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TRITERPENES OF *SALACIA PRINOIDES* DC[a]

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Abstract—From the root bark of *Salacia prinoides* DC. (Celastraceae), six closely related triterpenes, P, Q, R, S, T and U have been isolated. These have been shown to be 1,3-diketofriedelane derivatives. The structures of these compounds, **1**, **10**, **39**, **33**, **11** and **12**, have been established on the basis of spectroscopic as well as degradative evidence.

Salacia prinoides DC (Celastraceae) is a large sized shrub commonly found in the Western Ghats of India. Although the roots and bark of this plant have been used in native medicine for the treatment of diabetes, Antarkar *et al.* did not find any lowering of the blood sugar in their clinical investigations.[1]

Heymann *et al.*[2] reported the isolation of two crystalline compounds—A, $C_{30}H_{48}O_3$, m.p. 270–280° and B, $C_{30}H_{46}O_3$, m.p. 290–295°, by extraction of the phellem (root bark) of the plant with light petroleum. From the UV and IR spectral data they showed that these compounds were 1,3-diketones. They could not determine the nature of the third oxygen in these compounds nor could they convert these to any known compound. Huang Wei-Yuan[3] described the chromatographic separation of compounds A and B on alumina and prepared a few derivatives of A and B without arriving at any conclusion regarding the chemical nature of these compounds. Pillay *et al.*[4] reported the isolation from the root bark of a pale yellow compound, m.p. 271–272°, and identified it as mangiferin.

In two recent short communications, Rangaswami *et al.*[5,6] have reported the isolation of friedelin, friedel-1-ene-3-one, friedelane-1,3-dione, friedelane-1,3-dione-24-al and friedelane-1,3-dione-7α-ol from the root bark of *Salacia prinoides*. No details of the physical constants of these compounds or the methods employed for the transformation of these to known structures have been described in these publications.

We have been investigating the constituents of *Salacia prinoides* DC. since 1965 and we wish to present here our results on the isolation and structure elucidation of these compounds. Hexane extraction of the root bark gave a semicrystalline solid which was found by TLC to be a mixture of several compounds. Chromatographic separation of this solid on silica gel gave six crystalline compounds which we have designated as P, Q, R, S, T and U.

The UV spectra of all these compounds showed λ_{max} 261 nm, shifted to about 290 nm on addition of sodium hydroxide, and their IR spectra showed twin bands at about 1740 and 1700 cm^{-1}, indicating that these were all 1,3-diketones.[2] All the compounds showed in their NMR spectra an AB system at δ 3·5 and 3·2 ($J = 16$ Hz) assigned to the hydrogens of the methylene between the two carbonyls of the diketone system. The absence of double bonds in all the compounds was indicated by the lack of colouration with tetranitromethane. Their molecular formulae, established by mass spectra, showed that they were pentacarbocyclic, compound R alone having an additional cyclic ether function.

Compound P (**1**), $C_{30}H_{48}O_2$, indicated in its mass spectrum the presence of a friedelin skeleton.[7–9] Since an enolisable β-diketone group can be located only in ring A, P could be assigned structure **1**, the significant mass spectral fragments at *m/e* 316, 301, 288 and 205 being assigned as **a**, **b**, **c** and **d** respectively.

On the basis of structure **1** for P, correlation with friedelin was attempted in many ways. Methylation of P with diazomethane gave two enol-ethers separated by fractional crystallisation. The ether, m.p. 240°, could be assigned structure **2** since its NMR spectrum showed C_2—H as a doublet at δ 5·38 ($J = 2$ Hz) due to allylic coupling with C_{10}—H and C_{10}—H as a doublet ($J = 2$ Hz) at δ 2·5. The isomer, which was too insoluble for NMR determination, could, by elimination, be assigned structure **3**. LAH reduction of **3** followed by treatment with acid was expected[10] to give friedel-1-ene-3-one. In practice, however, this approach proved very unsatisfactory and gave a mixture of at least four compounds from which was obtained, in poor yield, by fractional crystallisation, an α,β-unsaturated ketone, m.p. 222°, λ_{max} 237 nm (log ε 3·79), M^+ 424. Its m.p., however, is different from the reported m.p., 247–248°, of friedel-1-ene-3-one.[11]

An attempt was then made without success to prepare **1** from friedelin by oxidation of the re-

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ported Δ^2-enol benzoate. Corey *et al.*[2a] have reported that treatment of friedelin with benzoyl chloride at 150–160° gives the Δ^2-enol benzoate, m.p. 260–263°, whereas at 180–190°, the Δ^3-enol benzoate, m.p. 268–275°, is formed. Although the structure of the latter was proved by oxidation to the 2,3-dione, that of the former was not established. We have repeated the benzoylation and find that the only product of the reaction is the Δ^3-enol benzoate, m.p. 265–270°. The NMR spectra of the products from different runs at 150–160° all showed the absence of an olefinic proton expected for the Δ^2-enol benzoate. The difference in the m.ps of the two enol-benzoates reported by Corey *et al.* is also not very marked. Rangaswami *et al.* have mentioned in their communication[5] that they were able to prepare friedelane-1,3-dione by oxidation of the Δ^2-enol benzoate but no details are reported as to how they prepared the latter. Sengupta *et al.*[13] have also reported that in the case of friedelane-3,7-dione (putranjivadione) only the $\Delta^{2,6}$-enol benzoate is formed and none of the Δ^2-isomer.

A successful correlation of P with friedelane was finally achieved by stepwise reduction of the carbonyl groups. Acetylation of P gave an acetate, shown by its UV and IR spectra (see experimental) to be an enol-acetate. Its NMR spectrum shows C_2—H at δ 5·7 as a doublet ($J = 2{\cdot}5$ Hz) due to allylic coupling with C_4—H and C_4—H as an octet at δ 2·5–3·1, in keeping with structure **4**. Hydrogenation of **4** over platinum oxide gave 1-oxo-friedelane (**5**) which was also obtained by desulfurisation of the monothioketal (**6**) of P. The mass spectrum of **5** shows the fragment (**d**) at *m/e* 205, the base peak at *m/e* 273 being (**e**). Wolff-Kishner reduction of **5** under the conditions used by Nagata and Itazaki[14] gave a mixture of friedelane (**7**) (identical in its m.m.p., IR and mass spectra with an authentic sample) and 1-hydroxyfriedelane (**8**), the OH being assigned the equatorial position since the reaction involves strong equilibrating conditions. Dehydration of **8** gave friedel-$\Delta^{1,10}$-ene (**9**) which was resistant to catalytic hydrogenation. The obtention of friedelane establishes the structure of P as **1**.

Compounds Q (**10**) ($C_{30}H_{48}O_2$), T (**11**) ($C_{30}H_{48}O_2$) and U (**12**) ($C_{30}H_{46}O_4$), were found to be closely related, differing only in the degree of oxidation of one of the angular Me groups.

The NMR spectrum of Q shows the AB quartet of the methylene of the β-diketone and a one-proton singlet at δ 10·3 due to an aldehyde group. The NMR spectrum of T shows the methylene of the β-diketone and a two-proton singlet at δ 4·1 due to the methylene hydrogens of an angular hydroxymethyl group. The mass spectra of both Q and T showed a peak at *m/e* 425 arising by loss of CHO and CH_2OH groups respectively from the molecular ion, the other significant peaks being at *m/e* 301 (**f**), *m/e* 273 (**g**), *m/e* 205 (**d**) and *m/e* 153 (**h**). The mass spectra of Q and T indicated that they belong to the friedelin group carrying a CHO and CH_2OH group respectively either at C_5 or C_9. Oxidation of T with pyridine-chromium trioxide gave Q thus showing that the substituents were at the same position in both the compounds.

Reduction of Q with excess sodium borohydride gave a mixture, the major product being the diol (**13**), the hindered C_1-ketone being unaffected. Treatment of this with acetic anhydride yielded an *α,β-unsaturated ketone* (**14**), $C_{32}H_{50}O_3$ (M^+ 482), λ_{max} 230 nm (log ϵ 3·76).

Acetylation of Q with pyridine and acetic anhydride at 60° gave the C-acetate (**15**) whereas at 0°, the product was an enol-acetate (**16**). Hydrogenation of **16** furnished the keto-aldehyde (**17**), $C_{30}H_{48}O_2$ (M^+ 440), which on vigorous Wolff–Kishner reduction under the conditions used by Barton *et al.*,[15] yielded friedelane, thus establishing the nature of the ring system in Q and T.

Methylation of T with diazomethane gave two enol-ethers separated by chromatography. The ether (**18**), m.p. 300–303°, in its NMR spectrum, showed C_2—H as a doublet at δ 5·2 ($J = 1{\cdot}5$ Hz) and C_4—H as a multiplet at δ 2·5 whereas the ether (**19**), m.p. 273–276°, showed C_2—H as a doublet at δ 5·37 ($J = 1$ Hz) and C_{10}—H as a doublet at δ 2·5 ($J = 3$ Hz). LAH reduction of **18** followed by acid treatment[10] gave a mixture from which no α,β-unsaturated ketone could be isolated in a pure state.

Acetylation of T gave the enol-acetates **20** and **21** which were separable by chromatography. Hydrogenation of **20** yielded the keto-acetate (**22**) whereas **21** gave the keto-alcohol (**23**). The mass spectra of **17** and **22** show strong peaks at *m/e* 411 due to M—CHO and M—CH_2OAc fragments respectively, other significant peaks present in both mass spectra being at *m/e* 205 (**d**) and *m/e* 259 (**i**). A peak at *m/e* 288 in **17** is assigned to fragment **j**.

Wolff–Kishner reduction of **22** under the Nagata–Itazaki conditions[14] yielded the diol (**24**) which gave a diacetate (**25**). Vigorous reduction of **22** under the Barton[15] conditions yielded a hydroxy-friedelane, m.p. 233–234°. Acetylation of the latter gave an acetate m.p. 161–162°, whereas oxidation with pyridine–chromium trioxide gave an aldehyde, m.p. 265–266°. Since the presence of a friedelane skeleton had been established and since the mass spectra of all these compounds showed strong peaks at *m/e* 205 (d) and *m/e* 245 (k), the substituent could be attached only to C_5 or C_9. Comparison of the physical properties of the three compounds with those reported for 24-hydroxyfriedelane and 25-hydroxyfriedelane (y-hydroxyfriedelane) and their derivatives[16] showed that the Wolff–Kishner reduction product of **22** was definitely different from 25-hydroxyfriedelane (Table 1). The alcohol and the acetate have fairly close physical properties with those reported for 24-hydroxyfriedelane and its acetate. The m.p. of the aldehyde however differs from the reported m.p. of friedelan-24-al and

Table 1

Compound	m.p.	$[\alpha]_D$
Alcohol from T	233–234°	+20°
24-Hydroxyfriedelane	238–241°	+23°
25-Hydroxyfriedelane	223–226°	+21°, +23°
Acetate from T	161–162°	+20·4°
24-Acetoxyfriedelane	173–175°	+19°
25-Acetoxyfriedelane	143–145°	+13°
Aldehyde from T	265–266°	+39·1°
Friedelan-24-al	180–182°	+25°
Friedelan-25-al	287–290°	−34°, −32°

this is possible only if they are dimorphic. TLC comparison of the acetate of the Wolff–Kishner reduction product with an old sample of synthetic 24-acetoxyfriedelane furnished by Professor Courtney showed that the latter was a mixture of two compounds, the major spot coinciding with our sample. Samples of synthetic 24-hydroxyfriedelane and friedelan-24-al were no longer available and hence no direct comparisons could be made with our products. Position 25 for the OH in our alcohol is also discounted by the absence of a peak at *m/e* 275 in its mass spectrum. A strong peak at *m/e* 275 has been reported in the mass spectrum of 25-hydroxyfriedelane and has been ascribed to the fragment **l**. Since the C_1-ketone of compounds Q and T could not be selectively reduced, comparison with the known friedelan-3-one-24-al[17] was not feasible.

The Wolff–Kishner reduction product is hence assigned structure **26**, the acetate being **27** and the aldehyde **28**. This leads to structures **10** and **11** for Q and T respectively. Comparison of the properties of compound A reported by Heymann *et al.*[2] indicate that this is identical with our compound Q (**10**).

Compound U (**12**) was found to be an acid. Methylation with diazomethane yielded a mixture of two isomeric dimethyl ethers. The ether, m.p. 230°, in its NMR spectrum, shows C_2—H as a doublet at δ 5·2 ($J = 2$ Hz) whereas the isomer, m.p. 240–245°, shows this at δ 5·35 (d, $J = 1·5$ Hz). Comparison of the values with the enol-ethers obtained from T favours structure **29** for the ether m.p. 230°, and **30** for the isomer, m.p. 240–245°.

Compound U was correlated with Q (**10**) by oxidation of both with potassium permanganate in acetone. The diketone group was oxidised to a diacid, the aldehyde in Q also getting oxidised to a carboxylic acid. The products (**31**) from both compounds were esterified with diazomethane to yield an identical tri-ester (**32**). This shows that the carboxyl group in U is in the same position as the aldehyde in Q (**10**) and leads to structure (**12**) for U.

The structure of compound S, $C_{30}H_{48}O_3$, was established as **33**. The compound, also a β-diketone, has the third O atom as a secondary OH group. The mass spectrum of S shows peaks at *m/e* 438 ($M^+ - H_2O$), *m/e* 332 (**m**) and *m/e* 314 (**n**), the base peak being at *m/e* 205 (**d**).

Methylation of S with diazomethane gave a mixture of two enol-ethers, one of which **34** could be obtained pure. Acetylation of S with acetic anhydride and pyridine at reflux temperature gave and C-acetate (**35**) whereas at 0°, the O-acetate (**36**) resulted. The NMR spectrum of the latter showed C_2—H as a doublet at δ 5·72 ($J = 2$ Hz) and C_7—H as a broad signal at δ 5·3. Catalytic hydrogenation of **36** gave **37**, Wolff–Kishner reduction of which yielded 7α-hydroxyfriedelane (epi-putranjivol)[9] (**38**), identical (m.m.p., TLC, IR) with an authentic sample.

Compound R (**39**), $C_{30}H_{46}O_3$, is also a β-diketone. Since it does not possess any additional CO or OH group, the third O atom must be present as an ether function. The NMR spectrum of R (100 MHz) (Fig 1) shows three AB quartets. The doublets (1H each) at δ 3·48 and 3·22 ($J = 16$ Hz) are assigned to the methylene (C_2—H) of the β-diketone system. The pair of doublets (1H each) at δ 4·56 and 4·01 ($J = 11$ Hz) and at δ 4·3 and 3·35 ($J = 11$ Hz) are assigned to protons of the group —CH_2—O—CH_2—. Of these, the proton at δ 4·01 shows a further splitting ($J = 2$ Hz) due to long-range coupling. On the basis of structure **39** for R, the most significant peaks in its mass spectra are considered to be *m/e* 329 (**o**), *m/e* 301 (**p**) and *m/e* 205 (**d**).

Methylation of R with diazomethane gave two enol-ethers separated by crystallisation and chromatography. The ether (**40**), m.p. 340°, in its NMR spectrum, showed C_2—H at δ 5·2 (d, $J = 2$ Hz) and C_4—H as a multiplet at δ 2·6. The isomer (**41**), m.p. 290°, showed C_2—H at δ 5·38 (d, $J = 2$ Hz) and C_{10}—H at δ 2·45 (d, $J = 2$ Hz). LAH reduction of **40** followed by treatment with acid gave an α,β-unsaturated ketone (**42**), $C_{30}H_{46}O_2$ (M^+ 438), λ_{max} 235 nm (log ε 3·83).

Acetylation of R gave the enol-acetate (**43**) whose NMR spectrum showed C_2—H at δ 5·7 (d, $J = 2$ Hz), C_4—H as a multiplet at δ 2·4–2·9 and the four ether hydrogens as a complex multiplet at δ 3–4·7. Catalytic reduction of **43** gave the ketone (**44**), $C_{30}H_{48}O_2$ (M^+ 440). The NMR (100 MHz) spectrum of **44** (Fig 2) showed a pair of doublets at δ 4·6 and 4·05 ($J = 11$ Hz) and another pair at δ 4·27 and 3·32 ($J = 11$ Hz). The C_2—H appears as a two-proton multiplet at δ 2·25 and C_{10}—H as a singlet at δ 2·1. Decoupling experiments showed that the protons at δ 4·6 and 4·05 are coupled to each other and the protons at δ 4·27 and 3·32 are also mutually coupled. The proton at δ 4·05 shows a further splitting ($J = 2$ Hz) due to long-range coupling. That this is not due to the C_{10}—H in any W-type conformation was shown by deuteration of **44** to a tri-deuterio derivative in which this coupling was found to persist. The mass spectrum of **44** shows the fragment (**q**) at *m/e*

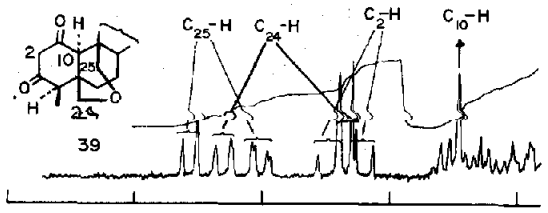


Fig 1.

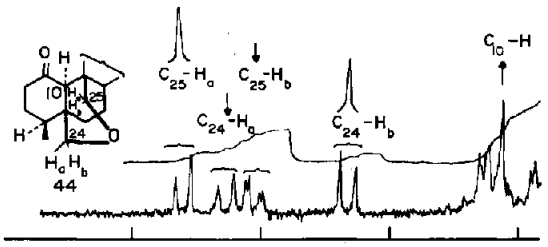


Fig 2.

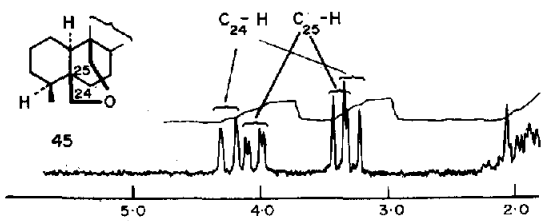
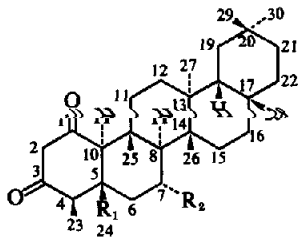


Fig 3.

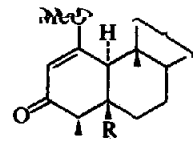
315 which is shifted to *m/e* 318 in the tri-deuterio derivative.

Vigorous Wolff–Kishner reduction of **44** yielded **45**, $C_{30}H_{50}O$ (M^+ 426) whose NMR spectrum (100 MHz) (Fig 3) showed the ether hydrogens as two pairs of doublets—the proton at δ 4·25 being coupled to the one at δ 3·28 (J = 11 Hz) and the proton at δ 4·05 being coupled to the one at δ 3·37 (J = 11 Hz). The proton at δ 4·05 shows, as in the case of **44**, an additional long-range coupling of 2 Hz. Comparison of the NMR spectrum with **44** shows that the protons in **45** at δ 4·25, 3·28 and 4·05 are occurring at virtually the same positions as in **44**. The fourth proton which appears in **44** at δ 4·6 is shifted in **45** to δ 3·37—a shift of 1·25 ppm due to the deshielding effect of the CO of **44** on one of the methylene hydrogens of the ether group. The spectral properties of R and its co-occurrence with the other compounds indicate it to possess a friedelin skeleton with two angular Me groups being modified to a CH_2—O—CH_2 group. The magnitude of the deshielding effect of the CO on one of the four protons of the ether system compares with the shift of 1·26 ppm reported for the C_1—H in compound **46** and such a shift is possible only for one of the hydrogens of C_{25} with a ketone at C_1.[18] The other proton on C_{25} shows the long-range coupling which could be due to the $C_{11\alpha}$—H (W-type). The second Me involved in the ether formation could be either C_{24} or C_{25}. The former is preferred since most of the congeners of R also have the methyl at C_5 in an oxidised state. In view of the difficulty of correlating R with known friedelan derivatives, an attempt is underway to establish its structure by an X-ray analysis of the dibromo-derivative of R, tentatively assigned structure **47**.* Comparison of the physical properties of compound B reported by Heymann *et al.*[2] indicate that this is identical with our compound R.

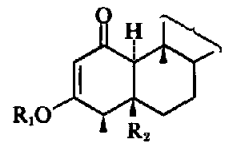
The CD of 1-oxofriedelane derivatives **5**, **22** and **44** and friedelin are presented in Fig 4.



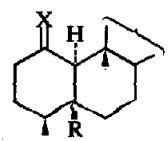
1: R_1 = Me; R_2 = H
10: R_1 = CHO; R_2 = H
11: R_1 = CH_2OH; R_2 = H
12: R_1 = COOH; R_2 = H
33: R_1 = Me; R_2 = OH



2: R = Me
19: R = CH_2OH
30: R = COOMe



3: R_1 = R_2 = Me
4: R_1 = Ac; R_2 = Me
16: R_1 = Ac; R_2 = CHO
18: R_1 = Me; R_2 = CH_2OH
20: R_1 = Ac; R_2 = CH_2OAc
21: R_1 = Ac; R_2 = CH_2OH
29: R_1 = Me; R_2 = COOMe



5: X = O; R = Me
7: X = H_2; R = Me
17: X = O; R = CHO
22: X = O; R = CH_2OAc
23: X = O; R = CH_2OH
26: X = H_2; R = CH_2OH
27: X = H_2; R = CH_2OAc
28: X = H_2; R = CHO

Note added in proof: X-ray diffraction study carried out by Professor D. Rogers has established that *R* is 25,26-oxido-friedel-1,3-dione.

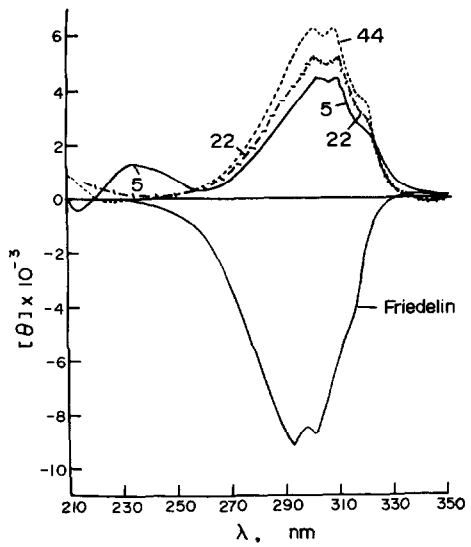
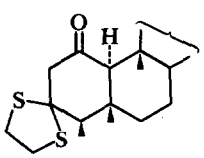


Fig 4. CD of compounds 5, 22, 44 and friedelin.



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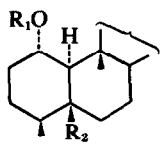
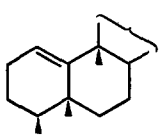


8: $R_1 = H$; $R_2 = Me$
24: $R_1 = H$; $R_2 = CH_2OH$
25: $R_1 = Ac$; $R_2 = CH_2OAc$



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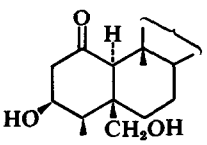

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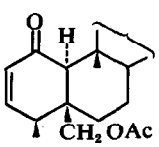
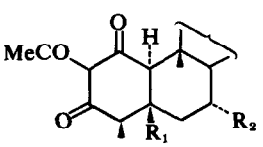
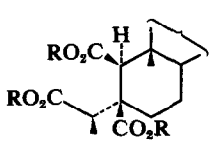


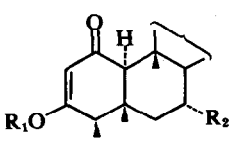
14



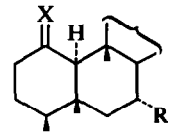
15: $R_1 = CHO$; $R_2 = H$
35: $R_1 = Me$; $R_2 = OAc$



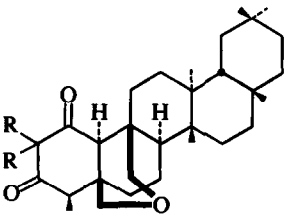
31: R = H
32: R = Me



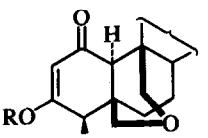
34: $R_1 = Me$; $R_2 = OH$
36: $R_1 = Ac$; $R_2 = OAc$



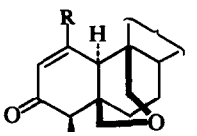
37: X = O; R = OAc
38: $X = H_2$; R = OH



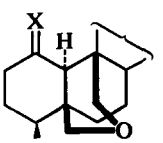
39: R = H
47: R = Br



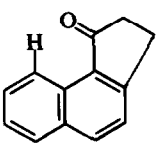
40: R = Me
43: R = Ac



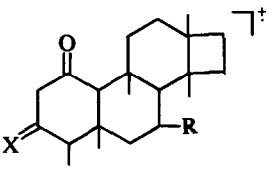
41: R = OMe
42: R = H



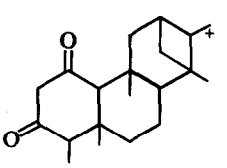
44: X = O
45: $X = H_2$



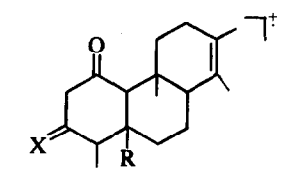
46



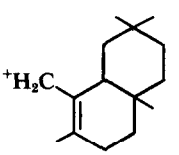
a X = O; R = H *m/e* 316
m X = O; R = OH *m/e* 332



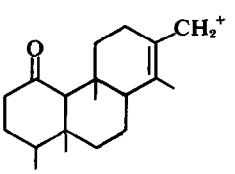
b *m/e* 301



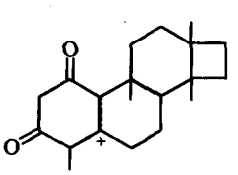
c X = O; R = Me *m/e* 288
j $X = H_2$; R = CHO *m/e* 288



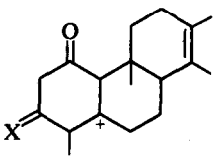
d *m/e* 205



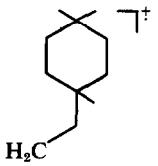
e *m/e* 273



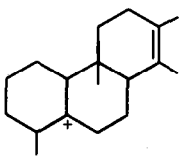
f *m/e* 301



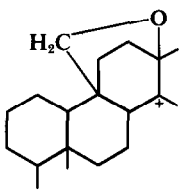
g X = O *m/e* 273
i X = H_2 *m/e* 259



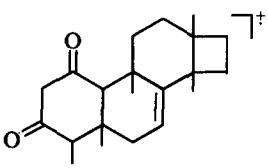
h *m/e* 153



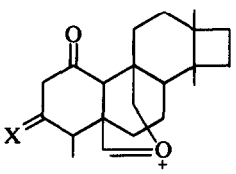
k *m/e* 245



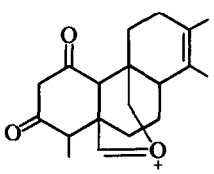
l *m/e* 275



n *m/e* 314



o X = O *m/e* 329
q X = H_2 *m/e* 315



p *m/e* 301

EXPERIMENTAL

Optical rotations were taken at 25° in $CHCl_3$ at c. 2% solns. UV spectra were determined in EtOH. λ^{NaOH} was taken in 0·01 NaOH in 70% EtOH. IR spectra, unless otherwise stated, were taken in nujol. NMR spectra were run in $CDCl_3$.

Isolation of compounds P, Q, R, S, T *and* U. The dried and powdered outer yellow phellem (6 kg) of the root bark of *Salacia prinoides* was repeatedly extracted with cold hexane (5 × 30 l). The pooled extracts gave an orange gummy residue (200 g) which was dissolved in minimum hot $CHCl_3$ and precipitated with hot hexane. The solid (46 g) obtained on cooling was seen by TLC to consist of at least six components. Separation of these was effected by chromatography. The solid (40 g) was chromatographed over silica gel (1200 g) in hexane–C_6H_6 (20 : 80), 50 ml fractions being collected and monitored by TLC.

Fractions corresponding to the same R_f value were combined, evaporated and the residue crystallised from $CHCl_3$–hexane.

(i) Fractions 31–47 gave P (**1**) (2 g), m.p. 280–283°, $[\alpha]_D$ −4·2°, λ_{max} 261 (log ε 3·63), shifted to λ_{max}^{NaOH} 290 nm (log ε 4·30), ν_{max} 1740, 1710, 1300, 1250, 1200, 1175, 1150, 1070, 1050, 1000, 960, 920, 800, 780, 720 cm^{-1} (Found: C, 81·4; H, 10·9. $C_{30}H_{48}O_2$ requires: C, 81·8, H, 11·0%). Mass spectrum: *m/e* 440 (M^+) (100), 425 (30), 397 (2), 369 (4), 316 (100), 301 (18), 288 (100), 287 (100), 273 (28), 261 (50), 260 (60), 246 (55), 205 (60); NMR: δ 3·5 (d, J = 16 Hz, 1H) and 3·15 (d, J = 16 Hz, 1H).

(ii) Fractions 62–89 gave Q (**10**) (3 g), m.p. 303–305°, $[\alpha]_D$ +14·3°, λ_{max} 261 nm (log ε 3·66), shifted to λ_{max}^{NaOH} 290 nm (log ε 4·30), ν_{max} 1740, 1710, 1300, 1280, 1250, 1200, 1180, 1075, 1005, 960, 920, 900, 820, 740, 720 cm^{-1} (Found: C, 79·3; H, 10·2. $C_{30}H_{46}O_3$ requires: C, 79·2; H, 10·2%). Mass spectrum: *m/e* 454 (M^+) (70), 439 (10), 436 (10), 425 (30), 409 (15), 393 (10), 370 (22), 302 (20), 301 (19), 287 (15), 273 (30), 259 (23), 245 (11), 217 (12), 205 (12), 193 (73), 191 (30), 153 (100), 149 (75), 119 (73), 111 (70), 105 (87); NMR: δ 10·3 (s, 1H, CHO), 3·5 (d, J = 16 Hz, 1H), 3·15 (d, J = 16 Hz, 1H).

(iii) Fractions 106–135 gave R (**39**) (8·5 g), m.p. 300–303°, $[\alpha]_D$ −4·3°, λ_{max} 261 nm (log ε 3·70), shifted to λ_{max}^{NaOH} 290 nm (log ε 4·32), ν_{max} 1740, 1700, 1300, 1260, 1205, 1195, 1180, 1120, 1100, 1070, 980, 945, 840, 815, 790, 755, 720, 660 cm^{-1} (Found: C, 79·1; H, 10·2. $C_{30}H_{46}O_3$ requires: C, 79·2; H, 10·2%). Mass spectrum: *m/e* 454 (M^+) (100), 439 (25), 422 (17), 407 (27), 393 (7), 329 (40), 301 (27), 271 (11), 259 (10), 247 (10), 235 (17), 217 (13), 205 (8), 204 (15), 163 (27), 139 (27); NMR (100 MHz): δ 4·56 (d, J = 11 Hz, 1H), 4·3 (d, J = 11 Hz, 1H), 4·01 (dd, J = 11, 2 Hz, 1H), 3·48 (d, J = 16 Hz, 1H), 3·35 (d, J = 11 Hz, 1H), 3·22 (d, J = 16 Hz, 1H), 2·45 (s, C_9—H).

(iv) Fractions 151–172 gave S (**33**) (1·9 g), m.p. 305–310°, $[\alpha]_D$ −5·0°, λ_{max} 261 nm (log ε 3·56), shifted to λ_{max}^{NaOH} 290 nm (log ε 4·33), ν_{max} 3530, 1730, 1700, 1300, 1270, 1250, 1200, 1170, 1100, 1065, 1005, 710 cm^{-1} (Found: C, 79·1; H, 10·9. $C_{30}H_{48}O_3$ requires: C, 78·9; H, 10·6%). Mass spectrum: *m/e* 456 (M^+) (64), 441 (25), 438 (12), 423 (6), 332 (15), 314 (11), 233 (31), 221 (26), 205 (100), 191 (35), 179 (43), 163 (57).

(v) Fractions 191–250 gave T (**11**) (8 g), m.p. 285–287°, $[\alpha]_D$ −14·7°, λ_{max} 261 nm (log ε 3·56), shifted to λ_{max}^{NaOH} 284 nm (log ε 4·33), ν_{max} 3580, 1730, 1700, 1350, 1300, 1200, 1180, 1070, 1040, 1000, 960, 920, 780, 720 cm^{-1} (Found: C, 78·7; H, 10·5. $C_{30}H_{48}O_3$ requires: C, 78·9; H, 10·6%). Mass spectrum: *m/e* 456 (M^+) (2), 438 (12), 425 (80), 407 (7), 315 (8), 301 (10), 287 (32), 273 (100), 261 (55), 259 (86), 231 (16), 205 (38), 191 (50), 179 (70), 153 (20), 151 (48); NMR: δ 4·1 (s, 2H, CH_2OH), 3·5 (d, J = 16 Hz, 1H), 3·18 (d, J = 16 Hz, 1H).

(vi) Fractions 261–280 gave U (**12**) (0·4 g), m.p. 330–335°, $[\alpha]_D$ −27·5°, λ_{max} 261 nm (log ε 3·49), shifted to λ_{max}^{NaOH} 284 nm, (log ε 4·03), ν_{max} 1740, 1700, 1240, 1200, 1170, 1000, 720 cm^{-1} (Found: C, 76·8; H, 10·0. $C_{30}H_{46}O_4$ requires: C, 76·6; H, 9·9%). Mass spectrum: *m/e* 470 (M^+) (52), 452 (55), 437 (35), 424 (19), 409 (17), 399 (12), 320 (48), 318 (26), 317 (28), 300 (17), 273 (15), 259 (16), 205 (16), 203 (16), 175 (25), 163 (45), 151 (100), 137 (55), 123 (90).

Methylation of P. Compound P (1; 400 mg) was suspended in MeOH (20 ml) and treated with excess ethereal CH_2N_2. The ppt was filtered and crystallised from CH_2Cl_2–hexane to yield **3** (160 mg), m.p. 327° (d), λ_{max} 253 nm (log ε 4·13), ν_{max} 1645, 1610 cm^{-1} (Found: C, 81·9; H, 11·3. $C_{31}H_{50}O_2$ requires: C, 81·9; H, 11·1%). Mass spectrum: *m/e* 454 (M^+) (12), 439 (6), 329 (3), 301 (10), 275 (10), 261 (15), 233 (8), 221 (12), 205 (10), 191 (5), 179 (10), 153 (100). A satisfactory NMR spectrum of this could not be obtained due to poor solubility. The mother liquor from **3** on evaporation gave a solid which

Fractions	Eluent	Wt. (g)	R_f TLC on Silica gel in C_6H_6–$CHCl_3$ (1:2)						
1–30	C_6H_6	—	—	—	—	—	—	—	
31–47	C_6H_6	5·4	0·8	—	—	—	—	—	
48–61	C_6H_6	2·5	0·8	0·65	—	—	—	—	
62–89	C_6H_6	3·4	—	0·65	—	—	—	—	
90–105	C_6H_6	2·0	—	0·65	0·57	—	—	—	
106–135	C_6H_6	9·0	—	—	0·57	—	—	—	
136–150	C_6H_6	—	—	—	—	—	—	—	
151–172	C_6H_6–$CHCl_3$ (90:10)	2·3	—	—	—	0·45	—	—	
173–190	C_6H_6–$CHCl_3$ (90:10)	2·0	—	—	—	0·45	0·4	—	
191–210	C_6H_6–$CHCl_3$ (90:10)	2·0	—	—	—	—	0·4	—	
211–250	C_6H_6–$CHCl_3$ (80:20)	7·0	—	—	—	—	0·4	—	
251–260	C_6H_6–$CHCl_3$ (80:20)	—	—	—	—	—	—	—	
261–280	C_6H_6–$CHCl_3$ (70:30)	0·5	—	—	—	—	—	0·2	
281–300	$CHCl_3$	—	—	—	—	—	—	—	
301–330	$CHCl_3$–MeOH (98:2)	2·0	Resinous mass						

crystallised from MeOH to yield the isomeric **2** (98 mg), m.p. 240°, λ_{max} 258 nm (log ϵ 4·12), ν_{max} 1650, 1590 cm^{-1} (Found: C, 81·5, H, 11·1. $C_{31}H_{50}O_2$ requires: C, 81·9; H, 11·1%); NMR: δ 5·38 (d, $J = 2$ Hz, C_2—H), 3·67 (s, 3H, OMe), 2·5 (d, $J = 2$ Hz, C_{10}—H).

LAH *reduction of enol-ether* (**3**). A soln of **3** (200 mg) in dry ether (40 ml) was added under stirring to LAH (300 mg) in ether (30 ml). The mixture was stirred at 50° for 2 hr, cooled and decomposed with HCl (2N, 10 ml). The ether layer was separated, washed with H_2O, dried and evaporated. The residue showed 4 spots on TLC. Fractional crystallisation from CH_2Cl_2–MeOH gave plates, m.p. 222° (30 mg), λ_{max} 237 nm (log ϵ 3·79). Mass spectrum: *m/e* 424 (M^+) (38), 409 (22), 302 (28), 300 (62), 287 (24), 285 (30), 273 (72), 271 (64), 259 (64), 231 (80), 218 (100).

Acetate (**4**). Compound P (**1**; 220 mg) was treated at 0° with Py (5·6 ml) and Ac_2O (0·05 ml). After 24 hr at 0°, the solid that separated was filtered and crystallised from CH_2Cl_2–MeOH to yield **4** (180 mg), m.p. 285°, λ_{max} 237 nm (log ϵ 4·44), ν_{max} 1770, 1665 cm^{-1} (Found: C, 79·6; H, 10·5. $C_{32}H_{50}O_3$ requires: C, 79·6; H, 10·4%); NMR: δ 5·7 (d, $J = 2·5$ Hz, C_2—H), 2·5–3·1 (octet, C_4—H), 2·2 (s, 3H, OAc).

Thioketal (**6**). Compound P (**1**; 200 mg) was treated with ethanedithiol (2 ml) and BF_3 etherate (2 ml) and kept at 25° for 4 days. The solid that separated was filtered and crystallised from CH_2Cl_2–hexane to yield **6** (60 mg), m.p. 301°, ν_{max} 1720 cm^{-1} (Found: C, 74·5; H, 10·3. $C_{32}H_{52}OS_2$ requires: C, 74·4; H, 10·1%). Mass spectrum: *m/e* 516 (M^+) (10), 501 (15), 456 (20), 441 (10), 423 (12), 369 (50), 356 (60), 233 (100).

1-*Oxofriedelane* (**5**): (i) The acetate (**4**; 100 mg) in EtOAc (50 ml) was hydrogenated over PtO_2 (100 mg) in a Parr apparatus at 40 lbs/in² for 7 hr. The soln was filtered, evaporated and the residue crystallised from MeOH to yield **5** (64 mg), m.p. 287°, $[\alpha]_D$ +22·1°, ν_{max} 1700 cm^{-1} (Found: C, 84·1; H, 12·0. $C_{30}H_{50}O$ requires: C, 84·4; H, 11·8%). Mass spectrum: *m/e* 426 (M^+) (60), 411 (30), 302 (60), 287 (15), 273 (100), 247 (70), 232 (88), 205 (85), 193 (55), 179 (60), 125 (100); CD (c, 0·031, dioxane): $[\theta]_{390}$ 0; $[\theta]_{309·5}$ +4430; $[\theta]_{306}$ +4260; $[\theta]_{302}$ +4430; $[\theta]_{259}$ +170; $[\theta]_{233}$ +1362; $[\theta]_{214}$ −469; $[\theta]_{210}$ 0.

(ii) The thioketal (**6**; 50 mg) in EtOH (20 ml) was refluxed for 16 hr with Raney Ni (1 g). The soln was filtered, evaporated and the residue crystallised from MeOH to yield **5** (25 mg), m.p. 287°, identical (m.m.p., IR) with the sample prepared from the enol-acetate.

Wolff–Kishner reduction of 1-*oxofriedelane*. The ketone **5** (200 mg) was heated in a sealed tube at 180° for 16 hr with anhyd hydrazine (5 ml) and NaOEt (2 g Na dissolved in 50 ml EtOH). Addition of H_2O and extraction with $CHCl_3$ gave a solid which consisted mainly of 2 compounds as seen by TLC. Preparative TLC (Silica gel, C_6H_6) gave **7** (15 mg), m.p. 250° (from CH_2Cl_2–MeOH), identical (m.m.p., IR, mass spectrum) with an authentic sample. Mass spectrum: *m/e* 412 (M^+) (81), 397 (13), 259 (30), 233 (20), 218 (25), 217 (27), 205 (27), 204 (30), 191 (30), 179 (32), 177 (36), 163 (40), 149 (100), 137 (58), 135 (56), 125 (80), 123 (100), 121 (60). The more polar fraction gave **8** (100 mg), m.p. 255° (from C_6H_6), ν_{max}^{KBr} 3620 cm^{-1}. The compound was used for dehydration.

Friedel-$\Delta^{1,10}$*-ene* (**9**). 1-Hydroxyfriedelane **8** (80 mg) was heated for 6 hr at 110° with Py (2 ml) and $MeSO_2Cl$ (0·5 ml), treated with dil HCl and extracted with CH_2Cl_2. The product was passed through a short column of Al_2O_3 in CH_2Cl_2 and then crystallised from CH_2Cl_2–MeOH to yield **9** (40 mg), m.p. 218–220°, ν_{max}^{KBr} 1630 cm^{-1}. Mass spectrum: *m/e* 410 (M^+) (18), 395 (27), 286 (35), 205 (32), 149 (35), 135 (32), 123 (100); NMR: δ 5·32 (t, $J = 3$ Hz, C_1—H), 2·05 (m, 2H, C_2—H). The compound was recovered after attempted catalytic reduction in AcOH over PtO_2 for 16 hr at 50° in a Parr apparatus at 45 lbs/in².

Py—CrO_3 *oxidation of compound* **T**. A soln of com-

pound T (**11**; 400 mg) in Py (3 ml) was added to Py—CrO_3 complex (from 500 mg CrO_3 and 6 ml Py) at 5°. The mixture was stirred at 10° for 12 hr and diluted with C_6H_6. The soln was filtered, the filtrate washed (dil HCl, H_2O), dried and evaporated. Chromatography of the residue over SiO_2 in C_6H_6–ether (3:1) gave a solid (200 mg), m.p. 302–304° (from $CHCl_3$–ether), identical (m.m.p., TLC, IR and NMR) with compound Q (**10**).

$NaBH_4$ *reduction of* Q. A soln of Q (**10**; 500 mg) in EtOH (30 ml) and C_6H_6 (10 ml) was refluxed for 16 hr with $NaBH_4$ (1·5 g). Addition of H_2O and extraction with CH_2Cl_2 gave a solid which was chromatographed over Al_2O_3 in C_6H_6. The major fraction gave **13** (130 mg), m.p. 290–295° (from CH_2Cl_2–MeOH), ν_{max}^{KBr} 3620, 3580, 1705 cm^{-1} (Found: C, 78·3; H, 11·3. $C_{30}H_{50}O$ requires: C, 78·6; H, 11·0%). Mass spectrum: *m/e* 458 (M^+) (28), 440 (20), 425 (20), 411 (28), 259 (25), 245 (28), 217 (30), 205 (37), 203 (30), 193 (100), 191 (72), 175 (28), 161 (28), 153 (33).

The diol **13** (100 mg) was acetylated with Py/Ac_2O at 80° for 12 hr to yield **14** (30 mg), m.p. 208–209° (from ether–MeOH), λ_{max} 230 nm (log ϵ 3·76), ν_{max} 1735, 1700, 1680 cm^{-1} (Found: C, 79·6; H, 10·7. $C_{32}H_{50}O_3$ requires: C, 79·6; H, 10·4%). Mass spectrum: *m/e* 482 (M^+) (10), 422 (100), 409 (80), 407 (50), 284 (25), 271 (37), 257 (37), 245 (36), 243 (30), 231 (37), 217 (25), 205 (25), 203 (37), 191 (38), 177 (50), 147 (50), 137 (37), 123 (75).

C-Acetylation of compound Q. Compound Q (**10**; 200 mg) in Py (5 ml) was heated at 60° for 6 hr with Ac_2O (2 ml), evaporated *in vacuo* and poured on to H_2O to yield **15** (150 mg), m.p. 170° (from EtOAc–MeOH), λ^{max} 234, 281 nm (log ϵ 3·93, 3·95), shifted to λ_{max} 275 nm (log ϵ 4·16) on addition of NaOH.

O-Acetylation of compound Q. A soln of Q (**10**; 220 mg) in Py (5 ml) was treated at 0° with Ac_2O (0·05 ml). After 24 hr at 0°, water was added, the solid filtered and crystallised from CH_2Cl_2–MeOH to yield **16** (110 mg), m.p. 260–262°, λ_{max} 238 nm (log ϵ 3·96), ν_{max} 1775, 1720, 1660 cm^{-1} (Found: C, 77·8; H, 10·0. $C_{32}H_{48}O_4$ requires: C, 77·4; H, 9·7%); NMR δ 10·35 (s, 1H, CHO), 5·7 (d, J = 2 Hz, C_2—H), 2·2 (s, 3H, OAc).

1,24-*Dioxofriedelane* (**17**). The acetate **16** (70 mg) in EtOAc (50 ml) was shaken with PtO_2 and H_2 at 35 lbs/in² in a Parr apparatus for 7 hr. The soln was filtered, evaporated and the residue crystallised from CH_2Cl_2–MeOH to yield **17** (30 mg), m.p. 285°, ν_{max}^{KBr} 1705 cm^{-1} (Found: C, 81·7; H, 11·3. $C_{30}H_{48}O_2$ requires: C, 81·8; H, 11·0%); NMR: δ 10·35 (s, 1H, CHO). Mass spectrum. *m/e* 440 (M^+) (90), 425 (30), 411 (60), 395 (28), 379 (25), 356 (30), 288 (80), 273 (50), 259 (70), 205 (60), 193 (100), 191 (85), 153 (85).

Wolff-Kishner reduction of **17**. The ketoaldehyde **17** (0·4 g) was heated with Na (1·8 g) in diethylene glycol (80 ml) and anhyd hydrazine (30 ml) at 210° for 16 hr to give friedelane (40 mg) identical (m.m.p., IR, mass spectrum) with an authentic sample.

Methylation of compound T. A soln of T (**11**; 1 g) in a mixture of $CHCl_3$ (20 ml) and MeOH (5 ml) was treated with excess CH_2N_2 and the product chromatographed over SiO_2 in C_6H_6. The column was eluted successively with C_6H_6, C_6H_6–$CHCl_3$ (1:1) and $CHCl_3$. The earlier fractions gave the ether **18** (500 mg), plates (from CH_2Cl_2–MeOH), m.p. 300–303°, λ_{max} 253 nm (log ϵ 4·13), ν_{max} 1640, 1615 cm^{-1} (Found: C, 78·5; H, 11·0. $C_{31}H_{50}O_3$ requires: C, 79·1, H, 10·7%). Mass spectrum: *m/e* 470 (M^+) (2), 455 (28), 453 (30), 439 (20), 287 (25), 278 (13), 273 (13), 261 (10), 251 (10), 249 (13), 235 (10), 233 (13), 221 (20), 207 (28), 205 (12), 153 (100), 121 (50); NMR: δ 5·2 (C_2—H, d, J = 1·5 Hz), 4·1 (2H, broad singlet), 3·6 (s, 3H, OMe), 2·5 (m, 1H, C_4—H), 2·05 (s, 1H, C_{10}—H).

The later fractions in the chromatography gave the ether **19** (250 mg), needles (from CH_2Cl_2–MeOH), m.p. 273–276°, λ_{max} 258 nm (log ϵ 4·17), ν_{max} 1640, 1600 cm^{-1} (Found: C, 79·4; H, 10·5. $C_{31}H_{50}O_3$ requires: C, 79·1; H, 10·7%). Mass spectrum: *m/e* 470 (M^+) (1), 439 (15), 287 (15), 275 (10), 273 (14), 261 (6), 153 (100), 123 (20), 121 (20); NMR: δ 5·37 (d, J = 1Hz, C_2—H), 4·1 (s, 2H), 3·67 (s, 3H, OMe), 2·5 (d, J = 1 Hz, C_{10}—H), 2·1 (m, 1H, C_4—H).

Acetylation of compound T. A soln of T (**11**; 600 mg) in Py (15 ml) was cooled to 5° and treated with Ac_2O (12 ml). After 16 hr at 5°, the solution was evaporated *in vacuo* below 40°, diluted with H_2O and extracted with ether. The ether extract was washed (dil HCl, H_2O), dried, evaporated and the product chromatographed over SiO_2 in C_6H_6. The column was eluted successively with C_6H_6, C_6H_6–$CHCl_3$ (1:1), $CHCl_3$ and $CHCl_3$–MeOH (98:2). The earlier fractions gave **20** (200 mg), m.p. 220–223° (from CH_2Cl_2–MeOH), λ_{max} 237 nm (log ϵ 3·97), shifted to λ_{max} 290 nm (log ϵ 4·15) on addition of NaOH, ν_{max}^{KBr} 1770, 1740, 1680 cm^{-1} (Found: C, 75·7; H, 9·8. $C_{34}H_{52}O_5$ requires: C, 75·5; H, 9·7%). The later fractions in the chromatography yielded **21** (130 mg), m.p. 248–251° (from CH_2Cl_2–MeOH), λ_{max} 237 nm (log ϵ 3·85) shifted to λ_{max} 290 nm (log ϵ 4·05) on addition of NaOH, ν_{max}^{KBr} 1775, 1670 cm^{-1} (Found: C, 76·9; H, 10·3. $C_{32}H_{50}O_4$ requires: C, 77·1; H, 10·1%).

1-*Oxo*-24-*acetoxyfriedelane* (**22**). A soln of **20** (700 mg) in EtOAc (120 ml) was reduced with H_2 at 40 lbs/in² in a Parr apparatus in presence of PtO_2 (200 mg) for 7 hr, filtered and evaporated. Crystallisation from CH_2Cl_2–MeOH gave **22** (380 mg), m.p. 196–198°, $[\alpha]_D$ +16·2°, ν_{max}^{KBr} 1735, 1700 cm^{-1} (Found: C, 79·6; H, 11·2. $C_{32}H_{52}O_3$ requires: C, 81·4; H, 11·4%); NMR: δ 4·1 (br, s, 2H, (M^+) (6), 469 (6), 442 (7), 424 (100), 411 (90), 393 (27), 286 (45), 273 (65), 272 (70), 259 (60), 247 (65), 232 (42), 231 (45), 217 (30), 206 (50), 205 (51), 203 (40), 191 (45), 177 (62), 163 (45), 147 (46), 133 (52), 125 (70), 123 (60); NMR: δ 4·52 (q, J = 4 Hz, 2H), 2·1 (s, 3H); CD (*c*, 0·059, dioxane) $[\theta]_{340}$ 0; $[\theta]_{310}$ +5082; $[\theta]_{305}$ +4840; $[\theta]_{301}$ + 5180; $[\theta]_{240}$ + 48; $[\theta]_{215}$ + 629.

1-*Oxo*-24-*hydroxyfriedelane* (**23**). The monoacetate **21** (250 mg) in EtOAc (120 ml) was reduced as above to yield **23** (100 mg), m.p. 274–275° (from CH_2Cl_2–MeOH), ν_{max}^{KBr} 3540, 1695 cm^{-1} (Found. C, 81·5; H, 11·7. $C_{30}H_{50}O_2$ requires: C, 81·4; H, 11·4%); NMR: δ 4·1 (br, s, 2H, C_{24}—H).

Wolff-Kishner reduction of **22**. (i) The ketoacetate **22** (200 mg) was heated in a sealed tube at 180° for 24 hr with hydrazine hydrate (98%; 4 ml) and NaOEt (2 g Na dissolved in 40 ml EtOH), cooled, diluted with H_2O and extracted with $CHCl_3$. Chromatography of the product over SiO_2 in C_6H_6 gave **24** (85 mg), m.p. 237–240° (from CH_2Cl_2–MeOH), $[\alpha]_D$ + 6·4°, ν_{max}^{KBr} 3620, 3500 cm^{-1}. Mass spectrum: *m/e* 444 (M^+) (1), 426 (3), 413 (50), 395 (50), 261 (30), 243 (35), 229 (25), 217 (20), 205 (35), 203 (30), 191 (32), 177 (30), 163 (30), 149 (30), 123 (50), 121 (40), 109 (75), 95 (100).

Acetylation of the diol with Py/Ac_2O at 60° for 4 hr gave **25** which could not be crystallised; NMR: δ 5·45 (1H, broad), 4·5 (s, 2H), 2·08 (s, 3H), 2·03 (s, 3H).

(ii) Sodium (1·5 g) in freshly distilled diethylene glycol (60 ml) was heated to 180° (all temps measured with thermometer in liquid) and anhydrous hydrazine (18 ml) added till the mixture refluxed at 180°. The soln was

cooled, the ketoacetate **22** (500 mg) added and the soln refluxed for 14 hr. Part of the hydrazine was then distilled off until a reflux temp of 210° was attained. After refluxing for 16 hr more, the soln was cooled, diluted with H_2O and extracted with CH_2Cl_2. Chromatography of the product over SiO_2 in C_6H_6 gave **26** (250 mg), m.p. 233–234° (from CH_2Cl_2–MeOH), $[\alpha]_D$ +20·0°, ν_{max}^{KBr} 3630 cm^{-1} (Found: C, 84·1; H, 12·3. Calc. for $C_{30}H_{52}O$: C, 84·0; H, 12·2%). Mass spectrum: *m/e* 428 (M^+) (1), 397 (65), 245 (35), 233 (25), 231 (50), 219 (15), 217 (18), 205 (95), 203 (22), 177 (27), 163 (22), 149 (45), 137 (36), 135 (35), 123 (80), 109 (100), 95 (45); NMR: δ 4·1 (d, $J = 3$ Hz, 2H, C_{24}—H). The above alcohol (100 mg) was acetylated with Py/Ac_2O at 60° for 6 hr to get **27** (60 mg), m.p. 161–162° (from CH_2Cl_2–MeOH), $[\alpha]_D$ +20·4°, ν_{max}^{KBr} 1735 cm^{-1} (Found: C, 81·7; H, 11·8. Calc. for $C_{32}H_{54}O_2$: C, 81·6; H, 11·6%). Mass spectrum: *m/e* (M^+ not seen), 410 (M–AcOH) (57), 397 (70), 395 (23), 259 (16), 245 (26), 233 (20), 231 (18), 218 (20), 205 (30), 191 (20), 177 (40), 163 (27), 149 (100), 137 (35), 135 (42), 123 (22), 109 (35), 95 (42); NMR: δ 4·48 (s, 2H, C_{24}—H), 2·05 (s, 3H, OAc).

Oxidation of **26** (120 mg) with Py–CrO_3 (from 200 mg CrO_3 and 2 ml pyridine) yielded **28** (90 mg), m.p. 265–266° (from CH_2Cl_2–MeOH), ν_{max}^{KBr} 1705 cm^{-1}, $[\alpha]_D$ +39·1° (Found: C, 83·9; H, 12·2. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). Mass spectrum: *m/e* 426 (M^+) (40), 411 (20), 397 (41), 274 (50), 273 (50), 245 (100), 231 (90), 219 (42), 217 (85), 205 (90), 203 (50), 193 (95), 177 (85), 163 (80), 153 (80), 149 (75). NMR: δ 10·3 (s, CHO).

Methylation of compound U (**12**) *with* CH_2N_2. Compound U (100 mg) in MeOH (5 ml) was treated with excess ethereal CH_2N_2 and the product crystallised from CH_2Cl_2–MeOH to yield **29** (35 mg), m.p. 230°, ν_{max} 1720, 1650, 1610 cm^{-1} (Found: C, 76·7; H, 10·2. $C_{32}H_{50}O_4$ requires: C, 77·1; H, 10·1%). Mass spectrum: *m/e* 498 (M^+) (26), 483 (13), 466 (15), 451 (22), 439 (35), 423 (40), 347 (17), 287 (35), 275 (15), 248 (18), 233 (20), 205 (10), 153 (100); NMR: δ 5·2 (d, $J = 2$ Hz, C_2—H), 3·65 (s, 6H, OMe). (The mother liquor on evaporation and crystallisation gave **30** (25 mg), m.p. 240–245°. Mass spectrum: *m/e* 498 (M^+) (85), 483 (12), 466 (15), 451 (25), 439 (33), 423 (60), 347 (20), 331 (25), 287 (85), 275 (25), 248 (10), 233 (15), 205 (10), 153 (100). NMR: δ 5·35 (d, $J = 1·5$ Hz, C_2—H), 3·62 (s, 6H, OMe).

$KMnO_4$ *oxidation of compound* Q. A soln of compound Q (**10**; 300 mg) in aldehyde-free acetone (70 ml) was treated with $KMnO_4$ (1 g), refluxed with stirring for 2 hr and evaporated. The residue in dil H_2SO_4 (6%) was treated with small amounts of $NaHSO_3$ and the white ppt filtered to yield the crude **31** (275 mg), m.p. 200° (d), ν_{max} 1710 cm^{-1} (broad). This was treated with excess ethereal CH_2N_2 and the product chromatographed over Al_2O_3 (6 g) in C_6H_6 to yield **32** (28 mg), m.p. 175–176° (from hexane), ν_{max}^{KBr} 1735 cm^{-1} (Found: C, 71·9; H, 10·1. $C_{32}H_{52}O_6$ requires: C, 72·1; H, 9·8%). Mass spectrum: *m/e* 532 (M^+) (4), 501 (25), 473 (33), 445 (100), 413 (33), 385 (75), 321 (20), 289 (12), 251 (20), 233 (46), 221 (25). NMR: δ 3·6 (s, 9H).

$KMnO_4$ *oxidation of compound* U. Compound U (**12**; 200 mg) in acetone (50 ml) was oxidised with $KMnO_4$ (500 mg) as above to yield the crude **31** (170 mg), m.p. 210° (d). Methylation of this with CH_2N_2 gave **32** (13 mg), identical (mixed m.p., IR, TLC) with the ester from compound Q.

Methylation of compound S. Compound S (**33**; 100 mg) in a mixture of MeOH and $CHCl_3$ was treated with excess CH_2N_2 and the solid that separated was filtered and crystallised from $CHCl_3$–MeOH to yield **34** (50 mg), m.p. 315–320°, ν_{max} 3520, 1640, 1610 cm^{-1} (Found: C, 79·1; H, 11·0. $C_{32}H_{52}O_3$ requires: C, 79·3; H, 10·8%). The mother liquor showed the presence of another compound but this could not be obtained pure even by chromatography.

C,O-*Diacetate* (**35**) *from compound* S. Compound S (**33**; 100 mg) was refluxed for 1 hr with AcOH (3 ml), Py (1·5 ml) and Ac_2O (3 ml) and left overnight at 30°. The solvents were removed *in vacuo* and the residue crystallised from CH_2Cl_2–MeOH to yield **35** (48 mg), m.p. 204°, λ_{max} 234, 281 nm (log ε 3·98, 4·01), ν_{max}^{KBr} 1730, 1670 cm^{-1} (Found: C, 75·0; H, 10·3. $C_{34}H_{52}O_5$ requires: C, 75·5; H, 9·7%). Mass spectrum: *m/e* 540 (M^+) (33), 525 (17), 481 (67), 465 (17), 335 (70), 317 (50), 275 (50), 247 (100), 205 (98), 181 (83); NMR: δ 5·4 (m, C_7—H), 2·55 (s, 3H, C_2—Ac), 2·05 (s, 3H, C_7—OAc).

O,O-*Diacetate* (**36**) *from compound* S. Compound S (**33**; 850 mg) in Py (14 ml) was cooled to 10° and treated with Ac_2O (13 ml) and stirred for 20 hr at 10°. The soln was evaporated *in vacuo* and the residue extracted with ether to yield **36** (450 mg), m.p. 248–251°, λ_{max} 238 nm (log ε 3·97), ν_{max}^{KBr} 1755, 1722, 1710, 1670 cm^{-1} (Found: C, 75·2; H, 10·0. $C_{34}H_{52}O_5$ requires: C, 75·5; H, 9·7%). Mass spectrum: *m/e* 540 (M^+) (100), 525 (36), 498 (60), 481 (80), 439 (88), 423 (24), 149 (96); NMR: δ 5·72 (d, $J =$ 2 Hz, C_2—H), 5·3 (br, 1H, C_7—H), 2·2 (s, 3H), 2·05 (s, 3H).

1-*Oxo-7-α-acetoxyfriedelane* (**37**). The diacetate (**36**; 450 mg) in EtOAc (120 ml) was reduced over PtO_2 in a Parr apparatus for 16 hr. The product crystallised from CH_2Cl_2–MeOH to yield **37** (250 mg), m.p. 262–265°, ν_{max}^{KBr} 1720–1705 cm^{-1} (broad) (Found: C, 78·9; H, 10·9. $C_{32}H_{52}O_3$ requires: C, 79·3; H, 10·8%); NMR: δ 5·3 (m, 1H, C_7—H), 2·02 (s, 3H, OAc).

7-*α-Hydroxyfriedelane* (**38**). Sodium (0·8 g) was added to diethylene-glycol (40 ml), heated to 180° and anhyd hydrazine (12 ml) added, followed by **37** (300 mg). The soln was refluxed for 16 hr at 180°, part of the hydrazine distilled off and the residual solution refluxed at 210° for 16 hr more. It was cooled, diluted with H_2O and extracted with $CHCl_3$. Chromatography of the product over SiO_2 in C_6H_6 yielded **38** (130 mg), m.p. 248–249° (from CH_2Cl_2–MeOH), $[\alpha]_D$ +13·1°, ν_{max}^{KBr} 3620 cm^{-1} (Found: C, 84·2; H, 12·3. Calc. for $C_{30}H_{52}O$: C, 84·0; H, 12·2%). Mass spectrum: *m/e* 428 (M^+) (2), 410 (28), 395 (19), 231 (12), 205 (32), 193 (30), 191 (19), 177 (72), 163 (32), 149 (22), 137 (32), 123 (39), 121 (35), 109 (67), 95 (100). It was identical (m.m.p., TLC, IR) with authentic epiputranjivol (7-α-hydroxyfriedelane).[9] It differs from putranjivol (7-β-hydroxyfriedelane)[9] in TLC and IR.

Methylation of compound R. Compound R (**39**; 1 g) in a mixture of MeOH (15 ml) and $CHCl_3$ (15 ml) was treated with excess ethereal CH_2N_2. The solid that separated was filtered and crystallised from $CHCl_3$-hexane to yield **40** (300 mg), m.p. 340°, λ_{max} 256 nm (log ε 4·14), ν_{max} 1645, 1610 cm^{-1} (Found: C, 79·6; H, 10·6. $C_{31}H_{48}O_3$ requires: C, 79·4; H, 10·3%); NMR: δ 5·2 (d, $J = 2$ Hz, C_2—H), 3·6 (s, 3H, OMe), 2·6 (m, 1H, C_4—H). The mother liquor on chromatography over SiO_2 in C_6H_6 and elution with C_6H_6–$CHCl_3$ (1:2) gave more of **40** (65 mg) and the isomer **41** (255 mg), m.p. 290° (from $CHCl_3$–hexane), λ_{max} 258 nm (log ε 4·14), ν_{max} 1640, 1600 cm^{-1} (Found: C, 79·3; H, 10·7. $C_{31}H_{48}O_3$ requires: C, 79·4; H, 10·3%); NMR: δ 5·38 (d, $J = 2$Hz, C_2—H), 3·7 (s, 3H, OMe), 2·45 (d, $J = 2$ Hz, C_{10}—H), 3·9–4·5 (m, 3H), 3·35 (d, $J = 12$ Hz, 1H).

LAH *reduction of* **40**. The ether **40** (300 mg) in ether (50 ml) was added to LAH (300 mg) in ether (50 ml) and the mixture was refluxed for 2 hr, cooled and decomposed with dil HCl. The product was chromatographed over SiO_2. C_6H_6 to yield **42** (105 mg), m.p. 205° (from CH_2Cl_2–hexane), λ_{max} 235 nm (log ϵ 3·82), ν_{max} 1680 cm^{-1} (Found: C, 82·0; H, 10·7. $C_{30}H_{46}O_2$ requires: C, 82·1; H, 10·6%. Mass spectrum: *m/e* 438 (M^+) (50), 423 (100), 393 (42), 391 (40), 314 (30), 313 (30), 301 (25), 286 (30), 269 (30), 255 (35), 217 (65), 205 (30), 189 (30).

Acetylation of compound R. Compound R (**39**, 300 mg) in Py (7 ml) was cooled to 5°, treated with Ac_2O (6 ml) and stirred at 5° for 20 hr. The soln was concentrated *in vacuo* to 3 ml, filtered and washed with ether to yield **43** (270 mg), m.p. 285–288° (from $CHCl_3$–MeOH), λ_{max} 239 nm (lg ϵ 3·97), ν_{max}^{KBr} 1770, 1750, 1660, 1610 cm^{-1} (Found: C, 77·3; H, 10·0. $C_{32}H_{48}O_4$ requires: C, 77·4; H, 9·7%). Mass spectrum: *m/e* 496 (M^+) (80), 454 (24), 439 (9), 426 (8), 407 (8), 301 (100), 259 (9), 218 (15), 205 (6), 163 (11), 139 (22); NMR: δ 5·7 (d, J = 2 Hz, C_2—H), 2·2 (s, 3H), 3–4·7 (complex multiplet, 4H, CH_2—O—CH_2), 2·4–2·9 (m, C_4—H).

Catalytic reduction of **43**. A solution of **43** (250 mg) in EtOAc (150 ml) was reduced in a Parr apparatus over PtO_2 (100 mg) for 3 hr, filtered and evaporated. Chromatography of the residue over Al_2O_3 in C_6H_6 gave **44** (170 mg), m.p. 295–300° (from CH_2Cl_2–MeOH), ν_{max}^{KBr} 1700 cm^{-1} (Found: C, 81·7; H, 11·2. $C_{30}H_{48}O_2$ requires: C, 81·8; H, 11·0%). Mass spectrum: *m/e* 440 (M^+) (70), 425 (28), 408 (63), 393 (40), 315 (100), 235 (28), 217 (40), 204 (70), 147 (36), 137 (30), 125 (30), 121 (30); NMR (100 MHz): δ 4·6 (d, J = 11 Hz, 1H), 4·27 (d, J = 11 Hz, 1H), 4·05 (dd, J = 11, 2 Hz, 1H), 3·32 (d, J = 11 Hz, 1H), 2·25 (m, 2H, C_2—H), 2·1 (s, 1H, C_9—H); CD (*c*, 0·046, dioxane): $[\theta]_{340}$ 0; $[\theta]_{308.5}$ +6122; $[\theta]_{305}$ +5906; $[\theta]_{300}$ +6193; $[\theta]_{223}$ −143; $[\theta]_{210}$ +909.

Deuteration of **44**. Ketone **44** (130 mg) was added to a soln of Na (300 mg) in C_2H_5OD (8 ml) and dry dioxane (5 ml). The soln was refluxed for 24 hr, evaporated *in vacuo*, treated with ice-cold dil HCl and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed quickly with cold H_2O, dried, evaporated and the residue crystallised from CH_2Cl_2–hexane to yield **44**-d_3 (100 mg), m.p. 295°. Mass spectrum: *m/e* 443 (M^+) (10), 428 (5), 412 (13), 411 (18), 396 (7), 318 (30), 290 (13), 273 (6), 261 (5), 260 (5), 235 (6), 220 (5), 217 (5), 204 (11), 163 (16), 151 (12), 149 (12), 145 (14), 128 (22), 81 (68), 69 (100); NMR (100 MHz): δ 4·6 (d, J = 11 Hz, 1H), 4·27 (d, J = 11 Hz, 1H), 4·05 (dd, J = 11, 2 Hz, 1H), 3·32 (d, J = 11 Hz, 1H).

Wolff–Kishner reduction of **44**. Na (1·6 g) was added to diethylene glycol (80 ml) and heated to 180°. Anhyd hydrazine (20 ml) was added followed by **44** (1·1 g). The soln was refluxed at 180° for 36 hr, part of the hydrazine distilled off and the residual soln refluxed at 210° for 12 hr more. Addition of H_2O and extraction with CH_2Cl_2 gave a solid which was chromatographed over SiO_2 in C_6H_6–hexane to yield **45** (480 mg), prisms (from CH_2Cl_2–MeOH), m.p. 244–246° (Found: C, 84·7; H, 12·2. $C_{30}H_{50}O$ requires: C, 84·4; H, 11·8%). Mass spectrum: *m/e* 426 (M^+) (21), 411 (18), 381 (21), 379 (32), 257 (25), 243 (26), 235 (23), 231 (20), 229 (25), 189 (12), 177 (15), 175 (13), 163 (13), 149 (15), 95 (78), 81 (90), 43 (100); NMR (100 MHz): δ 4·25 (d, J = 11 Hz, 1H), 4·05 (dd, J = 11, 2 Hz, 1H), 3·37 (d, J = 11 Hz, 1H), 3·28 (d, J = 11 Hz, 1H).

Bromination of R. Compound R (**39**, 232 mg) in $CHCl_3$ (4 ml) was treated with a soln of Br_2 in AcOH (0·603 M; 1·75 ml). After stirring at 30° for 30 min, MeOH was added and the solid filtered to yield **47** (140 mg), m.p. 340° (from $CHCl_3$–MeOH) (Found: C, 59·5; H, 7·4; Br, 27·2. $C_{30}H_{44}Br_2O_3$ requires: C, 58·8; H, 7·2; Br, 26·1%).

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