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SYNTHETIC STUDIES TOWARDS COMPLEX DITERPENOIDS-17[1] : SYNTHESIS AND OXIDATIVE CLEAVAGE OF (+)-19,20-CYCLOABIETA-19-OXO-8,11,13-TRIENE

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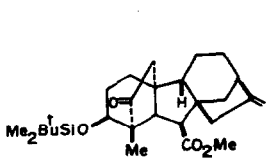
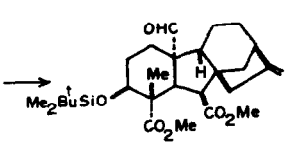
Abstract : Oxidative cleavage of the enolates of (+)-19,20-cycloabieta-19-oxo-8,11, 13-triene (1a) and the related tetracyclic ketone (1b) with molecular oxygen leads to (+)-abieta-8,11,13-triene-19,20-dioic acid (20a) and the dicarboxylic acid (20b), respectively. The synthesis of the tetracyclic ketone (1a) has been realized by two different methods through $Ni(acac)_2$ catalyzed intramolecular carbon-hydrogen insertion of the α-diazomethyl ketone (13), prepared from (+)-20-nor-4-epidehydroabietic acid (7) via lactone 6 and the stereo-specific rearrangement of the cyclobutanone (16), obtained from the easily accessible unsaturated acid (4) via the unsaturated cyclobutenone (15). Lithium-ammonia reduction of 4 gave (+)-20-nor-dehydroabietic acid (11) exclusively, whereas catalytic hydrogenation of 4 over Pd-C (10%) resulted in the A/B-ring cis-acid (9) as the major product, which was obtained exclusively from the lactone 6 by hydrogenolysis under the same condition.

Recently Mander and his co-workers[2] have reported an interesting and remarkably efficient oxidative cleavage of a hindered cyclopentanone (A) through its enolate by using molecular oxygen, to the respective seco aldehyde ester (B). In continuation to our interest in the synthesis of diterpenoids[3] we report here synthesis of tetracyclic ketone 1a and the results of its oxidative cleavage reactions in a projected general route to some C-4 and C-10 functionalized abietane diterpenoids[4,5].



A



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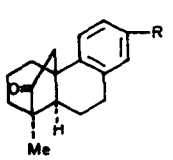
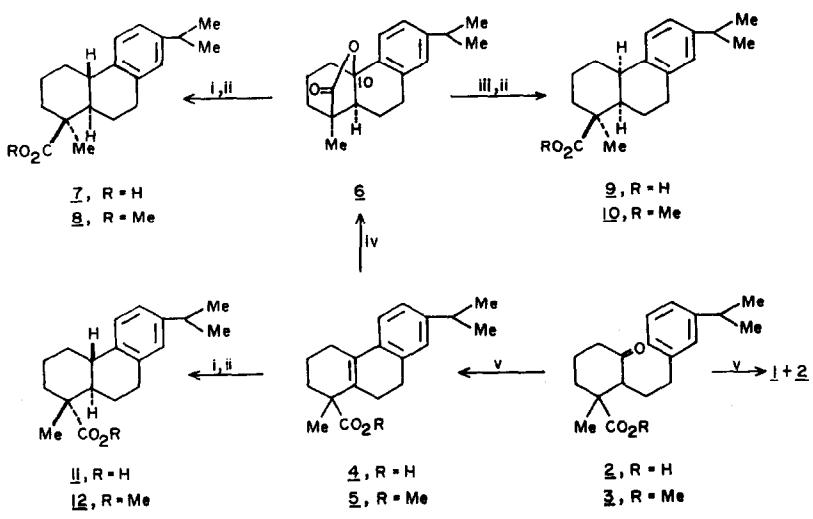


1g , R = i-Pr
1b , R = H

RESULTS AND DISCUSSIONS

Synthesis of the ketone 1a was realized through two routes (Scheme-1) developed earlier in this laboratory for 1b[6,7] through the acids 4 and 7. The tricyclic unsaturated acid 4 and the γ-lactone 6, precursor for 1a, have been prepared through cyclodehydration of the easily accessible known keto-acid 2 or the corresponding keto-ester 3[8]. Thus, treatment of a cold benzene solution of 2 with benzene-H_2SO_4 mixture[9] formed the easily separable mixture of the γ-lactone 6 and the unsaturated acid 4 in 67% and 21% yields, respectively. The assigned stereochemistry of 6 has been conclusively established from its further chemical transformations as described below. Cyclization of the keto-ester 3 with H_2SO_4 in benzene at low temperature[10] afforded theunsaturated ester 5 in 68% yield as the only isolable product, which on saponification gave 4 in 84% yield. The lactonization of 4 with H_2SO_4 proceeded cleanly to afford 6 in 75% yield. Hydrogenolysis of the lactone 6 with Li and NH_3(l) in the presence of NH_4Cl afforded (+)-20-nor-4-epi-dehydroabietic acid (7) in 99% yield. The homogenity of this acid was proved from the ^1H NMR spectrum (at 200 MHz) of the corresponding methyl ester 8 (Scheme-1). The reductive cleavage of lactone 6 leading to 7 with complete retention of stereochemistry at the benzylic asymmetric centre (at C-10) is in conformity with the earlier observations[9-11] with similar systems. The assigned stereochemistry of the acid 7 is keeping with its subsequent transformations to be described (Scheme-2). Formation of this acid 7 from the lactone 6 automatically established the depicted stereochemistry for the latter. The catalytic hydrogenolysis of the lactone 6 in ethanol in the presence of Pd-C(10%)

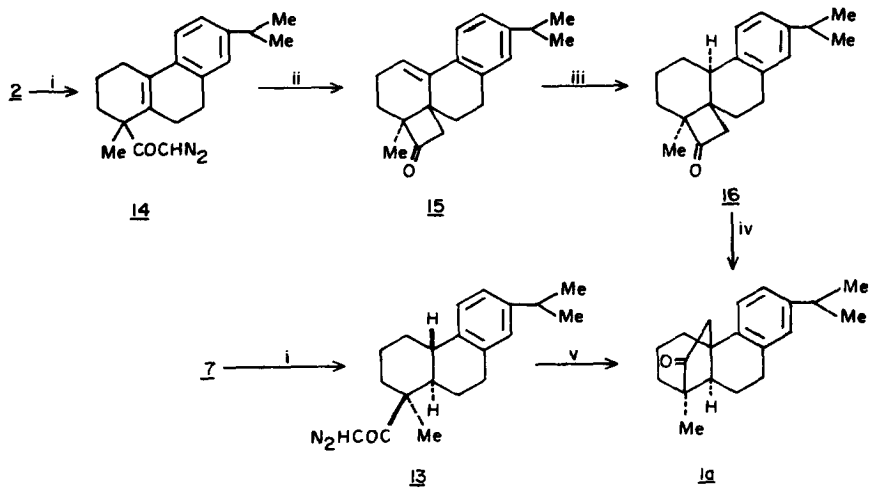
SCHEME-I



Reagents : (i) Li-NH_3(l), NH_4Cl (ii) CH_2N_2, Et_2O (iii) Pd-C (10%), EtOH
(iv) H_2SO_4 (v) H_2SO_4, C_6H_6

proceeded rapidly and yielded the acid 9 in 90% yield through inversion of configuration at the C-10 benzylic asymmetric centre as observed in similar substrates[10,11]. The homogenity of this acid was proved from the ^{1}H NMR spectrum of the corresponding methyl ester 10. Li-NH_3(l) reduction of the unsaturated acid 4 afforded (+)-20-nor-dehydroabietic acid (11) in 94% yield. The homogenity of this acid 11 was again established from the ^{1}H NMR spectrum of the corresponding methyl ester 12. The mechanism of the high stereoselectivity of this type of reduction has been discussed earlier[10,12].

SCHEME 2



Reagents : (i) NaOMe, MeOH, $(COCl)_2$, C_6H_6, CH_2N_2, Et_2O, TEA
(ii) TFA, $CHCl_3$ (iii) Pd-C (10%), EtOH
(iv) $Et_3\overset{+}{O}BF_4^-$, CH_2Cl_2 (v) Ni(acac)$_2$, C_6H_{12}

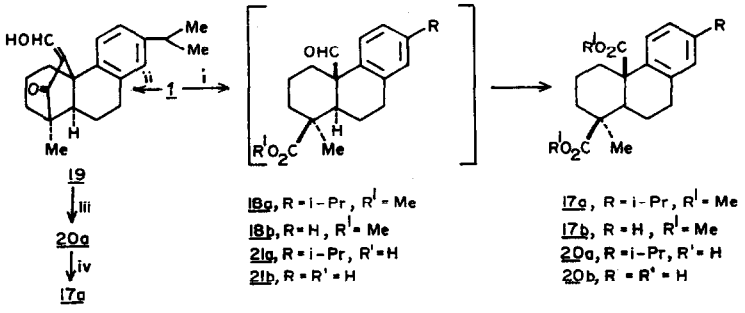
In the first approach 6, the diazoketone 13, prepared from 7 through the usual procedure[9], on decomposition in dilute cyclohexane solution in the presence of Ni(acac)$_2$[11] under irradiation with tungsten lamps and chromatographic purification of the crude product gave the ketone 1a in 81% yield as the only isolable product. The structure of this ketone 1a was established from its IR and ^{1}H NMR spectra (see Experimental).

In the second route 7, the unsaturated acid 4 was converted to the corresponding diazoketone 14 in 91% yield through the usual method[9]. Treatment of an ice-cold dilute solution of this diazoketone 14 in chloroform with an excess of trifluoroacetic acid afforded the cyclobutenone 15 in excellent yield after chromatography on neutral

alumina. Catalytic hydrogenation of 15 in the presence of Pd-C (10%) in ethanol proceeded stereospecifically to give the saturated cyclobutanone 16 in 94% yield. The stereochemical assignment of the newly generated C-10 chiral centre was based on analogy and has been confirmed from its further transformation to 1a in 75% yield by treatment with an excess of triethyloxoniumtetrafluoroborate in CH_2Cl_2.

The previously reported model tetracylic ketone 1b[6] was first subjected to oxidation with molecular oxygen in the presence of KH in DMF-THF and subsequent treatment with methyl iodide, following the method of Dawe et al[2], gave the known[6] dimethyl ester 17b, in 90% yield, as the only isolable product. The oxidation of 1b under various conditions again gave 17b. We were unable to detect any aldehyde ester 18b in the reaction products. Repeating the oxidation with the isopropyl ketone 1a gave only (+)-dimethyl abieta-8,11,13-triene-19,20-dioate (17a)* in excellent yield. This was also prepared through the oxidation[6] of the hydroxymethylene compound 19, derived from 1a, with alkaline hydrogen peroxide followed by esterification (CH_2N_2) (Scheme-3).

SCHEME - 3



Reagents : (i) KH, DMF, THF, O_2, MeI (ii) HCO_2Et, NaH, C_6H_6 (iii) H_2O_2 (30%), NaOH (iv) CH_2N_2-Et_2O

Our failure to isolate or identify the expected aldehyde ester 18a and 18b in the oxidation products of tetracyclic ketones 1a and 1b, unlike that reported[2] for oxidation of (A), might be due to rapid in situ oxidation of the relatively less hindered aldehyde acid intermediates 21a and 21b to the respective dicarboxylic acids 20a and 20b, under the reaction conditions. The present work thus, clearly indicates that the nature of the products in the oxidation process of the bridged ketones by molecular oxygen considerably depends upon the structure of the substrates.

* Diterpene numbering and nomenclature has been used for the compounds related to the natural products.

EXPERIMENTAL

The compounds described are all racemates. IR spectra were recorded on a Perkin-Elmer model PE 298 spectrometer. ^1H NMR spectra were taken on a Varian XL-200 instrument. Chemical shifts are referred to TMS on the δ scale. Analytical GC was performed on a Shimadzu GC-9A model with a flame ionisation detector employing 1.5% OV-17 (6.5 ft x 0.25 in) column with N_2 as the carrier gas. UV spectra were recorded on a Beckmann DU spectrometer for solutions in ethanol (95%). Elemental analyses were performed by P.P. Bhattacharyya of this laboratory. Column chromatography was performed on neutral alumina (Brockman Grade 1) or silica gel Glaxo Laboratories (India). Petroleum and petroleum ether refer to fractions of bp 60-80°C and 40-60°C respectively.

(+)-5,10-Dehydro-20-nor-4-epidehydroabietic Acid (4) and (+)-4a β-Hydroxy-1 α-methyl-7-isopropyl-1,2,3,4,4a,9,10,10a-trans-octahydrophenanthrene-1 β-carboxylic acid 1→4a lactone (6). Cyclization of the keto acid 2*. Method A : A solution of the keto acid 2 (6.0 g, 20 mmol) in dry thiophene free benzene (60 ml) was added to well stirred concentrated H_2SO_4 (70 ml), cooled in an ice-salt bath (-10°C to -5°C), during 10-15 min and stirring in cold was continued for 2 h. The reaction mixture was poured into crushed ice (1 kg) and extracted with EtOAc. The organic phase was thoroughly washed with NaOH aq (2%) and water, dried, and concentrated to afford the lactone (6) (3.8 g, 67%), mp 154°C (EtOAc-petroleum); IR (KBr) 1770 and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (6H, d, J = 7Hz); 1.30 (3H, s), 1.36-3.0 (total 12H, m), 7.06-7.56 (3H, m). Anal. calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found : C, 80.23; H, 8.48%.

The combined aqueous alkaline extracts were acidified with HCl (6N) and the separated gummy solid was extracted with EtOAc, washed with water, dried. The residual product was recrystallized twice from EtOAc to give the acid 4 (1.2 g, 21%), mp 142°C; IR (KBr) 1695, 1640, 1600 cm^{-1}; UV (EtOH) λ_{max} 266 nm (log ε 4.10). Anal. calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found : C, 80.52, H, 8.68%.

Method B : Repeating the cyclization of 2 (1.0 g, 3.31 mmol) in dry $CHCl_3$ (25 ml) at ca -15°C - -5°C with concentrated H_2SO_4 (17 ml) for 1 h and the usual work up afforded the lactone 6 (680 mg, 72%) mp and mmp 154°C and the acid 4 (80 mg, 9%) mp and mmp 142°C with the samples described above.

Cyclization of the keto ester 3 : (+)-Methyl 5,10-dehydro-20-nor-4-epi-dehydroabietate (5). To a well stirred solution of the keto ester 3 (7.8 g, 26 mmol) dissolved in dry thiophene free benzene (160 ml) and cooled in freezing mixture (-8°C to -5°c), ice-cold H_2SO_4 (96 ml) was added dropwise over a period of 1 h. Stirring was continued for 30 min more at 0°C. The reaction mixture was poured into crushed ice (1.2 kg). After work up and distillation gave the ester 5 (5.0 g, 69%), bp 170-180°C at 0.1 mm Hg; R_t 3.93 min at 240°C; UV (EtOH) λ_{max} 265 nm (log ε 4.10); IR (neat) 1725, 1600 cm^{-1}; ^1H NMR 1.22 (6H, d, J = 7 Hz),(1.34, 3H s), 1.45-2.98 (total 11H, m), 3.66 (3H, s).

*We thank Dr. A.K. Chakraborti for the initial experimental conditions of this cyclization method.

7.02-7.28 (3H, s). Anal. calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.79. Found : C, 80.21; H, 8.52%

The cyclized ester 5 (5 g, 16.7 mmol) was hydrolyzed in ethylene glycol (26 ml) with a solution of KOH (2.6 g, 46 mmol) in water (2.6 ml) by heating at 170-175°C under N_2-atmosphere. The homogeneous reaction mixture was poured into water (100 ml) and the neutral portion was extracted with ether, washed with water, and dried. Removal of solvent afforded the unchanged ester 5 (100 mg). The basic portion was chilled and acidified with cold HCl (6N), and the precipitated acidic product was extracted with EtOAc. The EtOAc layer was washed with water and dried. Removal of solvent afforded the acid 4 (4g, 84%); mp and mmp 142°C with the sample described above.

Lactone 6 from unsaturated acid 4. Unsaturated acid 4 (200 mg, 0.70 mmol) was added to concentrated H_2SO_4 (4 ml) at -10°C to -5°C. Stirring at that temperature was continued for 1 h. The homogeneous red mixture was poured into crushed ice (25 g), extracted ether, washed with Na_2CO_3 solution (5%) and water. After being dried, evaporation of solvent gave the lactone 6 (150 mg, 75%) mp and mmp 154°C, with the sample described above.

(+)-20-nor-4-epi-Dehydroabietic Acid (7). To a stirred solution of the lactone 6 (1.0 g, 3.5 mmol) in anhydrous Et_2O (20 ml) and anhydrous THF (20 ml) and anhydrous NH_3 (1) (distilled from Na) was added Li wire (147 mg, 21 mg atom) in several lots during 3-5 min and the stirring was continued for additional 2 min. The blue colour was discharged by the cautious addition of solid NH_4Cl. The ammonia was then allowed to evaporate completely at room temperature, 25 ml of moist ether was added and the reaction mixture was carefully acidified with an excess of HCl (6N). The product was extracted with EtOAc and washed with water followed by NaOH aq (2%) repeatedly. The trace of neutral product left after evaporation of EtOAc was discarded. The aqueous alkaline layer was acidified and the liberated acid was extracted with EtOAc. After the usual work up afforded the acid 7 (1.8 g, 99%) mp 185°C (EtOAc); UV (EtOH) λ_{max} 260 nm (log ε 2.73) and 274 nm (log ε 2.69); IR (KBr) 1690, 1600 cm^{-1}. Anal. calcd. for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found : C, 79.79; H, 9.09%.

(+)-Methyl 20-nor-4-epi-Dehydroabietate (8). The acid 7 (100 mg) in Et_2O (15 ml) was esterified with an excess of ethereal diazomethane to afford the pure ester 8 (95 mg, 91%) homogeneous in GC, (R_t 10.40 min at 140°C); UV (EtOH λ_{max} 267 nm (log ε 2.5) and 175.6 nm (log ε 2.15); IR (neat) 1725, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 1.23 (6H, d, J = 7 Hz), 1.27 (3H, s), 1.31-2.86 (total 13H, m), 3.63 (3H, s), 6.92-7.22 (3H, m). Anal. calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found : C, 80.21; H, 9.21%.

Catalytic hydrogenolysis of the lactone 6. (+) -20 nor-4-epi-10-epi-Dehydroabietic Acid (9). The lactone 6 (200 mg) in ethanol (95%, 10 ml) on hydrogenation with Pd-C (100 mg, 10%) at room temperature and pressure for 30 min afforded 9 (180 mg, 90%); mp 192°C after recrystallization from EtOAc-petroleum ether; UV (EtOH) λ_{max} 269 nm (log ε 2.7), 277 nm (log ε 2.77); IR (KBr) 1690 cm^{-1}. Anal. calcd. for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found : C, 79.59; H, 9.04%.

The acid 9 (100 mg) was esterified with CH_2N_2-Et_2O to afford 10 (100 mg, 99%); mp 72-73°C (petroleum ether) (homogeneous in GC, R_t 10.01 min at 140°C); UV (EtOH) λ_{max} 264 nm (log ε 2.62) and 2.73 nm (log ε 2.69); IR (KBr) 1720, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (6H, d, J = 7 Hz), 1.40 (3H, s), 1.50-3.04 (total 13H, m), 3.74 (3H, s), 6.96-7.30 (3H, m). Anal. calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found C, 80.0; H, 9.40.

Reduction of the unsaturated acid 4 : (+) -20-nor-Dehydroabietic Acid (11). To a well stirred solution of the unsaturated acid 4 (200 mg, 0.7 mmol) in dry THF (5 ml) and dry Et_2O (5 ml) and anhydrous NH_3 (1) (distilled from Na) Li-metal (90 mg, 13 mg atom) was added in small portions over about 5 min and stirred for an additional 10 min. The mixture was decomposed by addition of powdered NH_4Cl. Evaporation of NH_3 followed by the usual work up with ether afforded a solid (190 mg, 94%); mp 177-178°C. (EtOAc-petroleum ether). UV (EtOH) λ_{max} 260 nm (log ε 2.50) and 2.74 nm (log ε 2.50); IR (KBr) 1685, 1600 cm^{-1}. Anal. calcd. for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found : C, 79.60; H, 9.00%.

(+)-Methyl 20-nor-Dehydroabietate (12). The acid 11 (100 mg) was esterified with excess of CH_2N_2 inEt_2O in the usual way to afford the liquid ester 12 (95 mg, 91%) (homogeneous in GC, R_t 10.79 min at column temperature 140°C); UV (EtOH) λ_{max} 260 nm (log ε 2.74) and 272 nm (log ε 2.67); IR (neat) 1725, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) 0.9-2.92 (total 13H, m), 1.21 (6H, d, J = 7 Hz), 1.24 (3H, s), 3.68 (3H, s), 6.98-7.30 (3H m). Anal. calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found : C, 80.20; H, 9.54%.

(+) -19,20-Cycloabieta-19-oxo-8,11,13-triene (1a). Insertion reaction of the diazoketone 13. The acid 7 (1.0 g, 3.49 mmol) was converted to the diazoketone 13 (960 mg, 86%) as a yellow gum following the identical method as reported earlier[9]; IR (neat) 2060, 1630, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 1.18 (6H, d, J = 7 Hz). 1.60-3.54 (total 13H, m), 5.30 (1H, s), 6.72-7.24 (3H, m). A solution of the diazoketone 13 (960 mg, 3 mmol) in dry cyclohexane (100 ml) was added dropwise over a period of 3 h to a magnetically stirred refluxing solution of anhydrous $Ni(acac)_2$[11] (520 mg, 2 mmol) in dry cyclohexane (100 ml) under N_2-atmosphere, which was irradiated with two 250 W tungsten lamps. Refluxing under irradiation was continued for a further 10 h. The green solution was filtered through neutral alumina (40 g) and the column was eluted with petroleum ether-benzene mixture (9:1). Evaporation of the combined elutes under reduced pressure afforded the bridged cyclopentanone 1a (700 mg, 81%); mp 90-91°C. This was recrystallized from petroleum ether to give the analytically pure sample of 1a as a colourless solid, mp 94°C (homogeneous in GC, T_t 5.34 min at 150°C); IR (KBr) 1725, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 1.03 (3H, s), 1.23 (6H, d, J = 7 Hz), 1.65-2.0 (8H, m) 2.22-2.32 (1H m, C_5-H), 2.36 (δ_A) and 2.43 (δ_B) AB_q J = 20 Hz, $-COCH_2$), 2.75-3.0 (3H, m), 6.05-7.14 (3H, m). Anal. calcd. for $C_{20}H_{26}O$: C, 85.10; H, 9.22. Found: C, 85.17; H, 9.49%. The ketone 1a gave a 2,4-dinitrophenylhydrazone, mp 230°C. Onrecrystallization from methanol deep orange red crystals were obtained, mp 234°C. Anal. calcd. for $C_{26}H_{30}O_4N_4$: C, 67.51; H, 6.54. Found : C, 67.46; H, 6.21%.

Acid-catalyzed intramolecular alkylation reaction of the diazo-ketone 14 : (+)-1 α-Methyl-7-isopropyl-1,2,3,9,10-10a-hexahydro-1 β ,10a β ,11-oxo-ethanophenanthrene (15). The acid 4 (350 mg, 1.23 mmol) was converted to the diazoketone 14 (345 mg, 91%) as a light yellow solid mp 96°C following the identical method as described earlier[7] [IR (KBr) 2100, 1630, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 1.22 (6H, d, J = 7 Hz), 1.30 (3H, s), 1.54-2.96 (total 11H, m), 5.60 (1H, s) 7.04-7.30 (3H, m)]. To an ice cold solution of the diazoketone 14 (320 mg, 1.03 mmol) in dry $CHCl_3$ (50 ml), TFA (0.5 ml) was added with stirring. An immediate evolution of N_2 was observed. The mixture was stirred for 30 min at 0°C. The light brown solution was washed successively with water, Na_2CO_3 aq (5%) and water and then dried. Evaporation of the solvent under reduced pressure afforded a light brown mass. It was dissolved in minimum volume of benzene and chromatographed on neutral alumina (10 g). The product eluted with petroleum ether afforded the unsaturated cyclobutanone 15 (260 mg, 89%), mp 75°C (light petroleum); IR (KBr) 1770, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 1.21 (3H, s), 1.25 (3H, s), 1.46-2.36 (9H, m), 2.80-3.08 (5H, m), 6.4 (1H, t, J = 7 Hz), 7.02 (1H, brs), 7.11 (1H, dd, J = 8 and 3 Hz), 7.56 (1H, d, J = 8 Hz). Anal. calcd. for $C_{20}H_{24}O$: C, 85.66; H, 8.63. Found : C, 85.50; H, 8.41%.

(+)-1 α-Methyl-7-iso-propyl-1,2,3,4,4aα ,9,10,10a-octahydro-1 β ,10a β-11-oxo -ethanophenanthrene (16). The unsaturated cyclobutanone 15 (199 mg, 0.36 mmol) in ethanol (10 ml) was hydrogenated at room temperature and pressure in presence of Pd-C (50 mg, 10%) for 30 min. The usual work up afforded the saturated ketone 16 as a white solid (95 mg, 94%), mp 85°C, homogeneous in GC (R_t 3.67 min at 160°C); IR (KBr) 1765, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 1.11 (3H, s), 1.25 (6H, d, J = 7 Hz), 1.34-3.18 (14H, m), 6.68-7.32 (3H, m). Anal. calcd. for $C_{20}H_{26}O$: C, 85.10; H, 9.22. Found : C, 84.99; H, 9.40%.

Rearrangement of the saturated cyclobutanone 16 to the bridged cyclopentanone 1a. Triethyloxonium tetrafluoroborate was prepared by adding epichlorohydrin (2.2 ml) dropwise to a magnetically stirred mixture of BF_3Et_2O (1.3 g, 9.15 mmol) in dry ether (6 ml). The white solid thus obtained was dissolved in dry CH_2Cl_2 (4 ml) and to this was added the saturated cyclobutanone 16 (150 mg, 0.53 mmol in CH_2Cl_2 (4 ml) dropwise during 1 h at room temperature. The reaction mixture was stirred for another 24 h at room temperature, diluted with water and extracted with ether. The ethereal layer was washed with Na_2CO_3 aq (5%), water and finally dried. Removal of the solvent afforded a solid which was filtered through a column of neutral alumina (5 g). Petroleum elution afforded the bridged ketone 1a (125 mg, 83%) as white solid, mp 94°C, identical with the sample described earlier in all respect (^1H NMR, IR, GC).

Oxidation of ketone 1b with KH and O_2. (i) To a stirred suspension of KH (ca 300 mg, 7.5 mmol, 35%) (prewashed with dry petroleum) in dry THF (5 ml) and DMF (3 ml) under N_2 atmosphere at -25°C (bath temperature) was added ketone 1b (360 mg, 1.5 mmol) in THF (3 ml) and DMF (2 ml). The resulting red suspension was stirred at 0°C and O_2 was passed (dried with KOH) for 5 min. After cooling at -20°C, the mixture was quenched with excess MeI (ca 2 ml), decomposed with methnol and extracted with ether (4 x 15 ml). The ether extracts were washed with water, dried.

Removal of ether afforded (+)-dimethyl podocarpa-8,11,13- triene-19,20-dioate (17b) (426 mg, 90%); mp 135°C, indentical with the sample described earlier[6] [IR, NMR, GC].

(ii) Similar reaction of ketone 1b (240 mg) under oxygen atmosphere and decomposition with MeOH gave diacid 20b, which was esterified with an excess of CH_2N_2-Et_2O to afford the diester 17b in 80% overall yield.

Repeating the oxidation of 1b under various other temperatures from -78 to -10°C under controlled exposure to oxygen gave either the diacid 20b (or diester 17b) completely or a mixture with the recovered ketone 1b.

(+)-Dimethyl Abieta-8,11,13-triene-19,20-dioate (17a). Method A : Formylation and oxidation of 1a with alkaline H_2O_2. The hydroxymethylene ketone 19 (198 mg, 90%) [IR (neat) 1680, 1600 cm^{-1}; ^1H NMR 1.1 (3H, s), 1.26 (6H, d, J = 7 Hz), 1.60-3.42 (total 13H, m), 6.76 (1H, s), 7.02-7.42 (3H,m)] was prepared from 1a (200 mg, 0.71 mmol) with NaH (272 mg, 11.33 mmol) and HCOOEt (3.5 ml) under N_2 atmosphere following the procedure described[6] for 1b. The crude product 19 (190 mg, 0.61 mmol) was dissolved in NaOH aq (10%), 16 ml x 2 lots) and was oxidized with H_2O_2 (30%, 6 ml x 2 lots) at room temperature for 20 h as described earlier. Usual work up gave the diacid 20a (178 mg, 88%) mp 228°C (EtOAc-petroleum); IR (KBr) 1700, 1600 cm^{-1}. Anal. calcd. for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found : C, 72.60; H, 7.65%

The corresponding dimethyl ester 17a was prepared by esterification of 20a with CH_2N_2 in Et_2O in 95% yield; IR (neat) 1725, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) 1.24 (6H, d, J = 7 Hz), 1.34 (3H, s), 1.40-2.80 (9H, m), 2.82-3.20 (2H, m), 3.50-3.74 (1H, m), 3.58 (3H, s), 3.68 (3H, s), 6.90-7.38 (3H, m). Anal. calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found C, 73.61; H, 8.56%.

Method B : Oxidation of 1a with KH and O_2 : (i) To a stirred suspension of KH (ca 100 mg, 2.5 mmol, 35%) (prewashed with dry petroleum) in dry THF (1.5 ml) and DMF (1.0 ml) under N_2 atmosphere at -25°C (bath temperature) was added ketone 1a (200 mg, 0.71 mmol) in THF (1.5 ml) and DMF (1.0 ml). The resulting red suspension was stirred at -25°C for 2 h. The mixture was warmed at 0°C and oxygen was passed (dried with KOH) for 5 min. After cooling at -20°C, the mixture was quenched with excess MeI (ca 1 ml), decomposed with methanol and extracted with ether (4x10 ml). The ether ether extracts were washed with water, dried. Removal of ether gave the diester 17a (108 mg, 80%); identical with the sample described earlier (IR, ^1H NMR).

(ii) Similar reaction of ketone 1a (100 mg) under oxygen atmosphere and decomposition with MeOH gave diacid 20a which was esterified with an excess of CH_2N_2-Et_2O to afford the diester 17a in 74% overall, identical with the sample described earlier (IR, ^1H NMR).

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