Further Reactions of Sideridiol [(−)-Kaur-15-ene-7β,19-diol] †

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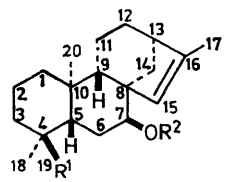
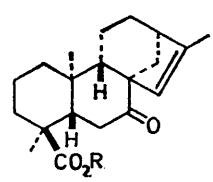
The secondary hydroxy-group of sideridiol [(−)-kaur-15-ene-7β,19-diol] (I) has been confirmed as being in the 7- rather than the 12-position. Bromination of methyl (−)-7-oxokauran-19-oate (IXb) gives methyl (−)-6β-bromo-7-oxokauran-19-oate (Xb); treatment of the latter with base gives (−)-7-oxokaur-5-en-19,6-olide (XII) mainly. Better yields of lactone (XII) are obtained by heating a solution of bromo-ester (Xb) in dimethyl sulphoxide under reflux. The n.m.r., o.r.d., and c.d. data for the bromo-ester (Xb) are discussed.

We have suggested[1] the structure (I) for sideridiol [(−)-kaur-15-ene-7β,19-diol], the simplest of the diterpenes from *Sideritis sicula* Ucria (Labiatae). The absolute configuration and the position of the primary hydroxy-group were proved by direct comparison with a known derivative of (−)-kaurene, while the choice of the 7-position for the axial secondary hydroxy-group was resolved mainly on the basis of spectroscopic results. We present further evidence which confirms the proposed structure.

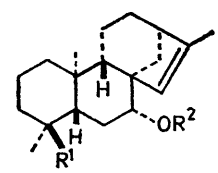
Comparison of the n.m.r. spectra of sideridiol (I) and its oxidation product (IIb) showed that the allylic 13-proton resonance from both compounds appeared as a broad signal, δ 2·35—2·40 p.p.m. A carbonyl group at C-12 would be expected to deshield the 13-proton.



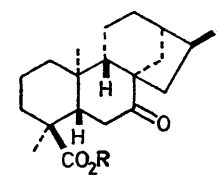
(I) $R^1 = CH_2{\cdot}OH$, $R^2 = H$
(IV) $R^1 = CO_2H$, $R^2 = H$
(V) $R^1 = CH_2{\cdot}OH$, $R^2 = Ac$
(VIII) $R^1 = CH_2{\cdot}OAc$, $R^2 = Ac$



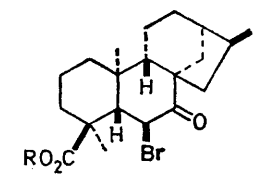
(IIa) R = H
(IIb) R = Me



(III) $R^1 = CO_2H$, $R^2 = H$
(VI) $R^1 = CH_2{\cdot}OH$, $R^2 = H$
(VII) $R^1 = CH_2{\cdot}OAc$, $R^3 = Ac$



(IXa) R = H
(IXb) R = Me



(Xa) R = H
(Xb) R = Me

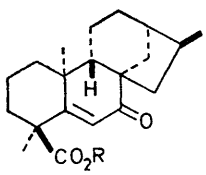
Reduction of the unsaturated keto-acid (IIa) with sodium borohydride afforded an equatorial hydroxy-acid (III), which was isomeric with the acid (IV) [obtained by oxidation and hydrolysis of siderol (V), and which must retain the original axial stereochemistry of the

† The results reported in this paper are part of a lecture delivered at the University of Zürich, 10th November, 1970: see F. Piozzi, *Chimia*, 1971, **25**, 30.

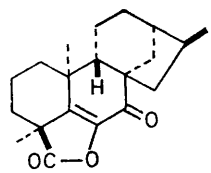
[1] F. Piozzi, P. Venturella, Z. Bellino, and R. Mondelli, *Tetrahedron*, 1968, **24**, 4073.

secondary hydroxy-group]. Reduction of other 7-oxokaurane derivatives gave [2] only the 7α-equatorial alcohol whereas reduction of 12-oxokauranes gave [3] a mixture of 60% axial and 40% equatorial products. The position and multiplicity of the 7-proton resonances in the n.m.r. spectra of the acids (III) and (IV), the corresponding diols and acetates, are in accord with these stereochemical assignments (see Experimental section). Surprisingly reduction of the keto-ester (IIb) with lithium aluminium hydride gave 90% 7-axial and only 10% 7-equatorial alcohol.

The oxo-acid (IXa) or its ester (IXb) was brominated to give the bromide (Xa) or (Xb), respectively. Dehydrobromination of the acid (Xa) with ethanolic potassium hydroxide or the ester (Xb) with either lithium



(XIa) R = H
(XIb) R = Me



(XII)

carbonate and lithium chloride or collidine gave only a small amount of the unsaturated ketone (XI). The main product was the βγ-unsaturated γ-lactone (XII) [$\nu_{max.}$ 1790 and 1675 cm^{-1}, $\lambda_{max.}$ 261 nm (ε 5500)]. This was obtained in better yield by the action of dimethyl sulphoxide under reflux on the oxo-ester (Xb).[4] Only a 7-oxo-compound could give rise to formation of the lactone (XII).

The stereochemistry of the ester (Xb) has been studied. Although there was no change in the carbonyl frequency in the i.r. on bromination of (IXb), the u.v. spectrum showed a bathochromic shift (Δλ +30 nm) in accord with an axial conformation for the bromine atom. The changes in the n.m.r. spectrum support this assignment. The 4α-methyl signal is at δ 1·20 p.p.m. in the ester (IXb) but at 1·36 in the bromide (Xb), while the signal for the 10α-methyl group is also at 1·20 in (IXb) but at 0·88 in (Xb). The strong shielding of the 10α-methyl group by the carbonyl group may be rationalised by assuming that ring B adopts a half-boat or boat conformation in the bromide (Xb). Moreover, the 6α-bromo-atom should also deshield the 10α-methyl-group even with ring B in a half-boat or boat conformation.[5,6]

The n.m.r. spectrum of (Xb) also showed two doublets at δ 2·70 and 4·42 p.p.m. which were assigned to the 5- and 6-protons respectively. Their coupling constant (10·5 Hz) corresponds to a dihedral angle of 0—10° or 140—150° associated with either a 6β-proton and ring B in a boat conformation or a 6α-proton and ring B in a half-boat conformation.*

The Nuclear Overhauser effect (NOE) has been already used to determine the configuration of 6-bromo-7-oxo-diterpenoids.[7] With the bromo-keto-ester (Xb), irradiation of the 10α-methyl group showed no significant increase in the 6-H signal, while irradiation of the 4α-methyl group gave an increase of *ca.* 18%. This suggests a 6α-configuration for 6-H. Whatever the conformation of ring B, a 6β-proton would be too far (>3 Å) from the methyl group for the effect to be observed. The 6α-proton and the 4α-methyl group are 1·6 Å apart in a half-boat and 1·7 Å apart in a chair conformation, while 6α-H and 10α-Me are 1·8 Å apart in chair and 2·2 Å in half-boat conformation. In the boat conformation the 10α-methyl group is even further away. Thus, the i.r., u.v., and n.m.r. data confirm the 6β-configuration for the bromine atom and that ring B is in the half-boat conformation.

The o.r.d. and c.d. curves of the keto-esters (IXb) and (Xb) have also been studied. The o.r.d. curve of the keto-ester (IXb) showed a positive Cotton effect at 287 nm (in ethanol) as did the c.d. at 291 nm ($\Delta\varepsilon_{max.}$ +2·73 in ethanol) and at 295 nm ($\Delta\varepsilon_{max.}$ +1·91 in n-heptane). The o.r.d. of the bromo-compound (Xb) shows two positive Cotton effects in ethanol (at 325 and 288 nm) but only one in n-heptane (at 324 nm). Similarly the c.d. shows two maxima ($\Delta\varepsilon_{max.}$ +0·65 at 320 and +0·81 at 289 nm) in ethanol and only one ($\Delta\varepsilon_{max.}$ +1·31 at 325 nm) in n-heptane. The c.d. curve of the bromo-ester (Xb) in ethanol is temperature-dependent: measurements at −20, 0, and +20° show that the maximum at 289 nm increases whilst that at 320 nm decreases as the temperature is lowered. These results imply an equilibrium of two conformers. However, n.m.r. studies (60 MHz, $CDCl_3$ or CS_2) over the temperature range from +30 to −70° reveal no splitting of the 5- and 6-H signals. N.m.r. spectra in CD_3OD at low temperature could not be recorded because of the poor solubility of the bromo-ester (Xb).

Previous reports [8] of o.r.d. and c.d. data for 6-bromo-7-oxoditerpenoids have been concerned only with compounds with an aromatic ring C and normal A/B junction, thereby rendering assumptions about the conformation of ring B based on Cotton effects uncertain. However, it is to be noted that bathochromic shifts in Cotton effect have only been observed for 6α-bromo-7-ketones with a normal A/B ring junction, *i.e.* those having an equatorial

* This discussion has not taken into consideration the fact that *J* values for the protons α and β to a cyclohexanone carbonyl group are reported to be greater than predicted by Karplus curve (see K. L. Williamson and W. S. Johnson, *J. Amer. Chem. Soc.*, 1961, **83**, 4623).

[2] J. R. Hanson and A. F. White, *Tetrahedron*, 1969, **25**, 2743.
[3] P. R. Jefferies and R. W. Retallack, *Austral. J. Chem.*, 1968, **21**, 2085.
[4] E. Wenkert, R. W. J. Carney, and C. Kaneko, *J. Amer. Chem. Soc.*, 1961, **83**, 4440.
[5] R. C. Cambie, G. R. Clark, D. R. Crump, and T. N. Waters, *Chem. Comm.*, 1968, 183.
[6] A. E. Lickei, A. C. Rieke, and D. M. S. Wheeler, *J. Org. Chem.*, 1967, **32**, 1647.
[7] R. A. Bell and E. N. C. Osakwe, *Chem. Comm.*, 1968, 1093.
[8] A. K. Bose, M. S. Manhas, and R. C. Cambie, *J. Org. Chem.*, 1965, **30**, 501.

bromine atom in a twisted conformation of ring B or an axial bromine atom in a boat conformation of ring B.*

The 60 MHz n.m.r. spectrum of the unsaturated keto-ester (IIb) showed a broad signal at δ 2·35 p.p.m. which was assigned to the allylic 13α-proton and two one-proton resonances at δ 2·45 (doublet) and 2·10 p.p.m. (multiplet). The saturated keto-ester (IXb) lacked the 13α-H signal but showed a triplet at δ 2·88 p.p.m. ($J_{gem} + J_{eclips}$ 26 Hz) assigned to the 15α-proton which is strongly deshielded by the 7-carbonyl group. A doublet at δ 2·56 p.p.m., assigned to the 6α-proton, is resolved into a quintet at 100 MHz and into a clean triplet ($J_{gem} + J_{ax,ax}$ 28 Hz) at 220 MHz. This signal is obviously the C part of an ABC system at 60 MHz and the X part of an ABX spectrum at 220 MHz. The signals at δ 2·15—2·0 must include resonances due to the 6β-proton since these and the signal at δ 2·56 p.p.m. disappear on deuteriation. This analysis and assignment is in agreement with previous results.[9,10] The downfield shift [2] of the 10α-methyl signal and the positive Cotton effects observed in the o.r.d. and c.d. measurements are consistent with a normal chair conformation of ring B in the oxo-ester (IXb).

Catalytic hydrogenation of the unsaturated oxo-ester (IIb) gave an unexpected result. Normally hydrogenation of (−)-kaur-15-enes occurs exclusively from the less-hindered α-face to give the 16β-methyl epimer. G.l.c. of the oxo-ester (IXb), prepared by oxidation of dihydrosideridiol followed by methylation, revealed the presence of only one epimer. However, hydrogenation of the unsaturated ester (IIb) afforded a 4 : 1 mixture of the C(16) epimers in which the 16β-epimer predominated. The acid (IIa) gave a similar result. The epimers could not be separated by crystallisation, preparative g.l.c., or column chromatography. It is probable that the partial addition from the β-side depends on the presence of the neighbouring carbonyl group at C(7).

EXPERIMENTAL

Kieselgel (0·05—0·2 mm; Merck) was used for column chromatography. T.l.c. plates were coated with silica gel G (Merck). G.l.c. was carried out with a Varian Aerograph model 1440-1 instrument, with nitrogen as carrier gas and a hydrogen-flame ion detector; preparative g.l.c. was performed with a Varian Aerograph model 202 instrument, with helium as carrier gas and a thermoconductivity detector. Optical rotations were determined with a Perkin-Elmer 141 polarimeter. I.r. spectra were recorded with a Perkin-Elmer 137 Infracord spectrophotometer and, unless otherwise stated, refer to Nujol mulls. U.v. spectra were recorded with Beckm DB and Cary 14 instruments. N.m.r. spectra at 60 MHz were measured with a Jeol C-60 H spectrometer and other n.m.r. spectra with Varian HA-100 and HR-220 spectrometers (courtesy of Prof. W. von Philipsborn, Institute of Organic Chemistry, University of Zürich) with tetramethylsilane as internal standard. Mass spectra were obtained with a Hitachi–Perkin-Elmer RMU6D spectrometer (courtesy of Dr. A. Selva, Institute of Chemistry, Politechnic School of Milano). O.r.d. measurements were made with a Cary model 60 spectropolarimeter and c.d. curves with a Roussel–Jouan 185 dichrograph.

(−)-7α-*Hydroxykaur*-15-*en*-19-*oic Acid* (III).—To a solution of (−)-7-oxokaur-15-en-19-oic acid [1] (IIa) (100 mg) in dry methanol (20 ml), sodium borohydride (200 mg) was added and the mixture was left overnight. After evaporation of the solvent and treatment with dilute hydrochloric acid, the *hydroxy-acid* (III) was extracted with ethyl acetate, m.p. 264—265° (from ethanol) (Found: C, 75·6; H, 9·4. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·50%), positive tetranitromethane test, $\nu_{max.}$ 3390 (OH) and 1700 (CO_2H) cm^{-1}, *m/e* 318 (83%), 303 (15), 300 (18), 285 (6), 272 (26) and 255 (15), δ ([$^2H_5$]pyridine, 60 MHz) 1·12 (s, 4α-Me), 1·44 (s, 10α-Me), 1·69 (d, *J* 1·5 Hz, 16-Me), 4·08br (1H, t, $W_{\frac{1}{2}}$ 19 Hz, 7β-H), and 5·30br (s, 15-H).

(−)-7β-*Hydroxykaur*-15-*en*-19-*oic Acid* (IV).—Methyl (−)-7β-acetoxykaur-15-en-19-oate [1] (100 mg) in 5% ethanolic potassium hydroxide (5 ml) was heated under reflux for 6 h. The solvent was evaporated off and the residue was treated with dilute hydrochloric acid to give the *hydroxy-acid* (IV), m.p. 266—268° (from aqueous ethanol) (Found: C, 75·7; H, 9·6. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·5%), positive tetranitromethane test, $\nu_{max.}$ 3500 (OH) and 1730 (CO_2H) cm^{-1}, *m/e* 318 (68%), 303 (14), 300 (80), 285 (32), 272 (42), and 255 (55), δ ([$^2H_5$]pyridine, 60 MHz) 1·12 (3H, s, 4α-Me), 1·45 (3H, s, 10α-Me), 1·71 (3H, d, *J* 1·5 Hz, 16-Me), 3·83br (1H, t, $W_{\frac{1}{2}}$ 6·5 Hz, 7α-H), and 6·04br p.p.m. (1H, s, 15-H).

(−)-*Kaur*-15-*ene*-7α,19-*diol* (*Episideridiol*) (VI).—Reduction of the hydroxy-acid (III) with lithium aluminium hydride [1] gave the diol (VI), m.p. 197—198° (from methanol–water), δ ($CDCl_3$, 60 MHz) 0·78 (s, 4α-Me), 1·10 (s, 10α-Me), 1·76 (d, *J* 1·5 Hz, 16-Me), 3·10 and 3·47 (2H, ABq, *J* 11·2 Hz, 4β-CH_2·OH), 3·74br (1H, t, $W_{\frac{1}{2}}$ 12 Hz, 7β-H), and 5·13br p.p.m. (1H, $W_{\frac{1}{2}}$ 4·5 Hz, 15-H).

Treatment of the diol (VI) with acetic anhydride–pyridine affords (−)-7α,19-*diacetoxykaur*-15-*ene* (VII), an oil which could not be crystallised, δ ($CDCl_3$, 60 MHz) 0·81 (s, 4α-Me), 1·09 (s, 10α-Me), 1·67 (d, *J* 1·5 Hz, 16-Me), 2·00 and 2·07 (3H each, s, 2 × AcO), 3·59 and 3·81 (2H, ABq, *J* 11·2 Hz, 4β-CH_2·OAc), 4·80br (7β-H), and 5·09br p.p.m. ($W_{\frac{1}{2}}$ 4·5 Hz, 15-H).

(−)-*Kaur*-15-*ene*-7β,19-*diol* (*Sideridiol*) (I).—Reduction of the hydroxy-acid (IV) with lithium aluminium hydride afforded sideridiol (I), m.p. 195—196° (from methanol–water), identical (m.p. and mixed m.p., t.l.c., i.r., and n.m.r.) with the natural product.[1] N.m.r. data for (I) and for its diacetyl-derivative (VIII) have already been reported.[1]

Methyl (−)-7-*Oxokauran*-19-*oate* (IXb).—This ester was prepared as previously described [1] (greater than 98% pure, g.l.c.), m.p. 82—83° (from ethanol–water), *m/e* 332 (50%), 317 (3), 300 (6), 272 (100), and 257 (10), $\nu_{max.}$ 1710 (CO) and 1735 (CO_2Me) cm^{-1}, $\lambda_{max.}$ (EtOH) 287 nm (ε 32), $\lambda_{max.}$ (n-heptane) 291 nm (ε 24), δ ($CDCl_3$, 60 MHz) 1·05 (d, *J* 6 Hz,

* After our manuscript had been submitted, a paper by R. C. Cambie and his co-workers (*Austral. J. Chem.*, 1971, **24**, 1237) referred to the configuration and conformation of some tricyclic 6-bromo-7-oxoditerpenoids. Our data and interpretations for the bromo-ester (Xb) are in agreement with the general discussion reported by Cambie.

[9] R. Beugelmans, R. H. Shapiro, L. J. Durham, D. H. Williams, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, 1964, **86**, 2832.

[10] A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *J. Amer. Chem. Soc.*, 1963, **85**, 2185.

16β-Me), 1·20 (s, 4α- .0α-Me), 2·15—2·0 (partially overlapped, 6β-H), 2·56 (q, 6α-H), 2·88 (t, $J_{15\alpha.15\beta} + J_{15\alpha.16\alpha}$ 26 Hz, 15α-H), and 3·64 p.p.m. (s, CO_2Me), δ ($CDCl_3$, 100 MHz) 2·0—2·15 (partially overlapped, 6β-H), 2·55 (quintet, 6α-H), and 2·83 p.p.m. (t, 15α-H), δ ($CDCl_3$, 220 MHz) 2·05 (1H, partially overlapped q, $J_{6\beta.5\beta}$ 2·5, $J_{6\beta.6\alpha}$ 15 Hz, 6β-H), 2·55 (1H, t, $J_{6\alpha.6\beta} + J_{6\alpha.5\beta}$ 28 Hz, 6α-H), and 2·89 p.p.m. (1H, t, 15α-H), $[\phi]_{308}^{27}$ +4300°, $[\phi]_{287}^{27}$ 0° (*c* 0·1 in ethanol), $\Delta\varepsilon_{291}^{27}$ +2·73 (*c* 0·19 in ethanol), $\Delta\varepsilon_{295}^{27}$ +1·91 (*c* 0·12 in n-heptane). The n.m.r. spectrum ($CDCl_3$, 60 MHz) of the [6,6-$^2H_2$]keto-ester [1] does not show signals at δ 2·56 (6α-H) and 2·15—2·0 p.m.r. (6β-H).

Hydrogenation of (−)-7-*Oxokaur*-15-*en*-19-*oic Acid* (IIa).—The unsaturated keto-acid [1] (IIa) (160 mg) in ethanol was hydrogenated over 10% Pd–C at atmospheric pressure and room temperature; hydrogen uptake ceased after 1 mol. equiv. had been absorbed. Usual work-up gave the saturated product, m.p. 171—173° (from ethanol–water) $\nu_{max.}$ 1730 and 1698 cm^{-1}. Treatment of the saturated keto-acid with ethereal diazomethane gave a product, which was purified on alumina (neutral, Merck, act. II, eluant cyclohexane–benzene 2 : 1), and had m.p. 68—70° (from cyclohexane). The product, before and after crystallisation, contained two components in the ratio *ca.* 4 : 1 (g.l.c.), separated by preparative g.l.c. The major portion was identical (m.p. and mixed m.p., i.r., and m.s.) with methyl (−)-7-oxokauran-19-oate (IXb); [1] the less abundant was an oil, *m/e* 332 (23%), 317 (2), 300 (4), 272 (49), and 257 (5·5), and was identified as *methyl* (−)-7-*oxo*-16α-*kauran*-19-*oate*.

Hydrogenation of Methyl (−)-7-*Oxokaur*-15-*en*-19-*oate* (IIb).—Hydrogenation, as before, of the unsaturated keto-ester [1] (IIb) gave a product, m.p. 68—70° (from cyclohexane), containing 80% of saturated keto-acid (IXb) and 20% of its 16α-epimer (g.l.c.).

Methyl (−)-6β-*Bromo*-7-*oxokauran*-19-*oate* (Xb).—Methyl (−)-7-oxokauran-19-oate [1] (IXb) (100 mg) was dissolved in acetic acid (5 ml) and treated with a solution of bromine (50 mg) in acetic acid (4 m). A drop of hydrobromic acid in acetic acid was added to the solution, which was left at room temperature for 5 days. After dilution with water, the ether extracts were washed with sodium thiosulphate, dried, and evaporated to give the *bromo-keto-ester* (pure by t.l.c.; eluant cyclohexane–ethyl acetate 3 : 1), m.p. 135° (from light petroleum) (Found: C, 61·6; H, 7·9. $C_{21}H_{31}BrO_3$ requires C, 61·3; H, 7·5%), *m/e* 412 (1%), 410 (1), 353 (2), 351 (2), 331 (63), 315 (8), 299 (11), and 271 (100), δ ($CDCl_3$, 60 MHz) 0·88 (s, 4α-Me), 1·36 (s, 10α-Me), 1·03 (d, *J* 6 Hz, 16β-Me), 2·70 (d, *J* 10·5 Hz, 5-H), 3·70 (s, CO_2Me), and 4·42 p.p.m. (1H, d, *J* 10·5 Hz, 6-H), $\lambda_{max.}$ (EtOH) 317 nm (ε 142), $\lambda_{max.}$ (n-heptane) 321nm (ε 139), $\nu_{max.}$ 1710 (CO) and 1730 (CO_2Me) cm^{-1}, $[\phi]_{343}^{27}$ +2070°, $[\phi]_{325}^{27}$ +1250°, $[\phi]_{306}^{27}$ +840°, $[\phi]_{288}^{27}$ 0°, $[\phi]_{272}^{27}$ −620° (*c* 0·24 in ethanol), $[\phi]_{348}^{27}$ +3000°, $[\phi]_{324}^{27}$ 0°, $[\phi]_{295}^{27}$ −1540° (*c* 0·23 in n-heptane), $\Delta\varepsilon_{320}^{27}$ +0·65 and $\Delta\varepsilon_{289}^{27}$ +0·81 (*c* 0·24 in ethanol), $\Delta\varepsilon_{325}^{27}$ +1·31 (*c* 0·23 in n-heptane).

(−)-6β-*Bromo*-7-*oxokauran*-19-*oic Acid* (Xa).—Bromination of the keto-acid (IXa) as described for its methyl ester gave the acid (Xa), m.p. 204—205° (from ethanol–water), $\nu_{max.}$ 1700—1725br cm^{-1}, *m/e* 398 (5%), 396 (5), 317 (100), 299 (47), and 271 (99), δ ($CDCl_3$, 60 MHz) 0·87 (s, 4α-Me), 1·04 (d, *J* 6 Hz, 16β-Me), 1·33 (s, 10α-Me), 2·75 (1H, d, *J* 10·5 Hz, 5-H), and 4·45 p.p.m. (1H, d, *J* 10·5 Hz, 6-H).

Dehydrobromination of Methyl (−)-6β-*Bromo*-7-*oxokauran*-19-*oate* (Xb) *to Methyl* (−)-7-*Oxokaur*-5-*en*-19-*oate* (XI) *and* (−)-7-*Oxokaur*-5-*en*-19(6)-*olide*.—(*a*) Methyl (−)-6β-bromo-7-oxokauran-19-oate (Xb) (90 mg) was dissolved in dimethylformamide (120 ml) and to the solution lithium chloride (105 mg) and lithium carbonate (375 mg) were added. The mixture was warmed at 100° for 36 h, then diluted with water and extracted with ether. Work-up gave a residue containing (t.l.c.; eluant cyclohexane–ethyl acetate 3 : 1) two main products, R_F 0·75 and 0·55. The more polar product, the *lactone* (XII) was isolated by crystallisation from cyclohexane and then from ethyl acetate and the less polar ester (XI) by p.l.c. of the residue from the mother liquors of the crystallisation of the lactone (XII) (30 mg), m.p. 252—253° (Found: C, 76·7; H, 8·5. $C_{20}H_{26}O_3$ requires C, 76·4; H, 8·3%), $\lambda_{max.}$ (EtOH) 261 nm (ε 5500), $\nu_{max.}$ 1790 and 1675 cm^{-1}, *m/e* 314 (35%), 299 (5), 286 (15), 271 (29), 258 (17), 243 (46), and 242 (100), δ ($CDCl_3$, 60 MHz) 1·08 (d, *J* 6 Hz, 16β-Me), 1·43 and 1·52 (s, 4α- and 10α-Me), and 2·93 p.p.m. (1H, t, $J_{15\alpha.15\beta} + J_{15\alpha.16\alpha}$ 24 Hz, 15α-H). The αβ-unsaturated ketone (XI) (5 mg) has m.p. 100—102° (from cyclohexane), $\lambda_{max.}$ (EtOH) 238 nm (ε 7000), *m/e* 330 (100%), 315 (85), and 271 (33), δ ($CDCl_3$, 60 MHz) 1·06 (3H, d, *J* 6 Hz. 16β-Me), 1·40 and 1·49 (3H each, s, 4α- and 10α-Me), 3·70 (s, CO_2Me), and 5·66 p.p.m. (1H, s, 6-H).

(*b*) A solution of bromo-compound (Xb) (50 mg) in collidine (3 ml) was heated under reflux for 6 h: usual treatment gave a mixture (t.l.c.) of the products with R_F 0·75 and 0·55, that were isolated and characterised as (XI) and (XII), respectively.

(*c*) A solution of bromo-acid (Xa) (50 mg) in methanolic potassium hydroxide (10%; 5 ml) was heated under reflux for 3 h. The solvent was evaporated, the residue was taken up in dilute hydroc acid and extracted with ether. The mixture was tre ith diazomethane and separated, as described above, into the ester (XI) and the lactone (XII).

(−)-7-*Oxokaur*-5-*en*-19(6)-*olide* (XII).—A solution of (Xb) (60 mg) in dimethyl sulphoxide (3 ml) and acetonitrile (3 ml) was heated for 10 days at 115°. Dilution with water and extraction with ether gave a crystalline residue of the lactone (XII) (45 mg), m.p. 252—253° (from ethyl acetate), identical with the product described above.

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