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HIGHER ISOPRENOIDS—XIII[a]

PARTIAL SYNTHESES FROM CYCLOARTENOL, CYCLOLAUDENOL—PART 5: TRANSFORMATION OF CYCLOLAUDENOL TO 31-NORCYCLOLAUDENONE[b,c]

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Abstract—A new general procedure for the functionalization of 4α-Me group in triterpenoids, reported earlier, has been utilized for the conversion of cyclolaudenol to 31-norcyclolaudenone a triterpene isolated from *Musa sapientum*. A convenient method for the cleavage of C=C bond in enamines with RuO_4 is reported.

We have recently reported[1] a novel method for the functionalization of 4α-Me group in triterpenoids. The salient features of the method involve the introduction of a 3β-hydroxymethyl side chain at C-3 (e.g. **1**→**2**) followed by photolytic decomposition of the derived hypohalite [$Pb(OAc)_4$–I_2] to give lactone **3**. The method has now been successfully used for the conversion of cyclolaudenol (**4**) to 31-norcyclolaudenone (**5**) a triterpane isolated from *Musa sapientum*.[2]

It was clear from the outset that the olefinic bond in the side chain of **4** would have to be protected in a manner that the sequence of reactions for the functionalisation of 4α-Me group and final removal of C-29 (from a lactone of the type **3**) can be easily carried out and after the operations, the double bond can be regenerated. Of the various possibilities,[3] the one which appeared more practical, was to convert the terminal methylene group to a hydroxymethyl function by hydroboration–oxidation and then selectively protect the primary OH group. For the latter purpose, tritylation was favoured for various reasons: (i) trityl group (Tr=Ph_3C), because of its bulky nature was expected to exhibit high selectivity in the protection of primary alcoholic group (ii) trityl ethers are stable to alkalies and other nucleophiles and a sequence of reactions can be so envisaged that the reagents used are compatible with the protective group (iii) detritylation can be effected under mild acidic conditions under which cyclopropane ring of cycloaudane derivatives was expected to be stable. The sequence of reactions employed to convert cyclolaudenol (**4**) to 31-norcyclolaudenone (**5**) is shown in Fig. 1.

Cyclolaudanol on hydroboration with diborane followed by oxidative work-up gave a mixture of epimeric 26-hydroxycyclolaudan-3β-ols[5] (**6**, 85%; PMR: C<u>H</u>OH, C<u>H</u>$_2$OH 3H, m, 3.24–3.84 ppm) which was smoothly converted to 26-trityloxycyclolaudan 3β-ols (**7**, 90%; PMR: C<u>H</u>$_2$OTr 2H, bt, 2,82–3.11 ppm). The latter on oxidation (CrO_3–pyridine) gave the corresponding 3-keto derivatives **8** (IR: C=O 1715 cm^{-1}; PMR[6]: cyclopropyl C<u>H</u>$_2$, 1H, d, 0.53 ppm, J = 4 Hz; 1H, d, >0.84 ppm, masked under the Me signals), which in turn were treated with methylenetriphenylphosphorane to get 26-trityloxy-3-methylenecyclolaudanes (**9**; IR: C=C<u>H</u>$_2$ 1637, 898 cm^{-1}). Hydrocarboration of **9** with 9-borabicyclo[3.3.1]nonane (9-BBN)[7] followed by oxidation (H_2O_2–NaOH) yielded a mixture of diastereomeric 26-trityloxy-3β-hydroxymethylcyclolaudanes (**10**, IR: OH 3440 cm^{-1}) and some 26-trityloxy-3α-hydroxymethylcyclolaudanes. The major pair (diastereomeric at C-26) was assigned 3β-configuration based on the expected preferential attack by the hydroborating agent from the less hindered α-face of olefins **9**. The PMR spectra of the aldehydes derived from these alcohols (Collin's reagent) lent further support to these assignments (equatorial[8] C<u>H</u>O 9.73 ppm; axial[8] C<u>H</u>O, 9.96 ppm; 7:3).

Irradiation (100 W tungstan lamp) of alcohols **10** along with the 3α-isomers, in presence of $Pb(OAc)_4$ and iodine followed by Collin's oxidation gave a product from which lactones **11** (IR: γ-lactone 1775 cm^{-1}) were isolated (30%) by inverted-dry-column-chromatography (IDCC).[9] The PMR spectrum of lactones **11** (C<u>H</u>$_2$OCO 2H, m, 3.81–4.29 ppm) bears a close resemblance to that of lactone **3**[1] (R=C_8H_{19}; C<u>H</u>$_2$OCO 2H, m, 3.78–4.28 ppm) prepared earlier, indicating that configurations at C-3 and C-4 in these lactones are similar. Further confirmation about the structure of **11** was forthcoming from the spectral characteristics of methyl 3β-hydroxymethyl-26-trityloxycyclolaudan-29-oates (**12**) and the corresponding formyl esters **13** (Fig. 1).

Lactones **11** were hydrolysed (10% KOH–THF) and esterified (CH_2N_2) to give hydroxyesters **12** (IR: OH 3500 cm^{-1}; CO_2Me 1730, 1250[10] cm^{-1}). Oxidation of **12** with Collin's reagent gave the formyl esters **13** (IR: CHO 2710, 1720 cm^{-1}. PMR: C<u>H</u>O 9.49 ppm). The latter were converted to their enamines[11] (piperidine, p-toluenesulphonic acid) which, without purification were directly oxidised (RuO_4–CCl_4)[12] to methyl 3-oxo-26-trityloxy-cyclolaudan-29-oates (**14**; IR: C=O 1705 cm^{-1}; CO_2Me, 1735, 1245 cm^{-1}. PMR[6]: cyclopropyl C<u>H</u>$_2$ 1H, d, 0.5 ppm, J = 4 Hz; 1H, >0.83 ppm, masked under other signals). Exposure of **14** to HCl methanolic resulted in detritylation to yield methyl 3-oxo-26-hydroxycyclolaudan-29-oates (**15**, IR: OH 3620 cm^{-1}), which were subjected to hydrolysis and decarboxylation[13] (LiI–DMF) to get 26-hydroxycycloeucalanones (**16**). The sequence was completed by the pyrolysis of acetates derived from **16** to give 31-norcyclolaudenone (**5**), the

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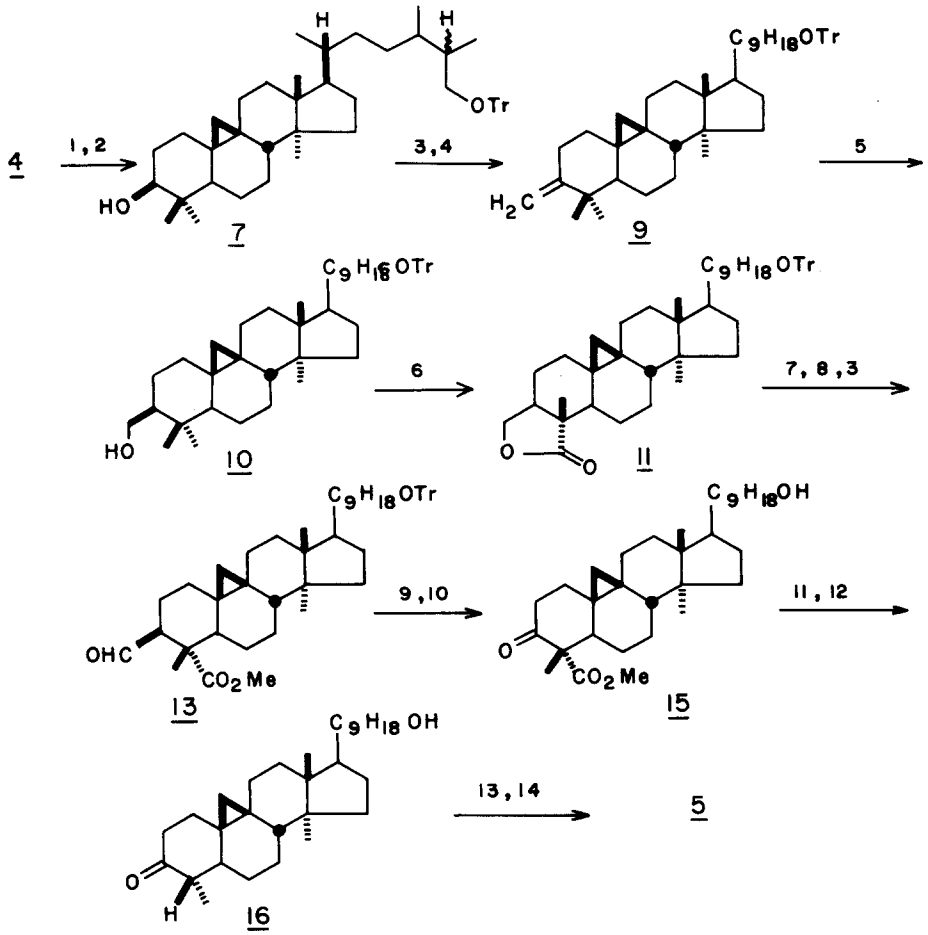
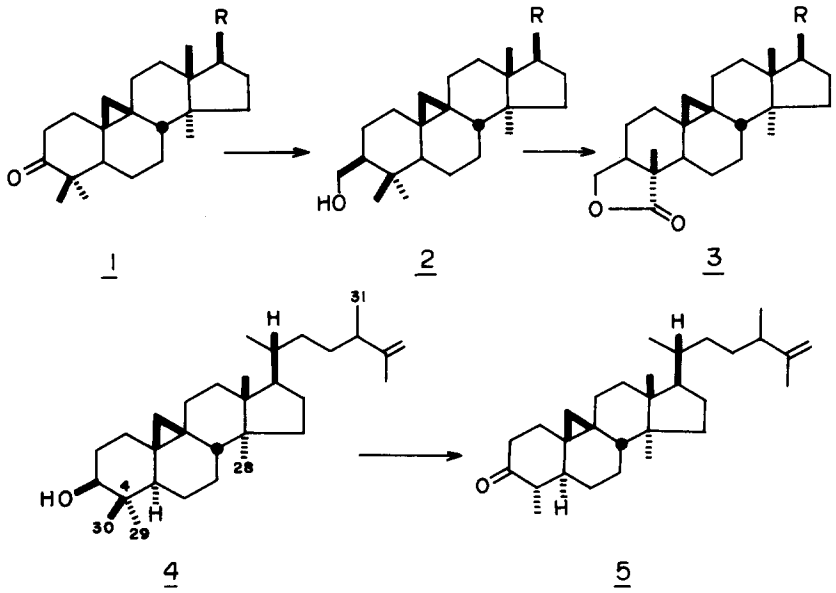
[c]Abstracted from the Ph.D Thesis of Manoj C. Desai (M.S.University, Baroda, 1980).



Reagents : (1) B_2H_6; H_2O_2– NaOH (2) Ph_3CCl –pyridine (3) CrO_3–pyridine (4) $Ph_3(Me)P^+I^-$ – t BuOK (5) 9-BBN; $H_2O_2^-$ NaOH (6) $Pb(OAc)_4$, I_2 / hν (7) KOH–THF aq. (8) CH_2N_2 (9) Piperidine, p-TSA (10) RuO_4 (11) HCl – MeOH (12) LiI - DMF (13) Ac_2O – pyridine (14) Δ

Fig. 1. Transformation of cyclolaudenol to 31-norcyclolaudenone.



physical data (m.p., IR, PMR, Mass) of which were identical with those reported[2] for the natural product.

EXPERIMENTAL

All m.ps are uncorrected. Light petroleum refers to fraction of b.p. 60–80°. Optical rotations were measured in $CHCl_3$ on a Schmidt-Haensch electronic polarimeter (model Polartronic-I).

The following instruments were used for spectral/analytical data: Perkin-Elmer spectrophotometer model 402(UV); Perkin-Elmer Infracord model 267; Perkin-Elmer model R32 (90 MHz) NMR spectrometer; Varian Mat CH7 Mass spectrometer (70 eV, direct inlet system). While citing PMR data, the following abbreviations have been used: s (singlet), d (doublet), t (triplet), m (multiplet) and b (broad). While summarising mass spectral data, besides the molecular ion, nine most abundant ions (*m/e*) are reported with their relative intensities.

Silica gel for column chromatography (−100, +200 mesh) was washed with hot water till sulphate-free, dried and activated at 125–130° for 6 hr and standarised.[14] Tlc was carried out on SiO_2-gel layers (0.25 mm) containing 15% gypsum and activated at 110–115° (2 hr).

Each of the 26-trityloxycyclolaudane derivatives (**7** to **13**), being a mixture of diastereomers, was isolated as a gum which could not be crystallised and was used as such for the next step.[5]

26-Hydroxycyclolaudan-3β-ols (**6**)

A soln of diborane in THF (2%, 52.3 ml ≡ 1.097 g of BH_3, 0.0795 mole) was slowly added to a stirred and cooled (10–15°) soln of **4** (35 g, 0.0795 mole) in anhyd THF (700 ml). Stirring was continued for another 4 hr at ~25°. The mixture was then cooled (0°), decomposed with water (15 ml, 10 min) and treated with 3N NaOH aq (30 ml) and H_2O_2 (30%, 30 ml). The contents were allowed to warm to 25° and stirred at that temp for 2 hr. After dilution with water (200 ml), the aqueous phase was extracted with ether (100 ml × 2). The combined organic extracts were worked up in the usual manner to get a solid (31 g, 85%) which was crystallised from Et_2O–MeOH to give **6**, m.p. 163–165°. IR (Nujol): OH 3330 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.36 ppm; 1H, d, 0.58 ppm; J = 4 Hz), C-Me's (singlets at 0.82, 0.84, 0.89, 0.91 and 0.98 ppm), CHOH, CH_2OH (3H, m, 3.24–3.84 ppm). Mass: *m/e* 458 (M^+, 84%), 443 (47%), 441 (39%), 440 (69%), 425 (100%), 315 (39%), 175 (57%), 109 (45%), 95 (69%) and 69 (39%) (Found: C, 81.35; H, 11.93. $C_{31}H_{54}O_2$ requires: C, 81.22; H, 11.79%).

26-Trityloxycylolaudan-3β-ols (**7**)

A soln of **6** (25 g, 0.055 mole), trityl chloride (18.7 g, 0.067 mole) and pyridine (6.63 g, 0.084 mole) in C_6H_6 (575 ml) was refluxed (N_2) for 19 hr during which pyridine hydrochloride precipitated out. The mixture was cooled, pyridine hydrochloride removed by filtration, the filtrate was stripped free of benzene and excess pyridine to give a product which was dissolved in petroleum ether (40–60°, 150 ml) and allowed to crystallise (0°, 12 hr). Unreacted trityl chloride which crystallised was removed by filtration and petroleum ether was flashed off from the filtrate to yield **7** (34.3 g, 89.8%) which could not be crystallised. IR (CCl_4): OH 3615 cm^{-1}; aromatic nucleus 3050, 3020, 1890, 1590, 1485 and 700 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.31 ppm; 1H, d, 0.56 ppm; J = 4 Hz); C-Me's (singlets at 0.78, 0.82, 0.89 and 0.96 ppm), CH_2 OTr (2H, bt, 2.82–3.11 ppm), CHOH (1H, m, 3.10–3.36 ppm) aromatic H (15H, m, 7.18–7.62 ppm). (Found: C, 85.87; H, 9.94. $C_{50}H_{68}O_2$ requires: C, 85.71; H, 9.71%).

26-Trityloxycyclolaudan-3-ones (**8**)

To a cooled (15–20°) soln of pyridine (14.98 g, 0.19 mole) in CH_2Cl_2 (350 ml), CrO_3 (19 g, 0.189 mole) was added slowly in small lots.[15] Afterwards, a soln of **7** (19 g, 0.027 mole) in CH_2Cl_2 (50 ml) was added and the mixture was stirred at 25° for 4 hr, diluted with ether (400 ml) and filtered. The organic phase was washed with 5% NaOH aq (200 ml × 2), water (250 ml × 3) and dried. Removal of solvents gave a gummy residue which was dissolved in light petroleum and passed through a small bed of Al_2O_3–II. The eluates were stripped free of solvent to provide **8** (14.9 g, 78.6%). IR (CCl_4): C=O 1715 cm^{-1}; aromatic nucleus 3050, 3020, 1900, 1600, 1495 and 700 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.53, J = 4 Hz; 1H, >0.84 ppm) C-Me's (singlets at 0.84, 0.91, 1.02 and 1.07 ppm) CH_2OTr (2H, bt, 2.82–3.11 ppm), aromatic H (15H, m, 7.22–7.67 ppm). (Found: C, 86.11; H, 9.52. $C_{50}H_{66}O_2$ requires: C, 85.96; H, 9.45%).

26-Trityloxy-3-methylenecyclolaudanes (**9**)

A soln of ketones **8** (13 g, 0.018 mole) in anhyd THF (40 ml) was added (25 min, N_2) to a suspension of methyltriphenyl phosphonium iodide (9.77 g, 0.024 mole) and t-BuOK (2.71 g, 0.024 mole) in THF (100 ml). The contents were stirred at 30° for another hr, after which most of THF was distilled off. The residue on usual work up using ether gave a product which was chromatographed over Al_2O_3–II (3.5 cm × 30 cm) with light petroleum to get the desired olefins **9** (10.3 g, 79.4%). IR (CCl_4): C=CH_2 1637, 898 cm^{-1}; aromatic nucleus 3040, 3010, 1900, 1600, 1495 and 700 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.29 ppm; 1H, d, 0.64 ppm, J = 4 Hz), C-Me's (singlets at 0.89, 1.0 and 1.05 ppm), CH_2OTr (2H, bt, 2.82–3.11 ppm), C=CH_2 (1H, bs, 4.62 ppm; 1H, bs, 4.67 ppm), aromatic H (15H, m, 7.07–7.58 ppm). Mass: *m/e* 453 (M^+-243, 34%), 311 (23%), 244 (48%), 243 (100%), 217 (12%), 173 (12%), 165 (12%), 109 (11%) and 95 (16%). (Found: C, 88.13; H, 9.91. $C_{51}H_{68}O$ requires: C, 87.93; H, 9.77%).

Hydroboration of olefins **9**

A mixture of **9** (5.7 g, 8.19 mmole) and 9-BBN[7] (1.2 g, 9.83 mmole) in THF (100 ml) was refluxed (N_2) for 3 hr. After cooling (~0°), the mixture was successively treated with EtOH (6 ml), 6N NaOH aq (10 ml) and H_2O_2 (30%, 20 ml), and the contents were stirred (27°) for 4 hr. The aqueous phase was extracted with ether (30 ml × 2). Usual work up gave a mixture of **10** and 3α-hydroxymethyl-26-trityloxycyclolaudanes. IR (Nujol): OH 3440 cm^{-1}, aromatic nucleus, 3040, 3020, 1900, 1600, 1490 and 700 cm^{-1}. PMR (CCl_4): cyclpropyl CH_2 (1H, d, 0.32 ppm, 1H, d, 0.52 ppm; J = 4 Hz), C-Me's (singlets at 0.71, 0.82, 0.89 and 0.96 ppm); CH_2OTr (2H, bt, 2.84–3.11), CH_2OH (2H, m, 3.18–3.46 and 3.67–3.98 ppm), aromatic H (15H, m, 7.11–7.60 ppm). (Found: C, 85.89; H, 9.93. $C_{51}H_{70}O_2$ requires: C, 85.71; H, 9.80%).

Photocyclisation of 3-hydroxymethyl-26-trityloxycyclolaudanes

A mixture of the above alcohols (4.0 g, 0.056 mole), $Pb(OAc)_4$ (7.0 g, 0.0159 mole) and I_2 (1.86 g, 0.014 g atom) in dry cyclohexane (150 ml) was irradiated (100 W, tungstan lamp) till refluxing ensued. The mixture was irradiated and refluxed for another 3 hr; cooled and filtered. The residue was washed with cyclohexane (100 ml). The combined organic extracts were washed successively with 10% $Na_2S_2O_3$ aq (50 ml), water (75 ml × 2) and then passed through a small bed of anhyd Na_2SO_4. To the filtrate, pyridine (3 ml) was added and the solvent was removed by distillation under reduced pressure (90 min, 35°). The residue was dissolved in CH_2Cl_2 (10 ml) and added to a soln of CrO_3 (3.9 g, 0.039 mole) and pyridine (3.08 g, 0.039 mole) in CH_2Cl_2 (75 ml) at 15–20°. After stirring for 1 hr, it was worked up in the usual manner to give a brown gummy product (4.2 g) which was subjected (2 × 2.0 g) to IDCC[9] on SiO_2-gel (6.6 cm × 22 cm) using 2% EtOAc in C_6H_6 as the solvent. A band at R_f: 0.57 yielded the lactones **11** (1.25 g, 31%). IR (CCl_4): OCO 1775 cm^{-1}; aromatic nucleus 3060, 3030, 1900, 1600, 1492 and 700 cm^{-1}; PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.2 ppm, J = 4 Hz; 1H, >0.78 ppm, masked under other signals), C-Me's (signals at 0.78, 0.82, 0.84, 0.89, 0.93 and 1.09 ppm); CH_2OTr (2H, bt, 2.82–3.11 ppm), CH_2OCO (2H, m, 3.78–4.28 ppm), aromatic H (15H, m, 7.13–7.58 ppm). Mass: *m/e* 483 (M^+-243, 21%), 341 (33%), 245 (19%), 244 (88%), 243 (71%), 242 (17%), 167 (50%), 166 (38%), 165 (100%), and 95 (21%). (Found: C, 84.33; H, 9.18. $C_{51}H_{66}O_3$ requires: C, 84.30; H, 9.09%).

Methyl 3β-formyl-26-trityloxycyclolaudan-29 oates (**13**)

Lactones **11** (0.5 g, 0.69 mmole) were hydrolysed by refluxing with KOH (0.5 g) dissolved in minimum quantity of water and diluted with THF (20 ml) for 6 hr. Most of THF was then distilled off and the residue, diluted with water (20 ml) and cooled to 0° was acidified with 10% oxalic acid aq. The aqueous phase was

extracted with ether (20 ml × 3), the ether extract was successively washed with water (25 ml × 4), and brine (20 ml), and after drying (Na_2SO_4) esterified (CH_2N_2). Removal of solvent provided **12** (0.46 g, 88%). PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.35 ppm; 1H, d, 0.49 ppm; J = 4 Hz), C-Me's (singlets at 0.84, 0.96, 0.98 and 1.07 ppm), CH_2OTr (2H, bt, 2.80–3.11 ppm); CH_2OH (2H, d, 3.42 ppm, J = 8 Hz), CO_2CH_3 (3H, s, 3.69 ppm), aromatic H (15H, m, 7.16–7.62 ppm).

To a stirred soln of CrO_3 (0.41 g, 4.15 mmole) and pyridine (0.33 g, 4.15 mmole) in CH_2Cl_2 (40 ml) was added in one lot, a soln of hydroxyesters **12** (0.45 g, 0.59 mmole) in CH_2Cl_2 (3 ml) at 15–30°. The mixture was stirred at 25° for 0.5 hr and worked up in the usual manner to give **13** (0.39 g, 87.7%). IR (CCl_4): CHO 2710, 1720 cm^{-1}, CO_2Me 1735, 1250 cm^{-1}, aromatic nucleus 3060, 3020, 1900, 1600, 1485 and 700 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.38 ppm; 1H, d, 0.58 ppm; J = 4 Hz), C-Me's (singlets at 0.82, 0.93, 0.96 and 1.07 ppm), CH_2OTr (2H, bt, 2.78–3.13 ppm), CO_2CH_3 (3H, s, 3.73 ppm), aromatic H (15H, m, 7.16–7.60 ppm), CHO (1H, s, 9.49 ppm). (Found: C, 82.57; H, 9.13. $C_{52}H_{68}O_4$ requires: C, 82.54; H, 8.99%).

Methyl 3-oxo-26-trityloxycyclolaudan-29-oates (**14**)

A soln of formyl-esters **13** (1.03 g, 1.36 mmole) and piperidine (0.94 g, 11.06 mmole) in benzene (25 ml) containing *p*-toluenesulphonic acid (90 mg) was refluxed (N_2) using Dean–Stark apparatus (filled with molecular sieves 5 Å type for 40 hr). The completion of reaction was monitored by disappearance of absorption at 2710 cm^{-1} in IR spectrum. At the end of the reaction, benzene was removed, the resulting enamines were dissolved in CCl_4 (40 ml) and treated with a soln of RuO_4 in CCl_4 [prepared from RuO_2 (0.9 g) and $NaIO_4$ (2 g)]. Black RuO_2 was immediately precipitated out of the mixture; the latter was stirred (~27°) for another 2 hr. Excess RuO_4 was decomposed by adding isopropanol (5 ml); RuO_2 precipitated was filtered and washed with CCl_4. The filtrate and washings were mixed, stripped free of CCl_4 and the residue was filtered through a small bed or Al_2O_3–II to yield the desired ketoesters **14** (0.84 g, 71.3%). IR (CCl_4): C=O 1705 cm^{-1}; CO_2Me 1735, 1245 cm^{-1}; aromatic nucleus 3040, 3020, 1900, 1594, 1490 and 700 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.5 ppm, J = 4 Hz; 1H, >0.83 ppm) C-Me's (singlets at 0.83, 0.86, 0.94 and 1.31 ppm); CH_2OTr (2H, bt, 2.86–3.12 ppm), CO_2CH_3 (3H, s, 3.76 ppm), aromatic H (15H, m, 7.20–7.67 ppm). (Found: C, 82.61; H, 9.07. $C_{51}H_{66}O_4$ requires: C, 82.48; H, 8.89%).

Methyl 3-oxo-26-hydroxycyclolaudan-29-oates (**15**)

The ketoesters **14** (0.7 g, 0.943 mmole) obtained above were dissolved in 1:1 MeOH–ether (40 ml) containing conc HCl (1.5 ml) and the contents were stirred at 25° for 6 hr. The mixture was diluted with ether (150 ml), the organic layer was washed with water (50 ml × 4). and dried. Removal of solvent, gave a yellow residue (0.561 g) which was chromatographed over SiO_2-gel (II, 1.3 cm × 20 cm); (i) C_6H_6, 10 ml × 4, 200 mg, trityl chloride (ii) 2% EtOAc in C_6H_6, 10 ml × 10, 361 mg, solid m.p. 145–148°. Frac. (ii) was crystallised from Et_2O–MeOH to give **15**, m.p. 154–156°. IR (CCl_4): OH 3620, 3520 cm^{-1}; C=O 1705 cm^{-1}; CO_2Me 1725, 1250 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.58 ppm, J = 4 Hz; 1H, >0.84 ppm, masked under other signals), C-Me's (singlets at 0.84, 0.93 and 0.98 ppm), $CH_3C.C=O$ (3H, s, 1.36 ppm) CH_2OH (2H, m, 3.20–3.67 ppm), CO_2CH_3 (3H, s, 3.71 ppm). Mass: *m/e* 500 (M^+, 100%), 357 (73%), 318 (41%), 297 (41%), 175 (40%), 121 (41%), 109 (44%), 107 (43%), 95 (86%) and 69 (50%). (Found: C, 77.03; H, 10.51. $C_{32}H_{52}O_4$ requires: C, 76.80; H, 10.40%).

26-Hydroxycycloeucalonones (**16**)

Compounds **15** (50 mg) and LiI (68 mg) were dissolved in DMF (5 ml) and the contents were refluxed (N_2) for 10 hr. After cooling, the mixture was poured into cold 2N HCl aq (50 ml) and extracted with ether (25 ml × 3). Usual work-up gave a gummy solid which was passed through a small bed of SiO_2-gel using C_6H_6 as eluant to give **16** (30 mg, 70%), m.p. 114–116° (Et_2O–MeOH). IR (CCl_4): OH 3640, 3520 cm^{-1}, C=O 1712 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.31 ppm; 1H, d, 0.55 ppm; J = 4 Hz), C-Me's (singlets at 0.69, 0.76, 0.80, 0.87 and 0.94 ppm), CH_2OH (2H, m, 3.26–3.67 ppm). (Found: C, 81.19; H, 11.73. $C_{30}H_{52}O_2$ requires: C, 81.03; H, 11.71%).

31-*Norcyclolaudenone* **5**

A soln of **16** (77 mg) and pyridine (80 mg) in Ac_2O (2 ml) was heated on water bath for 1 hr. After cooling the mixture was worked up in the usual manner to give 26-acetoxycycloeucalanones (73 mg).

The crude acetates, without purification, were pyrolysed by distilling it from a small bulb at 200° (air-bath temp)/1 mm and passing the vapours through a glass furnaces (2.0 mm i.d. × 15 cm) maintained at 480–500° over a period of 2 hr. The pyrolysate (63 mg) thus obtained was pyrolysed a second time under the same conditions to increase the amount of olefin formed (monitored by tlc). The pyrolysate (55 mg) thus obtained was chromatographed on SiO_2-gel (II, 0.7 cm × 17 cm) while monitoring with tlc (2% EtOAc in C_6H_6). After eluting with pet ether (20 ml), the column was eluted with 1:1 benzene–light petroleum (0.5 ml × 15) to get 31-norcyclolaudenone (20 mg), m.p. 128–130° (Et_2O–MeOH) $[\alpha]_D + 49.5$ ($CHCl_3$), [Lit.[2], m.p. 130–132° (acetone), $[\alpha]_D^{27} + 49.0°$ ($CHCl_3$)]. IR (CCl_4): C=O 1710 cm^{-1}, C=CH_2 (2H, s, 893 cm^{-1}. PMR (CCl_4): cyclopropyl CH_2 (1H, d, 0.44 ppm; 1H, d, 0.58 ppm; J = 4 Hz), C-Me's (singlets at 0.89, 0.96, 1.0 and 1.02 ppm), CH_3 C=C (3H, s, 1.64 ppm), C = CH_2 (2H, s, 4.67 ppm). Mass: *m/e* 424 (M^+, 100%) 299 (55%), 136 (35%), 123 (54%), 121 (37%), 109 (42%), 107 (39%), 95 (71%), 81 (37%) and 69 (52%).

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[3]See e.g. D. W. Young, *Protective Groups in Organic Chemistry* (Editor, J. F. W. McOmie), p. 309. Plenum Press, London (1973).

[4]Ref. 3, p. 95.

[5]Since the chirality at C-26 was to be destroyed in the end, no effort was made to separate these isomers.

[6]The conversion (3–OH → 3–CO) is marked by a downfield shift of cyclopropyl protons in PMR.

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