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SYNTHESIS OF (1R)-(+)-CIS-CHRYSANTHEMIC ACID

J.S. Yadav*, Sudha V. Mysorekar and A.V. Rama Rao
Indian Institute of Chemical Technology, Hyderabad 500 007, India

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Abstract : *A synthesis of (1R)-cis-chrysanthemic acid from (R,R)-tartaric acid is described. The diol* ***8*** *was converted to the mono MEM protected compound* ***8b****. Dehydration of the tertiary alcohol using methanesulfonyl chloride-triethylamine-DMAP and treatment of the resulting product with lithium in liquid ammonia afforded* ***10****. The diazoester of* ***10*** *was subjected to intramolecular cyclopropanation using a soluble copper complex to obtain* ***12****. Cleavage of the MEM ether, dehydration of the tertiary alcohol followed by reductive cleavage with lithium in liquid ammonia gave the title compound.*

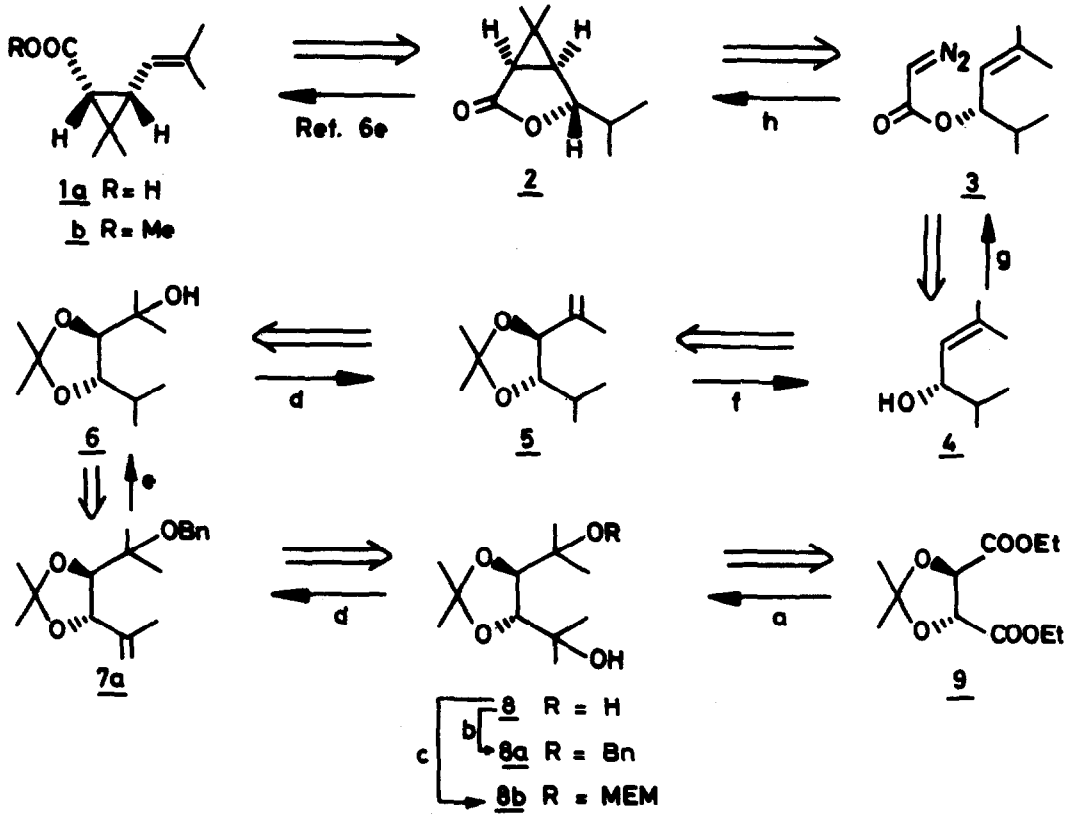
The high insecticidal activity of the pyrethroids coupled with their low mammalian toxicity has stimulated considerable activity towards their synthesis[1]. Most of this effort has been directed towards the esters of trans chrysanthemic acid[1,2]. It has been discovered[3] that certain esters of cis chrysanthemic acid possess superior activity relative to the trans chrysanthemates. Cis chrysanthemic acid esters are very important precursors for the synthesis[4] of caronaldehyde acid esters, which can be converted[5] to side-chain modified cis chrysanthemic acids. Several derivatives of cis chrysanthemic acid, particularly the halogenated compounds are some of the most effective insecticides known. Nevertheless, relatively few stereospecific total syntheses of cis chrysanthemic acid have been reported[6]. Obviously, the major obstacle inherent in this synthetic problem is the cis relationship of the carboxy and alkenyl substituents on the cyclopropane ring. In this paper we describe two routes to (+)-cis chrysanthemic acid from L-tartaric acid.

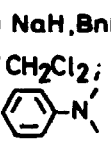
A retrosynthetic analysis of **1** shows that the required intermediary cyclopropanated lactone **2** (which has been converted to cis chrysanthemic acid by Franck-Neumann et al[6e]) could be obtained by intramolecular cyclopropanation[7] of the diazoester **3** as shown in Scheme 1. The diazoester **3** is conveniently prepared from the allylic alcohol **4**, which in turn could be derived from **5** by reductive cleavage of the acetonide. **5** could be procured by dehydrating the tertiary alcohol **6**, which can be obtained from L-tartaric acid by simple steps. Thus, cheaply and abundantly available natural tartaric acid makes an ideal starting material for the synthetic endeavour[2e,6f].

Accordingly, **8** was obtained by the Grignard reaction of (R,R)-2,3-O-isopropylidene-diethyl tartrate (**9**) with excess methylmagnesium iodide by the procedure of Seebach et al[8]. **8** was converted to the monobenzyl ether (**8a**) by using 1.1 eq. of sodium hydride and benzyl bromide. A crucial problem is the dehydration of the tertiary alcohol **8a** which needs to be carried out under mild conditions due to the presence of an acetonide group. After trying several combinations of reagents it was found that a system containing methanesulfonyl chloride (1.5 eq.), triethylamine (3 eq.) and N,N-dimethylaminopyridine (4 mol%) effected[9] the dehydration in excellent yield to afford **7a**. Exhaustive catalytic hydrogenation of **7a** over Raney nickel afforded **6** which was subjected to a second dehydration to obtain **5**. Reductive cleavage of the allylic C-O bond using lithium in liquid ammonia proceeded smoothly to afford the allylic alcohol **4**. It was converted[7] to the

diazoacetate (3) by treating it first with the acid chloride of glyoxylic acid p-toluenesulfonyl hydrazone in the presence of N,N-dimethylaniline and subsequently with triethylamine. The diazoester 3 on heating in a 3:2 mixture of dioxane and cyclohexane at high dilution in the presence of a soluble copper complex bis (acetylacetonato) Cu (II) underwent[11] intramolecular carbene addition

Scheme 1



Reagents : a) MeMgI (excess); b) NaH, BnBr (1.1eq) ; c) NaH, MEM-Cl (1.1eq) d) MsCl, Et_3N, DMAP / CH_2Cl_2; e) H_2 / Ra-Ni; f) Li / Liq. NH_3; g) pTsNH-N=CHCOCl,  , Et_3N / CH_2Cl_2; h) $Cu(acac)_2$. dioxane, cyclohexane.

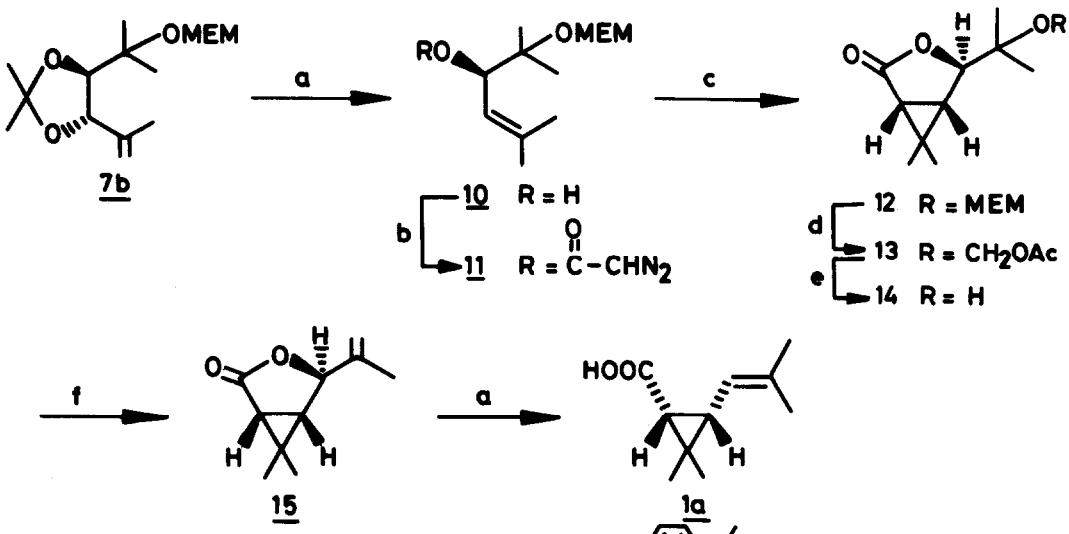
on the double bond in a stereospecific manner, resulting in the optically active bicyclic cyclopropanated lactone 2 (Scheme 1) in an overall yield of 9.5% from 8. 2 can be converted to (1R,3S)-(+)-chrysanthemic acid by known methods[6e]. Thus, this route constitutes a formal total synthesis of (+)-1.

It was however, still desirable to achieve the total synthesis of 1 by a more efficient method. It was envisaged that minor modifications in the route described above, i.e., scheme 1 could provide (+)-cis-chrysanthemic acid in a more expedient way while maintaining the original basic strategy

unaffected. It would be advantageous if the benzyl group was replaced by a protecting group which could survive reductive conditions. The β-methoxyethoxymethyl (MEM) ether was chosen as the protecting group because it possesses good stability and can be removed by using mild conditions, when desired.

Accordingly, the diol **8** was converted to the mono-MEM ether (**8b**) (Scheme 2). Dehydration of the tertiary alcohol afforded **7b**. Reductive cleavage of the isopropylidene group with lithium in liquid ammonia gave the allylic alcohol **10**. **10** was converted to the allylic diazoacetate (**11**) which underwent intramolecular cyclopropanation on heating in dioxane-cyclohexane mixture in the presence of $Cu(acac)_2$, to afford the optically active bicyclic lactone **12**.

Scheme 2



Reagents: a) Li / Liq. NH_3 ; b) pTsNH-N=CHCOCl ,  , Et_3N / CH_2Cl_2;
c) $Cu(acac)_2$, dioxane, cyclohexane; d) Ac_2O, AcOH, H_2SO_4; e) NaOMe / MeOH f) MsCl, Et_3N, DMAP / CH_2Cl_2

MEM ether cleavage was effected in two steps - i) conversion of **12** to the acetate **13** by treatment with a mixture of acetic anhydride-acetic acid and catalytic amount of sulfuric acid for 5 min, ii) hydrolysis of the acetate by catalytic sodium methoxide in methanol. Treatment of **14** with mesyl chloride-triethylamine-DMAP resulted in the olefin **15**. Thus, in essence, **15** was obtained by employing a modification which involved stepwise dehydration.

Compound **15** on reaction with lithium in liquid ammonia underwent reductive cleavage of the allylic C-O bond with concomitant shifting of the double bond to afford (1R)-(+)-cis-chrysanthemic acid in an overall yield of 5.6% from **8**. Esterification with ethereal diazomethane afforded (1R)-(+)-cis-methyl chrysanthemate, whose spectral data and $[\alpha]_D$ values were in agreement with the reported data.

Experimental

IR spectra were recorded on Perkin-Elmer 683 or 1310 spectrometers. ^1H NMR spectra

were recorded on Varian FT-80A or Jeol PMX-90 spectrometers, using TMS as internal standard. Mass spectra were recorded on a CEC-21-110B double focussing mass spectrometer operating at 70 eV using direct inlet system. Optical rotations were measured with a Jasco Dip 181 digital polarimeter.

(4R,5R)-4,5-Bis-(2-hydroxyprop-2-yl)-2,2-dimethyl-1,3-dioxolane (8)

This compound was obtained by the procedure of Seebach[8], from magnesium (11.5 g, 0.48 mol), methyl iodide (68.2 g, 0.48 mol) and **9** (24.6 g, 0.1 mol) as a white crystalline solid (20.2 g, 93%); m.p. 154.2°, lit.[8] m.p. 154.0-154.6°.

(4R,5R)-4-(2-Benzyloxyprop-2-yl)-2,2-dimethyl-5-(2-hydroxyprop-2-yl)-1,3-dioxolane (8a)

To a solution of **8** (10.9 g, 50 mmol) in a mixture of dry THF (80 ml) and HMPA (20 ml) was added sodium hydride (50% oil dispersion, 2.8 g, 60 mmol) at 0 °C under nitrogen. The mixture was stirred for 1 h at room temperature, then benzyl bromide (9.4 g, 55 mmol, 6.7 ml) was added dropwise over 45 min. After stirring at room temperature for 6 h, crushed ice was added to it and the mixture extracted with ethyl acetate (3 x 100 ml). The organic extracts were washed with water (2 x 100 ml), dried (Na_2SO_4) and concentrated. The residue was chromatographed over silica gel using light petroleum-ethyl acetate (4:1, 3:1) as eluent to afford **8a** (13.8 g, 89%): $[\alpha]_D$ + 11.48° (c 2.42, chloroform); ^1H NMR ($CDCl_3$) δ 1.2, 1.25 (2s, 6H, 2 x CH_3), 1.4 (s, 9H, 3 x CH_3), 1.44 (s, 3H, CH_3), 3.83 (s, 2H, H-4, H-5), 4.2 (s, 1H, OH), 4.58 (d, 2H, CH_2Ph), 7.35 (s, 5H, Ph); Mass m/z 293 (M^+ -15), 149 (100%), 91.

Anal. Calcd. for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 69.90; H, 9.08.

(4R,5S)-4-(2-Benzyloxyprop-2-yl)-2,2-dimethyl-5-(1-propen-2-yl)-1,3-dioxolane (7a)

A mixture of compound **8a** (12.3 g, 40 mmol), triethylamine (12.0 g, 120 mmol, 17.2 ml) and DMAP (0.20 g, 4 mol%) in CH_2Cl_2 (100 ml) was cooled to 0 °C and mesyl chloride (6.8 g, 60 mmol, 4.8 ml) was added dropwise to it. After 2 h at room temperature, crushed ice was added and the mixture stirred for 1 h. It was extracted with CH_2Cl_2 (3 x 100 ml), washed with water (2 x 100 ml), dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel using light petroleum-ethyl acetate (5:1) as eluent to yield **7a** (10.3 g, 89%): $[\alpha]_D$ + 1.8° (c 2.1, chloroform); ^1H NMR ($CDCl_3$) δ 1.25 (s, 6H, 2 x CH_3), 1.4 (s, 6H, 2 x CH_3), 1.8 (s, 3H, CH_3-C=C), 3.9 (d, 1H, H-4), 4.45 (d, 1H, H-5), 4.52 (s, 2H, CH_2Ph), 4.95, 5.07 (2s, 2H, CH_2=), 7.25 (s, 5H, Ph); Mass m/z 275 (M^+ -15), 149, 91 (100%).

Anal. Calcd. for $C_{18}H_{26}O_3$: C, 74.44; H, 9.03. Found: C, 74.15; H, 8.98.

(4R,5S)-2,2-Dimethyl-4-(2-hydroxyprop-2-yl)-5-(2-propyl)-1,3-dioxolane (6)

Compound **7a** (10 g) and Raney nickel (5 g) in ethanol (100 ml) were stirred under hydrogen at atmospheric pressure and room temperature for 3 days and then filtered to remove the catalyst. The filtrate was concentrated to give a residue which was chromatographed on silica gel using light petroleum-ethyl acetate (4:1) as eluent to furnish **6** (5.4 g, 78%): $[\alpha]_D$ -67.45° (c 2.87, chloroform); ^1H NMR ($CDCl_3$) δ 0.85, 0.95 (2d, 6H, 2 x CH-CH_3), 1.1, 1.16 (2s, 6H, 2 x CH_3), 1.3 (s, 6H, 2 x CH_3), 1.6-1.8 (m, 1H, $(CH_3)_2CH$), 3.5-3.78 (m, 2H, H-4, H-5); Mass m/z 187 (M^+ -15).

Anal. Calcd. for $C_{11}H_{22}O_3$: C, 65.31; H, 10.96. Found: C, 64.99; H, 10.90.

(4S,5S)-2,2-Dimethyl-4-(1-propen-2-yl)-5-(2-propyl)-1,3-dioxolane (5)

This compound was obtained by the procedure described above for **7a**, from **6** (4.04 g, 20 mmol), triethylamine (6.0 g, 60 mmol), DMAP (0.10 g, 4 mol%) and mesyl chloride (3.4 g, 30 mmol)

as an oil (2.8 g, 76%): $[\alpha]_D$ -30.86° (c 2.78, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.95, 1.02 (2d, 6H, 2 x CH-C$\underline{H}_3$), 3.56, 3.7 (dd, 1H, H-5), 4.22 (d, 1H, H-4), 5.0, 5.1 (2s, 2H, CH_2=); Mass m/z 169 (M^+ -15).

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.42; H, 10.88.

(4R)-2,5-Dimethyl-2-hexen-4-ol (4)

Ammonia (100 ml) was condensed into a flask containing compound **5** (2.5 g) in dry THF (5 ml). Lithium (0.62 g) was added in small pieces to this mixture, till it attained a blue colour. After stirring for 15 min, solid ammonium chloride was added to it till the blue colour disappeared. Ammonia was allowed to evaporate, the solid was dissolved in a minimum amount of water and extracted with ether. The organic extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel using pentane-ether (4:1) as eluent to give **4** (0.9 g, 52%): $[\alpha]_D$ + 8.8° (c 1.0, chloroform); ^1H NMR ($CDCl_3$) δ 0.85, 0.95 (2d, 6H, 2 x CH-C$\underline{H}_3$), 1.15-1.55 (m, 1H, $(CH_3)_2C\underline{H}$), 1.7, 1.75 (2d, 6H, 2 x CH_3), 4.0, 4.1 (dd, 1H, CH-O), 5.2 (dm, 1H, CH=).

(4R)-2,5-Dimethyl-2-hexen-4-yl diazoacetate (3)

Glyoxylic acid chloride p-toluenesulfonyl hydrazone (1.9 g, 7.29 mmol) was added to an ice cooled solution of dry alcohol **4** (0.50 g, 3.9 mmol) in dry CH_2Cl_2 (27 ml) under nitrogen. N,N-Dimethylaniline (0.91, 7.15 mmol) was added and the dark green solution was stirred for 15 min at 0 °C. Then triethylamine (2.75 ml, 20 mmol) was introduced and the resulting dark orange suspension was stirred for 10 min. at 0 °C, then for 15 min. at room temperature. An ice-cold saturated solution of citric acid was added and the mixture was extracted with CH_2Cl_2, washed with saturated citric acid solution, dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel using pentane-ether (8:1) as eluent, to furnish **3** (0.50 g, 65%): ^1H NMR ($CDCl_3$) δ 0.8, 0.9 (2d, 6H, 2 x CH-C$\underline{H}_3$), 1.65, 1.67 (2s, 6H, 2 x CH_3), 4.6 (s, 1H, C$\underline{H}N_2$), 5.0 (dm, 1H, CH=), 5.3 (dd, 1H, CH-O); IR (film) 2100 cm^{-1} (diazo), 1690 (COOR).

2,2-Dimethyl-3-(1-hydroxyprop-1-yl-2-methyl)-1-cyclopropanecarboxylic acid lactone (2)

A solution of **3** (0.40 g) in a mixture of dioxane (12 ml) and cyclohexane (8 ml) was added dropwise to a refluxing solution of bis-(acetylacetonato) Cu(II) (20 mg) in a mixture of dioxane (12 ml) and cyclohexane (8 ml). After the addition was complete, the mixture was refluxed for 2 h, the solvents were evaporated and the residue chromatographed on silica gel using pentane-ether (5:1) as eluent to afford **2** (0.20 g, 59%): $[\alpha]_D$ - 75.2° (c 0.52, chloroform), lit.[6e] $[\alpha]_D$ - 80° (c 1.2 chloroform); ^1H NMR ($CDCl_3$) δ 0.88, 0.96 (2s, 6H, 2 x CH_3), 1.15, 1.17 (2d, 6H, $(CH_3)_2CH$), 1.45-1.6 (m, 1H, H-5), 1.7, 1.85 (2d, 2H, cyclopropane), 4.2 (d, 1H, CH-O); IR (film) 1725 cm^{-1} (lactone); Mass m/z 168 (M^+), 167, 149 (100%).

(4R,5R)-2,2-Dimethyl-5-(2-hydroxyprop-2-yl)-4-(2- β -methoxyethoxymethoxyprop-2-yl)-1,3-dioxolane (8b)

This compound was obtained by the procedure described above for **8a**, from **8** (10.9 g, 50 mmol), sodium hydride (2.8 g, 60 mmol) and MEM chloride (6.85 g, 55 mmol) as an oil (13.0 g, 85%): $[\alpha]_D$ + 4.6° (c 2.91 chloroform); ^1H NMR ($CDCl_3$) δ 1.14, 1.15, 1.25 (3s, 9H, 3 x CH_3), 1.26 (s, 9H, 3 x CH_3), 3.3 (s, 3H, OCH_3), 3.35-3.65 (m, 4H, 2 x CH_2-O), 3.7 (s, 2H, H-4, H-5), 3.95 (s, 1H, OH), 4.8 (s, 2H, O-CH_2-O); Mass m/z 291 (M^+ -15), 89 (100%), 59.

Anal. Calcd. for $C_{15}H_{30}O_6$: C, 58.80; H, 9.87. Found: C, 58.64; H, 9.79.

(4R,5S)-2,2-Dimethyl-4-(2- β -methoxyethoxymethoxyprop-2-yl)-5-(1-propen-2-yl)-1,3-dioxolane (7b)

This compound was obtained by the procedure described above for **7a**, from **8b** (12.2 g, 40 mmol), triethylamine (12.0 g, 120 mmol), DMAP (0.20 g, 4 mol%), and mesyl chloride (6.8 g, 60 mmol) as an oil (10.1 g, 88%): $[\alpha]_D$ -8.15° (c 1.78, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.2 (s, 6H, 2 x CH_3), 1.35 (s, 6H, 2 x CH_3), 1.73 (s, 3H, CH_3-C=C), 3.3 (s, 3H, OMe), 3.4-3.7 (m, 4H, 2 x CH_2-O), 3.8 (d, 1H, H-4), 4.35 (d, 1H, H-5), 4.8 (s, 2H, O-CH_2-O), 4.9, 5.1 (2s, 2H, CH_2=); Mass m/z 273 (M^+ -15), 147, 112, 89 (100%).

Anal. Calcd. for $C_{15}H_{28}O_5$: C, 62.47; H, 9.79. Found: C, 62.12; H, 9.98.

2,5-Dimethyl-2-(β-methoxyethoxymethoxy)-4-hexen-3-ol (10)

This compound was obtained by the procedure described above for **4**, from **7b** (10.0 g) and lithium (2.5 g) in ammonia (500 ml), as an oil (5.7 g, 71%): $[\alpha]_D$ + 39.09° (c 1.76, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 6H, 2 x CH_3), 1.65, 1.68 (2d, 6H, 2 x CH_3), 3.1 (d, 1H, OH), 3.33 (s, 3H, OMe), 3.55-3.80 (m, 4H, 2 x CH_2-O), 4.12, 4.25 (dd, 1H, CH-OH), 4.80 (ABq, 2H, O-CH_2-O), 5.15 (dm, 1H, CH=).

2,5-Dimethyl-2-(β-methoxyethoxymethoxy)-4-hexen-3-yl diazoacetate (11)

This compound was obtained by the procedure described above for **3**, from **10** (3.62 g, 15.6 mmol), glyoxylic acid p-toluenesulfonyl hydrazone (7.6 g, 29.15 mmol), N,N-dimethylaniline (3.63 ml, 28.6 mmol) and triethylamine (11 ml, 80 mmol) as a yellow oil (3.5 g, 75%): ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 6H, 2 x CH_3), 1.7 (s, 6H, 2 x CH_3), 3.3 (s, 3H, OMe), 3.4-3.7 (m, 4H, 2 x CH_2-O), 4.65 (s, 1H, CHN_2), 4.75 (s, 2H, O-CH_2-O), 5.1 (dm, 1H, CH=), 5.45 (d, 1H, CH-O); IR (film) 2100 cm^{-1} (diazo), 1694 (COOR).

Anal. Calcd. for $C_{14}H_{24}N_2O_5$: C, 55.98; H, 8.05. Found: C, 55.83; H, 7.95.

2,2-Dimethyl-3-[(2- β-methoxyethoxymethoxy-2-methyl)-1-hydroxyprop-1-yl]-1-cyclopropanecarboxylic acid lactone (12)

This compound was obtained by the procedure described above for **2**, from **11** (3.0 g) and $Cu(acac)_2$ (0.15 g) as an oil (1.6 g, 59%): $[\alpha]_D$ -18.86° (c 0.88, chloroform); ^{1}H NMR ($CDCl_3$) δ1.1 (s, 6H, 2 x CH_3), 1.22, 1.25 (2s, 6H, 2 x CH_3), 1.85, 2.05 (2d, 2H, cyclopropane), 3.3 (s, 3H, OMe), 3.4-3.75 (m, 4H, 2 x CH_2-O), 3.95 (s, 1H, CH-O), 4.77 (s, 2H, O-CH_2-O); IR (film) 1760 cm^{-1} (lactone); Mass m/z 273 (M^+ +1), 199, 89, 59 (100%).

Anal. Calcd. for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.48; H, 8.92.

2,2-Dimethyl-3[2-hydroxy-2-methyl)-1-hydroxyprop-1-yl]-1-cyclopropanecarboxylic acid lactone (14)

A solution of **12** (1.5 g) in dry CH_2Cl_2 (10 ml) was cooled to 0 °C and treated with an ice-cold mixture of acetic anhydride (7 ml), glacial acetic acid (3 ml) and conc. H_2SO_4 (0.05 ml). After 10 min at 0 °C the mixture was poured into an ice-cold 10% solution of sodium bicarbonate. It was allowed to stand for 2 h and then extracted with CH_2Cl_2 (3 x 25 ml), washed successively with 10% $NaHCO_3$ (2 x 25 ml), water (1 x 25 ml), dried (Na_2SO_4) and evaporated to afford the acetate **13** which was used as such for the next step.

13 was dissolved in anhydrous methanol (10 ml) and treated with sodium methoxide (25 mg) for 16 h. The reaction mixture was deionized with Amberlite resin, filtered and concentrated to afford crude **14** which was purified on a column of silica gel using light petroleum-ethyl acetate

(1:1) as eluent to furnish **14** (0.65 g, 64% from **12**): $[\alpha]_D$ -58.57° (c 1.26, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.1 (s, 6H, 2 x CH_3), 1.2 (s, 6H, 2 x CH_3), 1.7, 1.95 (2d, 2H, cyclopropane), 3.95 (s, 1H, CH-O); IR (film) 3220 cm^{-1} (OH), 1760 cm^{-1} (lactone); Mass m/z 185 (M^+ +1), 169, 111, 59 (100%).

2,2-Dimethyl-3-(1-hydroxy-2-methyl-2-propen-1-yl)-1-cyclopropanecarboxylic acid lactone (15)

This compound was obtained by the procedure described above for **7a**, from **14** (0.55 g, 3 mmol), triethylamine (0.9 g, 9 mmol), DMAP (15 mg, 4 mol%) and mesyl chloride (0.51 g, 4.5 mmol) as an oil (0.37 g, 74%): $[\alpha]_D$ -53.57° (c 0.56, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.1, 1.15 (2s, 6H, 2 x CH_3), 1.7 (s, 3H, CH_3-C=), 1.8, 1.95 (2d, 2H, cyclopropane), 4.55 (s, 1H, CH-O), 4.95, 5.05 (2s, 2H, CH_2=).

(1R,3S)-(+)-Cis-chrysanthemic acid (1a)

A solution of compound **15** (0.33 g, 2 mmol) in dry ether (1 ml) was added in one lot to a solution of lithium (42 mg, 6 mmol) in liquid ammonia (20 ml). After stirring for 5 min the reaction mixture was quenched with solid ammonium chloride (0.1 g). Ammonia was allowed to evaporate, the mixture was dissolved in 5% NaOH and extracted with ether to remove unreacted **15**. The aqueous layer was cooled to 0 °C and acidified with ice-cold 5% HCl to pH 4. The mixture was extracted with ether, washed with water, dried (Na_2SO_4) and evaporated to give **1a** (0.15 g, 50%): ^{1}H NMR ($CDCl_3$) δ 1.17, 1.2 (2s, 6H, 2 x CH_3), 1.45 (d, 1H, H-1), 1.55, 1.67 (2s, 6H, 2 x CH_3), 2.0 (broad d, 1H, H-3), 5.3 (d, 1H, CH=).

(1R,3S)-(+)-Cis-methyl chrysanthemate (1b)

Compound **1a** (0.100 g) was treated with an ethereal solution of diazomethane at 0 °C till it attained a yellow colour. The solution was evaporated to dryness and the residue was repeatedly chromatographed on silica gel using pentane-ether (9:1) as eluent to afford **1b** (0.060 g, 55%): $[\alpha]_D$ + 63.2° (c 0.8, benzene), lit.[6e] $[\alpha]_D$ + 67.5° (c 1.8, benzene); ^{1}H NMR ($CDCl_3$) δ 1.2 (broad s with shoulder, 6H, 2 x CH_3), 1.47 (obscured d, 1H, H-1), 1.6, 1.67 (2s, 6H, 2 x CH_3), 1.8-2.2 (dd, 1H, H-3), 3.52 (s, 3H, OMe), 5.3 (dm, 1H, CH=).

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