ing 12% alumina, 325 mesh and finer, product from Nakarai Chemicals Inc., Kyoto) and eluted with ethyl acetate–methanol (9:1 v/v). Homogeneous fractions (checked by tlc) were combined and evaporated below 35° nearly to dryness. Crystallization resulted on standing under petroleum ether in a refrigerator. The crystals were crushed and filtered to give 330 mg (63%) of an almost colorless product: mp 148–150°; $[\alpha]^{20}D$ −16.5° (c 2.38, $CHCl_3$); R_f 0.83 (1); λ_{max} (EtOH) 250 nm (ε 7000), shoulder 280 (1470); ν_{max} ($CHCl_3$) 3435, 3300–3200 (broad), 3000, 1730, 1720, 1670, 1620, 1470, 1440, 1370, 1330 cm^{-1}; pmr (100 MHz, $CDCl_3$) δ 9.18 (broad, one proton, NH of oxindole, exchanges rapidly with D_2O), 6.86–7.52 (five protons, aromatic multiplet + NHAc, exchanges slowly over several hours with D_2O), 4.98 [one-proton quartet, $J \simeq 7$ Hz, α proton, changes slowly to two overlapping doublets, 4.95 (J = 6 Hz) and 4.87 (J = 7 Hz), on D_2O exchange], 3.70 (three-proton singlet, OCH_3), 3.50 (one-proton triplet, J = 6 Hz, 3-H), 2.38 (two-proton skewed triplet, $J \simeq 7$ Hz, collapses to doublet, J = 7 Hz, on irradiation at center of 4.96 triplet, β-CH_2 groups), 2.02 ppm (three-proton singlet, NAc) The fragmentation on low-resolution mass spectrometry is shown in Scheme II.

Anal. Calcd for $C_{14}H_{16}O_4N_2$: C, 60.86; H, 5.84; N, 10.14. Found: C, 61.12; H, 5.86; N, 10.05.

L-3-(2-Acetamido-2-ethoxycarbonylethyl)indolinone (5). The pyrroloindole 2[11] (400 mg, 1.47 mmol) was dissolved in 20% acetic acid (40 ml) with stirring. The solution was treated in the same manner as the methyl ester analog above. The crude product (150 mg) was chromatographed on silica gel and eluted with ethyl acetate–methanol (9:1 v/v). Homogeneous fractions were pooled and evaporated. The syrupy residue failed to crystallize and was stored under vacuum, then pulverized. The resulting amorphous powder was collected with petroleum ether to afford 112 mg: mp 113–117°; R_f 0.85 (1); λ_{max} (EtOH) 250 nm (ε 6800), shoulder 280 (1420); ν_{max} ($CHCl_3$) 3420, 3300–3200, 2950, 1720, 1670, 1620, 1470, 1440, 1370 cm^{-1}; M^+ m/e 290. The fragmentation pathways were similar to those of **4**.

Anal. Calcd for $C_{14}H_{18}O_4N_2$: C, 62.05; H, 6.25; N, 9.65. Found: C, 62.27; H, 6.51; N, 9.54.

Registry No.—**1**, 25690-48-6; **2**, 21018-88-2; **3**, 32999-55-6; **4**, 51806-22-5; **5**, 40846-93-3.

References and Notes

(1) Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan.
(2) The amino acid **3** has been variously referred to as hydroxytryptophan,[4,9] α-hydroxytryptophan,[3,5,6] 2-hydroxytryptophan,[8,10] β-oxindole-3-alanine,[5] and β-3-oxindolylalanine.[4] Current usage would seem to favor 2-hydroxytryptophan, although the oxindolealanine nomenclature would more correctly reflect the structure.
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New Syntheses in Dihydrojasmone Series

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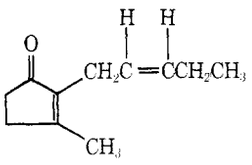
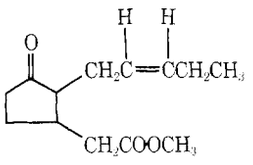
cis-Jasmone and methyl jasmonate are primary odorous principles of the flower oils of several varieties of *Jasminum*. Several syntheses of jasmone[1-5] and methyl jasmonates[6-8] have been published. Dihydrojasmone (**6**) is closely related to jasmone both in structure and in odor, is useful in perfumery, and has been synthesized by several procedures.[5,9-12]


cis-jasmone


methyl jasmonate

We wish now to describe an efficient five-step synthesis of dihydrojasmone (**6**) and tetrahydrojasmone (**7**), and a seven-step synthesis of methyl dihydrojasmonate (**12**). The starting point in the present synthetic scheme was the alkylation of 2-carbethoxycyclopentanone(**1**). This was accomplished by using NaH in DMF with RBr.[13] The key intermediate **3** was prepared by acid hydrolysis of **2**.[14] 2-Pentylcyclopentan-1-one (**3**) was then treated with isopropenyl acetate, yielding **4**, which was converted into **5** by the bromination–dehydrobromination method.[15] Methylation of **5** with methyllithium and oxidation of the resulting carbinol with chromium trioxide[8,16] led to the expected dihydrojasmone (**6**). The cuprous chloride catalyzed addition of a Grignard reagent, CH_3MgI, to **5** formed tetrahydrojasmone (**7**). Michael addition of dimethyl malonate to **5** yielded **8**, which upon hydrolysis and decarboxylation[8,17] was transformed to dihydrojasmonic acid (**9**), which was methylated to yield methyl dihydrojasmonate (**12**). We also explored a different route for synthesis of **12**, *via* intermediates **10** and **11**. Methyl-2-pentylcyclopent-2-en-1-ol acetate (**10**) was prepared either by treating **5** with lithium methyl acetate or with Reformatzky reagent.[18]

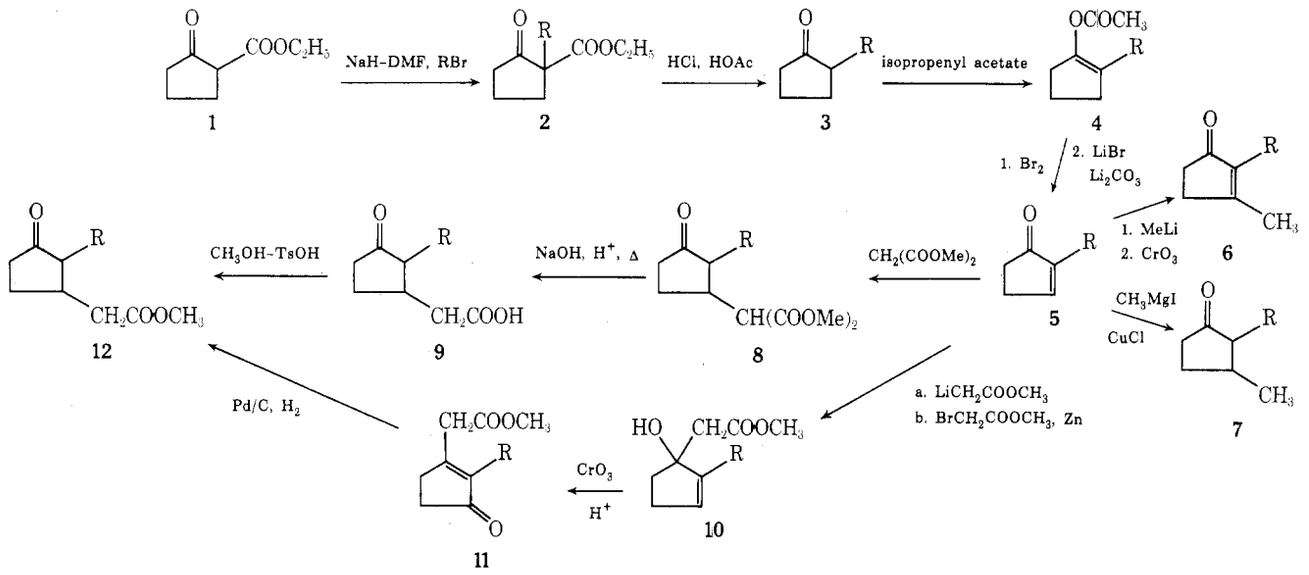
The lithium method seemed more elegant and attractive; it yielded 82% of **10**, as compared to 60% by Reformatzky's method. Oxidation of **10** with chromium trioxide afforded **11**, which was reduced catalytically to **12**.[17] Methyl dihydrojasmonate (**12**) prepared by both methods had identical spectroscopic (ir, nmr), and chromatographic properties.

It is noteworthy that compounds **6**, **11**, and **12** possess the characteristic long-lasting jasmone-like odors. The advantages of the present synthesis is that the starting materials are relatively inexpensive and easily accessible and the overall yields of the products are satisfactory.

Experimental Section

Microanalyses were performed at the Microanalytical Laboratory of the Hebrew University. Melting points were determined on a Thomas-Hoover apparatus. The following spectrometers were used: nuclear magnetic resonance (nmr), Varian T-60; infrared (ir), Perkin-Elmer Model 137; mass spectrometer (mass spectrum), Varian MAT-311; ultraviolet (uv), Unicam SP-800; vapor phase chromatography (vpc) analyses were performed on a Varian Aerograph 90-P instrument using a 3% SE-30 column. Infrared spectra were measured in sandwich cells (sc), uv spectra in ethanol, and nmr spectra in deuteriochloroform, unless otherwise stated.

2-Pentyl-2-carbethoxycyclopentan-1-one (2). 2-Carbethoxycyclopentanone(308 g, 1.97 mol) was added dropwise under a nitrogen atmosphere over a 3-hr period to a suspension of sodium hydride (100 g, 2.5 mol) in dry dimethylformamide (DMF) (1.2 l.) at 20°. After the addition was completed, the reaction mixture was stirred for 15 min at room temperature and then for 15 min at 50°. *n*-Pentyl bromide (300 g, 1.98 mol) was then added during 30 min. The reaction mixture was stirred overnight at room temperature, poured into water, and extracted thrice with ether. The organic layer was washed with a saturated solution of sodium chloride and dried over magnesium sulfate, and the solvents were removed *in vacuo*. Distillation through a small column afforded 2-pentyl-2-carbethoxycyclopentan-1-one: 284 g (64%); bp 100° (0.1 mm); ir



1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12

6, dihydrojasmone
7, tetrahydrojasmone
12, methyl dihydrojasmonate

(liquid) 1755, 1730, 1630, 1468, 1230, 1150, 1030, cm^{-1}; nmr ($CDCl_3$) δ 0.85 (3 H, t), 1.10–2.66 (17 H, m), 4.04 (2 H, 9).

Anal. Calcd for $C_{13}H_{22}O$: C, 68.99; H, 9.80. Found: C, 68.90; H, 9.65.

2-Pentylcyclopentan-1-one (3). 2-Pentyl-2-carbethoxycyclopentan-1-one (**2**, 280 g, 1.24 mol) in the presence of glacial acetic acid (350 ml) and hydrochloric acid (20%, 600 ml) was refluxed for 24 hr. The reaction mixture was cooled and water was added. It was then extracted with ether and the organic layer was washed with sodium bicarbonate and sodium chloride solutions and dried over magnesium sulfate. The solvents were removed *in vacuo* and the residue was distilled through a small column, affording 152 g (79.5%) of 2-pentylcyclopentan-1-one: bp 60–62° (0.5 mm); ir (liquid) 1738, 1470, 1455, 1410, 1155, 929 cm^{-1}; nmr ($CDCl_3$) δ 0.82 (3 H, t), 1.03–1.50 (8 H, m), 1.66–2.41 (7 H, m).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.69. Found: C, 78.08; H, 11.77.

1-Acetoxy-2-pentylcyclopent-1-ene (4). 2-Pentylcyclopentan-1-one (**3**, 145 g, 0.94 mol) and isopropenyl acetate (200 g, 2 mol) in the presence of *p*-toluenesulfonic acid (1 g) was refluxed overnight. The red-colored reaction mixture was poured into a cold solution of potassium bicarbonate (10%), extracted with ether, and dried over magnesium sulfate. The solvents were removed *in vacuo* and the residue was distilled through a small column, affording 155 g (84%) of 1-acetoxy-2-pentylcyclopent-1-ene: bp 65° (0.2 mm); ir (liquid) 1755, 1700, 1470, 1370, 1305, 1210 cm^{-1}; nmr ($CDCl_3$) δ 0.85 (3 H, t), 1.04–1.49 (4 H, m), 1.72–2.55 (10 H, m), 2.01 (3 H, s).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.50; H, 9.86.

2-Pentycyclopent-2-en-1-one (5). Bromine (120 g, 0.75 mol) in carbon tetrachloride (150 ml) was added dropwise during 1 hr to a mixture of 1-acetoxy-2-pentylcyclopent-1-ene (149 g, 0.76 mol), chloroform (450 ml), water (600 ml), and calcium carbonate (55 g). After stirring for 1 hr the organic layer was separated and washed with solutions of sodium thiosulfate and sodium chloride. The organic layer was dried over magnesium sulfate and the solvents were removed *in vacuo*. The residue was dissolved in dry DMF (750 ml) and in the presence of dry lithium bromide (130 g) and dry lithium carbonate (130 g) was refluxed for 45 min. Cold water (1 l.) was added and the red-colored solution was neutralized with hydrochloric acid (20%) and extracted with ether. The organic layer was washed with sodium chloride solution and dried over magnesium sulfate. Distillation afforded 90 g (78%) of 2-pentylcyclopent-2-en-1-one: bp 60° (0.2 mm); ir (liquid) 1700, 1633, 1445, 1253, 1198, 1050, 1000 cm^{-1}; nmr ($CDCl_3$) δ 0.85 (3 H, t), 1.08–1.63 (6 H, m), 1.88–2.72 (6 H, m), 7.05 (1 H, m); uv (EtOH) 230 nm (ϵ 9900).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.76; H, 10.60.

2-Pentyl-2-methylcyclopent-2-en-1-one (6, Dihydrojasmone). Methyllithium (14 ml, 20 mmol, of 1.9 *M* ethereal solution) was added dropwise with stirring at 0° and under a nitrogen atmosphere to 2-pentylcyclopent-2-en-1-one (**5**, 1.41 g, 9.28 mmol) in dry ether (30 ml). After the addition was completed, the reaction mixture was stirred for 15 min at room temperature, poured into cold water, and extracted with petroleum ether. The organic layer was washed with water and dried over magnesium sulfate, and the solvents were removed *in vacuo*. The residue of crude carbinol was dissolved in ether (30 ml), cooled to 0°, and treated with chromium trioxide (1 g) in sulfuric acid (10 ml, 5%). After a period of 15 min, water was added and the product was extracted with petroleum ether. The organic layer was washed with a solution of sodium bicarbonate (10%) and dried over magnesium sulfate, and the solvents were distilled off. The oily residue was distilled through a small column, yielding 0.6 g (39%) of 2-pentyl-2-methylcyclopent-2-en-1-one: bp 79–81° (0.2 mm); ir (liquid) 1700, 1645, 1445, 1388, 1180, 1070, 810 cm^{-1}; nmr ($CDCl_3$) δ 0.84 (3 H, t), 1.05–1.69 (6 H, m), 1.98 (3 H, s), 1.90–2.63 (6 H, m); uv (EtOH) 236 nm (ϵ 12,700).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.44; H, 10.64.

2-Pentyl-3-methylcyclopentan-1-one (7, Tetrahydrojasmone). Cuprous chloride (0.1 g) was added in one portion under a nitrogen atmosphere to methylmagnesium iodide, prepared from magnesium turnings (0.5 g, 0.021 g-atom) and methyl iodide (2.8 g, 0.02 mol) in dry ether. 2-Pentylcyclopent-2-en-1-one (**5**, 2 g, 0.013 mol) was then added dropwise over a period of 20 min. After addition was completed, stirring proceeded for 45 min and the reaction mixture was poured into ice-cold dilute hydrochloric acid. It was then extracted with ether. The organic layer was washed with solution of sodium bicarbonate and water, and dried over magnesium sulfate. Purification by preparative gas–liquid chromatography afforded 1.5 g (68%) of 2-pentyl-3-methylcyclopentan-1-one: ir (liquid) 1735, 1460, 1380, 1155, 790 cm^{-1}; nmr ($CDCl_3$) δ 0.63–0.98 (6 H, m), 1.00–1.70 (8 H, m), 1.82–2.63 (6 H, m).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.55; H, 11.60.

2-Pentyl-3-dimethylmalonylcyclopentan-1-one (8). 2-Pentylcyclopent-2-en-1-one (**5**, 15.2 g, 0.1 mol) in dry methanol (50 ml) was added dropwise (while stirring) during 30 min and under a nitrogen atmosphere to a cold (−5°) solution of sodiodimethyl malonate prepared from dimethyl malonate (16.5 g, 0.12 mol), sodium metal (0.3 g, 0.077 g-atom), and dry methanol (20 ml). After the addition was completed, the stirring was continued for 1 hr. Acetic acid (1.5 g, 0.025 mol) was added and the solvents were distilled off *in vacuo*. The residue was extracted with ether and the organic layer was washed with a solution of sodium chloride and dried over magnesium sulfate. Ether was distilled off and the residue was distilled, affording 13.4 g (63%) of 2-pentyl-3-dimethylmalonylcyclopentan-1-one: bp 126–127° (0.3 mm); ir (liquid) 1755, 1740, 1440, 1220, 1160 cm^{-1}; nmr (CCl_4) δ 0.85 (3 H, t), 1.04–1.55 (8 H, m), 1.78–2.29 (6 H, m), 3.39 (1 H, d), 3.61 (6 H, s).

Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.75; H, 8.47.

2-Pentyl-3-oxocyclopentylacetic Acid (9, Dihydrojasmonic

Acid). Sodium hydroxide (5.2 g) in water (50 ml) was added with vigorous agitation over a period of 1 hr and under a nitrogen atmosphere to 2-pentyl-3-dimethylmalonylcyclopentan-1-one (**8**, 17.5 g, 0.062 mol). The reaction mixture was stirred overnight at room temperature and extracted with ether, and the aqueous layer was acidified with sulfuric acid (7 g in 15 ml of water). The aqueous layer was refluxed until gas evolution ceased. The cold solution was extracted with ether, washed with water, and dried over magnesium sulfate. The solvents were removed *in vacuo* and the residue was distilled, affording 13.3 g (95%) of 2-pentyl-3-oxocyclopentylacetic acid: bp 168–170° (0.3 mm); ir (liquid) 3070–3020, 1740, 1712, 1465, 1410, 1165 cm^{-1}; nmr (CCl_4) δ 0.85 (3 H, t), 1.05–1.65 (8 H, m), 1.84–2.74 (8 H, m), 11.2 (1 H, s).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.08; H, 9.31.

Methyl-2-pentyl-3-oxocyclopentyl Acetate (12, Methyl Dihydrojasmonate). 2-Pentyl-3-oxocyclopentylacetic acid (**9**, 2 g, 0.094 mol), dry methanol (20 ml), and *p*-toluenesulfonic acid (10.05 g) were refluxed overnight. Methanol was distilled and the residue was extracted with ether. The ether solution was washed successively with a solution of sodium chloride, sodium bicarbonate, and again with sodium chloride and dried over magnesium sulfate. Distillation yielded 1.7 g (80%) of methyl-2-pentyl-3-oxocyclopentyl acetate: bp 105–107° (0.2 mm); ir (liquid) 1740, 1440, 1269, 1170 cm^{-1}; nmr (CCl_4) δ 0.85 (3 H, t), 1.01–1.58 (8 H, m), 1.82–2.51 (8 H, m), 3.55 (3 H, s).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.72; H, 9.60.

Methyl-2-pentylcyclopent-2-en-1-ol Acetate (10). Method A. Methyl acetate (1.71 ml, 25 mmol) was added dropwise over a period of 2 min (under a nitrogen atmosphere) into a THF solution of lithium bis(trimethylsilyl)amide (25 ml, 1.0 *M*) at −78°. After the addition was completed, the stirring proceeded for 15 min. 2-Pentylcyclopent-2-en-1-one (**5**, 3.8 g, 25 mmol) was injected through a septum inlet. After a period of 15 min, hydrochloric acid (5 ml, 20%) was injected. After the reaction was completed, the mixture was extracted with hexane. The organic layer was separated, washed with a saturated solution of sodium bicarbonate and water, and dried over sodium sulfate. Hexane was distilled off and the residue was distilled under reduced pressure, yielding 4.63 g (82%) of methyl-2-pentylcyclopent-2-en-1-ol-acetate: bp 97° (0.4 mm); ir (liquid) 3500, 1740, 1440, 1203 cm^{-1}; nmr (CCl_4) δ 0.93 (3 H, t), 1.13–1.50 (8 H, m), 1.71–2.24 (4 H, m), 2.42 (2 H, s), 2.52 (2 H, s), 3.31 (1 H, s), 3.69 (3 H, s), 5.42 (1 H, m).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 69.03; H, 9.74. Found: C, 69.10; H, 9.47.

Method B. 2-Pentylcyclopent-2-en-1-one (**5**, 1.52 g, 10 mmol) and methyl bromoacetate (1.1 ml, 10 mmol) in dry benzene (8 ml) were added slowly to activated zinc (0.65 g, 0.02 g-atom) in boiling benzene (2 ml). After the exothermic reaction had subsided, the mixture was refluxed for 30 min and cooled and acetic acid (5 ml, 10%) was added. The benzene layer was separated, washed with a solution of sodium bicarbonate and water, and dried over sodium sulfate. The solvent was removed *in vacuo* and the residue was distilled under reduced pressure affording 1.36 g (60%) of the product, bp 97° (0.4 mm), ir and nmr identical with those obtained by method A.

Methyl-2-pentyl-3-oxo-1-cyclopentenyl Acetate (11). Chromium trioxide (1 g) in sulfuric acid (10 ml, 5%) was added dropwise at 0° to methyl-2-pentylcyclopent-2-en-1-ol acetate (**10**, 2.03 g, 9 mmol) in ether (30 ml). After the addition was completed, the stirring proceeded for 45 min at 5°. Water was added and the product was extracted with hexane. The organic layer was separated, washed with a solution of sodium bicarbonate (10%) and water, and dried over sodium sulfate. The solvent was evaporated and the oil was distilled, affording 1.75 g (87%) of methyl-2-pentyl-3-oxo-1-cyclopentenyl acetate: bp 118–119° (0.4 mm); ir (liquid) 1740, 1705, 1645, 1435, 1175 cm^{-1}; uv (EtOH) 237 nm (ϵ 9200); nmr (CCl_4) δ 0.88 (3 H, t), 1.15–1.41 (8 H, m), 2.01–2.80 (4 H, m), 3.35 (2 H, s), 3.68 (3 H, s).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.64; H, 8.93. Found: C, 69.73; H, 9.20.

Methyl-2-pentyl-3-oxocyclopentyl Acetate (12, Methyl Dihydrojasmonate). Methyl-2-pentyl-3-oxo-1-cyclopentenyl acetate (**11**, 115 mg, 0.51 mmol), with sodium hydroxide (0.05 g) and methanol (15 ml) in the presence of Pd/C (0.21 g, 5%), was hydrogenated at room temperature. After the hydrogenation was completed, the catalyst was removed by filtration and the methanol was evaporated *in vacuo*. Methyl dihydrojasmonate (50 mg, 43%) was obtained by preparative glc. Its spectroscopic (ir, nmr) and chromatographic (glc) data were identical with those of methyl dihydrojasmonate prepared from compound **9**.

Registry No.—**1**, 611-10-9; **2**, 24852-03-7; **3**, 4819-67-4; **4**, 24851-93-2; **5**, 25564-22-1; **6**, 1128-08-1; **7**, 13074-63-0; **8**, 51806-23-6; **9**, 3572-64-3; **10**, 51806-24-7; **11**, 24863-70-5; **12**, 24851-98-7.

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Synthesis of Some Bridged Triterpene Ethers[1a]

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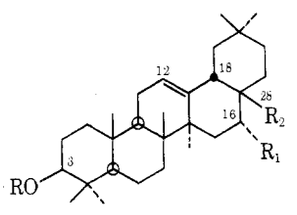
Several 13β,28-epoxyoleananes with additional oxygen functions in the molecule have recently been isolated from plants.[2-10] An unambiguous synthesis of the simplest of these, protoprimulagenin A (**21**), was desired to confirm this structural feature.

Although protoprimulagenin A was isolated from *Primula sieboldi* roots as recently as 1968,[10] Tschesche and coworkers had prepared such a compound from echinocystic acid (**3**) in 1964.[3,5] By heating in acetic and concentrated hydrochloric acids for several hours, **3** was converted to a 13β,28-lactone which was then reduced to a 13β,28-epoxide with boron trifluoride etherate and lithium aluminum hydride.[3]



1, R = R_1 = H; R_2 = CO_2H
2, R = R_1 = H; R_2 = CO_2CH_3
3, R = H; R_1 = OH; R_2 = CO_2H
4, R = H; R_1 = OH; R_2 = CO_2CH_3
5, R = Ac; R_1 = OAc; R_2 = CO_2H
6, R = R_1 = H; R_2 = CH_2OH
7, R = Ac; R_1 = H; R_2 = CH_2OH
8, R = R_1 = H; R_2 = CH_2OAc
9, R = Ac; R_1 = H; R_2 = CH_2OAc
10, R = H; R_1 = OH; R_2 = CH_2OH
11, R = H; R_1 = OH; R_2 = CH_2OH
with Br at 12 or OH at 13