From the Linden Flower to Linden Honey – Volatile Constituents of Linden Nectar, the Extract of Bee-Stomach and Ripe Honey

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Honey is produced by honeybees (*Apis mellifera*), which collect nectar from flowers, digest it in their bodies, and deposit it in honeycombs, where it develops into ripe honey. We studied the evolution of the volatile constituents from the nectar of linden blossoms (*Tilia cordata*) to honey *via* the 'intermediate' honeybee.

The sampling of the contents of the honey stomach or honey sack of the bee is unique. Extracts were prepared from nectar, from the liquid of the honey stomach, and from ripe honey. The chemistry is extremely complex, and compounds spanning from monoterpenes (hydrocarbons, ethers, aldehydes, acids, and bifunctional derivatives), isoprenoids, aromatic compounds (phenylpropanoids, phenols), and products degraded from fatty acids to alkaloids, were identified. Some compounds definitely stem from the plants, whereas other interesting constituents can be attributed to animal origin. Two derivatives of decanoic acid, 9-oxodec-2-enoic acid (**12**) and 9-hydroxydec-2-enoic acid, identified in the honey are known to be constituents of the so-called '*Queen's pheromone*'. Two metabolites of these acids were identified in the extract of the honey stomach: 8-oxononanal (**10**), a new natural product, and 8-oxononanol (**11**). There structures were confirmed by synthesis.

Nectar and honey stomach contain many aldehydes, which, due to the highly oxidative atmosphere in the honeycomb, are found as corresponding acids in the honey. Two acids were newly identified as 4-isopropenylcyclohexa-1,3-diene-1-carboxylic acid (**14**) and 4-(1-hydroxy-1-methylethyl)-cyclohexa-1,3-diene-1-carboxylic acid (**15**).

Introduction. – Ever since prehistoric times, honey has played an important role in human nutrition, principally as a flavorsome sweetener, but also for its medicinal properties, which include alleviating insomnia, lowering blood pressure and nervousness, and preventing arteriosclerosis. Honey is produced by the honeybees (*Apis mellifera*), which collect nectar, digest it, and stock it in honeycombs, where it is ripened. The nectar, a sticky liquid, is produced in the blossom by nectary glands and collected in cup-forming sepals (*Fig. 1*).

The nectar gathered is stocked in the honey stomach, which can contain up to 60 µl of liquid (*Fig. 2*). Enzymes in the saliva, produced in the cervical gland, degrade sucrose into glucose and fructose and cleave glycosides of the nectar into sugar moieties and volatile aglycones. Only a portion of the nectar is transferred to the intestines through a special valve and digested to produce energy for long-distance flights, or stored for hibernation.

On returning to the hive, the content of the stomach is regurgitated into the waxy honeycomb, either as feed for the bees carrying out their duties in the hive or to ripen into honey. In this investigation, we tried to follow the transformation of the volatiles from the nectar to the ripened honey. The volatile compounds of the nectar, and then of the liquid contained in the honey stomach of the bee, having collected nectar from

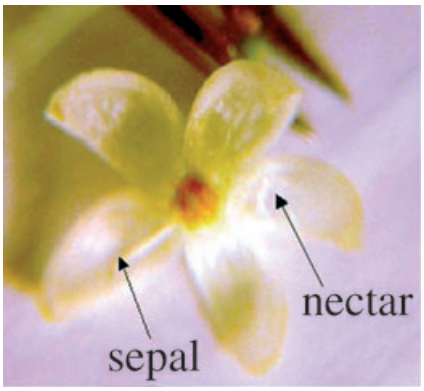


Fig. 1. *Sepals of a linden flower with a droplet of nectar*

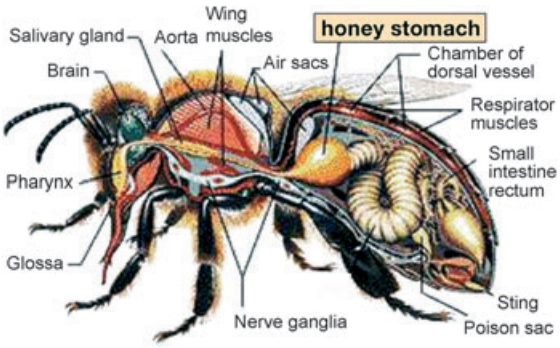


Fig. 2. *Anatomy of the bee* [1]

linden flowers (*Tilia cordata*), were studied. The only trees in bloom in the surrounding neighborhood of the honeycombs were linden trees, and it was, thus, assumed that the nectar preferentially gathered was from linden flowers, and that the honey sample was also monofloral. The nectar of 50 flowers was collected, extracted, and analyzed, as well as the contents of the stomach of 25 bees caught at the entrance of the hive on their way back from nectar gathering. Gentle pressure with two fingers applied on their backs ejected the liquid into a glass capillary tube (*Fig. 3*).

There are only a few studies in which the chemical constituents of the flower have been correlated with those of the corresponding honey or nectar: the volatiles of the flower, the nectar, and the honey of leatherwood, an endemic plant of Tasmania [2], and constituents of the nectar of *Citrus* flowers, concentrating, however, on the content of caffeine [3]. Most recently, a comparison of the components of extracts of entire *Citrus* flowers and of *Citrus* honey showed similar monoterpenoids as identified in our study [4]. The analyses of linden honey and the fresh linden flowers led to the identification of a unique monoterpenoid ether called '*linden ether*' (=2,4,5,7a-tetrahydro-3,6-dimethylbenzofuran; **1**) [5]. To the best of our knowledge, no

Fig. 3. *Manual sampling of the contents of the honey stomach of a bee*

investigation has described the isolation and analysis of linden nectar and of the liquid extracted from bee stomach.

The present paper will highlight some observations that seem relevant for the processing of nectar to honey. It is, however, out of the scope of this report to give the exhaustive results of the investigation, since *nearly 500 different compounds* have been identified!

Results and Discussion. – The extracts prepared from linden nectar, linden nectar recovered after being digested in the honeybee stomach, and of the ripe linden honey are extremely complex. An impressive number of unknown compounds show mass-spectral patterns that are characteristic for mono- and bifunctional monoterpenoids. Due to the minute quantities of samples of the first two types of extracts, fractionation and isolation of compounds for further analytical measurement could only be performed with the third sample, *i.e.*, the finished honey. Most results were established only by GC/MS injection and interpretation of the mass spectra, by comparison with reference substances, and by confirmation of their retention times.

Nectar. The nectar extract (see *Fig. 4*) is composed of all the essential groups of natural products: compounds of fatty acid degradation (nonanal, decanal, tetradec-1-ene), phenylpropanoids (3-(4-methoxyphenyl)propan-1-ol, 3-(4-methoxyphenyl)propanal, 3-(4-methoxyphenyl)prop-2-enal), isoprenoids (vomifolione, vomifoliol, and 3,5,5-trimethyl-4-(3-oxobutyl)cyclohex-2-en-1-one), alkaloids (caffeine, theophylline, a trace of nicotine), and a complex mixture of monoterpenes, among them the above mentioned linden ether (**1**), 1,8-cineole, diols **2** and **3**, and unknown compounds having molecular weights (MW) of 148, 150, 152, 166, 168, and 170, respectively (see *Fig. 5*). As a consequence of the results described later for the ripe honey, the following hypothetical structures might be proposed for two of the honey compounds: *p*-mentha-1,3,8-trien-7-al (**4**) and 8-hydroxy-*p*-mentha-1,3-dien-7-al (**5**). Their mass spectra are depicted in *Fig. 6*, *a* and *6*, *b*, respectively.

Honey Stomach. In the honey stomach (see *Fig. 7*), the aliphatic compounds, the isoprenoids, and the alkaloids all remain unchanged. The presumption that active

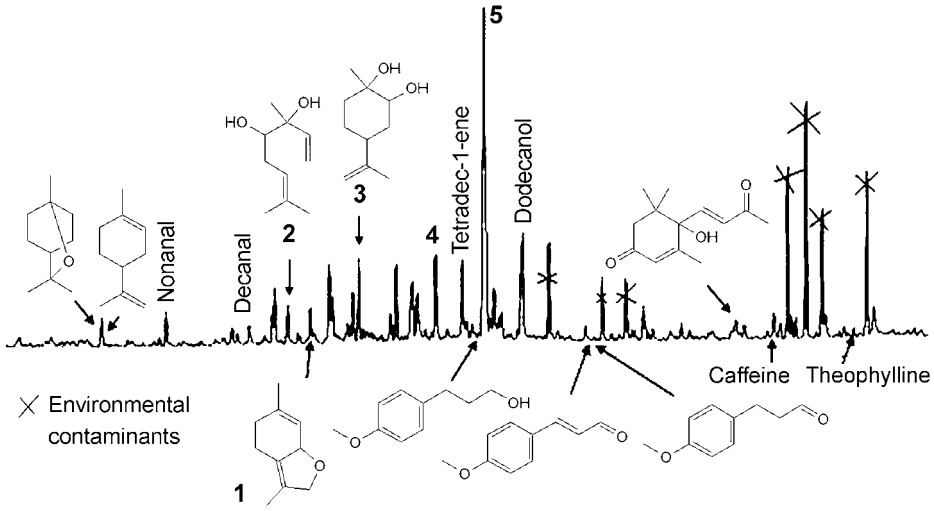


Fig. 4. *Gas-chromatographic* (GC) *profile of linden-flower nectar extract*

glycosidases are present in the saliva was confirmed by the appearance of new monoterpenic alcohols in the extract of the liquid isolated from the bee stomach: the three linalool derivatives 3,7-dimethylocta-1,5-dien-3,7-diol (**6**), 3,7-dimethylocta-1,6-dien-3,5-diol (**7**), and 2,6-dimethyl-6-hydroxyocta-2,7-dienal (**8**), also identified in *Citrus* honey [4]. The latter aldehyde, giving rise to the isomers of lilac aldehyde [4] (compounds identified in linden honey as well), has already been identified in lavandin oil; it is formed during the '*noble rot*' of grape must by *Botrytis cinerea* [6]. The most-abundant compound (MW 164) is highly unsaturated and, most probably, corresponds to the unknown aromatic compound 4-(1-hydroxy-1-methylethyl)benzaldehyde (**9**; see *Fig. 6,c*).

Two new *aliphatic* compounds, with mass fragments at *m/z* 43 and 58, respectively, typical for methyl ketones, and with molecular weights of 156 and 158, appeared as trace components. Their hypothetical structures, 8-oxononanal (**10**) and 9-hydroxynonan-2-one (**11**) were confirmed by synthesis (see *Exper. Part*); and their resemblance with the '*Queen's substance*' (= 9-oxodec-2-enoic acid; **12**) was evident. This semiochemical is the main constituent of the '*Queen's pheromone*', a well-equilibrated cocktail of fatty acids and aromatic compounds [7], produced in the mandibular gland of the queen and having the function of regulating the social behavior of the bee colony.

α-Oxidation of the '*Queen's substance*' (**12**), or of the saturated analog **13**, another constituent of the pheromone, to 2-hydroperoxy-9-oxodecanoic acid, followed by decarboxylation, leads to the keto aldehyde **10** [8] (see *Scheme 1*). These two compounds are the only metabolites of animal origin absorbed into the plant liquid extracted from the bee stomach. The alcohol **11** is known from milk [9], *Pimenta racemosa* [10], krill products [11], and, most interestingly, from the sternal gland of the elephant shrew [12]. The aldehyde **10** has been described in a synthetic context only [13], and is, therefore, a new natural product.

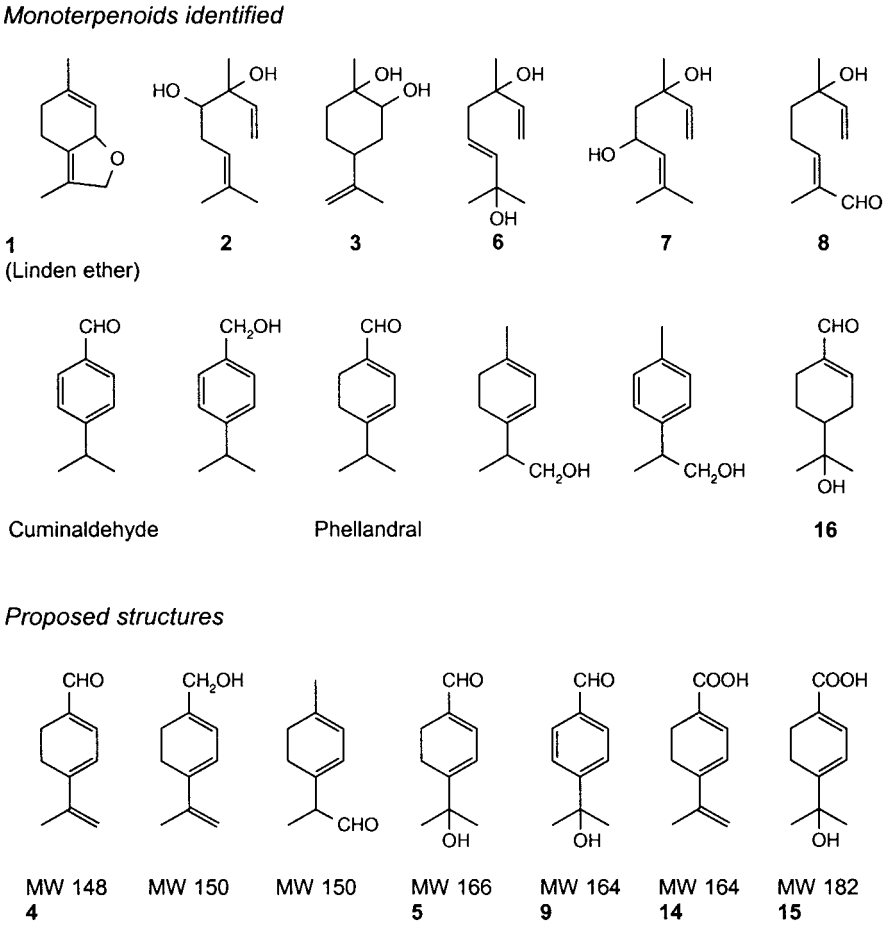


Fig. 5. *Identified and proposed strucutres of monoterpenoids*

Ripe Honey. After one month, the mature honey is recovered from the waxy honeycomb by centrifugation. The preparation of a sugar-free extract by solid-phase extraction (SPE) on an *OASIS®-HBL* cartridge (rather than solvent extraction with CH_2Cl_2 with the formation of nasty emulsions), provided a product with excellent organoleptic properties truly representing the starting material. The monoterpenoid diols **3** and **7**, vomifolione, caffeine, and theophylline remain intact under the highly oxidative atmosphere of the honeycomb (35° and abundant air (O_2) provided by 'ventilation' performed by the bees moving their wings at the entrance of the hive), whereas other compounds do undergo oxidation. Benzoic acid and phenylacetic acid, very characteristic of the honey-like smell, together with two new monoterpenic acids, 4-isopropenylcyclohexa-1,3-diene-1-carboxylic acid (**14**) and 4-(1-hydroxy-1-methyl-ethyl)cyclohexa-1,3-diene-1-carboxylic acid (**15**) are abundant components (see *Fig. 8*). The isolation, identification, and spectral data of **14** and **15** will be discussed in a separate paper. The structures of these compounds, established by NMR

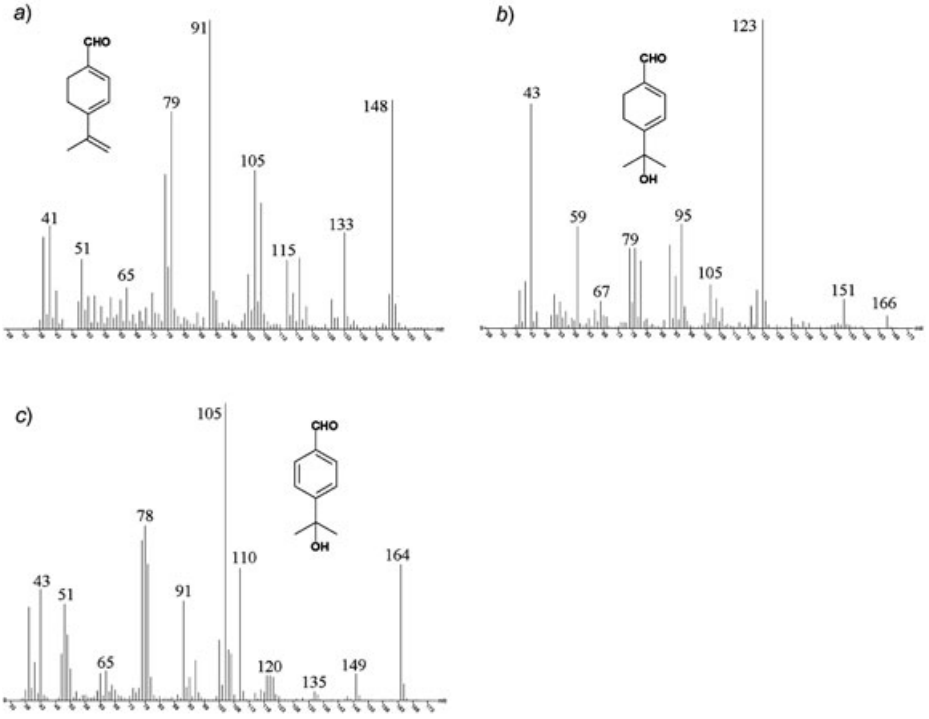
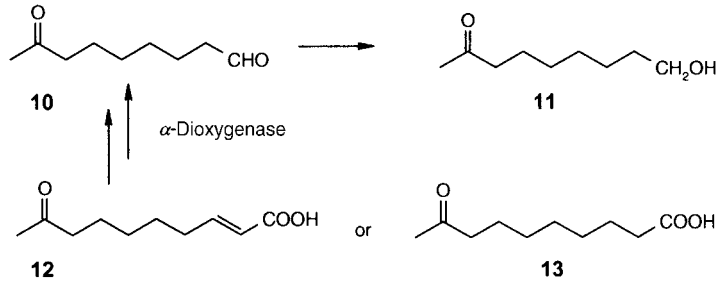


Fig. 6. *Mass spectra and anticipated chemical structures of the* (unknown) *compounds* **4** (*a*), **5** (*b*), and **9** (*c*)

Scheme 1. *Transformation of Compounds Related to* 'Queen's substance' (see text)



experiments, support the hypothetical structures of aldehydes **4** and **5** proposed in nectar. Compound **5** was still present in the ripe honey, eluting just after 8-hydroxy-*p*-menth-1-en-7-al (**16**), a known compound [14]. The content of linden ether (**1**) increased, and among the trace compounds, a series of further *p*-menthofuranoids, including dill ether and menthofuran, and rose oxide, are compounds with strong odor impacts (*Fig. 9*) [5][15].

Methyl syringate (**17**; see *Fig. 8*) is most probably absorbed into the lipophilic honey from propolis, a resinous material collected by the worker-bees from tree barks and used, mixed with beeswax, to construct and strengthen the combs. Within the methyl

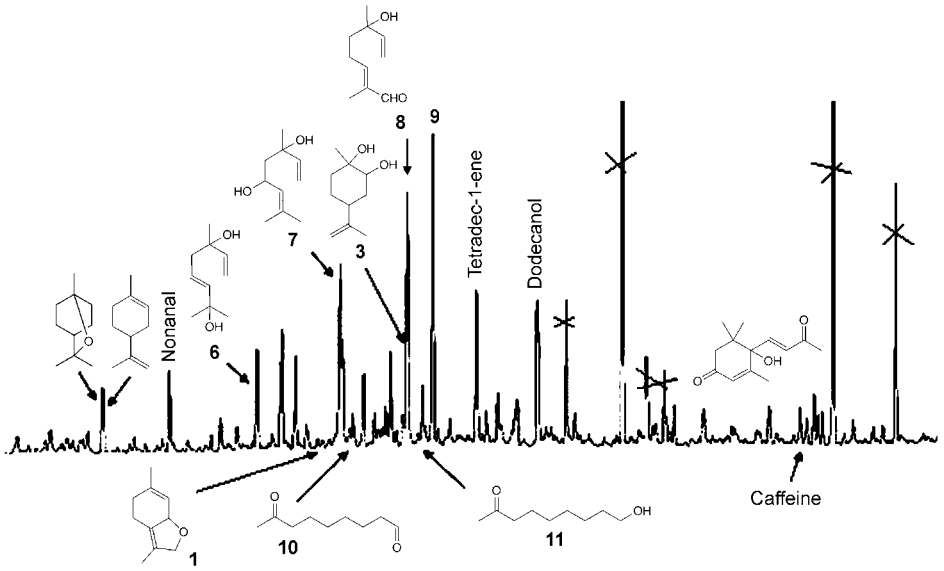


Fig. 7. *Gas-chromatographic profile of the extract of the honey stomach*

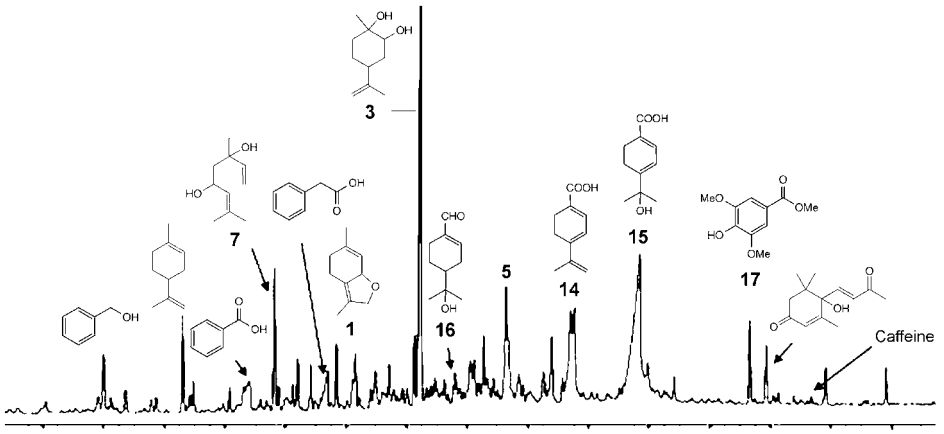


Fig. 8. *Gas-chromatographic profile of linden honey* (*OASIS*© extraction)

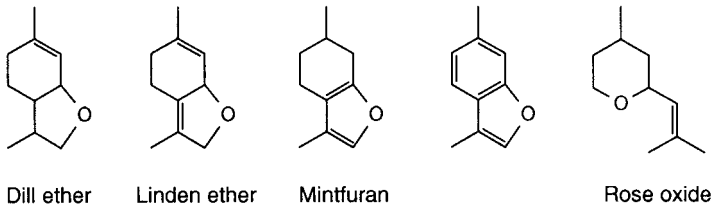


Fig. 9. *Structures of 'menthofurans' identified in linden honey*

ester fractions, among 115 acids, the '*Queen's substance*' (**12**) and 9-hydroxydec-2-enoic acid [16] (another compound of the '*Queen's pheromone*') were identified. This is, to our knowledge, the first report of these pheromones in finished honey. Many saturated (C_6 to C_{14}) and unsaturated (dec-2-enedioic and dodec-2-enedioic) diacids, having their origin in royal jelly [17][18] – a secretion of the pharyngal gland, and used as protein-rich feed for the larvae of the queen – are present together with a panoply of aromatic acids [19] and a trace amount of abscisic acid. The alkaloids caffeine and theophylline have been postulated as markers in *Citrus* honeys [3], where their concentration is significantly higher; and caffeine, together with theobromine, was identified in tea flowers [20].

Conclusions. – Our observations are based on the interpretation of restricted samples, quasi '*snapshots*' of a complex sequence of events. This report is a subjective selection of results that seem to delineate the evolution of the volatile constituents from the flower nectar to honey. Many compound structures could not be fully elucidated, and some hypothetical compounds were proposed. However, compounds **10** and **11**, related to the '*Queen's substance*', were confirmed. The monoterpenoid acids **14** and **15** as well as their glycosidic precursor, which could be isolated from various honeys, will be the subject of a detailed subsequent publication.

We are indebted to Dr. *F. Brühlmann* and Dr. *B. Maurer* (*Firmenich SA*) for stimulating discussions about natural-products chemistry.

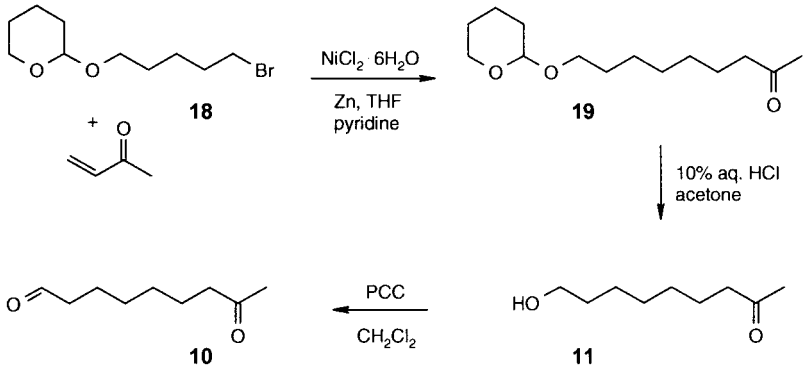
Experimental Part

General. GC/MS Experiments were performed on a *6890* gas chromatograph (*Agilent*) coupled to a quadrupole *5971* mass spectrometer (*Agilent*) equipped with an apolar column (*SPB-1* capillary column, 30 m × 0.25 mm, film thickness 1 μm; temp. program: 5 min at 60°, then 60° – 250° at 5°/min; injector temp. 250°, transfer-line temp. 250°; carrier gas: He), or on a *6890* gas chromatograph (*Agilent*) coupled to a quadrupole *5972* mass spectrometer (*Agilent*) equipped with a polar column (*Supelcowax*®; 30 m, film thickness 0.25 μm; temp. program: 5 min at 50°, 50 – 240° at 5°/min; carrier gas: He); EI mass spectra were generated at 70 eV at a scan range from *m*/*z* 27 – 350. Linear retention indices (*RI*) were determined after injection of a series of n-alkanes (C_5 – C_{28}) under identical GC conditions. ^{1}H- and ^{13}C-NMR Spectra were measured on a *Bruker AMX-360* instrument in $CDCl_3$; δ values in ppm rel. to Me_4Si as internal standard. Solid-phase-extraction cartridges: *OASIS*®*-HLB* (*Waters*), 20 ml, filled with 1 g of polymer. Linden flowers were picked in a linden trees path in Cormondrèche (Neuchâtel, Switzerland) on a dry, sunny day (June 2002) and immediately transferred to the laboratory for workup. Linden honey: ripe honey produced from the same trees with the same hives in 2001 was obtained ('*Les Miels Suisses*', Mr. *Boris Bachofen*). 9-Oxo-dec-2-enoic acid was purchased from *Maybridge Chemical*, Cornwall; 3,4-dihydro-2*H*-pyran from *Acros Organics*, Geel; 5-bromopentan-1-ol from *TCI Organic Chemicals*, Oregon; and Zn powder (< 45 μm) from *Merck*, Darmstadt. 9-Hydroxynonan-2-one (**11**) was prepared according to [21] and [22] (following *Scheme 2*).

Isolation and Extraction of the Nectar. – Approximately 50 flowers were dissected with tweezers to access the droplets of nectar situated in the concave sepals. These droplets were aspirated into a glass capillary (i.d. 0.7 mm); rich flowers gave up to 2 cm of liquid, which was blown into H_2O (25 ml) with Ar gas. The capillaries were rinsed with H_2O. The aq. layer was extracted with CH_2Cl_2 (5 ml), and the org. extract was dried and concentrated.

Isolation and Extraction of the Liquid from the Honey Stomach. 25 Worker-bees were caught at the entrance of the hive, and pressure was applied on their backs with two fingers, which pushed the contents of the honey-stomach back to the mouth where it could be aspirated with a small glass capillary (*Fig. 3*). The bees were then released without being harmed. The pieces of capillary tubes containing the extracted liquid were covered with deionized H_2O (25 ml), rinsed with H_2O, and covered with CH_2Cl_2 (10 ml). The aq. layer was extracted

Scheme 2. *Synthesis of Compounds* **10** *and* **11**



with CH_2Cl_2 (3 × 20 ml), and the combined org. extracts were dried ($MgSO_4$) and concentrated by distilling off the solvent (*Vigreux* column).

Preparation of the Extract of Ripe Linden Honey. – An *OASIS®-HLB* cartridge was put on top of a vial with a rubber adapter and branched to a water pump. It was conditioned with MeOH (10 ml), and equilibrated with deionized H_2O (10 ml), applying a slight vacuum. A soln. of linden honey (50 g) in H_2O (400 ml) was loaded, and the cartridge was rinsed with H_2O (100 ml) and then with 5% aq. MeOH (10 ml). The compounds were eluted with Et_2O (20 ml), and the solvent was dried ($MgSO_4$) and removed by distillation (*Vigreux* column).

Preparation of the Methyl Ester Fraction of the Honey Extract. The extract (780 mg), prepared as described above, was dissolved in Et_2O (150 ml) and treated with sat. aq. $NaHCO_3$ soln. (150 ml). After neutralization with 10% aq. HCl soln. (70 ml), drying, and concentration under reduced pressure, the fraction (300 mg) containing org. acids was treated with an ethereal soln. of diazomethane (CH_2N_2), until the yellow color persisted. Removal of the solvent afforded a mixture of methyl esters (240 mg), which were separated by column chromatography (CC; SiO_2; gradient of ether/pentane, twelve fractions).

*2-[(5-Bromopentyl)oxy]tetrahydro-2*H*-pyran* (**18**; *Scheme 2*). Conc. aq. HCl (0.1 ml) was added at r.t. to 3,4-dihydro-2*H*-pyran (1.76 g, 21.0 mmol). Then 5-bromopentan-1-ol (3.32 g, 20 mmol) was added dropwise with cooling in a water bath. After 4 h of stirring at r.t., conc. aq. HCl (0.2 ml) was added, and stirring was continued for 3 h. Then, Et_2O was added, and the org. phase was separated, washed with aq. Na_2CO_3, dried ($MgSO_4$), and concentrated (rotary evaporator). The resulting residue (4.94 g) was distilled to provide **18** (1.25 g, 25%). B.p. 131–136° (12 mm Hg). ^{1}H-NMR: 1.44–1.95 (*m*, 12 H); 3.35–3.90 (*m*, 6 H); 4.58 (*t*, 1 H). ^{13}C-NMR: 98.9 (*d*); 67.2 (*t*); 62.4 (*t*); 33.7 (*t*); 32.6 (*t*); 30.8 (*t*); 28.9 (*t*); 25.5 (*t*); 25.0 (*t*); 19.7 (*t*). EI-MS: 251 (4, M^+), 249 (5), 151 (10), 149 (11), 85 (100), 69 (47), 56 (23), 41 (54), 29 (18).

9-Hydroxynonan-2-one (**11**). Zn Powder (740 mg, 11.4 mmol) was introduced into a flame-dried flask under Ar. THF (8.0 ml), $NiCl_2 \cdot 6\,H_2O$ (120 mg, 0.505 mmol), pyridine (550 mg, 6.95 mmol), and but-3-en-2-one (660 mg, 9.42 mmol) were introduced. The mixture was heated to 60° for 30 min. Compound **18** (1.25 g, 4.98 mmol) was added, and the mixture was heated for 72 h at 80°. After cooling, Et_2O and THF were added, the soln. was filtered, and the filtrate was concentrated under reduced pressure. Acetone (100 ml) and 10% aq. HCl (200 ml) were added to the resulting crude mixture, which contained 9-(tetrahydro-2*H*-pyran-2-yloxy)nonan-2-one (**19**; 66%). The mixture was stirred for 30 min. at r.t., and saturated with NaCl, and extracted with Et_2O (3 ×). The org. layer was dried ($MgSO_4$), the solvent was removed *in vacuo*, and the resulting residue (580 mg) was purified by CC (SiO_2; pentane/ether 3 : 7) to provide **19** (190 mg, 15% from **18**) and the desired keto alcohol **11** (170 mg; 22% from **18**).

Data of **19**: ^{13}C-NMR: 209.3 (*s*); 98.9 (*d*); 67.6 (*t*); 62.4 (*t*); 43.8 (*t*); 30.8 (*t*); 29.9 (*q*); 29.7 (*t*); 29.2 (*t*); 29.1 (*t*); 26.1 (*t*); 25.5 (*t*); 23.8 (*t*); 19.7 (*t*). EI-MS: 242 (0, M^+), 157 (3), 141 (4), 123 (30), 85 (100), 67 (10), 55 (28), 43 (95), 29 (15).

Data of **11**: GC/MS Retention indices (RIs): 2223 (polar), 1337 (apolar). ^{1}H-NMR: 1.25–1.40 (*m*, 6 H); 1.52–1.62 (*m*, 4 H); 2.00 (br. *s*, 1 H); 2.14 (*s*, 3 H); 2.42 (*t*, 2 H); 3.62 (*t*, 2 H). ^{13}C-NMR: 209.6 (*s*); 62.8 (*t*); 43.7 (*t*); 32.7 (*t*); 29.9 (*q*); 29.2 (*t*); 29.1 (*t*); 25.6 (*t*); 23.7 (*t*). EI-MS: 140 (1, M^+), 125 (2), 111 (2), 101 (3), 97 (5), 82 (20), 71 (17), 58 (75), 55 (40), 43 (100), 31 (17).

8-Oxononanal (**10**; *Scheme 2*). A soln. of **11** (1.06 g, 6.70 mmol) in CH_2Cl_2 (10 ml) was added dropwise at r.t. to a stirred soln. of pyridinium chlorochromate (PCC; 2.18 g, 10.1 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 90 min. Then, Et_2O was added, the mixture was filtered through a pad of SiO_2, and the filtrate was concentrated *in vacuo*. The resulting residue (0.98 g) was purified by CC (SiO_2; pentane/ether 1:1) to afford **10** (550 mg; 53%). RI: 1967 (polar), 1266 (apolar). ^{1}H-NMR: 1.28–1.40 (*m*, 4 H); 1.55–1.68 (*m*, 4 H); 2.13 (*s*, 3 H); 2.42 (*m*, 4 H); 9.76 (*t*, 1 H). ^{13}C-NMR: 209.0 (*s*); 202.7 (*d*); 43.8 (*t*); 43.6 (*t*); 29.9 (*q*); 28.9 (*t*); 28.8 (*t*); 23.5 (*t*); 21.8 (*t*). EI-MS: 156 (0, M^+), 138 (6), 113 (3), 95 (10), 81 (4), 71 (13), 58 (52), 43 (100), 29 (12).

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