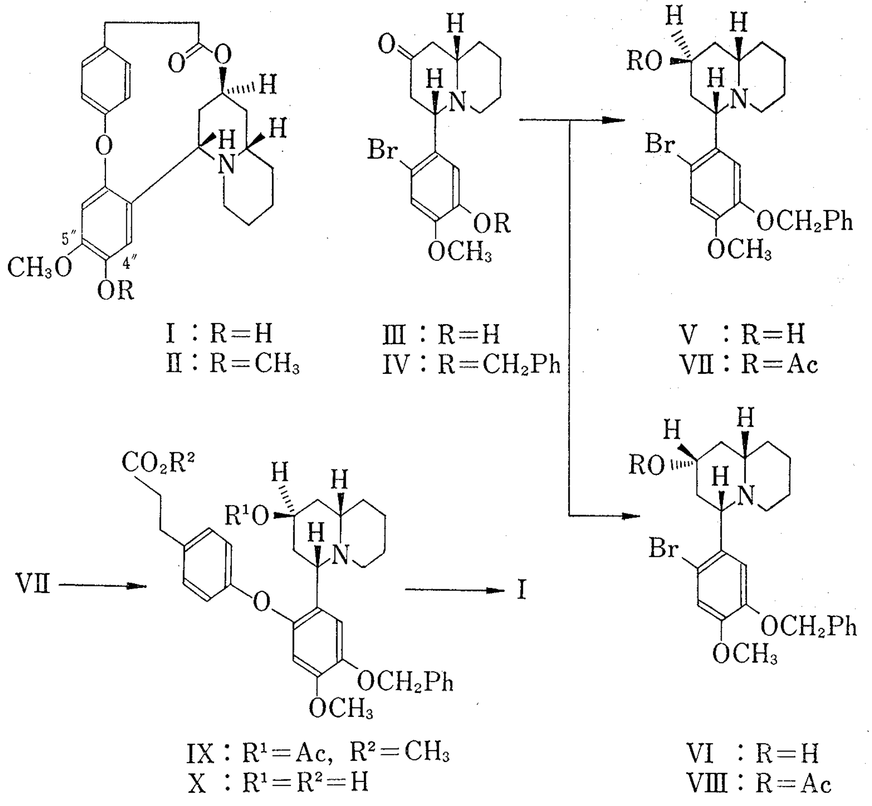

I : $R=H$
II : $R=CH_3$

III : $R=H$
IV : $R=CH_2Ph$

V : $R=H$
VII : $R=Ac$

IX : $R^1=Ac$, $R^2=CH_3$
X : $R^1=R^2=H$

VI : $R=H$
VIII : $R=Ac$

Ph=phenyl

Chart 1

Though we have not yet obtained the authentic natural desmethyldecaline for the comparison with the synthetic product (I), the above-mentioned synthesis will provide a final proof for the structure of desmethyldecaline.

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Volatile Metabolite of Aquatic Fungi. Identification of 6-Pentyl-α-pyrone from *Trichoderma* and *Aspergillus* Species

In continuation of a study on odorous compounds which are responsible for the unpleasant taste and odor of public water supplies,[1] we recently isolated two strains of fungi, a *Trichoderma* and an *Aspergillus* species, from the bottom deposits of Sengari Reservoir, Kobe City Water Supply Bureau, and their volatile metabolites were examined.

These fungi were cultured on Sabouraud agar medium (200 Petri dishes (10 cm i.d.)) at 27° for 5 days and each whole culture was submitted repeatedly to steam distillation.

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[1] T. Kikuchi, *Japan Analyst* (*Bunseki Kagaku*), **22**, 1530 (1973).

Extraction of the final distillate with methylene chloride and careful evaporation of the extract gave a small amount of oily substance in each case (about 50 mg).

Both of these substances showed a practically single peak in gas chromatography using a 10% PEG 20M column and the retention times were coincident with each other as shown in Fig. 1. Further, the mass spectra taken by GC–MS method[2] (see Fig. 2) were also fully identical with each other, indicating that the main volatile compounds produced by these two fungi are identical.

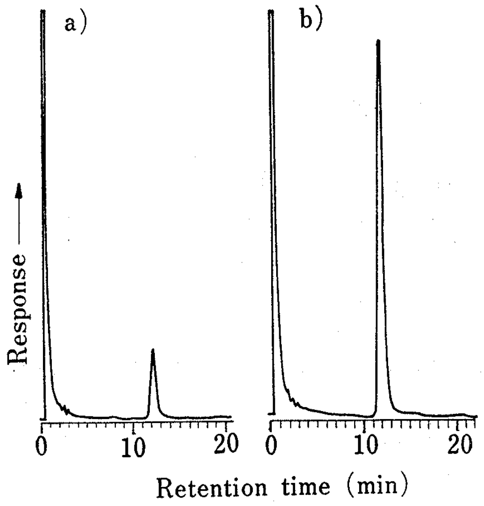

Fig. 1. Gas Chromatograms of the Volatile Metabolites of a) the *Trichoderma* sp. and b) the *Aspergillus* sp. isolated from Sengari Reservoir

condition: Hitachi Gas Chromatograph Model 063; column, 10% PEG20M on Chromosorb WNAW (2 m × 3 mm i.d. stainless steel); detector, FID; column temp., 180°; carrier gas, N_2 (30 ml/min)

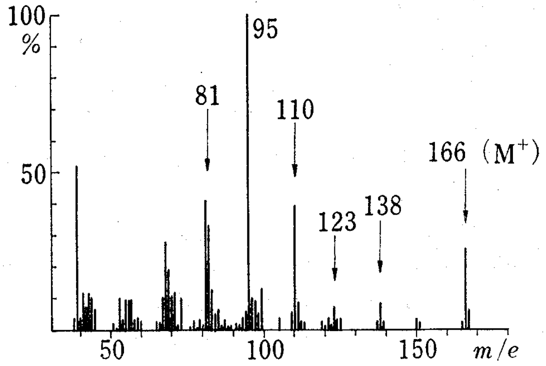

Fig. 2. Mass Spectrum arising from the Main Peak of the Volatile Metabolites of the *Trichoderma* sp.

condition: GC column, 20% PEG 20M on Chromosorb W(AW) (1.5 m × 2 mm i.d. glass tube); column temp., 180°; carrier gas, He (2 kg/cm²); MS ionization voltage, 70 eV; accelerator voltage, 1800 V

A portion (about 15 mg) of the oily substance obtained from the *Trichoderma* species was purified by preparative gas chromatography (10% PEG 20M, column temperature 165°) to give a colorless oil (4 mg) having a waxy flavor, the molecular formula of which was determined as $C_{10}H_{14}O_2$ by high-resolution mass spectrometry[3] (Calcd.: 166.0994; Found: 166.0980). The infrared (IR) spectrum (in chloroform) showed characteristic absorption bands[4] at 1725, 1630, and 1560 cm^{-1} and the ultraviolet (UV) spectrum (in ethanol) an absorption maximum[5] at 302 mμ (ε 6000), suggesting the presence of an α-pyrone skeleton. As shown in Fig. 3, its nuclear magnetic resonance (NMR) spectrum[6] (in deuterated methylene chloride) revealed signals for a primary methyl group at δ 0.91 (3H, triplet, $J=6$ Hz), methylene protons at δ 1.2—1.9 (6H) and δ 2.48 (2H, triplet, $J=7.5$ Hz), and olefinic protons at δ 5.96 (1H, doublet, $J=6.5$ Hz), δ 6.07 (1H, doublet, $J=9$ Hz), and δ 7.24 (1H, doublet of doublet, $J=9$ and

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2) GC–MS was performed on a Hitachi Mass Spectrometer Model RMU-6E combined with a Hitachi Gas Chromatograph Model K-53 and a Ryhage type molecular separator was used as the carrier gas separator.

3) High-resolution mass spectrometry was performed on a JMS–OISG double-focusing mass spectrometer. We wish to express our deep gratitude to Miss Y. Izumi of Institute for Chemical Research, Kyoto University, for the measurement of mass spectrum.

4) K. Nakanishi, "IR Absorption Spectroscopy (Practical)," Nankodo Co., Ltd., Tokyo, 1960, p. 56.

5) A.I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, Oxford, 1964, p. 140.

6) The NMR spectrum was measured on a Varian Associates HA-100 Spectrometer with tetramethylsilane as internal standard. The splitting pattern of olefinic protons was confirmed by the spin-decoupling experiments.

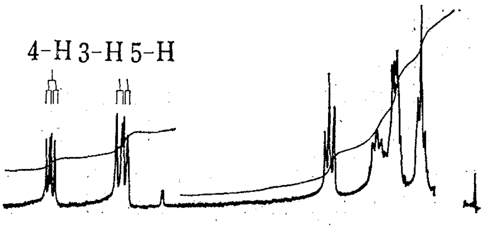
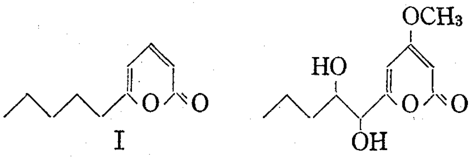


Fig. 3. NMR Spectrum of the Volatile Metabolite (I) of the *Trichoderma* sp.



I

II

Chart 1

J=6.5 Hz). On the basis of these spectral data, the compound was considered to be 6-pentyl-α-pyrone (I).[7]

Then, we synthesized 6-pentyl-α-pyrone (I) according to the Nobuhara's method[8] for the direct comparison. The IR, UV, NMR, and mass spectra of the synthetic sample and also the retention time in gas chromatography were entirely identical with those of the natural compound (I).

From the above observations, it was proved that the *Trichoderma* and *Aspergillus* species produce 6-pentyl-α-pyrone (I) as a major volatile component. This compound has been reported as a volatile component of the Red Globe variety of freestone peaches,[9] but our report is the first example of detection from the fungus metabolites. In this connection, it is interesting to note that a closely related compound (II) was recently isolated from a *Penicillium* species.[10] Several 5,6-dihydro-α-pyrone derivatives have also been reported as the metabolites of a few fungi.[10,11] Although 6-pentyl-α-pyrone (I) has only a waxy flavor, it may contribute to some extent to the unpleasant taste and odor in public water supplies.

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7) T.J. Batterham, "NMR Spectra of Simple Heterocycles," John Wiley and Sons, Inc., New York, 1973, p. 392.
8) A. Nobuhara, *Agr. Biol. Chem.* (Tokyo), **33**, 1264 (1969).
9) M.R. Sevenants and W.G. Jennings, *J. Food Sci.*, **36**, 536 (1971).
10) W.J. McGahren, G.A. Ellestad, G.O. Morton, and M.P. Kunstmann, *J. Org. Chem.*, **38**, 3542 (1973).
11) Y. Kimura, K. Katagiri, and S. Tamura, *Tetrahedron Letters*, **1971**, 3137; G.A. Ellestad, W.J. McGahren, and M.P. Kunstmann, *J. Org. Chem.*, **37**, 2045 (1972); G.M. Strunz, C.J. Heissner, M. Kakushima, and M.A. Stillwell, *Can. J. Chem.*, **52**, 825 (1974).