

Some Aspects of the Chemistry of Tea. A Contribution to the Knowledge of the Volatile Constituents

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After a review of recent advances in the knowledge of tea polyphenols, the identification of 83 vola-

tile constituents of black tea is reported.

The beverage produced from tea was introduced 57 centuries ago and, if one considers the economic importance of the tea plant, it is not surprising that its chemistry has attracted the attention of many investigators.

The available information was capably reviewed by Stahl (25) in 1962. The same year saw the publication of a monograph by Roberts, dealing with the changes undergone by the polyphenols during the processing steps necessary to transform the leaves into the black tea of commerce (21).

The process for the manufacture of black tea, in its orthodox form, involves four stages: withering, rolling, "fermenting," and firing. Numerous changes occur in the chemical composition of the system during each stage. For instance, since the tissues are not killed until the last step—firing—some metabolic processes can take place until that point (23).

In addition to obvious physical changes, significant chemical changes occur during the withering of the leaves. The present knowledge on the subject has been reviewed by Bhatia (2) and Sanderson (22), two important contributors to the understanding of the chemistry of tea.

Some of the chemical changes which occur during withering are the following. Protein breakdown results in a net increase of free amino acids which are continuously fed into and removed from an amino acid pool. The caffeine content increases, as the alkaloid is possibly formed enzymatically from the amino acids. Soluble carbohydrates increase, and changes in organic acids, typical of senescing plant tissue, also take place. The permeability of the cell membranes is reported to increase and the activity of the polyphenol oxidase to fluctuate.

Rolling triggers many other chemical changes, as it causes the breakdown of many cells and permits, *inter alia*, contact of the oxidases with the polyphenolic substrates, a prerequisite for fermentation.

Finally, firing may involve more than the inactivation of the enzymes, the elimination of water, and the loss of part of the aromatic constituents. The trade believes that tea continues to change after it has been dried and packed (2).

An understanding of all these changes and of the factors that govern them and affect the quality of the finished product is of importance to the tea industry. Moreover, in recent years, the soluble tea industry has come into its own, and its technologists require new knowledge in order to improve the present processes and design new ones. Thus, tea research continues to be a very active field, as evidenced by the number of papers that have appeared since 1962. Areas of particular interest are concerned with the chemistry of withering and fermentation, the nature and specificity of the complex enzymatic system of the leaves, and the study of the aromatic volatile constituents and of their contribution to the flavor of the beverage.

The availability of gas chromatographic instruments in the producing countries should facilitate studies on the formation of the volatile constituents, their concentration in various parts of the plant, their changes during processing, etc. Work along some of these lines was reported prior to the advent of gas chromatography; however, more reliable results could be obtained by modern techniques.

Structure and Origin of Theaflavin

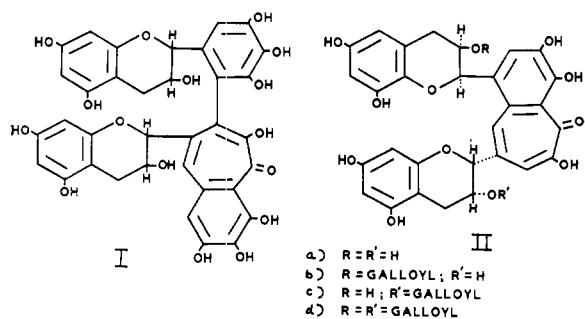
This paper, in the main, reports recent contributions to the understanding of the nature of the volatile constituents of tea flavor. However, mention will be made, first, of the structures of theaflavin and its gallate esters, compounds which contribute importantly to the color and brightness of tea infusions. These factors weigh fairly heavily in the commercial valuation of black tea. However, the role played in determining the flavor of tea infusions is not as easily demonstrated for the theaflavins as it is for the volatile constituents.

The structure of theaflavin, formulated by Roberts (21) as I, has now been shown by two independent groups (5, 28) to be IIa. This structure yielded only to the concerted attack of the spectral tools, in particular mass spectrometry and NMR. Without mass spectrometry, in fact, even the determination of the molecular weight and of the formula of this easily solvated molecule had appeared as very difficult tasks. However, while the authors' paper (27) and that of the Sheffield group (5) appeared in late 1965 and early 1966, respectively, Takino had proposed (28), although not unequivocally proved, the same structure in 1964.

Evidence for the structures of the three possible theaflavin gallates (IIb, IIc, and IId) and their pres-

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ence in black tea was put forward (26) at the meeting of the Japan Tea Association, in March 1966. This and other information regarding the *in vitro* oxidation of the polyphenols of tea leaf singly and in combination (17) clearly establish that the precursors of theaflavins are not only epigallocatechin and its gallate (IIIc and III d), as originally postulated by Roberts (21), but also epicatechin gallate (IIIb) and, perhaps, epicatechin (IIIa) (for structures, see Figure 1).

The involvement of epicatechin gallate in tea fermentation had been proved by Bhatia (3) in 1961, on the basis of his own work and the reports of Swiss and Russian investigators (8, 31). This finding shaped the thinking of chemists concerned with the structure of theaflavin and of its esters.

Molecules as large as the ones of these precursors of the theaflavins, after transformation into their silyl derivatives, can be pushed without too great difficulty through a gas chromatographic column (7) (Figure 1). This is rather remarkable, if one considers that the molecular weight of the completely trimethylsilylated epigallocatechin gallate is 1034.

With some difficulty, one can also obtain (7) the mass spectra of these molecules, as well as those of some other derivatives of tea polyphenols with molecular weights close to, or in excess of, 2000. The combination of these two techniques might have good potential in the study of plant polyphenols.

Volatile Constituents of Black Tea. By contrast with the voluminous literature on the chemistry of tea polyphenols, the aromatic constituents of black tea do not seem to have received sufficient attention. The results obtained by classical methods have been re-

cently reviewed by Stahl (25). A limited study of volatile acids contained in the essential oil of black tea has also been made (4). In fact, since the advent of gas chromatography and the spectral methods of structure elucidation, the only reports of a sustained effort in this field have been those of an excellent Japanese group headed by Yamanishi (13, 14, 33-35), which has divided its attention between green and black tea. Production of the green tea, popular in the Orient, is based upon rapid inactivation of the enzymatic system of tea leaves, whereas in the production of black tea the key step is an extensive fermentation. To choose a suitable starting material for this study, several varieties of black tea were surveyed, first by examining the gas chromatographic curves of their steam distillates obtained under standard conditions. A flame ionization detector, essentially insensitive to water, was employed. The results obtained with the sensitivity and resolution achievable with this type of dilute (aqueous) sample suggest that the compositions of the distillates of the various teas investigated may have been qualitatively similar in all cases; however, a considerably higher degree of chromatographic resolution would be necessary to establish definitely whether or not teas of various origin contain all the same volatile constituents. Even with the above limitations, substantial quantitative differences between the chromatograms of the various teas investigated are clearly apparent (Figure 2). If extended to a sufficient number of teas of different origin and known organoleptic properties, this type of study may yield practical results.

Finally, the authors decided to employ, as starting material, a commercial blend of black tea. Steam distillation, followed by enrichment of the aqueous solution of tea volatiles so obtained, ultimately afforded an oil which was used throughout this investigation. This material—0.017% yield, based upon the amount of black tea employed—when heavily diluted with water, had an odor reminiscent of tea, but which did not seem to be properly balanced. Chromatograms run to follow the concentration process indicate that not all constituents are recovered with the same efficiency. This is a problem that plagues many flavor chemists. An analytical GC curve of the above oil—the aroma complex—is reproduced in Figure 3.

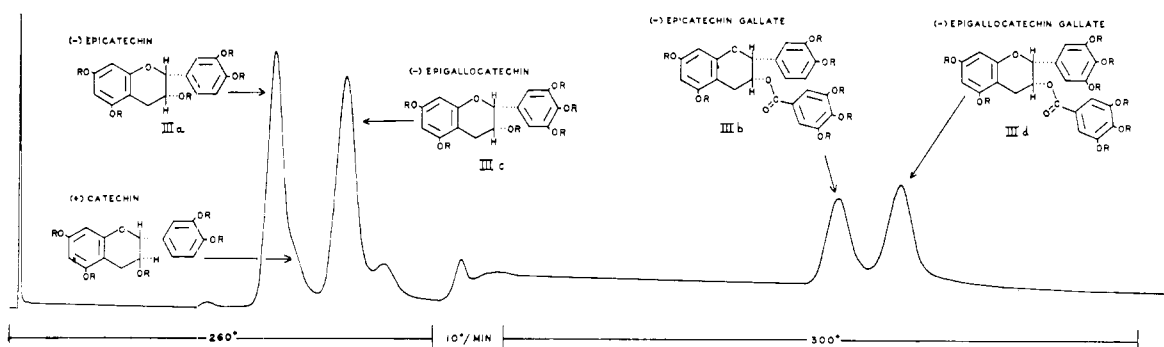


Figure 1. Gas chromatogram of an artificial mixture of trimethylsilyl derivatives of some tea polyphenols (7)

Conditions. 6-foot \times 0.125-inch glass column, 3% SE-30 on Chromosorb Q; program: 260° C. for 24 minutes, followed by programming to 300° at 10° per minute; flow: 70 ml. of helium per minute

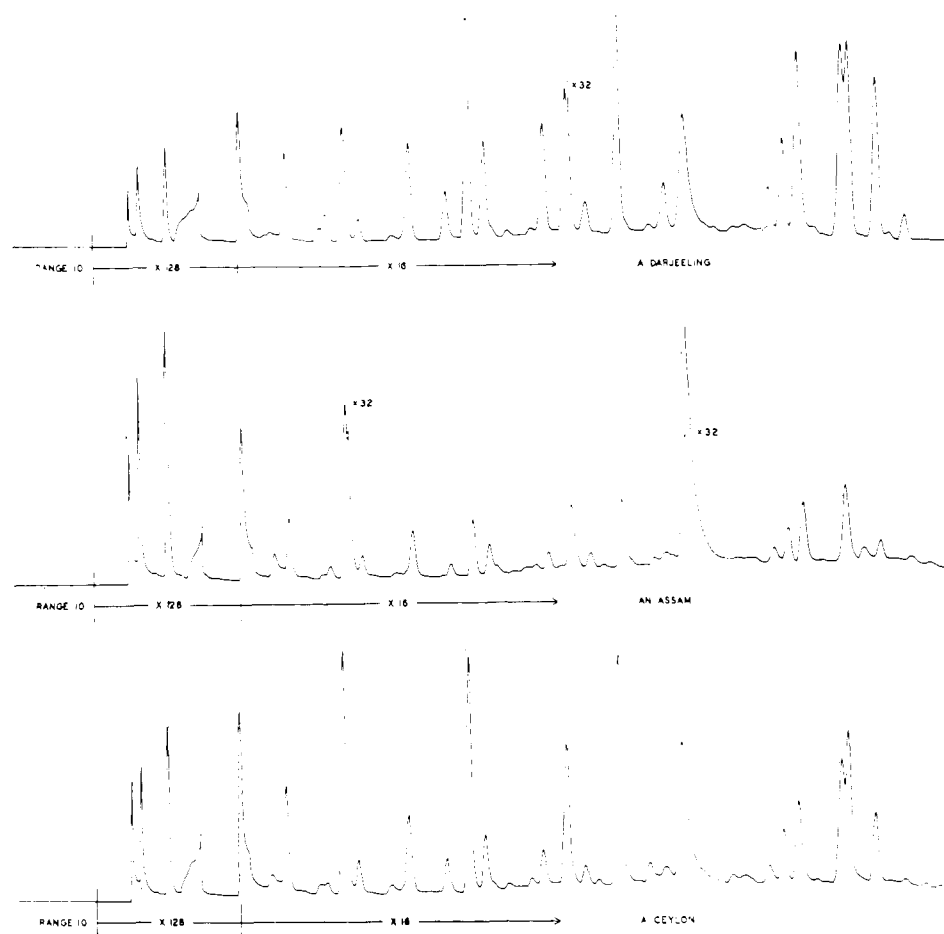


Figure 2 Gas chromatograms of steam

Separation and Identification. One of the most sophisticated methods of analysis available to chemists involved in flavor work is based upon the coupling of the outlet of a gas chromatographic column to the inlet of a fast scanning mass spectrometer (6, 15). This recently introduced analytical device, which should permit, at least in principle, the rapid and detailed study of any complex volatile mixture, has been used in some investigations of natural flavors (16, 29, 32).

However, the successful application of this technique depends primarily on meeting two basic requirements: The components of the volatile mixture should be completely separated so that each peak emerging from the gas chromatographic column represents a single substance, and the nature (and amount) of each of the compounds entering the mass spectrometer must be such that their identification is possible on the basis of chromatographic and mass spectral data alone. If either condition is not satisfied, the complexity of the interpretive work rapidly increases, and unequivocal results cannot always be obtained.

In the course of the present work, a more conservative approach has been adopted:

A. Separate the complex volatile mixture into an appropriate number of "cuts" by means of a preparative gas chromatographic column.

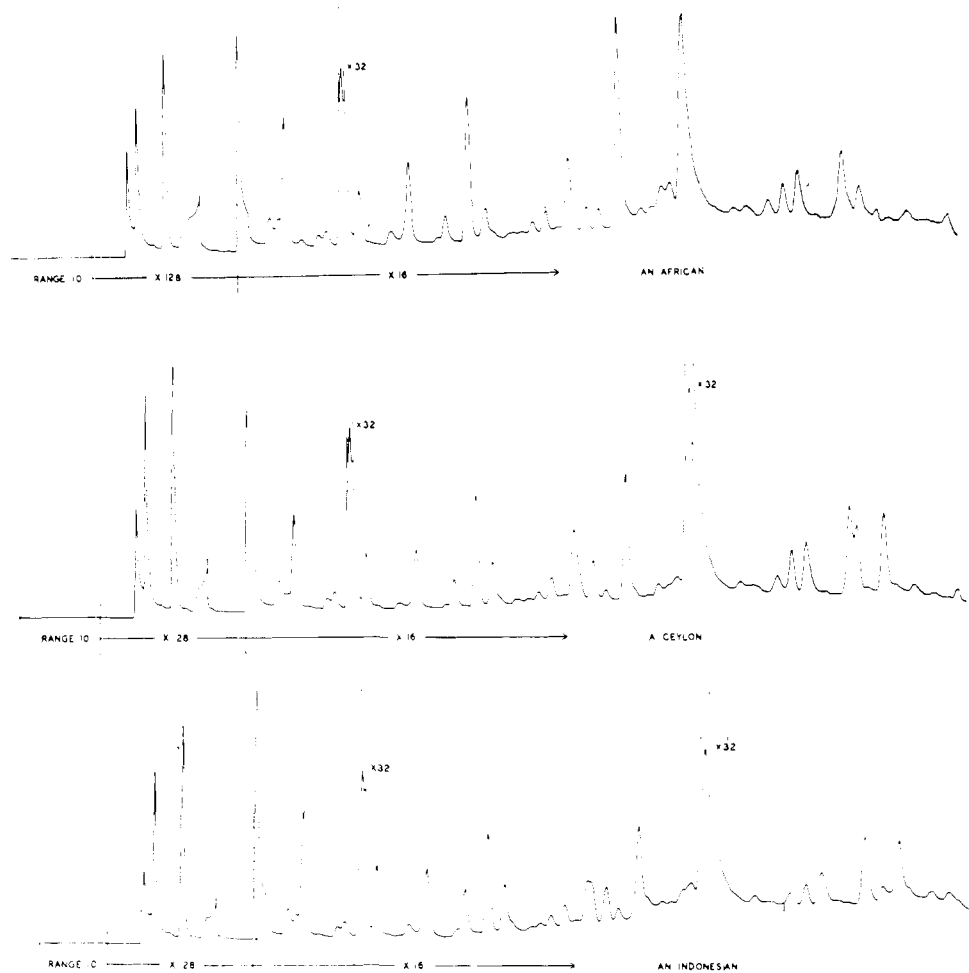
B. Separate the components of each "cut" from one another by means of an analytical gas chromatographic column having a polarity different from that of the preparative column.

C. When necessary, pass those peaks which are still uncompletely resolved (after elution from the first analytical column) through a second, and occasionally through a third, analytical column.

D. Compare retention times on two columns, infrared and, when indicated, ultraviolet and mass spectra of the natural products isolated in a chromatographically pure state with those of the appropriate synthetic materials.

In a few cases, cuts obtained in the preparative run have been injected into an efficient analytical column, and the peaks emerging have been directly introduced into a fast scanning mass spectrometer. However, confirmation of the tentative results so obtained has been sought, in all instances, via steps *A* to *D*.

Figure 4 shows a preparative gas chromatogram of the aroma complex used in our study (1-ml. injection, ballistic program) and an analytical chromatogram of the same oil (9- μ l. injection, conventional program), with the names of the compounds identified in the authors' laboratory and the trap numbering system employed.



distillates of six varieties of black tea

The compounds identified are listed in Table I, with their retention times on two columns of different polarity and the corresponding retention times of a series of ethyl esters of normal carboxylic acids used as internal standards. The above data should enable other investigators to repeat the isolations. Finally, the last column lists the compounds found in black tea by Yamanishi's group. Some of the compounds

found in black tea in the present investigation have previously been reported by Yamanishi's group as present in the oil obtained from unfermented fresh tea leaves and from green tea (35).

While the structural simplicity of the majority of the compounds identified (all previously known substances) does not warrant a discussion of the spectral data leading to their identification, the seven most intense infra-

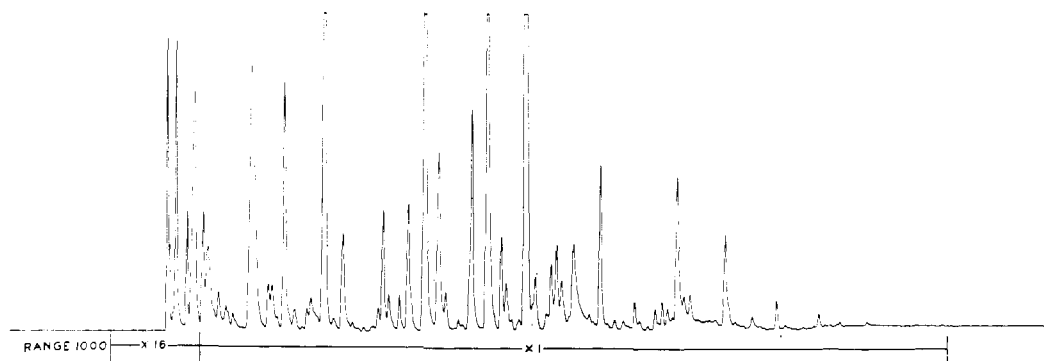


Figure 3. Hi-Pak gas chromatogram of an aroma complex of black tea

For conditions, see Experimental

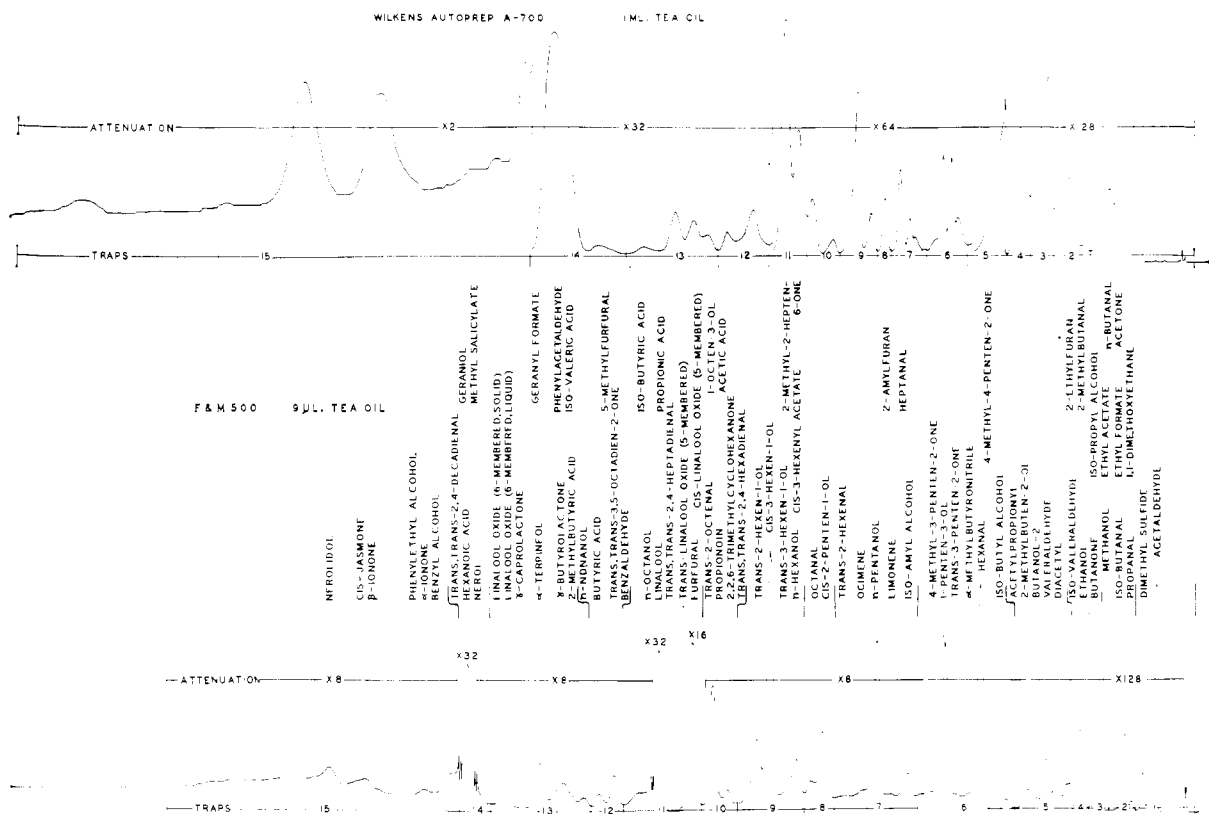


Figure 4. Preparative (top) and analytical (bottom) gas chromatograms of an aroma complex of black tea
For conditions, see Experimental

red absorption bands and the seven strongest mass spectral peaks of the black tea constituents identified in this laboratory are reported.

Although no attempt has been made to determine accurately the relative concentrations of the identified constituents of the aroma complex, work in progress suggests that trace components play an important role in determining the flavor of black tea. Moreover, one of the authors' few attempts to employ gas chromatography with capillary columns has revealed that many are the constituents of the aroma complex which remain unidentified (Figure 5).

Preliminary organoleptic tests seem to indicate that with tea, as with some other plant materials (1, 12), "character impact compounds" are found among the

constituents of the aroma complex which have fairly high boiling points; however, the role of some of the low boiling substances, although less striking, may also be important for the aroma of black tea.

At least from an academic viewpoint, knowledge of the nature of the aroma complex of tea cannot be claimed until the identification work is completed. However, the techniques developed for the basic investigations and the results reported so far from various laboratories may help tea technologists in their very valuable applied studies.

Experimental

The infrared spectra were determined in CCl_4 solution on a Beckman IR4 spectrophotometer employing

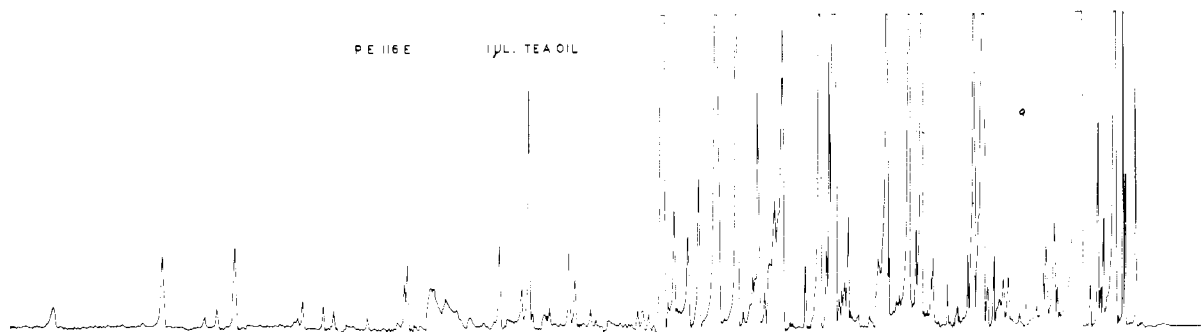


Figure 5. Capillary column gas chromatogram of an aroma complex of black tea

Table I. Gas Chromatographic Data of Some Volatile Constituents of Black Tea and Appropriate Markers^a

Compound	Molecular formula	Present Investigation		Trap No., preparative runs	Yamanishi and Collaborators
		R_T^a	R_T^b		
Acetaldehyde	C ₂ H ₄ O	0.5	2.4	1	
Dimethyl sulfide	C ₂ H ₆ S	1.6	3.4	1	
Propanal	C ₃ H ₆ O	1.3	4.1	2	
1,1-Dimethoxyethane	C ₄ H ₁₀ O ₂	2.7	4.4	2	
2-Methylpropanal	C ₄ H ₈ O	2.1	4.9	2	+
Acetone	C ₃ H ₆ O	1.1	4.9	2	
Ethyl formate	C ₃ H ₆ O ₂	1.6	4.9	2	
Ethyl formate	C ₃ H ₆ O ₂	1.6	4.9	...	
Butanal	C ₄ H ₈ O	2.7	6.8	3	+
Methanol	CH ₄ O	0.5	6.8	3	
Ethyl acetate	C ₄ H ₈ O ₂	3.0	6.8	3	
Ethyl acetate	C ₄ H ₈ O ₂	3.0	6.8	...	
2-Butanone	C ₄ H ₈ O	2.6	7.5	3	+
2-Propanol	C ₃ H ₈ O	1.2	7.6	3	
Ethanol	C ₂ H ₆ O	0.9	8.0	4	
2-Methylbutanal	C ₅ H ₁₀ O	4.1	8.1	4	
Isovaleraldehyde	C ₅ H ₁₀ O	3.9	8.2	4	+
2-Ethylfuran	C ₆ H ₈ O	5.3	9.3	4	
Ethyl propionate	C ₅ H ₁₀ O ₂	5.3	9.4	...	
Diacetyl	C ₄ H ₆ O ₂	2.4	10.0	5	
Valeraldehyde	C ₅ H ₁₀ O	5.0	10.8	5	+
2-Butanol	C ₄ H ₁₀ O	2.6	11.6	5	
2-Methyl-3-buten-2-ol	C ₅ H ₁₀ O	3.0	12.1	5	
Ethyl butyrate	C ₆ H ₁₂ O ₂	8.7	13.0	...	
Acetylpropionyl	C ₅ H ₈ O ₂	4.9	13.7	5	
2-Methyl-1-propanol	C ₄ H ₁₀ O	3.2	14.7	6	
4-Methyl-4-penten-2-one	C ₆ H ₁₀ O	7.0	15.8	6	
Hexanal	C ₆ H ₁₂ O	8.7	15.8	6	
α -Methylbutyronitrile	C ₅ H ₉ N	5.6	16.3	6	
Ethyl valerate	C ₇ H ₁₄ O ₂	13.2	18.1	...	
Isovaleronitrile	C ₅ H ₉ N	5.9	18.2	6	
<i>trans</i> -3-Penten-2-one	C ₅ H ₈ O	6.5	18.2	6	
1-Penten-3-ol	C ₅ H ₁₀ O	4.6	18.3	6	+
4-Methyl-3-penten-2-one	C ₆ H ₁₀ O	8.9	18.6	6	
Isoamyl alcohol	C ₅ H ₁₂ O	6.4	21.2	7	
Heptanal	C ₇ H ₁₄ O	13.4	21.4	7	+
Limonene	C ₁₀ H ₁₆	20.9	22.5	7	
2-Amylfuran	C ₉ H ₁₄ O	18.0	23.4	7	
1-Pentanol	C ₅ H ₁₂ O	7.7	23.5	7	+
Ethyl hexanoate	C ₈ H ₁₆ O ₂	18.3	23.5	...	
Ocimene	C ₁₀ H ₁₆	21.3	24.6	7	
<i>trans</i> -2-Hexenal	C ₆ H ₁₀ O	10.9	26.6	7	+
<i>cis</i> -2-Penten-1-ol	C ₅ H ₁₀ O	7.6	26.8	8	+
Octanal	C ₈ H ₁₆ O	18.7	27.0	8	
<i>cis</i> -3-Hexenyl acetate	C ₈ H ₁₄ O ₂	19.2	28.2	9	
Hexanol	C ₆ H ₁₄ O	11.9	29.0	9	+
Ethyl heptanoate	C ₉ H ₁₈ O ₂	23.7	29.0	...	
2-Methyl-2-hepten-6-one	C ₈ H ₁₄ O	17.7	29.4	9	
<i>trans</i> -3-Hexen-1-ol	C ₆ H ₁₂ O	11.3	29.9	9	
<i>cis</i> -3-Hexen-1-ol	C ₆ H ₁₂ O	11.6	30.1	9	+
<i>trans</i> -2-Hexen-1-ol	C ₆ H ₁₂ O	11.9	32.0	9	+
<i>trans,trans</i> -2,4-Hexadienal	C ₆ H ₈ O	13.7	33.6	10	
2,2,6-Trimethylcyclohexanone	C ₉ H ₁₆ O	21.0	33.7	10	
Acetic acid	C ₂ H ₄ O ₂	3.7	34.4	^b	+
Propionoin	C ₆ H ₁₂ O ₂	13.2	34.4	10	

(continued)

Table I. (Continued)

Compound	Molecular formula	Present Investigation			Yamanishi and Collaborators
		R_T^a	R_T^b	Trap No., preparative runs	
1-Octen-3-ol	C ₈ H ₁₆ O	17.6	34.4	10	
Ethyl octanoate	C ₁₀ H ₂₀ O ₂	28.9	34.4	...	
<i>trans</i> -2-Octenal	C ₈ H ₁₄ O	22.3	35.0	10	+
<i>cis</i> -Linalool oxide (5-membered) ^c	C ₈ H ₁₄ O ₂	23.2	35.4	11	+
Furfural	C ₅ H ₄ O	10.0	36.4	11	
<i>trans</i> -Linalool oxide (5-membered) ^c	C ₈ H ₁₄ O ₂	24.0	37.0	11	+
<i>trans,trans</i> -2,4-Heptadienal	C ₇ H ₁₀ O	19.1	38.4	11	
Propionic acid	C ₃ H ₆ O ₂	7.4	38.4	^b	+
1-Octanol	C ₈ H ₁₈ O	22.6	39.6	11	
Linalool	C ₁₀ H ₁₈ O	24.0	39.6	11	+
Ethyl nonanoate	C ₁₁ H ₂₂ O ₂	33.7	39.6	...	
Isobutyric acid	C ₄ H ₈ O ₂	10.1	39.8	^b	+
Benzaldehyde	C ₇ H ₆ O	16.5	40.4	12	+
<i>trans,trans</i> -3,5-Octadien-2-one	C ₈ H ₁₂ O	23.6	42.1	12	
5-Methylfurfural	C ₆ H ₆ O ₂	16.5	42.2	12	
Butyric acid	C ₄ H ₈ O ₂	11.2	43.0	^b	+
1-Nonanol	C ₉ H ₂₀ O	27.9	44.6	12	
Ethyl decanoate	C ₁₂ H ₂₄ O ₂	38.5	44.6	...	
Isovaleric acid	C ₅ H ₁₀ O ₂	13.6	45.2	^b	+
2-Methylbutyric acid	C ₅ H ₁₀ O ₂	14.4	45.3	^b	
γ -Butyrolactone	C ₄ H ₆ O ₂	13.4	46.1	13	
Phenylacetaldehyde	C ₈ H ₈ O	20.9	46.3	13	+
α -Terpineol	C ₁₀ H ₁₈ O	29.1	47.9	13	
Geranyl formate	C ₁₁ H ₁₈ O ₂	34.0	48.1	13	
γ -Caprolactone	C ₆ H ₁₀ O ₂	20.9	49.6	13	
Linalool oxide (6-membered, liquid) ^c	C ₈ H ₁₄ O ₂	28.1	49.6	13	+
Ethyl undecanoate	C ₁₃ H ₂₆ O ₂	43.0	49.6	...	
Linalool oxide (6-membered, solid) ^c	C ₈ H ₁₄ O ₂	28.1	50.3	13	+
Nerol	C ₁₀ H ₁₈ O	30.9	51.9	14	+
Methyl salicylate	C ₈ H ₈ O ₂	28.9	53.0	14	
Hexanoic acid	C ₆ H ₁₂ O ₂	21.3	53.3	^b	+
Geraniol	C ₁₀ H ₁₈ O	32.0	53.8	14	+
<i>trans,trans</i> -2,4-Decadienal	C ₁₀ H ₁₆ O	35.0	53.8	14	
Ethyl laureate	C ₁₄ H ₂₈ O ₂	47.5	54.2	...	
Benzyl alcohol	C ₇ H ₈ O	20.7	55.6	15	+
α -Ionone	C ₁₃ H ₂₀ O	40.7	56.1	15	
2-Phenylethanol	C ₈ H ₁₀ O	25.0	57.5	15	+
β -Ionone	C ₁₃ H ₂₀ O	43.0	59.8	15	
<i>cis</i> -Jasmone	C ₁₁ H ₁₆ O	38.5	60.1	15	
Nerolidol	C ₁₃ H ₂₀ O	46.7	61.9	15	
Ethyl myristate	C ₁₅ H ₃₂ O ₂	55.5	63.1	...	
Valeric acid	C ₅ H ₁₀ O ₂				+
Isocaproic acid	C ₆ H ₁₂ O ₂				+
<i>cis</i> -3-Hexenoic acid	C ₆ H ₁₀ O ₂				+
<i>trans</i> -2-Hexenoic acid	C ₆ H ₁₀ O ₂				+

^a Markers indented. Column A (R_T^a), nonpolar; column B (R_T^b), polar. For chromatographic conditions, see Experimental.

^b Acids isolated by bicarbonate extraction of an ether solution of freshly obtained steam distillate of tea.

^c For stereochemistry of the four linalool oxides, see (9).

a beam condenser and an ultramicrocell. The mass spectral data, determined on a CEC 21-110B spectrometer (ionizing voltage 70 e.v.; oven and source temperature 150° C.), refer to normal scanning speeds. Some variations in relative peak intensities were observed when the fast scanning mode was employed.

The GC retention times (R_T), expressed in minutes, were determined on a F & M 500 instrument, with thermal conductivity detector, and refer to the fol-

lowing conditions. Column A (R_T^a), 8 feet \times 0.25 inch, 25% silicone rubber (SE-30) on 60- to 100-mesh Chromosorb W, with a flow rate of 70 ml. of helium per minute, programmed from 75° to 250° C., at 2.1° per minute. Column B (R_T^b), 13 feet \times 0.25 inch, 15% Carbowax 20M on 60- to 80-mesh Diatoport S, with a flow rate of 70 ml. of helium per minute, programmed from 75° to 225° C. at 2.1° per minute. The retention times (R_T^a and R_T^b) of a series of ethyl esters

of straight-chain carboxylic acids, employed as markers, are listed in Table I.

The conditions employed for the analytical chromatograms of Figure 3 were as follows: 50-foot \times 0.125 inch o.d. packed stainless steel column, Carbowax 20M (F & M Hi-Pak); flow, 40 ml. of helium per minute; temperature, 65° C. for 8 minutes, followed by programming to 215° C. at the rate of 2° per minute; sample size 2.5 μ l.; instrument F & M 810, with flame ionization detection. This chromatographic system, while giving good resolution, causes partial adsorption of carboxylic acids and of some alcoholic and phenolic substances.

Isolation of Aroma Complex of Black Tea. A commercial blend of black tea was treated with steam until an amount of distillate equal to 40% of the weight of the charge had been collected, or until gas chromatographic analysis (flame ionization detector) showed that further steaming would yield only negligible amounts of volatiles. Flash evaporation of the steam distillate, continued until a volume of condensate equal to 10% of the charge had been obtained, yielded a clear residue, *A*, and a distillate, *B*, containing oily droplets in fine suspension. Residue *A* contained almost exclusively carboxylic acids (approximately 2.5 meq. per kg. of black tea employed or 66% of the volatile acids present in the original steam distillate), and was not further investigated. Boiling distillate *B* under a slight nitrogen pressure in a flask equipped with an oil separator (so modified as to permit refrigeration of the layer lighter than water, and connected with an efficient condensing system) yielded within a few minutes an oily fraction (oil fraction *A*, 0.014% yield based on the amount of black tea employed). Prolonging the distillation for as much as one hour improved the yield only slightly.

Rectification of the aqueous layer returning to the distillation flask from the oil separator gave a second oily fraction (oil fraction *B*, b.p. 47° to 90° C., 0.003% yield), containing some of the more water-soluble constituents. The combined oil fractions *A* and *B* constitute the aroma complex which is the object of the present investigation (Figure 3).

An alternative procedure by which the aroma complex of tea can be isolated in an essentially water-free condition is based upon solvent extraction of the original steam distillate, or of the condensate resulting from its flash evaporation. While the aroma complexes obtained by the different procedures are qualitatively similar, they are quantitatively different (GC). The chief advantage of the distillation procedure consists in its rapidity and in the fact that it eliminates the risk of contaminating the aroma complex with solvents and their impurities.

Preliminary Fractionation of Aroma Complex. Repeated 0.5- to 1.0-ml. injections of the above oil into a preparative GC unit led to the isolation of 15 cuts (see Table I). The conditions employed for the preparative runs were: instrument, Wilkens Autoprep A-700; column, 20 feet \times 0.375 inch, 30% Carbowax 20M on 30- to 60-mesh Chromosorb W; flow, 100 ml. of helium per minute; program, ballistic, from

75° to 225° C.; trapping, standard Autoprep A-700 trapping unit, with cooling bath at -60° C.; over-all trapping efficiency, 75% of charge (average of several 0.5 ml. runs). The contents of each trap were held under refrigeration in sealed vials until further fractionation was possible; however, analytical GC runs of each trap were obtained within 48 hours of the time of trapping, so that eventual formation of artifacts during storage could be monitored. Indeed, formation of artifacts was observed in a few of the low boiling cuts (oxidation of aldehydes to the corresponding acids, formation of 1,1-dimethoxypropane, 1,1-dimethoxyisobutane, 1,1-dimethoxybutane, and 1,1-dimethoxy-2-methylbutane from methanol and the appropriate aldehydes); the peaks resulting from artifacts were ignored during the next fractionation step (chromatography on column *A*).

Isolation of Pure Compounds from Aroma Complex

Criterion of Purity. Each of the 15 preparative cuts was fractionated on column *A*. The substances, often mixtures, corresponding to the peaks emerging from column *A* were trapped into dry ice-cooled glass capillaries, and the content of each trap was reinjected into column *B*. When the infrared spectra of the leading and trailing edge of any given peak were found to be identical, the material trapped from the central part of the peak was employed for the spectrometric determinations. This criterion of purity, which could not be applied to the very minor constituents, may be replaced in future work by a criterion based upon the identity of the mass spectra of the leading and trailing edge of the peaks. Peaks emerging from column *B* were generally found to be single substances; in a few cases, however, reinjection into column *A* or *B* (generally in isothermal conditions, at temperatures changing from case to case) was found to be necessary before the above criterion of purity could be satisfied.

Materials. The following compounds were obtained from commercial sources and purified by GC before comparing their chromatographic and spectral properties with those of the substances obtained from black tea. The wavelengths (microns) of the seven most intense infrared bands (between 2.5 and 12.2 microns) are reported in order of decreasing intensity. The seven strongest mass spectral peaks (*m/e*) are also listed for each compound; their intensities relative to that of the base peak (100%) are given in parentheses. The molecular ion peak, when observed, is reported in all cases, even if it was not among the seven most intense peaks.

Acetaldehyde, R_T^a : 0.5; R_T^b : 2.4; IR: 5.75, 7.39, 9.00, 6.98, 3.67, 3.53, 7.12; *m/e*: 29(100%), 44(molecular ion, 46%), 15(31%), 43(30%), 14(13%), 26(13%), 42(12%).

Propanal, R_T^a : 1.3; R_T^b : 4.1; IR: 5.76, 3.38, 3.57, 3.68, 7.18, 9.14, 11.79; *m/e*: 29(100%), 28(94%), 58(molecular ion, 81%), 27(62%), 57(27%), 26(20%), 30(9%).

2-Methylpropanal, R_T^a : 2.1; R_T^b : 4.9; IR: 5.75, 3.39, 6.80, 3.69, 3.57, 7.14, 7.30; *m/e*: 43(100%),

41(58%), 72(molecular ion, 45%), 27(40%), 29(20%), 39(20%), 42(8%).

Butanal, R_T^a : 2.7; R_T^b : 6.8; IR: 5.75, 3.38, 3.68, 3.54, 7.06, 6.80, 7.20; m/e : 44(100%), 43(77%), 72(molecular ion, 75%), 27(69%), 41(59%), 29(53%), 39(28%)

2-Methylbutanal, R_T^a : 4.1; R_T^b : 8.1; IR: 5.76, 3.36, 6.82, 3.68, 3.56, 7.20, 11.10; m/e : 57(100%), 29(86%), 41(73%), 58(47%), 27(33%), 86(molecular ion, 25%), 39(20%).

Isovaleraldehyde, R_T^a : 3.9; R_T^b : 8.2; IR: 5.76, 3.39, 6.80, 3.68, 7.28, 3.55, 7.19; m/e : 44(100%), 41(84%), 43(67%), 29(56%), 58(55%), 57(48%), 27(42%), 86(molecular ion, 17%).

Valeraldehyde, R_T^a : 5.0; R_T^b : 10.8; IR: 5.76, 3.38, 3.67, 3.55, 6.79, 7.05, 8.91; m/e : 44(100%), 29(46%), 58(34%), 41(32%), 27(27%), 57(24%), 43(19%), 86(molecular ion, 3%).

trans, trans-2,4-Hexadienal, R_T^a : 13.7; R_T^b : 33.6; IR: 5.88, 6.05, 8.92, 8.56, 10.11, 9.89, 9.21; m/e : 81(100%), 39(69%), 41(54%), 96(molecular ion, 45%), 53(41%), 67(40%), 27(23%); $\lambda_{\max}^{\text{EtOH}}$ 273 m μ .

Hexanal, R_T^a : 8.7; R_T^b : 15.8; IR: 3.37, 5.76, 3.47, 3.66, 3.52, 6.28, 7.15; m/e : 44(100%), 56(81%), 41(64%), 43(56%), 57(53%), 27(41%), 29(38%), 100(molecular ion, 2%).

Heptanal, R_T^a : 13.4; R_T^b : 21.4; IR: 5.76, 3.40, 3.69, 6.82, 7.09, 7.22; m/e : 70(100%), 44(87%), 43(77%), 41(76%), 42(53%), 55(52%), 29(48%), 114(molecular ion, 4%).

Octanal, R_T^a : 18.7; R_T^b : 27.0; IR: 3.40, 5.76, 3.69, 6.82, 3.55, 7.20, 7.09; m/e : 43(100%), 41(83%), 44(76%), 84(71%), 56(65%), 57(55%), 29(54%), 128(molecular ion, 1%).

Benzaldehyde, R_T^a : 16.5; R_T^b : 40.4; IR: 5.85, 8.31, 12.08, 7.62, 8.58, 7.77, 6.26; m/e : 106(molecular ion, 100%), 77(98%), 105(94%), 51(45%), 50(24%), 78(17%), 52(11%); $\lambda_{\max}^{\text{EtOH}}$ 245 m μ .

Furfural, R_T^a : 10.0; R_T^b : 36.4; IR: 5.82, 6.75, 9.78, 6.30, 8.57, 9.19, 7.10; m/e : 96(molecular ion, 100%), 95(85%), 39(58%), 38(19%), 29(17%), 37(11%), 40(6%); $\lambda_{\max}^{\text{EtOH}}$ 276 m μ .

5-Methylfurfural, R_T^a : 16.5; R_T^b : 42.2; IR: 5.91, 6.57, 9.78, 8.27, 7.16, 8.36, 8.09; m/e : 110(molecular ion, 100%), 109(89%), 53(52%), 27(25%), 51(15%), 39(13%), 50(12%); $\lambda_{\max}^{\text{EtOH}}$ 283 m μ .

Phenylacetaldehyde, R_T^a : 20.9; R_T^b : 46.3; IR: 5.78, 9.69, 6.65, 3.55, 6.83, 3.67, 3.29; m/e : 91(100%), 120(molecular ion, 25%), 92(23%), 65(19%), 39(16%), 27(11%), 63(9%).

Acetone, R_T^a : 1.1; R_T^b : 4.9; IR: 5.81, 8.20, 7.33, 7.04, 6.95, 3.32, 9.18; m/e : 43(100%), 58(molecular ion, 29%), 15(17%), 42(7%), 27(6%), 26(4%), 39(4%).

2-Butanone, R_T^a : 2.6; R_T^b : 7.5; IR: 5.80, 8.54, 7.32, 3.35, 7.03, 6.82, 3.40; m/e : 43(100%), 29(23%), 27(20%), 72(molecular ion, 18%), 15(10%), 42(8%), 57(8%).

Diacetyl, R_T^a : 2.4; R_T^b : 10.0; IR: 8.98, 7.39, 5.82, 7.04, 11.00, 7.20, 10.60; m/e : 43(100%), 15(15%), 86(molecular ion, 15%), 42(8%), 14(4%), 44(3%), 29(2%).

Acetylpropionyl, R_T^a : 4.9; R_T^b : 13.7; IR: 5.81,

9.13, 7.39, 11.01, 7.22, 7.07, 6.82; m/e : 43(100%), 29(68%), 57(42%), 27(22%), 100(molecular ion, 21%), 15(12%), 42(7%).

trans-3-Penten-2-one, R_T^a : 6.5; R_T^b : 18.2; IR: 5.93, 7.96, 10.27, 6.11, 7.34, 5.87, 6.91; m/e : 69(100%), 41(84%), 43(59%), 39(43%), 84(molecular ion, 31%), 15(12%), 42(10%); $\lambda_{\max}^{\text{EtOH}}$ 218 m μ .

4-Methyl-3-penten-2-one, R_T^a : 8.9; R_T^b : 18.6; IR: 6.12, 5.90, 8.55, 8.21, 7.37, 6.90, 7.23; m/e : 55(100%), 83(86%), 43(73%), 98(molecular ion, 72%), 29(41%), 39(36%), 27(30%); $\lambda_{\max}^{\text{EtOH}}$ 237.5 m μ .

4-Methyl-4-penten-2-one, R_T^a : 7.0; R_T^b : 15.8; IR: 5.80, 11.14, 7.35, 8.63, 8.20, 6.92, 6.05; m/e : 43(100%), 39(33%), 27(29%), 15(23%), 29(14%), 55(12%), 41(8%), 98(molecular ion, 5%).

2-Methyl-2-hepten-6-one, R_T^a : 17.7; R_T^b : 29.4; IR: 5.80, 7.35, 3.42, 7.24, 8.62, 6.91, 7.08; m/e : 43(100%), 41(53%), 69(39%), 55(34%), 108(23%), 58(20%), 39(19%), 126(molecular ion, 16%).

3-Methyl-2-(pent-2'-en)-cyclopent-2-en-1-one (*cis*-jas-mone), R_T^a : 38.5; R_T^b : 60.1; IR: 5.83, 6.03, 7.20, 3.37, 6.92, 7.45, 9.35; m/e : 164(molecular ion, 100%), 110(63%), 149(50%), 79(48%), 41(47%), 55(45%), 122(43%); $\lambda_{\max}^{\text{EtOH}}$ 235 m μ .

4 - (2,6,6 - Trimethyl - 2 - cyclohexen - 1 - yl) - 3 - buten-2-one (α -ionone), R_T^a : 40.7; R_T^b : 56.1; IR: 7.96, 5.94, 3.43, 7.32, 6.15, 10.17, 6.94; m/e : 121(100%), 93(83%), 43(75%), 136(68%), 192(molecular ion, 39%), 41(33%), 91(26%); $\lambda_{\max}^{\text{EtOH}}$ 227 m μ .

4 - (2,6,6 - Trimethyl - 1 - cyclohexen - 1 - yl) - 3 - buten-2-one (β -ionone), R_T^a : 43.0; R_T^b : 59.8; IR: 7.94, 5.95, 3.41, 7.32, 6.21, 10.19, 6.83; m/e : 177(100%), 43(75%), 41(24%), 91(16%), 135(15%), 178(14%), 39(14%), 192(molecular ion, 13%); $\lambda_{\max}^{\text{EtOH}}$ 294 and 221 m μ .

1,1-Dimethoxyethane, R_T^a : 2.7; R_T^b : 4.4; IR: 8.77, 8.87, 9.19, 9.54, 11.51, 7.18, 3.35; m/e : 59(100%), 75(41%), 31(28%), 29(25%), 43(20%), 15(15%), 47(9%), 90(molecular ion, 0.1%).

Propionoin, R_T^a : 13.2; R_T^b : 34.4; IR: 5.80, 9.00, 3.34, 10.30, 6.80, 2.84, 7.20; m/e : 59(100%), 31(45%), 57(36%), 29(32%), 58(24%), 41(23%), 27(15%), 116(molecular ion, 4%).

Methanol, R_T^a : 0.5; R_T^b : 6.8; IR: 9.70, 3.01, 3.42, 3.55, 6.90, 7.10, 9.00; m/e : 31(100%), 32(molecular ion, 76%), 29(45%), 15(15%), 30(7%), 28(5%), 14(3%).

Ethanol, R_T^a : 0.9; R_T^b : 8.0; IR: 9.51, 9.17, 3.39, 3.00, 11.36, 7.19, 6.84; m/e : 31(100%), 45(40%), 46(molecular ion, 23%), 27(22%), 29(16%), 43(9%), 15(8%).

2-Propanol, R_T^a : 1.2; R_T^b : 7.6; IR: 3.36, 10.51, 8.83, 8.60, 7.22, 2.97, 9.02; m/e : 45(100%), 27(15%), 43(14%), 29(10%), 39(9%), 41(8%), 31(6%), 60(molecular ion, 1%).

2-Methyl-1-propanol, R_T^a : 3.2; R_T^b : 14.7; IR: 9.65, 3.39, 6.79, 2.99, 9.98, 7.29, 7.17; m/e : 43(100%), 42(64%), 41(56%), 33(46%), 31(43%), 27(28%), 74(molecular ion, 18%).

2-Butanol, R_T^a : 2.6; R_T^b : 11.6; IR: 3.38, 10.98, 10.10, 2.99, 7.27, 9.00, 9.71; m/e : 45(100%), 27(33%),

29(24%), 31(24%), 43(24%), 59(24%), 41(20%), 74 (molecular ion, 0.4%).

1-Pentanol, R_T^a : 7.7; R_T^b : 23.5; IR: 3.39, 9.48, 2.99, 9.28, 9.92, 6.78, 7.21; m/e : 42(100%), 55(68%), 70(63%), 41(55%), 31(48%), 29(44%), 27(27%), 88(molecular ion, 0.02%).

Isoamyl alcohol, R_T^a : 6.4; R_T^b : 21.2; IR: 3.40, 9.46, 3.00, 6.81, 9.90, 7.21, 7.31; m/e : 41(100%), 70(78%), 55(73%), 42(68%), 43(56%), 27(51%), 39 (50%), 88(molecular ion, 0.2%).

1-Penten-3-ol, R_T^a : 4.6; R_T^b : 18.3; IR: 10.80, 10.05, 10.28, 3.33, 9.38, 2.98, 6.98; m/e : 57(100%), 29(26%), 27(18%), 31(14%), 41(9%), 39(8%), 43(7%), 86(molecular ion, 3%).

2-Methyl-3-buten-2-ol, R_T^a : 3.0; R_T^b : 12.1; IR: 3.36, 10.82, 10.53, 7.31, 8.57, 8.91, 8.40; m/e : 43 (100%), 71(87%), 41(30%), 27(28%), 59(27%), 39(17%), 31(15%), 86(molecular ion, 1.1%).

1-Hexanol, R_T^a : 11.9; R_T^b : 29.0; IR: 3.39, 9.47, 2.99, 9.64, 6.84, 7.24, 8.97; m/e : 56(100%), 43(62%), 55(50%), 42(45%), 41(41%), 31(29%), 29(25%), 102 (molecular ion, 0.1%).

1-Octanol, R_T^a : 22.6; R_T^b : 39.6; IR: 3.42, 9.54, 6.82, 9.75, 3.00, 7.24; m/e : 56(100%), 55(81%), 41(80%), 43(74%), 70(72%), 84(63%), 69(59%), 130 (molecular ion, 0.05%).

1-Octen-3-ol, R_T^a : 17.6; R_T^b : 34.4; IR: 3.42, 10.82, 10.09, 9.89, 6.82, 2.94, 7.02; m/e : 57(100%), 43(23%), 29(21%), 72(19%), 27(17%), 41(16%), 55(11%), 128(molecular ion, 0.1%).

1-Nonanol, R_T^a : 27.9; R_T^b : 44.6; IR: 3.41, 3.00, 9.48, 6.81, 7.24, 2.76, 8.94; m/e : 56(100%), 43(97%), 55(88%), 41(81%), 70(66%), 69(57%), 29(43%), 144 (molecular ion, 0.5%).

3,7-Dimethyl-1,6-octadien-3-ol (linalool), R_T^a : 24.0; R_T^b : 39.6; IR: 10.83, 3.41, 10.04, 7.25, 6.86, 9.00, 7.07; m/e : 71(100%), 93(65%), 41(64%), 43(56%), 55(49%), 69(42%), 80(28%), 154(molecular ion, 1%).

1-*p*-Menthen-8-ol (α -terpineol), R_T^a : 29.1; R_T^b : 47.9; IR: 3.35, 7.24, 8.62, 10.83, 8.85, 6.92, 9.02; m/e : 59(100%), 121(69%), 93(65%), 136(61%), 42 (50%), 81(37%), 41(27%), 154(molecular ion, 4%).

2,6-Dimethyl-2,6-octadien-8-ol (geraniol), R_T^a : 32.0; R_T^b : 53.8; IR: 3.41, 10.00, 7.22, 6.89, 2.98, 5.96, 9.01; m/e : 69(100%), 41(90%), 39(25%), 68(20%), 27(18%), 29(17%), 53(13%), 154(molecular ion, 4%).

2,6-Dimethyl-2,6-octadien-8-ol (nerol, geometrical isomer of geraniol), R_T^a : 30.9; R_T^b : 51.9; IR: 3.42, 10.02, 6.89, 7.24, 3.00, 2.75, 9.02; m/e : 69(100%), 41(92%), 39(25%), 93(22%), 68(21%), 27(18%), 29 (18%), 154(molecular ion, 4%).

Geranyl formate, R_T^a : 34.0; R_T^b : 48.1; IR: 5.78, 8.62, 3.42, 7.23, 9.02, 6.87, 11.16; m/e : 69(100%), 41(78%), 39(24%), 68(22%), 53(17%), 27(16%), 29 (15%), 182(molecular ion, 0.2%).

3,7,11-Trimethyl-1,6,10-dodecatrien-3-ol (nerolidol), R_T^a : 46.7; R_T^b : 61.9; IR: 3.42, 10.83, 6.86, 7.24, 9.02, 10.03, 2.88; m/e : 69(100%), 41(75%), 93(54%), 43(48%), 71(39%), 55(32%), 81(29%), 222(molecular ion, 0.2%).

Benzyl alcohol, R_T^a : 20.7; R_T^b : 55.6; IR: 9.81, 6.56, 9.66, 6.85, 2.99, 8.25, 7.21; m/e : 79(100%), 108

(molecular ion, 87%), 107(67%), 77(57%), 51(30%), 91 (19%), 50(16%).

2-Phenylethanol, R_T^a : 25.0; R_T^b : 57.5; IR: 9.52, 3.38, 2.93, 6.83, 7.19, 6.13, 3.28; m/e : 91(100%), 92(63%), 122(molecular ion, 33%), 65(16%), 39(11%), 41(8%), 51(8%).

cis-2-Vinyl-2-methyl-5-(1'-hydroxy-1'-methyl ethyl)-tetrahydrofuran (five-membered linalool oxide), R_T^a : 23.2; R_T^b : 35.4; IR: 3.37, 9.52, 10.82, 8.82, 7.29, 8.51, 10.08; m/e : 59(100%), 94(49%), 43(45%), 68(33%), 111(31%), 55(29%), 41(26%), 170(molecular ion, 0.05%).

trans-2-Vinyl-2-methyl-5-(1'-hydroxy-1'-methyl ethyl)-tetrahydrofuran (five-membered linalool oxide), R_T^a : 24.0; R_T^b : 37.0; IR: 3.37, 9.49, 10.84, 10.09, 7.30, 10.53, 9.70; m/e : 59(100%), 43(50%), 94(41%), 68(34%), 41(31%), 55(29%), 111(24%), 170(molecular ion, 0.05%).

Both *cis* and *trans* isomers of five-membered linalool oxide were supplied as a mixture by Aldrich Chemical Co., Inc., Milwaukee, Wis., under the name linalool oxide and separated by GC. The infrared and mass spectra of the two isomers were identical with those published by Felix *et al.* (9)

Ethyl formate, R_T^a : 1.6; R_T^b : 4.9; IR: 5.76, 8.41, 8.64, 3.34, 9.90, 11.87, 9.00; m/e : 31(100%), 28(98%), 29(45%), 27(44%), 45(34%), 74(molecular ion, 17%), 26(11%).

Ethyl acetate, R_T^a : 3.0; R_T^b : 6.8; IR: 8.06, 5.72, 9.54, 7.27, 3.35, 9.09, 7.18; m/e : 43(100%), 29(16%), 45(15%), 61(13%), 88(molecular ion, 10%), 15(9%), 27(9%).

Methyl salicylate, R_T^a : 28.9; R_T^b : 53.0; IR: 7.61, 8.19, 7.92, 5.88, 8.59, 6.89, 9.13; m/e : 120(100%), 152(molecular ion, 46%), 92(45%), 121(30%), 65(18%), 39(16%), 63(11%).

γ -Butyrolactone, R_T^a : 13.4; R_T^b : 46.1; IR: 5.59, 8.51, 9.60, 10.02, 7.24, 11.52, 3.32; m/e : 42(100%), 28(99%), 41(43%), 27(42%), 29(41%), 86(molecular ion, 36%), 56(29%).

γ -Caprolactone, R_T^a : 20.9; R_T^b : 49.6; IR: 5.59, 8.51, 10.28, 3.36, 7.39, 8.55, 9.80; m/e : 85(100%), 29(45%), 27(22%), 28(21%), 42(20%), 56(20%), 57 (17%), 114(molecular ion, 5%).

Acetic acid, R_T^a : 3.7; R_T^b : 34.4; IR: 5.78, 7.71, 7.04, 3.00-4.00, 10.61, 7.34, 9.83; m/e : 43(100%), 45(89%), 60(molecular ion, 69%), 15(25%), 42(15%), 29(11%), 28(10%).

Propionic acid, R_T^a : 7.4; R_T^b : 38.4; IR: 5.79, 8.02, 3.34, 3.00-4.00, 7.03, 7.72, 6.80; m/e : 74(molecular ion, 100%), 28(98%), 29(82%), 73(64%), 27(61%), 45(60%), 57(31%).

Isobutyric acid, R_T^a : 10.1; R_T^b : 39.8; IR: 5.82, 3.00-4.00, 3.36, 8.06, 7.04, 6.77, 7.73; m/e : 43(100%), 41(39%), 27(27%), 73(26%), 88(molecular ion, 15%), 39(14%), 45(12%).

Butyric acid, R_T^a : 11.2; R_T^b : 43.0; IR: 5.82, 3.38, 3.00-4.00, 8.19, 7.78, 7.05, 10.68; m/e : 60(100%), 73(32%), 27(20%), 41(18%), 43(13%), 45(13%), 42 (12%), 88(molecular ion, 5%).

2-Methylbutyric acid, R_T^a : 14.4; R_T^b : 45.3; IR: 5.83, 3.38, 8.13, 6.82, 7.75, 7.04, m/e : 74(100%),

57(58%), 29(48%), 41(42%), 27(25%), 87(25%), 60(21%), 102(molecular ion, 1%).

Isovaleric acid, R_T^a : 13.6; R_T^b : 45.2; IR: 5.82, 3.36, 3.00–4.00, 7.65, 8.14, 7.03, 6.80; m/e : 60(100%), 41(41%), 43(27%), 74(25%), 87(24%), 27(23%), 39(22%), 102(molecular ion, 1%).

Hexanoic acid, R_T^a : 21.3; R_T^b : 53.3; IR: 5.80, 3.37, 3.00–4.00, 7.02, 7.69, 7.87, 10.61; m/e : 60(100%), 73(44%), 41(30%), 27(25%), 43(18%), 29(17%), 39(16%), 116(molecular ion, 0.3%).

Isovaleronitrile, R_T^a : 5.9; R_T^b : 18.2; IR: 3.38, 6.81, 7.18, 7.28, 7.02, 8.97, 9.60 (C N at 4.45); m/e : 43(100%), 41(60%), 39(25%), 27(25%), 15(5%), 38(5%), 42(5%), 83(molecular ion, 0.1%).

Dimethyl sulfide, R_T^a : 1.6; R_T^b : 3.4; IR: 6.93, 3.42, 9.70, 7.60, 10.27, 3.50, 9.12; m/e : 62(molecular ion, 100%), 47(97%), 45(52%), 46(40%), 61(40%), 35(29%), 27(18%).

Samples of the following compounds were donated either by Philip Kratz, International Flavors and Fragrances, New York, or by J. Boldingh, Uniliver, Holland, whose cooperation in this matter is gratefully acknowledged. These samples were also purified by GC prior to the determination of their spectral properties.

Limonene, R_T^a : 20.9; R_T^b : 22.5; IR: 11.22, 3.40, 6.92, 6.85, 7.24, 6.06, 10.92; m/e : 68(100%), 93(56%), 136(molecular ion, 35%), 67(34%), 39(29%), 41(27%), 57(25%).

Ocimene, R_T^a : 21.3; R_T^b : 24.6; IR: 11.17, 3.42, 10.07, 6.88, 6.21, 9.03, 7.19; m/e : 93(100%), 80(31%), 41(30%), 79(29%), 91(27%), 77(23%), 39(22%), 136(molecular ion, 18%); $\lambda_{\max}^{\text{EtOH}}$ 232 μm .

trans-2-Hexenal, R_T^a : 10.9; R_T^b : 26.6; IR: 5.84, 10.24, 8.55, 3.35, 9.12, 3.52, 9.52; m/e : 41(100%), 55(63%), 42(61%), 69(58%), 39(54%), 27(50%), 57(47%), 98(molecular ion, 41%); $\lambda_{\max}^{\text{EtOH}}$ 221 μm .

trans-2-Octenal, R_T^a : 22.3; R_T^b : 35.0; IR: 5.89, 3.42, 10.22, 8.77, 9.12, 6.09, 6.82; m/e : 41(100%), 70(97%), 55(87%), 29(76%), 57(65%), 83(61%), 39(53%), 126(molecular ion, 2%); $\lambda_{\max}^{\text{EtOH}}$ 221 μm .

trans,trans-2,4-Decadienal, R_T^a : 35.0; R_T^b : 53.8; IR: 5.90, 6.08, 3.42, 9.00, 10.13, 9.91, 6.81; m/e : 81(100%), 41(31%), 29(19%), 39(17%), 67(16%), 27(16%), 152(molecular ion, 15%); $\lambda_{\max}^{\text{EtOH}}$ 275 μm .

cis-3-Hexen-1-ol, R_T^a : 11.6; R_T^b : 30.1; IR: 9.53, 3.36, 2.99, 9.76, 6.81, 7.20, 11.53; m/e : 41(100%), 67(72%), 55(41%), 82(40%), 39(31%), 31(28%), 69(27%), 100(molecular ion, 6%).

trans-2-Hexen-1-ol, R_T^a : 11.9; R_T^b : 32.0; IR: 10.30, 3.35, 10.01, 2.99, 9.13, 7.20, 9.55; m/e : 57(100%), 41(42%), 27(31%), 39(25%), 43(20%), 44(19%), 29(18%), 100(molecular ion, 3%).

trans-3-Hexen-1-ol, R_T^a : 11.3; R_T^b : 29.9; IR: 9.55, 10.32, 3.38, 2.97, 6.84, 7.21, 6.96; m/e : 41(100%), 67(50%), 69(42%), 55(39%), 82(33%), 39(26%), 31(24%), 100(molecular ion, 7%).

cis-3-Hexenyl acetate, R_T^a : 19.2; R_T^b : 28.2; IR: 8.06, 5.72, 9.66, 3.37, 7.31, 7.20, 6.84; m/e : 43(100%), 67(54%), 82(52%), 41(17%), 39(9%), 27(7%), 54(7%), 142(molecular ion, 0.05%).

The compounds listed below were synthesized following procedures described in the literature.

cis-2-Penten-1-ol. This compound was prepared by reaction (30) of methylmagnesium bromide and *cis*-4-chlorobut-2-en-1-ol—from commercially available *cis*-2-buten-1,4-diol and purified by GC. R_T^a : 7.6; R_T^b : 26.8; IR: 9.62, 3.37, 3.00, 9.99, 3.48, 3.31, 6.82; m/e : 57(100%), 41(27%), 44(26%), 29(25%), 27(22%), 39(21%), 68(19%), 86(molecular ion, 12%).

trans,trans-3,5-Octadien-2-one. This compound was prepared from *trans*-2-pentenal (30) and acetone, according to the procedure of Grunager and Grieco (11), and purified by GC. R_T^a : 23.6; R_T^b : 42.1; IR: 10.05, 8.00, 5.98, 6.28, 6.10, 7.37, 3.38; m/e : 95(100%), 43(54%), 81(42%), 124(molecular ion, 37%), 39(23%), 41(21%), 109(20%); $\lambda_{\max}^{\text{EtOH}}$ 274 μm .

trans,trans-2,4-Heptadienal. This compound was prepared by reaction of the commercially available 1-methoxy-1-buten-3-yne with ethylmagnesium bromide, followed by treatment of the product so obtained with propanal (20). A sample purified by GC had the following physical properties: R_T^a : 19.1; R_T^b : 38.4; IR: 5.92, 6.07, 8.58, 8.93, 10.13, 9.04, 9.89; m/e : 81(100%), 39(27%), 110(molecular ion, 25%), 41(25%), 53(22%), 27(17%), 67(14%); $\lambda_{\max}^{\text{EtOH}}$ 273 μm .

2,2,6-Trimethylcyclohexanone. This product was obtained by methylation of commercially available 2,6-dimethylcyclohexanone, according to the procedure of Newman, Waltcher, and Ginsberg (19). A sample purified by GC had the following physical properties: R_T^a : 21.0; R_T^b : 33.7; IR: 5.84, 3.42, 6.86, 10.07, 7.21, 8.87, 9.81; m/e : 82(100%), 56(46%), 41(36%), 69(36%), 55(31%), 140(molecular ion, 19%), 70(14%).

cis- and *trans*-2,6,6-Trimethyl-2-vinyl-5-hydroxy-tetrahydropyran (six-membered linalool oxides). Treatment of linalool with monoperphthalic acid in ether, as described by Naves and Bachman (18), followed by distillation, led to the isolation of a fraction rich in the two six-membered linalool oxides. The latter substances (a solid and a liquid at room temperature) were obtained in a pure state by preparative GC, and had infrared and mass spectra identical with those previously published (9). The physical properties of solid and liquid six-membered oxides were as follows: solid oxide: R_T^a : 28.1; R_T^b : 50.3; IR: 9.18, 9.27, 3.37, 10.94, 9.98, 10.18, 7.32; m/e : 68(100%), 59(75%), 43(58%), 94(46%), 41(33%), 67(29%), 27(27%), 170 (molecular ion, 0.1%). Liquid oxide: R_T^a : 28.1; R_T^b : 49.6; IR: 9.27, 9.36, 3.37, 10.93, 10.18, 10.01, 9.80; m/e : 68(100%), 59(71%), 94(54%), 43(50%), 67(30%), 41(30%), 27(21%), 170(molecular ion, 0.1%).

2-Ethylfuran. This product was prepared by Wolff-Kischner reduction of the commercially available 2-acetylfuran (10). A sample purified by GC had the following physical properties: R_T^a : 5.3; R_T^b : 9.3; IR: 9.93, 10.92, 8.72, 3.36, 6.26, 6.82, 9.18; m/e : 81(100%), 96(molecular ion, 55%), 53(20%), 39(11%), 41(8%), 95(8%), 27(6%).

2-Amylfuran. This product was prepared by Wolff-Kischner reduction of 2-valeroylfuran (10). A sample purified by GC had the following physical properties: R_T^a : 18.0; R_T^b : 23.4; IR: 3.41, 9.91, 8.71, 6.80, 6.27, 10.81, 7.23; m/e : 81(100%), 53(26%), 82(24%),

27(22%), 39(16%), 41(16%), 29(15%), 138(molecular ion, 13%).

α -Methylbutyronitrile. This product was prepared from 2-chlorobutane and sodium cyanide in DMSO, according to the procedure of Smiley and Arnold (24). A sample purified by GC had the following physical properties: R_T^a : 5.6; R_T^b : 16.3; IR: 3.37, 6.82, 6.86, 7.21, 4.46, 10.33, 9.88; m/e : 55(100%), 54(34%), 29(17%), 27(11%), 41(7%), 39(6%), 56(4%), 83(molecular ion, 0.2%).

Acknowledgment

For the chromatogram presented in Figure 5, the authors are indebted to Ernest Kugler, Coca-Cola G.m.b.H., Essen, Germany.

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Received for review August 15, 1966. Accepted November 10, 1966. Symposium on Chemical Aspects of Flavor, Division of Agricultural and Food Chemistry, 152nd Meeting, ACS, New York, N. Y., September 1966. Inquiries concerning this paper should be addressed to M. A. Gianturco.