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# The Constituents of Hops. V.[1] The Volatile Composition of *Humulus japonicus* Sieb. et Zucc.

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The steam-volatile constituents of *Humulus japonicus* Sieb. et Zucc. have been studied, and 50 compounds of the oil have been identified mainly by means of the temperature-programmed capillary GLC mass-spectra method. Beside the previously-reported principal components of hops (α-humulene, caryophyllene, α-copaene, α- and β-selinenes, γ-cadinene, caryophyllene-oxide, and humulene-epoxide-II), benzyl alcohol and phenethyl alcohol were found in high concentrations, whereas the myrcene was negligible. The proportion of the main compound, humulene, to the next highest one, caryophyllene, was approximately in the ratio of two to one, as in the essential oil of *H. lupulus*. As far as the chemical composition of the essential oils is concerned, *H. japonicus* seems to be related rather more closely to *H. lupulus* than to *H. cordifolius*.

The genus *Humulus* is represented by two species, the common hop, *Humulus lupulus* L., and the annual climbing plant from Japan, *H. joponicus* Sieb. et Zucc., which is synonymous with *H. scandens* Merr. and which belongs to the natural family *Cannabiaceae*. The wild hops of North America, *H. americanus* and *H. neomexicanus*, and the Asian *H. cordifolius*, the chemical composition of which was recently reported,[1] are generally considered to be varieties of *H. lupulus*. In this paper, the identification of the volatile constituents contained in the above-ground parts with the cones of *H. japonicus* is reported for the first time, and the chemical similarities between the above-mentioned species are discussed.

## Experimental

**Separation.** The above-ground parts with the cones of *H. japonicus* (18 kg) gathered in the suburbs of Osaka at the beginning of October, 1969, were extracted with

TABLE 1. THE CONSTITUENTS OF HYDROCARBONS

| Peak No. in Fig. 1 | Identity of Constituent | Peak No. in Fig. 1 | Identity of Constituent |
|---|---|---|---|
| 1 | α-Pinene | 37 | β-Selinene |
| 2 | β-Pinene | 38 | α-Selinene |
| 3 | Myrcene | 38 | α-Muurolene |
| 4 | *n*-Undecane | 39 | β-Bisabolene |
| 8 | *n*-Dodecane | 40 | α-Curcumene |
| 15 | *n*-Tridecane | 41 | γ-Cadinene |
| 20-1 | *n*-Tetradecane | 41 | δ-Cadinene |
| 22 | α-Ylangene | 43 | β-Sesquiphellandrene |
| 23 | α-Copaene | 47 | Calamenene |
| 25 | β-Bourbonene | 50 | γ-Calacorene |
| 27 | *n*-Pentadecane | 51 | α-Calacorene |
| 27 | β-Elemene | 62 | Cadalene |
| 27 | *trans*-α-Bergamotene | | * $C_{12}H_{24}$ 168 (43) |
| 28 | Caryophyllene | | * $C_{13}H_{26}$ 182 (43) |
| 32 | α-Humulene | | * $C_{14}H_{28}$ 196 (43) |
| 33 | β-Farnesene | | * $C_{15}H_{30}$ 210 (43) |
| 34 | γ-Muurolene | | * $C_{16}H_{32}$ 224 (43) |
| 35 | *n*-Hexadecane | | iso $C_{13}H_{28}$ 184 (57) |
| 35 | α-Amorphene | | iso $C_{14}H_{30}$ 198 (57) |

1) Previous paper of this series: Y. Naya and M. Kotake, This Bulletin, **43**, 2956 (1970).

TABLE 2. THE CONSTITUENTS OF OXYGENATED COMPOUNDS

| Peak No. | Identity of Constituent | Peak No. | Identity of Constituent |
|---|---|---|---|
| 6 | Hexanol | 35 | Phenethyl alcohol |
| 8 | *trans*-3-Hexenol-1 | 39 | Geraniol |
| 9 | *cis*-2-Hexenol-1 | 52 | Caryophyllene-oxide |
| 13 | 1-Octene-3-ol | 54 | Humulene-epoxide-I |
| 18 | Linalool | 55 | Humulene-epoxide-II |
| 20 | * $M^+$, *m/e* 124 (109) | 59 | Humulol |
| 24 | * $M^+$, *m/e* 124 (82) | 60 | T-Cadinol |
| 26 | * $M^+$, *m/e* 138 (95) | 64 | Humulenol-II |
| 26-1 | α-Terpineol | 66 | Humulene-dioxide |
| 29 | * $M^+$, *m/e* 138 (82) | 67 | α-Cyperone |
| 31 | Benzyl alcohol | | |

* Unknown compound together with molecular weight and base peak on MS spectrum.

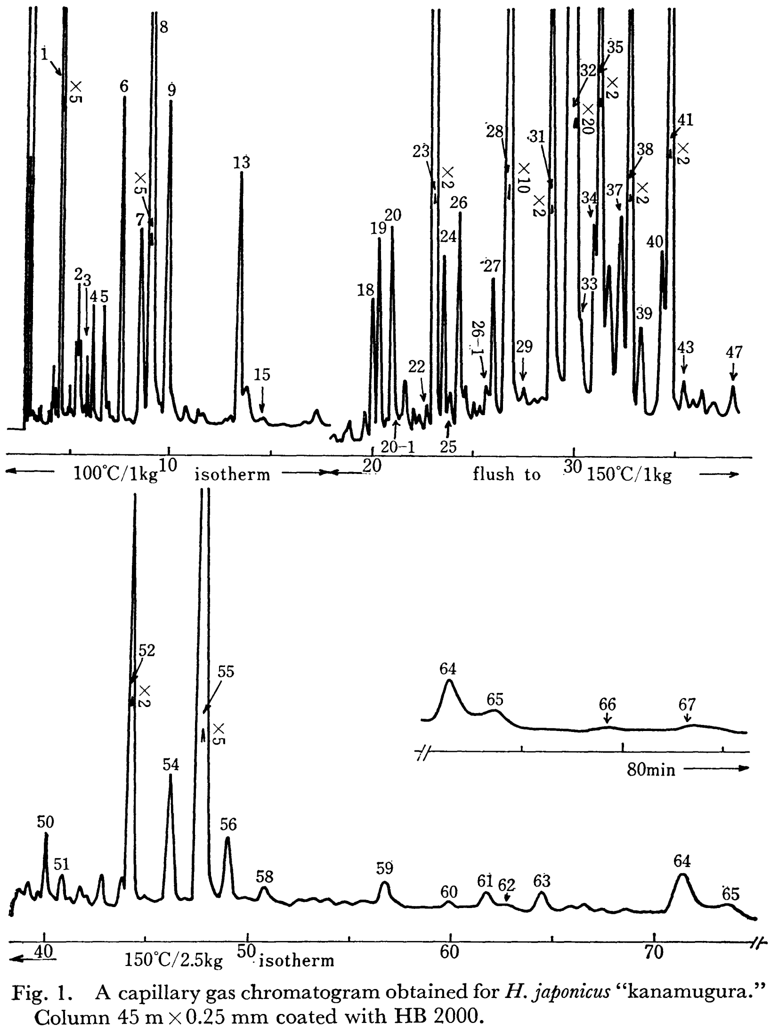


Fig. 1. A capillary gas chromatogram obtained for *H. japonicus* "kanamugura." Column 45 m × 0.25 mm coated with HB 2000.

ether. The extract was steam-distilled to obtain the essential oil (1.8 g). This oil was subjected to selective adsorption chromatography on neutral alumina to separate it into hydrocarbon (0.8 g) and oxygenated constituents (0.6 g). Each fraction was divided into several parts by programmed preparative gas-liquid chromatography (Carbowax 20 M), and then examined by means of the temperature-programmed capillary GLC mass spectra method. In addition, the major constituents were isolated by a combination of adsorption chromatography and preparative gas-liquid chromatography (Carbowax 20 M) and were identified by comparing their IR spectra with those of authentic samples.

**Apparatus.** The mass spectrometer employed was a Hitachi Model RMU-6 instrument; the operating conditions were as follows: ionization energy, 80 eV; accelerating voltage, 2000 V; ionization chamber, 150°C.

For the GLC, a Hitachi Model K-53 was used. The capillary column used for the analysis was 45 m long by 0.25 mm in I.D., made of stainless steel and coated with HB 2000; the column temperature was programmed non-linearly from 100 to 150°C. The helium-carrier gas-inlet pressure was set at 1.5 kg/cm$^2$ for initiation and 2.5 kg/cm$^2$ at the end.

For preparative gas-chromatography, a model 90-P Varian Aerograph equipped with a thermal conductivity detector was employed. A 10-ft. $\times$ 3/8 in. aluminum column packed with 20% Carbowax 20 M on Chromosorb W (60—80 mesh) was used. Helium was used as the carrier gas, and the column temperature was set at 100—220°C.

## Results and Discussion

The compounds identified from the oil of *H. japonicus* are listed in Table 1 and 2, together with the peak number on the programmed GLC (Fig. 1). The authentic compounds used for identification were obtained from reliable sources and were purified by GLC separation before use. α-Humulene and the related oxides, together with humulol and humulenol-II, were found in great abundance. α-Copaene, caryophyllene and its oxide, α- and β-selinenes, and γ-cadinene have been found to be the common major components of the "Shinshu-wase" (*H. lupulus*).[2,3] It is significant, compared with the composition of "Shinshu-wase," that myrcene is here found to be negligible, whereas benzyl alcohol and phenethyl alcohol are detected in abnormally high concentrations. Mention has been made previously of the botanical relationship among the *H. lupulus*, *H. cordifolius*, and *H. japonicus*. It is interesting that the similarities in the essential oil of *H. lupulus* and *H. japonicus*, are however, distinct from that of *H. cordifolius* to some extent; this seems to be in disagreement with the botanical relationship of the three concerned plants. That is, the former two are humulene-rich, and the later is caryophyllene-rich, in the ratio of approximately two to one. The proportion of humulene-epoxide-II to caryophyllene-oxide corresponds with that in the corresponding hydrocarbons. In addition, in *H. cordifolius*, bisabolene-type sesquiterpenes (zingiberene and α-curcumene, together with β-bisabolene and β-sesquiphellandrene), selina-3,7(11)-diene, and selina-4(14), 7(11)-diene were found in abnormally high concentrations, as has previously been reported.[1]

2) Y. Naya and M. Kotake, *Nippon Kagaku Zasshi*, **88**, 1307 (1967); **89**, 1113 (1968); **91**, 275 (1970).

3) R. G. Buttery and L. C. Ling, *Brewers Digest*, **1966**, 71.