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TERPENOIDS—X[1]

CHEMICAL CONVERSION OF ENMEIN INTO *ENANTIO*-ABIETANE AND TOTAL SYNTHESIS OF ABIETANE[2]

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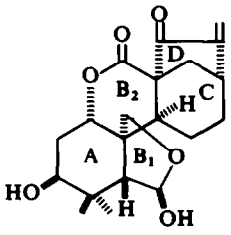
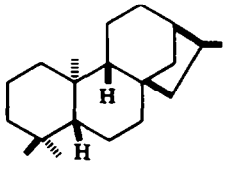
Abstract—The acyloin condensation of the lactone ester **13a** derived from enmein (**1**), a diterpenoid bitter principle from *Isodon trichocarpus* KUDO, was invesitgated. The acyloin products were converted into **33** through several steps of reactions, while abietic acid was transformed into **39**. We propose the name "abietane" for the compound **39**, hence "*enantio*-abietane" for the compound **33**. Since abietic acid has been synthesized, its conversion into abietane constitutes the total synthesis of the latter.

RECENTLY, we converted enmein (**1**), a major diterpenoid bitter principle from the leaves of *Isodon trichocarpus* KUDO (Japanese name: "Kurobana-hikiokoshi") and *I. japonicus* HARA ("Hikiokoshi"), into (−)-kaurene (**2**) as chemical evidence for the structure and absolute configuration of enmein.[4] The key reaction in the chemical conversion was the acyloin condensation with the lactone ester **3** derived from

CHART 1



1



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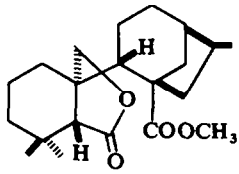
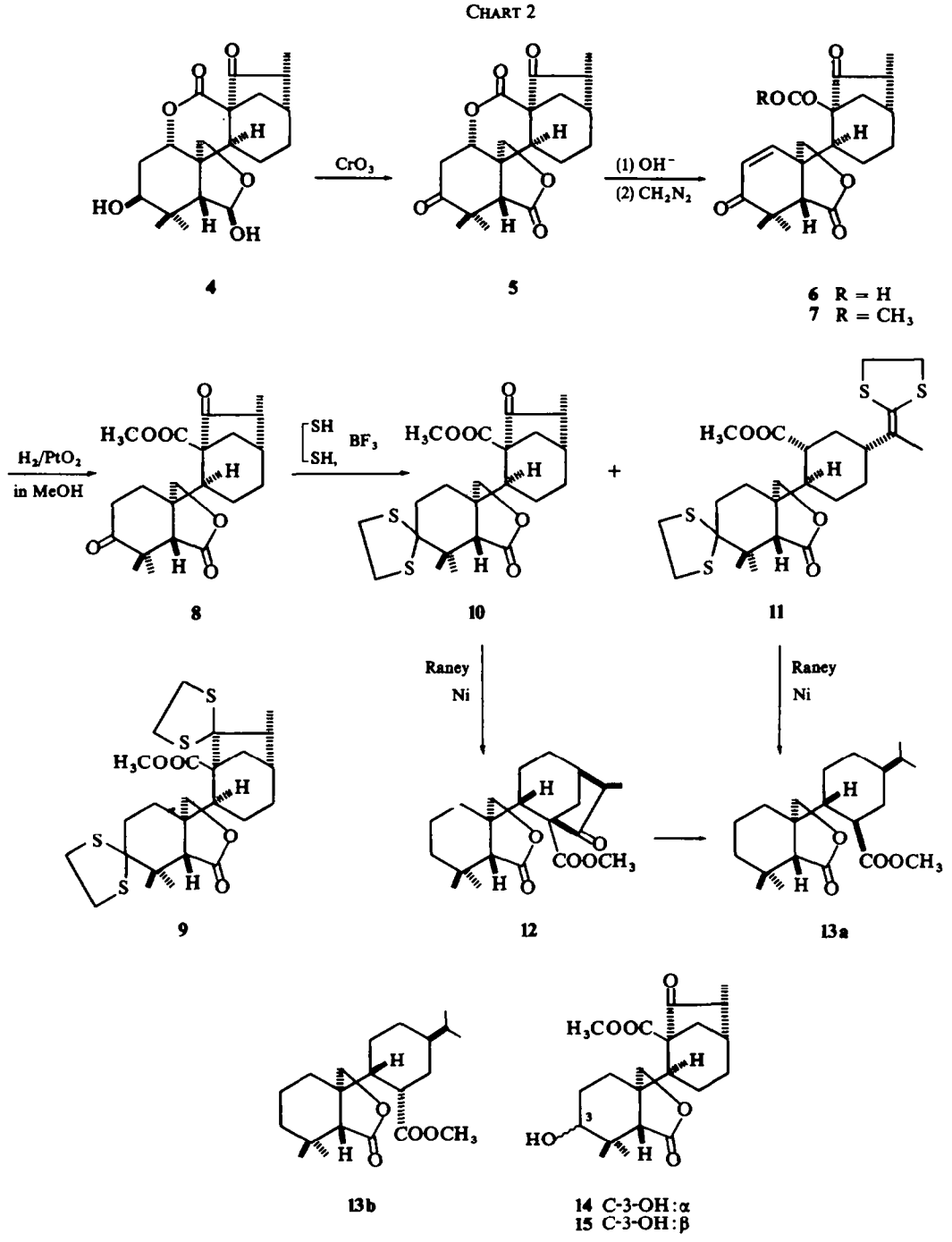


3

enmein (**1**) Dihydroenmein (**4**)[4,5] was oxidized with chromic acid to bisdehydrodihydroenmein (**5**), which was converted into enonoic acid **6**, a major product, by alkaline hydrolysis.[6] The methyl ester **7** of the latter was hydrogenated to the diketo lactone ester **8**. Thioketalization of **8** into bis(ethylene dithioketal) **9** and desulphurization of the latter with Raney nickel was attempted in order to prepare the key compound **3**, but the former reaction resulted in the formation of ethylene dithioketal **10** and undesired bis(ethylene dithioketal) **11**. On desulphurization with Raney nickel, compounds **10** and **11** gave **12** and **13a**, respectively. A further thioketalization-desulphurization of **12** gave only **13a** in a low yield, but no compound **3**. Consequently, another route was used for preparing **3**.

Before attempting to synthesize abietane from **13a**, the foregoing reactions, were checked.

CHART 2



4 **5** **6** R = H, **7** R = CH_3

8 **10** **11**

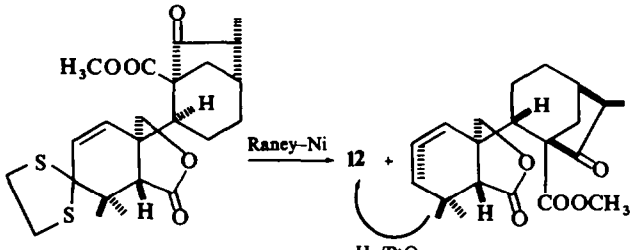
9 **12** **13a**

13b **14** C-3-OH:α, **15** C-3-OH:β

Hydrogenation of **7** on Adams' catalyst gave minor alcoholic products **14** and **15** in addition to a major product **8**. The structures of the alcohols were clarified by chromic acid oxidation into ketone **8** and also by NMR spectral analysis. In the thioketalization of **8**, easy formation of ethylene dithioketal **10**, but much more difficult formation of bis(ethylene dithioketal) **11** was observed by reexamination of the thin layer chromatograms. A mixture of **10** and **11**, on desulphurization with Raney nickel gave, **12** and **13a** in a ratio of about 6:1. Consequently, this experiment was repeated several times until sufficient **13a** was available for the following reactions. From the mother liquor after recrystallization of **13a**, compound **13b**, a C-8 epimer of **13a**, was obtained in crystalline form. On treatment with sodium methoxide followed by methylation, **13b** was easily epimerized into **13a**.[4]

Ester **7** on thioketalization[7] afforded crystalline 3-mono(ethylene dithioketal) **16** in a satisfactory yield. The latter was desulphurized with Raney nickel to a mixture of **12** and **17**, which was easily converted into a homogeneous compound **12** by catalytic hydrogenation. But, crystalline **17** could also be obtained by column chromatography and was subsequently characterized.

CHART 3

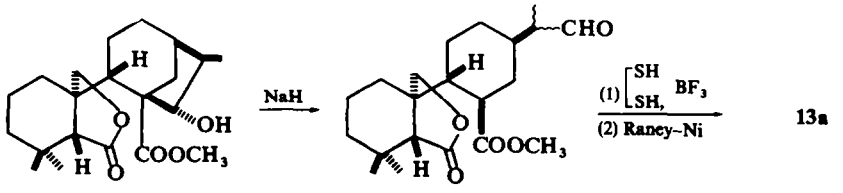


16 **17**

As the foregoing experiments afforded **12** in considerable amounts, thioketalization–desulphurization with a mixture of **8** and **12** was again carried out. In this experiment, compound **3** was also found among the reaction products though the yield was exceedingly low.

During the foregoing investigations, other methods were investigated in order to improve the yield of **13a**. The ketolactone ester **12** was reduced with $LiAl(t\text{-}BuO)_3H$ or $NaBH_4$ to the alcohol **18**[8,*] which through a retroaldol type reaction gave an

CHART 4



18 **19**

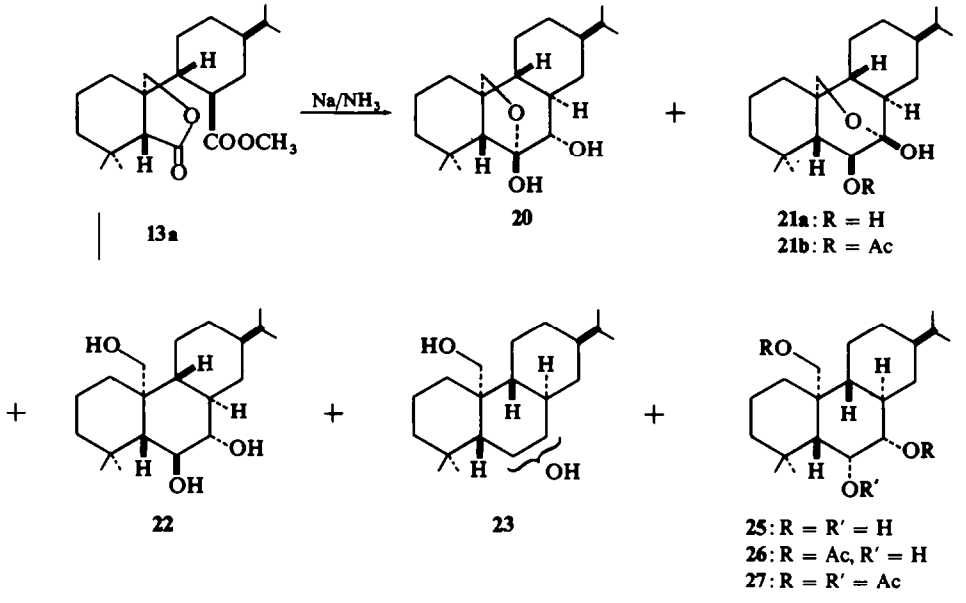
* During the treatment of the reaction mixture, C-15 β-alcohol which was originally formed epimerized into **18**.[9]

aldehyde **19** in a satisfactory yield. The aldehyde on thioketalization–desulphurization afforded **13a** in a good yield.

In addition, **18** when heated under reflux for 10 minutes in ethyleneglycol gave a very good yield of **19**.

Subsequently, acyloin condensation of **13a** using a large excess of metallic sodium resulted in formation of triol **22** and diol **23** accompanied with triol **25**.

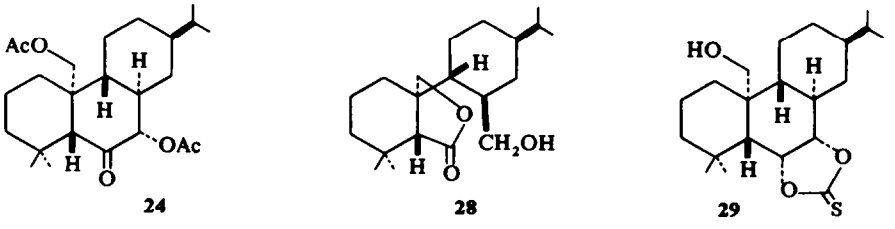
CHART 5



13a | **20** | **21a**: R = H, **21b**: R = Ac | **22** | **23** | **25**: R = R′ = H, **26**: R = Ac, R′ = H, **27**: R = R′ = Ac

If a 1·2 equivalents of sodium were used, 6-hemiketal-7-ol derivative **20** was the major product. The IR spectrum of **20** exhibits absorption of the OH groups at 3500 cm^{-1}, and the NMR spectrum shows an isopropyl group and two tertiary Me groups and a doublet signal (J = 8·0 c/s) assignable to a C-7 proton at δ 3·12 ppm. On acetylation the compound gave diacetate **24**. Based on this evidence, structure **20** was assigned to this compound.

CHART 6



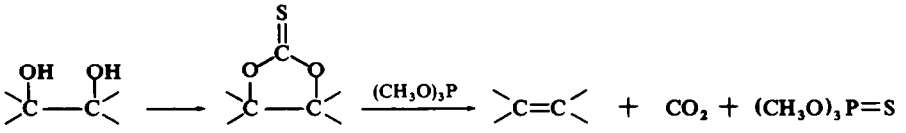
24 | **28** | **29**

The hemiketal **20** was reduced to the triol **25** which on acetylation gave the diacetate **26**, and a triacetate **27** under more vigorous conditions, while triol **22** on acetylation

easily afforded a triacetate. These experimental results and spectral data support the structures given to these alcohols. On reduction with sodium in methanol, compound **20** yeilded both triols **22** and **25**. In the acyloin condensation, a primary alcohol **28** was also found as a minor product.

Recently, Corey *et al.*[10] converted a 1,2-diol into a cyclic thionocarbonate which *via* desulphurization–decarboxylation yielded an olefin, as shown in Chart 7.

CHART 7

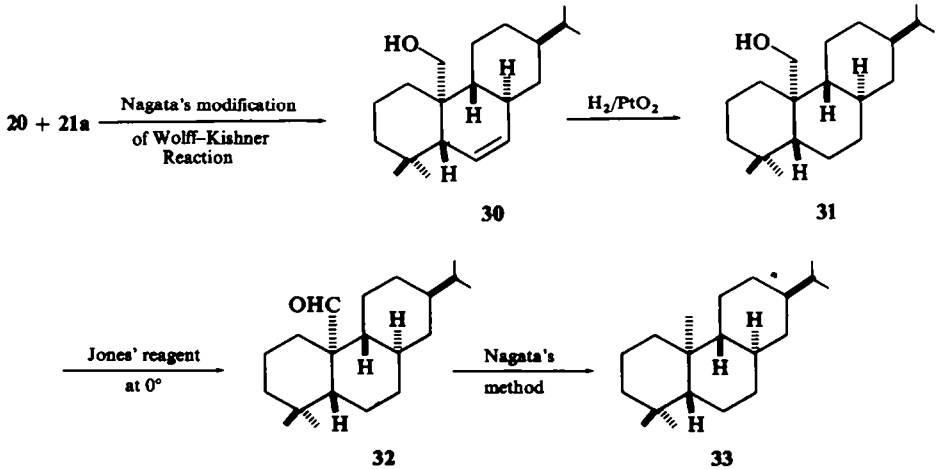


Application of this reaction to *cis*-triol **25** using N,N'-thiocarbonyldiimidazole[11] yielded a crystalline cyclic thionocarbonate **29**. The next elimination step, however, was unsuccessful because of insufficient material for a detailed investigation.

In the acyloin condensation if 1·3 to 1·6 equivalents of sodium were used, the 7-hemiketal-6-ol derivative **21a**, which had not been found previously, was isolated in crystalline form. The structure of this compound was based on the following data. (i) The IR (KBr) spectrum shows the absorption bands of the OH groups. (ii) The C-6 α-proton and C-20 ether-type methylene protons is present in the NMR spectrum. (iii) In the IR spectrum of the monoacetate **21b**, the absorption band of an OH group is still present. (iv) In the NMR spectrum of **21b** a tertiary hydroxy-, an acetyl- and methylene (C-20) groups are visible and (v) after acetylation to the monoacetate, a paramagnetic shift of the C-6 proton signal is observed.

A mixture of **20** and **21a** was subjected to Nagata's modification[12] of the Wolff–Kishner reduction to afford a crystalline unsaturated alcohol **30**. The IR spectrum shows the presence of an OH group and a double bond, and the NMR spectrum suggests the presence of an isopropyl group, two tertiary Me groups, a methylene group

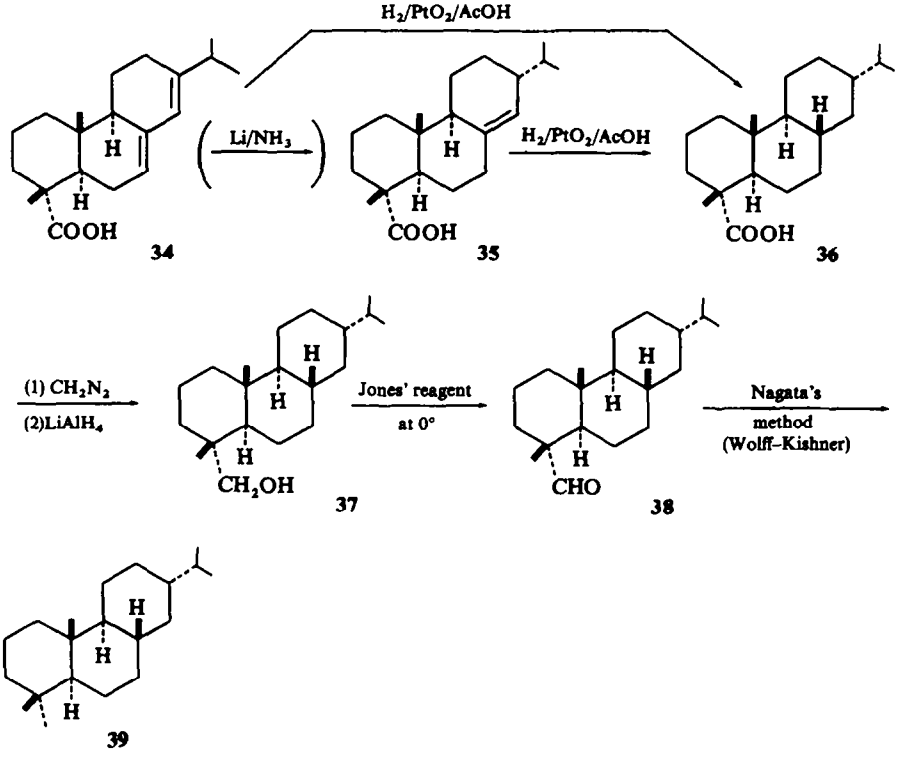
CHART 8



in a primary alcohol and a double bond. The alcohol **30** on hydrogenation with Adams' catalyst gave a crystalline saturated alcohol **31**. The latter on oxidation with Jones' reagent[13] yielded a crystalline aldehyde **32** which was again subjected to a modified Wolff–Kishner reduction to afford a dextrorotatory hydrocarbon. The compound had m.p. 38° and its mass spectrum showed M^+ 276. It was shown to be homogeneous on the VPC. The structure and absolute configuration of this compound can be represented as **33**, and this is supported by the experimental data.

Commercial abietic acid (**34**) was purified through the diisoamylamine salt and then hydrogenated on Adams' catalyst[14,15] to all-*trans*-tetrahydroabietic acid (**36**).[16] Similar catalytic hydrogenation of dihydroabietic acid (**35**)[14] also gave all-*trans*-tetrahydroabietic acid (**36**). The methyl ester of **36** on reduction with LAH gave a crystalline dextrorotatory alcohol **37**,* which was oxidized with Jones' reagent to an oily aldehyde **38**. Finally, the aldehyde **38** was subjected to a modified Wolff–Kishner reduction to afford a crystalline hydrocarbon **39** having m.p. 37–38° and $[\alpha]_D^{25}$ −5°. The analysis and mass spectrum (M^+ 276) confirmed the molecular formula $C_{20}H_{36}$ for the hydrocarbon, whose ORD showed (−)-plain curve.

CHART 9



The foregoing hydrocarbon **33** had $[\alpha]_D^{25}$ +5° and the same m.p. as described above, and exhibited a (+)-plain ORD curve. Its IR and mass spectra coincide with those

* This alcohol is known, but has not yet been crystallized.[16]

of **39**, and its retention time on vapour phase chromatogram was the same as that of **39**. These facts established that **39** and **33** were enantiomeric.

Since it is the first time that these hydrocarbons have been synthesized, we propose the name. "abietane"[17] for **39**, and "*enantio*-abietane" for **33**. The conversion of abietic acid into abietane constitutes the total synthesis of the latter, since (−)-abietic acid (**34**) has already been synthesized.[18]

EXPERIMENTAL

M.ps were determined by a micro m.p. apparatus (Yanagimoto) and are uncorrected. Unless otherwise stated, UV spectra were recorded in MeOH on a Hitachi model EPS-3 spectrophotometer, IR spectra in KBr on a Hitachi model EPI-S2 spectrophotometer and NMR spectra in $CDCl_3$ with TMS as an internal standard on a Varian A-60 spectrometer. Mass spectra were taken on a Hitachi RMU 6D mass spectrometer and ORD on JASCO model ORD/UV-5. Extracts were dried over Na_2SO_4. Mallinckrodt silicic acid was used for column chromatography. Thin layer chromatographic plates were coated with Nakarai Silica Layer G (0·1 mm).

Alcohols **14** *and* **15**. Compound **7** (14·5 g), dissolved in EtOAc–MeOH, was hydrogenated on Pd–C/PtO_2 catalyst. Concentration of the filtrate from the catalyst gave **8** (7·05 g) as crystals. Filtrate from **8**, after evaporation, was treated with MeOH–$CHCl_3$ to give a crude crystalline crop (A) (1·19 g). Filtrate from A was evaporated to give a solid residue, which was crystallized from $CHCl_3$ and recrystallized from MeOH to afford **14** (1·15 g). Further recrystallization from MeOH gave a pure sample for analysis as needles, m.p. 193–194·5°; IR ν_{max}: 3470; 1767; 1747; 1722 cm^{-1}, $\nu_{max}^{CHCl_3}$: 3530; 1763; 1716 cm^{-1}; NMR $\delta_{ppm}^{pyridine}$: 1·07 (3H, d, J = 6·0 c/s); 1·27 (3H, s); 1·56 (3H, s); 2·50 (1H, s, C-5-H); 3·63 (1H, m, C-3-H); 3·63 (3H, s); 4·14 (2H, s, C-20 H_2). (Found: C, 66·69; H, 8·18. $C_{21}H_{30}O_6$ requires: C, 66·64; H, 7·99%).

The substance A exhibited three spots on its thin layer chromatogram ($CHCl_3$ acetone, 95:5). It was chromatographed on silica gel (18 g) column (1·8 × 14 cm) and eluted with $CHCl_3$ to give a new crystalline compound (220 mg) in addition to **8** (237 mg) and **14** (132 mg). The new compound was recrystallized from $CHCl_3$–acetone to give a pure sample, m.p. 224–226°, which is an epimer of **14** and has the structure and absolute configuration **15**; IR ν_{max}: 3530; 3450; 1764; 1720 cm^{-1}, $\nu_{max}^{CHCl_3}$: 3610; 3520; 1762; 1750 (infl.); 1713 cm^{-1}, NMR δ_{ppm}: 0·96 (3H, s,); 1·11 (3H, d, J = 6·0 c/s); 1·22 (3H, s); 2·30 (1H, s, C-5-H); 3·57 (1H, broad tr, J = 3·0 c/s, C-3-H); 3·78 (3H, s, $COOCH_3$); 3·96 (2H, s, C-20 H_2). (Found: C, 66·76; H, 8·06. $C_{21}H_{30}O_6$ requires: C, 66·64; H, 7·99%).

Oxidation of **14** *and* **15**. Compound **14** (60 mg) was oxidized with CrO_3 (38 mg) in AcOH (4 ml). MeOH was added to decompose the excess of CrO_3, and after evaporation, water was added to the residue and extracted with EtOAc. After usual treatment, the solvent was evaporated off to give a neutral fraction. The latter was recrystallized from MeOH to give compound **8** (20 mg).

Compound **15** (48 mg) was subjected to the same oxidation as above with CrO_3 (33 mg) in AcOH (2 ml) to yield **8** (22 mg).

Thioketalization of **8**.[4] Compound **8** (6·027 g) was treated with ethanedithiol (10 ml) and BF_3–etherate (47%) (10 ml) at 57° for 3 days, adding BF_3–etherate (3 ml) each day. After further addition of BF_3–etherate (4 ml) and heating at 70° for 1 day followed by standing at room temp for 2 days, the reaction mixture was slowly added into Na_2CO_3 aq. containing ice and extracted with $CHCl_3$. After washing with H_2O and drying, the solvent was evaporated *in vacuo* to give a mixture (14 g) of **12** and **13a**, which was heated at reflux with W-2 Raney Ni (30 g) in EtOH for 22 hr. The catalyst was filtered off and again new Raney Ni (48 g) was added, then the mixture was heated at reflux in EtOH for 19 hr. The filtrate from the catalyst was evaporated to give a crude product (4·5 g), which was chromatographed on silica gel (100 g) column 3 × 38 cm) by eluting with $CHCl_3$ to yield **13a** (350 mg) and **12** (2·27 g) as crystals.

Unsaturated ethylenedithioketal **16**. Ester **7** (2·21 g) was allowed to react with ethanedithiol (7 ml) and BF_3–etherate (7 ml) at room temp for 2 hr. Treatment as usual gave a crude thioketal product (2·98 g), which was chromatographed on silica gel (110 g) column (4 × 25 cm) using $CHCl_3$ for elution to yield *ethylenedithioketal* **16** (2·1 g). The latter was recrystallized from $CHCl_3$-light petroleum to afford colourless crystals, m.p. 192–193·5°; IR ν_{max}: 1768; 1741 (infl.); 1713 cm^{-1}, ν_{max}^{Nujol}: 1770; 1738; 1713 cm^{-1}, NMR δ_{ppm}: 1·12 (3H, d, J = 6·0 c/s); 1·18 (3H, s); 1·50 (3H, s); 2·78 (1H, s, C-5-H); 3·36 (4H, m,

—S—CH_2—CH_2—S—); 3·78 (3H, s, $COOCH_3$); 3·96, 4·10 (each 1H, AB type, J = 10·5 c/s, C-20 H_2); 5·63, 6·12 (each 1H, AB type, J = 10·0 c/s, —CH=CH—). (Found: C, 61·59; H, 6·97. $C_{23}H_{30}O_5S_2$ requires: C, 61·32; H, 6·71%).

Desulphurization of **16**. Ethylenedithioketal **16** (1·270 g) was refluxed with W-2 Raney Ni (7·6 g) in EtOH (20 ml) for 16 hr. The filtrate from the catalyst was evaporated to dryness to give a crude desulphurized product (1 g), which was crystallized from $CHCl_3$–light petroleum to give a crystalline substance (657 mg) showing 2 spots on thin layer chromatogram. The mixture was subjected to hydrogenation on PtO_2 (100 mg) in MeOH to give a homogeneous product, which was recrystallized from $CHCl_3$–light petroleum to give pure **12**.

The filtrate from the crystals was evaporated and the residue (372 mg) was chromatographed on silica gel (30 g) (2 × 32 cm) using $CHCl_3$ for elution to separate *unsaturated ester* **17** and saturated ester **12**. One spot fraction of **17** (53 mg) was recrystallized from MeOH to give the analytical sample as colourless needles, m.p. 187·5–188°; IR ν_{max}: 1758; 1744 (infl.); 1713 cm^{-1}; NMR δ_{ppm}: 0·97 (3H, s); 1·12 (3H, d, J = 6·0 c/s); 1·30 (3H, s); 2·76 (1H, s, C-5-H); 3·73 (3H, s, $COOCH_3$); 5·73 (2H, m, —CH=CH—). (Found: C, 70·26; H, 8·10. $C_{21}H_{28}O_5$ requires: C, 69·97; H, 7·83%).

Isolation and identification of **3**. A mixture (3·1 g) of **8** and **12** were allowed to react with ethanedithiol (12.4 g) and BF_3–etherate (12·4 g), and the reaction mixture was treated as usual to give a crude thioketal mixture (5 g), which was column-chromatographed using silica gel (100 g), celite (100 g) and $CHCl_3$ to give a fraction (1·616 g) which consisted of bis-(ethylenedithioketal) **11**. The latter was recrystallized from EtOH to give pure crystals (702 mg) of **11**. Subsequently, the filtrate of **11** and other preceding fractions were combined and the mixture was again chromatographed on silica gel and celite to give a fraction (570 mg) which did not contain any compounds with a smaller R_f value than that of **11**. It was refluxed on Raney Ni (6·4 g) in EtOH to give the desulphurized product, which was treated with $NaOCH_3$ in MeOH at room temp for 15 hr and made acidic with HCl, then extracted with ether. The extract was methylated with CH_2N_2 and treated as usual to give a crude product (300 mg), which was chromatographed on silica gel (15 g; 1·8 × 16 cm) using $CHCl_3$ for elution. Thus, pure **13a** (40 mg) and **3** (22 mg) were isolated. The compound **3** was first obtained as an oil, but it was crystallized by addition of a small crystal and recrystallization twice from $CHCl_3$–light petroleum gave crystals, m.p. 147–155°,* whose IR (KBr) and NMR spectra coincided with those of an authentic sample.

Alcohol **18**[8, 9]

(i) Compound **12** (2·713 g) was dissolved in anhyd THF (60 ml) and a soln of LiAl $(t\text{-BuO})_3H$[19] (5·5 g) in THF (40 ml) was added. After the mixture was allowed to stand at room temp for 2·5 hr, MeOH was added and again allowed to stand for additional 1 hr. After concentration *in vacuo*, dil HCl was added and the whole extracted with $CHCl_3$. The extract was washed with H_2O and dried. The solvent was evaporated to dryness and the residue was crystallized (2·2 g) from $CHCl_3$–Et_2O–light petroleum. Recrystallization from Et_2O–light petroleum yielded colourless crystals, m.p. 157·5–158°; IR ν_{max}: 3500; 1766; 1735 (infl.); 1714 cm^{-1}, NMR δ_{ppm}: 0·98 (3H, s); 1·11 (3H, d, J = 7·0 c/s); 1·19 (3H, s); 2·07 (1H, s, C-5-H); 2·35 (1H, broad s, disappeared with D_2O); 3·62 (1H, d, J = 5·5 c/s, C-15-H); 3·74 (3H, s, $COOCH_3$); 3·92, 4·05 (each 1H, AB type, J = 10 c/s, C-20 H_2). (Found: C, 68·96; H, 9·11. Calc. for $C_{21}H_{32}O_5$: C, 69·20; H, 8·85%).

(ii) Ester **12** (500 mg) was dissolved in EtOH (10 ml) and $NaBH_4$ (53 mg) in EtOH (5 ml) was added. After standing at room temp for 4·5 hr, neutralization with 10% HCl and evaporation *in vacuo*, H_2O was added and the mixture extracted with $CHCl_3$. The extract on usual treatment gave the crude crystalline alcohol (510 mg), which was recrystallized twice from Et_2O–light petroleum to yield pure crystals, m.p. 154·5–155°. The IR (KBr) spectrum of this compound was superimposable with that of **18** which was prepared by the procedure described in (i). The mixture m.p. was 155–156°.

Mesylation of alcohol **18**. Alcohol **18** (90 mg) was dissolved in anhyd pyridine (2 ml), and mesyl chloride (0·5 ml) was added. The mixture was allowed to stand at room temp for 2·6 hr, then it was dropwise poured onto ice. After extraction with $CHCl_3$ three times, the extract was treated as usual to give the crude mesylate, which was recrystallized from acetone–Et_2O. The pure mesylate (40 mg) was obtained as colourless rods, m.p. 141–141·5°; IR ν_{max}: 1751, 1732 cm^{-1}, NMR δ_{ppm}: 0·99 (3H, s); 1·20 (3H, s); 1·20 (3H, d, J = 6·0 c/s); 2·08 (1H, s, C-5-H); 2·97 (3H, s, CH_3SO_2O—); 3·74 (3H, s, $COOCH_3$); 4·01, 3·93 (each 1H, AB type, J = 11·0 c/s, C-20 H_2); 4·54 (1H, indistinct d, J = 4·0 c/s, C-15-H). (Found: C, 59·51; H, 8·05. Calc. for $C_{22}H_{34}O_7S$: C, 59·71; H, 7·75%).

* m.p. 149–155°: E. Fujita *et al.*[4]; m.p. 117–118°: T. Okamoto *et al.*[8].

Sarett oxidation of alcohol **18**. A soln of **18** (105 mg) in pyridine (5 ml) was dropwise added over a period of 40 min to a slurry of CrO_3 (100 mg) in pyridine (10 ml) and kept stirred for 1·5 hr at room temp. The reaction mixture was dropwise added into H_2O and extracted with $CHCl_3$. The extract was washed with the sat $FeCl_2$ aq, and the ppt was filtered off. The $CHCl_3$ layer was treated as usual to give crude **12** (112 mg), which was purified by column (1·2 × 11 cm) chromatography on silica gel (4 g) using $CHCl_3$ as eluting solvent. The pure crystals (22 mg) proved to be identical with an authentic sample of **12**.

Aldehyde **19**

(i) To an ice-cold soln of NaH (15 mg) in dry THF (5 ml), a soln of **18** (200 mg) in dry THF (10 ml) was dropwise added over a period of 1 hr under N_2. Then, the mixture was heated for 6 hr under reflux in an oil bath. After neutralization with cold 10% HCl and concentration under N_2 stream at room temp, it was extracted with $CHCl_3$. The acidic substance was removed and the remaining $CHCl_3$ layer was washed with H_2O. Then, the usual treatment gave oily **19** (146 mg); IR $\nu_{max}^{CHCl_3}$: 2720; 1765; 1750; 1725 cm^{-1}, NMR δ_{ppm}: 0·98 (3H, s); 1·05 (3H, d, J = 7·5 c/s); 2·34 (1H, s, C-5-H); 3·68 (3H, s); 3·95 (2H, s, C-20 H_2); 9·62 (1H, d, J = 2·0 c/s, CHO).

(ii) Alcohol **18** (50 mg) was heated for 20 min under reflux in ethylene glycol (1 ml). Addition of H_2O, extraction with Et_2O and subequent treatment of the ethereal extract gave oily **19** (46 mg), whose IR spectrum in $CHCl_3$ was superimposable with that of the sample prepared in (i).

2,4-Dinitrophenylhydrazone of aldehyde **19**. Aldehyde **19** (50 mg) was dissolved in EtOH (2 ml) and to this a soln of 2,4-dinitrophenylhydrazone (27 mg) in EtOH (2 ml) was added. After addition of 2 drops of 35% HCl and standing, yellow crystals precipitated. Recrystallization from $CHCl_3$–EtOH yielded yellow needles, m.p. 107–110°; IR ν_{max}: 3280; 3080; 1767; 1753 (infl.); 1726; 1617; 1588 cm^{-1}. (Found: C, 59·09; H, 6·70. $C_{27}H_{37}O_8N_4$ requires: C, 59·54; H, 6·66%).

Thioketalization and desulphurization of aldehyde **19**. A mixture of aldehyde **19** (100 mg), BF_3–etherate (0·4 ml), and ethanedithiol (0·4 ml) was allowed to stand at room temp for 1 hr. The mixture was treated in the same way as described above to give crude thioketal, which was desulphurized with Raney Ni (600 mg) in EtOH as usual to yield ester **13a** (65 mg).

Diol **23** *and triol* **22**. A soln of **13a** (440 mg) in dry ether (20 ml) was dropwise added under stirring into a soln of Na (280 mg) in liquid ammonia (30 ml) over a period of 4 hr in a N_2 atmosphere. During the reaction the temp of the bath was kept at −70°. The reaction mixture was left at ca. −45° for 2 hr. Excess Na was decomposed by addition of a mixture of Et_2O–MeOH, then the ammonia was evaporated by a stream of N_2. The residue was made acidic with HCl, and extracted with Et_2O 3 times. The ethereal extract was treated as usual to give a neutral product (414 mg) in addition to an acidic fraction (11 mg). The neutral crude product was crystallized from $CHCl_3$–hexane to give a mixture (163 mg) of diol **23** and triol **22**, which was chromatographed on silica gel (8 g) column (1·5 × 10 cm) using $CHCl_3$ and $CHCl_3$–acetone for elution to give diol **23** (64 mg), a mixture (3 mg) of diol **23** and triol **22** and triol **21** (55 mg). The latter was eluted with $CHCl_3$ containing 1% of acetone. Diol **23** was recrystallized from $CHCl_3$–hexane to give colourless needles, m.p. 192–193·5°; IR ν_{max}: 3300; 1020 cm^{-1}, $\nu_{max}^{CHCl_3}$: 3630; 3450; 1008 cm^{-1}, NMR $\delta_{ppm}^{pyridine}$: 0·88 (6H, d, J = 6·0 c/s); 0·92 (3H, s); 0·99 (3H, s); 3·49 (1H, octet, J = 5·0, 10·0 c/s, C-6 or C-7-H); 4·18 (2H, s, C-20 H_2). ORD: (−)-plain curve. (Found: C, 77·71; H, 11·70. $C_{20}H_{36}O_2$ requires: C, 77·86; H, 11·76%).

Diol **23** (11 mg) on acetylation with Ac_2O-pyridine gave diacetate (7 mg); IR $\nu_{max}^{CHCl_3}$: 1725; 1028 cm^{-1}, NMR δ_{ppm}: 0·84 (6H, d, J = 6·0 c/s); 0·88 (6H, s); 2·05 (3H, s); 4·26, 4·40 (each 1H, AB type, J = 12·0 c/s, C-20 H_2).

Triol **22** was recrystallized from $CHCl_3$–hexane to give pure crystals, m.p. 80–85°; 146–147°; IR ν_{max}: 3380; 1028; 1016 cm^{-1}, $\nu_{max}^{CHCl_3}$: 3420; 1012 cm^{-1}, NMR δ_{ppm}: 0·88 (6H, d, J = 6·0 c/s); 1·12 (3H, s); 1·17 (3H, s); 3·00 (1H, qu, J = 8·0, 10·0 c/s, C-7-H); 3·72 (1H, qu, J = 7·5, 10·0 c/s, C-6-H); 3·89 (2H, s, C-20-H_2). ORD: (−)-plain curve (in MeOH). (Found: C, 73·95; H, 11·20. $C_{20}H_{36}O_3$ requires: C, 74·02; H, 11·20%). Triol **22** was acetylated to yield an acetate, which was recrystallized from hexane to give crystals, m.p. 164–165·5; IR ν_{max}: 1742; 1256; 1235; 1037 cm^{-1}, $\nu_{max}^{CHCl_3}$: 1722 cm^{-1}, NMR δ_{ppm} 0·84 (6H, d, J = 6·0 c/s); 0·96 (3H, s); 1·00 (3H. s); 1·79 (3H, s); 2·03 (3H, s); 2·12 (3H, s); 4·33 (2H, s, C-20 H_2); 4·72 (1H, qu, J = 9·0, 10·0 c/s, C-7-H); 5·57 (1H, qu, J = 12·0, 9·0 c/s, C-6-H). (Found: C, 69·57; H, 9·67. $C_{26}H_{42}O_3$ requires: C, 69·30; H, 9·40%).

Diol **23**, *triol* **22**, *and triol* **25**. Lactone ester **13a** (560 mg = 1·6 mmol.) was dissolved in dry ether (35 ml) and the soln was dropwise added to a soln of Na (441 mg = 10·2 mg atom) in NH_3 (40 ml) and dry ether (30 ml) over a period of 15 min under stirring (bath temp: −60°). The mixture was kept stirred for an addi-

tional 3 hr. During this period the bath temp was kept at −33°. After decomposition of excess Na, the usual treatment gave a neutral portion (600 mg) and an acidic product (45 mg), which was methylated with CH_2N_2 to give a methyl ester. The neutral product was chromatographed on silica gel (1·2 g) and eluted with $CHCl_3$ to give diol **23** (145 mg). It was identified by IR (KBr) comparison and mixture m.p. with an authentic sample. The following fraction consisted of diol **23** and triol **25**, and the subsequent fraction only of triol **25**. The latter was recrystallized from Me_2CO–hexane to give pure crystals of **25** (37 mg), which was identified with the sample obtained from **20** by IR (KBr) and mixture m.p. The following eluate (18 mg) with $CHCl_3$ consisted of triol **25** and triol **22**. Subsequent elution with $CHCl_3$ containing 10% of Me_2CO gave triol **22** (190 mg).

6-Hemiketal-7-ol **20**. A soln of **13a** (400 mg = 1·14 mmol) in dry Et_2O (25 ml) was dropwise added to a soln of Na (126 mg = 5·5 mg atom) in liquid ammonia (45 ml) and Et_2O (30 ml) under stirring over a period of 2 hr (bath temp: −70°). The mixture was stirred for an additional 2 hr. The usual treatment gave a neutral fraction (335 mg) and an acidic fraction (105 mg). The neutral fraction which gave three spots (TLC) and was chromatographed on silica gel (10 g; 1·2 × 5·5 cm) using $CHCl_3$ for elution to give a pure oil **20** (20 mg); IR $\nu_{max}^{CHCl_3}$: 3500; 3380; 1028; 1006 cm^{-1}, NMR δ_{ppm}: 0·88 (6H, d, J = 5·0 c/s); 1·15 (3H, s); 1·30 (3H, s); 3·12 (1H, d, J = 8·0 c/s, C-7-H); 3·53, 3·83 (each 1H, AB type, J = 8·0 c/s, C-20 H_2); 4·41 (1H,s, OH, disappeared with D_2O).

Acetylation of **20**. 6-Hemiketal-7-ol **20** (oil, 15 mg) was acetylated with Ac_2O–pyridine (equal volume) at room temp. The crude product was purified by silica gel (2 g; 1·2 × 5 cm) chromatography and elution with $CHCl_3$ to give a homogeneous acetate **24** (10 mg). The Legal test was positive (yellow to violet by addition of HCl); IR $\nu_{max}^{CHCl_3}$: 1737; 1047; 1038 cm^{-1}, NMR δ_{ppm}: 0·88 (6H, d, J = 6·0 c/s); 1·04 (3H, s); 1·18 (3H, s); 1·98 (3H, s); 2·20 (3H, s); 3·98, 4·38 (each 1H, AB type, J = 12·5 c/s, C-20 H_2); 4·87 (1H, d, J = 9·5 c/s, C-7-H).

Sodium borohydride reduction of **20**. 6-Hemiketal-7-ol **20** (20 mg) was dissolved in THF (20 ml), then a few drops of H_2O and $NaBH_4$ (49 mg) were added. The soln was stirred for 1 day. Neutralization with dil HCl, extraction with $CHCl_3$, washing the $CHCl_3$ layer with 10% Na_2CO_3 aq and NaCl aq, drying and evaporation gave a crystalline neutral residue, which was recrystallized from $CHCl_3$–hexane to give a homogeneous triol **25**, m.p. 190–193°; IR ν_{max}: 3270 cm^{-1}, $\nu_{max}^{CHCl_3}$: 3320, 1048 cm^{-1}, NMR $\delta_{ppm}^{COCl_3-D_2O}$: 0·87 (6H, d, J = 6·0 c/s); 1·02 (3H, s); 1·27 (3H, s); 3·01 (1H, qu, J = 3·0, 10·5 c/s, C-7-H); 3·53, 4·09 (eacn 1H, AB type, J = 12·0 c/s, C-20 H_2); 4·21 (1H, broad s, C-6-H), δ_{ppm}: 0·86 (6H, d, J = 5·5 c/s); 1·02 (3H, s); 1·27 (3H, s); 3·01 (1H, qu, J = 3·0, 10·5 c/s, C-7-H); 3·53, 4·09 (each 1H, AB type, J = 12·0 c/s, C-20 H_2); 4·21 (1H, broad s, C-6-H). (Found: C, 73·79; H, 11·15. $C_{20}H_{36}O_3$ requires: C, 74·02; H, 11·18%).

Diacetate **26**. Triol **25** on acetylation with Ac_2O–pyridine at room temp overnight gave diacetate **26**; IR $\nu_{max}^{CHCl_3}$: 3580; 3480; 1785 cm^{-1}, NMR δ_{ppm}: 0·88 (6H, d, J = 5·0 c/s); 0·99 (3H, s); 1·05 (3H, s); 2·05 (3H, s); 2·12 (3H, s); 4·26 (1H, broad s, C-6-H); 4·40, 4·73 (each 1H, AB type, J = 12·0 c/s, C-20 H_2); 4·52 (1H, qu, J = 10·5, 3·5 c/s, C-7-H), $\delta_{ppm}^{CCl_3-benzene(1:1)}$: 0·85 (6H, d, J = 5·0 c/s); 0·93 (3H, s); 1·26 (3H, s); 1·18 (3H, s); 1·92 (3H, s); 4·19 (1H, broad s, C-6-H); 4·45 (1H, qu, J = 10·5, 3·5 c/s, C-7-H); 4·41, 4·78 (each 1H, AB type, J = 12·0 c/s, C-20 H_2).

Triacetate **27**

(i) Triol **25** (32 mg) was allowed to react with Ac_2O (1·5 ml) in pyridine (1·5 ml) at room temp for 20 hr, then the mixture was heated at reflux for 8 hr. During this period Ac_2O (1 ml) and pyridine (1 ml) were added 3 times. Benzene and H_2O were added and evaporated *in vacuo* to give a residue, which was chromatographed on silica gel (2 g; 0·8 × 15 cm) using $CHCl_3$ as the eluting solvent to yield triacetate **27** (24 mg).

(ii) Triol (15 mg) was mixed with Ac_2O (1·5 ml) and anhyd NaOAc (20 mg), and the mixture was heated at reflux for 5 hr. NaOAc (10 mg) and Ac_2O (1 ml) was then added and refluxed for additional 2 hr. The usual treatment and chromatography of the crude product on silica gel (1·5 g; 0·8 × 8 cm) with $CHCl_3$ for elution gave triacetate **27**. Triacetates prepared by the procedures (i) and (ii) were combined (29 mg) and chromatographed on silica gel (2 g; 0·8 × 11·5 cm) with $CHCl_3$ as solvent to afford the pure triacetate (9 mg); IR $\nu_{max}^{CHCl_3}$: 1732 cm^{-1}, NMR δ_{ppm}: 0·85 (6H, d, J = 6·0 c/s); 0·98 (3H, s); 1·00 (3H, s); 2·00; 2·05; 2·12 (each 3H, s); 4·48 (1H, qu, J = 3·5, 10·5 c/s, C-7-H); 4·35, 4·71 (each 1H, AB type, J = 12·5 c/s, C-20 H_2); 5·66 (1H, qu, J = 1·0, 3·5 c/s, C-6-H).

Reduction of 6-hemiketal-7-ol **20** *with sodium in methanol.* Compound **20** (20 mg), dissolved in anhyd MeOH (4 ml), was allowed to stand with Na (160 mg) at room temp for 12 hr. Subsequently, the soln was heated under reflux for 1·5 hr. Neutralization with HCl, evaporation of the solvent, extraction with $CHCl_3$ after addition of H_2O, and the usual treatment of the extract gave crude neutral substance (17 mg), which

was chromatographed on silica gel (1·8 g; 0·8 × 11 cm) using $CHCl_3$ for elution to yield triol **25** as the first fraction and followed by triol **22**. Each crystalline product was identified with an authentic sample by IR ($CHCl_3$) comparison and mixture m.p.

Isolation of primary alcohol **28**. Crude 6-hemiketal-7-ol (contaminated with another by-product as shown on TLC; 17 mg) was reduced with $NaBH_4$ (40 mg). The crude neutral product (17 mg) was chromatographed on silica gel column using $CHCl_3$ for elution to give first the primary alcohol **28** (4 mg) and next the triol **25** (6 mg). Alcohol **28** did not crystallize but remained as oil; IR $\nu_{max}^{CHCl_3}$: 3600; 3470; 1748 cm^{-1}, NMR δ_{ppm}: 0·95 (6H, d, J = 5·0 c/s); 1·00 (3H, s); 1·20 (3H, s); 1·53 (1H, d, J = 1·5 c/s, $CH_2O\underline{H}$, disappeared by treatment with D_2O); 2·38 (1H, s); 3·70 (2H, m, C-7 $\underline{H}_2$); 4·09, 4·41 (each 1H, AB type, J = 9·5 c/s, C-20 $\underline{H}_2$).

Alcohol **28** after usual treatment with Ac_2O–pyridine gave an oily monoacetate; IR $\nu_{max}^{CHCl_3}$: 1767 (infl.), 1738 cm^{-1}, NMR δ_{ppm}: 0·85 (6H, d, J = 5·5 c/s); 0·99 (3H, s); 1·20 (3H, s); 2·09 (3H, s); 2·38 (1H, s); 4·10 (2H, AB part of ABX type, J_{AB} = 16·0, J_{AX} = 2·0, J_{BX} = 6·0 c/s, C-7 $\underline{H}_2$); 4·06 (2H, singlet, C-20 $\underline{H}_2$).

Oxidation of **28**. Alcohol **28** (58 mg), dissolved in AcOH, was mixed with a soln of CrO_3 (35 mg) in AcOH and a small quantity of H_2O, and allowed to stand at room temp for 4·3 hr. MeOH was added to decompose excess CrO_3. After evaporation *in vacuo* after addition of H_2O and extraction of the suspension in H_2O with $CHCl_3$, the extract was washed with 10% Na_2CO_3 aq, then with H_2O, and treated as usual to give neutral substance (42 mg). The aqueous layer was acidified with HCl and extracted with $CHCl_3$. The extract was treated as usual to yield an acidic substance (14 mg), which was chromatographed on silica gel (1 g) using $CHCl_3$ for elution to give purified acid (10 mg). Recrystallization from $CHCl_3$–hexane gave a crystalline acid, m.p. 141–144°; IR ν_{max} ~3150; 1773, 1751; 1737; 1713 cm^{-1}, $\nu_{max}^{CHCl_3}$: 3400 ~ 2500; 1754; 1747; 1678 cm^{-1}, NMR δ_{ppm}: 0·87 (6H, d, J = 5·5 c/s); 0·99 (3H, s); 1·21 (3H, s); 2·40 (1H, s); 4·01, 4·19 (each 1H, AB type, J = 10·0 c/s, C-20 $\underline{H}_2$); 8·67 (1H, broad s, disappeared with D_2O. $COO\underline{H}$). The acid was methylated with CH_2N_2 to afford ester **13a**.

Thionocarbonate **29**. Triol **25** (144 mg) and N,N'-thiocarbonyldiimidazole (91 mg) were dissolved in dry toluene (4 ml), and the soln was heated under reflux for 2 hr in N_2 atm. The reaction mixture, after washing with H_2O and drying, was evaporated to give a crude mixture (171 mg) of products, which exhibited 3 spots on TLC. It was chromatographed on silica gel (3·7 g; 1·3 × 10 cm) using $CHCl_3$ for elution to give **29** (29 mg) and a mixture (68 mg) containing **29**. The former (29 mg) was again chromatographed on silica gel (1 g; 0·8 × 10·5 cm) using $CHCl_3$ for elution to give pure **29** (10 mg), which was recrystallized from acetone–petroleum ether to afford colourless needles, m.p. 164–165°, $[\alpha]_D$ 1° (c, 2·08, MeOH); IR ν_{max}: 3500; 3450; 1270 cm^{-1}, UV λ_{max}^{MeOH}: 238 mμ (ε 31000), NMR δ_{ppm}: 0·86 (6H, d, J = 5·5 c/s); 1·06 (3H, s); 1·24 (3H, s); 1·37 (1H, d, J = 3·0 c/s, C-5-$\underline{H}$); 3·97 (2H, broad s, C-20 $\underline{H}_2$); 4·38 (1H, qu, J = 7·0, 8·0 c/s. C-7-$\underline{H}$); 5·12 (1H, qu, J = 7·0, 3·0 c/s, C-6-$\underline{H}$), ORD (C, 2·08; MeOH): $[\phi]_{328}^{trough}$ −3600, $[\phi]_{312·2}$ 0, $[\phi]_{262}^{shoulder}$ +1210, $[\phi]_{255}^{peak}$ +12500. (Found: C, 69·08; H, 9·60. $C_{21}H_{34}O_3S$ requires: C, 68·82; H, 9·35%).

Attempted elimination reaction of compound **29**. Thionocarbonate (9 mg), dissolved in $(MeO)_3P$ (10 ml), was heated under reflux in N_2 atm for 24 hr. NaOH aq soln was added and the mixture extracted with ether. The extract, after washing with dil HCl and H_2O, was treated as usual to give a crude product (14 mg), which was chromatographed on silica gel using $CHCl_3$ for elution to yield an oily substance with one spot on TLC; IR $\nu_{max}^{CCl_4}$: 3020; 1261; 976 cm^{-1}.

7-Hemiketal-6-ol **21a**

(i) A soln of **13a** (860 mg. 2·45 mmol), in dry Et_2O (60 ml) was dropwise added into a soln of Na (300 mg. 13 mg atom, 1·32 eq) in liquid NH_3 (90 ml) and dry Et_2O (60 ml) under stirring over a period of 1 hr at −60° (bath temp). The reaction mixture was stirred for an additional 2 hr at −60° (bath temp). The usual treatment gave neutral (744 mg) and acidic (9 mg) fractions. The neutral portion (700 mg) was chromatographed on silica gel (40 g; 2·5 × 18 cm) using $CHCl_3$ for elution to give almost pure **21a**, which was recrystallized from acetone and from acetone and ether to yield a pure sample as colourless crystals, m.p. 170–174° and 178–181°; IR ν_{max}: 3365; 3305 cm^{-1}. (Found: C, 74·25; H, 10·57. $C_{20}H_{34}O_3$ requires: C, 74·49; H, 10·63%).

(ii) Compound **13a** (720 mg; 2·05 mmol), Na (300 mg; 13·04 mg atom; 1·59 eq), NH_3 (100 ml) and dry Et_2O (70 ml) were employed for acyloin condensation just as in the case of (i). The usual treatment gave neutral (589 mg) and acidic (50 mg) fractions. The neutral fraction was crystallized from acetone to yield **21a** (68 mg) as colourless needles, which was recrystallized from acetone to afford pure colourless needles, m.p. 179–183°. ν_{max}: 3360; 3300 (infl.); 1039; 1002 cm^{-1}, NMR δ_{ppm}: 0·87 (6H, d, J = 5·0 c/s); 1·10 (3H, s); 1·26 (3H, s); 1·78 (1H, s, C-5-$\underline{H}$); 3·35 (1H, broad s, C-6-$\underline{H}$); 3·48 (1H, s, disappeared by D_2O treatment, $O\underline{H}$), 3·77 (2H, s, C-20 $\underline{H}_2$).

Acetate **21b**. Compound **21a** (15 mg) was acetylated with Ac_2O and pyridine and treated as usual. The crude crystalline product was recrystallized from MeOH to yield **21b** (6 mg), as colourless rods, m.p. 161–162°; IR ν_{max}: 3340; 1737; 1245 cm^{-1}, NMR δ_{ppm}: 0·82 (6H, d, J = 5·0 c/s); 0·96 (3H, s); 1·13 (3H, s); 1·95 (3H, s); 3·27 (1H, s, disappeared with D_2O); 3·66 (2H, s, C-20 $\underline{H}_2$); 4·45 (1H, s, C-6-$\underline{H}$).

Acidic fraction of acyloin reaction products. The acidic fractions from each batch of the acyloin condensation were collected together and methylated with CH_2N_2–ether to give crude methyl ester (310 mg), which was chromatographed on silica gel (8 g) column (2 × 7·5 cm) using $CHCl_3$ for elution to separate the crystalline ester (180 mg) and an oily substance (43 mg). The former was crystallized from MeOH to give colourless needles (127 mg), whose IR (KBr) spectrum was superimposable with that of **13a**. The latter was not identified; IR $\nu_{max}^{CHCl_3}$: 3580; 3430; 1724 cm^{-1}; ν_{max}^{film}: 3430; 1726 cm^{-1}.

Unsaturated alcohol **30**. A mixture (410 mg) of acyloin products (which mainly consisted of **21a** and **20** as shown on TLC) was heated with $NH_2NH_2 \cdot HCl$ (2·3 g), anhyd $NH_2 \cdot NH_2$ (11 ml) and triethylene glycol (20 ml) at 140–150° for 12 hr. After pellets of KOH (12 g) were added to the reaction mixture at room temp the mixture was heated to 200° over a period of 3 hr, and heated under reflux at 200–210° for 4 hr. The reaction mixture was dropwise added into H_2O, and extracted with Et_2O for 4 times. The extract on usual treatment gave crude product (300 mg), which was chromatographed on Al_2O_3 (Merck, Akt. 1. neu. 20 g) column. Elution with n-hexane and benzene followed by benzene–ether mixtures (95:5 → 90:10 → 80:20 → 50:50) gave the expected product **30** (200 mg). Recrystallization from CH_3CN yielded colourless prisms (65 mg), m.p. 114–115°; IR ν_{max}: 3330; 1640; 777 cm^{-1}, NMR δ_{ppm}: 0·82 (6H, d, J = 5·0 c/s); 0·87 (3H, s); 0·92 (3H, s); 3·88 (2H, s C-20 $\underline{H}_2$); 5·59 (2H, broad s, $W_{\frac{1}{2}}$ = 4·5 c/s). (Found: C, 82·44; H, 12·05. $C_{20}H_{34}O$ requires: C, 82·69; H, 11·86%). Mass spectrum: M^+ m/e 290.

Alcohol **31**. Unsaturated alcohol **30** (60 mg), dissolved in MeOH (50 ml), was hydrogenated with PtO_2 catalyst. At the end of the reaction the catalyst was filtered off. The usual treatment of the filtrate and recrystallization of the crude product from CH_3CN to yield alcohol **31**, m.p. 103 ~ 104°; IR ν_{max}: 3345; 1022 cm^{-1}, NMR δ_{ppm}: 0·84 (6H, d, J = 5·0 c/s); 0·89 (6H, s); 3·90 (2H, s) (Found: C, 81·21; H, 12·43. $C_{20}H_{36}O \cdot \frac{1}{4}H_2O$ requires: C, 80·89; H, 12·39%).

Aldehyde **32**. Alcohol **31** (62 mg), dissolved in acetone (15 ml), was ice-cooled, and a cold Jones' reagent was dropwise added to the soln under N_2 atm. As soon as the yellow colour failed to disappear, the reaction mixture was poured into NaCl aq, then the mixture was extracted with Et_2O (each 10 ml) three times. The usual treatment of the extract gave a crude aldehyde, which recrystallized from MeOH to yield the pure aldehyde as colourless rods or needles, m.p. 73–78·5°; IR ν_{max}: 2750, 1708 cm^{-1}, NMR $\delta_{ppm}^{CDCl_3+D_2O}$: 0·70 (3H, s); 0·82 (6H, d, J = 5·5 c/s); 0·90 (3H, s); 10·10 (1H, d, J = 2·0 c/s, C$\underline{H}$O). (Found: C, 82·54; H, 11·99. $C_{20}H_{34}O$ requires: C, 82·69; H, 11·80%).

Enantio-abietane **33**. Aldehyde **30** (42 mg) was mixed with anhyd NH_2NH_2 (1·2 ml), $NH_2NH_2 \cdot 2HCl$ (250 mg) and triethylene glycol (2·5 ml), and the mixture was heated at 140° for 14 hr. Pellets of KOH (1·3 g) were added and the mixture heated at 150° for 2 hr, then the temp was slowly raised to 200° over a period of 2 hr. After heating at 200–220° for an additional 3 hr, the reaction mixture was poured into sat NaCl aq. The mixture was extracted with n-hexane 4 times (total of solvent: 30 ml). The crude hydrocarbon obtained by a usual treatment was chromatographed on Al_2O_3 (neutral. Akt. 1; 4 g; 1 × 9·5 cm) using n-hexane for elution to give **33** (20 mg), which was recrystallized from MeOH to yield *enantio-abietane* (16 mg) as pure colourless crystals, m.p. 37–38°; IR ν_{max}: 1467; 1453; 1387; 1368 cm^{-1}, $\nu_{max}^{CCl_4}$: 1464; 1451; 1388; 1360 cm^{-1}, ORD: (+)- plain curve (c, 0·366; n-hexane). $[\alpha]_D^{25}$ +5° (calculated from ORD). (Mol. Wt. Found: 276 in mass spectrum. Calc. for $C_{20}H_{36}$: 276). Gas chromatography: SE-30 Golay type-capillary column (45 m); Oven temp: 208°; injection temp: 282°. Carrier gas: N_2. Retention time: *enantio*-abietane 6·6 min; *enantio*-abietane + abietane 6·6 min.

Tetrahydroabietic acid **36**

(i) Abietic acid, m.p. 130–159° (26 g), which was prepared by purification[20] of the crude commercial substance, was hydrogenated in AcOH on PtO_2 (235 mg). The filtrate from the catalyst after addition of H_2O was evaporated *in vacuo* to give a residue, which was crystallized from acetone to yield a crude acid **36**, m.p. 150–155° (1·331 g). The latter was converted into diisoamylamine salt and purified with recrystallization to give crystalline salt, m.p. 126·5–127·5°, from which a free acid **36** (179 mg), m.p. 168–172°, was obtained by addition of AcOH. Its recrystallization from 95% EtOH afforded the pure acid **36** (171 mg), m.p. 183–184°, $[\alpha]_D^{30}$ +11·3° (c, 2·01; EtOH). The IR comparison and mixture m.p. with an authentic sample* proved their identity. (ii) Dihydroabietic acid (**35**) supplied from Prof. A. W. Burgstahler was

* The sample kindly supplied by Prof. Burgstahler had m.p. 183·5–185°.

subjected to the catalytic hydrogenation on PtO_2 in AcOH as in (i) to give acid **36**. Recrystallization from acetone 5 times yielded pure acid **36**.†; NMR δ_{ppm}: 0·85 (6H, d, J = 5·0 c/s); 0·86 (3H, s); 1·18 (3H, s); 9·60 (1H, broad, disappeared with D_2O).

Alcohol **37**. To a soln of **36** (150 mg) in EtOH, an ethereal soln of CH_2N_2 was added. After standing for a while, the solvent together with excess of CH_2N_2 was evaporated off. The oily methyl ester (154 mg) was purified on a silica gel column; IR $\nu_{max}^{CHCl_3}$: 1718 cm^{-1}. The methyl ester (303 mg), dissolved in dry Et_2O (6 ml), was dropwise added into a soln of LAH (38 mg) in Et_2O (3 ml), and the mixture was heated under reflux for 45 min. The usual treatment gave a crude product, but TLC still exhibited a remaining material's spot. Hence, the crude neutral product (280 mg) was again subjected to LAH (180 mg) reduction in Et_2O. The reaction mixture was treated as usual to give neutral substance (257 mg), which was chromatographed on Al_2O_3 (Woelm, Akt. 1, 5 g; 1·2 × 5·7 cm) using petroleum benzine–benzene–Et_2O system for elution to yield a one spot substance (240 mg). The latter on standing a long time crystallized. Recrystallization from MeOH gave pure crystals, m.p. 33–33·5°, $[\alpha]_D^{29}$ +7°; IR $\nu_{max}^{CCl_4}$: 3640; 3350 cm^{-1}, ν_{max}: 3350 cm^{-1}, NMR δ_{ppm}: 0·79 (3H, s); 0·84 (6H, d, J = 6·0 c/s); 0·86 (3H, s); 1·55 (1H, disappeared with D_2O); 3·12, 3·40 (each 1H, AB type, J = 11·0 c/s). Mass spectrum: M^+ 292. (Found: C, 81·99; H, 12·48. $C_{20}H_{36}O$ requires: C, 82·12; H, 12·40%); ORD: (+)-plain curve (*c*, 1·087; n-hexane).

Acetylation of **37**. Alcohol **37** (29 mg) was mixed with excess Ac_2O and pyridine, and the mixture was kept overnight. Evaporation *in vacuo* after addition of H_2O and benzene gave a residue, which was chromatographed on Al_2O_3 (3·13 g; 0·8 × 11 cm). Elution was carried out with petroleum benzine, petroleum benzine–benzene, and benzene–Et_2O. The eluate from benzene–Et_2O (1 : 1) gave an acetate (22 mg), which was again chromatographed on Al_2O_3 (650 mg; 0·6 × 4 cm) to yield pure acetate (7 mg) of **37**; IR $\nu_{max}^{CCl_4}$: 1738 cm^{-1}, NMR δ_{ppm}: 0·84 (6H, d, J = 6·0 c/s); 0·82 (6H, s); 2·06 (3H, s); 3·65, 3·84 (each 1H, AB type, J = 11·0 c/s).

Tosylation of alcohol **37**. Alcohol **37** (47 mg) was dissolved in dry pyridine (2 ml), and *p*-toluenesulphonyl chloride (108 mg) was added and the mixture was kept overnight. Extraction with Et_2O and treatment as usual gave a neutral product (80 mg), which was purified by silica gel (1 g) chromatography using $CHCl_3$ for elution. Oily tosylate (74 mg) was obtained; IR $\nu_{max}^{CCl_4}$: 1600; 1500; 1187; 1178 cm^{-1}, NMR δ_{ppm}: 0·77 (3H, s); 0·79 (3H, s); 0·81 (6H, d, J = 5·5 c/s); 2·46 (3H, s); 3·51, 3·71 (each 1H, AB type, J = 9·0 c/s).

Aldehyde **38**. To an ice-cold soln of **37** (104 mg) in acetone (15 ml), cold Jones' reagent was slowly added until the yellow colour of the soln persisted. TLC of a sample from the reaction mixture was carried out in order to check the reaction. As soon as the starting material was absent, the reaction mixture was poured into sat NaCl aq, then extraction with Et_2O was carried out 3 times. The ethereal layer gave **38** (102 mg) but crystallization was not successful; IR $\nu_{max}^{CCl_4}$: 2690; 1726 cm^{-1}, NMR δ_{ppm}: 0·82 (6H, d, J = 5·0 c/s); 0·88 (3H, s); 1·06 (3H, s); 9·23 (1H, s).

Hydrazone of aldehyde **38**. Alcohol **37** (40 mg) was subjected to oxidation with CrO_3 (45 mg)–pyridine under N_2 atm over a period of 10 min, then the reaction mixture was allowed to stand for 2·5 hr. After usual treatment, a neutral product (39 mg; IR $\nu_{max}^{CCl_4}$: 2680; 1728 cm^{-1}) was obtained. After a rapid column chromatography on Al_2O_3, the neutral fraction (34 mg) was mixed with 98·5% NH_2NH_2 (470 mg), $NH_2NH_2 \cdot 2HCl$ (320 mg), and triethylene glycol (1 ml), and the mixture was heated at 130° for 5·5 hr. The reaction mixture was poured into H_2O and extracted with $CHCl_3$ 3 times. The product was crystallized from Et_2O. It was very slightly soluble in organic solvents. Recrystallization from MeOH–light petroleum gave crystals of m.p. 256–263° (dec); IR ν_{max}: 1639 cm^{-1}, NMR $\delta_{ppm}^{pyridine}$: 0·84 (6H, d, J = 5·5 c/s); 0·85 (3H, s); 0·90 (3H, s).

Abietane **39**. Aldehyde **38** (72 mg) was mixed with triethylene glycol (4 ml), anhyd NH_2NH_2 (1·5 ml), and $NH_2NH_2 \cdot 2HCl$ (350 mg), and the mixture was heated at 120–140° for 14 hr. After cooling, KOH pellets (2 g) were added, and the mixture was heated again. The temp was slowly raised to 220° over a period of 3 hr, then it was heated at that temp for 2·5 hr. The reaction mixture was poured into NaCl aq and extracted with n-hexane 5 times (total of the solvent: 30 ml). The usual treatment of the extract gave a crude product (62 mg), which was chromatographed on Al_2O_3 (neu. Akt. 1., 6 g; 1 × 10 cm) using dry hexane for elution to yield crude *abietane* **39** (50 mg). The latter on recrystallization from MeOH twice afforded colourless needles (33 mg), m.p. 37–38°, $[\alpha]_D$ −5° (MeOH, Calc. from ORD curve); IR ν_{max}: 1463; 1451; 1387; 1368 cm^{-1}. Mass spectrum; M^+ 276, ORD (−)-plain curve (c, 0·289; n-hexane). (Found: C, 86·88; H, 13·33. $C_{20}H_{36}$ requires: C, 86·88; H, 13·12%). GLC: SE-30, Golay-type capillary

† This sample was shown to have 96·5% purity from gas-liquid chromatographical investigation.

column (45 m); oven temp 203°; injection temp: 283°; carrier gas: N_2. Retention time, abietane **39**: 6·6 min.; abietane **39** + *enantio*-abietane **33**: 6·6 min.

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