Cigarette Smoke Formation Studies

I. Distribution and Mainstream Products From Added ^{14}C -Dotriacontane-16, 17*

by Robert W. Jenkins, Jr., Richard H. Newman, Robert D. Carpenter, and Thomas S. Osden

Philip Morris USA, Research Center, Richmond, Virginia, USA

INTRODUCTION

The paraffinic hydrocarbons present in tobacco leaf tissue have received considerable attention. Tobacco leaf contains many paraffins, with *n*-hentriacontane ($\text{C}_{31}\text{H}_{64}$) as the major component (1). The C_{27} , C_{29} , C_{30} , C_{32} , and C_{33} paraffins are also present, but in lesser concentrations. The total paraffin content is variable among the various types and grades of tobacco, but is about 0.3% of the dry weight of the tobacco. Mold et al. (2) found that over 70% of the paraffin fraction was made up of C_{31} , C_{32} , and C_{33} hydrocarbons.

Lam (3) reported in 1955 that the paraffin fraction of tobacco extract pyrolyzed over pumice at 800°C , yielded measurable quantities of polycyclic hydrocarbons. This finding led to numerous studies by other investigators (4–9) to determine both the amount of paraffins present and the amount of polycyclic hydrocarbons which might be generated from the paraffin in the burning cigarette. Wynder and Hoffmann (8) have discussed these findings in some detail in their consideration of the precursors of polyaromatic hydrocarbons in cigarette smoke.

Of the various reports concerning the pyrolysis of paraffins only that of Rayburn et al. (10) studied the paraffins in an actual smoking situation. They added ^{14}C -labeled paraffins extracted from tobacco grown in $^{14}\text{CO}_2$ to tobacco, smoked the cigarettes, and determined the ^{14}C -activity in the polycyclic hydrocarbon fraction of the cigarette smoke. They concluded that the contribution of the paraffin fraction to the formation of polycyclic hydrocarbons was unimportant.

The extrapolation of pyrolysis data to cigarette smoke must always be questioned. Such pyrolyses are usually done at a constant temperature in the range of the coal temperature of a burning cigarette, and with substantial residence times at that temperature. While the conclusions drawn regarding the identity of the products may be useful in predicting the possible presence of those compounds in smoke, no quantitative extrapolation can be made.

Jenkins et al. (11) and Newman et al. (12) have described methodology to determine the distribution of radioactively labeled compounds in the smoke from a single cigarette. These techniques were chosen to study the fate of a representative paraffin in the cigarette during smoking. The choice of ^{14}C -dotriacontane-16,17 was made because dotriacontane is present in tobacco, it is similar in structure and boiling point to hentriacontane and tritriacontane, and it is commercially available.

EXPERIMENTAL

Radiochemicals

^{14}C -Dotriacontane-16,17 was purchased from Mallinckrodt Nuclear. The chemical and radiochemical purities were 98% and 99% respectively, as determined by gas radiochromatography, and were sufficient for these studies.

Labeled Cigarette Preparation

Thirty-five grams of cased, blended tobacco were sprayed with 0.4 mCi ^{14}C -dotriacontane-16,17 (3.91 mCi/mM) in 25 ml of hexane. During the spraying, the tobacco was tumbled. After thorough mixing, the solvent was removed by evaporation and the tobacco was humidified at 60% R.H. and 75°F . Cigarettes were handmade using Excel 67 mm length paper. Cigarettes were selected for resistance to draw and total weight, and were equilibrated at 75°F and 60% R.H. for one week prior to their use.

Smoke Distribution Studies

The procedures and smoking machine instrumentation were described previously and were used to obtain ^{14}C -mass balance and activity distributions in the total cigarette smoke (11).

The sidestream and mainstream total particulate matter (TPM) were collected on separate Cambridge filter pads which were immediately extracted in 25 ml of hexane. The butt was also extracted in 25 ml of hexane.

* Presented at the 5th International Tobacco Scientific Congress, Hamburg, September 1970.

The combusted sidestream and mainstream gas phases were absorbed in Hyamine-10X (Rohm & Haas) and aliquoted directly for counting.

The amount of ^{14}C -dotriacontane-16,17 on the cigarettes was determined by extracting each of four cigarettes in 25 ml of hexane and the activity determined by liquid scintillation. The degree of uniformity of the coating of ^{14}C -dotriacontane along the cigarette axis was determined by sectioning several cigarettes into four equal portions and conducting wet combustions on each portion for total activity. The $^{14}\text{CO}_2$ from the wet combustions was counted on a Nuclear-Chicago Dynacon model R1000 using a 500 cc ionization chamber.

Mainstream ^{14}C -Smoke Analyses

The total mainstream cigarette smoke analyses were conducted on a smoking machine previously described (12). The effluent from the gas chromatographic column was split 20:1, with the smaller fraction going to a FID detector for mass detection. Mass areas and retention times were printed out on an Infotronics CRS-100 Digital Integrator. The larger fraction was passed immediately into a 3/8 O.D. $\times$ 18 inch CuO furnace (750°C) for conversion of each peak to $^{14}\text{CO}_2$. Cobalt oxide and magnesium perchlorate were used to remove sulfur oxides and water, respectively. Propane:helium (1:1) was used as a counting gas. The 2 cc flow proportional detector, the pre-amplifier, and amplifier were from the Laboratorium Prof. Dr. Berthold. A Hewlett-Packard 5201-L scaler-timer was used and data were printed on a Hewlett-Packard digital recorder.

Counting efficiencies were determined using ^{14}C -acetone and ^{14}C -toluene (New England Nuclear).

The distribution of activity in the mainstream smoke was determined by using the following columns and operating conditions:

a. Porapak® Q 1/8 inch O.D. $\times$ 3 meter SS column programmed from -190° C to 200° C at 10° C/min and with 30 cc/min helium flow. This column resolved compounds from C_1 to about C_7 , as well as CO and CO_2 .

b. Carbowax®-20M on Chromosorb-G-HMDS 1/8 inch O.D. $\times$ 3 meter SS column programmed at 6°/min from -190° to 225° C and held at 225° C. Helium flow was 30 cc/min. This column resolved compounds containing from 6 to 12 carbon atoms.

c. OV-17 10% on Chromosorb-G-HMDS 1/8 inch O.D. $\times$ 3 meter SS column programmed at 30° C/min

from -190° C to 300° C and held at 300° C. Helium flow was 30 cc/min. This column resolved compounds containing from 10-36 carbon atoms.

Nearly all the activity was eluted from the OV-17 column, with the compounds resolved on the other columns eluting from OV-17 as early peaks. The CO and CO_2 peaks from the Porapak column were not detected by FID; the radioactivity from these compounds was counted over the range of their retention times.

Liquid Scintillation Counting

A Packard Tricarb Model 3003 liquid scintillation spectrometer was used with optimized gain and window settings.

Aliquots of the hexane extract were counted in a scintillator solution containing 72 g of naphthalene, 216 ml of ethanol, 360 ml of p-xylene and 360 ml of dioxane. The Hyamine® 10-X aliquots were counted in an Insta-Gel® (Packard) scintillator cocktail. Counting times were regulated for proper counting statistics. An internal standard (^{14}C -toluene, New England Nuclear) was added to each sample and the data were used for applying the proper quenching corrections.

RESULTS AND DISCUSSION

The cigarettes containing ^{14}C -dotriacontane were first analyzed for the uniformity of the activity along the cigarette rod. These data are shown in Table 1 and demonstrate acceptable agreement for our studies. The value obtained by extracting entire cigarettes is also shown in Table 1.

Table 1. Axial- ^{14}C cigarette distribution.

Cigarette number	Activity- $\mu\text{Ci}/16.7$ mm section				Total μCi
	I	II	III	IV	
1	2.47	2.49	2.85	2.96	10.77
2	2.94	2.66	2.55	2.66	10.81
Extracted average (three entire cigarettes) 10.80 ± 0.19					

The distribution of activity in the various portions of smoke from the radioactive cigarettes is presented in Table 2. All cigarettes were smoked to a 20 mm

Table 2. Total smoke distribution.

Smoke phase	μCi						% Distribution
Cigarette number	1	2	3	4	5	Avg.	
Sidestream gas	0.92	1.09	1.24	1.13	1.32	1.14	10
Sidestream TPM	3.49	4.55	3.79	3.67	4.94	4.09	38
Mainstream gas	0.16	0.07	0.18	0.14	0.15	1.14	10
Mainstream TPM	2.31	2.24	1.85	2.23	1.84	2.09	20
Butt	2.85	2.77	4.76	2.37	3.52	3.25	30
Total recovery	9.73	10.72	11.82	9.54	11.77	10.71	99

Figure 1. Puff-by-puff TPM delivery.

butt. Based on a beginning length of 67 mm, this would correspond to an expected butt concentration of 29.9% of the initial activity. The experimental value of 30% in the butt indicates no filtration of ^{14}C -dotriacontane by the uncombusted tobacco. This lack of filtration of the dotriacontane by the butt indicated a reasonable straight line delivery of dotriacontane as a function of puff count. This was verified by switching a fresh TPM pad and holder into the mainstream smoke between each puff. These data are presented in Figure 1.

The mainstream smoke contributions by the ^{14}C -dotriacontane, its pyrolysis products, and its combustion products were investigated by smoking on a total mainstream smoking machine. Table 3 contains the results of this investigation. The 0.7% of activity found in the CO and CO_2 is a measure of the combustion products found in the mainstream smoke, and indicates that combustion products of paraffins contribute little to the mainstream smoke. The 4.2% of activity found in the $\text{C}_1\text{--C}_{10}$ compounds is indicative of pyrolysis. No single compound in this range contained over 0.5% of the total mainstream activity. The lack of activity in the range of C_{11} to C_{30} compounds indicates that the pyrolytic conditions must be intense and confined, since splitting of groups from the ends of the straight chain of dotriacontane would leave compounds of $\text{C}_{11}\text{--C}_{30}$ with activity. The 95% of the mainstream activity found in the $\text{C}_{31}\text{--C}_{33}$ region indicates that distillation of the dotriacontane is the major method of transfer of the activity from the tobacco to the mainstream smoke.

The agreement between the recovery of mainstream activity by the two methods of smoking (Table 2, mainstream TPM plus mainstream gas phase, and Table 3) indicates that the two methods are equivalent in smoking conditions and in radioactivity recovery. The agreement between the gas phase results and the TPM results is also good (20:1 TPM to gas phase

by total recovery machine, Table 2, and 24:1 TPM to gas phase by total mainstream machine, Table 3).

The boiling point of n -dotriacontane is 310°C at 15 mm. The stability of the saturated hydrocarbon chain is probably responsible for the finding that 95% of the mainstream activity is unchanged dotriacontane, proving that distillation is the major transfer process. It might be presumed that the high boiling point would cause deposition of the compound in the tobacco as the smoke cooled, thereby causing sharply increased delivery in the last puff and high concentrations of dotriacontane in the unsmoked portion of tobacco. The lack of high delivery in the last puff may be explained by the temperature profiles published by Egerton et al. (13). They reported a temperature gradient that becomes very sharp as more puffs are taken so that the temperature during the 8th or 9th puff drops from 800° to 50°C in about 10 mm. Since these cigarettes were smoked to a 20 mm butt, the dotriacontane in the butt did not distil into the smoke. The lack of build up in the butt can be accounted for only by assuming that the dotriacontane is entirely in the non-volatile portion of particulate phase smoke, and that filtration by the tobacco is by diffusion of the volatile portion of the particulate phase into the leaf rather than by impaction of the non-volatile particles onto the surface of the leaf.

It is more difficult to explain the transfer of nearly 50% of the activity to the sidestream smoke, but it is probable that as soon as the momentum of the smoke stream due to the puff is lost, the gas flow within the cigarette rod near the burning zone reverses and flows toward the burning zone, carrying with it the distilled dotriacontane from the appropriate isotherm. As the dotriacontane passes through the burning zone, some is combusted, some is pyrolyzed, and some escapes unchanged. The small amount of activity present in the mainstream gas phase may then be due to the sudden reversal of flow as the cigarette is puffed.

The pyrolysis technique has been used for some time to elucidate structures or to study fragmentation products. In the study of smoke chemistry, the latter is of prime importance. There has been much written on the pyrolysis of tobacco constituents, but most of these studies were conducted on the pure components fractionated over a catalytic surface. The correlation of pyrolysis products formed this way with those formed during the burning of a cigarette is extremely difficult, if not impossible, without knowing the quantitative relationship between the precursor and its products in the cigarette smoke. The methods employed in this paper make it possible to determine this quantitative relationship in the matrix of the burning cigarette, since the incorporation of a single radioactive compound in the cigarette prior to smoking will result in radioactive smoke components that could have originated only from the radioactive precursor. The actual amount of chemical mass that is added by the tracer is small and therefore does not alter the normal smoke formation chemistry.

Table 3. Distribution of activity in mainstream smoke.

Smoke component	Activity $n\text{Ci}$	% of total activity
CO--CO_2	16.8 ± 0.1	0.7
$\text{C}_1\text{--C}_{10}$	100.8 ± 0.6	4.2
$\text{C}_{11}\text{--C}_{30}$	0.0	0.0
$\text{C}_{31}\text{--C}_{33}$	$2300. \pm 24.$	95.1
$> \text{C}_{33}$	0.0	0.0
Total recovered	$2418. \pm 25.$	100.

SUMMARY

The distribution of ^{14}C -dotriacontane-16,17 and its combustion and pyrolytic products in cigarette smoke is described. Twenty-one percent of the activity is found in the mainstream smoke, 49% is found in the sidestream smoke, and 30% is found in the butt. Of the mainstream activity, 95% is in unchanged dotriacontane. The transfer of ^{14}C -dotriacontane to mainstream smoke is linear throughout the smoking of the cigarette, as shown by puff-by-puff data. Hypotheses to explain the results are presented.

ZUSAMMENFASSUNG

Die vorliegende Arbeit behandelt die Verteilung von 16,17- ^{14}C -Dotriacontan und von dessen Verbrennungs- und Pyrolyseprodukten im Cigarettenrauch. 21% der Aktivität wurden im Hauptstromrauch, 49% im Nebstromrauch und 30% im Stummel nachgewiesen. Die im Hauptstromrauch festgestellte Aktivität liegt zu 95% in unverändertem Dotriacontan vor. Die Ergebnisse von Analysen je Zug zeigen, daß der Übergang von ^{14}C -Dotriacontan in den Hauptstromrauch während des gesamten Abrauchvorganges der Cigarette linear verläuft. Hypothesen zur Erklärung der Ergebnisse werden dargelegt.

RESUME

La distribution du ^{14}C -dotriacontane-16,17 et de ses produits de combustion et de pyrolyse dans la fumée de cigarette a été déterminée; 21% de la radio activité ont été trouvés dans le courant principal de fumée, 49% dans le courant secondaire et 30% dans le mégot. De la radio activité du courant principal de fumée, 95,1% provenait du dotriacontane inchangé, 0,7% de produits gazeux de combustion ($\text{CO}-\text{CO}_2$) et 4,2% de produits de pyrolyse. De la radio activité du courant secondaire, 79% était dans la phase particulière et 21% dans la phase gazeuse. Le transfert du ^{14}C -dotriacontane dans le courant principal de fumée était linéaire, comme démontré par les données du fumage par bouffées individuelles, et n'augmentait que légèrement de la première à la dernière bouffée.

La prépondérance du ^{14}C -dotriacontane inchangé dans le courant principal de fumée montre que la distillation est son mode de transfert du tabac à la fumée. Pendant les bouffées, le produit de la distillation est soutiré de la zone de combustion, ce qui donne une grande proportion de l'activité en ^{14}C -dotriacontane inchangé dans

le courant principal. Entre les bouffées le flux de gaz à l'intérieur de la cigarette est inversé, et il en résulte que le dotriacontane passe dans la zone de combustion où une partie est brûlée, une partie pyrolysée et une partie distillée.

Les 30% de la radio activité trouvés dans le mégot correspondent théoriquement à 29,9% de la radio activité présente dans cette longueur de la cigarette avant le fumage. Cela indique qu'il n'y a pas de déposition de matière particulaire sur le tabac du mégot pendant le fumage. Ce qui est aussi traduit par les rendements par bouffées individuelles.

REFERENCES

1. Carruthers, W., and Johnstone, A. W.: *Nature* 184 (1959) 1131.
2. Mold, J. D., Stevens, R. K., Means, R. G., and Ruth, J. M.: *Biochemistry* 2 (1963) 605.
3. Lam, J.: *Acta Path. Microbiol. Scand.* 37 (1955) 421.
4. Spears, A. W., Lassiter, C. W., and Bell, J. H.: *J. Gas Chromatog.* 1 (1963) 34.
5. Stedman, R. L.: *Chem. Rev.* 68 (1968) 153.
6. Schlotzhauer, W. S., and Schmeltz, I.: *Beitr. Tabakforsch.* 5 (1969) 1.
7. Stedman, R. L., and Rusanowskyj, W.: *Tob. Sci.* 4 (1960) 17.
8. Wynder, E. L., and Hoffmann, D.: "Tobacco and Tobacco Smoke", Academic Press, New York, N.Y., 1967, Chapter 7.
9. Badger, G. M., Donnelly, J. K., and Spotswood, T. M.: *Aust. J. Chem.* 18 (1966) 1249.
10. Rayburn, C. H., Wartman, W. B., Jr., and Pedersen, P. M.: *Science* 128 (1958) 1344.
11. Jenkins, R. W., Chavis, M. K., Newman, R. H., and Morrell, F. A.: submitted to *Int. J. Appl. Radiat. Isotopes*.
12. Newman, R. H., Jones, W. L., and Jenkins, R. W.: *Anal. Chem.* 41 (1969) 543.
13. Egerton, A., Guban, K., and Weinberg, F. J.: *Combustion and Flame* 7 (1963) 63.

Acknowledgment

The authors wish to thank Mrs. M. K. Chavis for her contribution to this study.

The authors' address:

Philip Morris USA, Research Center, P.O. Box 3 D, Richmond, Va., 23206, USA.

Erratum

Table 2, page 296:

The correct values for mainstream gas average and for percent distribution are 0.14 and 1, respectively.