mu\text{g}/\text{cigar}$).

	Phenol			Total phenols ^a			Pyridine			Total pyridines ^b		
	I	II	III	I	II	III	I	II	III	I	II	III
Puerto-Rico	164	166	375	301	287	527	99	141	647	317	456	996
Manila	166	171	398	329	360	782	100	108	518	325	428	768
Colombia	101	145	367	207	293	489	223	240	689	701	516	1048
Domingo-Criollo	169	156	420	339	315	540	166	50	477	586	297	728
Pennsylvania	126	126	498	249	258	606	184	217	1313	627	425	2194
Average	145	153	412	285	303	589	154	151	729	511	424	1147
(average $\mu\text{g}/\text{puff}$)	17	16	6	34	33	8	18	17	11	60	45	16
(average $\mu\text{g}/\text{liter}$)	489	470	293	962	935	418	524	476	525	1714	1286	800

Key: I: Little cigar, cigar wrapper, II: Little cigar, paper wrapper, III: Large cigar.

a: Sum of phenol, cresols, 2,4- and 2,5-dimethylphenols and p-ethylphenol.

b: Sum of pyridine, α -picoline, 2,6-lutidine, β - and γ -picoline, 2,4-lutidine, 3,5- and 3,4-lutidine.

two types of cigars, for the little cigars ranging from 11 to 16%, whereas for the large cigars, they are notably only 3 to 4%. Currently we are investigating the fate of the leaf nicotine (and other constituents) during smoking of cigars and its distribution in mainstream and sidestream smoke and butt. We are already aware of the role played by tobacco and smoke pH on the fate of nicotine during smoking. The smoke pH also influences the ratio of protonated to unprotonated nicotine (21) as will be discussed below.

Other mainstream smoke constituents are also delivered in lower yields from large cigars although not nearly so marked as TPM, nicotine and BaP. In Table 8, for example, where values for phenols and pyridine are given for the three groups of cigars, we still note a disproportionately low level of smoke constituents generated from the large cigars. On a per cigar basis, large cigars deliver nearly twice the phenols as corresponding little cigars (about seven times would be expected based on tobacco weight), but on a per puff and per liter basis, only about 25 and 50% respectively, of the levels from little cigars. This delivery of relatively low levels of phenol from large cigars has been noted before in comparison to cigarettes and was also observed for volatile and non-volatile acids (7, 8, 10, 14, 15). Pyridine, as might ordinarily be expected, on a per cigar scale, appears in the mainstream of large cigars in about five times the amount as that from little cigars, but on a per puff or per liter of smoke basis these differences are less pronounced and for the most part disappear. Similar to cigarette smoke, cigar smoke also contains more than 80% of pyridine in unprotonated form ($pK_a = 5.19$). Also, HCN values whether per cigar, per puff or per liter appear to be lowest in the smoke of large cigars as indicated by present data in our laboratory (19, 45).*

CO/CO₂: Carbon dioxide and especially carbon monoxide are important indicators of tobacco combustion with regard to completeness of combustion and to biological activity of total smoke. We determined, therefore, their levels in the mainstream smoke. Data for these are given in Table 9 — where the little cigars are considered first. Here we see the effects of the more porous cigarette paper on concentration levels of CO, which are reduced by nearly 50% in the smoke from the cigars wrapped in cigarette paper, whereas the CO₂/CO ratio is higher. It appears that oxidation processes are more complete in the cigars wrapped in more porous paper, so that not only dilution by incoming air, but also enhanced oxidation to CO₂ contribute to the observed effect (38).

In Table 10, we compare little and large cigars with regard to CO and CO₂ levels, under the conditions described previously, i. e. standard smoking conditions for the little cigars, and cigar smoking conditions for

the large cigars. Again CO and CO₂ levels are elevated, about threefold for CO, and sevenfold for CO₂, per cigar. Perhaps even higher values should have been expected, taking into consideration the respective quantities of tobacco burned. When we compare values obtained on a per puff and per liter basis, we note

Table 9. CO and CO₂ in smoke from little cigars (standard smoking conditions).

	I: With cigar wrapper			II: With cigarette wrapper		
	CO	CO ₂	CO ₂ /CO	CO	CO ₂	CO ₂ /CO
(mg/cigar)						
Puerto-Rico	43.1	81.2	1.88	22.0	75.0	3.41
Manila	40.6	65.3	1.61	25.0	76.1	3.04
Colombia	44.1	69.5	1.58	25.5	77.4	3.04
Domingo-Criollo	42.9	67.1	1.56	26.6	80.0	3.01
Pennsylvania	40.8	69.3	1.70	20.4	61.2	3.00
Average	42.3	70.5	1.67	23.9	73.9	3.09
Ratios (I/II)						
	CO			CO ₂		
Puerto-Rico	1.96			1.08		
Manila	1.62			0.86		
Colombia	1.73			0.90		
Domingo-Criollo	1.61			0.84		
Pennsylvania	2.00			1.13		
Average	1.78			0.96		

Table 10. CO and CO₂ in cigar smoke: Little vs. large cigars.

	CO			CO ₂		
	I	III	III/I	I	III	III/I
(mg/cigar)						
Puerto-Rico	43.1	99	2.30	81.2	464	5.71
Manila	40.6	133	3.28	65.3	514	7.87
Colombia	44.1	121	2.74	69.5	509	7.32
Domingo-Criollo	42.9	118	2.75	67.1	507	7.56
Pennsylvania	40.8	119	2.92	69.3	473	6.83
Average	42.3	118	2.79	70.5	493	6.99

Key: I: Little cigar, cigar wrapper, III: Large cigar.

Table 19. Hydrogen cyanide: Sidestream vs. mainstream levels (μg/cigar*).

	Mainstream (MS)	Sidestream (SS)	SS/MS
Puerto-Rico	129	18	0.14
Manila	94	23	0.24
Colombia	214	24	0.11
Domingo-Criollo	234	28	0.12
Pennsylvania	51	33	0.65

* 137 mm.

* Note added in proof: Since submission of the manuscript we have obtained data for HCN in mainstream and sidestream smoke of cigars with the recently developed glc method (45). The values and the ratios of HCN in sidestream vs. mainstream are presented in Table 19.

how disproportionately low the levels of CO and CO₂ are in the smoke of large cigars (Table 11).

When both little and large cigars are smoked under identical cigar smoking conditions, the differences in CO and CO₂ levels are magnified, on a per cigar basis. Large cigars, under these conditions, deliver six times more CO and ten times more CO₂ than the corresponding little cigars. Of course, one should note that the large cigars require about 70 puffs compared to 13 puffs for the little cigars. Furthermore, it is noteworthy that the cigar smoking conditions, in this case, as compared to the standard cigarette smoking conditions, result in lower values for both CO and CO₂ (Table 12).

pH: The pH characteristics of the cigars were profiled on a puff by puff basis (Fig. 1). A profile typical of those obtained for the little cigars is shown in Figure 2. Generally, the pH starts out relatively low (6.78 to 7.36) in initial puffs, and rises to a maximum (7.50 to 8.19) in the final puffs; this occurs under standard

Figure 1. pH profile of the smoke of a large cigar (Manila) obtained under cigar smoking conditions.

cigarette smoking conditions. Under cigar smoking conditions, somewhat lower pH values are obtained, although the trend from lower to higher pH values during the course of puffing is still generally observed. However, in some instances, i. e. in Colombia or Domingo-Criollo cigars, a drop in the pH profile is noted during intermediate puffs (Tables 15 and 16). As noted previously (16), smoke pH from genuine tobacco products (assuming no additives) is principally dependent on the tobacco used. The smoke pH profile of a cigar wrapped in cigarette paper still behaves like that of a cigar and not of a cigarette.

The large cigars smoked according to their specific protocol (in about 70 puffs) produce a smoke pH profile typified in Figure 1. Like the little cigars, the large cigars initially generate smoke with a relatively low pH, eventually reaching a maximum in the final puffs. Compared to the little cigars, the smoke from the large cigars reaches somewhat higher pH values, although in early and intermediate puffs, the large cigars exhibit a somewhat lower pH. The pH is the determining factor for the ratio of protonated to un-

Table 11. CO and CO₂ in cigar smoke: Little vs. large cigars.

	CO		CO ₂	
	I	III	I	III
	(mg/puff)			
Puerto-Rico	4.8	1.5	9.1	6.8
Manila	4.9	1.8	7.8	7.0
Colombia	5.1	1.7	8.1	7.3
Domingo-Criollo	5.1	1.6	7.9	6.9
Pennsylvania	5.2	1.8	8.7	7.1
Average	5.0	1.7	8.3	7.0
	(mg/liter smoke)			
Puerto-Rico	138	73	260	341
Manila	139	91	223	352
Colombia	146	86	230	364
Domingo-Criollo	144	80	226	343
Pennsylvania	147	89	250	353
Average	143	84	238	351

Key: I: Little cigar, cigar wrapper, III: Large cigar.

Table 12. CO and CO₂ in cigar smoke: Little vs. large cigars (under cigar smoking conditions).

	CO			CO ₂		
	I	III	III/I	I	III	III/I
	(mg/cigar)					
Puerto-Rico	20.7	99	4.8	60.7	464	7.6
Manila	21.7	133	6.1	50.8	514	10.1
Colombia	21.7	121	5.6	52.6	509	9.7
Domingo-Criollo	20.9	118	5.7	48.4	507	10.5
Pennsylvania	19.3	119	6.2	48.3	473	9.8
Average	20.9	118	5.6	52.2	493	9.4

Key: I: Little cigar, cigar wrapper, III: Large cigar.

Figure 2. Average pH profile of the smoke of a little cigar (Colombia) obtained under cigarette and cigar smoking conditions.

Table 13. Smoke from little cigars — pH of individual puffs^a.

	Mainstream — standard smoking conditions										
	3		5		7		9		10		
	I	II	I	II	I	II	I	II	I	II	
Puerto-Rico	6.84	7.02	7.16	7.22	7.58	7.40	7.88	7.60		7.75	
Manila	6.78	7.00	7.12	7.21	7.40	7.36	7.56	7.66			
Colombia	7.07	6.88	7.12	7.00	7.41	7.16	7.69	7.55		7.68	
Domingo-Criollo	7.22	7.16	7.52	7.41	7.78	7.60	7.93	7.80		7.99	
Pennsylvania	7.36	7.32	7.74	7.74	8.06	8.02	8.19				

	Mainstream — cigar smoking conditions												
	3		5		7		9		11		12		
	I	II	I	II	I	II	I	II	I	II	I	II	
Puerto-Rico	6.84	6.79	6.99	6.96	7.06	7.00	7.12	7.04	7.32	7.12	7.58 ^b	7.21 ^b	
Manila	6.91	6.64	7.08	6.81	7.22	6.94	7.34	7.06	7.42	7.19	7.49	7.23	
Colombia	6.55	6.51	6.48	6.46	6.40	6.39	6.40	6.38	6.45	6.44	6.56		
Domingo-Criollo	6.74	6.63	6.65	6.76	6.72	6.86	6.84	6.98	7.08	7.10			
Pennsylvania	6.86	7.20	6.99	7.38	7.06	7.66	7.14	7.82	7.28 ^c	7.92 ^c			

a: Puff pH = mean of maximum and minimum.
b: 13th puff.

c: 10th puff.

I: Little cigars, cigar wrapper
II: Little cigars, paper wrapper

protonated nicotine and other tobacco alkaloids. As demonstrated by Armitage and Turner, unprotonated nicotine is more readily absorbed through mucous membranes than is protonated nicotine, a factor influencing the acute toxicity of nicotine (39).

Cigars vs. Cigarettes: With regard to pH, it is appropriate at this point to compare little cigars and cigarettes as was done previously (15, 16) and as is shown in Figure 3. Unlike smoke from little cigars, smoke from cigarettes made of Bright or blended tobacco (major portion Bright tobacco) exhibits a gradual

Table 14. pH of smoke from big cigars^c (puff by puff basis).

Puff no.	Manila	Puerto-Rico	Domingo-Criollo	Colombia	Pennsylvania
5	6.03	5.80	6.19	5.50	6.23
10	6.02	5.73	6.01	5.05	5.99
15	5.98	5.72	5.95	4.71	5.91
20	5.90	5.69	5.91	4.59	5.76
25	5.86	5.63	5.81	4.47	5.63
30	5.89	5.53	5.71	4.55	5.60
35	5.94	5.51	5.71	4.67	5.62
40	6.00	5.54	5.74	4.93	5.71
45	6.06	5.62	5.83	5.29	5.87
50	6.15	5.83	5.96	5.75	6.11
55	6.28	6.24	6.16	6.22	6.40
60	6.51	6.81	6.50	6.81	6.81
65	6.82	7.73	6.64	7.49	7.29
70	7.27	7.94 ^b	7.09	7.96 ^b	
75	7.78 ^a		7.38 ^a		

a: Puff No. 73.
b: Puff No. 68.

c: Cigar smoking schedule.

Figure 3. pH profiles of cigar and cigarette smoke (21).

decrease in pH during successive puffs, usually reaching a minimum in the final puffs. As noted earlier, pH is a function of the tobacco used, assuming all other factors to be equal, and cigarette tobacco may be distinguished from cigar tobacco by the pH of the smoke generated. Even when wrapped with cigarette

Table 15. Ammonia: Comparisons between cigars and cigarettes.

Key: I: Little cigar, cigar wrapper
II: Little cigar, paper wrapper
III: Large cigar

	μg NH ₃ /cigar or cigarette		
	I	II	III
Puerto-Rico	761	936	661
Manila	297	364	158
Colombia	659	804	494
Domingo-Criollo	641	699	529
Pennsylvania	607	644	400
Average	593	689	448
Commercial cigarette (85 mm, non-filter)	134		

Table 16. CO and CO₂: Cigars vs. cigarettes.

	CO (mg)*			CO ₂ (mg)*		
	A	B	C	A	B	C
Little cigar - I	42	5.0	143	71	8.3	238
Little cigar - II	24	2.6	74	74	8.0	227
Large cigar - III	118	1.7	84	493	7.0	351
Cigarette	18	1.6	46	68	6.0	172

* A: per cigar or cigarette.

Cigar values are averages.

B: per puff.

C: per liter.

paper, cigar tobacco gives rise to a pH profile expected from cigar smoke, as is also seen in smoke from cigarettes made exclusively from Burley tobacco (21). Like pH, ammonia levels in smoke seem also to be a function of tobacco type and are characteristically high in the smoke of cigars (vs. cigarettes). According to Johnson, during smoking part of the nitrate in tobacco is reduced to ammonia (40), and since most Burley and cigar tobaccos are relatively high in nitrate, this fact may at least partially explain the elevated ammonia levels in the smoke of little cigars and large cigars (24). Little cigars, for example (Table 15), whether wrapped in cigar wrapper or cigarette paper, give significantly higher values for ammonia than are obtained from a cigarette (593 and 689 mg/cigar vs. 134 mg/cigarette). Other volatile bases behave similarly.

Cigars also give characteristically high levels of CO and CO₂, although more so for CO since the porosity of the wrapper is a determining factor for the CO yield in the smoke (41, 42). Use of cigarette paper instead of cigar wrapper results in lowered CO, yet remains above the level of cigarette smoke. CO₂, on the other hand, seems to be less affected by the more porous wrapper. Overall, CO seems more sensitive to changes in "cigarette or cigar engineering" (Table 16).

Large Cigars vs. Little Cigars: As noted, the large cigar compared to the little cigar delivers relatively low concentrations of constituents in mainstream smoke,

Figure 4. Gas chromatogram of vapor phase of cigar smoke (little cigar, Puerto-Rico tobacco, cigarette wrapper).

especially in the mainstream particulates. This we noted to be particularly true for TPM, nicotine and BaP — but is also true for other constituents.

What happens then to cigar tobacco as it is exposed to the elevated temperatures associated with tobacco combustion? If the products generated do not become part of the mainstream particulates, then in order to maintain a material balance, we should expect to find greater concentrations of smoke constituents in the vapor phase (mainstream), and in the sidestream. Table 17 presents data for some of the vapor phase constituents. On a per cigar basis, large cigars generate 6 to 7 times more isoprene, 4 to 5 times more acetaldehyde, and 2 to 7 times more acrolein than the corresponding little cigars. However, these differences tend to disappear or reverse themselves when one looks at the data on a per puff basis. A gas chromatogram of cigar smoke vapor phase is illustrated in Fig. 4.

As for the sidestream "hypothesis", at the moment we have only NH₃ data, and again on a per cigar basis, more NH₃ is present in large cigar sidestream than in

Table 17. Gas phase constituents: Little vs. large cigars (μg/cigar)*.

	Isoprene			Acetaldehyde			Acrolein		
	I	II	III	I	II	III	I	II	III
Puerto-Rico	374	272	2766	904	804	4378	39	60	248
Manila	282	524	3083	822	1160	5777	21	81	186
Colombia	234	456	3933	844	1140	3228	35	102	183
Domingo-Criollo	421	567	2748	867	1048	3632	30	69	227
Pennsylvania	230	429	2384	708	1094	5918	19	74	222
Average	308	450	2983	829	1049	4587	29	77	213
(μg/puff [averages])	36	49	42	98	115	65	3.4	8.4	3.0
(μg/liter [averages])	1036	1404	2118	2792	3278	3270	96.4	239	152

Key: I: Little cigars, cigar wrapper, II: Little cigars, paper wrapper, III: Large cigars.

a: Reference cigarette (85 mm, non-filter): 733 μg isoprene, 1372 μg acetaldehyde, and 122 μg acrolein.

Table 18. Ammonia: Mainstream vs. sidestream levels ($\mu\text{g}/\text{cigar}$).

	Mainstream (MS)	Sidestream (SS)	SS/MS
Little cigar A*	148	6,980	47
Little cigar B*	288	11,600	40
Cigar**	158	106,000	670

* 85 mm, filter (commercial little cigar).

** 137 mm (Manilla).

little cigar sidestream. Furthermore, if one looks at the sidestream to mainstream ratio for NH_3 , the large cigar value is 670 as compared to 40 for the little cigar (Table 18). This is in line with an earlier finding by Johnson et al. showing the highest sidestream to mainstream ratio for NH_3 for the smoke of all Burley cigarettes (43).

It is obvious that to resolve the question of large cigar vs. little cigar, more data are needed, especially a material balance of constituents in mainstream, and sidestream, and in their respective particulate and vapor phases. The data presented indicate, however, that the cigar smoker on a per puff basis is exposed to relatively low levels of certain smoke constituents. On the other hand, large concentrations of constituents, including ammonia, in the sidestream smoke explain at least partially the effects of cigar smoke on non-smokers, as well as the lingering aroma characteristics associated with cigar smoke and butts. Another factor is the difference in axial and peripheral temperature profiles among various smoking products. A comprehensive study of cigar combustion temperatures indicates that these may differ significantly from those observed in other smoking products (e. g. cigarettes) and that different types of cigars show different combustion profiles as well (28, 44).

SUMMARY

Comparative data have been presented and evaluated on levels of various constituents in five different cigar tobaccos and in the smoke they generate when made into little and large cigars. Generally the large cigars deliver a significantly lower level of mainstream smoke particulates such as TPM, nicotine and benzo(a)pyrene, when compared to the little cigars. On a per cigar basis, however, large cigars (as opposed to little cigars) deliver substantially higher levels of CO and other gas phase constituents. A higher delivery of ammonia by large cigars is noted in the sidestream smoke. When little cigars are wrapped in cigarette paper, the major effects are lower levels of CO (reduced by 50%). Cigar smoke can be distinguished from cigarette smoke on the basis of pH characteristics, ammonia and CO levels. Future studies should be concerned with establishing the material balance for components in mainstream and sidestream smoke of little cigars and large cigars.

ZUSAMMENFASSUNG

Für fünf verschiedene Zigarrentabake und den Rauch, den diese nach Verarbeitung zu kleinen und großen Zigarren erzeugten, wurden von einer Reihe von Inhaltsstoffen vergleichende Daten vorgelegt und ausgewertet. Im Vergleich zu den kleinen Zigarren hatte der Hauptstromrauch der großen Zigarren im allgemeinen einen signifikant niedrigeren Gehalt an Gesamtkondensat, Nikotin und Benz(a)pyren. Im Gegensatz zu den kleinen Zigarren war der Gehalt der großen Zigarren an CO und anderen Verbindungen der Gasphase je Zigarre jedoch wesentlich größer. Im Nebenstromrauch enthielten die großen Zigarren mehr Ammoniak. Die Umwicklung kleiner Zigarren mit Cigarettenpapier hatte hauptsächlich einen niedrigeren Gehalt an Kohlenmonoxid zur Folge (Verminderung um 50%). Zigarrenrauch unterscheidet sich von Cigarettenrauch in der pH-Charakteristik und im Gehalt an Ammoniak und Kohlenmonoxid. Künftige Untersuchungen sollten sich mit der Stoffbilanz von Bestandteilen des Haupt- und Nebenstromrauches kleiner und großer Zigarren befassen.

RESUME

On présente et on discute des données comparatives sur les teneurs en différents constituants présents dans cinq différents tabacs pour cigares ainsi que dans la fumée produite par de petits et de grands cigares qui ont été fabriqués avec ces tabacs. En général, le flux principal de fumée d'un grand cigare produit significativement moins de matière particulaire totale, nicotine et benzo(a)pyrène que celui d'un petit cigare. Par cigare, par contre, les grands cigares produisent beaucoup plus de CO et d'autres constituants de la phase gazeuse. On note une plus grande production d'ammoniaque dans le flux secondaire des grands cigares. Quand de petits cigares sont enroulés dans du papier à cigarettes, l'effet principal est de réduire la production de CO (de 50%). On peut distinguer la fumée de cigare de celle de cigarette par le pH, et la teneur en ammoniaque et en CO. Des études futures devraient essayer d'établir le bilan matière des constituants du flux principal et du flux secondaire pour les grands et les petits cigares.

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