141. Synthesis of the Alleged Natural Monoterpenoid *a*-Santolinenone[1])

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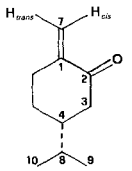
Summary

Authentic α-santolinenone (= (+)-(4*R*)-1(7)-*p*-menthen-2-one; (+)-**1**) is made available for the first time in 30% overall yield from (+)-(4*R*)-*p*-menthene ((+)-**2**) *via* the diastereoisomeric allylic alcohols (+)-**4a**/(+)-**4b**, which are oxidized to (+)-**1** with Ag_2CO_3/*Celite*. Yields are good, except for the last stage; indeed, only alcohol (+)-**4a**, with equatorial OH-group, undergoes oxidation, and (+)-**1** is partly subtracted *via* a hetero *Diels-Alder* dimerization giving a mixture of the diastereoisomeric dihydropyrans (+)-**5a**/(+)-**5b**. When Cr(VI) reagents are used, (+)-**4a**/(+)-**4b** mainly give phellandral (**6**) and carvotanacetone (**7**). MnO_2 reacts too sluggishly with (+)-**4a**/(+)-**4b**. A camphor pyrolyzate, previously thought to be **1** must be a different compound, probably **7**.

The structure (±)-**1** was proposed seventy years ago for an oily fraction from the steam volatiles of the plant *Santolina chamaecyparissus* and called α-santolinenone [1]. The evidence offered was poor [1], and repeated search for **1** from the same plant species with modern analytical methods has given negative results [2][2]). This notwithstanding, α-santolinenone (**1**) has been included, as originally formulated [1], in two authoritative compilations of natural products [4].

We became interested in **1** as a potentially useful chiral synthon for the synthesis of sesquiterpenoids recently isolated in our laboratory from a marine sponge [5]. To the



(+)-**1**

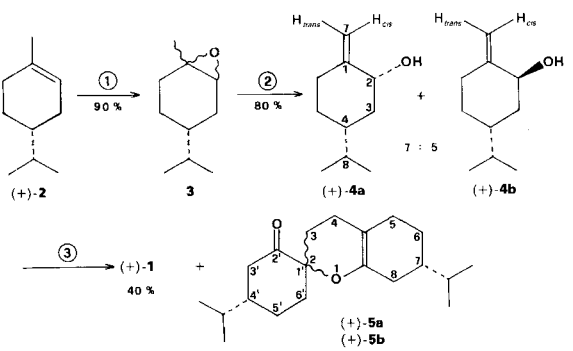
[1]) Presented by *F. P.* as part of a lecture at the University of Innsbruck on March 15th, 1984.

[2]) Astonishingly, α-santolinenone, as originally formulated ((±)-**1**) [1], has recently been proposed again as a component of the essential oils of *Santolina virus* and *S. chamaecyparissus* [3], on the basis of much the same earlier evidence [1]. All intervening literature has been ignored.

best of our knowledge, synthetic **1** has only been reported as a product of the flash pyrolysis of camphor [6]. However, the implied [6] high stability of the product, which is surprising for a simple α-methylidene-cyclohexanone [7], and the lack of NMR spectral data, make the structural attribution **1** of dubious value. Also, the extremely poor yield renders the method [6] synthetically unattractive. In fact, it is shown below that the structural attribution **1** for the camphor pyrolyzate [6] has to be revised.

An appraisal of current methods for the synthesis of α-methylidene ketones [8] did not suggest any easy route to enantiomerically pure (+)- or (−)-**1**. Therefore, we chose to synthesize it from (+)-(4*R*)-1-*p*-menthene ((+)-**2**) according to *Scheme 1*. The method involves epoxidation of (+)-**2** followed by base opening of the epoxides **3** to give the alcohols (+)-**4a**/(+)-**4b**[3]) which are finally oxidized to (+)-(4*R*)-1(7)-*p*-menthen-2-one ((+)-**1**). The yields are good, except for the last stage. Indeed, only (+)-**4a** undergoes oxidation, and (+)-**1** tends to dimerize to give a mixture of diastereoisomeric spiro compounds (+)-**5a**/(+)-**5b**. Though (+)-**1** could be cleanly separated from both (+)-**4b** and (+)-**5a**/(+)-**5b** by HPLC, it was not possible to record spectra of (+)-**1** completely free of the spirocompounds; the latter tend to be reformed even in the cold.

Scheme 1



① *m*-Chloroperbenzoic acid (1 mol-equiv.); $NaHCO_3$ (2 mol-equiv.) in CH_2Cl_2 at 5–10°, 1 h.
② LDA (2 mol-equiv.) in THF at reflux, 2 h.
③ Ag_2CO_3/*Celite* in hexane at reflux, 2 h.

Whereas the formation and opening of **3** are standard and straight-forward[4]), oxidation of the allyl alcohols (+)-**4a**/(+)-**4b** to (+)-**1** proved a very stringent test for the performance of current oxidizing agents for allyl alcohols [10]. In fact, both Cr(VI) and Mn(IV) reagents proved unsatisfactory. Thus, with pyridinium chlorochromate in CH_2Cl_2 [11], (+)-**4a**/(+)-**4b** mainly led to phellandral (**6**) [12]. Pyridinium chlorochromate/NaOAc 1:2 [11] or pyridinium dichromate [13] in CH_2Cl_2 gave a complex

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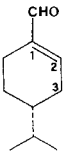
[3]) Alcohols (+)-**4a** and (+)-**4b** could be separated by *RP-18* reverse-phase chromatography with H_2O/MeOH 7:3, (+)-**4a** being eluted first. The relative configurations are supported by ^{1}H-NMR spectra which show for H–C(2) of (+)-**4a** a much broader *m* ($w_{1/2}$ = 19.0 Hz) than for (+)-**4b** ($w_{1/2}$ = 7.1 Hz). This is consistent with a larger diaxial coupling between H–C(2) and H–C(3) in (+)-**4a**.

[4]) A very hindered base has to be used for the epoxide opening, as independently known in the case of limonene epoxides [9a]. Potentially useful alternative routes for **3**→**4** exist [9b].

mixture containing **1** and **6**[5]) in a *ca.* 5:3 ratio, besides some carvotanacetone (**7**)[5]) [14]. Moreover, 4-(dimethylamino)pyridinium chlorochromate [15] gave (+)-**6**[5]) and (+)-**1** in a *ca.* 1:1 ratio, besides traces of **7**[6]). Other Cr(VI) reagents [16] also proved unsatisfactory for similar reasons. Finally, activated MnO_2 [17] reacted as expected too sluggishly, and the products were not investigated. Clearly, in view of the fact that (+)-**1** dimerizes, the oxidizing agent must also be rapid. The oxidizing reagent of choice proved to be Ag_2CO_3 on *Celite*, though, unpredictably [18], only (+)-**4a** underwent oxidation, while (+)-**4b** was recovered unchanged.



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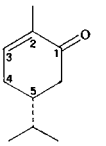

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The structure of (+)-**1**, which gives UV and IR spectra characteristic of enones, is proved by ^{1}H-NMR and mass spectra[7]). Thus, CH_2=C(1) appears as 2 broad *s* (further coupled to H–C(6)) at δ 5.82 (H_{cis}) and 5.12 ppm (H_{trans}). $(CH_3)_2$C(8) give a *d* at 0.90 ppm, while the remaining protons integrate correctly as a series of *m* between 2.5 and 1 ppm. The MS shows the M^+ at 152 with consecutive losses of isopropyl (*m/z* 109) and CO (*m/z* 81), whilst the peak *m/z* 82 is quite weak.

This MS fragmentation pattern for (+)-**1** is different from that reported for the camphor pyrolyzate of M^+ 152, where *m/z* 82 is the base peak whilst *m/z* 81 is quite weak [6c]. In the proposed fragmentation scheme [6c], *m/z* 82 is better accomodated *via* a *retro-Diels-Alder* fragmentation of carvotanacetone (**7**). In fact, both the published [14] and our MS of **7** exactly match the MS reported for the camphor pyrolyzate of M^+ 152, which, therefore, corresponds most probably to carvotanacetone (**7**).

The *Diels-Alder* dimers (+)-**5a**/(+)-**5b** could be nicely separated by HPLC on silica gel. MIKES mass spectra showed them to be diastereoisomers whose structure is sup-

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[5]) Both **6** and **7** from the pyridinium chlorochromate/NaOAc oxidation, though pure according to ^{1}H-NMR spectra, gave only weak optical rotations compared with reported values for the naturally occurring products [12] [14]. This suggests that some migration of the double bond has occurred. In contrast, **6** from the 4-(dimethylamino)pyridinium chlorochromate oxidation gave a higher optical rotation than that reported for the naturally occurring (+)-isomer [12a], but equal in absolute value to that reported for the naturally occurring (–)-isomer [12b].

[6]) Only alcohol (+)-**4b** with axial OH-group was oxidized to (+)-**1**, whilst (+)-**4a** was recovered unchanged.

[7]) Because of the spontaneous dimerization of (+)-**1**, its specific rotation could not be obtained directly. However, as (+)-**5a** and (+)-**5b** have not too dissimilar specific rotations, we simply evaluated the concentration ratio of (+)-**1**/(+)-**5a,b** by ^{1}H-NMR spectroscopy for a mixture of known total concentration in order to deduce $[\alpha]_D^{20} \approx +98°$ (c = 0.24, $CHCl_3$) for (+)-**1**.

ported by ^{13}C-NMR spectra[8]). However, superimposition of ^{1}H-NMR signals did not allow to assign unambiguously which is which[9]).

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Experimental Part

1. *General Remarks.* Silica-gel HPLC and reverse-phase HPLC were carried out with, respectively, *Merck LiChrosorb Si-60* (7 μm, 25 × 1 cm) and LiChrosorb RP-18 (7 μm, 25 × 1 cm) columns. NMR spectra were obtained with *Varian CFT20*, modified for ^{1}H and equipped with a capillary probe for ^{13}C, and *Bruker WP 200* spectrometers. Multiplicities in ^{13}C-NMR are from off-resonance decoupling. Chemical shifts are given in δ with respect to TMS and J are given in Hz. Electron impact mass spectra were taken with either a home-made computerized spectrometer, based on the *ELFS 4-162-8 Extranuclear* quadrupole and a *VG ZAB2F* spectrometer. IR and UV spectra were recorded with *Perkin-Elmer 337* and *Beckman DB-4* spectrometers, resp. Polarimetric data are from a *JASCO DIP-181* polarimeter.

2. *(+)-(2*R*,4*R*)-1(7)-*p*-Menthen-2-ol ((+)-***4a***) and (+)-(2*S*,4*R*)-1(7)-*p*-menthen-2-ol ((+)-***4b***).* Standard epoxidation of (+)-*p*-menthene ((+)-**2**; *Fluka;* stated $[\alpha]_D^{20} = +107.2°$ (c = 11.1, $CHCl_3$)), followed by lithium diisopropylamid treatment of the diastereoisomeric mixture of epoxides **3**, gave a 7:5 mixture (+)-**4a**/(+)-**4b** in 72% overall yield. Reverse-phase HPLC with MeOH/H_2O 7:3 gave pure (+)-**4a** followed by pure (+)-**4b**. *Data of (+)-***4a***:* Colourless liquid, $[\alpha]_D^{20} = +23.1°$ (c = 0.55, $CHCl_3$). IR (film): 3350*s*, 1660*m*, 1115*m*, 1090*s*, 1065*s*, 1032*m*, 1010*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 4.88 (br. *s*, further coupled to 2H–C(6), as shown by irradiation at 2.6, 1H, H_{cis}–C(7)); 4.73 (br. *s*, further coupled to 2H–C(6), 1H, H_{trans}–C(7)); 4.15 (*m*, $w_{1/2}$ = 19.0, 1H, H–C(2)); 2.6-1.0 (series of *m*, 9H); 0.85 (*d*, J = 6.0, 6H, $2CH_3$–C(8)); on irradiation at 2.6 (H_{eq}–C(6) as X of *ABX*), *s* at 4.88 and 4.73 sharpened (*ABX* changed into *AB* with J_{AB} = 2.2). MS: 154 (4, M^+), 136 (24, $M^+ - H_2O$), 111 (16, $M^+ - C_3H_7$), 93 (100, 111 $- H_2O$).

*Data of (+)-***4b***:* Colourless liquid, $[\alpha]_D^{20} = +29.8$ (c = 1.1, $CHCl_3$). IR (film): 3350*s*, 1660*m*, 1075*m*, 1048*m*, 1030*s*, 980*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 4.78 (br. *s*, 1H, H_{cis}–C(7)); 4.72 (br. *s*, 1H, H_{trans}–C(7), $J_{cis/trans}$ = 2.2); 4.30 (*m*, $w_{1/2}$ = 7.1, 1H, H–C(2)); 2.6-1.0 (series of *m*, 9H, *X* at 2.6); 0.84 (*d*, J = 5.5, 6H, $2CH_3$–C(8)). MS: superimposable to that of **4a**.

3. *Oxidation of the 7:5 Mixture (+)-***4a***/(+)-***4b***.* 3.1. *With Ag_2CO_3/Celite.* The mixture (+)-**4a**/(+)-**4b** (0.15 g, 1.0 mmol) and 5 mmol of the *Fetizon* reagent [18] in 35 ml of hexane were refluxed under N_2 for 2 h, then filtered, evaporated, and the residue was subjected to silica-gel HPLC with hexane $(i\text{-Pr})_2O$ 9:1. The mixture

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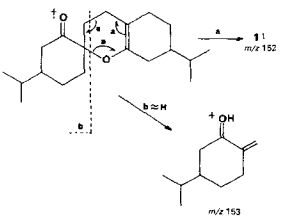
[8]) The MS reveals *(Scheme 2)* peaks of both protonated α-santolinenone and α-santolinenone radical cation. In fact, the spectrum of both (+)-**5a** and (+)-**5b** exactly matches that of α-santolinenone from m/z 152 downwards.

Scheme 2



[9]) Either the use of higher fields, or of shift reagents at 200 MHz, would allow to assign the ^{1}H-NMR spectra.

(+)-**5a**/(+)-**5b** was eluted first, followed by *(+)-(4R)-1(7)-*p*-menthen-2-one* ((+)-**1**), then by **6** in traces, and, finally, by a 95:5 mixture (+)-**4b**/(+)-**4a**. Preparatively, (+)-**1** could be best isolated from the mixture by flash chromatography. *Data of* ((+)-**1**)[10]: Colourless liquid, $[\alpha]_D^{20} \approx +98°$ ($c = 0.24$, $CHCl_3$). UV (95.5 hexane/(i-Pr)$_2$O; 233. IR (film): 1680, 1620. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.82 (br. *s*, further coupled to H_{eq}–C(6), as shown by irradiation at 2.8, 1H, H_{cis}–C(7)); 5.12 (br. *s*, further coupled to H_{eq}–C(6), 1H, H_{trans}–C(7), $J_{cis,trans} = 2.2$); 2.8 (*m*, 2H, H_{eq}–C(6), H_{eq}–C(3)); 2.5–1.0 (series of *m*, 6H); 0.90 (*d*, $J = 6.0$, 6H, $2CH_3$–C(8)). MS: 152 (1, M^+), 109 (23, $M^+ - C_3H_7$), 82 (24), 81 (100, 109 –CO), 69 (60), 41 (64).

3.2. *With Pyridinium Chlorochromate (PCC).* Standard conditions [11] with [PCC]/[**4**] = 1.5 in CH_2Cl_2 at r.t. for 2 h gave a mixture containing (^{1}H-NMR and HPLC) mainly **6**, together with some **1**, **5**, and **7**.

3.3. *With Pyridinium Chlorochromate/NaOAc 1:2 (PCC/NaOAc) or Pyridinium Dichromate (PDC).* Standard conditions with PCC/NaOAc 1:2 [13] using [PCC]/[**4**] = 1.5 in CH_2Cl_2 at r.t. for 2 h gave a mixture containing (^{1}H-NMR and HPLC) **1**, **6** and **7** in 5:3:2 relative ratios, besides some **5**. The relative amounts of **1** and **5** were found to depend on the time elapsed from the mixing of the reagents. Much the same results were obtained with PDC under standard conditions [14] with [PDC]/[**4**] = 0.8 in CH_2Cl_2 at r.t. for 6 h. HPLC purification on silica gel as above led to **6** and **7**. *(+)-(4R)-1-*p*-Menthen-7-al* (**6**): $[\alpha]_D^{20} = +33.0°$ ($c = 0.7$, $CHCl_3$). ^{1}H-NMR (80 MHz, C_6D_6): 9.33 (*s*, 1H, CHO); 6.05 (*m*, 1H, H–C(2)); 2.2–1.0 (series of *m*, 8H); 0.70 (*d*, $J = 5.8$, 6H, $(CH_3)_2CH$). MS: 151 (1, $M^+ - 1$), 123 (5, $M^+ - 29$), 109 (70, $M^+ - C_3H_7$), 81 (75), 43 (100). *(–)-(5R)-5-Isopropyl-2-methyl-2-cyclohexen-1-one* (**7**): $[\alpha]_D^{20} = -22.0°$ ($c = 0.51$, $CHCl_3$). ^{1}H-NMR (80 MHz, C_6D_6): 6.14 (*m*, 1H, H–C(3)); 2.5–1.0 (series of *m*, 6H); 1.8 (*s*, 3H, CH_3–C(2)); 0.67 (*d*, $J = 6.2$, 6H, $(CH_3)_2CH$) [14c]. MS: superimposable to reported spectra [14a].

3.4. *With 4-(Dimethylamino)pyridinium Chlorochromate.* Standard conditions [15] gave **6** which, after reverse-phase HPLC purification, showed $[\alpha]_D^{20} = +151.7°$ ($c = 0.20$, $CHCl_3$), besides to (+)-**1**, in equivalent amount, and traces of **7**.

4. *(4'S,7S)-4',7-Diisopropyl-5,6,7,8-tetrahydro-spiro[chroman-2,1'-cyclohexan]-2'-one ((+)-***5a** *and (+)-***5b***).* The mixture (+)-**5a**/(+)-**5b**, separated by HPLC from either the mixtures of oxidation of **4** or from α-santolinenone on standing (see above), was separated into its components (4:1 molar ratio of (+)-**5a**/(+)-**5b**) by silica gel HPLC (hexane/(i-Pr)$_2$O 96:4). *Data of (+)-***5a** (eluted first): Colourless liquid, $[\alpha]_D^{20} = +36.1°$ ($c = 0.45$, $CHCl_3$). IR (film): 1725*s*, 1700*m*[11]). ^{1}H-NMR (200 MHz, C_6D_6): 2.75 (*dd*, $J = 12.0$, 12.0, 1H); 2.4 (br. *m*, 1H); 2.2 (*m*, 3H); 2–1 (series of *m*, 15H); 0.87 (*d*, $J = 7.0$, 6H); 0.76 (*d*, $J = 7.0$, 3H); 0.72 (*d*, $J = 7.0$, 3H). On irradiation at 1.3, both the *d* at 0.87, 0.76, and 0.72 became *s*, whilst the *dd* at 2.75 became a *d*. ^{13}C-NMR (20 MHz, C_6D_6): 210.4 (*s*, C=O); 144.7 (*s*, C(8a)); 105.4 (*s*, C(4a)); 79.5 (*s*, C(2)); 20.2, 19.8, 19.8, 19.7 (4*q*); 42.1, 39.3, 31.7, 29.2, 27.9, 26.9, 24.0, 23.2 (8*t*); 48.1, 41.5, 33.1, 32.5 (4*d*). MS: 304 (27, M^+); HR found 304.2382 ± 0.005; calc. for $C_{20}H_{32}O_2$ 304.2402); 261 (1, $M^+ - C_3H_7$); 243 (1, 261 –CO); 153 (100, $M^+ - 151$; HR found 153.1242 ± 0.005; calc. for $C_{10}H_{17}O$ 153.1279); 152 (29, $M^+ - 152$); 135 (5, 153 –H_2O); 109 (24, 152 $- C_3H_7$); 81 (45, 109 –CO). Linked scans showed the following relationships 261→243 + 153 + 152; 153→135.

*Data for (+)-***5b** (eluted second): Colourless liquid, $[\alpha]_D^{20} = +54.8°$ ($c = 0.26$, $CHCl_3$). IR (film): 1725*s*, 1700*m*. ^{13}C-NMR (20 MHz, C_6D_6): 206.8, 146.0, 102.0, 81.3 (4*s*); 20.1, 20.1, 19.8, 19.8 (4*q*); 41.7, 36.7, 31.5, 29.3, 28.7, 26.9, 25.0, 23.1 (8*t*); 46.0, 41.2, 32.4, 31.5 (4*d*). MS: superimposable to that for (+)-**5a** (also the MIKES spectra).

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[10]) As the diastereoisomeric (+)-**5a**/(+)-**5b** are rapidly reformed, spectra of (+)-**1** always revealed a little of their mixture; the corresponding signals had to be subtracted from those of (+)-**1**.

[11]) Two C=O bands have already been observed with α-halogenated monoketo-steroids [19].

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