The Reducing Property of Tobacco Smoke

2. The Influence of Smoking Vehicle, with Particular Reference to the Pipe*

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INTRODUCTION

One of the objectives of our laboratory is the modification of yield and chemical composition of tobacco smoke. To monitor these changes we have developed relatively simple chemical and biochemical tests which are indicators of the chemical reactivity of tobacco smoke (1-5). Thus, we have found that monitoring the dichlorophenolindophenol⁺-reducing property of tobacco smoke is useful in studying such modifications of chemical composition of smoke and have used this property extensively (6).

As part of these studies, we have already shown that air-cured tobaccos, such as those used in the manufacture of cigars and pipe tobaccos, when smoked in the form of cigars or in stainless steel pipes, gave condensates that were much lower in DCIP-reducing activity than condensates obtained by smoking Canadian flue-cured cigarettes (1). However, we found that this difference between air- and flue-cured tobaccos is not as marked when these are ground and smoked in cigarette tubes. Also, some earlier preliminary studies had suggested that cigar filler tobacco, when crushed by hand and smoked in a stainless steel pipe, gave a condensate with such a low reducing activity as to be barely detectable under the conditions of our assay. These results suggested an important role for the smoking vehicle in generating reducing activity. Consequently, a systematic examination of different tobacco types as well as modes of smoking was undertaken, to determine what role these played in the generation of reducing activity of smoke and the results obtained are reported herein.

MATERIALS AND METHODS

Smoking Procedures

Standard smoking procedures — 35 ml puffs of 2-second duration taken every minute in the case of cigarettes, cigarillos and cigars, or taken every 10 seconds in the case of pipes — were employed. Different types of natural tobaccos smoked in stainless steel pipes were in a granulated form (7). The stainless steel pipes were

fabricated with the same hole and stem dimensions as the briar pipes used regularly by pipe smoking panels in the laboratory. In contrast to briar pipes, these are easy to clean and re-use. The condensates were collected and smoke solutions prepared as described previously (1). In this report wet TPM refers to total particulate matter collected on Cambridge pads. Dry TPM is obtained from wet TPM by drying over NaOH or CaCl₂ in an evacuated desiccator kept at 4° C.

Reduction of Dichlorophenolindophenol

The procedure followed has been described earlier (1).

RESULTS AND DISCUSSION

While we had smoked air-, flue-cured and fermented tobaccos in cigarette tubes, as well as pipe tobaccos in pipes, and found significant differences between them, we had never smoked pipe tobaccos in cigarette tubes. Consequently, we selected two commercially available brands of pipe tobaccos and smoked these in cigarette tubes. The reducing activities of condensates from these tobaccos are recorded in Table 1. Since these pipe tobaccos are cut to about 20 cuts per inch, we included a grade of flue-cured tobacco, cut as above, as control. From the results obtained, it will be seen that even though these pipe tobaccos give smoke with distinctly lower total as well as specific reducing activities, the

Table 1. DCIP⁺-reducing activity of pipe tobaccos smoked in cigarette tubes.

Tobacco	Weight of dry TPM from 5 cigarettes (mg)	No. of puffs per cigarette	DCIP-reducing activity	
			Total activity from 5 cigarettes	Specific activity- "units" per mg TPM
Plugged, flue-cured (20 cuts per inch)	110	14	595	5.40
Brand 1	117	13	286	2.46
Brand 2	79	12	285	3.62

* Received for publication: 16th April, 1975.

⁺ DCIP.

⁺ Dichlorophenolindophenol.

Figure 1. Effect of smoking time on total particulate matter (TPM) yield and DCIP*-reducing activity.

Pipe smoking

Cigar smoking

Cigarillo smoking

Cigarette smoking

values are still significantly higher than those of around 1 obtained in pipe smoking (1) suggesting, once again, an important role for the vehicle in which tobacco is smoked. The low reducing values obtained when these pipe tobaccos are smoked in cigarette form are not surprising when it is considered that they are blends of both flue- and air-cured tobaccos to which significant amounts of additives such as humectants and plasticizers are added. In the case of Brand 1, which is a Dutch type pipe tobacco, the processing calls for a step called

"plugging" in which the tobacco blend is held under pressure. A similar "plugging" of the flue-cured tobacco had to be carried out before it could be cut to 20 c.p.i. on a laboratory scale. The specific reducing activity of this flue-cured tobacco appears to be lower than is generally obtained for such a tobacco. This lower value for flue-cured tobacco along with the lower value obtained for Brand 1 than for Brand 2 which is not plugged before cutting, suggest that "plugging" itself involves changes which are reflected in the specific reducing activity of smoke, and merits further investigation.

* Dichlorophenolindophenol.

Table 2. DCIP*-reducing activities of air- and flue-cured tobacco smoked in stainless steel pipes.

Smoking time (min)	Weight of tobacco smoked (g)	Weight of wet TPM (mg)	Weight of dry TPM (mg)	Percent loss in weight on drying	DCIP-reducing activity Specific activity-"units" per mg dry TPM
Flue-cured					
5	0.21	6.2	5.8	7	6.9
10	0.55	17.5	14.8	15	3.4
20	0.80	43.7	20.0	54	1.9
40	1.55	183.2	36.7	80	2.2
60	2.19	358.2	46.5	87	0.6
Air-cured (cigar)					
5	0.40	5.4	4.9	9	2.9
10	0.61	6.8	6.0	12	1.4
20	0.94	41.5	10.0	76	1.9
40	2.00	192.0	45.6	76	0.2
60	2.60	475.6	74.3	84	0.2
Burley					
10	0.25	19.1	8.3	57	1.5
20	0.72	47.3	9.0	81	0.5
40	1.75	177.7	34.2	81	0.1
60	2.35	379.4	54.9	86	0.4

* Dichlorophenol/indophenol.

Next, in order to determine the role of the pipe in generating reducing activity of smoke, flue-cured, Burley and cigar tobaccos were smoked for different lengths of time in pipes and the total particulate matter was collected on Cambridge pads. The reducing activities of these tars were determined and from the results presented in Table 2 it will be seen that specific reducing activity dropped sharply with increase in smoking time. All three tobaccos showed this marked decrease in specific reducing activity indicating that pipe smoking does indeed give a tar of low reducing activity as found earlier. However, from Table 2 it will be seen that the specific reducing activities of the early TPM samples obtained from flue-cured tobacco were much higher than the early samples from cigar and Burley tobaccos. After the initial higher activity, all three tobaccos consistently gave very low specific activities. Large amounts of moisture accumulate and these values would even be lower if wet weights of TPM were used to calculate specific activity. Similar results were obtained using commercially available briar pipes. On the other hand, no such change in specific reducing activity with smoking time is observed in the case of cigarillo, cigar and cigarette smoking. Nor does moisture accumulate the way it does in pipe smoking, in any of these other modes of smoking. Results obtained in cigarette, cigarillo, cigar and pipe smoking are illustrated in Figure 1.

We wondered whether the decreasing specific activities with increasing smoking time recorded in pipe smoking were due to any change in the chemical nature of TPM as burning progressed in the pipe, or due to increased trapping of reducing substances by the water accu-

mulating in the pipe and on the unburned tobacco. To carry out this study, flue-cured tobacco was smoked for different lengths of time in the pipe, at the end of which the unsmoked tobacco and the Cambridge pad containing the TPM were extracted separately using 95% ethanol, and the pipe rinsed out using the same solvent. These extracts were then examined for their content of reducing activity. Corresponding amounts of fresh tobacco (equal in weight to the residual unsmoked tobacco in the pipe) served as controls. When these amounts of fresh tobacco are extracted using 95% ethanol, the extracts do not show any reducing activity, confirming that the activity trapped on the unsmoked tobacco in the pipe was generated during pipe smoking. The results obtained in a typical pipe smoking experiment are summarized in Table 3. From this table, it will be seen that pipe rinses, at all times, failed to show any reducing activity. However, it will be seen that a considerable amount of reducing activity was trapped by the unsmoked tobacco in the pipe, and if one adds this amount of activity to the activity obtained for the TPM on the pad, the specific activities for the total particulate matter are at least as high as those obtained for flue-cured tobacco smoked in cigarette form, but the total activities are still very low. When trapped reducing activity is included and specific activities are expressed as "units" per gram tobacco smoked, then once again pipe smoke appears to be similar to cigarette smoke, and both these are markedly lower than cigar and cigarillo smoke. In no other mode of smoking (cigarette, cigarillo or cigar) does the trapped reducing activity contribute significantly enough to change the

Table 3. Distribution of reducing activity between TPM, pipe rinse and unsmoked tobacco (flue-cured) in pipe smoking.

Time of smoking and source	Weight of tobacco smoked (g)	Weight of dry TPM (mg)	Weight of TPM per g tobacco smoked (mg)	DCIP* — reducing activity		
				Total activity—"units"	Specific activity	
					"Units" per mg dry TPM	"Units" per g tobacco smoked
5 min						
TPM	0.21	3.8	18.1	20	5.2	94
Rinse				Nil	Nil	Nil
Unsmoked tobacco				59	15	277
10 min						
TPM	0.45	7.8	17.3	52	6.7	116
Rinse				Nil	Nil	Nil
Unsmoked tobacco				110	14.1	245
20 min						
TPM	0.73	10.6	14.5	51	4.8	70
Rinse				Nil	Nil	Nil
Unsmoked tobacco				110	10.4	150
40 min						
TPM	1.69	13.5	8.0	50	3.7	30
Rinse				Nil	Nil	Nil
Unsmoked tobacco				71	5.3	42
60 min						
TPM	2.09	19.4	9.3	48	2.5	23
Rinse				Nil	Nil	Nil
Unsmoked tobacco				60	3.1	29
100 min						
TPM	3.45	222.5	64.9	172	0.8	50
Rinse				Nil	Nil	Nil
Unsmoked tobacco				Nil	Nil	Nil

* DichlorophenolIndophenol.

Table 4. Distribution of DCIP*-reducing activity between TPM, ash and butt in smoking.

Source	Weight of tobacco smoked (g)	Weight of dry TPM (mg)	Weight of TPM per g tobacco smoked (mg)	DCIP-reducing activity		
				Total activity-"units"	Specific activity	
					"Units" per mg dry TPM	"Units" per g tobacco smoked
Cigarettes						
TPM	3.06	119.3	38.9	895	7.5	292
Ash				Nil	Nil	Nil
Butt				154	1.3	50
Cigars						
TPM	7.06	64.4	9.1	92	1.4	13
Ash				Nil	Nil	Nil
Butt				51	0.8	7
Cigarillos						
TPM	11.41	311.0	27.3	588	1.9	51
Ash				Nil	Nil	Nil
Butt				53	0.2	5

* DichlorophenolIndophenol.

The tar weights and total activities are per 5 cigarettes, cigars or cigarillos.

Table 5. A summary of results — Mode of smoking and DCIP*-reducing activity.

Study of	Mode of smoking			
	Cigarette	Cigar	Cigarillo	Pipe
TPM/vehicle	High	High	High	Low (high at very end of smoking)
TPM/g tobacco smoked	High	Low	High	Low (high at very end of smoking)
TPM: DCIP-reducing specific activity	High	Low	Low	Low
Total DCIP-reducing activity	High	Low	High	Low
Unsmoked tobacco/butt — DCIP-reducing specific activity	Specific activity much lower than that of TPM	Specific activity close to that of TPM	Specific activity much lower than that of TPM	Specific activity higher than that of TPM
Contribution of trapped reducing activity	Slight	Considerable, but no significant increase toward flue-cured cigarette level	Slight	Considerable increase to flue-cured cigarette level

* Dichlorophenolindophenol.

specific activity so markedly (see Table 4). In cigar smoking the activity trapped in the cigar butt is about equal to that collected on the pad, but the total of these two still does not represent sufficient activity so as to change the specific activity to any extent as it does in the case of pipe smoking.

For comparative purposes, cigarette, cigarillo and cigar butts and ash were collected and extracted, along with TPM from these, using 95% ethanol. The results obtained are summarized in Table 4. That the reducing activity detected in the butts of these smoking vehicles was generated during smoking, was confirmed by extracting appropriate sections of tobacco rod of equal length to the butts, cut off from unsmoked cigarettes, cigars or cigarillos. These extracts did not show any reducing activity.

From all the experiments, it is evident that the specific activities of pipe, cigar and cigarillo smoke are indeed low and that filtration effects account for the low specific activities, but not total activities, only in the case of pipe smoking. The decreasing specific activities in the case of pipe smoking may be due to re-pyrolysis occurring to a greater extent in this mode of smoking than in the smoking of the cigarette or cigarillo. However, it may be stated that no such decreasing specific activities are obtained in cigar smoking in which case there is also considerable accumulation of reducing activity on the butt, relative to total activity. Thus, as far as total activity (pad plus butt) is concerned, pipe smoking is very similar to cigar smoking and both give considerably lower activity than cigarette and cigarillo smoking. For convenience, a summary of all these results is presented in Table 5.

In conclusion, it may be stated that in pipe smoking, the smoker is exposed to very low amounts of reactive

compounds as measured by DCIP reduction, and while part of this low delivery to the smoker is due to the type of tobacco generally smoked in a pipe, the smoking vehicle itself plays a major role. The biological significance of this extremely low delivery of reducing compounds in pipe smoking is as yet unknown.

SUMMARY

A detailed investigation of pipe smoking was undertaken to elucidate why this mode of smoking produced condensates of low DCIP*-reducing activity.

Pipe tobaccos, smoked in cigarette tubes, gave reducing activities distinctly lower than those obtained for flue-cured tobacco, but the values were still higher than those obtained in pipe smoking. In pipe smoking, using both flue- and air-cured tobaccos, the initial high specific reducing activities (during 5–10 minutes of smoking) dropped to very low values towards the end of smoking. The decreasing specific activities paralleled the formation of water. No reducing activity was trapped by the water accumulating in the pipe, but a considerable amount of activity was trapped by the unsmoked tobacco. Unlike cigarette and cigarillo smoking, the trapped activity in cigar and pipe smoking was sufficient to significantly alter specific activity, but still much too low to obtain, in cigar and pipe smoking, the large total activities obtained in cigarette and cigarillo smoking. In the other three modes of smoking, viz cigarette, cigarillo and cigar, there was no change in specific activity with increase in duration of smoking (or change in butt length).

* Dichlorophenolindophenol.

ZUSAMMENFASSUNG

Es wurde eine eingehende Untersuchung des Pfeifenrauchens unternommen, um zu klären, warum das bei dieser Abrauchart entstehende Kondensat eine geringe Dichlorophenolindophenol [DCIP] reduzierende Aktivität hat.

Pfeifentabake, die in Zigarettenröhren abgeraucht wurden, zeigten für die reduzierende Aktivität Werte, die eindeutig niedriger waren als diejenigen von „flue-cured“-Tabak, aber trotzdem noch über denen lagen, die sich beim Abrauchen in der Pfeife ergaben. Beim Veraschen von „flue-cured“- und „air-cured“-Tabaken in der Pfeife sank die anfänglich (in den ersten 5 bis 10 Minuten) hohe spezifische reduzierende Aktivität am Ende des Rauchvorganges auf sehr niedrige Werte. Die Verminderung der spezifischen Aktivität lief mit der Bildung von Wasser parallel. Das in der Pfeife angesammelte Wasser hatte keine, der unverrauchte Tabak hingegen eine beträchtliche Menge reduzierende Aktivität aufgefangen. Im Gegensatz zum Zigaretten- und Zigarillorauchen war beim Zigarren- und Pfeiferauchen die aufgefangene Aktivität zwar so stark, daß sie eine wesentliche Veränderung der spezifischen Aktivität hervorrufen konnte, dennoch aber viel zu gering, um die hohen Gesamtwerte zu erreichen, die beim Zigaretten- und Zigarillorauchen erhalten wurden. Bei den übrigen drei Abraucharten, d. h. Zigarette, Zigarillo und Zigarre, veränderte sich die spezifische Aktivität nicht mit der Zunahme der Rauchdauer (oder der Veränderung der Stummellänge).

RESUME

Des recherches détaillées sur la fumée de pipe ont été entreprises, pour trouver la raison pour laquelle ce mode de fumer produit des condensats de faible activité réductrice au dichlorophénolindophénol (DCIP).

Les tabacs de pipe, fumés dans des tubes à cigarettes, ont donné des activités réductrices nettement plus faibles que celles des tabacs «flue-cured», mais les valeurs sont encore plus élevées que quand on les fume à la pipe. En fumant à la pipe des tabacs «air-cured» et «flue-cured»,

l'activité réductrice spécifique initiale élevée (cinq à dix premières minutes) tombe à des valeurs extrêmement basses vers la fin. La chute des activités spécifiques va de pair avec la formation d'eau. Aucune activité réductrice n'est piégée par l'eau accumulée dans la pipe, mais des quantités importantes en sont retenues par le tabac non fumé. Contrairement à ce qui se passe dans la cigarette et le cigarillo, l'activité piégée dans la pipe et le cigare est suffisante pour modifier l'activité spécifique de façon significative, mais bien trop faible pour obtenir, dans le cigare et la pipe, les importantes activités totales de la cigarette et du cigarillo. Dans les trois autres modes de fumer, c'est-à-dire la cigarette, le cigarillo et le cigare, on n'a pas observé de changement dans l'activité spécifique en augmentant la durée de fumage (ou en changeant la longueur du mégot).

Acknowledgements

The author wishes to thank Mrs. Cathy K. Fletcher for skilled technical assistance.

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