Two New Diterpenoids from *Teucrium fruticans*

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Fruticolone (1) and isofruticolone (2), both isolated from *Teucrium fruticans*, have been shown by a combination of spectroscopic and *X*-ray methods (*R* 0.070; 1 620 observed diffractometer reflections) to be *ent*-19-acetoxy-4β,18:15,16-diepoxy-1β-hydroxycleroda-13(16),14-dien-6-one and *ent*-19-acetoxy-4β,18:15,16-diepoxy-6α-hydroxycleroda-13(16),14-dien-1-one, respectively.

A NUMBER of Teucrium species (Labiatae) have been used as medicinal herbs, particularly in the Mediterranean regions.[1] Many diterpenoids have been isolated from the Labiatae including a group of clerodane lactones from *Teucrium chamaedrys*[2] and *T. viscidum*.[3] In continuing our work[4] on diterpenoids from the Labiatae, we have examined *T. fruticans*. Extraction of the leaves with acetone afforded, after careful purification, two isomeric diterpenoids, $C_{22}H_{30}O_6$, fruticolone (1) and isofruticolone (2).

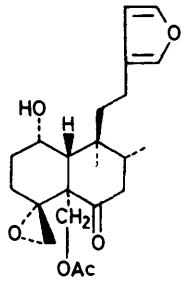
Both fruticolone and isofruticolone had i.r. absorption and ^{1}H n.m.r. signals indicative of $-\overset{|}{C}H(OH)$, $-\overset{|}{C}-CH_2OAc$, $>\overset{O}{\diagdown\diagup}C-CH_2$, a saturated ketone, a β-substituted furan ring, a $-\overset{|}{C}H-CH_3$, and a $-\overset{|}{C}-CH_3$ group. The multiplicity of the signals in the single-frequency off-resonance ^{13}C n.m.r. spectra (see Table 1) showed that the remaining carbon atoms were disposed as five methylenes and another methine. In view of the analytical data, the compounds were considered to be bicarbocyclic diterpenoids.[5] Since the clerodane skeleton can accommodate a furan ring and both a $>\overset{O}{\diagdown\diagup}C-CH_2$ and a secondary methyl group, whilst the labdane skeleton cannot, the former was adopted as a working basis for the structure. Further evidence for the presence of an exocyclic epoxide was obtained by reduction of fruticolone with lithium aluminium hydride. The product, which was characterized by the formation of a diacetate (4) and a triacetate (5), contained ^{1}H and ^{13}C n.m.r. signals from an additional tertiary methyl group and a tertiary alcohol. On treatment with hydrogen chloride fruticolone diketone (3) also gave an unstable chlorohydrin.

Spin-decoupling studies on fruticolone revealed the coupling of the secondary methyl group (δ 0.92, *J* 7 Hz) to a proton (δ 1.75). Irradiation at the epoxide signal (δ 3.43, *J* 2 and 4.5 Hz) led to the collapse of the other epoxide doublet (δ 2.25, *J* 4.5 Hz). The C*H*·OH (δ 3.43, m, $W_{\frac{1}{2}}$ 7 Hz) signal was shown to be coupled to signals at δ 1.75 within the methylene envelope. The other significant features of the spectrum were the AB $-CH_2OAc$ quartet (δ 4.92 and 5.40, *J* 15 Hz) and a triplet (δ 2.75, *J* 14 Hz) which was assigned to the 7-H. This was superimposed on a multiplet (δ 2.55) which showed long-range coupling (2 Hz) to the lower of the epoxide signals. Although tentative clerodane structures were assigned by examination of the n.m.r. spectra, the full structure was determined by *X*-ray analysis.

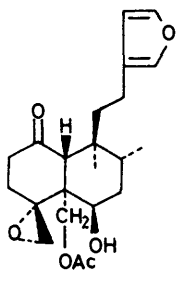
Satisfactory *X*-ray data could not be obtained on fruticolone as it decomposed on *X*-ray irradiation. However the triacetate (5) obtained by acetylation of

[1] 'A Dictionary of Plants Used by Man,' G. Usher, Constable, London, 1974, p. 572.
[2] D. P. Popa and A. M. Reinbold, *Khim. prirod. Soedinenii*, 1974, pp. 321, 589.
[3] I. Uchida, T. Fujita, and E. Fujita, *Tetrahedron*, 1975, **31**, 841.
[4] G. Savona, F. Piozzi, J. R. Hanson, and M. Siverns, *J.C.S. Perkin I*, 1976, 1607; 1977, 322, 497.
[5] J. R. Hanson, *Progr. Phytochemistry*, 1972, **3**, 231.

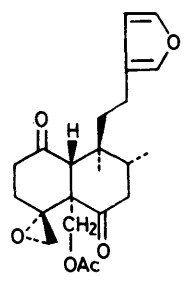
the lithium aluminium hydride reduction product of fruticolone, was crystalline and sufficiently stable. All



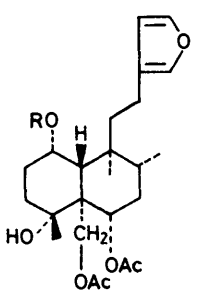
(1)



(2)



(3)



(4) R = H
(5) R = Ac

TABLE 1

^{13}C N.m.r. signals *

Atom	Compound (1)	(2)	(3)	(4)	(5)
1	66.7	210.9	206.9	65.5	68.1
2	38.5	37.0	37.9	38.7	38.8
3	34.7 †	35.9 †	36.9 †	32.8 †	32.5 †
4	61.8	60.5	58.4	75.8	76.6
5	55.2	47.1	56.8	48.9	48.6
6	207.0	69.3	205.9	77.8	77.0
7	45.1	36.9	44.7	32.8	32.8
8	38.5	28.8	39.4	35.9	35.9
9	39.9	37.7	38.2	39.7	39.7
10	52.8	48.8	57.5	47.7	49.6
11	28.6 †	30.7 †	30.3 †	32.3 †	29.1 †
12	18.1	19.0	18.8	18.3	18.2
13	124.0	125.1	124.3	124.6	124.3
14	110.8	111.1	110.8	110.8	110.8
15	138.5	138.6	138.6	138.5	138.6
16	143.0	142.7	143.0	142.9	143.0
17	15.5	14.4	15.0	15.0	15.0
18	49.3	50.4	52.4	24.9	24.1
19	64.3	63.9	62.9	63.5	63.0
20	19.2	16.7	17.3	19.6	19.5
OAc	21.0	20.3	20.3	21.4	21.4
	171.2	170.4	170.0	21.7	21.7
				169.6	21.8
				169.6	169.7
					169.7
					170.3

* In deuteriochloroform; p.p.m. from tetramethylsilane.
† These assignments may be interchanged.

the bond lengths and angles (Tables 2 and 3) were close to those expected for the formulation (5). The *trans*-decalin framework (Figure) possessed the all-chair conformation. Steric repulsion between the axial sub-

TABLE 2

Final atom positions (× 10^4), with estimated standard deviations in parentheses

	x	*y*	*z*
C(1)	3 559(6)	−0 168(7)	8 177(6)
C(2)	3 520(6)	−0 466(7)	9 390(5)
C(3)	2 456(6)	0 258(8)	9 732(6)
C(4)	2 575(6)	1 792(8)	9 647(5)
C(5)	2 536(5)	2 211(6)	8 372(5)
C(6)	2.946(5)	3 695(7)	8 315(6)
C(7)	3 160(6)	4 148(7)	7 199(6)
C(8)	4 246(6)	3 289(8)	6 912(6)
C(9)	3 905(6)	1 797(7)	6 811(5)
C(10)	3 601(5)	1 375(7)	7 973(5)
C(11)	5 052(6)	0 981(8)	6 648(5)
C(12)	6 260(6)	1 090(8)	7 530(6)
C(13)	7 320(6)	0 437(8)	7 134(5)
C(14)	7 793(6)	0 808(9)	6 171(6)
C(15)	8 690(6)	−0 031(10)	6 116(7)
C(16)	8 044(7)	−0 572(9)	7 598(7)
C(17)	4 620(9)	3 925(10)	5 853(8)
C(18)	3 717(6)	2 307(8)	10 517(5)
C(19)	1 263(6)	1 863(8)	7 596(6)
C(20)	2 888(6)	1 488(9)	5 728(5)
C(21)	2 604(7)	−1 896(7)	6 901(7)
C(22)	1 373(7)	−2 524(8)	6 363(7)
C(23)	−0 303(6)	3 575(8)	7 066(7)
C(24)	−1 293(8)	4 309(13)	7 394(11)
C(25)	2 363(6)	5 608(7)	9 269(6)
C(26)	1 285(7)	6 372(9)	9 513(8)
O(1)	8 913(5)	−0 875(7)	6 981(5)
O(2)	1 531(4)	2 345(6)	10 032(4)
O(3)	2 443(4)	−0 763(5)	7 452(4)
O(4)	1 971(4)	4 547(4)	8 622(4)
O(5)	0 272(4)	2 658(6)	7 824(4)
O(6)	3 577(5)	−2 344(7)	6 852(7)
O(7)	0 027(5)	3 787(8)	6 174(5)
O(8)	3 425(5)	5 934(5)	9 603(5)

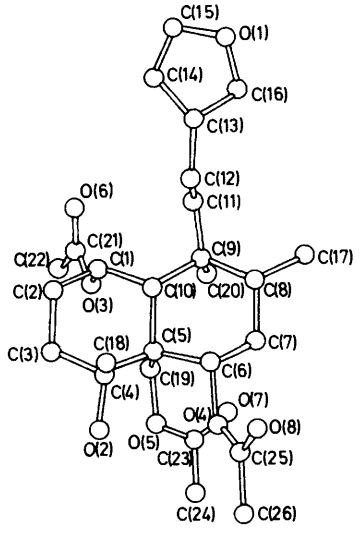


FIGURE *X*-Ray structure of the triacetate (5)

stituents O(3), C(20), and C(19) and between adjacent equatorial substituents O(2) and O(4) was minimised by a slight bending of the fused ring system along the line C(5)–C(10). Thus the planes defined by C(2),C(3),C(5),-C(10) and C(5),C(7),C(8),C(10), which would be coplanar in an undistorted molecule, are at an angle of *ca.* 12° to each other in this molecule. It was then necessary to locate the hydroxy and carbonyl functions of fruticolone on the clerodane skeleton.

Oxidation of both fruticolone (1) and isofruticolone (2) gave the same diketone (3). The spectral changes which accompanied this oxidation served to locate the hydroxy and carbonyl groups. In the case of fruticolone

TABLE 3

Bond lengths and angles, with estimated standard deviations in parentheses

(*a*) Bonds (Å)

C(1)–C(2)	1.500(10)	C(12)–C(13)	1.505(10)
C(1)–O(3)	1.465(7)	C(13)–C(14)	1.423(11)
C(1)–C(10)	1.553(10)	C(14)–C(15)	1.305(12)
C(2)–C(3)	1.510(11)	C(15)–O(1)	1.317(11)
C(3)–C(4)	1.533(11)	O(1)–C(16)	1.371(11)
C(4)–C(5)	1.583(9)	C(13)–C(16)	1.324(11)
C(4)–O(2)	1.442(9)	O(3)–C(21)	1.338(9)
C(4)–C(18)	1.536(9)	C(21)–C(22)	1.503(10)
C(5)–C(6)	1.547(9)	C(21)–O(6)	1.175(10)
C(5)–C(10)	1.598(9)	C(19)–O(5)	1.423(9)
C(5)–C(19)	1.542(8)	O(5)–C(23)	1.344(9)
C(6)–C(7)	1.486(10)	C(23)–C(24)	1.439(14)
C(7)–C(8)	1.570(10)	C(23)–O(7)	1.227(11)
C(8)–C(9)	1.526(11)	C(6)–O(4)	1.478(8)
C(8)–C(17)	1.559(13)	O(4)–C(25)	1.324(8)
C(9)–C(10)	1.568(9)	C(25)–C(26)	1.493(11)
C(9)–C(20)	1.549(8)	C(25)–O(8)	1.184(8)
C(9)–C(11)	1.551(10)	C(11)–C(12)	1.512(8)

(*b*) Angles (°)

C(1)–C(2)–C(3)	111.4(5)	C(8)–C(9)–C(10)	106.6(5)
C(2)–C(3)–C(4)	111.8(6)	C(8)–C(9)–C(20)	112.2(6)
C(3)–C(4)–C(5)	110.0(5)	C(8)–C(9)–C(11)	108.8(6)
C(3)–C(4)–O(2)	105.7(6)	C(11)–C(9)–C(20)	104.4(5)
C(3)–C(4)–C(18)	110.7(5)	C(9)–C(10)–C(1)	115.1(5)
C(5)–C(4)–O(2)	111.2(5)	C(9)–C(10)–C(5)	116.6(5)
C(5)–C(4)–C(18)	114.5(6)	C(1)–C(10)–C(5)	114.5(5)
C(4)–C(5)–C(6)	110.4(5)	C(9)–C(11)–C(12)	119.3(6)
C(4)–C(5)–C(10)	107.0(5)	C(11)–C(12)–C(13)	111.8(6)
C(4)–C(5)–C(19)	110.7(5)	C(12)–C(13)–C(14)	126.8(6)
C(10)–C(5)–C(19)	109.4(5)	C(13)–C(14)–C(15)	107.2(7)
C(5)–C(6)–C(7)	115.8(6)	C(14)–C(15)–O(1)	112.1(8)
C(5)–C(6)–O(4)	107.3(5)	O(1)–C(16)–C(13)	111.5(8)
C(7)–C(6)–O(4)	109.0(5)	C(16)–C(13)–C(14)	104.1(7)
C(6)–C(7)–C(8)	108.6(5)	C(5)–C(19)–O(5)	113.1(6)
C(7)–C(8)–C(9)	111.0(6)	O(3)–C(21)–C(22)	110.8(6)
C(7)–C(8)–C(17)	108.3(6)	O(3)–C(21)–O(6)	124.5(7)
C(9)–C(8)–C(17)	115.7(6)	C(22)–C(21)–O(6)	124.7(8)
C(19)–O(5)–C(23)	120.7(6)	C(6)–O(4)–C(25)	116.2(5)
O(5)–C(23)–C(24)	115.4(8)	O(4)–C(25)–C(26)	110.5(6)
O(5)–C(23)–O(7)	121.6(7)	O(4)–C(25)–O(8)	125.7(7)
C(24)–C(23)–O(7)	123.0(8)	C(26)–C(25)–O(8)	124.8(7)
C(10)–(C1)–C(2)	110.9(5)	C(2)–C(1)–O(3)	107.4(5)
C(10)–C(1)–O(3)	110.7(5)		

(1) a ^{13}C doublet and triplet resonance moved downfield and a ^1H n.m.r. multiplet collapsed to a singlet (δ 2.91). This would be in accord with the change $-CH_2\cdot CH(OH)\cdot CH\cdot\overset{|}{C}-$ to $-CH_2\cdot CO\cdot CH\cdot\overset{|}{C}-$. In isofruticolone ^{13}C singlet and triplet resonances were significantly deshielded by this change. Furthermore the ^1H n.m.r. spectrum of isofruticolone itself contained a one-proton singlet at δ 3.28. This would be in accord with the presence of the groupings $-\overset{|}{C}\cdot CH(OH)\cdot CH_2-$ and $-CO\cdot CH\cdot\overset{|}{C}-$ in isofruticolone. The 19-H_2 AB quartet appeared at considerably higher field in isofruticolone than in fruticolone. In the former it lies within the shielding cone of a C-1 ketone. Whereas the triacetate (5) retains the stereochemistry of fruticolone at C-1, a new chiral centre is generated at C-6. This centre also bears a hydroxy-group in isofruticolone. In the ^1H n.m.r. spectrum of isofruticolone, the H-6 signal appears as a triplet (δ 3.50, *J* 1.5 Hz) which moves downfield to δ 4.68 on acetylation. Spin-decoupling studies showed that this proton was coupled to a multiplet within the methylene envelope at δ 1.6. On the other hand the H-6 signal in the diacetate (4) and the triacetate (5) is a double-doublet, *J* 7 and 9 Hz. Hence isofruticolone is epimeric at this centre to the triacetate (5) and thus possesses the stereochemistry (2).

The absolute stereochemistry of these diterpenoids followed from an examination of the c.d. curve of fruticolone which showed a negative Cotton effect. C-6 Ketones in the clerodin and caryopterin series show a positive Cotton effect.[6] Hence these diterpenoids are antipodal to clerodin and are closely related to the ajugarins which have recently been isolated[7] from *Ajuga remota* (Labiatae).

EXPERIMENTAL

General experimental details have been described previously.[4] *Teucrium fruticans* (2 kg, dry flowers and leaves, collected near Palermo in early April, 1976) was extracted with acetone (10 l) at room temperature for 1 week. Solvent was evaporated, the residue extracted with ethyl acetate, and the extract washed with water and dried. Solvent was evaporated to give a gum which was subjected to dry column chromatography over silica gel (Merck, deactivated with 15% water). Elution with light petroleum gave plant waxes which were rejected. Elution with 30—50% ethyl acetate–light petroleum afforded *fruticolone* (1) (1 g) which crystallized as prisms, m.p. 150 °C, $[\alpha]_D$ +28.3° (*c* 0.3 in $CHCl_3$), $\Delta\varepsilon_{317}$ nm −0.23 (MeOH) (Found: C, 67.4; H, 7.8. $C_{22}H_{30}O_6$ requires C, 67.7; H, 7.7%); $\nu_{max.}$ 3 400, 1 725, 1 250, and 875 cm^{-1}; δ 0.94 (3 H, d, *J* 6 Hz, 17-H_3), 1.33 (3 H, s, 20-H_3), 2.02 (3 H, s, OAc), 3.43 and 2.27 (1 H each, d, *J* 4.5 Hz, 18-H_2), 4.43 (1 H, m, 1-H), 4.9 and 5.42 (1 H each, d, *J* 13.5 Hz, 19-H_2), 6.23 (1 H, m, H-14), 7.18 (1 H, m, H-16), and 7.32 (1 H, m, H-15); *m/e* 390 (M^+) 372, 330, 317, 312, 299, 243, 205, 149, 95, and 81 (100%). Further elution afforded an oil which was purified by t.l.c. in ethyl acetate–light petroleum (1 : 1) to give *isofruticolone* (2) (0.25 g) as an oil, $[\alpha]_D$ −87.8° (*c* 0.25 in $CHCl_3$) (Found: M^+ 390.204 035. $C_{22}H_{30}O_6$ requires M^+ 390.204 224); $\nu_{max.}$ 3 450, 1 750, 1 700, 1 250, and 875 cm^{-1}; δ 0.81 (3 H, d, *J* 6 Hz, 17-H_3), 1.07 (3 H, s, 20-H_3), 1.95 (3 H, s, OAc), 2.78 and 2.94 (1 H each, d, *J* 4.5 Hz, 18-H_2), 3.28 (1 H, s, H-10), 3.65 and 4.03 (1 H each, d, *J* 11 Hz, 19-H_2), 6.22 (1 H, m, H-14), 7.18 (1 H, m, H-16), and 7.29 (1 H, m, H-15); *m/e* 390 (M^+), 372, 330, 299 (100%), 95, and 81.

Oxidation of Fruticolone and Isofruticolone.—Fruticolone (300 mg) in dry pyridine (10 ml) was treated with chromium trioxide (500 mg) at room temperature for 24 h. The solution was poured into water and the organic product recovered in ethyl acetate. The extract was washed (aqueous acetic acid, sodium hydrogen carbonate solution, water) and dried. Evaporation of the solvent gave the

[6] D. H. R. Barton, N. T. Cheung, A. D. Cross, L. M. Jackman, and M. Martin-Smith, *J. Chem. Soc.*, 1961, 5061; S. Hosozawa, N. Kato, and K. Munakata, *Tetrahedron Letters*, 1974, 3753.

[7] I. Kubo, Y. Lee, V. Balogh-Nair, K. Nakanishi, and A. Chapya, *J.C.S. Chem. Comm.*, 1976, 949.

diketone (3) (200 mg) which crystallized from ethyl acetate–light petroleum as needles, m.p. 105 °C (Found: M^+, 388.189 052. $C_{22}H_{28}O_6$ requires M^+, 388.188 575); $\nu_{max.}$ 1 725, 1 700, 1 240, and 875 cm^{-1}; δ 0.95 (3 H, d, *J* 6 Hz, 17-H_3), 1132 (3 H, s, 20-H_3), 2.00 (3 H, s, OAc), 2.85 and 3.09 (1 H each, d, *J* 4.5 Hz, 18-H_2), 2.91 (1 H, s, H-10), 4.28 (2 H, dd, *J* 11.5 Hz, 19-H_2), 6.18 (1 H, m, 14-H), 7.11 (1 H, m, 16-H), and 7.28 (1 H, m, 15-H); *m/e* 388, 370, 357, 328, 315, 297, 184, 179, 151 (100%), 95, and 81. Treatment of isofruticolone (100 mg) under identical conditions afforded the same diketone (identified by m.p., t.l.c., i.r., and n.m.r.).

Hydrolysis of the Diketone (3) *with Hydrochloric Acid.*—The diketone (75 mg) in ethyl acetate (10 ml) was treated with 20% hydrochloric acid (10 ml) at room temperature with stirring for 1 h, and the solution then washed (aqueous sodium carbonate solution, water) and dried. Evaporation of solvent gave an unstable oil; δ 0.91 (3 H, d, *J* 6 Hz, 17-H_3), 1.19 (3 H, s, 20-H_3), 1.98 (3 H, s, OAc), 2.73 (1 H, s 10-H), 3.84 (2 H, s, 18-H_2), 4.49 (2 H, s 19-H_2), 6.18 (1 H, m, H-14), 7.15 (1 H, m, 16-H), and 7.32 (1 H, m, 15-H); *m/e* 424 ($C_{22}H_{29}O_6Cl$), 406, 388, 375, 364, 95, and 81.

Reduction with Lithium Aluminium Hydride.—Fruticolone (500 mg) in dry tetrahydrofuran (25 ml) was heated under reflux with lithium aluminium hydride (500 mg) for 12 h. Excess of reagent was destroyed by dropwise addition of aqueous sodium hydroxide and the organic product recovered in ethyl acetate and purified by chromatography on silica in 50% ethyl acetate–light petroleum. The tetraol crystallized from ethyl acetate–light petroleum as needles, m.p. 78 °C; δ 0.88 (3 H, d, *J* 6 Hz, 17-H_3), 1.22 (3 H, s), 1.40 (3 H, s), 18-H_3 and 20-H_3), 4.00 and 4.45 (1 H each, d, *J* 12 Hz, 19-H_2), 4.08 and 4.29 (1 H each, m, 1-H and 6-H), 6.25 (1 H, m, H-14), 7.20 (1 H, m, 16-H), and 7.32 (1 H, m, 15-H); *m/e* 352, 334, 316, 309, 298, 286, 270, 216, 99 (100%), 95, and 81. Acetylation of the tetraol (300 mg) with acetic anhydride (2 ml) in dry pyridine (5 ml) gave a mixture of di- and tri-acetates which were separated by dry column chromatography on silica (Merck, deactivated with 15% water) to afford the diacetate as an oil; $\nu_{max.}$ 3 450, 1 735br, and 875 cm^{-1}; δ 0.86 (3 H, d, *J* 6 Hz, 17-H_3), 1.18 (3 H, s), 1.29 (3 H, s, 18-H_3 and 20-H_3), 2.02 and 2.10 (3 H each, s, OAc), 4.10 (1 H, m, 1-H), 4.95 (1 H, m, 6-H), 4.73 and 5.22 (1 H each, d, *J* 13 Hz, 19-H_2), 6.24 (1 H, m, H-14), 7.19 (1 H, m, H-16), and 7.31 (1 H, m, H-15); *m/e* 418, 376, 365, 316, 298, 245, 203, 95, and 81.

The *triacetate* (5) crystallized from ethyl acetate–light petroleum, m.p. 156 °C (Found: C, 65.1; H, 7.9. $C_{26}H_{38}O_8$ requires C, 65.25; H, 8.00%); $\nu_{max.}$ 1 735br and 872 cm^{-1}; δ 0.88 (3 H, d, *J* 6 Hz, 17-H_3), 1.00 (3 H, s), 1.3 (3 H, s), (18-H_3 and 20-H_3), 2.02 (3 H, s), 2.09 (6 H, s, OAc), 4.93 and 5.125 (1 H each, d, *J* 13 Hz, 19-H_2), 5.10 (1 H, m) and 5.29 (1 H, m) 1-H and 6-H), 6.28 (1 H, m, 14-H), 7.20 (1 H, m, 16-H), and 7.31 (1 H, m, 15-H); *m/e* 418 (M − CH_3CO_2H), 376, 358, 316, 305, 298, 245, 240, 216, 203, 149, 121, 95, and 81.

Crystal Data.—$C_{26}H_{38}O_8$, M = 478.6. Monoclinic, a = 11.028(2), b = 9.924(2), c = 12.046(2) Å, β = 102.89(1)°, U = 1 285.1 Å^3, Z = 2, D_c = 1.24 g cm^{-3}, $F(000)$ = 576. Mo-K_α radiation λ = 0.709 26Å; μ(Mo-K_α) = 0.98 cm^{-1}. Space group $P2_1$ (No. 4) from systematic absences of $0k0$ for k odd.

Crystallographic Measurement.—A crystal 0.5 × 0.1 × 0.2 mm elongated along *b* was used for data collection on a Hilger and Watts four-circle diffractometer. Accurate cell parameters were derived from the setting angles of 12 reflections. Intensities for unique reflections with $2 < \theta < 22°$ were measured by an ω–2θ step scan with Mo-K_α radiation and a graphite-crystal monochromator. Standard deviations of intensities were calculated in the usual way with p 0.04.[8] Data were corrected for Lorentz and polarisation effects but not for absorption, and 1 620 reflections with $I > 3\sigma(I)$ were used in the structure analysis.

Structure Solution and Refinement.—Initial attempts at structure solution using the multiple-start tangent formula routine of the SHELX program system [9] produced several phase sets of low R_A values for which the E maps showed only the *trans*-decalin fragment with any certainty. When this was used as a partial structure to generate phases for the tangent formula, again nothing recognisable was produced. Finally the *trans*-decalin fragment in the specified orientation was repositioned in the unit cell using a translation function.[10] Several subsequent Fourier syntheses then allowed the location of the remaining non-hydrogen atoms of the molecule.

Least-squares refinement of all atoms with isotropic temperature factors reduced R to 0.16. In order to define the origin, the atoms list was divided into two halves which were refined in alternate cycles. Oxygen atoms were distinguished on the basis of bond lengths, stereochemistry, and temperature factors. Further refinement with anisotropic temperature factors converged at R 0.099 and a difference-Fourier map showed peaks at all atom positions expected for hydrogen atoms. The methyl hydrogen atom positions were idealised [d(C–H) 1.08 Å] and the methyl groups refined as rigid bodies. All other hydrogen atoms were held fixed at the positions taken from the difference map. Continued least-squares refinement with a common isotropic temperature factor for the methyl hydrogen atoms and with the other hydrogen atoms allowed individual isotropic temperature factors, converged at R 0.070, R' 0.102 [$R' = (\Sigma\omega\Delta^2/\Sigma|F_o|^2)^{\frac{1}{2}}$], and the maximum positional shift-to-error was 0.2. The weighting scheme used was $\omega = 0.164/[\sigma^2(F) + 0.0197|F^2|]$, and the scattering factors used were taken from ref. 11. A final difference-Fourier map showed peaks of up to Å^{-3} in the vicinity of the C(23) acetate group which were probably due to slight disorder in this area, but elsewhere it was featureless. Final non-hydrogen atom positions are listed in Tables 2 and 3. Anisotropic temperature factors and hydrogen-atom parameters have been deposited with the structure factor listing as Supplementary Publication No. SUP 22180 (14 pp., 1 microfiche).*

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