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STRUCTURES OF SOME ALIPHATIC COMPOUNDS IN THE ESSENTIAL OIL OF *MENTHA* × *GENTILIS* nm. *HIRTELLA*[*]

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Key Word Index—*Mentha* × *gentilis* nm. *hirtella*; Labiatae; 2,4-dimethylhexane-2-ol; 5-methylnonanal; 2-butylhexanal; tetrahydrogeranyl acetate.

Abstract—The structures of four new aliphatic compounds from the essential oil of *Mentha* × *gentilis* nm. *hirtella* have been elucidated as 2,4-dimethylhexane-2-ol, 5-methylnonanal, 2-butylhexanal and tetrahydrogeranyl acetate.

INTRODUCTION

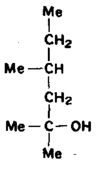
In an earlier study of the chemical composition of the essential oil of *Mentha* × *gentilis* L. nm. *hirtella* Markl. we distinguished four new aliphatic compounds not previously reported from natural sources. In the present study we describe the elucidation of the structures of these compounds.

RESULTS AND DISCUSSION

Compound 12 (numbering as in Ref. [1]) has a parent peak at *m/e* 130 in its MS. On carbon-skeleton chromatography it yields mainly 2,4-dimethylhexane. As skeletal rearrangements do not generally occur with aliphatic compounds on carbon-skeleton chromatography [2–4], compound 12 apparently possesses the same carbon skeleton as 2,4-dimethylhexane. The strong IR absorption at 3300 cm^{-1} is due to an alcoholic hydroxyl group. In the MS the occurrence and position of the hydroxyl group may be deduced from the rather small M$^+$-peak resulting from elimination of water, and the base peak at *m/e* 59 due to a more favoured α cleavage in respect to a –C (Me)$_2$OH grouping. Consequently compound 12 is 2,4-dimethylhexane-2-ol (**1**). This structure is also confirmed by a further study of the MS fragmentation of the compound.

Compound 14 has its parent peak in the MS at *m/e* 156. Its IR spectrum has a strong band at 1725 cm^{-1}, and bands at 2840 and 2860 cm^{-1}, which indicates an aldehyde group. On carbon-skeleton chromatography mainly 5-methylnonane and 4-methyloctane were formed. As carbons in aldehyde groups are rather easily removed on carbon-skeleton chromatography [2–4], the 5-methylnonane skeleton seems likely, and in addition the aldehyde group must be situated in the main chain, not in the side chain. When the above facts are taken into consideration 5-methylnonanal (**2**) seems a likely structure for compound 14, and this is also confirmed by a study of its MS fragmentation.

Compound 15 shows a parent peak at *m/e* 156, and has aldehyde bands in its IR spectrum at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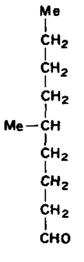
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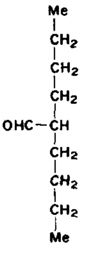
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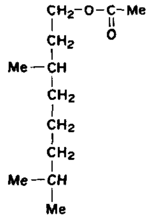
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[*] Part II in the series Studies on the essential oils of some taxa of the genus Mentha L. occurring in Fennoscandia. For part I see Ref. [1].

1725 cm^{-1} as well as 2680 and 2720 cm^{-1}. On carbon-skeleton chromatography it yields mainly 5-methylnonane and *n*-nonane. These facts suggest a 5-methylnonane skeleton, and a position in the side chain for the aldehyde group. The structure of compound 15 thus appears to be 2-butylhexanal (**3**). The fragmentation pattern of the MS gives further evidence for this structure.

Similarly spectroscopic analysis applied to compound 26 revealed it to be tetrahydrogeranyl acetate (**4**). Identical IR and MS were recorded on synthetic tetrahydrogeranyl acetate.

EXPERIMENTAL

Material. The compounds 12, 14, 15 and 26 were isolated from the essential oil of *Mentha* × *gentilis* L. nm. *hirtella* Markl. by a combination of column chromatography and preparative GLC [1]. The purity of each compound was checked by GLC using polar (Carbowax 20 M) and non-polar (OV-101) WCOT capillary columns. The plants were collected in the neighbourhood of Helsinki in S. Finland in August–September 1971. A herbarium voucher is deposited in the Botanical Museum of the University of Helsinki (H).

Spectroscopy. IR spectra of the compounds were run with the samples as liquid films between KBr pellets. MS were recorded using a GC-MS combination; GC column; Carbowax 20M WCOT stainless steel, 50 m × 0·25 mm i.d.; temps: injector 200°, manifold 200°, ion source (housing and chamber) 190°; electron energy: 70 eV.

Carbon-skeleton chromatography. For the determination of the carbon skeleton, procedure I and catalyst C of Widén [2] were used in combination with the GC-MS instrument.

Compound 12 (**1**). About 2 mg of compound 12 was obtained as a colourless liquid. $\mathrm{IR}_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3300, 1450, 1370, 1250, 1190, 1110, 1070, 1035, 1005, 965, 930, 870, 825, 810, 775, 760, 722. MS *m/e* (rel. int): 130 (M$^+$, 1), 41 (49), 43 (18), 55 (86), 59 (100), 69 (12), 70 (10), 83 (52), 101 (18), 112 (8). On carbon-skeleton chromatography mainly 2,4-dimethylhexane was formed. MS *m/e* (rel. int): 114 (M$^+$, 5), 41 (32), 43 (100), 55 (17), 57 (33), 71 (22), 85 (33).

Compound 14 (**2**). About 5 mg of compound 14 was available as a colourless liquid. $\mathrm{IR}_{\max}^{\mathrm{KBr}}$ cm^{-1}: 2860, 2840, 1725, 1460, 1378, 1363, 1352, 1289, 1241, 1178, 1162, 1115, 1091, 1066, 1040, 1000. MS *m/e* (rel. int.): 156 (M$^+$, 0·5), 41 (54), 43 (29), 55 (34), 57 (78), 67 (100), 81 (25), 82 (90), 83 (19), 85 (61), 136 (6). On carbon-skeleton chromatography 5-methylnonane, MS *m/e* (rel. int.): 142 (M$^+$, 2), 41 (33), 43 (100), 57 (95), 71 (30), 85 (17), 99 (4), 113 (1) and 4-methyloctane, MS *m/e* (rel. int.): 128 (M$^+$, 3), 41 (35), 43 (100), 57 (80), 71 (20), 85 (24), 99 (5) were formed.

Compound 15 (**3**). About 10 mg of colourless liquid was obtained. $\mathrm{IR}_{\max}^{\mathrm{KBr}}$ cm^{-1}: 2720, 2680, 1725, 1480, 1420, 1380, 1300, 1252, 1190, 1170, 1155, 1120, 1010, 945, 725, MS *m/e* (rel. int.): 156 (M$^+$, 0·5), 41 (89), 43 (100), 55 (65), 57 (90), 70 (43), 81 (29), 82 (34), 84 (20), 95 (23), 112 (24), 136 (5). On carbon-skeleton chromatography 5-methylnonane, and *n*-nonane, MS *m/e* (rel. int.): 128 (M$^+$, 3), 41 (31), 43 (100), 57 (72), 71 (20), 85 (18), 99 (4) were formed.

Compound 26 (**4**). About 15 mg of colourless liquid was available. $\mathrm{IR}_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1745, 1475, 1390, 1368, 1240, 1170, 1040, 980, 950, 898, 840, 725, 640. MS *m/e* (rel. int.): 200 (M$^+$, 0·5), 41 (43), 43 (100), 55 (59), 56 (58), 57 (30), 61 (27), 69 (44), 70 (54), 83 (35), 97 (21), 112 (15), 140 (7). Synthetic tetrahydrogeranyl acetate exhibits identical MS and IR spectra.

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