Neighbouring Group Participation in the Reduction of the Diterpenoid Fujenal

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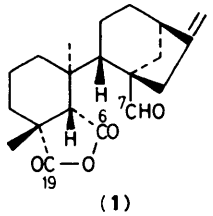
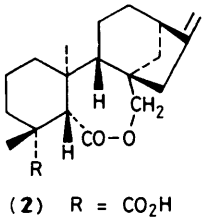
Hydride reduction of the aldehyde-anhydride, fujenal, proceeds first at the C-7 aldehyde. This generates a C-7 alkoxide which then participates in the reactions of the C-6 carbonyl groups. C-6 ⟶ C-7 and C-6 ⟶ C-19 Lactones are formed. The structure of a C-6 ⟶ C-7 lactone was confirmed by *X*-ray analysis.

The diterpenoid aldehyde-anhydride fujenal (**1**) may be obtained[1] from the fungus, *Gibberella fujikuroi*. Since it is relatively accessible and it possesses functionality on ring B of the molecule,[2] it has formed the starting material for a number of transformations.[3–6] The molecule contains three potentially distinguishable carbonyl groups with differing stereoelectronic environments. In the course of preparing inhibitors of gibberellin plant hormone biosynthesis[7–10] we have examined the reduction of fujenal (**1**) by various hydride reagents. These reactions have revealed not only the effect of the conformation of the molecule[11] on its reactivity but also a number of instances of neighbouring group participation involving C-7.

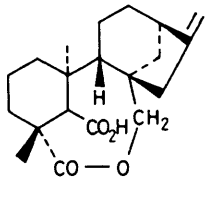
Reduction of fujenal (**1**) with the bulky lithium tri-t-butoxyaluminium hydride gave a carboxylic acid, $C_{20}H_{28}O_4$. This product ($\nu_{max.}$ 3 000br, 1 730, and 1 720 cm^{-1}) had lost not only the aldehyde CH absorption in its i.r. spectrum but also the anhydride absorption. The ^1H n.m.r. spectrum contained an AB doublet, δ 3.92 and 4.59, *J* 12.6 Hz, attributable to 7-H and a singlet, δ 2.96, which was assigned to 5-H.



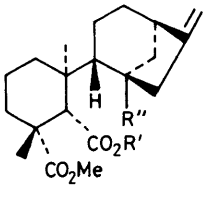
(**1**)



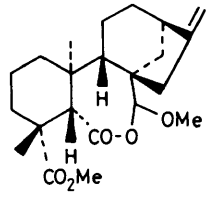
(**2**) R = CO_2H
(**4**) R = CO_2Me



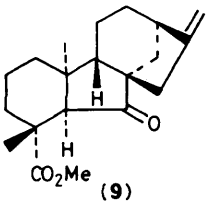
(**3**)



(**5**) R′ = H, R″ = CH_2OH
(**7**) R′ = H, R″ = CHO
(**8**) R′ = H, R″ = CO_2H
(**10**) R′ = Me, R″ = CHO
(**11**) R′ = Me, R″ = CH_2OH



(**6**)



(**9**)

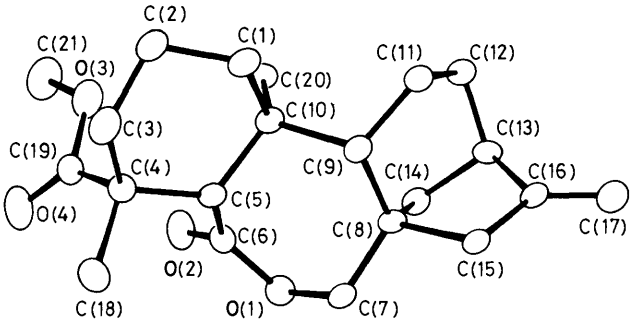


Figure. Crystal structure of compound (**4**)

Methylation with ethereal diazomethane gave a methyl ester (**4**) (δ 3.69, OMe). This methyl ester was unstable in solution slowly affording, as revealed by t.l.c., a mixture containing the open form (**5**). The acid was formulated as (**2**) rather than (**3**) in the light of an *X*-ray structure and chemical inter-relationships.

The structure of the lactone (**2**) was established by *X*-ray analysis of the methyl ester (**4**) (see Figure). This not only confirmed the termini of the lactone, but also confirmed the stereochemistry at C-5. Recent work has shown[12] that epimerisation at C-5 occurs rather easily in the kaurenolides.

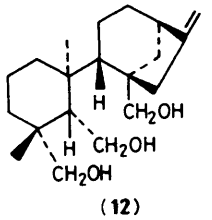
Although, as anticipated, the aldehyde has been reduced first, cleavage of the anhydride has also taken place. However for plant growth regulatory activity[7] we were interested in maintaining a free hydroxy group at C-7. The participation of the incipient alkoxides at C-7 in the cleavage of the anhydride may be overcome by its prior hydrolysis. Although acid-catalysed methanolysis of fujenal (**1**) affords[2] pseudo-esters [*e.g.* (**6**)], treatment with sodium methoxide in methanol affords the 19-methyl ester (**7**). The location of the methoxy group at C-19 rather than at C-6 followed from the conversion of the ester *via* the corresponding dicarboxylic acid (**8**) into the cyclopentanone (**9**).[5] Methylation of the methyl ester (**7**) with diazomethane gave the normal dimethyl ester (**10**) [δ 3.75 and 3.79 (each 3 H, OMe), 9.79 (1 H, s, 7-H, C*H*O]. Reduction of the aldehyde (**10**) with sodium borohydride gave the C-7 mono-ol (**11**) [δ 3.81 and 3.86 (each 3 H, OMe), 3.31 and 4.16 (each 1 H, d, *J* 11.5 Hz, 7-H)]. Reduction under more vigorous conditions with lithium aluminium hydride in tetrahydrofuran gave the triol, *ent*-6,7,19-trihydroxy-6,7-secokaur-16-ene (**12**) [δ 3.42 and 3.95 (each 1 H, d, *J* 10.8 Hz), 3.47 and 3.86 (each 1 H, d, *J* 11.5 Hz, 7-H and 19-H), and 3.80 (2 H overlapped with a d, *J* 7.4 Hz, 6-H)]. This n.m.r. spectrum suggests that the primary alcohols are subject to hindered rotation.

Reduction of the methyl ester (**7**) with sodium borohydride gave not only the ε-lactone (**4**) but also the corresponding 19-carboxylic acid (**2**) and the hydroxy acid (**5**). The axial 19-methyl ester of the diterpenoids is normally very difficult to

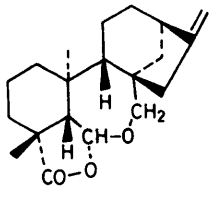
hydrolyse under basic conditions.[13,14] The formation of the free 19-carboxylic acid, which was observed on a number of occasions was, therefore, surprising. The formation of (**2**) may be accounted for by the neighbouring group participation of the carboxylate alkoxide anions. This would account for the fact that the hydrolysis does not occur to any detectable extent on reduction of the dimethyl ester (**10**).

Reduction of fujenal (**1**) in methanol–tetrahydrofuran with sodium borohydride afforded a chromatographically separable mixture of three compounds. The first minor product to be eluted from the column was the γ-lactol ether (**13**) ($\nu_{max.}$ 1 780 cm^{-1}, γ-lactone). The hemiacetal proton resonance (δ 5.86, 6-H) appeared as a doublet, *J* 4 Hz, coupled to 5-H (δ 1.98) whilst the 7-H signals formed an AB quartet (δ 3.48 and 3.66, *J* 12 Hz). The magnitude of $J_{5,6}$ suggests the C-6 stereochemistry shown in (**13**). The second product was the known γ-lactone (**14**)[3] whilst the third product was the isomeric ε-lactone (**16**). The ratio of these two major products varied with the ratio of methanol–tetrahydrofuran used for the reduction. Oxidation of the ε-lactone (**16**) with 2.67M chromium trioxide gave the acid (**2**) identical with the sample obtained by the lithium tri-t-butoxyaluminium hydride reduction of fujenal.

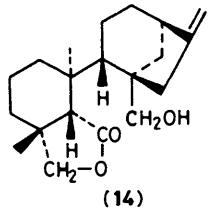
Throughout these reactions there is a surprising resistance of the C-6 carbonyl group to reduction. Two features may account for this. The *X*-ray crystallographic structure of fujenal (**1**) has shown[11] that it exists in a conformer in which rotation has occurred about the C(9)–C(10) bond. Nuclear Overhauser enhancement (n.O.e.) studies suggest[11] that this conformation also exists in solution. In this situation whilst the C-20 methyl group hinders the α-face of C-6 to attack, the β-face is hindered by the C-7 group. In the course of the hydride reductions the C-7 oxygen may bear a negative charge thus hindering the β-face trajectory for an incoming nucleophile at C-6. Indeed the alkoxide may participate in *ortho*-lactol formation (**15**) at C-6 thus protecting the C-6 carbonyl group from further nucleophilic attack. This leaves the C-19 carbonyl group exposed for reduction. The lactol (**15**) may be formed during the equilibration of the γ-lactone (**14**) and the ε-lactone (**16**). An interesting facet of this is found in the lithium aluminium hydride reduction of the ε-lactone (**4**) from which the major product is the ether (**13**). In this case the C-6 carbonyl is not protected by *ortho*-lactol formation and as the less-hindered of the two carbonyl groups, it is reduced first with attack from the β-face. The C-6α alkoxide which is formed can then facilitate the hydrolysis of the C-19 ester.



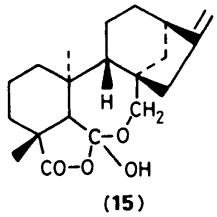
(**12**)



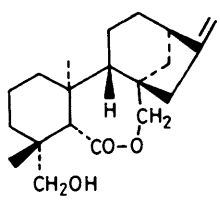
(**13**)



(**14**)



(**15**)



(**16**)

Experimental

Light petroleum refers to the fraction b.p. 60—80 °C, ether refers to diethyl ether. Extracts were dried over sodium sulphate; m.p.s were determined on a Kofler block; ^1H n.m.r. spectra were determined on a Bruker WH360 spectrometer for solutions in $CDCl_3$; i.r. spectra were recorded as Nujol mulls.

Reduction of Fujenal (**1**) *with Lithium Tri-t-butoxyaluminium Hydride.*—Lithium aluminium hydride (0.5 g) in diethyl ether (80 ml) was treated with t-butyl alcohol (10 ml) for 30 min. The solid was allowed to settle, the ether was decanted, and diglyme (100 ml) was added. Fujenal (5 g) in diglyme (50 ml) was added and the mixture was stirred at room temperature for 15 min. Water was added and the mixture concentrated under reduced pressure. More water was then added and the solution was acidified with concentrated hydrochloric acid and extracted with ethyl acetate. The extract was washed with water, dried, and evaporated. The resultant gum was chromatographed on silica to afford fujenal (346 mg) identified by its i.r. and n.m.r. spectra. Further elution gave ent-7-*hydroxy*-6,7-*secokaur*-16-*en*-6,19-*dioic acid* 6,7-*lactone* (**2**) which crystallized from methanol as needles (427 mg), m.p. 164—165 °C (Found: C, 72.0; H, 8.45. $C_{20}H_{28}O_4$ requires C, 72.3; H, 8.4%); $\nu_{max.}$ 3 000br, 1 730, 1 720, 1 660, and 880 cm^{-1}; δ 1.19 (3 H, s, 20-H), 1.29 (3 H, s, 18-H), 2.96 (1 H, s, 5-H), 3.92 and 4.59 (each 1 H, s, *J* 12.6 Hz, 7-H), and 4.81 and 4.90 (each 1 H, br s, 17-H). The *methyl ester* (**4**) prepared with diazomethane, crystallized from methanol as needles, m.p. 157—158 °C (Found: C, 72.6; H, 9.1. $C_{21}H_{30}O_4$ requires C, 72.8; H, 8.7%); $\nu_{max.}$ 1 720, 1 710, 1 660, and 880 cm^{-1}; δ 1.23 (3 H, s, 20-H), 1.34 (3 H, s, 18-H), 2.76 (1 H, s, 5-H), 3.69 (3 H, s, OMe), 3.76 and 4.48 (each 1 H, d, *J* 12.6 Hz, 7-H), 4.79 and 4.88 (each 1 H, br s, 17-H).

Dimethyl ent-7-*Oxo*-6,7-*secokaur*-16-*ene*-6,19-*dioate* (**10**).—The 19-methyl ester (**7**), prepared as described previously[5] was treated in methanol with an excess of ethereal diazomethane to afford the 6,19-*dimethyl ester* (**10**) which crystallized from ethyl acetate–light petroleum as needles, m.p. 154—155 °C (Found: C, 70.1; H, 8.6. $C_{22}H_{32}O_5$ requires C, 70.2; H, 8.6%); $\nu_{max.}$ 1 740, 1 720, 1 710, 1 655, and 890 cm^{-1}; δ 1.12 (3 H, s, 20-H), 1.36 (3 H, s, 18-H), 3.75 and 3.79 (each 3 H, s, OMe), 4.72 and 4.87 (each 1 H, br s, 17-H), and 9.79 (1 H, s, 7-H).

Reduction of the Dimethyl Ester (**10**).—(a) *With sodium borohydride.* The dimethyl ester (250 mg) in tetrahydrofuran (50 ml) was treated with sodium borohydride (900 mg) at 0 °C and stirred overnight. 30% Aqueous tetrahydrofuran (20 ml) was added and the solution was then concentrated under reduced pressure. The residue was acidified with dilute hydrochloric acid and the product was recovered in ethyl acetate to afford *dimethyl* ent-7-*hydroxy*-6,7-*secokaur*-16-*ene*-6,19-*dioate* (**11**) (193 mg) which crystallized as needles, m.p. 153—154 °C (Found: C, 69.8; H, 8.7. $C_{22}H_{34}O_5$ requires C, 69.8; H, 9.05%); $\nu_{max.}$ 3 440, 1 720, 1 710, 1 660, and 880 cm^{-1}; δ 1.15 (3 H, s, 20-H), 1.38 (3 H, s, 18-H), 3.81 and 3.86 (each 3 H, s, OMe),

3.31 and 4.16 (each 1 H, d, *J* 11.5 Hz, 7-H), and 4.69 and 4.80 (each 1 H, br, s, 17-H).

(b) *With lithium aluminium hydride.* The dimethyl ester (200 mg) in tetrahydrofuran (50 ml) was treated with lithium aluminium hydride (800 mg) with ice cooling. The mixture was then heated under reflux overnight after which it was treated with ethyl acetate and water. The solution was concentrated, diluted with water, acidified with hydrochloric acid, and extracted with ethyl acetate. Work-up of the latter afforded ent-6,7-*secokaur*-16-*ene*-6,7,19-*triol* (**12**) (75 mg) which crystallized from ethyl acetate as needles, m.p. 163—164 °C (Found: C, 74.3; H, 10.1. $C_{20}H_{34}O_3$ requires C, 74.5; H, 10.6%); $\nu_{max.}$ 3 500, 1 660, and 880 cm^{-1}; δ[$(CD_3)_2SO$] 1.10 (3 H, s, 20-H), 1.32 (3 H, 18-H), 2.13 (1 H, d, *J* 7.4 Hz, 5-H), 3.42 and 3.95 (each 1 H, d, *J* 10.8 Hz), 3.47 and 3.86 (each 1 H, d, *J* 11.5 Hz, 7-H and 19-H), 3.80 (2 H, s and overlapped d, *J* 7.4 Hz, 6-H), and 4.74 and 4.87 (each 1 H, br s, 17-H).

Reduction of ent-19-*Methoxycarbonyl*-7-*oxo*-6,7-*secokaur*-16-*en*-6-*oic Acid with Sodium Borohydride.*—The methyl ester (**7**) (500 mg) in methanol–tetrahydrofuran (1 : 1) (50 ml) was treated with sodium borohydride (1.21 g) for 3 h. The mixture was then treated with aqueous tetrahydrofuran (20 ml) and acidified with hydrochloric acid. The solution was concentrated under reduced pressure, diluted with water, and extracted with ethyl acetate. Work-up and chromatography of the latter on silica gave with 20% ethyl acetate–light petroleum as eluant *ent*-7-hydroxy-19-methoxycarbonyl-6,7-secokaur-16-en-6-oic acid 6,7-lactone (**4**) (102 mg) identical (i.r. and n.m.r.) to the material described above. Elution with 30% ethyl acetate–light petroleum gave ent-7-*hydroxy*-19-*methoxycarbonyl*-6,7-*seco-kaur*-16-*en*-6-*oic acid* (**5**) (84 mg), m.p. 244—246 °C (Found: C, 69.4; H, 8.9. $C_{21}H_{32}O_5$ requires C, 69.2; H, 8.8%); $\nu_{max.}$ 3 450, 3 300br, 1 740, 1 720, 1 660, and 880 cm^{-1}; δ 1.32 (3 H, s, 20-H), 1.43 (3 H, s, 18-H), 3.66 (3 H, s, OMe), 3.35 and 4.30 (each 1 H, d, *J* 12 Hz), and 4.79 (2 H, br d, 17-H).

Reduction of Fujenal (**1**) *with Sodium Borohydride.*—Fujenal (5 g) in dry tetrahydrofuran (20 ml) and dry methanol (20 ml) was cooled in ice and treated with sodium borohydride (1.49 g) for 30 min. 30% Aqueous tetrahydrofuran (20 ml) was added and the solvents were evaporated under reduced pressure. The residue was acidified with dilute hydrochloric acid and the products were recovered in ethyl acetate and chromatographed on silica. Elution with 20% ethyl acetate–light petroleum gave ent-6,7-*epoxy*-6-*hydroxy*-6,7-*secokaur*-16-*en*-19-*oic acid* 6,19-*lactone* (**13**) (93 mg) as needles, m.p. 256—258 °C (sublimes) (Found: C, 75.8; H, 8.9. $C_{20}H_{28}O_3$ requires C, 75.95; H, 8.9%); $\nu_{max.}$ 1 780, 1 660, and 890 cm^{-1}; δ 1.28 (6 H, s, 18-H and 20-H), 1.98 (1 H, d, *J* 4 Hz, 5-H), 3.48 and 3.66 (each 1 H, d, *J* 12 Hz, 7-H), 4.78 and 4.85 (each 1 H, br s, 17-H), 5.86 (1 H, d, *J* Hz, 6-H). Irradiation at δ 5.86 collapsed the signal at δ 1.98 to a singlet. Elution with 30% ethyl acetate–light petroleum gave *ent*-7,19-dihydroxy-6,7-secokaur-16-en-19-oic acid 6,19-lactone (**14**) (1.23 g), m.p. 146—148 °C (lit.,[3] 149—151 °C); δ 1.15 (3 H, s, 20-H), 1.32 (3 H, s, 18-H), 2.21 (1 H, s, 5-H), 3.46 and 4.42 (2 H, AB q, *J* 11.5 Hz, 7-H), 3.76 and 4.08 (each 1 H, d, *J* 9 Hz, 19-H), and 4.75 and 4.82 (each 1 H, br s, 17-H). Elution with methanol gave ent-7,19-*dihydroxy*-6,7-*secokaur*-16-*en*-6-*oic acid* 6,7-*lactone* (**16**) (1.95 g) which crystallized from methanol as

Table 1. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x	*y*	*z*
O(1)	−365(4)	3 706(3)	2 312(1)
O(2)	513(5)	4 590(2)	3 164(1)
O(3)	2 758(5)	3 848(2)	4 230(1)
O(4)	9(6)	3 993(3)	4 546(2)
C(1)	3 827(6)	1 246(4)	3 204(2)
C(2)	3 692(6)	1 343(4)	3 913(2)
C(3)	1 783(7)	1 379(4)	4 114(2)
C(4)	768(6)	2 416(4)	3 828(2)
C(5)	1 146(5)	2 518(3)	3 114(2)
C(6)	425(6)	3 678(4)	2 873(2)
C(7)	−252(6)	2 691(4)	1 901(2)
C(8)	1 566(4)	2 482(3)	1 672(2)
C(9)	2 826(5)	1 846(3)	2 141(2)
C(10)	3 026(5)	2 307(3)	2 837(2)
C(11)	4 582(5)	1 635(3)	1 816(2)
C(12)	5 251(5)	2 619(4)	1 383(2)
C(13)	3 795(5)	3 100(4)	960(2)
C(14)	2 371(6)	3 605(3)	1 385(2)
C(15)	1 444(5)	1 671(4)	1 082(2)
C(16)	2 862(6)	2 090(3)	641(2)
C(17)	3 178(7)	1 662(4)	77(2)
C(18)	−1 201(7)	2 138(5)	3 892(2)
C(19)	1 083(6)	3 514(4)	4 228(2)
C(20)	4 192(5)	3 392(4)	2 892(2)
C(21)	3 196(9)	4 884(4)	4 597(2)

Table 2. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Bonds

O(1)–C(6)	1.346(5)	O(1)–C(7)	1.447(5)
O(2)–C(6)	1.205(5)	O(3)–C(19)	1.339(6)
O(3)–C(21)	1.447(6)	O(4)–C(19)	1.198(6)
C(1)–C(2)	1.526(6)	C(1)–C(10)	1.558(5)
C(2)–C(3)	1.527(7)	C(3)–C(4)	1.533(6)
C(4)–C(5)	1.559(5)	C(4)–C(18)	1.549(7)
C(4)–C(19)	1.525(6)	C(5)–C(6)	1.512(6)
C(5)–C(10)	1.578(5)	C(7)–C(8)	1.497(6)
C(8)–C(9)	1.568(5)	C(8)–C(14)	1.538(5)
C(8)–C(15)	1.563(5)	C(9)–C(10)	1.585(5)
C(9)–C(11)	1.535(6)	C(10)–C(20)	1.522(5)
C(11)–C(12)	1.535(6)	C(12)–C(13)	1.537(6)
C(13)–C(14)	1.533(6)	C(13)–C(16)	1.509(6)
C(15)–C(16)	1.516(6)	C(16)–C(17)	1.322(6)

Angles

C(6)–O(1)–C(7)	119.8(3)	C(19)–O(3)–C(21)	116.9(4)
C(2)–C(1)–C(10)	114.8(3)	C(1)–C(2)–C(3)	110.3(4)
C(2)–C(3)–C(4)	113.3(4)	C(3)–C(4)–C(5)	110.6(3)
C(3)–C(4)–C(18)	107.8(4)	C(3)–C(4)–C(19)	108.5(3)
C(5)–C(4)–C(18)	106.4(3)	C(5)–C(4)–C(19)	117.4(3)
C(18)–C(4)–C(19)	105.7(4)	C(4)–C(5)–C(6)	109.3(3)
C(4)–C(5)–C(10)	121.8(3)	C(6)–C(5)–C(10)	109.7(3)
O(1)–C(6)–O(2)	117.7(4)	O(1)–C(6)–C(5)	119.3(3)
O(2)–C(6)–C(5)	123.0(4)	O(1)–C(7)–C(8)	112.3(4)
C(7)–C(8)–C(9)	116.0(3)	C(7)–C(8)–C(14)	112.0(3)
C(7)–C(8)–C(15)	107.5(3)	C(9)–C(8)–C(14)	112.7(3)
C(9)–C(8)–C(15)	106.6(3)	C(14)–C(8)–C(15)	100.6(3)
C(8)–C(9)–C(10)	120.7(3)	C(8)–C(9)–C(11)	108.8(3)
C(10)–C(9)–C(11)	113.1(3)	C(1)–C(10)–C(5)	106.7(3)
C(1)–C(10)–C(9)	105.0(3)	C(1)–C(10)–C(20)	110.3(3)
C(5)–C(10)–C(9)	108.3(3)	C(5)–C(10)–C(20)	112.7(3)
C(9)–C(10)–C(20)	113.2(3)	C(9)–C(11)–C(12)	117.0(3)
C(11)–C(12)–C(13)	111.6(3)	C(12)–C(13)–C(14)	107.4(3)
C(12)–C(13)–C(16)	110.1(3)	C(14)–C(13)–C(16)	102.2(3)
C(8)–C(14)–C(13)	102.5(3)	C(8)–C(15)–C(16)	106.1(3)
C(13)–C(16)–C(15)	107.2(3)	C(13)–C(16)–C(17)	127.0(4)
C(15)–C(16)–C(17)	125.8(4)	O(3)–C(19)–O(4)	122.0(4)
O(3)–C(19)–C(4)	112.5(4)	O(4)–C(19)–C(4)	125.2(4)

rhombs, m.p. 210—211.5 °C (Found: C, 71.55; H, 9.10. $C_{20}H_{30}O_3 \cdot H_2O$ requires C, 71.4; H, 9.5%); $\nu_{max.}$ 3 450, 3 280, 1 725, 1 658, and 880 cm^{-1}; δ([$^2H_5$]-pyridine) 1.45 (6 H, s, 18-H and 20-H), 3.35, 3.81 (2 H) and 4.27 (d, *J* 11 Hz) (7H and 19-H), 4.86 and 4.93 (each 1 H, br s, 17-H).

Reduction of the ent-7-*Hydroxy*-19-*methoxycarbonyl*-6,7-*secokaur*-16-*en*-6-*oic Acid* 6,7-*Lactone* (**4**) *with Lithium Aluminium Hydride*.—The ester (**4**) (50 mg) in dry tetrahydrofuran (25 ml) was heated under reflux with lithium aluminium hydride (70 mg) for 8 h. The solution was acidified with dilute hydrochloric acid and the product was recovered in ethyl acetate. Work-up of the latter and chromatography of the residue on silica gave *ent*-6,7-epoxy-6-hydroxy-6,7-secokaur-16-en-19-oic acid 6,19-lactone (**13**) (19 mg) which was identified by its i.r. and n.m.r. spectra (*vide supra*) and starting material (21 mg).

Oxidation of ent-7,19-*Dihydroxy*-6,7-*secokaur*-16-*en*-6-*oic Acid* 6,7-*Lactone*.—The lactone (**16**) (200 mg) in acetone (100 ml) was cautiously treated with the 2.67M chromium trioxide reagent (2 ml) over 2.5 h. The mixture was treated with methanol, concentrated, and extracted with ethyl acetate. Evaporation of the extract and crystallization of the residue afforded *ent*-7-hydroxy-6,7-secokaur-16-en-6,19-dioic acid 6,7-lactone (127 mg) as needles, m.p. 163—164.5 °C identified by its i.r. and n.m.r. spectra.

Crystal Structure Determination: Crystal Data.—$C_{21}H_{30}O_4$, M = 346.5, orthorhombic, a = 7.673(2), b = 11.289(5), c = 21.400(7) Å, U = 1 853.5 Å^3, Z = 4, D_c = 1.24 g cm^{-3}, monochromated Mo-K_α radiation, λ = 0.710 69 Å, μ = 0.8 cm^{-1}.

A crystal *ca.* 0.8 × 0.4 × 0.2 mm was mounted on an Enraf Nonius CAD4 diffractometer. Intensities for unique data with $2 < \theta < 25°$ were measured by an $\omega - 2\theta$ scan with a maximum scan time of 60 s. No correction was made for absorption. Out of 2 004 reflections measured, 1 379 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$.

The structure was solved by direct methods using 'MULTAN' and refined by full-matrix least-squares with anisotropic temperature factors. Hydrogen atoms were included at calculated positions (C–H 1.08 Å) and held fixed with a common B_{iso} of 6.0 Å^2. Refinement converged at R = 0.051, R' = 0.061 with a weighting scheme of $w = 1/\sigma^2(F)$. All calculations were done on a PDP11/34 computer using the Enraf Nonius SDP-Plus program package. Fractional atomic co-ordinates, intramolecular distances, and angles are given in Tables 1 and 2. Hydrogen atom co-ordinates, torsion angles, anisotropic temperature factors and structure factor tables are available on request from the Cambride Crystallographic Data Centre.*

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