Structural Studies in the Bruceol System

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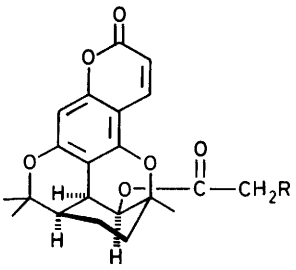
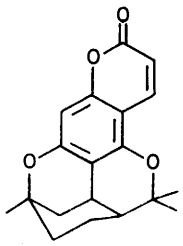
Single-crystal *X*-ray structure determinations of the chloro- and iodo-acetates of (−)-bruceol have been carried out, confirming the structure of (−)-bruceol and allowing a probable assignment of absolute configuration. The structure of (±)-deoxybruceol has also been determined.

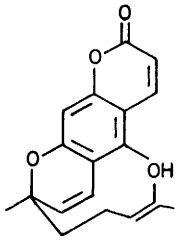
ALTHOUGH the assignment of structure to (−)-bruceol, the naturally occurring citran from *Eriostemon brucei* F. Muell (Rutaceae) rests on two independent *X*-ray studies,[1,2] its absolute configuration has not been determined. Two derivatives of the (−)-bruceol secondary alcohol function have been prepared, the chloroacetate (1) and the iodoacetate (2) and their structures determined in an attempt to establish the absolute configuration of the system. In closer examination of the extracts of *Eriostemon brucei* from which (−)-deoxybruceol had been isolated,[3] we were surprised to find a small amount of (±)-deoxybruceol, (3), m.p. 152°,



(1) R = Cl
(2) R = I



(3)



(4)

$[\alpha]_D$ −5°. An *X*-ray study of this compound has also been carried out, confirming the previous finding[2] regarding the orientation of the *p*-menthane segment of the coumarin ring. Of the various hypotheses that can be put forward to rationalize the occurrence of (±)-deoxybruceol, the more attractive one is that it arises by non-enzymatic cyclization of a small amount of an intermediate achiral chromen [*e.g.* (4)] or an immediate precursor, as has been previously described.[2] In this event (±)-isodeoxybruceol should have been present, but this could have been lost during crystallization as only a small amount would be formed.[2]

EXPERIMENTAL

(−)-*Bruceol Chloroacetate* (1).—A solution of chloroacetyl chloride (5 ml) in dry benzene (10 ml) was added dropwise to a stirred ice-cooled solution of (−)-bruceol (400 mg), pyridine (0.1 ml), and dry benzene (10 ml) and left for 2.5 h. The mixture was poured into aqueous 8% $NaHCO_3$ (100 ml) and the organic layer was separated, washed with aqueous 8% $NaHCO_3$ and water, and then dried. The product obtained was crystallised from dichloromethane–light petroleum and then from ethanol to give the chloroacetate (1) (336 mg) as light yellow *prisms*, m.p. 243—245°, $[\alpha]_D$ −313° (*c* 0.3, $CHCl_3$) (Found: C, 62.5; H, 5.4. $C_{21}H_{21}ClO_6$ requires C, 62.3; H, 5.2%), δ (60 MHz; $CDCl_3$) 1.08, 1.42, and 1.56 (s, tertiary Me), 2.92br (s, benzylic H), 4.08 (s, CH_2Cl), 5.15 (d, *J* 3 Hz, acetoxymethine H), 6.15 and 7.90 (AB q, *J* 10 Hz, vinylic H), and 6.40 (s, aromatic H), *m/z* 406 (M^+, 7%), 404 (M^+, 21), 360 (36), 323 (8), 321 (24), 310 (8), 295 (11), 245 (10), 229 (17), 191 (5), 181 (16), 149 (6), and 91 (100).

(−)-*Bruceol Iodoacetate* (2).—(−)-Bruceol chloroacetate (1) (350 mg) in dry acetone (35 ml) was treated with KI (1.1 g) and refluxed for 4 h. The compound isolated was recrystallized from ethanol as needles of the *iodoacetate*, m.p. 179—180° (Found: C, 50.8; H, 4.5. $C_{21}H_{21}IO_6$ requires C, 50.8; H, 4.25%).

The general crystallographic procedure has been outlined in the preceding paper;[4] abnormalities and difficulties specific to each compound are discussed below.†

Crystal Data.—(1), $C_{21}H_{21}ClO_6$, M = 404.9. Monoclinic, space group $P2_1$ (C_2^2, No. 4), a = 11.407(3), b = 7.654(3), c = 11.139(7) Å, β = 95.49(4)°, U = 968.1(7) Å^3, D_m = 1.37(1) g cm^{-3}, D_c = 1.38 g cm^{-3}, Z = 2. $F(000)$ = 424. μ_{Mo} = 2.32 cm^{-1}. $2\theta_{max.}$ = 45°. N = 1 387, N_o = 931, R = 0.038, R' = 0.040.

(2), $C_{21}H_{21}IO_6$, M = 496.3. Hexagonal, space group $P6_122$ (D_6^2, No. 178), a = 11.901(3), c = 49.89(1) Å, U = 6 120(4) Å^3. D_m = 1.61(1) g cm^{-3}, D_c = 1.62 g cm^{-3}, Z = 12. $F(000)$ = 2 976, μ_{Mo} = 15.1 cm^{-1}. $2\theta_{max.}$ = 40°. N = 1 248, N_o = 1 019, R = 0.034, R' = 0.042.

(3), $C_{19}H_{20}O_4$, M = 312.4. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 14.948(5), b = 10.757(4), c = 10.449(4) Å, α = 100.91(3), β = 96.23(3), γ = 103.92(3)°, U = 1 580(1) Å^3, D_m = 1.32(1) g cm^{-3}, D_c = 1.31 g cm^{-3}, Z = 4. $F(000)$ = 664. μ_{Mo} = 0.98 cm^{-1}. $2\theta_{max.}$ = 45°. N = 4 162, N_o = 2 640, R = 0.056, R' = 0.058.

Abnormal Features.—In attempting to assign the absolute configuration (1) was obtained preparatively more readily than (2) and an initial attempt made on that compound;

† See also Supplementary Publication No. SUP 22969 (33 pp.). For details, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 2*, 1979 Index Issue.

TABLE 1

Atomic co-ordinates of (1) and (2). Fractional cell parameters (x,y,z), $\times 10^3$, H; $\times 10^4$, others

(1)

Atom	x	y	z
O(1)	3 610(4)	−3 918(6)	6 664(3)
C(2)	4 453(6)	−5 182(11)	6 968(6)
O(2)	4 815(5)	−5 178(9)	8 043(4)
C(3)	4 772(7)	−6 311(13)	6 053(7)
H(3)	531(6)	−716(11)	640(6)
C(4)	4 295(7)	−6 209(11)	4 934(6)
H(4)	447(6)	−711(10)	431(6)
C(5)	3 443(5)	−4 885(10)	4 611(5)
C(6)	2 867(5)	−4 688(9)	3 432(5)
O(6)	3 054(3)	−5 916(6)	2 583(3)
C(7)	2 098(5)	−3 358(10)	3 174(5)
C(8)	1 372(6)	−3 166(11)	1 990(6)
H(8)	135(5)	−181(10)	174(5)
C(81)	2 108(5)	−6 067(10)	1 589(5)
C(82)	2 663(8)	−7 355(15)	0 763(8)
H(82a)	324(6)	−678(12)	042(7)
H(82b)	220(6)	−754(11)	006(6)
H(82c)	293(6)	−861(11)	126(6)
C(9)	0 144(5)	−3 698(10)	2 256(6)
H(9)	−043(5)	−370(9)	152(5)
C(10)	1 843(6)	−4 310(9)	1 038(6)
H(10)	119(5)	−448(8)	033(5)
O(10)	2 900(3)	−3 566(7)	0 610(3)
C(11)	0 971(6)	−6 815(10)	2 020(7)
H(11a)	052(5)	−722(9)	123(5)
H(11b)	111(5)	−801(10)	247(5)
C(12)	0 217(6)	−5 612(9)	2 742(6)
H(12a)	−066(5)	−612(9)	275(5)
H(12b)	047(5)	−550(8)	378(5)
C(13)	−0 316(5)	−2 319(10)	3 103(6)
C(131)	−0 892(7)	−0 797(12)	2 387(7)
H(131a)	−166(6)	−122(11)	201(6)
H(131b)	−041(5)	−033(10)	169(6)
H(131c)	−104(6)	036(11)	296(6)
C(132)	−1 147(7)	−3 019(12)	3 979(7)
H(132a)	−059(5)	−383(10)	456(5)
H(132b)	−181(5)	−378(10)	360(5)
H(132c)	−135(6)	−207(10)	451(6)
O(14)	0 678(3)	−1 445(6)	3 863(4)
C(15)	1 668(5)	−2 425(10)	4 114(5)
C(16)	2 184(6)	−2 557(10)	5 285(6)
H(16)	194(5)	−189(9)	586(5)
C(17)	3 087(5)	−3 752(9)	5 491(5)
C(18)	2 724(6)	−2 285(10)	−0 236(5)
O(18)	1 781(4)	−1 774(8)	−0 626(5)
C(19)	3 917(6)	−1 702(13)	−0 572(6)
H(19a)	435(6)	−280(10)	−093(6)
H(19b)	440(5)	−128(10)	016(6)
Cl	3 782(2)	0 000(—) *	−1 626(2)

(2)

Atom	x	y	z
O(1)	6 819(7)	0 953(6)	8 324(1)
C(2)	5 683(10)	0 857(10)	8 235(2)
O(2)	4 929(8)	−0 148(8)	8 115(1)
C(3)	5 470(10)	1 930(10)	8 295(2)
H(3)	466(—)	190(—)	823(—)
C(4)	6 376(10)	2 971(9)	8 434(2)
H(4)	625(—)	373(—)	848(—)
C(5)	7 532(9)	3 042(9)	8 516(2)
C(6)	8 526(9)	4 091(8)	8 663(1)
O(6)	8 254(6)	5 018(6)	8 756(1)
C(7)	9 678(9)	4 176(8)	8 716(1)
C(8)	10 736(8)	5 259(9)	8 869(1)
H(8)	1 157(—)	559(—)	878(—)
C(81)	9 046(10)	5 767(10)	8 983(1)
C(82)	8 640(11)	6 778(10)	9 026(2)
H(82a)	915(—)	738(—)	917(—)
H(82b)	887(—)	737(—)	887(—)
H(82c)	776(—)	650(—)	906(—)
C(9)	10 744(9)	4 619(9)	9 137(2)
H(9)	1 134(—)	527(—)	926(—)
C(10)	10 464(9)	6 336(9)	8 908(1)
H(10)	1 095(—)	685(—)	907(—)

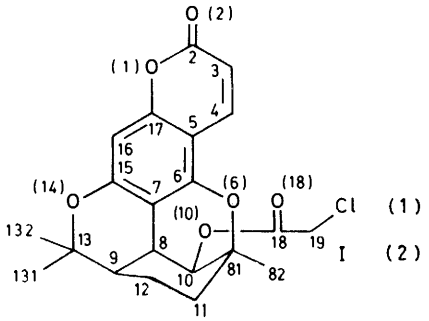
TABLE 1 (*continued*)

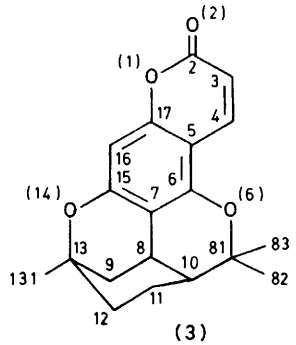
(2)

Atom	x	y	z
O(10)	10 690(6)	7 104(6)	8 674(1)
C(11)	8 814(9)	4 954(10)	9 247(2)
H(11a)	915(—)	566(—)	940(—)
H(11b)	786(—)	446(—)	928(—)
C(12)	9 389(10)	4 052(9)	9 261(2)
H(12a)	938(—)	376(—)	944(—)
H(12b)	881(—)	327(—)	915(—)
C(13)	11 214(9)	3 632(9)	9 073(2)
C(131)	12 675(10)	4 296(11)	9 059(2)
H(131a)	1 294(—)	491(—)	891(—)
H(131b)	1 307(—)	477(—)	922(—)
H(131c)	1 296(—)	370(—)	902(—)
C(132)	10 715(10)	2 521(10)	9 274(2)
H(132a)	1 094(—)	281(—)	945(—)
H(132b)	977(—)	205(—)	926(—)
H(132c)	1 096(—)	188(—)	923(—)
O(14)	10 752(6)	2 997(6)	8 809(1)
C(15)	9 742(9)	3 032(9)	8 693(1)
C(16)	8 805(9)	1 959(10)	8 557(2)
H(16)	892(—)	122(—)	852(—)
C(17)	7 789(9)	2 038(9)	8 460(2)
C(18)	11 911(10)	8 078(9)	8 628(2)
O(18)	12 800(7)	8 277(7)	8 771(1)
C(19)	11 950(11)	8 849(10)	8 391(2)
H(19a)	1 275(—)	913(—)	829(—)
H(19b)	1 125(—)	833(—)	826(—)
I	11 801.8(9)	10 474.5(8)	8 523.7(2)

* Defines origin.

subsequently (2) also became available and both determinations proceeded. In the case of (1), a unique data set was measured to $2\theta_{max.}$ 45°, with an accompanying set of 'Friedel pairs' to $2\theta_{max.}$ 25°. The small contribution of f'' in this case did not allow the definition of a set of individually significant Friedel pair sets to be selected; refinement on the unique data set in the chirality presented resulted in residuals R, R', and S of 0.038, 0.040, and 1.28. Refinement in the alternative chirality yielded residuals 0.039, 0.041, and 1.30. For (2), difficulties were also encountered





(3)

SCHEME

by virtue of the very long cell axis; data were measured within the limit $2\theta_{max.}$ 40° for a unique data set together with a similar set of ' Friedel pairs '. The ω-scan technique was used; nevertheless, significant overlap was found for 15 reflections which were deleted from both $\{hkl\}$ and $\{\bar{h}\bar{k}\bar{l}\}$. The structure was refined to convergence in both chiralities in both $\{hkl\}$ and $\{\bar{h}\bar{k}\bar{l}\}$, yielding residuals R, R', and S of 0.034, 0.042, and 1.21 ($\{hkl\}$, presented chirality); 0.036, 0.045, and 1.31 ($\{\bar{h}\bar{k}\bar{l}\}$, presented chirality); 0.037, 0.045, and 1.32 ($\{hkl\}$, alternative chirality), 0.040, 0.050, and 1.43 ($\{\bar{h}\bar{k}\bar{l}\}$, alternative chirality). The chirality resulting from the two determinations is thus consistent and also consistent with that of compound (3) presented in the previous paper; nevertheless, all absolute configuration determinations presented in these two papers have been carried out under somewhat non-ideal conditions and should further derivatives of suitable crystalline form present themselves on a future occasion, the opportunity should be taken to carry out an independent check. Axial systems in all diagrams are right-handed.

Non-hydrogen atom numbering is as in the Scheme, hydrogen atom numbering following that of the parent carbon, suffixed a—c for distinguishing purposes where necessary.

TABLE 2

Atomic co-ordinates of (3). Fractional cell parameters (x,y,z), × 10^3, H; × 10^4, C,O

Molecule	1		
Atom	x	y	z
O(1)	8 105(2)	5 377(3)	7 456(3)
C(2)	7 742(3)	4 255(4)	7 896(5)
O(2)	8 255(2)	3 556(3)	8 016(4)
C(3)	6 798(3)	4 032(5)	8 146(5)
H(3)	657(3)	332(4)	847(4)
C(4)	6 295(3)	4 888(4)	7 998(4)
H(4)	566(3)	469(4)	817(4)
C(5)	6 684(3)	6 052(4)	7 581(4)
C(6)	6 233(3)	7 032(4)	7 404(4)
O(6)	5 306(2)	6 812(3)	7 485(3)
C(7)	6 690(3)	8 185(4)	7 100(4)
C(8)	6 141(3)	9 166(4)	6 967(5)
H(8)	594(2)	943(3)	775(3)
C(81)	4 709(3)	7 322(4)	6 584(4)
C(82)	4 132(4)	7 948(7)	7 487(4)
H(82a)	384(3)	736(4)	798(4)
H(82b)	450(3)	867(5)	814(5)
H(82c)	365(4)	815(5)	693(5)
C(83)	4 094(4)	6 139(6)	5 579(7)
H(83a)	443(4)	564(5)	511(5)
H(83b)	375(3)	558(4)	598(4)
H(83c)	363(3)	643(5)	498(5)
C(9)	6 728(3)	10 340(4)	6 556(5)
H(9a)	632(3)	1 093(4)	626(4)
H(9b)	721(3)	1 094(4)	735(4)
C(10)	5 296(3)	8 361(4)	5 940(4)
H(10)	493(3)	895(4)	573(4)
C(11)	5 649(3)	7 847(5)	4 677(5)
H(11a)	514(3)	759(4)	388(4)
H(11b)	591(3)	709(4)	483(4)
C(12)	6 432(4)	8 888(5)	4 314(5)
H(12a)	615(3)	948(4)	390(4)
H(12b)	675(3)	844(4)	365(4)
C(13)	7 185(3)	9 825(4)	5 429(4)
C(131)	7 789(4)	10 909(6)	4 918(7)
H(131a)	835(3)	1 147(4)	569(5)
H(131b)	811(4)	1 061(5)	423(6)
H(131c)	741(4)	1 148(5)	459(5)
O(14)	7 858(2)	9 154(3)	5 923(3)
C(15)	7 525(3)	8 239(4)	6 623(4)
C(16)	8 016(3)	7 307(4)	6 770(5)
H(16)	861(3)	734(3)	651(4)
C(17)	7 599(3)	6 268(4)	7 292(4)

TABLE 2 (*continued*)

Molecule	2		
Atom	x	y	z
O(1)	5 665(2)	7 156(3)	1 084(3)
C(2)	5 500(3)	8 312(4)	0 846(4)
O(2)	4 728(2)	8 441(3)	0 939(3)
C(3)	6 263(3)	9 233(4)	0 529(4)
H(3)	613(3)	995(4)	028(4)
C(4)	7 111(3)	9 018(5)	0 528(4)
H(4)	765(3)	964(4)	031(4)
C(5)	7 278(3)	7 838(4)	0 806(4)
C(6)	8 130(3)	7 509(4)	0 825(4)
O(6)	8 920(2)	8 400(3)	0 703(3)
C(7)	8 218(3)	6 322(4)	1 047(4)
C(8)	9 183(3)	6 146(4)	1 124(5)
H(8)	940(3)	620(4)	030(4)
C(81)	9 762(3)	8 585(4)	1 714(5)
C(82)	10 580(4)	8 890(7)	0 977(7)
H(82a)	1 051(3)	809(4)	014(4)
H(82b)	1 059(3)	960(5)	061(5)
H(82c)	1 118(4)	910(5)	160(5)
C(83)	9 774(5)	9 770(6)	2 791(8)
H(83a)	982(3)	1 049(5)	243(5)
H(83b)	919(3)	954(4)	321(4)
H(83c)	1 038(5)	996(6)	352(6)
C(9)	9 189(4)	4 814(5)	1 427(6)
H(9a)	887(2)	413(4)	062(4)
H(9b)	984(3)	479(4)	167(4)
C(10)	9 750(3)	7 313(5)	2 235(5)
H(10)	1 039(3)	726(4)	239(4)
C(11)	9 331(4)	7 200(5)	3 501(5)
H(11a)	875(3)	744(4)	348(4)
H(11b)	978(3)	785(4)	432(4)
C(12)	9 138(4)	5 806(6)	3 745(6)
H(12a)	877(3)	572(4)	445(4)
H(12b)	975(4)	562(5)	405(5)
C(13)	8 673(3)	4 662(5)	2 567(5)
C(131)	8 616(5)	3 345(8)	2 946(10)
H(131a)	825(4)	329(5)	363(6)
H(131b)	828(4)	259(6)	213(6)
H(131c)	929(4)	327(4)	317(4)
O(14)	7 682(2)	4 601(3)	2 154(3)
C(15)	7 518(3)	5 567(4)	1 549(4)
C(16)	6 643(3)	5 813(5)	1 509(5)
H(16)	611(3)	524(4)	175(4)
C(17)	6 539(3)	6 921(4)	1 103(4)

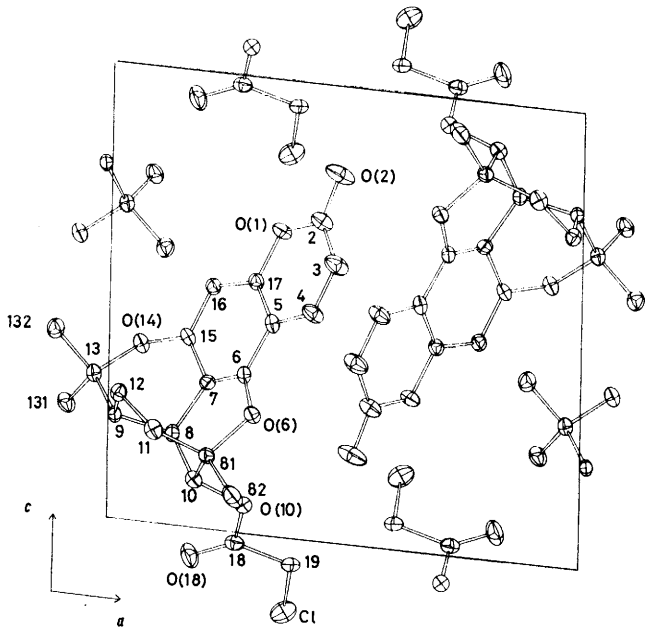


FIGURE 1 Unit cell-contents of (1) projected down b, showing non-hydrogen atoms with 20% thermal ellipsoids and labelling

TABLE 3

Molecular geometries (non-hydrogen atoms) of (1)—(3)

Compound/molecule	(1)	(2)	(3)/1	(3)/2
Distances (Å)				
O(1)–C(2)	1.383(9)	1.37(2)	1.382(6)	1.386(6)
O(1)–C(17)	1.390(7)	1.40(1)	1.380(6)	1.388(5)
C(2)–O(2)	1.228(8)	1.23(2)	1.209(6)	1.206(6)
C(2)–C(3)	1.411(12)	1.45(3)	1.434(7)	1.433(6)
C(3)–C(4)	1.314(10)	1.36(1)	1.342(8)	1.343(7)
C(4)–C(5)	1.426(10)	1.40(2)	1.416(6)	1.425(7)
C(5)–C(6)	1.419(8)	1.42(2)	1.411(7)	1.401(6)
C(5)–C(17)	1.397(9)	1.40(2)	1.407(6)	1.398(6)
C(6)–C(7)	1.357(9)	1.35(2)	1.376(6)	1.375(7)
C(6)–O(6)	1.364(8)	1.38(2)	1.363(5)	1.366(5)
O(6)–C(81)	1.475(7)	1.46(1)	1.495(6)	1.501(5)
C(7)–C(8)	1.496(8)	1.49(1)	1.502(7)	1.494(7)
C(7)–C(15)	1.395(9)	1.41(2)	1.386(6)	1.379(6)
C(8)–C(9)	1.515(9)	1.54(1)	1.518(7)	1.527(8)
C(8)–C(10)	1.513(10)	1.48(2)	1.525(5)	1.538(6)
C(81)–C(10)	1.496(10)	1.52(1)	1.554(6)	1.562(7)
C(81)–C(82)	1.527(12)	1.52(2)	1.517(8)	1.517(9)
C(81)–C(11)	1.537(10)	1.57(1)		
C(81)–C(83)			1.513(6)	1.528(8)
C(9)–C(12)	1.561(10)	1.53(1)		
C(9)–C(13)	1.540(10)	1.56(2)	1.506(7)	1.502(8)
C(10)–O(10)	1.455(8)	1.42(1)		
C(10)–C(11)			1.530(7)	1.537(8)
C(11)–C(12)	1.539(11)	1.54(2)	1.547(7)	1.533(9)
C(12)–C(13)			1.538(6)	1.530(7)
C(13)–O(14)	1.506(7)	1.48(1)	1.476(6)	1.479(6)
C(13)–C(131)	1.525(11)	1.51(1)		
C 13)–C(132)	1.521(11)	1.52(1)		
O(14)–C(15)	1.362(8)	1.35(1)	1.366(8)	1.370(6)
C(15)–C(16)	1.382(9)	1.38(1)	1.399(7)	1.394(7)
C(16)–C(17)	1.381(10)	1.35(2)	1.379(7)	1.375(7)
O(10)–C(18)	1.361(8)	1.35(1)		
C(18)–O(18)	1.187(8)	1.20(1)		
C(18)–C(19)	1.513(10)	1.49(1)		
C(19)–Cl,I	1.751(9)	2.13(1)		
Angles (°)				
C(17)–O(1)–C(2)	121.4(5)	124(1)	122.1(3)	122.3(3)
O(1)–C(2)–O(2)	113.4(7)	117(1)	116.1(4)	116.3(4)
O(1)–C(2)–C(3)	118.2(6)	117(1)	117.0(4)	116.8(4)
O(2)–C(2)–C(3)	128.4(8)	126(1)	126.8(5)	126.9(5)
C(2)–C(3)–C(4)	122.5(8)	120(1)	121.8(5)	121.6(5)
C(3)–C(4)–C(5)	119.5(7)	121(1)	120.6(4)	120.9(4)
C(4)–C(5)–C(6)	123.5(6)	124(1)	126.0(4)	125.7(4)
C(4)–C(5)–C(17)	120.0(6)	121(1)	118.5(4)	118.3(4)
C(6)–C(5)–C(17)	116.3(6)	114(1)	115.5(3)	116.0(4)
C(5)–C(6)–O(6)	118.7(6)	117(1)	119.1(4)	120.5(4)
C(5)–C(6)–C(7)	120.5(6)	122(1)	122.1(4)	121.9(4)
O(6)–C(6)–C(7)	120.7(5)	121(1)	118.8(4)	117.5(4)
C(6)–O(6)–C(81)	115.0(5)	114(1)	118.6(3)	115.8(3)
C(6)–C(7)–C(8)	123.5(6)	124(1)	117.1(4)	115.7(4)
C(6)–C(7)–C(15)	119.5(5)	117(1)	118.3(4)	118.5(4)
C(8)–C(7)–C(15)	114.0(6)	117(1)	122.7(4)	123.0(4)
C(7)–C(8)–C(10)	110.9(6)	111(1)	102.6(3)	102.9(4)
C(7)–C(8)–C(9)	104.2(5)	103(1)	110.4(4)	110.3(4)
C(10)–C(8)–C(9)	112.2(6)	112(1)	114.1(4)	113.2(4)
O(6)–C(81)–C(82)	100.8(5)	103(1)	103.6(4)	104.3(4)
O(6)–C(81)–C(10)	100.0(5)	108(1)	112.3(3)	111.9(3)
O(6)–C(81)–C(11)	111.9(5)	114(1)		
O(6)–C(81)–C(83)			106.6(4)	105.8(4)
C(82)–C(81)–C(10)	114.4(6)	114(1)		
C(82)–C(81)–C(11)	111.0(7)	110(1)		
C(83)–C(81)–C(10)				
C(10)–C(81)–C(11)	108.6(5)	107(1)		
C(83)–C(81)–C(82)			110.8(4)	111.1(4)
C(8)–C(9)–C(12)	107.5(5)	108(1)		
C(8)–C(9)–C(13)	108.1(6)	107(1)	107.7(4)	107.7(5)
C(12)–C(9)–C(13)	116.2(5)	116(1)		
C(8)–C(10)–C(81)	107.7(5)	109(1)	107.3(4)	106.8(4)
C(8)–C(10)–O(10)	111.4(6)	113(1)		
C(81)–C(10)–O(10)	110.2(5)	107(1)		
C(8)–C(10)–C(11)			108.1(4)	108.1(4)
C(81)–C(10)–C(11)			117.0(4)	116.9(4)
C(10–C(11)–C(12)			113.5(4)	112.6(5)
C(81)–C(11)–C(12)	118.1(6)	118(1)		
C(11)–C(12)–C(9)	113.2(6)	114(1)		
C(11)–C(12)–C(13)			118.6(4)	117.6(5)
C(12)–C(13)–C(9)			109.5(4)	109.3(4)
C(9)–C(13)–O(14)	111.5(5)	113(1)	108.8(4)	109.1(4)
C(12)–C(13)–O(14)			111.4(4)	112.0(4)
C(9)–C(13)–C(131)	111.0(5)	111(1)	112.9(4)	112.5(5)
C(12)–C(13)–C(131)			110.9(4)	110.9(5)
C(9)–C(13)–C(132)		113(1)		
O(14)–C(13)–C(131)	102.6(5)	105(1)	103.3(4)	103.0(4)
O(14)–C(13)–C(132)	106.1(5)	105(1)		
C(131)–C(13)–C(132)	109.0(6)	109(1)		
C(13)–O(14)–C(15)	115.8(5)	118(1)	116.0(3)	116.3(3)
O(14)–C(15)–C(7)	118.1(5)	118(1)	120.7(4)	120.7(4)
C(7)–C(15)–C(16)	121.5(6)	122(1)	120.8(4)	120.7(5)
O(14)–C(15)–C(16)	120.3(6)	120(1)	118.3(4)	118.6(4)
C(15)–C(16)–C(17)	116.7(6)	117(1)	117.7(4)	117.7(4)
C(16)–C(17)–O(1)	117.6(6)	118(1)	116.6(4)	116.8(4)
C(16)–C(17)–C(5)	123.8(6)	125(1)	123.3(4)	123.2(4)
O(1)–C(17)–C(5)	118.4(6)	117(1)	120.0(4)	119.9(4)
C(10)–O(10)–C(18)	115.9(5)	118(1)		
O(10)–C(18)–O(18)	124.0(6)	122(1)		
O(10)–C(18)–C(19)	107.9(5)	111(1)		
O(18)–C(18)–C(19)	128.1(7)	127(1)		
C(18)–C(19)–Cl,I	111.2(5)	109(1)		

TABLE 4

Least-squares planes for (1)—(3). Least-squares planes defined by the conjugated fragments in the form $pX + qY + rZ = s$. The R.H. orthogonal Å frame is defined with X parallel to a, Z in the ac plane. σ (defining atoms) and atom deviations, δ, are in Å

Compound/molecule	(1)	(2)	(3)/1	(3)/2
10^4p	7 145	−2 736	1 626	0 518
10^4q	−6 672	−4 300	5 112	4 962
10^4r	−2 104	8 604	8 439	8 667
s	−1.169	33.27	9.832	3.586
σ	0.10	0.11	0.13	0.12
δ (defining atoms)				
O(1)	−0.05	−0.03	0.05	−0.11
C(2)	0.00	−0.02	0.02	0.00
O(2)	0.04	−0.01	0.05	0.06
C(3)	0.04	0.01	−0.05	0.05
C(4)	0.03	0.02	−0.06	0.05
C(5)	−0.05	−0.03	0.00	−0.03
C(6)	−0.05	−0.01	0.04	−0.04
O(6)	0.16	0.22	0.02	0.17
C(7)	−0.18	−0.18	0.19	−0.19
C(8)	−0.05	−0.17	0.22	−0.09
O(14)	0.21	0.20	−0.26	0.27
C(15)	−0.02	0.02	0.00	−0.01
C(16)	−0.01	0.04	−0.02	−0.04
C(17)	−0.07	−0.07	0.04	−0.09
δ (other atoms)				
C(9)	1.30	1.15	0.34	−0.21
C(81)	0.70	0.73	−0.98	1.19
C(82)	0.65	0.76	−0.16	0.68
C(83)			−2.32	2.50
C(10)	−0.15	−0.22	−1.09	1.28
C(11)	2.15	2.16	−2.24	2.35
C(12)	2.37	2.29	−2.06	2.15
C(13)	1.23	1.00	−0.66	0.73

DISCUSSION

Structural Commentary.—The absolute configuration determination aside, new structural information arising out of the present study is minimal. In regard to the geometry of bruceol itself, the earlier study [2] is of superior precision, being carried out in the absence of a heavy atom. The present study of (±)-deoxybruceol is superior in precision to that of ref. 2 for the same reason,

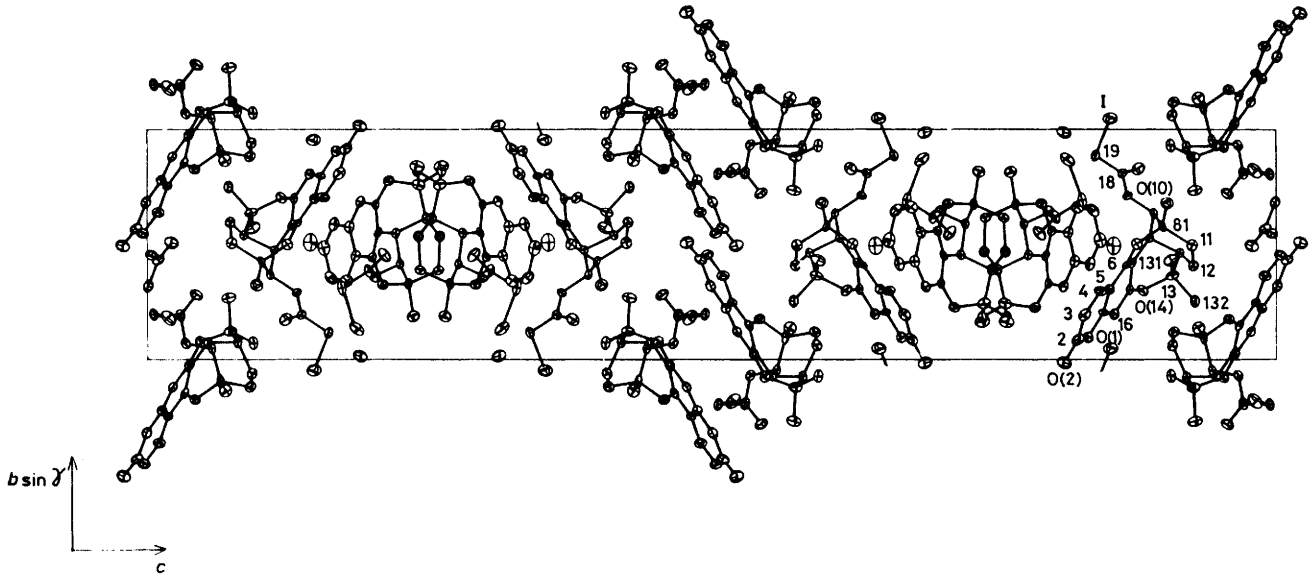


FIGURE 2 Unit-cell contents of (2) projected down *a*

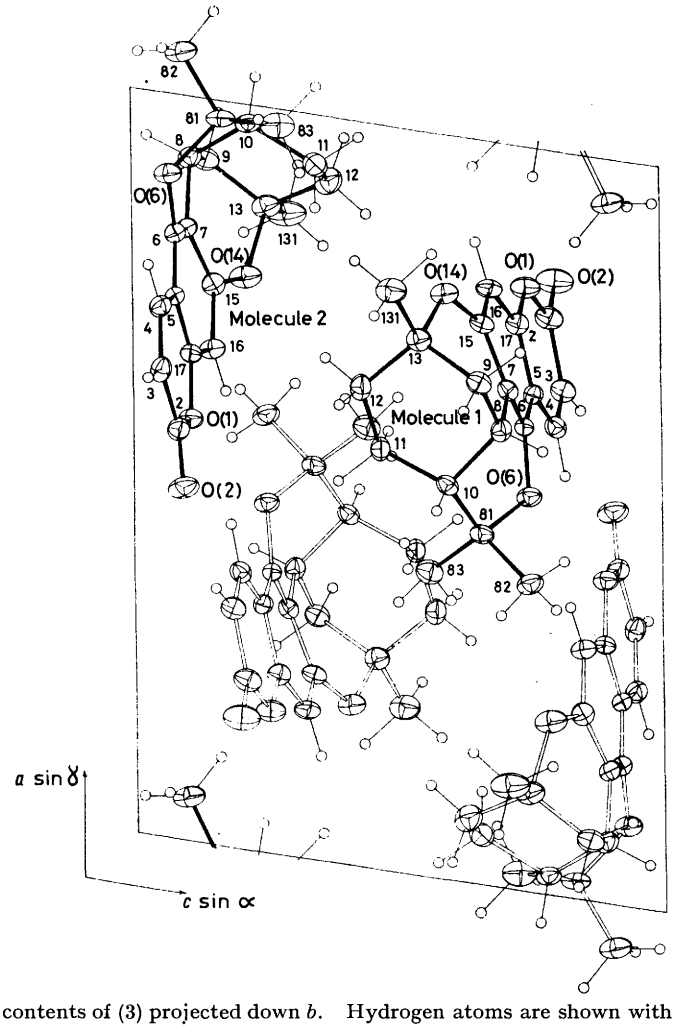


FIGURE 3 Unit-cell contents of (3) projected down *b*. Hydrogen atoms are shown with arbitrary radii of 0.1 Å

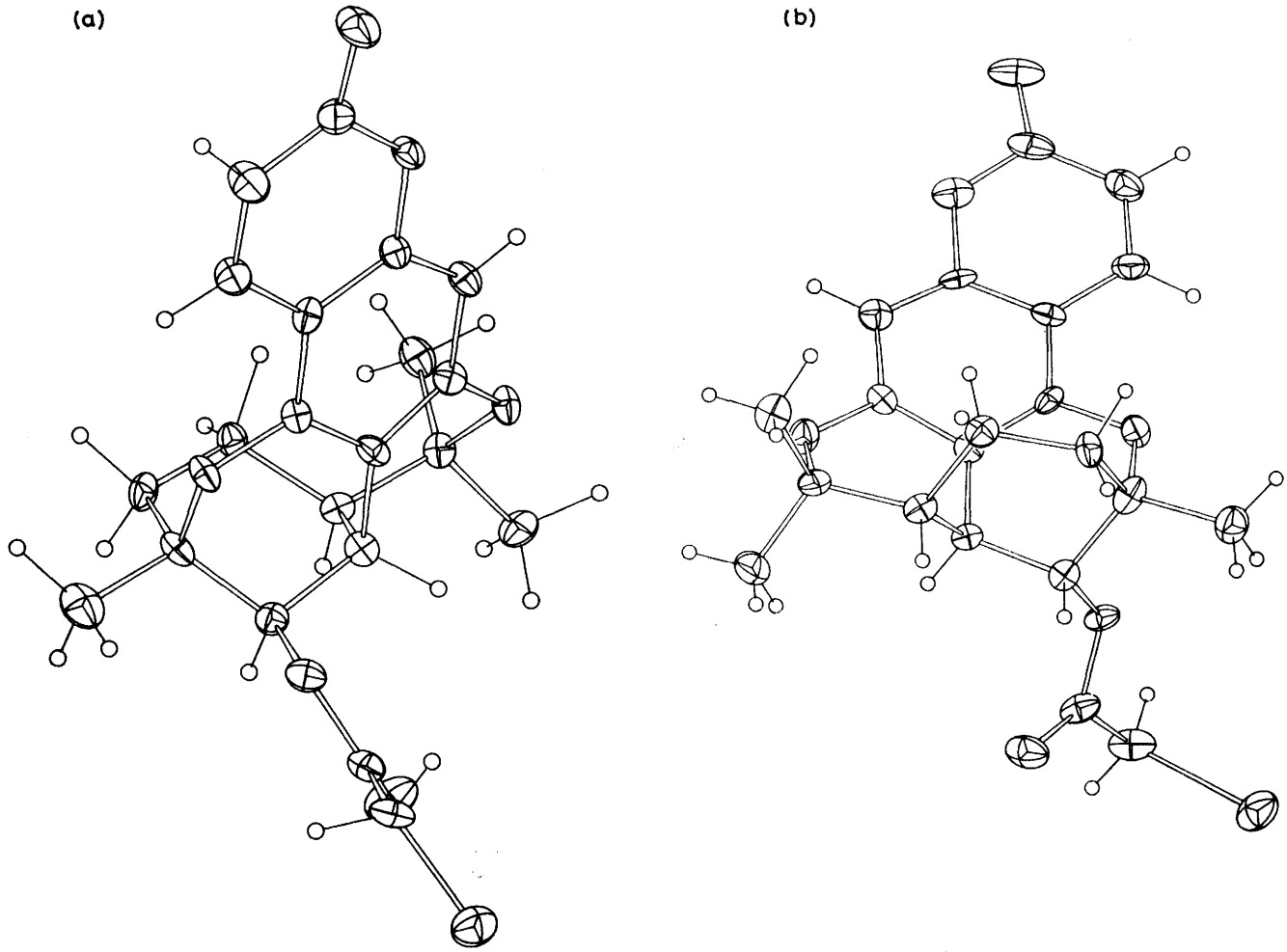


FIGURE 4 Individual molecules of compound (1)(a) and (2)(b)

TABLE 5

Torsion angles for (1)—(3). Torsion angles (°) within the fused alicyclic portion of the skeleton are given for compounds (1); (2); and (3), molecules 1,2, respectively

Atoms	Angles
C(6)–C(7)–C(15)–C(16)	14.1, 16.7; −16.7, 16.7
C(8)–C(7)–C(15)–C(16)	175.2, 179.3; 179.9, 176.9
C(6)–C(7)–C(15)–O(14)	−162.3, −163.3; 159.0, −160.2
C(8)–C(7)–C(15)–O(14)	−1.1, −0.6; −4.4, 0.0
O(6)–C(6)–C(7)–C(8)	2.7, −1.4; 3.9, −0.2
C(5)–C(6)–C(7)–C(8)	−173.8, −179.8; −178.6, −176.2
O(6)–C(6)–C(7)–C(15)	161.9, 159.8; −160.4, 161.4
C(5)–C(6)–C(7)–C(15)	−14.6, −18.6; 17.0, −14.6
C(81)–O(6)–C(6)–C(5)	155.7, 157.5; −143.5, 130.5
C(81)–O(6)–C(6)–C(7)	−20.9, −20.9; 34.1, −45.6
C(6)–C(7)–C(8)–C(9)	105.2, 108.9; −176.8, 177.7
C(6)–C(7)–C(8)–C(10)	−15.8, −11.2; −54.9, 56.7
C(15)–C(7)–C(8)–C(9)	−55.0, −52.5; −13.2, 17.1
C(15)–C(7)–C(8)–C(10)	−176.0, −172.6; 108.8, −104.0
C(7)–C(8)–C(10)–C(81)	44.8, 43.1; 67.9, −66.9
C(9)–C(8)–C(10)–C(81)	−71.4, −71.8; −172.8, 174.1
C(7)–C(8)–C(10)–C(11),-O(10)	−76.0, −76.3; −59.2, 59.8
C(9)–C(8)–C(10)–C(11),-O(10)	167.7, 168.8; 60.2, −59.3
O(6)–C(81)–C(10)–C(8)	−63.9, −65.2; −36.1, 27.4
O(6)–C(81)–C(10)–O(10),-C(11)	57.7, 57.8; 85.5, −93.8
C(82)–C(81)–C(10)–C(8)	−176.5, −179.5; 78.9, −87.8
C(82)–C(81)–C(10)–O(10),C(11)	−54.9, −56.5; −159.5, 151.0
C(11), C(83)–C(81)–C(10)–C(8)	58.8, 58.6; −156.6, 147.2
C(11), C(83)–C(81)–C(10)–O(10), C(11)	−179.6, −178.4; −35.1, 26.0

TABLE 5 (*continued*)

Atoms	Angles
C(12)–C(11)–C(81)–O(6)	75.3, 75.1
C(12)–C(11)–C(81)–C(82)	−173.1, −169.2
C(12)–C(11)–C(81)–C(10)	−46.3, −44.9
C(12)–C(11)–C(10)–C(8)	−43.3, 45.9
C(12)–C(11)–C(10)–C(81)	−164.5, 166.4
C(81), C(10)–C(11)–C(12)–C(9), C(13)	39.4, 39.6; 39.5, −44.5
C(7)–C(8)–C(9)–C(13)	67.1, 67.6; 47.0, −48.3
C(7)–C(8)–C(9)–C(12)	−59.0, −58.0
C(10)–C(8)–C(9)–C(13)	−172.7, −172.9; −67.9, 66.5
C(10)–C(8)–C(9)–C(12)	61.3, 61.6
C(8)–C(9)–C(13)–O(14)	−27.4, −35.3; −66.4, 65.2
C(12)–C(9)–C(13)–C(131)	−153.0, −157.4
C(8)–C(9)–C(13)–C(12)	55.5, −57.5
C(8)–C(9)–C(13)–C(131)	86.3, 82.6; 179.6, 178.9
C(8)–C(9)–C(13)–C(132)	−148.4, −153.8
C(12)–C(9)–C(13)–C(132)	−27.7, −33.8
C(12)–C(9)–C(13)–O(14)	93.3, 84.7
C(9)–C(13)–O(14)–C(15)	−28.7, −18.2; 50.7, −49.8
C(12)–C(13)–O(14)–C(15)	−70.1, 71.2
C(131)–C(13)–O(14)–C(15)	−147.5, −139.7; 170.8, −169.6
C(132)–C(13)–O(14)–C(15)	97.2, 104.8
C(13)–O(14)–C(15)–C(7)	45.6, 38.9; −14.9, 16.6
C(13)–O(14)–C(15)–C(16)	−130.8, −141.1; 161.0, −160.3
C(6)–O(6)–C(81)–C(10)	52.5, 53.8; −15.6, 28.9
C(6)–O(6)–C(81)–C(82)	173.7, 174.8; −134.6, 147.3
C(6)–O(6)–C(81)–C(11),-C(83)	−68.4, −65.6; 108.5, −95.4
C(11)–C(12)–C(9)–C(8)	−43.7, −44.1
C(11)–C(12)–C(9)–C(13)	−164.8, −163.7
C(11)–C(12)–C(13)–C(9)	−45.2, 50.0
C(11)–C(12)–C(13)–C(131)	−170.5, 174.6
C(11)–C(12)–C(13)–O(14)	75.1, −70.9

but in the case of both molecules the essential structural features already discussed [2] are confirmed. Attention is drawn to the fact that the pictorial representations of (−)-bruceol in ref. 2 are of opposite chirality to the present.

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