Heterocyclic Trace Components in the Essential Oil of Coriander

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The essential oil of coriander is obtained from the dried fruits of the plant *Coriandrum sativum* L. belonging to the family *Apiaceae*. It is marked by a very high percentage of linalool (approximately 70%), but the olfactory note of this monoterpene tertiary alcohol—when isolated by distillation—is quite different from the one of the purely synthetic counterpart. The special sensory effects of coriander oil have therefore always stirred the attention of flavorists and perfumers all over the world.

It is common knowledge that a great part of the annual crop of coriander seeds goes directly into classic spice blends such as the "Indian Curry" type whereas the essential oil is used for the flavoring of alcoholic beverages, candies, meat sauces and tobacco. Arctander[1] mentions that just the use in tobacco flavors has led to the fact that coriander oil is an interesting modifier in perfumes of the "Tabac" and "Fougère" types clearly dominating the men's line market.

With the very interesting progress of masculine notes in perfumery during the last 10 to 15 years, it was a "must" for research to look a little bit closer into the chemical composition of coriander oil, the estimated annual production of which lies around 100 metric tons according to the survey of B. M. Lawrence[2] given in 1985 on the basis of a worldwide estimation. The frequent mentioning of the essence in the well-known columns of the same author[3] reporting on progresses in the essential oil field, clearly indicates the interest to learn more about its olfactory properties. The already mentioned sensory effects must be related to trace components, because 18 main components constitute approximately 97% by weight of the total oil without giving the odor impression of coriander oil when reconstituted according to their percentages found in the natural specimen.

Thus, lower aliphatic aldehydes from C-5 to C-10 and some unsaturated analogs have been mentioned to have some influence odorwise[4]. The same may hold for α- and γ-campholenic acid first detected by D. de Rijke et al.[5] in coriander oil. Up to now, no publication has dealt with nitrogen-containing substances or heterocycles of the thiazole type occurring in this oil. Therefore this report covers the occurrence of such compounds as trace constituents in a commercial coriander seed oil. In addition, some furan derivatives will be mentioned too.

General Analytical Findings

A gas chromatogram of the complete oil is shown in figure 1. The main component linalool (compound 95) amounted to 69% followed by

*according to a lecture given at the 18th International Symposium on Essential Oils, Nordwijkerhout/Netherlands, September 1987.

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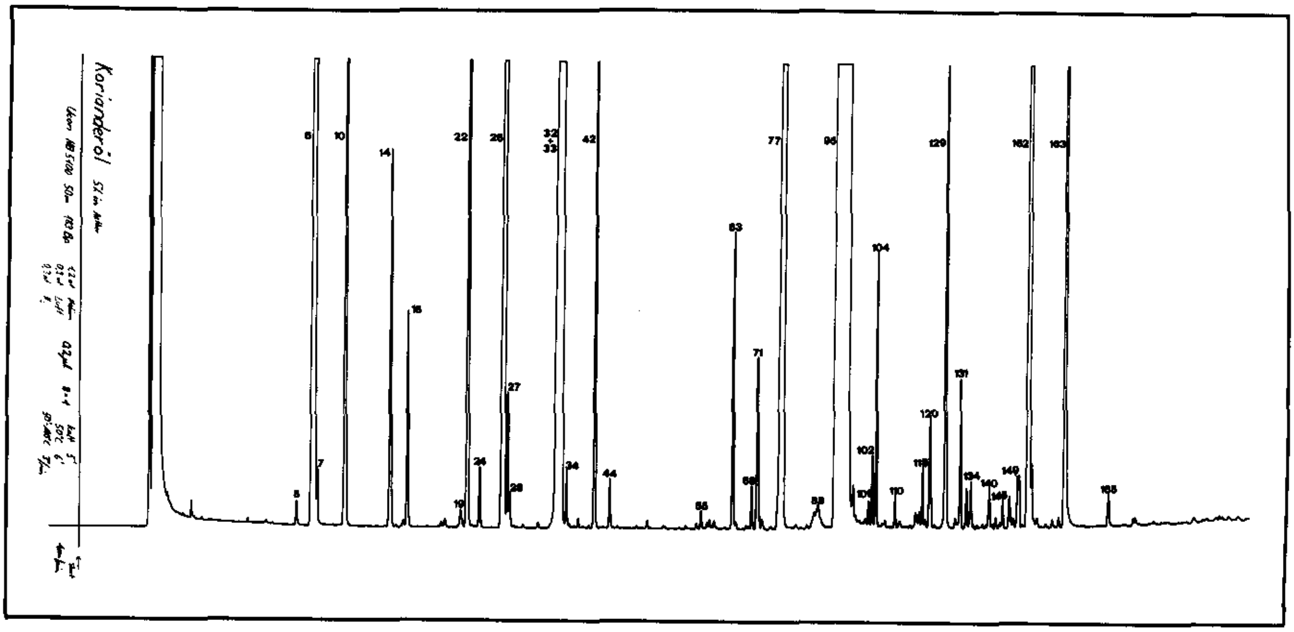


Figure 1. GLC of coriander oil

Conditions: glass capillary column (50 m length, 0.3 mm i.d.) coated with UCON HB 5100, temperature program: r.t. 5 min, 50°C 6 min, program 50-180°C with ΔT=3°/min, carrier gas helium (1,2-atm), injection 0,2 $\mu\ell$ of a 5% solution in diethyl ether.

camphor (compound 77) and geranyl acetate (compound 152) making together approximately 10%. Five monoterpene hydrocarbons exceed the 1% limit: γ-terpinene (compound 32; 4,7%), α-pinene (compound 6; 3,6%), limonene (compound 26; 1,9%), p-cymene (compound 33; 1,7%) and myrcene (compound 22; 1,35%).

A total of 50 compounds has been known from literature to occur in coriander seed oil[6]. The present in-depth analysis now reveals the presence of at least 203 components well distributed over a great number of chemical classes (see Table I). We will discuss the italicized groups of chemical compounds in more detail because we believe that they may contribute to a certain extent to the peculiar odor caused by the well-balanced bouquetting mother nature has done with such a simple alcohol like lanalool.

But before going into these details, some other aspects concerning the quantitative composition of coriander seed oil should be mentioned first. In a new TNO-series, H. Maarse and C. A. Visscher[7] compiled since 1982 the quantitative data of food ingredients. This annually up-dated compilation does not yet include the heading "coriander seed" or its oil, respectively. In view of the relatively broad distribution in condiments and flavorings it seems worthwhile to incorporate it also in a forthcoming volume and the quantitative data for selected constituents as given in Table II may serve as basis for the introduction. Such data will also support the constant endeavor

CONSTITUENTS OF CORIANDER OIL

	literature	our analysis
HYDROCARBONS	19	30
OXIDES, FURANS, ACETALS	4	23
ALCOHOLS	10	45
ALDEHYDES	9	22
KETONES	1	19
ESTERS	3	18
ACIDS	2	26
PHENOLS, PHENOL ETHERS	2	5
N-CONTAINING COMPOUNDS	-	15
	50	203

QUANTITATIVE DATA (%)

FOR SELECTED CONSTITUENTS OF CORIANDER OIL

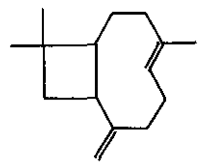
	Lawrence (1980)	Hirvi et al. (1985)	ours (1986)
α-Pinene	3.9	0.2	3.6
Camphene	0.7	-	0.87
β-Pinene	0.4	0.7	0.28
Sabinene	0.4	-	0.17
Myrcene	0.9	-	1.35
3-Carene	tr	-	tr
α-Phellandrene	tr	-	0.01
Limonene	1.6	1.6	1.9
α-Terpinene	tr	-	0.08
β-Phellandrene	-0.3	-	0.14
γ-Terpinene	6.9	10.5	4.7
p-Cymene	2.1	1.6	1.7
Linalool	70.0	70.3	69.1
Linalyl acetate	0.2	-	0.05
Camphor	7.7	2.4	5.2
Terpinene-4-ol	0.5	0.2	0.28
α-Terpineol	0.4	0.3	0.59
Borneol	-	-	0.18
Geraniol	0.8	3.4	0.9
Geranyl acetate	2.3	5.7	4.7

of J. Stofberg[8] with respect to the so-called consumption ratios as valuable criteria for the definition of safety aspects of nature-identical chemical substances.

Our quantitative data obtained from GLC-measurements correspond quite well to the ones of B. M. Lawrence[4] published in 1980 on the occasion of the 25th anniversary of the "Society of Flavor Chemists." The values given by T. Hirvi et al.[9] differ a little bit from both the others. But nevertheless these 18-20 compounds form 97% of the total oil so that 180 trace components will share the remaining 3%, i.e. they occur in concentrations corresponding to the average of 0.01% or less which means that we have 0.1 g of a single compound in 1 kg of coriander seed oil.

Specific Trace Components

It is interesting to note that the concentration of sesquiterpene hydrocarbons occurring in coriander oil is also very small. This specialty may be one of the reasons for the odor peculiarity of the oil since a great number of terpene-based essential oils owe at least part of their sensory impressions to an olfactory modification of monoterpene alcohols by a great variety of sesquiterpene hydrocarbons distilling together with the oxygenated compounds. At present, we could detect only α-humulene 2, trans-β-farnesene 3 and ar-curcumene 4 as traces besides the already known caryophyllene 1 (0.07%) and its epoxides.



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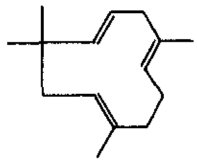
(0.07 %)



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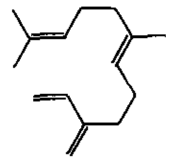

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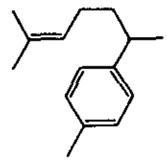

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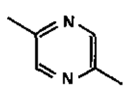
(traces)

Thus, it seemed to us that other trace components with a relatively high sensory impact should or must be responsible for the very typical odor of coriander oil. We believe that the class of nitrogen-containing heterocycles we detected by means of GLC-MS-coupling experiments in special fractions of the oil fulfills this aspect, at least to a certain extent.

In the neighborhood of p-cymene, for instance, 2,5- and 2,6-dimethyl pyrazine (5,6) immediately followed by 2,3-dimethyl pyrazine (7) could be



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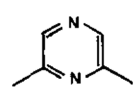

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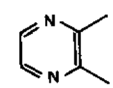

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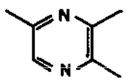
verified by comparison with authentic specimens. These heterocyclic substances are known to exhibit strong odor characteristics. They occur almost together in a great number of food flavor volatiles and alcoholic beverages[6], but interestingly enough also in the absolute oil of iris rhizomes[10] and in the fig leaf absolute[11]. Their odor notes are described as being roasted, herbaceous, nutty and chocolate-like with green undertones and an amine character not to be neglected.

Homologs in form of 2,3,5-trimethyl pyrazine (8), 2-ethyl 6-methyl pyrazine (9), 2-ethyl 5-methyl pyrazine (10), tetramethyl pyrazine (11), 2-ethyl 3,6-dimethyl pyrazine (12) and 2-ethyl 3,5-dimethyl pyrazine (13) constitute the next group of heterocyclic compounds we detected as trace components in coriander oil.



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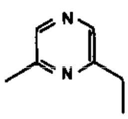

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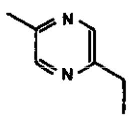

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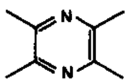

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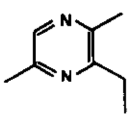

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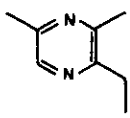

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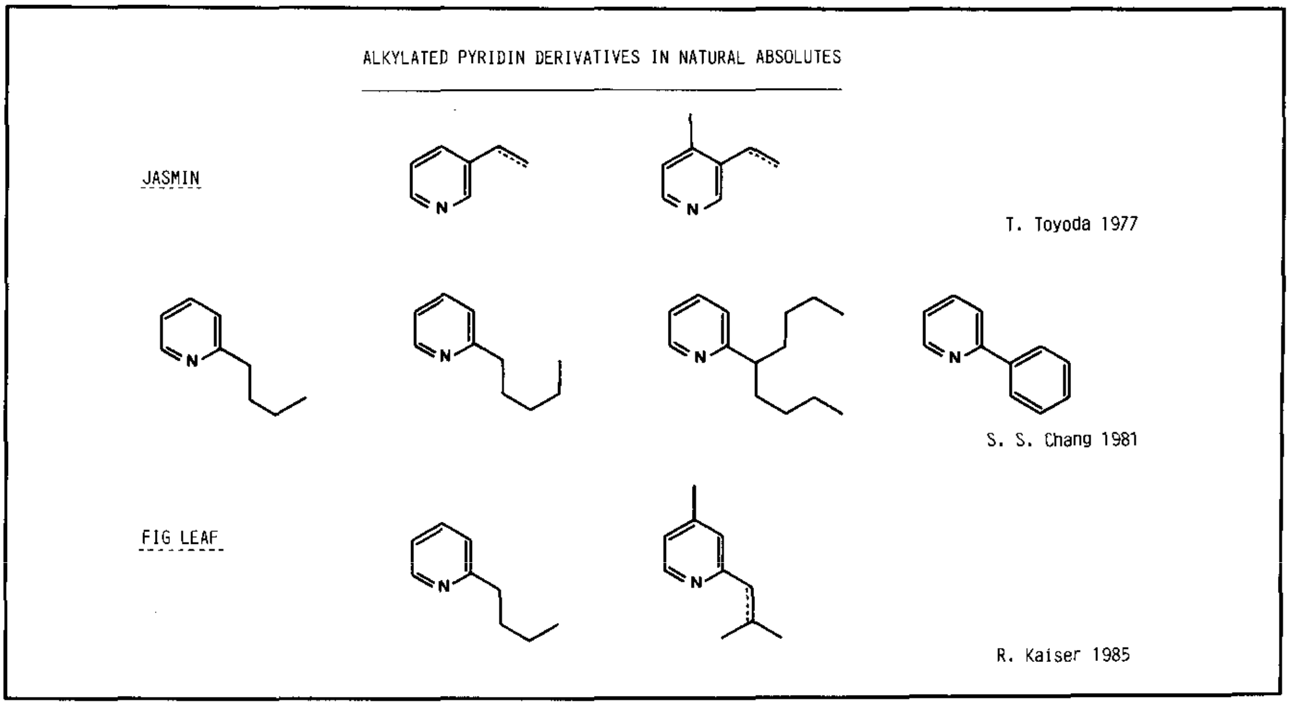
Notice practically the same distribution in various food and beverages as mentioned for the dimethylated pyrazines. We are also familiar with the occurrence of such compounds in absolute oils used in perfumery. Compound 11, for instance, was identified already in 1970 in galbanum[12] together with 2,3-dimethyl 5-ethyl pyrazine and similar substances. Furthermore, B. Maurer and G. Ohloff[13] have detected compounds 8 and 11 in the dried castoreum glands, i.e. in the perfumery material obtained from this natural source. Additionally, other plant rhizomes were reported to contain tetramethyl pyrazine, i.e. the rhizomes of *Glycyrrhiza glaubra* L.[14] giving the well-known licorice extract and the ones of *Curcuma aromatica*[15].

All the compounds of this group surely exert a sensory impact in coriander oil because there is, for instance, the description of a nutty, earthy odor character for the ethyl-dimethyl-substituted pyrazine and T. Shibamoto[16] reported very recently about the remarkably low odor threshold values of trisubstituted pyrazines and the use of such compounds not only in flavoring, but also in



perfume blending.

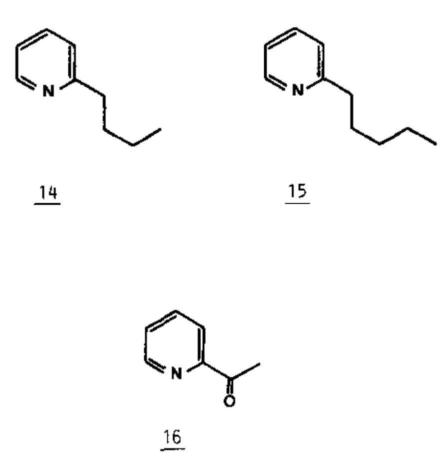
Switching from alkyl-substituted pyrazines to similar derivatives of pyridine, first have a look at the occurrence of such compounds in other natural perfume ingredients. At the Kyoto congress 1977, T. Toyoda and co-workers[17] reported that jasmin absolute of different geographical origin always contains nicotinic acid derivatives as well as alkyl pyridines bearing the alkyl substituents in the 3- and 4-position. It was found that these compounds played important roles in modulating the floral odor notes of other ingredients occurring in jasmin.

Some years later, S. S. Chang, et al.[18] published their results concerning new components in jasmin absolute of Egyptian origin. They identified alkyl pyridines substituted in the 2-position which may contribute to a specific, slightly burnt or roasted aroma touch found to be of interest in the odor profile of the absolute. Similar pyridine derivatives were finally identified in fig leaf absolute by R. Kaiser[11] and it was interesting to see that even the new 2,4-disubstituted pyridines have a relatively broad distribution as trace components in other essential oils such as verbena oil, geranium oil, boronia absolute and orange flower absolute.

This was underlined by a very recent report of H. Surburg[19] on minor constituents of palmarosa oil. He was able to detect more than 40 pyrazine and pyridine derivatives in this oil which represents a natural source of geraniol. His finding fit therefore very well into the framework of sensorially important heterocycles in essential oils.

PYRIDIN DERIVATIVES

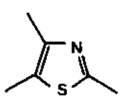
IN CORIANDER OIL



The pattern of a 2-substituted pyridine skeleton was now also detected in the essential oil of the fruits of *Coriandrum sativum*. We were able to confirm the presence of 2-butyl pyridine (14) and 2-pentyl pyridine (15) together with 2-acetyl pyridine (16) which is another important flavor component in nature. According to the so-called TNO-list[6] this compound was found in baked potatoes, heated meat, cocoa, coffee, tea, in roasted filberts and peanuts as well as in beer. Furthermore, it has to be mentioned that a chemical study of the Burley tobacco flavor concentrate revealed for the first time the presence of compound 16 in this natural substrate[20] and that very recently, the strong smelling substance could also be detected in headspace volatiles of flue-cured, American type tobacco, of Burley tobacco and of Turkish tobacco[21] thus confirming the former analytical result.

Next, three thiazole derivatives occurring in trace amounts in coriander oil have to be discussed. 2,4,5-Trimethyl thiazole (17) has a green,

THIAZOLE DERIVATIVES



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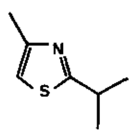

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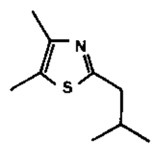

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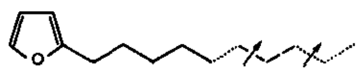
nutty, coffee- and cocoa-like, slightly quinolinic odor with a very high odor value based on an odor threshold value of less than 1 ng/ℓ air. Already in 1975, J. A. Maga[22] recognized the group of thiazoles as a group of extremely potent odorants and compound 17 bears today a FEMA-GRAS number (No. 3325) just underlining the high interest given to this substance in the flavoring business.

More recently, B. D. Mookherjee and co-workers[23] observed the formation of 2,4,5-trimethyl thiazole when cystin was thermally degraded in water. That most of the thiazoles found, for instance, in flavor concentrates of potatoes[24] or dry red beans[25]—when conducting the Likens-Nickerson-extraction under atmospheric pressure—are formed by heat, was first mentioned by R. G. Buttery and his co-workers[25]. Thus, compounds 17 and 19 were already detected by these authors in the mentioned flavor concentrates.

Compound 18 was first described by C. T. Ho and N. Ichimura[26] as constituent of tomatoes freshly mashed immediately after plucking. The flavor volatiles were transferred with nitrogen to cooling traps thus avoiding the influence of heat and opening another view with respect to the formation of thiazole derivatives in plant.

Last but not least, some oxygen-containing heterocycles such as furan or tetrahydrofuran derivatives will give an idea of the complexity of the chemical composition coriander oil has shown during its indepth analysis by instrumen-

FURAN DERIVATIVES



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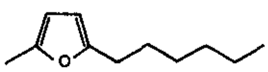

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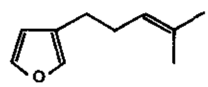

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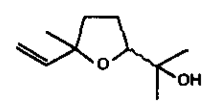
tal methods. 2-Pentyl furan (20) together with the higher homologs 2-hexyl-, 2-octyl- and 2-decyl furan (21-23) as well as the tentatively identified compound 24 are trace constituents eluting from the polar GLC-column before and in the neighborhood of the main component linalool or geraniol, respectively. With the exception of compounds 23 and 24, such furan derivatives are relatively often encountered in food flavor extracts[6], especially in flavors of the roasted type like the one of roasted filberts[27]. The 2n-alkyl furans have been known for a long time and synthetic specimens were described as liquids with fruity odor characteristics by E. Buchta and C. Huhn[28] already in 1965. The 2-n-decyl furan can be easily prepared according to M. D'Auria, et al[29] who described this compound for the first time as an intermediate for 2(3H)-furanone derivatives.

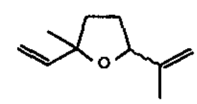
Perillen (25) represents a furan derivative of terpenoic origin and gives us a link to some tetrahydrofuran derivatives which may be correlated to linalool and the linalool oxides already described as constituents of coriander oil[30].

TETRAHYDRO FURAN DERIVATIVES



linalool oxides

(known)



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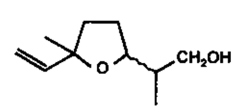

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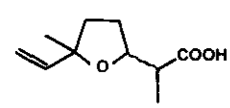

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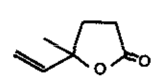

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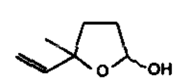

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The 2-methyl-2-vinyl-5-isopropenyl-THF (26) is today a commercial product also used in certain reconstitutions of essential oils. Lilac alcohol (27) and its corresponding acid, the davana acid (28), are further terpenoid trace constituents in the neutral or the acidic part, respectively, of coriander oil. They will surely be formed by an oxidative transformation of the main component linalool. We discussed such oxidative degradation steps on the occasion of our in-depth analysis of davana oil[31a,b]. This feature functioned as the "red thread" in the elucidation of a great number of constituents in this oil, all exhibiting an intact methyl-vinyl-substituted THF-ring moiety. The last step in such an oxidative process is the well-known lavender lactone (29). This is an olfactorily interesting lactone found by several authors for the first time in lavender and lavandin oil[32,33]. It now constitutes also a trace component of coriander oil. The same holds for compound 30 probably formed by the enzymic systems in the plant with lactone 29 as starting material. The lavender lactol has been revealed as a naturally occurring substance for the first time in davana oil[31b].

Final Remarks

With these terpene-like structures in mind, it may become clear that most of the remaining trace compounds belong to the monoterpene class numerically representing by far the most impressive part of coriander oil. But in the majority of cases, the sensory input of the just discussed heterocyclic compounds is surely more interesting than the one of the minor terpenoic substances already known from other natural sources.

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