

**414. Triterpenes of the Friedelane Series. Part I. Ketones.**

By J. L. COURTNEY and R. M. GASCOIGNE.

The bark of *Siphonodon australe* Benth. contains a mixture of over a dozen triterpenes of the friedelane series. The ketonic fraction of this mixture consists of friedelin, two diketones, and a triketone. These new ketones have been related to friedelin (friedelan-3-one) and to each other and are named friedelane-3 :  $x$ -dione, friedelane-3 :  $y$ -dione, and friedelane-3 :  $x$  :  $y$ -trione.

The hindrance of the  $x$ -oxo-group is comparable to that of the 11-oxo-group in steroids, and the  $y$ -oxo-group is even more hindered.

As part of an extensive investigation of alkaloids of the Australian flora Dr. J. R. Cannon, (the late) Dr. G. K. Hughes, and Dr. E. Ritchie of the University of Sydney examined the bark of the tree *Siphonodon australe* Benth. From it they isolated dulcitol and a crystalline mixture of neutral triterpenes which they very kindly passed on to us. The mixture contains over a dozen triterpenes of the friedelane series; it can be divided into three main fractions containing respectively ketones, monohydroxy-ketones, and polyhydroxy-compounds. This paper describes the ketonic constituents and the following paper the monohydroxy-ketones. The polyhydroxy-compounds will be dealt with later.

The ketonic fraction consists of friedelin (ca. 0.2% of the whole mixture), two diketones (ca. 15% and 1%), and a triketone (ca. 10%). None of the last compounds has the properties of an  $\alpha$ - or  $\beta$ -diketone. The structure and configuration of friedelin (friedelan-3-one) have recently been elucidated.<sup>1</sup> We assign the name friedelane-3 :  $x$ -dione to one of the diketones on the following grounds. When reduced by the Clemmensen method it yielded friedelane and a new ketone friedelan- $x$ -one. Reduction by sodium borohydride afforded two epimeric hydroxy-ketones,\* one of which, when reduced by the Wolff-Kishner method with anhydrous hydrazine, yielded *epifriedelinol* (friedelan-3 $\beta$ -ol). It follows that the two epimeric hydroxy-ketones are 3 $\alpha$ - and 3 $\beta$ -hydroxyfriedelan- $x$ -one and that the diketone contains a 3-carbonyl group.

Friedelan- $x$ -one was formed also on reduction of friedelane-3 :  $x$ -dione by the Huang-Minlon modification of the Wolff-Kishner reduction, with 85% hydrazine hydrate. In this case, however, no friedelane was obtained. The  $x$ -oxo-group is considerably hindered: thus friedelan- $x$ -one does not react with semicarbazide or 2 : 4-dinitrophenylhydrazine. Friedelane-3 :  $x$ -dione yields a monosemicarbazone which must be formed by the 3-oxo-group. The reduction experiments described above indicate that the hindrance of the  $x$ -oxo-group is comparable to that of the 11-oxo-group in steroids. Thus it is not reduced by sodium borohydride (at ordinary temperature) or by the Huang-Minlon procedure (with aqueous hydrazine); these methods do not reduce 11-oxo-steroids.<sup>2,3</sup> On the other hand it is reduced by the Clemmensen method (with heavily amalgamated zinc) and by the Wolff-Kishner method (with anhydrous hydrazine), both of which also reduce 11-oxo-steroids.<sup>4,5</sup>

The triketone is friedelane-3 :  $x$  :  $y$ -trione. It formed a monosemicarbazone and so contains two unreactive carbonyl groups. The reactive carbonyl group was identified as the 3-oxo-group in the following way. The group was protected by formation of the ethylene ketal (by the transfer procedure<sup>6</sup>) which was then reduced by the Wolff-Kishner method (anhydrous hydrazine). Removal of the protecting group and chromatography of the product yielded friedelin accompanied by a small amount of friedelane and a

\* Evidence that these two compounds are epimers is provided by their molecular rotation differences (given in the following paper) and their infrared absorption.

<sup>1</sup> Corey and Ursprung, *J. Amer. Chem. Soc.*, 1955, **77**, 3667, 3668; Brownlie, Spring, Stevenson, and Strachan, *Chem. and Ind.*, 1955, 686, 1156; Ourisson and Takahashi, *ibid.*, p. 1155; Dutler, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1955, **38**, 1268.

<sup>2</sup> Cf. Soloway, Deutsch, and Gallagher, *J. Amer. Chem. Soc.*, 1953, **75**, 2356.

<sup>3</sup> Huang-Minlon, *ibid.*, 1949, **71**, 3301.

<sup>4</sup> Steiger and Reichstein, *Helv. Chim. Acta*, 1938, **21**, 161.

<sup>5</sup> Moffett and Hunter, *J. Amer. Chem. Soc.*, 1951, **73**, 1973; Barton, Ives, and Thomas, *J.*, 1955, 2056.

<sup>6</sup> Dauben, Löken, and Ringold, *J. Amer. Chem. Soc.*, 1954, **76**, 1359.

hydroxy-ketone which is discussed below. Proof of the presence of the  $\alpha$ -oxo-group is given in the following paper.

Clemmensen reduction of the triketone under vigorous conditions (heavily amalgamated zinc) yielded a new ketone, friedelan- $\gamma$ -one, and a new diketone, friedelane- $\alpha$  :  $\gamma$ -dione; no friedelane was obtained. It is evident from this result that the  $\gamma$ -oxo-group is even more hindered than the  $\alpha$ -oxo-group. Probably as a consequence of this marked hindrance, the  $\gamma$ -oxo-group is partially converted into a hydroxyl group in the conditions of the Wolff-Kishner reduction with anhydrous hydrazine. Thus, when friedelane-3 :  $\alpha$  :  $\gamma$ -trione was reduced by this method it yielded friedelane and an alcohol which was shown to be friedelan- $\gamma$ -ol by oxidation to friedelan- $\gamma$ -one. Similarly the hydroxy-ketone obtained along with friedelin from the reduction of the ethylene ketal of friedelane-3 :  $\alpha$  :  $\gamma$ -trione is  $\gamma$ -hydroxyfriedelan-3-one.

The second diketone is friedelane-3 :  $\gamma$ -dione. It formed a monosemicarbazone and on reduction by the Huang-Minlon procedure yielded friedelan- $\gamma$ -one. Proof of the presence of the 3-oxo-group is provided by the oxidation of  $\gamma$ -hydroxyfriedelan-3-one which yielded the diketone.

The relations summarised in the names assigned to the several ketones described are substantiated by their infrared absorption, which will be discussed in a later paper, and by the molecular-rotation contributions of the carbonyl groups (Table).

*Molecular rotation contributions of carbonyl groups.*

	[ $M$ ] <sub>D</sub> with CO group	[ $M$ ] <sub>D</sub> without CO group	$\Delta$ CO
<i>3-Oxo-group</i>			
Friedelan-3-one .....	-94°	+91°	-185°
Friedelane-3 : $\alpha$ -dione .....	+506	+647	-141
Friedelane-3 : $\alpha$ : $\gamma$ -trione .....	+327	+453	-126
Friedelane-3 : $\gamma$ -dione .....	-273	-145	-128
<i><math>\alpha</math>-Oxo-group</i>			
Friedelan- $\alpha$ -one .....	-647	+91	+556
Friedelane-3 : $\alpha$ -dione .....	+506	-94	+600
Friedelane-3 : $\alpha$ : $\gamma$ -trione .....	+327	-273	+600
Friedelane- $\alpha$ : $\gamma$ -dione .....	+453	-145	+598
<i><math>\gamma</math>-Oxo-group</i>			
Friedelan- $\gamma$ -one .....	-145	+91	-236
Friedelane-3 : $\gamma$ -dione .....	-273	-94	-179
Friedelane-3 : $\alpha$ : $\gamma$ -trione .....	+327	+506	-179
Friedelane- $\alpha$ : $\gamma$ -dione .....	+453	+647	-194

The value of the specific rotation of friedelane observed in this investigation was that found by Bruun <sup>7</sup> and not the higher value recorded in the earlier literature.

#### EXPERIMENTAL

Analyses by Dr. E. Challen and Mr. D. Weedon, and infrared spectra by Mr. I. Reece.

Specific rotations were measured in CHCl<sub>3</sub> solution and, unless otherwise stated, in a 1 dm. tube. The m. p. of many of the compounds described was dependent on rate of heating, so the capillary tube was always placed in the apparatus at *ca.* 30° below the m. p. Identity of specimens was established by comparison of their infrared spectra. Alumina for chromatography had activity II, and the light petroleum had b. p. 40–60°.

Oxidation of hydroxyl to keto-groups was carried out with the chromium trioxide-pyridine reagent <sup>8</sup> as follows: a 5–10% solution of the compound to be oxidised, in dry pyridine, was added to an equal weight of chromium trioxide in pyridine (10% solution; prepared by slowly adding the chromium trioxide to the pyridine with cooling <sup>8</sup>). The mixture was occasionally shaken and left overnight. It was then diluted with benzene and filtered; the solid material was extracted twice with boiling benzene. The benzene filtrate and extracts were combined and washed with water, then with 5*N*-hydrochloric acid until the pyridine was removed, and then with sodium hydrogen sulphite solution. Evaporation of the benzene yielded the product, generally in almost quantitative yield.

<sup>7</sup> Bruun, *Acta Chem. Scand.*, 1954, **8**, 76.

<sup>8</sup> Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422; Herzog, Payne, Tully, and Hershberg, *ibid.*, p. 5751.

*Isolation of the Triterpene Mixture from Siphonodon australe* (with Mr. A. Z. SZUMER).—The air-dried, finely milled bark (55 kg.) was extracted by percolation with chloroform, and the extract, after removal of chloroform, was dissolved in hot alcohol (12 l.) and left for several days. Amorphous material which was deposited was filtered off and extracted twice with hot alcohol; the extracts were added to the alcoholic filtrate.

The amorphous material was extracted with hot *N*-sodium hydroxide (the extract yielded black acidic material which was discarded) and then with hot benzene which extracted crystalline triterpenes (79 g.). The undissolved material consisted of a mixture of sodium salts (70 g.) insoluble in sodium hydroxide solution.

The alcoholic filtrate on concentration yielded a mixture of triterpenes (339 g.) which was recrystallised from alcohol. Removal of alcohol from the concentrated filtrate with steam left a resin which was dissolved in benzene (10 l.). The benzene solution was extracted with 2*N*-sodium hydroxide [acidification of the extract yielded resin (764 g.)] and then filtered through a column of alumina (2 kg.); the filtrate contained a clear gum (214 g.). Elution of the column with benzene and then with chloroform–benzene gave a series of fractions from which crystalline triterpene material (39 g.) was obtained by treatment with light petroleum (lower fractions) and ethyl acetate (higher fractions).

The combined triterpene mixture (457 g.) had selective ultraviolet absorption only in the 285  $m\mu$  region ( $E_{1\text{cm}}^{1\%}$  3).

*Chromatography of the Triterpene Mixture*.—The mixture (140 g.) was dissolved in benzene (3 l.) and adsorbed on a column of alumina (4.1 kg.;  $5 \times 233$  cm.). The column was eluted with benzene, then with increasing concentrations of chloroform in benzene, and finally with chloroform to give 58 fractions, each of *ca.* 2 g. All the fractions except the first were crystalline and had the following specific rotations (*c* 2 to 3):

Fraction	$[\alpha]_D$	Fraction	$[\alpha]_D$	Fraction	$[\alpha]_D$	Fraction	$[\alpha]_D$
2	+55°	21	+61°	36	+1°	45	+12°
3	+97	22–28	+67–71	37	–11	46–53	+42–19
4	+105	29	+51	38	–20	54	+38
5–15	+110–113	30	+41	39	–27	55	+26*
16	+74	31	+36	40	–38	56	–8*
17	+14	32	+28	41	–50	57	+12
18	+31	33	+31	42	–42	58	–18
19	+47	34	+32	43	–29		
20	+57	35	+42	44	–9		

\* *c* 0.6, 2 dm. tube

Each fraction (except 2–4, 5–15, and 22–28) was examined separately, initially by recrystallisation from alcohol.

*Friedelin*.—Fractions 2–4 were combined, dissolved in 4 : 1 light petroleum–benzene, and chromatographed over alumina (200 g.). The first fraction (0.9 g.) had  $[\alpha]_D$   $-9^\circ$  and after three recrystallisations from alcohol–benzene yielded friedelin (0.28 g.), *m. p.* 261–264°,  $[\alpha]_D$   $-21^\circ$  (*c* 2.5) (Found : C, 84.3; H, 11.7. Calc. for  $C_{30}H_{50}O$  : C, 84.4; H, 11.8%). The product was identical with an authentic specimen (infrared spectra). Corks were not used in the extraction or the separation of the triterpene mixture.

*Friedelane-3 : x-dione*.—Fractions 5–15 were combined and recrystallised from alcohol, yielding *friedelane-3 : x-dione* in needles, *m. p.* 248–250°,  $[\alpha]_D$   $+115^\circ$  (*c* 2.6) (Found : C, 82.1; H, 10.7.  $C_{30}H_{46}O_2$  requires C, 81.8; H, 11.0%). An additional amount was obtained from fractions 2–4 and 16–17 by chromatography (total, 22.5 g.). The *monosemicarbazone* formed prisms (from alcohol), *m. p.* 247° (decomp.) (Found : C, 74.2, 74.2; H, 10.5, 10.4; N, 8.3, 8.5.  $C_{31}H_{51}O_2N_3 \cdot \frac{1}{2}C_2H_5 \cdot OH$  requires C, 74.4; H, 10.4; N, 8.3%).

*Friedelane-3 : y-dione*.—By virtue of its low solubility in alcohol, *friedelane-3 : y-dione* was isolated from fractions 16 and 17. An additional amount was obtained from fractions 18–21 by chromatography (total, 1.6 g.). It crystallised from alcohol–benzene in laths, *m. p.* 305–309°,  $[\alpha]_D$   $-62^\circ$  (*c* 2.3) (Found : C, 81.5; H, 10.9%). The *monosemicarbazone* formed plates (from alcohol–chloroform), *m. p.* 331° (decomp.) (Found : C, 74.8; H, 10.4; N, 8.6.  $C_{31}H_{51}O_2N_3$  requires C, 74.8; H, 10.3; N, 8.4%).

*Friedelane-3 : x : y-trione*.—Fractions 22–28 were combined and recrystallised from alcohol, yielding *friedelane-3 : x : y-trione* in needles or plates, *m. p.* 300–303°,  $[\alpha]_D$   $+72^\circ$  (*c* 2.4) (Found : C, 79.4; H, 10.2.  $C_{30}H_{46}O_3$  requires C, 79.2; H, 10.2%). An additional amount was obtained from fractions 18–21 and 29–35 by chromatography (total, 13.8 g.). The *monosemicarbazone* formed needles (from alcohol), *m. p.* 320° (decomp.) (Found : C, 72.8; H, 9.5; N, 8.3.  $C_{31}H_{49}O_3N_3$  requires C, 72.8; H, 9.65; N, 8.2%).

*Clemmensen Reduction of Friedelane-3 : x-dione*.—A hot solution of *friedelane-3 : x-dione*

(2 g.) in dioxan (500 ml.) was diluted with 10N-hydrochloric acid (290 ml.) and added to amalgamated zinc [prepared by leaving zinc needles (80 g.) in a solution of mercuric chloride (80 g.) in 50% aqueous alcohol (600 ml.) for 15 min.]. The mixture was heated on the steam-bath for 5 hr. and then cooled, whereupon the product separated out. Filtration of a solution of the product in 3 : 1 light petroleum-benzene through alumina (60 g.) yielded friedelane (0.2 g.), plates (from alcohol-benzene), m. p. 243—245°,  $[\alpha]_D + 22^\circ$  (*c* 0.7; 2 dm. tube) (Found : C, 87.05; H, 12.5. Calc. for  $C_{30}H_{52}$  : C, 87.3; H, 12.7%). Its identity was established by comparison (mixed m. p. and infrared spectra) with an authentic specimen.

Elution of the column with 3 : 1 light petroleum-benzene yielded *friedelan-x-one* (1.1 g.), needles (from alcohol), m. p. 241—243°,  $[\alpha]_D + 152^\circ$  (*c* 2.1) (Found : C, 84.4; H, 11.95.  $C_{30}H_{50}O$  requires C, 84.4; H, 11.8%).

*Huang-Minlon Reduction of Friedelane-3 : x-dione*.—A solution of friedelane-3 : *x*-dione (5 g.), potassium hydroxide (4.5 g.), and hydrazine hydrate (7 ml. of 85%) in diethylene glycol (32 ml.) was refluxed for 1½ hr. Hydrazine hydrate was then removed by distillation and the mixture was kept at 200° for 5 hr.; it was then cooled and acidified. The product, isolated with chloroform, was extracted with light petroleum which left high-melting nitrogen-containing material. The light petroleum extract was filtered through alumina (200 g.) which was eluted with 1 : 1 light petroleum-benzene, yielding *friedelan-x-one* (1.3 g.), m. p. 241—243°,  $[\alpha]_D + 152^\circ$  (*c* 2.2).

*Reduction of Friedelane-3 : x-dione with Sodium Borohydride*.—A solution of friedelane-3 : *x*-dione (2.0 g.) in pyridine (100 ml.) was added to a solution of sodium borohydride (0.55 g.) in methyl alcohol (50 ml.) containing *N*-sodium hydroxide (0.25 ml.). The solution was left for 24 hr. and then acidified with 5N-hydrochloric acid (400 ml.). The product, isolated with chloroform, was dissolved in benzene and chromatographed over alumina (100 g.). Elution with benzene gave eight fractions (each *ca.* 0.25 g.). Fraction 1 was starting material. Fraction 3 was recrystallised from alcohol, yielding *3β-hydroxyfriedelan-x-one*, prisms, m. p. 288—291°,  $[\alpha]_D + 159^\circ$  (*c* 1.0) (Found : C, 81.5; H, 11.1.  $C_{30}H_{50}O_2$  requires C, 81.4; H, 11.4%). The *acetate* formed plates (from alcohol), m. p. 271—273°,  $[\alpha]_D + 158^\circ$  (*c* 0.5; 2 dm. tube) (Found : C, 79.35; H, 10.8.  $C_{32}H_{52}O_3$  requires C, 79.3; H, 10.8%).

Fractions 4—6 consisted of mixtures which could not be separated. Fraction 7 was recrystallised from alcohol, yielding *3α-hydroxyfriedelan-x-one*, plates, m. p. 307—311°,  $[\alpha]_D + 145^\circ$  (*c* 1.0) (Found : C, 81.3; H, 11.2%). The *acetate* formed plates (from alcohol), m. p. 305—307°,  $[\alpha]_D + 114^\circ$  (*c* 0.7; 2 dm. tube) (Found : C, 79.3; H, 10.7).

When the reduction was repeated on a larger scale a 53% yield of the *3β*(axial)-epimer was isolated.

*Wolff-Kishner Reduction of 3β-Hydroxyfriedelan-x-one*.—A mixture of *3β*-hydroxyfriedelan-*x-one* (1.0 g.), anhydrous hydrazine (6.5 ml.), and a solution of sodium (2.5 g.) in methyl alcohol (30 ml.) was heated at 200° for 16 hr. The product, isolated with chloroform after the mixture had been acidified, was dissolved in 3 : 1 light petroleum-benzene and filtered through alumina (60 g.). The filtrate contained friedelane (0.20 g.), m. p. 244—246°,  $[\alpha]_D + 22^\circ$  (*c* 1.2). Elution with 3 : 1 light petroleum-benzene yielded *epifriedelinol* (0.35 g.), plates (from much alcohol), m. p. 281—283°,  $[\alpha]_D + 21^\circ$  (*c* 1.1) (Found : C, 84.2; H, 12.1. Calc. for  $C_{30}H_{52}O$  : C, 84.0; H, 12.2%). Its infrared spectrum was identical with that of an authentic specimen. The *acetate* formed plates (from alcohol-benzene), m. p. 290—293°,  $[\alpha]_D + 33^\circ$  (*c* 1.1) (Found : C, 81.3; H, 11.5. Calc. for  $C_{32}H_{54}O_2$  : C, 81.6; H, 11.6%).

*Conversion of Friedelane-3 : x : y-trione into Friedelin and Friedelane-3 : y-dione*.—A solution of friedelane-3 : *x* : *y*-trione (2.95 g.) in 2-ethyl-2-methyl-1 : 3-dioxolan<sup>6</sup> (60 ml.) containing toluene-*p*-sulphonic acid (45 mg.) was refluxed for 7 hr. The product, obtained by filtering the cooled reaction mixture, was recrystallised from benzene, yielding the ethylene *ketal*, prisms, m. p. 342—345°,  $[\alpha]_D + 76^\circ$  (*c* 1.2) (Found : C, 77.3; H, 10.3.  $C_{32}H_{50}O_4$  requires C, 77.1; H, 10.1%). It had strong infrared peaks at 1092, 1077, and 1067  $cm^{-1}$  (Nujol mull; cf. Page, *J.*, 1955, 2017).

A mixture of the *ketal* (1.3 g.), anhydrous hydrazine (8.5 ml.), and a solution of sodium (3.2 g.) in methyl alcohol (50 ml.) was heated at 200° for 16 hr. The product, isolated from the acidified mixture with chloroform, was dissolved in acetone (400 ml.) containing toluene-*p*-sulphonic acid (75 mg.), and the solution was refluxed for 14 hr., to remove the *ketal* group. The product, isolated by pouring the concentrated solution into water, was dissolved in 2 : 1 light petroleum-benzene and filtered through alumina (100 g.). The filtrate contained friedelane (30 mg.), m. p. 245—247°,  $[\alpha]_D + 21^\circ$  (*c* 0.3; 2 dm. tube). Elution with benzene gave *friedelin* (80 mg.), m. p. 261—264°,  $[\alpha]_D - 25^\circ$  (*c* 0.8) (Found : C, 84.3; H, 11.65%).

Elution with 20% chloroform in benzene yielded *y*-hydroxyfriedelane-3-one (450 mg.), laths (from alcohol), m. p. 301—305°,  $[\alpha]_D -20^\circ$  (*c* 0.7; 2 dm. tube) (Found: C, 81.4; H, 11.3%). The acetate formed needles (from aqueous alcohol), m. p. 175—176°,  $[\alpha]_D -25^\circ$  (*c* 1.2) (Found: C, 79.1; H, 10.7%).

Oxidation of *y*-hydroxyfriedelane-3-one with chromium trioxide in pyridine yielded friedelane-3 : *y*-dione, m. p. 306—310°,  $[\alpha]_D -60^\circ$  (*c* 0.8).

*Clemmensen Reduction of Friedelane-3 : x : y-trione.*—Friedelane-3 : *x* : *y*-trione (2 g.) was reduced in the same way as friedelane-3 : *x*-dione, and the product was chromatographed over alumina (100 g.). Elution with 3 : 1 light petroleum–benzene yielded *friedelane-y-one* (0.2 g.), prisms (from alcohol–benzene), m. p. 287—290°,  $[\alpha]_D -34^\circ$  (*c* 1.6) (Found: C, 84.7; H, 12.0%). Elution with 2 : 1 light petroleum–benzene yielded *friedelane-x : y-dione*, plates (from alcohol–benzene), m. p. 302—305°,  $[\alpha]_D +103^\circ$  (*c* 1.6) (Found: C, 81.7; H, 11.0%).

*Wolff–Kishner Reduction of Friedelane-3 : x : y-trione.*—Friedelane-3 : *x* : *y*-trione (1.64 g.) was reduced in the same way as 3 $\beta$ -hydroxyfriedelane-*x*-one, and the product was dissolved in 2 : 1 light petroleum–benzene and filtered through alumina (100 g.). The filtrate contained friedelane (0.61 g.), m. p. 245—247°,  $[\alpha]_D +22^\circ$  (*c* 1.0). Elution with 1 : 1 light petroleum–benzene yielded *friedelane-y-ol* (0.67 g.), plates (from alcohol), m. p. 223—226°,  $[\alpha]_D +20^\circ$  (*c* 1.8) [Found (after vacuum-sublimation): C, 84.3; H, 12.2. C<sub>30</sub>H<sub>52</sub>O requires C, 84.0; H, 12.2%]. The acetate formed prisms (from aqueous alcohol), m. p. 143—145°,  $[\alpha]_D +13^\circ$  (*c* 1.0) (Found: C, 81.6; H, 11.5. C<sub>32</sub>H<sub>54</sub>O<sub>2</sub> requires C, 81.6; H, 11.6%).

Oxidation of *friedelane-y-ol* with chromium trioxide in pyridine yielded *friedelane-y-one*, m. p. 290—292°,  $[\alpha]_D -30^\circ$  (*c* 1.0).

*Huang–Minlon Reduction of Friedelane-3 : y-dione.*—Friedelane-3 : *y*-dione (0.5 g.) was reduced in the same way as friedelane-3 : *x*-dione, and the product was chromatographed over alumina (50 g.). Elution with 2 : 1 light petroleum–benzene yielded *friedelane-y-one* (0.35 g.), m. p. 286—290°,  $[\alpha]_D -32^\circ$  (*c* 1.0).

We are indebted to Mr. L. J. Webb and Mr. J. G. Tracey, Division of Plant Industry, C.S.I.R.O., and to the Forester at Imbil, Queensland, for supplies of *Siphonodon australe* bark.