

Characterization of Acetylenes and Terpenoids Isolated from *Solidago altissima* L.

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Synopsis

Four acetylenes and three terpenoids were isolated from *Solidago altissima* L. and characterized by MS, ¹H-NMR and ¹³C-NMR spectroscopy as methyl (*Z*)-decaene-4,6,8-triynoate (*Z*-dehydromatricaria ester, **1**), methyl 10-[(*Z*)-2-methyl-2-butenoyloxy]-(2*Z*,8*Z*)-2,8-decadiene-4,6-dioate (**2**), (4*Z*)-2,4-decadiene-6,8-diyn-4-olide (*Z*-dehydromatricaria lactone, **3**), (4*E*)-2,4-decadiene-6,8-diyn-4-olide (*E*-dehydromatricaria lactone, **4**), 13*E*,7 α -acetoxyl kolavenic acid (solidagonic acid, **5**), kolavenol (**6**), and D:C-friedours-7-en-3 β -ol (ilexol, **7**). The polyacetylenes could be easily detected as yellowish brown spots on TLC plate following irradiation with blue black light for two to three minutes. The *Z* and *E* isomers of dehydromatricaria lactones were easily differentiated based on differences in melting points and chemical shifts of ¹H- and ¹³C-NMR spectroscopy. Bioassay of these compounds on the germination of lettuce seeds showed that compounds **1**, **2**, **3**, **4**, and **5** exhibited growth inhibitory activity, whereas compound **7** did not exhibit the activity. This study presents the first isolation of (*E*)-dehydromatricaria lactone from *Solidago altissima* L. in nature.

Introduction

As an approach to finding highly biofunctional natural molecules, we have been studying the characterization and structural determination of acetylenes and terpenoids in plants. In this report, structural characterization¹ and biological activities² of acetylenes and terpenoids, which were found in *Solidago altissima* L. are reviewed.

Acetylenes and terpenoids are common constituents of the tribe Astereceae (Compositae)³⁻⁵. Some acetylenes have biological activities such as antifungal⁶⁻⁸, allelopathic⁹, nematocidal¹⁰, and plant growth inhibitory¹¹⁻¹³ properties. Diterpenes exhibit insect antifeedant, antifungal, antibacterial, and antiviral activities⁹. One of the polyacetylenes, dehydromatricaria lactone was discovered in 1965 (Bohlmann et al.¹⁴) from *Anthemis brachycentros* F. Gay. Recently, Noda et al.¹⁵ reported that the *Z* isomer (**3**) of this lactone isolated from *Solidago altissima* L. and dehydromatricaria ester (**1**) strongly inhibited the growth of barnyard millet seedlings (*Panicum crus-galli* L. var. *frumentaceum* TRIN.).

We also found the *E* isomer (**4**) of the lactone in the same plant, *Solidago altissima* L., together with the *Z* isomer (**3**). We report here the characterization and a few information including the complete ¹H- and ¹³C-NMR assignments for the *Z* and *E* isomers of the lactone, which can serve for structural determination of related natural products. This paper also describes acetylenes and

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structural determination of related natural products. This paper also describes acetylenes and terpenoids found in the roots of *Solidago altissima* L., and their effect on the germination of lettuce seeds.

Experimental

Isolation of acetylenes and terpenoids

The fresh roots (290g) of *Solidago altissima* L. were chopped with a commercial blender, and extracted with 70% acetone-water (2 L) in the dark for one day. The 70% acetone-water extract was concentrated *in vacuo* to 80 mL at 38°C, and then extracted with ether and *n*-butanol, successively. The solvent-removed ether extract (1.53g) was chromatographed into 25 fractions over silica gel (Wako gel C-300, Wako Pure Chemical Industries Ltd.) with *n*-hexane-ethyl acetate (4 : 1, v/v) as an eluent. Three fractions (Frs. 3, 6, and 9) on the TLC plate (silica gel 60F₂₅₄, Merck) were irradiated for a few minutes by blue black light to generate yellowish brown spots. Each of these fractions were rechromatographed over silica gel (Wako gel C-300) with benzene as an eluent, and 93 mg of methyl (*Z*)-2-decaene-4,6,8-trienoate (dehydromatricaria ether, **1**) from fraction 3, 78 mg of methyl 10-[(*Z*)-2-methyl-2-butenyloxy]-(2*Z*,8*Z*)-2,8-decadiene-4,6-dienoate (**2**) from fraction 6, 33 mg of (4*Z*)-2,4-decadiene-6,8-diyne-4-olide ((*Z*)-dehydromatricaria lactone, **3**) from fraction 9, and 8 mg of (4*E*)-2,4-decadiene-6,8-diyne-4-olide ((*E*)-dehydromatricaria lactone, **4**) from fraction 9 were isolated, respectively.

Analytical instruments

Melting points (mp) were measured on Yanagimoto micro melting point apparatus. Optical rotations were measured with a JASCO DIP-1000. UV and IR spectra were recorded on a Shimadzu UV-160A spectrometer and a Perkin-Elmer 1760-X infrared fourier transform spectrometer, respectively. MS spectra were obtained with JEOL JMS-HX 100 and JMA-DA 5000 spectrometers.

¹H-NMR (500 MHz or 270 MHz), ¹³C-NMR (125.7 MHz or 67.5 MHz) and 2D NMR spectra were obtained by JEOL GSX-500 or JEOL EX-270 spectrometers, in a 5 mm ϕ tube at various temperatures. A 30 mg of **3** was used for 2D NMR (COLOC). Chemical shifts are reported as parts per million (ppm) downfield from internal tetramethylsilane as the standard.

(Z)-Dehydromatricaria lactone (3). IR spectrum was in accordance with lit. values^{14), 15)}. EI-MS 70 eV *m/z* (rel. int.): 158 ([M]⁺, 100), 130 (11), 102 (29), 82 (15), 76 (38), 75 (11), 74 (13), 61 (15), 54 (8), 50 (20), 44 (30), 40 (28). HR-MS found: 158.0381, Calcd. for C₁₀H₆O₂: 158.0368. ¹H-NMR (CDCl₃)(see also refs [14, 15, 17]): δ 2.05 (3H, d, *J*=1 Hz, Me-10), 5.33 (1H, br. s, H-5), 6.29 (1H, dd, *J*_{2,5}=0.8 and *J*_{2,3}=5.5 Hz, H-2), 7.41 (1H, *J*_{2,3}=5.5 Hz, H-3). ¹³C-NMR (CDCl₃): Table 1.

(E)-Dehydromatricaria lactone (4). IR spectrum was in accordance with lit. values^{17), 19)}. EI-MS 70 eV *m/z*: 158 (M⁺, 100), 130 (13), 102 (29), 82 (15), 76 (24), 75 (9), 74 (13), 61 (3), 54 (8), 50 (18), 44 (5), 40 (4). HR-MS found: 158.0380, Calcd. for C₁₀H₆O₂: 158.0368. ¹H-NMR (CDCl₃)(see also refs [17]): δ 1.98 (3H, d, *J*=1 Hz, Me-10), 5.67 (1H, br. s, H-5), 6.26 (1H, dd, *J*_{2,5}=1.8 and *J*_{2,3}=5.5 Hz, H-2), 7.67 (1H, *J*_{2,3}=5.5 Hz, H-3). ¹³C-NMR (CDCl₃): Table 1.

13E,7 α -acetoxyl kolavenic acid (solidagonic acid, 5). [α]_D²⁰ -76.15° (*c*=0.13, CHCl₃). EI-MS 70 eV *m/z* (rel. int.): 362 (M⁺, 2), 344 (18), 302 (29), 287 (25), 247 (31), 189 (43), 187 (100), 173 (28), 159 (26), 147 (25), 145 (24), 133 (36), 119 (70), 107 (44), 95 (47), 81 (23), 69 (19), 55 (22), 43 (49). IR (NaCl) ν max: 3500-2400, 3023, 2947, 1734, 1693, 1641, 1435, 1392, 1377, 1251, 1168, 1021 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃): δ 0.89 (3H, d, *J*=7Hz, H-17), 0.98 (3H, s, H-18), 1.16 (3H, s, H-19), 1.20-1.60 (8H, m), 1.54 (3H, br. s, H-20), 1.90-2.10 (4H, m), 2.02 (3H, s, Ac), 2.14 (3H,

s, H-16), 5.09 (1H, dd, $J=3.5, 7\text{Hz}$, H-7), 5.11 (1H, br. s, H-3), 5.68 (1H, br. s, H-14) ppm. $^{13}\text{C-NMR}$ (67.5 MHz, CDCl_3): δ 12.04 (q, C-17), 17.86 (t, C-11), 18.03 (q, C-20), 19.46 (q, C-16), 19.59 (q, C-18), 21.37 (q, C-19), 21.46 (q, C-2'), 26.62 (t, C-2), 35.01 (t, C-12), 37.18 (s, C-9), 37.29 (t, C-1), 38.13 (d, C-8), 38.35 (s, C-5), 39.82 (t, C-6), 46.24 (d, C-10), 75.19 (d, C-7), 114.93 (d, C-14), 120.09 (d, C-3), 144.40 (s, C-4), 163.83 (s, C-13), 170.82 (s, C-1'), 171.68 (s, C-15) ppm.

kolavenol (6). $[\alpha]_{\text{D}}^{20} -42.89^\circ$ ($c=0.14$, CHCl_3). *EL-MS* 70 eV m/z (rel. int.): 290 (M^+ , 36), 272 (21), 257 (20), 243 (5), 222 (4), 191 (32), 189 (100), 175 (24), 161 (16), 147 (16), 133 (21), 120 (65), 107 (62), 95 (92), 81 (35), 69 (25), 55 (33), 41 (33). *IR* (NaCl) ν max: 3600-3200, 2926, 2856, 1742, 1669, 1647, 1456, 1382, 1240, 1171, 1001 cm^{-1} . $^1\text{H-NMR}$ (270 MHz, CDCl_3): δ 0.69 (3H, s, H-18), 0.78 (3H, d, $J=7\text{Hz}$, H-17), 0.97 (3H, s, H-19), 1.25-1.55 (10H, m), 1.56 (3H, br. s, H-20), 1.66 (3H, s, H-16), 1.73-2.00 (4H, m), 4.13 (2H, d, $J=7\text{Hz}$, H-15), 5.17 (1H, br. s, H-3), 5.37 (1H, q, $J=7\text{Hz}$, H-14) ppm.

Bioassay with lettuce seeds

2 mL of each compounds at the requisite concentration in an aqueous solution containing tween 80 (100 ppm) was absorbed on filter paper in Petri dish. Ten germinated seeds of lettuce were placed on each filter paper in Petri dish and incubated at 25°C for 5 d. The relative germination ratio was calculated based on germination of ten seeds in Petri dish which contained only aqueous tween 80 without any other additives (control).

Results and Discussion

A crude mixture of acetylenes and terpenoids was obtained from a 70% acetone-water extract of the fresh roots (290 g) of *Solidago altissima* L. Four acetylenes and three terpenoids (Fig. 1) were purified by column chromatography on silica gel. The yields of isolated compounds are **1**: 93 mg, **2**: 78 mg, **3**: 33 mg, **4**: 8 mg, **5**: 26 mg, **6**: 4 mg, and **7**: 31 mg.

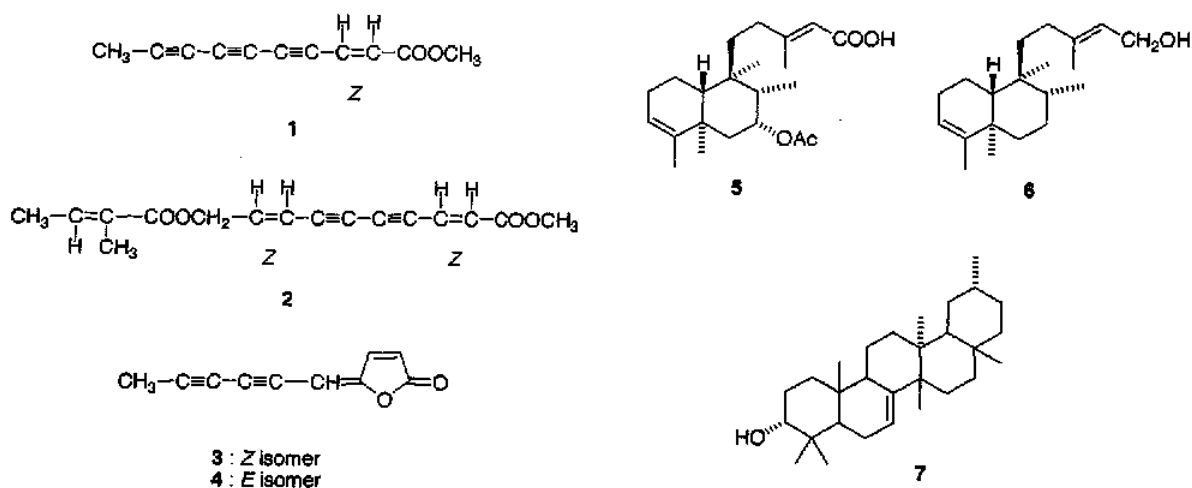


Fig. 1. Structures of acetylenes and terpenoids isolated from *Solidago altissima* L.

Table 1. ^{13}C -NMR data for **1** - **4** (δ in CDCl_3 , 125.7 MHz or 67.5 MHz)

Carbon No.	1	2	3	4
1	164.46 s	164.64 s	168.23 s	168.99 s
2	121.47 d	121.78 d	121.06 d	121.96 d
3	132.47 d	131.30 d	142.32 d	140.14 d
4	85.99 s*	81.30 s*	158.87 s	160.36 s
5	64.69 s*	81.30 s*	93.08 d	94.08 d
6	72.08 s*	78.88 s*	67.84 s	67.84 s
7	70.91 s*	84.87 s*	86.49 s	84.17 s
8	58.26 s*	111.07 d	64.44 s	64.28 s
9	80.86 s*	138.74 d	85.75 s	83.33 s
10	4.71 q	61.96 t	4.85 q	4.80 q
COOMe	51.66 q	51.75 q		
1'		167.53 s		
2'		127.35 s		
3'		141.37 d		
4'		15.91 q		
5'		20.52 q		

Signal assignments were based on ^{13}C - ^1H COSY, COLOC, and DEPT experiments.

*The assignments may be interchangeable.

The EI-MS and ^1H -NMR spectral data for **1** and **2** agreed with those of authentic samples of methyl (*Z*)-2-decane-4,6,8-triynoate (dehydromatricaria ester) and methyl 10-[(*Z*)-2-methyl-2-butenoyloxy]-(2*Z*,8*Z*)-2,8-decadiene-4,6-diyanoate, which had been previously isolated from *Solidago altissima* L. by Ichihara *et al.*¹⁶⁾. The ^{13}C -NMR and DEPT data of **1** and **2** are listed in Table 1.

Compound **3** was colorless crystals, became grayish blue at its mp 84°C, decomposed at 102°C, and showed a specific rotation of -3.60° ($c=0.12$, CHCl_3). The molecular formula of **3** was found to be $\text{C}_{10}\text{H}_{16}\text{O}_2$ by HR-MS, which showed a molecular ion peak at m/z 158.0368. The *B/E* constant linked scan spectrum of molecular ion (m/z 158) in **3** produced fragment ions at m/z 130, 102, and 82. The *B/E* constant linked scan spectrum of fragment ion at m/z 102 gave further peaks at m/z 76 and 52, but did not give a peak at m/z 82. Thus, fragment ion at m/z 82 is assigned to unsaturated-lactone ring. The IR spectrum of **3** exhibited a sharp absorption band at 2226 cm^{-1} , interpreted as a asymmetrically disubstituted $\text{C}\equiv\text{C}$ stretching frequency. Two very strong absorption bands at 1774 and 1744 cm^{-1} indicated the presence of an unsaturated-lactone ring. The ^1H -NMR spectrum of **3** indicated the presence of a methyl group (doublet at δ 2.05, $J=1$ Hz) and three olefinic protons at δ 5.33 (br. s), 6.29 ($J=0.8$, 5.5 Hz), and 7.41 ($J=5.5$ Hz). The ^1H -NMR spectrum of **3** closely resembled that of (*Z*)-dehydromatricaria lactone^{15), 17)}. The stereochemistry of the 4,5-double bond was verified by NOE difference experiment. Irradiation of H-5 affected H-3 showing that H-5 and H-3 reside on the same side of the diene. Upon irradiation of H-3, clear NOEs of the H-5 and H-2 signals were also observed, thus confirming the previously assigned stereochemistry of the 4,5-double bond^{14), 15), 18)}. The ^{13}C -NMR (Table 1) and DEPT showed ten carbon signals comprised of one carbonyl carbon signal, one carbonyl or olefinic carbon signal attached to an oxygen atom, three olefinic carbon signals, four acetylenic or carbon signals attached to an oxygen atom, and one methyl carbon signal¹⁸⁾. In the COLOC spectrum, long range couplings were observed as shown in Fig. 2, confirming the connection from C-1 to C-10. Based on the foregoing evidence, the structure of **3** was identified to be (*Z*)-dehydromatricaria lactone,

which had been previously isolated from *Solidago altissima* L. by Ichihara *et al.*¹⁵⁾.

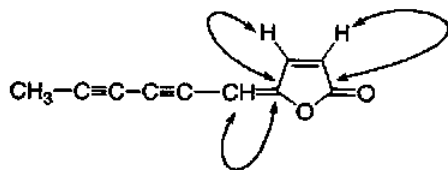


Fig. 2. Correlation peak in **3** by COLOC.

Compound **4** was colorless crystals, mp 99 - 101 °C, and showed a specific rotation of -54.76° ($c=0.03$, CHCl_3). The molecular formula of **4** was found to be $\text{C}_{10}\text{H}_6\text{O}_2$ by HR-MS, which showed a molecular ion peak also at m/z 158.0368. The B/E constant linked scan analyses of **4** gave similar results as those of compound **3**. The IR spectrum of **4** was in accordance with literature values^{17), 19)}. The $^1\text{H-NMR}$ spectrum of **4** indicated the presence of a methyl group at δ 1.98 (d, $J=1$ Hz) and three olefinic protons at δ 5.67 (br. s), 6.26 ($J=1.8, 5.5$ Hz), and 7.67 ($J=0.8, 5.5$ Hz). This $^1\text{H-NMR}$ result is in agreement with the recent findings of Lam and co-workers¹⁷⁾ who produced (*E*)-dehydromatricaria lactone by oxidation of 2,4-hexadiynyliden-1,6-dioxaspiro-[4.4]nona-2,8-dien-4-ol with activated MnO_2 . Thus compound **4** was identified as a new natural product. The stereochemistry of the 4,5-double bond was verified by NOE difference experiment. Irradiation of H-5 was no affect H-3 showing that H-5 and H-3 reside on the different side of the diene. Upon irradiation of H-3, clear NOE of the H-2 signal was observed. Thus the stereochemistry of the 4,5-double bond was confirmed *E* isomer. The $^{13}\text{C-NMR}$ and DEPT data of **4** are also listed in Table 1. Based on the evidence, the structure of **4** was determined to be (*E*)-dehydromatricaria lactone, a compound found for the first time in *Solidago altissima* L.

Compound **5**, a colorless crystal, had mp 143-144 °C, and showed a specific rotation of -76.15° ($c=0.13$, CHCl_3). The molecular weight of **5** was found to be 362 by EI-MS. The IR spectrum of **5** indicated the presence of an ester group at 1734 and 1251 cm^{-1} , and an α, β b-unsaturated acid at 3500-2400, 1693, and 1641 cm^{-1} . The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra data of **5** are identical with those of authentic sample of 13*E,7* α -acetoxyl kolavenic acid (solidagonic acid)²⁰⁾, which had been previously isolated from *Solidago altissima* L. as a bitter component by Kusumoto *et al.*²¹⁾.

Compound **6** was a colorless oil, and showed a specific rotation of -42.89° ($c=0.14$, CHCl_3). The molecular weight of **6** was found to be 290 by EI-MS. The IR spectrum of **6** indicated the presence of a primary alcohol at 3600-3200 and 1001 cm^{-1} . The $^1\text{H-NMR}$ spectral data for **6** agreed with that of authentic sample of kolavenol²⁰⁾, which had been previously isolated from *Hardwickia pinnata* by Misra *et al.*²²⁾.

Compound **7**, a white crystal, had mp 207-208 °C, and showed a specific rotation of -0.81° ($c=0.14$, CHCl_3). The molecular weight of **7** was found to be 426 by EI-MS. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectral data of **7** were identical with those of authentic sample of D:C-friedours-7-en-3 β -ol (ilexol), which had been previously isolated from *Solidago altissima* L. by Iseda²³⁾.

Thus, four acetylenes and three terpenoids have now been successfully isolated from the roots of *Solidago altissima* L.. Since it had been known that acetylenes had growth inhibitory activity for rice^{9, 12)} and barnyard millet seedings (*Panicum crusgalli* L. var. *frumentaceum* TRIN.)^{11, 13)}, compounds **1, 2, 3, 4, 5**, and **7** obtained in this study were subjected to bioassay on the germination of lettuce seeds (*Lactuca sativa* L.). As a result, compounds **1, 2, 3, 4**, and **5** exhibited growth inhibitory activity, whereas compound **7** did not exhibit the activity, as shown in Table 2. Compounds **3** and **4** which are geometric isomers showed almost the same activity. Moreover, the growth inhibitory

activities of compounds **3** and **4** for lettuce seeds were stronger than that of compound **1**. The growth inhibitory activities of compounds **4** and **5** are reported for the first time in this study.

Table 2. Effect of Compounds on the Germination of Lettuce seeds

Compound	Length of root (%)	Length of hypocotyl (%)	Length of cotyledon (%)	Weight (%)
Z-dehydromatricaria ester (1)				
1000 ppm	0	0	0	0
500 ppm	43.0	27.3	50.5	40.9
100 ppm	55.9	29.6	52.7	41.8
10-[(Z)-2-methyl-2-butenyloxy]- (2Z,8Z)-2,8-decadiene-4,6-dienoate (2)				
1000 ppm	73.4	48.2	75.5	63.3
500 ppm	113.1	62.3	91.8	79.1
100 ppm	143.7	67.5	90.8	95.5
Z-dehydromatricaria lactone (3)				
1000 ppm	0	0	0	0
500 ppm	0	0	0	0
100 ppm	1.3	6.9	64.2	37.5
E-dehydromatricaria lactone (4)				
1000 ppm	0	0	0	0
500 ppm	0	0	0	0
100 ppm	8.4	12.3	42.8	48.3
13E-7α-acetoxyl kolavenic acid (5)				
1000 ppm	74.7	58.0	73.1	69.3
500 ppm	78.0	51.2	81.7	80.0
100 ppm	85.8	72.8	88.2	82.0
D:C-friedours-7-en-3β-ol (7)				
1000 ppm	88.7	126.5	105.5	78.3
500 ppm	93.7	145.8	105.4	87.8
100 ppm	101.6	141.4	117.1	109.1
Control	100.0	100.0	100.0	100.0

Conclusions

Characterization of polyacetylenes including the *Z* and *E* isomers of dehydromatricaria lactones is summarized as follows. 1) Polyacetylenes could be easily detected as yellowish brown spots on TLC plate following irradiation with blue black light for two to three minutes. 2) The *Z* and *E* isomers of dehydromatricaria lactones were easily differentiated based on the differences in melting points and chemical shifts of ^1H - and ^{13}C -NMR spectroscopy.

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Solidago altissima L. から単離されたアセチレン類およびテルペン類の特性

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摘 要

Solidago altissima L. から単離した4種のアセチレンおよび3種のテルペン, methyl (Z)-decaene-4,6,8-triynoate (Z-dehydromatricaria ester, **1**), methyl 10-[(Z)-2-methyl-2-butenoyloxy]-(2Z,8Z)-2,8-decadiene-4,6-dioate (**2**), (4Z)-2,4-decadiene-6,8-diyn-4-olide (Z-dehydromatricaria lactone, **3**), (4E)-2,4-decadiene-6,8-diyn-4-olide (E-dehydromatricaria lactone, **4**), 13E,7 α -acetoxyl kolavenic acid (solidagonic acid, **5**), kolavenol (**6**), D:C-friedours-7-en-3 β -ol (ilexol, **7**) について発芽に対する影響をレタスを用いて検討した。その

結果, 化合物 **1**, **2**, **3**, **4** および **5** は生長阻害作用を示し, 化合物 **7** は活性を示さなかった。ポリアセチレンは, TLC上で2, 3分ブルーブラックライトの照射によって黄茶色のスポットとして, 容易に確認できた。Dehydromatricaria lactones のZ体およびE体は, 融点の違い, また, ¹H- および¹³C-NMRのケミカルシフトの違いによって, 容易に確認できた。なお, 単離した成分のうち, (E)-dehydromatricaria lactone (**4**) は天然物として *Solidago altissima* L. から初めて見出した成分である。