Note

High-boiling Constituents of Clove Oil (*Eugenia caryophyllata* THUNB.) and Hop Oil (*Humulus lupulus* LINN.)

Toshikazu UCHIDA, Yoshiharu MATSUBARA
and Akemi ADACHI

Department of Applied Chemistry,
Faculty of Science and Engineering,
Kinki University, Kowakae,
Higashiosaka-shi 577

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Clove oil (*Eugenia caryophyllata* THUNB.) and hop oil (*Humulus lupulus* LINN.) are used as materials for eugenol and beer. Of the oxygenated derivatives of β -caryophyllene found in their essential oils, there have been reported caryophyllene oxide, caryophylla-3(12), 7(13)-dien-6 α -ol and caryophylla-3(12), 6-dien-4-ol in clove oil,¹⁾ and caryophyllene oxide,^{1,2)} caryophyllene alcohol²⁾ and caryophylla-3(12), 6-dien-4-ol¹⁾ in hop oil. Both clove and hop neutral oil contain β -caryophyllene as the major component in their high boiling fraction. Thus, it can be expected that the oxygenated derivatives of β -caryophyl-

lene by a biosynthetic route may exist in their neutral essential oils. We have extensively examined these essential oils, using clove and hop oils supplied by the Takasago Perfumery Co., Ltd.

The removal of acids and phenols from the respective essential oils gave the neutral oils. More than 49 and 82 peaks were respectively observed in the gas chromatograms of these neutral oils (Figs. 1 and 2). As shown in Table I, four compounds were identified as sesquiterpene alcohols by comparing their GC-MS with those of authentic samples. The authentic samples were synthesized by well-established methods. Thus, oxidation of β -caryophyllene in acetic acid with lead tetraacetate followed by hydrolysis gave **45**,³⁾ **46** (=71'),⁴⁾ **48** (=73')⁴⁾ and **49** (=75')⁴⁾ as minor products. These were purified by means of preparative GLC before use.

Compounds **46** (=71'), **48** (=73') and **49** (=75') have not previously been found in the essential oils of clove and hop, and 4,4-dimethyltricyclo[6.3.2.0^{2,5}]trideca-8-ene-1-ol (**45**) was shown to be present in the natural products for the first time.

Apparatus

Gas chromatography. We used a Yanaco model G 180-TFP gas chromatograph equipped with a flame-ionization detector. A glass capillary column (inside diameter, 0.28 mm; length, 20 m) coated with PEG 20 M was used. The column temperature was programed at 2°C per minute from 60 to 180°C, and was held isothermally at 180°C for 0.5 hr. The inlet pressure for the nitrogen carrier gas was 1.0 kg/cm². The gas chromatogram was obtained

FIG. 1. Gas Chromatogram of Clove Oil.

FIG. 2. Gas Chromatogram of Hop Oil.

FIG. 3.

TABLE I. SESQUITERPENE COMPONENTS OF CLOVE AND HOP OILS

Clove oil	
Peak No.	Compound
45 ⁽³⁾	4,4-Dimethyltricyclo[6.3.2.0 ^{2,5}]trideca-8-ene-1-ol
46 ⁽⁴⁾	Caryophylla-4(12),8(13)-dien-5 β -ol (10,10-Dimethyl-2,6-dimethylenbicyclo[7.2.0]undecan-5 β -ol)
48 ⁽⁴⁾	Caryophylla-3,8(13)-dien-5 α -ol (11,11-Dimethyl-8-methylenbicyclo[7.2.0]undeca-3-ene-5 α -ol)
49 ⁽⁴⁾	Caryophylla-3,8(13)-dien-5 β -ol (11,11-Dimethyl-8-methylenbicyclo[7.2.0]undeca-3-ene-5 β -ol)
Hop oil	
Peak No.	Compound
71 ⁽⁴⁾	Caryophylla-4(12),8(13)-dien-5 β -ol (10,10-Dimethyl-2,6-dimethylenbicyclo[7.2.0]undecan-5 β -ol)
73 ⁽⁴⁾	Caryophylla-3,8(13)-dien-5 α -ol (11,11-Dimethyl-8-methylenbicyclo[7.2.0]undeca-3-ene-5 α -ol)
75 ⁽⁴⁾	Caryophylla-3,8(13)-dien-5 β -ol (11,11-Dimethyl-8-methylenbicyclo[7.2.0]undeca-3-ene-5 β -ol)

under these conditions by injecting 0.4 μ l of neutral oil.

Mass spectrometry. Mass spectra were obtained on a JEOL JMS HX-100 mass spectrometer. The operating conditions were: ionization voltage, 70eV; ion-accelerating voltage, 5000 V; temperatures of the ionization chamber and sample injection block, 270 and 230°C, respectively.

MS spectral data

45: m/z 220 (M^+ , 4%), 205 ($M - CH_3$, 5), 202 ($M - H_2O$, 3), 191 (6), 187 ($M - CH_3 - H_2O$, 13), 177 (8), 173 (4), 163 (7), 162 (33), 159 (11), 149 (10), 147 (48), 145 (11), 136 (11), 135 (48), 133 (19), 131 (18), 121 (22), 119 (38), 117 (8), 107 (52), 105 (33), 95 (12), 93 (40), 91 (49), 85 (10), 81 (15), 79 (33), 77 (24), 71 (28), 67 (26), 65 (12), 55 (26), 53 (19), 51 (6), 43 (100), 41 (48), 39 (20).

46 and 71': m/z 220 (M^+ , 1%), 205 ($M - CH_3$, 3), 202 ($M - H_2O$, 2), 187 ($M - CH_3 - H_2O$, 6), 177 (6), 159 (11), 149 (9), 136 (100), 123 (12), 121 (13), 119 (15), 117 (13), 109 (22), 107 (20), 105 (21), 95 (19), 93 (25), 91 (30), 81 (25), 79 (28), 77 (16), 69 (38), 67 (20), 55 (22), 53 (13), 43 (9), 41 (48), 39 (14).

48 and 73': m/z 220 (M^+ , 9%), 205 ($M - CH_3$, 13), 202 ($M - H_2O$, 11), 187 ($M - CH_3 - H_2O$, 16), 177 (10), 173 (9), 164 (14), 160 (15), 149 (20), 146 (26), 135 (20), 133 (34),

131 (26), 123 (79), 121 (33), 119 (18), 117 (11), 109 (37), 107 (58), 105 (42), 97 (11), 95 (48), 93 (94), 91 (50), 84 (56), 81 (100), 79 (55), 77 (33), 71 (39), 69 (43), 67 (37), 65 (14), 55 (36), 53 (23), 43 (12), 41 (88), 39 (25).

49 and 75': m/z 220 (M^+ , 6%), 205 ($M - CH_3$, 14), 202 ($M - H_2O$, 14), 187 ($M - CH_3 - H_2O$, 46), 177 (9), 173 (10), 164 (17), 161 (40), 159 (34), 151 (29), 149 (33), 147 (40), 135 (42), 133 (47), 131 (49), 123 (72), 119 (33), 117 (18), 109 (79), 107 (82), 105 (67), 95 (13), 93 (93), 91 (74), 81 (74), 79 (64), 77 (48), 69 (43), 67 (43), 59 (10), 55 (61), 53 (37), 43 (30), 41 (100), 39 (36).

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