oleic acid. However, the results showed that the monoene consisted of ca. 75% petroselinic acid and only 8% oleic acid. When the dibasic oxidation products are analyzed as methyl esters the methyl ester of the C_{12} monobasic acid also appears (between C_5 and C_6 dibasic esters) and if the amount is calculated relative to the C_6 dibasic ester it gives an additional check on the petroselinic acid present. The average molar ratio of the C_6 dibasic acid to the C_{12} monobasic acid was 50.5 to 49.5. Christian and Hilditch (5) reported that the oil of *Coriandrum sativum* L. contained 53% petroselinic acid and 32% oleic acid but they were using a much less accurate procedure and also they may have been working with a different variety of coriander seed. The variety of seed used in this work would be a good source of petroselinic acid. The percentage of C_6 monobasic acid agreed quite well with the calculated value and the percentage of C_9 dibasic acid agreed with the sum of the percentages of the C_6 and C_9 monobasic acids, both of which are derived from acids with unsaturation commencing at carbon 9. Thus there was no evidence for the presence of any appreciable amount of acids, other than petroselinic acid, with the first double bond in the 6,7 position. Again ca. 0.5–1% 11-octadecenoic acid was probably present.

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Relationship Between Molecular Structure and Flavor Perceptibility of Aliphatic Aldehydes

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Abstract

The mean threshold values for odor and taste of some aliphatic aldehydes are determined in solutions of paraffin oil. These threshold values lie at low concn and display a distinct alternating effect in the same homologous series. Moreover it appears from experiments with mixtures of various aldehydes that in the case of certain ratios a masking effect in odor and taste occurs.

Introduction

OILS AND FATS, which are present in our daily diet, may develop during the induction period of the autoxidation the so-called reversion flavors (1,2). These flavor carriers formed from the odor- and tasteless-hydroperoxides (3) are mainly aldehydes. An investigation on odors is difficult, because the odor carriers and their precursors are present in very low concn. Although they can be clearly observed organoleptically, the picture of the composition of the volatile substances can be obtained only with very sensitive gas chromatographic methods (head space analysis).

Since it appears that this volatile part contains a large number of components, the question arises how and to what extent the type of reversion flavors is determined by these components. Does a single component with a "top fragrance" with respect to the other components in the same system play a predominant role? Are there other factors such as synergism and/or antagonism (intensifying respectively masking effects) which influence the taste of the fat in question? As aldehydes are important as flavor carriers, an investigation has been initiated into the relationship between the molecular structure and taste and odor of saturated and unsaturated aldehydes.

Results of a similar investigation in the field of perfumes have been published by Beets (4). Lea and Swoboda (5) have determined the flavor threshold value in water, in groundnut oil, and in paraffin oil, of a number of saturated and of two unsaturated aldehydes.

Our experiments were carried out with aldehydes of various homologous series and the mean threshold values for odor and taste in paraffin oil were determined in order to investigate the influence of chain length, of number and position of the double bonds and of stereo-isomerism (*cis-trans*).

Moreover, by means of experiments with mixtures of various aldehydes the mutual influence in some cases was demonstrated

Experimental

Saturated aldehydes. Saturated unbranched aliphatic aldehydes (C_3–C_{12}) were purified by distilling commercially available products respeatedly; if necessary the purification took place via their sodium bisulphite addition product. The purity (according to the GLC analysis) was increased to 98% or more. The substances dosed gravimetrically were dissolved in paraffin oil with concn of 0.0001, 0.001 etc. up to 1000 ppm inclusive, and to guarantee a homogeneous

TABLE I

Flavor Potential of Saturated and Unsaturated Aldehydes Dissolved in Paraffin Oil

Substance	Threshold in ppm		Lea and Swoboda (5) (taste)
	Odor	Taste	
Propanal	3.6	1.6	1.0
Butanal	0.15	0.024	0.7
Pentanal	0.24	0.15	....
Hexanal	0.32	0.15	0.6
Heptanal	3.2	0.042	....
Octanal	0.32	0.068	0.6
Nonanal	13.5	0.32	....
Decanal	6.7	1.0	0.7
Undecanal	6.8	0.1	....
Dodecanal	3.0	0.046	0.4
2 *trans*-pentenal	2.3	0.32	....
2 *trans*-hexenal	10.0	2.5	....
2 *trans*-heptenal	14.0	0.63	....
2 *trans*-octenal	7.0	1.0	....
2 *trans*-nonenal	3.2	0.1	0.4
2 *trans*-decenal	33.8	5.5	....
2 *trans*-undecenal	150.0	4.2	....
2 *trans*-dodecenal	36.0	6.3	....
3 *cis*-hexenal	0.11	0.11	....
3 *trans*-hexenal	1.2	1.2	....
2 *trans*,4 *trans*-hexadienal	0.27	0.036	....
2 *trans*,4 *trans*-heptadienal	10.0	0.46	....
2 *trans*,4 *trans*-octadienal	1.0	0.15	....
2 *trans*,4 *trans*-nonadienal	2.5	0.46	....
2 *trans*,4 *trans*-decadienal	2.15	0.28	....
2 *trans*,4 *cis*-heptadienal	3.6	0.055	....
2 *trans*,5 *cis*-octadienal	15.0	0.21	....
2 *trans*,6 *cis*-nonadienal	0.01	0.002	....
2 *trans*,7 *cis*-decadienal	0.048	0.02	....
2 *trans*,6 *trans*-nonadienal	0.21	0.018	....
2 *trans*,7 *trans*-decadienal	1.0	0.32	....

solution, the mixture was stirred magnetically for ca. 20 min in brown, wide mouthed bottles (capacity 50 ml) which had been thoroughly cleaned and steamed.

These solutions were assessed for odor and taste by a test panel of 10 persons who were not specially trained; a sample of pure paraffin oil was used as a blank.

The results were obtained in accordance with the method by Patton (6), by plotting the percentage of positive responses against the logarithm of the concn, after which the mean threshold value (50% positive response) for odor and taste could be read from the graph obtained. The aldehydes investigated show in Table I.

Unsaturated aldehydes. The unsaturated aldehydes investigated were synthesized in our laboratory. (Some of these have not yet been mentioned in the literature and will be published elsewhere). To prepare the solutions known amounts of pure fractions were collected by means of gas chromatography in a column filled with glass beads and a small amount of paraffin oil. Subsequently the contents were transferred with 10 g paraffin oil into a 50-ml brown wide mouthed bottle after which the mixture was stirred magnetically for ca. 20 min. The dilutions of this stock solution were prepared in the same way as stated above and the odor and taste assessments were again carried out by the same test panel.

The determined threshold values show in Table I.

Experiments with mixtures of various aldehydes. Known amounts of 3 *cis*-hexenal, likewise in paraffin oil, were added to a known amount of 2 *trans*,4 *trans*-decadienal in paraffin oil and the mixture assessed for flavor. The results show in Table II.

TABLE II

Antagonistic Effect on the Odor of 3 *cis*-hexenal

Odor assessment	Composition of the mixture in paraffin oil	
	3 *cis*-hexenal (ppm)	2 *trans*, 4 *trans*-decadienal (ppm)
Decadienal	3.3	26.3
Decadienal	6.2	24.7
Decadienal	8.8	23.3
Decadienal	11.1	22.1
Decadienal + weakly green beans	13.2	21.0
Decadienal + weakly green beans	9.2	10.5
Only weakly green beans	1.4	1.6
Weakly green beans	0.1	.....
Green beans	1.0	.....

Results and Discussion

Table I shows the result of the taste and odor experiments with saturated unbranched aldehydes and unsaturated unbranched aldehydes. From propanal up to dodecanal, the concn of the threshold values for the odor lie in the order of 10–0.1 ppm and for the taste of 1–0.01 ppm. Lea and Swoboda (5) have found considerably higher threshold values for some of these aldehydes. Since the authors give no details about the substances they used, the differences might be attributed to differences in purity of the aldehydes. A definite relation between the threshold value and the chain length of the compound cannot be concluded from values in Table I. This is in correspondence with the work by Lea and Swoboda. Since the bp in the series of investigated aldehydes rise monotonously with increasing chain length ($bp_{1\,atm}$ C_3 : 21C; $bp_{1\,atm}$ C_{12} : 235C) the conclusion might be that at least in the interval C_9–C_{12}, the number of molecules required to stimulate the olfactory receptors decreases with increasing mol wt. In all cases the threshold values for taste are lower than those for odor; this also is found with the unsaturated aldehydes.

In this respect it may be noted that for aldehydes also the gradually more accepted rule applies that the taste assessment takes in fact place on the odor receptors in the nose, and consequently can be qualified as odor.

In the series of the 2 *trans*-alkenals for the odor threshold values at concn ranging between 100–1 ppm and for the taste between 1–0.1 ppm were found. If the separate values are compared with those of the saturated aldehydes with the same chain length, it appears that on introducing a *trans*-double bond in the α-β position the threshold value rises. The C_9-homologue forms an exception to this rule.

The investigation into the influence of the double bond (*cis* or *trans*) in another position in the chain is being carried out. From the threshold value found for the 3 *trans*-hexenal it appears that the position of the double bond in alkenals influences the flavor intensity. If the threshold values for taste of these alkenals are plotted as a function of the chain length it appears that there is an alternating effect (Fig. 1). The aldehydes in this series with an uneven number of carbon atoms have a lower threshold value than the corresponding aldehydes with even numbers.

An extension of the investigation in the series of the 2-alkenals into the influence of the *cis*-double bond in the α-β position cannot be realized; attempts to synthesize the 2 *cis*-alkenals resulted in formation of the stabler *trans*-alkenals (7).

In the series of 2 *trans*,4 *trans*-alkadienals an analogous effect was observed. If the threshold values for the odor (10–0.1 ppm) and for the taste (0.1–0.01 ppm) are plotted against the chain length, lower threshold values are found for the aldehydes with an even number of carbon atoms than for those with uneven number in contrast with the previous series (Table I). The investigation is also here restricted to the 2 *trans*,4 *trans*-alkadienals, since the 2 *cis*,4 *trans* and 2 *cis*, 4 *cis* compounds are no more stable than the 2 *cis*-alkenals.

In addition, a homologous series of alkadienals with the *trans*-double bond in the α-β-position and a *cis*-

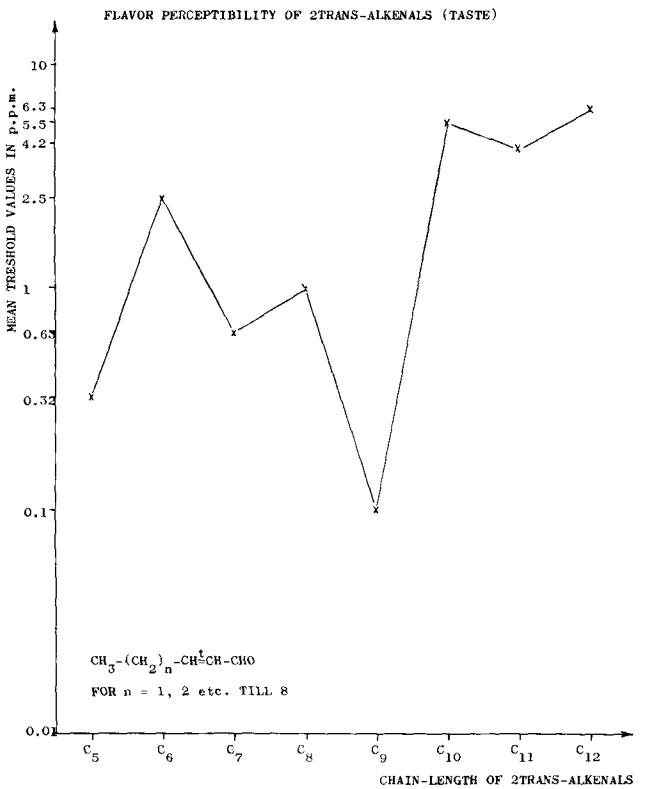

FIG. 1. Flavor perceptibility of 2*trans*-alkenals (taste).

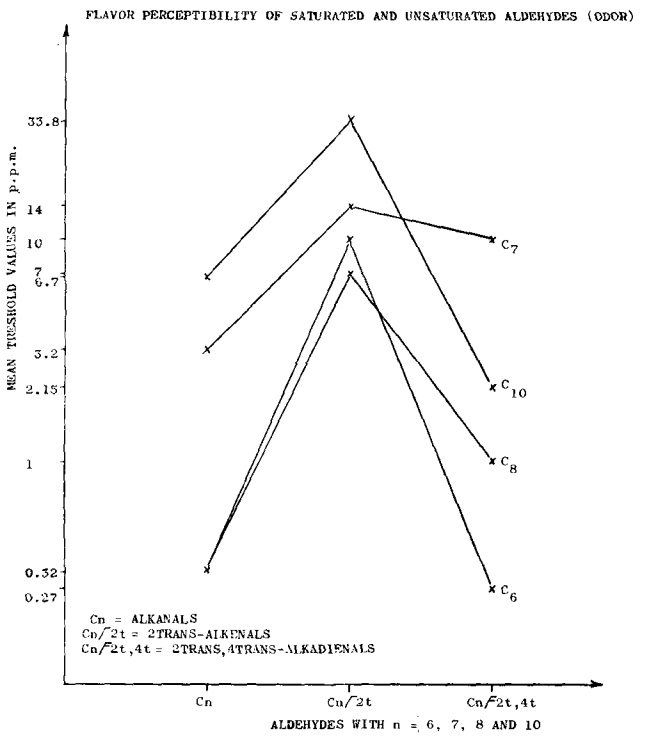

FIG. 2. Flavor perceptibility of saturated and unsaturated aldehydes (odor).

C_n = alkanals.
$C_n\lceil 2t$ = 2*trans*-alkenals.
$C_n\lceil 2t,4t$ = 2*trans*,4*trans*-alkadienals.

double bond between carbon atoms 3 and 4 (terminal position), was investigated. Also here this alternating effect was observed and was again in correspondence with that of the 2 *trans*-alkenals (Table I).

We have found this alternating effect in various series of odor and taste experiments, but an explanation for this phenomenon has not yet been found. However, it is generally known that various homologous series display alternating effects in the case of certain physical properties as for instance the melting points, and heat of crystallization. Such alternating effects usually refer to a physical property of the crystalline state of the substance in question. It is therefore not impossible that during the odor and taste perception molecular orientation plays a part.

Further it appears from Table I that when in the chain of the 2 *trans*-alkenal a *trans*-double bond is introduced in the 4th position (conjugated diene system) the threshold value decreases with respect to the alkenal (Fig. 2).

The fact that also here the position of this second double bond is of great importance appears from the threshold value of the alkadienals having a double bond in the 3-4 position, terminally. The difference in threshold value, is considerable in some cases.

With respect to the *cis-trans* isomerism it appears by comparing the threshold values of:

2 *trans*,4 *cis*-heptadienal
2 *trans*,6 *cis*-nonadienal
2 *trans*,7 *cis*-decadienal
3 *cis*-hexenal

with those of their respective *trans*-isomers that the *cis*-double bond in these cases yields a higher flavor intensity (8). However, this is no proof at all that we can speak of a general rule.

From Table II it can be deduced that in the presence of larger amounts of decadienal, the 3 *cis*-hexenal in a concentration of 13.2 ppm is only weakly observed whereas the threshold value is 0.1 ppm.

Such an antagonistic effect on the odor of 3 *cis*-hexenal is also displayed by the 2 *trans*-nonenal. At a concentration of 4.5 ppm the 3 *cis*-hexenal is only weakly observed, when 2 *trans*-nonenal is present in a concentration of 2.8 ppm. The latter concn lies even below its threshold value.

On mixing 3 *cis*-hexenal and 2 *trans*,4 *trans*-heptadienal (respectively concentrations of 13.2 and 12.5 ppm) an odorless and almost tasteless mixture likewise was obtained.

From the above experiments with aldehydes it appears that during the reversion extinguishing or masking effects of odor and taste properties may occur. A similar effect was illustrated by Wright (9) with a mixture of nitro-benzene and methyl-salicylate. However, with respect to the reversion flavor, also additive effects may be expected, which assumption is supported by observations made by Lillard et al. (10).

In order to gain a better insight into this complicated interplay of various known and as yet unknown components, a thorough knowledge of the relationship between molecular structure and perception of aldehydes is indispensable.

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