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144. An Investigation of the Tea Aroma
Part I. New Volatile Black Tea Constituents

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(15. V. 74)

Summary. A total of 68 constituents, mainly aldehydes, ketones and esters, have been identified for the first time in a black tea aroma concentrate using coupled gas-chromatography/mass spectrometry.

Introduction. – Tea is one of the world's most widely consumed beverages [1] [2]. The volatile substances that are present in the tea leaves play an important role in determining the overall flavor impression received [2]. Despite the identification of many constituents of green and black tea leaves[1]), a satisfactory reconstitution of black tea aroma proved to be impossible. We therefore undertook a detailed analysis of this aroma and would like to report here on the occurrence of 68 newly identified constituents. Using the direct coupling technique of a mass spectrometer with a glass capillary column, we were able to identify these new components by their mass spectra and their respective retention times. The reference samples were either commercially available or were synthesized.

Results. – New substances are listed in the Table, including the *m/e* values of substances whose mass spectra have not been reported.

The first group in the Table consists of 21 aldehydes, the majority being straight chain alkenals and alkadienals. These represent an expected extension of the few that were already known to exist in tea aroma, since they can be considered as degradation products from lipid precursors [7–11]. β-Cyclocitral and safranal have probably carotenoids as their precursors [12], whereas 2-methylbenzaldehyde and 4-methoxybenzaldehyde might be regarded as degradation products from polyphenolic substances, the largest chemical class found in the young tea shoot [3]. The two 2-phenyl-2-alkenals identified might be derived from the amino acid pairs leucine/phenylalanine and valine/phenylalanine, all known to occur in green tea leaves [13].

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[1]) Two recent reviews by *Sanderson & Graham* [2] and *Sanderson* [3] are a good introduction to the tea literature. For the most recent work on black tea aroma since the latest review [2], see [4] [5] [6].

Table. *New Volatile Black Tea Constituents*

	MW	MF	source of reference sample	mass spectra or references	
				8 strongest m/e values (relative abundance)	other characteristic peaks
1. ALDEHYDES					
cis-3-pentenal	84	C_5H_8O	1 [36]	55(100), 29(69), 27(45), 41(44), 39(40), 84(36), 56(24), 43(18)	83(14), 69(10)
trans-2-heptenal	112	$C_7H_{12}O$	2	3	
trans-2-nonenal	140	$C_9H_{16}O$	1	3, 4, 5a	
trans-2-decenal	154	$C_{10}H_{18}O$	1	3	
trans-2-undecenal	168	$C_{11}H_{20}O$	1	70(100), 41(98), 57(88), 55(83), 43(81), 83(71), 29(55), 69(53)	97(22), 150(4), 168(2)
trans-2,cis-4-hexadienal	96	C_6H_8O	7	7	
trans-2,trans-4-octadienal	124	$C_8H_{12}O$	2	81(100), 39(26), 41(26), 67(18), 27(18), 53(16), 54(13), 124(12)	95(7)
trans-2,cis-4-octadienal	124	$C_8H_{12}O$	7	7	
trans-2,trans-4-nonadienal	138	$C_9H_{14}O$	2	3, 4, 5a	
trans-2,cis-4-nonadienal	138	$C_9H_{14}O$	7	7	
trans-2,cis-6-nonadienal	138	$C_9H_{14}O$	2	41(100), 70(67), 69(65), 39(26), 27(18), 67(18), 53(11), 55(11)	81(7), 109(4), 138(0)
trans-2,cis-4-decadienal	152	$C_{10}H_{16}O$	7	7	
neral	152	$C_{10}H_{16}O$	1	3	
β-cyclocitral	152	$C_{10}H_{16}O$	1	4	
safranal	150	$C_{10}H_{14}O$	1	[37]	
2-methylbenzaldehyde	120	C_8H_8O	2	3, 4, 5a	
4-methoxybenzaldehyde	136	$C_8H_8O_2$	2	3, 4, 5a	
4-methyl-2-phenyl-2-pentenal	174	$C_{12}H_{14}O$	1	4	
5-methyl-2-phenyl-2-hexenal	188	$C_{13}H_{16}O$	1	4	
4-ethyl-7,11-dimethyl-trans-2, trans-6,10-dodecatrienal (1a)	234	$C_{16}H_{26}O$	6	69(100), 41(50), 98(37), 81(27), 55(10), 95(9), 67(9), 137(9)	234(2), 205(1), 216(1)
1b, trans-2,cis-6 isomer of 1a	"	"	6	"	
2. KETONES					
2-heptanone	114	$C_7H_{14}O$	2	3, 4, 5a, c	
5-isopropyl-2-heptanone	156	$C_{10}H_{20}O$	1	43(100), 58(22), 57(20), 71(19), 41(16), 69(15), 98(15), 55(14)	113(7), 123(3), 156(3)
2-octanone	128	$C_8H_{16}O$	2	3, 4, 5a	
3-octanone	128	$C_8H_{16}O$	2	3, 4, 5b	
trans-3,cis-5-octadien-2-one	124	$C_8H_{12}O$	1	95(100), 43(89), 81(66), 39(32), 124(31), 53(30), 41(29), 79(29)	27(22), 109(20)
2-nonanone	142	$C_9H_{18}O$	2	3, 4, 5a	
6,10-dimethyl-2-undecanone	198	$C_{13}H_{26}O$	1	[38]	
benzyl ethyl ketone	148	$C_{10}H_{12}O$	2	57(100), 29(40), 91(39), 65(13), 148(12), 92(10), 39(8), 27(6)	-
2,6,6-trimethylcyclohex-2-en-1-one	138	$C_9H_{14}O$	1	82(100), 54(24), 138(14), 39(10), 41(8), 83(6), 27(5), 53(4)	95(4), 110(2), 123(1)
2,6,6-trimethylcyclohex-2-en-1,4-dione	152	$C_9H_{12}O_2$	1	68(100), 96(88), 40(45), 152(41), 39(37), 41(21), 69(11), 109(10	137(7), 124(4)
β-damascenone (7)	190	$C_{13}H_{18}O$	1	[17]	
α-damascone (8)	192	$C_{13}H_{20}O$	1	69(100), 123(22), 81(19), 41(18), 192(15), 39(7), 43(5), 107(5)	135(4), 177(3)
β-damascone (9)	192	$C_{13}H_{20}O$	1	177(100), 69(79), 41(73), 121(60), 192(58), 123(55), 43(46), 81(42)	107(39), 135(26), 149(18)
1,5,5,9-tetramethylbicyclo[4.3.0] non-8-en-7-one (10)	192	$C_{13}H_{20}O$	1	110(100), 123(57), 177(48), 41(26), 192(24), 109(22), 121(19), 95(16)	135(7), 149(6), 164(4)
3. ESTERS					
hexyl formate	130	$C_7H_{14}O_2$	1	3, 4, 5a	
trans-2-hexenyl formate	128	$C_7H_{12}O_2$	1	67(100), 41(99), 57(91), 82(73), 27(49), 39(43), 55(43), 29(40)	99(20), 71(10), 128(1)
cis-3-hexenyl formate	128	$C_7H_{12}O_2$	1	[39]	
trans-2-hexenyl acetate	142	$C_8H_{14}O_2$	1	3, 4, 5a	
ethyl phenylacetate	164	$C_{10}H_{12}O_2$	2	3, 4, 5a	
hexyl phenylacetate	220	$C_{14}H_{20}O_2$	1	43(100), 91(77), 136(32), 92(27), 41(19), 57(15), 137(14), 65(11)	129(11), 220(3)
trans-2-hexenyl propionate	156	$C_9H_{16}O_2$	1	57(100), 29(32), 67(23), 41(19), 55(19), 82(15), 27(10), 39(7)	100(5), 156(2)
trans-3-hexenyl propionate	156	$C_9H_{16}O_2$	1	57(100), 67(77), 82(66), 29(46), 41(21), 27(15), 55(15), 39(10)	105(2), 156(0)
cis-3-hexenyl propionate	156	$C_9H_{16}O_2$	1	[39]	

Table, continuation

	MW	MF	source of reference sample	mass spectra or references	
				8 strongest m/e values (relative abundance)	other characteristic peaks
cont. ESTERS					
hexyl butyrate	172	$C_{10}H_{20}O_2$	1	3, 4, 5b	
trans-2-hexenyl butyrate	170	$C_{10}H_{18}O_2$	1	71(100), 43(51), 41(27), 67(24), 55(23), 82(18), 27(14), 39(11)	100(5), 170(3)
trans-3-hexenyl butyrate	170	$C_{10}H_{18}O_2$	1	67(100), 82(94), 43(91), 71(86), 41(39), 27(25), 55(20), 39(19)	170(0)
benzyl butyrate	178	$C_{11}H_{14}O_2$	1	3, 4, 5a	
cis-3-hexenyl 2-methylbutyrate	184	$C_{11}H_{20}O_2$	2	82(100), 57(89), 67(79), 41(33), 85(32), 29(23), 55(19), 27(11)	103(3), 184(0)
trans-2-hexenyl hexanoate	198	$C_{12}H_{22}O_2$	1	3, 4, 5a	
cis-3-hexenyl trans-2-hexenoate	196	$C_{12}H_{20}O_2$	1	3, 4, 5a	
trans-3-hexenyl cis-3-hexenoate	196	$C_{12}H_{20}O_2$	1	82(100), 67(75), 41(73), 69(62), 55(61), 83(24), 39(18), 27(14)	97(11), 114(4), 196(0)
methyl octanoate	158	$C_9H_{18}O_2$	2	3, 4, 5a, b	
ethyl octanoate	172	$C_{10}H_{20}O_2$	2	3, 4, 5a, b	
methyl trans-dihydrojasmonate	226	$C_{13}H_{22}O_3$	1	83(100), 156(29), 153(28), 82 (27), 55(21), 41(20), 96(11), 43(11)	195(5), 226(5)
4. MISCELLANEOUS					
2-ethyl-1-hexanol	130	$C_8H_{18}O$	1	3, 4, 5a, b	
4-terpineol	154	$C_{10}H_{18}O$	1	3, 4	
4-methyl-5-hexen-4-olide	126	$C_7H_{10}O_2$	1	111(100), 43(86), 55(77), 71(53), 27(42), 67(42), 56(34), 41(29)	99(28), 83(24), 126(15)
carvacrol	150	$C_{10}H_{14}O$	2	3, 4	
thymol	150	$C_{10}H_{14}O$	2	3, 4, 5a	
2-acetylfuran	110	$C_6H_6O_2$	2	3, 4, 5a, b	
safrole	162	$C_{10}H_{10}O_2$	1	4	
2, 6, 10, 10-tetramethyl-1-oxa-spiro [4, 5]dec-6-ene (**11**, "theaspirane")	194	$C_{13}H_{22}O$	1	138(100), 82(33), 96(24), 83(16), 109(15), 41(15), 43(13), 55(12)	123(11), 179(4), 194(1)
6, 7-epoxy-2, 6, 10, 10-tetramethyl-1-oxa-spiro[4, 5]decane (**12**, "6, 7-epoxy-dihydrotheaspirane")	210	$C_{13}H_{22}O_2$	1	43(100), 126(63), 154(62), 55(60), 125(51), 41(50), 69(46), 111 (33)	85(29), 139(27), 210(25)
6-hydroxy-2, 6, 10, 10-tetramethyl-1-oxa-spiro[4, 5]decane (**13**, "6-hydroxy-dihydrotheaspirane")	212	$C_{13}H_{24}O_2$	1	85(100), 43(89), 126(89), 86(72), 84(52), 69(46), 41(44), 109(29)	170(13), 197(7), 212(5)
phenylacetic acid	136	$C_8H_8O_2$	2	3, 4, 5a	
trans-geranic acid	168	$C_{10}H_{16}O_2$	1	69(100), 41(79), 39(21), 100(19), 27(15), 123(10), 29(10), 53(9)	168(4), 150(2), 153(2)
trans-2-octenoic acid	142	$C_8H_{14}O_2$	1	41(100), 73(99), 29(93), 55(84), 70(71), 42(57), 27(48), 82(47)	86(39), 124(16), 142(1)

1) Own collection.

2) Commercially available.

3) 'Atlas of Mass Spectral Data', Vol. 1, 2 and 3, 1969, edited by *E. Stenhagen, S. Abrahamsson & F. W. McLafferty*, Interscience Publishers, John Wiley & Sons.

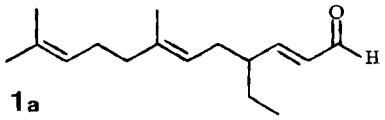
4) 'Eight Peak Index of Mass Spectra', Vol. 1 and 2, 1970, 1st Edition, published by: Mass Spectrometry Data Centre, AWRE, Aldermaston, Reading, RG7 4PR, U.K.

5) a) 'Compilation of Mass Spectral Data', *A. Cornu & R. Massot*, 1966, published by: Heyden & Son Limited (in corporation with Presses Universitaires de France), Great Britain; b) First supplement to 5a, 1967; c) Second supplement to 5a, 1971.

6) See Experimental Part: B. Synthesis.

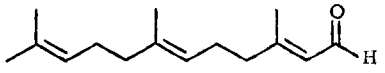
7) Identification of all *trans*-2, *cis*-4-alkadienals was based on the fact that a) there was almost no difference in mass spectral fragmentation pattern between the *trans*-2,*trans*-4 and the *trans*-2,*cis*-4 isomers; the spectral data of which have been described in detail in the case of *trans*-2,*trans*-4-decadienal and its *trans*-2,*cis*-4 isomer [16], and b) the availability of the latter substance [16] allowed us to establish the retention times for the other *trans*-2,*cis*-4 isomers in relation to their *trans*-2,*trans*-4-dienals.

The same two alkenals occur in cocoa and are considered to originate from the same amino acids [14]. Among the aldehydes identified, 4-ethyl-7,11-dimethyl-*trans*-2,*trans*-6,10-dodecatrienal (**1a**) is a unique homosesquiterpene aldehyde (*cf.* farnesal (**2**)).



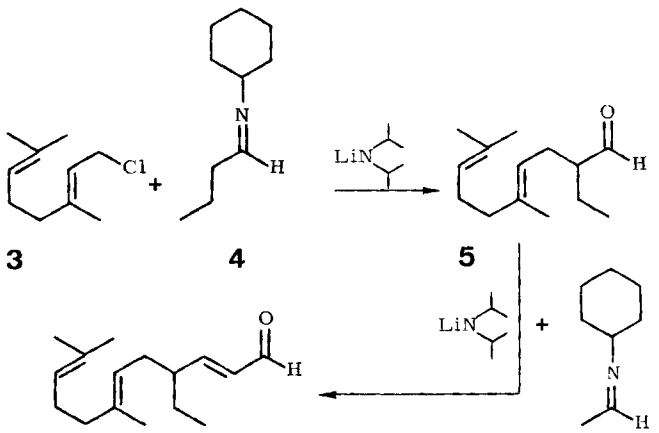
1a

1b ***trans*-2,*cis*-6 isomer of 1a**



2

Starting with geranyl chloride, compound **1** was synthesized in two steps using *Wittig's* 'directed aldol condensation'[2]).



3 **4** **5**

1a ***trans*-2, *trans*-6**

1b ***trans*-2, *cis*-6**

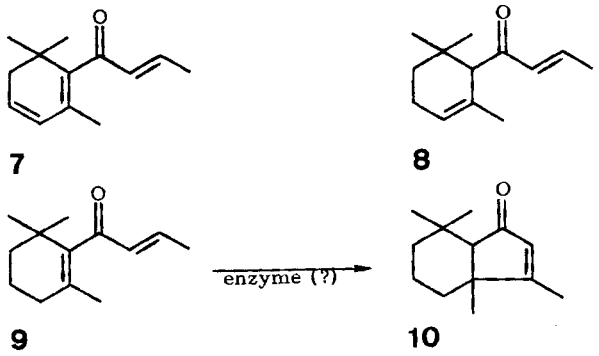
6

The major product of the synthesis, obtained as a 3:1 mixture of the *trans*-2,*trans*-6-(**1a**) and *trans*-2,*cis*-6-(**1b**) isomer (see Exper. Part), was identical in retention time and mass spectral fragmentation with the natural material. In addition, a second peak in the tea aroma concentrate corresponded to the *trans*-2,*cis*-6-(**1b**) isomer of the synthetic substance. The natural occurrence of the latter compound, **1b**, could be due to partial isomerization of **1a**, but we cannot exlude the possibility of its presence in the green tea leaf[3]).

[2]) For a similar application, see the synthesis of β-sinensal by *Büchi & Wüest* [15].

[3]) In addition, the natural existence of the *cis*-2,*trans*-6- and the *cis*-2,*cis*-6 isomers of **1** is implied by the presence of two minor peaks having a mass spectral fragmentation similar to **1a**. Not having been separated from some other compounds of unknown structure, their positive identification was impossible.

A total of 14 newly identified ketones are listed in the second group in the Table. 2- and 3-Alkanones may be derived from oxidized lipids [10] and it would therefore not be surprising to encounter them in tea aroma. The 5-isopropyl-2-heptanone is probably derived from a menthene precursor. Contrary to recently published results [5], we were able to positively identify a 3,5-octadien-2-one, as the *trans*-3,*cis*-5 isomer[4]). β-Damascenone (**7**), isolated for the first time from Bulgarian rose essential oil [17], α-damascone (**8**) and β-damascone (**9**), have now also been identified in tea. This finding further substantiates the importance of carotenoids as precursors of tea volatiles [12], and from which these three ketones **7**, **8** and **9** are thought to be derived [18]. Interestingly enough, a cyclization product from β-damascone, namely the bicyclic ketone (**10**) [19], has been shown to exist in the tea aroma concentrate. The occurrence of this ketone might be accounted for by an enzymatic cyclization of



β-damascone, either biosynthetically at the green leaf stage or during the actual black tea manufacturing process, rather than by the known acid catalyzed cyclization (*cf.* [19]), which necessitates drastic reaction conditions (85% H_3PO_4). 2,6,6-Trimethylcyclohex-2-ene-1,4-dione is the result of a 'logical' oxidative extension of 2,6,6-trimethylcyclohex-2-en-1-one.

Several new esters (the third group in the Table) have also been identified. Most of them are hexenyl esters of lower straight chain saturated and unsaturated acids, the corresponding alcohols and acids having been among the first constituents to be identified in tea aroma [20–24]. Besides methyl jasmonate, recently found in tea [4], an ester we have also encountered, we identified methyl *trans*-dihydrojasmonate[5]). This substance, a well known fragrance [25] [26], has thus, as far as we know, been identified in nature for the first time. Dihydro compounds corresponding to many of the unsaturated substances present in tea volatiles have been identified[6]). For example 2,6,6-trimethylcyclohexanone accompanies 2,6,6-trimethylcyclohex-2-en-1-one, and both alkenals and alkanals occur.

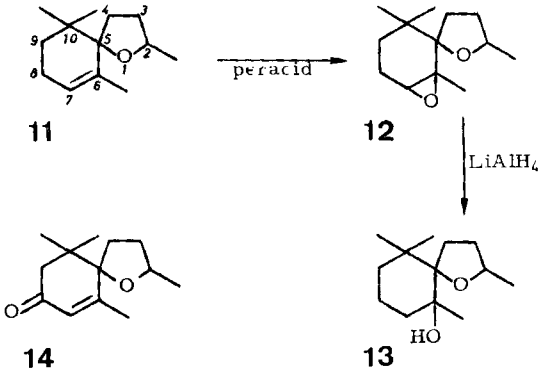
The last and fourth group in the table lists several classes of substances together. Some of them deserve more comment, namely the three 1-oxa-spiro[4,5]decane

[4]) Prepared *via* a stereoselective synthesis, see [16].

[5]) Hedione® (trade mark of *Firmenich SA*, Geneva).

[6]) This relationship has also been observed, for example, in an analysis of the oil of Bergamot [27] where a related compound, dihydrojasmone (3-methyl-2-pentyl-cyclopent-2-en-1-one) has been found as a trace component together with *cis*- and *trans*-jasmone.

derivatives, 2,6,10,10-tetramethyl-1-oxa-spiro[4,5]dec-6-ene (**11**, 'theaspirane'), 6,7-epoxy-2,6,10,10-tetramethyl-1-oxa-spiro[4,5]decane (**12**, '6,7-epoxy-dihydrotheaspirane') and 6-hydroxy-2,6,10,10-tetramethyl-1-oxa-spiro[4,5]decane (**13**, '6-hydroxydihydro-theaspirane').



11 **12** **14** **13**

'Theaspirone' (**14**) [28] was until now the only known member of this class found in tea aroma. Starting with 2,6,10,10-tetramethyl-1-oxa-spiro[4,5]dec-6-ene (**11**, 'theaspirane') [29], **12** and **13** were synthesized as indicated in the above scheme[7]). Linalool or linalool oxides are probable precursors for 4-methyl-5-hexen-4-olide, a product also identified in *Burley* tobacco [30] and the oil of *Artemisia pallens* [31].

With the identification of these 68 new constituents, the total number of known volatile tea aroma ingredients has now been increased to well over 200.

Experimental Part

A. Analysis[8]). – 1. *Extraction Procedure.* In a typical experiment, a total of 500 g black tea leaves[9]) was added under nitrogen and with vigorous stirring to 5 l of boiling water during $1^1/_2$ h. At the same time, there was introduced within 2 h 1.5 l of *n*-hexane (purified by extraction with conc. sulfuric acid, washing to neutrality with H_2O, followed by a distillation). The *n*-hexane/water vapors that continuously distilled were condensed and the water phase was reintroduced into the tea infusion at the rate it distilled. The *n*-hexane layer was dried over anhydrous magnesium sulfate, filtered and evaporated to a volume of about 150 ml using a thin film evaporator. After removal of most of the *n*-hexane, using a small column filled with glass helices, the remaining solvent was continuously evaporated under a flow of nitrogen. An acetone dry-ice trap was always used to prevent possible aroma losses during the entire extraction process, as well as during the concentration steps. In this manner there was obtained a black tea aroma concentrate, the taste of which was judged typical of the particular tea used by a panel of experts. Based on 500 g tea leaves used, the yields obtained varied between 60 to 100 ppm depending on the origin of the tea sample (*e.g.* Ceylanese, Indian and Kenyan black teas) and, in part, the variability of the conditions used.

2. *Separation of the black tea aroma concentrate.* Several combined black tea aroma concentrates, obtained as described above, were distilled yielding three fractions: b.p. < 20°/10 Torr, 22%; b.p. 20–30°/0.2 Torr, 41%; b.p. 30–60°/0.001 Torr, 9% and a residue b.p. > 60°/0.001 Torr, 28%.

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[7]) Experimental details, including stereochemical assignments, will be published in due course.

[8]) With the partial technical assistance of Mr. *C. Vanrietvelde.*

[9]) Scale-up of this extraction procedure to 15 kg black tea leaves per batch was possible and we would like to thank Dr. *H. Strickler* and Mr. *S. Riesen* of our Pilot Plant for carrying out these experiments.

These fractions were then subjected to ascending dry column chromatography [32] [33] using methylene chloride as the migrating solvent. After the column had been cut, the different zones were extracted with diethylether, evaporated and concentrated. At this stage a particular fraction could be further divided by a gas-chromatographic (GC.) separation on a packed column using a polar or nonpolar stationary phase. These dry column and gas-chromatographic subfractions and the fractions from the distillation were analyzed using the direct GC./MS.-coupling system described below.

3. *Gas-chromatography (GC.) conditions.* – a) *Capillary columns.* Instrument *Carlo Erba* GT 450, glass capillary column, type *Grob* [34][10], length 33 m × 0.31 mm i.d., coated with UCON HB 5100, a similar column, but of length 50 m × 0.31 mm i.d., temp. 50–160° and 100–180°, Δt = 2°/min., initial temp. isothermal for 3 min., injection port temp. 200°, carrier gas (He) inlet pressure 0.4 kg/cm² and 0.8 kg/cm². – b) *Mass spectrometer coupled directly with gas chromatograph. Atlas* CH4B with a *Becker-Ryhage*-type helium separator at temp. 250°, ionisation source temp. 250°, electron energy 70 eV. – c) *Verification of retention times.* Peaks identified by MS. as new black tea aroma constituents were always verified with at least 2 internal standards having retention times close to the peak in question and being themselves present in the aroma concentrate. – d) *Packed columns for subdividing of fractions.* Instrument *Hewlett-Packard* 5700 A, column length 2.5 m × 2 mm i.d., 15% SP-1000 or 15% SOMB on chromosorb W (80–100 mesh AW/DMCS), temp. 100–220°, Δt = 4°/min., injection port temp. 250°, TCD-temp. 250°.

B. Synthesis. – 1. *General.* GC.-conditions as described under 3d). NMR. spectra were measured in CCl_4 on a *Hitachi Perkin-Elmer* R-20 B and a *Bruker*-HFX-90, chemical shifts are given in ppm with tetramethylsilane as 0.00 ppm. IR. spectra were recorded on a *Perkin-Elmer* 21 spectrometer and analyses were carried out in our microanalytical laboratory.

2. *Butylidenecyclohexylamine* (**4**) *and ethylidenecyclohexylamine* (**6**) were prepared according to *Wittig & Frommeld* [35].

3. *2-Ethyl-5,9-dimethyl*-trans-*4,8-decadienal* (**5**). The reaction sequence below was carried out under N_2. All reagents, except *n*-butyllithium, were dried over molecular sieves before use. To a precooled solution (–70°) of 5.63 g diisopropylamine (55.7 mmol) in 20 ml dry ether there were added all at once with stirring 31.4 ml of a 1.75 N *n*-butyllithium/hexane solution. The mixture was further stirred at –70° for 10 min., then for 15 min. at +3°. After cooling to –10°, a solution of 10.78 g freshly distilled butylidenecyclohexylamine (**4**, 70.5 mmol) in 5 ml dry ether was added dropwise with stirring within 15 min. Stirring was then continued for another 20 min. at +3°. The mixture was precooled to –20° and a solution of 8.63 g geranyl chloride[11] (**3**, 50.4 mmol) in 5 ml ether was added with stirring during 15 min. After further stirring for 20 min. at –10°, the mixture was allowed to reach room temperature overnight. An ice-cold solution of 30 g oxalic acid in 400 ml H_2O was added dropwise with stirring over 30 min. to the precooled (ice-bath) reaction mixture. The mixture was extracted several times with ether; the combined ether layers were washed with H_2O, saturated $NaHCO_3$ sol. and saturated NaCl sol., dried ($MgSO_4$), filtered and evaporated to yield 11.0 g of a yellowish oil, which distilled b.p. 126–128°/10 Torr; yielding 7.39 g of compound **5**. Capillary GC. indicated the expected isomeric mixture of 75% *trans*-4- and 25% *cis*-4 isomers of **5**.

Spectra of **5**. NMR. (60 MHz, CCl_4): 0.90 (3 H, *t*, J = 7 Hz); 1.60 (6 H, *s*); 1.68 (3 H, *s*); 5.05 (2 H, *broad t*); 9.54 (1 H, *d*, J = 2 Hz). – IR. (neat): 2970 s, 2930 s, 2700 m, 1728 s, 1445 m, 1375 m. – MS.: M^+ 208 (1.5): *m/e*: 69 (100), 41 (64), 57 (44), 55 (23), 44 (17), 29 (13), 43 (13), 81 (13), 39 (10), 93 (10).

4. *4-Ethyl-7,11-dimethyl*-trans-*2*,trans-*6,10-dodecatrienal* (**1a**). Except for the addition of compound **5** (in place of geranyl chloride) at –60° instead of –20°, the foregoing experiment (B. 3) was repeated using 2.07 g diisopropylamine (20.5 mmol) in 20 ml dry ether, 14.3 ml of a 1.75 N *n*-butyllithium/hexane solution, 3.80 g ethylidenecyclohexylamine (**6**, 30.4 mmol) in 10 ml dry ether (in place of compound **4**) and 4.17 g compound **5** (20.0 mmol) in 10 ml dry ether. After the dropwise addition of an ice-cold solution of 10 g oxalic acid in 160 ml H_2O, followed by the usual work-up, there was obtained 5.0 g of an oily residue. A GC. indicated the presence of ca. 60%

[10] Prepared by *H. & G. Jaeggi*, Labor für Gas-Chromatographie, CH–9043 Trogen, Switzerland.

[11] A mixture of ca. 75% *trans*-2- and 25% *cis*-2 isomers.

of compound **1**. Two consecutive column chromatographies on silica gel in hexane/ethyl acetate 20:1 followed by bulb distillation yielded pure **1**, b.p. 108–110°/0.5 Torr. Capillary GC. indicated the presence of 75% *trans-2,trans*-6- (**1a**) and 25% *trans-2,cis*-6- (**1b**) isomer.

Spectra of **1**. NMR. (90 MHz, $CDCl_3$): 0.89 (3 H, *t*, J = 7.5 Hz); 1.61 (6 H, *s*); 1.70 (3 H, *s*); 5.12 (2 H, *broad t*); 6.12 (1 H, $d \times d$, J = 8 Hz and 16 Hz); 6.72 (1 H, $d \times d$, J = 8 Hz and 16 Hz); 9.53 (1 H, *d*, J = 8 Hz). – IR. (neat): 2970 s, 2940 s, 2720 m, 1685 s, 1630 m, 1450 m, 1375 m, 975 m. – MS.: see Table.

$C_{16}H_{26}O$ (234) Calc. C 81.99 H 11.18% Found C 82.03 H 11.40%

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