Triterpenoids of Lanostane Group from Fruit Bodies of Nine Basidiomycetous Species

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Eight species of Aphyillorphorales and one species of Agaricales of Basidiomycetes were examined for the triterpenoidal constituents and six compounds (I, II, III, IVa, VIIIa, IXa) were isolated and identified (Table I). The new acid from Melanoporia rosea (as the methyl ester) (IVa) was suggested to be 12β-hydroxy carbomethoxyacetyl quercinic acid methyl ester.

More than thirty tetracyclic triterpenes of lanostane group have so far been obtained from fruit bodies or mycelia of Polyporaceae, Basidiomycetes. Most of these compounds possess a carboxyl group at C₂₀ with or without one carbon unit at C₂₄.

We have examined on the fruit bodies of 97 species of wood-rotting fungi, especially of Polyporaceae and related families for the distribution of triterpenes and sterols. The studies on the constituents of Poria cocos (Fr.) Wolf and Echinodontium tsugicola (P. Henn.) Imaiz. have been reported in the previous papers.

In this paper, isolation of the triterpenoids from nine species as shown in Table I will be reported.

Fresh, ripe fruit bodies of each species were air-dried, crushed and extracted with ether for one week at room temperature. In order to facilitate the identification and the separation of the triterpenes the hexane insoluble part of the extracts was methylated with diazo-

<table>
<thead>
<tr>
<th>Species (Japanese name)</th>
<th>Family</th>
<th>Compound identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daedalea tanakaë (Murr.) Aoshima (Himeshiroamitake)</td>
<td>Polyporaceae</td>
<td>I</td>
</tr>
<tr>
<td>Melanoporia rosea (Alb. et Schw. ex Fr.) Aoshima (Barairosarunokoshikake)</td>
<td>Polyporaceae</td>
<td>I, II, III, IVa</td>
</tr>
<tr>
<td>Melanoporia juniperina Aoshima (Nikuamitake)</td>
<td>Polyporaceae</td>
<td>I, II, III</td>
</tr>
<tr>
<td>Gloeophyllum abietinum (Bull. ex Fr.) Karst. (Kogeiroukaragatake)</td>
<td>Polyporaceae</td>
<td>VIIIa, IXa</td>
</tr>
<tr>
<td>G. sepiarium (Wulf. ex Fr.) Karst. (Kiikaragatake)</td>
<td>Polyporaceae</td>
<td>VIIIa, IXa</td>
</tr>
<tr>
<td>G. striatum (Swartz. ex Fr.) Murr. (Hirohanokikaigaragatake)</td>
<td>Polyporaceae</td>
<td>VIIIa, IXa</td>
</tr>
<tr>
<td>Lentinus tepidus Fr. (Matsurofuji)</td>
<td>Tricholomataceae</td>
<td>VIIIa, IXa</td>
</tr>
<tr>
<td>Sporangium appendiculatus (Berk. et Br.) Aoshima (Shirokaimentake)</td>
<td>Polyporaceae</td>
<td>II, VIIIa, IXa</td>
</tr>
<tr>
<td>Veluticeps angularis (Lloyd) Aoshima et Furukawa (Chizugatasarunokoshikake)</td>
<td>Veluticepsaceae</td>
<td>IXa</td>
</tr>
</tbody>
</table>

1) Location: Kamiyoga-1-chome, Setagayaku, Tokyo.
methane and separated by column and preparative thin-layer chromatographies (TLC) to give each compound as the methyl ester as shown in Table I. Sterol fraction from the hexane soluble part will be reported in a forth-coming paper.

From the white, small fruit bodies of *Daedalea tanakae* grown on conifers and broad-leaved trees, methyl polypropenate C (I) was isolated. The isolation of the acid from *D. dickinsii* had been reported.\(^5\)

In the case of two species of *Melanoporia*, producing perennial fruit bodies and growing on conifers and broad-leaved trees, the same constituent (I) was isolated together with methyl tumulosate (II) contaminated with the corresponding 7,9(11)-diene (III). In addition, a new triterpene was obtained from *M. rosea*. The methyl ester of the new acid (IVA), \(C_{36}H_{56}O_{8}\), \([\alpha]_D^2 +4.66^\circ\), showed one spot in TLC, gave an oily monoacetate (IVB), \(C_{37}H_{58}O_{9}\), \([\alpha]_D^2 -5.26^\circ\), and was converted into a diol monomethyl ester (VA), \(C_{32}H_{58}O_{9}\), \([\alpha]_D +19.0^\circ\), by the hydrolysis with methanolic potassium hydroxide, followed by the methylation. The diol (Va) was further derived to the diacetate (Vb) and the ketone (VII). Thus the methyl ester (IVA) was proved to be an acyl ester of the compound (VA) having two secondary hydroxyls and one

\[I : R = O, \text{methyl polypropenate C}]
\[III : R = \text{H, methyl dehydrorutulosate}]

\[\text{CH}_3\text{OOC} \cdot \text{CH}_2\cdot \text{CO} \cdot \text{O}]

\[\text{IVA : } R_1 = \text{OH}, R_2 = \text{CH}_3\]
\[\text{IVB : } R_1 = \text{OAc}, R_2 = \text{CH}_3\]
\[\text{IVA : } R_1 = \text{H}, R_2 = \text{H}\]
\[\text{IVB : } R_1 = \text{H}, R_2 = \text{CH}_3\]

\[\text{Va : } R_1 = \text{H}, R_2 = \text{OH}\]
\[\text{Vb : } R_1 = \text{OAc}, R_2 = \text{H}\]
\[\text{VII : } R_1 = \text{=O}, R_2 = \text{=O}\]

\[\text{II : } R_1 = \text{OH}, R_2 = \text{OH, methyl tumulosate}
\[\text{VIIa : } R_1 = \text{OH}, R_2 = \text{H, methyl ebiricoate}
\[\text{VIIb : } R_1 = \text{OAc}, R_2 = \text{H}
\[\text{VIIc : } R_1 = \text{OTMS}, R_2 = \text{H}

\[\text{IXa : } R = \text{OH, methyl trametelenolate}
\[\text{IXb : } R = \text{OAc}
\[\text{IXc : } R = \text{OTMS}

\[\text{Chart 1}\]

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methoxycarbonyl group. Since there exist no olefinic proton observed in the nuclear magnetic resonance (NMR) spectra, one double bond was accommodated at the 8-position as in the case of most of the fungal triterpenes. From the molecular formulae and infrared (IR) spectra the remaining oxygen function was assumed to be a carbonyl. The acyl group was suggested to be methoxycarbonylacetyl by the mass spectrum of IVa, m/e 498 (M+–C4H9O4), 483 (M+–CH3–C4H9O4), 465 (M+–CH2–H2O–C4H9O4), the loss of C4H9O2 by the hydrolysis, and by the NMR spectrum (δ 3.70 (3H), 3.38 (2H)). As the malonate conjugate of fungal triterpene the structure of carboxyacetylergocryptic acid (VIIa) was elucidated.6 The spectral data of IVa and the derivatives showed close similarities with those of the methyl ester (VIIb) of VIIa, except the presence of an additional secondary hydroxyl group in IVa (δ, 4.10). Especially the fragments caused by the loss of 158 mass units in the mass spectra (Chart 2) and the presence of two secondary methyl groups appearing in rather lower fields (δ 1.12, 1.08) in the NMR spectra suggested the presence of the same side chain.

These results showed that the methyl ester of the new acid (IVa) correspond to a monohydroxy derivative of carboxyacetylergocryptic acid dimethyl ester (VIIb).

**Table II. NMR Spectra of the Triterpenoids (δ in ppm in CDCl₃ solution)**

<table>
<thead>
<tr>
<th></th>
<th>CH₃</th>
<th>H</th>
<th>OCH₃ COCH₃ CO</th>
<th>OCOCH₃</th>
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<tbody>
<tr>
<td>18</td>
<td>1.01</td>
<td>0.92</td>
<td>1.03 (d)</td>
<td>3.62</td>
</tr>
<tr>
<td>19</td>
<td>0.87</td>
<td>1.04 (d)</td>
<td>4.66 (m)</td>
<td>3.10 (m)</td>
</tr>
<tr>
<td>30, 31</td>
<td>1.12 (d)</td>
<td>6.68 (m)</td>
<td>3.62</td>
<td>3.38</td>
</tr>
<tr>
<td>32</td>
<td>27, 28</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>3</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

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\(a) J = 6 \text{ Hz}, \quad b) J = 7 \text{ Hz.} \\
In IVa–VIIb the C₄H₉-methyls appears at 0.9–1.0 ppm overlapping with other methyl signals.

Although there exists no decisive evidence for the location of the hydroxyl group, 12β-position was assumed to be most preferable from the following evidences. As shown in Table II the additional hydroxyl group does not effect the chemical shifts of any of the angular methyl groups.7–10 The ketone (VII) does not show the properties of 1,2-diketone and \(\alpha,\beta-\)

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unsaturated carbonyl. These facts favour 1β-, 6α- and 12β-positions. By the acetylation (IVa→IVb, Va→Vb), the highest methyl signals (assigned as C₁₅-methyls) were deshielded while, by the oxidation (Va→VII), one of the methyl groups (assigned as C₂₉-methyl) was shielded (Table II). Therefore we propose the structure, 12β-hydroxycarbomethoxyacetyl quercinic acid methyl ester (IVa) for the methyl ester of the new compound as a more preferable formulation. Lack of the material prevented further examination.

**Table III.** The GLC of the Methyl Esters of the Triterpene Acids

<table>
<thead>
<tr>
<th>Compound or origin</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IXa</td>
<td>15.6</td>
</tr>
<tr>
<td>VIIIa</td>
<td>15.5</td>
</tr>
<tr>
<td><em>Gloosphyllum abietinum</em></td>
<td>16.9</td>
</tr>
<tr>
<td><em>G. sepiarium</em></td>
<td>17.1</td>
</tr>
<tr>
<td><em>G. striatum</em></td>
<td>17.1</td>
</tr>
<tr>
<td><em>Lentinus lepidus</em></td>
<td>17.1</td>
</tr>
<tr>
<td><em>Velluticeps angularis</em></td>
<td>15.6</td>
</tr>
</tbody>
</table>

1.5% OV-1, column temp. 200°, N₂ flow 50 ml/min

The three species of *Gloosphyllum*, grown on conifers, afforded a mixture of triterpenes as the methyl esters, which were proved to be methyl eburiolate (VIIIa) and methyl trametenolate (IXa) by gas chromatography (GLC) (Table III, Fig. 1). Although taxonomically situated rather different, *Lentinus lepidus* (Tricholomataceae in Agaricales) grown on conifers, afforded the same mixture. In this occasion further identification was carried out by gas chromatograph—mass spectrometry (GC-MS) (Fig. 1). Namely, trimethylsilyl ethers of the mixture from *L. lepidus* showed two peaks in GLC and each component revealed the fragment peaks, *m/z* 542, 527, 437 and *m/z* 566, 541, 451, respectively, agreeing with M⁺, M⁺-CH₃, M⁺-CH₃-ROH of methyl trametenolate trimethylsilyl ether (IXc), C₃₀H₅₀O₃Si, and methyl eburiolate trimethylsilyl ether (VIIIc), C₃₀H₄₀O₃Si. The NMR spectrum of the triterpene mixture also supported the result. The signals at δ 5.03 and at δ 4.71, 4.63 were assigned as the C₁₅ vinylic proton of IXa and the C₂₅ vinylic protons of VIIIa respectively and the ratio of the intensities was about 1:2. The isolation of the same mixture was reported from *Gloosphyllum trabeum* (Lenzies trabeum, *Daedalea trabea*)¹¹,¹² and the separation as the methyl esters was reported to be practically

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hard. The fractional crystallization of methyl ester acetates of the mixture has been found to be effective for the separation. Recently the separation by the dihydro derivatives was reported.\textsuperscript{13)} As for the metabolites of \textit{Lentinus lepideus}, some phenolics were reported\textsuperscript{10,14)} and eburicoic acid (VIIIa) has been listed up,\textsuperscript{15)} but there has been no original report concerning about the triterpene constituents. The same result was also obtained from the fungus mycelia of the same species cultured in liquid media.

\textit{Spongiporus appendiculatus}, grown mostly on oak trees, produces annual, large fruit bodies, reddish yellow or orange, becoming paler with age. From the fungus methyl eburioate (VIIa) contaminated with methyl trametenolate (IXa) and methyl tumulosate (II) were isolated.

\textit{Veluticeps angularis} grows on cedar and cypress trees and forms perennial, woody and dark brown fruit bodies. Methyl trametenolate (IXa) was isolated from the fungus. In this case methyl eburioate (VIIa) was not accompanied.

Two general types of decay of woods by wood-rotting fungi are known; the white-rots and the brown-rots. All the nine species reported here for the presence of triterpenes belong to the brown-rotting fungi which attack cellulose and hemicellulose but leave lignin.

This point will be precisely discussed in a forthcoming paper.

**Experimental**

\textbf{Daedalea tanakae (Murr.) Aoshima}—Fruit bodies of the fungus (6 g), collected at Minakami, Gunma Prefecture, were air-dried, crushed and extracted with ether for one week at room temperature. The hexane insoluble part (0.10 g) of the etheral extract (0.12 g) was treated with CH$_2$N$_2$ and separated by preparative layer chromatography to afford methyl polylophanec C (I), mp 178–180° (MeOH), 4.45 mg. UV $\lambda_{	ext{max}}$ nm (log e): 237 (4.08), 244 (4.14), 252 (3.98). IR $\nu_{	ext{max}}$ cm$^{-1}$: 3420, 1735, 1687, 895. NMR (CDCl$_3$) $\delta$: 3.66 (3H, s), 4.08 (1H, m), 4.68 (1H, m), 4.72 (1H, m), 5.4 (2H, m). Identified with the authentic sample by TLC, GLC, IR, and NMR.

\textbf{Melanoporia rosea (Alb. et Schw. ex Fr.) Aoshima}—Fruit bodies of the fungus (15 g), collected at Sounkyo, Hokkaido, gave the etheral extract (6.27 g). The methylated products obtained by the same procedure were separated by preparative layer chromatography to afford the following compounds:

i) Methyl polylophanec C (I), mp 198–198.5° (MeOH), 250.8 mg. UV $\lambda_{	ext{max}}$ nm (log e): 236 (4.20), 244 (4.24), 252 (4.11). IR $\nu_{	ext{max}}$ cm$^{-1}$: 3420, 1735, 1710 (sh), 1685, 890. NMR (CDCl$_3$) $\delta$: 3.65 (3H, s), 4.10 (1H, m), 4.63 (1H, m), 4.70 (1H, m), 5.2 (1H, m), 5.35 (1H, m). Identified with the authentic sample by TLC, GLC, IR, and NMR.

ii) The mixture of methyl tumulosate (II) and methyl dehydrotumulosate (III), mp 135–137° (MeOH), 169.5 mg. UV $\lambda_{	ext{max}}$ nm (log e): 236 (3.91), 244 (3.92), 252 (3.73). (The ratio of II: III, 52: 48). IR $\nu_{	ext{max}}$ cm$^{-1}$: 3440, 1715, 1648, 890. NMR (CDCl$_3$) $\delta$: 3.66 (3H, s), 3.22 (1H, m), 4.06 (1H, m), 4.65 (1H, m), 5.4 (2H, m). Identified with the authentic sample by TLC, GLC, IR, and NMR.

iii) 12β-Hydroxyxarboxyamethoxyacetquericinic acid methyl ester (IVA), mp 116–117° (MeOH), 72.7 mg, $\varepsilon_{589}^B +4.66$° (CHCl$_3$, $c = 0.97$). IR $\nu_{	ext{max}}$ cm$^{-1}$: 3420, 1750, 1735, 1708, 1700. Mass Spectrum $m/e$: 416.409 (calcd, for C$_{35}$H$_{48}$O$_4$: 416.398), 598 (M$^+$-H$_2$O), 583 (M$^+$-CH$_3$-H$_2$O), 498 (M$^+$-CH$_3$O), 483 (M$^+$-CH$_2$-CH$_2$O), 865 (M$^+$-CH$_3$-H$_2$O-C$_2$H$_4$O), 325 (M$^+$-CH$_3$-H$_2$O-C$_4$H$_4$O), 307 (M$^+$-CH$_2$-H$_2$O-C$_2$H$_4$O). NMR (Table II).

IVA gave the acetate (IVB) by the conventional method, an oily substance, $\varepsilon_{589}^B -5.26$° (CHCl$_3$, $c = 0.76$). Mass Spectrum $m/e$: 658 (M$^+$, C$_{35}$H$_{50}$O$_4$), 643 (M$^+$-CH$_3$), 598 (M$^+$-C$_2$H$_4$O), 583 (M$^+$-CH$_2$-H$_2$O), 468 (M$^+$-C$_2$H$_4$O-C$_2$H$_4$O), 465 (M$^+$-CH$_3$-C$_2$H$_4$O), 440 (M$^+$-C$_2$H$_4$O-C$_2$H$_4$O), 307 (M$^+$-CH$_3$-H$_2$O-C$_2$H$_4$O). NMR (Table II). IVA (50.19 mg) was hydrolysed with boiling 5% KOH-MeOH (10 ml) for 1 hr. After working up usual and methylation with CH$_2$N$_2$, the reaction product was purified by preparative layer chromatography to give the diol (VA) as colorless powder (36.86 mg), mp 53–55° (MeOH), $\varepsilon_{589}^B +19.0$° (CHCl$_3$, $c = 1.0$). IR $\nu_{	ext{max}}$ cm$^{-1}$: 3480, 1740, 1720. $\nu_{	ext{max}}$ cm$^{-1}$: 1723, 1708. Mass Spectrum $m/e$: 516.379 (calcd, for C$_{36}$H$_{50}$O$_4$: 516.381), 498 (M$^+$-H$_2$O), 483 (M$^+$-CH$_2$=CH$_2$O), 325 (M$^+$-CH$_2$=CH$_2$O-C$_2$H$_4$O), 307 (M$^+$-CH$_2$=CH$_2$O-C$_2$H$_4$O). NMR (Table II). The diol (VA) (49.41 mg) was acetylated by Ac$_2$O-pyridine by the conventional method to give the diacetate (Vb) as colorless powder.
(43.70 mg), mp 56—57°C (MeOH). IR ν_{max} cm⁻¹: 1740, 1720, 1240. NMR (Table II). The diol (Va) (36.88 mg) in acetone (3 ml) was added with Jones' reagent (0.1 ml). After standing at room temperature for 10 min, the reaction products were extracted with ether, washed, and separated by preparative layer chromatography to give the ketone (VII), an oily substance (10.60 mg), IR ν_{max} cm⁻¹: 1725(sh), 1715(sh), 1705, 1700, NMR (Table II), and the minor product, an oily substance (1.4 mg), IR ν_{max} cm⁻¹: 1722(sh), 1715(sh), 1705, 1700.

**M. juniperina Aoshima**—Fruit bodies (15 g), collected at Kiso, Nagano Prefecture, gave the ethereal extract (0.1 g). The preparative layer chromatography of the methylated products give two compounds; methyl polypropenolate (I), 1.27 mg, IR ν_{max} cm⁻¹: 3440, 1735, 1687, 895, and methyl tenuolootane (II), 1.41 mg, UV λ_{max} nm (log ε): 243 (3.62), 252 (3.53) (contaminated with methyl dehydrotumelol (III) about 25%), IR ν_{max} cm⁻¹: 3440, 1735, 1645, 890. Identified with the authentic sample by TLC, GLC, and IR, respectively.

**Gloeophyllum spp.**—Fruit bodies of *Gloeophyllum abietinum* (Bull. ex Fr.) KARST. (14 g), collected at Yoga, Tokyo, *G. septarium* (Wulf. ex Fr.) KARST. (10 g), collected at the foot of Mt. Teshio, Hokkaido, and *G. striatum* (Swartz. ex Fr.) Murr. (7.2 g), collected at Marunuma, Gumma Prefecture, were used for the study. The ethereal extracts (0.27 g, 0.30 g, and 0.27 g, respectively) were treated with the same procedure as before and separated by preparative layer chromatography to give the mixture of methylated products (27.87 mg, 21.50 mg and 8.34 mg, which were shown to be the same mixture of methyl trametenol (IXa) and methyl eburoricate (VIIa) by GLC (Table III) and by comparison with IR and NMR. The ratio (VIIa: IXa) of the two compounds determined by gas chromatograms are 73: 27, 78: 22 and 77: 23 respectively.

**Lentinus lepideus Fr.**—Fruit bodies (78 g), collected at Aobayama, Sendai, gave the ethereal extract (1.0 g). The hexane insoluble part (0.95 g), methylated with CH₃₂N₂, was separated by preparative layer chromatography to give a mixture of methyl trametenolate (IXa) and methyl eburoricate (VIIa) (147.0 mg). According to GLC, the mixed ratio (IXa: VIIa) is 41: 59. The identification was carried out by GC-MS (Table III, Fig. 1). NMR (CDCl₃) δ: 3.22 (1H, m), 3.62 (3H, s), 4.63, 4.71 (each 1H, m), 5.03 (1/2H, m).

**Spongiporus appendiculatus** (Berk. et Br.) Aoshima—Fruit bodies (32.5 g), collected at Nayoro, Hokkaido, gave the ethereal extract (0.32 g). The hexane insoluble part (0.21 g), methylated with CH₃₂N₂, was chromatographed on a column of alumina (Woelm, neutral, 200 g) and eluted successively with benzene, 2% ether-benzene, ether and MeOH. The 2% ether-benzene fraction was further separated by preparative layer chromatography into two components. i) Methyl eburoricate (VIIa), mp 110—113° (MeOH), 8.33 mg, IR ν_{max} cm⁻¹: 3440, 1735, 1645, 890. Identified with the authentic sample by TLC, GLC, and IR. The mother liquor showed the presence of methyl trametenol (IXa) by GLC. ii) Methyl tenuolootane (II), mp 138—140° (MeOH), 11.49 mg, UV λ_{max} nm (log ε): 237 (3.77), 244 (3.83), 252 (3.67). IR ν_{max} cm⁻¹: 3440, 1735, 1645, 890.

**Veluticeps angularis** (Lloyd) Aoshima et Furukawa—Fruit bodies (20 g), collected at Kiso, Nagano Prefecture, gave the ethereal extract (2.03 g). The hexane insoluble part (2.38 g), methylated with CH₃₂N₂, was separated by column chromatography of alumina (Woelm, neutral, 100 g) and eluted successively benzene, 2% ether-benzene, 5% ether-benzene, ether and MeOH. The 2% ether-benzene fraction was further purified by preparative layer chromatography. Methyl trametenololate (IXa), mp 132—135° (MeOH), 110.1 mg, IR ν_{max} cm⁻¹: 3860, 1735. NMR (CDCl₃) δ: 1.57 (3H, m), 1.66 (3H, m), 3.62 (3H, s), 3.20 (1H, m), 5.05 (1H, m). Identified with the authentic sample by TLC, GLC, IR, and NMR. The acetate (IXb), colorless needles of mp 140—142° (MeOH), IR ν_{max} cm⁻¹: 1738, 1245, NMR (CDCl₃) δ: 2.03 (3H, s), 4.50 (1H, m), was identified with methyl acetyltrametenolate (IXb) (mixed mp, TLC, GLC, and IR).

**The Culture of Lentinus lepideus Fr.**—The fungus culture was grown in potato-dextrose medium in Roux bottles for 45 days. The dried mycelium (29.5 g) was extracted successively with hexane and ether. The ethereal extract (1.25 g) treated with CH₃₂N₂ was separated by preparative layer chromatography to give the same mixture as the fruit bodies. The fraction was acetylated by Ac₂O-pyridine to give colorless needles of mp 120—130° showing 2 peaks by GLC. Fractional crystallization from MeOH afforded colorless needles, mp 152—153°, IR ν_{max} cm⁻¹: 1730, 1245, 890. NMR (CDCl₃) δ: 2.05 (2H, s), 4.05 (1H, m), 4.75, 4.67 (each 1H, m), which was identified with methyl acetylpyridurate (VIIIb) by the ordinary methods. By the further fractional crystallization by GLC, another colorless needles, mp 145—147° (MeOH), was obtained from the mother liquor. IR ν_{max} cm⁻¹: 1730, 1245. NMR (CDCl₃) δ: 1.60 (3H, m), 1.70 (3H, m), 2.05 (3H, s), 4.52 (1H, m), 5.12 (1H, m). Identified with methyl acetyltrametenolate (IXb) by the ordinary methods.

**Thin-Layer Chromatography**—For thin-layer chromatography Silicagel H or HF₆₃₄ were used. Hexane—AcOEt (7: 3) and CHCl₃—MeOH (9: 1) were employed for the solvent and the detection was carried out by heating on a hot plate after spraying 20% vanillin-phosphoric acid.

17) Identified and provided by Dr. K. Aoshima, Government Forest Experiment Station.
Gas Chromatography—Gas chromatography was carried out on 1.5% OV-1 on Shimapite W and 1.5% QF-1 on Chromosorb W on a Hitachi F6-D Gas Chromatograph.

Acknowledgement. The authors thank Prof. T. Takemoto, Tohoku University and Dr. K. Aoshima, Government Forest Experiment Station, for showing interest to this work and the supply of the specimens of fungi. The author indebted to Prof. H. Inouye and Dr. K. Tokura, Kyoto University, and Dr. W. Lawrie, The University of Strathclyde, for the donation of the authentic samples, to Prof. M. Tomoeda, Kanazawa University, Prof. H. Agata, Showa College of Pharmaceutical Sciences, and Prof. N. Ikegawa, Tokyo Institute of Technology, for their help in spectral determinations, and to the members of Laboratory of Mycology, this Institute, for their help in culture of the fungus mycelia.