Tetrahedron. Vol. 24, pp. 6259 to 6264. Pergamon Press 1968. Printed in Great Britain

TERPENOIDS AND RELATED COMPOUNDS—XI[1]

THE STRUCTURE OF ROXBURGHOLONE, A NEW TRITERPENOID CONSTITUENT OF *PUTRANJIVA ROXBURGHII*

P. SENGUPTA and J. MUKHERJEE

Organic Chemistry Laboratory, University of Kalyani, Kalyani, Nadia, W. Bengal, India

(*Received in the UK* 7 *May* 1968; *accepted for publication* 28 *May* 1968)

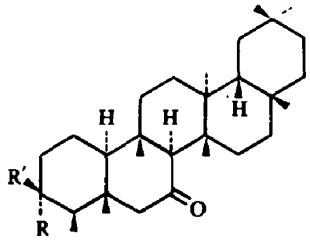
Abstract—The isolation of friedelin, putranjivadione (I), friedelanol and a new triterpenoid Roxburgholone, $C_{30}H_{50}O_2$, from the bark of *P. roxburghii* has been described. Roxburgholone has been shown to be 3α-hydroxyfriedelan-7-one (II). The hydroxyketone obtained by sodium borohydride reduction of putranjivadione (I) has been shown to be 3β-hydroxyfriedelan-7-one (XIII).

IN A previous communication[1] we have reported the isolation of friedelin and putranjivadione, a new pentacyclic triterpene diketone obtained as the major components of the whole plant of *Putranjiva roxburghii* (Euphorbiaceae) and have established the structure of the latter as friedelan-3,7-dione (I) from chemical transformations coupled with mass spectrometric fragmentation pattern and NMR and IR data. We have now chemically examined the bark of *P. roxburghii* and report the isolation of friedelin and putranjivadione (I) as the major triterpenoid constituents and friedelanol and a new triterpenoid, named Roxburgholone as the minor constituents.

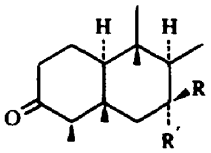
The benzene extract of the bark of *P. roxburghii* was separated into an ether soluble gum and an ether insoluble crystalline mass. The ether soluble fraction yielded only friedelin and putranjivadione[1] (I). The chloroform soluble portion of the ether insoluble part on chromatography over activated alumina yielded first friedelin and putranjivadione (I) as the less polar fractions. The more polar fraction melting over a range above 300° could not be resolved into purer components by chromatography and crystallization. However, when converted into acetate, the mixture could be separated on chromatography over deactivated alumina followed by crystallization into two pure components. The less polar constituent, $C_{32}H_{54}O_2$, m.p. 316–318°, $[\alpha]_D$ −12·5° was identified as friedelanol acetate,[2] which on deacetylation afforded friedelanol,[2] m.p. 299–300°. The more polar component, m.p. 322–328°, $[\alpha]_D$ −26° did not yield reproducible C,H-analytical data (see below) and consequently was hydrolysed to a new hydroxy compound, $C_{30}H_{50}O_2$, m.p. 312–318°, $[\alpha]_D$ −7·8°. This new compound, named Roxburgholone has been shown by the following transformations to be 3α-hydroxyfriedelan-7-one (II).

The presence of a hydroxyl function and a keto group was demonstrated by the IR spectra of roxburgholone (II) which showed bands at 3480 (OH) and 1700 cm^{-1} (6-membered ring saturated ketone). Roxburgholone (II) could be acetylated to an acetate (III), m.p. 322–328°, $[\alpha]_D$ −26° which also did not yield reproducible C,H-analytical data. The IR spectra of this acetate showed bands at 1700 cm^{-1} (6-membered ring saturated ketone) and 1735 and 1240 cm^{-1} (acetate) with no peak

CHART 1

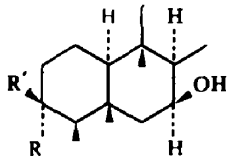


I, $\begin{cases} R' = O \\ R \end{cases}$

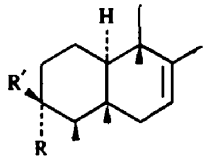


IV: R = OH, R′ = H
V: R = H, R′ = OH

II: R = OH, R′ = H
III: R = OAc, R′ = H
XIII: R = H, R′ = OH



VI: R = OH, R′ = H
VII: R = OAc, R′ = H
XII: R = R′ = H
XIV: R = H, R′ = OH
XV: R = H, R′ = OAc



VIII: R = OAc, R′ = H
IX: R = OH, R′ = H
X: $\begin{cases} R \\ R' \end{cases}$ = O
XI: R = R′ = H
XVI: R = H, R′ = OAc
XVII: R = H, R′ = OH

in the hydroxyl region. The acetate (III) on hydrolysis furnished roxburgholone (II).

The presence of a friedelane skeleton and the location of the oxygen functions in roxburgholone (II) could be easily demonstrated by its oxidation (chromic acid–pyridine complex[3]) to a diketone, $C_{30}H_{48}O_2$, m.p. 285–289° found to be identical (mixed m.p. and IR) with putranjivadione[1] (I). However, the 3-hydroxyfriedelan-7-one[1] obtained by sodium borohydride reduction of putranjivadione (I) was found to differ from roxburgholone (II). This led us to assume the following possibilities that (a) roxburgholone is still a 3-hydroxyfriedelan-7-one but epimeric at C_3 with the borohydride reduction product of putranjivadione or (b) it is either one of the epimeric pair (IV or V) of 7-hydroxyfriedelan-3-one. Since the ketonic group of roxburgholone could not be reduced by Huang-Minlon's method, the possibility of structures IV or V was ruled out.

Roxburgholone (II) was reduced with LAH to a diol, Roxburghadiol (VI), $C_{30}H_{52}O_2$, m.p. 286–288°, $[\alpha]_D$ ±0°, the IR spectra of which showed two bands in the hydroxyl region at 3480 and 3620 cm^{-1} but no band in the carbonyl region. This diol (VI), which was different from putranjivadiol,[1] obtained by LAH reduction of putranjivadione had, like putranjivadiol, one OH group hindered, since it formed a monoacetate (VII), $C_{32}H_{54}O_3$, m.p. 290–294°, $[\alpha]_D$ −4·8° on treatment with acetic anhydride and pyridine. In the IR spectra the acetate (VII) still showed a peak at

3580 cm^{-1} (OH) besides the acetate peaks, and on hydrolysis regenerated roxburghadiol (VI). However, on treatment with acetic anhydride and a drop of perchloric acid roxburghadiol (VI) or its monoacetate (VII) eliminated a molecule of water and yielded the same ene-acetate (VIII), $C_{32}H_{52}O_2$, m.p. 147–148°, $[\alpha]_D$ −86° having IR bands at 1740 and 1250 cm^{-1} (acetate) and 818 cm^{-1} (trisubstituted ethylenic linkage). The acetate (VIII) on hydrolysis afforded the ene-alcohol (IX), $C_{30}H_{50}O$, m.p. 176–180°, $[\alpha]_D$ −74° having IR bands at 3400 cm^{-1} (OH) and 818 cm^{-1} (trisubstituted ethylenic linkage). The alcohol (IX) on oxidation with chromic acid–pyridine complex[3] furnished the ketone (X), $C_{30}H_{48}O$, m.p. 140–141°, $[\alpha]_D$ −87·8° having an IR band at 1725 cm^{-1} (6-membered ring saturated ketone) and no band in the hydroxyl region. This ketone (X) on Huang-Minlon reduction yielded the known putranjivene[1] (friedel-7-ene) (XI) thus locating the exact position of the ethylenic linkage in VIII, IX and X. This would mean that the hindered free OH group in roxburghadiol monoacetate (VII) is at C_7. The axial (β) orientation attributed to this free OH group in VII is consistent with the fact that only such a configuration could undergo smooth proton catalysed 1,2-elimination involving the axial α H atom at C_8. It may be mentioned here that putranjivol (XII) having the OH in axial β orientation yielded almost exclusively putranjivene (XI) on treatment with acetic anhydride and perchloric acid.[1] Since roxburgholone (II) did not have any non-acylable hindered OH group, this OH group must have been derived from a ketonic group at C_7 of roxburgholone (II) during LAH reduction. Hence roxburgholone (II) and the 3-hydroxyfriedelan-7-one,[1] obtained by sodium borohydride reduction of putranjivadione must be epimeric at C_3. Further that the OH group at C_3 in roxburgholone (II) is equatorial (α) was demonstrated by the reduction of the ene-one (X) with sodium and isoamyl alcohol under equilibrating conditions, when the same ene-alcohol (IX), m.p. 176–180° derived from roxburgholone (II) was obtained. Thus the assigned structure of roxburgholone as 3α-hydroxyfriedelan-7-one (II) is correct. The hydroxyketone, obtained by borohydride reduction of putranjivadione (I) must then be 3β-hydroxyfriedelan-7-one (XIII). This conclusion was further substantiated by the following transformations with this hydroxyketone (XIII).

The hydroxyketone (XIII) on reduction with LAH furnished putranjivadiol,[1] m.p. 270–274° whose correct stereochemistry can now be represented by structure XIV. This diol also contains, like roxburghadiol, a hindered or axial β OH group at C_7, since as reported earlier[1] it forms a monoacetate (XV). Putranjivadiol (XIV) or its monoacetate (XV) on treatment with acetic anhydride and a drop of perchloric acid underwent elimination of water to give 3β-acetoxyfriedel-7-ene (XVI), m.p. 152–156°, $[\alpha]_D$ −35·8° epimeric with the acetate (VIII) reported above. The IR spectra of XVI shows bands at 1740 and 1250 cm^{-1} (acetate) and 825 cm^{-1} (trisubstituted ethylenic linkage) but no band in the hydroxyl region. This acetate (XVI) on hydrolysis yielded 3β-hydroxyfriedel-7-ene (XVII), m.p. 162–165°, $[\alpha]_D$ −51° having IR bands at 3600 cm^{-1} (OH) and 820 cm^{-1} (trisubstituted ethylenic linkage). The alcohol (XVII) on oxidation with chromic acid–pyridine complex[3] gave friedel-7-en-3-one (X) identical (mixed m.p. and IR) with the ketone X obtained above from the epimeric alcohol (IX).

Thus we have described both the epimers II and XIII of 3-hydroxy-friedelan-7-one and have shown that roxburghadiol is friedelan-3α,7β-diol (VI) and is epimeric at C_3 with putranjivadiol which is friedelan-3β,7β-diol (XIV).

EXPERIMENTAL

All m.ps are uncorrected. The pet. ether used had b.p. 60–80°.

Benzene extraction of the bark of Putranjiva roxburghii

(a) *Examination of the ether soluble part.* Finely pulverized bark (4 Kg) of *P. roxburghii* was extracted with benzene in a soxhlet apparatus for 18 hr. The gummy residue obtained after the removal of benzene was separated into ether soluble and ether insoluble fractions. The ether soluble portion was washed with cold 5% KOH aq, then with water and dried (Na_2SO_4). The neutral gummy mass (55·5 g) obtained after the evaporation of ether was chromatographed over activated alumina (500 g). Elution with a mixture of pet. ether and benzene (3:2) yielded a fraction, m.p. 248–252° (0·38 g), which on crystallization from $CHCl_3$–acetone yielded pure friedelin, m.p. 259–261°, $[\alpha]_D$ −22° ($CHCl_3$), identical with an authentic specimen (mixed m.p. and IR). (Found: C, 84·60; H, 11·91. Calc. for $C_{30}H_{50}O$: C, 84·44; H, 11·81%).

Further elution of the column with benzene:ether (3:2) gave a solid, m.p. 276–280° (5·3 g), which on crystallization from $CHCl_3$–acetone afforded pure I, m.p. 284–289°, $[\alpha]_D$ −36°, identical with an authentic specimen[1] (mixed m.p. and IR). (Found: C, 81·99; H, 10·97. Calc. for $C_{30}H_{48}O_2$: C, 81·76; H, 10·98%).

(b) *Examination of the ether insoluble part—friedelin and putranjivadione* (I). The ether insoluble part (7·1 g) was boiled with $CHCl_3$ and filtered over a bed of alumina. The residue (4·2 g) obtained after the removal of solvent, was chromatographed over activated alumina (300 g). Elution with pet. ether:benzene (2:3) furnished the first fraction, m.p. 248–256° (0·1 g), which on crystallization from $CHCl_3$–acetone gave pure friedelin (40 mg), m.p. 257–261° identical with an authentic specimen. Elution with benzene:ether (4:1) yielded the second fraction (2·5 g), m.p. 276–282°, which on crystallization from $CHCl_3$–acetone furnished I (1·8 g), m.p. 285–289° identical with an authentic specimen.

Friedelanol acetate and roxburgholone acetate (III)

Further elution of the column in the above chromatogram with ether–$CHCl_3$ (3:2) gave a crystalline mass (1·1 g) melting above 300°. This mixture could not be further resolved by rechromatography and crystallization and was acetylated with Ac_2O (40 cc) and pyridine (40 cc) in the usual manner. The crude acetate (0·86 g), m.p. 312–316°, that crystallized out of the reaction mixture was chromatographed over deactivated alumina (100 g). Elution with pet. ether:benzene (3:2) gave the first acetate (120 mg), m.p. 308–310°, which on crystallization from benzene–MeOH yielded friedelanol acetate (35 mg), m.p. 316–318°, $[\alpha]_D$ −12·5° ($CHCl_3$), identical with an authentic specimen[2] (mixed m.p. and IR). (Found: C, 82·18; H, 11·28. Calc. for $C_{30}H_{54}O_2$: C, 81·64; H, 11·56%).

Further elution of the column with the same solvent mixture yielded the more polar fraction (0·65 g), m.p. 318–322°, which on crystallization from $CHCl_3$–MeOH gave III (0·16 g), m.p. 322–328°, $[\alpha]_D$ −26° ($CHCl_3$). IR peaks at 1735 and 1240 cm^{-1} (acetate) and 1700 cm^{-1} (6-membered ring saturated ketone).

Friedelanol. The above friedelanol acetate (0·1 g) in benzene (5 cc) was refluxed for 5 hr with 3·6 cc of 10% methanolic KOH. On cooling the mixture was diluted with ether and the organic layer was washed with water, dried (Na_2SO_4) and evaporated. The residue (90 mg) was chromatographed over activated alumina (10 g). Elution with benzene:$CHCl_3$ (9:1) furnished a solid (70 mg), m.p. 294–300°, which on crystallization from acetone gave pure friedelanol (50 mg), m.p. 299–300° identical with an authentic specimen. (Found: C, 84·36; H, 12·12. Calc. for $C_{30}H_{52}O$: C, 84·04; H, 12·23%).

Roxburgholone (II). Compound III (1 g) in benzene (56 cc) was refluxed for 5 hr with 40 cc of 10% methanolic KOH. The reaction mixture was cooled, diluted with water and taken up in $CHCl_3$. The organic layer on evaporation yielded a crystalline mass (1 g), which was chromatographed over activated alumina (40 g). Elution with benzene–ether (4:1) furnished a solid (0·77 g), m.p. 308–314°, which after crystallization from $CHCl_3$–MeOH yielded II (0·4 g), m.p. 312–318°, $[\alpha]_D$ −7·8° ($CHCl_3$). (Found: C, 81·63; H, 11·49. $C_{30}H_{50}O_2$ requires: C, 81·39; H, 11·38%). IR peaks at 3480 cm^{-1} (OH) and 1700 cm^{-1} (6-membered ring saturated ketone).

Acetylation of roxburgholone. A mixture of II (0·13 g), Ac_2O (3 cc) and pyridine (3 cc) was heated on the water bath for 2 hr and allowed to stand at room temp overnight. The crude acetate (0·12 g), m.p. 318–322°, on crystallization from $CHCl_3$–MeOH afforded III (0·1 g), m.p. 322–328°, $[\alpha]_D$ −26° ($CHCl_3$).

Oxidation of roxburgholone—Putranjivadione (I). A soln of II (0·2 g) in pyridine (6 cc) cooled to 15° was added to CrO_3–pyridine complex,[3] prepared from CrO_3 (0·2 g) and pyridine (2 cc) at 15°. The reaction mixture was allowed to stand at room temp for 18 hr. Excess CrO_3 was decomposed by addition of MeOH. The mixture was then digested with EtOAc and filtered. The filtrate after working up as usual, yielded a solid (0·19 g), which was chromatographed over activated alumina (20 g). Elution with pet. ether:benzene

(2:3) afforded a solid (0·14 g), m.p. 276–282° which after crystallization from $CHCl_3$–acetone furnished I (80 mg), m.p. 285–289°, identical with an authentic specimen[1] (mixed m.p. and IR). (Found: C, 81·99; H, 10·97. Calc. for $C_{30}H_{48}O_2$: C, 81·76; H, 10·98%).

Attempted Huang-Minlon reduction of roxburgholone. A mixture of II (0·2 g), di-ethylene glycol (16 cc) and 85% hydrazine hydrate (2 cc) was refluxed at 200–210° for 1 hr and then after the addition of KOH (0·2 g) the mixture was refluxed for 1 hr. The condenser was then removed and the mixture was heated until the temp of the mixture was 190°. Finally, the condenser was reattached and the mixture was refluxed for 2½ hr, cooled and diluted with water. Usual work-up furnished a solid, which on chromatography over activated alumina (20 g) gave only the unchanged roxburgholone (0·18 g), m.p. 316–318°.

Lithium aluminium hydride reduction of roxburgholone—Roxburghadiol (VI). LAH (0·6 g) was added in portions to an ice cooled soln of II (0·5 g) in THF (80 cc) and the mixture refluxed for 6 hr. The mixture, after cautious addition of cold water, was extracted with $CHCl_3$. The $CHCl_3$ soln was washed with water, dried (Na_2SO_4) and evaporated to yield a crude product (0·5 g), m.p. 278–280°, which was chromatographed over activated alumina (40 g). Elution with benzene:ether (4:1) gave a solid (0·4 g), m.p. 278–282°, which after crystallization from $CHCl_3$–acetone furnished VI (0·12 g), m.p. 286–288°, $[\alpha]_D$ ±0° ($CHCl_3$). (Found: C, 81·25; H, 11·83. $C_{30}H_{52}O_2$ requires: C, 81·02; H, 11·79%); IR peaks at 3480 and 3620 cm^{-1} (OH) but no bands in the carbonyl region.

Acetylation of Roxburghadiol—Roxburghadiol monoacetate (VII). Roxburghadiol (0·1 g) was acetylated with Ac_2O (1 cc) and pyridine (1 cc). The crude acetate (65 mg), m.p. 288–292° crystallized out of the reaction mixture. Recrystallization from $CHCl_3$–acetone yielded pure VII (50 mg), m.p. 290–294°, $[\alpha]_D$ −4·8° ($CHCl_3$). (Found: C, 79·23; H, 11·32. $C_{32}H_{54}O_3$ requires: C, 78·96; H, 11·18%); IR peaks at 3580 cm^{-1} (OH) and 1700 and 1250 cm^{-1} (acetate).

3α-Acetoxyfriedel-7-ene (VIII). A drop of $HClO_4$ was added to an ice cold suspension of VII (0·13 g) in Ac_2O (6 cc). The mixture was stirred at room temp for 20 min and poured into cold $NaHCO_3$ aq (10 cc). The ppt was taken up in $CHCl_3$, washed with water and dried (Na_2SO_4). Evaporation of solvent gave a solid (0·15 g), which was chromatographed over deactivated alumina (10 g). Elution with pet. ether yielded a fraction (0·12 g), which on crystallization from acetone–MeOH furnished VIII (50 mg), m.p. 147–148°, $[\alpha]_D$ −86° ($CHCl_3$). (Found: C, 81·80; H, 11·30. $C_{32}H_{52}O_2$ requires: C, 81·99; H, 11·18%); IR peaks at 1740 cm^{-1} and 1250 cm^{-1} (acetate) and 818 cm^{-1} (trisubstituted ethylenic linkage) and no band in the hydroxyl region. It gave yellowish brown colour with tetranitromethane.

Acetic anhydride and perchloric acid treatment of roxburghadiol (VI). A drop of $HClO_4$ was added to an ice cold suspension of VI (0·17 g) in Ac_2O (6 cc). After working up as above the crude solid (0·15 g) was chromatographed over deactivated alumina (12 g). Elution with pet. ether yielded a solid (0·12 g), which on crystallization from acetone–MeOH furnished VIII (0·1 g), identical with VIII described above.

Friedel-7-en-3 α-ol (IX). A mixture of VIII (0·11 g), benzene (3·6 cc) and 10% methanolic KOH (2·5 cc) was refluxed for 5 hr. After working up as usual the crude alcohol (90 mg) was crystallized from MeOH to furnish IX (40 mg), m.p. 176–180°, $[\alpha]_D$ −74° ($CHCl_3$). (Found: C, 84·41; H, 11·57. $C_{30}H_{50}O$ requires: C, 84·44; H, 11·72%); IR peaks at 3400 cm^{-1} (OH) and 818 cm^{-1} (trisubstituted ethylenic linkage) but no peak in the carbonyl region. It gave positive tetranitromethane test.

Oxidation of friedel-7-en-3 α-ol (IX)—*friedel-7-en-3-one* (X). A soln of IX (0·16 g) in pyridine (1·6 cc) was cooled to 15° and added to CrO_3–pyridine complex,[3] prepared from CrO_3 (0·16 g) and pyridine (1·6 cc) cooled to 15°. After working up as usual the crude solid (0·15 g), m.p. 124–128° was chromatographed over activated alumina (8 g). Elution with pet. ether afforded a solid (0·13 g), m.p. 132–134°, which on crystallization from $CHCl_3$–MeOH gave X (40 mg), m.p. 140–141°, $[\alpha]_D$ −87·8° ($CHCl_3$). (Found: C, 84·84; H, 11·50. $C_{30}H_{48}O$ requires: C, 84·84; H, 11·39%); IR peak at 1725 cm^{-1} (6-membered ring saturated ketone) but no peak in the hydroxyl region.

Sodium and isoamyl alcohol reduction of friedel-7-en-3-one (X)—*Friedel-7-en-3 α-ol* (IX). Na (0·64 g) was slowly added to a refluxing soln of X (0·16 g) in isoamyl alcohol (8 cc) and refluxing continued until all the Na had dissolved. After steam distillation the ppt was extracted with ether. The organic layer was washed with water, dried (Na_2SO_4) and evaporated to give a gummy solid (0·16 g), which was chromatographed over activated alumina (8 g). Elution with pet. ether:benzene (4:1) afforded a solid (0·1 g), m.p. 174–178°, which on crystallization from MeOH furnished IX (20 mg), identical (mixed m.p. and IR) with the sample derived from roxburgholone.

Huang-Minlon reduction of friedel-7-en-3-one (X)—*Friedel-7-ene* (XI). Compound X (90 mg) in diethylene glycol (8 cc) was refluxed with 85% hydrazine hydrate (2 cc) for 1 hr. KOH (0·1 g) was added and the mixture refluxed for 1 hr, when the condenser was removed and the mixture heated to 190°. After refluxing

for an additional 2½ hr, the mixture was worked up as usual to furnish a solid (75 mg), which was then chromatographed over activated alumina (2 g). Elution with pet. ether yielded a fraction (30 mg), which on crystallization from MeOH furnished friedel-7-ene (15 mg), m.p. 160–162°, identical (mixed m.p. and IR) with an authentic sample of XI.[1]

Lithium aluminium hydride reduction of 3β-*hydroxyfriedelan-7-one* (XIII)—*Putranjivadiol* (XIV). LAH (0·22 g) was added in portion to an ice cold soln of XIII (0·17 g) in THF (30 cc) and the mixture was refluxed for 6 hr. Usual work up yielded a crude product (0·15 g), m.p. 254–260° which was then chromatographed over activated alumina (4 g). Elution with benzene–ether (4:1) furnished a solid (80 mg), which on crystallization from $CHCl_3$–MeOH afforded XIV (30 mg), m.p. 270–274° identical with an authentic sample[1] (mixed m.p. and IR).

Acetic anhydride and perchloric acid treatment of putranjivadiol monoacetate (XV)—3β-*Acetoxyfriedel-7-ene* (XVI). A drop of $HClO_4$ was added to an ice cold suspension of XV[1] (0·15 g) in Ac_2O (6 cc). After working up as above the crude solid (0·14 g) was chromatographed over deactivated alumina (10 g). Elution with pet. ether gave a fraction (0·12 g), which on crystallization from acetone–MeOH furnished XVI (60 mg), m.p. 152–156°, $[\alpha]_D$ −35·8° ($CHCl_3$). (Found: C, 82·29; H, 11·24. $C_{32}H_{52}O_2$ requires: C, 81·99; H, 11·18%); IR peaks at 1740 and 1250 cm^{-1} (acetate), 825 cm^{-1} (trisubstituted ethylenic linkage) and no peak in the hydroxyl region. It gave positive tetranitromethane test.

3β-*Acetoxyfriedel-7-ene* (XVI) *from putranjivadiol* (XIV). A drop of $HClO_4$ was added to an ice cold suspension of XIV (0·16 g) in Ac_2O (6 cc). After working up as above the crude product was chromatographed over deactivated alumina (10 g). Elution with pet. ether gave a solid (0·1 g), which on crystallization from acetone–MeOH furnished XVI (60 mg), m.p. 152–156° identical with XVI (mixed m.p. and IR) described above.

Friedel-7-en-3β-*ol* (XVII). A mixture of XVI (0·1 g), benzene (1 cc) and 10% methanolic KOH (1·5 cc) was refluxed for 5 hr. After working up the crude alcohol (90 mg) was chromatographed over activated alumina (10 g). Elution with pet. ether–benzene (4:1) yielded a solid (80 mg), which on crystallization from MeOH afforded XVII (20 mg), m.p. 162–165°, $[\alpha]_D$ −51° ($CHCl_3$). (Found: C, 84·53; H, 11·71. $C_{30}H_{50}O$ requires: C, 84·44; H, 11·72%); IR peaks at 3600 cm^{-1} (OH) and 820 cm^{-1} (trisubstituted ethylenic linkage) and no peak in the carbonyl region.

Oxidation of friedel-7-en-3β-*ol* (XVII)—*Friedel-7-en-3-one* (X). A soln of XVII (0·16 g) in pyridine (1·6 cc) cooled to 15° was added to CrO_3–pyridine complex[3] prepared from CrO_3 (0·2 g) and pyridine (2 cc) at 15°. After working up the crude product (0·14 g), m.p. 122–126° was chromatographed over activated alumina (6 g). Elution with pet. ether afforded a solid (0·12 g), which on crystallization from $CHCl_3$–MeOH yielded X identical with X (mixed m.p. and IR) described above.

Acknowledgement—We are highly indebted to Prof. D. K. Banerjee of Indian Institute of Science, Bangalore and to Prof. J. N. Chatterjea of Patna University for the IR spectra of our compounds. We are also indebted to Dr. S. K. Sengupta of East India Pharmaceutical Works Ltd., Calcutta for the optical rotation values.

REFERENCES

[1] Part X: P. Sengupta, A. K. Chakraborty, A. M. Duffield, L. J. Durham and Carl Djerassi, *Tetrahedron* **24**, 1205 (1968).

[2] J. Simonsen and W. C. J. Ross, *The Terpenes* Vol. IV; p. 469. University Press, Cambridge (1957).

[3] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.* **75**, 427 (1953).