Biosci. Biotechnol. Biochem., **64** (9), 1988–1992, 2000

Note

Syntheses of Stereochemically Restricted Lactone-type Analogues of Jasmonic Acids

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Received March 2, 2000; Accepted April 10, 2000

5-Oxa-7-*epi*-jasmonic acid and 5-oxa-jasmonic acid, which are stereochemically restricted lactone-type analogues of jasmonic acids, were synthesized *via* three-component coupling of 2(5*H*)-furanone, *tert*-butyl acetate and 1-bromo-2-pentyne. After acidic deprotection of the *tert*-butyl esters, the (*Z*)-olefin was introduced by catalytic partial reduction with the Lindlar catalyst to give the desired analogues.

Key words: 7-*epi*-jasmonic acid; jasmonic acid; phytohormone; jasmonic acid analogue

Jasmonoids have recently been postulated as a class of phytohormones.[1] The *cis*-isomer, 7-*epi*-jasmonic acid (7-*epi*-JA, **1**) is first biosynthesized and readily isomerizes to the thermodynamically stable *trans*-isomer, jasmonic acid (JA, **2**). Therefore, **1** is considered to be an essential endogenous plant regulator. In fact, it has been reported that the methyl ester of **1** when exogenously supplied exhibited higher biological activities than those of **2**.[2] We have previously reported that the natural product, coronafacic acid, can be regarded as a stereochemically *cis*-restricted bicyclic analogue of **1**.[3] Furthermore, some analogues (7-methyl-, 7-fluoro-, 3-methyl-, 2-methyl- and 3,7-didehydro-) have been synthesized to restrict the *cis*-configuration and conformation of two side chains on the cyclopentanone ring of **1** and **2**.[4–8] However, these analogues exhibited no or weak activities in a jasmonate-bioassay system, except for the strong inhibitory activity of methyl 3,7-didehydrojasmonate taword the germination of lettuce seeds.[8] Thus, the 5-oxa-JA analogues (**3** and **4**), which are considered to have almost the same molecular size as **1** and **2** and to prevent epimerization under the physiological conditions of bioassays, were designed to clearly confirm the structure-activity relationship of JAs.

Three-component coupling[9] of 2(5*H*)-furanone, *tert*-butyl acetate and 1-halo-2-pentyne is an appropriate route to construct the required carbon skeleton, except for stereocontrol. Since the use of commercially available 1-chloro-2-pentyne as an alkylating agent gave none of the desired product in several attempts, the corresponding bromide obtained *via* substitution with lithium bromide was next used. Treatment of 2(5*H*)-furanone with an enolate of *tert*-butyl acetate provided a lactone-enolate which was alkylated with 1-bromo-2-pentyne to give *cis*-isomer **5** and *trans*-isomer **6** in 2% and 52% yields, respectively. Both isomers could be readily separated by silica gel column chromatography. By considering the transition state during alkylation, it is readily understandable that **6** would be predominantly formed because the electrophile (1-bromo-2-pentyne) would approach the lactone-enolate from the opposite direction to that of the bulky substituent (the *tert*-butoxycarbonylmethyl group). The structural validity of **5** and **6** was confirmed from several reasonable NOE enhancements in their ^{1}H–^{1}H-NOE difference spectra. When H_{4a} and H_{4b} were respectively irradiated in *cis*-isomer **5**, NOE enhancement of both H_{2a}/H_{2b} and H_7 was observed. When H_{4a} and H_3 were respectively irradiated in *trans*-isomer **6**, NOE enhancement of H_{2a}/H_{2b}/H_7 and H_{8a}/H_{8b} was observed. In order to increase the yield of **5**, isomerization of **6** was carried out. After treating **6** with 2.2 equiv. of lithium diisopropylamide (LDA), the resulting bis-enolate was protonated by adding several proton sources; for example, MeOH, AcOH, aq. HCl, aq. NH_4Cl and H_2O. The highest ratio (**5**:**6** = 1:7.6) was obtained when H_2O was used as the proton source. Acidic deprotection of the *tert*-butyl ester of **5** with trifluoroacetic acid (TFA) gave desired carboxylic acid **7** in a 97% yield. Partial reduction of **7** in the presence of the Lindlar catalyst in EtOAc quantitatively gave **3**. No epimerization at the α-position of the lactone was apparent in the process of the reactions and durig purification from the following results: In the ^{1}H-NMR spectra of the three *cis*-isomers (**5**, **7** and **3**), each isomer was regarded as a single stereoisomer, and their proton signals (H_7, H_3, H_{4a} and H_{4b}) attached to lactone rings were commonly observed around δ (ppm) 2.8, 3.0, 4.2 and 4.4,

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Abbreviations: JA, jasmonic acid; LDA, lithium diisopropylamide; TFA, trifluoroacetic acid

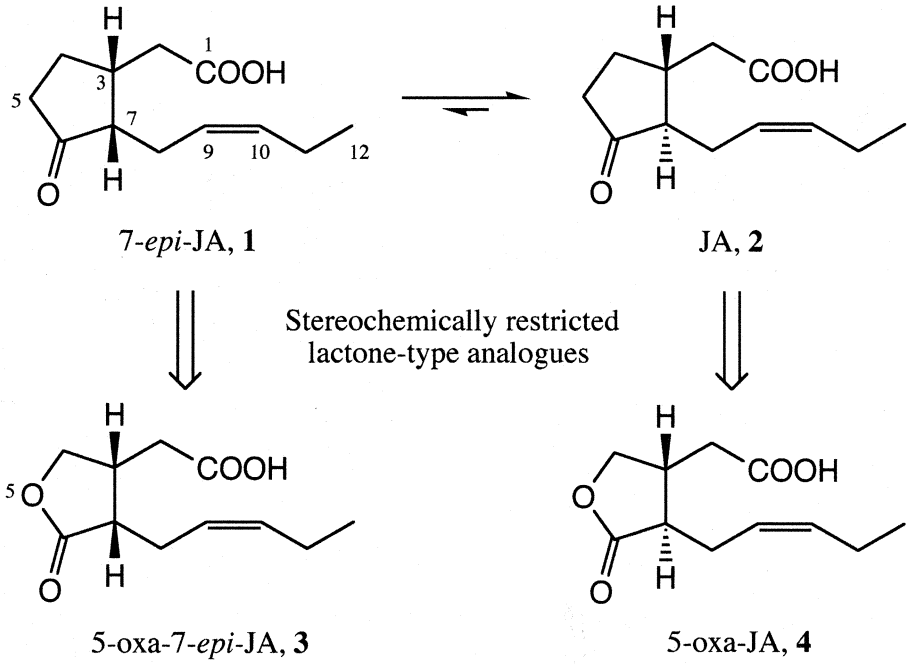
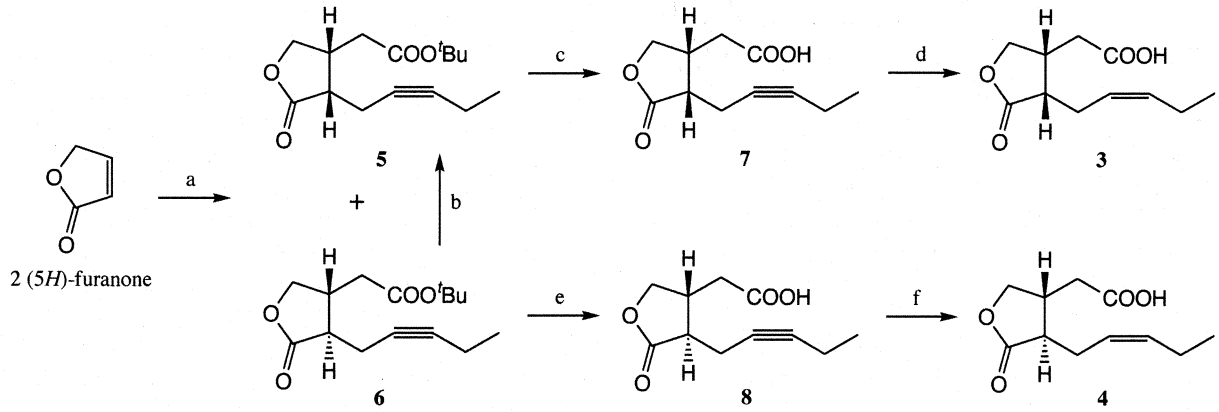


Fig. 1. Structures of Jasmonic Acids and Their Stereochemically Restricted Lactone-type Analogues.



Scheme. (a) $CH_3COOtBu$, LDA (1.0 eq.)/THF, then 1-bromo-2-pentyne, **5** (2%) and **6** (52%); (b) LDA (2.2 eq.)/THF, then H_2O, **5** (8.4%) and **6** (64%); (c) TFA/CH_2Cl_2 (97%); (d) H_2, Lindlar cat./EtOAc (100%); (e) TFA/CH_2Cl_2 (94%); (f) H_2, Lindlar cat./EtOAc (100%).

respectively, with similar multiplicity and coupling constants. In the same manner, **6** was converted into **4** in a 94% yield (2 steps) without epimerization. In the ^{1}H-NMR spectra of the three *trans*-isomers (**6**, **8** and **4**), each isomer was regarded as a single stereoisomer and was clearly distinguishable from the corresponding *cis*-isomers. Their proton signals (H_{4a} and H_{4b}) attached to lactone rings were commonly observed around δ (ppm) 3.9 and 4.6, respectively, with similar multiplicity and coupling constants. Therefore, the lacton-type analogues were chemically stable enough to prevent epimerization under acidic and neutral reaction conditions.

In conclusion, **3** and **4**, hitherto unknown and stereochemically restricted lactone-type analogues of JAs, were synthesized in 3 steps *via* three-component coupling. Unfortunately, neither **3** nor **4**, like 3,7-didehydro-JA,[10] exhibited any activities in the potato cell expansion-inducing[11] and tuber-inducing[12] assays in the concentration range from 10^{-6} to 10^{-4} M. It seems that epimerization of **3** and **4** would not occur under the physiological conditions of these bioassays with the medium adjusted to pH 5.6.[11,12] However, both **3** and **4** would provide significant information in other jasmonate-bioassay systems because they have almost the same molecular size as those of JAs.

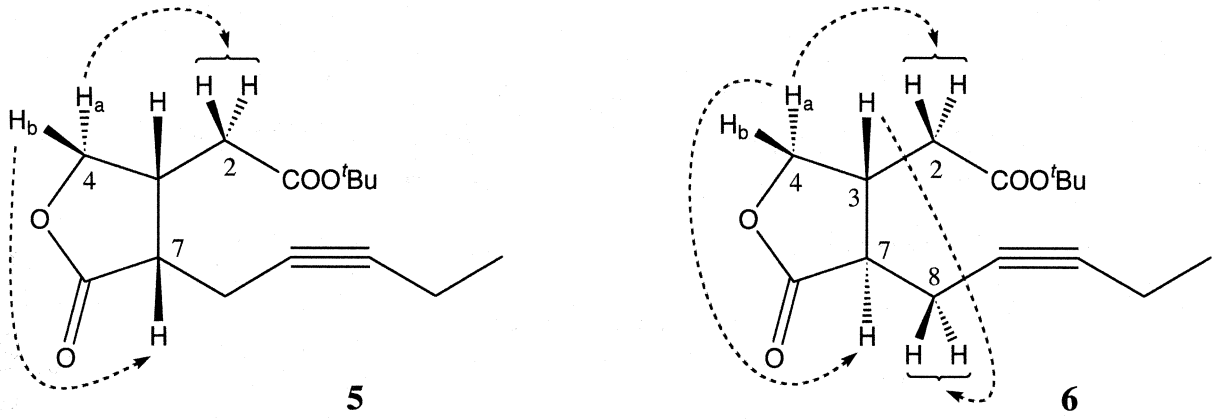


Fig. 2. Selected NOE Enhancement in **5** and **6**.

Experimental

General methods. ^{1}H- and ^{13}C-NMR spectra were recorded with a Jeol JNM-EX-270 spectrometer (^{1}H at 270 MHz; ^{13}C at 67.5 MHz) and a Brucker AM-500 spectrometer (^{1}H at 500 MHz; ^{13}C at 125 MHz). In the ^{1}H-NMR spectra, chemical shifts are reported as δ (ppm) values relative to the residual proton (δ 7.26 ppm) of $CDCl_3$. In the ^{13}C-NMR spectra, chemical shifts are reported as δ (ppm) values relative to the carbon signal (δ 77.0 ppm) of $CDCl_3$. IR spectra were measured with a Perkin Elmer System 2000 FT-IR spectrometer, and mass spectra were recorded with a Jeol JMS-AX500 or Jeol JMS-SX102A spectrometer. Column chromatography was carried out with silica gel 60 (spherical, 70–140 mesh ASTM; Kanto Chemical Co., Japan).

1-Bromo-2-pentyne. A mixture of 1-chloro-2-pentyne (10.0 g, 97.5 mmol) and lithium bromide monohydrate (61.3 g, 585 mmol) in DMF (200 ml) was stirred at 60°C for 3 days. The mixture was partitioned between Et_2O (400 ml) and water (600 ml). The organic layer was successively washed with water (300 ml × 2) and brine (100 ml), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure below 25°C. The crude product was distilled under reduced pressure to give 1-bromo-2-pentyne (7.35 g, 51%) as a colorless oil. Bp 42–45°C (12 mm Hg); IR ν_{max} (film) cm^{-1}: 2979, 2939, 2920, 2879, 2846, 2238, 1456, 1431, 1377, 1319, 1264, 1210, 1154, 1137, 1063, 1012, 958, 719, 691, 610; ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.13 (3H, t, J=7.3 Hz, *Me*), 2.25 (2H, tq, J=2.4, 7.3 Hz, CH_2Me), 3.91 (2H, t, J=2.4 Hz, BrCH_2); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 12.8, 13.6, 15.8, 74.6, 89.4; EI-MS m/z: 149 (15.6, MH$^+$ for ^{81}Br), 148 (16.3, M$^+$ for ^{81}Br), 147 (16.0, MH$^+$ for ^{79}Br), 146 (16.3, M$^+$ for ^{79}Br), 67 (100, $C_5H_7^+$); HR-MS m/z (M$^+$): calcd. for $C_5H_7^{79}Br$, 145.9731; found, 145.9701.

(2S,3S*)-3-(tert-Butoxycarbonylmethyl)-2-(2-pentynyl)-4-butanolide* (**5**) and *(2R*,3S*)-3-(tert-Butoxycarbonylmethyl)-2-(2-pentynyl)-4-butanolide* (**6**). *[A] Three-conponent coupling*: To a stirred solution of diisopropylamine (0.84 ml, 6.00 mmol) in dry THF (14 ml) at 0°C in an argon atmosphere was added dropwise an *n*-hexane solution of *n*-butyllithium (3.72 ml, 5.95 mmol as 1.6 M). The solution was stirred for 30 min at 0°C. To the resulting LDA solution at −78°C was added dropwise *tert*-butyl acetate (0.80 ml, 5.94 mmol), and the mixture was stirred for 30 min at −78°C. To the resulting lithium enolate solution at −78°C was added dropwise 2(5*H*)-furanone (0.42 ml, 5.92 mmol) and the mixture was stirred for 2 h at the same temperature. To the resulting lactone enolate solution at −78°C was added dropwise 1-bromo-2-pentyne (0.89 g, 6.05 mmol), and the mixture was gradually allowed to warm to room temperature while stirring over 5 h. The reaction mixture was quenched by adding sat. aq. NH_4Cl (20 ml) and extracted with EtOAc (30 ml × 3). The combined extracts were washed with brine (30 ml), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane:Et_2O = 3:1) to give **5** (24 mg, 2%) as a colorless oil and **6** (826 mg, 52%) as a colorless oil. *[B] Isomerization*: To an LDA solution (4.93 mmol) in dry THF (10 ml) prepared by the same method as that just described, a solution of **6** (596 mg, 2.24 mmol) in dry THF (4.0 ml) was added dropwise at −78°C in an argon atmosphere. The mixture was allowed to warm to room temperature and stirred for 30 min. To the resulting bis-enolate solution was added H_2O (2.0 ml). After partitioning the mixture between EtOAc (30 ml) and H_2O (30 ml), the organic layer was washed with brine (10 ml), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a crude mixture of **5** and **6**. This mixture was separated by silica gel column chromatography (*n*-hexane:Et_2O = 3:1) to give **5** (50 mg, 8.4%) and **6** (380 mg, 64%).

Data for **5**. IR ν_{max} (film) cm^{-1}: 2978, 2936, 2920, 2875, 2233, 1778, 1728, 1480, 1457, 1418, 1393, 1369, 1321, 1305, 1285, 1250, 1156, 1117, 1058, 1024, 994, 939, 847, 760; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.11 (3H, t, J=7.5 Hz, CH_2*Me*), 1.46 (9H, s, CO_2CMe_3), 2.16 (2H, tq, J=2.4, 7.5 Hz, C*H*$_2$Me), 2.35 (1H, dd, J=16.5, 9.6 Hz, C*H*HCO$_2$CMe$_3$), 2.38 (1H, m, C*H*HCC), 2.58 (1H, m, CH*H*CC), 2.66 (1H, dd, J=16.5, 5.0 Hz, CH*H*CO$_2$CMe$_3$), 2.86 (1H, dt, J=4.6, 9.6 Hz, C$_2$-*H*), 3.06 (1H, m, C$_3$-*H*), 4.19 (1H, dd, J=9.3, 4.2 Hz, OC*H*H), 4.38 (1H, dd, J=9.3, 8.3 Hz, OCH*H*); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 12.4, 14.0, 16.1, 28.1, 33.1, 34.9, 42.1, 75.1, 81.3, 81.4, 84.0, 170.6, 176.9; EI-MS m/z: 267 (0.87, MH^+), 251 (2.04, M^+-CH_3), 211 (72.9, $M^+-C_4H_7$), 210 (94.0, $M^+-C_4H_8$), 193 (42.1, $M^+-C_4H_9O$), 165 (14.4), 151 (13.2), 124 (87.1), 82 (39.0), 57 (100); HR-MS m/z (MH^+): calcd. for $C_{15}H_{23}O_4$, 267.1596; found, 267.1582.

Data for **6**. IR ν_{max} (film) cm^{-1}: 2978, 2935, 2919, 2875, 2233, 1770, 1732, 1480, 1456, 1429, 1393, 1368, 1354, 1283, 1252, 1225, 1156, 1074, 1019, 977, 946, 922, 846, 758; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.11 (3H, t, J=7.5 Hz, CH_2*Me*), 1.46 (9H, s, CO_2CMe_3), 2.16 (2H, tq, J=2.4, 7.5 Hz, C*H*$_2$Me), 2.38 (1H, dd, J=16.2, 9.6 Hz, C*H*HCO$_2$CMe$_3$), 2.40 (1H, ddd, J=3.6, 4.6, 6.4 Hz, C$_2$-*H*), 2.61 (2H, m, C*H*$_2$CC), 2.77 (1H, dd, J=4.8, 16.2 Hz, CH*H*CO$_2$CMe$_3$), 2.89 (1H, m, C$_3$-*H*), 3.92 (1H, t, J=9.1Hz, OC*H*H), 4.60 (1H, dd, J=9.1, 8.3 Hz, OCH*H*); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 12.4, 14.1, 19.1, 28.1, 36.3, 38.2, 43.9, 71.3, 74.6, 81.4, 84.7, 170.1, 176.8; EI-MS m/z: 267 (0.14, MH+), 251 (0.55, M^+-CH_3), 211 (13.0, $M^+-C_4H_7$), 210 (38.9, $M^+-C_4H_8$), 193 (27.1, $M^+-C_4H_9O$), 165 (4.70), 151 (9.60), 124 (58.4), 82 (28.0), 57 (100); HR-MS m/z (MH^+): calcd. for $C_{15}H_{23}O_4$, 267.1596; found, 267.1566.

(2S,3S*)-3-Carboxymethyl-2-(2-pentynyl)-4-butanolide* (**7**). To a solution of **5** (38.0 mg, 143 μmol) in CH_2Cl_2 (0.3 ml) was added TFA (0.1 ml) at room temperature. After being kept for 4 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$:MeOH=10:1) to give **7** (29.0 mg, 97%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 3400–2500 (br.), 2977, 2920, 2232, 1771, 1733, 1480, 1414, 1348, 1320, 1278, 1210, 1170, 1101, 1083, 1059, 1024, 993, 948, 920, 890, 825, 757; ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.10 (3H, t, J=7.4 Hz, CH_2*Me*), 2.13 (2H, tq, J=2.4, 7.5 Hz, C*H*$_2$Me), 2.20–2.72 (3H, m), 2.76–2.95 (2H, m), 3.10 (1H, m, C$_3$-*H*), 4.20 (1H, dd, J=9.4, 4.5 Hz, OC*H*H), 4.41 (1H, dd, J=9.4, 6.6 Hz, OCH*H*), 10.2 (1H, br. s, COO*H*); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 12.4, 14.0, 16.2, 31.7, 34.6, 42.0, 71.4, 74.9, 84.4, 177.0, 177.3; EI-MS m/z: 211 (11.2, MH^+), 210 (3.90, M^+), 195 (5.27, M^+-CH_3), 193 (2.24, M^+-OH), 165 (4.20, M^+-CO_2H), 151 (6.32), 124 (100), 82 (74.1); HR-MS m/z (MH^+): calcd. for $C_{11}H_{15}O_4$, 211.0970; found, 211.0956.

(2S,3S*)-3-Carboxymethyl-2-[(Z)-2-pentenyl]-4-butanolide* [*(3S*,7S*)-5-oxa-7-epi-jasmonic acid* (**3**)]. **7** (27.0 mg, 129 μmol) was hydrogenated in the presence of the Lindlar catalyst (15 mg) in EtOAc (3.0 ml) for 24 h. After filtering off the catalyst, the filtrate and washings were combined and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$:MeOH=10:1) to give **3** (27.3 mg, 100%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 3400–2500 (br.), 3010, 2967, 2934, 2876, 1771, 1713, 1482, 1412, 1379, 1302, 1208, 1166, 1119, 1058, 1022, 994, 941, 797; ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.97 (3H, t, J=7.3 Hz, CH_2*Me*), 2.07 (2H, quint., J=7.3 Hz, C*H*$_2$Me), 2.16–2.62 (4H, m), 2.76 (1H, m), 2.99 (1H, m, C$_3$-*H*), 4.13 (1H, dd, J=9.3, 4.2 Hz, OC*H*H), 4.35 (1H, dd, J=9.3, 8.3 Hz, OCH*H*), 5.30 (1H, m, vinyl-*H*), 5.51 (1H, m, vinyl-*H*), 10.24 (1H, br. s, COO*H*); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 14.0, 20.9, 23.4, 31.8, 34.8, 42.6, 70.9, 123.9, 134.7, 177.0, 177.7; EI-MS m/z: 213 (2.05, MH^+), 212 (4.57, M^+), 211 (16.6, M^+-H), 194 (7.07, M^+-H_2O), 167 (1.69, M^+-CO_2H), 153 (4.39), 144 (34.6), 126 (34.8), 85 (100); HR-MS m/z (MH^+): calcd. for $C_{11}H_{17}O_4$, 213.1127; found, 213.1149.

(2R,3S*)-3-Carboxymethyl-2-(2-pentynyl)-4-butanolide* (**8**). According to the same method as that described for **7**, **6** (380 mg, 1.43 mmol) was converted into **8** (282 mg, 94%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 3400–2500 (br.), 2978, 2920, 2236, 1770, 1730, 1481, 1431, 1413, 1350, 1320, 1285, 1204, 1168, 1110, 1077, 1020, 974, 925, 885, 817, 758; ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.01 (3H, t, J=7.5 Hz, CH_2*Me*), 2.06 (2H, tq, J=2.4, 7.5 Hz, C*H*$_2$Me), 2.30–2.63 (4H, m), 2.74–2.94 (2H, m), 3.87 (1H, t, J=8.9 Hz, OC*H*H), 4.54 (1H, dd, J=8.9, 8.1 Hz, OCH*H*), 11.2 (1H, br. s, COO*H*); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 12.3, 14.0, 19.1, 36.3, 36.5, 43.7, 71.2, 74.4, 84.9, 176.9, 177.3; EI-MS m/z: 211 (3.85, MH^+), 210 (0.96, M^+), 195 (3.24, M^+-CH_3), 193 (1.24, M^+-OH), 165 (2.61, M^+-CO_2H), 151 (9.14), 124 (100), 82 (70.0); HR-MS m/z (MH^+): calcd. for $C_{11}H_{15}O_4$, 211.0970; found, 211.0986.

(2R,3S*)-3-Carboxymethyl-2-[(Z)-2-pentenyl]-4-butanolide* [*(3S*,7R*)-5-oxa-jasmonic acid* (**4**)]. According to the same method as that described for **3**, **8** (282 mg, 1.34 mmol) was converted into **4** (284 mg, 100%) as a colorless oil. IR ν_{max} (film) cm^{-1}: 3400-2500 (br.), 3012, 2966, 2934, 2876, 1770, 1713, 1482, 1412, 1349, 1304, 1284, 1202, 1167, 1102, 1072, 1020, 997, 940, 920, 883, 798; ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.94 (3H, t, J=7.3 Hz, CH_2*Me*), 2.03

(2H, quint., $J=7.3$ Hz, CH_2Me), 2.30–2.80 (6H, m), 3.92 (1H, t, $J=9.1$ Hz, OC*H*H), 4.54 (1H, dd, $J=9.1$, 8.3 Hz, OCH*H*), 5.32 (1H, m, vinyl-*H*), 5.54 (1H, m, vinyl-*H*), 10.84 (1H, br. s, COO*H*); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 14.1, 20.6, 26.5, 36.4, 36.6, 44.4, 71.1, 123.3, 135.3, 176.5, 177.8; EI-MS *m/z*: 213 (1.83, MH^+), 212 (2.36, M^+), 211 (0.94, M^+-H), 194 (10.1, M^+-H_2O), 167 (1.56, M^+-CO_2H), 153 (5.02), 144 (55.6), 126 (52.4), 84 (100); HR-MS *m/z* (M^+): calcd. for $C_{11}H_{16}O_4$, 212.1048; found, 212.1060.

Acknowledgments

We are grateful to Mr. K. Watanabe and Dr. E. Fukushi in our faculty for measuring the MS data, and also to Dr. Y. Koda in our faculty for evaluating biological activities. We thank the Ministry of Education, Science and Culture (Japan) for grant-aid for scientific research, No. 11760082.

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