Triterpenes of the Root-bark of *Salacia prenoides* DC

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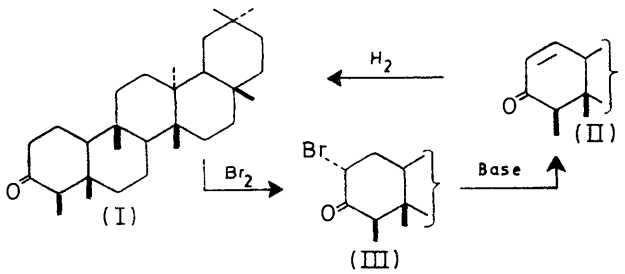
The isolation of six friedelane derivatives from the root-bark of *Salacia prenoides*, and the identification of four of them as friedel-1-en-3-one (II), friedelane-1,3-dione (V), 1,3-dioxofriedelan-24-al (VI), and 7α-hydroxyfriedelane-1,3-dione (VII) by chemical and spectroscopic means, is described.

Salacia prenoides (DC) (Celastraceae) is an Indian shrub whose roots and leaves are used in Indian medicine as an oral antidiabetic. Heymann and his co-workers [1] isolated two crystalline compounds from the root bark, 'compound A' $C_{30}H_{48}O_3$, and 'compound B' $C_{30}H_{46}O_3$. Both compounds possess a β-diketone system. Wei-Yuan Huang [2] reported the preparation of their dideoxo derivatives. Pillay and Lekshmi [3] isolated dulcitol and mangiferin, and Krishnan [4] isolated a naphthoquinone pigment and gutta percha.

We recently reported [5] the isolation of five crystalline compounds from this plant and indicated their structures. We now describe the elucidation of these structures. The compounds were isolated by fractionating the petroleum extract of the root bark into methanol-soluble and -insoluble portions. The methanol-soluble portion after further purification was chromatographed over silica gel. Six compounds (A—F) were eluted from the column. Our 'compound E', which appears to be the same as 'compound B' of Heymann, was not mentioned in our earlier communication, and our work on the structure of our 'compound E' is not yet complete.

Compounds A *and* B.—Compound A was identified as friedelin (I). Compound B, $C_{30}H_{48}O$, had u.v. and i.r. spectra showing the presence of an αβ-unsaturated carbonyl group, and catalytic hydrogenation yielded friedelin. Hence compound B could be friedel-1-en-3-one (II). A compound with this structure is already known synthetically [6] but there was considerable difference in the m.p.s (reported m.p. 247—248°, our m.p. 228—230°). Compound (II) was synthesised by us



by the method of Shoppee and Johnston,[6] and the synthetic and natural compounds were identical. The mass spectrum of compound B agreed with that of friedelin except that fragments containing ring A had 2 mass units less than the corresponding fragments from friedelin.

Compound C.—Compound C, $C_{30}H_{48}O_2$, showed i.r. and u.v. absorptions characteristic of a β-diketone system, having an acidic function between two carbonyls (see Experimental section). The n.m.r. spectrum showed an AB quartet centred at δ 3·38 (*J* 21 Hz) which can be attributed to the system $-CO-CH_2-CO-$ [7] which is possible only in ring A of a triterpenoid. The presence of such a system was confirmed by the reaction of compound C with acetic anhydride and diazomethane. With acetic anhydride and pyridine at 0° it yielded an enol acetate (XI) (proof of its structure is given below), and with pyridine, acetic anhydride, and acetic acid at 100° it yielded the *C*-acetyl derivative (VIII). With diazomethane, compound C yielded two isomeric methyl ethers (XIV) and (XVII).

The mass spectral fragmentation pattern (discussed later) of compound C and its derivatives showed that it could be a friedelane derivative.[8] Hence compound C appeared to be friedelane-1,3-dione (V). This was proved chemically by its conversion into friedelin by selective reduction at C-1 and conversely by its synthesis from friedelin.

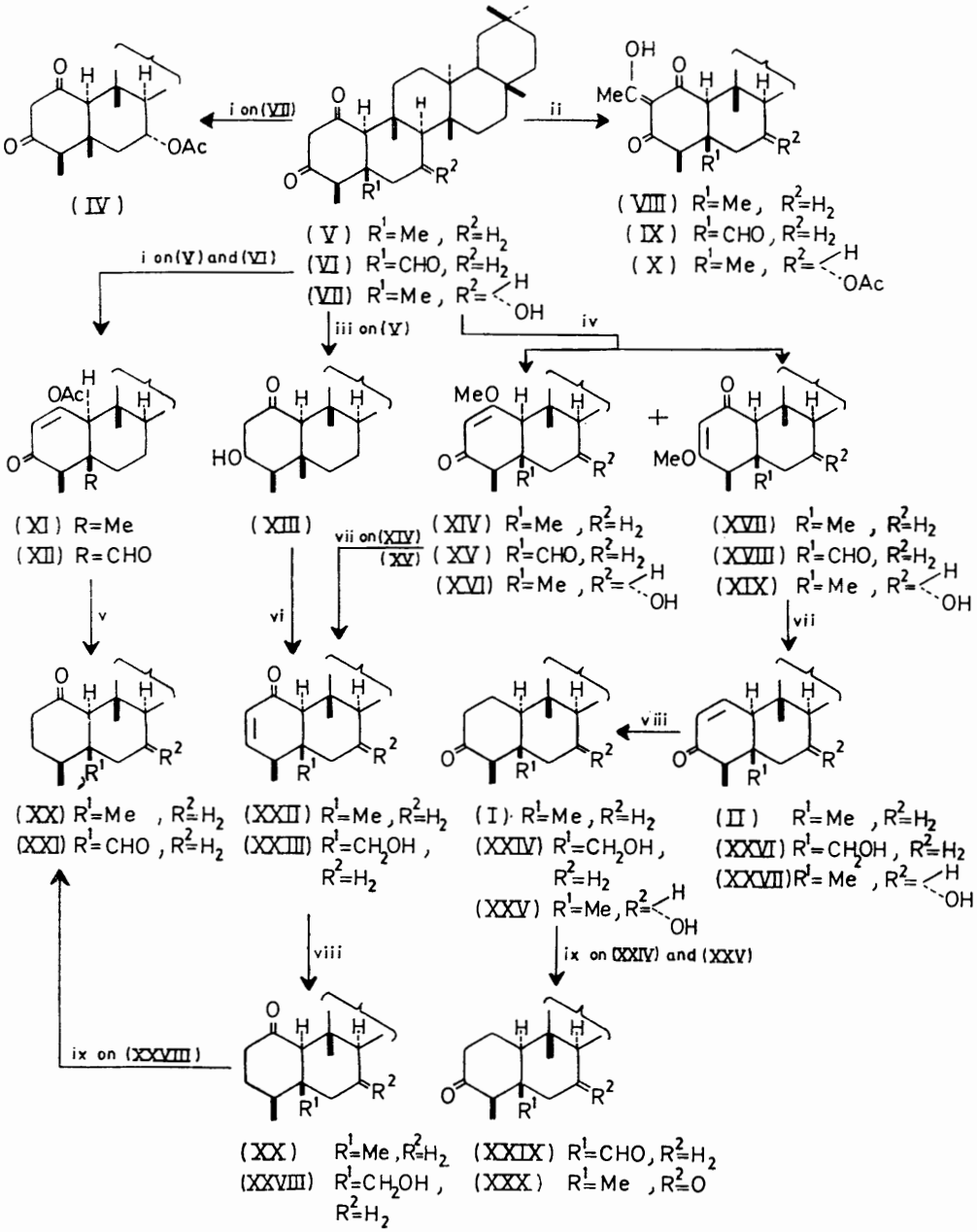
When the enol acetate of compound C was hydrogenated with Adams catalyst, a monodeoxo-compound was obtained which was different from friedelin and should therefore be friedelan-1-one (XX), a compound not previously reported. Its mass spectrum agrees with structure (XX), and hence the enol acetate should be (XI).

Reduction of compound C with sodium borohydride gave a β-hydroxy-ketone which underwent ready dehydration with acid to an αβ-unsaturated ketone, and this on hydrogenation gave only friedelan-1-one (XX). Hence the β-hydroxy-ketone should be (XIII) and its dehydration product should be (XXII). Thus in the above two methods, reduction took place at C-3.

The desired selective reduction at C-1 was finally achieved by treating one of the two isomeric methyl

[1] H. Heymann, S. S. Bhatnagar, and L. F. Fieser, *J. Amer. Chem. Soc.*, 1954, **76**, 3689.
[2] Wei-Yuan Huang, *Hua Hsueh Hsueh Pao*, 1962, **28**, 365 (*Chem. Abs.*, 1963, **59**, 15,602).
[3] P. P. Pillay and A. Lekshmi, *Bull. Res. Inst., Univ. Kerala, Trivandrum*, 1957, **5**, 29 (*Chem. Abs.*, 1958, **52**, 20,423).
[4] V. Krishnan, Ph.D. Thesis, Delhi University, 1968.
[5] S. Rangaswami and N. C. Tewari, *Current Sci.*, 1971, **40**, 36; N. C. Tewari, K. N. N. Ayengar, and S. Rangaswami, *ibid.*, p. 601.
[6] C. W. Shoppee and G. A. R. Johnston, *J. Chem. Soc.*, 1962, 1246.
[7] N. S. Bhacca and D. H. Williams, 'Application of N.M.R. Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, pp. 45, 61.
[8] H. Budzikewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 3668.

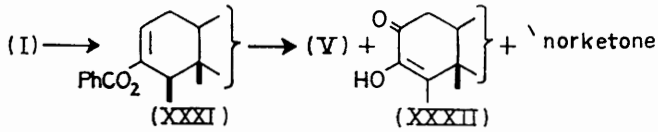
ethers (XVII) with lithium aluminium hydride, followed by catalytic hydrogenation. In the same way, the other methyl ether (XIV) gave (XX).



Reagents: i, Ac_2O–Py, 0—4°; ii, Ac_2O–AcOH–Py, 100°; iii, $NaBH_4$; iv, CH_2N_2; v, H_2/PtO_2; vi, H^+; vii, $LiAlH_4$; viii, H_2/Pd–C; ix, CrO_3–Py

For the synthesis of compound C, friedelin was benzoylated to give the benzoate (XXXI) and then oxidized by sodium dichromate.[9] The crude product was saponified and then separated into acidic and neutral parts. The acidic part yielded compound C (V), and the neutral part gave the known friedelane-2,3-dione which exists in the form of the diosphenol (XXXII)[10] and the substance referred to as 'norketone' by Corey and Ursprung.[9]

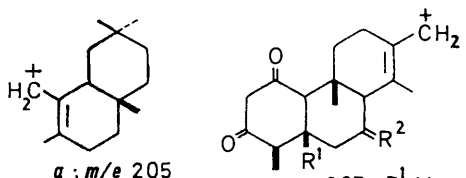
Mass spectral data of compound C and its derivatives were in full agreement with the structure (V), the most



significant being, *a* (*m/e* 205), *b* (*m/e* 287), and *c* (*m/e*

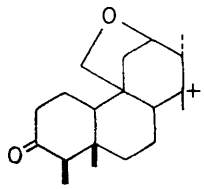
[9] E. J. Corey and J. J. Ursprung, *J. Amer. Chem. Soc.*, 1956, **78**, 5041.
[10] V. V. Kane and R. Stevenson, *J. Org. Chem.*, 1960, **25**, 1394.

139). Fragment *c* was given also by compound F described below.

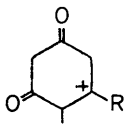


a ; *m/e* 205

b ; *m/e* 287 ; R^1=Me ; R^2=H_2
d ; *m/e* 301 ; R^1=CHO; R^2=H_2
g ; *m/e* 303 ; R=Me ; R=



f ; *m/e* 289



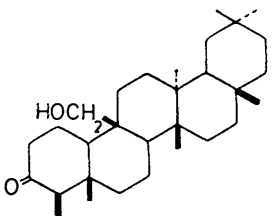
c ; *m/e* 139 ; R=Me
e ; *m/e* 153 ; R=CHO

Compound D.—The properties of our compound D and its derivatives resembled those reported by Heymann [1] for his 'compound A' and its derivatives. However, the molecular formula reported by them as $C_{30}H_{48}O_3$ has to be revised to $C_{30}H_{46}O_3$ (M^+ 454). Heymann had reported that this compound contains a β-diketone system and also an isolated carbonyl group. Our i.r. and u.v. data were in complete agreement with his. The β-diketone system can only be in ring A as in the case of compound C. The n.m.r. spectrum showed an AB quartet centred at δ 3·33 (*J* 21 Hz) attributable to the methylene protons between two carbonyls. The third oxygen atom appeared to be present as an aldehyde from the colour reaction with triphenyltetrazolium chloride reagent and the n.m.r. spectrum. The aldehyde proton signal was not split, and the presence of a friedelane skeleton and the position of the aldehyde function were deduced as follows.

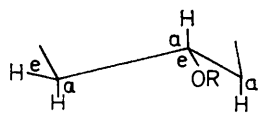
The mass spectrum of compound D largely resembled that of friedelin and it further ruled out the possibility of the aldehyde function being in rings D and E and limited its position to rings A, B, and C. In this connection the fragments *a*, *d*, and *e* are noteworthy. The loss of CHO in the mass spectrum showed that the CHO group is at an angular position. This is only possible at C-5 and C-9, and that it is at C-5 and not at C-9 was proved by converting compound D into its 1-deoxo derivative and obtaining 24-hydroxyfriedelan-3-one (XXIV) and 3-oxofriedelan-24-al (XXIX) in the following manner. The methyl ether (XVIII) of compound D was subjected to lithium aluminium hydride reduction, followed by acid hydrolysis, when the αβ-unsaturated keto-alcohol (XXVI) was obtained. This was catalytically reduced, and the product, a saturated keto-alcohol, differed in its m.p. and mass spectrum from 25-hydroxyfriedelan-3-one (XXXIII) described in the literature.[11] The main difference in the mass spectrum was a strong peak at *m/e* 289 (*f*) which is diagnostic of (XXXIII) and is absent in the mass spectrum of our keto-alcohol, which should therefore have structure (XXIV). Hence the aldehyde function in question should be only at C-5. This was further confirmed by oxidation of the keto-alcohol (XXIV) to the corresponding known keto-aldehyde (XXIX), m.p. 247—250° $C_{30}H_{48}O_2$ (M^+ 440), $\nu_{max.}$ 1724 (CHO) and 1709 cm^{-1} (six-membered ring ketone) [lit.,[12] m.p. 248—249°, $\nu_{max.}$ (Nujol) 1724 and 1709 cm^{-1}]. Hence compound D can be formulated as 1,3-dioxofriedelan-24-al (VI).

By a similar series of reactions the isomeric methyl ether (XV) of compound D gave a product which was isomeric with (XXIX). It could thus only be 1-oxofriedelan-24-al (XXI) which was also obtained by hydrogenating the enol acetate (XII) of compound D.

Compound F.—Compound F, $C_{30}H_{48}O_3$, contained a $-CO-CH_2-CO-$ group as was evident from the spectral data and appropriate chemical transformations as in



(XXXIII)



(XXXIV)
a, R=H
b, R=Ac

the case of compounds C and D (see Experimental section). In addition, there is a hydroxy-group ($\nu_{max.}$ 3690 cm^{-1}; $m/e = M - 18$ in the mass spectrum). In the n.m.r. spectrum the proton adjacent to the hydroxy-group appeared as a sextet at δ 4·11 with a splitting pattern indicating an environment as shown in (XXXIVa).[13] The hydroxy-group was readily acylated. In the n.m.r. spectrum of the *O,C*-diacetyl derivative (X) (formed by the action of acetic anhydride, acetic acid, and pyridine at 100°) the C*H*OAc proton again appeared as a sextet, centred at δ 5·41, indicating an environment as in (XXXIVb). Such a situation can be encountered in the friedelane skeleton only at C-7. On the basis of these data compound F may be represented as 7α-hydroxyfriedelane-1,3-dione (VII). This was confirmed by eliminating the oxygen function at C-1 as in the case of compounds C and D and isolating friedelane-3,7-dione (XXX). This is a naturally occurring compound (putranjivadione),[14] with which our product was identical.

The mass spectrum of compound F agrees with the structure (VII). A peak at *m/e* 205 (fragment *a*)

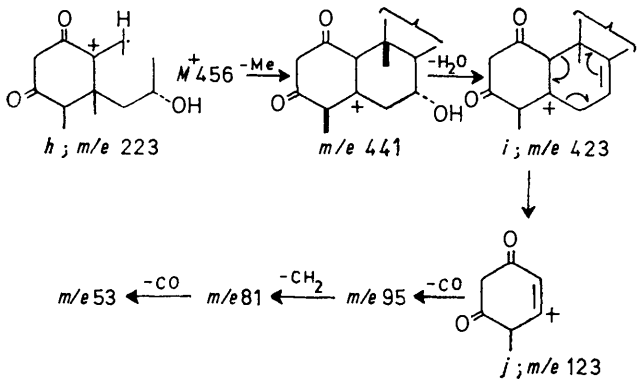
[11] J. L. Courtney, R. M. Gascoigne, and A. Z. Szumer, *J. Chem. Soc.*, 1956, 2119; J. S. Shannon, C. G. MacDonald, and J. L. Courtney, *Tetrahedron Letters*, 1963, 173.

[12] T. Hoshino, T. Tsuyuki, and T. Takahasi, *Bull. Chem. Soc. Japan*, 1967, **40**, 389.

[13] Ref. 7, p. 83.

[14] P. Sengupta, A. K. Chakraborty, A. M. Duffield, L. J. Durham, and C. Djerassi, *Tetrahedron*, 1968, **24**, 1205.

ruled out the presence of an oxygen function in rings D or E while the fragments *c*, *g*, and *h* clearly limit the hydroxy-function to ring B (position 6 or 7). The



fragment *j* (*m/e* 123) from which those at 95, 81, and 53 are derived is evidently formed from *i* by retro-Diels–Alder fission which is possible only when the hydroxy-group is at C-7 and not at C-6.

EXPERIMENTAL

M.p.s were taken on a Kofler hot-stage apparatus. Rotations were taken in chloroform. U.v. spectra were recorded in methanolic solution on a Hilger Uvispek spectrophotometer. I.r. spectra were recorded on a Perkin-Elmer Infracord 137 machine in KBr unless otherwise stated. N.m.r. spectra were taken in [^{2}H]chloroform using tetramethylsilane as internal standard on a Varian A-60 instrument. All compounds gave a positive Liebermann–Burchard test except A and reacted with 2,4-dinitrophenylhydrazine hydrochloride spray reagent.

Extraction and Isolation of Pure Compounds.—Scrapings (2 kg) of the root bark were extracted with boiling petroleum (5 × 3 l). The yellow viscous concentrate was macerated with hot methanol (2 l). The methanol-soluble portion was concentrated under reduced pressure and left in a refrigerator overnight. The solid that separated was filtered off, dissolved in chloroform, and precipitated with methanol. The pale yellow solid (2 g) was chromatographed over silica gel (100 g). Petroleum–benzene (8 : 2 v/v) eluted compound A (I) which crystallized from chloroform–ethyl acetate as needles (0·02 g), m.p. 264—266°, $[\alpha]_D$ −24·2° (*c* 0·912) (M^+ 426, $C_{30}H_{50}O$). It was identified as friedelin (m.p., t.l.c., and i.r. spectrum). Petroleum–benzene (7 : 3) eluted compound B (II), needles (from chloroform–methanol), (0·01 g). Petroleum–benzene (1 : 1) eluted compound C (V), needles (from chloroform–methanol) (0·05 g). Petroleum–benzene (4 : 6) eluted compound D (VI), needles (from chloroform–methanol) (0·20 g). Petroleum–benzene (3 : 7) eluted compound E, needles (from chloroform–methanol) (0·50 g). Petroleum–benzene (1 : 9) eluted compound F (VII), silky needles (from chloroform–benzene) (0·10 g).

Compound B (II).—*Friedel-1-en-3-one* (II) had m.p. 228—230°, $[\alpha]_D$ −73·8° (*c* 0·948) (Found: C, 84·7; H, 11·2. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%), $\lambda_{max.}$ 233 nm (log ε 3·98), $\nu_{max.}$ 1686 cm^{-1}, *m/e* 424 (M^+, 28%), 301 (10), 300 (8), 285 (3), 273 (6), 271 (5), 218 (8), 205 (56), 191 (16), and 123 (100).

Hydrogenation of Compound B (II).—A solution of (II) (5 mg) in ethyl acetate (10 ml) was hydrogenated over 10% Pd–C (5 mg). The solution was filtered and evaporated. The residue (5 mg) gave (I), m.p. 264—266° (from chloroform–ethyl acetate), identical (mixed m.p., t.l.c., and i.r. spectrum) with authentic friedelin.

2α-*Bromofriedelin* [9] (III).—This was prepared by the literature method,[9] and had δ 0·71—1·2 (24H, 8 × Me), 2·1 (2H, m, 1β-H, 4α-H), 3·11 (1H, q, *J* 14 Hz, 1α-H), and 4·36 (1H, t, *J* 6 Hz, 2β-H).

Friedel-1-en-3-one (II) *from* (III).—A solution of (III) (0·10 g) in freshly distilled 2,4,6-collidine (3 ml) was heated at 180° for 3 h in a nitrogen atmosphere. The mixture was cooled and diluted with ether (30 ml). The ethereal layer was washed with dil. hydrochloric acid, water, and dried (Na_2SO_4). Evaporation gave a solid (0·06 g) which was chromatographed over silica gel (3 g). Petroleum–benzene (9 : 1) eluted compound (II) (0·03 g) identical with the sample obtained above.

Compound C (V).—*Friedelane-1,3-dione* (V) had m.p. 275—290°,* $[\alpha]_D$ +2·1° (*c* 0·930) (Found: C, 81·4; H, 10·6. $C_{30}H_{48}O_2$ requires C, 81·7; H, 10·9%), $\lambda_{max.}$ 260 nm (log ε 3·66), $\lambda_{max.}$ (0·01N-NaOH) 289 nm (log ε 4·31), $\lambda_{max.}$ (0·01N-NaOH + HCl) 260 nm, $\nu_{max.}$ 1742 and 1718 cm^{-1}, δ 0·70—1·21 (24H, 8 × Me), 2·48 (2H, m, 4α-H, 10α-H), and 3·38 (2H, q, *J* 21 Hz, –CO–CH_2–CO–), *m/e* 440 (M^+, 100%), 316 (91), 301 (21), 287 (91), 273 (61), 218 (20), 207 (63), 205 (87), 139 (74), and 123 (74).

1-*Acetoxyfriedel-1-en-3-one* (XI).—Acetic anhydride (1·5 ml) was added to an ice-cold solution of (V) (0·03 g) in pyridine (1·6 ml) and the solution was kept at 0—4° for 30 h. The solution was poured into water and the solid was filtered off, washed with water, and dried. The *acetate* (XI) was crystallized from chloroform–methanol (0·03 g), m.p. 270—272°, $[\alpha]_D$ +53·0° (*c* 0·830) (Found: C, 79·9; H, 10·8. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%), $\lambda_{max.}$ 237 nm (log ε 3·90), $\lambda_{max.}$ (0·01N-NaOH) 290 nm (log ε 4·33), $\lambda_{max.}$ (0·01N-NaOH + HCl) 260 nm, $\nu_{max.}$ 1789, 1672, and 1642 cm^{-1}, *m/e* 482 (M^+, 34%) 440 (34), 329 (19), 287 (58), 273 (22), 207 (32), 205 (24), 181 (24), 139 (100), and 123 (39).

2-*Acetylfriedelane-1,3-dione* (VIII).—To a solution of (V) (0·02 g) in glacial aetic acid (0·5 ml) and pyridine (0·25 ml), acetic anhydride (0·25 ml) was added and the mixture heated on an oil-bath (100°) for 1 h. After working up in the manner described earlier the crude acetyl compound was crystallized from chloroform–methanol as *needles* (0·015 g), m.p. 198—200°, $[\alpha]_D$ −10·0° (*c* 0·812) (Found: C, 79·4; H, 10·2. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%), $\lambda_{max.}$ 235 and 281 nm (log ε 3·96 and 4·04), $\lambda_{max.}$ (0·01N-NaOH) 274 nm (log ε 4·22), $\lambda_{max.}$ (0·01N-NaOH + HCl) 235 and 281 nm, $\nu_{max.}$ 1669 and 1553 cm^{-1}, *m/e* 482 (M^+, 32%), 439 (2), 358 (33), 343 (15), 329 (40), 273 (17), 205 (25), 181 (100), and 123 (36).

1-*Methoxyfriedel-1-en-3-one* (XIV) *and* 3-*Methoxyfriedel-2-en-1-one* (XVII).—A suspension of (V) (0·05 g) in methanol–ether (1 : 1) (20 ml) was treated with excess of ethereal diazomethane and the mixture was left in a refrigerator overnight. Evaporation afforded a crude solid (0·045 g) which was separated by preparative t.l.c. (solvent, chloroform) into (XIV) and (XVII). The *methyl ether* (XIV) crystallized from chloroform–methanol as needles, m.p.

* The wide melting point range seems to be a characteristic of some of the components of the plant material under study, and a similar observation has been made and commented on previously.[1] The material was homogeneous to t.l.c. in three different solvent systems.

252—254°, $[\alpha]_D$ −59·6° (*c* 0·704) (Found: C, 81·6; H, 10·8. $C_{31}H_{50}O_2$ requires C, 81·8; H, 11·0%), $\lambda_{max.}$ 258 nm (log ε 4·18), $\nu_{max.}$ 1661 and 1600 cm^{-1}, *m/e* 454 (M^+, 30%), 330 (6), 315 (4), 301 (6), 221 (9), 205 (13), 153 (100), and 123 (18). The *methyl ether* (XVII) crystallized from chloroform–methanol as needles, m.p. >310°, $[\alpha]_D$ −28·0° (*c* 1·14) (Found: C, 82·0; H, 11·2. $C_{31}H_{50}O_2$ requires C, 81·8; H, 11·0%), $\lambda_{max.}$ 253 nm (log ε 4·12), $\nu_{max.}$ 1658 and 1616 cm^{-1}, *m/e* 454 (M^+, 29%), 301 (6), 221 (11), 205 (8), 153 (100), and 123 (11).

Friedelan-1-*one* (XX) *from* (XI).—A solution of (XI) (0·02 g) in ethyl acetate (10 ml) was stirred with Adams catalyst (0·01 g) in an atmosphere of hydrogen for 2 h. The catalyst was filtered off and the solution evaporated. The residue (0·015 g) was chromatographed over a column of silica gel (0·50 g). Elution with petroleum–benzene (9 : 1) afforded a solid which furnished (XX) as *needles*, m.p. 294—298° (from chloroform–methanol), $[\alpha]_D$ −10·0° (*c* 0·946) (Found: C, 84·1; H, 11·3. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%), $\nu_{max.}$ 1709 cm^{-1}, *m/e* 426 (M^+, 100%), 302 (96), 287 (12), 273 (63), 218 (20), 205 (35), and 123 (41).

3-*Hydroxyfriedelan*-1-*one* (XIII).—To a solution of (V) (0·02 g) in methanol–dioxan (1 : 1; 5 ml) was added sodium borohydride (0·02 g) and the solution was set aside for 1 h. It was concentrated under reduced pressure and poured into water (20 ml) containing conc. hydrochloric acid (2 ml). The precipitate was filtered off, washed, and crystallized from chloroform–methanol yielding (XIII) as *silky needles*, m.p. >300°, $[\alpha]_D$ −10·2° (*c* 0·790) (Found: C, 81·6; H, 11·7. $C_{30}H_{50}O_2$ requires C, 81·3; H, 11·3%), $\nu_{max.}$ 3663 and 1701 cm^{-1}.

Friedel-2-*en*-1-*one* (XXII) *from* (XIII).—A solution of (XIII) (0·03 g) in dioxan (5 ml) was treated with 2N-sulphuric acid (1 ml) and the mixture was allowed to stand at 40° for 24 h. Removal of the solvent under reduced pressure and addition of water gave a solid which was filtered off, washed, dried, and chromatographed over silica gel (0·50 g). Petroleum–benzene (7 : 3) eluted (XXII) as *needles*, m.p. 277—279° (from chloroform), $[\alpha]_D$ −20·0° (*c* 1·10) (Found: C, 84·5; H, 11·2. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%), $\lambda_{max.}$ 229 nm (log ε 3·98), $\nu_{max.}$ 1675 cm^{-1}, *m/e* 424 (M^+, 32%), 300 (47), 285 (15), 273 (22), 271 (55), 218 (12), 205 (30), 123 (100), and 91 (39).

Friedelan-1-*one* (XX) *from* (XXII).—A solution of (XXII) (0·01 g) in ethyl acetate (10 ml) was hydrogenated over 10% Pd–C (0·01 g) for 1 h. The product was crystallized from chloroform–methanol yielding (XX) as needles, m.p. 296—299°, identical (mixed m.p. and t.l.c.) with (XX) described earlier.

Friedel-1-*en*-3-*one* (II) *from* (XVII).—To a well stirred solution of (XVII) (0·03 g) in dry ether (20 ml) was added dropwise a suspension of lithium aluminium hydride (0·03 g) in dry ether (10 ml). After stirring for 0·5 h at room temperature, water was added, followed by 2N-sulphuric acid (10 ml). The ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were washed with water, dried, and evaporated. The crude product was purified by preparative t.l.c. (solvent, chloroform) and crystallized from chloroform–methanol yielding (II) as needles, m.p. 227—229°, identical (mixed m.p., t.l.c., and i.r. spectrum) with (II) obtained from the plant.

Friedel-2-*en*-1-*one* (XXII) *from* (XIV).—A suspension of lithium aluminium hydride (0·015 g) in dry ether (10 ml) was added to a solution of (XIV) (0·015 g) in dry ether (10 ml) and the reaction was left for 0·5 h. On working up as described above a crude product was obtained which was purified by preparative t.l.c. (solvent, chloroform–methanol, 99 : 1) and crystallization to get (XXII) as needles, m.p. 276—278°, identical (mixed m.p. and t.l.c.) with (XXII) described earlier.

Friedel-2-*en*-3-*yl Benzoate* (XXXI).—This was prepared by the literature method [9] and was obtained as shining plates (0·30 g), m.p. 262—264° (lit.,[9] 260—263°) (Found: C, 83·4; H, 10·7. Calc. for $C_{37}H_{54}O_2$: C, 83·7; H, 10·2%), $\nu_{max.}$ 1724 cm^{-1}.

Sodium Dichromate Oxidation of (XXXI).—A solution of (XXXI) (0·50 g) in benzene (40 ml) and acetic acid (20 ml) was treated with a solution of sodium dichromate (0·20 g) in acetic acid (10 ml) and the mixture was allowed to reflux gently for 52 h. Benzene was removed under reduced pressure and the acetic acid solution was diluted with ether. The ethereal solution was washed with cold aqueous 10% sodium hydroxide solution (10 × 10 ml), water, and dried (Na_2SO_4). Evaporation yielded a crude product (0·35 g) which was dissolved in methanol (40 ml) containing potassium hydroxide (0·15 g) and refluxed for 3 h. The reaction mixture was cooled and diluted with ether (200 ml). The ethereal solution was washed with water till neutral and aqueous portions were used to get the acidic fraction. The ethereal solution was dried (Na_2SO_4). Evaporation yielded a crude solid (0·25 g) which was chromatographed over alumina (8 g). Elution with petroleum–benzene (1 : 1) afforded a solid which after crystallization from chloroform–methanol furnished 3-hydroxyfriedel-3-en-2-one (XXXII) as needles, m.p. 266—267° (lit.,[9] m.p. 267—269°) (Found: C, 81·4; H, 10·4. Calc. for $C_{30}H_{48}O_2$: C, 81·7; H, 10·9%), $\lambda_{max.}$ 275 nm (log ε 4·06), $\nu_{max.}$ 1661 and 1634 cm^{-1}, *m/e* 440 (M^+, 81%), 316 (4), 301 (3), 287 (7), 218 (7), 207 (13), 205 (100), and 123 (46). It gave dark brown colour with ferric chloride.

Further elution with benzene afforded a solid which after crystallization from chloroform–methanol furnished Corey's 'norketone' as needles, m.p. 215—217°, $\nu_{max.}$ 1739 cm^{-1} [lit.,[9] m.p. 215—217°, $\nu_{max.}$ (CS_2) 1735 cm^{-1}].

The aqueous alkaline solution described above was acidified with ice-cold conc. hydrochloric acid and extracted with ether. The ethereal solution was washed with water and dried (Na_2SO_4). Evaporation gave a crude solid (0·05 g) which was chromatographed over silica gel (2 g). Petroleum–benzene (1 : 1) eluted a solid which on crystallization from chloroform–methanol furnished needles, m.p. 278—290°, identical (mixed m.p., t.l.c., and i.r. spectrum) with (V).

Compound D (VI).—1,3-*Dioxofriedelan*-24-*al* (VI) had m.p. 270—290° (decomp.), $[\alpha]_D$ +18·3° (*c* 1·089) (lit.,[1] m.p. 255—270°, $[\alpha]_D$ +6·6°) (Found: C, 79·4; H, 10·5. $C_{30}H_{46}O_3$ requires C, 79·2; H, 10·2%), $\lambda_{max.}$ 261 nm (log ε 3·67) $\lambda_{max.}$ (0·01N-NaOH) 289 nm (log ε 4·32), $\lambda_{max.}$ (0·01N-NaOH + HCl) 261 nm, $\nu_{max.}$ 1730 and 1701 cm^{-1}, δ 0·63—1·1 (21H, 7 × Me), 2·48 (2H, m, 4α-H, 10α-H), 3·33 (2H, q, *J* 21 Hz, –CO–CH_2–CO–), and 10·35 (1H, s, CHO), *m/e* 454 (M^+, 100%), 425 (57), 315 (20), 301 (57), 273 (82), 205 (26), 153 (91), and 123 (55).

1-*Acetoxy*-3-*oxofriedel*-1-*en*-24-*al* (XII).—Acetic anhydride (0·6 ml) was added to an ice-cold solution of (VI) (0·04 g) in pyridine (0·7 ml) and the mixture was left in a

refrigerator overnight. Working up as described earlier gave (XII) as *plates*, m.p. 225—227° (from chloroform–methanol), $[\alpha]_D$ +20·5° (*c* 0·712) (Found: C, 77·1; H, 9·3. $C_{32}H_{48}O_4$ requires C, 77·3; H, 9·7%), $\lambda_{max.}$ 237 nm (log ε 3·88), $\lambda_{max.}$ (0·01N-NaOH) 289 nm (log ε 4·36), $\lambda_{max.}$ (0·01N-NaOH + HCl) 260 nm, $\nu_{max.}$ 1779, 1724 and 1667 cm^{-1}.

1-*Oxofriedelan*-24-*al* (XXI) *from* (XII).—A solution of (XII) (0·02 g) in ethyl acetate (10 ml) was hydrogenated using Adams catalyst (0·02 g) for 1 h. The product after working up was crystallized from chloroform–methanol to get (XXI) as *needles*, m.p. 262—264°, $[\alpha]_D$ −2·4° (*c* 0·512) (Found: C, 81·5; H, 10·5. $C_{30}H_{48}O_2$ requires C, 81·7; H, 10·9%), $\nu_{max.}$ 1706 cm^{-1}, *m/e* 440 (M^+, 84%), 411 (26), 273 (16), 205 (25), 193 (100), and 123 (32).

2-*Acetyl*-1,3-*dioxofriedelan*-24-*al* (IX).—A solution of (VI) (0·02 g) in glacial acetic acid (0·5 ml), pyridine (0·25 ml), and acetic anhydride (0·25 ml) was heated for 2 h at 100°. The product obtained after working up as described earlier was chromatographed over silica gel (1·5 g). Elution with petroleum–benzene (3 : 2) yielded a solid which after crystallization from chloroform–methanol furnished (IX) as *plates*, m.p. 165—167°, $[\alpha]_D$ −10·2° (*c* 0·812) (Found: C, 77·6; H, 10·0. $C_{32}H_{48}O_4$ requires C, 77·3; H, 9·7%), $\lambda_{max.}$ 240 and 282 nm (log ε 3·99 and 4·04), $\lambda_{max.}$ (0·01N-NaOH) 274 nm (log ε 4·20), $\lambda_{max.}$ (0·01N-NaOH + HCl) 240 and 282 nm, $\nu_{max.}$ 1709, 1667 and 1563 cm^{-1}.

1-*Methoxy*-3-*oxofriedel*-1-*en*-24-*al* (XV) *and* 3-*Methoxy*-1-*oxofriedel*-2-*en*-24-*al* (XVIII).—A suspension of (VI) (0·20 g) in ether (20 ml) was treated with excess of ethereal diazomethane. On working up in the way described above a solid (0·20 g) was obtained which was found by t.l.c. to be a mixture of two compounds. These were separated by preparative t.l.c. (solvent, chloroform–methanol, 98 : 2). *Aldehyde* (XV) was obtained as plates, m.p. 223—225° (from chloroform–methanol), $[\alpha]_D$ +10·0° (*c* 0·780) (lit.,[1] m.p. 223—229°, $[\alpha]_D$ +2·6°) (Found: C, 79·2; H, 10·6. $C_{31}H_{48}O_3$ requires C, 79·4; H, 10·3%), $\lambda_{max.}$ 258 nm (log ε 4·26), $\nu_{max.}$ 1709, 1661, and 1592 cm^{-1}. The *aldehyde* (XVIII) was obtained as needles, m.p. >310° (from chloroform–methanol), $[\alpha]_D$ +5·0° (*c* 0·790) (lit.,[1] m.p. 315—317°) (Found: C, 79·6; H, 10·0. $C_{31}H_{48}O_3$ requires C, 79·4; H, 10·3%), $\lambda_{max.}$ 253 nm (log ε 4·08), $\nu_{max.}$ 1712, 1645, and 1613 cm^{-1}, *m/e* 468 (M^+, 47%), 439 (28), 301 (43), 273 (22), 205 (30), 153 (100), and 123 (53).

24-*Hydroxyfriedel*-1-*en*-3-*one* (XXVI) *from* (XVIII).—The methyl ether (XVIII) (0·20 g) was treated with lithium aluminium hydride (0·20 g). The crude product (0·14 g) was purified by preparative t.l.c. (solvent, chloroform–methanol, 98 : 2) to get the *hydroxy-ketone* (XXVI) as needles (from chloroform–methanol), m.p. 240—242° (decomp.), $[\alpha]_D$ −22·6° (*c* 0·968) (Found: C, 81·5; H, 10·5. $C_{30}H_{48}O_2$ requires C, 81·7; H, 10·9%), $\lambda_{max.}$ 230 nm (log ε 3·95), $\nu_{max.}$ 3662 and 1672 cm^{-1}.

24-*Hydroxyfriedelan*-3-*one* (XXIV).—A solution of (XXVI) (0·03 g) in ethyl acetate (10 ml) was hydrogenated over 10% Pd–C. The product obtained after working up was crystallized from chloroform–methanol to get the *hydroxy-ketone* (XXIV) as plates, m.p. 260—262° (Found: C, 81·1; H, 11·0. $C_{30}H_{50}O_2$ requires, C, 81·3; H, 11·3%), $\nu_{max.}$ 3676 and 1706 cm^{-1}, *m/e* 442 (M^+, 3%), 411 (100), 301 (17), 273 (3), 205 (13), and 123 (11).

3-*Oxofriedelan*-24-*al* (XXIX).—A solution of (XXIV) (0·02 g) in pyridine (0·5 ml) cooled to 15° was added to chromium trioxide–pyridine complex [prepared from chromium trioxide (0·03 g) and pyridine (0·6 ml)]. The mixture was left at room temperature for 18 h, water was added, and it was extracted with ether. The ethereal solution was washed with water and dried (Na_2SO_4). Evaporation gave a crude product (0·015 g) which was chromatographed over silica gel (1 g). Elution with petroleum–benzene (4 : 6) afforded (XXIX) as needles (from chloroform–methanol), m.p. 247—250° (lit.,[11] 248—249°), $\nu_{max.}$ (Nujol) 1724 and 1709 cm^{-1}, *m/e* 440 (M^+, 25%), 411 (9), 273 (11), 205 (27), 193 (100), and 123 (45).

24-*Hydroxyfriedel*-2-*en*-1-*one* (XXIII).—A solution of (XV) (0·10 g) in dry ether (30 ml) was treated with lithium aluminium hydride (0·10 g). The crude product (0·06 g) was purified by preparative t.l.c. (solvent, chloroform–methanol, 98 : 2) to get (XXIII) as *plates*, m.p. 260° (decomp) (from chloroform–methanol) (Found: C, 81·5; H, 10·5. $C_{30}H_{48}O_2$ requires C, 81·7; H, 10·9%), $\lambda_{max.}$ 230 nm (log ε 3·95), $\nu_{max.}$ 3660 and 1667 cm^{-1}.

24-*Hydroxyfriedelan*-1-*one* (XXVIII).—A solution of (XXIII) (0·01 g) in ethyl acetate (10 ml) was hydrogenated for 2 h using 10% Pd–C catalyst (0·01 g). The product (XXVIII) crystallized from chloroform–methanol as *plates*, m.p. 290—292° (Found: C, 81·1; H, 11·6. $C_{30}H_{50}O_2$ requires C, 81·3; H, 11·3%), $\nu_{max.}$ 3660 and 1701 cm^{-1}.

1-*Oxofriedelan*-24-*al* (XXI) *from* (XXVIII).—An ice-cold solution of (XXVIII) (0·01 g) in pyridine (0·25 ml) was added to chromium trioxide–pyridine complex [prepared from chromium trioxide (0·01 g) and pyridine (0·2 ml)] and the mixture was left at room temperature for 18 h. After working up as described above the product was crystallized from chloroform–methanol as plates, m.p. 263—265°, identical (mixed m.p. and t.l.c.) with (XXI) obtained from (XII) as described above.

Compound E.—This had m.p. 290—295°, $[\alpha]_D$ −11·0° (*c* 1·033) (lit.,[1] m.p. 290—295°, $[\alpha]_D$ −0·5°) (Found: C, 78·9; H, 10·5. Calc. for $C_{30}H_{46}O_3$: C, 79·2; H, 10·2%), $\lambda_{max.}$ 260 nm (log ε 4·10), $\lambda_{max.}$ (0·01N-NaOH) 289 nm (log ε 4·40), $\lambda_{max.}$ (0·01N-NaOH + HCl) 260 nm, $\nu_{max.}$ 1739, 1709, 1189, 1178, 1099, and 1064 cm^{-1}.

Compound F (VII).—7α-*Hydroxyfriedelane*-1,3-*dione* had m.p. 306—310°, $[\alpha]_D$ +10·7° (*c* 0·924) (Found: C, 78·6; H, 10·2. $C_{30}H_{48}O_3$ requires C, 78·8; H, 10·5%), $\lambda_{max.}$ 260 nm (log ε 3·65), $\lambda_{max.}$ (0·01N-NaOH) 289 nm (log ε 4·29), $\lambda_{max.}$ (0·01N-NaOH + HCl) 260 nm, $\nu_{max.}$ 3690, 1736, and 1698 cm^{-1}, δ 0·72—1·25 (24H, 8 × Me), 2·47 (2H, m, 4α-H, 10α-H), 3·31 (2H, q, *J* 20 Hz, $-CO-CH_2-CO-$), and 4·11 (1H, sextet, $J_{ax,ax}$ 10, $J_{ax,eq}$ 5 Hz, 7β-H), *m/e* 456 (M^+, 25%), 441 (39), 438 (10), 423 (15), 332 (35), 303 (14), 273 (16), 223 (31), 205 (100), 139 (52), 123 (73), 95 (68), 81 (59), and 53 (37).

7-*Acetoxy*-2-*acetylfriedelane*-1,3-*dione* (X).—A solution of (VII) (0·05 g) in glacial acetic acid (1·4 ml), pyridine (0·7 ml), and acetic anhydride (0·7 ml) was heated for 2 h at 100°. The product was chromatographed over silica gel (3 g). Elution with petroleum–benzene (1 : 1) afforded a solid (0·03 g) which on crystallization furnished (X) as *needles*, m.p. 245—247°, $[\alpha]_D$ −30·0° (*c* 0·917) (Found: C, 75·3; H, 9·9. $C_{34}H_{52}O_5$ requires C, 75·5; H, 9·6%), $\lambda_{max.}$ 235 and 280 nm (log ε 3·92 and 4·05), $\lambda_{max.}$ (0·01N-NaOH) 274 nm (log ε 4·26), $\lambda_{max.}$ (0·01N-NaOH + HCl) 235 and 280 nm, $\nu_{max.}$ 1727, 1686, 1563, and 1248 cm^{-1}, δ 0·96—1·26 (24H, 8 × Me) 2·09 (3H, s, Ac), 2·56 (3H, s, MeC(OH)=, and 5·41 (1H, sextet, $J_{ax,ax}$ 10, $J_{ax,eq}$ 5 Hz, 7β-H).

7α-*Acetoxyfriedelane*-1,3-*dione* (IV).—Acetic anhydride (1·5 ml) was added to an ice-cold solution of (VII) (0·05 g) in pyridine (1·6 ml) and the mixture was left in a refrigerator overnight. The crude solid (0·04 g) was chromatographed over silica gel (2·5 g). Elution with petroleum–benzene (8 : 2) afforded (IV) which crystallized from chloroform–methanol as *needles*, m.p. 265—267°, $[\alpha]_D$ −50·5° (*c* 0·512) (Found: C, 77·2; H, 10·4. $C_{32}H_{50}O_4$ requires C, 77·0; H, 10·1%), $\lambda_{max.}$ 260 nm (log ε 3·56), $\lambda_{max.}$ (0·01N-NaOH) 290 nm (log ε 4·25), $\lambda_{max.}$ (0·01N-NaOH + HCl) 260 nm, $\nu_{max.}$ 1724, 1709, and 1250 cm^{-1}.

7α-*Hydroxy*-3-*methoxyfriedel*-2-*en*-1-*one* (XIX) *and* 7α-*Hydroxy*-1-*methoxyfriedel*-1-*en*-3-*one* (XVI).—A solution of (VII) (0·10 g) in ether (20 ml) was treated with excess of ethereal diazomethane. Working up as described above afforded a mixture containing two compounds which were separated by preparative t.l.c. (solvent, chloroform–methanol, 97 : 3). The *enone* (XIX) crystallized from chloroform–methanol as plates, m.p. >310°, $[\alpha]_D$ −51·2° (*c* 0·468) (Found: C, 79·3; H, 10·4. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·7%), $\lambda_{max.}$ 254 nm (log ε 4·04), $\nu_{max.}$ 3630, 1653, and 1618 cm^{-1}. The *isomeric enone* (XVI) crystallized from chloroform–methanol as silky needles, m.p. 274—276°, $[\alpha]_D$ −90·6° (*c* 0·861) (Found: C, 78·9; H, 10·3. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·7%), $\lambda_{max.}$ 258 nm (log ε 4·28), $\nu_{max.}$ 3600, 1645, and 1587 cm^{-1}.

7α-*Hydroxyfriedel*-1-*en*-3-*one* (XXVII).—A solution of (XIX) (0·06 g) in dry ether was treated with lithium-aluminium hydride (0·05 g) and the mixture was left at room temperature for 0·5 h. The crude product (0·04 g) was purified by preparative t.l.c. (solvent, chloroform–methanol, 95 : 5) to give (XXVII) as *plates*, m.p. 249—251°, $[\alpha]_D$ −5·0° (*c* 0·728) (Found: C, 81·5; H, 11·4. $C_{30}H_{48}O_2$ requires C, 81·7; H, 10·9%), $\lambda_{max.}$ 228 nm (log ε 3·95), $\nu_{max.}$ 3676 and 1669 cm^{-1}.

7α-*Hydroxyfriedelan*-3-*one* (XXV).—A solution of (XXVII) (0·02 g) in ethyl acetate (10 ml) was hydrogenated using 10% Pd–C catalyst (0·02 g). The product (XXV) crystallized from chloroform–methanol as *plates*, m.p. 285—288° (Found: C, 81·6; H, 11·5. $C_{30}H_{50}O_2$ requires C, 81·3; H, 11·3%), $\nu_{max.}$ 3571 and 1721 cm^{-1}.

Friedelane-3,7-*dione* (XXX).—An ice-cold solution of (XXV) (0·015 g) in pyridine (0·4 ml) was added to chromium trioxide–pyridine complex [prepared from chromium trioxide (0·015 g) and pyridine (0·4 ml)] and the reaction mixture was left at room temperature for 18 h. The crude product was chromatographed over a column of silica gel (0·5 g). Elution with petroleum–benzene (1 : 1) afforded (XXX) as needles, m.p. 285—287° (from chloroform–methanol), identical (mixed m.p., t.l.c., and i.r. spectrum) with an authentic sample of putranjivadione.[14]

We thank Professor T. R. Seshadri for his interest, the Central Council for Research in Indian Medicine and Homoeopathy for financial assistance, Dr. M. L. Dhar and Dr. Nitya Nand of the Central Drug Research Institute, Lucknow, for n.m.r. and mass spectra of some of the samples, and Dr. N. K. Panikkar and Dr. A. H. Parulekar of the National Institute of Oceanography, Panaji, Goa, for help in procuring the plant material.

[3/1432 *Received*, 9*th July*, 1973]