Extractives from New Zealand Honeys. 4. Linalool Derivatives and Other Components from Nodding Thistle (*Carduus nutans*) Honey

Alistair L. Wilkins,* Yinrong Lu, and Seng-To Tan

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Sixteen linalool derivatives and a variety of aliphatic acids and diacids, aromatic acids, and phenols (total of 61 components) were identified in the methylated diethyl ether extracts of New Zealand nodding thistle (*Carduus nutans*) honeys using GC-FID and combined GC-MS methods. Separation of the diethyl ether extracts afforded three dominant linalool derivatives which were identified using one- and two-dimensional NMR procedures as (*E*)-2,6-dimethyl-3,7-octadiene-2,6-diol (3), (*Z*)-2,6-dimethyl-6-hydroxy-2,7-dienal (8), and (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoic acid (characterized as methyl ester, 6). The minor components, α,5-dimethyl-5-ethenyl-2-tetrahydrofuranacetaldehydes [lilac aldehydes (11), four isomers] and β,5-dimethyl-5-ethenyl-2-tetrahydrofuranethanols [lilac alcohols (10), four isomers], were identified by comparison with synthetic samples. The total level of linalool derivatives in the nodding thistle honey samples was between 15 and 87 μg/g of honey (average level 43 μg/g of honey).

INTRODUCTION

Our previous investigations (Tan et al., 1988, 1989a, 1990) of the extractable organic substances present in New Zealand unifloral honeys have shown that the floral source of some New Zealand honeys can be reliably determined from the gas chromatographic (GC) analysis of the noncarbohydrate extractable organic substances recovered from honey samples by liquid-liquid extraction with diethyl ether. We have reported that manuka (*Leptospermum scoparium*) honeys are characterized by the presence of high levels of 2-hydroxy-3-phenylpropionic acid and syringic acid (Tan et al., 1988; Wilkins et al., 1992), while degraded carotenoid-like substances are known to occur in heather (*Calluna vulgaris*) honeys (Tan et al., 1989a). We now report the characterization of a series of linalool derivatives occurring in New Zealand nodding thistle honeys using GC-FID, combined GC-MS, one- and two-dimensional NMR spectroscopy, and synthetic procedures.

METHODS AND MATERIALS

Ten nodding thistle honey samples (1986-1987 season) were obtained directly from beekeepers. The floral integrity of the samples was established from a combination of parameters including organoleptic characteristics, taste, appearance, hive location, and available floral sources. Pollen data were available for three of the samples (see Table I). The honey samples were extracted during 1987-1989. Bulk extraction was performed using the NT2 sample.

Methods and procedures used in the analysis of the nodding thistle honey samples were as described in part 1 of this series (Tan et al., 1988), other than the use of 250 mL of extractor with a 12-h extraction time. Gas chromatography with flame ionization detection (GC-FID) of the methylated extracts was performed on a 16 m × 0.22 mm (i.d.) column, coated with dimethylsilicone (BP-1; SGE Ltd., Melbourne), installed in Pye 4500 or HP 5980 GC instruments. Combined gas chromatographic/mass spectroscopic (GC-MS) analyses were carried out on a Hewlett-Packard 5890/5970 GC-MSD system interfaced to a 12-m HP-1 methylsilicone column. Quantification was performed using the GC-FID instruments, with methyl heptadecanoate (methyl marginate) as internal standard, using response factors determined for other constituents as described in part 1 (Tan et al., 1988). The response factor of linalool (1.01) was also determined relative to methyl heptadecanoate. Addition of linalool (112 μg) to a nodding thistle honey sample (10 g) dissolved into water (200 mL), followed by diethyl ether liquid-liquid extraction, and GC-FID quantification resulted in a 84.8% recovery of linalool. Repetition of the recovery experiment using distilled water (200 mL) (and no honey sample) resulted in a 99% recovery of linalool. High-resolution GC-MS was performed on a Kratos MS80RFA instrument coupled to a Carlo Erba Mega GC. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were determined on a Bruker AC-300 instrument.

Table I. Pollen Data for Three Nodding Thistle Honeys

	NT1	NT3	NT10
nodding thistle	20	19	7
white clover type	61	64	77
lotus	8	8	6
other	11	9	10

A bulk extraction of sample NT2 (900 g) afforded a mixture of extractives which were separated by multiple preparative layer chromatography (PLC) on silica gel (Merck $PF_{254+366}$) with *n*-hexane/ether (4:1) (three developments). Twenty fractions were recovered from the PLC plate. Three of the fractions, corresponding to peaks 17, 30, and 34, were recovered in sufficient quantity and purity for structural elucidation using one- and two-dimensional NMR spectroscopy (structures are shown in Chart I).

The fraction corresponding to peak 17 afforded (*E*)-2,6-dimethyl-3,7-octadiene-2,6-diol (3) (Takaoka and Hiroi, 1976; Etoh et al., 1980): MS (see Table III); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25, 1.27, 1.31 (3 s, 3 × CH_3), 2.23 (dd, J = 14.1, 7.8 Hz, 5-H′), 2.28 (dd, J = 14.1, 6.3 Hz, 5-H″), 5.05 (dd, J = 10.7, 1.2 Hz, 8-H′), 5.20 (dd, J = 17.3, 1.2 Hz, 8-H″), 5.64 (ddd, J = 15.6, 7.2, 6.3 Hz, 4-H), 5.71 (d, J = 15.6 Hz, 3-H), 5.92 (dd, J = 17.3, 10.7 Hz, 7-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5, 29.87, 29.93 (3 × CH_3), 45.1 (C-5), 70.8 (C-2), 72.7 (C-6), 112.1 (C-8), 121.8 (C-4), 142.7 (C-7), 144.8 (C-3).

The fraction corresponding to peak 34 afforded methyl (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoate (6) (Okada et al., 1980; Konoshima and Sawada, 1982): MS (see Table III); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 6-CH_3), 1.61-1.68 (m, 5-CH_2), 1.82 (s, 2-CH_3), 2.19-2.24 (m, 4-CH_2), 3.72 (s, OCH_3), 5.09 (dt, J = 10.8, 1.1 Hz, 8-H′), 5.23 (dd, J = 17.4, 1.1 Hz, 8-H″), 5.91 (dd, J = 17.4, 10.8 Hz, 7-H), 6.75 (t, J = 7.5 Hz, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (2-CH_3), 23.5 (C-4), 28.0 (6-CH_3), 40.7 (C-5), 51.7 (OCH_3), 73.1 (C-6), 112.2 (C-8), 127.7 (C-2), 142.4 (C-7), 144.6 (C-3), 168.7 ($COOCH_3$).

The fraction corresponding to peak 30 afforded (*Z*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (8): MS (see Table III); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 6-CH_3), 1.58 (s, 2-CH_3), 1.60

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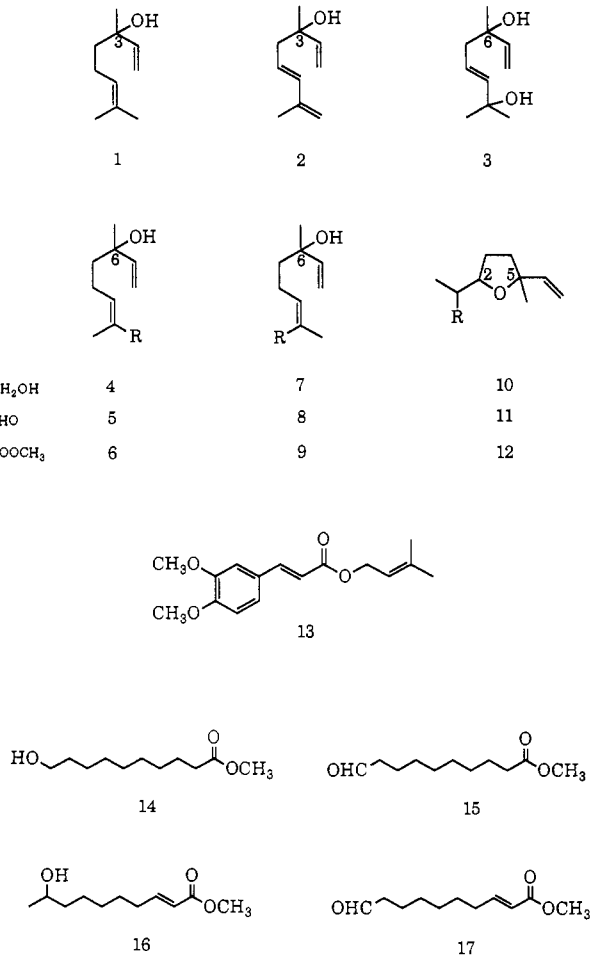
Chart I



(m, 5-CH_2), 2.10 (m, 4-CH_2), 5.08 (d, J = 10.7 Hz, 8-H′), 5.22 (d, J = 17.3 Hz, 8-H″), 5.42 (t, J = 7.3 Hz, 3-H), 5.91 (dd, J = 17.3, 10.7 Hz, 7-H), 9.62 (s, CHO).

Selenium Dioxide Oxidation of Linalool (1) (Hirata et al., 1981). A solution of linalool (1) (410 mg) in dioxane (2 mL) was stirred with selenium dioxide (225 mg) under reflux for 6 h. Workup and separation by radial PLC on silica gel gave (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**5**) (80 mg) and α,5-dimethyl-5-ethenyl-2-tetrahydrofuranacetaldehydes (lilac aldehydes **11**, four isomers) (50 mg).

(E)-2,6-Dimethyl-6-hydroxy-2,7-octadienal (5): MS (see Table III); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 2-CH_3), 1.60 (m, 5-CH_2), 1.65 (s, 6-CH_3), 2.33 (m, 4-CH_2), 2.65 (br s, OH), 5.02 (dd, J = 10.7, 1.1 Hz, 8-H′), 5.17 (d, J = 17.3 Hz, 8-H″), 5.83 (dd, J = 17.3, 10.7 Hz, 7-H), 6.44 (t, J = 7.3 Hz, 3-H), 9.29 (s, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.0 (2-CH_3), 23.8 (C-4), 27.9 (6-CH_3), 40.2 (C-5), 72.7 (C-6), 112.3 (C-8), 139.0 (C-2), 144.3 (C-7), 155.1 (C-3), 195.3 (CHO).

α,5-Dimethyl-5-ethenyl-2-tetrahydrofuranacetaldehydes (Lilac Aldehydes 11, Four Isomers): MS (see Table III); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36–1.42 (m, α-CH_3), 1.49–1.51 (s, 5-CH_3), 1.64–1.76 (m, CH_2CH_2), 2.4–2.6 (m, C*H*CHO), 4.09–4.25 (m, 2-CH), 4.93–4.99, 5.10–5.19, 5.76–5.91 (m, CH=CH_2), 9.72, 9.73, 9.75, 9.76 (C*H*O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.9, 10.3, 10.4, 10.9 (α-CH_3), 22.7, 23.0, 23.7, 23.9 (C-3), 26.6, 26.7, 26.9, 27.0 (5-CH_3), 28.6, 28.9, 29.2, 29.3 (C-4), 36.6, 36.9, 37.4, 37.6 (C-5), 50.7, 51.1, 51.7, 51.9 (C-2), 78.4, 78.7, 79.2, 79.6 (*C*HCHO), 111.6, 111.7, 111.8, 111.8 (CH=CH_2), 143.3, 143.4, 144.1, 144.2 (*C*H=CH_2), 204.6, 204.8, 204.8, 204.9 (*C*HO).

Preparation of Lilac Aldehydes (11) from (E)-2,6-Dimethyl-6-hydroxy-2,7-octadienal (5) (Wakayama et al., 1973). A solution of (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**5**) (40 mg) in methanol (2 mL) was stirred with sodium hydride (80%) (20 mg) for 2 h. Workup afforded lilac aldehydes (**11**) (four isomers) (15 mg) (spectroscopic data see above).

Preparation of β,5-Dimethyl-5-ethenyl-2-tetrahydrofuranethanols (Lilac Alcohols 10, Four Isomers) from Lilac Aldehydes (11) (Wakayama et al., 1973). A solution of lilac aldehydes (**11**) (10 mg) in tetrahydrofuran (THF) (2 mL) was stirred with lithium aluminum hydride ($LiAlH_4$) (10 mg) for 2 h. Workup afforded lilac alcohols (**10**) (four isomers) (9 mg). MS (see Table III).

Preparation of Methyl α,5-Dimethyl-5-ethenyl-2-tetrahydrofuranacetates (Lilac Acid Methyl Esters 12, Four Isomers) from Methyl (E)-2,6-Dimethyl-6-hydroxy-2,7-octadienoate (6) (Bidan et al., 1977). A solution of methyl (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoate (**6**) (10 mg) in methanol (1 mL) was stirred with sodium hydride (80%) (5 mg) for 10 min. Workup afforded lilac acid methyl esters (**12**) (four isomers) quantitatively (GC determined). MS (see Table III).

RESULTS AND DISCUSSION

Figure 1 is a representative GC-FID profile of the methylated extractable organic substances recovered from a representative nodding thistle honey sample (NT8). Table II lists the levels of the substances detected in the methylated diethyl ether extracts of the 10 nodding thistle honey samples. Nodding thistle honeys typically also include significant clover and lotus contributions, as indicated by the pollen data (Table I). Nodding thistle pollen appears to be underrepresented, and even a 7% contribution is considered indicative of a substantial nodding thistle contribution (Moar, personal communication). It is accepted that the 10 samples utilized in this study are most appropriately classified as predominantly nodding thistle honeys, rather than unifloral grade honeys.

Since unifloral grade clover honey samples are characterized (Tan et al., 1988) by very low levels of extractable organic substances (typically less than 50 μg/g of honey), the peaks attributable to the nodding thistle input (e.g., peaks 17, 26, 28, 30, and 34) can be readily recognized. Peaks eluting after stearic acid (peak 61) were found to be higher chain length hydrocarbons (>C_{21}) or fatty acids (detected as the corresponding methyl esters). Since these substances are primarily constituents of beeswax, the composition of which is well-known (Tan et al., 1988; Bonaga et al., 1986; Graddon et al., 1979; Tulloch and Hoffmann, 1972), details of their characterization and concentration are not presented here.

The most striking characteristic of the 10 nodding thistle honey samples was the dominance of peaks 17, 26, 30, and 34 (see Figure 1), each of which exhibited an intense mass spectral ion of m/z 71, reminscent of that exhibited by linalool (**1**). A bulk extraction of sample NT2 afforded a mixture of extractives which were separated by multiple preparative layer chromatography on silica gel. Three fractions, corresponding to peaks 17, 30, and 34, were recovered in sufficient quantity and purity for structural elucidation using one- and two-dimensional NMR spectroscopy. Other constituents of the diethyl ether extracts were identified by comparisons (GC-FID, GC–MS, and NMR analyses) with synthetic specimens prepared in our laboratory.

Peak 17. ^{13}C NMR revealed the presence of 10 carbon signals, assignable to three methyl carbons, the carbons of two olefinic double bonds (one disubstituted, the other monosubstituted), and two oxygenated carbons. ^{1}H NMR indicated the presence of three aliphatic methyl groups, two methylene protons, which showed an AB system consistent with their location adjacent to a chiral center, and five olefinic protons. Three of the olefinic protons were mutually coupled and exhibited coupling constants and chemical shifts typical of the vinyl group of linalool (**1**), while the other pair of olefinic protons were mutually trans coupled (J = 17.3 Hz). These observations, in combination with two-dimensional COSY NMR data, established peak 17 to be (*E*)-2,6-dimethyl-3,7-octadiene-2,6-diol (**3**). The ^{1}H NMR spectrum of **3** compared well with that reported for this compound by Takaoka and

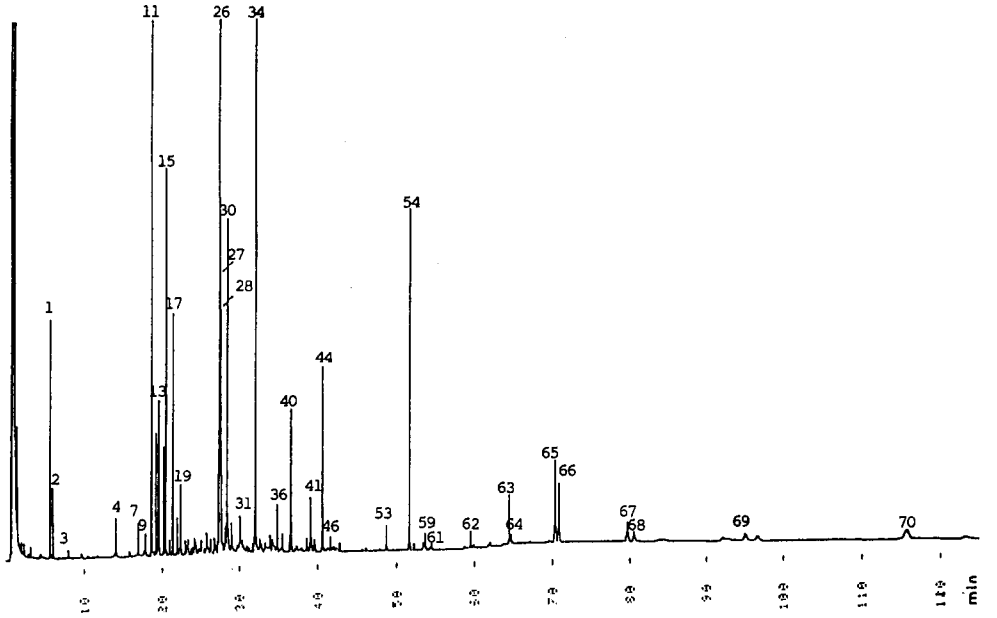


Figure 1. Gas chromatographic profile of methylated nodding thistle honey extractives (sample NT8). For peak identifications see Table I. GC conditions: 16-m BP-1 column, H_2 as carrier gas (μ 46 cm/s); 40 °C (3-min hold) raised at 4 °C/min to 250 °C (65-min hold).

Hiroi (1976) and Etoh et al. (1980). (*E*)-2,6-Dimethyl-3,7-octadiene-2,6-diol (**3**) was first prepared by photosensitized oxidation of linalool (**1**) (Matsuura and Butsugan, 1968) and later isolated from the essential oil of ho-leaf (Takaoka and Hiroi, 1976). It has also been identified as a constituent of grapes, grape juice, and wines (Rapp and Knipser, 1979; Williams et al., 1980; Wilson et al., 1984; Strauss et al., 1987) and tea (Etoh et al., 1980).

Peak 34. High-resolution mass spectroscopy established the molecular formula $C_{11}H_{18}O_3$ (found *m/z* 198.1250; required *m/z* 198.1256) while a fragment ion of *m/z* 180 was shown to arise from the molecular ion by loss of a water molecule (found *m/z* 180.1170; required *m/z* 180.1150). ^{13}C NMR spectroscopy demonstrated the presence of 11 carbon signals, assignable to two methyl carbons, one conjugated carbonyl group, and the carbons of two olefinic double bonds (one trisubstituted, the other monosubstituted), and an oxygenated carbon signal (see Methods and Materials). ^1H NMR indicated the presence of an aliphatic tertiary methyl group, an olefinic methyl group, a carboxymethyl group, two pairs of methylene protons, and four olefinic protons, three of which were mutually coupled.

The 300-MHz two-dimensional double quantum filtered COSY spectrum of peak 34 revealed the presence of an isolated vinyl group, and the coupling of the olefinic proton (6.75 ppm) to a pair of methylene protons (2.21 ppm) and to the olefinic methyl group (1.82 ppm). Additionally, the olefinic methyl group was found to be long range coupled to the foregoing methylene protons (2.21 ppm), which were in turn coupled to the other pair of methylene protons (1.65 ppm). ^1H and ^{13}C NMR chemical shifts were also correlated in a both conventional and long range correlated two-dimensional experiments. These observations identified peak 34 as methyl (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoate (**6**). The trans disposition of the $COOCH_3$ group was defined by comparison with ^1H NMR data reported for the methyl (+)-2,6-dimethyl-6-(*S*)-hydroxy-2-*trans*-2,7-octadienoate (Okada et al., 1980; Konoshima and Sawada, 1982).

Peaks 26 and 30. ^1H NMR demonstrated that peak 30 possessed a tertiary methyl group, an olefinic methyl group, two pairs of methylene protons, four olefinic protons, and an aldehyde group (9.62 ppm). These data, compared with those determined for methyl (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoate (**6**) (see above) and a synthetic specimen of (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**5**) (see Methods and Materials), established peak 30 to be (*Z*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**8**). In a like manner peak 26 was identified as (*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**7**). It is noteable that the mass spectrum of (*Z*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**8**) differs significantly from that of its *E* isomer (**5**). In a like manner we have observed that the mass spectrum of (*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**7**) (see Table III) differs significantly from that of its *E* isomer (**4**) (Hirata et al., 1981).

Peak 9. Peak 9 was identified as 3,7-dimethyl-1,5,7-octatrien-3-ol (**2**) (hotrienol). The mass spectrum of **2** (see Table III) was very similar to that determined for (*E*)-2,6-dimethyl-3,7-octadiene-2,6-diol (**3**). This compound was first isolated from tea (Nakatani et al., 1969) and has also been detected in grapes (Schreier et al., 1974; Ribereau-Gayon et al., 1975) and in the distillate of beeswax (Ferber and Nursten, 1977).

Peaks 12–14, 19, 22, and 23. Since peaks 12–14 exhibited essentially identical mass spectra, they were considered to be stereoisomers, as were peaks 19, 22, and 23. Their determinations as α,5-dimethyl-5-ethenyl-2-tetrahydrofuranacetaldehydes (lilac aldehydes, **11**) (peaks 12–14) and β,5-dimethyl-5-ethenyl-2-tetrahydrofuranethanols (lilac alcohols, **10**) (peaks 19, 22, and 23), respectively, were achieved by comparison with synthetic specimens prepared as described under Methods and Materials. Oxidation of linalool (**1**) with selenium dioxide (Hirata et al., 1981) afforded a mixture of (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**5**) (17%) and lilac aldehydes (**11**) (11%, four isomers). Lilac aldehydes (**11**) were also prepared from (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**5**) by intramolecular Michael addition (Wakayama et al., 1973). ^1H and ^{13}C NMR analyses indicated both the synthetic and natural specimens of **11** and **10** to be mixtures of four diastereomers in the ratio ca. 1:1:1:0.5, three of which were adequately resolved in GC-FID and GC–MS analyses.

Wakayama et al. (1973) first synthesized lilac alcohols (**10**) from linalool acetate. Oxidization afforded (*E*)-2,6-dimethyl-6-acetoxy-2,7-octadienal, which was converted

Table II. Concentration (Micrograms per Gram) of Components from 10 Methylated Nodding Thistle Honey Samples

peak	compd (prominent MS peaks)	honey sample									
		NT1	NT2	NT3	NT4	NT5	NT6	NT7	NT8	NT9	NT10
1	butane-1,3-diol[a]	1.9	3.7	2.6	4.2	4.0	4.6	1.7	2.8	1.7	3.7
2	diacetone alcohol[a]	2.1	2.7	1.6	0.8	0.6	1.1	0.3	1.0	0.6	0.8
3	methyl 3-furancarboxylate	0.2	0.3	–[b]	–	0.2	0.2	–	0.1	–	0.1
4	dimethyl butanedioate	2.4	1.2	0.1	0.2	4.9	3.2	0.1	0.6	0.2	0.8
5	benzyl alcohol	0.3	tr[c]	–	tr	tr	0.1	tr	tr	tr	0.1
6	methyl 2-furancarboxylate	0.2	0.1	–	–	0.5	0.2	0.1	0.1	–	0.4
7	methyl benzoate	1.0	0.4	0.3	0.5	0.4	0.3	0.2	0.2	0.1	0.4
8	2-phenylethanol	tr	tr	0.3	0.1	0.2	0.1	tr	0.1	tr	0.1
9	3,7-dimethyl-1,5,7-octatrien-3-ol (**2**) (hotrienol)[a]	1.4	1.4	1.0	0.2	0.5	0.2	0.2	0.4	0.3	0.4
10	methyl pyridinecarboxylate	0.1	tr	–	tr	0.2	0.3	0.1	tr	tr	0.1
11	*n*-undecane (C_{11}) (internal standard)										
12	lilac aldehyde (**11**) (isomer 1)	1.3	2.6	1.1	0.4	0.7	0.5	0.3	2.0	0.7	–
13	lilac aldehyde (**11**) (isomer 2)	2.6	5.0	2.1	0.8	1.3	1.7	0.4	3.7	1.2	–
14	lilac aldehyde (**11**) (isomer 3)	1.5	2.7	1.2	0.4	0.7	0.5	0.2	1.9	0.5	–
15	methyl 2-phenylethanoate	3.6	5.5	3.7	1.5	3.0	1.3	1.0	3.0	1.7	1.9
16	unknown (43, *59*, 83, 116, 141, 159)	1.0	1.4	1.3	0.4	0.2	0.2	0.2	0.3	0.3	0.5
17	3,7-dimethyl-1,5-octadiene-3,7-diol (**3**)	3.5	6.0	2.8	1.9	2.5	1.0	0.8	2.9	1.8	1.0
18	5-(hydroxymethyl)-2-furfural	2.1	0.2	0.2	0.2	1.4	1.9	1.0	0.5	0.4	2.1
19	lilac alcohol (**10**) (isomer 1)	2.4	2.3	0.8	0.6	0.7	0.5	0.2	0.9	0.6	0.6
20	4-methoxybenzaldehyde	–	1.1	0.7	–	–	–	–	–	0.3	1.0
21	dimethyl hexanedioate	0.6	–	–	0.1	0.4	0.1	–	0.2	–	–
22	lilac alcohol (**10**) (isomer 2)	–	–	–	0.1	–	–	tr	0.2	0.3	–
23	lilac alcohol (**10**) (isomer 3)	–	–	–	–	–	–	0.1	0.4	0.4	0.4
24	methyl *cis*-3-phenylpropenoate	–	–	–	0.1	0.5	tr	0.1	–	–	–
25	unknown (43, *59*, 60, 69, 87, 118, 130, 159)	0.2	0.3	0.2	0.3	0.6	0.2	0.1	0.2	0.1	0.7
26	(*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**7**)[d]	5.8	12	6.0	3.0	4.9	2.1	1.6	8.7	6.5	2.1
27	unknown (43, 55, *71*, 96, 109, 139, 157)	2.2	6.0	3.7	1.7	2.7	1.1	0.8	2.8	2.2	1.6
28	(*E*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**4**)[a]	5.3	7.0	3.5	1.8	2.3	1.3	0.9	3.0	2.0	1.6
29	methyl 2-hydroxy-3-phenylpropanoate	–	–	0.7	–	0.4	0.2	–	–	–	–
30	(*Z*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**8**)	9.1	11	8.3	3.1	6.1	3.0	1.9	4.6	4.2	3.4
31	methyl *trans*-3-phenylpropenoate	4.7	3.3	4.2	1.5	1.6	3.7	6.5	0.7	0.3	2.5
32	unknown (*43*, 55, 69, 97, 109, 129, 155)	–	–	0.2	0.5	1.2	0.6	0.5	1.0	1.7	1.3
33	dimethyl octanedioate	0.7	0.3	0.2	0.4	0.4	0.3	0.1	0.1	0.1	0.3
34	(*E*)-methyl 2,6-dimethyl-6-hydroxy-2,7-octadienoate (**6**)	30	29	28	9.9	14	6.5	6.4	11	8.6	13
35	dimethyl 2-*trans*-octenedioate	–	–	–	0.2	0.7	0.3	–	–	–	–
36	methyl 10-oxodecanoate (**15**)[a]	0.7	1.2	0.9	0.2	0.5	0.1	0.4	1.0	1.0	0.7
37	methyl laurate (12:0)	0.1	tr	–	–	0.2	0.1	–	0.2	0.3	–
38	methyl nonanedioate	0.1	0.1	tr	0.1	0.4	0.2	0.1	0.3	0.3	0.1
39	methyl 9-hydroxy-2-*trans*-decenoate (**16**)[a]	0.2	0.1	0.1	0.6	0.6	0.3	0.4	0.3	–	0.5
40	methyl 10-oxo-2-*trans*-decenoate (**17**)[a]	2.3	4.6	1.8	1.7	1.3	0.5	0.6	2.4	1.9	1.3
41	dimethyl decanedioate	4.3	1.6	0.3	1.5	2.3	1.4	0.1	0.9	0.8	2.2
42	methyl 3-(4′-methoxyphenyl)-*trans*-propenoate	1.0	0.5	0.4	0.4	0.3	0.1	0.1	0.3	0.5	0.9
43	methyl 3-hydroxy-3-(4′-methoxyphenyl)propanoate	0.1	0.6	0.6	0.2	0.4	0.3	0.1	0.2	0.1	0.3
44	dimethyl 2-*trans*-decenedioate	15	6.8	6.1	6.7	7.6	5.4	4.4	2.9	2.4	8.8
45	methyl 3,4,5-trimethoxybenzoate	0.1	0.2	0.2	–	0.1	tr	0.1	–	0.1	0.5
46	methyl 3-(4′-hydroxyphenyl)-*trans*-propenoate	1.6	0.2	0.5	0.2	0.4	0.2	0.3	0.4	0.3	0.9
47	methyl myristate (14:0)	0.4	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.1	0.2
48	methyl 4-hydroxy-3,5-dimethoxybenzoate	1.5	0.6	0.6	–	0.6	0.5	–	–	0.4	0.9
49	methyl 3-(3′,4′-dimethoxyphenyl)-*cis*-propenoate	1.2	0.3	0.8	0.3	0.4	0.7	1.1	0.2	0.2	1.2
50	methyl pentadecanoate (15:0)	0.4	0.1	0.3	0.1	0.2	tr	0.3	tr	tr	0.1
51	methyl 3-(3′,4′-dimethoxyphenyl)-*trans*-propenoate	1.1	0.4	0.6	0.1	0.4	1.7	2.2	0.1	0.1	1.2
52	methyl palmitoleate (16:1)	0.2	0.3	0.2	0.1	0.5	0.1	0.2	0.1	0.1	0.1
53	methyl palmitate (16:0)	2.4	1.8	1.5	1.0	1.9	1.2	1.1	0.8	0.7	1.1
54	methyl margarate (17:0) (internal standard)										
55	methyl abscisate	0.3	0.5	0.7	0.2	0.2	0.2	0.2	0.2	0.2	0.2
56	prenyl 3-(3′,4′-dimethoxyphenyl)-*trans*-propenoate (**13**)	–	–	0.2	–	–	0.1	0.2	–	–	0.3
57	methyl linoleate (18:2)	0.8	0.4	0.4	0.2	0.7	0.5	0.5	0.2	0.3	0.5
58	methyl α-linolenate (18:3)	1.4	0.7	0.8	0.4	1.5	1.0	0.5	0.2	0.3	0.2
59	methyl oleate (18:1)	2.7	2.1	1.7	1.0	1.8	1.3	1.1	0.7	0.8	1.3
60	*n*-heneicosane (C_{21})	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.2
61	methyl stearate (18:0)	0.7	0.5	0.5	0.2	0.3	0.2	0.3	0.2	0.2	0.3

[a] Identified by comparison with NBS library mass spectrum or with mass spectrum published. [b] A dash (–) indicates that the compound was not present. [c] Tr indicates that the compound was present at a level of <0.1 μg/g of honey. [d] Tentatively identified.

to (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**5**) and isomerized (intramolecular Michael addition) to lilac aldehydes (**11**), which on reduction gave lilac alcohols (**10**). Likewise, methyl (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoate (**6**) undergoes an intramolecular Michael addition to give lilac acid methyl esters (**12**), reduction of which afforded lilac alcohols (**10**) (Bidan et al., 1977). Recently, lilac alcohols (**10**) were synthesized by intramolecular reactions of allyloxy radicals (John et al., 1989).

Lilac aldehydes (**11**) were first isolated from lilac flower oil (Wakayama and Namba, 1974) and later found as fragrant components in gardenia flower (Hattori et al., 1978), in *Platanthera stricta* (Patt et al., 1988), and in *Artemisia pallens* (Misra et al., 1991). Lilac alcohols (**10**) were also isolated from lilac flower oil (Wakayama et al., 1973) and found to be fragrant components of gardenia flowers (Hattori et al., 1978), *P. stricta* (Patt et al., 1988), and *A. pallens* (Misra et al., 1991). The absolute configurations of lilac alcohols a, b, c, and d (βS,2S,5S; βR,2S,5S; βR,2R,5S; and βS,2R,5S, respectively), were determined by synthesis and ^{1}H NMR spectroscopy (Wakayama et al., 1973). Notwithstanding the presence of the

Table III. Mass Spectral Data of Linalool Derivatives

compd	EIMS at 70 eV, m/z
linalool (1)	41 (100), 71 (98), 93 (92), 43 (88), 55 (67), 69 (54), 80 (33), 121 (21)
3,7-dimethyl-1,5,7-octatrien-3-ol (2)	71 (100), 43 (80), 82 (60), 67 (39), 41 (27), 55 (19), 53 (13), 79 (7)
2,6-dimethyl-3,7-octadiene-2,6-diol (3)	82 (100), 43 (87), 71 (76), 67 (56), 41 (17), 55 (15), 83 (9), 85 (8)
(*E*)-2,6-dimethyl-2,7-octadiene-1,6-diol (4)	43 (100), 71 (55), 67 (45), 55 (33), 82 (14), 96 (12), 119 (112), 137 (10)
(*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (5)	71 (100), 43 (96), 41 (38), 55 (37), 87 (24), 82 (23), 83 (22), 98 (12)
(*E*)-methyl 2,6-dimethyl-6-hydroxy-2,7-octadienoate (6)	43 (100), 71 (63), 41 (42), 55 (35), 67 (23), 97 (13), 121 (10), 138 (5)
(*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (7)[a]	71 (100), 43 (73), 55 (32), 41 (28), 83 (13), 87 (12), 82 (10), 95 (9)
(*Z*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (8)	43 (100), 71 (53), 67 (43), 41 (33), 55 (30), 82 (13), 93 (12), 79 (11)
lilac alcohol (10) (isomer 1)	55 (100), 43 (85), 41 (59), 93 (47), 111 (41), 67 (39), 71 (25), 69 (21)
lilac alcohol (10) (isomer 2)	55 (100), 43 (88), 41 (55), 93 (51), 111 (48), 67 (42), 71 (27), 81 (22)
lilac alcohol (10) (isomer 3)	55 (100), 43 (86), 41 (56), 93 (42), 67 (39), 111 (34), 71 (22), 69 (20)
lilac aldehyde (11) (isomer 1)	55 (100), 43 (83), 41 (53), 67 (41), 93 (34), 71 (33), 69 (25), 111 (20)
lilac aldehyde (11) (isomer 2)	55 (100), 43 (80), 41 (52), 67 (39), 93 (38), 71 (32), 111 (28), 69 (25)
lilac aldehyde (11) (isomer 3)	55 (100), 43 (81), 41 (52), 67 (37), 93 (36), 71 (37), 69 (25), 111 (23)
lilac acid methyl ester (12) (isomer 1)	55 (100), 43 (68), 41 (50), 111 (48), 93 (42), 67 (39), 69 (34), 88 (23)
lilac acid methyl ester (12) (isomer 2)	55 (100), 43 (76), 41 (54), 111 (47), 93 (42), 67 (35), 69 (34), 88 (22)
lilac acid methyl ester (12) (isomer 3)	55 (100), 43 (61), 41 (49), 111 (46), 93 (42), 67 (33), 69 (33), 88 (25)

[a] Tentatively identified.

corresponding linaloolic acid (determined as methyl ester 6), lilac acids [as methyl esters (12) in the methylated extractive with diazomethane prior to analysis] were not detected in the nodding thistle honey extracts analyzed in this study. Hitherto lilac acids have, for example, been identified in the essential oil of coriander (Lamparsky and Klimes, 1988).

While linalool (1) and α,α,5-trimethyl-5-ethenyl-1-(hydroxymethyl)-2-tetrahydrofuran (linalool oxide), an isomer of lilac alcohol (10), have been reported to occur in Australian honeys (Graddon et al., 1979), they were not found in New Zealand honeys investigated in this study.

Other Components. In addition to a number of linalool derivatives, an array of aromatic acids including benzoic acid (peak 7), phenylacetic acid (peak 15), 2-hydroxy-3-phenylpropionic acid (peak 29), 3,4,5-trimethoxybenzoic acid (peak 45), 3,5-dimethoxy-4-hydroxybenzoic acid (syringic acid, peak 48), *cis*- and *trans*-3-phenylpropenoic acid (cinnamic acid, peaks 24 and 31), 3-(4′-methoxyphenyl)propenoic acid (peak 42), and *cis*- and *trans*-3-(3′,4′-dimethoxyphenyl)propenoic acid (peaks 49 and 51) (each of which were identified as the corresponding methyl esters) were detected in the nodding thistle honey samples. Steeg and Montag (1988) have concluded that many of the aromatic carboxylic acids detected in honey samples are secondary plant metabolites. Peak 56, a minor component of some of the extracts, was identified as prenyl 3-(3′,4′-dimethoxyphenyl)propenoate (13). This substance has been shown to be a constituent of bee propolis (Ghisalberti, 1979; Greenaway et al., 1990).

Variable concentrations of an array of methylated aliphatic acids and diacids including methyl laurate (peak 37), methyl myristate (peak 47), methyl palmitoleate (peak 52), methyl palmitate (peak 53), methyl linoleate (peak 57), methyl α-linolenate (peak 58), methyl oleate (peak 59), methyl stearate (peak 61), dimethyl butanedioate (peak 4), dimethyl hexanedioate (peak 21), dimethyl octanedioate (peak 33), dimethyl 2-*trans*-octenedioate (peak 35), dimethyl nonanedioate (peak 38), dimethyl decanedioate (peak 41), and dimethyl 2-*trans*-decenedioate (peak 44) were also detected in the methylated nodding thistle honey extracts. Since these compounds, with the exception of dimethyl 2-*trans*-octenedioate, have previously been identified in a variety of other unifloral grade honeys including New Zealand clover (*Trifolium repens*), heather, manuka, thyme (*Thymus vulgaris*), willow (*Salix* sp.), and vipers bugloss (*Echium vulgare*) honeys (Tan et al., 1988, 1989a, 1990), their detection in the nodding thistle honey samples does not assist in the discrimination of floral sources.

Methyl 10-oxodecanoate (15) (peak 36), methyl 9-hydroxy-2-decenoate (16) (peak 39), and methyl 10-oxo-2-decenoate (17) (peak 40) were also identified in most of the extracts. These compounds and other C_8–C_{12} oxygenated saturated and unsaturated fatty acids such as 10-hydroxydecanoic acid are well-known royal jelly components (Lercker et al., 1981). Significant levels of these compounds also occur in mushrooms (Tressl et al., 1982).

Conclusions. Hitherto our investigations of the extractable noncarbohydrate organic substances present in New Zealand honeys have identified a range of compounds, including some unique degraded carotenoid-like substances, which appear characteristic of the floral source. Provided suitable marker substances can be identified, we believe chemical analysis (GC-FID or GC–MS methods) (Tan et al., 1989b) to be a plausible alternative to pollen analysis for floral source verification, especially so for honeys that exhibit low pollen counts. In the case of New Zealand nodding thistle honey samples, the 16 linalool derivatives identified in this study are proposed as suitable marker compounds. We have examined the extracts of more than 300 unifloral grade New Zealand honey samples and found the occurrence of linalool and lilac alcohol analogues to be confined to samples possessing a nodding thistle input.

Our results indicate that (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoic acid [detected as methyl ester (6) in this study] should be present at a level of 20 μg/g of honey, or greater, in a unifloral grade nodding thistle honey. Lesser levels (in total a further 20 μg/g of honey) of (*E*)-2,6-dimethyl-3,7-octadiene-2,6-diol (3), (*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (7), (*Z*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (8), α,5-dimethyl-5-ethenyl-2-tetrahydrofuranacetaldehydes (lilac aldehydes) (11), and β,5-dimethyl-5-ethenyl-2-tetrahydrofuranethanols (lilac alcohols) (10) should also be present.

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Registry No. Supplied by the Author: 3,7-Dimethyl-1,6-octadien-3-ol (linalool, **1**), 78-70-6; 3,7-dimethyl-1,5,7-octatrien-3-ol (**2**), 29957-43-5; 2,6-dimethyl-3,7-octadiene-2,6-diol (**3**), 13741-21-4; (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienal (**5**), 108943-16-4; (*E*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**4**), 75991-61-6; (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoic acid, 83945-54-4; methyl (*E*)-2,6-dimethyl-6-hydroxy-2,7-octadienoate (**6**), 75979-27-0; (*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**7**), 103619-06-3; α,5-dimethyl-5-ethenyl-2-tetrahydrofuranacetaldehyde (lilac aldehyde, **11**), 67920-63-2; β,5-dimethyl-5-ethenyl-2-tetrahydrofuranethanol (lilac alcohol, **10**), 35997-39-8; α,5-dimethyl-5-ethenyl-2-tetrahydrofuranacetic acid (lilac acid), 116181-55-6; α,α,5-trimethyl-5-ethenyl-1-(hydroxymethyl)-2-tetrahydrofuran (linalool oxide), 60047-17-8; decanoic acid, 334-48-5; methyl decanoate, 110-42-9; 10-hydroxydecanoic acid, 1679-53-4; methyl 10-hydroxydecanoate (**14**), 2640-94-0; 10-oxodecanoic acid, 5578-80-3; methyl 10-oxodecanoate (**15**), 14811-73-5; decanedioic acid, 111-20-6; dimethyl decanedioate, 106-79-6; 9-hydroxy-2-decenoic acid, 1422-28-2; 2-decenedioic acid, 72879-22-2; dimethyl 2-decenedioate, 28598-91-6; methyl 10-oxo-2-decenoate (**17**), 81550-30-3.