is not entirely unexpected.[11] The absence of any group with elements heavier than carbon reduces intersystem crossing by spin orbit coupling to a minimum making hyperfine induced mixing and spin lattice relaxation the major pathways. Analysis of the decay kinetics of the biradical signals requires the knowledge of the spin lattice relaxation times (T_1), and most likely the lifetimes of the biradicals are even longer than the decay constants of the signals. A detailed analysis is in progress.

Registry No. 1 (n = 10; $R_1 = R_2 = CH_3$), 110015-80-0; **1** (n = 9; $R_1 = R_2 = CH_3$), 60010-87-9; **1** (n = 8; $R_1 = R_2 = CH_3$), 110015-81-1; **2** (n = 10; $R_1 = R_2 = CH_3$), 110015-82-2; **2** (n = 9; $R_1 = R_2 = CH_3$), 110015-83-3; **2** (n = 8; $R_1 = R_2 = CH_3$), 110015-84-4; **3** (n = 10; $R_1 = R_2 = CH_3$), 110015-85-5; **3** (n = 9; $R_1 = R_2 = CH_3$), 110015-86-6; **3** (n = 8; $R_1 = R_2 = CH_3$), 110015-87-7.

(11) Zimmt, M. B.; Doubleday, C.; Gould, I. R.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724.

Total Synthesis of (±)-Atractyligenin

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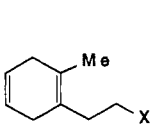
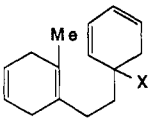
The thistle *Atractylis gummifera*, known since ancient times for its deadly toxicity, produces two poisonous principles which are derivatives of the diterpenoid atractyligenin (**1**).[1] These substances, atractyloside (**2**) and 4-carboxyatractyloside, function by blocking the transport of adenosine diphosphate (ADP) into mitochondria, thereby decreasing ATP production.[1-3] Atractylosides also occur in the coffee plants *Coffea arabica* and *Coffea robusta* and are consumed in non-negligible amounts by coffee drinkers.[4,5] Our awareness of the anomalous situation in which a known toxin is unknowingly ingested by a large and metabolically variable human population and previous work on the ATP translocation inhibitor[3] bongkrekic acid[6] aroused our interest in the synthesis and biochemistry of atractyligenin and its glycosides. The successful achievement of total synthesis of (±)-**1**[7] is reported herein. A novel approach to the construction of the ring system developed for this problem has also been applied recently to the total synthesis of cafestol.[8]

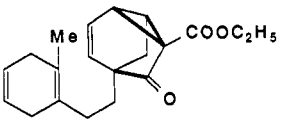
o-Tolylethanol (formed in 97% yield by lithium aluminum hydride reduction in ether of *o*-tolylacetic acid) was reduced with excess lithium in tetrahydrofuran (THF)–ammonia–*tert*-amyl alcohol (1:1:1)[9] at −45 °C for 5 h to give the Birch product **3** (89%)



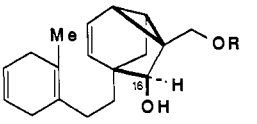
3 X = OH
4 X = I



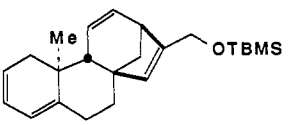
5 X = $COOCH_3$
6 X = CHO
7 X = $COCH_2COOC_2H_5$
8 X = $COCN_2COOC_2H_5$



9



10 R = H
11 R = TBMS



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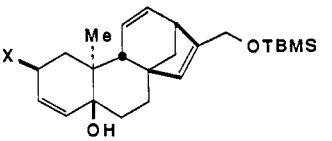
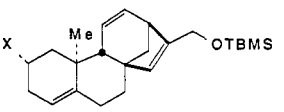
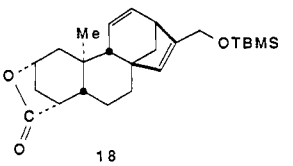


13 X = OH
14 −X = =O



15 −X = =O
16 X = OH
17 X = $OCOSeC_6H_5$



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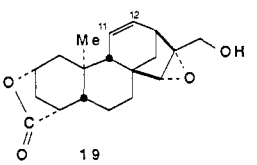

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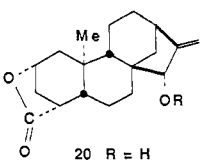
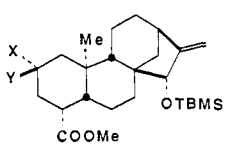
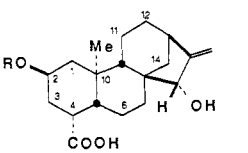


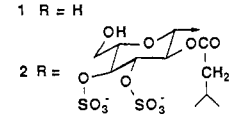
20 R = H
21 R = TBMS



22 X = OH, Y = H
23 X = H, Y = OH



1 R = H



which by treatment with 3 equiv each of triphenylphosphine, imidazole, and iodine in ether–acetonitrile (3:1) at 25 °C for 30 min produced iodide **4** (93%). Methyl cyclohexa-1,3-diene-5-carboxylate[10] was deprotonated (1.1 equiv of lithium diisopropylamide (LDA) in THF at −78 °C for 1 h) and alkylated with iodide **4** (1.1 equiv) in the presence of 1 equiv of hexamethylphosphoric triamide at −78 °C for 5 h and −78 °C to −20 °C for 9 h to afford bicyclic ester **5** (82%). Appendage elaboration to form the β-keto ester **7** was accomplished by the following sequence: (1) reduction by 5 equiv of diisobutylaluminum hydride in methylene chloride at −78 °C for 2.5 h to give the corresponding primary alcohol (90%); (2) Swern oxidation with 1.2 equiv of oxalyl chloride, 2.6 equiv of dimethyl sulfoxide, and 5.5 equiv of

(1) For an outstanding treatise on atractylosides and atractyligenin; see: *Atractyloside: Chemistry, Biochemistry, and Toxicology*; Santi, R.; Luciani, S., Eds.; Piccin Medical Books: Padova, Italy, 1978.
(2) Klingenberg, M. in ref 1, pp 69–107.
(3) Klingenberg, M. *Trends Biochem. Sci.* **1979**, *4*, 249–252.
(4) See: Richler, H.; Spiteller, G. *Chem. Ber.* **1978**, *111*, 3506–3509, and references cited therein for the occurrence of atractyligenin and its glycosides in human urine as a consequence of absorption from ingested coffee.
(5) An excellent summary of the literature on potential harmful effects of dietary atractylosides from coffee which has been provided by Pegel (Pegel, K. H. *Chem. Eng. News* **1981** (July 20) p 4) seems to have been largely ignored.
(6) Corey, E. J.; Tramontano, A. *J. Am. Chem. Soc.* **1984**, *106*, 462–463.
(7) For structure determination and chemistry of atractyligenin, see: (a) Piozzi, F.; Quilico, A.; Mondelli, R.; Ajello, T.; Sprio, V.; Malera; A. *Tetrahedron* **1966**, Suppl. 8, Part II, 515–529. (b) Piozzi, F., Quilico, A.; Fuganti, C.; Ajello, T.; Sprio, V. *Gazetta Chem. Ital.* **1967**, *97*, 935–954. (c) Piozzi, F. in ref. 1, pp 13–32.
(8) Corey, E. J.; Wess, G.; Xiang, Y. B.; Singh, A. K. *J. Am. Chem. Soc.* **1987**, *109*, 4717–4718.
(9) Corey, E. J.; Katzanellenbogen, J. K.; Gilman, N. W.; Roman, S.; Erickson, B. W. *J. Am. Chem. Soc.* **1968**, *90*, 5618–5620.
(10) Hoare, J. H.; Policastro, P. O.; Berchtold, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 6264–6267.

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triethylamine in methylene chloride at −60 °C for 30 min to form aldehyde **6** (95%); (3) reaction of a mixture of **6** and ethyl diazoacetate with 1 equiv of LDA in THF at −78 °C for 2 h to produce the crossed aldol adduct (86%) which upon stirring with a solution of rhodium diacetate[11] in dimethoxyethane at 25 °C for 5 h provided **7** (72%). The diazo ester **8**, generated from **7** in 96% yield by using 1.3 equiv of tosyl azide in 1:5 triethylamine–ethanol at 25 °C for 5 h,[12] was converted with position- and stereospecificity to the cyclopropyl keto ester **9** (67%) by addition over 10 min to a solution of copper(II) bis(salicylidene-*tert*-butylamine) in toluene at reflux.[13] Reduction of **9** with 4 mol equiv of lithium aluminum hydride in ether at −20 °C for 1.5 h produced diol **10**, mp 55–56 °C, (86%) together with a small amount of the 16-epimeric secondary alcohol, mp 88–89 °C, (6%).[14] Silylation of **10** with 1 equiv of *tert*-butyldimethylsilyl chloride and 2.5 equiv of imidazole in dimethylformamide at 20 °C for 1.5 h gave after silica gel (sg) chromatography (5% ether–petroleum ether) the mono *tert*-butyldimethylsilyl (TBMS) ether **11** (91%).

Conversion of **11** to the tetracyclic tetraene **12** could be achieved with good efficiency in a single step. Reaction of **11** (0.04 M in 1-nitropropane) with 2.5 equiv of 2,6-di-*tert*-butyl-4-methylpyridine and 1.1 equiv of triflic anhydride at 0 °C for 10 min, quenching with excess triethylamine, and sg chromatography (0.25% ether in petroleum ether) gave **12** (69%), UV $_{max}$ 268 nm. The stereochemistry of the cyclization product **12** was ascertained by ^{1}H NMR NOE experiments on the further transformation product **15** which was synthesized from **12** by the following sequence: (1) stereospecific conversion of **12** to the corresponding 2β,5β-endoperoxide derivative by selective addition of singlet oxygen to the A-ring diene (O_2, rose bengal, G.E. sunlamp irradiation in 7:3 methylene chloride–methanol, 0.004 M in **12**, at −20 °C for 45 min) (79% yield after sg chromatography with 5% ether in hexane); (2) reduction with excess aluminum amalgam in 95:5 THF–water at 20 °C for 15 min to give diol **13**, mp 139–140 °C; and (3) oxidation with 7 equiv of chromium trioxide in pyridine at 20 °C for 15 min to form hydroxy enone **14**, mp 128–129 °C; (4) trifluoroacetate formation (3 equiv of trifluoroacetic anhydride, 0.5 equiv of 4-(dimethylamino)pyridine in pyridine–methylene chloride at 0 °C, 1 h) followed by reduction with excess zinc powder in 1:1 THF–acetic acid (20 °C, 8 h) to give **15** (81%). ^{1}H NMR NOE difference spectra measured with the β,γ-unsaturated enone **15** showed positive NOE effects between the C(10) angular methyl protons, C(11) olefinic proton, C(1)-α-proton, and C(14) methylene α-proton, thereby establishing that the cyclization of **11** proceeded stereospecifically to form **12**, a conclusion which was confirmed by the conversion of **12** via **15** to (±)-atractyligenin (**1**) as described below.

Reduction of **15** by L-selectride (5 equiv, THF at −78 °C for 1 h) afforded alcohol **16** after sg chromatography (2:1 petroleum ether–ether) which was converted to the selenocarbonate **17** in 80% overall yield by reaction with phosgene (5 equiv) and triethylamine (2.5 equiv) in THF at 20 °C for 2 h, evaporation of solvent, and further reaction with selenophenol and pyridine in benzene at 20 °C for 14 h. Slow addition over 12 h of 1.5 equiv of tri-*n*-butyltin hydride and 0.03 equiv of azoisobutyronitrile in benzene to a solution of selenocarbonate **17** in benzene at reflux led to a novel free radical cyclization across the A-ring to afford the γ-lactone **18**, mp 110–111 °C[15] (73% yield after sg chromatography to separate ca. 10% of an isomeric δ-lactone).[16] Desilylation of **18** (0.24 M tetrabutylammonium fluoride in THF at 20 °C for 30 min) gave the corresponding primary allylic alcohol, mp 177–178 °C, which was stereospecifically converted by oxidation (3 equiv of trityl hydroperoxide, 0.03 equiv of vanadyl acetylacetonate, and 1 equiv of 2,6-lutidine in 3:2 toluene–benzene at 20 °C for 3 h) into epoxy alcohol **19**, mp 159–160 °C (96%).[17] Transformation of **19** into hydroxy γ-lactone **20** was effected by the following sequence: (1) catalytic reduction of the 11,12-olefinic linkage of **19** with 5% Pd–C catalyst, H_2 (1 atm) in ethyl acetate at 20 °C for 1.5 h to provide the corresponding saturated hydroxy γ-lactone, mp 180–181 °C (85%); (2) conversion of the primary alcohol to the corresponding primary bromide (1.05 equiv of carbon tetrabromide and 1.2 equiv of triphenylphosphine in acetonitrile at 20 °C for 1 h); (3) direct reduction of the epoxy bromide in this acetonitrile solution by addition of excess zinc powder and 1:1 THF–acetic acid (final concentration of acetic acid 0.08 M) and stirring at 20 °C for 18 h to give **20**, mp 105–106 °C (65% from epoxy alcohol). The methyl ester TBMS ether of atractyligenin (**23**) was synthesized from **20** by the following sequence: (1) silylation (*tert*-butyldimethylsilyl triflate and 2,6-lutidine in methylene chloride at −78 °C for 2 h) to form **21**, mp 159–160 °C (89%); (2) methanolysis (catalytic amount of anhydrous potassium carbonate in dry methanol at 20 °C for 6 h) to give hydroxy methyl ester **22** (95%); (3) oxidation of the secondary hydroxyl function (pyridinium chlorochromate) to give the corresponding keto methyl ester, mp 166–167 °C (88%); (4) ketone reduction (samarium diiodide[18] in 5:1 THF–H_2O at 20 °C for 10 min) to give after sg chromatography 90% yield of the 2β-alcohol **23** in addition to 7% of the 2α-alcohol **22** (sg TLC R_f values with 1:1.5:2.5 ethyl acetate–ether–petroleum ether as eluent were 0.25 and 0.43, respectively, for **23** and **22**). Desilylation of **23** (0.03 M tetra-*n*-butylammonium fluoride in THF at 20 °C for 14 h) produced the methyl ester of atractyligenin (**1**) (97%), identical with a sample prepared by reaction of ethereal diazomethane with authentic atractyligenin,[19] by infrared, 500 MHz ^{1}H NMR, and mass spectroscopy as well as by sg TLC chromatographic comparison in a number of different solvent systems. The assignment of each proton in the ^{1}H NMR spectrum of **1** methyl ester was possible by the COSY method; in addition, irradiation of the C(10) angular methyl group in **1** methyl ester produced positive NOE effects on the following protons: COO-CH_3, 1α-H, 6α-H, 11α-H, 12α-H, and 14α-H. The new NMR data totally support the structure originally assigned to **1**, which follows as well from the synthesis reported herein. Conversion of the methyl ester of atractyligenin to the free acid **1** was accomplished by treatment with 9 equiv of lithium *n*-propylthiolate[20] (0.044 M in hexamethylphosphoric triamide) at 0 °C for 1 h and 20 °C for 9 h (84% yield after sg chromatography with 9:1 ether–ethanol for elution). Synthetic (±)-atractyligenin was indistinguishable from a naturally derived sample by spectroscopic and chromatographic comparison.

The synthesis of (±)-atractyligenin (**1**) reported here proceeds with uniformly good yields and good control of stereochemistry. Noteworthy features from the viewpoint of synthetic methodology include the following: (1) successful alkylative assembly of the major carbon unit (**4** → **5**) in an effective process which can potentially be made enantioselective as well; (2) selective internal cyclopropanation (**8** → **9**); (3) stereospecific ring closure to generate the required ring system and stereochemistry (**11** → **12**); specific A-ring functionalization (**12** → **13**); internally directed introduction of the 4α-carboxylic acid function (**17** → **18**); specific allylic hydroxyl transposition (**18** → **20**); stereoselective inversion

(11) Pelliciari, R.; Fringuelli, R.; Ceccherelli, P.; Sisani, E. *J. Chem. Soc., Chem. Commun.* **1979**, 959–960. All synthetic products beyond this point were racemic.

(12) (a) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 733–749. (b) Regitz, M.; Menz, F.; Rüter, J. *Tetrahedron Lett.* **1967**, 739–742.

(13) Corey, E. J.; Myers, A. G. *Tetrahedron Lett.* **1984**, *25*, 3559–3562.

(14) The major diol **10** and minor diol were readily separated by silica gel (sg) chromatography; R_f values are 0.43 and 0.25, respectively on TLC–sg plates with 1:1 ethyl acetate–ether. Analysis of the ^{1}H NMR spectra of **10** and its epimer allowed assignment of configuration since the carbinol proton of **10** showed a positive NOE effect with the methylene group attached to the three-membered ring, an effect not observed in the epimer; see also ref 8.

(15) Similar cyclizations to form monocyclic or fused bicyclic γ-lactones from acetylenes (but not olefins) have recently been reported by Bachi and Bosch (Bachi, M. D.; Bosch, E. *Tetrahedron Lett.* **1986**, *27*, 641–644).

(16) Slow addition of the tin hydride reagent is important, since at high steady-state concentrations of this reagent the isomeric δ-lactone is formed by an interesting anti-Markovnikov addition route.

(17) This reaction was not stereospecific when *tert*-butyl hydroperoxide was used.

(18) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698.

(19) We are deeply grateful to Prof. Franco Piozzi, University of Palermo, for a generous gift of atractyligenin.

(20) Bartlett, P. A.; Johnson, W. S. *Tetrahedron Lett.* **1970**, 4459–4462.

of hydroxyl from axial to equatorial (**22** → **23**) by SmI_2 reduction of a cyclohexanone.[21]

Supplementary Material Available: Experimental data for compounds listed in the paper (8 pages). Ordering information is given on any current masthead page.

(21) This research was assisted financially by grants from the National Institutes of Health and the National Science Foundation. We are most grateful to Dr. Günther Wess for many helpful discussions and early studies on the crucial cationic cyclization step in the series leading to successful synthesis of cafestol.[8]

Asymmetric Hydrooligomerization of Propylene

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Received April 8, 1987

Recently optically active homogeneous catalysts have been used to polymerize propylene to isotactic polymers;[1] the synthesized high polymer did not have a detectable optical activity in solution and in the melt as expected.[2] However, with the same catalysts optically active isotactic oligomers of propylene with detectable optical rotation should be produced.[2] Knowing the sign of optical rotation of the isotactic oligomers it is possible to relate enantioface of the α-olefin, prevailingly reacting, with the known structure[3] of the chiral catalyst precursor, thus obtaining further important indications on the regio- and stereospecific polyinsertion mechanism.

The polymerization of propylene at 0 °C in toluene solution (400 cm^3; C_3H_6 = 2.4 mol/L) for 72 h in the presence of hydrogen (eq 1) (p_{H_2} between 1 and 4 bar during the polymerization) using

$$CH_2{=}CHR \xrightarrow[H_2]{\text{catalyst}} H\text{-}[CH_2\text{-}CH(R)]_n\text{-}H \qquad (1)$$

R = H, alkyl

a catalyst obtained from a mixture of (−)-(*R*)-ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)dimethylzirconium,[3] **1** [42 mg, $[\alpha]_{436}^{25°} = -540°$ (*c* = 3.4 mg/mL in benzene)], and methylaluminoxane[4] (388 mg; $\bar{M}_n$ = 1200) yields a mixture of hydrogenated isotactic polypropylenes and liquid hydrogenated oligomers (288.5 g). The solid high polymers (230.2 g) were purified and fractionated as usual[5] (Table I, fractions F–J). From the toluene solution, after elimination of the catalyst residues, the low-boiling oligomers were separated by distillation[6] (1.4 g, fraction A, Table I). The higher boiling oligomers (56.9 g) were fractionated by dissolution with a series of solvents at room temperature (fractions B–E, Table I). The IR and ^{13}C NMR spectra of the fractions indicate the presence of *n*-butyl, *n*-propyl, and isobutyl groups with a large prevalence of *n*-propyl groups; no bands corresponding to olefinic carbon atoms could be detected, and therefore the reaction can be considered as a "hydrooligomerization". The above results show that (i) hydrogenolysis of zirconium–carbon bonds is much faster than β-hydrogen elimination, (ii) polypropylene chains start and grow according to "1-2"-insertion (presence of *n*-propyl groups and isopropyl groups as chain ends; no detectable amount of $-CH(CH_3)-CH_2-CH_2-CH(CH_3)$ sequences[7] in fraction J), and

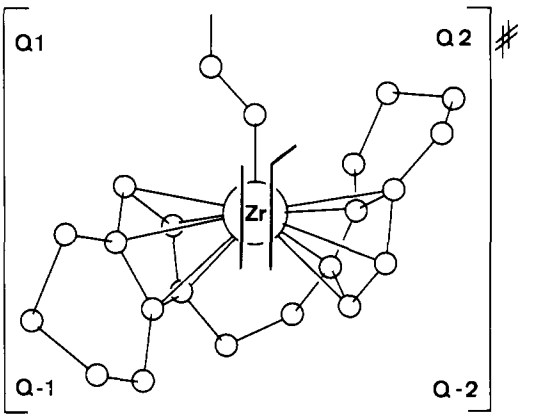

Figure 1. Simplified stereochemical model of a transition state for propylene insertion in the Zr–C< bond of the catalytic system prepared from **1**. The Zr atom and the first carbon atom of the growing chain lie in the plane of the drawing, and the incoming propylene molecule, with the *Re* enantioface directed toward the catalyst, is projected on the same plane.

(iii) occasional "2-1"-insertions lead, after reaction with hydrogen, to chain termination (presence of *n*-butyl groups as chain ends). Furthermore ^{13}C (Table I footnote *o*) and ^1H NMR spectra indicate that the oligomers have an isotactic structure.[8,9]

The molar rotation of all the fractions, $[\Phi]_D^t$, (Table I) is positive and not very different, as expected for polymer chains which do not have largely preferred (e.g., helical) conformations in solution.[10,2] The gas chromatograms of fractions A and B (Carbowax 15%, 4 m) at 200 °C revealed a series of peaks that appeared as pairs. Fraction A was reexamined with GC–MS at lower temperature (80–150 °C), and three pairs of peaks were observed. The products corresponding to the two peaks[11] of each pair have the same molecular weight, that is for the three pairs 128, 170, and 212, respectively. The two compounds having MW 128 were identified as 2,4-dimethylheptane, **2**, and 4-methyloctane, **3**, respectively, by comparison of the ^{13}C NMR spectrum of their mixtures and of their mass spectrum with that of the corresponding authentic samples.

The isomer of molecular weight 170 with the shorter retention time[6] was identified by ^{13}C NMR as a single diastereoisomer of the 2,4,6-trimethylnonane, **4**. The ^1H NMR spectrum of this compound when compared to the spectrum of meso and racemic 2,4,6,8-tetramethylnonane[12] reveals that the asymmetric carbon atoms in position 4 and 6 have opposite absolute configuration[13] and is therefore the u[13] diastereoisomer. The isomer with higher retention time was identified as (u)-4-6-dimethyldecane, **5**, on the basis of ^1H and ^{13}C NMR spectra of its mixture with **4** (75% of **5** by GC analysis) by subtracting the spectrum of **4** from the spectrum of the mixture of **4** and **5**. The identification was

(1) Kaminsky, W. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Kodanska: Tokyo, 1986; p 293.
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