

178. A Chemical Study of *Burley Tobacco Flavour* (*Nicotiana tabacum L.*)**II. Medium-Volatile, free Acidic Constituents****(b. p. ~ 84 – $114^\circ/0.001$ Torr)**by **Eduard Demole** and **Dominique Berthet**

Firmenich & Cie, Research Laboratory, Geneva

(24 VI 72)

Summary. The acidic part of a fraction b.p. 84 – $114^\circ/0.001$ Torr from *Burley Tobacco* condensate was investigated. Among the 22 compounds identified, 9 appeared to be new tobacco flavour components. This result increased to 208, the total number of *Burley tobacco* constituents so far isolated and identified in this laboratory.

The first publication of this series [1] dealt with a study of the 'volatile to medium-volatile (b.p. $\leq 84^\circ/0.001$ Torr) constituents' of *Burley tobacco* condensate, i.e. with the so-called *fractions B1* and *B2* from this essential oil¹). In this second paper, we describe further results obtained by similarly investigating the acidic constituents of the somewhat less volatile *fraction B3*¹) (b.p. 84 – $114^\circ/0.001$ Torr).

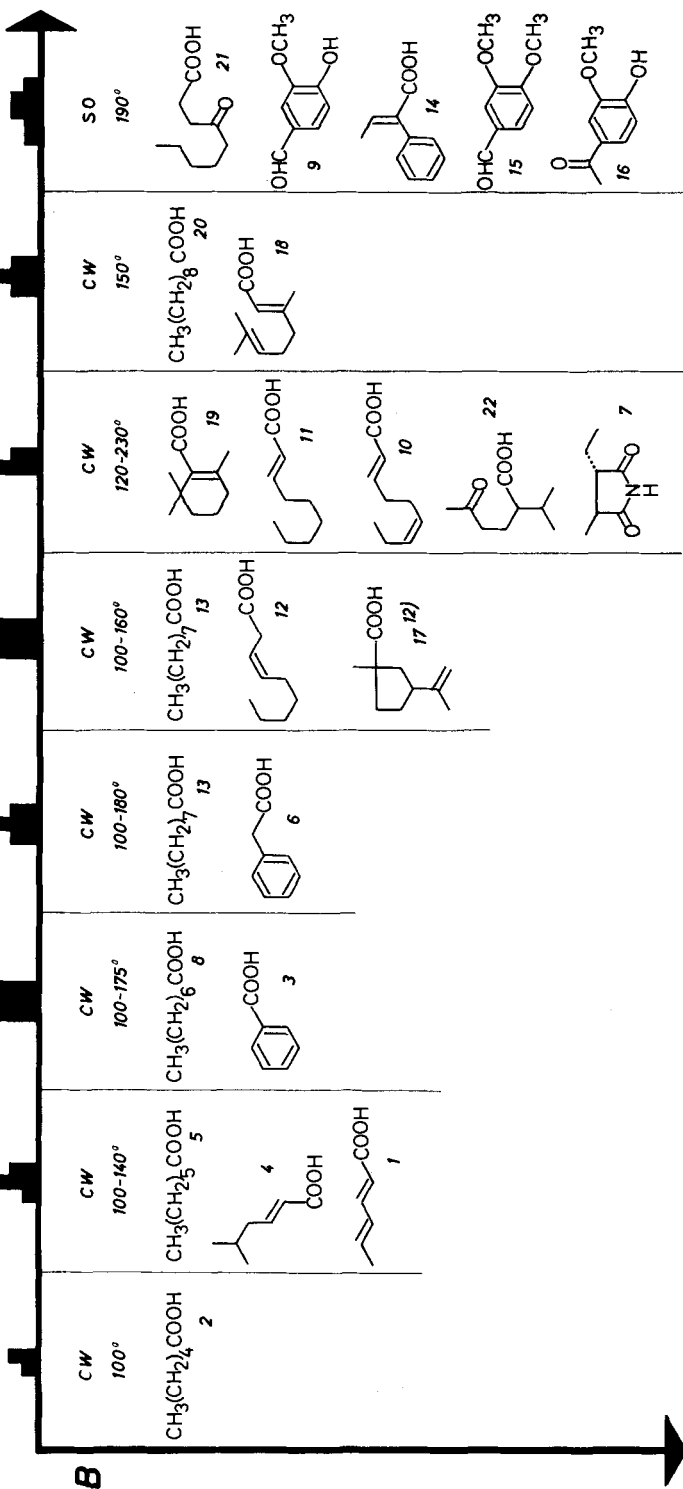
Fraction **B3** represented an exceedingly complex mixture of compounds possessing a powerful and excellent tobacco flavour, and which was characterized by the following general data: $d_4^{20} = 0.8918$; $n_D^{20} = 1.4923$; $\alpha_D^{23} = + 0.9^\circ$ (CHCl_3 , $c = 27.5$); found, C 81.23, H 11.82, N 6.80%. An ethereal solution of this fraction (37.2 g) was first washed with 6×75 ml of 10% sodium carbonate. After the usual processing (acidification of the combined alkaline extracts, re-extraction, etc.), there was isolated 0.823 g of acidic (= *fraction B3-PA*) and 36.382 g of neutral compounds (= *fraction B3-PN*). While the latter was put aside for further work²), *fraction B3-PA* was esterified with diazomethane and directly subjected to a semi-preparative separation by gas liquid chromatography³) (GLC.) using a conventional, analytical column (0.6×350 cm) packed with 15% of silicone oil (SO)⁴) on Chromosorb W⁵). This separation is symbolized by arrow *A* in the *Scheme* shown below (above this arrow, the peaks of this preliminary chromatogram in their proper ratios have been drawn and the experimental parameters used are given.) The 'peaks' trapped in the course of separation *A* were then re-injected onto Carbowax (CW.)⁶) (except for the less volatile group which was more conveniently resolved on SO again), and this resulted in the final separations corresponding to arrow *B* in the *Scheme*. In rows parallel to

- 1) *Burley tobacco* condensate and fractions **B1**, **B2** and **B3** were obtained as previously described [1].
- 2) To be published later.
- 3) Using a gas chromatograph 'Aerograph', Model 1820-3 (*Varian* Aerograph AG).
- 4) 'Embaphase' (*May & Baker Ltd.*).
- 5) 'Acid washed' grade (*Johns-Manville*).
- 6) A 0.4×250 cm column packed with 5% of 'Carbowax' 20 M (*Varian* Aerograph AG) on Chromosorb W⁵) was used for this second set of separations.

SCHEME

GLC separations of fraction B3-PA after esterification with CH_2N_2 ;
only the corresponding acids are shown.

A SO Program, 120-300° + 6°/min.



this arrow, the formulae of the compounds isolated⁷⁾ and identified⁸⁾ in each of these sub-separations are indicated according to the order of elution, as are the experimental conditions used.

The 22 compounds identified in the course of these separations make up about 94.4% by weight of starting fraction **B3-PA**. They are listed according to their molecular weights in the *Table* given below. The substances which, to the best of our knowledge, should be considered as new tobacco constituents, are marked by a cross in the 4th column.

Medium-volatile, free acidic constituents of Burley Tobacco condensate
(Identified from fraction **B3-PA**)

	Formula	M ⁺	New in tobacco	Ref.
Sorbic acid	1	112		[2]
Hexanoic acid	2	116		[2]
Benzoic acid ⁹⁾	3	122		[2]
5-Methylhex-2-enoic acid (<i>trans</i>) ¹⁰⁾	4	128		[3]
Heptanoic acid	5	130		[2]
Phenylacetic acid ⁹⁾	6	136		[2]
2-Ethyl-3-methylsuccinimide (<i>trans</i>) ¹¹⁾	7	141	+	[4]
Octanoic acid	8	144		[2]
Vanillin	9	152		[2]
Nona-2,6-dienoic acid (<i>trans, cis</i>)	10	154	+	
Non-2-enoic acid (<i>trans</i>)	11	156	+	
Non-3-enoic acid (probably <i>cis</i>) ¹⁰⁾	12	156		[3]
Nonanoic acid	13	158		[2]
α -Phenylcrotonic acid ⁹⁾	14	162	+	
Veratraldehyde	15	166	+	
Acetovanillone	16	166	+	
3-Isopropenyl-1-methylcyclopentancarboxylic acid ¹²⁾	17	168	+	[5]
Geranic acid	18	168	+	
β -Cyclogeranic acid ⁹⁾	19	168	+	
Decanoic acid ⁹⁾	20	172		[2]
4-Oxononanoic acid ¹⁰⁾	21	172		[3]
2-Isopropyl-5-oxohexanoic acid	22	172		[6]

⁷⁾ In most cases, the substances thus isolated were still further purified by a third GLC. separation (on SO).

⁸⁾ For ensuring proper identification of these tobacco constituents, their mass spectra, and, whenever necessary, their IR. and NMR. spectra were checked against those of authentic, synthetic compounds. The IR. spectra were run in our own laboratory on a Model 720 *Perkin-Elmer* spectrometer. Other spectra were measured in our specialized laboratories under the supervision of Dr. B. Willhalm, on the following instruments: mass spectrometer *Atlas* CH4 IV 58 (*Atlas-Werke* AG); NMR. spectrometers *Bruker* HFX-90/3 – 15 inch (90 MHz) and *Hitachi Perkin-Elmer* R 20 B (60 MHz).

⁹⁾ The corresponding aldehyde had been previously identified in *Burley tobacco* condensate [1].

¹⁰⁾ Independently found in *Burley tobacco* essential oil by Drs. D. L. Roberts and W. A. Rohde [3], to whom we express our best thanks for having made their manuscript available before publication.

¹¹⁾ Analogous compounds have also been found to occur in *Greek tobacco*. We thank Dr. C. R. Enzell (*Swedish Tobacco Company*, Stockholm) for having kindly informed us of this result before publication.

¹²⁾ Undetermined stereochemistry.

At first glance, the presence of the *neutral* compounds *trans* 2-ethyl-3-methylsuccinimide (7) and veratraldehyde (15) among the acidic constituents of fraction **B3** may appear surprising. In fact, it is well known that *small amounts* of polar, neutral impurities are very often solubilized and extracted together with acids during the classical fractionation with aqueous bases.

In general, the chemical origin of the compounds isolated from fraction **B3-PA** of *Burley tobacco* condensate does not require any particular comment, except for 2-isopropyl-5-oxohexanoic acid (22) which most probably is a metabolite of *solanone*, and for *trans* 2-ethyl-3-methylsuccinimide (7)¹³⁾ which apparently should derive from some precursor related to chlorophyll¹³⁾.

BIBLIOGRAPHY

- [1] E. Demole & D. Berthet, *Helv.* **55**, 1866 (1972).
 [2] R. L. Stedman, *Chem. Reviews* **68**, 153 (1968).
 [3] D. L. Roberts & W. A. Rohde, *Tobacco Science* (1972), in press.
 [4] C. H. Gray, G. A. Lemmon & D. C. Nicholson, *J. chem. Soc. [C]* **1967**, 178.
 [5] R. L. Settime, G. L. Parks & G. L. K. Hunter, *J. org. Chemistry* **29**, 616 (1964).
 [6] Tetsuo Fukuzumi, *Okayama Tab. Shikensho Hokoku* **30**, 103 (1971); *Chem. Abstr.* **76**, 56807-e (1972).
 [7] H. Brockmann Jr., *Liebigs Ann. Chem.* **754**, 139 (1971); H. Brockmann Jr. & D. Müller-Enoch, *Chem. Ber.* **104**, 3704 (1971).

¹³⁾ See for instance [7].

179. Beiträge zur Chemie der Si-N-Bindung, XXII¹⁾ N,N'-Tetrakis(trimethylsilyl)methylendiamin

von Walter Fink

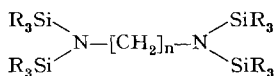
Monsanto Research S.A., Eggbühlstrasse 36, CH-8050 Zürich

Herrn Prof. Dr. M. Schmeisser zum 60. Geburtstag gewidmet

(5. VII. 72)

Summary. N,N'-Tetrakis(trimethylsilyl)methylendiamine is prepared by the reaction of lithium-bis(trimethylsilyl)amide with tris(chloromethyl)amine.

Von den N,N'-Tetrakis-silyl-Derivaten geradkettiger Alkylendiamine sind Verbindungen mit $n = 2$ [2], 3²⁾ [3] und höher [4] bekannt.



Ihre Darstellung geht in jedem Falle von den entsprechenden Alkylendiaminen aus und erfolgt durch die Silylierung der Aminogruppen, entweder durch die Uminierung von Silylaminen [2c] oder über die N-Alkali-Verbindungen bereits partiell silylierter Diamine [2a, b].

Das erste Glied dieser Verbindungsreihe mit $n = 1$, ein N,N'-Tetrakis(silyl)methylendiamin, konnte bisher wegen der Unbeständigkeit des Methylendiamins nicht hergestellt werden.

¹⁾ XXI. Mitt. s. [1].

²⁾ [(CH₃)₃Si]₂N-(CH₂)₃-N[Si(CH₃)₃]₂: Sdp. 96°/0.3 Torr, n_D^{20} 1,4538; chem. Verschiebung δ (in CCl₄ gegen TMS): (CH₃)₃Si 0,087, CH₂, 1,39, NCH₂ 2,57. C₁₅H₄₂N₂Si₄ (362,9) Ber. C 49,65 H 11,67 N 7,72%; Gef. C 49,53 H 11,74 N 7,62%.