

Lignans and Polyacetylenes from *Bupleurum acutifolium*

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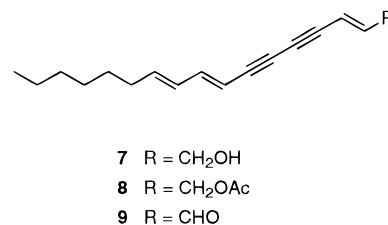
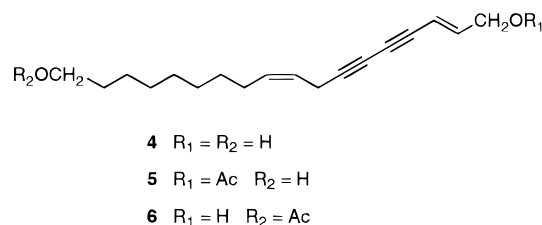
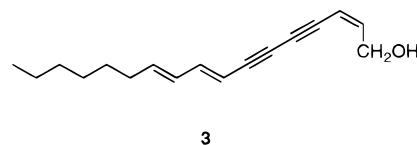
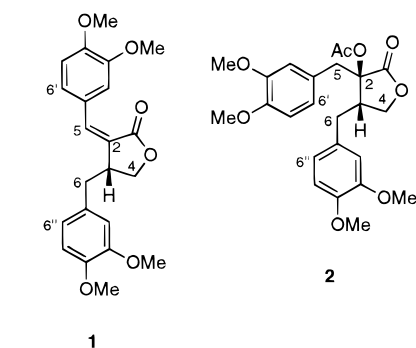
Two new lignans (*R,Z*)-3-(3,4-dimethoxybenzyl)-2-(3,4-dimethoxybenzylidene)- γ -butyrolactone (**1**) and (2*R*,3*S*)-2-acetoxy-2,3-bis(3,4-dimethoxybenzyl)- γ -butyrolactone (**2**), and four new polyacetylenes, (2*Z*,8*E*,10*E*)-heptadeca-2,8,10-triene-4,6-diyn-1-ol (**3**), (2*E*,9*Z*)-octadeca-2,9-diene-4,6-diyn-1,18-diol (**4**), (2*E*,9*Z*)-18-hydroxy-octadeca-2,9-diene-4,6-diyn-1-yl acetate (**5**), and (2*E*,9*Z*)-1-hydroxy-octadeca-2,9-diene-4,6-diyn-18-yl acetate (**6**), were isolated and identified from the hexane extract of aerial parts of *Bupleurum acutifolium* Boiss. Their structures were elucidated by NMR and MS analyses.

As part of our research into *Bupleurum* species,^{1,2} we have studied *Bupleurum acutifolium* Boiss. (*Umbelliferae*), a perennial plant that grows in the South of Spain. This paper describes the isolation and the identification of six new natural products, two lignans (**1**, **2**) and four polyacetylenes (**3–6**), from hexane extract of the aerial parts of this plant. Compounds **4–6** are the first polyacetylenes with a skeleton of eighteen carbon atoms isolated from the *Bupleurum* genus.

Results and Discussion

Compound **1** had molecular formula C₂₂H₂₄O₆ (HRMS). Its IR spectrum showed α,β -unsaturated γ -lactone (1740 cm⁻¹), olefinic double bond (1629 cm⁻¹), and aromatic ring (1595 and 1514 cm⁻¹) absorptions. The ¹H NMR spectrum showed signals of an 2,3-disubstituted γ -lactone moiety δ 3.31 (m, H-3), 4.13 (dd, H-4 α), 4.34 (dd, H-4 β), and of an olefinic proton δ 6.56 (d, H-5). The ¹H NMR spectrum also had signals corresponding to six benzene protons characteristic of two 1,2,4-trisubstituted aromatic rings, four methoxy groups and two benzylic protons. Two-dimensional NMR experiments were carried out (HMQC and HMBC) and they established that **1** was a 3-(3,4-dimethoxybenzyl)-2-(3,4-dimethoxybenzylidene)- γ -butyrolactone. The *Z* stereochemistry of the double bond C-3/C-5 was established on the basis of strong deshielding experienced by H-2' (δ 8.09) due to the proximity of the carbonyl group, similar to other lignans with a *Z* stereochemistry for that double bond.³ The negative specific rotation of **1** was similar to that of related lignans^{3–5} and allowed us to assign the absolute configuration of C-3 as *R*.⁵ Compound **1** is the 4',4''-dimethoxy derivative of salicifoline, isolated from *Bupleurum salicifolium*.⁶

Compound **2** had molecular formula C₂₄H₂₈O₈ (HRMS) and negative specific rotation. The IR, ¹H, and ¹³C NMR spectra showed the presence of a 2,3-disubstituted γ -lactone moiety, two 3,4-dimethoxybenzyl groups, and an acetoxy group. Connectivities among the different moieties were determined on the basis of two-dimensional experiments (DQF-COSY, HETCOR, and HMBC), establishing for **2** a structure of 2-acetoxy-2,3-bis(3,4-dimethoxybenzyl)- γ -butyrolactone. The *cis* orientation between H-3 and the acetate group was determined on the basis of the chemical



shift of H-3 (δ 3.64).^{7,8} This *cis* stereochemistry was confirmed by correlations between H-5a and H-6a, and H-5b and H-6a observed in its NOESY spectrum. The absolute configuration of **2** was established as 2*R*,3*S*.⁶

Compound **3** had molecular formula C₁₇H₂₂O (HRMS) and its IR spectrum contained hydroxyl (3406 cm⁻¹), triple bond (2198 cm⁻¹), and olefinic double bond (1673 and 1632 cm⁻¹) absorptions. These data together with the NMR were very similar to those of **7**, which led to the conclusion that they were stereoisomers. The stereochemistry change was

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located about the double bond C-2/C-3, which had a Z stereochemistry ($J_{2,3} = 10.6$ Hz). This stereochemistry was confirmed by the shielding experienced by C-1 and C-4 (δ C-1, 60.9 vs 62.2 for 7; C-4, 65.8 vs 81.7 for 7) in the ^{13}C NMR spectrum.

Compound 4 had molecular formula $\text{C}_{18}\text{H}_{26}\text{O}_2$ (HRMS). Its IR spectrum showed hydroxyl (3385 cm^{-1}), triple bond (2233 cm^{-1}), and double bond (1671 and 1630 cm^{-1}) absorptions. ^1H NMR and ^{13}C NMR signals were unequivocally assigned by two-dimensional experiments (DQF-COSY, HMQC, and HMBC). Comparison of ^1H NMR spectra of 4 and 7 allowed us to identify the $\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$ moiety (δ 6.35, dt, H-2; 5.76, da, H-3; 4.21, dd, H-1) in the spectrum of 4 with the same stereochemistry about the double bond ($J_{2,3} = 15.9$ Hz). In the ^1H NMR spectrum, a triplet at δ 3.62 ($J = 6.7$ Hz) was assigned to a methylene group linked to a hydroxyl group and adjacent to a methylene group; two signals at δ 5.49 and 5.38 were characteristic of two olefinic protons linked to methylene group and with Z stereochemistry; a doublet at δ 3.04 was attributed to a methylene adjacent to a double bond and to a triple bond and three signals at δ 2.02, 1.55, and 1.29 corresponding to seven contiguous methylene groups were also observed. In the ^{13}C NMR spectrum, four quaternary carbon signals between δ 82.5 and 64.9, characteristic of acetylene carbons, were observed. Thus, the structure of 4 was established as (2*E*,9*Z*)-octadeca-2,9-diene-4,6-diyne-1,18-diol.

Compounds 5 and 6 both had molecular formula $\text{C}_{20}\text{H}_{28}\text{O}_3$ (HRMS) indicating that they were isomers. Their IR and NMR spectra were very similar to those of 4, with the difference being the presence of an acetate group in both compounds. The location of the acetate group was made on the basis of the value of the chemical shift of H-1 and H-18 in the ^1H NMR spectra. Thus, in the compound 5, the acetate group was placed at C-6 due to deshielding experienced by the signal corresponding to H-1 (δ 4.60 vs 4.21 for 4). In compound 6, the acetate group was placed at C-18 on the basis of deshielding experienced by the signal due to H-18 (δ 4.03 vs 3.62 for 4).

Polyacetylenes 7–9 were previously isolated from *Bupleurum ranunculoides* and *Opopanax chironium* Kch. by Bohlmann et al.,^{9,10} but they published only partial ^1H NMR and no ^{13}C NMR data. Here, we report both the ^1H and ^{13}C NMR data, and unequivocal assignments were made using two-dimensional experiments (DQF-COSY, HETCOR, and HMBC).

Experimental Section

General Experimental Procedures. Optical rotations were measured on a 141 Perkin-Elmer polarimeter. IR spectra were recorded on a 983G Perkin-Elmer spectrometer. High-resolution MS were determined on an Autospec-Q VG-Analytical (FISONS) mass spectrometer and low-resolution MS were determined on a 5988A Hewlett-Packard mass spectrometer. NMR spectra were recorded on Bruker ARX 400 or Bruker AMX 300 spectrometers (δ values given in ppm relative to internal TMS and J values in Hz). HPLC was performed on a Spherisorb ODS-2 column (250×10 mm) eluting with $\text{MeOH}-\text{H}_2\text{O}$ 85:15. Column chromatography was carried out using silica gel 60 Chromagel (35–70 microns), eluting with mixtures of hexane/*tert*-butylmethyl ether, *tert*-butylmethyl ether/*MeOH* of increasing polarity. Analytical TLC was performed on layers of silica gel Merck 60G 0.25 mm thick, using a 7% phosphomolybdic acid solution (EtOH) to visualize the spots.

Plant Material. *B. acutifolium* Boiss. was collected in Sierra Bermeja (Málaga, Spain) in May 1995 and identified by Dr. J. Molero, Profesor Titular of the Department of

Vegetable Biology, University of Granada. A voucher specimen (MGC 21268) is available for inspection at the herbarium of the Faculty of Science of the University of Málaga.

Extraction and Isolation. Air-dried and powdered aerial parts (2.5 kg) of *B. acutifolium* Boiss. were extracted in a Soxhlet with hexane (12h) and subsequently with EtOH (12h). From hexane extract (88.3 g), fatty acids (36.8 g) were removed by precipitation in MeOH at low temperature. The defatted hexane extract (51.5 g) was column chromatographed, affording the sesquiterpenes γ -muurolene, α -muurolene, α -humulene, α -calcorene, γ -calcorene, *trans*-calamenene, δ -cadinene, γ -cadinene, β -caryophyllene, α -copaene, ylangene, plus caryophyllene oxide, α -humulene oxide (292 mg), squalene (68 mg), compound 8 (607 mg), lupeol¹¹ (20 mg), compound 9 (24 mg), compound 7 (2544 mg), compound 3 (10 mg), compound 5 (348 mg), compound 6 (622 mg), ferulic acid¹² (62 mg), chinensin⁶ (300 mg), compound 4 (266 mg), compound 1 (216 mg), and compound 2 (83 mg). The known compounds were identified by direct comparisons with standards or with literature data.

(*R,Z*)-3-(3,4-Dimethoxybenzyl)-2-(3,4-dimethoxybenzylidene)- γ -butyrolactone (1): crystalline solid (Bu^tOMe); mp 120°C ; $[\alpha]_D^{25} -227^\circ$ (c 1, CHCl_3); IR (film) ν_{max} 2999, 2937, 2837, 1740, 1629, 1595, 1514, 1463, 1327, 1271, 1239, 1175, 1145, 1089, 1026, 853, 807 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.09 (1H, d, $J = 2.0$ Hz, H-2'), 7.14 (1H, dd, $J_1 = 2.0$ Hz, $J_2 = 8.3$ Hz, H-6'), 6.82 (2H, d, $J = 8.3$ Hz, H-5', H-5''), 6.73 (1H, dd, $J_1 = 1.9$ Hz, $J_2 = 8.3$ Hz, H-6''), 6.69 (1H, d, $J = 1.9$ Hz, H-2''), 6.56 (1H, d, $J = 1.5$ Hz, H-5), 4.34 (1H, dd, $J_1 = 7.3$ Hz, $J_2 = 9.1$ Hz, H-4 β), 4.13 (1H, dd, $J_1 = 3.6$ Hz, $J_2 = 9.1$ Hz, H-4 α), 3.93 (3H, s, 3'-OMe), 3.90 (3H, s, 4'-OMe), 3.87 (3H, s, 4'-OMe), 3.82 (3H, s, 3''-OMe), 3.31 (1H, m, H-3), 2.94 (1H, dd, $J_1 = 7.1$ Hz, $J_2 = 13.7$ Hz, H-6b), 2.83 (1H, dd, $J_1 = 8.5$ Hz, $J_2 = 13.7$ Hz, H-6a); ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.4 (s, C-1), 150.6 (s, C-4'), 149.1 (s, C-3'), 148.5 (s, C-4''), 148.1 (s, C-3''), 140.9 (d, C-5), 130.4 (s, C-1'), 126.9 (s, C-2), 125.8 (d, C-6'), 124.7 (s, C-1'), 121.3 (d, C-6''), 113.7 (d, C-2'), 112.6 (d, C-2''), 111.5 (d, C-5'), 110.5 (d, C-5''), 70.1 (t, C-4), 56.9 (q, 3'-OMe, 3''-OMe), 56.0 (q, 4'-OMe, 4''-OMe), 44.6 (d, C-3), 40.8 (t, C-6); HRFABMS m/z 407.1469 (calcd for $\text{C}_{22}\text{H}_{24}\text{O}_6\text{Na}$, 407.1471).

(2*R,3S*)-2-Acetoxy-2,3-bis(3,4-dimethoxybenzyl)- γ -butyrolactone (2): white amorphous powder; $[\alpha]_D^{25} -19.3^\circ$ (c 1, CHCl_3); IR (film) ν_{max} 2938, 1786, 1740, 1591, 1516, 1466, 1368, 1259, 1238, 1157, 1079, 1028, 813 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 6.84 (1H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.2$ Hz, H-6'), 6.81 (1H, d, $J = 1.8$ Hz, H-2'), 6.79 (1H, d, $J = 8.2$ Hz, H-5'), 6.78 (1H, d, $J = 8.2$ Hz, H-5''), 6.65 (1H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.2$ Hz, H-6''), 6.60 (1H, d, $J = 1.8$ Hz, H-2''), 4.22 (1H, t, $J = 7.5$ Hz, H-4 β), 3.85 (9H, s, 3'-OMe, 3''-OMe, 4'-OMe), 3.84 (3H, s, 4'-OMe), 3.64 (2H, m, H-3, H-4 α), 3.25 (1H, d, $J = 14.3$ Hz, H-5b), 3.06 (1H, d, $J = 14.3$ Hz, H-5a), 3.03 (1H, dd, $J_1 = 5.6$ Hz, $J_2 = 13.7$ Hz, H-6b), 2.77 (1H, dd, $J_1 = 9.5$ Hz, $J_2 = 13.7$ Hz, H-6a), 2.04 (3H, s, COCH_3); ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.1 (s, C-1), 169.2 (s, COCH_3), 149.3 (s, C-4'), 148.6 (s, C-3'), 148.5 (s, C-3''), 148.1 (s, C-4''), 130.0 (s, C-1'), 125.3 (s, C-1'), 123.0 (d, C-6'), 120.4 (d, C-6''), 113.9 (d, C-2'), 111.6 (d, C-2''), C-5''), 110.9 (d, C-5'), 81.6 (s, C-2), 69.2 (t, C-4), 56.0 (q, 3'-OMe, 3''-OMe), 55.9^a (q, 4''-OMe), 55.8^a (q, 4'-OMe), 42.8 (d, C-3), 37.2 (t, C-5), 32.0 (t, C-6), 21.2 (q, COCH_3), assignments with the same letter may be interchanged; HREIMS m/z 444.1795 (calcd for $\text{C}_{24}\text{H}_{28}\text{O}_8$, 444.1784).

(2*Z,8E,10E*)-Heptadeca-2,8,10-triene-4,6-diyne-1-ol (3): orange syrup; IR (film) ν_{max} 3406, 2959, 2927, 2856, 2198, 1717, 1673, 1632, 1457, 1376, 1261, 1033, 801 cm^{-1} ; ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 300 MHz) δ 6.75 (1H, dd, $J_1 = 10.7$ Hz, $J_2 = 15.6$ Hz, H-9), 6.27 (1H, dt, $J_1 = 6.0$ Hz, $J_2 = 10.6$ Hz, H-2), 6.21 (1H, dd, $J_1 = 10.7$ Hz, $J_2 = 15.2$ Hz, H-10), 5.97 (1H, dt, $J_1 = 7.3$ Hz, $J_2 = 15.2$ Hz, H-11), 5.68 (1H, d, $J = 15.6$ Hz, H-8), 5.65 (1H, br d, $J = 10.6$ Hz, H-3), 4.31 (2H, br d, $J = 6.0$ Hz, H-1), 2.17 (2H, q, $J = 7.3$ Hz, H-12), 1.30 (8H, m, H-13, H-14, H-15, H-16), 0.87 (3H, t, $J = 6.5$ Hz, H-17); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 75 MHz) δ 148.5 (d, C-2), 146.6 (d, C-9), 141.1 (d, C-11), 130.4 (d, C-10), 108.1 (d, C-3), 107.8 (d, C-8), 80.1 (s, C-7), 79.5 (s, C-6), 70.2 (s, C-5), 65.8 (s, C-4), 60.9 (t, C-1), 33.3 (t, C-12), 32.3 (t,

C-15), 29.5 (t, C-13, C-14), 23.1 (t, C-16), 14.2 (q, C-17); HRCIMS m/z 243.1750 (calcd for $C_{17}H_{23}O$, 243.1749).

(2E,9Z)-Octadeca-2,9-diene-4,6-diyn-1,18-diol (4): yellow syrup; IR (film) ν_{\max} 3385, 3020, 2928, 2855, 2233, 1671, 1630, 1508, 1464, 1263, 1159, 1094, 1032, 949 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 6.35 (1H, dt, $J_1 = 5.0$ Hz, $J_2 = 15.9$ Hz, H-2), 5.76 (1H, br d, $J = 15.9$ Hz, H-3), 5.49 (1H, dt, $J_1 = 7.1$ Hz, $J_2 = 10.5$ Hz, H-10), 5.38 (1H, dt, $J_1 = 6.8$ Hz, $J_2 = 10.5$ Hz, H-9), 4.21 (2H, dd, $J_1 = 1.9$ Hz, $J_2 = 5.0$ Hz, H-1), 3.62 (2H, t, $J = 6.7$ Hz, H-18), 3.04 (2H, d, $J = 6.8$ Hz, H-8), 2.01 (2H, q, $J = 7.1$ Hz, H-11), 1.55 (2H, quint., $J = 6.7$ Hz, H-17), 1.29 (10H, m, H-12, H-13, H-14, H-15, H-16); ^{13}C NMR (CDCl_3 , 75 MHz) δ 144.9 (d, C-2), 133.1 (d, C-10), 122.6 (d, C-9), 109.3 (d, C-3), 82.5 (s, C-7), 74.5 (s, C-4), 73.4 (s, C-5), 64.9 (s, C-6), 63.2 (t, C-18), 62.8 (t, C-1), 32.9 (t, C-17), 29.5^a (t, C-15), 29.4^a (t, C-14), 29.3^a (t, C-13), 29.2^a (t, C-12), 27.2 (t, C-11), 25.8 (t, C-16), 18.0 (t, C-8), assignments with the same letter may be interchanged; HRCIMS m/z 275.2011 (calcd for $C_{18}H_{27}O_2$, 275.2011).

(2E,9Z)-18-Hydroxyoctadeca-2,9-diene-4,6-diyn-1-yl acetate (5): yellow syrup; IR (film) ν_{\max} 3406, 2929, 2856, 2243, 2236, 1742, 1597, 1513, 1460, 1364, 1240, 1031, 949 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 6.26 (1H, dt, $J_1 = 5.8$ Hz, $J_2 = 15.9$ Hz, H-2), 5.75 (1H, br d, $J = 15.9$ Hz, H-3), 5.50 (1H, dt, $J_1 = 7.2$ Hz, $J_2 = 10.5$ Hz, H-10), 5.38 (1H, dt, $J_1 = 6.8$ Hz, $J_2 = 10.5$ Hz, H-9), 4.60 (2H, dd, $J_1 = 1.9$ Hz, $J_2 = 5.8$ Hz, H-1), 3.63 (2H, t, $J = 6.7$ Hz, H-18), 3.06 (2H, d, $J = 6.8$ Hz, H-8), 2.07 (3H, s, COCH_3), 2.02 (2H, q, $J = 7.2$ Hz, H-11), 1.57 (2H, quint., $J = 6.7$ Hz, H-17), 1.30 (10H, m, H-12, H-13, H-14, H-15, H-16); ^{13}C NMR (CDCl_3 , 100 MHz) δ 170.5 (s, COCH_3), 139.2 (d, C-2), 133.0 (d, C-10), 122.1 (d, C-9), 112.2 (d, C-3), 83.0 (s, C-7), 72.6 (s, C-5), 69.9 (s, C-4), 64.7 (s, C-6), 63.7 (t, C-1), 63.1 (t, C-18), 32.8 (t, C-17), 29.4^a (t, C-14, C-15), 29.2^a (t, C-13), 29.1^a (t, C-12), 27.2 (t, C-11), 25.7 (t, C-16), 20.8 (q, COCH_3), 18.0 (t, C-8), assignments with the same letter may be interchanged; HRFABMS m/z 339.1933 (calcd for $C_{20}H_{28}O_3\text{Na}$, 339.1936).

(2E,9Z)-1-Hydroxyoctadeca-2,9-diene-4,6-diyn-18-yl acetate (6): yellow syrup; IR (film) ν_{\max} 3398, 2924, 2851, 2243, 2159, 1735, 1466, 1243, 1095, 1035, 949 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 6.35 (1H, dt, $J_1 = 5.0$ Hz, $J_2 = 15.9$ Hz, H-2), 5.76 (1H, br d, $J = 15.9$ Hz, H-3), 5.49 (1H, dt, $J_1 = 7.1$ Hz, $J_2 = 10.5$ Hz, H-10), 5.38 (1H, dt, $J_1 = 6.7$ Hz, $J_2 = 10.5$ Hz, H-9), 4.21 (2H, dd, $J_1 = 1.9$ Hz, $J_2 = 5.0$ Hz, H-1), 4.03 (2H, t, $J = 6.8$ Hz, H-18), 3.04 (2H, d, $J = 6.7$ Hz, H-8), 2.03 (3H, s, COCH_3), 2.02 (2H, q, $J = 7.1$ Hz, H-11), 1.60 (2H, quint., $J = 6.8$ Hz, H-17), 1.29 (10H, m, H-12, H-13, H-14, H-15, H-16); ^{13}C NMR (CDCl_3 , 75 MHz) δ 171.4 (s, COCH_3), 144.9 (d, C-2), 132.9 (d, C-10), 122.3 (d, C-9), 109.2 (d, C-3), 82.4 (s, C-7), 73.3 (s, C-4), 72.1 (s, C-5), 64.7 (t, C-18), 63.1 (s, C-6), 62.8 (t, C-1), 29.4^a (t, C-15), 29.2^a (t, C-13, C-14), 29.1^a (t, C-12), 28.6 (t, C-17), 27.2 (t, C-11), 25.9 (t, C-16), 21.0 (q, COCH_3), 18.0 (t, C-8), assignments with the same letter may be interchanged; HRFABMS m/z 339.1937 (calcd for $C_{20}H_{28}O_3\text{Na}$, 339.1936).

(2E,8E,10E)-Heptadeca-2,8,10-triene-4,6-diyn-1-ol (7): orange amorphous powder; ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz) δ 6.74 (1H, dd, $J_1 = 10.7$ Hz, $J_2 = 15.6$ Hz, H-9), 6.44 (1H, dt, $J_1 = 4.6$ Hz, $J_2 = 15.9$ Hz, H-2), 6.20 (1H, dd, $J_1 = 10.8$ Hz, $J_2 = 15.1$ Hz, H-10), 5.96 (1H, dt, $J_1 = 7.3$ Hz, $J_2 = 15.1$ Hz, H-11), 5.89 (1H, br d, $J = 15.9$ Hz, H-3), 5.67 (1H, d, $J = 15.6$ Hz, H-8), 4.15 (2H, dd, $J_1 = 1.8$ Hz, $J_2 = 4.6$ Hz, H-1), 2.10 (2H, q, $J = 7.4$ Hz, H-12), 1.38 (2H, quint., $J = 7.1$ Hz, H-13), 1.28 (6H, m, H-14, H-15, H-16), 0.86 (3H, t, $J = 7.3$ Hz, H-17); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz) δ 148.5 (d, C-2), 146.3 (d, C-9),

140.9 (d, C-11), 130.4 (d, C-10), 107.9 (d, C-8), 107.6 (d, C-3), 81.7 (s, C-4), 81.6 (s, C-7), 76.2 (s, C-6), 74.6 (s, C-5), 62.2 (t, C-1), 33.4 (t, C-12), 32.3 (t, C-15), 29.5 (t, C-13, C-14), 23.1 (t, C-16), 14.3 (q, C-17). IR, UV, and MS data are in accordance with those published.^{9,10}

(2E,8E,10E)-Heptadeca-2,8,10-triene-4,6-diyn-1-yl acetate (8): orange syrup; ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 300 MHz) δ 6.78 (1H, dd, $J_1 = 10.7$ Hz, $J_2 = 15.6$ Hz, H-9), 6.38 (1H, dt, $J_1 = 5.5$ Hz, $J_2 = 16.0$ Hz, H-2), 6.23 (1H, dd, $J_1 = 10.7$ Hz, $J_2 = 15.0$ Hz, H-10), 5.99 (1H, dt, $J_1 = 7.0$ Hz, $J_2 = 15.0$ Hz, H-11), 5.95 (1H, br d, $J = 16.0$ Hz, H-3), 5.73 (1H, d, $J = 15.6$ Hz, H-8), 4.65 (2H, dd, $J_1 = 1.4$ Hz, $J_2 = 5.5$ Hz, H-1), 2.14 (2H, q, $J = 7.2$ Hz, H-12), 2.06 (3H, s, COCH_3), 1.41 (2H, quint., $J = 6.9$ Hz, H-13), 1.29 (6H, m, H-14, H-15, H-16), 0.90 (3H, t, $J = 7.1$ Hz, H-17); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 75 MHz) δ 170.4 (s, COCH_3), 146.8 (d, C-9), 141.7 (d, C-2), 141.1 (d, C-11), 130.4 (d, C-10), 111.7 (d, C-3), 107.7 (d, C-8), 82.5 (s, C-4), 80.6 (s, C-7), 75.7 (s, C-6), 73.6 (s, C-5), 63.9 (t, C-1), 33.5 (t, C-12), 32.3 (t, C-15), 29.5 (t, C-13, C-14), 23.1 (t, C-16), 20.5 (q, COCH_3), 14.3 (q, C-17). IR, UV and MS data in accordance with those published.^{9,10}

(2E,8E,10E)-Heptadeca-2,8,10-triene-4,6-diyn-1-al (9): orange syrup; ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 400 MHz) δ 9.68 (1H, d, $J = 7.5$ Hz, H-1), 6.95 (1H, d, $J = 16.0$ Hz, H-3), 6.83 (1H, dd, $J_1 = 10.7$ Hz, $J_2 = 15.6$ Hz, H-9), 6.50 (1H, dd, $J_1 = 7.5$ Hz, $J_2 = 16.0$ Hz, H-2), 6.25 (1H, dd, $J_1 = 10.7$ Hz, $J_2 = 15.1$ Hz, H-10), 6.15 (1H, dt, $J_1 = 7.3$ Hz, $J_2 = 15.1$ Hz, H-11), 5.78 (1H, d, $J = 15.6$ Hz, H-8), 2.18 (2H, q, $J = 7.3$ Hz, H-12), 1.38 (8H, m, H-13, H-14, H-15, H-16), 0.92 (3H, t, $J = 7.3$ Hz, H-17); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 100 MHz) δ 193.5 (d, C-1), 148.4 (d, C-9), 142.7 (d, C-2), 142.3 (d, C-11), 130.8 (d, C-3), 128.4 (d, C-10), 107.9 (d, C-8), 88.7 (s, C-7), 87.4 (s, C-6), 84.7 (s, C-5), 78.9 (s, C-4), 33.5 (t, C-12), 32.3 (t, C-15), 29.5 (t, C-13, C-14), 23.2 (t, C-16), 14.2 (q, C-17). IR, UV, and MS data are in accordance with those published.⁹

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