Synthetic Studies on Terpenoids. Part 7.[1] Synthetic Studies leading to the Total Synthesis of Eudesmane Sesquiterpenes

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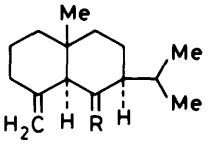
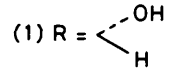
The synthesis of two naturally occurring sesquiterpenes, (±)-junenol (1) and (±)-acolamone (2), from the bicyclic ketone (3) is described. The introduction of an isopropyl chain at C-7 † of the bicyclic ketone was attempted by three different procedures and yielded ketone (5) which, on reduction with sodium and ethanol, gave the alcohol (12). This, on oxidation with lead tetra-acetate and iodine in cyclohexane, yielded the cyclic ether (13) and regenerated the ketone (5). Oxidation of compound (13) with chromium(VI) oxide in acetic acid afforded the keto-acid (15) which, on oxidative decarboxylation with lead tetra-acetate, furnished acolamone which was reduced with sodium borohydride in ethanol to (±)-junenol.

DURING the last two decades a considerable amount of synthetic chemistry has been directed towards eudesmane sesquiterpenes [2,3] which confront organic chemists with a variety of interesting problems. Junenol [4] and acolamone,[5] which belong to the eudesmane group of sesquiterpenes, have been assigned the structures and stereochemistries (1) and (2), respectively. The sesquiterpene alcohol (1) has elicited considerable attention from synthetic chemists, resulting in two syntheses.[6,7] Recently, the chemical correlation of α-santonin with (±)-junenol (1) and (±)-acolamone (2) has been carried out.[8] These experimental observations corroborate fully the structure and stereochemistry suggested for both junenol (1) and acolamone (2).



(1) R = 

(2) R = O

As part of our synthetic studies on diterpenes, we recently reported [9] the synthesis of the ketone (3). To demonstrate the utility of this ketone in the synthesis of sesquiterpenes, we now report [10,] ‡ a total synthesis of (±)-junenol (1) and (±)-acolamone (2). The present approach proceeds *via* intermediates which may be useful for the synthesis of other eudesmane sesquiterpenes.

RESULTS AND DISCUSSION

The cyclohexylimine (4), formed by condensation of the ketone (3) and cyclohexylamine, was treated with ethylmagnesium bromide followed by isopropyl bromide and the resulting alkylated enamine on acid hydrolysis [11] furnished the ketone (5) in 15% overall yield. The assignment of configuration at C-7 of compound (5) was confirmed by its chemical transformation into the natural products junenol (1) and acolamone (2). The 15% yield of the ketone (5) was clearly unacceptable for our projected multistage synthesis and thus an alternative approach was sought.[12] The ketone (3) was converted into the oily n-butylthiomethylene derivative (6) following Ireland's general procedure.[13] Treatment of compound (6) with $LiMe_2Cu$ yielded the ketone (5) in 22% yield. As this yield of the ketone (5) was not a significant improvement over that obtained before, further synthetic routes were investigated.

Treatment of the ketone (3) with sodium hydride and diethyl carbonate in 1,2-dimethoxyethane furnished principally the keto-ester (7) whose ^1H n.m.r. spectrum was complicated, probably because of contamination with a small amount of the enol tautomer (8) whose formation is not unlikely. Although there are reasons to expect a dynamic equilibrium of the esters (7) and (8), no attempt was made to separate these, nor to determine their percentages in the reaction mixture. Direct reaction of the keto-ester (7) with methyl-lithium in diethyl ether yielded the crystalline ketol (9) in 72% yield. It appears that the sterically hindered environment of the C-6 ketonic carbonyl group of the keto-ester (7) is responsible for the selective reaction at the ester function § and thus in the present case the use of a ketone-protecting group was not necessary.[14] Dehydration of the ketol (9) with acid yielded the ketones (10) and (11) in 78 and 3% yield, respectively, though the exact proportions of compounds (10) and (11) varied somewhat from run to run. Separation of the ketones (10) and (11) could be effected by chromatography; however, the mixture of ketones was used directly for the next step.¶ The configurational assignment at C-7 of the ketone (11) was demonstrated by its hydrogenation with plati-

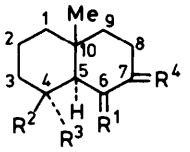
† Compounds in this paper are numbered by the steroid–terpenoid convention, as shown for compounds (1) and (2), with the *geminally* substituted decalin ring being defined as ring A.

‡ A portion of this work was presented by A. K. Banerjee at the 1st European Congress in Organic Chemistry, Cologne, West Germany, August 17—20, 1979.

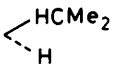
§ We have observed that the methyl-lithium reaction sequence, when applied to either ethyl 2-oxocyclohexanecarboxylate or ethyl 2-oxocyclohexaneacetate, gives a mixture of products, in contrast to the reaction with compound (7).

¶ For the purpose of synthesizing the ketone (5) the separation of compounds (10) and (11) was unnecessary since both compounds would ultimately lead to the same product on hydrogenation.

num(IV) oxide in methanol which smoothly and rapidly yeilded the desired ketone (5) in almost quantitative yield, the product being identical with the sample described previously. The formation of compound (5) provided clear evidence for the stereochemistry at C-7



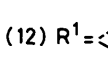
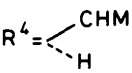
(3) $R^1=O, R^2=R^3=Me, R^4=H,H$

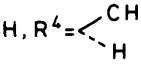
(5) $R^1=O, R^2=R^3=Me, R^4=$ 

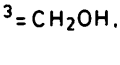
(6) $R^1=O, R^2=R^3=Me, R^4=CHSBu^n$

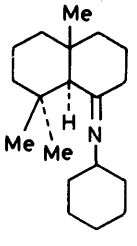
(7) $R^1=O, R^2=R^3=Me, R^4=\sim CO_2C_2H_5, H$

(9) $R^1=O, R^2=R^3=Me, R^4=\sim C(OH)Me_2$

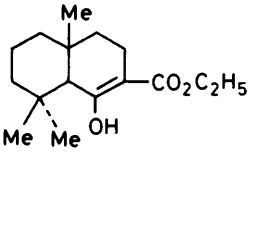
(12) $R^1=$  , $R^2=R^3=Me, R^4=$ 

(15) $R^1=O, R^2=Me, R^3=CO_2H, R^4=$ 

(16) $R^1=\sim OH, H$, $R^2=Me, R^3=CH_2OH, R^4=$ 



(4)



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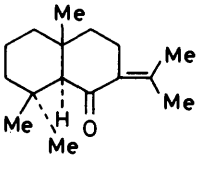
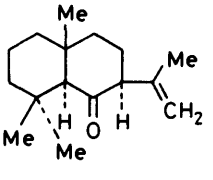
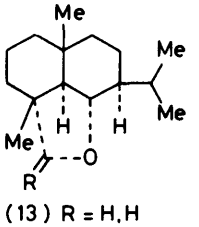


(10)



(11)



(13) R = H,H

(14) R = O

of the ketone (11). Larger-scale hydrogenations were carried out with a mixture of the ketones (10) and (11) to afford the ketone (5) in excellent yield.

Next, our attention was directed towards the functionalization of the C-4 α-methyl group of the ketone (5) by the use of an intramolecular free-radical reaction [15] and for this we required the alcohol (12). Sodium in ethanol reduced the carbonyl group of the ketone (5) to afford the alcohol (12) in 80% yield; the stereochemical assignment for C-6 was based on an analysis of the ^1H n.m.r. spectrum which exhibited a multiplet at δ 3.86 with a half-width of 18 Hz, thus indicating the axial nature [16] of the proton at C-6 of the alcohol (12). Irradiation of a refluxing cyclohexane solution of compound (12), lead tetra-acetate, and iodine with a tungsten lamp afforded a product mixture consisting of the desired cyclic ether (13) (65%) (major product) along with the ketone (5) (30%), unchanged alcohol (12) (3% recovery), and impure polar fractions. Oxidation of the cyclic ether (13) with chromium(VI) oxide–acetic acid yielded the keto-acid (15) and the lactone (14) in 32 and 48% yield, respectively, though the exact proportions of compounds (14) and (15) varied somewhat in repeated experiments.

As the lactone (14) was obtained in appreciable amounts, an attempt was made to convert it into the keto-acid (15). Reduction of the lactone (14) with lithium aluminium hydride in refluxing tetrahydrofuran (THF) furnished an oily diol (16) which, on oxidation with Jones' reagent [17] at room temperature, furnished the desired keto-acid (15) in only 25% yield. The rest of the oxidation product could not be identified.

It now remained to convert the keto-acid (15) into junenol (1) and acolamone (2) and, to accomplish this, compound (15) was subjected to oxidative decarboxylation [18] with lead tetra-acetate in benzene–pyridine. A mixture of products was obtained from which the desired acolamone (2) was obtained as a viscous liquid in 17% yield by chromatography over 10% silver nitrate-impregnated silica gel.[19,20] The product was found to be identical (i.r., n.m.r.) with natural acolamone.[5] Reduction of (±)-acolamone with sodium borohydride in methanol, followed by sublimation of the resultant product, afforded (±)-junenol (1), identical [i.r. (CCl_4)] with authentic junenol.[7] Unfortunately, no direct comparison was possible due to our lack of authentic specimens of junenol and acolamone.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage and are uncorrected. Unless otherwise stated, i.r. spectra were taken on a Perkin-Elmer 337 spectrometer for KBr discs or liquid films, and ^1H n.m.r. spectra, recorded on a Varian A-90 spectrometer, were measured in CCl_4 with tetramethylsilane as internal standard. Column chromatography was carried out with Neutral Brockman alumina or silica gel (B.D.H.). Thin-layer chromatography (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 iodine vapour. Unless otherwise stated, all organic extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. Microanalyses were carried out in Franz Pasher Microanaltiches Laboratorium at Bonn, Germany. All compounds described herein are racemic although the prefix (±) is omitted and only one enantiomer is depicted in the structural formulae.

The Ketone (5).—*Method A*. The ketone (3) (1 g) and cyclohexylamine (2.81 g) were refluxed in dry benzene

(25 ml) in a Dean–Stark trap for 48 h. On removal of the solvent, the ketimine (4) was obtained as dense liquid (1.32 g) contaminated with a small amount of the starting ketone (3), as shown by its i.r. spectrum. No attempt was made to purify the ketimine (4).

To a solution of ethylmagnesium bromide, prepared from magnesium turnings (59 mg), ethyl bromide (625 mg), and dry THF (15 ml), was added dropwise a solution of the crude ketimine (4) (675 mg) in dry THF (10 ml). The mixture was heated under reflux for 1.5 h, and then cooled to room temperature. The stirred solution was treated with isopropyl bromide and the resulting mixture was stirred and heated under reflux for 18 h; it was then cooled and treated with a solution of sodium acetate (1 g) in glacial acetic acid (2 ml). The mixture was heated under reflux for a further 5 h and was then cooled; the organic layer was separated and the aqueous phase was extracted several times with benzene. The combined organic extracts were washed successively with 15% hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and brine till the washings were neutral, and were then dried. The solvent was removed and the residue was distilled to yield the ketone (5) (170 mg, 15% overall), b.p. 112—115 °C (bath) at 0.2 mmHg; *m/z* 236 (M^+); δ 0.85, 0.90, and 0.96 (each 3 H, 3 × s, 4-, 4-, and 10-Me) and 1.16 (6 H, d, *J* 3 Hz, CH*Me*$_2$) (Found: C, 81.1; H, 11.8. Calc. for $C_{16}H_{28}O$: C, 81.29; H, 11.94%).

Method B. To an ice-cooled, stirred mixture of ethyl formate (1.24 g), sodium acetate (550 mg), and benzene (20 ml) was added a solution of the ketone (3) (1 g) in reagent-grade benzene (5 ml). The mixture was stirred overnight at room temperature, water (25 ml) was then added, and the separated benzene layer was washed with 8% aqueous NaOH (2 × 20 ml). The combined alkaline extracts were cooled, acidified with 5% hydrochloric acid, and extracted with diethyl ether. The extract was washed, dried, and evaporated to dryness to yield a dense, oily material (1.25 g) which was mixed with butane-1-thiol (1 ml), dry benzene (25 ml), and toluene-*p*-sulphonic acid (18 mg); the mixture was then heated under reflux for 32 h with removal of water in a Dean–Stark trap (1 drop was collected). The cooled benzene solution was washed in turn, with water, aqueous potassium hydrogen carbonate, and brine, and was then dried and evaporated to dryness to yield the crude oily sulphide (6) (1.29 g) which was heated at 165 °C and 10 mmHg pressure for 1 h with the flask completely immersed in the oil-bath in order to remove all low-boiling materials; the residue was used directly in the next step.

To an ice-cold solution of $LiMe_2Cu$ in diethyl ether, prepared from purified copper(I) iodide (1.61 g) and 1.4M of methyl-lithium in diethyl ether (Aldrich Chemical Company) (2.21 ml), was added the crude sulphide (6) (1.92 g) under dry nitrogen. The mixture was stirred for 55 min at 0 °C and was then quenched cautiously by the slow dropwise addition of saturated aqueous ammonium chloride (20 ml). After further dilution with water the entire mixture was vacuum-filtered to remove all solids, the ethereal layer of the filtrate was separated, and the aqueous portion was extracted with diethyl ether (2 × 20 ml). The combined ethereal solutions were washed, dried, and evaporated to dryness to afford a yellow oil which, on distillation, afforded the ketone (5) (259 mg, 22%), identical with the sample previously described.

The Keto-ester (7).—A stirred mixture of the ketone (3) (1 g), a 50% dispersion of sodium hydride (245 mg), diethyl carbonate (2.41 g), and dry 1,2-dimethoxyethane (10 ml) was heated at 80—85 °C for 2 h under nitrogen. The mixture was cooled and a little absolute ethanol was added dropwise to destroy excess of sodium hydride. A solution of 10% aqueous acetic acid (6 ml) was added to the stirred, cold reaction mixture under nitrogen. The resulting solution was extracted with diethyl ether and the extract was washed in turn with 5% aqueous sodium hydrogen carbonate and brine, and was then dried and evaporated to dryness. A red oil was obtained which was distilled to afford the keto-ester (850 mg, 68%), b.p. 82—83 °C (bath) at 0.3 mmHg; *m/z* 221 ($M^+ - CO_2H$); $\nu_{max.}$ (film) 1 713 and 1 745 cm^{-1} (ketonic and ester C=O, respectively) (Found: C, 71.95; H, 9.7. Calc. for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84%).

The Ketol (9).—A solution of methyl-lithium was prepared from methyl iodide (12.67 g) and lithium metal (1.26 g) in diethyl ether (72 ml). To the stirred solution was added dropwise, during 15 min, a solution of the keto-ester (7) (1.46 g) in diethyl ether (5 ml). The solution was then washed, dried, and evaporated to dryness to yield a yellow oil which, on cooling, crystallised to give the ketol (9) (901 mg, 72%), m.p. 55—56 °C (from hexane); *m/z* 234 ($M^+ - H_2O$); $\nu_{max.}$ (KBr) 3 485 (OH) and 1 710 cm^{-1} (C=O) (Found: C, 75.95; H, 11.05. Calc. for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18%).

The Ketones (10) *and* (11).—A solution of the ketol (9) (805 mg) in absolute methanol (15 ml) was treated with 10% hydrochloric acid (5 ml) under reflux under nitrogen for 2 h; the mixture was then cooled, diluted with water, and extracted with diethyl ether. The extract was washed in turn with 3% aqueous sodium hydrogen carbonate and brine, then dried and evaporated to dryness to yield an oily material which was dissolved in cold hexane, whence crystallization occurred. After the completion of crystallization at room temperature (12 h), the ketone (10) was obtained (598 mg, 78%), m.p. 24—26 °C (from hexane); *m/z* 234 (M^+); $\nu_{max.}$ (KBr) 1 696 and 1 676 (split C=O) and 1 625 cm^{-1} (C=C); δ 0.88 (3 H, s) and 0.90 (6 H, s) (altogether, 4-, 4-, and 10-Me), and 1.18 (6 H, s, C=C*Me*$_2$) (Found: C, 81.9; H, 11.1. Calc. for $C_{16}H_{26}O$: C, 81.99; H, 11.18%).

Evaporation of the mother liquor from the crystallization of the ketone (10) furnished the ketone (11) (23 mg, 3%) as a dense liquid, *m/z* 234 (M^+); $\nu_{max.}$ 1 710 (C=O) and 1 640 cm^{-1} (C=C); δ 0.84 (3 H, s) 0.91 (6 H, s,) (altogether, 4-, 4-, and 10-Me), 1.64 (3 H, s, CH_2=C*Me*), and 4.78 and 4.92 (total 2 H, C=CH_2) (Found: C, 81.85; H, 11.1. Calc. for $C_{16}H_{26}O$: C, 81.99; H, 11.18%).

Hydrogenation of the Ketone (11).—A stirred solution of the ketone (11) (30 mg) in methanol (5 ml) was hydrogenated over 5% Pd–C (4 mg) under 8 atm of hydrogen for 20 min. Work-up afforded a reddish, oily material which, on filtration through a column of neutral alumina (hexane as eluant) afforded the ketone (5) (28 mg), identical (i.r. spectrum; t.l.c.) with an authentic specimen.

Hydrogenation of the Ketones (10) *and* (11).—A mixture of compounds (10) and (11) (500 mg) in methanol (20 ml) containing 5% Pd–C (50 mg) was stirred under 8 atm of hydrogen for 12 h. The mixture was filtered and the filtrate was evaporated to dryness to give an oil which, on distillation, yielded the ketone (5) (443 mg, 88%), identical with the sample previously described. The overall yield of the ketone (5) from compound (3) [(3) ⟶ (7) ⟶ (9) ⟶ (10) + (11) ⟶ (5)] was 36%.

The Alcohol (12).—A solution of the ketone (5) (200 mg) in

warm, dry ethanol (5 ml) was quickly added to sodium metal (500 mg). After 25 min, the mixture was heated at 100—110 °C (bath) until all the sodium had dissolved. The solution was cooled to room temperature, diluted with water, and saturated with sodium chloride; it was then extracted with diethyl ether. The extract was washed, dried, and evaporated to dryness to give a yellow oil which solidified on trituration with hexane and a little benzene. Recrystallization from hexane afforded the alcohol (12) (176 mg, 80%), m.p. 61 °C; *m/z* 238 (M^+) and 220 ($M^+ - H_2O$); $\nu_{max.}$ (KBr) 3 450 cm^{-1} (OH); δ 0.86 (3 H, s), 0.92 (3 H, s), 0.94 (3 H, s) (altogether, 4-, 4-, and 10-Me), 1.07 (6 H, d, *J* 2 Hz, $CHMe_2$), and 3.86 (1 H, m, $W_{\frac{1}{2}}$ 18 Hz, 6-H) (Found: C, 80.5; H, 12.55. Calc. for $C_{16}H_{30}O$: C, 80.60; H, 12.68%).

Lead Tetra-acetate Oxidation of the Alcohol (12).—A mixture of lead tetra-acetate (2.22 g) and anhydrous calcium carbonate (2.22 g) suspended in cyclohexane (30 ml) was heated under reflux for 25 min. To the suspension was added in turn a solution of the alcohol (12) (500 mg) in cyclohexane (20 ml) followed immediately by iodine (560 mg) and the resulting mixture was heated under reflux for 1.5 h whilst under irradiation from two Phillips 250 W photo-lamps. The mixture was cooled, filtered, and the insoluble solid was washed thoroughly with diethyl ether. The combined filtrate and washings were washed in turn with 1% aqueous NaOH and aqueous sodium thiosulphate to remove the colour of iodine. Subsequently, further washes, followed by evaporation to dryness, afforded a dense liquid which was chromatographed on alumina (hexane as eluant) to give the cyclic ether (13) (321 mg, 65%) as a dense liquid, b.p. 140—152 °C (bath) at 0.25 mmHg; *m/z* 236 (M^+) and 191 ($M^+ - CH_2OMe$); δ 0.82 (3 H, s, Me), 0.97 (3 H, s, Me), 108 (6 H, d, *J* 2 Hz, $CHMe_2$), and 3.45 (2 H, q, *J* 3 Hz, CH_2O) (Found: C, 81.15; H, 11.9. Calc. for $C_{16}H_{28}O$: C, 81.29; H, 11.94%).

Elution with hexane–benzene (9 : 1) then afforded the ketone (5) (148 mg, 30%), identical (i.r., t.l.c.) with the sample previously described.

Further elution with hexane–benzene (1 : 1) gave the starting alcohol (12) (15 mg, 3% recovery), identical (m.p., i.r.) with the sample previously described.

Oxidation of the Cyclic Ether (13).—To a solution of the cyclic ether (13) (310 mg) in 99% acetic acid (5 ml) was added a solution of chromium(VI) oxide (180 mg) in 80% acetic acid (1 ml) and the mixture was kept at room temperature for 60 h. The mixture was diluted with water and extracted with diethyl ether. The extract was washed several times in turn with 2% aqueous sodium hydrogen carbonate and brine until the washings were neutral, and was then dried. Removal of the solvent afforded the lactone (14) (151 mg, 48%), m.p. 50—51 °C (from diethyl ether–hexane); *m/z* 250 (M^+) and 235 ($M^+ - Me$); $\nu_{max.}$ (KBr) 1 760 cm^{-1} (γ-lactone); δ 0.84 (3 H, s) and 0.92 (3 H, s) (together, 4- and 10-Me) and 1.08 (6 H, d, *J* 2 Hz, $CHMe_2$) (Found: C, 76.6; H, 10.5. Calc. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47%).

The sodium hydrogen carbonate washings mentioned above were acidified and extracted with chloroform. The extract was washed until the washings were neutral and was then dried. Evaporation of the solvent afforded the keto-acid (15) (103 mg, 32%), m.p. 48—49 °C (from diethyl ether); *m/z* 221 ($M^+ - CO_2H$) and 206 ($M^+ - CO_2H - Me$); $\nu_{max.}$ (KBr) 1 710 cm^{-1} (acid and ketonic CO); δ 0.81 (3 H, s) and 0.91 (3 H, s) (together, 4- and 10-Me) and 1.06 (6 H, d, *J* 2 Hz, $CHMe_2$) (Found: C, 72.05; H, 9.35. Calc. for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84%).

The Diol (16) *and its Oxidation to the Keto-acid* (15). To lithium aluminium hydride (125 mg) in THF (25 ml) was added a solution of the lactone (14) (200 mg) in THF (5 ml). The mixture was heated under reflux for 10 h and then cooled and cautiously diluted with water to destroy the excess of the hydride. The precipitate was filtered off and the filtrate was dried. Removal of the solvent yielded the oily diol (16) (199 mg, 98%), *m/z* 354 (M^+) and 236 ($M^+ - H_2O$); $\nu_{max.}$ 3 540 cm^{-1} (OH).

To a solution of the diol (16) (199 mg) in acetone (5 ml) was added Jones' reagent (2 ml) and the mixture was stirred at room temperature for 6 h. Isopropyl alcohol was added to destroy the excess of oxidant and the mixture was then extracted with diethyl ether. The extract was washed several times with 5% aqueous sodium hydrogen carbonate. The alkaline washings were acidified (5% cold hydrochloric acid, 7 ml) to afford the keto-acid (15) (76 mg, 25%), identical with the sample previously described. The dark red, oily material obtained from the neutral, ethereal extract could not be identified.

Acolamone (2).—To a solution of the keto-acid (15) (300 mg) in a mixture of dry benzene (30 ml) and dry pyridine (2 ml) was added lead tetra-acetate (582 mg). The mixture was stirred for 1 h at room temperature and then for 3 h at reflux it was then cooled, filtered through Celite, and the residue washed several times with benzene. The filtrate and washing were combined, washed in turn with dilute hydrochloric acid and brine, and dried. Removal of the solvent afforded a dark, oily material which, on chromatographic purification over 10% $AgNO_3$–impregnated silica gel (eluant hexane–benzene 8 : 2), yielded acolamone (2) as a liquid (16 mg, 17%); *m/z* 220 (M^+), 205 ($M^+ - Me$), and 177 ($M^+ - Me_2CH$); $\nu_{max.}$ (film) 1 715 (CO) and 1 645 cm^{-1}; δ 0.82 (3 H, s, 10-Me), 0.95 (6 H, d, *J* 3 Hz, $CHMe_2$), and 5.02 (1 H, s) and 5.95 (1 H, s) (together, $C{=}CH_2$) (Found: C, 81.7; H, 10.8. Calc. for $C_{15}H_{24}O$: C, 81.76; H, 10.98%).

Junenol (1).—To a solution of acolamone (2) (12 mg) in ethanol (3 ml) was added sodium borohydride (10 mg). The mixture was stirred for 10 h and was then diluted with water, and extracted with diethyl ether. The extract was washed and dried. Removal of the solvent afforded a yellow-white solid which, on sublimation, gave junenol (1) (6 mg), m.p. 76—78 °C (lit.,[7] 77.5—79 °C); *m/z* 222 (M^+), 204 ($M^+ - H_2O$), and 179 ($M^+ - Me_2CH$); $\nu_{max.}$ (CCl_4) 3 575, 2 990, 1 770, 1 640, 1 452, 1 262, 1 244, 1 185, 1 145, 1 070, 1 022, 995, 962, 920, 892, 872, 850, 832, and 772 cm^{-1} [almost identical with the i.r. spectrum of authentic [7] (±)-junenol]. The extremely small yield of junenol prevented us from obtaining its n.m.r. spectrum (Found: C, 80.85; H, 11.7. Calc. for $C_{15}H_{26}O$: C, 81.02; H, 11.79%).

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