Composition of Australian Honey Extractives. 1. Norisoprenoids, Monoterpenes, and Other Natural Volatiles from Blue Gum (*Eucalyptus leucoxylon)* and Yellow Box (*Eucalyptus melliodora)* Honeys

Bruce R. D'Arcy,*,† Gavin B. Rintoul,† Catherine Y. Rowland,‡ and Adrian J. Blackman‡

Department of Food Science and Technology, The University of Queensland, Gatton College, 4345, Queensland, Australia, and Department of Chemistry, University of Tasmania, Hobart, GPO Box 252C, 7001, Tasmania, Australia

Chemical fingerprinting of Australian honey requires information on the composition of natural honey volatiles if it is to be useful as a honey-sourcing method. The naturally occurring volatiles of Australian blue gum (*Eucalyptus leucoxylon*) and yellow box (*Eucalyptus melliodora*) honeys were isolated by solvent (ethyl acetate) extraction. Compounds in the extracts were analyzed by gas chromatography (GC) and gas chromatography−mass spectrometry (GC−MS). These procedures have permitted the identification of 55 compounds that include norisoprenoids, monoterpenes, benzene derivatives, aliphatic compounds, and Maillard reaction products. The following 13 compounds were quantitatively identified for the first time in honey: four isomeric 3,4-dihydro-3-oxoactinidols; 8,9-dehydrotheaspirone; two isomeric 3-oxoretro-α-ionols; megastigm-4-ene-3,9-dione; 1-phenylbutane-2,3-diol; 1-phenylbutane-2,3-dione; 18-hydroxyoleic acid lactone; 3,5-dihydroxy-2-methyl-4*H*-pyran-4-one; and 2,5-dimethyl-2,4-dihydroxy-3(2*H*)-furanone. The nature of the volatiles and semivolatiles in these two Australian honeys suggests that Australian honeys are quite distinctive relative to the other honeys that have been chemically studied by GC−MS.

Keywords: *Australian blue gum (Eucalyptus leucoxylon) honey; yellow box (Eucalyptus melliodora); natural volatiles; norisoprenoids; extractives; monoterpenes; composition*

INTRODUCTION

No information is presently available on the identity of those honey constituents that are useful for chemically authenticating the floral origin of Australian blue gum (*Eucalyptus leucoxylon*) and yellow box (*Eucalyptus melliodora*) honeys. Naturally occurring volatile flavor compounds are largely responsible for the strong, distinctive aroma and flavor of Australian honeys (Graddon et al., 1979; Wootton et al., 1978). Thus, the chemical analysis of natural honey volatiles using gas chromatography (GC) combined with mass spectrometry (GC−MS) (chemical fingerprinting) may identify compounds that are useful for objectively authenticating the floral origin of Australian honeys. To confirm such an hypothesis, it is important to first examine the previous studies of natural honey volatiles.

One of these studies is our recent GC investigation of natural volatiles among the total organic extractives in methylated extracts of Australian leatherwood (*Eucryphia lucida*) honey (Rowland et al., 1995). This study identified few natural honey volatiles (volatiles in the honey extracts prior to methylation). In addition, there have been only two other detailed studies of Australian honey volatiles (Graddon et al., 1979; Wootton et al., 1978); however, both studies identified few significant natural volatiles. Thus, these three previous studies of Australian honeys have provided only limited data on the chemistry of natural honey volatiles. The characterization of these volatiles is, therefore, of interest in the search for possible floral source descriptors for Australian honeys.

In contrast to the limited chemical data available on Australian honey volatiles, studies of other honeys have identified many natural volatiles, with the early GC work (pre-1966) being well reviewed by White (1975), Graddon et al. (1979), and Maga (1983). However, later GC studies of honey volatiles have not been so well reviewed. The following examination highlights the three main categories of natural volatiles that are dominant in, or source specific for, honeys throughout the world; norisoprenoids, terpenes, and benzene derivatives.

Firstly, some honeys are known to contain degraded carotenoid-like norisoprenoids with a 3,5,5-trimethylcyclohex-2-ene ring structure (Broom et al., 1992b). Examples of honeys that contain a variety of these norisoprenoids are New Zealand heather (*Calluna vulgaris*) honey (Tan et al., 1989a,b; Tan, 1989; Sun, 1995), Asian longan (*Euphoria longana*) honey (Ichimura, 1994), and Australian leatherwood honey (Rowland et al., 1995). The norisoprenoids in these three honeys appear to originate from the floral source. Furthermore, an individual norisoprenoid that is a floral source descriptor is dehydrovomifoliol (**80**); it characterizes European heather honeys (Häusler and Montag, 1989, 1991). In another study of honey volatiles, the norisoprenoid, 1-(2-oxo-*trans*-1-butenyl)-2,6,6-trimethylcyclohexane-*trans*,*cis*-1,2,4-triol was found to characterize New Zealand thyme honey (Tan et al., 1990; Broom et al., 1992a). Therefore, the results of these various studies suggest that volatile norisoprenoids are one of the important categories of natural honey volatiles.

Additionally, many honey types throughout the world contain volatile terpenes, of which some are floral source

* Author to whom correspondence should be addressed. E-mail: bd@burger.uqg.uq.edu.au. Facsimile: + 61 7 5460 1171.

† The University of Queensland.

‡ University of Tasmania.

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descriptors. One of the best examples of the occurrence of honey terpenes is in New Zealand nodding thistle (*Carduus nutans*) honey, where volatile monoterpenes such as hydroxylated linalool derivatives and lilac alcohols and aldehydes characterize this honey (Wilkins et al., 1993b). Also, Asian longan honey (Ichimura, 1994) and Australian leatherwood honey (Rowland et al., 1995) contain some of these linalool derivatives. The variety of monoterpenes in these three honeys suggests such compounds are floral source descriptors. Furthermore, it appears that the individual volatile terpenes, *trans*-8-*p*-menthene-1,2-diol (Tsuneya et al., 1974), linden ether, and *cis*-rose oxide are floral source descriptors for shina (linden; *Tilia* spp; lime tree) honey (Blank et al., 1989). In addition, separate studies of the volatiles in Georgian (Tschogowadse et al., 1973) and Hungarian honeys (Tóth et al., 1987) have identified honey terpenes. Both these studies characterized compounds normally found in plant essential oils, which seems to indicate that plant nectar is the source of the terpenes in these honeys. Also, volatile terpenes were recently reported in honey as part of a detailed headspace GC−MS investigation of aroma volatiles (Bouseta et al., 1992). The two identified terpenes (α-pinene and limonene) are not floral source specific for any honeys; however, other aroma volatiles appear to be characteristic of particular honeys (Bouseta et al., 1992, 1996). A similar study (purge-and-trap GC−MS analysis) that identified honey terpenes was important since it detailed source specific volatile monoterpenes, including linalool derivatives, in honeys from the United States of America (Overton and Manura, 1994); this is the only recent study of natural volatiles in honeys from this country. In conclusion, all of these studies indicate that volatile terpenes, particularly monoterpenes, are another category of natural honey volatiles.

In addition to honey norisoprenoids and monoterpenes, volatile benzene derivatives are important since many are dominant in some honeys. One study of such honeys attempted to chemically source three European honeys based on differences in the occurrence and quantity of volatile aromatic aldehydes and acetophenone (Häusler and Montag, 1990). Similarly, the GC analysis of volatile aromatic compounds characterized the floral type of honeys sourced from Spain (Aguar et al., 1991). Two important earlier studies of honey volatiles found that phenylacetaldehyde is the dominant component in honeys from Piedmont, Italy (Bicchi et al., 1983), and 3-aminoacetophenone is the major volatile component that distinguishes Italian chestnut honey (Bonaga and Giumanini, 1986). On the other hand, a family of 4-methoxyphenyl compounds is a dominant feature of New Zealand manuka (*Leptospermum scoparium*) honey (Visser et al., 1988), although, curiously, other investigations of this honey did not find many of these compounds (Tan et al., 1988; Wilkins et al., 1993a). Finally, a recent study of New Zealand vipers bugloss honey is important since it showed, for the first time, that 1,4-dihydroxybenzene (hydroquinone) is a floral source descriptor for honey (Wilkins et al., 1995b). The results of all these studies, therefore, indicate that volatile benzene derivatives are also a major category of the natural volatiles that are dominant in honey.

These studies, and other work on honey volatiles (Radosevic et al., 1976; Tateo, 1982; Artem'ev and Chepurnoi, 1984a,b), provide a starting point for studies of Australian honeys, where the chemistry of natural volatiles remains largely unknown. This paper examines the chemistry of natural volatiles extracted from samples of Australian blue gum (*E. leucoxylon*) and yellow box (*E. melliodora*) honeys and determines if any of these compounds are useful for authenticating the floral origin of each honey type.

MATERIALS AND METHODS

Reagents. Analytical grade ethyl acetate was redistilled and checked by GC. Standards and authentic materials were obtained as analytical grade commercial chemicals and were at least 95% pure by GC. Dehydrovomifoliol (**80**) and 3-oxo-α-ionone (**71**) were donated, and methyl syringate was synthesized from a commercial sample of the corresponding acid by treatment with diazomethane.

Honey Samples. Eight replicate samples of yellow box (*E. melliodora*) honey and seven replicate samples of blue gum (*E. leucoxylon*) honey were the important commercial floral honeys collected for this study. During the 1994−1995 flowering season, individual Australian apiarists supplied six blue gum honey samples (BG1−BG6) sourced from different geographical areas of Victoria (southern Australia) and seven yellow box honey samples (YB1−YB7) sourced from different areas in south-east Queensland and northern New South Wales, Australia. These 13 honey samples were heated to 30−40 °C during centrifugal extraction from the combs. The seventh sample of blue gum honey, BG7, and the eighth sample of yellow box honey, YB8 ("Leabrook Farms", Coopers Fine Foods Pty. Ltd., South Australia) were sourced during the 1993−1994 flowering season. These two samples were obtained from retail outlets and were heated at temperatures up to 58 °C during transfer, filtering, and bottling.

The taste, aroma, and color characteristics, together with information about the hive location, season, and available floral sources, were used by the supplying apiarists and the honey packer to accurately identify the floral source of the Australian honey samples. This procedure is the standard honey-sourcing method used by the Australian honey industry.

Honey Sample Preparation. Before extraction, the honey samples were centrifuged at 2500 rpm for 15 min to remove any beeswax.

Honey Extraction. The procedure for the preparation of unmethylated honey extracts was a modification of the method reported by Rowland et al. (1995). This modified method was used since it reproducibly extracts natural honey volatiles and semivolatiles (high-boiling volatiles) with good recoveries and without the excessive application of heat. An extract from 30 g (3 × 10 g) of each of the eight replicate samples of yellow box honey and the seven replicate samples of blue gum honey was prepared using the following procedure.

In a typical extraction, an aliquot (200 μL) of an internal standard of methyl undecanoate in ethyl acetate (0.152 mg/mL) was added to honey (10 g). The internal standard was thoroughly mixed with the honey using a mechanical stirrer (750 rpm) for 2 min. This honey was left to equilibrate at room temperature for 10 min. The honey was then extracted by initially stirring rapidly (mechanical stirrer at 750 rpm) with ethyl acetate (16 mL) at room temperature for 5 min. The solvent was decanted, and the honey residue was exhaustively extracted by stirring (mechanical stirrer at 750 rpm) with ethyl acetate (3 × 8 mL) for 3 min. Finally, this whole procedure was repeated with two other samples (10 g) from the same bulk honey replicate (overall a triplicate extraction; combined total of 30 g of honey). All of the ethyl acetate extracts from the triplicate extraction (3 × 10 g of honey) were then combined. An aliquot (600 μL) of methyl heptadecanoate in ethyl acetate (0.144 mg/mL) was added to this combined ethyl acetate extract. The combined extract (with both internal standards) was then carefully concentrated under reduced pressure in an all-glass rotary evaporator at 30 °C. When the volume was suitably reduced (to 1 mL), the extract was dried over anhydrous sodium sulfate. The filtered extract was then diluted to 2 mL with ethyl acetate, and stored at −18 °C. One microlitre of this extract was analyzed by GC and GC−MS. Also, some of the honey extracts (2 mL) were evaporated to dryness (under a stream of nitrogen), after the GC and GC−

Table 1. Mean Concentrations and Coefficients of Variance (CV) Obtained for 20 Volatiles for Seven 30 g Extractions of the Same Bulk Sample of the Yellow Box Honey, YB2

compd no.	retent index	compound (prominent MS peaks)	mean (mg/kg of honey)	CV(%)
4	804	*levo*-butane-2,3-diol	4.8	9.7
5	811	*meso*-butane-2,3-diol	3.7	20.1
13	947	unknown (41, 43, 45, 57, 69, 74, 85)	0.3	11.6
14	953	unknown (41, 43, 45, 55, 57, 69, 74, 87)	0.4	19.4
27	1081	*cis*-linalool oxide (furan type)	0.5	10.8
34	1167	2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one	2.0	5.0
50	1340	unknown isomer of trimethylphenol (77, 91, 121, 156 M^+)	4.7	13.9
53	1375	3-hydroxy-4-phenylbutan-2-one	3.2	8.3
56	1410	monoterpene (43, 55, 59, 67, 68, 93, 94, 111, 137, 155)	3.6	11.1
57	1412	monoterpene (43, 55, 59, 67, 68, 93, 94, 111, 137, 155)	1.9	8.2
59	1446	1-phenylbutane-2,3-diol	0.9	12.1
63	1605	3,4-dihydro-3-oxoactinidol (isomer 1)	3.2	11.0
64	1610	3,4-dihydro-3-oxoactinidol (isomer 2)	0.7	11.6
65	1633	3,4-dihydro-3-oxoactinidol (isomer 3)	2.2	11.3
71	1675	3-oxo-α-ionone	1.2	10.1
74	1719	unknown (43, 65, 77, 91, 105, 149, 178)	3.1	14.1
75	1738	3-oxoretro-α-ionol (isomer 1)	0.6	21.4
80	1822	dehydrovomifoliol	13.3	13.0
85	1958	unknown (45, 93, 109, 123, 138, 153, 181, 196)	48.3	11.6
91	2208	18-hydroxyoleic acid lactone	4.2	6.7

MS analyses were completed. The overall odor of each totally evaporated extract was then determined by sniffing.

Capillary GC Analysis. An unmethylated extract was analyzed to ensure the nonvolatile carboxylic acids, which were also extracted, were not detected by GC. A standard GC analysis procedure for flavor volatiles was used. This procedure involved the use of a Perkin-Elmer Autosystem gas chromatograph equipped with a flame ionization detector and interfaced to a computerized Perkin-Elmer data management system. The volatile compounds in the unmethylated honey extracts were analyzed by GC on a 50 m × 0.22 mm (i.d.) fused silica capillary column, coated with 5% phenylpolysilaphenylene−siloxane of film thickness 0.25 μm (BPX-5; SGE Ltd., Melbourne, Australia). A splitless injection system was used. Also, helium was used as carrier gas at a linear flow velocity of 25 cm/s. The column oven was temperature programmed to rise from 50 °C (1 min initial hold) to 250 °C (10 min final hold) at 3 °C/min. Injector and detector temperatures were 240 and 280 °C, respectively. Retention indices were determined by interpolation of the GC retention times to those of *n*-alkanes (C_5−C_{22} mixture) under identical conditions.

Capillary GC−MS Analysis. The concentrated unmethylated extracts were analyzed by a standard GC−MS procedure using a Hewlett-Packard (HP) 5890 Series II gas chromatograph interfaced to a HP 5970 mass selective detector operating in the scan mode (*m*/*z* 30−300). Also, the GC−MS system was interfaced to an identical column and analyzed under the same conditions to that used for the GC analysis, except for the flow of helium carrier gas which was set at a lower linear flow velocity (21 cm/s) because of instrument limitations. Here, electron impact mass spectral analysis was carried out at an ionization energy of 70 eV and an ion source temperature of 300 °C. Retention indices were determined by interpolation of the GC−MS retention times, in the same manner as for the GC analysis.

Identification and Quantification of Volatile Compounds. The mass spectra and retention indices of the volatile components were compared to those of commercial or donated authentic compounds and to those reported in particular data (Tan, 1989; Sun, 1995). In other cases, the structural assignments of volatiles were accomplished solely by comparing the mass spectra of compounds with published mass spectral data, and with those in the *NBS Registry of Mass Spectral Data* using a computer system. Quantification (100% recovery factor) was performed using the GC instrument and an internal standard (methyl undecanoate), without consideration of response factors (calibration factor 1.00).

Repeatability of Honey Extraction. To determine the repeatability (form of precision) of the extraction procedure, seven consecutive extractions of 30 g (i.e. 7 × 30 g) of the same bulk sample of yellow box honey (YB2) were performed, followed by quantification of the volatile extractives. The 20 volatiles chosen for quantification were representative of the different boiling points, compound types, and concentrations that were encountered, and are detailed in Table 1.

Statistical Comparison of Compound Concentrations. Data were analyzed by an unpaired *t*-test comparison (with unequal variances), to detect significant differences between the mean concentrations of individual volatiles that were extracted from samples of the two honey types. Significance was reported with $P < 0.05$. Additionally, some of the natural volatiles with significantly different mean concentrations for each honey type were assigned as possible floral source descriptors; the minimum concentration (mg/kg of honey) required for such an assignment was the lower limit of the 95% confidence interval.

RESULTS AND DISCUSSION

Honey Extraction. The totally evaporated honey extracts had a strong floral honey aroma which suggests that aroma volatiles were extracted. For all the extractions of honey samples, the percent recovery of the internal standard added to the honey (methyl undecanoate) relative to the internal standard added to the final extract (methyl heptadecanoate) averaged 82%. Table 1 lists the mean concentrations (mg/kg of honey) and variance coefficients (CV%) for 20 representative volatiles that were extracted during seven consecutive 30 g (3 × 10 g) analyses of the same bulk yellow box honey (YB2). This repeatability experiment for the extraction method yielded a median value of 11.5% for the variance coefficients (CV%) obtained for the 20 selected honey volatiles. The repeatability (CV%) was not the same for all the classes of natural volatiles included in the 20 selected compounds. However, except for the three compounds **5**, **14**, and **75**, the repeatability (CV) varied in the acceptable range of 5.0−14.1%. In addition, there were no differences in repeatability (CV%) related to compound volatility (Table 1). With respect to concentration, minor components (compounds with levels less than 0.6 mg/kg of honey) such as the compounds **13**, **14**, and **27** exhibited similar repeatability (CV%) characteristics to those for the major components such as dehydrovomifoliol (**80**) and the unknown **85**. Thus, there is no pattern of repeatability related to the concentration of the honey components. In conclusion, the data listed in Table 1 indicate that the ethyl acetate extraction of liquid honey, described earlier, is a rapid and efficient method for the isolation of honey volatiles, including aroma volatiles and semivolatiles, without the use of excessive heating. Such conditions are in contrast to those used in the steam distillation−solvent extrac-

tion technique (Bicchi et al., 1983; Visser et al., 1988; Bouseta and Collin, 1995) where excessive heating is involved.

Analysis of Unmethylated Honey Extracts. Tables 2 and 3 contain details of the concentrations (mg/kg of honey, fresh weight) of the natural volatiles and semivolatiles that were detected in the unmethylated extracts from the eight Australian yellow box honey samples, YB1−YB8, and the seven Australian blue gum honey samples, BG1−BG7. Although the nonvolatile carboxylic acids were not detected here due to analyzing unmethylated extracts, our solvent extraction method does extract an array of nonvolatile carboxylic acids, the analysis of which is presently proceeding. Volatiles eluting after 18-hydroxyoleic acid lactone (**91**) are not detailed here since they were found to be long-chain hydrocarbons ($>C_{21}$). These hydrocarbons were of limited interest to this study since they originate from beeswax (Tan et al., 1988).

The listed volatiles (Tables 2 and 3) are in the concentration range 0.1−51.3 mg/kg of honey. These concentrations (mg/kg levels), although comparable to the levels of volatiles in New Zealand honeys (Tan et al., 1988, 1989a,b, 1990; Wilkins et al., 1993a,b, 1995a,b), are much greater than the μg/kg levels in honeys from Europe (Bouseta et al., 1992) and the United States of America (Overton and Manura, 1994). This finding is the reason why Australian honeys are more strongly flavored than European honeys. Tables 2 and 3 do not contain volatiles detected at concentrations of less than 0.1 mg/kg of honey, since these were considered to be trace levels. All of these trace compounds were unidentified. Additionally, Tables 2 and 3 list the 55 compounds identified by GC−MS out of a total of 91 natural honey volatiles. However, 61 of the 91 constituents were extracted from both honey types, indicating that some similarity exists between these two Australian honey types with respect to natural volatiles. The fact that 13 of the 55 identified compounds are new honey volatiles highlights the distinctiveness of Australian yellow box and blue gum honeys relative to other honeys throughout the world. Also, Tables 2 and 3 list the evidence used to identify the volatiles; the literature reports that contain reference mass spectra; and details of the mass spectral data for those compounds where assignments were not made (unknowns). Figure 1 details the structures of the compounds that are discussed.

The natural honey volatiles identified in the extracts from blue gum and yellow box honeys are mainly neutral compounds that fall into the following five broad structural categories: norisoprenoids; monoterpenes; benzene derivatives; aliphatic compounds; and Maillard reaction products. These volatiles are the focus of the discussion below.

Norisoprenoids. Of the five categories of natural honey volatiles, the norisoprenoids are dominant in number and concentration. Most of the volatile norisoprenoids that were detected are C_{13} compounds, with the identified components occurring in concentrations up to 14.7 mg/kg of honey. Eight of these compounds were identified in honey for the first time. Also, the norisoprenoids found in this study contain a 3,5,5-trimethylcyclohex-2-en-1-one structure and are referred to as degraded carotenoids.

*3,4-Dihydro-3-oxoactinidols (**63**, **64**, **65**, and **67**).* The four bicyclic diastereoisomers **63**, **64**, **65**, and **67** are of great interest since they have not been reported as components of honey, other than for Australian honeys. Sun (1995) recently identified two of these diastereoisomers in extracts of four types of Australian honey. We now report the quantitative identification of all four 3,4-dihydro-3-oxoactinidols **63**, **64**, **65**, and **67** for blue gum and yellow box honeys. The concentrations were similar ($P > 0.05$) between the two honey types, indicating that these norisoprenoids are not floral source descriptors. Moreover, previous studies of Australian honeys detected some of these compounds (identical mass spectra), but they were incorrectly named as (5′-carbaldehyde)-2-furyl butyl ketone (Graddon et al., 1979; Rowland et al., 1995). Because the four 3,4-dihydro-3-oxoactinidols **63**, **64**, **65**, and **67** are also neutral volatiles of tobacco (Uegaki et al., 1979), they may contribute to the aroma of Australian yellow box and blue gum honeys.

*8,9-Dehydrotheaspirone (**61**).* Another bicyclic compound **61** is new to honey. In this study, the mean level of 8,9-dehydrotheaspirone (**61**) for the blue gum honey samples (1.9 mg/kg of honey) was significantly higher ($P < 0.05$) than that for the yellow box honey samples (0.4 mg/kg of honey). This result suggests that the norisoprenoid **61** may be a floral source descriptor for blue gum honey. Additionally, compound **61** has a strong flowery-woody odor (Fujimori et al., 1981) that may contribute to the aroma of blue gum honey.

*3-Oxoretro-α-ionols (**75**, **78**).* The norisoprenoids **75** and **78** (9-hydroxymegastigma-4,6-dien-3-ones) are also new honey volatiles and were found in low concentrations (0.1−0.7 mg/kg of honey) and at similar mean levels ($P > 0.05$) in the extracts of replicate samples of each honey type. Thus, the compounds **75** and **78** are not floral source descriptors. The free and bound forms of the compounds **75** and **78** are grape juice components (Sefton et al., 1989, 1993), while one of the isomers is a free volatile of tobacco (Lloyd et al., 1976); therefore, the isomers **75** and **78** appear to be plant derived.

*Megastigm-4-ene-3,9-dione (**73**).* The norisoprenoid **73** with the saturated side chain is a new honey volatile. It was detected in small but similar ($P > 0.05$) mean levels (0.2 mg/kg of honey) in extracts of samples of both honey types. Thus, megastigm-4-ene-3,9-dione (**73**) is not a floral source descriptor for Australian yellow box or blue gum honeys. However, it is worth noting that megastigm-4-ene-3,9-dione (**73**) was observed without its reduced form 9-hydroxymegastigm-4-en-3-one. This result is the reverse of that found for tobacco (Lloyd et al., 1976; Fujimori et al., 1976) and grapes (Sefton et al., 1989; Winterhalter et al., 1990) where only 9-hydroxymegastigm-4-en-3-one was detected and indicates that different conditions are involved in the formation of compound **73** from plant to hive.

*3-Oxo-α-ionone (**71**).* The dione **71** is a constituent of New Zealand clover honey (Sun, 1995) and Australian leatherwood honey (Rowland et al., 1995). 3-Oxo-α-ionone (**71**) (megastigma-4,7-diene-3,9-dione) appears to characterize Australian blue gum honey, since the mean concentration of 3-oxo-α-ionone (**71**) for the blue gum honey samples (6.8 mg/kg of honey) was significantly greater ($P < 0.05$) than that for the yellow box honey samples (1.4 mg/kg of honey). Also, the allene **71a** coeluted (GC−MS) with compound **71** for yellow box honey; the allene **71a** is a known heather honey volatile (Tan et al., 1989a).

*3-Oxo-α-ionol (**69**).* The reduced form of 3-oxo-α-ionone (**71**) was detected in both Australian honey types as the degraded carotenoid **69** (9-hydroxymegastigma-

Table 2. Concentration (Milligrams per Kilogram of Honey) of Components Detected in Unmethylated Extracts of Australian Yellow Box Honey

compd no.	retent index	compound (prominent MS peaks)	yellow box honey samples								evidence for assgnt[d]	ref[e]
			YB1	YB2	YB3	YB4	YB5	YB6	YB7	YB8	mean	
1	759	3-hydroxybutan-2-one (acetoin)	6.9	2.9	8.3	8.3	0.9	0.8	7.0	0.5	4.5	A	
2	763	1,1-diethoxyethane (acetal)	0.7	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.3	A	
3	793	toluene	0.4	0.2	0.2	0.2	0.4	0.3	0.1	0.2	0.3	A	
4	804	*levo*-butane-2,3-diol	11.1	5.1	9.5	14.5	11.9	18.4	9.7	10.0	11.3	A	
5	811	*meso*-butane-2,3-diol	5.6	3.5	6.4	7.8	6.8	10.5	5.7	6.9	6.6	A	
6	817	1,1-diethoxypropane	0.2	0.2	0.1	0.3	0.3	0.5	0.2	0.2	0.2	D	
7	843	isovaleric acid	0.2	0.1	0.4	0.2	0.1	0.1	0.6	0.1	0.2	A	
8	848	furfural	0.2	0.4	0.2	0.3	0.3	0.3	0.2	0.2	0.3	A, C	*f*
9	855	unknown (41, 43, 45, 61, 73, 74)	0.6	–[b]	0.6	0.1	0.1	0.8	0.6	0.1	0.4		
10	892	unknown (39, 41, 43, 45, 58, 61, 69, 84, 87)	0.3	0.1	0.3	0.2	0.3	0.5	0.2	0.6	0.3		
11	898	unknown (41, 43, 53, 69, 97, 112)	0.4	0.5	0.5	0.5	0.4	0.6	0.5	0.2	0.5		
12	934	unknown (41, 42, 43, 55, 57, 69, 70, 85, 98)	1.0	1.4	1.4	1.0	1.7	3.0	0.5	0.9	1.4		
13	947	unknown (41, 43, 45, 57, 69, 74, 85)	0.5	0.3	0.5	0.6	0.1	0.6	0.7	0.2	0.4		
14	953	unknown (41, 43, 45, 55, 57, 69, 74, 87)	0.7	0.3	1.2	0.9	0.3	1.0	1.5	0.5	0.8		
15	986	phenol	6.5	0.4	0.2	4.2	6.6	3.4	0.3	3.6	3.1	A, B	*f*
16	989	2,5-dimethyl-2,4-dihydroxy-3(2*H*)-furanone[a]	0.1	–	–	–	0.1	0.1	–	–	0.1	C	*g*
17	1003	acetophenone	0.1	–	–	0.1	0.2	–	–	–	0.1	C, D	*h*
18	1013	δ-3-carene	0.4	0.2	0.3	0.6	0.7	1.6	0.4	0.9	0.6	A	
19	1032	unknown (41, 43, 45, 56, 57, 69, 70, 83, 98)	0.1	0.1	0.1	0.1	0.1	0.4	0.1	0.2	0.2		
20	1034	*p*-isopropyltoluene (*p*-cymene)	0.1	0.2	0.1	0.2	0.2	0.2	0.2	–	0.1	A	
21	1044	unknown (41, 43, 45, 55, 56, 57, 69, 71, 87)	0.3	0.3	0.6	0.4	0.3	0.5	0.6	0.3	0.4		
22	1051	benzyl alcohol	0.6	0.2	0.3	0.4	0.1	0.2	0.3	0.2	0.3	A, C	*f, h*
23	1059	unknown (43, 57, 71, 86, 88, 89, 99, 131)	0.4	0.2	0.8	0.4	0.2	0.4	0.7	0.2	0.4		
24	1061	unknown (43, 45, 57, 72)	0.5	0.5	0.4	0.4	0.4	0.9	0.4	0.6	0.5		
25	1063	phenylacetaldehyde	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	A	
26	1075	unknown (43, 45, 55, 59, 71, 86, 88)	0.4	0.2	0.7	0.3	0.1	0.4	0.6	0.1	0.3		
27	1081	*cis*-linalool oxide (furan type)	0.9	0.5	0.2	0.6	0.7	0.7	0.2	0.4	0.5	C, D	*f, i*
28	1098	*trans*-linalool oxide (furan type)	0.6	0.6	0.2	0.5	0.2	0.6	0.2	0.2	0.4	C, D	*f, i*
29	1102	unknown (38, 39, 53, 67, 95, 123, 124)	1.9	1.6	0.4	1.0	0.7	1.2	0.4	0.8	1.0		
30	1109	linalool	0.2	–	0.1	0.2	0.1	0.2	0.1	0.3	0.1	A, C	*f, h, j*
31	1114	3,7-dimethylocta-1,5,7-trien-3-ol (hotrienol)	0.4	0.1	0.1	0.4	0.2	0.6	0.2	0.3	0.3	C	*j*
32	1115	unknown (41, 43, 55, 57, 68, 69, 70, 71, 82)	0.2	0.2	0.3	0.2	0.2	0.4	0.3	0.3	0.3		
33	1134	2-phenylethanol	0.2	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1	A	
34	1167	2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one	1.9	2.1	1.4	1.8	0.7	2.2	1.7	1.3	1.6	C, D	*g*
35	1169	3,5,5-trimethylcyclohex-2-ene-1,4-dione (4-oxoisophorone)	–	–	–	–	0.4	–	–	0.5	0.1	A, B, C	*h, k*
36	1196	2,2,6-trimethylcyclohexane-1,4-dione	1.0	0.3	0.5	0.4	0.3	0.5	0.7	0.3	0.5	A, B	
37	1204	2,6-dimethylocta-3,7-diene-2,6-diol	1.0	0.3	1.0	1.2	0.8	1.1	1.0	0.9	0.9	C	*j*
41	1230	1-phenylbutane-2,3-dione[a]	0.1	–	–	–	–	–	0.1	–	0.1	C	*l*
42	1235	6-methylheptyl prop-2-enoate	0.3	0.2	0.2	0.3	0.2	0.5	0.3	1.6	0.5	D	
43	1247	unknown (39, 43, 45, 57, 85, 86)	0.8	0.5	0.3	0.5	0.5	0.5	0.5	0.5	0.5		
44	1256	5-(hydroxymethyl)-2-furfural (HMF)	12.4	13.2	1.5	6.6	5.7	8.1	1.3	3.9	6.6	A, B	
45	1264	phenylacetic acid	–	0.3	0.1	–	0.1	–	0.1	0.6	0.2	A	
49	1336	2-methoxyacetophenone	0.5	0.4	0.2	0.3	0.3	0.4	0.2	0.2	0.3	B	
50	1340	unknown isomer of trimethylphenol (77, 91, 121, 156 M^+)	3.3	5.0	1.8	3.1	1.8	3.7	2.0	1.6	2.8	B	
51	1344	unknown (39, 41, 43, 55, 67, 69, 70, 82, 98, 121)	0.5	0.7	0.3	0.3	0.6	0.4	0.2	0.3	0.4		
52	1362	unknown (41, 43, 59, 60, 69, 71, 95, 97, 99, 118, 171)	1.5	0.4	0.9	1.3	1.7	2.2	0.9	1.5	1.3		
53	1375	3-hydroxy-4-phenylbutan-2-one	2.0	3.3	2.4	2.8	1.1	4.2	2.7	2.5	2.6	C	*m*
54	1381	unknown (41, 43 55, 67, 71, 82, 98)	0.7	0.2	0.5	0.5	0.5	0.7	0.8	0.5	0.5		
56	1410	monoterpene (43, 55, 59, 67, 68, 93, 94, 111, 137, 155)	7.8	3.7	1.8	5.9	6.6	5.3	3.1	4.8	4.9		
57	1412	monoterpene (43, 55, 59, 67, 68, 93, 94, 111, 137, 155)	3.0	2.0	1.8	3.0	3.2	3.3	2.0	3.2	2.7		
58	1430	methyl undecanoate (11:0) (internal standard)											
59	1446	1-phenylbutane-2,3-diol[a]	0.3	0.9	0.6	0.6	0.6	0.7	0.5	0.5	0.6	C	*m*
60	1499	*n*-pentadecane (C_{15})	0.1	0.3	0.1	0.1	0.1	1.8	0.2	0.1	0.4	A	
61	1518	8,9-dehydrotheaspirone[a]	0.4	0.4	0.3	0.3	0.7	0.4	0.3	0.3	0.4	C	*n, o*
63	1605	3,4-dihydro-3-oxoactinidol (isomer 1)[a]	3.5	3.3	1.9	2.7	1.9	3.2	1.9	2.1	2.6	C	*p*
64	1610	3,4-dihydro-3-oxoactinidol (isomer 2)[a]	1.0	0.7	0.7	0.8	0.5	0.9	0.7	0.6	0.7	C	*p*
65	1633	3,4-dihydro-3-oxoactinidol (isomer 3)[a]	2.3	2.2	1.1	1.7	1.1	2.0	1.2	2.7	1.8	C	*p*
66	1641	monoterpene (43, 59, 71, 95, 107, 125)	1.4	0.6	0.6	1.2	0.4	1.2	0.7	2.2	1.0		
67	1645	3,4-dihydro-3-oxoactinidol (isomer 4)[a]	0.2	0.2	0.1	0.2	0.1	0.3	0.2	0.2	0.2	C	*p*
68	1650	monoterpene (43, 59, 71, 95, 107, 125)	0.7	0.3	0.2	0.6	0.2	0.9	0.3	0.5	0.5		
69	1668	3-oxo-α-ionol	0.4	0.4	0.2	1.1	0.5	2.7	0.2	0.6	0.8	B, C	*h, q–t*
70	1671	unknown (43, 108, 123, 137, 179)	0.6	0.6	0.3	0.5	0.3	0.4	0.3	0.2	0.4		
71a	1673	4-(3-oxobut-1-enylidene)-3,5,5-trimethylcyclohex-2-en-1-one	*[c]	*	*	*	*	*	*	*	*	B	
71	1675	3-oxo-α-ionone	1.2	1.3	0.9	1.2	1.9	2.1	1.4	1.2	1.4	A, B, C	*q, r*
72	1696	*n*-heptadecane (C_{17})	0.2	0.2	0.1	0.2	0.1	0.3	0.1	0.1	0.2	A	
73	1699	megastigm-4-ene-3,9-dione[a]	0.1	0.2	0.3	0.3	0.3	0.5	0.1	0.1	0.2	E	
74	1719	unknown (43, 65, 77, 91, 105, 149, 178)	1.6	3.3	0.7	1.6	0.9	2.5	1.0	1.2	1.6		
75	1738	3-oxoretro-α-ionol (isomer 1)[a]	0.5	0.6	0.4	0.7	0.4	0.7	0.3	0.7	0.6	C	*k, t*
76	1791	*n*-octadecane (C_{18})	1.0	1.0	0.5	0.9	0.8	1.5	0.5	0.7	0.9	A	
77	1796	methyl syringate	0.2	0.3	0.2	0.3	0.3	3.4	0.2	1.5	0.8	A, B, C	*u*
78	1802	3-oxoretro-α-ionol (isomer 2)[a]	0.2	0.1	0.1	0.2	0.2	0.3	0.1	0.6	0.2	C	*k, t*
79	1814	vomifoliol	0.3	0.3	0.2	0.2	0.3	0.3	0.3	0.2	0.3	B, C	*s, t, v, w*
80	1822	dehydrovomifoliol	10.7	13.9	7.5	9.0	11.1	14.7	7.7	8.6	10.4	A, B, C	*t, x, y*
80b	1831	unknown (43, 93, 109, 121, 149, 164)	*	*	*	*	*	*	*	*	*		
81	1857	unknown (43, 54, 69, 83, 95, 109, 123, 180, 185)	2.4	3.3	1.6	2.2	1.8	2.8	1.7	6.4	2.8		
82	1899	*n*-nonadecane (C_{19})	0.3	0.3	0.1	0.2	0.2	0.2	0.2	0.2	0.2	A	
84	1939	unknown (43, 45, 69, 77, 93, 123, 147, 165, 180)	5.0	5.1	4.4	5.6	3.9	7.5	3.7	4.2	4.9		
85	1958	unknown (45, 93, 109, 123, 138, 153, 181, 196)	44.7	45.7	25.3	41.6	24.2	51.3	20.1	27.9	35.1		

Table 2 (Continued)

compd no.	retent index	compound (prominent MS peaks)	yellow box honey samples									evidence for assgnt[d]	ref[e]
			YB1	YB2	YB3	YB4	YB5	YB6	YB7	YB8	mean		
86	1964	unknown (43, 55, 77, 93, 123, 137, 181, 195, 224)	–	–	–	–	0.9	1.2	–	0.9	0.4		
87	2002	*n*-eicosane (C_{20})	0.7	0.3	–	0.4	0.1	0.2	0.2	–	0.2	A	
88	2037	methyl heptadecanoate (17:0) (internal standard)											
89	2108	*n*-heneicosane (C_{21})	0.3	0.4	0.2	0.4	0.5	0.5	0.3	2.1	0.6	A	
90	2121	unknown (41, 43, 69, 98, 111, 142, 167, 181, 196)	1.3	1.1	0.6	1.3	0.5	1.7	0.9	2.8	1.3		
91	2208	18-hydroxyoleic acid lactone[a]	8.7	4.1	26.9	11.1	6.2	19.8	24.2	15.9	14.6	C	*z*

[a] New in honey. [b] A dash (–) indicates that the compound was not detected. [c] *Unresolved peak, the presence of which was verified by GC–MS analysis. [d] Key: A, comparison of retention index and mass spectrum with that of an authentic sample recorded under the same conditions; B, comparison of retention index and mass spectrum with that reported by Tan (1989), or in unpublished data supplied by A. L. Wilkins, Chemistry Department, University of Waikato, Hamilton, New Zealand; C, comparison of mass spectrum with a published spectrum; D, comparison of mass spectrum with NBS library (computer) spectrum; E, comparison of mass spectrum with Wiley Index spectrum. [e] References containing mass spectral data. [f] Lee et al. (1975). [g] Mills (1978). [h] Fujimori et al. (1976). [i] Felix et al. (1963). [j] Wilkins et al. (1993b). [k] Sefton et al. (1989). [l] Joulain (1987). [m] Watanabe et al. (1986). [n] Fujimori et al. (1981). [o] Winterhalter et al. (1990). [p] Uegaki et al. (1979). [q] Aasen et al. (1973). [r] Enzell and Wahlberg (1986). [s] Strauss et al. (1987a). [t] Winterhalter (1990). [u] Russell et al. (1990). [v] Demole and Enggist (1974). [w] Strauss et al. (1987b). [x] Etoh et al. (1980). [y] Häusler and Montag (1989). [z] Sun (1995).

4,7-dien-3-one). 3-Oxo-α-ionol (**69**) is also a constituent of New Zealand heather honey (Tan et al., 1989a) and Asian longan honey (Ichimura et al., 1994). In the present study, the mean concentration of compound **69** for the blue gum honey samples (1.3 mg/kg of honey) was not significantly greater ($P > 0.05$) than that for the yellow box honey samples (0.8 mg/kg of honey). Thus, 3-oxo-α-ionol (**69**) is not suitable for identifying either honey type.

*Dehydrovomifoliol (**80**) and Vomifoliol (**79**).* The other two norisoprenoids detected in yellow box and blue gum honeys, dehydrovomifoliol (6-hydroxymegastigma-4,7-diene-3,9-dione, **80**) and vomifoliol (6,9-dihydroxymegastigma-4,7-dien-3-one, **79**), have similar mass spectra. However, the distinguishing features of their mass spectra, when the molecular ions are not available, are the *m/z* 166 ion for compound **80** and the *m/z* 168 ion for the diol **79**. In this study, dehydrovomifoliol (**80**) was detected at comparable levels (means of 6.1 and 10.4 mg/kg of honey) to that found previously for Australian leatherwood honey (mean of 10.2 mg/kg of honey) (Rowland et al., 1995) and Australian *Eucalyptus* honey (6.02 mg/kg of honey) (Häusler and Montag, 1991). These data suggest that dehydrovomifoliol (**80**) is not a floral source descriptor for any Australian honey. It is important to note that these concentrations are well below the levels (56–264 mg/kg of honey) that characterize heather honeys (Häusler and Montag, 1989, 1991; Tan et al., 1989a). Other occurrences of dehydrovomifoliol (**80**) in natural tissues are detailed elsewhere (Häusler and Montag, 1989; Rowland et al., 1995). During the present study, vomifoliol (**79**) was found in small but similar ($P > 0.05$) concentrations in the yellow box and blue gum honey samples (0.1–0.6 mg/kg of honey). These data, together with the fact that compound **79** is also a component of Asian longan honey (Ichimura et al., 1994), indicate that vomifoliol (**79**) is not a source descriptor for yellow box or blue gum honeys.

Unidentified Norisoprenoids. Compounds **84**, **85**, and **86** possess mass spectra (see Tables 2 and 3) that are suggestive of norisoprenoids, but we were unable to identify them using mass spectral data alone. The dominance of compound **85** [*m/z* 45 (98), 93 (100), 109 (38), 123 (70), 138 (53), 153 (41), 181 (2), 196 (8)] was the major characteristic of the unmethylated extracts of the eight yellow box honey samples. The mean concentration of compound **85** for the yellow box honey samples (35.1 mg/kg of honey) was significantly greater ($P < 0.05$) than that for the blue gum honey samples (0.7 mg/kg of honey); thus, the unknown compound **85** may be a floral source descriptor for Australian yellow box honey. The isolation and identification of this unknown is continuing.

The norisoprenoids of this study have also been observed in tobacco (free volatile) (Fujimori et al., 1976; Lloyd et al., 1976; Enzell and Wahlberg, 1986), and in grape juice and wine (bound form or free volatile) (Strauss et al., 1987a,b; Sefton et al., 1989, 1993; Winterhalter et al., 1990), which suggest that the honey norisoprenoids are plant-derived.

Monoterpenes. An examination of the compounds listed in Tables 2 and 3 indicates that the unmethylated honey extracts also contained hydroxylated monoterpenes related to linalool, in addition to linalool (**30**). Here, the linalool derivatives, 3,7-dimethylocta-1,5,7-trien-3-ol (hotrienol, **31**) and 2,6-dimethylocta-3,7-diene-2,6-diol (**37**) are of most importance because they are also constituents of Australian leatherwood honey (Rowland et al., 1995), New Zealand nodding thistle honey (Wilkins et al., 1993b), and Asian longan honey (Ichimura, 1994). Other occurrences of hotrienol (**31**) in plant tissues are reviewed elsewhere (Wintoch et al., 1993). Also, linalool (**30**) is a constituent of other Australian honeys (Graddon et al., 1979), New Zealand manuka honey (Visser et al., 1988), and Asian longan honey (Ichimura, 1994). In conclusion, the low concentrations of compounds **30**, **31**, and **37**, combined with their occurrence in other honeys, indicate that these compounds are not useful for the floral sourcing of yellow box or blue gum honeys.

*Linalool Oxides (**27**, **28**).* Of particular interest among the monoterpenes are the cyclic ethers **27** and **28**; only the yellow box honey samples contained the two isomers **27** and **28**. Linalool oxides are also components of New Zealand manuka honey (Visser et al., 1988), some honeys from the United States of America (Overton and Manura, 1994), and Asian longan honey (Ichimura, 1994). Identification of these two compounds was possible since their mass spectra were identical with those for the *cis*- and *trans*-furan linalool oxides **27** and **28** (α,α,5-trimethyl-5-vinyltetrahydrofurfuryl alcohols) as reported by Felix et al. (1963) and Lee et al. (1975). These identifications were further aided by the fact that the retention indices for compounds **27** and **28**, relative to authentic linalool (**30**), agree with that reported by Demarne (1989) for the *cis*- and *trans*-linalool oxides in geranium oil. Additionally, the isomers **56** and **57** have mass spectra that are very similar to those of the furan linalool oxides **27** and **28** and remain unidentified. The mean concentrations of the unknown isomers **56** and **57** for the yellow box honey samples (4.9 and 2.7 mg/kg of honey) were significantly greater ($P < 0.05$) than

Table 3. Concentration (Milligrams per Kilogram of Honey) of Components Detected in Unmethylated Extracts of Australian Blue Gum Honey

compd no.	retent index	compound (prominent MS peaks)	blue gum honey samples								evidence for assgnt[d]	mass spectral ref[e]
			BG1	BG2	BG3	BG4	BG5	BG6	BG7	mean		
1	759	3-hydroxybutan-2-one (acetoin)	7.5	7.7	8.3	14.6	9.3	8.1	11.8	9.6	A	
2	763	1,1-diethoxyethane (acetal)	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.2	A	
3	793	toluene	0.2	0.1	0.1	0.2	0.1	0.2	0.2	0.2	A	
4	804	*levo*-butane-2,3-diol	10.0	10.4	18.7	9.5	9.6	12.3	9.2	11.4	A	
5	811	*meso*-butane-2,3-diol	8.5	9.2	13.1	9.1	7.7	10.5	7.6	9.4	A	
6	817	1,1-diethoxypropane	–[c]	–	–	–	–	–	1.3	0.2	D	
7	843	isovaleric acid	0.2	0.2	0.1	0.4	0.3	0.2	0.6	0.3	A	
8	848	furfural	0.2	0.3	0.2	0.3	0.2	0.2	–	0.2	A	*f*
9	855	unknown (41, 43, 45, 61, 73, 74)	0.3	0.5	0.2	0.6	0.1	0.5	0.3	0.4		
10	892	unknown (39, 41, 43, 45, 58, 61, 69, 84, 87)	0.4	0.5	0.2	0.3	0.2	0.3	1.2	0.4		
11	898	unknown (41, 43, 53, 69, 97, 112)	1.0	0.8	0.9	0.9	1.0	0.9	3.1	1.2		
12	934	unknown (41, 42, 43, 55, 57, 69, 70, 85, 98)	1.5	0.9	1.6	1.4	1.0	0.8	2.5	1.4		
13	947	unknown (41, 43, 45, 57, 69, 74, 85)	0.3	0.2	0.2	0.3	0.3	0.3	0.2	0.3		
14	953	unknown (41, 43, 45, 55, 57, 69, 74, 87)	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1		
15	986	phenol	0.4	0.4	0.3	0.3	0.3	0.3	1.1	0.5	A, B	*f*
16	989	2,5-dimethyl-2,4-dihydroxy-3(2*H*)-furanone[a]	–	0.2	0.1	0.1	–	–	–	0.1	C	*g*
18	1013	∂-3-carene	0.5	0.9	1.0	0.4	0.4	0.8	0.2	0.6	A	
19	1032	unknown (41, 43, 45, 56, 57, 69, 70, 83, 98)	0.2	0.2	0.2	0.2	0.1	0.2	–	0.2		
23	1059	unknown (43, 57, 71, 86, 88, 89, 99, 131)	0.4	0.2	0.3	0.3	0.2	0.2	0.6	0.3		
24	1061	unknown (43, 45, 57, 72)	0.2	0.5	0.5	0.5	0.4	0.4	0.8	0.5		
25	1063	phenylacetaldehyde	1.6	0.9	0.7	1.3	1.1	1.2	0.8	1.1	A	
26	1075	unknown (43, 45, 55, 59, 71, 86, 88)	0.4	0.2	0.3	0.3	0.2	0.1	0.5	0.3		
29	1102	unknown (38, 39, 53, 67, 95, 123, 124)	0.4	0.3	0.2	0.5	0.4	0.6	1.1	0.5		
32	1115	unknown (41, 43, 55, 57, 68, 69, 70, 71, 82)	0.4	0.8	0.9	0.4	0.7	0.5	0.3	0.6		
34	1167	2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one	1.2	2.6	1.2	3.2	1.2	2.3	2.6	2.0	C, D	*g*
37	1204	2,6-dimethylocta-3,7-diene-2,6-diol	–	0.2	0.4	0.2	0.1	0.3	0.2	0.2	C	*h*
38	1205	3,5-dihydroxy-2-methyl-4*H*-pyran-4-one[a]	0.1	0.1	–	0.2	0.1	0.2	–	0.1	C	*i*
39	1223	unknown[b]	0.8	0.6	0.4	1.5	1.1	1.5	0.4	0.9		
40	1227	unknown (43, 45, 48, 57, 58, 61, 75, 85, 86)	0.4	0.9	0.4	0.8	0.6	0.7	0.4	0.6		
42	1235	6-methylheptyl prop-2-enoate	0.3	0.3	0.3	0.3	0.4	0.2	0.2	0.3	D	
43	1247	unknown (39, 43, 45, 57, 85, 86)	0.2	0.3	0.4	0.5	0.3	0.5	0.5	0.4		
44	1256	5-(hydroxymethyl)-2-furfural (HMF)	1.0	2.1	1.2	2.6	1.8	3.1	6.1	2.5	A, B	
45	1264	phenylacetic acid	–	–	–	0.1	–	–	0.3	0.1	A	
46	1301	unknown (1) (43, 45, 57, 61, 71, 74, 75, 85, 132)	0.1	0.1	0.2	0.6	0.3	0.5	0.2	0.3		
47	1304	*n*-tridecane (C_{13})	–	0.1	–	–	–	–	0.2	0.1	A	
48	1312	unknown (2) (43, 45, 57, 61, 71, 74, 75, 85, 132)	0.1	0.1	0.1	0.6	0.2	0.3	0.2	0.2		
49	1336	2-methoxyacetophenone	0.2	0.2	0.3	0.3	0.3	0.2	0.5	0.3	B	
52	1362	unknown (41, 43, 59, 60, 69, 71, 95, 97, 99, 118, 171)	–	0.1	0.4	0.2	0.1	0.5	0.8	0.3		
53	1375	3-hydroxy-4-phenylbutan-2-one	0.2	1.6	0.5	0.6	1.2	0.7	1.1	0.8	C	*j*
55	1402	*n*-tetradecane (C_{14})	0.1	0.2	0.6	0.1	0.3	0.2	0.2	0.3	A	
56	1410	monoterpene (43, 55, 59, 67, 68, 93, 94, 111, 137, 155)	0.5	0.8	1.1	0.7	0.6	1.2	1.1	0.9		
57	1412	monoterpene (43, 55, 59, 67, 68, 93, 94, 111, 137, 155)	0.2	0.6	0.7	0.5	0.5	0.8	0.1	0.5		
58	1430	methyl undecanoate (11:0) (internal standard)										
59	1446	1-phenylbutane-2,3-diol[a]	–	1.4	0.1	0.2	0.6	0.5	–	0.4	C	*j*
60	1499	*n*-pentadecane (C_{15})	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	A	
61	1518	8,9-dehydrotheaspirone[a]	2.0	1.6	1.6	2.5	2.0	2.0	1.3	1.9	C	*k, l*
62	1597	*n*-hexadecane (C_{16})	0.1	0.1	0.1	0.1	0.2	0.2	0.5	0.2	A	
63	1605	3,4-dihydro-3-oxoactinidol (isomer 1)[a]	0.2	0.3	1.2	0.3	0.3	0.2	0.5	0.4	C	*m*
64	1610	3,4-dihydro-3-oxoactinidol (isomer 2)[a]	0.1	0.3	0.4	0.3	0.2	0.2	1.3	0.4	C	*m*
65	1633	3,4-dihydro-3-oxoactinidol (isomer 3)[a]	0.2	0.1	0.5	0.1	0.2	0.2	0.5	0.3	C	*m*
66	1641	monoterpene (43, 59, 71, 95, 107, 125)	0.4	0.5	0.7	0.6	0.5	0.6	0.4	0.5		
67	1645	3,4-dihydro-3-oxoactinidol (isomer 4)[a]	0.1	–	0.3	–	0.1	0.1	0.7	0.2	C	*m*
68	1650	monoterpene (43, 59, 71, 95, 107, 125)	0.2	0.3	0.4	0.4	0.3	0.3	0.4	0.3		
69	1668	3-oxo-α-ionol	1.9	0.5	1.6	1.0	1.2	1.3	2.0	1.3	B, C	*n*–*r*
71	1675	3-oxo-α-ionone	4.6	4.8	7.3	8.9	6.9	7.9	7.3	6.8	A, B, C	*o, p*
72	1696	*n*-heptadecane (C_{17})	0.4	0.3	0.5	0.6	0.5	0.6	0.5	0.5	A	
73	1699	megastigm-4-ene-3,9-dione[a]	–	0.3	0.1	0.1	0.3	0.1	0.4	0.2	E	
75	1738	3-oxoretro-α-ionol (isomer 1)[a]	0.1	0.1	0.1	0.1	0.1	0.2	0.7	0.2	C	*s, r*
76	1791	*n*-octadecane (C_{18})	0.3	0.2	0.7	0.3	0.2	0.3	1.6	0.5	A	
77	1796	methyl syringate	1.1	0.2	1.8	2.9	0.9	0.2	1.2	1.2	A, B, C	*t*
78	1802	3-oxoretro-α-ionol (isomer 2)[a]	0.2	0.2	0.3	0.3	0.2	0.3	0.7	0.3	C	*s, r*
79	1814	vomifoliol	0.6	0.1	0.2	0.1	0.1	0.2	0.4	0.3	B, C	*q, r, u, v*
80	1822	dehydrovomifoliol	5.6	4.0	9.9	4.4	5.4	5.6	7.7	6.1	A, B, C	*r, w, x*
82	1899	*n*-nonadecane (C_{19})	0.2	0.3	0.3	0.1	0.2	0.1	0.4	0.2	A	
83	1935	unknown (39, 43, 45, 77, 147, 180)	0.4	0.5	2.8	0.2	0.6	0.4	1.5	0.9		
84	1939	unknown (43, 45, 69, 77, 93, 123, 147, 165, 180)	0.4	0.2	–	0.2	0.3	0.4	0.6	0.3		
85	1958	unknown (45, 93, 109, 123, 138, 153, 181, 196)	0.2	0.3	3.3	0.1	0.3	0.7	0.2	0.7		
86	1964	unknown (43, 55, 77, 93, 123, 137, 181, 195, 224)	1.6	1.2	1.0	1.8	1.5	2.2	0.9	1.5		
87	2002	*n*-eicosane (C_{20})	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	A	
88	2037	methyl heptadecanoate (17:0) (internal standard)										
89	2108	*n*-heneicosane (C_{21})	1.0	1.2	0.6	0.4	1.2	0.7	1.0	0.9	A	
91	2208	18-hydroxyoleic acid lactone[a]	4.7	2.7	37.6	5.3	1.8	4.5	0.8	8.2	C	*y*

[a] New in honey. [b] Unknown was detected in GC but not in GC–MS. [c] A dash (–) indicates that the compound was not detected. [d] Key: A, comparison of retention index and mass spectrum with that of an authentic sample recorded under the same conditions; B, comparison of retention index and mass spectrum with that reported by Tan (1989), or in unpublished data supplied by A. L. Wilkins, Chemistry Department, University of Waikato, Hamilton, New Zealand; C, comparison of mass spectrum with a published spectrum; D, comparison of mass spectrum with NBS library (computer) spectrum; E, comparison of mass spectrum with Wiley Index spectrum. [e] References containing mass spectral data. [f] Lee et al. (1975). [g] Mills (1978). [h] Wilkins et al. (1993b). [i] Jurch and Tatum (1970). [j] Watanabe et al. (1986). [k] Fujimori et al. (1981). [l] Winterhalter et al. (1990). [m] Uegaki et al. (1979). [n] Fujimori et al. (1976). [o] Aasen et al. (1973). [p] Enzell and Wahlberg (1986). [q] Strauss et al. (1987a). [r] Winterhalter (1990). [s] Sefton et al. (1989). [t] Russell et al. (1990). [u] Demole and Enggist (1974). [v] Strauss et al. (1987b). [w] Etoh et al. (1980). [x] Häusler and Montag (1989). [y] Sun (1995).

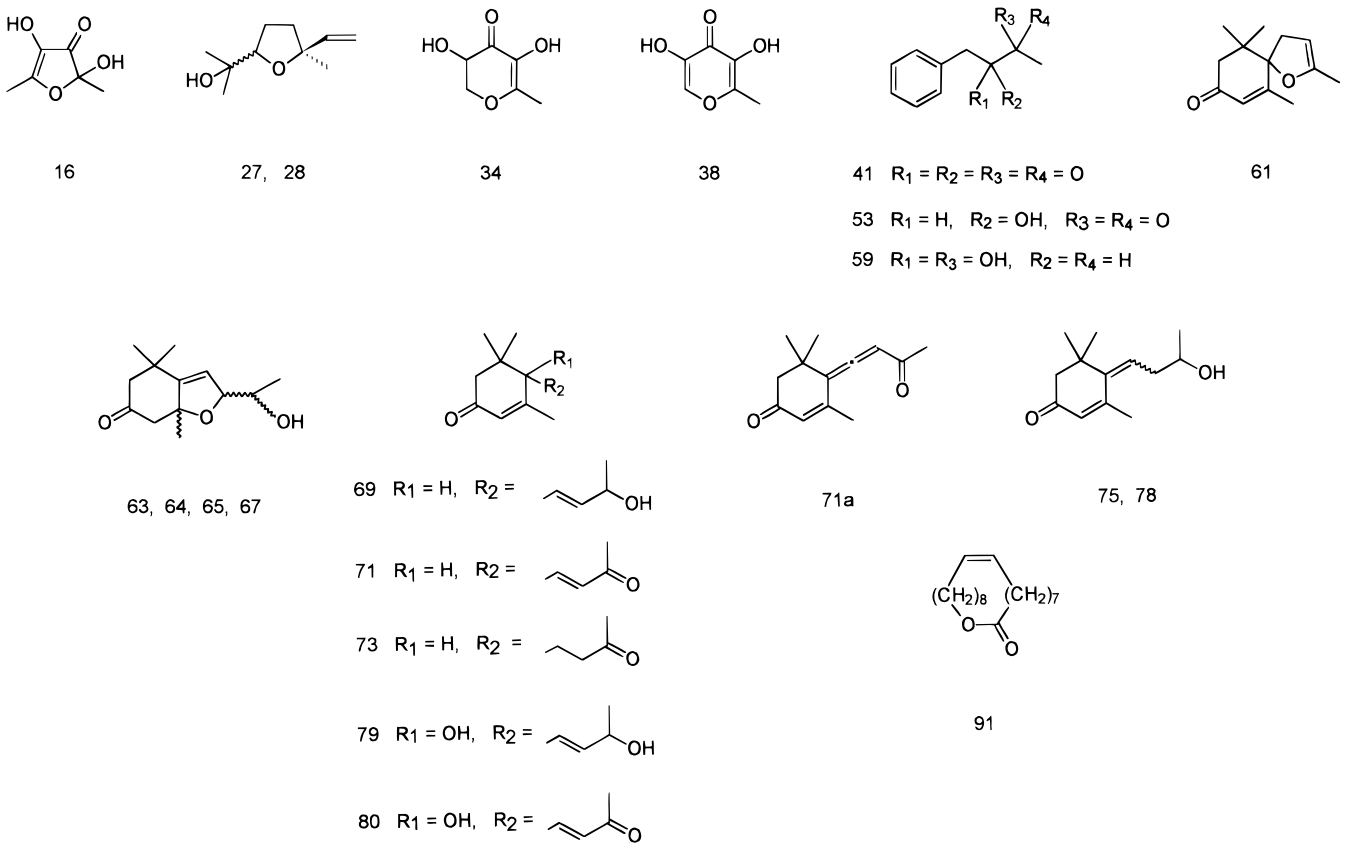

Figure 1. Structures of some compounds referred to in this work.

those for the blue gum honey samples (0.9 and 0.5 mg/kg of honey); thus, the unknown monoterpenes **56** and **57** may be floral source descriptors for Australian yellow box honey. Finally, some of the monoterpenes in Australian honeys are also components of grapes and wine (Williams et al., 1980a,b), indicating that these honey monoterpenes may originate from plant nectar.

Nonvolatile flavor precursors such as glycosides of norisoprenoids (Strauss et al., 1987a,b; Sefton et al., 1989, 1993; Winterhalter et al., 1990) and monoterpenes (Winterhalter et al., 1990) are well-known components of other natural products such as grape juice and wine. Thus, it is not possible to conclude whether the honey volatiles originate from the plant nectar in the free form or from the bound form through acid or enzymatic hydrolysis in the honeybee's stomach or the hive during honey ripening.

Benzene Derivatives. Additionally, the results in Tables 2 and 3 indicate that many benzene derivatives were among the volatiles extracted from the honey samples. These compounds included the following three related honey extractives that are known constituents of flowers (Watanabe et al., 1986; Joulain, 1987): 1-phenylbutane-2,3-dione (**41**), 3-hydroxy-4-phenylbutan-2-one (**53**), and 1-phenylbutane-2,3-diol (**59**), with compounds **41** and **59** being new honey volatiles. Interestingly, the pleasant odor of the wisteria flower is due to compound **53** (Watanabe et al., 1986). In this study, the mean level of the keto alcohol **53** for the yellow box honey samples (2.6 mg/kg of honey) was significantly higher ($P < 0.05$) than that for the blue gum honey samples (0.8 mg/kg of honey). However, 3-hydroxy-4-phenylbutan-2-one (**53**) is probably not specific for any one floral type of Australian honey since it was previously found in extracts from unripe (8.8 mg/kg of honey) and ripe (0.2 mg/kg of honey) Australian leatherwood honey (Rowland et al., 1995) and in extracts from a range of other Australian honeys (compound E, Graddon et al., 1979). Due to their previous isolation from flowers, the three honey compounds **41**, **53**, and **59** appear to originate from the plant nectar, and may contribute to the aroma of Australian yellow box and blue gum honeys, even though they appear not to be useful for the sourcing of these honeys. Finally, the following benzene derivatives extracted from yellow box and blue gum honeys are also known volatiles in Australian honeys (Wootton et al., 1978; Graddon et al., 1979; Rowland et al., 1995), New Zealand honeys (Tan et al., 1989a,1990; Wilkins et al., 1993b), and European honeys (Bicchi et al., 1983; Bonaga and Giumanini, 1986): toluene (**3**), phenol (**15**), *p*-cymene (**20**), benzyl alcohol (**22**), 2-phenylethanol (**33**), 2-methoxyacetophenone (**49**), and methyl syringate (**77**).

Aliphatic Compounds. One aliphatic compound of interest is 18-hydroxyoleic acid lactone (**91**). Sun (1995) identified this semivolatile during a study of extracts of four Australian honeys. However, the present work is the first to report the quantification of this new honey compound **91**. Other aliphatic compounds identified here are the low-boiling volatiles, acetoin (**1**), acetal (**2**), and *levo*- and *meso*-butane-2,3-diols (**4** and **5**), which are all known honey volatiles (Wootton et al., 1978; Graddon et al., 1979; Bonaga and Giumanini, 1986; Ichimura, 1994; Rowland et al., 1995). However, the origin of these volatiles is not clear from previous studies of honey, so their potential for use as floral source descriptors is uncertain. The hydrocarbons **47**, **55**, **60**, **62**, **72**, **76**, **82**, **87**, and **89** are high-chain-length *n*-alkanes (C_{13}–C_{21}). Detailed studies of these compounds in honey (Graddon et al., 1979; Bonaga et al., 1986; Tan et al., 1988) indicate that hydrocarbons originate from beeswax and are not useful as floral source descriptors.

Maillard Reaction Products. Through mass spectral comparison, the Maillard-type products 2,5-dimethyl-2,4-dihydroxy-3(2*H*)-furanone (**16**) (Mills, 1978) and 3,5-dihydroxy-2-methyl-4*H*-pyran-4-one (**38**) (Jurch and Tatum, 1970) were identified in the unmethylated honey extracts. These two compounds are new honey volatiles. Another Maillard reaction product, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (**34**), is a known constituent of Australian honeys (Graddon et al., 1979; Rowland et al., 1995). These Maillard-type compounds are heat-generated products of honey sugars (Shaw et al., 1971; Mills, 1978) and are, thus, not floral source descriptors for Australian yellow box or blue gum honeys.

CONCLUSIONS

There is great diversity among the natural volatiles that are extractable from Australian blue gum and yellow box honeys, including a variety of distinctive norisoprenoids, monoterpenes, benzene derivatives, aliphatic compounds, and Maillard reaction products. Moreover, these two honey types contain 13 new honey volatiles.

A chemical fingerprinting procedure using GC and GC−MS shows great potential for the objective sourcing of Australian honeys, since some floral source descriptors were found during this study. Australian yellow box honey is characterized by the unknown compound **85** when present at concentrations greater than 12.4 mg/kg of honey and the two unknown monoterpenes **56** and **57** when present at levels higher than 1.2 and 1.6 mg/kg of honey, respectively. Similarly, 8,9-dehydrotheaspirone (**61**) and 3-oxo-α-ionone (**71**) are indicative of Australian blue gum honey when present at concentrations greater than 1.2 and 3.8 mg/kg of honey, respectively. These conclusions are based on the results of the GC analysis of extracts of more than 60 Australian honey samples, including eight different floral types. The results of this study are important to the development of a chemical fingerprinting procedure that will be used to objectively authenticate the floral origin of Australian honeys.

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