captan, which were without effect on curly dock. These observations are based on our screening data and must be considered tentative until definitive structure–activity studies can be made.

The mechanism of action postulated for the stimulation of uredospores of *Puccinia graminis* f. sp. *tritici* by nonanal or nonanol has been that of overcoming an endogenous inhibitor, methyl-cis ferulate, identified by Macko et al. (1971). In uredospores of the bean rust organism, *Uromyces phaseoli*, another endogenous inhibitor, methyl-cis-3,4-dimethoxy cinnamate (Macko et al., 1970, 1972), is overcome by β-ionone, the most effective compound of many tested (French et al., 1977).

Another type of biological activity for some of the fatty alcohols has been reported by Sinohara (1973), who found that 1-octanol was the most effective of the one–eight C alcohols in inducing de novo formation of glucose dehydrogenase in dormant spores of *Aspergillus oryzae*. Octanol is almost as active as nonanol as a stimulator of fungal spores germination (French et al., 1975a). Similarly, Feofilova and Arbuzov (1975) reported that β-ionone, another rust spore stimulator (French et al., 1977), induced de novo formation of carotogenic enzymes in *Blakeslea trispora*.

In this connection, it is interesting to note the effects of nonanal and other aldehydes on the swelling phenomenon of smartweed and the effects of citral and other compounds on the formation and excretion of gels in morningglory seed. As previously mentioned in fungal spores, perhaps certain enzyme systems are being activated in seeds. With smartweed, an end product accumulates which greatly increases osmotic intake of water. With morningglory, an increase in gel-forming enzymes may occur. In both cases the growth process appears to be bypassed. Research on these effects is in progress.

While our studies of the 28 volatile flavor compounds on 18 species of weed seed have not shown effects on all species, several responses are worthy of note and further study, particularly the stimulatory effects of nonanenitrile, octyl thiocyanate, and 2-nonanone. Perhaps these compounds could be used to induce premature germination, under conditions in which the seedlings could not survive, such as just before onset of winter. Compounds such as nonanal and citral, and related chemicals, might be used to develop methods for inactivating species like smartweed and morningglory by inducing swelling or exudation, short-circuiting the growth process, and promoting microbial destruction of the seed. Such speculative possibilities suggest the value of continued screening for activity in compounds related to the flavor group, and of a detailed study of structure–activity relationships and mechanism of action. Besides the organoleptic responses induced by all of the compounds, some of them have previously shown activity as insect pheromones, as inducers of de novo enzyme synthesis, and as stimulators of fungal spore and pollen germination. This study shows that some of the flavor compounds also stimulate germination of seed of two *Rumex* species.

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Volatile Constituents of Some Unifloral Australian Honeys

Anthony D. Graddon, James D. Morrison,* and John F. Smith

A study has been made of the volatile constituents of some unifloral Australian honeys, using a gas chromatograph–mass spectrometer–computer system. The extracts of honey volatiles prove to be complex mixtures of at least 100 compounds. A surprising range of hydrocarbons and oxygenated compounds are present, some of which may be unique to the floral sources.

Honey has played a part in the diet of mankind since the earliest recorded times. Honeys are often very distinctive, each country producing varieties which are sometimes highly prized. Australia, with a flora somewhat different from the rest of the world, produces several rather unusual honeys.

The composition of honey has been studied extensively. Most of the studies reported in the literature have been directed toward quality control and establishing standards for the honey industry and these studies have usually been

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limited to the analysis of the major constituents (glucose, fructose, and water) and enzyme activity. There are also some reports of more detailed analyses of minor constituents, which are summarized in a comprehensive review of the composition of honey by White (1975). A recent report by Chandler et al. (1974) presented analytical results for a large number of Australian honeys.

Unifloral honeys possess highly characteristic aromas, indicating the presence of various volatile components. Some of these probably derive from the original sources of nectar; some will be dependent on the physiology of the bee, and others arise in processing after harvest. Orange blossom honey, for example, contains about 2–4 ppm of methyl anthranilate (MA) which is virtually absent from other honeys (White, 1975). By contrast, hydroxymethylfurfural (HMF) is found in all honeys at varying concentrations. HMF is produced by the decomposition of fructose and the rate of formation is exponentially dependent on the temperature, so the level of HMF is higher in honey which has been overheated in processing or storage, or which has been adulterated with acid-hydrolyzed invert sugar. Both MA and HMF can be determined spectrophotometrically but most other volatile compounds can only be studied adequately by gas chromatography. The volatiles of honey have been studied less comprehensively than those of many other foodstuffs.

Dörrsheidt and Friedrich (1962) identified methyl acetate and methyl propionate in a honey distillate using gas chromatography (GC) but were unable to identify 29 other components. ten Hoopen (1963) used a vacuum distillation technique to capture low-molecular-weight carbonyls as their 2,4-dinitrophenylhydrazones and was able to identify five compounds by GC. Merz (1962) made a qualitative gas chromatographic study of an ether extract and attempted to relate the quality of the honey to the HMF content. His report also included an organoleptic evaluation of eluting GC peaks and it was observed that compounds eluting after HMF had the most distinctive honey-like aromas.

Cremer and Riedmann (1965) extracted honey volatiles with a stream of hydrogen gas at temperatures of 70 to 90 °C and were able to separate about 120 compounds by GC, of which more than half were identified. The major constituents included alcohols, their oxidation products, and esters. It was suggested that the alcohols were produced from free amino acids by enzymic reactions. Phenylalanine was therefore indicated as a precursor of 2-phenylethanol and phenylacetic acid and its esters which are used in honey essences [Furia and Bellanca (1971)]. Honeys in which 2-phenylethanol and benzyl alcohol could not be found were considered to be organoleptically weak.

Cremer and Riedmann (1965) observed that they were unable to detect HMF or any of the late eluting honey aroma components reported by Merz (1962). It is probable that their apparatus was unsuitable for the study of such compounds. For example, the latest eluting compound which was identified in their analyses was 2-phenylethanol which has a retention index, under similar GC conditions, of about 0.4 relative to HMF. It is apparent that there is a conflict between the work of Merz and that of Cremer and Riedmann.

Two more recent reports have indicated the presence of compounds which probably originate directly from the floral source. Chogovadze et al. (1973) used GC to detect various terpenoids and esters in honeys of the Georgian S.S.R. Tsuyena et al. (1974) identified 8-*p*-menthene-1,2-diol as the major component of Linden honey and also identified several other terpenoid compounds by IR, MS, NMR, and GC. They also identified several compounds which had been reported by Cremer and Riedmann (1965), but, as in previous reports, about half of the components detected by GC could not be identified.

Table I. Honey Samples Analyzed

abbrev.	plant of origin, common name	botanical name	source
BA1	Saw Banksia	*Banksia serrata*	AHC
BA2	Desert Banksia	*Banksia ornata*	AHC
YB	Yellow Box	*Eucalyptus melliodora*	THA
SB	Stringy Bark	*Eucalyptus* [mixed]	THA
SWB	Sweet Bursaria	*Bursaria spinosa*	GAY
CL1	Clover	*Trifolium repens*	AHC
CL2	Clover	*Trifolium repens*	AHC

Ferber and Nursten (1977) used GC–MS to analyze beeswax volatiles extracted by vacuum distillation. They identified about 50 compounds, about half of which were hydrocarbons and the remainder were oxygenated compounds including significant amounts of benzyl alcohol and 2-phenylethanol which have consistently been identified in honey.

The work described in this paper contains detailed analyses of extracts of seven Australian honeys, four from native flora and three from exotics, as part of a preliminary study on the aroma of honey.

EXPERIMENTAL SECTION

1. Source of Honey Samples. Unifloral honey samples were obtained from a retail outlet [True Health Aids (THA), Sydney, NSW] and from a honey merchant [Archibald Honey Co. (AHC), Dingley, Victoria] (see Table I). Both sources specialize in straight line honeys from individual apiarists. Sweet Bursaria honey was obtained from a local apiarist (W.R. Gay, Rosanna, Vic.).

2. Preparation of Honey Extracts. Ten milliliters of dichloromethane was thoroughly mixed with 50 g of honey and then decanted. This was repeated with four more 5-mL aliquots of solvent and the combined extract was concentrated by evaporating the solvent with a stream of high-purity nitrogen. When the volume was suitably reduced, concentration was completed in a vial which was then sealed with a septum to retain the inert atmosphere of nitrogen. The concentrates had an intense honey aroma and a yellow color and were typically solid below 30 °C.

For two honeys, a duplicate extract was prepared with the addition of methyl anthranilate (MA) to the honey (1 μg/g) prior to extraction to allow an approximate quantification of the volatiles detected but the difference in extraction efficiency for the various compounds makes the estimation of concentrations uncertain.

Blank analyses were performed by concentrating 30 mL of the CH_2Cl_2 (Merck A.R.) to the same volume as the final honey extracts, using the same apparatus. The GC–MS analysis showed the presence of $CHCl_3$, CCl_4, and a trace of benzyl chloride (approximate ratio 10:3:1). The first two could only be detected by mass chromatography since they eluted in the tail of the wide solvent peak.

The dilution of honey with either one part or three parts (w/w) of distilled water prior to solvent extraction gave less satisfactory results. The extraction was complicated by the formation of emulsions and, more important, the final extracts did not contain some of the compounds found as major components in the extracts made without dilution (notably HMF and methyl furoate), presumably because the partition between aqueous and CH_2Cl_2 phases was altered.

3. Gas Chromatography. Honey extracts were analyzed on a Pye Model 104 gas chromatograph interfaced

Table II.

	SCOT	PACKED
phase	Carbowax 20M	SP1000 (1.5%)
support		60-80 mesh Chromosorb G
column length	50 m	2 m
column diameter	0.5 mm i.d.	3.1 mm o.d., ca. 2 mm i.d.
helium flow, mL/min	2.0	12-15
initial period	various up to 8 min	none
program range, °C	60-210	150-220
program rate, °C	4 or 6	6

by a silicone membrane to a 12-in. magnetic-sector single-focusing mass spectrometer constructed in these laboratories.

Two columns were used for this work (Table II).

The first analyses were carried out using only the support coated open tubular (SCOT) column. Later it was realized that a major portion of the extracts did not elute from this column. Subsequent analyses using the packed column showed that most of the extract consisted of high-molecular-weight hydrocarbons. The retention of these compounds and probably some others on the SCOT column is believed to have contributed to the progressive deterioration observed in its performance throughout these analyses.

4. GC–MS–Computer Analysis. During a GC–MS analysis, the mass spectrometer was scanned under computer control (Digital Equipment Corporation PDP 11/40) from about m/e 10 to an upper mass limit specified by the operator. Scan repetition rates were 1.5 s for scans up to m/e 200, 2.0 s for scans to m/e 300, and 2.5 s for scans to m/e 400. Spectra were stored on magnetic disk cassette for processing after completion of the GC analysis.

The data were processed using a combination of mass fragmentography and background subtraction. The processed mass spectra could be plotted in bar-graph form on a Tektronix 4006-1 terminal with hard copy facility, which was also used to display the mass fragmentograms. The spectra could also be compared with reference spectra from small user-created libraries of up to 300 ten-peak mass spectra, using a similarity ranking reverse-search routine. Software for the GC–MS–computer system was written entirely by one of the authors (A.G.).

Mass spectra were first checked by computer search against a library of about 100 previously identified spectra or checked if necessary against a large computer library (of about 30 000 spectra) or against compilations of mass spectral data (Cornu and Massot, 1966; or Stenhagen et al., 1974). When a compound could not be identified in this way, an attempt was made to elucidate the structure from its fragmentation pattern. Attempting to ascertain elemental formulae by isotope ratios was generally not possible since fast scanning during data acquisition results in large statistical uncertainties for low intensity ions.

Where reference compounds were available, identifications were checked by retention data and mass spectra.

RESULTS

About 160 compounds were detected of which approximately 100 have been identified with various degrees of certainty. For the purpose of presentation, the compounds have been divided into two classes, hydrocarbons and oxygenated compounds. No compounds were identified containing other elements.

In Tables III–VI the concentration is indicated on a three-point scale, each division differing by a factor of 10. In absolute terms, a major component represents more than 5 ppm of the honey but this limit can only be regarded as approximate since it is based on the peak size of only one introduced compound (MA) in only two analyses.

1. Hydrocarbons. *(a) Retention Times Up to Hexadecane.* In six of the extracts, these compounds formed between 3 and 13% of the total eluant from the SCOT

Table III. Hydrocarbons,[a] Yellow Box Extract

formula	name		formula	name	
C_9H_{20}	branched alkane	**[b]	C_9H_{12}	methylethylbenzene	**
$C_{10}H_{22}$	branched alkane	**	$C_{10}H_{14}$	alkylbenzene (C_4)	**
C_9H_{18}	bisubst. cyclohexane	*	C_9H_{12}	alkylbenzene (C_3)	***
$C_{10}H_{22}$	branched alkane	*	$C_{10}H_{14}$	alkylbenzene (C_4)	*
$C_{10}H_{22}$	branched alkane	***	$C_{10}H_{14}$	alkylbenzene (C_4)	*
$C_{10}H_{22}$	branched alkane	**	$C_{10}H_{14}$	alkylbenzene (C_4)	**
$C_{10}H_{22}$	decane	***	C_9H_{12}	1,2,3-trimethylbenzene	**
$C_{11}H_{24}$	branched alkane	**	$C_{10}H_{14}$	alkylbenzene (C_4)	**
$C_{10}H_{20}$	monosubst. cyclohexane	*	$C_{10}H_{14}$	alkylbenzene (C_4)	**
C_7H_8	toluene	*	$C_{10}H_{14}$	alkylbenzene (C_4)	**
$C_{11}H_{24}$	branched alkane	**	C_9H_{10}	allylbenzene (?)	*
$C_{11}H_{24}$	branched alkane	**	$C_{11}H_{16}$	alkylbenzene (C_5)	*
$C_{10}H_{20}$	monosubst. cyclohexane	**	$C_{10}H_{12}$	alkenylbenzene (C_4)	*
$C_{11}H_{24}$	undecane	***	$C_{11}H_{16}$	alkylbenzene (C_5)	*
C_8H_{10}	ethylbenzene	**	$C_{10}H_{12}$	methylindane	*
C_8H_{10}	*p*-xylene	**	$C_{11}H_{16}$	alkylbenzene (C_5)	*
C_8H_{10}	*m*-xylene	**	$C_{10}H_{14}$	alkylbenzene (C_4)	*
$C_{10}H_{18}$	decalin	*	$C_{11}H_{16}$	alkylbenzene (C_5)	*
C_9H_{12}	isopropylbenzene	*	$C_{14}H_{30}$	tetradecane	**
C_8H_{10}	*o*-xylene	**	$C_{11}H_{16}$	alkylbenzene (C_5)	*
$C_{11}H_{22}$	monosubst. cyclohexane	*	$C_{10}H_{14}$	alkylbenzene (C_4)	**
C_9H_{12}	propylbenzene	*	$C_{11}H_{16}$	alkylbenzene (C_5)	*
$C_{12}H_{26}$	dodecane	**	$C_{10}H_{14}$	alkylbenzene (C_4)	**
C_9H_{12}	methylethylbenzene	***	$C_{10}H_{12}$	alkenylbenzene (C_4)	*
C_9H_{12}	trimethylbenzene	**	$C_{10}H_{12}$	tetralin	*
$C_{10}H_{14}$	alkylbenzene (C_4)	*	$C_{16}H_{34}$	hexadecane	*
C_8H_8	styrene	*			

[a] Hydrocarbon levels were much lower in all other honey extracts. [b] (*) Trace component, (**) minor component, (***) major component.

Table IV. Compounds Positively Identified[a]

	SW	YB	BA1	BA2	CL1	CL2	SWB
acetoin	***	***	***	**	*	*	*
hydroxyacetone	*	*	*	*	*	*	*
furfuraldehyde	*	*	*	*	*	**	*
methyl furyl ketone			*			*	*
linalool	*						*
benzaldehyde		*					*
isobutyric acid				*			
γ-valerolactone			*			*	
phenylacetaldehyde						*	*
butyrolactone	*	*	*		*	*	*
benzyl alcohol	*	*	*	*	*	*	*
2-phenylethanol	*	*	*	*	*	*	*
phenol						***	***
o-methoxybenzyl alcohol							**
p-methoxybenzyl alcohol							*
5′-hydroxymethyl-2-furaldehyde	**	**	**	**	***	*	***
methyl syringate		?	**	*	**	?	***

[a] See footnote *b* of Table III.

Table V. Compounds Tentatively Identified

	ref	SB	YB	BA1	BA2	CL1	CL2	SWB
3-hydroxypentan-2-one (P)	*a*	**	**	*	*	*		
2-hydroxypentan-3-one (P)	*a*	**	*	*	*			
1-hydroxybutan-2-one (P)	*a*	*	*	*	*			
linalool oxide		*	*					
butane-2,3-diol		*		*				
5-methyl-2-furaldehyde (P)		*						
furfuryl alcohol		*	*					*
hexenyl butyrate (I)	*b*	**	**	*				
methylmethoxyfuran (P)		*				*	*	*
phenylfuran	*c*							*
ionol		*		*	*		*	*
hexenyl butyrate (II)	*b*	***	***	**		**	*	*
furan-2,5-dicarbaldehyde (P)	*d*					*	*	***
methyl furoate	*e*	*	*	*	*	**	**	**
methoxybenzaldehyde							*	*
propylanisole								*
α-hydroxyacetophenone					*			**
3,5-dihydroxy-2-methyl-2,6-dihydropyran-4-one		*		*			*	
methyl 2,5-dimethoxybenzoate								**
3,5-dimethoxybenzaldehyde								*
trimethoxybenzaldehyde								**
palmitic acid				*	*	*	?	*

[a] The three α-hydroxy ketones in this table are homologues of acetoin and hydroxyacetone (Table IV). Their mass spectra (see Figure 1) indicate very similar fragmentation mechanisms. [b] The mass spectra obtained for these two compounds are most similar to reference spectra (CSIRO) of the two hex-3-enyl butyrates, but the match is not perfect and it is possible that the structure of the alkenyl moiety may be different. [c] Stenhagen et al. list several compounds with very similar mass spectra; α-naphthol, β-naphthol, phenylfuran, and 2-vinylbenzofuran. Of these, the two naphthols have been excluded because their retention time is much greater than the unknown. [d] No reference mass spectrum was available but the proposed structure is almost certain, especially considering the high content (in all honeys) of the alcohol analogue 5′-hydroxymethylfurfural. The mass spectrum is shown in Figure 1. [e] A reference sample of methyl-2-furoate was obtained but it eluted much earlier than the unknown. However, the mass spectra were very similar, differing only in the abundance of the molecular ion (126$^+$) which was 44% in the standard and 20% in the unknown. It is probable that the unknown is the isomer, methyl-3-furoate.

Table VI. Unidentified Compounds[a]

	M_r	SB	YB	BA1	BA2	CL1	CL2	SWB
A	?	*	*	*	*			
B	138	*				**		
C	152	*	*		*	*		*
D	?	*	*	*	*	**	*	**
E	164		*	***	*			*
F	?	**	*	*	*	**	*	*
G	180	*	*	*	*	*	?	*
H	206	**	**	**	**	*	*	**

[a] These compounds are listed in order of GC elution, and their mass spectra are presented in Figures 2 and 3. Proposed structures: (A) C_8 or C_9 alcohol, (B) 4-butylcyclopenten-3-one, (C) 4-butylcyclohexen-3-one, (E) 1-phenylpentan-2-ol, (G) (5′-carbaldehyde)-2-furyl butyl ketone. Structures B and C are proposed after comparison of the mass spectra with that of piperitone (Stenhagen et al., 1974).

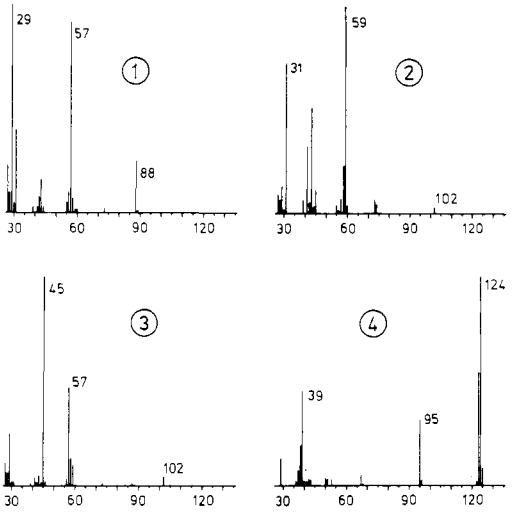

Figure 1. Mass spectra of tentatively identified compounds which do not appear in reference compilations. (1) 1-hydroxybutan-2-one, (2) 3-hydroxypentan-2-one, (3) 2-hydroxypentan-3-one, (4) furan-2,5-dicarbaldehyde.

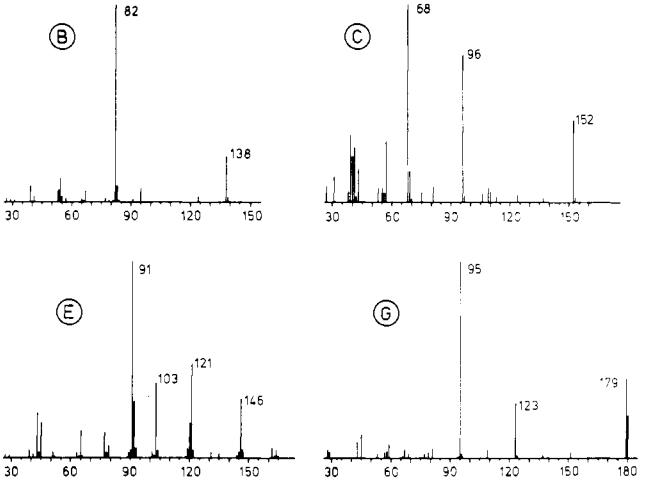

Figure 2. Mass spectra of unidentified compounds for which a structure has been suggested. (B) 4-butylcyclopenten-3-one, (C) 4-butylcyclohexen-3-one, (E) 1-phenylpentan-2-ol, (G) (5′-carbaldehyde)-2-furyl butyl ketone.

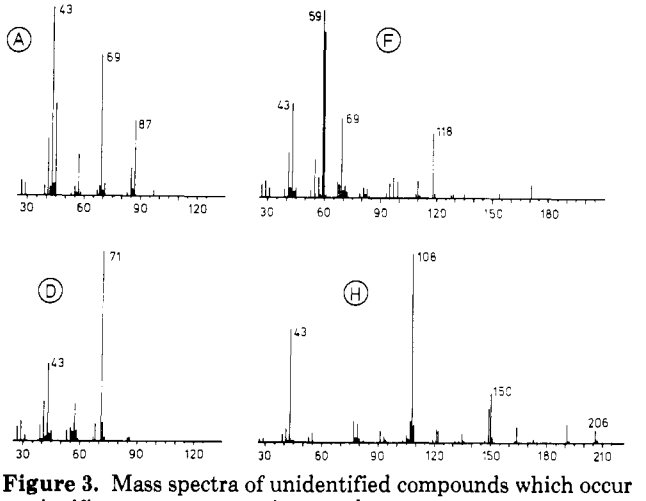

Figure 3. Mass spectra of unidentified compounds which occur as significant components in most honey extracts.

column, but in Yellow Box honey this figure was about 50%. Although the hydrocarbon spectra are easy to recognize, it is difficult to distinguish between isomers because of the similarity of their mass spectra. This is especially true for the higher alkyl benzenes and branched alkanes. The complete identification of every hydrocarbon would require extensive retention-time studies, and this has not been attempted since it is not at present believed that any of these compounds contribute to the honey aroma.

The hydrocarbons detected in the YB extract are listed in Table III. Because of the deteriorating column performance and the much lower hydrocarbon content, fewer compounds were detected in the other extracts but the results indicated that the hydrocarbon composition was similar in all cases.

(*b*) *Hydrocarbons with Retention Times Greater than Hexadecane.* As stated previously, these compounds were not all detected in early analyses because they were not eluted from the SCOT column. They were identified using the 6-ft packed column and consist mainly of *n*-alkanes, C_{23}, C_{25}, C_{27}, C_{29}, and C_{31} in the approximate ratio 1:2:6:3:3. Even-number alkanes were in much lower concentrations.

2. Oxygenated Compounds. For purposes of presentation, these compounds are divided into (a) compounds definitely identified, (b) compounds partially or tentatively identified, and (c) unknown compounds. Data for some of the less volatile components are only available for extracts which were analyzed using the short-packed column as well as the SCOT column.

(*a*) *Compounds Positively Identified.* The compounds listed in Table IV have been identified by mass spectral and retention time data by comparison with reference compounds.

In the case of methyl syringate, its mass spectrum did not appear in reference libraries. However, it was present as a major component in Sweet bursaria honey extract and it was possible to trap the compound from a GC column for examination in a double-focusing mass spectrometer with peak matching facilities (Japan Electron Optics Laboratories Model JMS D-100). The accurate mass of the molecular ion (m/z 212) and the major fragment ion (m/z 181) was obtained, and this information led to the proposed structure which was subsequently confirmed by formation of the compound from methanol and syringic acid on Dowex 50 cation-exchange resin (H^+ form) and GC–MS analysis.

(*b*) *Compounds Tentatively or Partially Identified.* This group includes compounds which have been identified by comparison of their mass spectra with reference spectra but have not yet been confirmed by retention time data (Figure 1).

Also included in Table V are compounds whose structure has been deduced from their mass spectra and for which it is believed that the given structure is highly likely. These compounds are indicated (P).

(*c*) *Unidentified Compounds.* In the course of the analyses, about 60 compounds have been detected whose mass spectra do not appear in either of the catalogues. The quality of these mass spectra is variable and about half of them are poor spectra of trace components which are poorly resolved from column bleed and neighboring GC elutants. Most of the others have been detected with good reproducibility in several honeys and must be considered as detailed spectra of single compounds. So far it has not been possible to trap enough of these compounds for high-resolution mass measurement.

Molecular structures have been proposed for five of the unknowns but with a low degree of confidence (Figures 2 and 3). Table VI also includes three other unknowns which have been detected in every honey.

DISCUSSION

The GC–MS analysis of these honey extracts has shown that they are extremely complex mixtures containing about 100 compounds, each present in amounts between 20 ppb and 20 ppm of honey.

Of the compounds identified, only a few have been reported in previous studies. Acetoin, 2-phenylethanol, benzyl alcohol, and furfural were reported by Cremer and Riedmann (1965) and these were detected in all extracts. Some of the more volatile compounds mentioned in their study and in the earlier papers would not be detected in our analyses because they would be evaporated with the solvent during concentration or eluted with the solvent peak in GC–MS analysis. The methyl and ethyl esters of phenylacetic acid which Cremer and Riedmann (1965) implicated as honey-aroma compounds have not been detected, possibly because their concentration is too low. Of the terpenoids reported by Chogovadze et al. (1973) and Tsuyena et al. (1974), only linalool has been identified.

The hydrocarbons found in the honey extracts almost certainly come from beeswax which has not been completely separated during harvest and processing. The relative amounts of alkanes C_{23}–C_{31} are nearly identical with those reported by Tulloch (1972) in the GC analysis of whole beeswax. Tulloch (1972) also reported the presence of a C_{16} acid in beeswax and palmitic acid has been detected in most of our honey extracts. The lighter hydrocarbons identified in our analyses agree with those reported in the volatile fraction of beeswax by Ferber and Nursten (1977) except that the honey extracts contained comparatively low levels of C_{12}–C_{20} alkanes and methylated naphthalenes were not detected. Ferber and Nursten also identified several other oxygenated aromatics which had not been reported in honey, but of these we have detected only phenol.

One of the main aims of the series of analyses was to establish which components were present in all of the extracts. Excluding the hydrocarbons, ten such compounds have been found: acetoin, hydroxyacetone, furfuraldehyde, methyl furoate, HMF, 2-phenylethanol, benzyl alcohol, and three unidentified D, F, and G. It is probable that other compounds should be included but may have escaped detection in some analyses because of low concentration or premature termination of the MS data acquisition.

HMF was present in all of the extracts as a major component and the calculated concentration (5–20 ppm) agrees well with results published by Chandler et al. (1974) and other sources. The level of methyl furoate and furfural was approximately proportional to the HMF content, which suggests that these, and probably some other furan compounds, are derived from the same source, probably the nonenzymic degradation of monosaccharides.

Hydroxyacetone, benzyl alcohol, phenylethanol, and unknown D were found at about the same level in all the extracts but the acetoin content varied dramatically: honeys from exotic flora (clover and Sweet Bursaria) contained only traces, whereas the native honeys contained large amounts and also contained substantial amounts of the other hydroxy ketones (See Table V). Unknown F was found in more variable amounts and the detection of other very similar spectra within the same analysis indicates the existence of three or more isomers. Unknown H was present in significant amounts in all extracts and two other compounds with very similar spectra were detected in most cases.

The other compounds of special interest are those which occur in high concentration (>5 ppm) in one or more honeys and are apparently absent from others: hexenyl butyrates (I) and (II) in SB and YB, phenol in Cl1 and SWB, unknown E in BA2, various methoxy aromatics in SWB.

Phenol is sometimes used as a bee repellent during harvest but it is likely that the other compounds come directly from the floral source or environment since it is doubtful that such uniqueness could be due to difference between the hives or in the processing. More data are required before this can be confirmed.

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