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Total Synthesis of (-)-Kjellmanianone from Tricyclodecadienone. A Revision of its Absolute Configuration

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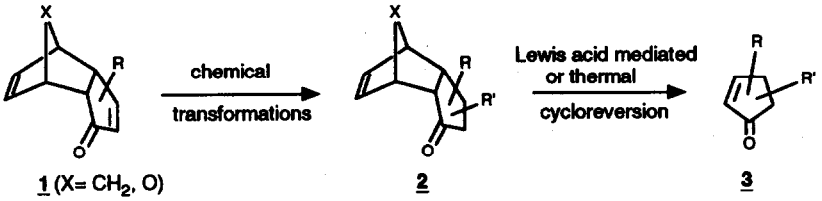
Abstract: *A stereocontrolled total synthesis of the naturally occurring cyclopentenoid (-)-kjellmanianone* **8** *has been accomplished starting from enantiopure (+)-tricyclo[5.2.1.$0^{2,6}$]decadienone 2-carboxylic ester* **5**. *Key steps in this approach to* **8** *include Barton's halodecarboxylation of* **17** *followed by methoxylation to produce* **20**, *nucleophilic epoxidation of enolacetate* **26** *to introduce the α-hydroxyketone moiety and thermal fragmentation of* **27** *using flash vacuum thermolysis (FVT) to give* **8**. *The R configuration of synthetic (-)-kjellmanianone was unequivocally established by an X-ray diffraction analysis of its precursor* **27**, *implying that the previously assigned absolute configuration of (+)-kjellmanianone is incorrect.*

Natural products containing an oxygenated cyclopentanone or cyclopentenone substructure may show significant biological activity. Notable examples of biologically active monocyclic cyclopentanoids are prostaglandins[1], pentenomycins[2], methylenomycins[3] and the marine eicosanoids[4]. In recent papers we[5] and others[6] demonstrated that tricyclodecadienones **1** are excellent synthons for the synthesis of a great variety of functionalized cyclopentenones. Conjugate addition to the enone moiety of **1**, followed by electrophilic substitution and appropriate group transformations, allows the stereoselective introduction of various functional groups. The obtained tricyclodecenones **2** (X= CH_2, O) can then be converted into the desired cyclopentenones **3** by Lewis acid mediated or thermal [4+2] cycloreversion. The overall reaction sequence, which is summarized in Scheme 1, leads to cyclopentenoids **3** in a highly stereoselective manner. The

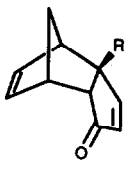
Scheme 1



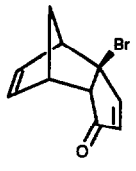
1 (X= CH_2, O) **2** **3**

availability of both antipodes of **1** (X= CH_2) in enantiopure form, either by enzymatic resolution[6b,7] or asymmetric synthesis[8], completes this strategy and makes it extremely useful for the enantioselective synthesis of a variety of cyclopentenoids.

Key structure in our route to cyclopentanoids is tricyclic carboxylic acid **4** which is conveniently accessible from cyclopentadiene and benzoquinone[9]. Recently we discovered[10] that acid **4**, notwithstanding its highly unsaturated character, readily and efficiently undergoes radical decarboxylation using Barton's methodology[11]. A variety of synthetically interesting and promising 6-substituted tricyclodecadienones has now become easily available. Using this approach 6-methoxytricyclodecadienone **7** is obtained in an excellent overall yield by bromodecarboxylation of **4** followed by alkaline methanolysis of initially produced tricyclic bromide **6**. The strategy as depicted in Scheme 1 suggests that tricyclic alkyl ethers, such



4 R= CO_2H
5 R= CO_2Et



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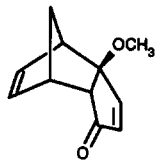

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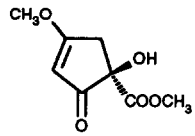
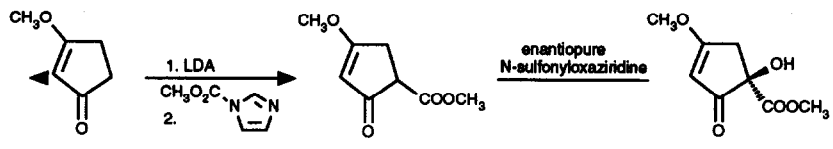


8

as **7**, offer excellent prospects for the enantioselective synthesis of cyclopentanoids containing an β-alkoxy enone moiety. In this paper[12], we will disclose an efficient route to enantiopure (R)-kjellmanianone **8**, a naturally occurring cyclopentenoid possessing such a β-alkoxy enone functionality, starting from homochiral (+)-ethyl tricyclodecadienone carboxylate **5**[7a,9]. In addition, it will be shown that the absolute configuration of (+)-kjellmanianone, as established previously, is incorrect.

Kjellmanianone **8**, a highly oxygenated cyclopentenoid, was isolated by Nakayama et al.[13] in 1980 from the marine brown algae, *sargassum kjellmanianum* and shown to possess moderate activity against gram positive bacteria such as *E.Coli* K12 and *Bacillus subtilis var niger*. The structure of kjellmanianone was established by single crystal X-ray analysis. Using the Bijvoet method this study also provided its absolute configuration as R. Interestingly, the optical rotation measured for the natural product appeared to be extremely low, *viz.* $[\alpha]_D$= +1.6 (c 1.8, $CHCl_3$). Shortly after its isolation, an enantioselective synthesis of (+)-kjellmanianone **8** was achieved by Smith *et al.* by asymmetric hydroxylation of 5-carbomethoxy-3-methoxy-cyclopent-2-enone **10** using enantiopure N-sulfonyloxaziridines[14] (Scheme 2). Optical yields up

Scheme 2



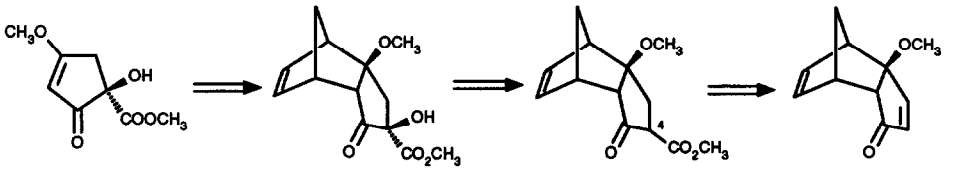
9 **10** cy: 68% **8** cy: 60% ee: 68.5%

to 68.5% ee were obtained. Although enantiopure (+)-kjellmanianone was not obtained, its optical rotation

was calculated to be *ca.*$[\alpha]_D$= ≈100 indicating that natural kjellmanianone, as isolated by Nakayama, is almost completely racemic. By applying the exciton chirality method as developed by Mason[15] and Nakanishi[16], the absolute configuration of (+)-kjellmanianone was again established as R. Enantiopure kjellmanianone has hitherto not been prepared.

Retrosynthetic analysis of kjellmanianone using the strategy as depicted in Scheme 1, reveals that a most efficient route to this cyclopentenoid would involve three major steps: (i) regioselective 1,4-reduction of the enone moiety in 6-methoxy tricyclodecadienone **7** followed by methoxycarbonylation to form **12**; (ii) hydroxylation at the ketone C_α-position (C_4 in the tricyclic system) in **12** which should stereoselectively lead to **11**; (iii) thermal [4+2]-cycloreversion of **11** to afford kjellmanianone **8** (Scheme 3). In order to

Scheme 3



8 **11** **12** **7**

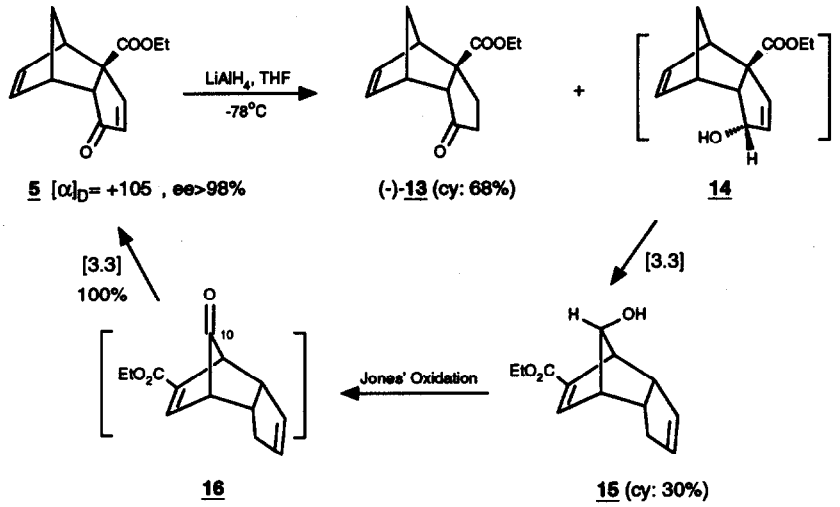
obtain natural (R)-kjellmanianone **8**, this synthetic scheme necessitates the use of enantiopure (+)-tricylic ester **5** as the starting material. The absolute configuration of this ester is as depicted in the Schemes.

The regioselective enone reduction of **7** appeared to be unexpectedly troublesome. The use of zinc in acetic acid as a typical 1,4-enone reducing agent did not meet with any success[17]. At room temperature no reaction was observed at all, whereas at elevated temperatures mixtures of products were obtained which did not contain any of the desired reduction product. With lithium aluminum hydride in tetrahydrofuran at -78 °C the predominant product turned out to be the 1,2-reduction product in nearly qantitative yield. With lithium in ammonia the 1,4-reduction product was formed, however only in a maximum yield of 25%.

These disappointing results prompted us to change our synthetic strategy. We figured that the desired reduction of the enone double bond could equally well be accomplished at the very beginning of our synthetic route, *viz.* at the stage of the starting ester **5**. Both Barton's bromodecarboxylation and the subsequent methanolysis of the bridgehead bromide were not expected to be affected by the absence of the enone double bond. Attempted reduction of ester **5** with zinc in acetic acid under a variety of conditions again did not result in appreciable amounts of desired ketone **13**. Ester **5** was recovered almost quantitatively even after prolonged heating of the mixture for more than eighteen hours. This reluctance of **5** to undergo zinc reduction is in remarkable contrast with the zinc reduction of parent tricyclodecadienone **1** (X=CH_2, R=H) which, under identical conditions, proceeds smoothly in a 1,4-enone fashion. The presence of a substituent at the C_6-position in the *endo*-tricyclodecadienone system apparently severely hampers this reduction with zinc. Other metal reduction methods, such as lithium in ammonia or the use of copper hydride, did not lead to significant yields of **13** either.

Much better results were obtained when lithium aluminum hydride was used. At -78 °C in THF, ester **5** gave a mixture of the desired keto-ester **13** and bridge alcohol **15** in a 7:3 ratio, in almost quantitative yield

Scheme 4

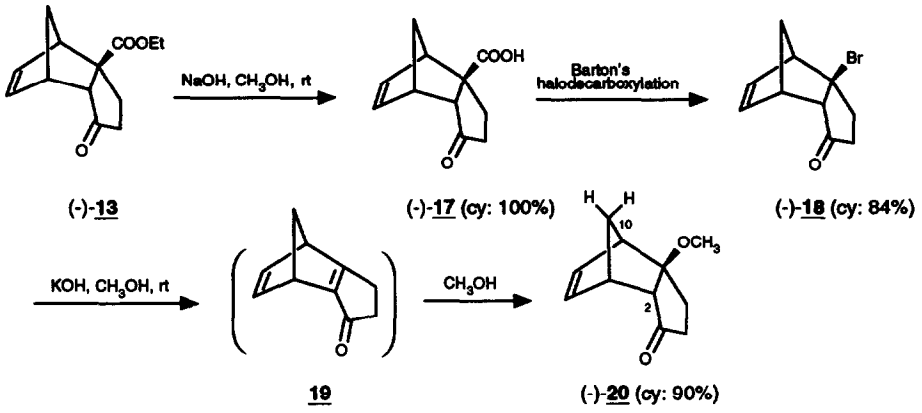


(Scheme 4). Both compounds could readily be separated by flash chromatography to give keto-ester **13** in 68% yield. Minor alcohol **15**, the formation of which is conveniently explained by initial stereoselective 1,2-reduction of **5** to give **14** followed by a fast Cope rearrangement[18], could quantitatively be reconverted into **5** by a Jones oxidation. Oxidation of **15** gives the corresponding bridge ketone **16**, which, due to an increased angle strain at C_{10}, immediately rearranges to the thermodynamically more stable ketone **5** in a Cope fashion[18]. The predominant formation of the 1,4-addition product in the hydride reduction of **5** can be rationalized by assuming initial coordination of lithium aluminum hydride with the γ-ester function placing it in a favorable position for hydride transfer to the β-carbon of the enone moiety. If such coordination is absent, as is the case in methyl ether **7**, conjugate addition is disfavored due to van der Waals interactions between the adjacent *exo*-γ-substituent and the incoming nucleophile, and 1,2-addition will be the preferred reduction pattern.

Having established the best conditions for an effective reduction of the enone double bond in racemic **5**, enantiopure (+)-**5** ($[\alpha]_D$= +105 , ee>98%) was subjected to lithium aluminum hydride reduction to give tricyclic ketone (-)-**13** without any loss of optical purity.

Hydrolysis of ester (-)-**13** with sodium hydroxide in methanol at room temperature smoothly gave carboxylic acid (-)-**17** in quantitative yield (Scheme 5). The bromodecarboxylation of (-)**17** was carried out under identical conditions as used for the transformation of carboxylic acid **4** into enone bromide **6**[10]. Conversion of **17** into the corresponding acid chloride with oxalyl chloride, followed by treatment with the sodium salt of N-hydroxypyridine-2-thione afforded the N-acyloxypyridine-2-thiono ester which was not isolated but immediately reacted with bromotrichloromethane. An almost quantitative formation of bromide **18** was achieved when the reaction was carried out at reflux temperature and using a 250 W tungsten lamp to initiate the radical decomposition of the hydroxamic ester. In contrast to enone bromide **6**, this bromoketone **18** could readily be purified by flash column chromatography without too much loss of material. Enantiopure bromide (-)-**18** was thus obtained in an excellent overall yield of 84%.

Scheme 5

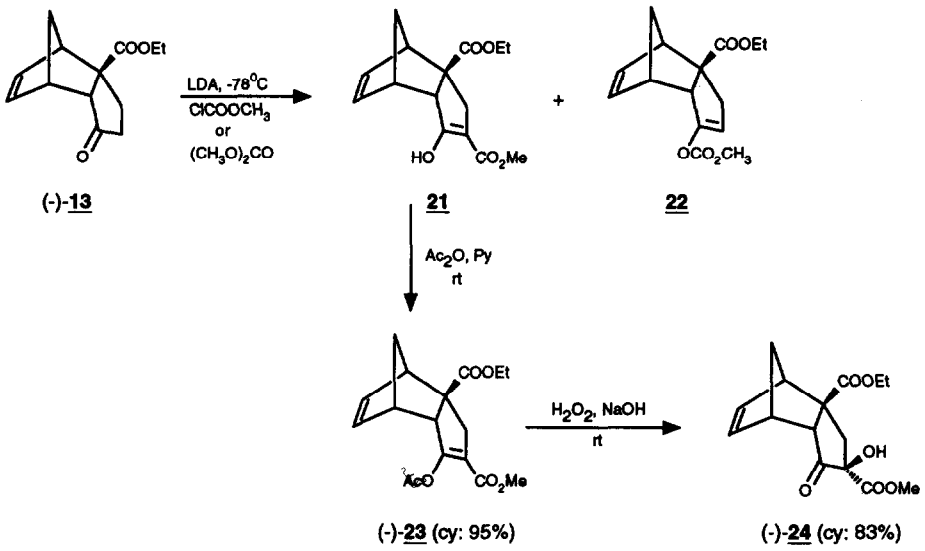


Bromide (-)-18 was rapidly methoxylated upon treatment with potassium hydroxide in methanol to give a single tricyclic methoxy-compound in 90% yield. In analogy with the methoxylation of tricyclic bromide **6**, this transformation is assumed to involve the intermediacy of cyclopentanone annulated norbornadiene **19**, which, notwithstanding the relative mild reaction conditions used, immediately undergoes complete conjugate addition of methanol[10] (Scheme 5). The absence of any enone **19** in the reaction mixture is indicative of the high reactivity of this annulated enone system which is much more strained than its non-annulated isomer **1**. In principle, the addition of methanol to the central enone unit in **19** can lead either to 6-methoxy substituted *endo*- or *exo*-tricyclodecenone. Since only a single methoxy compound is formed the steric accessibility of the two faces of the enone unit in **19** is apparently quite different. Molecular modeling indicates that methoxide addition *syn* to the methylene bridge in **19**, thus retaining the original *endo*-configuration of the tricyclodecenone skeleton, is indeed more favorable than addition *syn* to the unsaturated ethylene bridge. This conclusion was confirmed by a detailed 2-D ^{1}HNMR spectroscopic analysis which unequivocally revealed that the addition product isolated from this methanolysis of **18** is *exo*-6-methoxy-*endo*-tricyclodecenone **20**. Especially indicative is the observation of a strong NOE-effect for one of methylene bridge C_{10}-protons on irradiation of the C_2-proton in **20**. Such a magnetic interaction is only conceivable for *endo*-structure **20**. At a later stage of this study, unequivocal confirmation of the correctness of this assignement was obtained from the photochemical cage closure of enol carbonate **28** and the X-ray diffraction analysis of **27** *(vide infra)*.

Having attained an effective and stereoselective synthesis of **20**, the next task involves the stereoselective introduction of the *endo*-C_4-methoxycarbonyl- and the *exo*-C_4-hydroxy group. It seems logical to introduce the methoxycarbonyl group first and then find methods to hydroxylate the active C_4-methylene position of the β-ketoester. This sequence of reactions was first studied for tricyclic ester **13** as a model system (Scheme 6).

Deprotonation of keto-ester **13** using lithium diisopropylamide at -78 °C followed by the addition of methyl chloroformate gave a mixture of the desired methoxycarbonylation product **21** and the O-alkylated compound **22** in about equal amounts and in 75% total yield. Almost exclusive formation of **21** was

Scheme 6



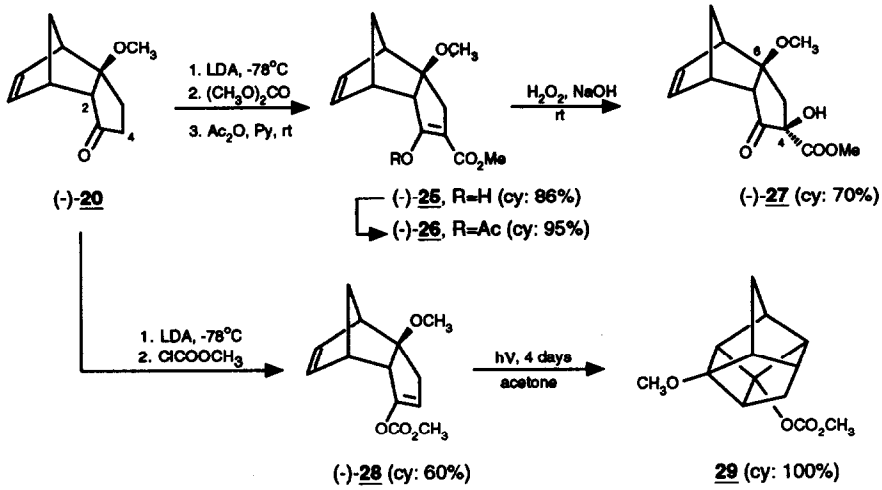
achieved by using dimethyl carbonate instead of methyl chloroformate as the methoxycarbonylation reagent. The ^{1}HNMR spectrum of **21** showed that this compound is almost entirely enolized.

For the introduction of an hydroxylic function at the C_4-position in **21**, common methods for the hydroxylation of β-ketoesters employing electrophilic oxidation reagents, *e.g.* carboxylic peresters and transition metal peroxides,[19] were considered. However, such electrophilic reactions are not feasible for the α-hydroxylation of tricyclodecenone derivatives such as **21** as the rather strained norbornene double bond will probably compete in such an electrophilic oxidation reaction[20]. Since enol esters derived from a β-ketoester can be considered as Michael acceptors, a nucleophilic epoxidation of such esters is an attractive alternative for the regioselective hydroxylation of tricyclodecenone ester **21**. For this purpose acetate **23** was prepared in nearly quantitative yield by acylation of enolate **21** with acetic anhydride and pyridine. The nucleophilic epoxidation of enol acetate **23** was carried out under the usual conditions using hydrogen peroxide and sodium hydroxide in a dichloromethane/methanol mixture as the solvent at room temperature for 16 hr. In this manner the desired α-hydroxyester **24** was obtained as a single compound in 83% yield after chromatography on silica gel. This rewarding result shows that nucleophilic hydroxylation of ester enolates derived from β-keto-esters is an alternative for the synthesis of α-hydroxyketones in those cases where *m*-CPBA cannot be used. The isolation of a single hydroxy ester indicates the high stereoselectivity of this alkaline epoxidation of **23**. Assuming initial attack at the C_3 position in **23** addition of the hydroperoxide anion from the *exo*-face of the tricyclodecadiene system is much more favored than from the *endo*-face due to severe steric interaction of the nucleophile with the C_8-C_9 norbornene double bond. The preference for *exo*-atack at this C_3-position is convincingly demonstrated by the hydride reduction of ester **5** which stereospecifically leads to the corresponding *exo*-alcohol (see Scheme 4). This consideration suggests the formation of **24** as the ultimate product in this reaction. This assignment is confirmed by the ^{1}HNMR spectral data of **24** and at a later stage by an X-ray diffraction analysis of the corresponding 6-methoxy

congener **27** *(vide infra).*

The methoxycarbonylation of enantiopure methoxy ketone (-)-**20** with dimethyl carbonate and lithium diisopropyl amide proceeded with the same efficiency as is observed for ester **13**. No elimination of the methoxy group, which could be envisaged here by initial competitive deprotonation at the C_2-position, is observed (Scheme 7). Interestingly, the use of methyl chloroformate instead of dimethyl carbonate leads

Scheme 7



predominantly to O-acylation affording enol carbonate **28**. This enol carbonate could quantitatively be converted into 1,3-bishomocubane ester **29** by photolysis in benzene containing 10% of acetone, which provides additional evidence for the *endo*-configuration of the 6-methoxytricyclodecenone (-)-**20**.

β-Keto ester (-)-**25**, which is completely enolized, was quantitatively converted into acetate (-)-**26** using standard methodology. Nucleophilic epoxidation of (-)-**26**, under identical conditions as used above for the epoxidation of enolester **23**, proceeded smoothly to give the desired α-hydroxy-β-keto ester (-)-**27** as a white crystalline material in 70% yield after flash column chromatography on silica gel. To exclude any ambiguity about the stereochemisty around C_4 in (-)-**27** an X-ray diffraction analysis was performed. The structure of (-)-**27** was indeed fully confirmed (Figure)[21].

In the final step, thermal [4+2]cycloreversion of (-)-**27** should now lead directly to kjellmanianone **8** (Scheme 8). When (-)-**27** is subjected to thermolysis at 500 °C and 0.03 mbar, applying the technique of flash vacuum thermolysis, a smooth retro-Diels-Alder reaction was observed. The expected 2-hydroxycyclopentenone ester **8** was produced in almost quantitative yield as solid material. Recrystallization from diisopropyl ether gave an optically pure sample with $[\alpha]_D$= -115.0 (c 1.15, $CHCl_3$) and melting point 157-158 °C. The spectral data of **8** are in full agreement with its proposed structure and identical to those reported for kjellmanianone[13,14]. However, with respect to the optical properties of this cyclopentenoid considerable differences came to light. The optical rotation observed for enantiopure kjellmanianone is considerably higher than expected on the basis of the rotation found by Smith *at al.*[14] for their (+)-kjellmanianone (m.p.= 126-128 °C, ee= 68.5%, $[\alpha]_D$= +67.9). Strikingly and unexpectedly, the sign of rotation of kjellmanianone synthesized according to our route appeared to be opposite to that

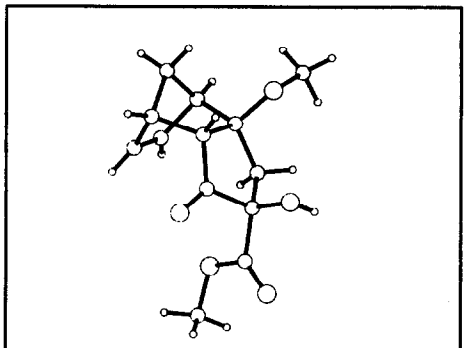
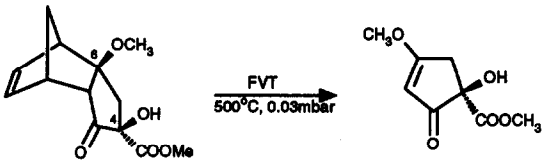


Figure. X-ray structure of (-)-27

Scheme 8



(-)-27 (-)-(R)-8 (c.y.: >90%; $[\alpha]_D$= -115.0)

observed by Nakayama and Smith[13,14].

Based on the well-established absolute configuration of starting tricyclic ester (+)-5[7a,b,22], the absolute configuration of our (-)-kjellmanianone is R at C_4 (Scheme 8). As a consequence, the absolute configuration of (+)-kjellmanianone as established earlier by Nakayama[13] and Smith[14] using X-ray diffraction and the exciton chirality method, respectively, must be incorrect and has to be revised to S. Although there is no doubt about the correctness of the X-ray structure analysis of natural kjellmanianone, a reliable determination of its absolute configuration is in fact impossible because the isolated kjellmanianone is almost completely racemic with an ee of less than 1.5%. At that time the racemic nature of natural kjellmanianone was probably not realized. Our result also shows that the exciton chirality method as used by Smith *et al.* should be handled with great care, certainly for those compounds for which no precedents are available[23].

In conclusion, we have realized an effective and completely enantioselective synthesis of kjellmanianone, a rather sensitive and labile cyclopentenoid, illustrating the high synthetic potential of the tricyclodecadienone system as a chiron for cyclopentenoid synthesis.

Experimental

General remarks

Melting points were measured with a Reichert Thermopan microscope and are uncorrected. IR spectra were

recorded on a Perkin-Elmer 298 infrared spectrometer. ^1H and ^{13}C-NMR spectra were recorded on a Bruker AM-400 spectrometer, using TMS as an internal standard. For mass spectra a double focussing VG 7070E mass spectrometer was used. Capillary GC analyses were performed using a Hewlett-Packard 5890A, containing a cross-linked methyl silicone column (25m). Flash chromatography were carried out at a pressure of ca. 1.5 bar, a column length of 15-25 cm and a column diameter of 1-4 cm, using Merck Kieselgel 60H. Elemental analyses were performed on a Carlo Erba Instruments CHNS-O 1108 Elemental analyzer. Optical rotation were determined on a Perkin-Elmer 241 polarimeter. All solvents used were dried and distilled according to the standard procedures.

(-)-(1R,2R,6R,7S)-*Ethyl 5-oxo*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-ene-2-carboxylate* **13** *and ethyl* anti-*10-hydroxy*-endo-*tricyclo[5.2.1.0^{2,6}]deca-4,8-diene-8-carboxylate* **15**

A suspension of $LiAlH_4$ [1.0 g (0.26 mol) in 100 ml dry THF] was kept at room temperature overnight. A clear top layer solution of $LiAlH_4$ (~90 ml) was transferred to a three-necked flask equipped with thermometer and stirring magnetic bar and a solution of enone **5** (2.18 g, 10 mmol, $[\alpha]_D$= +105, ee > 98 %) in THF (10 ml) added at -78 °C (5 min.) using a syringe. After 10 min, an excess of acetone was added, followed by 3 % HCl aq. Extraction with ether (3x), several washings (brine), drying (Na_2SO_4) and concentration *in vacuo* produced 1.07 g of an oil. Purification by flash chromatography (n-hexane /EtOAc = 2/1) gave pure **13** (1.5 g, 68%) as a colorless oil and **15** (0.66 g, 30%).

13: $[\alpha]_D^{25}$= -87.3 (c 1.14, CH_3OH). ^1H-NMR (400 MHz, $CDCl_3$): δ 6.29 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 6.25 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.8 Hz, 1H, H_8 or H_9), 4.22 (q, J=7.1 Hz, 2H, OCH_2), 3.35 (m, 2H, two of H_1, H_6 and H_7), 3.24 (brs, 1H, one of H_1, H_6 and H_7), 2.00-2.60 (m, 4H, H_3 and H_4), 1.61 A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H_{10a} or H_{10s}), 1.57 B A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H_{10a} or H_{10s}), 1.30 (t, J=7.1 Hz, 3H, OCH_2CH_3). IR (CH_2Cl_2): ν 3010-2820 (C-H, sat.), 1735 (C=O), 1725 (C=O) cm^{-1}. EI/MS: *m/e* (%) 220 (0.6, M^+), 192 (0.3, M^+-CO), 175 (6, M^+-OEt), 155 (52, M^++1-C_5H_6), 66 (100, $C_5H_6^+$). EI/HRMS *m/e*: 221.1168 [calc.for $C_{13}H_{17}O_3(M^+$+1): 221.1178].

15: ^1H-NMR (400 MHz, $CDCl_3$): δ 6.77 (d, $J_{1,9}$=3.7 Hz, 1H, H_9), 5.50 (s, 2H, H_4 and H_5), 4.18 (q, J=7.0 Hz, 2H, OCH_2), 2.80-2.31, 3.38-3.72, 3.87 (m, 5H, H_1, H_6, H_7, H_{10} and OH), 1.49-1.56 (m, 3H, H_2 and H_3), 1.29 (t, J=7.1 Hz, 3H, OCH_2CH_3). IR (CH_2Cl_2): ν 3620 (free OH), 3480 (H-bond OH), 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1710 (C=O), 1590 (C=C, conj.) cm^{-1}.

(-)-(1R,2R,6R,7S)-*5-Oxo*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-ene-2-carboxylic acid* **17**

Ester **13** (2.2 g, 10 mmol) in a 10% solution of NaOH in methanol (30 ml, 10% was stirred at room temperature for 2h. The mixture was neutralized and concentrated to nearly dryness. Water (50 ml) was added, followed by extraction with ethyl acetate (3x), several washings with brine and water, drying (Na_2SO_4) and concentration *in vacuo* to give **17** (2 g, ~100%) as a white solid.

17: m.p.: 115-118 °C (diisopropyl ether), $[\alpha]_D^{25}$= -114.4 (c 1.12, CH_3OH). ^1H-NMR (400 MHz, $CDCl_3$): δ 9.5 (brs, 1H, COOH), 6.29 (m, 2H, H_8 and H_9), 3.40 (brs, 1H, H_1 or H_7), 3.37 (d, $J_{6,7}$=4.5 Hz, 1H, H_6), 3.28 (brs, 1H, H_1 or H_7), 2.41, 2.26, 2.14 and 1.86 (4 x m, 4H, H_3 and H_4), 1.66 (m, 2H, H_{10}). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 218.8/183.0 (quat.), 138.3/135.1/59.0 (tert.), 58.2 (quat.), 51.4 (sec.), 51.1/46.5 (tert.), 40.7/27.8 (sec.). IR (CH_2Cl_2): ν 3500-2300 (COOH), 3010-2820 (C-H, sat.), 1725 (C=O), 1695 (C=O) cm^{-1}. CI/MS: *m/e* (%) 193 (6, M^++1), 127 (62, M^++1-C_5H_6), 66 (100, $C_5H_6^+$). EI/HRMS *m/e*: 193.0863 [calc.for $C_{11}H_{13}O_3(M^+$+1): 193.0865].

(-)-(1S,2R,6R,7R)-*6-Bromo*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **18**

Oxalyl chloride (5 ml) and 10 drops of dimethyl formamide were added to a solution of acid **17** (2.9 g, 15 mmol) in benzene (25 ml) at room temperature. After stirring for 1h with protection from moisture, the solvent and excess oxalyl chloride were evaporated. Benzene (10 ml) was added and resulting solution added dropwise (20 min.) to a dried, stirred suspension of N-hydroxypyridin-2-thione sodium salt (2.9 g, 19 mmol) in benzene (50 ml) and bromotrichloromethane (50 ml) which was kept at reflux temperature and under nitrogen while irradiating with a 250 w tungsten lamp . After completion of the addition the reaction mixture was cooled to room temperature and evaporated to dryness. The crude product was purified by flash chromatography (n-hexane /EtOAc = 9/1) to give pure **18** (2.85, 84%) as a colorless oil.

18: $[\alpha]_D^{25}$= -117.9 (c 1.97, CH_3OH). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.23 (m, 2H, H_8 and H_9), 3.41 (brs, 1H, H_1 or H_7), 3.32 (d, $J_{1,2}$=4.5 Hz, 1H, H_2), 3.25 (m, 1H, H_1 or H_7), 2.69, 2.57, 2.33 and 2.11 (4xm, 4H, H_4 and H_5), 2.26 A of AB (d, $J_{10a,10s}$=8.9 Hz, 1H, H_{10s}), 1.91 B A of AB (d, $J_{10a,10s}$=8.9 Hz, 1H, H_{10a}). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 216.5 (quat.), 138.0/134.5 (tert.), 71.1 (quat.), 66.0/57.9 (tert.), 52.7 (sec.), 47.0 (tert.), 41.8/37.4 (sec.). IR (CH_2Cl_2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1730 (C=O) cm^{-1}. CI/MS: *m/e* (%) 229/227 (0.1/0.1, M^++1), 163/161 (12/13, M^++1-Br), 147 (12, M^+-C_5H_6), 66 (29, $C_5H_6^+$). EI/HRMS *m/e*: 227.0071 [calc.for $C_{10}H_{12}O^{79}Br(M^+$+1): 227.0072].

(-)-(1S,2R,6R,7R)-*6-Methoxy*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one* **20**

A solution of bromide **18** (2.3 g, 10 mmol) in methanol (10 ml) was added dropwise (10 min.) to a solution of 20% KOH in methanol (50 ml) at 5 °C. After the addition was complete stirring was continued for another 5 min. The reaction mixture was neutralized with HCl aq. (10 %), concentrated *in vacuo* and the residue extracted with ethyl acetate (3x), washed with brine, dried (Na_2SO_4) and concentrated to give a crude oil. Flash chromatography (n-hexane /EtOAc = 6/1) gave **20** (1.6 g, 90%) as a pure colorless oil.

20: $[\alpha]_D^{25}$= -137.2 (c 2.31, CH_3OH). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.22 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$resp. $J_{7,8}$=2.7 Hz, 1H, H_8 or H_9), 6.14 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$resp. $J_{7,8}$=3.4 Hz, 1H, H_8 or H_9), 3.33 (s, 3H, OCH_3), 3.16 (brs, 2H, H_1 and H_7), 2.70 (m, $J_{1,2}$=4.2 Hz, 1H, H_2), 2.46, 2.21, 2.12 and 1.81 (4xm, 4H, H_4 and H_5), 1.99 A of AB (d, $J_{10a,10s}$=8.3 Hz, 1H, H_{10s}), 1.72 B A of AB (d, $J_{10a,10s}$=8.3 Hz, 1H, H_{10a}). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 219.0 (quat.), 138.6/134.4 (tert.), 92.9 (quat.), 61.9/50.7 (tert.), 50.4 (sec.), 49.2, 45.4, 42.3/27.5 (sec.). IR (CH_2Cl_2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1725 (C=O), 1080 (C-O) cm^{-1}. CI/MS: *m/e* (%) 178 (1, M^+), 149 (100, M^+-CO), 113 (39, M^++1-C_5H_6), 66 (9, $C_5H_6^+$). EI/HRMS *m/e*: 178.0994 [calc.for $C_{10}H_{14}O_2(M^+)$: 178.0994].

(-)-(1R,2R,6R,7S)-*Ethyl 5-acetoxy-4-methoxycarbonyl*-endo-*tricyclo[5.2.1.0^{2,6}]deca-4,8-diene-2-carboxylate* **23**

A solution of **13** (330 mg, 1.5 mmol) in 10 ml of THF was slowly added to a solution of lithium diisopropylamide [1.78 mmol, generated from diisipropylamine (180 mg, 1.78 mmol) and 1.1 ml of 1.6 M n-butyllithium] in 10 ml of THF at -78°C. After the addition was complete, stirring was continued for 15 min. An excess of methyl chloroformate (500 mg, 5 mmol) in 5 ml of THF was added and stirring was continued at -78°C for another 1h. The reaction mixture was poured into saturated NH_4Cl aq. and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (n-hexane /EtOAc = 6/1) gave a mixture (150 mg) of **21** and **22** and together with starting material **13** (≅ 180 mg).

The mixture of **21** and **22** in dichloromethane (5 ml), acetic anhydride (1 ml), pyridine (3 ml) and DMAP

(10 mg) was stirred at room temperature for 3h. Concentration *in vacuo* and subsequent flash chromatography (n-hexane /EtOAc = 5/1) gave **23** (75 mg, 34% based on consumed 24) as a colorless oil.

23: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.25 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.0 Hz, 1H, H_8 or H_9), 6.18 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.3 Hz, 1H, H_8 or H_9), 4.20 (m, 2H, OCH_2CH_3), 3.82 (dd, $J_{6,7}$=3.8 Hz, $J_{6,3exo}$=3.7 Hz, 1H, H_6), 3.65 (s, 3H, $COOCH_3$), 3.27 and 3.00 (2xbrs, 2H, H_1 and H_7), 2.71 A of AB (d, $J_{a,b}$=17.1 Hz, 1H, H_{3endo}), 2.31 B of AB (dd, $J_{a,b}$=17.1 Hz, $J_{6,3exo}$=3.7 Hz, 1H, H_{3exo}), 2.24 (s, 3H, $COCH_3$), 1.58 A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H_{10s}), 1.50 B A of AB (d, $J_{10a,10s}$=8.8 Hz, 1H, H_{10a}), 1.29 (t, J=7.1 Hz, 3H, OCH_2CH_3). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 176.0/167.0/163.2/158.8 (quat.), 138.0/133.7 (tert.), 117.1 (quat.), 61.1 (sec.), 57.7 (tert.), 54.4 (sec.), 51.3/50.5 (tert.), 48.7 (sec.), 44.6 (prim.), 36.1 (sec.), 20.9/14.2 (prim.). IR (CH_2Cl_2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1765 (C=O), 1710 (C=O), 1655 (C=C, conj.) cm^{-1}. EI/MS: *m/e* (%) 320 (0.4, M^+), 255 (31, M^++1-C_5H_6), 212 (100,M^++1-$COCH_3$-C_5H_6), 66 (40, $C_5H_6^+$), 43 (CH_3CO^+). EI/HRMS *m/e*: 320.1260 [calc.for $C_{17}H_{20}O_6$(M^+): 320.1260].

(-)-(1R,2R,4R,6R,7S)-*Ethyl 4-methoxycarbonyl-4-hydroxy-5-oxo*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-ene-2-carboxylate* **24**

A solution of **23** (110 mg, 0.33 mmol) in dichloromethane (4 ml), methanol (4 ml), hydrogen peroxide aq. (35 %, 2 ml) and NaOH (0.2 N, 2 ml) was stirred at room temperature overnight. Addition of water (10 ml), extraction with ethyl acetate (3x), several washing with brine, drying over Na_2SO_4 and concentration gave a crude oil. Flash chromatography (n-hexane /EtOAc = 4/1) gave pure **24** (65 mg, 83% based on recovered **23**) and **23** (25 mg).

24: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.28 (brs, 2H, H_8 or H_9), 4.28 (m, 2H, OCH_2CH_3), 3.92 (d, $J_{6,7}$=4.5 Hz, 1H, H_6), 3.85 (s, 1H, OH), 3.78 (s, 3H, $COOCH_3$), 3.31 and 3.19 (2xbrs, 2H, H_1 and H_7), 2.50 A of AB (d, $J_{a,b}$=15.0 Hz, 1H, one of H_3), 2.28 B of AB (dd, $J_{a,b}$=15.0 Hz, 1H, one of H_3), 1.84 A of AB (d, $J_{10a,10s}$=8.9 Hz, 1H, H_{10s}), 1.68 B A of AB (d, $J_{10a,10s}$=8.9 Hz, 1H, H_{10a}), 1.32 (t, J=7.1 Hz, 3H, OCH_2CH_3). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 208.9/176.2/170.6 (quat.), 138.2/135.5 (tert.), 84.9 (quat.), 61.6 (sec.), 56.9 (quat.), 56.1/53.1 (tert.), 51.3 (sec.), 50.6/44.8, 39.9 (sec.), 14.1 (prim.). IR (CH_2Cl_2): ν 3500 (free OH), 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1755 (C=O), 1725 (C=O) cm^{-1}. EI/MS: *m/e* (%) 294 (2, M^+), 228 (22, M^+-C_5H_6), 66 (40, $C_5H_6^+$). EI/HRMS *m/e*: 294.1104 [calc.for $C_{15}H_{18}O_6$(M^+): 294.1103].

(-)-(1S,2R,6R,7R)-*Methyl 3-hydroxy-6-methoxy*-endo-*tricyclo[5.2.1.0^{2,6}]dec-3,8-diene-4-carboxylate* **25**

A solution of **20** (180 mg, 1 mmol) in THF (2 ml) was slowly added to a solution of lithium diisopropylamide [2 mmol, prepared from diisipropylamine (200 mg, 2 mmol) and 1.2 ml of 1.6 M n-butyllithium] in 5 ml of THF at -78°C. After the addition was complete, stirring was continued for 30 min. An excess dimethyl carbonate (1 ml) was added and stirring was continued for 2 hrs at -78°C. The reaction mixture was then poured into saturated NH_4Cl aq. and repeatedly extracted with ethyl acetate . The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (n-hexane /EtOAc = 6/1) gave **25** (70 mg, 86% based on recovered **20**) and **20** (115 mg, 65%).

25: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.16 (s, 1H, enol), 6.11 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.5 Hz, 1H, H_8 or H_9), 6.03 B of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.3 Hz, 1H, H_8 or H_9), 3.73 (s, 3H, $COOCH_3$), 3.36 (d, $J_{1,2}$=4.5 Hz, 1H, H_2), 3.26 (s, 3H, OCH_3), 3.07 and 3.04 (2xbrs, 2H, H_1 and H_7), 2.55 A of AB (d, $J_{a,b}$=15.6 Hz, 1H, one of H_5), 2.10 B of AB (dd, $J_{a,b}$=15.6 Hz, J=1.6 Hz, 1H, one of H_5), 1.88 A of AB (d,

$J_{10a,10s}$=8.4 Hz, 1H, H_{10s}), 1.72 B A of AB (d, $J_{10a,10s}$=8.4 Hz, 1H, H_{10a}). IR (CH_2Cl_2): ν 3600-3100 (H-bond OH), 3010-2820 (C-H, sat.), 1725 (C=O), 1660 (C=C, conj.) cm^{-1}. CI/MS: *m/e* (%) 237 (3, M^++1), 171(100, M^+-C_5H_6), 66 (13, $C_5H_6^+$). EI/HRMS *m/e*: 237.0756 [calc.for $C_{13}H_{17}O_4$(M^++1): 237.0749].

(-)-(1S,2R,6R,7R)-*Methyl 3-acetoxy-6-methoxy*-endo-*tricyclo[5.2.1.0^{2,6}]deca-3,8-diene-4-carboxylate* **26**

A mixture of **25** (240 mg, 1 mmol) in dichloromethane (20 ml), acetic anhydride (2 ml), pyridine (10 ml) and DMAP (50 mg) was stirred at room temperature for 3h. Concentration *in vacuo* and subsequent flash chromatography (n-hexane /EtOAc = 5/1) gave **26** (250 mg, 92%) as a colorless oil.

26: $[\alpha]_D^{25}$= -59.6 (c 1.71, CH_3OH). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.18 A of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.8 Hz, 1H, H_8 or H_9), 6.06 B of AB (dd, $J_{8,9}$=5.6 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.3 Hz, 1H, H_8 or H_9), 3.67 (s, 3H, $COOCH_3$), 3.29 (s, 3H, OCH_3), 3.22 (m, 1H, H_2), 3.02 and 2.94 (2xbrs, 2H, H_1 and H_7), 2.70 A of AB (d, $J_{a,b}$=17.4 Hz, 1H, one of H_5), 2.25 B of AB (d, $J_{a,b}$=17.4 Hz, 1H, one of H_5), 2.24 (s, 3H, $COCH_3$), 1.84 A of AB (d, $J_{10a,10s}$=8.4 Hz, 1H, H_{10s}), 1.72 B A of AB (d, $J_{10a,10s}$=8.4 Hz, 1H, H_{10a}). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 167.3/162.5/158.7 (quat.), 137.9/133.7 (tert.), 119.0/89.7 (quat.), 58.5/51.3/51.149.9 (tert.), 48.5 (sec.), 43.6 (prim.), 35.3 (sec.), 20.9 (prim.). IR (CH_2Cl_2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1760, 1700 (C=O), 1650 (C=C, conj.) cm^{-1}. EI/MS: *m/e* (%) 279 (1, M^++1), 235(4, M^+-$COCH_3$), 170 (100, M^++1-$COCH_3$-C_5H_6), 66 (10, $C_5H_6^+$), 43 (40, $COCH_3^+$). EI/HRMS *m/e*: 170.0578 [calc.for $C_8H_{10}O_4$(M^++1-$COCH_3$-C_5H_6): 170.0579].

(-)-(1S,2R,4R,6R,7R)-*Methyl 4-hydroxy-6-methoxy-3-oxo*-endo-*tricyclo[5.2.1.0^{2,6}]dec-8-ene-4*-endo-*carboxylate* **27**

A solution of **26** (190 mg, 0.68 mmol) in dichloromethane (5 ml), methanol (5 ml), hydrogen peroxide aq. (35 %, 2 ml) and aq. NaOH (0.2 N, 2 ml) was stirred at room temperature for 2h. After adding 10 ml of water, the reaction mixture was extracted with ethyl acetate (3x), the organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* to give a solid material. Flash chromatography (n-hexane /EtOAc = 4/1) gave pure **27** (120 mg, 70%) as a white crystalline solid.

27: m.p.: 103.5-105.5 °C (ether), $[\alpha]_D^{25}$= -113.5 (c 1.10, CH_3OH). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.22 A of AB (dd, $J_{8,9}$=5.2 Hz, $J_{1,9}$ resp. $J_{7,8}$=1.9 Hz, 1H, H_8 or H_9), 6.12 B of AB (dd, $J_{8,9}$=5.2 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.4 Hz, 1H, H_8 or H_9), 3.78 (s, 3H, $COOCH_3$), 3.74 (s, 1H, OH), 3.39 (s, 3H, OCH_3), 3.22 and 3.14 (2 x brs, 3H, H_1, H_2 and H_7), 2.37 A of AB (d, $J_{a,b}$=15.6 Hz, 1H, one of H_5), 2.25 B of AB (dd, $J_{a,b}$=15.6 Hz, 1H, one of H_5), 2.13 A of AB (d, $J_{10a,10s}$=8.6 Hz, 1H, H_{10s}), 1.81 B A of AB (d, $J_{10a,10s}$=8.6 Hz, 1H, H_{10a}). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 209.7/171.0 (quat.), 138.9/134.7 (tert.), 91.3/85.2 (quat.), 60.6/53.2/51.3 (tert.), 50.9 (sec.), 48.3/43.7 (prim.), 38.0 (sec.). IR (CH_2Cl_2): ν 3500 (free OH), 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1750 (C=O), 1730 (C=O), 1090 (C-O) cm^{-1}. EI/MS: *m/e* (%) 187 (100, M^++1-C_5H_6), 169 (14, M^++1-C_5H_6-H_2O), 66 (63, $C_5H_6^+$). EI/HRMS *m/e*: 187.0606 [calc.for $C_8H_{11}O_5$(M^++1): 187.0606].

(-)-(R)-*Methyl 1-hydroxy-4-methoxy-2-oxo-cyclopent-3-ene-carboxylate* **8**

Flash vacuum thermolysis of **27** (90 mg, 0.35 mmol) [sample temp.: 80 °C, oven temp.: 500 °C, cold trap temp.: -78 °C and P: $3x10^{-2}$ mbar] produced solid **8** in quantitative yield (65 mg).

8: m.p.: 157-158 °C (EtOAc), $[\alpha]_D^{25}$= -115 (c 1.15, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.35 (s, 1H, H_3), 3.94 (s, 3H, OCH_3), 3.87 (s, 1H, OH), 3.80 (s, 3H, $COOCH_3$), 3.18 A of AB (d, $J_{a,b}$=17.6 Hz, 1H, one of H_5), 2.75 B of AB (d, $J_{a,b}$=17.6 Hz, 1H, one of H_5). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 199.4/189.9/171.5 (quat.), 101.0 (tert.), 79.0 (quat.), 59.2/53.4 (prim.), 40.5 (sec.). IR (CH_2Cl_2): ν 3510

(free OH), 3700-3100 (H-bond OH), 3010-2820 (C-H, sat.), 1740 (C=O), 1700 (C=O), 1595 (C=C, conj.) cm^{-1}. EI/MS: *m/e* (%) 186 (55, M^+), 158 (5, M^+-H_2O), 127 (62, M^+-$COOCH_3$), 98 (100, M^++1-$COOCH_3$-CO). EI/HRMS *m/e*: 186.0527 [calc.for $C_8H_{10}O_5(M^+)$: 186.0528].

(-)-(1S,2R,6R,7R)-3-Methoxycarbonyloxy-6-methoxy-endo-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene **28**

A solution of **20** (1.52 g, 8.5 mmol) in 10 ml of THF was slowly added to a solution of lithium diisopropylamide [14 mmol, prepared from diisipropylamine (1.4 g, 14 mmol) and 8.5 ml of 1.6 M n-butyllithium] in THF (100 ml) at -78°C. After the addition was complete, stirring was continued for 30 min. Excess methyl chloroformate (2 g) was added and stirring continued for 4h. The reaction mixture was then poured into saturated NH_4Cl aq. and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (n-hexane /EtOAc = 6/1) gave a mixture (1.58 g) of **25** and **28** and recovered **20** (240 mg, 16%).

The above mixture of **25** and **28** was dissolved in a mixture solvent of dichloromethane (20 ml), pyridine (10 ml) and acetic anhydride (5 ml) and stirred at room temperature for 1h. Concentration *in vacuo* followed by flash chromatography (n-hexane /EtOAc = 6/1) gave pure **28** (1.11 g, 71% based on recovered **20**) and **26** (460 mg, 25%).

28: $[\alpha]_D^{25}$= -21.6 (c 1.91, CH_3OH). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.14 A of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=2.9 Hz, 1H, H_8 or H_9), 6.02 B of AB (dd, $J_{8,9}$=5.7 Hz, $J_{1,9}$ resp. $J_{7,8}$=3.3 Hz, 1H, H_8 or H_9), 5.35 (d, J=1.0 Hz, 1H, H_4), 3.83 (s, 3H, $COOCH_3$), 3.28 (s, 3H, OCH_3), 3.15, 2.94, 2.90 (3 x m, 3H, H_1, H_2 and H_7), 2.42 A of AB (dd, $J_{a,b}$=17.6, J=6.4 Hz, 1H, one of H_5), 1.96 B of AB (dd, $J_{a,b}$=17.6 Hz, J=2.7 Hz, 1H, one of H_5), 1.85 A of AB (d, $J_{10a,10s}$=8.4 Hz, 1H, H_{10s}), 1.71 B of AB (d, $J_{10a,10s}$=8.4 Hz, 1H, H_{10a}). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 153.0/150.2 (quat.), 137.8/133.5/113.7 (tert.), 92.4 (quat.), 55.5/55.0/51.0 (tert.), 50.1 (prim.), 48.4 (sec.), 43.0 (prim.), 34.3 (sec.). IR (CH_2Cl_2): ν 3100-3020 (C-H, unsat.), 3010-2820 (C-H, sat.), 1760 (C=O), 1660 (C=C, conj.), 1085 (C-O) cm^{-1}. CI/MS: *m/e* (%) 236 (0.2, M^+), 170(100, M^+-C_5H_6), 111 (M^+-C_5H_6-$COOCH_3$), 66 (19, $C_5H_6^+$). EI/HRMS *m/e*: 236.1047 [calc.for $C_{13}H_{16}O_4(M^+)$: 236.1049].

2-Methoxy-4-methoxycarbonyloxypentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane **29**

A solution of **28** (30 mg) in 10% acetone in benzene (2.5 ml) was irradiated for four days using a high-pressure mercury arc and a Pyrex filter. Concentration *in vacuo* gave **29** in quantitative yield.

29: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H, $COOCH_3$), 3.35 (s, 3H, OCH_3), 3.22, 2.99, 2.88, 2.72 and 2.44 (5xm, 6H, tert.H), 1.93 and 1.76 2 x AB (2 x d, J=10.4 Hz, 2H, H_6 or H_{10}), 1.91 and 1.35 2 x AB (2 x d, J=11.2 Hz, 2H, H_6 or H_{10}). ^{13}C-NMR (100 MHz, H-dec., $CDCl_3$): δ 153.9/93.9/83.5 (quat.), 54.5/53.1/49.3/48.1/45.1/41.8/39.0 (tert.), 37.2/25.1 (sec.), 35.3 (tert.). IR (CH_2Cl_2): ν 3010-2820 (C-H, sat.), 1750 (C=O) cm^{-1}. CI/MS: *m/e* (%) 236 (0.9, M^+), 170(100, M^+-C_5H_6), 111 (43,M^+-C_5H_6-$COOCH_3$), 66 (6, $C_5H_6^+$). EI/HRMS *m/e*: 236.1047 [calc.for $C_{13}H_{16}O_4(M^+)$: 236.1049].

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