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IRIDOIDS : ENANTIOSELECTIVE SYNTHESIS OF LOGANIN VIA AN ASYMMETRIC DIELS-ALDER REACTION

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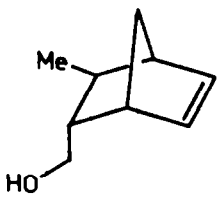
Abstract - Starting from (-)-camphor-10-sulfonic acid (5) the crystalline sultam 9 was readily prepared. $TiCl_4$-mediated Diels-Alder addition of the N-crotonoyl sultam 11 to cyclopentadiene, crys- tallization of the resulting adduct 12 and subsequent reduction gave virtually pure (1S, 4R, 5R, 6S)-1 together with recovered auxiliary 9. The loganin precursor 1 was transformed into norbornanone 20, which upon Baeyer-Villiger oxidation led to the suitably substituted cyclo- pentane 22 from which 1-B-O-methyl loganin aglucone (2) was rea- dily available.

INTRODUCTION

The iridoids[1], with ca 300 known naturally occurring compounds, represent a class of highly oxygenated monoterpenes with loganin ii as one of the best known members. This class has attracted considerable interest of synthetic organic chemists[2].

Recently, one of our laboratories reported a novel[3] and flexible[4] strategy based on readily available bicyclo 2.2.1 heptanone intermediates. The choice of the strategy was inter alea influenced by its facile adaptation to asymmetric total synthesis. The diastereoselective transformation of the racemic norbornene 1 to 1-O-methyl-epiloganin aglucone i has already been described[3].



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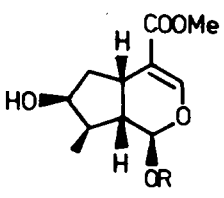
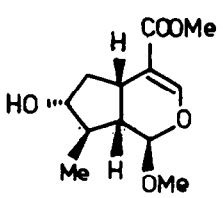


ii R = D-glu
2 R = Me

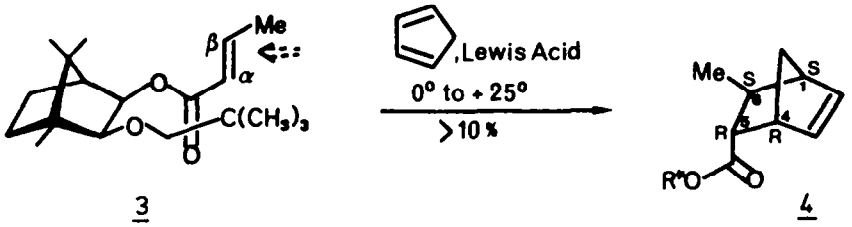


i

SCHEME 1

Aiming at the synthesis of enantiomerically pure 1-O-methyl-loganin aglucone 2[5,6] we decided to create the desired (1S, 4R, 5R, 6S)-configuration of 1 by an asymmetric Diels-Alder addition[7] of cyclopentadiene to a chiral (E)-crotyl derivative. Initial attempts to achieve a -face differentiated 4+2 cycloaddition to the neopentylether-shielded crotyl ester 3 were dis-

appointing[8]. Apparently, the slow rate of reaction 3 - 4, relative to that of diene polymerization, was due to steric effects.

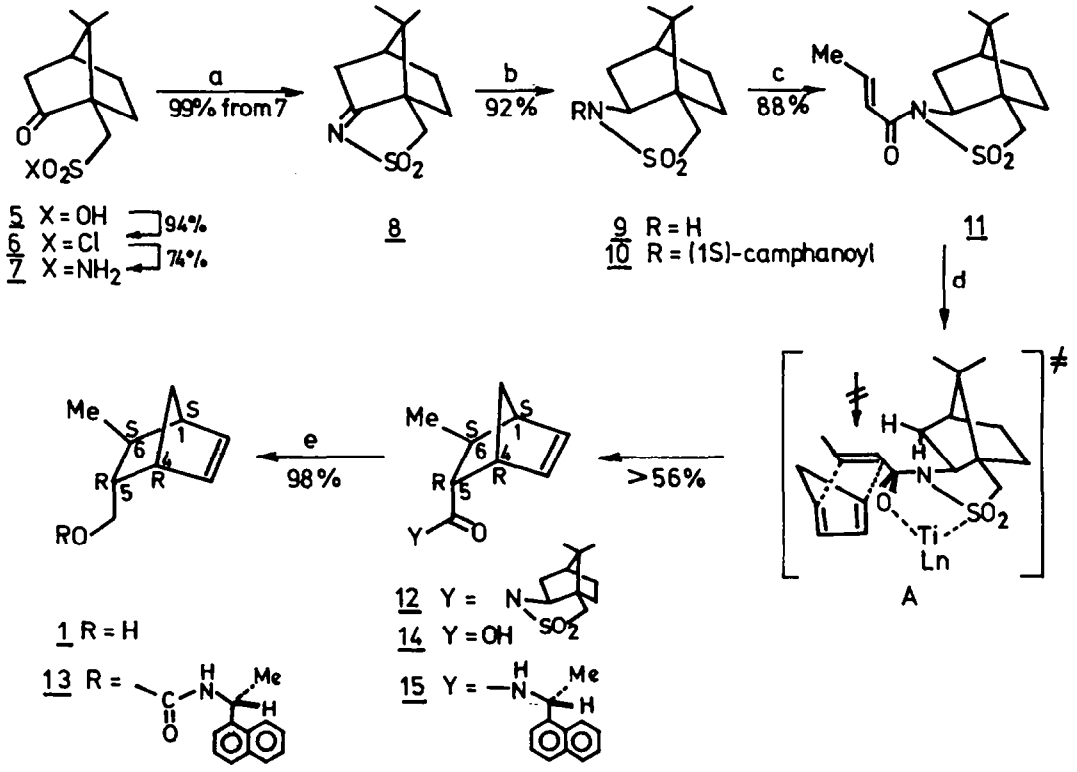


3 4

SCHEME 2

We then exploited the electronically enhanced dienophilicity of crotylimide 11[9]. The efficient and highly π-face selective Diels-Alder reaction 11 - 12 (Scheme 3) has been described by one of our laboratories in a preliminary communication[10].

Preparation of Enantiomerically Pure Norbornene 1 via an Asymmetric Diels-Alder Reaction



a) NaOMe, MeOH, r.t.; b) $LiAlH_4$, THF, 0°C; c) NaH, toluene, r.t.; $CH_3CH{=}CHCOCl$, r.t.; d) $TiCl_4$, C_5H_6, CH_2Cl_2, -78°C; e) $LiAlH_4$, THF, r.t.

SCHEME 3

The appropriate chiral auxiliary 9 was readily prepared starting from (-)-camphor-10-sulfonic acid (5). Treatment of 5 with PCl_5[11] gave the sulfonyl chloride 6 which upon successive amidation with NH_3 (6- 7), base catalyzed cyclization (7 - 8)[12], and reduction of imine 8 with $LiAlH_4$ furnished sultam 9 in 63 % overall yield. From a practical point of view it is worth noting that 5 is commercially available and that each compound, 5 to 9, can be purified efficiently by simple crystallization. The sharp melting point (182-183) of sultam 9 indicated its high enantiomeric purity which was confirmed to be 100 % based on GC analysis of the (1S)-camphanoyl imide 10. N-Acylation of 9 by successive treatment with NaH and crotonoyl chloride

gave the pure imide 11 in 88 % yield after recrystallization. The crucial Diels-Alder reaction 11 - 12 proceeded smoothly at -78° after successive addition of $TiCl_4$ (0.5 eq) and cyclopentadiene (10 eq) to a solution of dienophile 11 in CH_2Cl_2. Removal of polymers by treatment with charcoal furnished crude adduct 12 (93.5 % from 11). Under these reaction conditions the predominant (98 %) C=O-endo product 12 has been formed with > = 94 % α-face differentiation (as determined by analyses of 1 (GC) and 13 (HPLC)[13] which were prepared from crude 12). Furthermore, 12 was obtained virtually pure (m.p. 185-186°) after flash chromatography and crystallization (57 % from 11). Reduction of purified adduct 12 with $LiAlH_4$ gave the alcohol 1 together with the crystalline auxiliary 9 which was recovered by precipitation with pentane. The desired (1S, 4R, 5R, 6S)-alcohol 1 (98 % from 12 after bulb-to-bulb distillation) was shown to contain 0.5 % of its C=O-exo isomer (GC of 1) and, apparently, 1.5 % of its enantiomer (HPLC of 14). However, not even a trace of (1R, 4S, 5S, 6R) - 1 could be detected by HPLC analysis of 15 (obtained via the oxidation/amidation sequence 1 - 14 - 15). It thus follows that the crucial iridoid precursor 1 has been obtained in 97 to 100 % enantiomeric purity.

As postulated previously[10], we believe that the observed reactivity and π-face differentiation in the Diels-Alder step 11 - 12 is based on chelation of the SO_2 and C=O groups by the metal. The chelated dienophile would be locked into conformation A which directs the diene to the less hindered bottom face (C -Si).

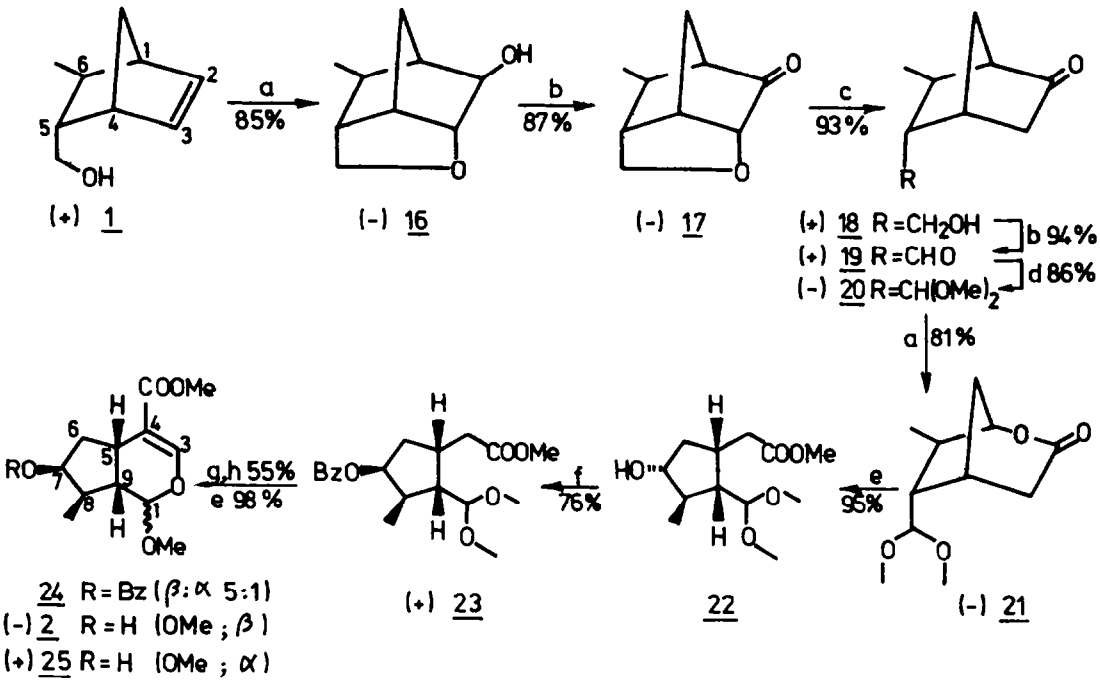
The predicted sense of induction follows from the chiroptic properties of 1, the HPLC measurements of 13 and, last but not least, the conversion of 1 to loganin 1-O-methyl-aglucone (2) as described below.

Transformation of 1 into (-)-1-O-methyl-loganin aglucone (2)

In the starting norbornene 1, the absolute configuration at the three contiguous centers 4, 5 and 6 is identical to that at C-5, C-9 and C-8 in the target molecule 2. Thus, formation of the substituted cyclopentane ring in 2 necessitates cleavage of the 1-2 bond in precursor 1. As this can be performed by a Baeyer-Villiger oxidation at the stage of a norbornanone (such as 18, 19 or 20) the regioselective transformation of the double bond in 1 to a carbonyl function at position 2 becomes the first objective. The endo-alcohol 1 cyclized to 16 upon treatment with mCPBA; Swern oxidation[14] followed by reductive cleavage of the α-ether bond in 17 afforded the desired norbornanone 18 in an overall yield of 68 % from 1. At this stage the hydroxyl group in 18 had first to be transformed into a protected aldehyde function, as Baeyer-Villiger oxidation of 18 led[3], via translactonisation, to the less strained fused δ-lactone, which constitutes a dead-end. Originally[3], racemic aldehyde 19 had been protected as a dioxolane. In view of the presence of a 1-methoxy group in the target 2 an overall more practical approach via the dimethoxyacetal 20 was selected. Swern oxidation of 18 and selective acetalization of the aldehyde function in 19, using Noyori's procedure[15], led to 20; treatment with mCPBA afforded lactone 21, methanolysis of which produced the desired ester 22 (62 % overall from 18. This ester was contaminated with a trace of 21 from which it could not be separated; therefore no rotation was measured.

Subsequent transformations of 22 have to involve inversion at C-7 and introduction of the remaining C-3 atom. In our preliminary report[3] we aimed at the racemic precursor i of the naturally occuring epiloganin which has previously been transformed into loganin[6b]. A conceptually shorter approach to 2 would consist of inversion at C-7, with simultaneous protection of the hydroxyl group, at the stage of 22, prior to the formylation. This was smoothly effected using Mitsunobu's procedure[16]. Although the benzoate ester in 23 is not an excellent protective group for the projected Claisen condensation, this is of little consequence as the ester must subsequently be removed. The formylation of 23 caused more problems than expected; only metallation with a 1:1 mixture of tBuOK-LICA gave an acceptable result. The crude formylated product was directly subjected to acid catalyzed ring closure producing 24 as a C-1 epimeric mixture (B: ratio 5:1; 55 % combined yield) which could easily be separated by prep. HPLC. (Small amounts of 2

and its C-1 epimer, arising from benzoate ester cleavage, caused by the methoxy anions formed during the Claisen condensation, were also isolated).



a) mCPBA, CH_2Cl_2, -10°C to r.t.; b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -60°C; c) Al-Hg, THF, EtOH, r.t.; d) $MeOSiMe_3$, Me_3SiOTf, CH_2Cl_2, -78°C; e) NaOMe, MeOH, r.t.; f) DEAD, ØCOOH, $Ø_3P$, CH_2Cl_2, r.t.; g) KOt.Bu, LICA, THF, -78°C; HCOOMe, -78°C to -40°C; h) $BF_3.OEt_2$, CH_2Cl_2, 0°C.

SCHEME 4

Finally, methanolysis of the major isomer 24 afforded (-)-1-O-methyl-loganin aglucone (2); no trace of the (+)-2 enantiomer could be detected on a Pirkle I HPLC column. Coinjection of a sample of (-)-2 and racemic 2 (obtained from racemic 1) indicates that ca. 3-5 % of the (+)-enantiomer can be seen on the chromatogram. Product 2 was completely identical (spectral data, rotation and retention time on coinjection on a Pirkle I HPLC column) with a sample of (-)-2 obtained[6a] from natural loganin, kindly provided by Dr. J. J. Partridge. The transformation of (-)-2 into loganin (ii) has previously been described[6a].

EXPERIMENTAL PART

General : All reactions were carried out under Ar with magnetic stirring, unless otherwise specified. Temperatures are expressed as degrees Celsius. "Work-up" denotes extraction with an org. solvent, washing of the org. phase with sat. aq. NaCl soln., drying over anh. $MgSO_4$, and removal of solvent by distillation in vacuo using a rotatory evaporator. Column chromatography : SiO_2 (Merck, Kieselgel 60). GC, HPLC : retention time in min (area-%). M.p.: Kofler stage; uncorrected. IR : in $CHCl_3$, unless otherwise specified max in cm^{-1}. ^1H NMR : at 360 MHz in $CDCl_3$, unless otherwise specified standard tetramethylsilane (δ=0 ppm); J in Hz. MS : m/z (rel.-%).

Preparation of Enantiomerically Pure Norbornene 1 via an Asymmetric Diels-Alder reaction

(1R)-7,7-Dimethyl-2-oxo-bicyclo|2.2.1|heptane-1-methanesulfonyl chloride (6)

(1R)-(-)-camphor-10-sulfonic acid (5) was either prepared by oxidation of (-)-borneol (Aldrich)[17] followed by sulfonation[18] of the resulting (1S)-(-)-camphor, or, alternatively, obtained commercially (Aldrich) and recrystallized from HOAc. A mixture of 5 (40 g, 0.172 mol) and PCl_5 (49.7 g, 0.239 mol) was stirred first manually then mechanically for 1 h at 0° and for 2 h at r.t.. Pouring of the reaction mixture into ice, filtration, washing of the insoluble residue

with ice water and drying in vacuo gave crude 6 (colorless solid 41.12 g) which was recrystallized from ligroin yielding pure sulfonyl chloride 6 (34.65 g, 80.5 %), m.p. 65-66°. ^{1}H NMR : 0;94 (s, 3H); 1.16 (s, 3H); 1.40 (m, 1H); 1.79 (m, 1H); 2.0 (d, J = 18, 1H); 2.05-2.2 (2H); 2.4-2.55 (2H); 3.74 (d, J = 17, 1H); 4.33 (d, J = 17, 1H).

(1R)-7,7-Dimethyl-2-oxo-bicyclo|2.2.1|heptane-1-methanesulfonamide (7).

A mechanically stirred soln of sulfonyl chloride 6 (105 g, 0.42 mol) in toluene (1 l) was saturated with gaseous NH_3 under cooling with ice. Filtration, washing of the insoluble residue with toluene, recrystallization from water (1.5 l) followed by addition of toluene, azeotropic removal of water (4x) and drying gave sulfonamide 7 (71.6 g, 74 %), m.p. 133-134°. IR : 3400, 1740, 1350, 1150. ^{1}H NMR (100 MHz) : 0.95 (s, 3H); 1.03 (s, 3H); 1.7-2.6 (7H); 3.13 (d, J = 15, 1H); 3.49 (d, J = 15, 1H); 5.1-5.5 (2H). MS : no $C_{10}H_{17}NO_3S^{+\cdot}$, 153 (67), 125 (51), 111 (100), 110 (39), 109 (34), 97 (16), 95 (42), 83 (78).

(7R)-10,10-Dimethyl-5-thia-4-azatricyclo|5.2.1.03,7|dec-3-ene-5,5-dioxide (8)

A 1 % soln of NaOMe in dry MeOH (7.6 ml) was added to a soln of 7 (71 g, 0.307 mol) in MeOH (distilled over $Mg(OMe)_2$, 2.7 l). Stirring of the mixture at r.t. for 4 h, addition of another portion of 1 % NaOMe in MeOH (3 ml - slow formation of a colorless precipitate), stirring of the mixture for 60 h, evaporation, shaking of the residue with $CHCl_3$/water, drying of the organic phase (Na_2SO_4), evaporation and crystallization of the residue gave pure 8 (65 g, 99.3 %), m.p. 225 . IR : 1652, 1340, 1168, 1133. ^{1}H NMR : 0.87 (s, 3H); 1.08 (s, 3H); 1.48 (t, J = 10, 1H); 1.78 (t, J = 10, 1H); 2.0-2.13 (2H); 2.26 (m, 1H); 2.38 (d, J = 19, 1H); 2.77 (d, br, J = 10, 1H); 2.98 (d, J = 13, 1H); 3.29 (d, J = 13, 1H). MS : 213 ($C_{10}H_{15}NSO_2^{+\cdot}$, 1), 149 (7), 148 (5), 134 (26), 109 (42), 108 (100), 93 (54), 82 (28), $[\alpha]_D$ = +32.1°, $[\alpha]_{578}$ = +33.2° (c = 0.982, $CHCl_3$, T = 21°C).

(7R)-10,10-Dimethyl-5-thia-4-azatricyclo|5.2.1.0^{3,7}|decane-5,5-dioxide (9)

$LiAlH_4$ (12.5 g, 0.329 mol) was added at 0° to a stirred soln. of imine 8 (70.0 g, 32.9 mmol) in THF (1.35 l). Stirring of the mixture at r.t. for 1 h, quenching by addition of 1 N aq. HCl during 4 h at 0 , filtration, washing of the insoluble residue with $CHCl_3$, extraction of the aq. phase with CH_2Cl_2, work-up and crystallization of the residue from EtOH gave the pure sultam 9 (64.7 g, 92 %), m.p. 182-183 . IR : 3340, 1340, 1312, 1135. ^{1}H NMR : 0.94 (s, 3H); 1.14 (s, 3H); 1.33 (m, 1H); 1.47 (m, 1H); 1.8-1.05 (5H); 3.09 (d, J = 14, 1H); 3.14 (d, J = 14, 1H); 3.43 (m, 1H); 4.12 (s, br, 1H). MS : no $C_{10}H_{17}NO_2S^{+\cdot}$, 162 (17), 151 (70), 136 (100), 134 (72), 119 (100), 108 (75), 93 (100), 83 (90). $[\alpha]_D$ = +31.1 ; $[\alpha]_{578}$ = +32.5 ; $[\alpha]_{546}$ = +37.1°; $[\alpha]_{436}$ = +65.4 ; $[\alpha]_{365}$ = +107.8 (c = 1.01, $CHCl_3$, T = 21.6°C).

4-((1S)-3-Oxo-4,7,7-trimethyl-2-oxabicyclo|2.2.1|heptan-1-oyl)-(7R)-10,10-dimethyl-5-thia-4-aza-tricyclo|5.2.1.0^{3,7}|decane-5,5-dioxide (10)

A soln of sultam 9 (25.4 mg, 0.116 mmol) in toluene (1 ml) was added at r.t. to a stirred suspension of NaH (55-60 % dispersion in mineral oil, 7.5 mg, 0.17 mmol) in dry toluene (1 ml). After 30 min a soln. of (-)-camphanoyl chloride (58.6 mg, 0.29 mmol) in toluene (1.5 ml) was added. Stirring of the mixture at r.t. for 10 h, addition of water (1 ml), washing of the organic phase with water, work-up and chromatography (hexane/EtOAc 6:1) gave crude 10 (43.7 mg, 98 %), colorless solid, GC (capillary column fused silica, 0.2 mm ID x 12 m, OV1, 10 psi H_2, 60 - 10 /min - 250) : 19.9 (100). IR : 1797, 1670, 1350, 1315, 1278, 1170, 1140, 1095. ^{1}H NMR : 0.98 (s, 3H); 1.00 (s, 3H); 1.11 (s, 3H); 1.14 (s, 3H); 1.24 (s, 3H); 1.3-1.45 (2H); 1.7 (m, 1H); 1.8-2.05 (5H); 2.1-2.3 (2H); 2.35 (m, 1H); 3.40 (d, J = 14, 1H); 3.54 (d, J = 14, 1H); 4.18 (dd, J = 5 and 8, 1H). MS : 395 ($C_{20}H_{29}NO_5S^{+\cdot}$, 1), 367 (2), 349 (3), 331 (3), 152 (15), 134 (49), 125 (20), 108 (40), 97 (35), 83 (100), 67 (34), 55 (90). GC-comparison samples were synthesized following the same procedure from (-)-camphanoyl chloride and either the antipode of 9 (GC : 20.6 (100)), or racemic 9 (GC : 19.9 (55), 20.6 (45)).

((E)-2-Butenoyl)-(7R)-10,10-Dimethyl-5-thia-4-azatricyclo|5.2.1.0^{3,7}|decane-5,5-dioxide (11)

A soln of sultam 9 (2.102 g, 9.77 mmol) in toluene (50 ml) was added dropwise at r.t. to a stirred suspension of NaH (55-60 % dispersion in mineral oil, 0.646 g, 14.66 mmol). After 1 h a soln of (E)-crotonoyl chloride (1.89 ml, 19.54 mmol) in toluene (50 ml) was added slowly and the mixture was stirred at r.t. for 3 h. Addition of water (20 ml), separation of the organic phase, work-up, chromatography (hexane/EtOAc 4:1) and crystallization from MeOH gave crotylimide 11 (2.44 g, 88 %), m.p. 186-187°. IR : 1685, 1643, 1335, 1299, 1264, 1230, 1210, 1135. ^{1}H NMR : 0.98 (s, 3H); 1.18 (s, 3H); 1.3-1.4 (2H); 1.8-2.0 (6H); 2.05-2.2 (2H); 3.45 (d, J = 13.5, 1H); 3.52 (d, J = 13.5, 1H); 4.95 (dd, J = 5 and 7.5, 1H); 6.61 (dq, J = 15 and 2, 1H); 7.11 (dt, J = 7, 1H). MS : 283 ($C_{14}H_{21}NO_3S^{+\cdot}$, 14), 204 (11), 134 (11), 108 (7), 69 (100). $[\alpha]_D$ = +103.7°, $[\alpha]_{578}$ = +108.2°; $[\alpha]_{546}$ = +123.5 ; $[\alpha]_{436}$ = +383.9 (c = 3.9, $CHCl_3$, T = 20°C).

4-((5R,6S)-6-Methylbicyclo|2.2.1|hept-2-en-5-carbonyl)-(7R)-10,10-dimethyl-5-thia-4-azatricyclo |5.2.1.0^{3,7}|-decane-5,5-dioxide (12)

The crotonoyl sultam 11 (2.234 g, 7.89 mmol) was placed under argon into a flame-dried 100 ml-reaction flask, equipped with a spiral addition tube which surrounds the flask and enters close to its bottom. After injection of dry CH_2Cl_2 (40 ml) the flask (and the surrounding tube) were cooled to -78° and freshly distilled $TiCl_4$ (0.433 ml, 3.95 mmol) was added. 15 Min later a soln of freshly distilled cyclopentadiene (7.0 ml, 79 mmol) in CH_2Cl_2 (5 ml) was added during 20 min

via the addition spiral (thus ensuring that the diene soln had been cooled to -78° before entering the reaction flask). Stirring the mixture at -78°C for 20 h, subsequent addition of water (10 ml) at -78° and work-up gave a crude mixture which was dissolved in toluene. Filtration of this solution through a column (3 cm ID x 5 cm) of charcoal and evaporation of the filtrate gave crude adduct 12 (2.575 g, 93.5 % from 11, 98 % C=O-endo, 94 % e.e.). Flash chromatography furnished 12 (2.40 g, 87 % from 11, 99 % C=O-endo) which was recrystallized (5 x EtOH) to give pure 12 (1.556 g, 57 % from 11, 99.5 % C=O-endo, 97-100 % e.e.), m.p. 185-186°. IR : 1695, 1332, 1279, 1262, 1162, 1130, 1110, 1050, 990. ^{1}H NMR : 0.97 (s, 3H); 1.15 (d, J = 7, 3H); 1.19 (s, 3H); 1.27-1.5 (3H); 1.68 (d, J = 4.5, 1H); 1.8-2.1 (6H); 2.52 (s, br, 1H); 2.98 (t, J = 3.5, 1H); 3.34 (s, br, 1H); 3.44 (d, J = 14, 1H); 3.52 (d, J = 14, 1H); 3.85 (dd, J = 4.5 and 7.5, 1H); 5.75 (dd, J = 2.5 and 6, 1H); 6.37 (dd, J = 3 and 6, 1H). MS : 349 ($C_{19}H_{27}NO_2S^{+\cdot}$, 10), 284 (52), 135 (40), 107 (20), 69 (100). $[\alpha]_D$ = +242.7°; $[\alpha]_{578}$ = +253.6°; $[\alpha]_{546}$ = +289.6 ; $[\alpha]_{436}$ = +509; $[\alpha]_{365}$ = +847 (c = 0.95, $CHCl_3$, T = 20°C).

(5R, 6S)-5-Hydroxymethyl-6-methylbicyclo|2.2.1|hept-2-ene (1)

A soln of the recrystallized adduct 12 (7.35 g, 21.06 mmol) in THF (130 ml) was added over 15 min at r.t. to a stirred suspension of $LiAlH_4$ (800 mg, 21.06 mmol) in THF (70 ml). Stirring of the mixture at r.t. for 30 min, subsequent quenching by addition of sat. aq. Na_2SO_4, drying with $MgSO_4$, evaporation, trituration of the residue with pentane and filtration gave insoluble auxiliary 9 (3.39 g, 75 %); evaporation of the filtrate and bulb-to-bulb distillation (140 , 11 Torr) of the residue gave alcohol 1 (2.858 g, 98 %). GC (glass column, 3 mm ID x 3 m, Chromosorb W/10 % Carbowax, 1 atm N_2, 140) : 15.7 (99.5), 17.8 (0.5); (capillary column fused silica, 0.2 mm ID x 25 m, Carbowax 20M, 10 psi H_2, 60 - 10 /min - 250) : 7.66 (99.5), 7.99 (0.5). The major CH_2OH-endo isomers (1 + antipode) were separated from the minor CH_2OH-exo products by prep. GC (15 mm ID x 2 m, Chromosorb W, 10 % OV-225, 1 atm N_2, 130) : 24.0 (99.5), 26.0 (0.5). IR(film) : 3360 (br.), 2960, 2880, 1470, 1380, 1345, 1220, 1052, 1030, 760, 710. ^{1}H NMR : 0.96 (m, 1H); 1.12 (d, J = 6.5, 3H); 1.42 (dd, J = 8.5 and 2, 1H); 1.51 (d, J = 8.5, 1H); 1.69 (m, 1H); 1.90 (s, br., 1H); 2.37 (s, 1H); 2.84 (s, 1H); 3.24 (dd, J = 10.5 and 9, 1H); 3.40 (dd, J = 10.5 and 6.5, 1H); 5.97 (dd, J = 3 and 5.5, 1H); 6.20 (dd, J = 3 and 5.5, 1H). MS : 138 ($C_9H_{14}O^{+\cdot}$, 9), 120 (15), 105 (9), 91 (7), 79 (7), 71 (12), 67 (9), 66 (100). $[\alpha]_D$ = +86.6°; $[\alpha]_{578}$ = +90.1°; $[\alpha]_{546}$ = +102.5°; $[\alpha]_{436}$ = +175.0°; $[\alpha]_{365}$ = +277.3° (c = 1.21, EtOH, T = 24.7°C).

O-((5R,6S)-6-Methylbicyclo|2.2.1|hept-2-en-5-yl)methyl N-|(1R)-1-(1-naphthyl)ethyl| carbamate (13)

(-)-(R)-1(1-naphthyl)ethyl isocyanate (25 ml, 0.11 mmol) and 2-N,N-(dimethylamino)ethanol (1 drop) were added to a soln of 1 (10 mg, 0.072 mmol) in toluene (0.1 ml). Then the mixture was heated in a closed Pyrex tube at 90° for 15 h. Evaporation and flash chromatography of the residue (hexane/EtOAc 3:1) gave crude carbamate 13 (24.2 mg, 100 %). HPLC (Hibar SiO_2 60, 5 um, 0.5 ID x 25 cm) : a) hexane/EtOAc 96:4, 1.0 ml/min: 33.4 (98.5), 36.4 (1.5); b) hexane/t.butylmethyl ether 94:6, 1.0 ml/min: 30.8 (98.5), 34.1 (1.5). IR : 3450, 3030, 2980, 1710, 1510, 1200, 1060. MS : 335 ($C_{22}H_{25}NO^{+\cdot}$, 19), 214 (77), 200 (100), 170 (25), 155 (35), 129 (36), 79 (20), 66 (59), 55 (100).
A HPLC-comparison sample was synthesized following the same procedure from (-)-(R)-1-(1-naphthyl)ethyl isocyanate and either, racemic 1 : HPLC (hexane/EtOAc 96:4, 0.8 ml/min); 30.0 (49.7), 33.4 (50.3), or (5S, 6R)-1 (99 % e.e. 5): HPLC : 30.0 (0.5), 33.4 (99.5).

N-|(1R)-1-(1-Naphthyl)ethyl|-(5R,6S)-6-methylbicyclo|2.2.1|hept-2-ene-5-carboxamide (15)

Jones reagent (37 ul, 0.028 mmol) was added to a vigorously stirred (Vibromix) soln of alcohol 1 (2.0 mg, 0.0145 mmol) in acetone (2 ml) at r.t.. Stirring of the mixture for 4 min followed by injection of i-PrOH (1 ml), stirring for 1 min and work-up gave carboxylic acid 14 (2.1 mg, 96 %). IR : 3400 (br), 2980, 2940, 2880, 1720, 1450, 1380, 1264, 1110. MS : 152 ($C_9H_{12}O_2^{+\cdot}$, 0.3), 79 (4), 77 (3.5), 67 (3.5), 66 (100), 65 (6), 43 (6), 39 (7). To a stirred mixture of crude acid 14 (11.3 mg, 0.074 mmol) and (1R)-1-(1-naphthyl)ethylamine (25.4 mg, 0.148 mmol) was added successively N-ethylmorpholine (37 ul, 0.296 mmol), a 50 % soln of propylphosphonic anhydride[19] in CH_2Cl_2 (79 mg, 0.124 mmol) and DMF (1 ml). The mixture was allowed to warm up to r.t. and kept at r.t. for 15 h. Evaporation of the reaction mixture, work-up and flash chromatography (hexane/EtOAc 10:1) gave crude 15 (21.5 mg, 95 % from 14). HPLC (Hibar SiO_2 60, 5 um, 0.5 x 25 cm, hexane/EtOAc 9:1, 2.0 ml/min) : 16.6 (100). A HPLC-comparison sample was synthesized following the same procedure from (R)-1-(1-naphthyl)ethylamine and racemic 14 : HPLC : 16.6 (41), 18.5 (59).

Transformation of (+)-1 into (-)-1-O-methyl-loganin aglucone (2)

(1R,2R,4R,5R)-4-Exo-methyl-tricyclo|3.2.1.$1^{3,8}$|-7-oxa-2-exo-nonanol (16)

To a soln of 1 (2.6 g, 18.8 mmol) in CH_2Cl_2 (153 ml) was added, at -10°C, mCPBA (4.77 g, 22.1 mmol; 80 %); the mixture was then stirred for 2.5 h at r.t.. Et_2O was added and the soln was washed successively with conc Na_2SO_3, conc $NaHCO_3$ and was worked up. The residue was taken up in THF (20 ml) and 10 % HCl (10 ml). The mixture was stirred for 15 min, then Et_2O and brine were added. Work-up and HPLC purification (Waters LC/system 500; EtOAc/hexane, 85:15) gave 16 (2.47 g; 85 %), Rf (Et_2O) : 0.23; IR (neat) : 3600-3200, 2950, 2860, 1465, 1350, 1315, 1125, 1100, 1075, 1050, 1025, 995, 925, 905; ^{1}H NMR : 3.93 (dd, J = 5 and 1 Hz, 1H); 3.77 (dd, J = 8 and 3.5 Hz, 1H), 3.70 (d, J = 8 Hz, 1H), 3.45 (m, 1H), 2.58 (m, 1H), 2.23 (s, 1H), 1.87 (d, J = 11 Hz, 1H), 1.80 (m, 2H), 1.71 (dd, J = 11 and 1 Hz, 1H), 1.28 (m, 1H), 1.02 (d, J = 7 Hz, 3H); MS : 154 ($C_9H_{14}O_2^{+\cdot}$, 16; calculated : 154.0994, found : 154.1012), 136 (5), 123 (35), 95 (28), 94 (30), 93

(40), 81 (31), 79 (33), 71 (36), 70 (27), 69 (100), 67 (31), 55 (77). $[\alpha]_D$ = -67.3° (c = 1.55, CH_2Cl_2, T = 18°C).

(1R,4R,5R)-4-Exo-methyl-tricyclo|3.2.1.$1^{3,8}$|-7-oxa-2-nonanone (17)

To a stirred soln of $(COCl)_2$ (3 ml, 33 mmol) in CH_2Cl_2 (75 ml) was added, at -60°C, a soln of DMSO (5.1 ml, 66 mmol) in CH_2Cl_2 (15 ml). After 2 min, a soln of 16 (2.1 g, 13.6 mmol) in CH_2Cl_2 (15 ml) was added during 5 min at -60°C. After 15 min at -60°C, Et_3N (23 ml, 165 mmol) was added (5 min), the mixture was allowed to warm up to r.t. and stirring was continued for 1 h. Water was added, after separation and extraction (CH_2Cl_2) the organic layer was washed with 10 % HCl and conc $NaHCO_3$. Work-up and column chromatography (Et_2O/hexane, 3:7) gave 17 (1.8 g, 87 %), m.p. 41 . Rf (ether) : 0.43; IR (KBr) : 2960, 2880, 1760, 1470, 1450, 1375, 1255, 1173, 1135, 1060, 1030, 1000, 905; ^1H NMR : 4.02 (q, J = 4 Hz, 1H), 3.85 (m, 2H), 3.0 (m, 1H), 2.23 (s, 1H), 2.18 (dt, J = 5 and 1.5 Hz, 1H), 2.08 (m, J = 12 Hz, 1H), 1.72 (m, 2H), 1.1 (d, J = 7 Hz, 3H); MS : 152 ($C_9H_{12}O_2^{+\cdot}$, 4; calculated : 152.0843, found : 152.0837), 124 (10), 79 (7), 77 (5), 70 (6), 69 (100), 68 (6). $[\alpha]_D$ = -157° (c = 1.2, CH_2Cl_2, T = 18°C).

(5R,6S)-5-Endo-hydroxymethyl-6-exo-methylbicyclo|2.2.1|-2-heptanone (18)

To a susp of Al-Hg (from 10.2 g Al; 0.375 mol) in THF (90 ml) and EtOH (35 ml) was added, at 0°C, ketone 17 (1.9 g, 12.5 mmol). After stirring 1 h at 0°C and 2 h at r.t. the mixture was centrifugated and the liquid decanted. The solid was washed with EtOAc. Usual work-up and column chromatography (Et_2O/hexane, 6:4) yielded 18 (1.79 g; 93 %). Rf (Et_2O) : 0.25; IR (neat) : 3650-3100, 2960, 2880, 1740, 1405, 1370, 1260, 1220, 1170, 1130, 1105, 1060, 1040, 980, 960; ^1H NMR : 3.71 (dd, J = 10 and 6.5 Hz, 1H), 3.54 (t, J = 10 Hz, 1H), 2.73 (m, 1H), 2.29 (s, 1H), 2.14 (dd, J = 4 and 18 Hz, 1H), 2.02-1.71 (m, 5H), 1.44 (m, 1H), 1.12 (d, J = 7 Hz, 3H); MS : 154 ($C_9H_{14}O_2^{+\cdot}$, 4; calculated : 154.0993, found : 154.1013), 136 (6), 110 (100), 95 (71), 94 (64), 93 (53), 92 (36), 91 (33), 81 (98), 80 (67), 79 (89), 77 (37), 67 (67), 55 (51); $[\alpha]_D$ = -11.2° (c = 2.0, CH_2Cl_2, 20°C).

(5R,6S)-5-Endo-formyl-6-exo-methylbicyclo|2.2.1|-2-heptanone (19)

From 18 (1.36 g, 8.83 mmol) as described for the oxidation of 16 to 17. Column chromatography (Et_2O/hexane, 1:1) yielded 19 (1.26 g; 94 %). Rf (Et_2O) : 0.40; IR (neat) : 2960, 2870, 2830, 2720, 1745, 1715, 1455, 1410, 1260, 1170, 1090, 1040, 800; ^1H NMR (90 MHz) : 9.83 (s, 1H), 3.08 (m, 1H), 2.64-2.16 (m, 3H), 2.05-1.65 (m, 4H), 1.13 (d, J = 6 Hz, 3H); MS : 152 ($C_9H_{12}O_2^{+\cdot}$, 15; calculated : 152.0837, found : 152.0840), 98 (54), 97 (100), 81 (43), 79 (36), 69 (54), 67 (30), 55 (41), 53 (30), 41 (54), 39 (64); $[\alpha]_D$ = +26.2° (c = 2.5, CH_2Cl_2, 20°C).

(5R,6S)-5-Endo-dimethoxymethyl-6-exo-methylbicyclo|2.2.1|-2-heptanone (20)

A soln of 19 (727 mg, 4.78 mmol) in anhydrous CH_2Cl_2 (0.5 ml) was treated at -78°C with Me_3SiOMe (1.24 g, 11.96 mmol) and Me_3SiOTf (20 ul). After stirring for 3 h at -78°C, dry pyridine (0.1 ml) was added at the same temperature. After 10 min the reaction mixture was poured into sat. aq. $NaHCO_3$ solution, and extracted with ether. After work-up, the residue was purified by HPLC (EtOAc/hexane 2:8), affording 20 (814 mg, 86 %). Rf (Et_2O/hexane 1:1) : 0.24; IR (neat) : 3100-2740, 1745, 1500-1380, 1130, 1105, 1060, 1040; ^1H NMR (200 MHz) : 4.17 (d, J = 8.75, 1H); 3.36 (s, 3H), 3.33 (s, 3H), 2.64 (m, 1H), 2.29 (m, 1H), 2.08 (m, 1H), 2.01 (m, 1H), 1.91 (m, 1H), 1.83 (m, 1H), 1.74-1.56 (2H), 1.11 (d, J = 6.75, 3H); MS : no $C_{11}H_{18}O_3^{+\cdot}$, 167 ($C_{10}H_{15}O_2^+$, 11; calculated : 167.1071, found : 167.1096), 143 (52), 101 (44), 85 (30), 75 (100), 47 (22), 41 (22); $[\alpha]_D$ = -12.9° (c = 1.9, CH_2Cl_2, T = 20°C).

(6R,7S)-6-Endo-dimethoxymethyl-7-exo-methyl-2-oxabicyclo|3.2.1|-3-octanone (21).

To a soln of norbornanone 20 (250 mg, 1.26 mmol) in CH_2Cl_2 (3 ml) was added mCPBA (409 mg, 1.89 mmol; 80 %). The mixture was then stirred for 16 h at r.t. Me_2S (2 ml) was added, followed by ether (6 ml). The soln was washed successively with sat. aq. $NaHCO_3$ and with brine. After drying and evaporation of the solvent, the residue was purified by column chromatography (Et_2O/hexane 1:1), yielding 21 (219 mg; 81 %).
Rf (Et_2O/hexane 1:1) : 0.09; IR (neat) : 3400-2800, 1735, 1380, 1230, 1125, 1090, 1070, 1040, 970; ^1H NMR (200 MHz) : 4.39 (m, 1H), 4.34 (d, J = 8.5, 1H), 3.40 (s, 3H), 3.35 (s, 3H), 2.70 (m, 1H), 2.61 (m, 1H), 2.54-2.44 (m, 1H), 2.22 (ddd, J = 1.75, 5.5 and 7.5, 1H), 2.00-1.81 (3H), 1.05 (d, J = 7.5, 3H); MS : 214 ($C_{11}H_{18}O_4^{+\cdot}$, < 1), 213 (1), 183 ($C_{10}H_{15}O_3^+$, 7; calculated : 183.1021, found : 183.1027), 151 (19), 85 (34), 81 (27), 75 (100), 47 (25), 41 (30); $[\alpha]_D$ = -28.0° (c = 3.3, CH_2Cl_2, T = 20°C).

(1R,2S,3R,4R)-2-(Dimethoxymethyl)-4-hydroxy-3-methyl-1-cyclopentane acetic acid methyl ester (22)

To a soln of the lactone 21 (215 mg, 1.01 mmol) in super dry MeOH (4 ml) was added NaOMe (27.3 mg, 0.51 mmol) in MeOH (0.6 ml). After stirring for 16 h at r.t., a sat. aq. NH_4Cl soln was added, and the solvent was evaporated under reduced pressure. Water was added, and the water-layer extracted with ether. After work-up the residue was purified by column chromatography (Et_2O/hexane 1:1), yielding 22 (246 mg; 95 %).
Rf (Et_2O/hexane 1:1) : 0.10; IR (neat) : 3420 (br), 2950, 2830, 1730, 1435, 1370, 1195, 1160, 1060, 1005, 960, 880; ^1H NMR (200 MHz) : 4.27 (d, J = 5 Hz, 1H), 3.68 (s, 3H), 3.7 (m, 1H), 3.37 (s, 3H), 3.34 (s, 3H), 2.68-2.35 (3H), 2.16 (ddd (dt), J = 7, 7 and 13 Hz, 1H), 2.04-1.86 (3H), 1.41 (ddd, J = 6.25, 9 and 13 Hz, 1H), 1.10 (d, J = 6.75, 3H).

(1R,2S,3R,4R)-4-Benzoyloxy-2-(dimethoxymethyl)-3-methyl-1-cyclopentaneacetic acid methyl ester (23)

To a soln of 22 (216 mg, 0.88 mmol), benzoic acid (214 mg, 1.75 mmol) and triphenylphosphine (459 mg, 1.75 mmol) in THF (5.6 ml) was added at r.t. diethyldiazodicarboxylate (DEAD, 277 ul, 1.76 mmol). After stirring for 16 h at r.t., the solvent was removed under reduced pressure. The residue was taken up in ether and washed successively with sat. aq. $NaHCO_3$ and brine. After drying and evaporation, the residue was purified by column chromatography (Et_2O/hexane 2:8) and HPLC (Et_2O:hexane 4:6), yielding benzoate 23 (234 mg; 76 %).
Rf (Et_2O/hexane 1:1) : 0.36; IR (neat) : 3100-2800, 1730, 1715, 1450, 1435, 1275, 1170, 1115, 1070, 710; ^1H NMR (200 MHz) : 8.04 (m, 2H), 7.50 (m, 3H), 5.43 (ddd, J = 2.25, 5 and 5, 1H), 4.25 (d, J = 5.3, 1H), 3.68 (s, 3H), 3.38 (s, 3H), 3.367 (s, 3H), 2.88 (m, 1H), 2.67 (dd, J = 7.5 and 15.8, 1H), 2.32 (dd, J = 8 and 15.8 Hz, 1H), 2.44-2.18 (2H), 2.01 (ddd, J = 2.25, 7 and 13.8, 1H), 1.80 (ddd, J = 5, 9.8 and 13.8, 1H), 1.10 (d, J = 7, 3H); MS : 350 ($C_{19}H_{26}O_6^{+\cdot}$, < 1; calculated : 350.1729, found : 350.1753), 165 (17), 105 (94), 77 (64), 75 (100), 47 (26); $|\alpha|_D$ = +30.7° (c = 3.7, CH_2Cl_2, T = 20°C).

7-O-Benzoyl-1-O-methyl-loganin aglucone (24)

To a suspension of KOt.Bu (48 mg, 0.429 mmol) in THF (0.8 ml) was added at -78°C N,N-isopropylcyclohexylamine (78 ul, 0.471 mmol) and n.BuLi (296 ul, 0.429 mmol, 1.45 M in hexane). After 10 min of stirring, a soln of 23 (50 mg, 0.143 mmol) in THF (0.8 ml) was added dropwise, at -78°C, during 5 min. The mixture was stirred for 30 min at -78° C. Methyl formate (176 ul, 2.86 mmol) was added, and the mixture was allowed to warm up to -40°C over 30 min. After an additional 60 min of stirring at -40°C, the reaction mixture was quenched with 5 % H_3PO_4. After work-up the crude formylation product was dissolved in anhydrous CH_2Cl_2 (6 ml), and treated at 0°C with $BF_3.OEt_2$ (20 ul). After 30 min, sat. $NaHCO_3$ (2 ml) was added and the water layer was extracted (Et_2O). The residue obtained after work-up was purified by HPLC (Et_2O:hexane 2:8), giving rise to 24 as a C-1 epimeric mixture (β-isomer : 22 mg, 45 %; α-isomer : 5 mg, 10 %).

β-isomer :

Rf (Et_2O/hexane 1:1) : 0.38; IR (neat) : 3020-2800, 1715, 1640, 1630, 1450, 1280, 1120, 1090, 715; ^1H NMR (200 MHz) : 8.08-7.99 (m, 2H), 7.63-7.40 (4H), 5.43 (m, 1H), 4.71 (d, J = 3.75, 1H), 3.71 (s, 3H), 3.52 (s, 3H), 3.18 (m, 1H), 2.47 (ddd, J = 1.5, 8 and 15, 1H), 2.27-2.10 (2H), 1.85 (ddd, J = 5.5, 7.25 and 15, 1H), 1.13 (d, J = 6.5, 3H); MS : no $C_{19}H_{22}O_6$, 224 (12), 192 (29), 160 (24), 105 (85), 85 (100), 77 (50), 55 (19); $|\alpha|_D$ = 5.30°(c = 0.92, $CHCl_3$, T = 22°C).

α-isomer :

Rf (Et_2O/hexane 1:1) : 0.40; IR (neat) : 3000-2800, 1710 (br), 1640, 1450, 1275, 1140-1040, 1030, 715; ^1H NMR (200 MHz) : 8.08-8.01 (2H), 7.61-7.39 (4H), 5.48 (m, 1H), 4.97 (d, J = 3.5, 1H), 3.72 (s, 3H), 3.47 (s, 3H), 3.15 (m, 1H), 2.65-2.45 (m, 1H), 2.43-2.09 (m, 1H), 2.05-1.91 (m, 1H), 1.13 (d, J = 7 Hz, 3H); MS : no $C_{19}H_{22}O_6$, 315 (< 1), 224 (7), 192 (20), 105 (100), 85 (64), 77 (53).

(-)1-β-O-methyl loganin aglucone (2)

To a soln of 24B (20 mg, 0.058 mmol) in super dry MeOH (2 ml) was added at r.t. NaOMe (31 mg, 0.58 mmol) in MeOH (0.4 ml). After stirring for 24 h at r.t., the mixture was diluted (Et_2O), acidified (5 % H_3PO_4), and the water layer was extracted with ether. The combined organic layers were washed with sat. aq. $NaHCO_3$. Work-up and purification by HPLC (Et_2O/hexane 7:3) afforded (-)-2 (13.7 mg, 98 %). The diastereoisomeric purity was checked on a RSiLC18HL-D 5 u column 0.46 x 25 cm, MeOH/H_2O, 55:45, 1.0 ml/min : 9.6 (100) . The optical purity was determined on a Pirkle I 5 u column by separate injection 0.46 x 25 cm, CH_2Cl_2/hexane 1:1, 0.8 ml/min : 20.4 (100) and by coinjection with (±)-2 (retention times 19.5 and 20.4).
Rf (Et_2O/hexane 1:1) : 0.11; IR (neat) : 3400 (br), 3040-2800, 1710, 1630, 1440, 1285, 1185, 1135, 1090 (br), 1030, 1000, 770; ^1H NMR (200 MHz) : 7.39 (d, J = 1.25, 1H), 4.63 (d, J = 4, 1H), 4.12 (m, 1H), 3.71 (s, 3H), 3.49 (s, 3H), 3.05 (m, 1H), 2.28 (ddd, J = 1.5, 8 and 14, 1H), 1.64 (ddd, J = 5, 7.5 and 14, 1H), 2.07 (ddd (td), J = 4, 9 and 9, 1H), 1.82 (m, 1H), 1.12 (d, J = 7, 1H); MS : 242 ($C_{12}H_{18}O_5^{+\cdot}$, < 1), 224 ($C_{12}H_{16}O_4^{+\cdot}$, 1; calculated : 224.1049, found : 224.1056), 211 (2), 139 (10), 85 (100), 55 (25), 45 (18), 41 (23); $|\alpha|_D$ = -44.5°(c = 0.75, $CHCl_3$, T = 20°C) (lit.[6a] -45°, c = 1.16, $CHCl_3$).

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