7,9,9-Trimethyl-1,4-dithiaspiro[4.5]dec-6-ene (3). Isophorone and 1,2-ethanedithiol gave **3** in 54% yield: bp 144–146 °C (8 mm); ^{1}H NMR δ 5.55 (m, 1 H), 3.32 (s, 4 H), 2.18 (s, 2 H), 1.75 (s, 2 H), 1.66 (br s, 3 H), 1.00 (s, 6 H). Anal. Calcd for $C_{11}H_{18}S_2$: C, 61.66; H, 8.47. Found: C, 61.75; H, 8.52.

8-Methyl-1,5-dithiaspiro[5.4]dec-7-ene (4). 3-Methylcyclopent-2-en-1-one and 1,3-propanedithiol gave **4** in 43% yield: bp 180–185 °C (30 mm); ^{1}H NMR δ 5.60 (m, 1 H), 3.10–1.25 (m, 8 H), 1.78 (br s, 3 H). Anal. Calcd for $C_9H_{14}S_2$: C, 58.05; H, 7.58. Found: C, 58.00; H, 7.45.

8,10,10-Trimethyl-1,5-dithiaspiro[5.5]undec-7-ene (5). Isophorone and 1,3-propanedithiol gave **5** in 64% yield: bp 156–158 °C (8 mm); ^{1}H NMR δ 5.68 (m, 1 H), 3.10–2.75 (m, 4 H), 2.15–1.60 (m, 2 H), 2.00 (s, 2 H), 1.78 (s, 2 H), 1.70 (br s, 3 H). Anal. Calcd for $C_{12}H_{20}S_2$: C, 63.13; H, 8.83. Found: C, 62.85; H, 8.78.

Cycloenlargement Reaction. General Procedure. A solution of cyclic thioketal (2.7×10^{-2} mol) and dichloroacetyl chloride (3.0×10^{-2} mol) in *n*-hexane (60 mL) was stirred at room temperature under nitrogen and a solution of triethylamine (3.3×10^{-2} mol) in *n*-hexane (20 mL) was slowly added during 1 h. After 3–4 h of reaction at room temperature dichloromethane (250 mL) and water (100 mL) were added and the brown organic layer was washed with an aqueous solution of HCl (5%, 3 × 30 mL), water (2 × 30 mL), an aqueous solution of Na_2CO_3 (5%, 3 × 50 mL), and a saturated solution of NaCl (2 × 30 mL). The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The reaction mixture was purified by crystallization from *n*-hexane and decolorized with charcoal. White crystals were collected by filtration and dried.

2,2-Dichloro-1-methyl-4,7-dithiabicyclo[6.2.1]undec-8-(11)-en-3-one (1a). Cyclic thioketal **1** gave **1a**: 6.49 g, 85% yield; mp 120–121 °C; IR (KBr) 1680 (vs), 1605 (m) cm^{-1}; ^{1}H NMR δ 6.15 (m, 1 H), 4.00–1.60 (m, 8 H), 1.52 (s, 3 H); mass spectrum, *m/e* 282 ($M^{+\cdot}$). Anal. Calcd for $C_{10}H_{12}Cl_2OS_2$: C, 42.42; H, 4.27. Found: C, 42.51; H, 4.31.

2,2-Dichloro-1-methyl-4,7-dithiabicyclo[6.3.1]dodec-8-(12)-en-3-one (2a). Cyclic thioketal **2** gave **2a**: 6.41 g, 80% yield; mp 93–95 °C IR (KBr) 1680 (vs), 1610 (m) cm^{-1}; ^{1}H NMR δ 6.40 (m, 1 H), 4.00–3.10 (m, 2 H), 3.08–2.86 (m, 2 H), 2.30–1.22 (m, 4 H), 1.36 (s, 3 H); mass spectrum, *m/e* 296 ($M^{+\cdot}$). Anal. Calcd for $C_{11}H_{14}Cl_2OS_2$: C, 44.46; H, 4.74. Found: C, 44.52; H, 4.78.

2,2-Dichloro-1,10,10-trimethyl-4,7-dithiabicyclo[6.3.1]dodec-8(12)-en-3-one (3a). Cyclic thioketal **3** gave **3a**: 7.64 g, 87%; mp 90–92 °C; IR (KBr) 1675 (vs), 1625 (w) cm^{-1}; ^{1}H NMR δ 6.32 (m, 1 H), 3.80–1.80 (m, 8 H), 1.52 (s, 3 H), 1.06 (s, 6 H); ^{1}H NMR (C_6D_6) δ 6.20 (m, 1 H), 3.50–2.78 (m, 4 H), 2.4–1.5 (m, 4 H), 1.3 (s, 3 H), 0.82 (s, 3 H), 0.70 (s, 3 H); mass spectrum, *m/e* 324 ($M^{+\cdot}$). Anal. Calcd for $C_{13}H_{18}Cl_2OS_2$: C, 48.01; H, 5.57. Found: C, 48.24; H, 5.61.

2,2-Dichloro-1-methyl-4,8-dithiabicyclo[7.2.1]dodec-9-(12)-en-3-one (4a). Cyclic thioketal **4** gave **4a**: 6.25 g, 78% yield; mp 124–126 °C; IR (KBr) 1685 (vs), 1590 (w) cm^{-1}; ^{1}H NMR δ 5.85 (m, 1 H), 3.55–1.40 (m, 10 H), 1.52 (s, 3 H); mass spectrum, *m/e* 296 ($M^{+\cdot}$). Anal. Calcd for $C_{11}H_{14}Cl_2OS_2$: C, 44.46; H, 4.74. Found: C, 4.55; H, 4.81.

2,2-Dichloro-1,11,11-trimethyl-4,8-dithiabicyclo[7.3.1]tridec-9(13)-en-3-one (5a). Cyclic thioketal **5** gave **5a**: 8.05 g, 88% yield; mp 127–128 °C; ^{1}H NMR δ 5.87 (m, 1 H), 3.72–1.22 (m, 10 H), 1.45 (s, 3 H), 1.02 (s, 3 H), 0.95 (s, 3 H); mass spectrum, *m/e* 338 ($M^{+\cdot}$). Anal. Calcd for $C_{14}H_{20}Cl_2OS_2$: C, 49.57; H, 5.94. Found: C, 49.35; H, 5.85.

X-ray Analysis of 1a. Precise unit-cell dimensions were determined by a least-squares fit on 23 independent 2θ values. The crystal used was 0.1 × 0.6 × 0.4 mm. Crystal data: $C_{10}H_{12}Cl_2OS_2$, M = 282.0, monoclinic, space group $P2_1/n$ a = 15.138 (3) Å, b = 12.035 (2) Å, c = 6.579 (5) Å, β = 93.41 (3)°, V = 1196.5 Å^3, Z = 4, d_c = 1.57 g cm^{-3}. Intensity data were collected by a Philips 1100 diffractometer out to 240° by use of Mo Kα radiation with a graphite monocromator and with a scan speed of 0.06° s^{-1}, a scan width of 0.8°, a take-off angle of 2°, a 0.6-mm window, and a counting background for 20 s on either side of the peak. Of 1888 independent reflections, 1492 having $I > 2.5\sigma(I)$ were considered observed.

Structure Determination and Refinement. After correction for Lorentz and polarization factors of 1492 independent reflections, 1264, for which $\sin\theta \leq 0.40$, were used in the analysis. The structure was solved by direct methods with the crystallographic program system SHELX (Sheldrick, 1976); the first E map indicated positions for all the nonhydrogen atoms. Subsequent difference Fourier synthesis indicated positions for all the hydrogen atoms. The structure, except the hydrogen atoms, was refined anisotropically, using full-matrix least squares. The weighting scheme was $w = 3.2835/(\delta^2 F_{obsd} + 0.000\,131 F_{obsd}^2)$. The final coonventional agreement factor was 0.041 for 1280 reflections (R_w = 0.039; R_G = 0.041; R_M = 0.041). Drawings were made with PLUTO (Motherwell, 1976).

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Registry No. 1, 76793-90-3; **1a**, 76793-91-4; **2**, 76793-92-5; **2a**, 76793-93-6; **3**, 76793-94-7; **3a**, 76793-95-8; **4**, 76793-96-9; **4a**, 76793-97-0; **5**, 76793-98-1; **5a**, 76793-99-2; dichloroketene, 4362-56-5; dichloroacetyl chloride, 79-36-7; 3-methylcyclopent-2-en-1-one, 2758-18-1; 3-methylcyclohex-2-en-1-one, 1193-18-6; isophorone, 78-59-1; 1,2-ethanedithiol, 540-63-6; 1,3-propanedithiol, 109-80-8.

Supplementary Material Available: Data for the X-ray structure of **1a** are available as bond lengths with estimated standard deviations (Table II), bond angles with estimated standard deviations (Table III), fractional atomic coordinates with estimated standard deviations (Table V), isotropic and anisotropic thermal parameters with estimated standard deviations (Table VI), fractional atomic coordinates with estimated standard deviations (Table VII). ^{13}C NMR data for compounds **1a–5a** are available as Table IV (5 pages). Ordering information is given on any current masthead page.

General Approach to the Synthesis of Naturally Occurring δ-Lactones[1]

Marek Chmielewski and Janusz Jurczak*

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

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The adducts from thermal and/or high-pressure Diels–Alder reactions between 1-methoxybuta-1,3-diene and carbonyl compounds (glyoxylates, aldehydes) are utilized as the starting materials for the syntheses of naturally occurring δ-lactones. Total syntheses of massoilactone, 6-phenyl-2-pyrone, and 2-methoxy-6-undecyl-5,6-dihydro-2*H*-pyran are described. A general approach to these syntheses is presented.

It has been shown[2] that butyl 2-methoxy-5,6-dihydro-2*H*-pyran-6-carboxylate (**1a**), easily obtainable via the Diels–Alder reaction of 1-methoxybuta-1,3-diene and butyl glyoxylate, can be utilized as the starting material for the

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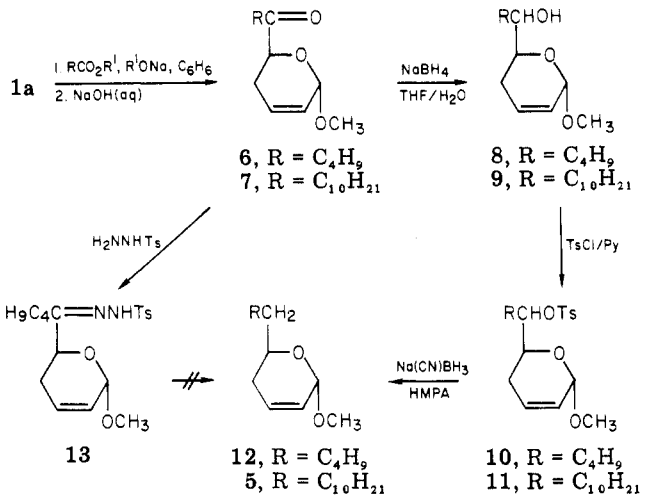
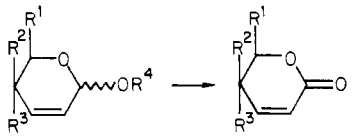
Scheme I[a]



[a] For the sake of simplicity all formulas in this paper refer to the monosaccharide D series although they represent, in fact, racemic compounds.

synthesis of monosaccharides.

Recently, we have reported[3] the oxidation of the derivatives of 6-substituted 2-methoxy-5,6-dihydro-2*H*-pyran (1), leading to unsaturated δ-lactones **2**, which represent



1 2

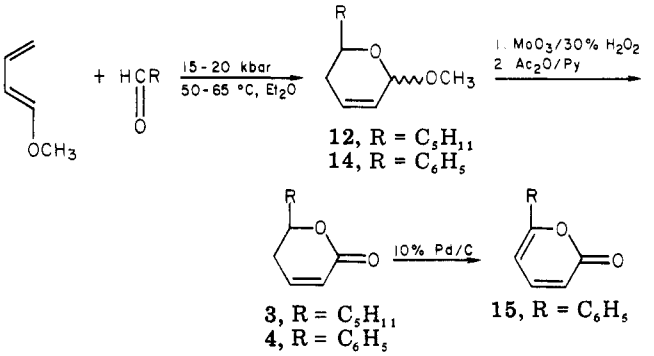
a, $R^1 = CO_2Bu$, $R^2 = R^3 = H$, $R^4 = Me$; b, $R^1 = CH_2OAc$, $R^2 = H$, $R^3 = OAc$, $R^4 = Et$; c, $R^1 = CH_2OAc$, $R^2 = OAc$, $R^3 = H$, $R^4 = Et$; d, $R^1 = CH_2OAc$, $R^2 = R^3 = H$, $R^4 = Me$; e, $R^1 = CH_2NHAc$, $R^2 = R^3 = H$, $R^4 = Me$.

a class of simple sugar compounds but which are also 2-pyrone derivatives. 6-Substituted 2-pyrones or their dihydro and tetrahydro derivatives occur in nature as pheromones[4] and as components of essential oils.[5]

Our objective was the extension of the preparative applicability of the Diels–Alder reaction between 1-methoxybuta-1,3-diene and carbonyl compounds to the synthesis of naturally occurring δ-lactones. This can be achieved by a suitable transformation of the butoxycarbonyl group of **1a** or by direct cycloaddition of an appropriate aldehyde and the 1,3-diene employed, followed by oxidation of the acetal carbon atom. [2 + 4] cycloaddition with heterodienophiles containing an active carbonyl group (e.g., butyl glyoxylate) can be achieved thermally at about 100 °C.[6] For cycloaddition with simple aldehydes, however, high pressure is necessary.[7]

In this paper we report the total syntheses of massoilactone (**3**), 6-phenyl-2-pyrone (**4**), and 2-methoxy-6-undecyl-5,6-dihydro-2*H*-pyran (**5**), the precursor of the pheromone from *Vespa orientalis*,[8] by the general approach given above.

Scheme II



Results

The mixed ester condensation of **1a** with ethyl valerate or methyl undecanoate, followed by ester cleavage of the crude β-keto esters according to the procedure described earlier,[9] led to ketones **6** or **7**, respectively (Scheme I). The ketones were reduced with sodium borohydride to give diastereomeric mixtures of the corresponding alcohols **8** or **9**, both in a ratio of 1:1 according to ^1H NMR spectra. The hydroxyl groups of **8** and **9** were subsequently tosylated, and the tosylates **10** and **11** were reduced with sodium cyanoborohydride to give 6-alkyl-2-methoxy-5,6-dihydro-2*H*-pyrans **12** and **5**, respectively. Deoxygenation of ketone **6** via LAH reduction of the tosylhydrazone **13**, failed to give compound **12**.

Compound **12** was oxidized with 30% hydrogen peroxide in the presence of molybdenum trioxide catalyst, followed by dehydration of the resulting hydroperoxide with acetic anhydride and pyridine to give racemic massoilactone (**3**, Scheme II).

Compounds **12** and **14**, precursors of naturally occurring δ-lactones, can be obtained by direct high-pressure cycloaddition of 1-methoxybuta-1,3-diene and appropriate aldehydes at 50–65 °C.[7] The high-pressure heterodiene synthesis is a convenient method for the preparation of various substituted derivatives of 5,6-dihydro-2*H*-pyran, which are not readily, if at all, obtainable by other procedures. Application of high pressure to the cycloadditions of 1-methoxybuta-1,3-diene and hexanal or benzaldehyde as dienophiles led, in moderate yields (16–79%), to 2-methoxy-6-pentyl-5,6-dihydro-2*H*-pyran (**12**) and 2-methoxy-6-phenyl-5,6-dihydro-2*H*-pyran (**14**), respectively. Compound **14** was subsequently oxidized by using the method described above to give 6-phenyl-5,6-dihydro-2-pyrone (**4**). Lactone **4** was dehydrogenated with 10% palladium-on-charcoal catalyst,[10] yielding 6-phenyl-2-pyrone (**15**).

The results presented here show that the Diels–Alder reaction of 1-methoxybuta-1,3-diene and carbonyl compounds can be used for the preparation of naturally occurring δ-lactones as a general route.

Experimental Section

Boiling points refer to air-bath temperatures. Melting points (uncorrected) were determined on a Kofler block. ^1H NMR spectra were recorded with a JEOL JNM-4H-100 spectrometer for $CDCl_3$ solutions (δ scale, Me_4Si 0 ppm). IR spectra were

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(10) D. Rosenthal, P. Grabowich, E. F. Sabo, and J. Fried, *J. Am. Chem. Soc.*, **85**, 3971 (1963).

recorded on Unicam SP-200 spectrophotometer. Silica gel G (Merck) was used for TLC and 100–200-mesh Macherey-Nagel silica gel for column chromatography. Typical TLC systems were *n*-hexane–ethyl acetate (7:3 v/v) and *n*-hexane–ether (7:3 v/v).

Compound **1a** was prepared as reported previously.[6] Compound **6** was obtained by mixed-ester condensation of **1a** with ethyl valerate followed by ester cleavage of the crude β-keto ester according to the procedure described earlier.[9]

***trans*-2-Methoxy-6-undecanoyl-5,6-dihydro-2*H*-pyran (7).** To a boiling suspension of sodium methoxide (18 g) in absolute benzene (40 mL) was added a mixture of ester **1a** (25 g) and methyl undecanoate (27 g) in benzene (80 mL) dropwise. The azeotrope formed from benzene and methanol was distilled off during the addition. After total removal of the azeotrope and about 80–90% of the benzene, the oily residue was cooled and then treated with 3% sodium hydroxide (100 mL). The mixture was refluxed for 7 h and extracted with ether. The extract was dried ($MgSO_4$) and evaporated to dryness. The oily residue was purified on a silica gel column with petroleum ether–ether (8:2 v/v) as eluent to give **7**: 5 g (15%); bp 140 °C (0.4 torr); IR (film) 1715 (C=O), 1180, 1100, 1040, 960 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 6.1–5.6 (2 H, m, olefin), 4.95 (1 H, m, H-2), 4.28 (1 H, pd, $\sum J$ = 15 Hz, H-6), 3.46 (3 H, s, OCH_3), 2.62 (2 H, t, CH_2CO), 2.3–2.0 (2 H, m, H-5, H-5′), 1.8–1.1 (16 H, m, $(CH_2)_8$), 0.90 (3 H, t, CH_3). Anal. Calcd for $C_{17}H_{30}O_3$: C, 72.3; H, 10.7. Found: C, 72.1; H, 10.5.

***trans*-2-Methoxy-6-(1-hydroxypent-1-yl)-5,6-dihydro-2*H*-pyran (8).** A solution of **6** (5.0 g, 25 mmol) in THF–water (4:1 v/v, 30 mL) was stirred with sodium borohydride (2 g) for 1 h at room temperature, and the mixture was then extracted with ether. The extract was dried, filtered, and concentrated to dryness. The oily residue was purified on silica gel column with petroleum ether–ethyl acetate (8:2 v/v) to give **8**: 4.0 g (79%); bp 110 °C (0.4 torr); IR (film) 3500 (OH), 1180, 1100, 1040 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 6.1–5.5 (2 H, m, olefin), 4.85 (1 H, br s, H-2), 3.9–3.4 (2 H, m, H-6, CHOH), 3.40 (3 H, s, OCH_3), 2.5–1.7 (2 H, m, H-5, H-5′), 1.7–1.1 (6 H, m, $(CH_2)_3$), 0.92 (3 H, t, CH_3). Anal. Calcd for $C_{11}H_{20}O_3$: C, 66.0; H, 10.1. Found: C, 66.0; H, 10.3.

***trans*-2-Methoxy-6-(1-hydroxyundec-1-yl)-5,6-dihydro-2*H*-pyran (9).** Compound **9** was prepared from ketone **7** in the same way as described above: yield 85%; bp 160 °C (0.4 torr); IR (film) 3500 (OH), 1180, 1105, 1050 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 6.1–5.6 (2 H, m, olefin), 4.85 (1 H, br s, H-2), 3.9–3.4 (2 H, m, H-6, CHOH), 3.41 (3 H, s, OCH_3), 2.5–1.7 (2 H, m, H-5, H-5′), 1.7–1.0 (18 H, m, $(CH_2)_9$), 0.90 (3 H, t, CH_3). Anal. Calcd for $C_{17}H_{32}O_3$: C, 71.8; H, 11.3. Found: C, 71.8; H, 11.4.

***trans*-2-Methoxy-6-(1-tosyloxypent-1-yl)-5,6-dihydro-2*H*-pyran (10).** A solution of **8** (1 g, 5 mmol) in pyridine (10 mL) was treated with tosyl chloride (1.1 g) and left at room temperature overnight. The mixture was worked up as usual to give a residue which was puridied on a silica gel column with petroleum ether–ether (7:3 v/v) as eluent to give **10**, 1.5 g (85%). Anal. Calcd for $C_{18}H_{26}O_5S$: C, 61.0; H, 7.4. Found: C, 60.8; H, 7.6.

A sample (0.8 g) of the mixture **10** was separated into pure diastereomers on a silica gel column with petroleum ether–ethyl acetate (9:1 v/v) as eluent. Two fractions were obtained: A, less polar isomer (0.4 g), and B, more polar isomer (0.35 g). Fraction A: IR (film) 1360, 1170 cm^{-1} (tosyl); ^1H NMR ($CDCl_3$) 7.9–7.3 (4 H, m, tosyl), 6.1–5.5 (2 H, m, olefin), 4.70 (1 H, br s, H-2), 4.65 (1 H, m, CHOTs), 3.95 (1 H, m, $\sum J$ = 20.0 Hz, H-6), 3.35 (3 H, s, OCH_3), 2.46 (3 H, s, tosyl), 2.2–1.1 (8 H, m, $(CH_2)_3$, H-5, H-5′), 0.86 (3 H, t, CH_3). Fraction B: IR (film) 1370, 1175 cm^{-1} (tosyl); ^1H NMR ($CDCl_3$) 8.0–7.3 (4 H, m, tosyl), 6.3–5.6 (2 H, m, olefin), 4.82 (1 H, br s, H-1), 4.69 (1 H, br q, $\sum J$ = 17.0 Hz, CHOTs), 3.99 (1 H, dt, $\sum J$ = 19.0 Hz, H-6), 3.31 (3 H, s, OCH_3, 2.45 (3 H, s, tosyl), 2.4–1.1 (8 H, m, $(CH_2)_3$, H-5, H-5′), 0.87 (3 H, t, CH_3).

***trans*-2-Methoxy-6-(1-tosyloxyundec-1-yl)-5,6-dihydro-2*H*-pyran (11).** Compound **11** was obtained and separated into diastereomers as described above for **10**. Less polar component: IR (film) 1370, 1180 cm^{-1} (tosyl); ^1H NMR ($CDCl_3$) 7.8–7.2 (4 H, m, tosyl), 6.0–5.5 (2 H, m, olefin), 4.63 (1 H, br s, H-2), 4.57 (1 H, m, CHOTs), 3.91 (1 H, dt, $\sum J$ = 19.1 Hz, H-6), 3.30 (3 H, s, OCH_3), 2.41 (3 H, s, tosyl), 2.1–1.9 (2 H, m, H-5, H-5′), 1.9–1.0 (18 H, m, $(CH_2)_9$), 0.98 (3 H, t, CH_3). Anal. Calcd for $C_{24}H_{38}O_5S$: C, 65.7; H, 8.7. Found: C, 66.0; H, 8.8. More polar component: IR (film) 1370, 1180 cm^{-1} (tosyl); ^1H NMR ($CDCl_3$) 7.9–7.2 (4 H, m, tosyl), 6.1–5.5 (2 H, m, olefin), 4.78 (1 H, br s, H-2), 4.62 (1 H, br q, $\sum J$ = 16.7 Hz, CHOTs), 3.95 (1 H, dt, $\sum J$ = 18.6 Hz, H-6), 3.28 (3 H, s, OCH_3), 2.42 (3 H, s, tosyl), 2.4–1.0 (20 H, m, $(CH_2)_9$, H-5, H-5′), 0.90 (3 H, t, CH_3). Anal. Calcd for $C_{24}H_{38}O_5S$: C, 65.7; H, 8.7. Found: C, 65.7; H, 8.8.

***trans*-2-Methoxy-6-pentyl-5,6-dihydro-2*H*-pyran (12).** A solution of **10** (1.0 g, 2.8 mmol) in HMPA (10 mL) was treated with sodium cyanoborohydride (0.1 g) and kept at 70 °C for 7 h. The solution was then poured into water and extracted with ether. The extract was dried ($MgSO_4$) and evaporated to dryness. The oily residue was purified on silica gel column with petroleum ether–ether (9:1 v/v) to give **12**: 0.2 g (38%); colorless oil; bp 100 °C (0.4 torr); IR (film) 1640 (C=C), 1150, 1060, 1045 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 6.2–5.6 (2 H, m, olefin), 4.92 (1 H, br s, H-2), 3.95 (1 H, m, H-6), 3.45 (3 H, s, OCH_3), 2.2–1.1 (10 H, m, $(CH_2)_4$, H-5, H-5′), 0.95 (3 H, t, CH_3). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.7; H, 10.9. Found: C, 71.7; H, 11.2.

***cis*-/*trans*-2-Methoxy-6-pentyl-5,6-dihydro-2*H*-pyran (12) Mixture.** The high-pressure apparatus,[7] closed on the bottom side with a stopper, was filled with *n*-hexanal (7.5 g, 75 mmol) and 1-methoxybuta-1,3-diene (12.5 g, 150 mmol) in ether (55 mL), and the mobile piston was inserted. Then the whole assembly was placed between the pistons of a hydraulic press and the pressure was raised to 19.7 kbar. After stabilization of the pressure, the heater was switched on, whereupon the temperature was raised to 65 °C and the pressure to 20.0 kbar. The reaction mixture was kept under these conditions for 5 h, cooled to room temperature, and left under high pressure for additional 15 h. After decompression, the solvent was evaporated, and the residue was dissolved in *n*-hexane (200 mL) and filtered to remove a small amount of polymers. The filtrate was concentrated under reduced pressure and distilled to give a cis/trans mixture of **12**: 3.9 g (28%); colorless oil; bp 90–93 °C (12 torr); IR (film) 1640 (C=C), 1150, 1055, 1040 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 6.15–5.55 (2 H, m, olefin), 5.04, 4.87 (1 H, 2 br s, cis and trans H-2), 3.75 (1 H, m, H-6), 3.48, 3.43 (3 H, 2 s, cis and trans OCH_3), 2.01 (2 H, m, H-5, H-5′), 1.9–0.7 (11 H, m, C_5H_{11}). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.7; H, 10.9. Found: C, 71.8; H, 11.1.

***trans*-2-Methoxy-6-undecyl-5,6-dihydro-2*H*-pyran (5).** Compound **5** was obtained according to the procedure described above for **12**: colorless oil; bp 140 °C (0.4 torr). Samples of **5** obtained from different experiments which were puridied independently and which were identical (TLC and ^1H NMR data) gave inconsistent elemental analyses: ^1H NMR ($CDCl_3$) 6.2–5.6 (2 H, m, olefin), 4.92 (1 H, br s, H-2), 3.95 (1 H, m, H-6), 3.45 (3 H, s, OCH_3), 2.2–1.1 (22 H, m, $(CH_2)_{10}$, H-5, H-5′), 0.90 (3 H, t, CH_3).

***trans*-2-Methoxy-6-pentanoyl-5,6-dihydro-2*H*-pyran Tosylhydrazone (13).** A solution of **6** (4.0 g, 20 mmol) and tosylhydrazine (4.0 g) in pyridine was kept at room temperature overnight. The mixture was poured into water and extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated to dryness to give **13**: 7.2 g (97%); colorless crystals; mp 112–113 °C (hexane–ether); IR (KBr) 3270 cm^{-1} (NH); ^1H NMR ($CDCl_3$) 7.9–7.2 (4 H, m, tosyl), 6.1–5.5 (2 H, m, olefin), 4.83 (1 H, br s, H-2), 4.37 (1 H, pd, $\sum J$ = 14.5 Hz, H-6), 3.40 (3 H, s, OCH_3), 2.44 (3 H, s, tosyl), 2.5–2.0 (4 H, m, CH_2, H-5, H-5′), 1.8–1.1 (4 H, m, $(CH_2)_2$), 0.87 (3 H, t, CH_3). Anal. Calcd for $C_{18}H_{26}O_4N_2S$: C, 59.0; H, 7.2; N, 7.7. Found: C, 59.0; H, 7.4; N, 7.7.

6-Pentyl-5,6-dihydro-2-pyrone (3). A mixture of **12** (0.9 g, 4.9 mmol), molybdenum trioxide (30 mg), and 30% hydrogen peroxide (20 mL) was stirred at room temperature for 16 h. The product was extracted with chloroform, and the extract was dried ($MgSO_4$) and concentrated to dryness. The crude oily product was treated with acetic anhydride–pyridine (1:5 v/v, 15 mL) and kept overnight at room temperature. The mixture then was poured into water and extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated to dryness, and the crude residue was purified on a silica gel column with *n*-hexane–ether (95:5 v/v) as eluent, yielding **3**: colorless syrup; 0.4 g (53%); bp 100 °C (0.4 torr); IR (film) 1730 (C=O), 1630 (C=C), 1250 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 6.94 (1 H, double pd, $J_{4,5} + J_{4,5'}$ = 8.5 Hz, H-4), 5.99 (1 H, pt, $J_{3,4}$ = 9.9, $J_{3,5} + J_{3,5'}$ = 3.7 Hz, H-3), 4.45 (1 H, m, H-6), 2.38 (2 H, m, H-5, H-5′), 2.0–1.1 (8 H, m, $(CH_2)_4$), 0.92 (3 H, t, CH_3). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.3; H, 9.8.

***cis*-/*trans*-2-Methoxy-6-phenyl-5,6-dihydro-2*H*-pyran (14) Mixture.** The cis/trans mixture of compound **14** was prepared from benzaldehyde (5.3 g, 50 mmol) and 1-methoxybuta-1,3-diene (8.3 g, 100 mmol) under a pressure of 19.5 kbar at 50 °C in the same way as described for compound **12**: yield 6.8 g (80%); bp 119-120 °C (1.2 torr); IR (film) 1660 (C=C), 1160, 1050, 1035 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 7.7-7.0 (5 H, m, phenyl), 6.15-5.4 (2 H, m, olefin), 5.12, 4.85 (1 H, 2 br s, cis and trans H-2), 4.66 (1 H, 2 d, H-6), 3.40, 3.30 (3 H, 2 s, cis and trans OCH_3), 2.18 (2 H, m, H-5, H-5'). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.7; H, 7.4. Found: C, 75.3; H, 7.4.

6-Phenyl-5,6-dihydro-2-pyrone (4). Compound **4** was obtained from **14** according to the procedure described above for **3**: colorless crystals; mp 56-57 °C (hexane); IR (KBr) 1720 (C=O), 1635 (C=C), 1245 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 7.6-7.3 (5 H, m, phenyl), 6.99 (1 H, double pd, $J_{4,5} + J_{4,5'} = 8.2$ Hz, H-4), 6.12 (1 H, dt, $J_{3,4} = 8.9$, $J_{3,5} + J_{3,5'} = 3.5$ Hz, H-3), 5.45 (1 H, pd, $\sum J = 16.4$ Hz, H-6), 2.62 (2 H, m, H-5, H-5'). Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.8. Found: C, 75.8; H, 5.8.

6-Phenyl-2-pyrone (15). A suspension of 360 mg of 10% palladium-on-charcoal in 50 mL of *p*-cymene was dried by azeotropic removal of approximately 5 mL of solvent until the temperature of the vapor was over 170 °C. To this mixture was added 174 mg (1 mmol) of **4**, and the resulting suspension was heated under reflux with stirring for 8 h under a blanket of nitrogen. The mixture was cooled and filtered, and the solvent was removed in vacuo. The residual oily material was purified on a silica gel column with petroleum ether-ethyl acetate (8:2 v/v) to give 79 mg (46%) of the pure α-pyrone **15**: mp 65-67 °C (hexane); IR (KBr) 1720 (C=O), 1625 (C=C), 1105, 1070 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 8.2-7.1 (5 H, m, phenyl), 7.55 (1 H, invisible, chemical shift was assigned by double-resonance experiment, H-4), 6.71 (1 H, d, $J_{3,4} = 7.0$ Hz, H-3), 6.33 (1 H, d, $J_{4,5} = 9.0$ Hz, H-5).

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Spatane Diterpenoids from the Tropical Marine Alga *Stoechospermum marginatum* (Dictyotaceae)

William H. Gerwick and William Fenical*

Institute of Marine Resources, Scripps Institution of Oceanography, La Jolla, California 92093

M. U. S. Sultanbawa

Department of Chemistry, University of Sri Lanka, Peradeniya Campus, Peradeniya, Sri Lanka

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Ten new metabolites, **2**-**11**, are described as natural products of the tropical marine alga *Stoechospermum marginatum* from Sri Lanka. These new compounds all possess the novel "spatane" tricyclic diterpenoid ring system, and their structures were defined by spectral analyses and by interconversion with derivatives of spatol, a metabolite recently defined fully by X-ray crystallography.

Marine algae of the family Dictyotaceae (Phaeophyta) are prolific producers of interesting secondary metabolites, consisting of C_{11} acetate-derived compounds,[1] compounds of mixed biosynthesis,[2-9] sequiterpenoids,[10-14] and diterpenoids.[15-31] The diterpenoids from this group are particularly unique, as the novel ring systems produced represent unconventional diterpenoid cyclizations not yet

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