A New Synthetic Method of Methyl Ketones

Part III.* Syntheses of cis- and trans-Jasmone

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A simple and stereospecific method has been developed for the synthesis of cis-jasmone. 3-Methyl-2-cyclopentenone (V) was condensed with cis-2-pentenyl chloride, which was prepared from propargyl alcohol, by means of sodium amide in liquid ammonia to yield stereoelectronically pure cis-jasmone (VIb) in 39-40% yield. By the similar direct alkylation, trans-jasmone (VIc) and dihydrojasmone (VIA) were also synthesized in moderate yields.

cis-Jasmone was isolated in 1899 from the essential oil of Jasminum grandiflorum L (jasmine oil) by Hesse, and its structure was determined in 1933 by Treff and Werner, and by Ruzicka and Pfeiffer, independently. It was also isolated from the essential oil of Citrus bigaradia Risso (orange flower oil), Mentha piperita L (peppermint oil) and Citrus bergamia Risso (bergamot oil). Its presence has also been reported in the oil of American spearmint and in jonquil absolute. cis-Jasmone, although present in small amount, is believed to be a characteristic, powerful and exceedingly important odoriferous constituent of these essential oils.

Since cis-jasmone was first synthesized from cis-β,γ-hexenol by Treff and Werner in 1935, various methods have been described.

Hunsdiecker, Crombie and Harper, and Harper and Smith have effected another synthesis of cis-jasmone from cis-β,γ-hexenol through γ-lactone or γ-diketone. Recently, Stork and Borch have devised a new synthetic method of γ-diketone, in which 5-oxoacetylene compound was hydrated with aqueous methanolic sulfuric acid in the presence of mercuric sulfate. Moreover, by the application of this method the syntheses of cis-jasmone and dihydrojasmone were also achieved. Sisido and co-workers have also reported the synthesis of trans-jasmone via substituted paraconic acid. All these syntheses of cis-jasmone involved the cyclization of suitably constituted γ-diketone of γ-lactone. Therefore, it was necessary to prepare these compounds without effecting the cis-double bond, but these syntheses have resulted generally in the production of mixture of isomers. Moreover, they require many stages and the final yield is ultimately low. Therefore, our purpose was to find a perfectly stereospecific synthesis of cis-jasmone via simpler procedure.

* Part II. M. Matsui and T. Yoshida, This Journal, 28, 105 (1964). The paper was presented at the 8th Annual Meeting of Chemistry of Perfume, Terpene and Essential Oil in Japan in Tohoku University at Sendai (1964).

1) A. Hesse, Ber., 32, 2617 (1899).
2) W. Treff und H. Werner, ibid., 66, 1521 (1933).
3) L. Ruzicka and M. Pfeiffer, Helv. chim. acta, 16, 208 (1933).
8) F. Ehre, Riechstoffindustrie, 19, 30, 181 (1929).
9) W. Treff und H. Werner, Ber., 68, 640 (1935).

10) H. Hunsdiecker, Ber., 75, 447, 455, 460 (1942).
One of the authors reported in the previous paper\textsuperscript{15} that many alkyl or alkenyl halides condense with mesityl oxide (I) at \( \alpha \)-methine group in liquid ammonia in the presence of sodium amide to afford \( \alpha \)-alkyl or \( \alpha \)-alkenyl mesityl oxides, (II) and (III), which are the useful intermediates of methyl ketones (IV).

\[
\begin{align*}
\text{(I)} & \quad \text{RX, NaNH}_2 \text{ in} \quad \text{liq. NH}_3 \quad \text{(II)} \quad \text{H}^+ \quad \text{CH}_3\text{COOH} \quad \text{(III)} \quad \text{R} \quad \text{O} \quad \text{(IV)}
\end{align*}
\]

Although attempts by Conia\textsuperscript{16} to obtain \( \beta \)-jasmine directly from 3-methyl-2-cyclopentenone and pentenyl bromide with sodium tert-amylate in tert-amyl alcohol have proved unsuccessful, alkylation of 3-methyl-2-cyclopentenone (V), alicyclic \( \alpha,\beta \)-unsaturated methyl etone, was accomplished by means of sodium amide in liquid ammonia in the present investigation.

In order to investigate the reaction, V was first directly condensed with \( n \)-amyl bromide under the conditions mentioned above. The product obtained in 37\textendash 38\% yield was identical with dihydrojasmine (VIa, 2-\( n \)-amyl-3-methyl-2-cyclopentenone) by physical properties as shown in Table I, formation of its semicarbazone and 2,4-dinitrophenylhydrazone,

\begin{table}[h]
\centering
\caption{Physical Properties and Derivatives of Jasmones}
\begin{tabular}{|l|c|c|c|c|c|c|c|}
\hline
& b.p. (°C/mm) & \( \delta^\text{D} \) & \( \rho^\text{20} \) & \( \lambda^\text{max} \text{at} \text{nm} \) & m.p. of 2,4-D.N.P. & m.p. of SEMI, \( \text{SEMII.} \) \textsuperscript{**} \\
& (°C/mm) & (g/cm\textsuperscript{3}) & (g/cm\textsuperscript{3}) & (\text{m/1}) & (°C) & (°C) \\
\hline
Dihydrojasmine (VIa) & 72.5 ~ 73.5/0.6 & 1.4795 & 0.9147 & 235(14,100) & 122 ~ 123 & 174 ~ 175 \\
\textit{cis}-Jasmine (VIIb) & 73 ~ 79 & 0.5 & 1.4991 & 0.9391 & 233(13,200) & 129 ~ 130 & 205 ~ 206.5 \\
\textit{trans}-Jasmine (VIIIc) & 83 ~ 84 & 0.8 & 1.4979 & 0.9349 & 233(13,600) & 133.5 ~ 136.5 & 200 ~ 201.5 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{*} 2,4-D.N.P.=2,4-dinitrophenylhydrazone, \textsuperscript{**} SEMI.=semicarbazone

![IR Spectrum of Synthetic Dihydrojasmine (VIIb) (Film)](image-url)

\textsuperscript{15} M. Matsui, T. Yoshida and H. Mori. This Journal, 28, 105 (1964).

carbazone, m.p. 174–175°C. These dates completely agreed with the reported ones.

In alkylation of V with n-amyl bromide alkyl group entered in the 2-position to give the desired product (VI), and the major part of by-product was not unconjugated product (VII), but dialkylation product (VIII). Consequently, direct alkylation of V with cis-(XIV) or trans-2-pentenyl chloride (XVI) under similar conditions was considered to give cis-(VIb) or trans-jasmone (Vlc) in moderate yield.

Both cis- and trans-2-pentenyl chlorides were prepared from propargyl alcohol (IX) in 54% yield based upon (IX) by the scheme below. IX was converted into tetrahydropyranyl ether (X) in the presence of phosphorus oxychloride in 86.2% yield. X was treated in liquid ammonia with ethyl bromide in the presence of sodium amide to afford 2-pentynyl-2-tetrahydropyranyl ether (XI) in 95.7% yield, XI was then treated with phosphoric acid to give 2-pentyn-1-ol (XII) in 82% yield. cis-2-Penten-1-ol (XIII) was obtained in 89.2% by means of semi-hydrogenation of the acetylenic carbinol (XII) using Lindlar’s catalyst. trans-2-Penten-1-ol (XV) was also prepared in 90% yield by reduction of XII with sodium in liquid ammonia.

cis Isomer (XIII) showed infrared absorption at 3378 and 1000 cm\(^{-1}\) due to primary alcohol group and at 1656 cm\(^{-1}\) due to ethylenic group and showed no band at 972 cm\(^{-1}\) due to trans-CH=CH—. The infrared spectrum of trans isomer (XV) showed the typical strong band at 972 cm\(^{-1}\) (trans-CH=CH—) besides at 3346, 1007 (CH\(_2\)OH) and 1667 cm\(^{-1}\) (C=C). Both cis- and trans-2-penten-1-ol were then converted into the corresponding chloride with phosphorus trichloride in 85–90% yields. These chlorides proved to be almost free from isomer each other by infrared spectra and by gas chromatography. The physical properties of these intermediates mentioned above are shown in Table II.
TABLE II. PHYSICAL PROPERTIES OF THE INTERMEDIATES (X)-(XVI)

<table>
<thead>
<tr>
<th>Intermediate</th>
<th>b.p. (°C/mm)</th>
<th>nD</th>
<th>dD</th>
<th>MRd</th>
<th>Found</th>
<th>Calcd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propargyl Ether (X)</td>
<td>85~ 86/20</td>
<td>1.4583</td>
<td>1.0086</td>
<td></td>
<td>37.95</td>
<td>38.24</td>
</tr>
<tr>
<td>2-Pentynyl Ether (XI)</td>
<td>120~121/20</td>
<td>1.4658</td>
<td>0.9779</td>
<td></td>
<td>47.63</td>
<td>47.48</td>
</tr>
<tr>
<td>2-Pentyn-1-ol (XII)</td>
<td>86~ 87/47</td>
<td>1.4521</td>
<td>0.9034</td>
<td></td>
<td>25.12</td>
<td>24.82</td>
</tr>
<tr>
<td>cis-2-Penten-1-ol (XIII)</td>
<td>59~ 60/19</td>
<td>1.4368</td>
<td>0.8498</td>
<td></td>
<td>26.54</td>
<td>26.35</td>
</tr>
<tr>
<td>trans-2-Penten-1-ol (XV)</td>
<td>59~ 60/22</td>
<td>1.4349</td>
<td>0.8485</td>
<td></td>
<td>26.48</td>
<td>26.35</td>
</tr>
<tr>
<td>cis-2-Pentenyl Chloride (XIV)</td>
<td>106~108</td>
<td>1.4391</td>
<td>0.9137</td>
<td></td>
<td>30.11</td>
<td>29.69</td>
</tr>
<tr>
<td>trans-2-Pentenyl Chloride (XVI)</td>
<td>107~110</td>
<td>1.4381</td>
<td>0.9085</td>
<td></td>
<td>30.22</td>
<td>29.69</td>
</tr>
</tbody>
</table>

FIG. 2. IR Spectrum of Synthetic cis-Jasmone (VIb) (Film).

Alkylation of 3-methyl-2-cyclopentenone (V) with cis-(XIV) or trans-2-pentenyl chloride (XVI) by the same procedure described above gave cis-(VIb, 2-(cis-2-pentenyl)-3-methyl-2-cyclopentenone) or trans-jasmone (VIc, 2-(trans-2-pentenyl)-3-methyl-2-cyclopentenone) in 38~40% yields. The physical properties and melting point of derivatives of jasmones are shown in Table I. Each jasmone showed a main peak on gas chromatography as shown in Fig. 4. The infrared spectrum of VIb shows maxima at 1695 cm⁻¹ due to α,β-unsaturated carbonyl group, 1645 and 751 cm⁻¹ due to cis-CH=CH— as shown in Fig. 2, and absorption at 971 cm⁻¹ was neglisible, showing the absence of trans-CH=CH—. It also showed the absorption peak at 233 mμ (ε=13,200) in ultraviolet spectrum, and gave 2,4-dinitrophenylhydrazone as reddish orange needles, m.p. 129~130°C (Lit. 121~122.5°C,¹³ 118.5~119.5°C,¹³ 117.5°C¹¹,¹²) and semicarbazone as leaflets, m.p. 205~206.5°C (Lit. 204~206°C,¹⁰~¹² 209.5~210°C³¹). Although the 2,4-dinitrophenylhydrazone of the synthetic cis-jasmone showed higher melting point than that of reported one, the natural cis-jasmone also gave the same 2,4-dinitrophenylhydrazone after the recrystallization from ethanol several times. The identity of the product with natural cis-jasmone was established by the identity of the infrared spectra of the ketone and its semicarbazone with those of authentic specimens, and by the non-depression of melting point on admixture of the semicarbazones and 2,4-dinitrophenylhydrazones.

On the other hand, trans-jasmone (VIc) shows absorption peaks at 1692 cm⁻¹ (C=O), 1645 and 971 cm⁻¹ (trans-CH=CH—) in infrared spectrum as shown in Fig. 3 and at 233 mμ (ε=13,600) in ultraviolet absorption. It gave 2,4-dinitrophenylhydrazone, m.p. 135.5~136.5°C, as red fine needles and semicarbazone,

FIG. 3. IR Spectrum of Synthetic trans-Jasmone (VIc) (Film).

m.p. 200°C - 201.5°C, as leaflets, which was identical with the reported one (Lit. m.p. 200°C - 202°C [11]). Crombie and Harper [11] recorded m.p. 128.5°C and Sisido [14] reported m.p. 127°C for the 2,4-dinitrophenylhydrazone. These may have been impure specimens.

The odor of VIc was fairly different from that of VIb. The cis isomer possesses more characteristic, persisting and fresh green note of jasmin oil than trans isomer, which has only weak floral note. Dihydrojasmone (VIa) possesses more pleasant and cis-jasmone-like odor than trans-jasmone.

An attempt to prepare the dehydrojasmone (VID) by the use of 2-pentynyl bromide under the same operation was unsuccessful.

EXPERIMENTAL

All melting and boiling points were uncorrected. Infrared spectra were measured in the state of liquid film.

3-Methyl-2-cyclopentenone (V)

In accordance with the procedure devised by Acheson and Robinson, [18] 3-methyl-2-cyclopentenone (V), b.p. 74°C - 80°C/14 mm, (31.1 g), was prepared from commercial acetylacetone (60 g). The product consisted of 83.7% V and 14.3% acetylacetone by gas chromatography.

Propargyl 2-Tetrahydropyranyl Ether (X)

To a mixture of propargyl alcohol (IX) (42 g, 0.75 mol) and 3,5-dihydropyran (63 g) cooled in an ice-water bath, was added phosphorus oxychloride (0.5 g). [19] The evolution of heat was observed. After the reaction mixture had been kept at room temperature for 2 hr., potassium hydroxide solution was added and the product was extracted with ether. The ether extract, without washing, was dried over sodium sulfate. After the evaporation of the ether, the residue was distilled through a Widmer column (15 cm) in the presence of a few pellets of potassium hydroxide to afford propargyl 2-tetrahydropyranyl ether (X) as a colorless liquid, (90.4 g, 86.2%), b.p. 75°C - 78°C/24 mm, \( \nu_{\text{max}}^{\text{film}} \) 3356 (\( \equiv \text{CH} \)), 2123 (C=CH), 1125 and 1036 cm\(^{-1} \) (C-O-C). The physical properties of analytical sample are given in Table II.

2-Pentynyl 2-Tetrahydropyranyl Ether (XI)

Sodium amide was prepared from sodium (17.7 g, 0.77 mol) in anhydrous liquid ammonia (700 ml) by the usual way. [15] To the stirred ammonia suspension in a dry-ice acetone bath X (98 g, 0.7 mol) was dropwise added, and the mixture was stirred for 1 hr. in order to complete formation of the sodio-derivative. Then, ethyl bromide (84 g, 0.77 mol) was added to the mixture and stirred for 3 hr. in a dry-ice acetone bath and for additional 1 hr. at room temperature under the evaporation of ammonia. After the reaction mixture was kept overnight at room temperature, water was added, and the product was extracted with ether. The ether was washed with saturated sodium chloride solution, and dried over sodium sulfate. The ether was recovered and the residue was distilled through a Widmer column.

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(15 cm) in the presence of a few pellets of potassium hydroxide to yield 2-pentynyl 2-tetrahydropyranyl ether (XI) as a colorless liquid (112.3 g, 95.7%), b.p. 120-121°C/20 mm; ν\text{\textsubscript{\text{max}}} 2217 (—C=C—), 1120 and 1022 cm\textsuperscript{-1} (C—O—C). Further physical data are given in Table II. Its gas chromatogram showed a main peak at the retention time of 9.5 min. under the same conditions mentioned above.

Diethyl sulfate, in place of ethyl bromide, was similarly used to give XI in 87% yield.

2-Pentyn-1-ol (XII)
A mixture of XI (100 g) and 85% phosphoric acid (2 g) in a flask attached with a Widmer column (13 cm) was heated at 145-155°C for 2 hr. Then, the mixture was gradually distilled under the reduced pressure of 35-40 mmHg. A mixture of 2-pentyn-1-ol and 2,3-dihydropyran, collected mainly at 85°C/23 mm in a flask containing a few pellets of potassium hydroxide, was dried over sodium sulfate. The product was distilled to give 2-pentyn-1-ol (XII) (40.9 g, 82%), b.p. 86-92°C/47 mm; ν\text{\textsubscript{\text{max}}} 3390 (OH), 1016 (CH\textsubscript{2}OH), 2283 and 2227 cm\textsuperscript{-1} (C—C). Its gas chromatogram showed one peak at the retention times of 3.5 min, under the same conditions mentioned above. The sample showed the physical properties given in Table II.

cis-2-Penten-1-ol (XIII)
XII (60 g) in methyl acetate (400 ml) was hydrogenated during 1.5 hr. at atmospheric pressure over Lindlar’s catalyst (12 g) until 1724 ml of hydrogen was absorbed (Calcd. for semi-hydrogenation, 1698 ml at 17°C). The product was separated from the catalyst and distilled through a Widmer column to afford pure cis-2-penten-1-ol (XIII) (54.6 g, 89.2%) as a colorless liquid, b.p. 55-65°C/19 mm; ν\text{\textsubscript{\text{max}}} 3378 (OH), 1007 (CH\textsubscript{2}OH) and 1656 cm\textsuperscript{-1} (trans-CH=CH-). The analysed sample showed the constants given in Table II, and its gas chromatogram showed a main peak of XIII and a peak of n-amyl alcohol (trace), but showed no peak of starting 2-pentyn-1-ol.

cis-2-Pentenyl Chloride (XIV)
XIII (120.4 g, 1.4 mol) in dry pyridine (24.5 g, 0.31 mol) was added during 5 hr. to a stirred solution of phosphorus trichloride (76.9 g, 0.56 mol) with cooling below about 8°C. After the addition was complete, the mixture was stirred for additional 30 min. in an ice-water bath and for 1 hr. at room temperature, and distilled to afford the crude chloride, b.p. 105-107°C. The chloride was washed with 1% sodium hydroxide solution and then water, dried over calcium chloride, and distilled through a Widmer column (13 cm) to give cis-2-pentenyl chloride (XIV) as a colorless liquid (131.5 g, 89.7%), b.p. 103-110°C; ν\text{\textsubscript{\text{max}}} 3441 (OH), 1007 (CH\textsubscript{2}OH), 1667 and 972 cm\textsuperscript{-1} (trans-CH=CH—). The physical properties are given in Table II. Its infrared spectrum showed little peaks at 970 cm\textsuperscript{-1} due to trans-CH=CH—, 910 and 990 cm\textsuperscript{-1} due to —CH=CH\textsubscript{2}, indicating the absence of allyl rearrangement products, namely trans-2-pentenyl or 1-penten-3-yl chloride. Gas chromatography showed a main peak of the cis-chloride.

Since the allyl rearrangement easily occurred in the case of cis-2-pentenyl bromide, the bromide obtained was a mixture of isomers.

trans-2-Penten-1-ol (XV)
XII (25.2 g, 0.3 mol) in dry ether (30 ml) was during 30 min. added dropwise to a stirred and cooled (dry-ice acetone) solution of sodium (27.6 g, 1.2 mol) in liquid ammonia (600 ml). The mixture was stirred for an additional 3 hr., whichafter ammonium chloride (about 90 g) was cautiously added until the blue color was discharged, and ammonia was allowed to evaporate overnight. Then water was added just enough to dissolve the crystals and the product was extracted with ether. The ether extract was dried over sodium sulfate and distilled through a Widmer column (13 cm) to afford trans-2-penten-1-ol (XV) as a colorless liquid (25.4 g, 90%), b.p. 59-60°C/22 mm; ν\text{\textsubscript{\text{max}}} 1650 (C=C) and 751 cm\textsuperscript{-1} (cis-CH=CH—). Further data are given in Table II. Its gas chromatogram showed a main peak of trans-2-penten-1-ol and a trace of n-amyl alcohol.

By the method of Bharucha and Weedon using LiAlH4, trans-2-penten-1-ol was also obtained in lesser yield, but a fairly amount of unchanged 2-pentyn-1-ol was recovered.

trans-2-Pentenyl Chloride (XVI)
In a manner similar to that used for the preparation of cis-2-pentenyl chloride, trans-2-pentenyl chloride (XVI) was obtained as a colorless liquid (53.0 g, 84.5%), b.p. 107-110°C by a reaction of trans-2-penten-1-ol (XV) (51.6 g, 0.6 mol) in pyridine (10.6 g, 0.133 mol) with phosphorus trichloride (33 g, 0.24 mol). ν\text{\textsubscript{\text{max}}} 1667 (C=C) and 966 cm\textsuperscript{-1} (trans-CH=CH—).

20) A. Juvala, Ber., 68, 1989 (1930).


CH=CH—). Gas chromatogram showed a single peak, and other physical properties are shown in Table II.

cis-Jasmone (VIb)
To a stirred suspension of 0.3 mol of sodium amide in anhydrous liquid ammonia (600 ml) prepared from sodium (6.9 g) and a catalytic amount of ferric nitrate 3-methyl-2-cyclopentenone (V) (44.1 g 0.39 mol as 85% purity) was added with cooling in a dry-ice acetone bath. The mixture was stirred for 30 min. In order to complete formation of the sodio-derivative. Then cis-2-pentenyl chloride (XIV) (31.5 g, 0.3 mol) in dry ether (50 ml) was added during 1 hr. Stirring was continued for 1 hr in a dry-ice acetone bath and for an additional 1 hr. at room temperature under the evaporation of ammonium. Ammonium chloride (5 g) was cautiously added to the mixture, which was stirred for several minutes and kept overnight under the evaporation of ammonia. Water was added and then the product was extracted with ether. The ether extract was thoroughly washed with 5% hydrochloric acid and saturated sodium chloride solution, successively. The ether solution was dried over sodium sulfate, and the solvent was removed. The residue was distilled through a Widmer column (15 cm) to yield two main fractions; (a) b.p. 73.-79°C/0.5 mm, nearly pure cis-jasmone (VIb) (19.2 g, 39%) and (b) b.p. 130.-160°C/ 1 mm (13.5 g). The fraction (a) possessed the following constants; n_D^20 = 1.4991 (Lit. 1.4978), d_20 = 0.9391, d_25 = 0.9507 (Lit. d_20 = 0.9422), A_max = 233 m_u (¢=13,200) [Lit. 235 m_u (¢=12,000)], 237 m_u (¢=11,000), A_max 1695 (C=C—C=O) and 1645 cm^-1 (C=C) as shown in Fig. 2 (Lit,11) 5.875, 6.05 m_u (respectively). Anal. Found: C, 79.99; H, 9.85. Calcd. for C_11H_18O: C, 80.44; H, 9.83%. 2,4-Dinitrophenylhydrazone was obtained as red fine needles m.p. 135.5-136.5°C from ethanol, (Lit. 128.5°C,11 127°C14)). Anal. Found: C, 59.47; H, 5.87; N, 16.01. Calcd. for C_17H_20O_4N_4: C, 59.29; H, 5.85; N, 16.27%. The semicarbazone formed from leaves m.p. 200--201.5°C (decomp.) from ethanol (Lit. 200~202°C11)). Anal. Found: C, 65.78; H, 8.38; N, 18.48. Calcd. for C_12H_19O_3N_3: C, 65.12; H, 8.65; N, 18.99%. A mixture of the semicarbazone (4 g) and phthalic anhydride (4 g) was steam-distilled to afford pure trans-jasmone, b.p. 77~79°C/0.5 mm, as a colorless liquid (2.5 g).

Dihydrojasmone (VIa)
In a similar manner mentioned above, dihydrojasmone (VIa) (18.6 g, 37.4%), b.p. 72.5--73.5°C/0.6 mm was obtained from 3-methyl-2-cyclopentenone (V) (44.1 g), n-amylobromide (45.3 g) and sodium amide (0.3 mol) in liquid ammonia (600 ml). n_D^20 = 1.4795 (Lit. n_D^20 = 1.4801), d_20 = 1.4805, d_25 = 1.4875; d_20 = 1.4771, d_25 = 1.4760, d_20 = 1.4760, d_25 = 1.4760, d_20 = 0.9147, d_25 = 0.9163 (Lit. d_20 = 0.9201, d_25 = 0.9200, d_25 = 0.9157), A_max = 235 m_u (¢=14,100) [Lit. 237 m_u (¢=12,000)], 236 m_u (¢=13,300), 236 m_u (¢=12,000), A_max 1692 (C=C—C=O) and 1642 cm^-1 (C=C) as shown in Fig. 1. Anal. Found: C, 79.23; H, 10.68. Calcd. for C_{11}H_{16}O_3: C, 79.46; H, 10.92%. It yielded 2,4-dinitrophenylhydrazone as red fine needles m.p. 122--129°C from ethanol (Lit. 122°C29,30,31 121.5°C,29 123°C28)). Anal. Found: C, 59.23; H, 6.30; N, 16.16. Calcd. for C_{12}H_{18}O_3N_3: C, 59.29; H, 6.85; N, 16.27%. The semicarbazone was recrystallized from ethanol to give leaflets, m.p. 200=201.5°C (decomp.) from ethanol (Lit. 200~202°C11)). Anal. Found: C, 59.47; H, 5.87; N, 16.01. Calcd. for C_{12}H_{18}O_3N_3: C, 59.29; H, 5.85; N, 16.27%. The semicarbazone formed from leaves m.p. 200--201.5°C (decomp.) from ethanol (Lit. 200~202°C11)). Anal. Found: C, 65.78; H, 8.38; N, 18.48. Calcd. for C_{12}H_{19}O_3N_3: C, 65.12; H, 8.65; N, 18.99%. A mixture of the semicarbazone (4 g) and phthalic anhydride (4 g) was steam-distilled to afford pure trans-jasmone, b.p. 77~79°C/0.5 mm, as a colorless liquid (2.5 g).
Fig. 4. Gas Chromatogram of Jasmones, (VIa), (VIb) and (VIc).

Temperature: 200°C; Helium flow rate: 50 ml/min; Stationary Phase: Reoplex on celite 545 (50~80 mesh) 10% w/w; Column: Stainless-steel column 2 m by 3 mm i.d.

N, 16.08. Calcd. for C_{17}H_{22}O_{4}N_{4}: C, 58.94; H, 6.40; N, 16.18%. The semicarbazone melted at 174~175°C (Lit. 173~174°C,25) 175~176°C,2,3,10,13,31,32 176°C,26 176.5~177°C,29 30) 173°C,24). Anal. Found: C, 64.56; H, 9.31; N, 18.59. Calcd. for C_{12}H_{21}O_{3}: C, 64.54; H, 9.48; N, 18.82%. Dihydrojasmine showed a single peak on gas chromatogram.

Gas Chromatography of Jasmones

Jasmones were introduced through a 200 x 0.32 cm i.d. stainless steel column packed with 10 wt% Reoplex on celite 545 (50~80 mesh) at 200°C, 50 ml of helium per min. as carrier gas. As shown in Fig. 4, the retention times of dihydrojasmine (VIa), trans-jasminone (VIc) and cis-jasmon (VIb) were 5.3, 6.8 and 7.4 min., respectively.

Acknowledgement. The authors wish to acknowledge useful guidance and comments of Dr. M. Matsui, the University of Tokyo.