Three New Phenolic Amides from the Roots of Eggplant (*Solanum melongena* L.)

Teruhiko YOSHIHARA, Seiji TAKAMATSU and Sadao SAKAMURA

Department of Agricultural Chemistry, Faculty of Agriculture,
Hokkaido University, Sapporo 060, Japan

Received October 6, 1977

The isolation of four phenolic amides, four phenolic compounds and an aromatic amine from the roots of eggplant is described. The phenolic amides were identified as *N-trans*-feruloyl tyramine (V), *N-trans-p*-coumaroyl tyramine (VII), *N-trans*-feruloyl octopamine (VIII) and *N-trans-p*-coumaroyl octopamine (IX). The three amides V, VIII and IX are new compounds. Furthermore, four phenolic compounds were identified as vanillin (I), isoscapoletin (II), ethyl caffeate (IV) and ferulic acid (VI). The aromatic amine was identified as *p*-aminobenzaldehyde (III).

It is generally recognized that some crops do not thrive when cropped annually on the same field. This phenomenon has been named "Iyachi" in Japanese and used to be avoided by rotating crops on the soil. In this connection, phytotoxic compounds originating from crops itself by excretion and decomposition of organic materials are regarded as one of the causal agents. In fact, it has been claimed by investigators that phenolic carboxylic acids in upland rice¹⁾ and isoflavones in red clover²⁾ act as the causal agent for affected crops. A typical example affected by continuous cropping can be seen in the plant family (*Solanaceae*) such as eggplant and tomatoes. Therefore, we first attempted to survey phenolic compounds in the roots of eggplant (*Solanum melongena* L.). This paper deals with the isolation and structure elucidation of four phenolic amides, four other phenolic compounds and an aromatic amine occurring in the roots of eggplant.

Fresh roots of eggplant were chopped and extracted with 70% ethanol. The extract was concentrated and the resulting aqueous solution was extracted with ether. The ether extract was concentrated and applied to a silica gel column. Eight fractions were obtained; three fractions (compound, $F_1 \sim F_3$) from the eluent of chloroform and five fractions (compound, $F_4 \sim F_8$) from the eluent of 5% methanol

in chloroform. The F_6 compound shown to be a mixture of two polyphenols by means of paper chromatography was further chromatographed over a silica gel column and separated into two compounds referred to F_{6a} and F_{6b} . All the compounds, except the F_3 compound, gave positive reactions to the phenol reagent.

The F_1 compound (I), $M^+ 152$, was an aldehyde compounds, as evidenced by the positive reaction with 2,4-dinitrophenylhydrazine and identified as vanillin (I) by means of UV, PMR and IR. The F_2 compound (II) was yellow crystals, mp $185 \sim 187^\circ\text{C}$, $M^+ 192$ and was considered to be isoscapoletin (II) by means of MS, UV, PMR and IR. Their identity was confirmed by comparison of these spectral data with those of the authentic specimens.³⁾ The F_3 compound (III), C_7H_7NO , $M^+ 121$, melted at $98 \sim 100^\circ\text{C}$ and gave positive reactions to the ninhydrin reagent and 2,4-dinitrophenylhydrazine, but not to the phenol reagent. In the IR spectrum of III, bands at 1603 and 780 cm^{-1} were attributed to an aromatic ring, bands at 1650 cm^{-1} to an aromatic amine group and bands at 1670 cm^{-1} to an aromatic aldehyde group. From these data, the structure of III was elucidated to be amino-benzaldehyde. In the PMR spectrum of III, the signals of a typical *p*-substituted benzene was observed; a doublet at $\delta 7.0$ and 7.85 ($J=9\text{ Hz}$) of each two aromatic protons. Thus, the F_3 compound

was elucidated to be *p*-aminobenzaldehyde (III), which has not been isolated from any higher plant.

The F_4 compound was obtained as crystals, mp $140\sim 141^\circ\text{C}$, M^+ 208, whose UV spectrum indicated the F_4 compound to be one of the derivatives of caffeic acid. By means of MS, PMR and IR, the F_4 compound was identified as ethyl caffeate (IV). The ester IV seems to be an artifact formed from caffeic acid during the isolation procedure. The F_{6a} compound showed the UV spectrum similar to that of caffeic acid. The PMR spectrum revealed the presence of an aromatic methoxy group ($\delta 3.92$), and a mass spectrum showed M^+ ion peak at m/e 194. From these data, the F_{6a} compound was elucidated to be ferulic acid (VI).

The F_{6b} compound (VII) obtained as crystals, mp $240\sim 245^\circ\text{C}$, showed λ_{max} at 294 and 312 nm, indicating it to be a compound having a double bond conjugated to a benzene ring (e.g. *p*-coumaric acid, ferulic acid, caffeic acid etc.). Indeed, their IR spectra revealed the presence of an aromatic ring ($1605, 1515\text{ cm}^{-1}$) and *trans*-olefin (980 cm^{-1}). In addition, VII had absorption bands of an amide group at 1670 cm^{-1} in the IR spectrum. The PMR spectrum of VII was evident for the existence of eight aromatic protons at $\delta 6.6\sim 7.5$, an amine proton at $\delta 8.0$ and two *trans*-coupled vinylic protons at $\delta 6.4$ and 7.35 ($J=15\text{ Hz}$). An acetylated derivative (XI) of VII was prepared with acetic anhydride-pyridine, which gave a positive reaction to the Dragendorff reagent. This colour reaction suggested the F_{6b} compound to be an amide compound. The PMR spectrum of XI was evident for the existence of two acetyl groups ($\delta 2.3$, s, 6H). A mass spectrum of XI showed peaks at m/e 367 (M^+), 147 ($\text{HO}-\text{C}_6\text{H}_4-\text{CH}=\text{CHCO}^+$) derived from acidic moiety and 120 ($\text{HO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2^+$) derived from amine moiety. From these data, the structure of the F_{6b} compound was assigned to *N-trans-p*-coumaroyl tyramine (VIII), which had been isolated from the bark of *Evodia belahe* B.⁴⁾ The validity of the structure assignment was confirmed by com-

parison of IR, MS, PMR and UV spectra with those of the synthetic specimen (XI) which was obtained from tyramine and acetyl *p*-coumaric acid.

The F_5 compound (V) obtained as syrup showed the IR and UV spectra similar to those of VII. The PMR spectrum of the F_5 compound showed signals similar to those of the F_{6b} compound except a peak assigned to a methoxy group ($\delta 3.8$). The difference of 30 mass units of molecular ion peak between the F_5 compound (M^+ 313) and the F_{6b} compound (M^+ 283) indicated the presence of a methoxy group on the phenolic moiety of the F_5 compound. The F_5 compound was therefore assigned as *N-trans*-feruloyl tyramine (V). This structure was also confirmed by synthesis.

The F_7 compound (VIII) and the F_8 compound (IX) showed the UV spectra similar to those of the F_5 and F_{6b} compounds. On acetylation, VIII and IX furnished the triacetyl derivative (XII and XIII, respectively), which gave a positive reaction to the Dragendorff reagent. The PMR spectrum of XII exhibited signals of $-\text{CH}_2\text{CH}-$ moiety at $\delta 3.7$ and 5.9 instead of those of $-\text{CH}_2\text{CH}_2-$ moiety at $\delta 2.9$ and 3.65 in XI. The methine signals of XII and XIII were observed at $\delta 5.9$ and 5.87 respectively, the functional groups in $-\text{CH}-$ of XII and XIII being assigned as secondary alcohol. The PMR spectrum of XII was evident for the existence of two acetyl ($\delta 2.3$), one methoxy ($\delta 3.83$), one amine ($\delta 5.7\sim 6.1$), one *trans*-olefinic ($\delta 6.26, 7.53, J=16\text{ Hz}$) and seven aromatic protons ($\delta 6.9\sim 7.4$) other than $-\text{CH}_2\text{CH}-\text{OAc}$. A mass spectrum of XII showed a molecular ion peak at m/e 455, and base peak at m/e 177 which corresponded to

the mass of $\text{HO}-\text{C}_6\text{H}_4-\text{CH}=\text{CHCO}^+$. From these data, the structure of VIII was elucidated to be *N-trans*-feruloyl octopamine. On the other hand, the PMR spectrum of XIII was evident for the existence of two acetyl ($\delta 2.26$), one methoxy ($\delta 3.7$), two *trans*-olefinic ($\delta 6.25, 7.54, J=15\text{ Hz}$) and eight aromatic protons ($\delta 6.9\sim 7.5$) other than $-\text{CH}_2-\text{CH}-\text{OAc}$. A mass spectrum of XIII showed a molecular

ion peak at m/e 425, and base peak at m/e 147 which corresponded to the mass of $\text{HO}-\text{C}_6\text{H}_4-\text{CH}=\text{CHCO}^+$. From these data, the structure of IX was elucidated to be *N-trans-p-coumaroyl* octopamine. The stereochemistry of octopamine in F_7 and F_8 compounds remains obscure.

The presence of amides of *p*-coumaric and ferulic acids in some plants has been reported previously; *p*-coumaroyl agmatine,⁶⁾ feruloyl putrescine,⁶⁾ *p*-coumaroyl serotonin,⁷⁾ and feruloyl serotonin.⁷⁾ However V, VIII and IX are new compounds which have never been previously encountered in nature.

EXPERIMENTAL

Melting points were measured with an electrical apparatus (Yanagimoto MP 30) and uncorrected. Optical rotations were taken on Hitachi POB. UV spectra were recorded using HITACHI PERKIN-ELMER 139 UV-VIS spectrophotometer. IR spectra were measured with HITACHI EPI-S2. Mass spectra were run on Hitachi RMU-7 in the direct way. PMR spectra were run on Hitachi R-22 (90Mc/sec).

Isolation and separation

The chopped fresh roots (15 kg) of eggplant were extracted with 70% EtOH. The filtrates were concentrated to approx. 400 ml and then extracted with ether (400 ml $\times$ 7). The ether extracts were concentrated under reduced pressure to a syrup (15 g), which was chromatographed over silica gel (200 g). The solvent system used was 4000 ml of CHCl_3 and 6000 ml of 5% MeOH in CHCl_3 . The fractions collected were monitored by UV absorption at 280 nm and separated the eluate of CHCl_3 into three fractions ($F_1 \sim F_3$) and the eluate of 5% MeOH in CHCl_3 into five fractions ($F_4 \sim$

F_8). The F_8 compound was further chromatographed over a silica gel column using CHCl_3 -MeOH- CH_3COOH (100:5:5); and two compounds, referred to as F_{8a} and F_{8b} , in their order of elution were obtained.

F_1 compound (vanillin, I)

The F_1 compound was rechromatographed on a silica gel column with 50% ether in petroleum ether and resulted in pale yellow crystals of vanillin (I) from CHCl_3 , 70 mg (0.0005% yield). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 277, 305 (sh). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1700, 1590, 1290, 870, 830. MS m/e : 152 (M^+), 151 (100%), 149, 137, 123, 109, 81. PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 4.0 (3H, s, $-\text{OCH}_3$), 6.45 (1H, br, $-\text{OH}$), 6.9~7.5 (3H, ArH), 9.85 (1H, s, $-\text{CHO}$).

F_2 compound (isoscopoletin, II)

The F_2 compound was rechromatographed on a silica gel column and resulted in yellow crystals of isoscopoletin (II) from CHCl_3 , 140 mg (0.001% yield), mp 185~187°C. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 299, 346. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1700 (α -pyrone ring), 1600, 1450. MS m/e : 192 (M^+), 177, 164, 149 (100%), 121, 79, 69, 51. PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 3.95 (3H, s, $-\text{OCH}_3$), 6.12 (1H, d, $J=10\text{Hz}$, $=$), 6.74 (1H, s, ArH), 7.12 (1H, s, ArH), 7.77 (1H, d, $J=10\text{Hz}$, $=$).

F_3 compound (*p*-aminobenzaldehyde, III)

The F_3 compound was rechromatographed on a silica gel column with CHCl_3 - $\text{CH}_3\text{COOC}_2\text{H}_5$ (1:1) and resulted in white crystals of *p*-amino benzaldehyde (III) from CHCl_3 , 70 mg (0.0005% yield), mp 98~100°C. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 286 (20,000). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1670, 1650, 1603, 780. MS m/e : 122, 121 (M^+ , 100%), 93, 65. PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 6.6 (2H, m, $-\text{NH}_2$), 7.0 (2H, d, $J=9\text{Hz}$, ArH), 7.85 (2H, d, $J=9\text{Hz}$, ArH), 9.85 (1H, s, $-\text{CHO}$).

F_4 compound (ethyl caffeate, IV)

The F_4 compound was rechromatographed on a silica gel column with 30% ethyl acetate in CHCl_3 and resulted in crystals of ethyl *trans*-caffeate (IV) from CHCl_3 , 95 mg (0.0006% yield), mp 140~141°C. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 246, 300 (12,000), 331 (16,000). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1710, 1270, 970, 870, 810. MS m/e : 208 (M^+), 180, 163 (100%), 145, 136, 117, 89. PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 1.27 (3H, t, CH_3), 4.2 (2H, q, $-\text{CH}_2-$), 6.2 (1H, d, $J=16\text{Hz}$, $=$), 6.85 (1H, d, $J=9\text{Hz}$, ArH), 7.0 (1H, dd, $J=2\text{Hz}$, 9Hz, ArH), 7.12 (1H, d, $J=2\text{Hz}$, ArH), 7.5 (1H, d, $J=16\text{Hz}$, $=$), 8.25 (2H, br, $-\text{OH}$).

F_{8a} compound (*trans*-ferulic acid, VI)

The F_{8a} compound was crystallized from CHCl_3 , and *trans*-ferulic acid (VI) was obtained as plates, 95 mg (0.0006% yield) mp 152~156°C. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 294 (11,700), 320 (12,200). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1690, 1600, 970. MS m/e : 194 (M^+ , 100%), 179, 150, 135.

PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3/\text{CO}}$: 3.92 (3H, s, $-\text{OCH}_3$), 6.35 (1H, d, $J=15$ Hz, $=\backslash$), 6.85 (1H, d, $J=8$ Hz, ArH), 7.1 (1H, dd, $J=2$ Hz, 8 Hz, ArH), 7.3 (1H, d, $J=2$ Hz, ArH), 7.6 (1H, d, $J=15$ Hz, $=\backslash$).

F₆ compound (N-trans-feruloyl tyramine, V)

The F_6 fraction was evaporated to dryness under reduced pressure and rechromatographed on a silica gel column with $\text{CHCl}_3-(\text{CH}_3)_2\text{CO}-\text{CH}_3\text{COOH}$ (40:10:1) and resulted in a syrup of *N-trans*-feruloyl tyramine (V), 60 mg (0.0004% yield). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 290 (10,700), 320 (12,700). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1705, 1590, 1430, 970. MS m/e : 315, 313 (M^+), 194, 193, 192, 177 (100%), 149, 145, 120. PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3/\text{CO}}$: 2.75 (2H, m, $-\text{CH}_2-$), 3.45 (2H, m, $-\text{CH}_2-$), 3.8 (3H, s, $-\text{OCH}_3$), 6.4 (1H, d, $J=15$ Hz, $=\backslash$), 6.6~7.2 (7H, m, ArH), 7.4 (1H, d, $J=15$ Hz, $=\backslash$), 7.8 (1H, d, $>\text{NH}$), 8.1 (2H, m, OH).

Acetylation of F_6 compound (V) (50 mg) with acetic anhydride and pyridine yielded diacetyl *N*-feruloyl tyramine (X) (40 mg, 63% yield) as syrup. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 278 (14,800). IR $\nu_{\text{max}}^{\text{thin film}}$ cm^{-1} : 3400, 1760, 1660, 1610, 1410, 1220, 970. MS m/e : 397 (M^+), 355, 192, 177, 149, 120, 107, 43 (100%). PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 2.34 (6H, s, $\text{CH}_3\text{CO}-\text{O}-\text{Ar}$), 2.84 (2H, m, $-\text{CH}_2-$), 3.6 (2H, m, $-\text{CH}_2-$), 3.85 (3H, s, $-\text{OCH}_3$), 5.85 (1H, m, $>\text{NH}$), 6.28 (1H, d, $J=16$ Hz, $=\backslash$), 6.9~7.3 (7H, ArH), 7.56 (1H, d, $J=16$ Hz, $=\backslash$).

F_{6b} compound (N-p-coumaroyl tyramine, VII)

The F_{6b} fraction was evaporated to dryness under reduced pressure and the residue was crystallized from CHCl_3 to give *N-p*-coumaroyl tyramine (VII) as powder 98 mg (0.0006% yield), mp 240~245°C. Anal. Found: C, 71.44; H, 6.14; N, 4.98. Calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_3$: C, 72.08; H, 6.01; N, 4.95%. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 294 (26,400), 312 (26,000). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1670, 1605, 1515, 980, 830. MS m/e : 284, 283 (M^+), 164, 147, 119, 107, 91 (100%). PMR $\delta_{\text{Me}_4\text{Si}}^{\text{DMSO}}$: 6.4 (1H, d, $J=15$ Hz, $=\backslash$), 6.7 (1H, d, $J=10$ Hz, ArH), 6.8 (1H, d, $J=10$ Hz, ArH), 7.02 (1H, d, $J=10$ Hz, ArH), 7.4 (1H, d, $J=10$ Hz, ArH), 7.35 (1H, d, $J=15$ Hz, $=\backslash$), 8.0 (1H, m, $>\text{NH}$).

Acetylation of F_{6b} compound (VII) by the usual way gave diacetyl *N-p*-coumaroyl tyramine (XI) (45 mg, 77% yield), mp 160°C (from CHCl_3). Anal. Found: C, 66.9; H, 5.71; N, 3.76. Calcd. for $\text{C}_{21}\text{H}_{21}\text{NO}_5$: C, 68.66; H, 5.72; N, 3.81%. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 281 (26,600). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3300, 1770, 1680, 1620, 1220, 970. MS m/e : 367 (M^+), 325, 283, 206, 189, 162, 147 (100%), 120, 107, 91. PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 2.3 (6H, s, $\text{CH}_3\text{CO}-\text{O}-\text{Ar}$), 2.9 (2H, t, $J=6$ Hz, 6 Hz, $-\text{CH}_2-$), 3.65 (2H, t, $J=6$ Hz, $-\text{CH}_2-$), 5.7 (1H, m, $>\text{NH}$), 6.78 (1H, d, $J=15$ Hz, $=\backslash$), 6.9~7.6 (8H, m, ArH), 7.6 (1H, d, $J=15$ Hz, $=\backslash$).

F₇ compound (N-trans-feruloyl octopamine, VIII)

Acetylation of F_7 compound (VIII) (60 mg) by the usual way gave triacetyl *N*-feruloyl octopamine (XII) (21 mg, 25% yield), mp 155~157°C (from CHCl_3), $[\alpha]_D^{25}-5.3$ ($c=1.75$, EtOH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 281 (17,000). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3300, 1770, 1660, 1620, 1410, 1210, 970. MS m/e : 455 (M^+), 413, 395, 353, 352, 311, 249, 177 (100%). PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 2.13 (3H, s, $\text{CH}_3\text{CO}-\text{O}-\text{Ar}$), 2.3 (6H, s, $\text{CH}_3\text{CO}-\text{O}-\text{Ar}$), 3.7 (2H, m, $-\text{CH}_2-$), 3.83 (3H, s, $-\text{OCH}_3$), 5.9 (1H, m, $-\text{CH}$), 5.7~6.1 (1H, br, NH), 6.26 (1H, d, $J=16$ Hz, $=\backslash$), 6.5~7.4 (7H, m, ArH), 7.53 (1H, d, $J=16$ Hz, $=\backslash$).

F₈ compound (N-p-coumaroyl octopamine, IX)

Acetylation of F_8 compound (IX) (11 mg) by the usual way gave triacetyl *N-p*-coumaroyl octopamine (XIII) (8 mg, 51% yield), mp 154~156°C (from CHCl_3), $[\alpha]_D^{25}+8.0$ ($c=2.75$, EtOH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 281 (9800). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3300, 1760, 1660, 1620, 1420, 1210, 970. MS m/e : 425 (M^+), 365, 323, 281, 219, 189, 177, 147 (100%), 135, 119. PMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$: 2.1 (3H, s, $\text{CH}_3\text{CO}-\text{O}-\text{Ar}$), 2.26 (6H, s, $\text{CH}_3\text{CO}-\text{O}-\text{Ar}$), 3.7 (2H, m, $-\text{CH}_2-$), 5.87 (1H, m, $-\text{CH}$), 6.25 (1H, d, $J=15$ Hz, $=\backslash$), 6.9~7.5 (8H, m, ArH), 7.54 (1H, d, $J=15$ Hz, $=\backslash$).

Synthesis of the acetyl derivatives of the amides (V, VII, VIII and IX)

a) *Diacetyl N-feruloyl tyramine*. To a solution of 593 mg of *O*-acetyl ferulic acid (2.5 mmole) and 0.5 ml of triethylamine in 5 ml of absolute tetrahydrofuran 0.25 ml of ethylchlorocarbonate (2.6 mmole) was added, and allowed to stand for 1 hr. After that 456 mg of tyramine hydrochloride (2.5 mmole) and 0.5 ml of triethylamine were added. The reaction mixture was stirred overnight at room temperature.

The mixture was evaporated to a solid, and dissolved in 2 ml of acetic anhydride and 2 ml of dry pyridine, which was allowed to stand overnight. The solution was evaporated to a solid, chromatographed over silica gel (70 g) with 2% MeOH in CHCl_3 and yielded diacetate of the amide (470 mg, 47% yield) as white powder. This was identical with diacetate of natural *N*-feruloyl tyramine in all respects.

b) *Diacetyl N-p-coumaroyl tyramine*. *O*-Acetyl *p*-coumaric acid (82 mg) and tyramine hydrochloride (72 mg) were treated as described above, and diacetyl *N-p*-coumaroyl tyramine was obtained (360 mg, 41% yield).

c) *Triacetyl N-feruloyl octopamine*. *O*-Acetyl ferulic acid (60 mg) and *dl*-octopamine hydrochloride (60 mg) were treated as described above, and triacetyl *N*-feruloyl *dl*-octopamine was obtained (30 mg, 26% yield).

d) *Triacetyl N-p-coumaroyl octopamine*. *O*-Acetyl *p*-coumaric acid (62 mg) and *dl*-octopamine hydro-

chloride (72 mg) were treated as described above, and triacetyl N-*p*-coumaroyl *dl*-octopamine was obtained (170 mg, 75% yield).

REFERENCES

- 1) K. Munakata and T. Yamada, *Nogyo Oyobi Engei*, **34**, 1117 (1959).
- 2) S. Tamura, C.-F. Chang, A. Suzuki and S. Kumai, *Agric. Biol. Chem.*, **33**, 391 (1969); C.-F. Chang, A. Suzuki, S. Kumai and S. Tamura, *ibid.*, **33**, 398 (1969).
- 3) F. Shafizadeh and A. B. Melnikoff, *Phytochemistry*, **9**, 1311 (1970).
- 4) J. Rondest, B. C. Das and J. Polonsky, *Bull. Soc. Chim. Fr.*, **1968**, 2411.
- 5) A. Stoessl, *Phytochemistry*, **4**, 973 (1965).
- 6) T. A. Wheaton and I. Stewart, *Nature*, **206**, 620 (1965).
- 7) Y. Terayama, A. Ichihara and S. Sakamura, Abstracts of papers, the Annual Meeting of the Agricultural Chemical Society of Japan, Yokohama, April, p. 343 (1977).