Thus, a straightforward three-step method has been developed for the preparation of the synthetic spearmint-flavoring ingredient, (−)-carvone. A second product, piperitenone, which is useful as an intermediate in the synthesis of menthol, was also produced in a good yield and partially purified.

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Olfactive Properties of a Number of Polysubstituted Pyrazines

Henk J. Takken,* Leendert M. van der Linde, Mans Boelens, and Johannes M. van Dort

Alkoxyalkylpyrazines have previously been reported to be very potent naturally green smelling compounds. A number of this type of pyrazines have been identified in natural products. We have synthesized the following series of pyrazines: two monomethoxy- and four dimethoxy(di)alkylpyrazines; 2-methyl-, 2-methoxy-, 2-methylthio-, and 2-dimethylamino-3-isobutylpyrazine; 2-methylamino-3-methyl-, 2-dimethylamino-3(and 6)-methyl- and 2-dimethylamino-3(and 6)-isobutylpyrazine; four methoxyacetylalkylpyrazines and two methoxy-(α-hydroxyisopropyl)methylpyrazines. Odor descriptions are given and compared within each series. Odor threshold values of a number of these pyrazines are measured and presented together with threshold values of pyrazines reported in the literature.

The occurrence of pyrazine derivatives in natural products was indicated for the first time by Morin in 1888. Not before 1928, however, was it discovered that these types of compounds were useful aroma constituents. Then a patent was granted to Reichstein and Staudinger (1928); the use of pyrazines in combination with other compounds was claimed for the preparation of a synthetic coffee oil. After the introduction of advanced analytical methods in aroma research around 1960, it was found that pyrazines occur widely in natural products, particularly in roasted products like coffee, cocoa, and nuts.

The concentration of pyrazine derivatives in these products is often very low. However, their contribution to the odor complex may still be essential because many of them have very low threshold values.

Until 1969 only pyrazines with substituents consisting of carbon and hydrogen have been found. In this report we will pay attention to pyrazines with at least one substituent containing a heteroatom, viz. methoxy-, methylthio-, dimethylamino-, and acetylpyrazines.

In 1969 (a,b) Buttery et al. reported the isolation of 2-methoxy-3-isobutylpyrazine from green bell peppers. The extremely potent odor of this compound was shown to be characteristic for the aroma of bell peppers. Also in 1969 Bramwell et al. reported the identification of two alkoxypyrazines in the oil of galbanum, viz. 2-methoxy-3-*sec*-butylpyrazine and 2-methoxy-3-isobutylpyrazine. Apart from these two pyrazines Murray et al. (1970) showed the presence of 2-methoxy-3-isopropylpyrazine in green peas and in galbanum oil. In this oil Burrell et al. (1970) detected 2-methoxy-3-isopropyl-5-methylpyrazine, 2,6-dimethoxy-3-isopropyl-5-methylpyrazine, and some alkyl-substituted pyrazines.

Duprey and Janes (1971) reported the existence of 2-methoxy-3-isopropyl-, 2-methoxy-3-isobutyl-, and 2-methoxy-3-isopropyl-5-methylpyrazine in the oil of petit grain. Buttery and Ling (1973) have proven the presence of 2-methoxy-3-isopropylpyrazine in potatoes, while in potato sprouts 2-methoxy-3-ethylpyrazine is identified by Nursten and Sheen (1974).

Very recently an extensive review was published in this journal by Maga and Sizer (1973) concerning pyrazines identified in foods. Patent literature clearly shows the importance of pyrazines as flavor constituents or perfume components. An investigation of some essential oils in our laboratory (Timmer, 1973) revealed the occurrence of a number of polysubstituted mono- and dimethoxyalkylpyrazines, as well as methoxyacetyl- and methoxy-α-hydroxyisopropylpyrazines.

For an olfactive study we have synthesized some representatives of these classes of pyrazines, as well as a number of alkylaminopyrazines. Odor descriptions will be given. We measured the odor threshold values of some of these pyrazines. These figures will be given together with threshold values of pyrazines reported in the literature.

EXPERIMENTAL SECTION

Synthesis and Spectral Data. Descriptions of the syntheses as well as the infrared, mass spectral, and nuclear magnetic resonance (NMR) data of the pyrazines mentioned in this report have been deposited in the microfilm edition of this volume of the journal (see paragraph at end of paper).

Odor Evaluation. Descriptions of the olfactive properties were given by three expert perfumers. The compounds were smelled on blotters at appropriate dilutions in diethyl

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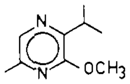
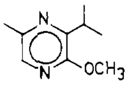
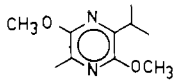
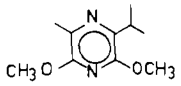
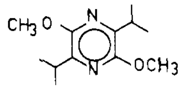
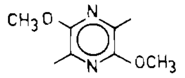
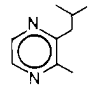
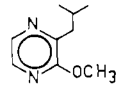
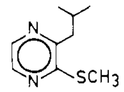
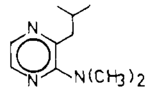
Table I. A Number of Mono- and Dimethoxyalkylpyrazines; Their Natural Occurrence and Odor Quality

No.	Pyrazine derivative	Formula	Identified in oil of	Odor description
I	2-Methoxy-3-isopropyl-6-methyl			Strongly green (green bean like), no nutty or floral notes
II	2-Methoxy-3-isopropyl-5-methyl		Galbanum,[a,b] absinth,[b] rosemary,[b] clary sage,[b] angelica root,[b] coriander seed,[b] carrot seed,[b] petit grain,[c] parsley seed[b]	Strongly green (green bean like), floral and ethereal undertone, no nutty notes
III	2,5-Dimethoxy-3-isopropyl-6-methyl			Green (bell pepper like), nutty notes
IV	2,6-Dimethoxy-3-isopropyl-5-methyl		Galbanum,[a,b] angelica root,[b] geranium[b]	Nutty, green (bell pepper like), woody bynote
V	2,5-Dimethoxy-3,6-diisopropyl			Green (bell pepper like), nutty notes, weakly sweet
VI	2,5-Dimethoxy-3,6-dimethyl			Green (bell pepper like), nutty notes, floral and ethereal undertone

[a] Burrell et al. (1970). [b] Timmer (1973). [c] Duprey and Janes (1971).

Table II. Isobutylpyrazines with Different Substituents on the 2 Position and Their Natural Occurrence

No.	Pyrazine derivative	Formula	Identified in oil of	Odor description
VII	2-Methyl-3-isobutyl		Coffee,[a] potato chips,[b] coriander seed[c]	Green (bell pepper like), dry and sweet notes
VIII	2-Methoxy-3-isobutyl		Bell peppers,[d,e] green peas,[f] coffee,[g] galbanum,[c,f,h] petit grain,[c,i] clary sage,[c] angelica root[c]	Strongly green (bell pepper like)
IX	2-Thiomethyl-3-isobutyl			Weakly green, roasted peanuts, cheese like (Camembert) note
X	2-Dimethylamino-3-isobutyl			Strong cocoa note, reminds of fusel oil, green and burnt undertone

[a] Goldman et al. (1967). [b] Buttery et al. (1971). [c] Timmer (1973). [d] Buttery et al. (1969b). [e] Buttery et al. (1969a). [f] Murray et al. (1970). [g] Friedel et al. (1971). [h] Bramwell et al. (1969). [i] Duprey and Janes (1971).

phthalate (1% solutions). Odor threshold values were measured according to the method described by Guadagni et al. (1963). The polyethylene bottles used were deodorized by rinsing them for 24 hr with warm water. All samples were purified by gas–liquid chromatography. The appropriate concentrations in water were made by diluting solutions of the pyrazine in diethylene glycol monomethyl ether. This solvent was also added in the same concentration to the reference solutions.

The compounds were tested in at least six concentrations, while each concentration was submitted to the panel together with three samples without the pyrazine. A choice between the four bottles had to be made. The panel consisted of 24 judges who were not specially selected or trained for the evaluation of the compound under study. We defined the odor threshold value as that concentration for which the level of correct responses is halfway between the 25 and 100% levels, i.e. 62.5%.

RESULTS AND DISCUSSION

Odor Characteristics. Odor descriptions and natural occurrence of four dimethoxy- and two monomethoxypyrazines are listed in Table I. Special attention was paid to the odor aspects: green (bean or bell pepper like), nutty, and floral.

A comparison of the odor descriptions leads us to the following remarks. All these methoxyalkylpyrazines have green odors. The three-substituted pyrazines have a more green bean like odor, while the tetrasubstituted ones have a more bell pepper like character. These also have a nutty note, which is most pronounced in IV.

At the time Buttery et al. (1969a,b) reported that 2-methoxy-3-isobutylpyrazine had a characteristic bell pepper like odor, it was already known to us that 2-methyl-3-isobutylpyrazine has a pronounced bell pepper like character (Naarden International N.V., 1968). Therefore, we wondered how the odor characteristics would change by replac-

Table III. Survey of the 2-Dimethylaminoalkylpyrazines Described

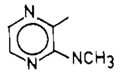
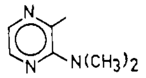
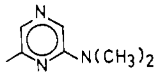
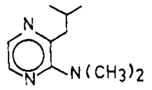
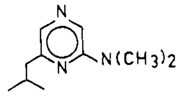
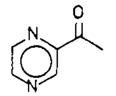
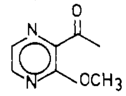
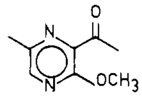
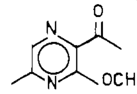
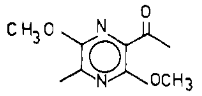
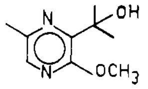
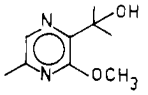
No.	Pyrazine derivative	Formula	Odor description
XI	2-Methylamino-3-methyl		Weak, reminds of roasted peanuts, green and cocoa notes
XII	2-Dimethylamino-3-methyl		Like XI, more green and peanut like, less cocoa notes
XIII	2-Dimethylamino-6-methyl		Reminds of unburnt coffee, peanut like and sweet notes, no cocoa note
X	2-Dimethylamino-3-isobutyl		Strong cocoa note, reminds of fusel oil, green and burnt undertone
XIV	2-Dimethylamino-6-isobutyl		Weakly green, cocoa note, no peanut note

Table IV. Some Differently Substituted Methoxyacetyl- and Methoxy-(α-hydroxyisopropyl)pyrazines and Their Natural Occurrence

No.	Pyrazine derivative	Formula	Identified in	Odor description
XV	2-Acetyl		Roasted peanuts,[a] sesame oil,[b] roasted filberts,[c] pressure cooked beef[d]	Breadcrust like, nutty, no green notes, reminiscent of acetamide
XVI	2-Methoxy-3-acetyl			Weak breadcrust like, green and nutty notes
XVII	2-Methoxy-3-acetyl-5-methyl		Galbanum oil[e]	Weak, breadcrust like, green musky note, chimney soot[f]
XVIII	2-Methoxy-3-acetyl-6-methyl			Weakly green, unpleasant, not breadcrust like, no nutty notes, chimney soot[f]
XIX	2,5-Dimethoxy-3-acetyl-6-methyl			Unpleasant, weakly green, earthy notes, chimney soot[f]
XX	2-Methoxy-3-(α-hydroxyisopropyl)-5-methyl		Galbanum oil[e]	Weak, green (bellpepper like), earthy undertone, chimney soot[f]
XXI	2-Methoxy-3-(α-hydroxyisopropyl)-6-methyl			Like XX, even weaker, nutty note

[a] Walradt et al. (1971). [b] Takei et al. (1969). [c] Kinlin et al. (1972). [d] Mussinan et al. (1973). [e] Timmer (1973). [f] It is striking that all compounds with an odor reminiscent of chimney soot have been prepared via an oxidation step with selenium dioxide. Although these compounds are thoroughly purified by preparative gas–liquid chromatography this typical note might be due to the presence of selenium compounds with a very high odor potency.

ing the methoxyl group by other functional groups such as methylthio and dimethylamino. In Table II these compounds are listed together with their odor descriptions and natural occurrence.

Replacement of the methoxyl group in 2-methoxy-3-isobutylpyrazine by a methyl group has only a small influence on the odor character. However, a change to methylthio or dimethylamino causes a sharp alteration of the odor properties. This is in contrast with the observations of Parliment and Epstein (1973), who found that the intensity changes from high to moderate going from 2-methoxy- to 2-methylthio-3-isobutylpyrazine, while the bell pepper note remains similar. As a consequence of our synthesis of 2-dimethylamino-3-isobutylpyrazine we also obtained some other dimethylaminoalkylpyrazines. The odor descriptions of these pyrazines and of one monomethylaminopyrazine are given in Table III. A comparison of these odor descriptions shows that these alkylaminopyrazines have weakly green odors, while the lower homologs have a more peanut-like and the higher a more cocoa-like character.

Investigations in our laboratory (Timmer, 1973) demonstrated the occurrence of 2-methoxy-3-acetyl-5-methylpyrazine and of 2-methoxy-3-(α-hydroxyisopropyl)-5-methylpyrazine in the oil of galbanum. We have synthesized these compounds and their methyl isomers. In Table IV the odor descriptions are given together with those of acetyl- and 2-methoxy-3-acetylpyrazine. It is shown that acetyl- and α-hydroxyisopropylpyrazines are weakly scenting compounds with a green and rather unpleasant odor type. Acetyl-, 2-methoxy-3-acetyl-, and 2-methoxy-3-acetyl-5-methylpyraz-

Table V. Odor Threshold of Pyrazine Solutions in Water

Pyrazine derivative	Threshold in parts per 10^{12} parts of water	Ref
Parent compound	500×10^6	*a*
2-Methyl	(105×10^6	*b*
	(100×10^6	*a*
2-Ethyl	22×10^6	*b*
2-*n*-Pentyl	1×10^6	*b*
2,3-Dimethyl	400×10^3	*a*
2,5-Dimethyl	(35×10^6	*b*
	(1.8×10^6	*c*
	(1×10^6	*d*
2,6-Dimethyl	54×10^6	*b*
2,3,5-Trimethyl	(9×10^6	*b*
	(400×10^3	*a*
2,5-Dimethyl-3-ethyl	43×10^6	*b*
2,6-Dimethyl-3-ethyl	15×10^6	*b*
2,3,5,6-Tetramethyl	10×10^6	*b*
2-Isobutyl	400×10^3	*c*
2-Methoxymethyl	150×10^3	*a*
2-Methoxy	700×10^3	*c*
2-Methoxy-3-methyl	4×10^3	*c*
2-Methoxy-3-ethyl	425	*c*
2-Methoxy-3-propyl	6	*c*
2-Methoxy-3-isopropyl	(1	*e*
	(2	*c*
2-Methoxy-3-*sec*-butyl	1	*e*
2-Methoxy-3-isobutyl (VIII)	(2	*c*
	(16	*f*
2-Methoxy-3-hexyl	1	*c*
2-Methoxy-5-methyl	15×10^3	*a*
2-Ethoxy-3-ethyl	11×10^3	*g*
2-Methoxy-3,5-dimethyl	3×10^3	*a*
2-Isobutyl-3-methoxy-5-methyl	260	*g*
2-Isobutyl-3-methoxy-6-methyl	2600	*g*
2-Isobutyl-3-methoxy-5,6-dimethyl	315×10^3	*g*
2-Methoxy-3-isopropyl-5-methyl (II)	50	*f*
2-Methoxy-3-isopropyl-6-methyl (I)	45	*f*
2,5-Dimethoxy-3-isopropyl-6-methyl (III)	250×10^3	*f*
2,6-Dimethoxy-3-isopropyl-5-methyl (IV)	70×10^3	*f*
2,5-Dimethoxy-3,6-dimethyl (VI)	180×10^3	*f*
2,5-Dimethoxy-3,6-diisopropyl (V)	670×10^3	*f*
2-Methyl-3-isobutyl (VII)	130×10^3	*f*
2-Methylthio-3-isobutyl (IX)	330	*f*
2-Dimethylamino-3-isobutyl (X)	1600×10^3	*f*
2-Dimethylamino-6-isobutyl (XIV)	5000×10^3	*f*
2-Dimethylamino-3-methyl (XII)	180×10^3	*f*
2-Dimethylamino-6-methyl (XIII)	1200×10^3	*f*
2-Methylthio-3-methyl	1×10^3	*a*
2-Methylthio-5-methyl	4×10^3	*a*
2-Methylthiomethyl	20×10^3	*a*

[a] Calabretta (1973). [b] Koehler et al. (1971). [c] Seifert et al. (1970). [d] Deck and Chang (1965). [e] Murray et al. (1970). [f] This report. [g] Seifert et al. (1972).

ine have breadcrust-like odor aspects.

Table V lists the odor threshold data of a number of substituted pyrazines collected from literature and our own measurements (footnote *f* of the table). One should be careful in drawing conclusions from a comparison of threshold values determined by different groups, even when they have used the same procedure (see, for instance, the different values reported for 2,5-dimethylpyrazine and 2-methoxy-3-isobutylpyrazine). Moreover we want to point out that if we state that the odor potency of one compound is lower than that of another based on their different threshold values this does not necessarily mean that the odor intensities at higher concentrations or in other media, like a complete perfume or flavor, will show the same differences. This is very well illustrated by comparing the odor threshold values published by Koehler et al. (1971) for solutions of a number of alkylpyrazines in water and the figures given by Collins (1971) for solutions of the same pyrazines in dark Irish beer. However, some general remarks still can be made.

Seifert et al. (1972) already mentioned that the most potent odors were found when an alkyl substituent stands in ortho position to a methoxyl function, for isobutylpyrazine and methoxypyrazine both had threshold values 10^5 times higher than 2-methoxy-3-isobutylpyrazine. The length of the alkyl side chain in methoxyalkylpyrazines may change from propyl to hexyl without great influence in the odor potency. However, methyl and ethyl give relatively weak odorants. This tendency seems to be confirmed by the figures given by Koehler et al. (1971) for some alkylpyrazines. Ethyl- and particularly methylpyrazine are less potent odorants than pentylpyrazine.

In connection with their measurements of the threshold of methoxydi- and -trialkyl substituted pyrazines, Seifert et al. (1970) proposed that one side of the ring must be unsubstituted to obtain extremely potent odorants. Our measurements are in agreement with this supposition, although we found only a minor drop in odor potency when a methyl group is introduced at the opposite side of the molecule (compare 2-methoxy-3-isopropyl-5-methylpyrazine or 2-methoxy-3-isopropyl-6-methylpyrazine with 2-methoxy-3-isopropylpyrazine). Also, the figures published by Calabretta (1973) demonstrate that introduction of an extra methyl group has little effect on the odor threshold.

Tetrasubstitution, also when a second methoxyl function is introduced, gives a remarkable decrease in odor potency. This is not confirmed by the threshold value of tetramethylpyrazine in relation to other alkylpyrazines reported by Koehler et al. (1971). The effect of exchange of methoxy by ethoxy in 2-methoxy-3-ethylpyrazine is reported by Seifert et al. (1970, 1972). The threshold value increases by a factor of 26. Also Parliment and Epstein (1973) have observed a marked reduction of the odor intensity by substitution of the methoxy group by other alkoxy groups. We considered the influence of more radical changes of the ortho substituent in isobutylpyrazines.

2-Methoxy-3-isobutylpyrazine is the most potent odorant of this series. 2-Methylthio-3-isobutylpyrazine has only a little higher threshold, while the odor potency of 2-methyl-3-isobutylpyrazine is much lower (about $10^4\times$); the threshold value of 2-dimethylamino-3-isobutylpyrazine is even a factor of 10^5 higher. Comparison of the threshold values of the 2-methylthiopyrazines given by Calabretta (1973) with the corresponding 2-methoxypyrazines also shows only small differences between these values. It is worthwhile mentioning that in the 2-dimethylamino series the 3-methyl has a 10 times lower threshold than the 3-isobutyl compound. The threshold values of the four dimethylaminopyrazines seem to confirm the statement of Seifert et al. (1970), namely that the most potent odorant is found when both substituents are on the same side of the molecule.

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Supplementary Material Available. Descriptions of the syntheses as well as the ir, MS, and NMR data of the pyrazines mentioned will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JAFC-75-638.

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Mass Spectrometry of Some Ethane- and Propanediol Diesters

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Mass spectral data of 9 ethanediol diesters and 18 propanediol diesters are presented. Ions arising from the two-step expulsion of aldehydes from the diol portion of the molecule can be used to differentiate between the 1,2-propanediol diesters and their 1,3 isomers. The ions at *m/e* 86 in the spectra of ethanediol diesters and at *m/e* 100 for the propanediol diesters are characteristic and can be used to distinguish between the two homologous series. Also distinctive are the fragments corresponding to the ion $[RCOCH_2OC(OH){=}CH_2]^+$. These are formed in ethanediol diesters and 1,2-propanediol diesters but not in 1,3-diol diesters.

In our work on the radiolysis of simple triglycerides, we identified some medium-chain esters of diols (LeTellier and Nawar, 1972). In certain respects, the mass spectral fragmentation patterns of these compounds were found to differ from those reported by Baumann et al. (1969) for the longer chain compounds, and also from those established by Sasâki et al. (1967) for acyclic α-glycol diesters. To clarify these anomalies, the homologous series of ethanediol diesters of C_2–C_{10} fatty acids and those of propanediol diesters of C_2–C_8 fatty acids were synthesized and their spectra carefully studied.

EXPERIMENTAL SECTION

The 1,2-ethanediol diesters, 1,2-propanediol diesters, and 1,3-propanediol diesters were synthesized, according to Mattson and Volpenhein (1962), by treating the appropriate acyl chlorides with 1,2-ethanediol, 1,2-propanediol, and 1,3-propanediol, respectively. A better than 99% purity of the diesters was obtained by preparative gas chromatography on a 10% SE 30 column. The mass spectra were determined with a Hitachi Perkin-Elmer combined gas chromatograph–mass spectrometer, Model RMU-6A. The ionizing voltage was 80 eV.

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