Crystal Structures of (5*E*,12*E*)-7β-Acetoxy-15β-hydroxybertya-5,12-diene-3,14-dione and (5*E*,12*E*)-7β-Acetoxybertya-5,12-diene-3,14-dione

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The crystal structures of the title compounds, $C_{22}H_{30}O_5$ (I) and $C_{22}H_{30}O_4$ (II), have been determined by *X*-ray diffraction by direct methods and refined by least squares to *R* 0.036 and 0.043 for 1 211 and 1 204 reflections respectively. Crystals of (I) and (II) are both orthorhombic, space group $P2_12_12_1$, $Z = 4$; for (I), $a = 23.095(3)$, $b = 10.987(1)$, $c = 8.224(1)$ Å; for (II), $a = 21.199(4)$, $b = 11.160(3)$, $c = 8.998(2)$ Å. The structure determinations confirm the stereochemistry previously assigned by other chemical and physical methods to the novel diterpene, bertyadionol.

In previous studies,[1] chemical and physical evidence has been presented for the structure of bertyadionol, a novel diterpene isolated from *Bertya cuppressoidea*, and the absolute configuration deduced from its degradation to (−)-*cis*-homocaronic acid. In order to confirm the suggested stereochemistry, a crystallographic study was undertaken; examination of bertyadionol itself showed the crystals to be triclinic with the unhelpful space group $P\bar{1}$ and $Z=2$. Further studies were undertaken on (5*E*, 12*E*)-7β-acetoxy-15β-hydroxybertya-5,12-diene-3,14-dione (I) which proved difficult to solve, so that the structure determination of a second derivative, (5*E*, 12*E*)-7β-

[1] E. L. Ghisalberti, P. R. Jefferies, R. F. Toia, and G. K. Worth, *Tetrahedron*, 1974, **30**, 3269, and refs. therein.

TABLE 1

Atomic positional ($\times 10^4$, for H $\times$ 10^3) and thermal parameters ($\times 10^3$ Å^2), with least-squares estimated standard deviations in parentheses

(*a*) For (I)

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	3 091(1)	−0 713(3)	7 251(5)	44(2)	34(2)	57(2)	−6(2)	4(2)	2(2)
C(2)	3 324(1)	−0 859(3)	8 962(5)	43(2)	38(2)	58(2)	0(2)	6(2)	8(2)
C(3)	3 870(2)	−0 087(3)	8 934(4)	48(2)	40(2)	41(2)	8(2)	4(2)	−2(2)
C(4)	3 854(1)	0 758(3)	7 472(4)	40(2)	31(2)	39(2)	−3(2)	0(2)	−2(2)
C(5)	4 049(1)	2 023(3)	7 881(4)	40(2)	40(2)	33(2)	−3(2)	−7(2)	0(3)
C(6)	4 446(1)	2 676(3)	7 131(4)	34(2)	41(2)	39(2)	2(2)	−5(2)	3(2)
C(7)	4 545(1)	3 983(3)	7 669(5)	48(2)	44(2)	39(2)	−10(2)	−8(2)	1(2)
C(8)	4 014(2)	4 791(3)	7 402(5)	57(2)	41(2)	53(2)	3(2)	−13(2)	−1(2)
C(9)	3 903(2)	5 063(3)	5 640(5)	50(2)	41(2)	53(2)	−4(2)	−8(2)	7(2)
C(10)	3 320(2)	5 443(3)	4 982(5)	76(3)	34(2)	62(3)	−3(2)	−21(3)	7(2)
C(11)	3 579(2)	4 213(3)	4 465(5)	55(2)	43(2)	50(2)	−6(2)	−6(2)	7(2)
C(12)	3 357(1)	3 023(3)	5 043(3)	38(2)	39(2)	42(2)	−2(2)	−7(2)	4(2)
C(13)	3 359(1)	1 996(3)	4 182(4)	38(2)	42(2)	39(2)	−6(2)	−5(2)	1(2)
C(14)	3 219(1)	0 808(3)	4 930(5)	31(2)	40(2)	51(2)	3(2)	−11(2)	−11(2)
C(15)	3 238(1)	0 602(3)	6 783(4)	34(2)	33(2)	41(2)	0(2)	5(2)	−4(2)
C(16)	3 326(2)	6 419(4)	3 703(7)	109(4)	47(3)	88(4)	−9(2)	−40(3)	19(3)
C(17)	2 807(2)	5 475(4)	6 078(6)	62(3)	68(3)	88(3)	15(2)	−12(3)	−2(3)
C(18)	3 525(2)	1 944(4)	2 414(5)	69(3)	70(3)	40(2)	−11(2)	3(2)	−3(2)
C(19)	3 417(2)	−2 151(4)	9 552(6)	74(3)	54(3)	94(4)	−6(2)	3(3)	26(3)
C(20)	4 787(2)	2 271(3)	5 690(5)	53(2)	60(2)	53(2)	−7(2)	12(2)	−6(2)
C(21)	5 170(2)	3 577(4)	9 886(6)	63(3)	60(3)	51(3)	−17(2)	−22(3)	14(2)
C(22)	5 250(3)	3 641(6)	11 673(6)	100(4)	132(5)	57(3)	1(4)	−20(3)	10(3)
O(3)	4 262(1)	−0 145(2)	9 898(3)	57(1)	64(2)	48(1)	3(1)	−9(1)	10(2)
O(7)	4 661(1)	4 029(2)	9 414(3)	58(2)	50(2)	44(1)	−7(1)	−12(1)	−2(1)
O(14)	3 133(1)	−0 081(2)	4 060(3)	68(2)	48(1)	56(2)	−4(1)	−18(1)	−12(1)
O(15)	2 854(1)	1 436(2)	7 605(3)	41(1)	38(1)	61(2)	4(1)	13(1)	−1(1)
O(21)	5 528(1)	3 157(3)	8 964(4)	56(2)	91(2)	68(2)	−3(2)	−5(2)	21(2)

	x	*y*	*z*		*x*	*y*	*z*
H(1α) *	334(2)	−122(3)	639(6)	H(17a)	247(2)	549(4)	554(5)
H(1β)	264(2)	−083(4)	716(6)	H(17b)	284(2)	484(4)	690(6)
H(2β)	309(2)	−044(4)	974(5)	H(17c)	279(2)	628(4)	668(6)
H(4α)	414(2)	036(4)	666(5)	H(18a)	387	147	241
H(5)	380(2)	237(4)	887(5)	H(18b)	365	266	189
H(7α)	487(2)	436(4)	713(5)	H(18c)	329	146	167
H(8α)	405(2)	566(4)	793(5)	H(19a)	373(2)	−256(4)	881(6)
H(8β)	369(2)	435(5)	798(6)	H(19b)	301(2)	−262(4)	959(5)
H(9α)	417(2)	547(4)	503(5)	H(19c)	355(2)	−217(4)	1 063(5)
H(11α)	375(2)	427(4)	328(6)	H(20a)	464(2)	270(4)	480(6)
H(12)	322(2)	295(4)	619(5)	H(20b)	469	151	539
H(15)	245(2)	107(4)	800(6)	H(20c)	520(2)	233(4)	598(5)
H(16a)	295(2)	641(4)	297(6)	H(22a)	493(2)	416(4)	1 214(6)
H(16b)	371	626	306	H(22b)	568(2)	379(4)	1 200(6)
H(16c)	337(2)	731(4)	400(5)	H(22c)	510(2)	290(4)	1 197(5)

(*b*) For (II)

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	6 509(2)	6 999(4)	5 596(6)	98(4)	68(3)	86(3)	−3(3)	0(3)	5(3)
C(2)	7 214(2)	6 964(4)	5 668(5)	93(3)	73(3)	68(3)	−13(3)	−3(3)	−1(3)
C(3)	7 337(2)	5 846(5)	6 546(5)	95(3)	90(4)	73(3)	14(3)	−14(3)	−9(3)
C(4)	6 779(2)	5 027(4)	6 577(5)	90(3)	60(3)	59(3)	2(3)	3(3)	−3(2)
C(5)	6 909(2)	3 772(4)	6 141(5)	84(3)	77(3)	49(2)	3(2)	7(2)	−1(2)
C(6)	6 701(2)	2 757(4)	6 721(4)	70(2)	65(3)	49(2)	3(2)	−4(2)	3(2)
C(7)	6 827(2)	1 586(4)	5 927(5)	84(3)	71(3)	71(3)	10(2)	5(3)	−1(3)
C(8)	6 457(2)	1 452(4)	4 455(5)	109(4)	74(3)	63(3)	4(3)	7(3)	−9(3)
C(9)	5 765(2)	1 279(4)	4 661(6)	111(4)	71(3)	68(3)	−1(3)	−9(3)	−11(3)
C(10)	5 299(2)	1 555(5)	3 474(5)	112(3)	71(3)	67(3)	−1(3)	−14(3)	−18(3)
C(11)	5 301(2)	2 280(4)	4 915(5)	86(3)	76(3)	56(2)	0(3)	−5(2)	−9(2)
C(12)	5 508(2)	3 536(4)	4 996(5)	75(3)	68(3)	57(3)	−2(2)	−7(2)	−2(3)
C(13)	5 302(2)	4 367(4)	5 938(5)	77(3)	69(3)	59(3)	13(2)	1(2)	−6(3)
C(14)	5 621(2)	5 499(4)	6 111(5)	88(3)	59(3)	76(3)	8(3)	10(3)	−14(2)
C(15)	6 288(2)	5 694(4)	5 577(5)	84(3)	58(3)	65(3)	3(2)	4(2)	−2(2)
C(16)	4 752(2)	0 696(6)	3 359(7)	163(5)	95(4)	109(4)	−16(4)	−25(4)	−29(4)
C(17)	5 478(2)	2 107(5)	2 034(5)	140(4)	95(3)	60(3)	14(3)	−13(3)	−12(3)
C(18)	4 736(2)	4 187(5)	6 958(6)	80(3)	92(3)	94(3)	−7(3)	19(2)	−12(3)
C(19)	7 533(3)	8 094(5)	6 219(6)	124(4)	88(3)	84(3)	−18(3)	−5(3)	−13(3)
C(20)	6 301(2)	2 655(5)	8 094(4)	100(3)	89(3)	52(2)	8(3)	5(2)	4(3)
C(21)	7 907(3)	1 311(5)	6 493(9)	87(4)	84(4)	124(5)	23(3)	12(4)	−7(4)
C(22)	8 548(3)	1 272(7)	5 956(10)	119(5)	159(6)	170(7)	18(5)	2(5)	−9(6)
O(3)	7 840(2)	5 628(4)	7 207(6)	128(3)	113(3)	147(3)	−8(2)	−44(3)	6(3)
O(7)	7 479(2)	1 518(3)	5 450(3)	92(2)	82(2)	73(2)	18(2)	5(2)	0(2)
O(14)	5 374(2)	6 303(3)	6 845(5)	119(3)	88(2)	177(4)	−7(2)	46(3)	−51(3)
O(21)	7 775(2)	1 139(4)	7 787(5)	116(3)	116(3)	100(3)	28(2)	−16(2)	−3(3)

TABLE 1 (*Continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
H(1α) *	633(2)	729(4)	651(5)	H(17a)	580	264	234
H(1β)	642(2)	762(4)	489(5)	H(17b)	521(2)	269(4)	165(5)
H(2β)	733(2)	663(4)	449(5)	H(17c)	563(2)	150(4)	132(4)
H(4α)	665(2)	509(4)	773(5)	H(18a)	497(2)	413(4)	796(5)
H(5)	714(2)	370(3)	526(5)	H(18b)	439(2)	486(4)	701(5)
H(7α)	674(2)	078(4)	676(5)	H(18c)	448(2)	338(4)	675(5)
H(8α)	667(2)	053(4)	407(5)	H(19a)	731(2)	823(4)	710(5)
H(8β)	666(2)	228(4)	396(5)	H(19b)	798	787	633
H(9α)	559(2)	044(4)	540(5)	H(19c)	757(2)	879(4)	545(4)
H(11α)	492(2)	202(4)	568(5)	H(20a)	628(2)	344(4)	851(5)
H(12)	586(2)	369(4)	422(5)	H(20b)	653(2)	218(4)	872(5)
H(15)	644(2)	543(4)	459(5)	H(20c)	586(2)	233(4)	776(5)
H(16a)	458	038	431	H(22a)	873	200	559
H(16b)	480	007	269	H(22b)	880	090	671
H(16c)	439	110	292	H(22c)	853	083	502

* H atom isotropic thermal parameters fixed at 0.1Å². Certain methyl H atoms were located geometrically and constrained (see text); standard deviations are not given for these atoms.

acetoxybertya-5,12-diene-3,14-dione (II) was also undertaken. Eventually the structures of both derivatives were successfully determined and are now reported. Diagrams throughout the present paper conform to the absolute configuration previous proposed.

EXPERIMENTAL

The derivation of (II) from the parent bertyadionol has been previously described; the alcoholic precursor of (I) is

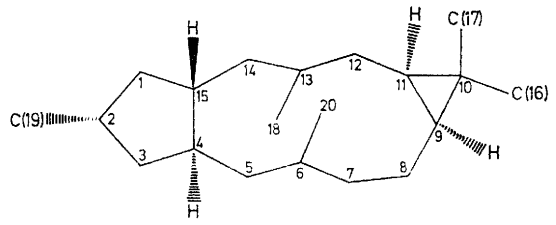

FIGURE 1 Bertyane, showing the skeleton numbering system

naturally occurring and its extraction has also been described. Large prismatic crystals of (I) and (II) were obtained as described previously by cooling ether–n-pentane. Nomenclature is based on the bertyane skeleton, defined in Figure 1.

Approximately spherical crystal fragments, *ca.* 0.30 mm diam., were used for cell calibration and data collection for both (I) and (II). In both cases, cell calibration was carried out by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex P$\bar{1}$ four-circle diffractometer; unique data sets in the range $2\theta < 100°$ [Ni-filtered Cu-K_α radiation ($\lambda = 1.5418$ Å)] were collected by a conventional 2θ—θ scan. For (I) 1 265 independent reflections were obtained, of which 1 211 having $I > 2\sigma(I)$ were used in the structure solution and refinement; for (II) corresponding values are 1 280 and 1 204. Absorption corrections were not applied.

Crystal data: (I) $C_{22}H_{30}O_5$, $M = 374.5$. Orthorhombic, $a = 23.095(3)$, $b = 10.987(1)$, $c = 8.224(1)$ Å, $U = 2086.7(4)$ Å³, $D_m = 1.18(1)$, $Z = 4$, $D_c = 1.19$ g cm^{-3}, $F(000) = 808$, μ(Cu-K_α) = 6.0 cm^{-1}. Space group $P2_12_12_1$ (D_2^4, No. 19). (II) $C_{22}H_{30}O_4$, $M = 358.5$, Orthorhombic, $a = 21.199(4)$, $b = 11.160(3)$, $c = 8.998(2)$ Å, $U = 2129(1)$ Å³, $D_m = 1.14(1)$, $Z = 4$, $D_c = 1.12$ g cm^{-3}, $F(000) = 776$. μ(Cu-K_α) = 5.3 cm^{-1}. Space group $P2_12_12_1$.

The structures were solved by the normal method of selecting four origin- and enantiomorph-defining reflections, including well-defined Σ^1 relations and one or two symbolic phases which were assigned numerical values for the start of tangent refinement. After a number of unsuccessful trial solutions were obtained, it being necessary in the case of (I) to identify powerful but contradictory phase-generating relationships which inhibited the solution, the correct solution was obtained by choosing a set of starting phases which did not introduce the contradictory relationships until a late stage in the phase-determining process. An almost complete molecular skeleton was obtained in both cases.

Refinement of the structure was carried by 9 × 9 block-diagonal least-squares, the molecular skeleton being refined as a full matrix in the final stages; anisotropic thermal parameters were of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. It was not possible to refine the hydrogen-atom thermal parameters in a meaningful manner and these were fixed isotropically during refinement; although they were clearly located in difference maps, it was also not possible to refine certain methyl hydrogen atoms and they were located geometrically and constrained (see Table 1). In both cases a weighting scheme of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ was found appropriate for $n = 4$. At convergence,

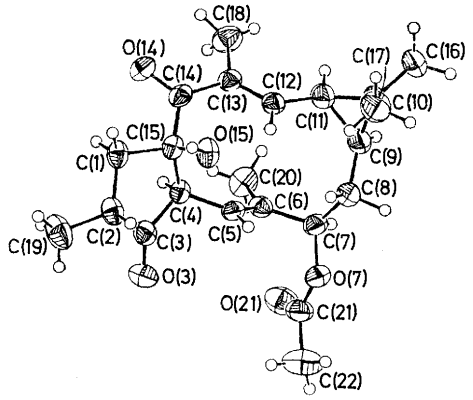

FIGURE 2 Molecule (I), showing 50% thermal ellipsoids

no non-hydrogen parameter shift exceeded 0.1σ, R and R' [$= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] being 0.036 and 0.048 for (I), and 0.043 and 0.061 for (II). Scattering factors used were for the neutral atoms.[2,3] Structure-factor tables are depo-

[2] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

TABLE 2

(*a*) Bond lengths (Å) and angles (deg.), with least squares estimated standard deviations in parentheses. Values for (II) follow those for (I)

C(1)–H(1α)	1.07(4), 0.96(4)
C(1)–H(1β)	1.05(4), 0.95(4)
C(1)–C(2)	1.514(6), 1.497(7)
C(1)–C(15)	1.534(5), 1.530(6)
C(2)–H(2β)	0.96(4), 1.15(4)
C(2)–C(19)	1.516(6), 1.514(7)
C(2)–C(3)	1.520(6), 1.500(7)
C(3)–O(3)	1.206(4), 1.245(6)
C(3)–C(4)	1.520(5), 1.496(7)
C(4)–H(4α)	1.04(4), 1.07(4)
C(4)–C(5)	1.500(5), 1.481(6)
C(4)–C(15)	1.541(5), 1.564
C(5)–H(5)	1.07(4), 0.93(4)
C(5)–C(6)	1.317(5), 1.324(6)
C(6)–C(7)	1.520(5), 1.513(6)
C(6)–C(20)	1.491(5), 1.504(6)
C(7)–H(7α)	0.96(4), 1.19(4)
C(7)–C(8)	1.530(5), 1.547(7)
C(7)–O(7)	1.461(4), 1.451(6)
C(8)–H(8α)	1.05(4), 1.18(4)
C(8)–H(8β)	1.02(5), 1.12(4)
C(8)–C(9)	1.502(5), 1.491(7)
C(9)–H(9α)	0.91(5), 1.21(4)
C(9)–C(10)	1.510(6), 1.487(7)
C(9)–C(11)	1.537(5), 1.506(7)
C(10)–C(11)	1.539(5), 1.529(6)
C(10)–C(16)	1.502(6), 1.508(9)
C(10)–C(17)	1.489(6), 1.484(7)
C(11)–H(11α)	1.05(4), 1.11(4)
C(11)–C(12)	1.483(5), 1.470(6)
C(12)–H(12)	1.00(4), 1.03(4)
C(12)–C(13)	1.332(5), 1.330(6)
C(13)–C(14)	1.479(5), 1.443(6)
C(13)–C(18)	1.505(5), 1.524(6)
C(14)–O(14)	1.227(4), 1.230(6)
C(14)–C(15)	1.541(5), 1.510(6)
C(15)–H(15β)	0.99(4) *
C(15)–O(15)	1.443(4) †
O(15)–H(15)	1.06(4) †
C(16)–H(16a)	1.06(4), 1.00
C(16)–H(16b)	1.05, 0.93(4)
C(16)–H(16c)	1.02(4), 0.96
C(17)–H(17a)	0.90(4), 0.95
C(17)–H(17b)	0.97(4), 0.94(4)
C(17)–H(17c)	1.02(4), 0.99(4)
C(18)–H(18a)	0.95, 1.02(4)
C(18)–H(18b)	0.95, 1.04(4)
C(18)–H(18c)	0.98, 1.08(4)
C(19)–H(19a)	1.06(4), 0.94(4)
C(19)–H(19b)	1.08(4), 0.98
C(19)–H(19c)	0.94(4), 1.05(4)
C(20)–H(20a)	0.93(5), 0.96(4)
C(20)–H(20b)	0.90, 0.91(4)
C(20)–H(20c)	0.99(4), 1.04(4)
C(21)–O(7)	1.336(5), 1.326(7)
C(21)–O(21)	1.212(6), 1.214(9)
C(21)–C(22)	1.483(7), 1.442(9)
C(22)–H(22a)	1.01(4), 0.96
C(22)–H(22b)	1.03(4), 0.96
C(22)–H(22c)	0.92(4), 0.98
C(13)–C(14)–O(14)	119.7(3), 119.8(4)
C(13)–C(14)–C(15)	122.3(3), 122.0(4)
O(14)–C(14)–C(15)	117.7(3), 117.8(4)
C(10)–C(16)–H(16a)	112(2), 117
C(10)–C(16)–H(16b)	104, 115
C(10)–C(16)–H(16c)	121(2), 109
H(16a)–C(16)–H(16c)	104(3), 103
C(10)–C(17)–H(17a)	113(3), 101
H(17a)–C(17)–H(17b)	115(4), 97
C(10)–C(17)–H(17c)	110(3), 111(2)
H(17a)–C(17)–H(17c)	102(4), 112
C(13)–C(18)–H(18b)	119, 119(2)
C(2)–C(19)–H(19a)	108(2), 101(2)
C(2)–C(19)–H(19c)	112(3), 115(2)
H(18a)–C(18)–H(18c)	100, 111(3)

TABLE 2 (*Continued*)

H(19a)–C(19)–H(19b)	115(3), 116
H(19b)–C(19)–H(19c)	105(4), 101
C(6)–C(20)–H(20b)	111, 105(2)
H(20a)–C(20)–H(20b)	100, 108(4)
H(20b)–C(20)–H(20c)	112, 116(3)
O(7)–C(21)–O(21)	124.0(4), 123.2(5)
O(21)–C(21)–C(22)	123.6(5), 122.4(6)
C(21)–C(22)–H(22b)	113(3), 107(7)
H(22a)–C(22)–H(22b)	120(3), 112
H(22b)–C(22)–H(22c)	116(3), 115
C(4)–C(15)–O(15)	109.0(3) †
C(1)–C(15)–O(15)	110.1(3) †
H(1α)–C(1)–H(1β)	114(3), 105(4)
H(1α)–C(1)–C(2)	112(2), 111(2)
H(1β)–C(1)–C(2)	114(2), 104(2)
C(2)–C(1)–C(15)	104.8(3), 106.3(4)
H(1α)–C(1)–C(15)	102(2), 102(2)
H(1β)–C(1)–C(15)	109(2), 128(2)
C(1)–C(2)–C(3)	102.8(3), 102.6(4)
C(1)–C(2)–C(19)	116.5(3), 116.0(4)
C(1)–C(2)–H(2β)	112(3), 100(2)
H(2β)–C(2)–C(19)	108(3), 119(2)
H(2β)–C(2)–C(3)	102(2), 100(2)
C(3)–C(2)–C(19)	114.1(3), 116.3(4)
C(2)–C(3)–C(4)	109.5(3), 112.4(4)
C(2)–C(3)–O(3)	125.7(3), 124.3(5)
O(3)–C(3)–C(4)	124.8(3), 123.3(5)
C(3)–C(4)–H(4α)	103(2), 100(2)
C(3)–C(4)–C(5)	112.4(3), 115.2(4)
C(3)–C(4)–C(15)	104.2(3), 103.0(4)
C(4)–C(5)–H(5)	110(2), 114(2)
C(4)–C(5)–C(6)	127.5(3), 130.0(4)
C(1)–C(15)–C(14)	112.4(3), 114.8(4)
C(4)–C(15)–C(14)	112.0(3), 111.7(4)
C(1)–C(15)–C(4)	102.5(3), 104.0(4)
C(4)–C(15)–H(15β)	99(2) *
H(15β)–C(15)–C(14)	123(2) *
C(1)–C(15)–H(15β)	101(2) *
H(4α)–C(4)–C(15)	108(2), 111(2)
H(4α)–C(4)–C(5)	110(2), 111(2)
C(5)–C(4)–C(15)	117.5(3), 114.9(4)
H(5)–C(5)–C(6)	122(2), 116(2)
C(5)–C(6)–C(7)	119.0(3), 119.6(4)
C(5)–C(6)–C(20)	125.2(3), 125.3(4)
C(7)–C(6)–C(20)	115.0(4), 115.7(3)
C(6)–C(7)–C(8)	112.6(3), 113.5(4)
C(6)–C(7)–H(7α)	113(2), 109(2)
C(6)–C(7)–O(7)	110.3(3), 110.6(4)
O(7)–C(7)–C(8)	105.5(3), 103.0(4)
H(7α)–C(7)–C(8)	108(2), 113(2)
O(7)–C(7)–H(7α)	107(3), 107(2)
C(7)–C(8)–C(9)	113.1(3), 113.9(4)
C(7)–C(8)–H(8α)	114(2), 98(2)
C(7)–C(8)–H(8β)	105(2), 94(2)
H(8α)–C(8)–H(8β)	107(3), 117(3)
H(8α)–C(8)–C(9)	103(2), 108(2)
H(8β)–C(8)–C(9)	114(2), 123(2)
C(8)–C(9)–H(9α)	120(3), 118(2)
C(8)–C(9)–C(10)	123.6(3), 122.5(4)
C(8)–C(9)–C(11)	124.7(3), 124.4(4)
H(9α)–C(9)–C(10)	106(3), 110(2)
H(9α)–C(9)–C(11)	106(3), 107(2)
C(10)–C(9)–C(11)	60.7(2), 61.4(3)
C(9)–C(10)–C(11)	60.5(2), 59.9(3)
C(9)–C(10)–C(16)	116.1(4), 115.3(4)
C(9)–C(10)–C(17)	120.0(4), 122.8(5)
C(16)–C(10)–C(11)	115.4(4), 113.4(4)
C(16)–C(10)–C(17)	114.5(4), 113.7(4)
C(11)–C(10)–C(17)	119.9(3), 121.4(4)
C(10)–C(11)–H(11α)	110(2), 113(2)
C(10)–C(11)–C(12)	123.4(3), 123.2(4)
C(9)–C(11)–H(11α)	111(2), 112(2)
C(9)–C(11)–C(12)	120.1(3), 121.3(4)
H(11α)–C(11)–C(12)	119(2), 116(2)
C(9)–C(11)–C(10)	58.8(3), 58.7(3)
C(11)–C(12)–H(12)	119(2), 110(2)
C(11)–C(12)–C(13)	125.1(3), 126.7(4)
C(13)–C(12)–H(12)	116(2), 123(2)
C(12)–C(13)–C(18)	123.2(3), 123.4(4)

TABLE 2 (*Continued*)

C(12)–C(13)–C(14)	121.7(3), 121.8(4)
C(18)–C(13)–C(14)	115.1(3), 114.7(4)
H(16a)–C(16)–H(16b)	114, 110
H(16b)–C(16)–H(16c)	100, 100
C(10)–C(17)–H(17b)	110(3), 117(3)
H(17b)–C(17)–H(17c)	107(4), 116(4)
C(13)–C(18)–H(18a)	104, 99(2)
C(13)–C(18)–H(18c)	118, 114(2)
C(2)–C(19)–H(19b)	110(2), 105
H(18a)–C(18)–H(18b)	101, 109(3)
H(18b)–C(18)–H(18c)	110, 105(3)
H(19a)–C(19)–H(19c)	108(4), 118(3)
C(6)–C(20)–H(20a)	106(3), 106(2)
C(6)–C(20)–H(20c)	108(3), 107(2)
H(20a)–C(20)–H(20c)	120(4), 114(3)
C(7)–O(7)–C(21)	115.7(3), 116.9(4)
O(7)–C(21)–C(22)	112.3(4), 114.4(7)
C(21)–C(22)–H(22a)	108(3), 118
C(21)–C(22)–H(22c)	100(3), 105
H(22a)–C(22)–H(22c)	97(4), 99
C(14)–C(15)–O(15)	110.6(3) †
C(15)–O(15)–H(15)	116(2) †

(*b*) Intermolecular O · · · H contacts less than the van der Waals distance (2.6 Å)

(I)			
O(14) · · · H(15^{I})	1.94(4)	O(14) · · · H(1β^{I})	2.58(4)
O(21) · · · H(4α^{II})	2.59(4)		
(II)			
O(21) · · · H(8α^{III})	2.48(4)	O(21) · · · H(19c^{IV})	2.50(4)
O(14) · · · H(11α^{V})	2.44(4)		

Roman numeral superscripts denote the following transformations of the asymmetric unit relative to reference molecules at *x*,*y*,*z*:

I $\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$ II $1 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$
III $1\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ IV $1\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
V $1 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$

* For (II) only. † For (I) only.

sited as Supplementary Publication No. SUP 21399 (12 pp., 1 microfiche).* All data processing and computation was carried out on a CDC 6200 computer at this University, with a local adaptation of the '*X*-Ray' system.[4] The carbon skeleton of the molecules is labelled (Figure 1) as before in bertyadionyl acetate. In (I) (Figure 2) O(15) is attached to C(15); the remaining oxygen-atoms are labelled according to the carbon to which they are attached. Hydrogen atoms are labelled according to the carbon atom to which they are attached followed by α or β depending on the configuration, or a, b, c where configuration is irrelevant.

DISCUSSION

In both cases, the unit cell (Figures 3 and 4) is comprised of discrete molecules of the compound; the chief intermolecular interactions in both cases are possible hydrogen bonds to the ester and ketone carbonyl oxygens from a diverse array of hydrocarbon hydrogen atoms (Table 2), and a very short hydrogen bond [1.94(4) Å] from a hydroxy-group to the carbonyl oxygen in (I).

The structure determinations confirm the suggested composition, structure, and relative stereochemistry of the macrocyclic eleven-membered ring and its fused associated three- and five-membered rings, and the substituent groupings. Bond lengths and angles (Table 2) are generally as expected although the somewhat short C(11)–C(12) distance in both structures [1.483(5), 1.470(6) Å] suggest that the conjugation through O(14)=C(14)-C(13)=C(12) extends through to C(11) as suggested on the basis of spectroscopic evidence.[5] A close correlation is found between H–C–C–H torsion angles (Table 3)

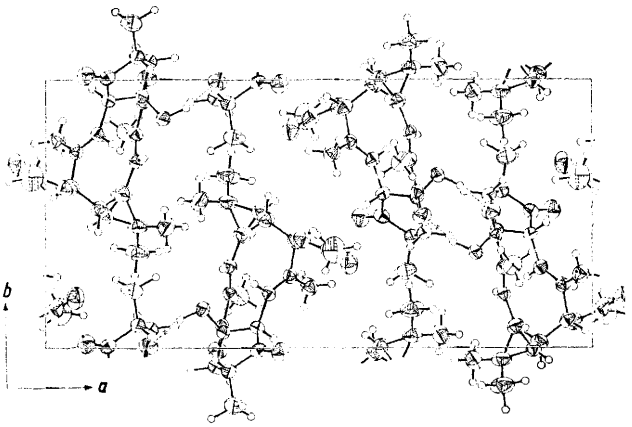

FIGURE 3 Unit-cell contents of (I), projected down *c*, showing 50% ellipsoids; close hydrogen-bonding contacts are shown as dotted lines. Here and in Figure 4 hydrogen atoms are shown as spheres of arbitrary radius 0.1 Å. Right-handed axial systems are used

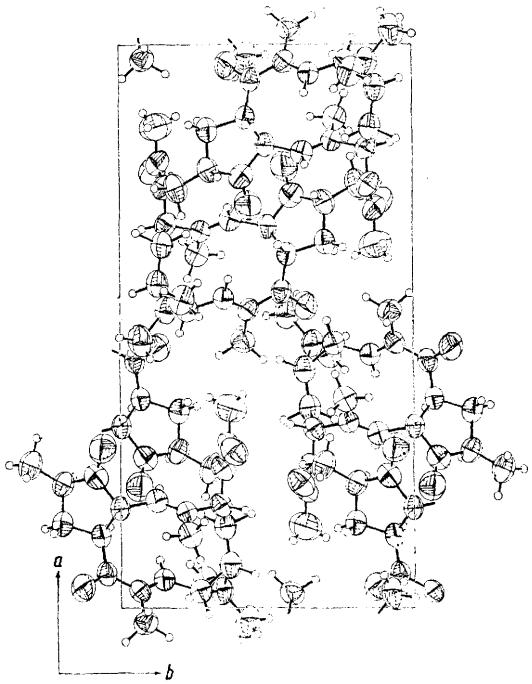

FIGURE 4 Unit-cell contents of (II), projected down *c*, showing 50% ellipsoids

* For details, see Notice to Authors, No. 7, in *J.C.S. Perkin II*, 1974, Index issue.

[4] '*X*-Ray' system of programs, Technical Report, TR 192, Computer Science Centre, University of Maryland, U.S.A., version of June 1972.

[5] E. L. Ghisalberti, P. R. Jefferies, T. G. Payne, and G. K. Worth, *Tetrahedron*, 1973, **29**, 403.

TABLE 3

Torsion angles (deg.) for the non-hydrogen molecular skeleton; values for (II) follow those for (I)

C(15)–C(1)–C(2)–C(3)	−35.3, −32.0
C(15)–C(1)–C(2)–C(19)	−160.9, −159.8
C(1)–C(2)–C(3)–C(4)	16.5, 18.4
C(1)–C(2)–C(3)–O(3)	−162.2, −160.0
C(19)–C(2)–C(3)–C(4)	143.6, 146.0
C(19)–C(2)–C(3)–O(3)	−35.1, −32.4
C(2)–C(3)–C(4)–C(5)	136.8, 128.2
C(2)–C(3)–C(4)–C(15)	8.5, 2.3
O(3)–C(3)–C(4)–C(5)	−44.5, −53.4
O(3)–C(3)–C(4)–C(15)	−172.8, −179.3
C(3)–C(4)–C(5)–C(6)	128.3, 138.7
C(15)–C(4)–C(5)–C(6)	−110.7, −101.8
C(4)–C(5)–C(6)–C(7)	175.4, 170.8
C(4)–C(5)–C(6)–C(20)	0.0, −4.8
C(5)–C(6)–C(7)–C(8)	−63.5, −69.2
C(5)–C(6)–C(7)–O(7)	54.0, 46.1
C(20)–C(6)–C(7)–C(8)	112.4, 106.9
C(20)–C(6)–C(7)–O(7)	−130.1, −137.9
C(6)–C(7)–C(8)–C(9)	−71.5, −70.4
O(7)–C(7)–C(8)–C(9)	168.2, 169.9
C(7)–C(8)–C(9)–C(10)	157.9, 157.8
C(7)–C(8)–C(9)–C(11)	82.7, 82.4
C(8)–C(9)–C(10)–C(11)	−114.2, −114.6
C(8)–C(9)–C(10)–C(16)	140.0, 142.0
C(8)–C(9)–C(10)–C(17)	−4.6, −4.6
C(11)–C(9)–C(10)–C(11)	0.0, 0.0
C(11)–C(9)–C(10)–C(16)	−105.9, −103.5
C(11)–C(9)–C(10)–C(17)	109.6, 110.0
C(9)–C(10)–C(11)–C(9)	0.0, 0.0
C(9)–C(10)–C(11)–C(12)	107.7, 109.2
C(16)–C(10)–C(11)–C(9)	106.9, 106.7
C(16)–C(10)–C(11)–C(12)	−145.4, −144.0
C(17)–C(10)–C(11)–C(9)	−109.7, −112.4
C(17)–C(10)–C(11)–C(12)	−2.0, −3.2
C(8)–C(9)–C(11)–C(10)	112.6, 111.6
C(8)–C(9)–C(11)–C(12)	−0.6, −0.7
C(10)–C(9)–C(11)–C(10)	0.0, 0.0
C(10)–C(9)–C(11)–C(12)	−113.1, −112.3
C(9)–C(11)–C(12)–C(13)	−142.1, −139.2
C(10)–C(11)–C(12)–C(13)	147.4, 150.0
C(11)–C(12)–C(13)–C(14)	169.8, 167.7
C(11)–C(12)–C(13)–C(18)	−7.6, −9.4
C(12)–C(13)–C(14)–C(15)	−18.4, −16.6
C(12)–C(13)–C(14)–O(14)	168.2, 170.6
C(18)–C(13)–C(14)–C(15)	159.2, 160.8
C(18)–C(13)–C(14)–O(14)	−14.2, −12.1
C(13)–C(14)–C(15)–C(1)	−178.4, 169.4
C(13)–C(14)–C(15)–C(4)	−63.7, −72.4
C(13)–C(14)–C(15)–O(15)	58.0 *
O(14)–C(14)–C(15)–C(1)	−5.0, −17.6
O(14)–C(14)–C(15)–C(4)	109.7, 100.6
O(14)–C(14)–C(15)–O(15)	−128.5 *
C(3)–C(4)–C(15)–C(1)	−29.7, −21.7
C(3)–C(4)–C(15)–C(14)	−150.3, −146.2
C(3)–C(4)–C(15)–O(15)	87.0 *
C(5)–C(4)–C(15)–C(1)	−154.9, −147.8
C(5)–C(4)–C(15)–C(14)	84.5, 87.8
C(5)–C(4)–C(15)–O(15)	−38.2 *
C(2)–C(1)–C(15)–C(4)	41.0, 34.2
C(2)–C(1)–C(15)–C(14)	161.4, 156.6
C(2)–C(1)–C(15)–O(15)	−74.8 *
C(6)–C(7)–O(7)–C(21)	70.4, 74.5
C(8)–C(7)–O(7)–C(21)	−167.7, −163.8
C(22)–C(21)–O(7)–C(7)	−179.2, −179.1
O(21)–C(21)–O(7)–C(7)	0.5, 2.6

* (I) only.

and those H · · · H proton n.m.r. coupling constants which are observable (Table 4). The results of the NOE experiments on (I) [1] are of interest in the context of the structural results, predicting H(4α), C(20), and H(7α) to be on the same side of the ring, as is found. C(20) and its associated hydrogens are predicted correctly to be in close proximity to H(4α) [H(4α) · · · H(20b) 2.06(4) Å]. C(20) and H(7α) are predicted to be almost coplanar with C(6) and C(7), also correctly, their torsion angle about C(6)–C(7) being 10°. H(15) is also predicted to be in close proximity to H(5) and H(12); this latter effect is most dramatically demonstrated by the very close proximity [2.20(4) Å] of O(15) to H(12).

The introduction of O(15) exercises a considerable effect on the geometry of the skeleton; whereas the heavy-atom torsion angles from the C(7)–C(8) bond around the macrocycle to the C(13)–C(14) bond are in very good agreement (usually ±1° between values for the two derivatives, indicative of considerable rigidity in the macrocycle), considerable deviations are observed in the vicinity of the five-membered ring. The proximity of O(15) to H(12) is also reflected in the n.m.r. proton shifts of H(12); for (II), H(12) is at δ 6.09 while in (I) it is at 7.32. The close proximity of H(12) to O(15) was taken to imply the necessity of a *trans* double-bond C(12)–C(13) with O(15) and H(12) *cis*, also a correct prognosis.

TABLE 4

Observed HC–CH proton-proton n.m.r. coupling constants J/Hz,[1] tabulated with the associated H–C–C–H torsion angles (deg.). Values for (II) follow those for (I)

H–C–C–H system	Torsion angle	J
H(8α)–C(8)–C(9)–H(9α)	62.6, 49.9	4.3, 4
H(8β)–C(8)–C(9)–H(9α)	179.2, −169.6	11.9, 12.5
H(7α)–C(7)–C(8)–H(8α)	−63.6, −58.9	2.6, 3
H(7α)–C(7)–C(8)–H(8β)	179.3, −176.6	11.0, 11
H(11)–C(11)–C(12)–H(12)	175.1, −178.3	11.8, 11.5
H(4)–C(4)–C(15)–H(15)	−171.1 *	11 *
H(4)–C(4)–C(5)–H(5)	−169.7, −161.9	10, 10

* Figures refer to II only.

Crystal structures of somewhat similar compounds have been reported [6,7] but they are insufficiently similar and reported in insufficient detail to justify a detailed comparison.

[5/266 *Received, February 10th,* 1975]

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