

# Identification of the Volatile Constituents of Cyprian Latakia Tobacco by Dynamic and Static Headspace Analyses

by

John C. Leffingwell<sup>1</sup>, E. D. Alford<sup>2</sup>, Diane Leffingwell<sup>1</sup> and Roger Penn<sup>3</sup>

<sup>1</sup> Leffingwell & Associates, Canton, GA 30115 USA

<sup>2</sup> Alford Consulting, Louisville, KY 40207 USA

<sup>3</sup> Mane SA, Route de l'Industrie 21, Vouvry 1896, Switzerland

## Summary

The volatile constituents of Cyprian Latakia tobacco were determined by both dynamic and static headspace GC-MS analyses. In excess of 500 volatile constituents were identified, with the majority of volatiles being phenolics, polycyclic and related aromatic hydrocarbons, sesquiterpenoids and known tobacco constituents. Notably, five ambrettolide isomers and dihydroambrettolide, as well as (Z)-Octadec-9-en-18-olide, were identified.

## Previous work:

No comprehensive analysis of the volatile constituents of Latakia tobacco has been previously published. In the late 1960's, publications by Irvine & Saxby reported identification of 38 phenols (1,2) and 22 carboxylic acids (3) of Latakia tobacco. Another study by these authors led to the identification of 27 anilines and aliphatic amines (4). In 1972, Elmenhorst identified the methyl & ethyl cyclopentenolones (5) and in 1980 found 28 alkylnaphthalenes in Latakia tobacco (6). The most extensive previous work on Latakia tobacco was carried out by Tolman at British American Tobacco during 1982-1983 in a series of unpublished reports (7-9).

## Introduction:

Latakia tobacco is a minor tobacco type produced by subjecting the leaf of Oriental tobacco to the smoke from "controlled fires of aromatic woods and fragrant herbs". During the process, of "smoke-curing" the tobacco acquires a black color and peculiar tarry-smoky exotic aroma and flavor.

Latakia tobacco was originally produced in the northern part of Syria near the port city of Latakia, using primarily nearby hardwoods and pines - probably from the Baer forest that is comprised of Aleppo pine (*Pinus halepensis*) and both Turkey oak (*Quercus cerris*) and Valonia oak, (*Quercus macrolepis*). During the period 1850-1950 extreme damage to the forests in Syria was done, first by the construction of the Baghdad and Hedjaz railways, both of which were still operated with wood for fuel during the first world war and later from the ravages of overharvesting and the second world war,

during which forest fires were purposefully set as a protest against the controlling foreign regime. The forests were also extensively used for the tobacco-curing industry. By the 1970's, production of Latakia tobacco essentially ceased in Syria as the government attempted to conserve and revitalize its forest area ecosystem system. Since that time, the primary producing area for Latakia tobacco has been Cyprus.

Syrian Latakia tobacco is reputed to have been smoke cured primarily by burning the green leafy branches and twigs of the Aleppo pine (*Pinus halepensis*) and Oak (*Quercus* species), along with lesser amounts of other aromatic species [e.g. Lebanon cedar (*Cedrus libani*), and *Juniperus excelsa*].

The Oriental tobacco type used for production of Cyprian Latakia tobacco is generally from "Smyrna" type seed. Anecdotally it is mentioned that in addition to hardwoods, some pine and aromatic shrubs and woods such as "myrtle" are used in the smoke-curing process.

We initially suspected that one of the main aromatic woods used was *Juniperus oxycedrus*, as the exotic, tarry aroma of Latakia has a similarity to the empyreumatic Cade oil produced by the destructive distillation of *Juniperus oxycedrus* (10,11-12). While *J. oxycedrus* contains nearly all of the sesquiterpenoids found in our analyses, the absence of cedrol, humulene oxide II, cedrenes and thujopsene in the Cyprian Latakia tobacco headspace would tend to indicate that it is not a major aromatic wood used (11-14). However, as the amounts of these sesquiterpenoids in *J. oxycedrus*, *J. excelsa* and *J. phoenicea* (which are all present in Cyprus) can vary dramatically by species, subspecies and location, their possible use to some degree cannot be totally dismissed.

It has been reported that the Mastic shrub (*Pistacia lentiscus*) is primarily used in the smoke generation for Cyprian Latakia tobacco (15). The following formula, based on this report, may approximate the shrubs and woods used for the smoke-curing process.

Mastic ( <i>Pistacia lentiscus</i> )	90%
Myrtle - <i>Myrtus communis</i>	4%
Cypress - <i>Cupressus sempervirens</i>	4%
Stone Pine ( <i>Pinus pinea</i> or <i>Pinus pinaster</i> )	4%
Other	1%

Virtually all of the terpenoids and sesquiterpenoids found in our headspace analyses are also known constituents of *Pistacia lentiscus* which leads credence to Mastic being a primary smoke contributor. *Pistacia lentiscus* not only grows wild in Cyprus but is also commercially cultivated.

Following the smoke curing process, the tobacco is usually bulked in large piles of bales which allows fermentation to proceed over a period of 3-6 months (16). Fermentation is said to improve the flavor.

## **Experimental:**

**Plant Name:** *Nicotiana tabacum*

**Source:** Commercial sample of Latakia tobacco from Cyprus.

**Plant Part:** Granulated leaves after smoke curing / processing.

**Sample Preparation:** Four analyses of the Latakia tobacco were conducted as described below.

**SAMPLE-1 (5.D):** 200 mg of the Latakia Tobacco was placed in a 5" X ¼" O. D. Stainless tube with Swagelok nuts & ferrules attached. The Top of the tube was fitted with a ¼" Swagelok union with the top nut hole diameter increased to allow the easy introduction of a Hewlett-Packard injection port liner (HP part #5181-3316) and sealed with an injection port O-Ring. The injection port liner had been packed with 100 mg of Tenax TA (20-35 mesh) (glass-wool plugs on top and bottom) and previously baked out at 260C for 2.5 hours. Helium (50 cc/min) was introduced into the bottom of the tube. The Latakia tobacco was purged for 30 minutes at 40°C, trapping the volatiles on the Tenax containing Injection port liner. The Liner was then placed in the GC injection port for direct injection of the volatiles into the GC.

**SAMPLE-2 (8.D):** A "TEABAG" (1 ½ " X 1 ½ ") was constructed from unscented tissue paper. 100 milligrams of prebaked-out Tenax TA (20-35 mesh) was placed in the Teabag and the Teabag was suspended above 10 grams of Latakia tobacco (in a 16oz jar) for 31 hours at room temperature. 24.5 mg Tenax was then removed and packed into an injection port liner. The Liner was then placed in the GC injection port for direct injection of the volatiles into the GC.

**SAMPLE-3 (10.D):** A "TEABAG" (1 ½ " X 1 ½ ") was constructed from unscented tissue paper. 100 milligrams of prebaked-out Tenax TA (20-35 mesh) was placed in the Teabag and the Teabag was suspended above 10 grams of Latakia tobacco (in a 16oz jar) for 45 days at room temperature. 24.5 mg of the Tenax was then removed and packed into an injection port liner. The Liner was then placed in the GC injection port for direct injection of the volatiles into the GC.

**SAMPLE-4 (6.D)** A "TEABAG" (1 ½ " X 1 ½ ") was constructed from unscented tissue paper. 100 milligrams of prebaked-out Tenax TA (20-35 mesh) was placed in the Teabag and the Teabag was suspended above 10 grams of Latakia tobacco (in a 16oz jar) for 23 hours at room temperature. 24.5 mg of the Tenax was then removed and packed into an injection port liner. The Liner was then placed in the GC injection port for direct injection of the volatiles into the GC.

**GC and GC/MS:** The GC-MS was a Hewlett-Packard 6890/5973 High Performance combination. A HP-5ms 60m X 0.32mm I. D. fused silica column coated with a 0.25 micron film thickness, a DB-5 equivalent column, was used in all analyses. The column was held isothermally at 30°C for 2 minutes, then programmed from 30°C to 260°C at 2°C/min, with a final hold time of 28 minutes to give a total analysis time of 145

minutes, except for Sample-4 (6.D) where the sample analysis was terminated prematurely at 55 minutes. The Injection port was held at 260°C. Helium Carrier Gas was used with a flow rate of 3.5 ml/min. The Mass spectrometer was scanned in the EI mode from 26m/z to 350m/z using 70eV ionizing voltage. Additionally, FID spectra were obtained. Percentages are FID percentages without correction for response factors. Where overlapping component peaks were present, the NIST AMDIS program was utilized to estimate peak percentages, when possible.

Analysis was done on the HP MS Enhanced Chemstation program (Version D.03.00.611) employing both normal and selective ion modes. The NIST AMDIS deconvolution program (Version 2.71) was also employed in both normal and high resolution modes using the MSP file format from data imported from the Wiley and NIST MS libraries as well as the authors libraries.

**Component Identification:** Identifications were based on mass spectra from the Wiley 6 and NIST 05 MS libraries as well as from the authors MS library. Standard classic Kovats Indices (KI) based on n-Alkanes (17) were calculated using the formula:

$$I_x = 100n + 100[\log(t_x) - \log(t_n)] / [\log(t_{n+1}) - \log(t_n)]$$

Additionally Linear Retention Indices (LRI), sometimes referred to as the Arithmetic Index (AI), based on n-alkanes using the methodology of Van den Dool and Kratz (18) were calculated using the formula:

$$LRI_x = 100n + 100(t_x - t_n) / (t_{n+1} - t_n)$$

Lee's Retention indices (Lee RI) were determined by analogy with the LRI indices for the following reference compounds: benzene, naphthalene, phenanthrene, chrysene (19).

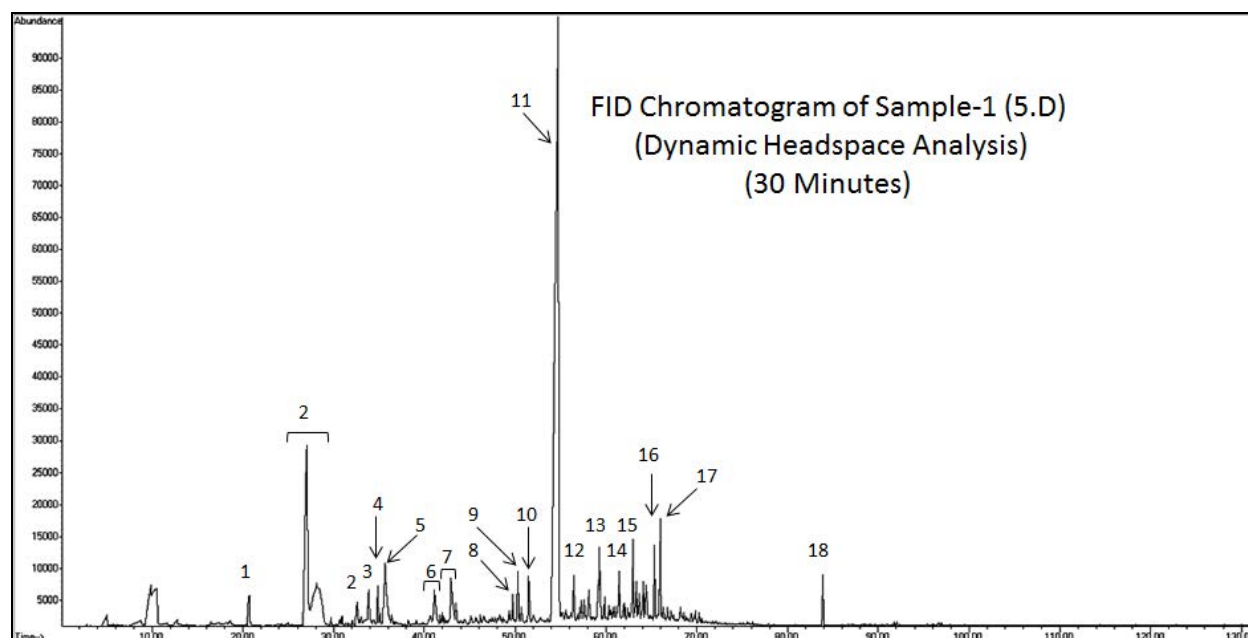
Where available, retention time comparisons were used employing primarily the Retention Indices compilations of the NIST Mass Spec Data Center (20), as well as those of Boelens (21) and Adams (22). Both the calculated Kovats KI and the LRI retention indices are provided in our tables because some of the reported literature does not specify which RI calculations were actually employed. The NIST and Adams values used for comparison were both the van den Dool and Kratz temperature programmed LRI values and the Kovats (KI) values. The Boelens values in the ESO 2000 (Update 2006) database that were derived from the literature do not specify the method of RI calculation. In most cases the RI values by both methods are quite similar, but can vary by 1-9 units. The Lee retention index values were used as a further corroboration. As with all such reported retention index values, those below 500-700 KI/LRI must be considered as somewhat approximate as such values are subject to greater instrumental experimental fluctuations between laboratories.

### Retention time shifts of polar constituents:

In Table 1., [GC-MS results of Sample 2 (8.D)], in the area containing high concentrations of phenolics and acids, fairly large retention time shifts were observed of polar constituents such as certain amides, pyridines, lactones, ketones, pyrazines, etc. In Table 2, the retention time shifts were validated by comparison with the other samples containing less of the phenolics and acids. In contrast, non-polar compounds (e.g. terpenes, benzenes etc. were not subject to such retention time shifts.

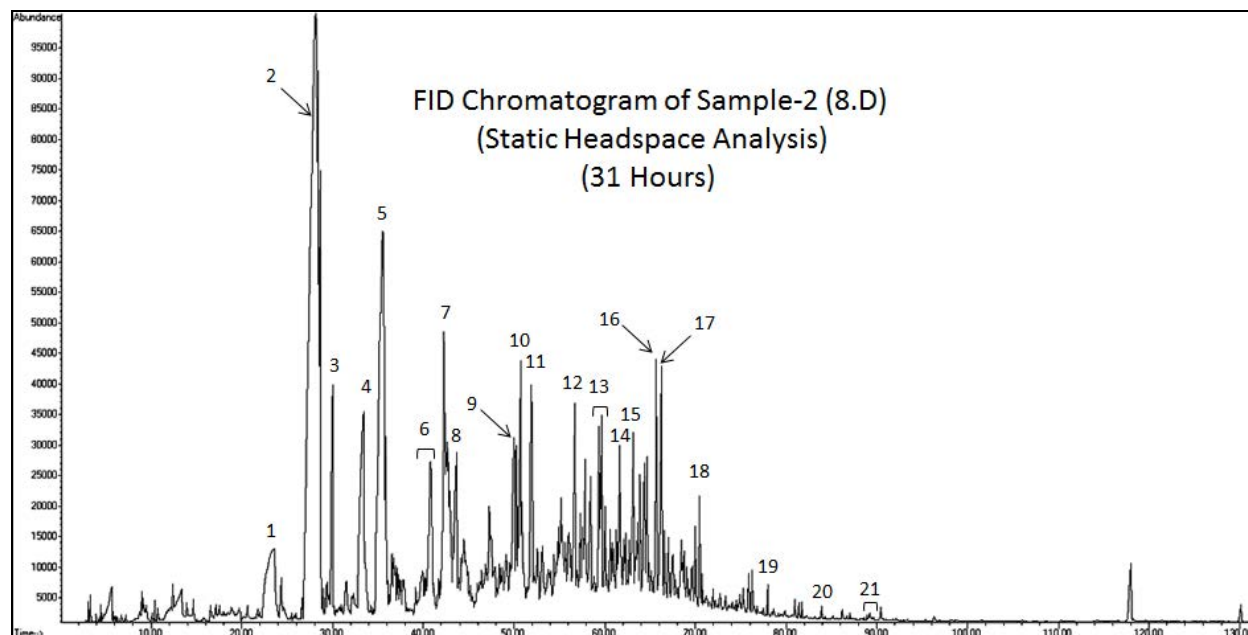
Figures 1-3 give the chromatograms of Samples 1-3 showing the rather dramatic differences obtained from the different headspace techniques.

Figure 1.



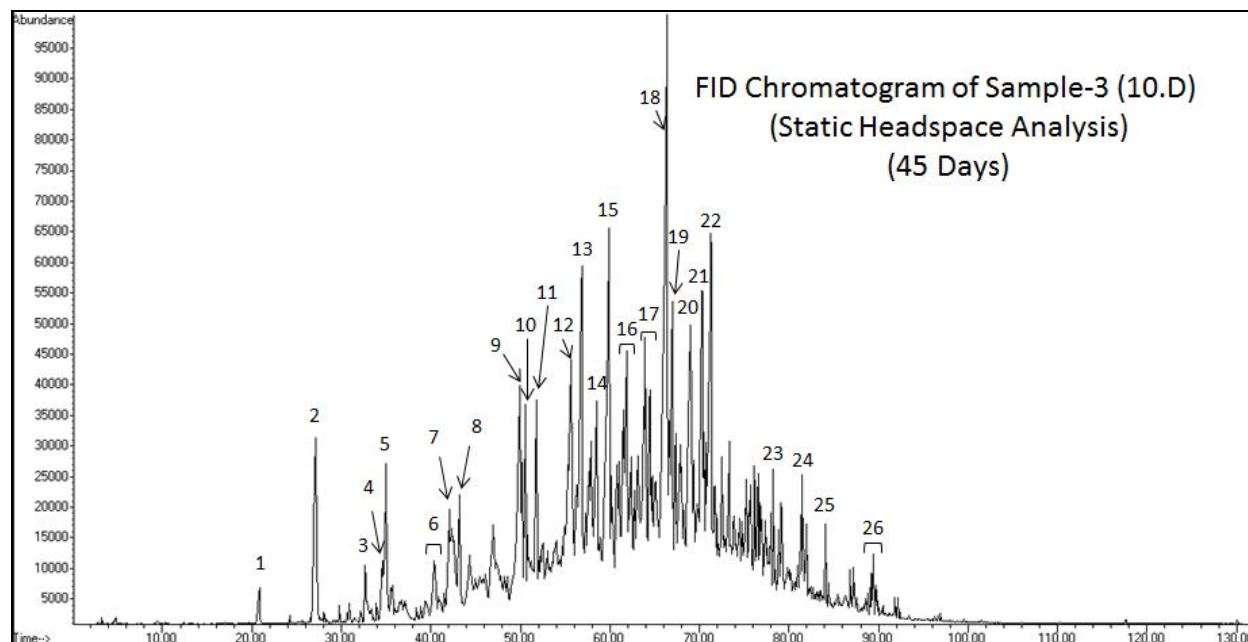
1. Butyrolactone; 2. Phenol; 3. 2-Methylphenol; 4. Guaiacol; 5. 3- & 4-Methylphenol; 6. 2-Ethylphenol + Dimethylphenols; 7. 3- & 4-Ethylphenol + 4-Methylguaiacol + Dimethylphenols; 8. 4-Ethylguaiacol; 9. 2-Methylnaphthalene; 10. 1-Methylnaphthalene; 11. Nicotine; 12. 1,1'-Bipenyl; 13. beta-Caryophyllene + Dimethylnaphthalenes; 14. alpha-Humulene + Dimethylnaphthalenes; 15. Germacrene D + alpha-Amorphene; 16. Dibenzofuran; 17. delta-Cadinene + cis-Calamenene; 18. Neophytadiene

Figure 2.



1. Butyrolactone; 2. Phenol; 3. Limonene; 4. 2-Methylphenol; 5. 3- & 4-Methylphenol + Guaiacol; 6. 2-Ethylphenol + Dimethylphenols; 7. 3 & 4-Ethylphenol + Naphthalene; 8. 4-Methylguaiacol; 9. 4-Ethylguaiacol; 10. 2-Methylnaphthalene; 11. 1-Methylnaphthalene; 12. 1,1'-Biphenyl; 13. beta-Caryophyllene + Dimethylnaphthalenes; 14. alpha-Humulene + Dimethylnaphthalenes; 15. Germacrene D + alpha-Amorphene; 16. Dibenzofuran; 17. delta-Cadinene + cis-Calamenene; 18. Diethyl phthalate + others; 19. 1-Pristene; 20. Neophytadiene; 21. Ambrettolide isomers

Figure 3.



1. Butyrolactone; 2. Phenol; 3. 2-Ethylphenol; 4. 4-Ethylphenol; 5. 3-Methylphenol + Guaiacol; 6. 2-Ethylphenol + Dimethylphenols; 7. 3 & 4-Ethylphenol + Naphthalene; 8. 4-Methylguaiacol; 9. 4-Ethylguaiacol; 10. 2-Methylnaphthalene; 11. 1-Methylnaphthalene; 12. Syringol; 13. 1,1'-Biphenyl; 14. Dimethylnaphthalenes; 15. Dimethylnaphthalenes; 16. alpha-Humulene + Dimethylnaphthalenes; 17. Acenaphthene + Methylbiphenyls; 18. Dibenzofuran + delta-Cadinene + cis-Calamenene; 19. A Trimethylnaphthalene; 20. n-Nonylbenzene + a Trimethylnaphthalene; 21. Diethyl phthalate; 22. 9H-Fluorene; 23. 1-Pristene; 24. Phenanthrene; 25. Neophytadiene; 26. Ambrettolide isomers

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
2.854		401	401	Acetaldehyde	0.002	MS,RI	381-407
3.076		486	485	Ethanol	0.014	MS,RI	427-482
3.159		500	500	Pentane	0.003	MS,RI	
3.287		511	510	Acetone	0.018	MS,RI	487-503
3.317		514	512	Isopropyl alcohol	0.010	MS,RI	500-515
3.390		520	518	Isoprene	0.002	MS,RI	502-520
3.552		534	530	Formic acid	0.001	MS	
3.602		538	534	Methyl acetate	0.001	MS,RI	515-536
3.635		540	536	Dichloromethane	0.001	MS,RI	520-531
3.800		553	549	Allyl alcohol (2-Propen-1-ol)	0.002	MS,RI	519-555
3.906		561	557	Isobutyraldehyde (2-Methylpropanal)	0.006	MS,RI	530-558
3.927		563	559	1-Propanol	0.003	MS,RI	536-568
3.982		567	563	2-Methylpentane	0.004	MS,RI	556-569
4.038		571	567	2-Methoxy-2-methylpropane	0.002	MS,RI	555-568
4.189		581	579	3-Methylpentane	0.004	MS,RI	576-585
4.336		591	590	2,3-butanedione	0.007	MS,RI	579-613
4.396		595	594	Butanal	0.003	MS,RI	582-600
4.468		600	600	Hexane	0.003	MS,RI	
4.472		600	600	2-Butanone	0.014	MS,RI	592-606
4.590		606	604	2-Methylfuran	0.006	MS,RI	608-629
4.764		613	611	3-Methylfuran	0.002	MS,RI	611-614
4.840		617	614	Ethyl acetate	0.014	MS,RI	605-628
5.073		627	622	Methylcyclopentane	0.044	MS,RI	622-635
5.635		649	643	Acetic acid <sup>b</sup>	0.327	MS,RI	600-663
5.687		651	645	2-Butenal	trace	MS,RI	632-657
5.793		655	649	3-Methylbutanal	0.015	MS,RI	642-666
5.971	100.0	661	655	Benzene	0.009	MS,RI	648-663
6.077	100.3	665	659	2-Methylbutanal	0.010	MS,RI	640-670
6.140	100.5	667	661	1-Hydroxy-2-propanone	trace	MS,RI	658-674
6.195	100.6	669	663	n-Butanol	0.008	MS,RI	653-673
6.277	100.8	671	666	5-Methyl-2,3-dihydrofuran <sup>tent</sup>	0.004	MS	
6.730	102.1	686	683	1-Penten-3-ol	0.010	MS,RI	683-688
6.813	102.3	689	686	1-Penten-3-one	0.004	MS,RI	680-691
6.850	102.4	690	687	2-Pentanone	0.009	MS,RI	680-699
7.191	103.4	700	700	Pentanal* + 2,3-Pentanedione** + Heptane	0.014	MS,RI	*691-705; **680-704
7.341	103.8	704	703	2-Ethylfuran	0.003	MS,RI	695-712
7.606	104.5	712	709	2,5-Dimethylfuran	0.003	MS,RI	704-711
7.730	104.8	715	712	3-Hydroxy-2-butanone	trace	MS,RI	701-720
8.145	106.0	726	722	Methylcyclohexane	0.002	MS,RI	718-726
8.667	107.4	739	733	Propanoic acid <sup>b,f</sup>	0.072	MS,RI	680-745
8.705	107.5	740	734	Pyrazine	0.040	MS,RI	730-740
8.765	107.7	741	736	3-Hydroxy-3-methyl-2-butanone	0.002	MS	
8.954	108.2	746	740	Isoamyl alcohol (3-Methyl-1-butanol)	0.080	MS,RI	737-759
9.081	108.6	749	743	2-Methyl-4-pentanone	0.002	MS,RI	730-742
9.136	108.7	750	744	1-Methylpyrrole	0.113	MS,RI	735-750
9.455	109.6	757	751	Pyridine	0.097	MS,RI	740-755

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
10.114	111.4	771	766	4-Penten-1-ol	0.026	MS	765 <sup>(55)</sup>
10.384	112.2	777	772	Toluene	0.038	MS,RI	758-780
10.717	113.1	783	780	1-Pentanol	0.040	MS,RI	758-781
10.930	113.7	787	784	cis-2-Pentenol	0.023	MS,RI	763-783
11.310	114.7	794	793	Propylene glycol <sup>b</sup>	0.557	MS,RI	732-850
11.620	115.6	800	800	Octane	trace	MS,RI	
11.812	116.1	803	802	Cyclopentanone	0.051	MS,RI	791-808
11.830	116.1	803	803	2-Hexanone	0.020	MS,RI	788-806
12.190	117.1	809	807	Isobutyric acid <sup>f</sup>	0.129	MS,RI	765-804
12.422	117.8	813	810	Hexanal <sup>b</sup>	0.128	MS,RI	796-812
12.632	118.3	816	813	Ethyl butyrate	0.065	MS,RI	796-812
12.873	119.0	820	816	Tetrachloroethylene	trace	MS,RI	804-816
12.922	119.1	820	816	Dihydro-2-methylfuran-3(2H)-one	trace	MS,RI	810-821
13.509	120.8	829	824	Butyl acetate	0.034	MS,RI	800-820
13.835	121.7	833	828	Butyric acid <sup>f</sup>	0.087	MS,RI	790-840
13.944	122.0	835	829	2-Methylpyrazine	0.081	MS,RI	826-839
14.593	123.7	844	837	(Z)-2-Butenoic acid <sup>(f, isomer not identified)</sup>	0.009	MS	
14.602	123.8	844	837	Cyclopentenone	trace	MS,RI	835
14.660	123.9	844	838	Furfural <sup>b</sup>	0.075	MS,RI	830-851
15.098	125.1	850	844	2-Methylcyclopentanone	0.009	MS,RI	836-848
15.558	126.4	856	849	3-Methylcyclopentanone	0.007	MS,RI	846-858
16.104	127.9	862	856	(E)-2-Hexenal	0.006	MS,RI	848-860
16.524	129.1	867	861	Ethylbenzene	0.026	MS,RI	855-869
16.565	129.2	868	862	Furfuryl alcohol <sup>b</sup>	0.050	MS,RI	850-866
16.763	129.7	870	864	4-Methyl-3-penten-1-ol	0.027	MS,RI	868
17.018	130.4	873	868	5-Hexen-1-ol	0.037	MS,RI	879
17.117	130.7	874	869	m-xylene and/or p-Xylene	0.050	MS,RI	860-878
17.393	131.5	877	872	2-Methylpyridine	0.033	MS,RI <sup>g</sup>	816-826
17.519	131.8	878	874	1-Hexanol	0.082	MS,RI	858-888
17.855	132.7	882	878	Isovaleric acid <sup>b</sup>	0.028	MS,RI	834-889
17.948	133.0	883	879	Isoamyl acetate (3-Methylbutyl acetate)	0.036	MS,RI	875-888
18.129	133.5	885	881	2-Methylbutyl acetate	0.058	MS,RI	875-885
18.425	134.3	888	885	Protoanemonin (5-methylenefuran-2(5H)-one)	0.004	MS,RI	878
18.617	134.8	890	888	3-Heptanone	trace	MS,RI	887-894
18.738	135.2	891	889	Styrene	0.037	MS,RI	888-904
18.879	135.6	893	891	o-Xylene	0.045	MS,RI	890-905
18.914	135.6	893	891	2-Heptanone	0.020	MS,RI	889-898
18.974	135.8	894	892	Cyclohexanone	0.020	MS,RI	891-897
19.121	136.2	895	894	(E)-2-Butenoic acid <sup>(f, isomer not identified)</sup>	0.043	MS	
19.362	136.9	898	897	2-Methylbutyric acid <sup>b,f</sup>	0.125	MS,RI	846-898
19.609	137.6	900	900	Nonane	0.051	MS,RI	900
19.706	137.8	901	901	Heptanal	0.052	MS,RI	899-907
20.036	138.7	906	905	2-Methyl-2-cyclopenten-1-one <sup>b</sup>	0.002	MS,RI	901-915
20.168	139.1	908	907	2-Butoxyethanol <sup>(b-tent)</sup>	0.065	MS,RI	904-909
20.173	139.1	908	907	Acetamide <sup>b</sup>	0.048	MS	
20.452	139.9	912	911	2-Acetylfuran <sup>(b-tent)</sup>	0.060	MS,RI	906-916
20.479	140.0	913	911	2,5-Dimethylpyrazine	0.006	MS,RI	910-923



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R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
20.541	140.1	914	912	2,6-Dimethylpyrazine	trace	MS,RI	910-926
20.626	140.4	915	913	gamma-Butyrolactone <sup>b</sup> (note smearing)	2.217	MS,RI	910-920
21.000	141.4	920	918	2-Ethylpyrazine	0.005	MS,RI	913-929
21.095	141.7	922	919	2,3-Dimethylpyrazine <sup>b</sup>	trace	MS,RI	915-930
21.382	142.4	925	922	Isopropylbenzene	0.023	MS,RI	917-930
22.020	144.2	934	930	alpha-Pinene <sup>a</sup>	0.002	MS,RI	928-941
22.312	145.0	938	934	2-Methyl-5-isopropenylfuran (2-methyl-5-(prop-1-en-2-yl)furan)	0.002	MS,RI	943
22.498	145.5	940	936	Valeric acid <sup>f</sup>	0.158	MS,RI	893-934
22.693	146.1	943	939	3-Methyl-2-butenic acid <sup>tent</sup>	0.001	MS	953
22.796	146.3	944	940	(E)-2-Methyl-2-butenic acid	trace	MS,RI	941 <sup>(51)</sup>
23.145	147.3	949	945	3-Methylpyridine	0.008	MS,RI <sup>g</sup>	864-868
23.688	148.8	956	951	n-Propylbenzene	0.002	MS,RI	950-959
24.050	149.8	960	956	6-Methyl-2-heptanone	trace	MS,RI	949-963
24.312	150.5	963	959	Benzaldehyde <sup>b</sup>	0.168	MS,RI	953-965
24.363	150.7	964	960	1-Ethyl-3-methylbenzene	0.040	MS,RI	957-967
24.415	150.8	965	961	4-Methylpyridine	0.012	MS,RI <sup>g</sup>	864-868
24.466	150.9	965	961	1-Ethyl-4-methylbenzene	0.020	MS,RI	957-967
24.651	151.5	967	964	N-Methylacetamide <sup>b</sup>	0.097	MS	
24.923	152.2	971	967	1,3,5-Trimethylbenzene	0.030	MS,RI	964-975
25.294	153.2	975	972	Sabinene <sup>a,b</sup>	0.002	MS,RI	969-978
25.496	153.8	977	974	beta-pinene <sup>a</sup>	0.003	MS,RI	973-985
25.540	153.9	978	975	2,6-Dimethylpyridine <sup>b</sup>	0.025	MS,RI <sup>g</sup>	884-890
25.708	154.4	980	977	Propionamide <sup>b</sup>	0.015	MS	
25.803	154.6	981	978	1-Ethyl-2-methylbenzene	0.019	MS,RI	977-986
25.924	155.0	982	980	5-Methylfurfural <sup>b</sup>	0.025	MS,RI <sup>g</sup>	956-967
25.984	155.1	983	980	2-Ethylpyridine	0.020	MS,RI <sup>g</sup>	904-908
26.291	156.0	986	984	Benzonitrile <sup>b</sup>	0.012	MS,RI	983-990
26.422	156.3	988	986	beta-angelicalactone <sup>b</sup> (5-Methyl-2(5H)-furanone)	0.014	MS,RI <sup>g</sup>	942-946
26.632	156.9	990	989	6-Methylhept-5-en-2-one <sup>b</sup>	0.069	MS,RI	984-989
26.800	157.4	992	991	Phenol <sup>b,c</sup> (broad peak from R.T. 26.80-28.68 min)	18.263	MS,RI	980-996
26.824	157.4	992	991	beta-myrcene <sup>a</sup>	0.005	MS,RI	983-995
26.860	157.5	993	991	1,2,4-Trimethylbenzene	0.010	MS,RI	990-998
26.891	157.6	993	992	2-Pentylfuran	0.002	MS,RI	990-996
27.220	158.5	997	996	Benzofuran	trace	MS,RI	995-1007
27.250	158.6	997	996	3-methyldihydrofuran-2(3H)-one <sup>b</sup>	0.006	MS,RI <sup>g</sup>	948-957
27.540	159.4	1000	1000	Decane	0.001	MS,RI	1000
27.570	159.5	1000	1000	N,N-Dimethylacetamide <sup>b</sup>	0.004	MS	
27.610	159.6	1001	1001	5,5-Dimethyl-2[5H]-furanone <sup>b</sup>	0.020	MS,RI <sup>g</sup>	952-962
27.700	159.8	1002	1002	gamma-valerolactone	0.029	MS,RI <sup>g</sup>	950-965
28.144	161.1	1008	1007	N-Methylpropionamide	0.007	MS	
28.224	161.3	1009	1008	2,5-dimethylpyridine	0.006	MS,RI <sup>g</sup>	926
28.269	161.4	1010	1009	2,4-dimethylpyridine	0.080	MS,RI <sup>g</sup>	932-941
28.380	161.7	1012	1010	2-Pyrone <sup>b</sup>	0.001	MS,RI <sup>g</sup>	973-985
28.398	161.8	1012	1011	2,3-dimethylpyridine	0.020	MS,RI <sup>g</sup>	945-952
28.570	162.2	1014	1013	3-Methyl-2[5H]-furanone	0.050	MS,RI <sup>g</sup>	977-989
28.650	162.5	1015	1014	3-methylpentanoic acid <sup>f</sup>	0.025	MS,RI <sup>g</sup>	994-1014

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
28.670	162.5	1016	1014	3-Methyl-2-cyclopenten-1-one <sup>b</sup>	0.030	MS,RI <sup>g</sup>	973-976
28.680	162.5	1016	1014	3-ethylpyridine	0.006	MS,RI <sup>g</sup>	959-966
28.705	162.6	1016	1014	3-vinylpyridine	0.020	MS,RI <sup>g</sup>	971-975
28.715	162.6	1016	1014	4-ethylpyridine	0.006	MS,RI <sup>g</sup>	954-968
28.720	162.7	1016	1015	3,5-dimethylpyridine	0.001	MS,RI <sup>g</sup>	970-980
28.768	162.8	1017	1015	4,4-Dimethyldihydro-2(3H)-furanone <sup>tent</sup>	0.001	MS	
28.911	163.2	1019	1017	3,4-dimethylpyridine	0.005	MS,RI <sup>g</sup>	999-1003
28.978	163.4	1020	1018	4,4-Dimethyl-2-cyclopenten-1-one <sup>tent</sup>	0.056	MS	
29.149	163.8	1022	1020	2-Ethyl-6-methylpyrazine	0.045	MS,RI <sup>g</sup>	997-1010
29.293	164.2	1024	1022	3,5-dimethylfuran-2(5H)-one	0.086	MS	RI long
29.360	164.4	1025	1022	1,2,3-trimethylbenzene	trace	MS,RI	998-1027
29.369	164.4	1025	1023	Trimethylpyrazine <sup>b</sup>	0.027	MS,RI <sup>g</sup>	1007-1014
29.469	164.7	1026	1024	2-Formyl-1-methylpyrrole	0.098	MS,RI	1010-1024
29.500	164.8	1027	1024	3-Pyridylcarbonitrile	0.009	MS,RI <sup>g</sup>	1007-1012
29.571	165.0	1028	1025	3-Methoxypyridine	trace	MS,RI <sup>g</sup>	998-1006
29.596	165.1	1028	1025	2-Propionylfuran	0.004	MS,RI <sup>g</sup>	1005-1022
29.601	165.1	1028	1025	p-Cymene <sup>a,b</sup>	0.124	MS,RI	1022-1028
29.984	166.1	1033	1030	Limonene <sup>a,b</sup>	0.823	MS,RI	1027-1035
30.196	166.7	1036	1033	Hexanoic acid <sup>f</sup>	0.027	MS,RI	998-1037
30.259	166.9	1036	1034	2-Acetylpyrazine	0.021	MS,RI <sup>g</sup>	1021-1029
30.413	167.3	1038	1035	2-Ethyl-1-hexanol* + 1,8-cineole <sup>**a</sup>	0.015	MS,RI	*1029-1045; **1031-1046
30.558	167.7	1040	1037	2-Formylpyrrole	0.148	MS,RI <sup>g</sup>	1013-1031
31.021	169.0	1046	1043	2-Acetylpyridine	0.083	MS,RI	1031-1046
31.440	170.1	1051	1048	2-Hydroxybenzaldehyde	0.020	MS,RI	1041-1054
31.536	170.4	1052	1049	Benzyl alcohol <sup>b</sup>	0.356	MS,RI	1024-1051
31.615	170.6	1053	1050	2-Acetyl-5-methylfuran	0.009	MS,RI <sup>g</sup>	1039-1054
31.760	171.0	1055	1052	1-Methyl-4-n-propylbenzene	0.002	MS,RI	1053-1061
31.900	171.4	1057	1054	5-ethenyl-5-methyl-2(3H)-furanone <sup>d</sup>	0.054	MS,RI <sup>g</sup>	1041-1046
32.000	171.7	1058	1055	1-Methyl-3-propylbenzene	0.001	MS,RI	1052-1065
32.136	172.1	1060	1057	2,3-Dimethyl-2-cyclopenten-1-one	0.103	MS,RI <sup>g</sup>	1040-1043
32.342	172.6	1062	1059	gamma-Terpinene <sup>a</sup>	0.283	MS,RI	1054-1065
32.630	173.4	1066	1063	Amyl isobutyrate <sup>tent</sup>	trace	MS,RI	1054-1057
32.973	174.4	1070	1067	1-Methyl-2-propylbenzene	0.001	MS,RI	1074-1075
33.200	175.0	1072	1070	2-Methylphenol <sup>b,c</sup>	2.680	MS,RI	1042-1076
33.326	175.3	1074	1071	3-Methylbenzaldehyde	0.006	MS,RI <sup>g</sup>	1047-1059
33.360	175.4	1074	1072	2-Bromophenol	trace	MS	1064
33.520	175.9	1076	1074	gamma-Hexalactone	0.008	MS,RI <sup>g</sup>	1047-1068
33.619	176.2	1077	1075	2-Hydroxybenzonitrile <sup>tent</sup>	0.006	MS	
33.641	176.2	1077	1075	3-Methyl-2-cyclohexenone <sup>tent, (b-tent)</sup>	0.035	MS	
33.668	176.3	1078	1076	Acetophenone <sup>b</sup>	0.171	MS,RI <sup>g</sup>	1062-1068
33.853	176.8	1080	1078	2,3,4-Trimethyl-2-cyclopenten-1-one	0.105	MS,RI <sup>g</sup>	1071
34.237	177.9	1084	1083	1-Octanol	0.016	MS,RI	1064-1084
34.438	178.4	1087	1085	1-Methyl-2-acetylpyrrole	0.003	MS,RI <sup>g</sup>	1050-1100
34.498	178.6	1087	1086	2-Ethyl-1,4-dimethylbenzene	0.041	MS,RI	1085-1093
34.640	179.0	1089	1087	4-Methylbenzaldehyde	0.003	MS,RI <sup>g</sup>	1076-1081
34.646	179.0	1089	1088	alpha-Terpinolene <sup>a</sup>	0.021	MS,RI	1082-1092

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
34.860	179.6	1091	1090	4-Isopropenyl-1-methylbenzene	trace	MS,RI	1088-1095
35.150	180.4	1094	1094	4-Methylphenol <sup>b,c</sup>	3.433	MS,RI	1074-1093
35.279	180.7	1096	1095	2-Acetylpyrrole <sup>b</sup>	0.050	MS,RI <sup>g</sup>	1060-1072
35.410	181.1	1097	1097	1-Methyl-2-pyrrolidone	0.017	MS,RI <sup>g</sup>	1042-1046
35.523	181.4	1099	1098	Guaiacol <sup>b,c</sup>	1.310	MS,RI	1087-1102
35.655	181.8	1100	1100	Undecane	0.010	MS,RI	
35.690	181.9	1100	1100	3-Methylphenol <sup>b,c</sup>	1.499	MS,RI	1075-1091
35.800	182.2	1102	1102	2-Nonanone <sup>a</sup>	trace	MS,RI	1091-1104
35.820	182.2	1102	1102	Methyl benzoate <sup>b</sup>	0.003	MS,RI	1091-1106
35.930	182.5	1104	1104	A Trimethylpyridine	0.008	MS	
35.960	182.6	1104	1104	2-Methyl-5-ethyl and/or 2-Ethyl-5-methylpyridine	0.006	MS,RI <sup>g</sup>	Both 1023
36.047	182.8	1106	1105	3,5-dimethylfuran-2(5H)-one <sup>tent</sup>	0.070	MS	
36.192	183.2	1108	1107	4-Hydroxybenzonitrile <sup>tent</sup>	0.067	MS	
36.267	183.4	1109	1108	An ethyldimethylpyridine	0.001	MS	
36.392	183.8	1110	1110	An ethyldimethylpyridine	0.017	MS	
36.455	184.0	1111	1110	3,4,5-Trimethyl-2-cyclopenten-1-one <sup>tent</sup>	0.217	MS	
36.587	184.3	1113	1112	1-Methyl-2,5-pyrrolidinedione (N-methylsuccinimide)	0.051	MS,RI <sup>g</sup>	1090 <sup>(52)</sup>
36.659	184.5	1114	1113	4,5-Dimethyl-4-hexen-3-one <sup>tent</sup>	trace	MS	
36.774	184.8	1116	1114	2,6-dimethylphenol <sup>c</sup>	0.512	MS,RI	1108-1117
36.322	183.6	1109	1109	1,2,4,5-Tetramethylbenzene	0.006	MS,RI	1114-1130
37.200	186.0	1122	1120	Heptanoic acid <sup>f</sup>	0.050	MS,RI <sup>g</sup>	1078-1097
37.410	186.6	1124	1123	6,7-Dihydro-5H-cyclopentapyrazine	0.033	MS,RI <sup>g</sup>	1104-1111
37.472	186.8	1125	1123	3-Acetylpyridine	trace	MS,RI <sup>g</sup>	1109-1117
37.755	187.5	1129	1127	3,4-Dimethylfuran-2(5H)-one <sup>tent</sup>	0.152	MS	
37.810	187.7	1130	1128	2-Phenethyl alcohol <sup>b</sup>	0.193	MS,RI <sup>g</sup>	1111-1121
38.208	188.8	1135	1133	Maltol (2-hydroxy-3-methyl-4H-pyran-4-one)	0.008	MS,RI	1110-1141
38.335	189.1	1137	1135	Isophorone	0.036	MS,RI	1118-1135
38.802	190.4	1143	1141	1-(5-methyl-2-furyl)propan-1-one	0.004	MS,RI	1136-1151
39.030	191.1	1146	1144	1,2-Dimethoxybenzene	trace	MS,RI	1142-1149
39.132	191.3	1147	1145	A Trimethyl-2-cyclopenten-1-one <sup>tent</sup>	0.051	MS	
39.333	191.9	1150	1147	Benzeneacetonitrile	0.073	MS,RI	1135-1148
39.486	192.3	1152	1149	1-methyl-1(H)-indene	0.010	MS,RI	Lee 191.7-193.4
39.596	192.6	1153	1151	6,7-Dihydro-5-methyl-5H-cyclopentapyrazine	trace	MS,RI	1139-1157
39.602	192.6	1153	1151	1,2,3,4-Tetramethylbenzene	0.002	MS,RI	1148-1152
39.743	193.0	1155	1153	4-Ketoisophorone <sup>b</sup>	0.002	MS,RI <sup>g</sup>	1139-1147
39.838	193.3	1156	1154	2,4- and/or 2,5-dimethylphenol <sup>c</sup>	0.012	MS,RI	1150-1167
39.887	193.4	1157	1155	2-Ethylphenol <sup>c</sup>	0.681	MS,RI	1138-1169
40.117	194.0	1160	1158	Pentylbenzene	trace	MS,RI	1150-1163
40.235	194.4	1161	1159	3-Ethyl-2-hydroxycyclopent-2-en-1-one <sup>b,e</sup>	trace	MS,RI <sup>g</sup>	1119-1140
40.764	195.8	1168	1166	3,5-dimethylphenol <sup>c</sup>	1.939	MS,RI	1169-1171
40.860	196.1	1169	1167	2'-Hydroxyacetophenone	0.030	MS,RI <sup>g</sup>	1167
41.113	196.8	1172	1170	gamma-Heptalactone	0.011	MS,RI <sup>g</sup>	1159-1163
41.190	197.0	1173	1171	Benzyl acetate	trace	MS,RI	1160-1172
41.470	197.8	1177	1175	endo-Borneol <sup>a</sup>	trace	MS,RI	1162-1175
41.920	199.0	1182	1181	3-Methylacetophenone	0.015	MS,RI	1172-1182
42.170	199.7	1185	1184	1,4-Dimethoxybenzene	0.153	MS,RI	1163-1192

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
42.230	199.9	1186	1185	4-Terpeneol <sup>a</sup>	trace	MS,RI	1175-1186
42.278	200.0	1187	1185	Naphthalene <sup>b</sup>	0.980	MS,RI	1182-1190
42.400	200.3	1188	1187	4-Ethylphenol <sup>c</sup>	3.410	MS,RI	1168-1192
42.635	200.9	1191	1190	3-Ethylphenol <sup>c</sup>	0.443	MS,RI	1171-1184
42.798	201.3	1193	1192	3-Methylguaiacol <sup>c</sup>	0.157	MS	
42.901	201.6	1194	1193	2,3-Dimethylphenol <sup>c</sup>	0.749	MS,RI	1181-1190
43.030	201.9	1196	1195	4-Methylacetophenone	0.020	MS,RI <sup>g</sup>	1180-1193
43.248	202.5	1198	1198	3,4-Dimethylphenol <sup>c</sup> + unknowns	0.182	MS	1190-1198
43.260	202.5	1198	1198	Methyl salicylate	0.019	MS,RI	1190-1203
43.410	202.9	1200	1200	Dodecane	0.029	MS,RI	
43.510	203.2	1201	1201	2-Decanone	0.002	MS,RI	1194-1201
43.559	203.3	1202	1202	4-Methylguaiacol <sup>c</sup>	1.285	MS,RI	1190-1207
43.614	203.5	1203	1203	alpha-Terpeneol <sup>a</sup>	0.060	MS,RI	1190-1207
43.705	203.7	1204	1204	A Dimethylbenzofuran	0.023	MS	
44.160	204.9	1211	1210	A Dimethylbenzofuran	0.283	MS	
44.170	204.9	1211	1210	6,7-Dihydro-2-methyl-5H-cyclopentapyrazine	trace	MS,RI <sup>g</sup>	1188
44.275	205.2	1212	1212	Octanoic acid <sup>f</sup>	0.020	MS,RI	1180-1203
44.457	205.6	1215	1214	2,4,6-Trimethylphenol	0.766	MS,RI	1202-1216
44.712	206.3	1219	1217	A Dimethylbenzofuran	0.114	MS	
44.840	206.6	1220	1219	Quinoxaline	0.070	MS,RI	1229
44.942	206.9	1222	1221	Benzoic acid <sup>f</sup>	0.520	MS,RI <sup>g</sup>	1170-1210
44.978	207.0	1222	1221	5,6,7,8-Tetrahydroquinoxaline	0.177	MS,RI	1212-1226
45.150	207.4	1225	1223	4,7-Dimethylbenzofuran or isomer	0.134	MS	1220-1240
45.450	208.2	1229	1227	2-Hydroxycineole (exo)	trace	MS,RI	1218-1228
45.653	208.7	1232	1230	4,7-Dimethylbenzofuran or isomer	0.077	MS	1220-1240
46.189	210.1	1239	1237	Hexylcyclohexane	0.005	MS,RI	1234-1238
46.249	210.3	1240	1238	2-Propylphenol <sup>c</sup>	0.184	MS,RI	1224-1244
46.409	210.7	1242	1240	4-Methoxyphenol <sup>c</sup>	0.030	MS,RI <sup>g</sup>	1235
46.438	210.8	1242	1241	2,3,6-Trimethylphenol <sup>c</sup>	0.274	MS,RI	1239-1246
46.649	211.3	1245	1243	2-Ethyl-5-methylphenol	0.161	MS	1242
46.764	211.6	1247	1245	A Dihydromethylnaphthalene or a dimethylindene	0.060	MS	
46.864	211.9	1248	1246	Carvacrol methyl ether	0.009	MS,RI	1244-1246
46.869	211.9	1248	1246	3-Ethyl-5-Methylphenol	0.414	MS,RI	1247
46.909	212.0	1249	1247	6,7-Dihydro-3,5-dimethyl-5H-cyclopentapyrazine	trace	MS,RI <sup>g</sup>	1243
47.293	213.0	1254	1252	Quinoline <sup>b</sup>	0.725	MS,RI <sup>g</sup>	1233-1242
47.467	213.4	1256	1254	An Ethyldimethylphenol	0.476	MS	
47.550	213.6	1257	1255	1,2-Dihydro-6-methylnaphthalene	0.150	MS,RI	Lee 213.69
47.801	214.3	1261	1259	An Ethyldimethylphenol	0.247	MS	
47.880	214.5	1262	1260	Hexylbenzene	0.135	MS,RI	1255-1267
47.960	214.7	1263	1261	A Dihydromethylnaphthalene or a dimethylindene	0.295	MS	
48.320	215.6	1268	1266	A Dihydromethylnaphthalene or a dimethylindene	0.370	MS	
48.421	215.9	1269	1267	1-Methyl-2-n-pentylbenzene	0.398	MS	
48.672	216.5	1272	1270	gamma-Octalactone* + A Dihydromethylnaphthalene	0.376	MS,RI	*1255-1266
49.001	217.4	1276	1275	3- and/or 4-Propylphenol <sup>c</sup>	0.282	MS,RI	1260-1285
49.156	217.8	1278	1277	4-Ethyl-3-Methylphenol + unknown	0.423	MS	
49.526	218.7	1283	1282	2,3,5-Trimethylphenol <sup>c</sup>	0.275	MS,RI	1275-1280
49.833	219.5	1287	1286	A Trimethylphenol?	0.100	MS,RI	

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
50.015	220.0	1289	1288	4-Ethylguaiacol <sup>c</sup>	1.569	MS,RI	1281-1288
50.267	220.7	1292	1292	2,3-Dihydro-1H-inden-1-one (Indan-1-one) <sup>b</sup>	0.594	MS,RI	1292-1307
50.450	221.1	1295	1294	Thymol <sup>a</sup>	0.001	MS,RI	1282-1295
50.640	221.6	1297	1297	Nonanoic acid <sup>f</sup>	0.004	MS,RI	1270-1297
50.731	221.9	1298	1298	2-Methylnaphthalene <sup>(b, isomer not identified)</sup>	1.653	MS,RI	1291-1315
50.733	221.9	1298	1298	2-Undecanone <sup>a</sup>	trace	MS,RI	1285-1298
50.874	222.2	1300	1300	Tridecane	0.365	MS,RI	
50.993	222.5	1302	1302	Carvacrol <sup>a</sup> + unknowns	0.278	MS,RI	1295-1305
51.005	222.6	1302	1302	2-Methyl-5,6,7,8-tetrahydroquinoxaline <sup>tent</sup>	trace	MS	
51.180	223.0	1305	1304	2,3,4-trimethylphenol <sup>c</sup> or 2,4,5-trimethylphenol	0.108	MS	
51.336	223.4	1307	1307	2-Methylquinoxaline	0.012	MS,RI	1304 <sup>(53)</sup>
51.479	223.8	1309	1309	3-Methoxyacetophenone <sup>tent</sup>	0.230	MS,RI <sup>g</sup>	1295-1301
51.882	224.8	1315	1315	1-Methylnaphthalene <sup>(b, isomer not identified)</sup> + unknown	1.378	MS,RI	1299-1325
52.267	225.8	1321	1320	1,2,3-Trimethoxybenzene <sup>(b, isomer not identified)</sup>	0.007	MS,RI <sup>g</sup>	1309-1317
52.417	226.2	1323	1322	8-Methylquinoline	0.007	MS,RI	1314-1323
53.097	228.0	1334	1332	3-Methyl-1-indanone <sup>tent</sup>	0.643	MS	
53.353	228.6	1337	1336	1-Ethyl-2-pentylbenzene	trace	MS	
53.766	229.7	1343	1342	Heptylcyclohexane + unknown(s)	0.446	MS,RI	1345-1350
54.028	230.4	1347	1346	Methyl 2-methoxybenzoate	0.196	MS,RI	1335-1351
54.408	231.4	1353	1351	alpha-Cubebene <sup>a</sup>	0.376	MS,RI	1349-1354
54.888	232.6	1360	1358	4-Methyl-1-indanone <sup>tent</sup>	0.404	MS	
54.960	232.8	1361	1359	Nicotine	trace	MS,RI	1355-1379
55.204	233.4	1364	1363	Syringol <sup>c</sup> (2,6-Dimethoxyphenol)	0.381	MS,RI	1353-1367
55.213	233.4	1364	1363	7-Methylquinoline	0.005	MS,RI <sup>g</sup>	1355
55.308	233.7	1366	1364	Heptylbenzene <sup>b</sup>	0.307	MS,RI	1363-1369
55.434	234.0	1367	1366	Eugenol <sup>a,b,c</sup>	0.306	MS,RI	1356-1370
55.693	234.7	1371	1370	1-Methyl-2-n-hexylbenzene + 6-Methylquinoline*	0.336	MS,RI* <sup>g</sup>	*1358 <sup>(53)</sup>
55.870	235.1	1373	1372	gamma-Nonalactone	0.009	MS,RI	1358-1373
55.943	235.3	1374	1373	Solanone <sup>b</sup>	0.381	MS,RI	1374
55.969	235.4	1375	1374	alpha-Ylangene <sup>a</sup>	0.145	MS,RI	1363-1376
56.103	235.7	1377	1376	4-Propylguaiacol <sup>b,c</sup>	0.343	MS,RI	1369-1371
56.196	236.0	1378	1377	4-Methylquinoline	0.040	MS,RI	1362-1363, Lee 236.6
56.200	236.0	1378	1377	A Trimethylindene	0.010	MS	
56.268	236.2	1379	1378	alpha-Copaene <sup>a</sup>	0.212	MS,RI	1374-1383
56.500	236.8	1382	1381	Decanoic acid <sup>f</sup>	0.012	MS,RI	1372-1387
56.716	237.3	1385	1384	1,1'-Biphenyl <sup>b</sup>	1.344	MS,RI	1371-1397
57.267	238.7	1393	1392	1-Tetradecene* + 4-(3-Methylphenyl)-but-3-en-2-one <sup>tent</sup>	0.395	MS,RI	*1389-1394
57.437	239.2	1395	1395	beta-Elemene <sup>a</sup>	0.052	MS,RI	1388-1395
57.605	239.6	1397	1397	2-Ethyl-naphthalene	0.655	MS,RI	1390-1398
57.795	240.1	1400	1400	Tetradecane	0.174	MS,RI	
57.814	240.2	1400	1400	1-Ethyl-naphthalene	0.795	MS,RI	1394-1406
57.899	240.4	1402	1402	2-Methyl-1,1'-biphenyl + unknown	0.030	MS,RI	1397-1404
58.194	241.1	1406	1406	Diphenyl ether	0.085	MS,RI	1390, Lee 241.7
58.385	241.6	1409	1409	6,10-Dimethylundecan-2-one	0.013	MS,RI	1400-1410
58.435	241.8	1410	1410	2,6- and 2,7-Dimethylnaphthalene <sup>d</sup>	0.902	MS,RI	1400-1409
58.501	241.9	1411	1411	5-Methyl-1,2,3-trimethoxybenzene	0.013	MS,RI	1400-1419
58.630	242.3	1413	1413	A Methylindanone	0.094	MS	

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
59.017	243.3	1419	1418	(1-Methylheptyl)benzene (2-phenyloctane)	0.005	MS	
59.374	244.2	1425	1424	beta-Caryophyllene <sup>*a,b</sup> + Calarene <sup>**a</sup> (beta-Gurjunene) + 1,3-Dimethylnaphthalene <sup>***d</sup>	1.081	MS,RI	*1415-1429; **1419-1432; ***1415-1427; Lee 243.0-243.9
59.500	244.5	1427	1426	1,7-Dimethylnaphthalene <sup>d</sup>	0.367	MS,RI	1419; Lee 243.0-244.3
59.690	245.0	1430	1429	1,6-Dimethylnaphthalene <sup>d</sup>	0.712	MS,RI	1419-1428; Lee 243.0-244.1
59.975	245.7	1434	1433	2-Ethenylnaphthalene	0.065	MS,RI	Lee 245.4-246.2
60.013	245.8	1435	1433	beta-Copaene <sup>a</sup>	0.390	MS,RI	1428-1435
60.186	246.3	1437	1436	Diphenylmethane	0.307	MS,RI	Lee 245.8-249.0
60.636	247.5	1444	1443	1,4- and 2,3-Dimethylnaphthalene <sup>d</sup>	0.478	MS,RI	1435-1446
60.668	247.5	1445	1443	1-Ethyl-2-hexylbenzene	0.030	MS	
60.851	248.0	1447	1446	1,5-Dimethylnaphthalene <sup>*d</sup> + Octylcyclohexane <sup>**</sup> (trace)	0.296	MS,RI	*1440-1450; **1447-1451
60.959	248.3	1449	1448	Aromadendrene <sup>a</sup>	0.240	MS,RI	1438-1449
61.072	248.6	1451	1449	1-(1,5-dimethylhexyl)-4-methylbenzene (dihydro-ar-Curcumene)	0.080	MS	
61.301	249.2	1454	1453	Acenaphthylene <sup>b</sup>	0.349	MS,RI	1447-1456; Lee 248.3-249.5
61.350	249.3	1455	1454	4-Methylsyringol <sup>c</sup>	0.100	MS,RI	1149-1461
61.515	249.7	1457	1456	(E)-Geranylacetone [(E)-6,10-dimethyl-5,9-undecadien-2-one]	trace	MS,RI	1452-1458
61.685	250.2	1460	1459	1,8-Dimethylnaphthalene <sup>*d</sup> + alpha-Humulene <sup>**a</sup>	1.233	MS,RI	*Lee 250.7; **1451-1460
61.857	250.6	1463	1461	2-Phenylpyridine	0.025	MS,RI	1466; Lee 248.9-249.7
62.090	251.2	1466	1465	Alloaromadendrene <sup>a</sup>	0.310	MS,RI	1453-1468
62.232	251.6	1468	1467	cis-Muurolo-4(14),5-diene <sup>a</sup>	trace	MS,RI	1455-1478
62.254	251.6	1468	1467	3-Phenylpyridine	0.006	MS,RI	1465-1470; Lee 249.8-250.0
62.300	251.8	1469	1468	Octylbenzene <sup>b</sup>	0.425	MS,RI	1462-1468
62.692	252.8	1475	1474	1-Methyl-2-n-heptylbenzene	0.377	MS	
62.833	253.1	1477	1476	A dimethylindanone + unknown	0.089	MS	
63.170	254.0	1482	1481	Germacrene D <sup>a</sup>	1.214	MS,RI	1477-1485
63.355	254.5	1485	1484	alpha-Amorphene <sup>a</sup>	0.182	MS,RI	1470-1486
63.495	254.8	1487	1486	ar-Curcumene	0.015	MS,RI	1479-1488
63.590	255.1	1488	1487	2-Propylnaphthalene	0.015	MS,RI	1493 <sup>(54)</sup> ; Lee 254.5
63.612	255.1	1488	1488	1,2-Dihydroacenaphthalene (Acenaphthene)	0.104	MS,RI	1480-1493
63.656	255.3	1489	1488	3-Methyl-1,1'-Biphenyl	0.294	MS,RI	1484-1490; Lee 254.8-255.9

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
63.833	255.7	1492	1491	1-Propylnaphthalene	0.200	MS,RI	Lee 255.1
63.855	255.8	1492	1491	1,2,3,4-tetrahydro-2,2,5,7-tetramethylNaphthalene	0.232	MS	
63.927	256.0	1493	1493	1-Pentadecene	0.268	MS,RI	1489-1493
64.222	256.7	1497	1497	4-Methyl-1,1'-Biphenyl	0.248	MS,RI	1492-1501
64.358	257.1	1499	1499	gamma-Amorphene <sup>a</sup>	0.282	MS,RI	1495-1499
64.419	257.2	1500	1500	Pentadecane + 1-Cyanonaphthalene*	0.279	MS,RI	*1500
64.603	257.7	1503	1503	Epizonarene* + A C3-naphthalene	0.302	MS,RI	*1497-1502
64.631	257.8	1504	1504	alpha-Muurolene* <sup>a</sup> + A C3-naphthalene	0.480	MS,RI	*1495-1505
64.865	258.4	1508	1507	An Ethylmethylnaphthalene	0.225	MS	
65.020	258.8	1510	1510	An Ethylmethylnaphthalene	0.056	MS	
65.087	259.0	1512	1511	(1-Methyloctyl)benzene (2-phenylnonane) <sup>(b, isomer not identified)</sup>	0.240	MS	
65.183	259.2	1513	1513	1-Ethyl-2-methylnaphthalene (or isomer)	0.029	MS	Lee 260.5
66.511	262.6	1536	1535	5-(or 4)-n-Pentylindane	0.001	MS	
65.669	260.5	1521	1521	gamma-Cadinene <sup>a,(b-tent)</sup>	0.013	MS,RI	1510-1526
65.697	260.5	1522	1521	1,3,7-Trimethylnaphthalene	0.018	MS,RI	Lee 259.2-261.0
65.730	260.6	1523	1522	Dibenzofuran <sup>b</sup>	0.366	MS,RI	1515-1526
65.976	261.3	1527	1526	An Ethylmethylnaphthalene or Trimethylnaphthalene	0.020	MS	
66.030	261.4	1528	1527	2-Cyanonaphthalene	0.010	MS,RI	Lee 261.4
66.087	261.5	1529	1528	An Ethylmethylnaphthalene or Trimethylnaphthalene	0.010	MS	
66.247	262.0	1531	1530	1,3,6-Trimethylnaphthalene	0.104	MS,RI	Lee 260.0-262.1
66.248	262.0	1531	1530	delta-Cadinene <sup>a,b</sup>	0.398	MS,RI	1518-1539
66.280	262.0	1532	1531	cis-Calamenene <sup>a,b</sup>	1.201	MS,RI	1519-1538
66.271	262.0	1532	1531	4-Ethylsyringol	0.310	MS,RI	1528-1539 (1539 our RI)
66.662	263.0	1538	1537	1,3,5-(or 1,4,6)-Trimethylnaphthalene <sup>d</sup>	0.110	MS,RI	Lee 262.7-264.7
66.747	263.3	1540	1539	Dihydroactinidiolide	0.005	MS,RI	1525-1548; 1539
66.982	263.9	1544	1542	An Ethylmethylnaphthalene + unknown	trace	MS	
67.013	263.9	1544	1543	alpha-Cadinene <sup>a,(b-tent)</sup>	0.321	MS,RI	1530-1542
67.159	264.3	1547	1545	1-Ethyl-2-heptylbenzene	0.115	MS	
67.408	265.0	1551	1550	alpha-Calacorene <sup>a,b</sup> + unknown	0.236	MS,RI	1540-1550
67.503	265.2	1552	1551	2,3,6-Trimethylnaphthalene* <sup>d</sup> + Nonylcyclohexane	0.211	MS,RI	*Lee 264.8-265.4
67.659	265.6	1555	1554	1,6,7-Trimethylnaphthalene <sup>d</sup>	0.109	MS,RI	Lee 265.6-266.5
67.800	266.0	1557	1556	Elemol <sup>a,(b-tent)</sup>	0.151	MS,RI	1545-1555
68.028	266.6	1561	1560	Elemicin <sup>a</sup>	trace	MS,RI	1547-1565
68.444	267.6	1568	1567	1,2,7-Trimethylnaphthalene <sup>d</sup>	0.490	MS,RI	Lee 266.6-267.5
68.531	267.9	1569	1568	1H-Phenalene	0.023	MS,RI	Lee 267.2-268.0
68.630	268.1	1571	1570	1,2,4-Trimethylnaphthalene <sup>d</sup>	0.275	MS,RI	Lee 268.3-268.5
68.791	268.5	1573	1572	Nonylbenzene <sup>b</sup>	0.302	MS,RI	1570-1579
69.078	269.3	1578	1577	1-Methyl-2-n-octylbenzene	0.253	MS	
69.555	270.5	1586	1585	N,N-diethyl-3-methylbenzamide (DEET)	0.176	MS	

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
69.670	270.8	1588	1587	9H-Fluorene* + 1-Methyl-7-isopropyl-naphthalene** <sup>b</sup>	0.190	MS,RI	*1580-1591; **1578
69.886	271.4	1591	1591	3,3'-Dimethyl-1,1'-biphenyl (or isomer)	trace	MS,RI	1589-1597; Lee 270.8- 271.3
69.926	271.5	1592	1591	Caryophyllene oxide <sup>a</sup>	trace	MS,RI	1577-1592
70.014	271.7	1593	1593	1-Hexadecene* + 1,2,5-Trimethylnaphthalene** + 1-Butylnaphthalene	0.485	MS,RI	*1579-1593; ** Lee 269.5- 270.5
70.088	271.9	1594	1594	3,3'-Dimethyl-1,1'-biphenyl (or isomer)	trace	MS,RI	1589-1597; Lee 270.8- 271.3
70.452	272.8	1600	1600	Hexadecane +2-Butylnaphthalene	0.118	MS	2-BN=MS
70.495	272.9	1601	1601	Diethyl phthalate	0.114	MS,RI	1595-1604
70.726	273.5	1605	1605	4,4'-Dimethyl-1,1'-biphenyl* + unknown	0.194	MS,RI	*1597-1608 ; Lee 274.1- 274.5
71.301	275.0	1615	1615	4-Propylsyringol	0.090	MS,RI	1612-1620
71.615	275.8	1621	1620	(1-Methylnonyl)benzene (2-Phenyldecane)	0.080	MS	
71.762	276.2	1623	1623	(6E,8E)-Megastigma-4,6,8-trien-3-one (Isomer III) <sup>(b, isomer not identified)</sup>	trace	MS,RI	1621 <sup>(56)</sup>
72.290	277.6	1633	1632	(6E,8Z)-Megastigma-4,6,8-trien-3-one (Isomer IV) <sup>(b, isomer not identified)</sup>	trace	MS,RI	1633 <sup>(56)</sup>
72.317	277.7	1633	1632	A Dimethyl-1,1'-biphenyl	0.034	MS	
72.438	278.0	1635	1634	A Dimethyl-1,1'-biphenyl	0.042	MS	
72.408	277.9	1635	1634	An Isopropylmethylnaphthalene	0.020	MS	
72.438	278.0	1635	1634	Benzophenone	0.026	MS,RI	1621-1644
72.528	278.2	1637	1636	Cubanol <sup>a</sup>	0.048	MS,RI	1632-1645
72.640	278.5	1639	1638	5-(or 4)-Hexylindane	0.010	MS	
72.750	278.8	1641	1640	4-Methyldibenzofuran	0.096	MS,RI	1639
73.016	279.5	1645	1644	An Isopropylmethylnaphthalene	0.041	MS	
73.277	280.1	1650	1649	1-Ethyl-2-octylbenzene + 2,6,10-Trimethylpentadecane* (Norpristane)	0.021	MS,RI	*1641-1649
73.313	280.2	1650	1649	A Methyldibenzofuran + T-Muurolo <sup>*a</sup>	0.163	MS,RI	*1640-1648
73.579	280.9	1655	1654	An Isopropylmethylnaphthalene	0.040	MS	
73.680	281.2	1657	1656	Decylcyclohexane	0.094	MS,RI	1656
74.030	282.1	1663	1662	4-Phenylbenzaldehyde <sup>(b, isomer not identified)</sup> + alpha-Cadinol <sup>*a</sup>	0.102	MS,RI	*1653-1668
74.214	282.6	1666	1665	A Methyldibenzofuran	trace	MS	
74.893	284.3	1677	1676	Decylbenzene	0.147	MS,RI	1670-1678
75.147	285.0	1681	1681	1-methyl-2-n-nonylbenzene	0.044	MS	
75.271	285.3	1684	1683	Cadalene <sup>a,b</sup> (1,6-Dimethyl-4-isopropyl-naphthalene)	0.124	MS,RI	1671-1684
75.856	286.8	1693	1693	1-Heptadecene	0.165	MS,RI	1687-1696
76.002	287.2	1696	1696	1-Pentylnaphthalene	0.050	MS	
76.259	287.8	1700	1700	Heptadecane	0.161	MS,RI	
76.299	287.9	1701	1701	A Methylfluorene <sup>b</sup>	0.015	MS	
76.447	288.3	1704	1703	2-Methylfluorene* + [(Methyldecyl)benzene isomer]	0.095	MS	*Lee 288.2- 288.7
76.552	288.6	1705	1705	2-Pentylnaphthalene	0.060	MS	



**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
76.578	288.7	1706	1706	Pristane = Norphytane (2,6,10,14-Tetramethylpentadecane)	trace	MS,RI	1702-1706
76.740	289.1	1709	1709	A Methylfluorene <sup>b</sup> + (1-Methyldecyl)benzene*	trace	MS,RI	*Lee 289.0
76.940	289.6	1713	1712	1-Methylfluorene* + unknown	0.117	MS	*1719; Lee 289.1-290.4
77.466	291.0	1723	1722	Chamazulene* + A (1-Methyldecyl)benzene isomer	0.079	MS, RI	*1718-1735
77.506	291.1	1723	1723	An Isopropylmethyl-naphthalene or Tetramethylnaphthalene	0.003	MS	
77.984	292.3	1732	1731	1-Pristene = 1-Norphytene (2,6,10,14-tetramethylpentadec-1-ene)	0.110	MS	1731 <sup>(26)</sup>
78.044	292.5	1733	1732	5-(or 4)-n-Heptylindane	0.020	MS	
78.578	293.8	1743	1742	2-Pristene = 2-Norphytene (2,6,10,14-tetramethylpentadec-2-ene)	0.005	MS	
78.610	293.9	1744	1743	9H-Fluoren-9-one <sup>b</sup>	0.093	MS,RI	1746; Lee 293
79.151	295.3	1753	1752	1-Ethyl-2-n-nonylbenzene	0.042	MS	
79.599	296.5	1761	1761	Undecylcyclohexane + unknown	0.019	MS,RI	1760
79.887	297.2	1767	1766	Myristic acid	0.075	MS,RI	1760-1780
80.193	298.0	1772	1771	Benzyl benzoate <sup>a</sup>	0.003	MS,RI	1765-1785
80.701	299.3	1781	1781	Undecylbenzene	0.038	MS,RI	1780-1789
80.962	300.0	1786	1785	Phenanthrene <sup>ab</sup> + 1-Methyl-2-n-decylbenzene <sup>(b, isomer not identified)</sup>	0.100	MS,RI	*1772-1794
81.404	301.4	1794	1793	1-Octadecene	0.077	MS,RI	1786-1795
81.471	301.6	1795	1795	Anthracene* + unknowns	0.014	MS,RI	*1786-1801
81.769	302.5	1800	1800	Octadecane* + 1-Hexylnaphthalene	0.061	MS,RI	*Lee 301.7
82.297	304.1	1810	1810	Phytane (2,6,10,14-Tetramethylhexadecane)	0.043	MS,RI	1806-1811
82.447	304.6	1813	1813	2-Hexylnaphthalene	trace	MS	
82.748	305.5	1819	1818	A Dimethylfluorene	0.002	MS	
82.850	305.8	1821	1820	A Dimethylfluorene	0.002	MS	
83.140	306.7	1827	1826	2,3-Dimethylfluorene	0.002	MS,RI	Lee 300-307.3
83.580	308.1	1835	1834	A Dimethylfluorene + 3,7,11,15-Tetramethyl-2-hexadecene* (a phytene isomer)	0.002	MS,RI	*1830-1838
83.903	309.1	1841	1840	Neophytadiene <sup>b</sup>	0.050	MS,RI	1836-1855
84.258	310.2	1848	1847	6,10,14-Trimethylpentadecanone* + 2-Phytene** (2,6,10,14-Tetramethyl-2-hexadecene)	0.029	MS,RI	*1842-1855; **1849-1859
84.272	310.2	1848	1847	5-(or 4)-n-Octylindane	0.001	MS	
84.350	310.5	1850	1849	A Dimethylfluorene	0.001	MS	
84.445	310.8	1851	1851	A Dimethylfluorene	0.001	MS	
84.746	311.7	1857	1856	1-Ethyl-2-n-decylbenzene	trace	MS	
85.191	313.1	1865	1865	1-Phenylnaphthalene* + Dodecylcyclohexane**	0.042	MS,RI	*1858-1872; **1864
85.274	313.3	1867	1866	9H-Xanthen-9-one	trace	MS,RI	Lee 312.3- 313.1
85.625	314.4	1873	1873	Di-isobutylphthalate + unknown	0.019	MS,RI	1871-1881
85.802	315.0	1877	1876	Benzyl salicylate	0.010	MS,RI	1863-1877
86.159	0.0	1883	1883	1-Methyl-2-n-undecylbenzene	0.024	MS	
86.160	316.1	1883	1883	1-Hexadecanol	0.063	MS,RI	1876-1886
86.280	316.4	1886	1885	Dodecylbenzene	trace	MS	
86.721	317.8	1894	1894	1-Nonadecene	0.028	MS,RI	1890-1899

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
87.062	318.9	1900	1900	Nonadecane + 3-methylphenanthrene <sup>(b, isomer not identified)</sup>	0.034	MS,RI	*Lee 318.6-319.5
87.250	319.4	1904	1904	2-Heptadecanone	trace	MS,RI	1900-1906
87.374	319.8	1906	1906	2-methylphenanthrene <sup>(b, isomer not identified)</sup>	0.029	MS,RI	Lee 319.8-320.3
87.418	320.0	1907	1907	1-Heptylnaphthalene	trace	MS	
87.804	321.1	1915	1915	4H-Cyclopenta[def]phenanthrene	0.010	MS,RI	Lee 320.0-322.2
88.094	322.0	1921	1920	2-Heptylnaphthalene	trace	MS	
88.174	322.3	1922	1922	(E,E)-Farnesylacetone	trace	MS,RI	1915-1927
88.230	322.5	1924	1923	9-(or 4-)-methylphenanthrene <sup>(b, isomer not identified)</sup>	0.001	MS	Lee 322.78-323.06
88.387	322.9	1927	1926	4-(or 9-)-methylphenanthrene <sup>(b, isomer not identified)</sup>	0.004	MS	322.87-323.3
88.446	323.1	1928	1927	Methyl palmitate	0.008	MS,RI	1915-1930
88.643	323.7	1932	1931	Ambrettolide* (Z-hexadec-7-en-16-olide) <sup>b</sup> + 1-Methylphenanthrene**	0.014	MS,RI	*1929-1930; **Lee RI 323.5-324
88.960	324.7	1938	1938	Ambrettolide <sup>b</sup> (isomer)	0.022	MS	
89.100	325.1	1941	1940	Dihydroambrettolide (Oxacycloheptadecan-2-one=16-Hexadecanolide)	trace	MS,RI	1928-1935
89.208	325.5	1943	1942	Ambrettolide <sup>b</sup> (isomer)	0.031	MS	
89.341	325.9	1946	1945	9-Hexadecenoic acid	0.013	MS,RI	1938-1949
89.523	326.5	1949	1949	Ambrettolide <sup>b</sup> (isomer)	0.014	MS	
89.684	327.0	1953	1952	Ambrettolide <sup>b</sup> (isomer)	0.015	MS	
89.969	327.8	1958	1958	(3Z)-Cembrene A	0.010	MS,RI	1959-1965
90.167	328.4	1962	1961	1-Ethyl-2-n-undecylbenzene	trace	MS	
90.467	329.4	1968	1967	Palmitic acid	0.040	MS,RI	1962-1991
90.475	329.4	1968	1968	Dibutyl phthalate	0.030	MS,RI	1957-1973
90.558	329.7	1970	1969	Phytofuran; 3-(4,8,12-Trimethyltridecyl)furan	trace	MS,RI	1971
91.026	331.1	1979	1978	2-Phenyl-naphthalene <sup>b</sup>	0.005	MS,RI	1987; Lee 330.5-331.2
91.628	333.0	1991	1990	n-Tridecylbenzene	trace	MS	
91.799	333.5	1994	1994	A Dimethylphenanthrene	trace	MS	
91.855	333.7	1995	1995	1-Methyl-2-n-dodecylbenzene	trace	MS	
91.808	333.5	1994	1994	1-Eicosene	0.007	MS,RI	1986-1996
92.036	334.2	1998	1998	A Dimethylphenanthrene	0.002	MS	
92.115	334.5	2000	2000	n-Eicosane	0.009	MS,RI	
92.287	335.0	2004	2004	Manoyl oxide	0.006	MS,RI	1987-2007
92.736	336.4	2013	2013	A Dimethylphenanthrene	trace	MS	
93.250	338.0	2024	2023	A Dimethylphenanthrene	trace	MS	
93.388	338.4	2027	2026	13-epi-manoyl oxide* + Isopropyl palmitate**	0.014	MS,RI	*2009-2023; **2017-2027
94.139	340.7	2042	2042	A Dimethylphenanthrene	trace	MS	
94.432	341.6	2048	2048	A Dimethylphenanthrene	trace	MS	
94.734	342.6	2055	2054	2,3- (or 1,7)-Dimethylphenanthrene	trace	MS,RI	Lee 342.0-343.9
95.356	344.5	2067	2067	Manool	0.007	MS,RI	2054-2070
95.430	344.7	2069	2068	Fluoranthene	0.002	MS,RI	2053-2080
96.100	346.8	2083	2082	Norambreinolide (Sclareolide) <sup>(b, isomer not identified)</sup>	trace	MS	2065

**Table 1. Identified Constituents of Latakia Tobacco Dynamic Headspace Analysis - Sample-2 (8.D)**

R.T (min.)	HP-5 Lee RI	HP-5 Kovats RI	HP-5 LRI	Compound	FID %	Ident.	LRI - KI Lit.
96.343	347.5	2088	2087	1-Heneicosene	0.024	MS,RI	2080-2098
96.736	348.7	2096	2095	9,10-Dimethylphenanthrene	trace	MS,RI	Lee 347.9-348.5
96.958	349.4	2100	2100	n-Heneicosane	0.007	MS,RI	
97.970	352.6	2122	2122	Pyrene	0.001	MS,RI	2113-2136; Lee 351.5-352.8
98.281	353.5	2129	2129	Methyl stearate	0.008	MS,RI	2117-2138
99.557	357.5	2157	2156	(Z)-Octadec-9-en-18-olide (Oxacyclonadec-10-en-2-one)	0.003	MS	
99.623	357.7	2158	2158	m-Terphenyl	trace	MS,RI	2140-2162
101.324	362.9	2194	2194	1-Docosene	trace	MS,RI	2190-2196
101.480	363.4	2198	2198	p-Terphenyl	trace	MS,RI	2191-2208
101.588	363.7	2200	2200	n-Docosane	0.003	MS,RI	
105.799	376.8	2295	2295	1-Tricosene	trace	MS,RI	2289-2296
106.027	377.5	2300	2300	Tricosane	0.003	MS,RI	
108.510	385.1	2359	2358	Benzyl butyl phthalate	0.001	MS,RI	2350-2359
110.091	390.0	2395	2395	1-Tetracosene	trace	MS,RI	2391-2396
110.304	390.7	2400	2400	Tetracosane + Di(n-Octyl)adipate	0.004	MS,RI	
113.322	400.0	2474	2474	Chrysene	trace	MS,RI	2472-2496
114.397		2500	2500	Pentacosane + unknown	0.006	MS,RI	
116.587		2557	2556	Di(2-ethylhexyl)phthalate	0.004	MS,RI	2546-2563
118.297		2600	2000	Hexacosane	0.002	MS,RI	
122.810		2700	2700	Heptacosane	trace	MS,RI	
128.112		2800	2800	Octacosane	0.002	MS,RI	
130.121		2832	2832	10-Demethylsqualene	0.074	MS,RI	2813-2832
134.480		2900	2900	Nonacosane	0.001	MS,RI	
Total Identified (%)					92.775		

a) Previously identified as a Pistacia lenticus constituent; References 21, 28-49.

b) Identified by T.M. Tolman in Latakia tobacco; References 7-9.

c) Identified by W. J. Irvine and M. J. Saxby in Latakia tobacco; References 1-2.

d) Identified by G. Nicolaus and H. Elmenhorst in Latakia tobacco; Reference 6.

e) Identified by H. Elmenhorst in Latakia tobacco; Reference 5.

f) Identified by P.J. Creasy and M.J. Saxby in Latakia tobacco; Reference 3.

g) Long retention time - see Table 2 for validation of the retention time shifts

**Table 2. Observed Retention Time Shift of Polar Components in Samples with Decreasing Phenolic (Acidity) Content**

Compound	Sample 2 R.T. 8.D	Sample 2 LRI 8.D	Sample 4 R.T. 6.D	Sample 4 LRI 6.D	Sample 3 R.T. 10.D	Sample 3 LRI 10.D	Sample 1 R.T. 5.D	Sample 1 LRI 5.D	Literature KI - LRI
Acetamide	20.173	907	16.755	864	12.924	817	12.657	814	NA
2-Methylpyridine	17.393	872	15.147	844	14.018	830	13.605	825	816-826
N-Methylacetamide	24.651	964	21.542	912	17.543	875	16.087	857	NA
3-Methylpyridine	23.145	945	20.331	909	17.653	875	16.645	864	864-868
4-Methylpyridine	24.415	961	21.124	920	17.829	877	16.774	865	864-868
2,6-Dimethylpyridine	25.540	975	23.077	944	19.892	904	18.333	885	884-890
Propionamide	25.708	977	23.087	944	19.268	895	18.729	890	NA
N,N-Dimethylacetamide	27.570	1000	25.434	973	21.118	928	19.144	895	883
2-Ethylpyridine	25.984	980	23.767	952	20.722	914	19.890	904	904-908
2-Methyl-2-cyclopenten-1-one	20.021	905	19.985	903	19.966	905	19.971	905	901-915
2,5-Dimethylpyrazine	20.479	911	20.470	911	20.391	910	20.337	910	910-916
2-Acetylfuran	20.452	911	20.411	910	20.399	910	20.381	910	906-916
2,6-Dimethylpyrazine	20.541	912	20.488	912	20.604	913	20.406	911	910-924
alpha-Pinene	22.020	930	21.983	930	ND	ND	21.982	930	928-941
beta-Angelicalactone (5-Methyl-2(5H)-furanone)	26.422	986	24.486	962	23.123	942	22.849	941	942-946
2,4-Dimethylpyridine	28.269	1009	27.364	997	24.944	967	22.900	941	932-941
n-Propylbenzene	23.688	951	23.671	952	23.644	951	23.640	951	950-959
gamma-Valerolactone (5-Methyldihydro-2(3H)-furanone)	27.700	1002	26.153	983	23.805	953	23.818	953	950-965
5,5-Dimethyl-2[5H]-furanone	27.610	1001	26.065	981	24.129	958	23.817	954	952-962
2,3-Dimethylpyridine	28.398	1011	27.608	1001	26.155	983	23.817	954	945-952
3-Methyldihydrofuran-2(3H)-one	27.250	996	25.250	971	ND	ND	23.495	949	948-957
Benzaldehyde	24.312	959	24.251	959	24.209	958	24.214	958	953-965
1-Ethyl-3-methylbenzene	24.363	960	24.340	960	24.312	959	24.324	960	957-967
1-Ethyl-4-methylbenzene	24.466	961	24.435	961	24.422	961	24.420	961	956-969
5-Methylfurfural	25.924	980	24.626	964	24.701	965	24.646	964	956-967
3-Ethylpyridine	28.680	1014	27.790	1004	26.926	992	26.733	990	959-966
1,3,5-Trimethylbenzene	24.923	967	24.890	967	24.877	967	24.875	966	964-975
Sabinene	25.294	972	25.265	971	ND	ND	25.250	971	969-978
3-Methyl-2-cyclopenten-1-one	28.67	1014	27.705	1002	26.111	984	24.949	967	973-976
3-Vinylpyridine	28.705	1014	27.886	1003	27.080	994	25.184	970	971-975
3,5-Dimethylpyridine	28.720	1015	27.790	1004	27.227	996	27.203	996	970-980
2-Pyrone	28.380	1010	ND	ND	25.736	977	25.404	973	973-983
beta-Pinene	25.496	974	25.434	973	ND	ND	25.418	973	973-985
1-Ethyl-2-methylbenzene	25.803	978	25.771	978	25.751	977	25.764	978	977-986
3-Methyl-2[5H]-furanone	28.570	1013	27.812	1004	26.500	987	26.032	981	977-989
Benzonitrile	26.291	984	26.256	984	26.228	983	26.226	983	983-990
beta-Myrcene	26.824	991	26.829	991	ND	ND	ND	ND	983-995
6-Methylhept-5-en-2-one	26.632	989	26.578	988	26.529	988	26.558	988	984-989
1,2,4-Trimethylbenzene	26.860	991	26.895	992	26.867	991	26.872	992	990-998

**Table 2. Observed Retention Time Shift of Polar Components in Samples with Decreasing Phenolic (Acidity) Content**

Compound	Sample 2 R.T. 8.D	Sample 2 LRI 8.D	Sample 4 R.T. 6.D	Sample 4 LRI 6.D	Sample 3 R.T. 10.D	Sample 3 LRI 10.D	Sample 1 R.T. 5.D	Sample 1 LRI 5.D	Literature KI - LRI
4,4-Dimethyldihydro-2(3H)-furanone <sup>tent</sup>	28.768	1015	27.989	1006	27.315	997	ND	ND	NA
2-Ethyl-6-methylpyrazine	29.149	1020	28.458	1012	27.866	1003	27.922	1005	997-1010
2-Formyl-1-methylpyrrole	29.469	1024	28.826	1016	28.299	1010	28.018	1007	1010-1022
3,5-Dimethylfuran-2(5H)-one	29.293	1022	28.613	1013	28.079	1007	28.135	1007	NA
3-Methoxypyridine	29.571	1025	28.613	1013	27.998	1006	28.120	1008	998-1006
Trimethylpyrazine	29.369	1023	28.871	1016	28.130	1007	28.230	1009	1007-1014
3-Pyridylcarbonitrile	29.500	1024	28.870	1016	28.365	1023	28.377	1011	1007-1012
3,4-Dimethylpyridine	28.911	1017	27.922	1006	28.960	1017	28.429	1012	999-1003
4-Ethylpyridine	28.715	1014	27.893	1005	27.109	995	27.078	1014	954-968
2-Formylpyrrole	30.558	1037	30.004	1030	29.024	1018	29.009	1018	1013-1031
1,2,3-Trimethylbenzene	29.360	1022	29.273	1022	29.202	1021	29.200	1021	1021-1028
2-Acetylpyrazine	30.259	1034	ND	ND	29.396	1023	29.354	1023	1021-1029
2-Methyl-5-ethyl and/or 2-Ethyl-5-methylpyridine	35.960	1104	ND	ND	29.863	1029	30.022	1031	Both 1023
p-Cymene	29.601	1024	29.611	1024	29.437	1023	29.449	1024	1022-1028
Limonene	29.984	1030	29.853	1029	29.745	1027	29.750	1027	1027-1035
2-Acetylpyridine	31.021	1043	30.609	1038	30.602	1038	30.286	1034	1031-1046
5-Ethenyl-5-methyl-2(3H)-furanone	31.900	1054	31.300	1044	30.942	1042	30.937	1043	1041-1046
2,3-Dimethyl-2-cyclopenten-1-one	32.136	1057	31.285	1044	30.232	1033	30.934	1043	1040-1043
1-Methyl-2-pyrrolidone	35.410	1097	34.207	1082	32.557	1061	31.641	1051	1042-1046
gamma-Hexalactone	33.52	1074	32.489	1061	32.102	1057	32.107	1056	1047-1068
gamma-Terpinene	32.342	1059	32.276	1058	32.227	1058	32.225	1058	1054-1065
2,3,4-Trimethyl-2-cyclopenten-1-one	33.853	1078	33.376	1072	32.814	1065	32.805	1065	1071
Acetophenone	33.645	1075	33.201	1070	32.924	1066	32.922	1067	1062-1068
2-Acetylpyrrole	35.279	1095	34.156	1082	33.306	1071	33.034	1069	1060-1072
1-Methyl-2-acetylpyrrole	34.438	1085	34.053	1080	33.761	1077	33.708	1076	1050-1100
4-Methylbenzaldehyde	34.640	1087	34.325	1084	34.084	1081	34.060	1080	1076-1081
1-Methyl-2,5-pyrrolidinedione	36.587	1112	35.808	1106	35.744	1101	35.148	1095	1090
4,5-Dimethyl-4-hexen-3-one <sup>tent</sup>	36.659	1113	35.977	1105	ND	ND	35.367	1098	NA
Heptanoic acid	37.200	1120	35.645	1100	36.045	1105	35.587	1100	1078-1097
6,7-Dihydro-5H-cyclopentapyrazine	37.410	1123	36.762	1114	36.550	1111	36.219	1107	1104-1111
3-Acetylpyridine	37.472	1123	35.918	1103	36.706	1104	36.322	1109	1109-1117
3,4-Dimethylfuran-2(5H)-one <sup>tent</sup>	37.755	1127	37.063	1118	36.963	1117	36.615	1112	NA
2-Phenethyl alcohol	37.810	1128	37.276	1121	37.051	1118	36.872	1116	1111-1121
Maltol (2-hydroxy-3-methyl-4H-pyran-4-one)	38.208	1133	37.203	1120	37.124	1119	ND	ND	1110-1141
Isophorone	38.335	1135	37.717	1127	37.543	1124	37.356	1123	1118-1135
6,7-Dihydro-5-methyl-5H-cyclopentapyrazine	39.596	1151	39.068	1142	38.901	1141	38.774	1140	1139-1157

**Table 2. Observed Retention Time Shift of Polar Components in Samples with Decreasing Phenolic (Acidity) Content**

Compound	Sample 2 R.T. 8.D	Sample 2 LRI 8.D	Sample 4 R.T. 6.D	Sample 4 LRI 6.D	Sample 3 R.T. 10.D	Sample 3 LRI 10.D	Sample 1 R.T. 5.D	Sample 1 LRI 5.D	Literature KI - LRI
3-Ethyl-2-hydroxycyclopent-2-en-1-one	40.235	1159	39.420	1149	39.297	1147	39.060	1144	1119-1140
Benzeneacetonitrile	39.333	1147	38.987	1149	38.864	1141	38.781	1142	1135-1145
4-Ketoisophorone	39.743	1153	39.354	1148	39.195	1142	39.083	1146	1139-1147
gamma-Heptalactone	41.113	1170	40.331	1160	40.952	1168	39.912	1155	1159-1163
2'-Hydroxyacetophenone	40.860	1167	40.632	1165	40.516	1164	40.462	1163	1167
Naphthalene	42.278	1185	42.100	1183	42.021	1182	41.968	1181	1180-1190
Quinoline	47.293	1252	46.594	1243	46.874	1246	46.123	1237	1233-1242
3-Methylacetophenone	41.92	1181	41.579	1176	41.441	1175	41.272	1173	1172-1182
1,4-Dimethoxybenzene	42.798	1192	42.577	1189	42.513	1188	42.393	1187	1168-1192
4-Methylacetophenone	43.03	1195	42.548	1189	42.396	1187	42.225	1185	1178-1189
6,7-Dihydro-2-methyl-5H-cyclopentapyrazine	44.17	1210	43.502	1201	43.372	1199	42.934	1194	1188
5,6,7,8-Tetrahydroquinoxaline	44.978	1221	44.376	1213	44.283	1212	43.928	1209	1212-1226
Quinoxaline	44.84	1219	44.347	1213	44.290	1212	44.016	1210	1209?-1229
Benzoic acid	44.942	1221	42.235	1185	44.656	1204	ND	ND	1170-1210
4-Methoxyphenol	46.409	1240	45.720	1231	ND	ND	ND	ND	1235
6,7-Dihydro-3,5-dimethyl-5H-cyclopentapyrazine	46.909	1247	46.608	1243	46.581	1242	46.417	1241	1243
Quinoline	47.293	1252	46.604	1243	46.868	1246	46.099	1236	1233-1242
gamma-Octalactone	48.672	1270	48.135	1263	48.534	1269	47.834	1259	1255-1266
2,3-Dihydro-1H-inden-1-one	50.267	1292	49.721	1285	50.164	1291	49.302	1278	1292-1307
2-Methyl-5,6,7,8-tetrahydroquinoxaline	51.005	1302	50.551	1296	50.861	1297	ND	ND	NA
2-Methylquinoxaline	51.336	1307	50.925	1301	51.170	1304	50.661	1297	1304
3-Methoxyacetophenone <sup>tent</sup>	51.479	1309	ND	ND	51.419	1308	51.167	1304	1295-1301
1,2,3-Trimethoxybenzene	52.267	1320	51.961	1316	52.212	1319	51.982	1316	1309-1317
8-Methylquinoline	52.417	1322	52.115	1318	52.249	1320	51.894	1315	1314-1323
7-Methylquinoline	55.213	1363	54.707	1355	54.664	1355	ND	ND	1355
6-Methylquinoline	55.693	1370	NA	NA	55.192	1362	54.868	1358	1358
gamma-Nonalactone	55.87	1372	NA	NA	56.28	1378	55.352	1365	1358-1373
4-Methylquinoline	56.196	1377	NA	NA	56.192	1377	56.483	1381	1382-1383

ND = Not detected

NA = Not available

**Table 2. Observed Retention Time Shift of Polar Components in Samples with Decreasing Phenolic (Acidity) Content**

Compound	Sample 2 R.T. 8.D	Sample 2 LRI 8.D	Sample 4 R.T. 6.D	Sample 4 LRI 6.D	Sample 3 R.T. 10.D	Sample 3 LRI 10.D	Sample 1 R.T. 5.D	Sample 1 LRI 5.D	Literature KI - LRI
4,4-Dimethyldihydro-2(3H)-furanone <sup>tent</sup>	28.768	1015	27.989	1006	27.315	997	ND	ND	NA
2-Ethyl-6-methylpyrazine	29.149	1020	28.458	1012	27.866	1003	27.922	1005	997-1010
2-Formyl-1-methylpyrrole	29.469	1024	28.826	1016	28.299	1010	28.018	1007	1010-1022
3,5-Dimethylfuran-2(5H)-one	29.293	1022	28.613	1013	28.079	1007	28.135	1007	NA
3-Methoxypyridine	29.571	1025	28.613	1013	27.998	1006	28.120	1008	998-1006
Trimethylpyrazine	29.369	1023	28.871	1016	28.130	1007	28.230	1009	1007-1014
3-Pyridylcarbonitrile	29.500	1024	28.870	1016	28.365	1023	28.377	1011	1007-1012
3,4-Dimethylpyridine	28.911	1017	27.922	1006	28.960	1017	28.429	1012	999-1003
4-Ethylpyridine	28.715	1014	27.893	1005	27.109	995	27.078	1014	954-968
2-Formylpyrrole	30.558	1037	30.004	1030	29.024	1018	29.009	1018	1013-1031
1,2,3-Trimethylbenzene	29.360	1022	29.273	1022	29.202	1021	29.200	1021	1021-1028
2-Acetylpyrazine	30.259	1034	ND	ND	29.396	1023	29.354	1023	1021-1029
2-Methyl-5-ethyl and/or 2-Ethyl-5-methylpyridine	35.960	1104	ND	ND	29.863	1029	30.022	1031	Both 1023
p-Cymene	29.601	1024	29.611	1024	29.437	1023	29.449	1024	1022-1028
Limonene	29.984	1030	29.853	1029	29.745	1027	29.750	1027	1027-1035
2-Acetylpyridine	31.021	1043	30.609	1038	30.602	1038	30.286	1034	1031-1046
5-Ethenyl-5-methyl-2(3H)-furanone	31.900	1054	31.300	1044	30.942	1042	30.937	1043	1041-1046
2,3-Dimethyl-2-cyclopenten-1-one	32.136	1057	31.285	1044	30.232	1033	30.934	1043	1040-1043
1-Methyl-2-pyrrolidone	35.410	1097	34.207	1082	32.557	1061	31.641	1051	1042-1046
gamma-Hexalactone	33.52	1074	32.489	1061	32.102	1057	32.107	1056	1047-1068
gamma-Terpinene	32.342	1059	32.276	1058	32.227	1058	32.225	1058	1054-1065
2,3,4-Trimethyl-2-cyclopenten-1-one	33.853	1078	33.376	1072	32.814	1065	32.805	1065	1071
Acetophenone	33.645	1075	33.201	1070	32.924	1066	32.922	1067	1062-1068
2-Acetylpyrrole	35.279	1095	34.156	1082	33.306	1071	33.034	1069	1060-1072
1-Methyl-2-acetylpyrrole	34.438	1085	34.053	1080	33.761	1077	33.708	1076	1050-1100
4-Methylbenzaldehyde	34.640	1087	34.325	1084	34.084	1081	34.060	1080	1076-1081
1-Methyl-2,5-pyrrolidinedione	36.587	1112	35.808	1106	35.744	1101	35.148	1095	1090
4,5-Dimethyl-4-hexen-3-one <sup>tent</sup>	36.659	1113	35.977	1105	ND	ND	35.367	1098	NA
Heptanoic acid	37.200	1120	35.645	1100	36.045	1105	35.587	1100	1078-1097
6,7-Dihydro-5H-cyclopentapyrazine	37.410	1123	36.762	1114	36.550	1111	36.219	1107	1104-1111
3-Acetylpyridine	37.472	1123	35.918	1103	36.706	1104	36.322	1109	1109-1117
3,4-Dimethylfuran-2(5H)-one <sup>tent</sup>	37.755	1127	37.063	1118	36.963	1117	36.615	1112	NA
2-Phenethyl alcohol	37.810	1128	37.276	1121	37.051	1118	36.872	1116	1111-1121
Maltol (2-hydroxy-3-methyl-4H-pyran-4-one)	38.208	1133	37.203	1120	37.124	1119	ND	ND	1110-1141
Isophorone	38.335	1135	37.717	1127	37.543	1124	37.356	1123	1118-1135
6,7-Dihydro-5-methyl-5H-cyclopentapyrazine	39.596	1151	39.068	1142	38.901	1141	38.774	1140	1139-1157

**Table 2. Observed Retention Time Shift of Polar Components in Samples with Decreasing Phenolic (Acidity) Content**

Compound	Sample 2 R.T. 8.D	Sample 2 LRI 8.D	Sample 4 R.T. 6.D	Sample 4 LRI 6.D	Sample 3 R.T. 10.D	Sample 3 LRI 10.D	Sample 1 R.T. 5.D	Sample 1 LRI 5.D	Literature KI - LRI
3-Ethyl-2-hydroxycyclopent-2-en-1-one	40.235	1159	39.420	1149	39.297	1147	39.060	1144	1119-1140
Benzeneacetonitrile	39.333	1147	38.987	1149	38.864	1141	38.781	1142	1135-1145
4-Ketoisophorone	39.743	1153	39.354	1148	39.195	1142	39.083	1146	1139-1147
gamma-Heptalactone	41.113	1170	40.331	1160	40.952	1168	39.912	1155	1159-1163
2'-Hydroxyacetophenone	40.860	1167	40.632	1165	40.516	1164	40.462	1163	1167
Naphthalene	42.278	1185	42.100	1183	42.021	1182	41.968	1181	1180-1190
Quinoline	47.293	1252	46.594	1243	46.874	1246	46.123	1237	1233-1242
3-Methylacetophenone	41.92	1181	41.579	1176	41.441	1175	41.272	1173	1172-1182
1,4-Dimethoxybenzene	42.798	1192	42.577	1189	42.513	1188	42.393	1187	1168-1192
4-Methylacetophenone	43.03	1195	42.548	1189	42.396	1187	42.225	1185	1178-1189
6,7-Dihydro-2-methyl-5H-cyclopentapyrazine	44.17	1210	43.502	1201	43.372	1199	42.934	1194	1188
5,6,7,8-Tetrahydroquinoxaline	44.978	1221	44.376	1213	44.283	1212	43.928	1209	1212-1226
Quinoxaline	44.84	1219	44.347	1213	44.290	1212	44.016	1210	1209?-1229
Benzoic acid	44.942	1221	42.235	1185	44.656	1204	ND	ND	1170-1210
4-Methoxyphenol	46.409	1240	45.720	1231	ND	ND	ND	ND	1235
6,7-Dihydro-3,5-dimethyl-5H-cyclopentapyrazine	46.909	1247	46.608	1243	46.581	1242	46.417	1241	1243
Quinoline	47.293	1252	46.604	1243	46.868	1246	46.099	1236	1233-1242
gamma-Octalactone	48.672	1270	48.135	1263	48.534	1269	47.834	1259	1255-1266
2,3-Dihydro-1H-inden-1-one	50.267	1292	49.721	1285	50.164	1291	49.302	1278	1292-1307
2-Methyl-5,6,7,8-tetrahydroquinoxaline	51.005	1302	50.551	1296	50.861	1297	ND	ND	NA
2-Methylquinoxaline	51.336	1307	50.925	1301	51.170	1304	50.661	1297	1304
3-Methoxyacetophenone <sup>tent</sup>	51.479	1309	ND	ND	51.419	1308	51.167	1304	1295-1301
1,2,3-Trimethoxybenzene	52.267	1320	51.961	1316	52.212	1319	51.982	1316	1309-1317
8-Methylquinoline	52.417	1322	52.115	1318	52.249	1320	51.894	1315	1314-1323
7-Methylquinoline	55.213	1363	54.707	1355	54.664	1355	ND	ND	1355
6-Methylquinoline	55.693	1370	NA	NA	55.192	1362	54.868	1358	1358
gamma-Nonalactone	55.87	1372	NA	NA	56.28	1378	55.352	1365	1358-1373
4-Methylquinoline	56.196	1377	NA	NA	56.192	1377	56.483	1381	1382-1383

ND = Not detected

NA = Not available



## Results and Discussion:

A series of purge and trap and static headspace analyses of Latakia tobacco were conducted using different conditions for sample collection.

In excess of 500 volatile constituents were identified, with the majority of volatiles being phenolics, polycyclic and related aromatic hydrocarbons, sesquiterpenoids and known tobacco constituents. Notably, 5 ambrettolide isomers and dihydroambrettolide, as well as (Z)-Octadec-9-en-18-olide, were identified.

**Tobacco Specific constituents:** The main tobacco specific constituents were neophytadiene, solanone and nicotine, although the amount of the latter is almost totally diminished in the static headspace analyses. Among constituents previously found in Oriental tobacco leaf identified were Manool, Manoyl oxide, 13-epi-Manoyl oxide, sclareolide (23) and (Z)-Octadec-9-en-18-olide (24). It appears that some degradation of nicotine during the smoke-curing process has produced an extensive series of substituted pyridines. This phenomenon has previously been observed on the pyrolysis of nicotine (25).

**Phenolics:** The phenolic composition of Latakia is similar to that reported previously for Kentucky Dark Fired-cured tobacco, except that the ratio of guaiacol to syringyl lignin pyrolysis derivatives is much greater (26). In Sample 3 (8.D) the total phenols exceeded 42% (FID) of the GC (which contributed to the retention time shifts previously mentioned – see Table 2) while the other samples contained considerably less total phenols.

**Polycyclic & related aromatic hydrocarbons:** This group of compounds along with substituted benzenes comprised the largest group of constituents in number. Of the polycyclic aromatic hydrocarbons, virtually all have been previously reported in tobacco smoke, but only a relatively few in tobacco types other than Latakia. A number of these are present at low levels in wood smoke and it would appear that these are probably due to pyrolytic decomposition of the woods and shrubs, as well as tobacco used in the smoke curing process. In many respects, the polycyclic and benzenoid compounds are quite similar to those found in pyrolyzates / distillates from shale oil deposits, see for example, Gallegos, 1986 (27).

**Terpenoids & Related primarily from the aromatic woods and shrubs:** The sesquiterpenoids comprised 5-9% of volatiles in the various headspace analyses (8.8% in 5.D and 5.1% in 8.D). Of these, alpha-Cubebene, alpha-Ylangene, alpha-Copaene, beta-Caryophyllene, beta-Elementene, beta-Copaene, Aromadendrene, cis-Muurolo-4(14),5-diene, Germacrene D, alpha-Amorphene, gamma-Amorphene, alpha-Muuroloene, gamma-Cadinene, delta-Cadinene, cis-Calamenene, alpha-Cadinene, alpha-Calacorene, Cadalene, Elemol, Caryophyllene oxide, T-Muurolol, alpha-Cadinol and Cubenol are all known constituents of *Pistacia lentiscus* (28-49) and all but gamma-Amorphene and Elemol are present in *Juniperus oxycedrus*. Of the monoterpenoids (alpha-Pinene, Sabinene, beta-Pinene, beta-Myrcene, p-Cymene, 1,8-Cineole, gamma-

Terpinene, alpha-Terpinolene, endo-Borneol, 4-Terpineol, alpha-Terpineol, Thymol and Carvacrol), all are also present in *Pistacia lentiscus*.

**Lactones:** The macrocyclic musk compounds pentadecan-15-olide and (Z)-octadec-9-en-18-olide have previously been identified in Oriental tobacco (24). In this study, in addition to the previously reported Oriental constituent, (Z)-octadec-9-en-18-olide, it was notable that Ambrettolide (hexadec-7-en-16-olide) and four isomeric materials as well as Dihydroambrettolide (hexadecan-16-olide) were found. This confirms the findings of unpublished reports of Tolman (7-9) who also found the presence of 5 isomers of ambrettolide.

**Other:** To the best of our knowledge, this is the first time that the C<sub>19</sub> branched hydrocarbons, Pristane (2,6,10,14-Tetramethylpentadecane) and 2-Pristene (2-Norphytene = 2,6,10,14-tetramethylpentadec-2-ene) and the C<sub>20</sub> branched hydrocarbons 2-Phytene (2,6,10,14-tetramethyl-2-hexadecene) and 3,7,11,15-Tetramethyl-2-hexadecene (a phytene isomer) have been reported as tobacco constituents although several are found in tobacco smoke. These materials, along with Phytane (2,6,10,14-tetramethyl-hexadecane) and 1-Pristene (1-Norphytene = 2,6,10,14-tetramethylpentadec-2-ene) are classic biomarkers of petroleum and coal deposits (50).

### Conclusions:

The dynamic and static headspace analyses of Latakia tobacco by GC-MS provided a convenient method for the identification of the complex tobacco volatiles. The use of the NIST AMDIS program allows the automated and accurate identification of overlapping constituents in the many overlapping GC peaks.

More than 500 constituents were identified and the terpenoids and sesquiterpenoids present suggests that *Pistacia lentiscus* (Mastic) is an important contributor to the smoke curing process.

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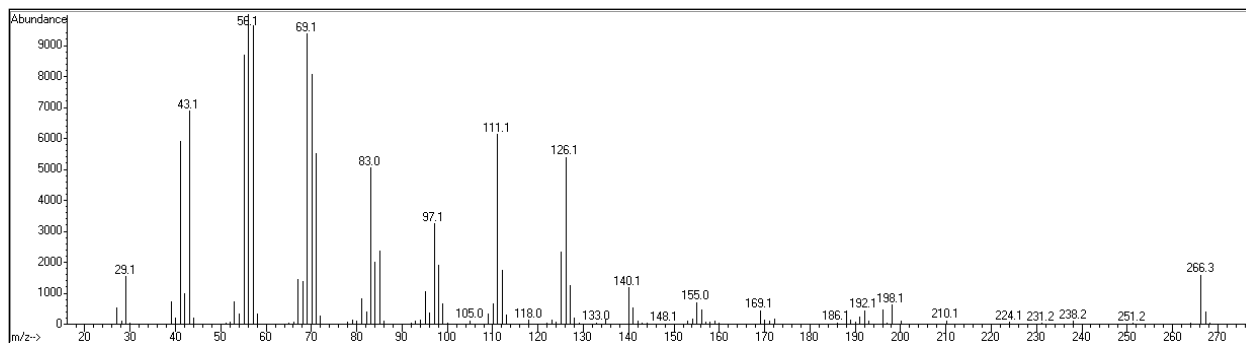
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### Supplementary Material

#### Mass Spectrum of 1-Pristene = 1-Norphytene (2,6,10,14-tetramethylpentadec-1-ene)



#### Mass Spectrum of 2-Pristene = 2-Norphytene (2,6,10,14-tetramethylpentadec-2-ene)

