Synthetic Photochemistry. Part 44.† Total Synthesis of Ceroplastol II and Albolic Acid, 5-8-5-Membered Tricyclic Sesterterpenoid Insect Wax Constituents, *via* Stereocontrolled Silyloxy-Cope Rearrangement with a Normally Disfavoured Transition State‡

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To a 1,5-diene, prepared by $CrCl_2$-mediated condensation of two iridoid synthons, was appended a lactol moiety, which was subjected to a stereocontrolled silyloxy-Cope rearrangement to give, *via* a normally disfavoured boat transition geometry, a thermolysate, from which the total synthesis of optically active ceroplastol II and albolic acid, 5-8-5-membered tricyclic sesterterpenoids, was accomplished for the first time.

Ceroplastol II (**1**)[1] and its congener albolic acid (**2**)[2] are sesterterpenoid alcohol and acid, respectively, isolated from the wax secretion of a scale insect, *Ceroplastes albolineatus*. The ceroplastanes, to which compounds (**1**) and (**2**) belong, the ophiobolanes,[3] and the fusicoccanes[4] are examples of the 5-8-5-membered tricyclic family, whose total synthesis currently attracts considerable interest. However, except for our achievement with cycloaraneosene.[5] no total synthesis of these natural products has been reported.[6] Herein, we report the synthesis of compounds (**1**) and (**2**).

Results and Discussion

As previously described,[7] the carbon framework of structure (**1**) can be constructed by the chromium(II) chloride condensation of two iridoid synthons, Cope rearrangement, and intramolecular eight-membered-ring formation. Since the absolute configuration of C-6 and C-14§ of compounds (**1**) and (**2**) are transferred from (3*R*)-irida-1,8-dien-7-al (**3**)[8] and (3*S*,8*R*)-9-benzyloxy-7-chloroirid-1-ene (**4**),[7] the starting material must be the condensate (**5**) from (**3**) and (**4**). Then, to set the correct stereochemistry at C-11, the lactol-regulated Cope rearrangement developed in our recent dictymal synthesis[9] is utilized. With this method, although the direct silyloxy-Cope rearrangement of the condensate proceeded stereoselectively through a chair transitional geometry,[7] the rearrangement of the same condensate modified by the fused lactol system can proceed *via* the desired boat transitional geometry (Scheme 1).

The best selectivity (70% *vs* 1%) for formation of (**5**), colourless prisms, m.p. 56.5–57.5 °C, over an epimeric by-product (**6**), a colourless oil, was obtained when the condensation was carried out with addition of isopropyl alcohol.¶ In this case, addition of Pr^iOH was essential for obtaining a good product distribution in favour of (**5**). Otherwise, the ratio of (**5**):(**6**) was variable. The product (**5**) was converted into the trimethylsilyl (TMS) ether (**7**), which upon treatment with disiamylborane and alkaline hydrogen peroxide yielded regio-and stereospecifically a hydroxymethyl derivative (**8**). Oxidation of compound (**8**) with pyridinium chlorochromate (PCC) gave a silyloxy aldehyde (**9**). As already shown, hydroboration of irida-1,8-diene derivatives always occurs stereoselectively to give (3*S**,8*R**)-irid-1-en-9-ols without exception,[10] the configuration of C-15 in (**9**) was proposed to be unnatural, the compound was epimerized to an isomeric aldehyde (**10**) by treatment with potassium fluoride–Florisil. The ^{13}C n.m.r. chemical shifts of the methyl carbons adjacent to the α-carbon of the aldehydes, δ 13.0 for (**9**) and 7.4 for (**10**), being in the same order as 10.7 for dehydroiridodial and 7.8 for chrysomelidial, are consistent with the stereochemical formulations.[8] The product (**10**) was further hydrolysed with pyridinium toluene-*p*-sulphonate (PPTS) to form a hydroxy aldehyde (**11**) (Scheme 2).

Upon heating at 190 °C, TMS ethers (**12a**) and (**12b**), derived from (**11**), respectively underwent Cope rearrangement with retention of the lactol ring as expected, to give the same mixture of thermolysates (**13a**) and (**13b**). From isomer (**12a**), a third thermolysate (**13c**) was obtained in 32% yield, and its ^1H n.m.r. spectrum showed signals due to trimethylsilyl enol ether and aldehyde groups. Therefore, a partial 1,3-silyl migration had occurred prior to the Cope rearrangement, and compound (**13c**) must be a thermolysate *via* the chair-formed transition state. Hydrolysis and subsequent sodium borohydride reduction of products (**13a**) and (**13b**) produced, *via* enol lactol (**14**), a single compound (**15**); separation of compounds (**12**) and (**13**) was, therefore, unnecessary. The C-ring in structure (**15**) was unambiguously determined to possess the natural configuration from ^{13}C n.m.r. comparison with the spectra of the related compounds (**A**)[5] and (**B**),[9] which have both been converted into natural products, cycloaraneosene and dictymal. Namely, an upfield shift for the signal ascribable to the methyl carbon at C-11 and a downfield shift for that of the methylene carbon of C-1 of compound (**15**) compared with those of (**A**) clarified the relationship of C-10 and C-11 in structure (**15**) as being opposite to that in (**A**). Similar comparison with (**B**) further supported the above conclusion. Furthermore, the *trans* relationship between C-10 and C-14 is a common feature in all three structures (**15**), (**A**), and (**B**) since the C-9 atoms have similar δ values.[11] Therefore, the Cope rearrangement of compound (**12**) proceeded *via* a normally disfavoured boat transitional geometry.

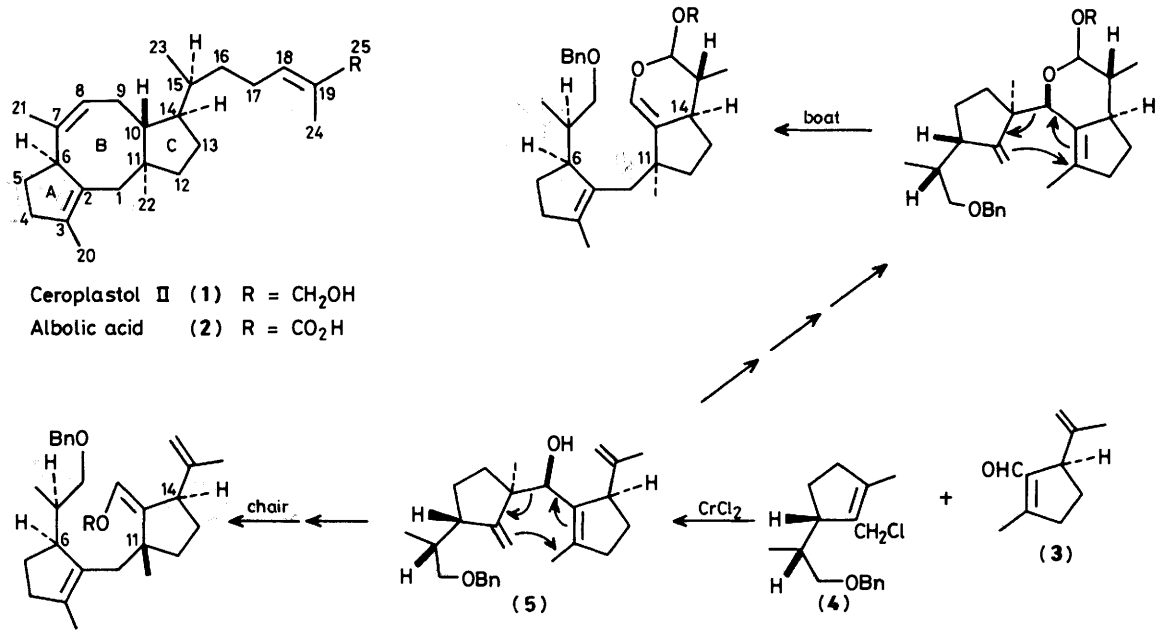
One of the two primary alcohol functions in compound (**15**) was preferentially protected by pivaloyl chloride to give a monoester (**16b**). Undesired by-products, dipivaloate and iso-

† Part 43: N. Kato, X. Wu, S. Ohbuchi, H. Miyagawa, S. Tanaka, H. Kataoka, T. Imaoka, and H. Takeshita, *Kyushu Diagaku Kinou Busshitsu Kagaku Kenkyusho Hokoku*, (Repts. Inst. Adv. Material Study, Kyushu Univ.), 1988, **2**, in the press.

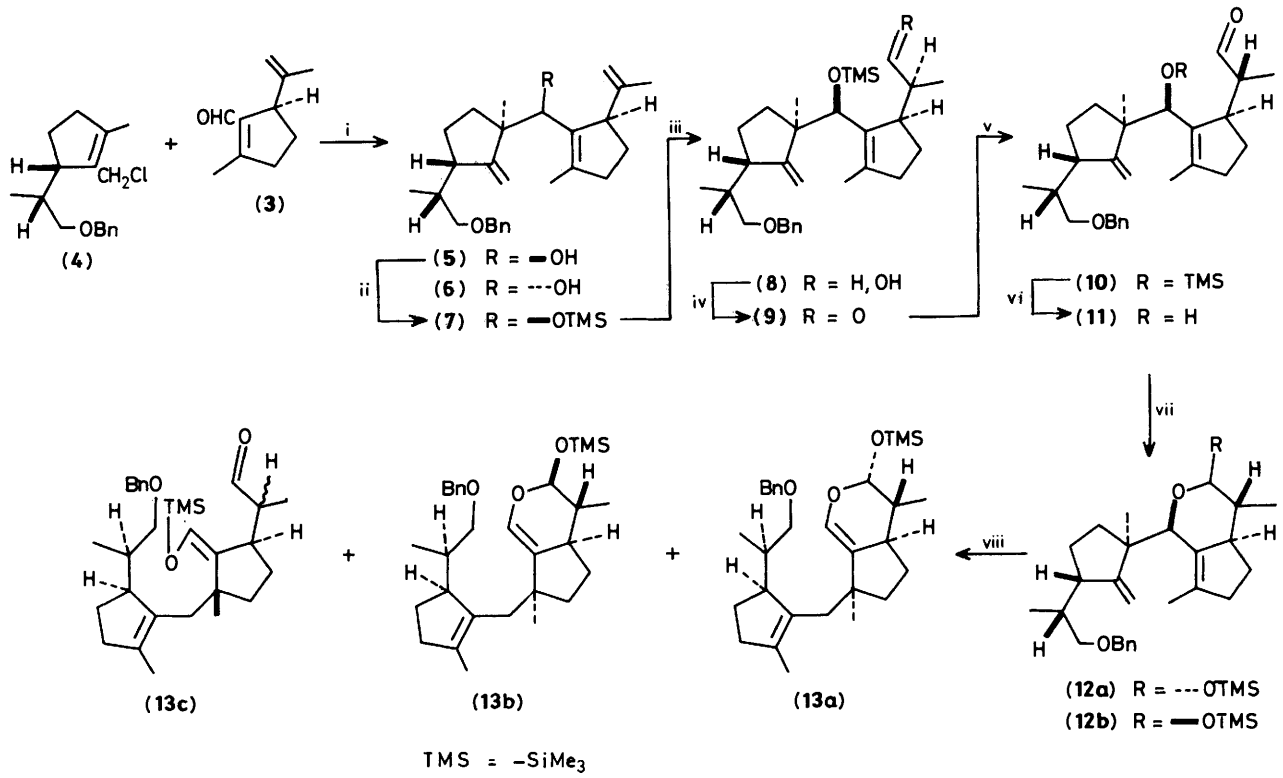
‡ The contents of the present paper were reported in preliminary form in *J. Chem. Soc., Chem. Commun.*, 1988, 354.

§ The positional numbers and ring letters shown in structure (**1**) are used throughout.

¶ In our preliminary communication, ref. 2, we described the run giving the highest yields for compounds (**5**) and (**6**), 88 and 3% respectively.

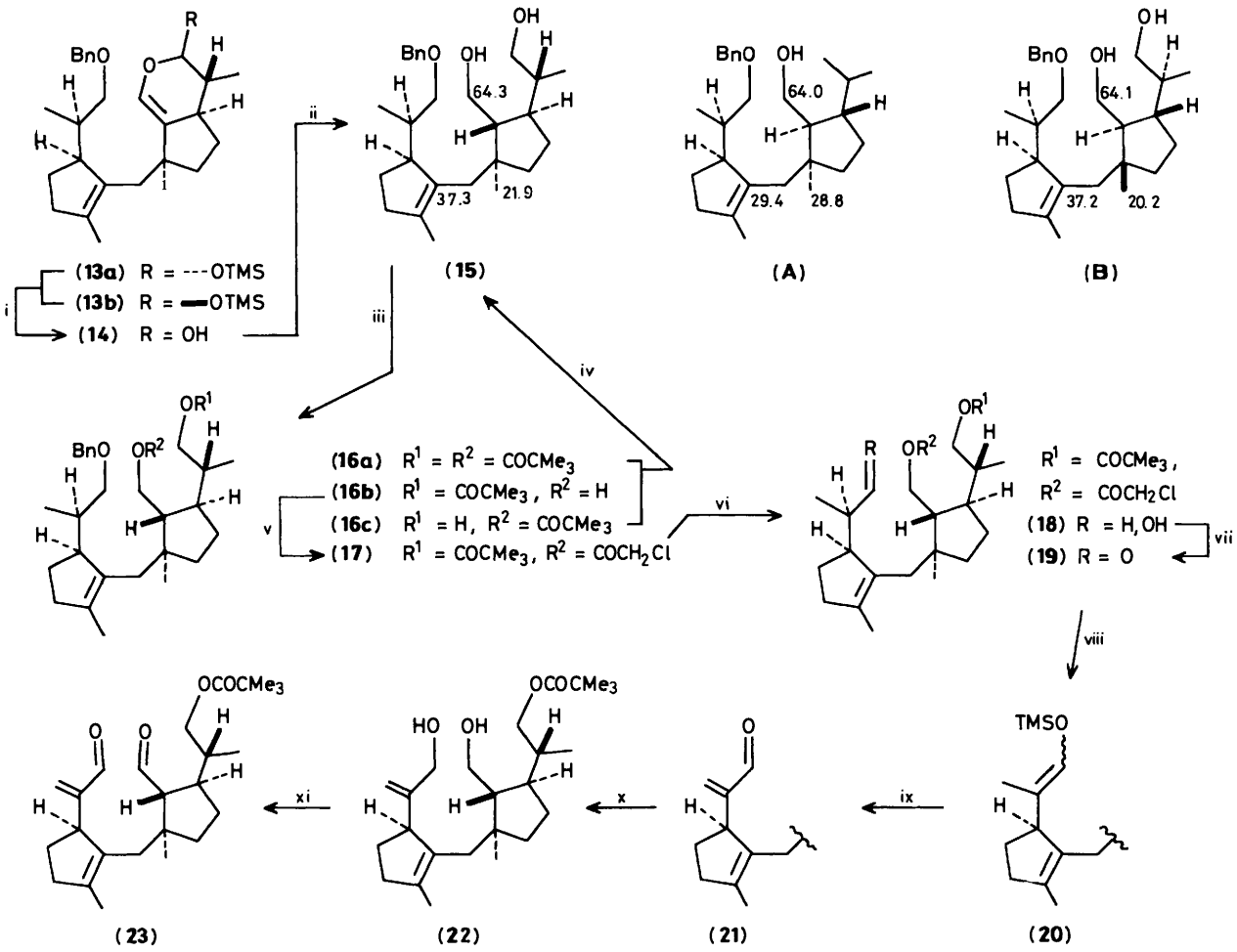


Scheme 1. Synthetic strategy for the synthesis of compounds (**1**) and (**2**)



Scheme 2. *Reagents and conditions:* i, $CrCl_3$–½LAH, THF–DMF (Pr^iOH) [(**5**), 70%; (**6**), 1%]; ii, TMSCl, Py (100%); iii, $[Me_2CH–CH(Me)]_2BH$, H_2O_2, ^-OH (95%); iv, PCC, CH_2Cl_2 (81%); v, KF–Florisil, MeOH (90%); vi, PPTS, aq. THF (100%); vii, TMSCl, Py [(**12a**), 27%; (**12b**), 67%]; viii, 190 °C [From (**12a**); (**13a**) + (**13b**) (4:1), 48%; (**13c**), 32%. From (**12b**); (**13a**) + (**13b**), (3:2), 72%]

meric monopivaloate (**16a**) and (**16c**), were quantitatively reduced to diol (**15**) by lithium aluminium hydride. After treatment of monoester (**16b**) with chloroacetyl chloride, the resultant chloroacetate (**17**) was debenzylated to the alcohol (**18**), and this was oxidized to an aldehyde (**19**). The TMS enol ether (**20**), prepared by treatment with trimethylsilyl trifluoromethanesulphonate, was oxidized with palladium(II) acetate[12] to afford an α,β-unsaturated aldehyde (**21**) in good yield. Differentiative deacylation, along with a reduction of the enal moiety, of compound (**21**) by means of sodium borohydride and cerium(III) chloride[13] easily produced a diol (**22**), which was converted into the dialdehyde (**23**) (Scheme 3). The titanium(II) chloride-mediated reductive cyclization[14] of compound (**23**) under dilute conditions gave a single glycol (**24**). The stereo-



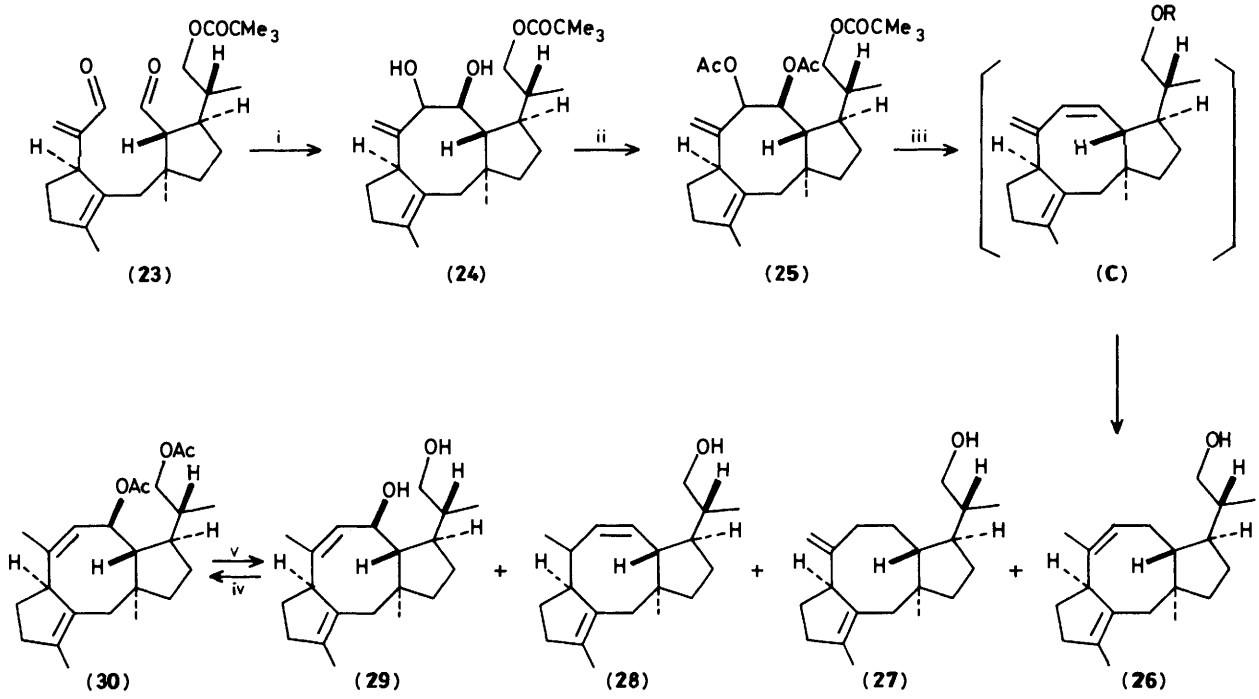
Scheme 3. *Reagents and conditions:* i, PPTS, aq. THF (97%); ii, $NaBH_4$, aq. $NaHCO_3$–MeOH (95%); iii, Me_3CCOCl, Py [(**16a**), 8%; (**16b**), 48%; (**16c**), 35%]; iv, LAH (98%); recycling iii and iv 3 times, (**15**) → (**16b**) (89%); v, $ClCH_2COCl$, Py (95%); vi, H_2/Pd–C (99.5%); vii, $(COCl)_2$–DMSO, Et_3N (95%); viii, CF_3SO_3TMS, Et_3N (98%); ix, $Pd(OAc)_2$, MeCN (94%); x, $NaBH_4$–$CeCl_3$, MeOH (93%); xi, = reagent vii (93%)

chemistry of this glycol was deduced spectroscopically as depicted. Namely, in the ^1H n.m.r. spectrum, a singlet signal ascribable to the α-oriented C-11 methyl group appeared at δ 0.81, indicating the secondary hydroxy group at C-9 to be β-oriented; because, if it were α-oriented, the C-11 methyl should appear at δ 1.1—1.2 by the anisotropic effect of a *syn*-oriented hydroxy group.[5,7] The stereochemistry of another hydroxy group (at C-8), however, could not be deduced unambiguously, although $J_{8,9}$ and $J_{9,10}$ were determined as 8.5 and 8.0 Hz, respectively.* Birch reduction of the diacetate (**25**) of diol (**24**) gave the bis-deacetoxylated compound (**26**) as a major product. The double-bond isomers (**27**) and (**28**) and a diol (**29**) were also obtained as minor by-products (Scheme 4). Since the diacetate (**30**) of diol (**29**) afforded none of the products (**26**)—(**28**) under the same conditions, it is clear that the bis-deacetoxylation was performed *via* the conjugate diene (**C**). The n.m.r. spectral data of compound (**26**) assured us that it possessed the correct C_{15}-C_{16}-degraded pentanor-derivative structure of target molecules (1) and (**2**).

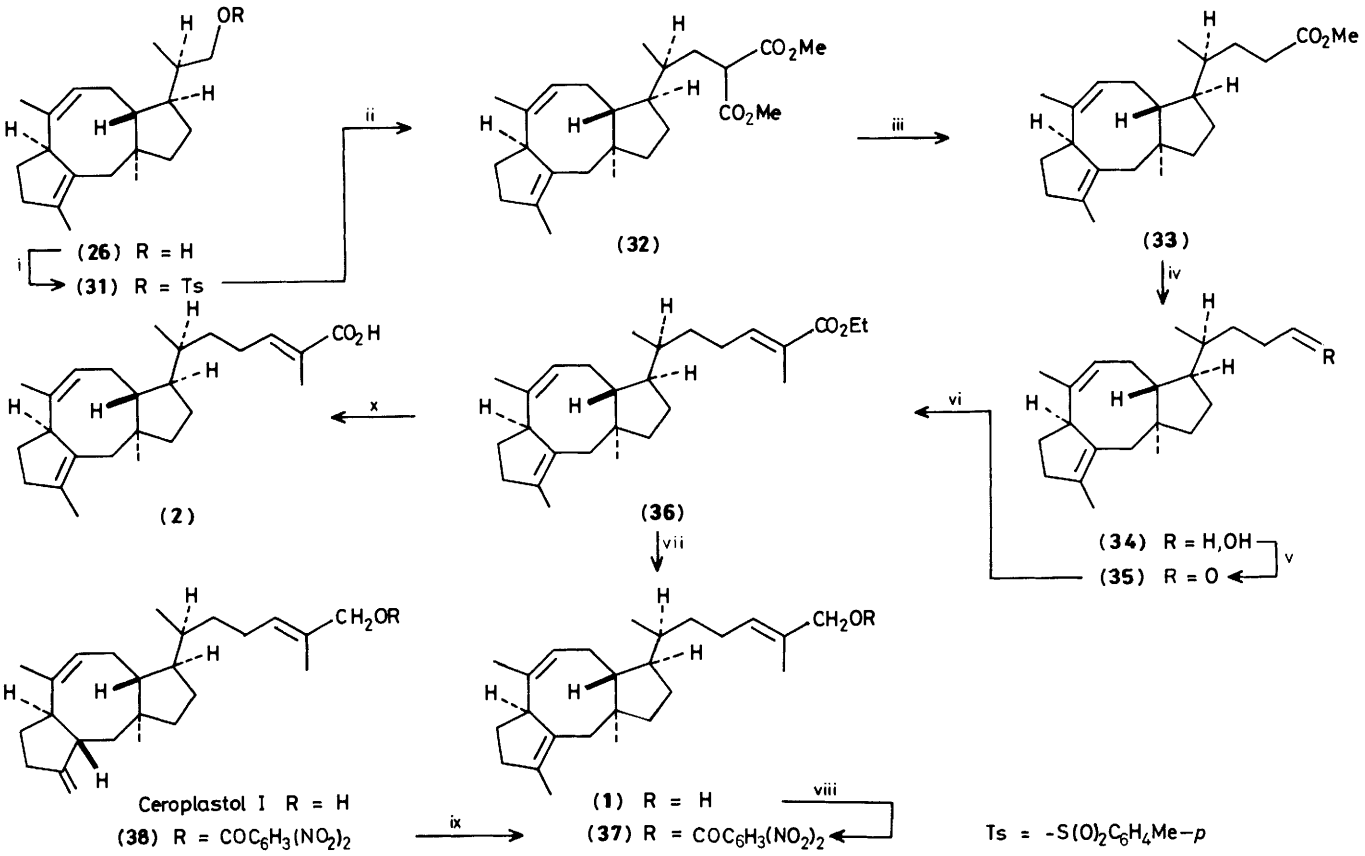
The final step of the synthesis was a conventional C_5-elongation of the side chain; *i.e.*, the toluene-*p*-sulphonyl ester (**31**) of the alcohol (**26**) was condensed with dimethyl sodiomalonate to give (**32**), which was decarboxylated to ester (**33**), $LiAlH_4$ (LAH) reduction of which gave the alcohol (**34**), which was oxidized with oxalyl dichloride–dimethyl sulphoxide (DMSO) to an aldehyde (**35**). Wittig reaction of (**35**) with ethyl 2-(triphenylphosphoranylidene)propionate gave the (*E*)-α,β-unsaturated ester, ethyl albolate (**36**), a portion of which was reduced to the alcohol which was thought to be (**1**).[1] Since sufficient data were not reported in ref. 1, the identity of synthetic (**1**) with the natural product was confirmed by derivation to the same 3,5-dinitrobenzoate (**37**) from the synthetic (**1**) and from isomerization of the natural 3,5-dinitrobenzoate (**38**) of ceroplastol I,[15] which was kindly provided by Drs. I. T. Harrison and S. Harrison. Further, synthetic (**1**) was identical in every respect, including the ^1H and ^{13}C n.m.r. spectral data with a sample prepared by saponification of natural (**37**). The rest of compound (**36**) was hydrolysed with base to give the acid (**2**) (Scheme 5) which was almost identical with the natural albolic acid, although its n.m.r. data showed some minor discrepancies with those reported.[2]

In conclusion, the 5-8-5-membered tricyclic sesterterpenoids have now been totally synthesized for the first time. The lactol-regulated Cope rearrangement is certainly versatile and can be applied on various occasions.

* Although, in the preliminary report,[2] the glycol moiety was assigned to have *cis* stereochemistry, the opposite conclusion is more likely judging from vicinal coupling constants.



Scheme 4. *Reagents and conditions:* i, $TiCl_4$–Zn, THF (96%); ii, Ac_2O, Py (93%); iii, Li, liq. NH_3–EtOH [(**26**), 76%; (**27**), 10%; (**28**), 7%; (**29**), 4%]; iv, = reagent ii (99.5%); v, = reagent iii (97%)



Scheme 5. *Reagents and conditions:* i, TsCl, Py (100%); ii, $NaCH(CO_2Me)_2$, DMF (81%); iii, NaCN, DMF, CH_2N_2 (71%); iv, LAH, THF (100%); v, $(COCl)_2$–DMSO, Et_3N (80%); vi, $Me(PPh_3{=})CCO_2Et$, C_6H_6 (93%); vii, = reagent iv (75%); viii, 3,5-$(NO_2)_2(C_6H_3)COCl$, Py (100%); ix, TsOH, acetone (82%); x, 3M NaOH, MeOH (95%).

Experimental

Elemental analyses were carried out by Miss S. Hirashima, of the Institute of Advanced Material Study, Kyushu University. N.m.r. spectra were measured by a JEOL FX 100 spectrometer for solutions in $CDCl_3$ solution, unless otherwise specified. Mass spectra were measured with a JEOL 01SG-2 spectrometer. I.r. spectra were taken as KBr disks or as a liquid film inserted between NaCl plates using a Jasco IR-A 102 spectrometer. The optical rotations were measured with a Union Model PM-101 apparatus. The solvents used in the reactions were carefully dehydrated and distilled under N_2 atmosphere immediately before use; therefore, they were anhydrous unless otherwise stated.

Improved Chromium(II) *Chloride-mediated Condensation*[16] *of Compounds* (**3**)[8] *and* (**4**).[7] *Formation of Alcohols* (**5**) *and* (**6**).—A stirred tetrahydrofuran (THF) suspension (100 ml) of $CrCl_3$ (10.29 g) was treated with powdered $LiAlH_4$ (LAH) (1.24 g) at 0—5 °C. After the evolution of H_2 had ceased, the mixture was allowed to attain room temperature and Pr^iOH (2.5 ml) was added. While the mixture was agitated by ultrasonic vibration, *N*,*N*-dimethylformamide (DMF) (100 ml) was added. To the mixture at 0—5 °C were consecutively added the compounds (**3**) (6.10 g) and (**4**) (7.55 g). The mixture was diluted with water, extracted with EtOAc, and the extract was dried over K_2CO_3. Silica gel column chromatography of the extract yielded alcohol (**5**) as *prisms* (7.45 g, 70%), m.p. 56.5—57.5 °C (Found: C, 82.4; H, 9.7. $C_{27}H_{38}O_2$ requires: C, 82.18; H, 9.71%); *m*/*z* 394 (M^+); $[\alpha]_D^{19}$ −144.9° (*c* 2.07 in $CHCl_3$); δ_H 1.07 (3 H, s), 1.09 (3 H, d, *J* 7 Hz), 1.62 (3 H, br s), 1.93 (3 H, br s), 3.18 (1 H, t, *J* 8.5 Hz), 3.22 (1 H, br m), 3.45 (1 H, dd, *J* 8.5, 4 Hz), 3.88 (1 H, br s), 4.42 (1 H, d, *J* 12 Hz), 4.46 (1 H, d, *J* 12 Hz), 4.64 (1 H, br s), 4.67 (1 H, m), 4.93 (1 H, d, *J* 2.5 Hz), 4.99 (1 H, d, *J* 3 Hz), and 7.27 (5 H, br s); δ_C 16.70 (q), 17.24 (q), 19.34 (q), 23.29 (q), 25.29 (t), 28.47 (t), 34.67 (t), 35.35 (d), 39.11 (t), 48.29 (d), 52.73 (s), 58.79 (d), 72.80 (t), 73.09 (t), 75.10 (d), 106.39 (t), 110.89 (t), 127.54 (d), 127.64 (d, 2 C), 128.41 (d, 2 C), 135.98 (s), 138.96 (s), 139.06 (s), 148.77 (s), and 160.64 (s); $\nu_{max.}$ 3 515, 2 950, 2 860, 1 639, 1 444, 1 365, 1 086, 1 074, 881, and 727 cm^{-1}; and alcohol (**6**) as an *oil*, (110 mg, 1%) (Found: C, 82.1; H, 9.8%); $[\alpha]_D^{18}$ −106.4° (*c* 1.25 in $CHCl_3$); δ_H 0.87 (3 H, s), 1.11 (3 H, d, *J* 7 Hz), 1.73 (6 H, br s), 2.22 (1 H, d, *J* 5 Hz), 3.21 (1 H, t, *J* 8.5 Hz), 3.38 (1 H, br m), 3.48 (1 H, dd, *J* 8.5, 3.5 Hz), 4.41 (1 H, d, *J* 12 Hz), 4.48 (1 H, d, *J* 12 Hz), 4.55 (1 H, d, *J* 5 Hz), 4.65 (1 H, m), 4.73 (1 H, m), 4.93 (1 H, d, *J* 2.5 Hz), 4.97 (1 H, d, *J* 3 Hz), and 7.27 (5 H, br s); δ_C 15.04 (q), 17.28 (q), 20.17 (q), 25.49 (t), 25.88 (q), 29.59 (t), 33.15 (t), 34.37 (d), 37.30 (t), 50.00 (d), 52.20 (s), 53.76 (d), 72.95 (t), 73.09 (t), 75.88 (d), 104.59 (t), 109.57 (t), 127.54 (d), 127.64 (d, 2 C), 128.46 (d, 2 C), 135.55 (s), 139.11 (s), 139.59 (s), 152.29 (s), and 160.74 (s); $\nu_{max.}$ 3 565, 2 950, 2 865, 1 640, 1 454, 1 369, 1 100, 890, 735, and 697 cm^{-1}.

TMS Ether (**7**) *of Compound* (**5**).—A pyridine solution (60 ml) of compound (**5**) (7.07 g) was treated with TMSCl (4.5 ml) under N_2 at 20 °C for 15 h. The mixture was then diluted with aq. $NaHCO_3$ and extracted with hexane–ether (1:1). Silica gel column chromatography of the extract with hexane–EtOAc (100:1) yielded the silyl ether (**7**) as an *oil* (8.33 g, 100%) (Found: C, 77.4; H, 10.1. $C_{30}H_{46}O_2Si$ requires: C, 77.20; H, 9.93%); $[\alpha]_D^{18}$ −152.0° (*c* 2.21 in $CHCl_3$); δ_H 0.05 (9 H, s), 1.00 (3 H, s), 1.09 (3 H, d, *J* 7 Hz), 1.60 (3 H, br s), 1.86 (3 H, br s), 3.18 (1 H, t, *J* 8.5 Hz), 3.22 (1 H, br m), 3.47 (1 H, dd, *J* 8.5, 4 Hz), 4.04 (1 H, br s), 4.42 (1 H, d, *J* 12 Hz), 4.47 (1 H, d, *J* 12 Hz), 4.63 (2 H, m), 4.86 (1 H, d, *J* 2.5 Hz), 4.89 (1 H, d, *J* 3 Hz), and 7.27 (5 H, br s); δ_C 0.39 (q, 3 C), 16.60 (q), 17.38 (q), 19.38 (q), 25.78 (t), 26.51 (q), 28.56 (t), 33.50 (t), 34.86 (d), 39.21 (t), 49.46 (d), 52.54 (s), 57.76 (d), 73.05 (t, 2 C), 77.93 (d), 106.25 (t), 111.08 (t), 127.54 (d, 3 C), 128.46 (d, 2 C), 136.77 (s), 138.33 (s), 139.11 (s), 148.77 (s), and 160.01 (s); $\nu_{max.}$ 2 955, 2 865, 1 640, 1 451, 1 368, 1 248, 1 073, 883, and 838 cm^{-1}.

Hydroboration of Alkene (**7**) *to Alcohol* (**8**) *and Further PCC Oxidation to Aldehyde* (**9**).—A THF solution (70 ml) of compound (**7**) (5.00 g) was treated with disiamylborane [prepared from 2-methylbut-2-ene (7.2 ml), $BF_3{\cdot}OEt_2$ (3.9 ml), and $NaBH_4$ (1.1 g)] at room temperature for 3.5 h and then treated with alkaline hydrogen peroxide [35% H_2O_2 (21 ml) and 3M NaOH (25 ml)] to give, after usual work-up and chromatography, alcohol (**8**) as an *oil* (4.94 g, 95%) (Found: C, 74.2; H, 9.95. $C_{30}H_{48}O_3Si$ requires: C, 74.33; H, 9.98%); $[\alpha]_D^{25}$ −6.2° (*c* 0.33 in $CHCl_3$); δ_H 0.13 (9 H, s), 0.90 (3 H, d, *J* 7 Hz), 1.03 (3 H, s), 1.08 (3 H, d, *J* 7 Hz), 1.85 (3 H, br s), 2.58 (1 H, br m), 3.19 (1 H, t, *J* 9 Hz), 3.28 (1 H, dd, *J* 11, 8.5 Hz), 3.47 (1 H, dd, *J* 9, 3 Hz), 3.61 (1 H, dd, *J* 11, 4.5 Hz), 4.23 (1 H, br s), 4.43 (1 H, d, *J* 12 Hz), 4.46 (1 H, d, *J* 12 Hz), 4.83 (1 H, d, *J* 2.5 Hz), 4.89 (1 H, d, *J* 3 Hz), and 7.27 (5 H, br s); δ_C 0.35 (q, 3 C), 16.82 (q), 17.18 (q), 17.35 (q), 23.35 (t), 25.77 (t), 27.12 (q), 33.00 (t), 34.77 (d), 37.36 (t), 39.18 (t), 49.71 (d), 52.71 (s), 53.77 (d), 64.83 (t), 73.12 (t, 2 C), 78.18 (d), 105.66 (t), 127.71 (d, 3 C), 128.48 (d, 2 C), 137.07 (s), 138.13 (s), 139.07 (s), and 160.60 (s); $\nu_{max.}$ 3 500, 2 960, 2 880, 1 640, 1 450, 1 252, 1 121, 1 070, 880, and 840 cm^{-1}.

Subsequently, a stirred CH_2Cl_2 solution (100 ml) of compound (**8**) (2.86 g) was treated with AcONa (1.3 g), Celite (2.14 g), and PCC (2.54 g) consecutively under N_2 for 6 h. The mixture was then passed through a short Florisil column, and further chromatography on a silica gel column [hexane–EtOAc (30:1)] gave aldehyde (**9**) as an *oil* (2.30 g, 81%) (Found: C, 74.4; H, 9.7. $C_{30}H_{46}O_3Si$ requires: C, 74.64; H, 9.60%); *m*/*z* 482 (M^+); $[\alpha]_D^{18}$ −25.9° (*c* 0.62 in $CHCl_3$); δ_H 0.09 (9 H, s), 0.97 (3 H, d, *J* 7 Hz), 1.05 (3 H, s), 1.09 (3 H, d, *J* 7 Hz), 1.87 (3 H, br s), 3.40 (1 H, t, *J* 8.5 Hz), 3.48 (1 H, dd, *J* 8.5, 4 Hz), 4.27 (1 H, br s), 4.43 (1 H, d, *J* 12 Hz), 4.48 (1 H, d, *J* 12 Hz), 4.87 (1 H, d, *J* 2.5 Hz), 4.90 (1 H, d, *J* 3 Hz), 7.27 (5 H, br s), and 9.68 (1 H, d, *J* 1 Hz); δ_C 0.35 (q, 3 C), 13.00 (q), 16.77 (q), 17.30 (q), 24.94 (t), 25.88 (t), 27.30 (q), 32.94 (t), 34.83 (d), 38.89 (t), 47.94 (d), 49.89 (d), 52.71 (s), 52.71 (d), 73.12 (t, 2 C), 78.34 (d), 105.77 (t), 127.66 (d, 3 C), 128.48 (d, 2 C), 135.83 (s), 139.07 (s), 139.78 (s), 160.83 (s), and 206.30 (d); $\nu_{max.}$ 2 955, 2 875, 1 725, 1 645, 1 476, 1 251, 1 070, 881, and 840 cm^{-1}.

KF-*catalysed Epimerization of* (**9**) *to* (**10**).—An MeOH solution (75 ml) of aldehyde (**9**) (1.61 g) was treated with KF (6 g) and Florisil (6 g) at room temperature for 15 h. The mixture was then diluted with ether and solid materials were filtered off. The filtrate was diluted with water and extracted with EtOAc, and the extract was dried on K_2CO_3. The residue obtained by evaporation of the solvent was chromatographed on a silica gel column to give compound (**10**) as an *oil* (1.44 g, 90%) [94% based on the consumed aldehyde (**9**)] (Found: C, 74.7; H, 9.8. $C_{30}H_{46}O_3Si$ requires: C, 74.64; H, 9.60%); $[\alpha]_D^{18}$ −102.3° (*c* 2.17 in $CHCl_3$); δ_H 0.09 (9 H, s), 0.95 (3 H, d, *J* 7 Hz), 1.04 (3 H, s), 1.10 (3 H, d, *J* 7 Hz), 1.88 (3 H, br s), 2.67 (1 H, br qd, *J* 7, 3 Hz), 3.18 (1 H, br m), 3.20 (1 H, dd, *J* 9, 8 Hz), 3.48 (1 H, dd, *J* 9, 4 Hz), 4.09 (1 H, br s), 4.43 (1 H, d, *J* 12 Hz), 4.47 (1 H, d, *J* 12 Hz), 4.87 (1 H, d, *J* 2.5 Hz), 4.91 (1 H, d, *J* 3 Hz), 7.27 (5 H, br s), and 9.50 (1 H, br s); δ_C 0.35 (q, 3 C), 7.35 (q), 16.82 (q), 17.30 (q), 23.35 (t), 25.94 (t), 27.24 (q), 33.00 (t), 34.88 (d), 39.53 (t), 48.18 (d), 48.65 (d), 49.89 (d), 52.71 (s), 73.18 (t, 2 C), 77.89 (d), 105.71 (t), 127.66 (d, 3 C), 128.48 (d, 2 C), 134.42 (s), 139.07 (s), 139.95 (s), 160.89 (s), and 205.01 (d); $\nu_{max.}$ 2 955, 2 870, 2 700, 1 726, 1 640, 1 454, 1 249, 1 064, 884, 838, 745, 735, and 698 cm^{-1}; and some recovered aldehyde (**9**) (76 mg, 5%).

Formation of Lactol TMS Ether (**12**) via *Alcohol* (**11**) *from TMS Ether* (**10**).—A solution of compound (**10**) (1.74 g) in a

mixture of THF (200 ml) and water (50 ml) containing pyridinium toluene-*p*-sulphonate (PPTS) (5 g) was kept at room temperature for 48 h. After dilution with water, the mixture was extracted with ether and chromatographed on a silica gel column to give, from hexane–EtOAc (10:1), the alcohol (**11**) as an *oil* (1.595 g, 100%) (Found: C, 78.8; H, 9.5. $C_{27}H_{38}O_3$ requires: C, 78.98; H, 9.33%); $[\alpha]_D^{18}$ −72.1° (*c* 1.22 in $CHCl_3$); $\nu_{max.}$ 3 410, 2 950, 2 865, 1 718, 1 640, 1 452, 1 364, 1 097, 1 043, 732, and 698 cm^{-1}; the n.m.r. spectra were too complicated to be assigned due to the tautomeric nature of compound (**11**).

Subsequently, alcohol (**11**) (440 mg) was converted into the TMS ethers (**12a**), an *oil* (142 mg, 27%); (Found: C, 74.4; H, 9.5. $C_{30}H_{46}O_3Si$ requires: C, 74.64; H, 9.60%]; $[\alpha]_D^{19}$ +14.6° (*c* 2.26 in $CHCl_3$); δ_H 0.12 (9 H, s), 0.78 (3 H, d, *J* 7 Hz), 1.10 (3 H, d, *J* 7 Hz), 1.12 (3 H, s), 1.60 (3 H, br s), 2.6 (2 H, m), 3.25 (1 H, t, *J* 8.5 Hz), 3.53 (1 H, dd, *J* 8.5, 4 Hz), 4.39 (1 H, br s), 4.43 (1 H, d, *J* 12 Hz), 4.48 (1 H, d, *J* 12 Hz), 4.82 (1 H, d, *J* 2.5 Hz), 4.86 (1 H, d, *J* 3 Hz), 4.98 (1 H, d, *J* 3 Hz), and 7.27 (5 H, br s); δ_C 0.20 (q, 3 C), 14.75 (q), 17.09 (q), 18.31 (q), 25.59 (t), 26.22 (q), 26.76 (t), 34.52 (t), 36.33 (d), 40.48 (t), 45.70 (d), 47.46 (d), 48.63 (s), 50.20 (d), 73.14 (t), 73.44 (t), 73.78 (d), 95.41 (d), 106.39 (t), 127.54 (d), 127.68 (d, 2 C), 127.68 (s), 128.46 (d, 2 C), 131.45 (s), 139.06 (s), and 159.08 (s); $\nu_{max.}$ 2 960, 2 880, 1 642, 1 454, 1 367, 1 252, 1 002, 894, and 840 cm^{-1}; and (**12b**), an *oil* (327 mg, 62%) (Found: C, 74.4; H, 9.55%); $[\alpha]_D^{18}$ −73.0° (*c* 2.37 in $CHCl_3$); δ_H 0.16 (9 H, s), 0.86 (3 H, d, *J* 7 Hz), 1.11 (3 H, d, *J* 7 Hz), 1.18 (3 H, s), 1.60 (3 H, br s), 2.60 (1 H, br m), 3.27 (1 H, dd, *J* 9, 8 Hz), 3.52 (1 H, dd, *J* 9, 4 Hz), 3.88 (1 H, br s), 4.38 (1 H, d, *J* 8 Hz), 4.43 (1 H, d, *J* 12 Hz), 4.45 (1 H, d, *J* 12 Hz), 4.83 (1 H, d, *J* 2.5 Hz), 4.85 (1 H, d, *J* 3 Hz), and 7.26 (5 H, br s); δ_C 0.41 (q, 3 C), 14.71 (q), 16.94 (q), 18.06 (q), 25.77 (t), 26.65 (q), 27.00 (t), 34.30 (t), 36.36 (d), 40.94 (t), 47.71 (d, 2 C), 49.00 (s), 55.42 (d), 73.12 (t), 73.42 (t), 81.65 (d), 102.42 (d), 106.01 (t), 127.54 (d), 127.66 (d, 2 C), 128.42 (d, 2 C), 128.95 (s), 131.19 (s), 139.07 (s), and 159.36 (s); $\nu_{max.}$ 2 955, 2 925, 1 642, 1 454, 1 248, 1 045, 880, and 840 cm^{-1}.

Cope Rearrangement of Compound (**12a**) *to Isomers* (**13a**) *and* (**13b**).—(*a*) A toluene solution (4.9 ml) of compound (**12a**) (98 mg) was heated in a sealed tube at 190 °C for 24 h. Silica gel column chromatography of the mixture gave the isomers (**13a**) and (**13b**) (4:1) as an *oil* (47 mg, 48%) [Found: C, 74.5; H, 9.6 (mixture). $C_{30}H_{46}O_3Si$ requires: C, 74.64; H, 9.60%]; *m/z* 482 (M^+); δ_H (**13a**) 0.12 (9 H, s), 0.94 (3 H, d, *J* 7 Hz), 1.02 (3 H, d, *J* 7 Hz), 1.12 (3 H, s), 1.57 (3 H, br s), 2.80 (1 H, br m), 3.10 (1 H, t, *J* 9 Hz), 3.27 (1 H, dd, *J* 9, 4 Hz), 4.40 (1 H, d, *J* 12 Hz), 4.44 (1 H, d, *J* 12 Hz), 5.07 (1 H, d, *J* 2.5 Hz), 6.04 (1 H, d, *J* 3 Hz), and 7.28 (5 H, br s); δ_H (**13b**) 0.19 (9 H, s), 0.97 (3 H, d, *J* 7 Hz), 1.03 (3 H, d, *J* 7 Hz), 1.09 (3 H, s), 1.57 (3 H, br s), 2.78 (1 H, br m), 3.10 (1 H, t, *J* 9 Hz), 3.26 (1 H, dd, *J* 9, 4 Hz), 4.40 (1 H, d, *J* 12 Hz), 4.44 (1 H, d, *J* 12 Hz), 4.78 (1 H, d, *J* 8 Hz), 6.17 (1 H, d, *J* 3 Hz), and 7.27 (5 H, br s); $\nu_{max.}$ 2 960, 1 675, 1 455, 1 372, 1 255, 1 085, 1 015, 962, 937, 842, 735, and 698 cm^{-1}; together with liberated aldehyde (**13c**) as an oily *mixture* of epimers at C-15 (31 mg, 32%) (5:3) (Found: C, 74.8; H, 9.8%); δ_H 0.81 (9 H, s), 1.01 (3 H, d, *J* 7 Hz), 1.04 and 1.08 (5:3; 3 H, d, *J* 7 Hz), 1.09 (3 H, s), 3.12 (1 H, t, *J* 9 Hz), 3.27 (1 H, dd, *J* 9, 3.5 Hz), 4.37 (1 H, d, *J* 12 Hz), 4.47 (1 H, d, *J* 12 Hz), 5.97 and 6.04 (5:3; 1 H, d, *J* 2.5 Hz), 7.30 (5 H, br s), and 9.68 and 9.71 (5:3; 1 H, d, *J* 2 Hz); $\nu_{max.}$ 2 955, 2 870, 2 700, 1 728, 1 667, 1 454, 1 155, 1 111, 844, and 695 cm^{-1}.

(*b*) Similarly, a toluene solution (10.4 ml) of compound (**12b**) (208 mg) was heated in a sealed tube at 180 °C for 24 h to give compounds (**13a**) and (**13b**) (3:2; 150 mg, 72%).

PPTS Hydrolysis of Compound (**13**) *to Alcohol* (**14**) *and its Reduction to Diol* (**15**).—A mixture of compounds (**13**) (613 mg) was hydrolysed in THF (15 ml) and water (4 ml) with PPTS (200 mg) at room temperature for 15 h. The mixture was diluted with water, extracted with ether, and chromatographed on a silica gel column to give an oily epimeric mixture of lactol (**14**) (507 mg, 97%), of which the β-anomer was crystallized from hexane as *prisms*, m.p. 81—83 °C (Found: C, 78.9; H, 9.3. Calc. for $C_{27}H_{38}O_3$; C, 78.98; H, 9.33%); $\nu_{max.}$ 3 380, 2 955, 2 875, 1 673, 1 453, 1 119, 736, and 693 cm^{-1}.

Then, an MeOH solution (30 ml) of alcohol (**14**) (998 mg) was treated with a mixture of aq. $NaHCO_3$ (8 ml) and $NaBH_4$ (260 mg) at 0—5 °C for 1 h. The mixture was then diluted with water, extracted with EtOAc, and the extract was dried over K_2CO_3. Silica gel chromatography of the extract gave diol (**15**) as an *oil* (985 mg, 95%) (Found: C, 78.0; H, 10.4. $C_{27}H_{42}O_3$ requires: C, 78.21; H, 10.21%); $[\alpha]_D^{21}$ −22.7° (*c* 1.32 in $CHCl_3$); δ_H 0.84 (3 H, s), 0.91 (3 H, d, *J* 7 Hz), 1.02 (3 H, d, *J* 7 Hz), 1.60 (3 H, br s), 2.72 (1 H, br m), 3.10 (1 H, t, *J* 9 Hz), 3.25 (1 H, dd, *J* 9, 4.5 Hz), 3.41 (1 H, dd, *J* 11, 5 Hz), 3.44 (1 H, dd, *J* 10.5, 8.5 Hz), 3.66 (1 H, dd, *J* 11, 4 Hz), 3.72 (1 H, dd, *J* 10.5, 5 Hz), 4.40 (1 H, d, *J* 12 Hz), 4.43 (1 H, d, *J* 12 Hz), and 7.25 (5 H, br s); δ_C 13.82 (q), 15.09 (q), 17.04 (q), 21.92 (q), 23.58 (t), 25.73 (t), 37.26 (t, 2 C), 34.72 (d), 39.60 (d), 39.60 (t), 43.41 (d), 46.44 (s), 51.22 (d), 53.12 (d), 64.26 (t), 66.41 (t), 72.41 (t), 73.09 (t), 127.49 (d), 127.59 (d, 2 C), 128.37 (d, 2 C), 135.16 (s), 135.49 (s), and 138.87 (s); $\nu_{max.}$ 3 310, 2 955, 1 454, 1 372, 1 048, 730, and 695 cm^{-1}.

Selective Esterification of Diol (**15**) *by Pivaloyl Chloride to give Monoester* (**16b**).—A CH_2Cl_2 solution (10 ml) of diol (**15**) (588 mg), Et_3N (0.2 ml), and 4-(dimethylamino)pyridine (DMAP) (20 mg) was treated with Me_3CCOCl (0.17 ml) at 0 °C. The mixture was then treated with aq. $NaHCO_3$ and extracted with ether. The residue obtained by removal of the solvent was chromatographed on a silica gel column to give mono ester (**16b**) as an *oil* (339 mg, 48%) (Found; C, 77.0; H, 10.1. $C_{32}H_{50}O_4$ requires; C, 77.06; H, 10.10%); $[\alpha]_D^{15}$ −16.3° (*c* 1.53 in $CHCl_3$); δ_H 0.89 (3 H, d, *J* 7 Hz), 0.90 (3 H, s), 1.02 (3 H, d, *J* 7 Hz), 1.19 (9 H, s), 1.61 (3 H, br s), 3.10 (1 H, dd, *J* 9, 8 Hz), 3.27 (1 H, dd, *J* 9, 4.5 Hz), 3.55 (1 H, dd, *J* 11, 6 Hz), 3.70 (1 H, dd, *J* 11, 6 Hz), 3.83 (1 H, dd, *J* 11, 6.5 Hz), 3.97 (1 H, dd, *J* 11, 6.5 Hz), 4.40 (1 H, d, *J* 12 Hz), 4.44 (1 H, d, *J* 12 Hz), and 7.28 (5 H, br s); δ_C 11.72 (q), 15.04 (q), 16.94 (q), 21.97 (q), 23.68 (t, 2 C), 27.15 (q, 3 C), 34.67 (d), 35.11 (d), 37.16 (t), 37.60 (t), 38.72 (s), 39.60 (t), 43.16 (d), 46.04 (s), 51.90 (d), 53.03 (d), 63.82 (t), 69.04 (t), 72.36 (t), 73.00 (t), 127.39 (d), 127.49 (d, 2 C), 128.27 (d, 2C), 135.30 (s, 2 C), 138.87 (s), and 178.66 (s); $\nu_{max.}$ 3 460, 2 955, 1 728, 1 455, 1 283, 1 160, 736, and 698 cm^{-1}; together with dipivaloate (**16a**) (62 mg, 8%) (Found: C, 76.2; H, 10.0. $C_{37}H_{58}O_5$ requires: C, 76.25; H, 10.03%); *m/z* 582 (M^+); δ_H 0.86 (3 H, d, *J* 7 Hz), 0.89 (3 H, s), 1.02 (3 H, d, *J* 7 Hz), 1.19 (18 H, s), 1.59 (3 H, br s), 2.69 (1 H, br m), 3.10 (1 H, t, *J* 9 Hz), 3.45 (1 H, dd, *J* 9, 4 Hz), 3.8—4.1 (4 H, m), 4.39 (1 H, d, *J* 12 Hz), 4.43 (1 H, d, *J* 12 Hz), and 7.28 (5 H, br s); $\nu_{max.}$ 2 960, 1 728, 1 481, 1 453, 1 280, 1 145, 733, and 696 cm^{-1}; and an isomeric monoester (**16c**) as an *oil* (249 mg, 35%) (Found: C, 76.8; H, 10.0. $C_{32}H_{50}O_4$ requires: C, 77.06; H, 10.10%); δ_H 0.84 (3 H, d, *J* 7 Hz), 0.91 (3 H, s), 1.03 (3 H, d, *J* 7 Hz), 1.19 (9 H, s), 1.60 (3 H, br s), 2.70 (1 H, br m), 3.10 (1 H, t, *J* 9 Hz), 3.44 (1 H, dd, *J* 9, 4.5 Hz), 3.98 (1 H, dd, *J* 11, 5.5 Hz), 4.08 (1 H, dd, *J* 11, 3 Hz), 4.40 (1 H, d, *J* 12 Hz), 4.42 (1 H, d, *J* 12 Hz), and 7.26 (5 H, br s); $\nu_{max.}$ 3 430, 2 955, 1 727, 1 481, 1 455, 1 282, 1 157, 734, and 698 cm^{-1}; and recovered diol (**15**) (33 mg, 6%). A mixture of esters (**16a**) and (**16c**), obtained as undesired by-products, was reduced with LAH (50 mg) in THF (5 ml) at 0 °C for 1 h. Usual work-up afforded diol (**15**) (246 mg, 98%). Using the combined recovered quantities of diol (**15**), the procedure was repeated twice to give the required monoester (**16b**) [573 mg, 89%; 91% conversion of diol (**15**)].

Chloroacetate (**17**) *of* (**16b**).—A CH_2Cl_2 solution (5 ml) of monoester (**16b**) (682 mg) and pyridine (0.33 ml) was treated

with $ClCH_2COCl$ (0.22 ml) at 0 °C for 30 min. The mixture was then diluted with aq. $NaHCO_3$ and extracted with hexane–EtOAc (5:1). The extract was washed successively with aq. $KHSO_4$, aq. $NaHCO_3$, and brine. Silica gel column chromatography of the extract yielded the mixed diester (**17**) as an *oil* (746 mg, 95%) (Found: C, 71.0; H, 9.0. $C_{34}H_{51}ClO_5$ requires: C, 70.99; H, 8.94%); *m/z* 574 and 576 (3:1; M^+); $[\alpha]_D^{25}$ −18.2° (*c* 2.09 in $CHCl_3$); δ_H 0.85 (3 H, d, *J* 7 Hz), 0.89 (3 H, s), 1.02 (3 H, d, *J* 7 Hz), 1.19 (9 H, s), 1.60 (3 H, br s), 2.69 (1 H, br m), 3.09 (1 H, t, *J* 9 Hz), 3.25 (1 H, dd, *J* 9, 4.5 Hz), 3.88 (2 H, m), 4.02 (2 H, s), 4.15 (2 H, m), 4.40 (1 H, d, *J* 12 Hz), 4.43 (1 H, d, *J* 12 Hz), and 7.28 (5 H, br s); δ_C 11.67 (q), 15.14 (q), 17.04 (q), 22.07 (q), 23.73 (t, 2 C), 27.20 (q, 3 C), 34.81 (d, 2 C), 37.21 (t), 37.50 (t), 38.67 (s), 39.60 (t), 40.77 (t), 43.26 (d), 46.19 (s), 48.34 (d), 53.12 (d), 67.53 (t), 68.50 (t), 72.27 (t), 73.05 (t), 127.44 (d, 3 C), 128.32 (d, 2 C), 135.01 (s), 135.74 (s), 139.06 (s), 167.23 (s), and 178.12 (s); $\nu_{max.}$ 2 955, 1 763, 1 740, 1 730, 1 482, 1 455, 1 261, 1 164, 1 150, 980, 735, and 697 cm^{-1}

Catalytic Hydrogenolysis of Ether (**17**) *to Alcohol* (**18**).—An EtOH solution (6 ml) of the benzyl ether (**17**) (355 mg) was hydrogenolysed with Pd/carbon (5%; 50 mg) at room temperature for 3 h. After removal of the catalyst by filtration, the mixture was heated under reduced pressure and the residue was chromatographed on a silica gel column to give the alcohol (**18**) as an *oil* (298 mg, 99.5%) (Found: C, 66.8; H, 9.35. $C_{27}H_{45}ClO_5$ requires: C, 66.85; H, 9.35%); *m/z* 484 and 486 (3:1; M^+); $[\alpha]_D^{18}$ −10.3° (*c* 2.23 in $CHCl_3$); δ_H 0.87 (3 H, d, *J* 7 Hz), 0.91 (3 H, s), 0.94 (3 H, d, *J* 7 Hz), 1.19 (9 H, s), 1.62 (3 H, br s), 2.72 (1 H, br m), 3.23 (1 H, br dd, *J* 11, 8 Hz), 3.49 (1 H, br dd, *J* 11, 6 Hz), 3.89 (2 H, m), 4.05 (2 H, s), and 4.15 (2 H, m); δ_C 11.62 (q), 15.14 (q), 16.50 (q), 22.17 (q), 23.34 (t), 23.73 (t), 27.20 (q, 3 C), 34.77 (d), 37.06 (d), 37.30 (t), 37.50 (t), 38.77 (s), 39.70 (t), 40.87 (t), 43.36 (d), 46.24 (s), 48.29 (d), 53.17 (d), 64.50 (t), 67.68 (t), 68.65 (t), 135.53 (s), 136.03 (s), 167. 52 (s), and 178.56 (s); $\nu_{max.}$ 3 430, 2 955, 1 764, 1 742, 1 722, 1 452, 1 280, 1 164, 1 145, 1 023, 978, and 788 cm^{-1}.

Swern Oxidation of Alcohol (**18**) *to Aldehyde* (**19**).—To a CH_2Cl_2 solution (8 ml) of $(COCl)_2$ (0.15 ml) at −80 °C was added dropwise a CH_2Cl_2 solution (0.5 ml) of DMSO (0.24 ml) and the mixture was stirred at −80 to −70 °C for 15 min. To this mixture was added a CH_2Cl_2 solution (4 ml) of alcohol (**18**) (522 mg). After the mixture had been stirred for 30 min at −70 to −60 °C, Et_3N (1.5 ml) was added and the mixture was gradually warmed to −10 °C. The mixture was then diluted with aq. $NaHCO_3$ and extracted with ether. The extract was chromatographed on a silica gel column to give aldehyde (**19**) as an *oil* (499 mg, 95%) (Found: 67.2; H, 8.95. $C_{27}H_{43}ClO_5$ requires: C, 67.13; H, 8.97%); $[\alpha]_D^{16}$ −43.3° (*c* 1.94 in $CHCl_3$); δ_H 0.88 (3 H, d, *J* 7 Hz), 0.92 (3 H, s), 1.02 (3 H, d, *J* 7 Hz), 1.19 (9 H, s), 1.63 (3 H, br s), 2.66 (1 H, qdd, *J* 7, 4, 1 Hz), 3.01 (1 H, br m), 3.89 (2 H, m), 4.07 (2 H, s), 4.17 (2 H, br d, *J* 5.5 Hz), and 9.58 (1 H, d, *J* 1 Hz); δ_C 11.65 (q, 2 C), 15.18 (q), 22.00 (q), 23.65 (t), 25.30 (t), 27.18 (q, 3 C), 34.83 (d), 37.12 (t), 37.77 (t), 38.77 (s), 39.65 (t), 40.83 (t), 43.18 (d), 46.42 (s), 48.30 (d), 48.65 (d), 51.89 (d), 67.42 (t), 68.48 (t), 133.77 (s), 137.60 (s), 167.36 (s), 178.19 (s) and 205.60 (d); $\nu_{max.}$ 2 950, 2 720, 1 760, 1 722, 1 480, 1 455, 1 280, 1 165, 1 148, and 982 cm^{-1}.

TMS Etherification of Aldehyde (**19**) *to TMS Vinyl Ether* (**20**).—A CH_2Cl_2 solution (5 ml) of aldehyde (**19**) (318 mg) was treated with CF_3SO_3TMS (0.22 ml) in the presence of Et_3N (0.18 ml) at 0 °C for 48 h. The mixture was poured into aq. $NaHCO_3$ and extracted with hexane–EtOAc (20:1). The extract was chromatographed on a Florisil column to give compound (**20**) as an *oil* (358 mg, 98%) (an isomeric mixture, *E*:*Z* 5:2) (Found: C, 65.1; H, 9.3. $C_{30}H_{51}ClO_5Si$ requires: C, 64.89; H, 9.26%); δ_H 0.15 and 0.17 (2:5; 9 H, s), 0.87 (3 H, d, *J* 7 Hz), 0.87 (3 H, s), 1.19 (9 H, s), 1.47 and 1.55 (2:5; 3 H, d, *J* 1 Hz), 1.64 (3 H, br s), 3.14 (1 H, br m), 3.88 (2 H, m), 4.03 (2 H, s), 4.13 (2 H, m), and 6.01 (1 H, m); $\nu_{max.}$ 2 955, 1 766, 1 732, 1 658, 1 481, 1 281, 1 252, 1 156, 880, and 842 cm^{-1}.

$Pd(OAc)_2$ *Oxidation of Vinyl Ether* (**20**) *to Enal* (**21**).—A CH_3CN solution (5 ml) of the silylvinyl ether (**20**) (580 mg) was treated with $Pd(OAc)_2$ (280 mg) at room temperature for 12 h. The mixture was diluted with hexane–EtOAc (2:1) and metallic solid was removed by filtration. The filtrate was washed with aq. $NaHCO_3$ and dried over $MgSO_4$. The residue obtained by evaporation of the solvent under reduced pressure was chromatographed on a silica gel column to give enal (**21**) as *needles* (470 mg, 94%), m.p. 55—55.5 °C (Found: C, 67.2; H, 8.55. $C_{27}H_{41}ClO_5$ requires: C, 67.41; H, 8.59%); *m/z* 480 and 482 (3:1; M^+); $[\alpha]_D^{22}$ +5° (*c* 2.19 in $CHCl_3$); δ_H 0.85 (3 H, s), 0.86 (3 H, d, *J* 7 Hz), 1.19 (3 H, s), 1.71 (3 H, br s), 3.76 (1 H, br m), 3.88 (2 H, m), 4.02 (2 H, s), 4.12 (2 H, m), 5.96 (2 H, m), and 9.58 (1 H, s); δ_C 11.56 (q), 15.16 (q), 21.97 (q), 23.54 (t), 27.21 (q, 3 C), 30.31 (t), 34.66 (d), 36.44 (t), 38.06 (t), 38.80 (s), 39.67 (t), 40.82 (t), 43.34 (d), 45.87 (s), 47.07 (d), 48.32 (d), 67.69 (t), 68.55 (t), 133.43 (s), 133.80 (t), 138.50 (s), 152.67 (s), 167.29 (s), 178.47 (s), and 194.90 (d); $\nu_{max.}$ 2 950, 1 755, 1 726, 1 680, 1 308, 1 280, 1 160, 983, and 972 cm^{-1}.

Reduction of Enal (**21**) *with* $NaBH_4$ *and* $CeCl_3$ *to Allyl Alcohol* (**22**).—To an MeOH solution (4 ml) of enal (**21**) (156 mg) were added $CeCl_3 \cdot 7H_2O$ (100 mg) and $NaBH_4$ (10 mg) and the mixture was stirred for 10 min at 0 °C. Further additions of the reagents were repeated 5 times after every 10 min. The mixture was then diluted with 0.5M HCl and extracted with EtOAc. Silica gel column chromatography of the extract afforded allyl alcohol (**22**) as an *oil* (122 mg, 93%) (Found: C, 73.7; H, 10.55. $C_{25}H_{42}O_4$ requires: C, 73.85; H, 10.41%); *m/z* 406 (M^+); $[\alpha]_D^{21}$ +22.8° (*c* 1.62 in $CHCl_3$); δ_H 0.88 (3 H, s), 0.89 (3 H, d, *J* 7 Hz), 1.20 (9 H, s), 1.68 (3 H, br s), 3.42 (1 H, br m), 3.49 (1 H, br dd, *J* 11, 5.5 Hz), 3.67 (1 H, br dd, *J* 11, 6 Hz), 3.79 (1 H, dd, *J* 11, 7 Hz), 4.01 (2 H, s), 4.02 (1 H, br dd, *J* 11, 5.5 Hz), 4.71 (1 H, br s), and 5.00 (1 H, m); δ_C 12.35 (q), 15.10 (q), 21.71 (q), 24.23 (t), 27.23 (q, 3 C), 29.30 (t), 35.62 (d), 36.92 (t), 38.57 (t), 38.85 (s), 40.72 (t), 43.77 (d), 45.72 (s), 51.98 (d), 53.35 (d), 64.38 (t), 64.72 (t), 69.00 (t), 109.26 (t), 134.70 (s), 136.96 (s), 151.54 (s), and 178.81 (s); $\nu_{max.}$ 3 350, 2 950, 1 720, 1 481, 1 457, 1 283, 1 160, 1 030, and 896 cm^{-1}.

Swern Oxidation of Allyl Alcohol (**22**) *to Dial* (**23**).—In a similar manner as the conversion of (**18**) into (**19**), allyl alcohol (**22**) (122 mg) was converted, using $(COCl)_2$ (0.06 ml), DMSO (0.1 ml), and Et_3N (0.75 ml), into dial (**23**), which was obtained as an *oil* (103 mg, 93%) (Found: C, 74.1; H, 9.5. $C_{25}H_{38}O_4$ requires: C, 74.59; H, 9.51%); $[\alpha]_D^{21}$ −21.1° (*c* 1.61 in $CHCl_3$); δ_H 0.88 (3 H, d, *J* 7 Hz), 0.96 (3 H, s), 1.19 (9 H, s), 1.75 (3 H, br s), 3.76 (1 H, dd, *J* 11, 6.5 Hz), 3.77 (1 H, br m), 3.93 (1 H, dd, *J* 11, 6 Hz), 5.98 (2 H, m), 9.59 (1 H, s), and 9.65 (1 H, d, *J* 3 Hz); δ_C 13.53 (q), 15.26 (q), 23.12 (q), 25.73 (t), 27.18 (q, 3 C), 30.21 (t), 36.03 (d), 36.49 (t), 38.13 (t), 38.79 (s), 40.07 (t), 40.34 (d), 47.05 (d), 48.93 (s), 62.88 (d), 67.82 (t), 132.74 (s), 133.88 (t), 139.36 (s), 152.46 (s), 178.27 (s), 194.77 (d), and 204.92 (d); $\nu_{max.}$ 2 960, 2 710, 1 728, 1 695, 1 618, 1 482, 1 456, 1 283, and 1 157 cm^{-1}.

$TiCl_2$*-Mediated Cyclization of Dial* (**23**) *to Glycol* (**24**).—To a mixture of $TiCl_2$ [prepared from $TiCl_4$ (0.28 ml) and Zn dust (350 mg)] and pyridine (0.21 ml) in THF (50 ml) was added dropwise a THF solution (30 ml) of compound (**23**) (103 mg) at room temperature during 3 h. The mixture was then treated with aq. K_2CO_3 and extracted with hexane–EtOAc (5:1). The extract was chromatographed on a silica gel column to give the

glycol (**24**) as an *oil* (99 mg, 96%) (Found: C, 74.1; H, 10.1. $C_{25}H_{40}O_4$ requires: C, 74.22; H, 9.96%); $[\alpha]_D^{22}$ +74.7° (*c* 0.91 in $CHCl_3$); δ_H 0.81 (3 H, s), 0.83 (3 H, d, *J* 6.5 Hz), 1.20 (9 H, s), 1.64 (3 H, br s), 3.23 (1 H, br m), 3.64 (1 H, dd, *J* 8.5, 8 Hz), 3.77 (1 H, d, *J* 8.5 Hz), 3.86 (1 H, dd, *J* 10.5, 7.5 Hz), 3.92 (1 H, dd, *J* 10.5, 7.5 Hz), 5.04 (1 H, br s), and 5.27 (1 H, br s); δ_C 10.42 (q), 14.69 (q), 21.24 (q), 21.57 (t), 27.24 (q, 3 C), 32.11 (t), 36.03 (d), 37.28 (t), 38.70 (t), 38.80 (s), 41.34 (d), 43.99 (s), 45.76 (t), 50.47 (d), 50.88 (d), 69.46 (t), 74.94 (d), 80.80 (d), 115.59 (t), 134.73 (s), 136.44 (s), 151.56 (s), and 178.83 (s); $\nu_{max.}$ 3 475, 2 955, 1 727, 1 705, 1 644, 1 481, 1 283, 1 165, 1 035, and 904 cm^{-1}.

Diacetate (**25**) *of Glycol* (**24**).—A pyridine solution (2 ml) of glycol (**24**) (126 mg) and DMAP (10 mg) was treated with Ac_2O (0.15 ml) at 0 °C for 2 h. The mixture was then diluted with aq. $NaHCO_3$ and extracted with hexane–EtOAc (10:1). Silica gel column chromatography of the extract gave diacetate (**25**) as an *oil* (142 mg, 93%) (Found: C, 71.1; H, 9.3. $C_{29}H_{44}O_6$ requires: C, 71.28; H, 9.08%); *m/z* 488 (M^+); $[\alpha]_D^{25}$ +76.8° (*c* 0.69 in $CHCl_3$); δ_H 0.86 (3 H, d, *J* 7 Hz), 0.89 (3 H, s), 1.20 (9 H, s), 1.66 (3 H, br s), 2.00 (3 H, s), 2.06 (3 H, s), 3.26 (1 H, br m), 3.70 (1 H, dd, *J* 10.5, 9 Hz), 3.96 (1 H, dd, *J* 10.5, 6 Hz), 5.14 (1 H, br s), 5.20 (1 H, d, *J* 9 Hz), 5.40 (1 H, t, *J* 9 Hz), and 5.43 (1 H, br s); δ_C 10.45 (q), 14.80 (q), 20.64 (q), 21.15 (q), 21.26 (q), 21.33 (t), 27.38 (q, 3 C), 32.72 (t), 35.37 (d), 37.30 (t), 38.63 (t), 38.93 (s), 42.90 (d), 44.53 (s), 45.83 (t), 49.67 (d), 49.94 (d), 69.35 (t), 74.10 (d), 80.57 (d), 119.08 (t), 135.27 (s), 135.99 (s), 146.44 (s), 169.98 (s), 170.56 (s), and 178.56 (s); $\nu_{max.}$ 2 955, 1 740, 1 730, 1 646, 1 481, 1 371, 1 240, 1 150, and 1 021 cm^{-1}.

Birch Reduction of Diacetate (**25**) *to give Compounds* (**26**)—(**29**).—Li metal (50 mg) was dissolved in a mixture of liq. NH_3 (20 ml) and THF (15 ml) at −78 °C. Into this blue-coloured solution was added a THF solution (5 ml) of diacetate (**25**) (137 mg) together with EtOH (0.5 ml). After the mixture had been stirred for 1 h at −78 °C, an excess of NH_4Cl (solid) was added and NH_3 was removed in a hood. The residue was diluted with aq. NH_4Cl and extracted with ether. Silica gel column chromatography of the extract afforded a mixture of dienols (**26**)—(**28**), and a diol (**29**) as an *oil* (3 mg, 4%) (Found: C, 78.7; H, 10.8. $C_{20}H_{32}O_2$ requires: C, 78.90; H, 10.84%); *m/z* 304 (M^+); δ_H 0.78 (3 H, s), 0.84 (3 H, d, *J* 6.5 Hz), 1.59 (3 H, br s), 1.62 (3 H, d, *J* 1 Hz), 2.39 (1 H, d, *J* 14.5 Hz), 3.35 (1 H, dd, *J* 10.5, 8.5 Hz), 3.51 (1 H, dd, *J* 10.5, 5.5 Hz), 3.57 (1 H, br, m), 4.58 (1 H, dd, *J* 9.5, 7.5 Hz), and 5.38 (1 H, br d, *J* 7.5 Hz); δ_C 10.97 (q), 14.59 (q), 18.08 (q), 20.06 (q), 21.67 (t), 25.66 (t), 37.19 (t), 37.34 (t), 39.02 (d), 39.78 (d), 44.15 (s), 44.23 (t), 50.39 (d), 59.31 (d), 67.63 (t), 69.98 (d), 133.18 (d), 133.91 (s), 134.37 (s), and 136.37 (s); $\nu_{max.}$ 3 335, 2 955, 2 920, 1 450, 1 380, and 1 037 cm^{-1}.

The mixture of products (**26**)—(**28**) was separated by high-pressure liquid chromatography (h.p.l.c.) [Micropolasil/hexane–EtOAc (25:2)] to give the required dienol (**26**) as an *oil* (61 mg, 76%) (Found: C, 83.4; H, 11.4. $C_{20}H_{32}O$ requires: C, 83.27; H, 11.18%); *m/z* 288 (M^+); $[\alpha]_D^{25}$ +218° (*c* 1.61 in $CHCl_3$); δ_H 0.71 (3 H, s), 0.83 (3 H, d, *J* 7 Hz), 1.57 (3 H, br s), 1.64 (3 H, br s), 2.06 (1 H, ddd, *J* 14, 10.5, 9.5 Hz), 2.26 (2 H, br m), 2.39 (1 H, d, *J* 14.5 Hz), 3.46 (2 H, d, *J* 7 Hz), 3.70 (1 H, br m), and 5.47 (1 H, br t, *J* 7.5 Hz); δ_C 10.41 (q), 14.66 (q), 17.25 (q), 20.17 (q), 20.17 (t), 24.62 (t), 25.54 (t), 35.92 (d), 37.42 (t), 37.54 (t), 42.42 (d), 42.50 (t), 44.39 (s), 49.27 (d), 54.63 (d), 68.10 (t), 126.50 (d), 133.19 (s), 136.87 (s), and 137.12 (s); $\nu_{max.}$ 3 330, 2 950, 2 870, 1 658, 1 450, 1 381, 1 042, 1 020, and 837 cm^{-1}; dienol (**27**) as an *oil* (8 mg, 10%) (Found: M^+, 288.2454. $C_{20}H_{32}O$ requires: *M*, 288.2452); δ_H 0.74 (3 H, d, *J* 6.5 Hz), 0.84 (3 H, s), 1.63 (3 H, br s), 3.11 (1 H, br m), 3.42 (2 H, br d, *J* 7 Hz), 4.80 (1 H, m), and 4.83 (1 H, br t, *J* 1.5 Hz); $\nu_{max.}$ 3 360, 2 920, 2 870, 1 445, 1 380, 1 040, and 895 cm^{-1}; and dienol (**28**) as an *oil* (6 mg, 7%) (Found: M^+, 288.2454); δ_H 0.80 (3 H, s), 0.87 (3 H, d, *J* 7 Hz), 1.13 (3 H, d, *J* 7.5 Hz), 1.71 (3 H, br s), 2.18 (1 H, ddd, *J* 11, 9.5, 1 Hz), 2.39 (1 H, d, *J* 13.5 Hz), 2.52 (1 H, dqd, *J* 9, 7.5, 4.5 Hz), 2.66 (1 H, br m), 3.46 (1 H, dd, *J* 10.5, 6.5 Hz), 3.54 (1 H, dd, *J* 10.5, 5.5 Hz), 5.32 (1 H, dd, *J* 11, 9.5 Hz), and 5.86 (1 H, ddd, *J* 11, 9, 1 Hz); $\nu_{max.}$ 3 320, 2 955, 2 925, 2 870, 1 452, 1 376, 1 035, 1 024, and 718 cm^{-1}.

Attempted Reduction of Diol (**29**) via *its Diacetate* (**30**).—A pyridine solution (0.5 ml) of diol (**29**) (29 mg) was treated with Ac_2O (0.3 ml) at room temperature for 12 h. The mixture was then diluted with aq. $NaHCO_3$ and extracted with hexane–EtOAc (3:1). The extract was purified by silica gel column chromatography to give diacetate (**30**) as an *oil* (37 mg, 99.5%) (Found: C, 74.3; H, 9.5. $C_{24}H_{36}O_4$ requires: C, 74.19; H, 9.34%); *m/z* 388 (M^+); δ_H 0.84 (3 H, s), 0.87 (3 H, d, *J* 7 Hz), 1.59 (3 H, br s), 1.63 (3 H, br s), 2.04 (3 H, s), 2.05 (3 H, s), 2.42 (1 H, d, *J* 14.5 Hz), 3.69 (1 H, br m), 3.81 (1 H, dd, *J* 11, 7 Hz), 3.89 (1 H, dd, *J* 11, 8 Hz), 5.31 (1 H, br d, *J* 7 Hz), and 5.78 (1 H, dd, *J* 10, 7 Hz); δ_C 9.98 (q), 14.56 (q), 17.97 (q), 19.96 (q), 20.98 (q, 2 C), 21.27 (t), 25.76 (t), 34.47 (d), 37.13 (t), 37.29 (t), 40.32 (d), 44.13 (s), 44.40 (t), 50.19 (d), 57.38 (d), 69.07 (t), 72.14 (d), 128.97 (d), 134.42 (s), 135.69 (s), 135.83 (s), 170.52 (s), and 171.14 (s); $\nu_{max.}$ 2 955, 1 740, 1 448, 1 372, 1 240, 1 036, and 958 cm^{-1}, which was reduced with Li in liq. NH_3–THF as described above. Although traces of compound (**26**) were detected on t.l.c., the diol (**29**) (28 mg, 97%) was recovered after chromatographic purification.

Malonate Synthesis from Dienol (**26**) *to Diester* (**32**) via *the Tosyl Derivative* (**31**).—To a pyridine solution (1 ml) of compound (**26**) (21 mg) and DMAP (5 mg) was added TsCl (40 mg) at room temperature and the solution was stirred for 6 h. The mixture was then diluted with aq. $NaHCO_3$ and extracted with hexane–EtOAc (3:1). The organic layer was successively washed with aq. $KHSO_4$, aq. $NaHCO_3$, and brine. Removal of the solvents afforded essentially pure tosyl ester (**31**) as an oil (32 mg, 100%); δ_H 0.65 (3 H, s), 0.79 (3 H, d, *J* 7 Hz), 1.55 (3 H, d, *J* 1 Hz), 1.63 (3 H, br s), 2.26 (2 H, br m), 2.35 (1 H, d, *J* 15 Hz), 2.45 (3 H, s), 3.65 (1 H, br, m), 3.83 (2 H, d, *J* 7 Hz), 5.40 (1 H, br t, *J* 8 Hz), 7.34 (2 H, dm, *J* 8 Hz), and 7.79 (2 H, dm, *J* 8 Hz).

Without further purification, compound (**31**) (32 mg) was treated with dimethyl sodiomalonate [prepared from dimethyl malonate (0.15 ml) and 55% NaH (50 mg, dispersed in an oil)] in DMF (4 ml) at 100 °C for 5 h. The mixture was then diluted with aq. $NaHCO_3$ and extracted with hexane–EtOAc (3:1). Silica gel column chromatography of the extract afforded diester (**32**) as an *oil* (24 mg, 81%) (Found: C, 74.6; H, 9.55. $C_{25}H_{38}O_4$ requires: C, 74.59; H, 9.51%); *m/z* 402 (M^+); $[\alpha]_D^{25}$ +159° (*c* 1.80 in $CHCl_3$); δ_H 0.70 (3 H, s), 0.81 (3 H, d, *J* 6.5 Hz), 1.55 (3 H, d, *J* 1 Hz), 1.63 (3 H, br s), 2.37 (1 H, d, *J* 14.5 Hz), 3.47 (1 H, t, *J* 7.5 Hz), 3.68 (1 H, br m), 3.73 (3 H, s), 3.74 (3 H, s), and 5.44 (1 H, br t, *J* 8 Hz); δ_C 13.13 (q), 14.66 (q), 17.26 (q), 19.97 (t), 20.17 (q), 24.55 (t), 25.51 (t), 30.48 (t), 35.55 (d), 37.44 (t), 37.57 (t), 42.30 (d), 44.58 (s), 45.20 (t), 49.27 (d), 49.91 (d), 52.40 (q), 52.48 (q), 54.56 (d), 126.38 (d), 133.19 (s), 136.89 (s), 137.07 (s), 170.09 (s), and 170.19 (s); $\nu_{max.}$ 2 955, 2 870, 1 758, 1 739, 1 435, 1 235, 1 148, and 833 cm^{-1}.

Decarboxylation of Diester (**32**) *to Monoester* (**33**).—A DMF solution (0.5 ml) of compound (**32**) (23.6 mg) was treated with NaCN (13 mg) at 160 °C for 30 min. The mixture was diluted with 1M HCl and extracted with EtOAc. After removal of the solvents, the residue was treated with an excess of an ethereal solution of CH_2N_2. Chromatographic purification *via* a silica gel column gave ester (**33**) as an *oil* (14.4 mg, 71%) (Found: C, 80.1; H, 10.7. $C_{23}H_{36}O_2$ requires: C, 80.18; H, 10.53%); *m/z* 344

(M^+); $[\alpha]_D^{27}$ +185° (*c* 0.78 in $CHCl_3$); δ_H 0.69 (3 H, s), 0.79 (3 H, d, *J* 6.5 Hz), 1.56 (3 H, br s), 1.63 (3 H, br s), 2.03 (1 H, ddd, *J* 13.5, 10.5, 9 Hz), 2.37 (1 H, d, *J* 13.5 Hz), 3.67 (3 H, s), 3.68 (1 H, br m), and 5.46 (1 H, br t, *J* 8.5 Hz); δ_C 13.16 (q), 14.67 (q), 17.28 (q), 20.10 (t), 20.19 (q), 24.64 (t), 25.54 (t), 31.76 (t), 32.25 (t), 32.56 (d), 37.45 (t), 37.62 (t), 42.36 (d), 44.56 (s), 45.50 (t), 49.29 (d), 51.47 (q), 54.66 (d), 126.53 (d), 133.13 (s), 136.83 (s), 137.19 (s), and 174.52 (s); $\nu_{max.}$ 2 955, 2 875, 1 743, 1 436, 1 382, and 1 170 cm^{-1}.

LAH Reduction of Ester (**33**) *to Alcohol* (**34**).—A THF solution (2 ml) of compound (**33**) (23.9 mg) was treated with LAH (5 mg) at room temperature for 30 min. The mixture was then diluted with aq. NH_4Cl and extracted with EtOAc. Silica gel column chromatography of the extract afforded alcohol (**34**) as an *oil* (22.0 mg, 100%) (Found: C, 83.4; H, 11.6. $C_{22}H_{36}O$ requires: C, 83.48; H, 11.46%); *m/z* 316 (M^+); $[\alpha]_D^{27}$ +194° (*c* 0.73 in $CHCl_3$); δ_H 0.70 (3 H, s), 0.79 (3 H, d, *J* 6.5 Hz), 1.56 (3 H, d, *J* 1 Hz), 1.63 (3 H, br s), 2.02 (1 H, ddd, *J* 13.5, 10.5, 9 Hz), 2.26 (2 H, m), 2.37 (1 H, d, *J* 15 Hz), 3.63 (2 H, t, *J* 6.5 Hz), 3.69 (1 H, br m), and 5.47 (1 H, br t, *J* 8.5 Hz); δ_C 13.72 (q), 14.93 (q), 17.56 (q), 20.37 (t), 20.44 (q), 24.90 (t), 25.80 (t), 31.33 (t), 32.62 (d), 33.00 (t), 37.71 (t), 37.91 (t), 42.64 (d), 44.82 (s), 45.94 (t), 49.54 (d), 54.93 (d), 63.68 (t), 126.90 (d), 133.32 (s), 137.01 (s), and 137.51 (s); $\nu_{max.}$ 3 350, 2 930, 2 875, 1 448, 1 382, 1 055, and 837 cm^{-1}.

Wittig Olefination of Compound (**34**) via *the Aldehyde* (**35**). *Formation of Ethyl Albolate* (**36**).—With the usual Swern oxidation conditions as described above, compound (**34**) (10.3 mg) was converted into the aldehyde (**35**) as an oil (8.2 mg, 80%): δ_H 0.70 (3 H, s), 0.81 (3 H, d, *J* 6 Hz), 1.56 (3 H, br s), 1.63 (3 H, br s), 2.04 (1 H, ddd, *J* 14, 10.5, 9 Hz), 2.26 (2 H, m), 2.38 (1 H, d, *J* 15 Hz), 2.44 (2 H, m), 3.67 (1 H, br m), 5.45 (1 H, br t, *J* 8 Hz), and 9.78 (1 H, t, *J* 2 Hz); $\nu_{max.}$ 2 955, 2 925, 2 875, 1 728, 1 448, 1 383, 1 148, and 838 cm^{-1}, which was then treated with ethyl 2-(triphenylphosphanylidene)propionate (30 mg) in refluxing benzene (1 ml) for 8 h. After removal of the solvent, the residue was chromatographed on a silica gel column to afford ethyl albolate (**36**) as an *oil* (9.7 mg, 93%) (Found: M^+, 398.3187. $C_{27}H_{42}O_2$ requires: *M*, 398.3183); $[\alpha]_D^{27}$ +153° (*c* 0.15 in $CHCl_3$); δ_H 0.70 (3 H, s), 0.80 (3 H, d, *J* 6.5 Hz), 1.29 (3 H, t, *J* 7 Hz), 1.58 (3 H, br s), 1.64 (3 H, br s), 1.84 (3 H, br s), 2.03 (1 H, m), 2.17 (2 H, m), 2.26 (2 H, m), 2.37 (1 H, d, *J* 14.5 Hz), 3.69 (1 H, br m), 4.18 (2 H, q, *J* 7 Hz), 5.47 (1 H, br t, *J* 8 Hz), and 6.75 (1 H, tm, *J* 7.5 Hz); δ_C 12.34 (q), 13.23 (q), 14.31 (q), 14.66 (q), 17.29 (q), 20.13 (q), 20.13 (t), 24.62 (t), 25.53 (t), 26.94 (t), 32.28 (d), 35.42 (t), 37.45 (t), 37.65 (t), 42.36 (d), 44.58 (s), 45.46 (t), 49.29 (d), 54.66 (d), 60.37 (t), 126.58 (d), 127.56 (s), 133.11 (s), 136.80 (s), 137.20 (s), 142.57 (s), and 168.35 (s); $\nu_{max.}$ 2 955, 2 920, 2 870, 1 713, 1 647, 1 446, 1 383, and 1 263 cm^{-1}; and its *Z*-isomer as an oil (0.4 mg, 4%) (Found: M^+, 398.3191); δ_H 0.69 (3 H, s), 0.79 (3 H, d, *J* 6 Hz), 1.30 (3 H, t, *J* 7.5 Hz), 1.57 (3 H, br s), 1.63 (3 H, br s), 1.89 (3 H, br s), 2.26 (2 H, m), 2.37 (1 H, d, *J* 14.5 Hz), 2.46 (2 H, m), 3.70 (1 H, br m), 4.20 (2 H, q, *J* 7.5 Hz), 5.46 (1 H, br t, *J* 8 Hz), and 5.91 (1 H, tm, *J* 7.5 Hz).

LAH Reduction of Ester (**36**) *to Ceroplastol II* (**1**).—A THF solution (1.5 ml) of ethyl albolate (**36**) (9.7 mg) was treated with LAH (5 mg) at 0 °C for 30 min. The mixture was then diluted with aq. NH_4Cl and extracted with hexane–EtOAc (6:1). The extract was chromatographed on a silica gel column to give ceroplastol II (**1**) as an oil (6.5 mg, 75%); *m/z* 356 (M^+); $[\alpha]_D^{27}$ +154° (*c* 0.12 in $CHCl_3$); δ_H 0.70 (3 H, s), 0.79 (3 H, d, *J* 6.5 Hz), 1.57 (3 H, br s), 1.63 (3 H, br s), 1.67 (3 H, br s), 2.05 (3 H, m), 2.26 (2 H, m), 2.37 (1 H, d, *J* 14.5 Hz), 3.69 (1 H, br m), 4.00 (2 H, br s), 5.40 (1 H, tm, *J* 7.5 Hz), and 5.47 (1 H, br t, *J* 8 Hz); $\delta_H(CCl_4)$ 0.68 (3 H, s), 0.78 (3 H, d, *J* 6.5 Hz), 1.53 (3 H, br s), 1.63 (6 H, br s), 3.64 (1 H, br m), 3.88 (2 H, br s), and 5.33 (2 H, m); δ_C 13.46 (q), 13.68 (q), 14.66 (q), 17.31 (q), 20.16 (q), 20.16 (t), 24.65 (t), 25.53 (t), 25.76 (t), 32.08 (d), 36.40 (t), 37.45 (t), 37.67 (t), 42.40 (d), 44.58 (s), 45.48 (t), 49.30 (d), 54.66 (d), 69.13 (t), 126.68 (d), 126.91 (d), 133.07 (s), 134.45 (s), 136.76 (s), and 137.27 (s); $\nu_{max.}$ 3 300, 2 970, 2 920, 2 860, 1 660, 1 448, 1 381, 1 010, and 839 cm^{-1}.

3,5-*Dinitrobenzoate* (**37**) *of Ceroplastol II* (**1**).—A pyridine solution (0.5 ml) of synthetic compound (**1**) (6.5 mg) was treated with 3,5-dinitrobenzoyl chloride (15 mg) at 0 °C for 1.5 h. The mixture was then diluted with aq. $NaHCO_3$ and extracted with hexane–EtOAc (8:1). The extract was chromatographed on a silica gel column to give the dinitrobenzoate (**37**) as needles (10 mg, 100%), m.p. 116—116.5 °C (lit.,[1] 116—118 °C); *m/z* 550 (M^+); $[\alpha]_D^{15}$ +110° (*c* 0.23 in $CHCl_3$); δ_H 0.68 (3 H, s), 0.79 (3 H, d, *J* 6.5 Hz), 1.52 (3 H, br s), 1.62 (3 H, br s), 1.77 (3 H, br s), 2.25 (2 H, m), 2.36 (1 H, d, *J* 14.5 Hz), 3.61 (1 H, br m), 4.82 (1 H, br d, *J* 11.5 Hz), 4.86 (1 H, br d, *J* 11.5 Hz), 5.35 (1 H, br t, *J* 8 Hz), 5.62 (1 H, br t, *J* 7.5 Hz), 9.15 (2 H, d, *J* 2 Hz), and 9.21 (1 H, t, *J* 2 Hz); $\nu_{max.}$ 3 120, 2 955, 2 875, 1 722, 1 625, 1 545, 1 448, 1 343, 1 292, 1 168, 1 073, 730, and 719 cm^{-1}.

Formation of Compound (**37**) *from the* 3,5-*Dinitrobenzoate* (**38**) *of Ceroplastol I*.—A refluxing acetone solution (3 ml) of natural compound (**38**) (50.8 mg) was treated with TsOH (15 mg) for 2 h. The mixture was then diluted with aq. $NaHCO_3$ and extracted with ether. The extract was chromatographed on a silica gel column to give the isomeric compound (**37**) as needles (41.8 mg, 82%), m.p. 116—116.5 °C; $[\alpha]_D^{21}$ +102.2° (*c* 0.91 in $CHCl_3$)], which was identical with the synthetic sample in every respect.

Hydrolysis of Compound (**37**) *from the Natural Source*.—A mixed solution of (**37**) [derived from the natural source (49.3 mg)] in 3M NaOH (0.5 ml) and MeOH (5 ml) was refluxed for 1 h. The mixture was then diluted with water and extracted with ether. Silica gel column chromatography of the extract gave ceroplastol II (**1**) as an oil (28.2 mg, 88%); $[\alpha]_D^{19}$ +157° (*c* 0.93 in $CHCl_3$), which was identical with the synthetic sample in every respect.

Saponification of Ethyl Albolate (**36**). *Formation of Albolic Acid* (**2**).—A mixed solution of compound (**36**) (5.0 mg) in 3M NaOH (2 ml) and MeOH (0.2 ml) was refluxed for 1 h. The mixture was acidified and then extracted with EtOAc. Silica gel column chromatography of the extract afforded albolic acid (**2**) as an oil (4.4 mg, 95%); *m/z* 370 (M^+); $[\alpha]_D^{27}$ +166° (*c* 0.21 in $CHCl_3$); δ_H 0.70 (3 H, s), 0.80 (3 H, d, *J* 6.5 Hz), 1.56 (3 H, br s), 1.63 (3 H, br s), 1.84 (3 H, br s), 2.03 (1 H, m), 2.2—2.3 (4 H, m), 2.38 (1 H, d, *J* 15 Hz), 3.69 (1 H, br m), 5.46 (1 H, br t, *J* 8 Hz), and 6.90 (1 H, tm, *J* 7.5 Hz); $\delta_H(CCl_4)$ 0.69 (3 H, s), 0.81 (3 H, d, *J* 6.5 Hz), 1.54 (3 H, br s), 1.63 (3 H, br s), 1.82 (3 H, br s), 3.64 (1 H, br m), 5.40 (1 H, br t, *J* 8 Hz), and 6.86 (1 H, br t, *J* 8 Hz); δ_C 12.05 (q), 13.38 (q), 14.66 (q), 17.29 (q), 20.14 (q), 20.14 (t), 24.62 (t), 25.53 (t), 27.16 (t), 32.28 (d), 35.25 (t), 37.45 (t), 37.64 (t), 42.36 (d), 44.59 (s), 45.46 (t), 49.30 (d), 54.66 (d), 126.56 (d), 126.65 (s), 133.13 (s), 136.81 (s), 137.20 (s), 145.45 (d), and 172.51 (s); $\nu_{max.}$ 3 000, 2 960, 2 925, 2 880, 1 688, 1 642, 1 450, 1 383, 1 276, 1 150, and 834 cm^{-1}.

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