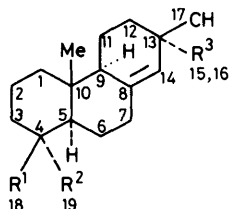


Synthetic Studies on Terpenoids. Part 6. Synthesis of (\pm)-4,13-Dimethyl-13-vinylpodocarp-8(14)-en-4 α - and -4 β -ols

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The podocarpa-8,11,13-trien-4-one (6) was converted into the corresponding 4-methylpodocarpatrien-4-ol (7) with MeLi. Birch reduction of the alcohol (7) with Li-liquid NH_3 yielded the podocarpenone (8) and the podocarpadienones (9) and (10). Condensation of (8) with ethyl cyanoacetate followed by conjugate addition of Me_2CuLi afforded the 13-cyano(ethoxycarbonyl)methyl ester (12) which on alkaline hydrolysis, esterification and reduction with LiAlH_4 afforded the corresponding 13-hydroxyethyl compound. Conversion of the latter, into its tosylate and elimination of the resulting tosylate by alumina gave 4,13-dimethyl-13-vinylpodocarp-8(14)-en-4 β -ol (1). Dehydration of 13-methoxycarbonylmethyl-4,13-dimethylpodocarp-8(14)-en-4-ol furnished the 4-methylene compound (16) which on epoxidation and then reduction with LiAlH_4 produced alcoholic material whose transformation to the tosylate followed by its elimination with alumina yielded the 4,13-dimethyl-13-vinylpodocarp-8(14)-en-4 α -ol (2). Hydrolysis of compounds (1) and (2) with PtO_2 in ethanol afforded the corresponding 13-ethyl compounds (3) and (4) respectively.

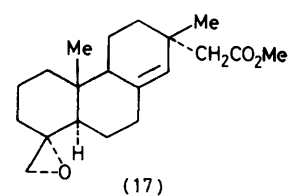
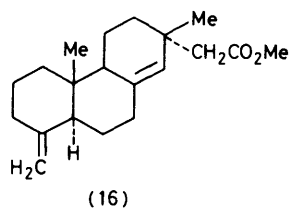
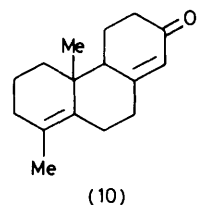
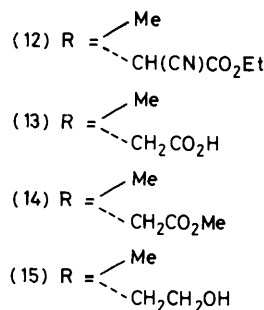
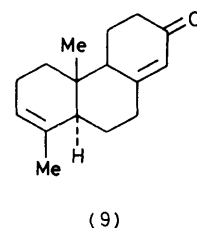
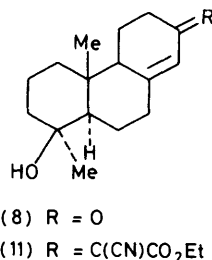
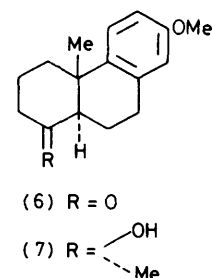
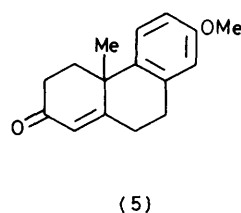
THE Western red cedar, *Thuja plicata* Donn, has been the subject of extensive chemical investigation because of its medicinal and industrial importance,² terpenes, essential oils, antibiotics, and antifungal compounds having been isolated from it.³ In 1969 two norditerpene alcohols were isolated from the bark of the Western cedar.⁴ One was transformed⁴ into dihydroisopimaric acid and then the alcohol (3) [dihydro-derivative of (1)] and the other into isopimarol and then the alcohol (4) [dihydro-derivative of (2)]. On the basis of these transformations their structures were assigned as the alcohols (1) and (2) respectively.



- (1) $\text{R}^1 = \text{OH}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{CH}=\text{CH}_2$
 (2) $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{OH}$, $\text{R}^3 = \text{CH}=\text{CH}_2$
 (3) $\text{R}^1 = \text{OH}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Et}$
 (4) $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{OH}$, $\text{R}^3 = \text{Et}$

In the course of a continuing synthetic interest^{5,6} in tricyclic diterpenes we have synthesized⁷ the alcohols (1) and (2).

In considering approaches to the synthesis of the alcohols (1) and (2), we reasoned that the ketone (6), prepared⁸ from the ketone (5), would be an attractive starting material since it contains all the structural and stereochemical characteristics necessary for efficient conversion into the target molecules. Reaction of compound (6) with MeLi yielded a single tertiary carbinol (7) in 80% yield; there was no marked increase in the yield of (7) when a mixture of Me_2LiCu and MeLi⁹ or an organoaluminium reagent¹⁰ like Et_3Al or Me_3Al was used. Tentative assignment of stereochemistry to the



hydroxy-group of the alcohol (7) rested upon spectral evidence and analogy with other cases in the literature.¹¹ In its n.m.r. spectrum the alcohol (7) exhibited methyl signals at δ 1.17 and 1.25. The observation that in the Eu(fod)₃-shifted n.m.r. spectrum of the alcohol (7) both the methyl signals moved downfield rapidly, provided evidence for the β -axial character of the 4-hydroxy-group, since with an α -orientation only the 4-methyl signal would have moved downfield. The chemical transformation of the alcohol (7) into alcohol (1) confirmed the foregoing assumption.

Reduction of the alcohol (7) by the Birch procedure¹² using Li-liq. NH₃ and Bu^tOH followed by treatment with methanolic hydrochloric acid yielded the ketones (8), (9), and (10) in yields of 28%, 45%, and 4% respectively; the structures of these were confirmed on the basis of spectroscopic evidence. Various attempts to improve the yield of the ketone (8) and to suppress the yields of the ketones (9) and (10) were to no avail.

Condensation¹³ of the ketone (8) with CNCH₂CO₂Et in the presence of NH₄OAc afforded the oily ester (11) (45%). The conjugate addition¹⁴ of LiMe₂Cu to the ester (11) was expected to produce one or both of two diastereoisomers depending on the stereochemistry of conjugate addition and on the configurational stability of the metal enolate. The conjugate addition yielded an oily material which on chromatographic purification yielded compound (12) in 28% yield. The nature of the remaining material was elusive. Compound (12) could have the alternative configuration but from considerations of a molecular model as well as the results in a closely related work^{15,16} it was considered that the product obtained was (12). Final confirmation of the foregoing assignment was achieved in the conversion of (12) into the alcohol (1). The cyanoester (12) when heated with KOH in diethylene glycol gave a single crystalline acid (13) which was converted into the ester (14) by diazomethane; this on reduction with LiAlH₄ gave the alcohol (15). Various attempts were made to dehydrate the latter to obtain the alcohol (1), but in most cases the results were disappointing owing to the formation of complex mixtures which contained negligible amounts of the alcohol (1). Thus an alternative route was sought to increase the yield of the alcohol (1).

The alternative approach consisted in the conversion of the alcohol (15) into its tosylate by treatment with TsCl and pyridine. The resulting tosylate obtained almost in quantitative yield, was subjected to an elimination reaction¹⁷ effected by chromatographic alumina. This mild procedure gave the alcohol (1) as colourless liquid and this was identified by spectral comparison (i.r.) with authentic natural alcohol (1). The rest of the product was a mixture of unchanged alcohol (15) (t.l.c. comparison) and olefinic products (evidenced by n.m.r. spectroscopy). There was no marked improvement in the yield of the alcohol (1) when the sulphonate ester elimination was attempted with different grades of alumina, different solvents (CCl₄, hexane, benzene), or an alteration in the reaction temperature (20–60 °C).

Hydrogenation of the alcohol (1) with PtO₂ in EtOH yielded the oily alcohol (3) the spectral characteristics of which (i.r. and n.m.r.) were indistinguishable from those of an authentic specimen.⁴

The ester (14) on treatment with thionyl chloride and pyridine yielded a mixture of olefins from which the desired olefin* (16) was obtained in 12% yield *via* chromatography over AgNO₃-impregnated silica gel.^{18,19} The modified Chugev reaction²⁰ when applied to the ester (14) produced a complex mixture of products from which a small amount of the olefin (16) was isolated. Epoxidation of the latter with *m*-chloroperbenzoic acid (MCPBA) provided the epoxide (17) whose stereochemistry was based on analogy with previously described systems.^{21,22} It was assumed that because of steric reasons the exocyclic methylene double-bond of the olefin (16) would be preferentially epoxidized and this was confirmed by spectroscopic evidence. Reduction of compound (17) with LiAlH₄ afforded material which without purification was converted into its tosyl derivative. The latter underwent an elimination reaction, effected by chromatographic alumina, to yield the alcohol (2) which was found to be identical (i.r. spectral evidence) with authentic natural material. The synthesis of the alcohol (2) also indicated that opening of the epoxide ring of (17) with LiAlH₄ proceeded with predictable stereochemistry.²³ Hydrogenation of compound (2) with PtO₂ in EtOH afforded compound (4) which was found to be identical (i.r. and n.m.r.) by direct comparison with an authentic specimen.⁴

EXPERIMENTAL

M.p.s were determined on a Köfler hot stage apparatus and are uncorrected. Unless otherwise stated i.r. spectra were taken on a 337 spectrometer for KBr discs or liquid films and n.m.r. spectra recorded on a Varian A-90 spectrometer were measured in CDCl₃ with SiMe₄ as an internal standard. Mass spectra were recorded on Dupont 21-492B and Hitachi Perkin-Elmer RMU-6H at 70 eV using a direct-inlet system. Column chromatography was carried out with Neutral Brockman alumina and silica gel (B.D.H.). T.l.c. plates were coated with silica gel having a thickness of ca. 0.2 mm and the spots were located by exposing the dried plates to I₂ vapour. Unless otherwise stated all organic extracts were washed with brine, dried (MgSO₄), and evaporated under reduced pressure. Microanalyses were carried out in Franz Pascher Microanalytisches Laboratorium at Bonn, Germany. All compounds described here are racemic although the prefix (\pm) is omitted and only one enantiomer is depicted in the structural formulae.

17-Methoxy-18-methylpodocarpa-8,11,13-trien-19-ol (7).—Under a nitrogen atmosphere, an ethereal solution of methyl-lithium (2.05M; 5 ml) (Alfa Inorganics Inc) was added dropwise to a stirred solution of the ketone (6) (2.01 g) at 0–5 °C; the resulting mixture was stirred for 4 h at 20–25 °C. Hydrolysis was achieved with saturated aqueous ammonium chloride and the resulting product was taken up in ether. The ethereal extract was dried and concentrated to

* The olefin (16) was found to be extremely unstable to light, its colour changing rapidly from faint yellow to deep red. It was, therefore, used immediately in the next step.

obtain a dark-red oil which was chromatographed on silica gel (25 g). Benzene-ether (95 : 5) eluted the alcohol (7) (1.78 g, 80%), m/e 260 (M^+) and 242 ($M^+ - H_2O$); ν_{max} (KBr) 3 380 (OH) and 1 610 cm^{-1} (C=C); δ 1.17 (s, 3 H), 1.25 (s, 3 H) (4-Me and 10-Me), 3.81 (s, 3 H, OCH_3), and 6.67—7.45 (m, 3 H, ArH) (Found: C, 78.1; H, 9.05. Calc. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29%).

The Podocarpene (8) and the Podocarpadienones (9) and (10).—A solution of the alcohol (7) (1 g) in dry THF (8 ml) was slowly added to a stirred solution of lithium wire (880 mg) in dry THF (20 ml). After the addition was complete, dry *t*-butyl alcohol (20 ml) diluted with dry THF (2 ml) was added dropwise during 15 min and the reaction mixture was stirred until the deep blue colour of the unchanged lithium had been dissipated (ca. 4 h). The reaction mixture was then treated with methanol (7 ml) and stirred under a stream of nitrogen until most of the ammonia had evaporated. The white residue was partitioned between water and benzene after which the organic layer was separated, washed with brine, dried, and evaporated. The residue was dissolved in methanol (25 ml) and the solution treated with hydrochloric acid (5*N*; 8 ml) under reflux for 1 h. The cooled solution was diluted with water and extracted with ether. The organic extract was then washed, dried, and evaporated. A pale yellow oil thus obtained was chromatographed over alumina.

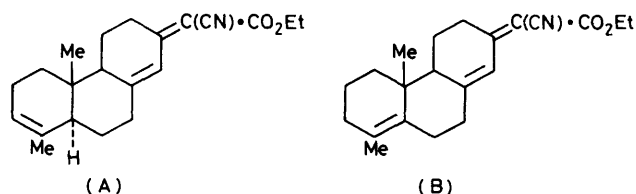
(i) Hexane-benzene (50 : 50) eluted the ketone (10) (59 mg, 4%), a mobile oil, m/e 230 (M^+); ν_{max} (film) 1 665 (C=C-C=O) and 1 610 cm^{-1} (C=C); δ 0.96 (s, 3 H, 10-Me), 1.65 (s, 3 H, 4-Me), and 5.75 (s, 1 H, 14-H) (Found: C, 82.95; H, 9.2. Calc. for $C_{16}H_{22}O$: C, 83.43; H, 9.63%).

(ii) Hexane-benzene (48 : 52) eluted the ketone (9) (395 mg, 45%) as a yellow oil, b.p. 110—118 °C/0.2 mmHg (bah), m/e 230 (M^+); ν_{max} (film) 1 670 (C=C-C=O) and 1 630 cm^{-1} (C=C); δ 0.97 (s, 3 H, 10-Me), 1.63 (s, 3 H, 4-Me), 5.12 (m, 1 H, 3-H), and 5.79 (s, 1 H, 14-H) (Found: C, 83.2; H, 9.4. Calc. for $C_{16}H_{22}O$: C, 83.43; H, 9.63%).

(iii) Elution with benzene-ether (95 : 5) afforded the ketone (8) (266 mg, 28%) as a dense liquid, m/e 248 (M^+); ν_{max} (film) 3 400 (OH), 1 670 (C=C-C=O) and 1 620 cm^{-1} (C=C); δ 0.90 (s, 3 H), 1.23 (s, 3 H) (4-Me and 10-Me), and 5.81 (s, 1 H, 14-H) (Found: C, 77.1; H, 9.5. Calc. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.4%).

The Podocarpene Ester (11).—The ketone (532 mg), $CNCH_2COOC_2H_5$ (272 mg), glacial AcOH (96 mg), and benzene (20 ml) were refluxed under a Dean-Stark water separator with addition of NH_4OAc (8 mg) at 3 h intervals. Heating was stopped after 12 h when the separation of water had ceased. The reaction mixture was cooled, washed, and dried. Removal of solvent yielded a dark oily material which on distillation* yielded the ester (11) (329 mg, 45%), b.p. 150—156 °C/0.8 mmHg (bath), m/e 343 (M^+); ν_{max} (film)

* The low boiling fractions [156 mg, 130—140 °C/0.8 mmHg (bath)] exhibited a molecular ion at m/e 325 (M^+) in the mass spectrum. In the n.m.r. spectrum, which was very complicated, there were signals at δ 1.63, 1.68, and 5.18 (m, 1 H). Based on these spectroscopic data it was concluded that the above-mentioned product was a mixture of compounds (A) and (B).



3 410 (OH), 2 220 (C≡N), 1 730 (C=O), and 1 610 and 1 600 cm^{-1} (C=C); δ 0.83 (s, 3 H), 1.35 (s, 3 H) (4-Me and 10-Me), 1.33 (t, 3 H, CO_2Et), 4.23 (q, 2 H, CO_2Et), and 5.12 (s, 1 H, 14-H) (Found: C, 73.2; H, 8.25. Calc. for $C_{21}H_{29}NO_3$: C, 73.43; H, 8.51%).

The Podocarpene Carboxylic Acid (13).—A solution of $LiMe_2Cu$ in anhydrous ether (20 ml) was prepared from CuI (Alfa) (336 mg) and 2.3*M*- $MeLi$ (Ventron) in ether (6 ml). After 15 min at -10 °C, the ester (11) (290 mg) in ether (8 ml) was added dropwise. The mixture was maintained at the same temperature with stirring for 2 h, and then 10 h at room temperature (25—28 °C). The reaction mixture was poured into aqueous NH_4Cl (15%; 30 ml) and extracted with ether. The combined organic extracts were washed, dried, and evaporated to yield a gummy material which was chromatographed on silica gel. Elution with benzene-ether (85 : 15) yielded the cyanoester (12) (84 mg, 28%) as a dense liquid, m/e 359 (M^+) and 341 ($M^+ - H_2O$); ν_{max} (film) 3 400 (OH), 2 240 (C≡N), 1 725 (C=O), and 1 610 cm^{-1} (C=C).

The cyanoester (12) (84 mg) was hydrolysed by refluxing it for 48 h with KOH (62 mg) in ethylene glycol (15 mg). Work-up afforded oily material which on trituration with ether gave the acid (13) (53 mg, 63%), m.p. 98—100 °C (ether-hexane); ν_{max} (KBr) 3 410 (OH), 1 700 (C=O), and 1 610 cm^{-1} (C=C); m/e 306 (M^+), 288 ($M^+ - H_2O$), and 229 ($M^+ - H_2O - Me - CO_2H$) (Found: C, 74.25; H, 9.6. Calc. for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87%).

Esterification of the acid (13) (75 mg) with CH_2N_2 in ether gave the ester (14) (82 mg), b.p. 148—154 °C/0.3 mmHg (bath), m/e 320 (M^+) and 302 ($M^+ - H_2O$); ν_{max} (film) 4 310 (OH), 1 748 (ester CO), and 1 610 cm^{-1} (C=C); δ 0.88 (s, 3 H), 1.32 (s, 3 H), and 1.35 (s, 3 H) (4-Me, 10-Me, and 15-Me), 3.65 (CO_2Me), and 5.22 (s, 1 H, 14-H) (Found: C, 74.8; H, 9.9. Calc. for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06%).

The Podocarpene (1).—A solution of the ester (14) (75 mg) in dry THF (10 ml) was added dropwise to $LiAlH_4$ (75 mg) in THF (25 ml). After 10 h at reflux the complex was decomposed with aqueous KOH (40%; 5 ml). The resulting white precipitate was filtered off and washed with THF. The cooled filtrate was dried and evaporated to yield oily material which on filtration through a short column of silica gel (2 g, benzene) yielded the oily alcohol (15) (62 mg); m/e 292 (M^+), 274 ($M^+ - H_2O$), 259 ($M^+ - Me - H_2O$), and 241 ($M^+ - Me - 2H_2O$); ν_{max} (film) 3 420 (OH) and 1 608 cm^{-1} (C=C).

Toluene-*p*-sulphonyl chloride (65 mg) was added to a solution of the alcohol (15) (60 mg) in pyridine (5 ml). The mixture was stirred at room temperature for 25 h after which it was poured onto ice and extracted with ether. The extracts were washed with ice-cold HCl (1%), aqueous $NaHCO_3$ (5%), and brine, and then dried and evaporated. The resulting tosylate (84 mg, 100%) was used in subsequent reactions without further purification.

A solution of the above tosylate (84 mg) in anhydrous ether (50 ml) was stirred with commercially available † Woelm aluminium oxide (12 g) (W-200 neutral activity) at 25 °C for 48 h. The mixture was then filtered through Celite and washed with ether (100 ml); and evaporation of the solvent from the eluate yielded a yellow oil, purification of which by chromatography on silica gel with benzene as eluant gave the alcohol (1) (10 mg, 20% from tosylate) as a

† When the elimination reaction was attempted⁷ with basic aluminium (Woelm activity 1) the yield of the alcohol (1) was 5%.

colourless liquid, m/e 274 (M^+) and 256 ($M^+ - H_2O$); ν_{\max} (film) 3 400 (OH), 1 640, 1 610, 1 000, and 906 ($CH=CH_2$), and 1 660 and 910 cm^{-1} ($C=CH$) [indistinguishable from the i.r. spectrum of the neutral alcohol (1)].

The Podocarpenol (3).—The alcohol (1) (8 mg) was hydrogenated at 2 atm and room temperature for 12 min in ethanol (5 ml) in the presence of PtO_2 (3 mg). Work-up afforded the oily alcohol (3) (8 mg); m/e 276 (M^+) and 258 ($M^+ - H_2O$); ν_{\max} (film) 3 400 (OH), 1 660, and 920 ($C=CH$) cm^{-1} [superimposable upon the spectrum of an authentic specimen of the alcohol (3)]; δ 0.83, 0.86, 0.93 (t, J 6 Hz) and 1.21 (Me at C-4, C-10, and C-13), and 5.09 ($C=CH$) [identical with the n.m.r. spectrum of an authentic specimen of the alcohol (3)].

The Podocarpenol (2).—To the ester (14) (200 mg) dissolved in dry pyridine (8 ml) was added $POCl_3$ (0.6 ml). The homogeneous solution was set aside at room temperature for 20 h after which it was poured onto ice; the resulting mixture was extracted with ether. The ether extracts were washed, dried, and evaporated to give a red oil which was chromatographed on 25% $AgNO_3$ -impregnated silica gel in hexane. Elution with hexane–benzene (1 : 1) gave the oily olefin (16) (22 mg, 12%); ν_{\max} (film) 1 720 (CO), 3 080, 1 640, and 899 cm^{-1} ($C=CH_2$).

The olefin (16) (50 mg) in $CHCl_3$ (10 ml) was treated with *m*-chloroperbenzoic acid (38 mg) at ca. 0 °C for 24 h. The solution was washed with aqueous $NaHCO_3$ and then brine to give the epoxide (17) (52 mg); ν_{\max} (film) 1 740 (ester CO) and 1 610 cm^{-1} ($C=C$); no exocyclic methylene absorption.

The crude epoxide (50 mg) was dissolved in ether (15 ml) and added to a stirred solution of $LiAlH_4$ (60 mg) in ether (20 ml). The mixture was refluxed for 3 h under N_2 . Work-up gave oily alcoholic material which was converted into its tosyl derivative by treatment with toluene-*p*-sulphonyl chloride and pyridine. The resulting tosylate (76 mg) was used in subsequent reactions without further purification.

A solution of the above tosylate (76 mg) in anhydrous ether (45 ml) was stirred with Woelm aluminium oxide (10 mg) (W-200 neutral activity) at 25 °C for 48 h. Filtration through Celite followed by elution with ether (75 ml) and evaporation of the solvent afforded oily material. Purification by chromatography on silica gel and elution with hexane–benzene (20 : 80) gave the alcohol (2) (8 mg, 18% from tosylate) a colourless liquid, m/e 274 (M^+) and 256 ($M^+ - H_2O$); ν_{\max} (film) 3 400 (OH), 3100, 1 600, 1 100, and 825 ($C=CH_2$), and 1 675 and 910 ($C=CH$) cm^{-1} [indistinguishable from the i.r. spectrum of the natural alcohol (2)].

The Podocarpenol (4).—The alcohol (2) (6 mg) in ethanol (6 ml) and PtO_2 (4 mg) was stirred under hydrogen at 2 atm and room temperature for 12 min. Work-up yielded the oily alcohol (4) (7 mg); m/e 276 (M^+) and 258 ($M^+ - H_2O$);

ν_{\max} (film) 3 400 (OH), 1 660, and 915 cm^{-1} ($C=CH$) [superimposable upon the spectrum of an authentic specimen of the alcohol (4)]; δ 0.83 (s, 3 H), 1.23 (s, 3 H), 1.26 (t, 3 H, J 6 Hz), and 1.30 (s, 3 H) (Me signals at C-4, C-10, and C-13), and 5.26 ($C=CH$).

We are most grateful to Professor E. P. Swan for providing the i.r. spectra of the naturally occurring alcohols (1) and (2) and authentic specimens of the alcohols (3) and (4). We gratefully acknowledge the financial support of this work provided by Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT). We express our thanks to Miss Idoia Isasi for typing the manuscript.

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