Studies on the Glycosides of *Epimedium grandiflorum* MORR. var. *thunbergianum* (MIQ.) NAKAI. I

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A new phenolic glycoside, icariside A1 (IV), and six new terpenic glycosides, icariside B1 (V), B2 (VI), C1 (VII), C2 (VIII), C3 (IX), and C4 (X), have been isolated from *Epimedium grandiflorum* MORR. var. *thunbergianum* (MIQ.) NAKAI, together with three known glycosides, salidroside (I), thalictoside (II) and benzyl glucoside (III). The structures of IV—X were established on the basis of chemical evidence and spectral data.

Keywords—*Epimedium grandiflorum* var. *thunbergianum*; 9,10-dihydrophenanthrenol glycoside; ionone derivative; sesquiterpene glycoside; icariside A; icariside B; icariside C

The aerial parts of *Epimedium grandiflorum* MORR. var. *thunbergianum* (MIQ.) NAKAI have been used since ancient times as a tonic in China and Japan. The constituents of this plant were investigated by Takemoto et al. (flavonoids and lignans)1) and Tomita and Ishii (alkaloid).2)

Our interest has been directed to the reinvestigation of the constituents of the aerial parts, with the aim of isolating some biologically active substances.3) In this paper, we wish to describe the isolation of seven new glycosides, icariside A1 (IV), B1 (V), B2 (VI), C1 (VII), C2 (VIII), C3 (IX), and C4 (X), along with three known glycosides, salidroside (I), thalictoside (II), and benzyl glucoside (III). The structures of these compounds were determined on the basis of chemical evidence and spectroscopic studies.

Salidroside (I) was identified by direct comparison [thin layer chromatography, infrared (IR), proton nuclear magnetic resonance (1H-NMR), and carbon-13 nuclear magnetic resonance (13C-NMR) spectra] with an authentic sample.4)

Thalictoside (II), C14H19NO8, mp 138—139 ºC was identified by comparison of various data (mp, IR, 1H-NMR) with reported values.5)

Benzyl glucoside (III), C13H18O6·1/4H2O, [α]D−59.2 º, was obtained as colorless needles, mp 123—124 ºC. The 1H-NMR spectrum exhibited AB-type signals due to a benzylic methylene at δ 4.85 (1H, J= 12 Hz) and 5.17 (1H, J= 12 Hz), a doublet signal due to an anomic proton at δ 5.75 (1H, J= 7 Hz) and multiplet signals due to aromatic protons at δ 7.25—7.65 (5H). These data led us to conclude the structure of this compound to be III, previously synthesized by Bonner et al. (lit. mp 121 ºC).6) This is the first isolation of III from this plant.

Icariside A1 (IV), C24H30O10, [α]D−22.9 º, was obtained as colorless needles, mp 220—222 ºC. The ultraviolet (UV) spectrum showed absorption maxima at 280 (4.27), 302 (4.17) and 312 (4.19) nm (log ε). The 1H-NMR spectrum exhibited a broad singlet signal due to benzylic methylene protons at δ 2.68 (4H), four singlet signals due to methoxyl protons at δ 3.84, 3.87, 3.91 and 4.11 (each 3H), a doublet signal due to an anomic proton at δ 5.75
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(1H, J = 7 Hz) and three singlet signals due to aromatic protons at \( \delta 6.92, 7.43 \) and \( 8.31 \) (each 1H). From these data, IV was assumed to be a 9,10-dihydrophenanthrene derivative having four methoxyl groups and a glucosyl residue.\(^7\) The \(^{13}\)C-NMR spectrum exhibited four methoxyl carbon signals at \( \delta 56.1, 56.5, 60.8 \) and \( 61.5 \), the latter two signals might be due to ortho-disubstituted methoxyl groups because of the downfield shifts.\(^8\) Acid hydrolysis afforded glucose as the sugar moiety and enzymatic hydrolysis afforded an aglycone IVa. Acetylation of IVa afforded a monoacetate IVb and methylation of IVa afforded a methyl ether IVc. In the \(^1\)H-NMR spectrum of IVa, two aromatic proton signals (\( \delta 6.66 \) and \( 6.76 \)) were long-range-coupled with a benzylic methylene proton signal at \( \delta 2.71 \) (4H, br s) and another one was deshielded at \( \delta 7.97 \).\(^7\) Nuclear Overhauser effects (NOE) were observed at the proton signals at \( \delta 6.76 \) (21%) and \( 7.97 \) (24%) on irradiation at the methoxyl signals. From these data, IVa was assumed to be 7-hydroxy-2,3,4,6-tetramethoxy-9,10-dihydrophenanthrene, previously isolated from *Combretum psidoides*.\(^9\) The identities of IVa, IVb and IVc were established by comparison of the physical and spectral data (mp, UV, \(^1\)H-NMR) with reported data. Therefore, the structure of icariside A\(_1\) was concluded to be IV.

Icariside B\(_1\) (V), C\(_{19}\)H\(_{20}\)O\(_8\) 1/2H\(_2\)O, \([\alpha]_D -73.5\)°, was obtained as an amorphous powder. The UV spectrum showed an absorption maximum at 232 (4.16) nm (log \( \varepsilon \)) and the IR spectrum showed the presence of hydroxyl groups (3450 cm\(^{-1}\)), an allenic structure (1945 cm\(^{-1}\)) and a conjugated ketone group (1670 cm\(^{-1}\)). The \(^1\)H-NMR spectrum exhibited four singlet methyl signals at \( \delta 1.09 \) (3H), \( 1.51 \) (6H), \( 2.21 \) (3H), the last one being due to a methyl ketone, a carbinol proton signal at \( \delta 4.95 \) (1H, m), an anomeric proton signal at \( \delta 5.12 \) (1H, d, \( J = 7 \) Hz) and an olefinic proton signal at \( \delta 5.92 \) (1H, s). Acid hydrolysis afforded glucose as the sugar moiety and enzymatic hydrolysis afforded an aglycone Va. In the \(^1\)H-NMR spectrum, a carbinol proton signal was observed at \( \delta 4.32 \) (m, \( W_{1/2} = 17.5 \) Hz). From these data, Va was assumed to be grasshopper ketone, previously isolated from *Romalea microptera*.\(^10\) The identity of Va was established by comparison of the physical and spectral data (mp, UV, IR, \(^1\)H-NMR) with reported data. In the \(^{13}\)C-NMR spectrum of Va, two carbinol carbon signals were observed at \( \delta 63.8 \) (d) and \( 72.3 \) (s). The former was shifted downfield by 8.2 ppm in the \(^{13}\)C-NMR spectrum of V, but the latter was shifted downfield by only 1.0 ppm. Therefore, the glucosidation position was decided to be at C-3. These results led us to conclude the structure of icariside B\(_1\) to be V.

Icariside B\(_2\) (VI), C\(_{19}\)H\(_{30}\)O\(_8\) 1/2H\(_2\)O, \([\alpha]_D -102.1\)°, was obtained as colorless needles, mp 172.5—174.0 °C. The UV spectrum showed an absorption maximum at 230 (4.06) nm (log \( \varepsilon \))

![Chart 1](https://example.com/chart1.png)

\( \text{I: } R = \text{Glc} \)
\( \text{II: } R = \text{Glc} \)
\( \text{IIa: } R = \text{Glc(OAc)}_4 \)
\( \text{III: } R = \text{Glc} \)
\( \text{IV: } R = \text{Glc} \)
\( \text{IVa: } R = \text{H} \)
\( \text{IVb: } R = \text{Ac} \)
\( \text{IVc: } R = \text{Me} \)
\( \text{V: } R = \text{Glc} \)
\( \text{Va: } R = \text{H} \)
\( \text{VI: } R = \text{Glc} \)
\( \text{VIa: } R = \text{H} \)
\( \text{VIb: } R = \text{Ac} \)
and the IR spectrum showed the presence of hydroxyl groups (3500, 3400 cm⁻¹) and a conjugated ketone group (1685 cm⁻¹). The ¹H-NMR spectrum exhibited four singlet methyl signals at δ 0.96 (3H), 1.13 (6H), 2.29 (3H), the last one being due to a methyl ketone, an anomic proton signal at δ 4.95 (1H, d, J=7.7 Hz) and a pair of trans olefinic proton signals at δ 6.51 (1H, d, J=15 Hz) and 7.21 (1H, d, J=15 Hz). In the ¹³C-NMR spectrum, three oxygen-bearing carbon signals were observed at δ 71.5 (d), and the former two signals were assigned to epoxy carbons. Acid hydrolysis afforded glucose as the sugar moiety and enzymatic hydrolysis afforded an aglycone VIIa, which was acetylated immediately, to give an acetate VIIb. The ¹H-NMR spectrum of VIIb exhibited an acetyl methyl signal at δ 1.97 (3H, s) and a carbinol proton signal at δ 4.84 (1H, m, W₁/₂=18 Hz) suggesting that VIIb has an equatorial acetoxyl group. From these data, VIIb was assumed to be 3α-acetoxy-5α,6α-epoxy-β-ionone, previously synthesized from a constituent of Nicotiana tabacum L.¹¹) The identity of VIIb was established by comparison of the physical and spectral data [mp, [α]D, UV, IR, ¹H-NMR, circular dichroism (CD)] with reported data. These results led us to conclude the structure of icariside B₂ to be VI.

Icariside C₁ (VII), C₂₁H₃₈O₈, [α]D = -22.5°, was obtained as an amorphous powder. The IR spectrum showed the presence of hydroxyl groups (3450 cm⁻¹) and double bonds (1645 cm⁻¹). The ¹H-NMR spectrum exhibited three singlet methyl signals at δ 1.36, 1.46, 1.49, a vinyl methyl signal at δ 1.66 (brs), an anomic proton signal at δ 5.16 (1H, d, J=8 Hz), an olefinic proton signal at δ 5.51 (1H, brt, J=7 Hz) and three olefinic proton signals at δ 5.16 (1H, dd, J=11, 2 Hz), 5.52 (1H, dd, J=18, 2 Hz), 6.17 (1H, dd, J=18, 11 Hz)
which were due to a vinyl group. In the $^{13}$C-NMR spectrum, twenty-one carbon signals were observed, including six signals due to a glucopyranosyl moiety. Acid hydrolysis afforded glucose as the sugar moiety and enzymatic hydrolysis afforded an aglycone VIIa, colorless oil, $\{\alpha\} D = -13.4^\circ$. The $^1$H-NMR spectrum of VIIa exhibited a carbinol proton signal at $\delta 3.76$ (1H, dd, $J = 10, 2$ Hz), while the $^{13}$C-NMR spectrum of VIIa exhibited fifteen carbon signals including three carbinol carbon signals at $\delta 72.4$ (s), 72.7 (s), 78.5 (d). From a comparison of these spectral data with those of nerolidol, VIIa was assumed to be 3,7,11-trimethyl-1,6-dodecadien-3,10,11-triol. The identity of VIIa was established by chemical synthesis of XIII from (+)-nerolidol (XI). Compound XIII was obviously a mixture of $10S$ and $10R$ from the synthetic process, but the two isomers were not distinguishable in the $^1$H- and $^{13}$C-NMR spectra. Thus, in order to decide the stereochemistry at C-10, the Cotton effect of the $\alpha$-glycol in the presence of a shift reagent Eu(fod)$_3$ was examined. The CD spectrum of VIIa showed a positive Cotton effect, $[\theta]_{305} + 41322$, and a negative Cotton effect, $[\theta]_{285} - 27716$, suggesting C-10 to be $S$. In the $^{13}$C-NMR spectrum of VIIa, three carbinol carbon signals were observed at $\delta 72.4$ (s), 72.7 (s), 78.5 (d). The last one was shifted downfield at $\delta 90.7$ (d) in the $^{13}$C-NMR spectrum of VII, so the glucosidation position was decided to be C-10. These results led us to conclude the structure of icariside C$_1$ to be VII.

Icariside C$_2$ (VIII), C$_{21}$H$_{38}$O$_8$$\cdot\frac{1}{2}$H$_2$O, $[\alpha] D = -19.3^\circ$, was obtained as an amorphous powder. The IR and $^1$H-NMR spectra were very similar to those of VII. Acid hydrolysis afforded glucose as the sugar moiety and enzymatic hydrolysis afforded an aglycone VIIa. On comparison of the $^{13}$C-NMR spectra of VIII and VIIa, the signal of C-10 (delta 76.9) of VIII was shifted upfield by 1.6 ppm and that of C-11 (delta 80.9) was shifted downfield by 8.2 ppm. Therefore, the structure of icariside C$_2$ was concluded to be VIII, with a glucosyl residue at C-11.

Icariside C$_3$ (IX), C$_{21}$H$_{38}$O$_8$$\cdot\frac{1}{2}$H$_2$O, $[\alpha] D = -34.7^\circ$, was obtained as an amorphous powder.
## Table III. \(^1\)H-NMR Chemical Shifts and Coupling Constants

<table>
<thead>
<tr>
<th>Proton No.</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>5.52 (1H, dd, J = 18, 2 Hz)</td>
<td>5.54 (1H, dd, J = 17, 2 Hz)</td>
<td>5.39 (1H, dd, J = 18, 1.5 Hz)</td>
<td>5.58 (1H, dd, J = 17, 2 Hz)</td>
</tr>
<tr>
<td>lb</td>
<td>5.16 (1H, dd, J = 11, 2 Hz)</td>
<td>5.17 (1H, dd, J = 10, 2 Hz)</td>
<td>5.23 (1H, dd, J = 11, 1.5 Hz)</td>
<td>5.18 (1H, dd, J = 10, 2 Hz)</td>
</tr>
<tr>
<td>2</td>
<td>6.17 (1H, dd, J = 18, 11 Hz)</td>
<td>6.17 (1H, dd, J = 17, 10 Hz)</td>
<td>6.28 (1H, dd, J = 18, 11 Hz)</td>
<td>6.18 (1H, dd, J = 17, 10 Hz)</td>
</tr>
<tr>
<td>6</td>
<td>5.51 (1H, br t, J = 7 Hz)</td>
<td>a)</td>
<td>a)</td>
<td>a)</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>1.36 (3H, s)</td>
<td>1.49 (6H, s)</td>
<td>1.48 (3H, s)</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.46 (3H, s)</td>
<td>1.51 (3H, s)</td>
<td>1.52 (3H, s)</td>
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<tr>
<td></td>
<td>15</td>
<td>1.49 (3H, s)</td>
<td>1.58 (3H, s)</td>
<td>1.48 (3H, s)</td>
</tr>
<tr>
<td>14</td>
<td>1.66 (3H, br s)</td>
<td>1.67 (3H, br s)</td>
<td>1.65 (3H, br s)</td>
<td>1.67 (3H, br s)</td>
</tr>
<tr>
<td>Anomeric</td>
<td>5.16 (1H, d, J = 8 Hz)</td>
<td>5.23 (1H, d, J = 7 Hz)</td>
<td>4.95 (1H, d, J = 8 Hz)</td>
<td>5.01 (1H, d, J = 8 Hz)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proton No.</th>
<th>VIIa</th>
<th>XIII</th>
<th>Xa</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>5.56 (1H, dd, J = 18, 2 Hz)</td>
<td>5.53 (1H, dd, J = 17, 2 Hz)</td>
<td>5.56 (1H, dd, J = 17, 2 Hz)</td>
</tr>
<tr>
<td>lb</td>
<td>5.17 (1H, dd, J = 11, 2 Hz)</td>
<td>5.16 (1H, dd, J = 11, 2 Hz)</td>
<td>a)</td>
</tr>
<tr>
<td>2</td>
<td>6.17 (1H, dd, J = 18, 11 Hz)</td>
<td>6.17 (1H, dd, J = 17, 11 Hz)</td>
<td>6.17 (1H, dd, J = 17, 11 Hz)</td>
</tr>
<tr>
<td>6</td>
<td>5.45 (1H, br t, J = 7 Hz)</td>
<td>5.43 (1H, br t, J = 7 Hz)</td>
<td>a)</td>
</tr>
<tr>
<td>10</td>
<td>3.76 (1H, dd, J = 10, 2 Hz)</td>
<td>3.74 (1H, dd, J = 10, 2 Hz)</td>
<td>3.77 (1H, dd, J = 10, 2 Hz)</td>
</tr>
<tr>
<td>12</td>
<td>1.48 (3H, s)</td>
<td>1.48 (6H, s)</td>
<td>1.49 (3H, s)</td>
</tr>
<tr>
<td>13</td>
<td>1.49 (3H, s)</td>
<td>1.51 (3H, s)</td>
<td>1.50 (3H, s)</td>
</tr>
<tr>
<td>15</td>
<td>1.53 (3H, s)</td>
<td>1.54 (3H, s)</td>
<td>1.54 (3H, s)</td>
</tr>
<tr>
<td>14</td>
<td>1.71 (3H, br s)</td>
<td>1.69 (3H, br s)</td>
<td>1.70 (3H, br s)</td>
</tr>
</tbody>
</table>

Run at 89.55 MHz in pyridine-\(d_5\) solution. a) Overlapped with H\(_2\)O.
The IR and $^1$H-NMR spectra were similar to those of VII and VIII. Acid hydrolysis afforded glucose as the sugar moiety and enzymatic hydrolysis afforded an aglycone VIIa. In the $^{13}$C-NMR spectrum of IX, the signal of C-3 ($\delta$ 80.1) was shifted downfield by 7.7 ppm, while those of C-2 ($\delta$ 144.6), C-4 ($\delta$ 42.3) and C-13 ($\delta$ 23.6) were shifted upfield by 2.6, 1.1 and 4.9 ppm, respectively, compared with those of VIIa. Therefore, the structure of icariside C$_3$ was concluded to be IX, with a glucosyl residue at C-3.

Icariside C$_4$ (X), C$_{21}$H$_{38}$O$_8$·1/2H$_2$O, $[\alpha]_D^0$ +3.4°, was obtained as an amorphous powder. The $^1$H- and $^{13}$C-NMR spectra were very similar to those of VII, though C-11 and C-12 showed small differences in the chemical shifts. Therefore, X was assumed to be an epimer of VII at C-10. The aglycone Xa obtained by enzymatic hydrolysis of X gave the same IR and $^{1}$H-NMR spectra as a synthetic product, XIII. The CD spectrum of Xa in the presence of Eu(fod)$_3$ showed a negative Cotton effect, $[\text{I}]_{305}$ -32768, and a positive one, $[\text{I}]_{284}$ +20480, opposite to those in the case of VIIa. Thus, the stereochemistry at C-10 was decided to be R and the structure of icariside C$_4$ to be X.

This is the first report of the isolation of a dihydrophenanthrene derivative and terpenic glycosides from Epimedium species. Studies on the structures of other minor glycosides (polar) are in progress.

**Experimental**

Melting points were taken on a Yanaco MP-500 micromelting point apparatus and are uncorrected. Optical rotations were determined with a JASCO DIP-140 digital polarimeter. IR spectra were run on a JASCO A-202 IR spectrometer and UV spectra on a Shimadzu UV-360 recording spectrometer. Mass spectra (MS) were measured on a JEOL JMS-100 mass spectrometer. CD spectra were recorded on a JASCO J-20A spectropolarimeter. $^1$H- and $^{13}$C-NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer (89.55 and 22.5 MHz, respectively).
shifts are given on the δ scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad). Gas chromatography (GC) was done on a Hitachi K53 gas chromatograph. High-performance liquid chromatography (HPLC) was done on a Kyowa Seimitsu model K880 instrument.

**Isolation**——Aerial parts of *E. grandiflorum* MRR. var. *thunbergianum* (MIQ.) NAKAI (15 kg), collected in summer 1985, in Niigata prefecture, Japan, were extracted twice with hot water. The extract was absorbed on Amberlite XAD-2 and the resin was eluted with methanol after being washed with water. After repeated chromatography of the methanol eluate (420 g) on silica gel with a chloroform–methanol system and HPLC (column; Develosil ODS-10, 20 × 250 mm) with a water–acetonitrile system, ten glycosides were isolated.

**Enzymatic Hydrolysis of Icariside A1 (IV)**—A solution of icariside A1 (IV, 13 mg) in water (2 ml) was treated with β-glucosidase (50 mg) at 37°C for a day. The reaction mixture was diluted with water and extracted with ethyl acetate 3 times. Ethyl acetate was evaporated off and the residue was recrystallized from methanol to give colorless with β-glucosidase (50 mg) at 37°C for a day. The reaction mixture was diluted with water and extracted with ethyl acetate 3 times. Ethyl acetate was evaporated off and the residue was recrystallized from methanol to give colorless

**Acetylation of Thalictoside (II)**—Thalictoside (II) (10 mg) was dissolved in pyridine and acetic anhydride (each 3 ml), and the reaction mixture was left at room temperature. The reagents were evaporated off in vacuo and the residue was recrystallized from methanol to give colorless.
Acetylation of VIa—A solution of IVa (5 mg) was acetylated in the usual way as described for II. A monoacetate IVb (6 mg) was obtained.

Methylation of VIa—A mixture of IVa (5 mg), dimethyl sulfate (0.2 ml) and anhydrous potassium carbonate (100 mg) in dry acetone (2 ml) was refluxed for 3h with stirring. After removal of the precipitate by filtration, the filtrate was concentrated to give a syrup, which was chromatographed on a thin layer plate (Kiesel gel GF254; benzene:isopropanol, 100:1) to yield a methyl ether (IVc, 3 mg) as colorless needles (methanol), mp 108-109°C.

Enzymatic Hydrolysis of Icariside B, (V) — A solution of icariside B, (V, 27 mg) in water (2 ml) was treated with cellulase (30 mg) at 37°C overnight. The reaction mixture was worked up in the same way as described for IV to give an aglycone (Va, Vm 5 mg) as an amorphous powder. This was acetylated in the usual way with pyridine and acetic anhydride (each 1 drop) at room temperature overnight. The reagents were evaporated off in vacuo.

Acetylation of VIa—A solution of IVa (5 mg) was acetylated in the usual way as described for II. A monoacetate IVb (6 mg) was obtained.

Methylation of VIa—A mixture of IVa (5 mg), dimethyl sulfate (0.2 ml) and anhydrous potassium carbonate (100 mg) in dry acetone (2 ml) was refluxed for 3h with stirring. After removal of the precipitate by filtration, the filtrate was concentrated to give a syrup, which was chromatographed on a thin layer plate (Kiesel gel GF254; benzene:isopropanol, 100:1) to yield a methyl ether (IVc, 3 mg) as colorless needles (methanol), mp 108-109°C.

Acetylation of VIa—A solution of IVa (5 mg) was acetylated in the usual way as described for II. A monoacetate IVb (6 mg) was obtained.
Synthesis of 3,7,11-Trimethyl-1,6-dodecadien-3,10,11-triol (XIII)—m-Chloroperbenzoic acid (2.5 g) was added to a stirred solution of (+)-nerolidol (XI, 2.8 g) in dichloromethane (25 ml) and saturated aqueous sodium hydrogen carbonate (25 ml). The mixture was stirred for 17 h at room temperature, then the dichloromethane layer was washed with saturated aqueous sodium chloride and dried over sodium sulfate. Removal of the solvent afforded a crude product, which was chromatographed on silica gel using benzene-acetone (9:1) as the eluent to give 10,11-epoxynerolidol (XII, 2.6 g) as a colorless oil. A solution of XII (850 mg) in 0.1 M sulfuric acid (33 ml) and tetrahydrofuran (33 ml) was stirred for 5.5 h at room temperature. The reaction mixture was diluted with water and passed through an Amberlite XAD-2 column. After washing of the column with water, the methanol eluate was purified by HPLC (Develosil ODS-10, 20 x 250 mm; H₂O–CH₃CN (70:30)) to give 3,7,11-trimethyl-1,6-dodecadien-3,10,11-triol (XIII, 150 mg) as a colorless oil. Anal. Calcd for C₁₅H₂₈O₃: C, 70.27; H, 11.01. Found: C, 70.24; H, 11.03. IR νKBr cm⁻¹: 3450, 1610, 1460, 1380, 1165, 1080, 1000, 930. ¹H- and ¹³C-NMR: Tables III and IV.

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