Acta Cryst. (1985). C**41**, 1272–1274

Structure of 3,3,5-Trimethyl-4-(3-oxo-1-butenyl)-4,5-epoxycyclohexyl 2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranoside, $C_{27}H_{38}O_{12}$

By F. Pavelčík and K. Havetta

Department of Analytical Chemistry, Faculty of Pharmacy, Komenský University, 832 32 *Bratislava, Czechoslovakia*

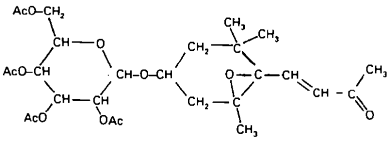
and V. Suchý

Department of Pharmacognosy and Botany, Faculty of Pharmacy, Komenský University, 832 32 *Bratislava, Czechoslovakia*

(*Received* 30 *January* 1985; *accepted* 25 *March* 1985)

Abstract. $M_r = 554{\cdot}6$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}702\ (8)$, $b = 13{\cdot}432\ (14)$, $c = 18{\cdot}263\ (12)$ Å, $V = 3115{\cdot}9\ (43)$ Å^3, $Z = 4$, $D_m = 1{\cdot}19\ (2)$, $D_x = 1{\cdot}18$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 7{\cdot}0$ cm^{-1}, $F(000) = 1184$, room temperature, $R = 0{\cdot}061$ for 2261 observed reflections. The epoxycyclohexane ring has an unsymmetrical sofa conformation, distorted towards a half-chair. Bond lengths and angles are normal. The discrete molecules are held together by van der Waals forces.

Introduction. The title compound (I) was isolated from the aerial part of *Veratrum album* subsp. *Lobelianum* and its structure was proposed on the basis of UV, IR, mass, and ^{1}H NMR spectra (Suchý *et al.*, to be published). Because the assignment of substitutents on the cyclohexane ring was not unique we performed an X-ray structure determination.



(I)

Experimental. Crystals suitable for X-ray analysis were obtained by slow evaporation of methanol solution. Density measured by flotation in aqueous KI solution. Crystal $0{\cdot}5 \times 0{\cdot}3 \times 0{\cdot}1$ mm. Weissenberg photographs showed the crystal to be orthorhombic; systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, $00l$ for $l = 2n + 1$ uniquely indicate space group $P2_12_12_1$. Unit-cell parameters refined by a least-squares fit of positional angles of 10 strong independent reflections measured on the diffractometer. 2501 reflections measured for $0{\cdot}0° < 2\theta \leq 115{\cdot}0°$. Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Intensities measured by the ω–2θ scan technique. Scan rate 4·88 to 29·3° min^{-1} in 2θ. Background measured at each end of the scan for one half of the scan time. Two standard reflections monitored after every 98 scans showed that no correction for instrument instability or crystal decay was required. Lp corrections applied. Data averaged to give 2416 unique and 2261 observed reflections $[|F| > 3{\cdot}92\sigma(F)]$. $R_{\rm int} = 0{\cdot}025$. No correction for absorption. Structure solved by direct method with *MULTAN*80 (Main *et al.*, 1980) and by weighted Fourier syntheses of electron density. Refinement on F by block-diagonal least squares with anisotropic thermal parameters assigned to all nonhydrogen atoms. A difference synthesis showed positions of all skeletal H atoms as well as partial disorder of one ester group (see Fig. 1). Both disordered positions were refined as a rigid group. During this refinement R dropped considerably and occupation factors converged to 0·71 and 0·29, respectively. Later all nonhydrogen atoms were refined independently with fixed occupation factors. Some bond lengths of disordered groups are stereochemically unrealistic (Table 2), probably due to overlap of atoms in both groups. H atoms, some at their calculated positions, with isotropic temperature factors were used for calculations of structure factors in final stages of refinement, but not all H atoms were located. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Weighting scheme $w^{-1} = \sigma^2(F) + (0{\cdot}04|F|)^2$. The five strongest reflections, affected by extinction, were assigned zero weights. In final refinement cycle $(\Delta/\sigma)_{\max} = 0{\cdot}2$. Final $R = 0{\cdot}061$ and $wR = 0{\cdot}079$ for observed, and 0·069 or 0·084 for all reflections, respectively. Final difference map revealed no significant regions of electron density with max. 0·17 and min. −0·22 e Å^{-3}. All standard crystallographic calculations carried out with *XRC*83 program package (Pavelčík, Kettmann, Zeman & Majer, 1983).

0108-2701/85/081272-03$01.50

Discussion. The refined positonal parameters of the heavy atoms are in Table 1,* bond distances and angles in Table 2. Fig. 1 is a drawing of the molecule.

Bond lengths and bond angles in Table 2 are normal. The C—O bond lengths involving the ring and glycosidic O atoms show the usual variation associated with the C(15)—O(4)—C(14)—O(1)—C(1) sequence as a result of the anomeric effect (Jeffrey, Pople & Radom, 1974): 1·420, 1·415, 1·397 and 1·441 Å. The conformation is *ap*, *sc* with torsion angle O(4)—C(14)—O(1)—C(1) −86·6°.

The conformation of the major part of the disordered ester group with torsion angles C(15)—C(19)—O(5)—C(26) and C(19)—O(5)—C(26)—C(27) close to 180° (see Table 3) resemble the most stable conformation of the ester group (Schweizer & Dunitz, 1982). The conformation of the minor part is similar to that of

Table 1. *Final atomic coordinates* (×10^4) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters*

$$(B_{eq} = \tfrac{4}{3}\textstyle\sum_i B_{ii}a_i^2)$$

	x	y	z	B_{eq}(Å^2)
O(1)	6420 (2)	624 (2)	6635 (2)	5·19
O(2)	4570 (3)	−1531 (2)	5534 (2)	5·98
O(3)	2742 (4)	−4881 (3)	5334 (2)	10·27
O(4)	8202 (2)	402 (2)	6662 (2)	5·18
O(5)	9735 (4)	−1115 (4)	6373 (3)	7·19
O(105)	9861 (11)	−903 (14)	6773 (7)	9·72
O(6)	10406 (3)	1957 (3)	6066 (2)	6·32
O(7)	11282 (3)	2118 (6)	7109 (2)	12·97
O(8)	8764 (3)	3356 (2)	6234 (2)	6·73
O(9)	8855 (6)	3688 (4)	5051 (2)	15·30
O(10)	6716 (3)	2536 (2)	5999 (2)	5·58
O(11)	6095 (4)	3269 (4)	7007 (2)	10·36
O(12)	10947 (5)	−1800 (4)	7066 (3)	8·26
O(112)	10569 (10)	−916 (10)	5637 (7)	7·45
C(1)	5952 (3)	−269 (3)	6341 (2)	4·86
C(2)	6315 (4)	−1183 (4)	6763 (3)	5·76
C(3)	5890 (4)	−2176 (3)	6452 (3)	5·62
C(4)	4720 (4)	−2064 (3)	6224 (2)	5·10
C(5)	4190 (4)	−1071 (4)	6203 (2)	5·36
C(6)	4775 (4)	−142 (4)	6426 (3)	5·69
C(7)	6503 (4)	−2474 (4)	5770 (4)	7·62
C(8)	6011 (5)	−2980 (5)	7058 (4)	8·45
C(9)	2996 (4)	−963 (5)	6267 (4)	7·96
C(10)	4032 (4)	−2957 (4)	6305 (2)	5·52
C(11)	3644 (4)	−3491 (4)	5769 (2)	5·92
C(12)	2972 (4)	−4377 (4)	5860 (3)	6·29
C(13)	2528 (5)	−4616 (5)	6595 (3)	8·13
C(14)	7367 (3)	905 (3)	6306 (2)	4·91
C(15)	9194 (4)	594 (4)	6332 (2)	5·39
C(16)	9448 (4)	1710 (3)	6438 (2)	5·37
C(17)	8579 (4)	2304 (3)	6091 (2)	5·10
C(18)	7517 (4)	2023 (3)	6405 (2)	4·91
C(19)	9996 (5)	−64 (4)	6698 (4)	7·55
C(20)	11283 (4)	2172 (5)	6456 (3)	7·79
C(21)	12139 (5)	2486 (6)	5984 (5)	10·89
C(22)	8883 (7)	3957 (4)	5676 (3)	10·06
C(23)	9143 (11)	4991 (6)	5929 (5)	14·72
C(24)	6057 (4)	3145 (4)	6361 (3)	7·13
C(25)	5282 (6)	3617 (6)	5846 (4)	10·06
C(26)	10245 (6)	−1899 (5)	6622 (4)	6·05
C(126)	10197 (14)	−1447 (19)	6171 (8)	7·49
C(27)	9847 (7)	−2789 (7)	6327 (4)	8·13
C(127)	10153 (13)	−2546 (14)	6134 (11)	6·76

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·521 (7)	C(16)—C(17)	1·502 (6)
C(1)—C(6)	1·513 (6)	C(16)—O(6)	1·433 (6)
C(1)—O(1)	1·441 (5)	C(17)—C(18)	1·513 (7)
C(2)—C(3)	1·546 (7)	C(17)—O(8)	1·457 (5)
C(3)—C(4)	1·551 (7)	C(18)—O(10)	1·434 (5)
C(3)—C(7)	1·522 (8)	C(19)—O(5)	1·567 (8)
C(3)—C(8)	1·554 (8)	C(19)—O(105)	1·148 (20)
C(4)—C(5)	1·494 (7)	C(20)—C(21)	1·450 (10)
C(4)—C(10)	1·492 (7)	C(20)—O(6)	1·353 (7)
C(4)—O(2)	1·461 (5)	C(20)—O(7)	1·196 (7)
C(5)—C(6)	1·509 (7)	C(22)—C(23)	1·500 (10)
C(5)—C(9)	1·528 (7)	C(22)—O(8)	1·309 (7)
C(5)—O(2)	1·451 (5)	C(22)—O(9)	1·198 (8)
C(10)—C(11)	1·310 (6)	C(24)—C(25)	1·502 (9)
C(11)—C(12)	1·473 (7)	C(24)—O(10)	1·344 (6)
C(12)—C(13)	1·491 (7)	C(24)—O(11)	1·193 (6)
C(12)—O(3)	1·211 (6)	C(26)—C(27)	1·406 (12)
C(14)—C(18)	1·525 (6)	C(26)—O(5)	1·317 (9)
C(14)—O(1)	1·397 (5)	C(26)—O(12)	1·213 (9)
C(14)—O(4)	1·415 (5)	C(126)—C(127)	1·478 (32)
C(15)—C(16)	1·546 (7)	C(126)—O(105)	1·387 (24)
C(15)—C(19)	1·504 (8)	C(126)—O(112)	1·298 (23)
C(15)—O(4)	1·420 (5)		

C(2)—C(1)—C(6)	109·7 (4)	C(15)—C(16)—C(17)	108·0 (4)
C(2)—C(1)—O(1)	111·0 (3)	C(15)—C(16)—O(6)	110·0 (4)
C(6)—C(1)—O(1)	106·0 (3)	C(17)—C(16)—O(6)	107·5 (4)
C(1)—C(2)—C(3)	113·9 (4)	C(16)—C(17)—C(18)	111·3 (4)
C(2)—C(3)—C(4)	110·4 (4)	C(16)—C(17)—O(8)	108·7 (4)
C(2)—C(3)—C(7)	110·4 (4)	C(18)—C(17)—O(8)	108·6 (3)
C(2)—C(3)—C(8)	107·7 (4)	C(14)—C(18)—C(17)	108·2 (3)
C(4)—C(3)—C(7)	107·2 (4)	C(14)—C(18)—O(10)	108·9 (3)
C(4)—C(3)—C(8)	110·7 (4)	C(17)—C(18)—O(10)	108·5 (3)
C(7)—C(3)—C(8)	110·5 (4)	C(15)—C(19)—O(5)	102·6 (4)
C(3)—C(4)—C(5)	121·7 (4)	C(15)—C(19)—O(105)	121·9 (9)
C(3)—C(4)—C(10)	117·2 (4)	C(21)—C(20)—O(6)	111·5 (5)
C(3)—C(4)—O(2)	113·8 (4)	C(21)—C(20)—O(7)	127·7 (6)
C(5)—C(4)—C(10)	117·2 (4)	O(6)—C(20)—O(7)	120·8 (6)
C(5)—C(4)—O(2)	58·8 (3)	C(23)—C(22)—O(8)	110·9 (7)
C(10)—C(4)—O(2)	113·8 (4)	C(23)—C(22)—O(9)	125·5 (7)
C(4)—C(5)—C(6)	120·6 (4)	O(8)—C(22)—O(9)	123·5 (7)
C(4)—C(5)—C(9)	122·0 (4)	C(25)—C(24)—O(10)	111·0 (5)
C(4)—C(5)—O(2)	59·5 (3)	C(25)—C(24)—O(11)	125·9 (6)
C(6)—C(5)—C(9)	112·9 (4)	O(10)—C(24)—O(11)	123·1 (5)
C(6)—C(5)—O(2)	114·6 (4)	C(27)—C(26)—O(5)	111·8 (6)
C(9)—C(5)—O(2)	115·8 (4)	C(27)—C(26)—O(12)	127·9 (7)
C(1)—C(6)—C(5)	111·5 (4)	O(5)—C(26)—O(12)	120·4 (7)
C(4)—C(10)—C(11)	125·9 (4)	C(127)—C(126)—O(105)	123·4 (17)
C(10)—C(11)—C(12)	125·1 (4)	C(127)—C(126)—O(112)	121·9 (17)
C(11)—C(12)—C(13)	119·7 (4)	O(105)—C(126)—O(112)	114·7 (17)
C(11)—C(12)—O(3)	120·0 (5)	C(1)—O(1)—C(14)	114·8 (3)
C(13)—C(12)—O(3)	120·1 (5)	C(4)—O(2)—C(5)	61·7 (3)
C(18)—C(14)—O(1)	108·8 (3)	C(14)—O(4)—C(15)	112·5 (3)
C(18)—C(14)—O(4)	108·8 (3)	C(19)—O(5)—C(26)	119·0 (5)
O(1)—C(14)—O(4)	108·6 (3)	C(19)—O(105)—C(126)	112·1 (15)
C(16)—C(15)—C(19)	111·9 (4)	C(16)—O(6)—C(20)	119·9 (4)
C(16)—C(15)—O(4)	107·9 (4)	C(17)—O(8)—C(22)	118·6 (4)
C(19)—C(15)—O(4)	107·8 (4)	C(18)—O(10)—C(24)	118·6 (4)

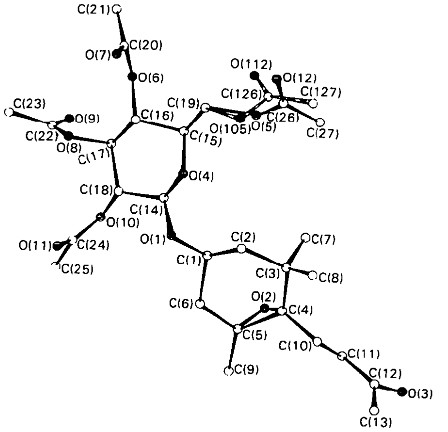


Fig. 1. The molecular structure of $C_{27}H_{38}O_{12}$.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42151 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Torsion angles* (°)

C(6)—C(1)—C(2)—C(3)	66·2 (4)	C(4)—C(5)—C(6)—C(1)	24·4 (5)	C(15)—C(16)—C(17)—O(8)	175·8 (3)
O(1)—C(1)—C(2)—C(3)	−177·0 (3)	C(9)—C(5)—C(6)—C(1)	−178·8 (4)	O(6)—C(16)—C(17)—C(18)	174·9 (5)
C(2)—C(1)—C(6)—C(5)	−54·7 (4)	O(2)—C(5)—C(6)—C(1)	−43·4 (5)	O(6)—C(16)—C(17)—O(8)	−65·6 (4)
O(1)—C(1)—C(6)—C(5)	−174·7 (3)	C(4)—C(10)—C(11)—C(12)	179·5 (5)	C(15)—C(16)—O(6)—C(20)	−109·7 (5)
C(2)—C(1)—O(1)—C(14)	91·7 (4)	C(10)—C(11)—C(12)—C(13)	11·2 (8)	C(17)—C(16)—O(6)—C(20)	133·0 (5)
C(6)—C(1)—O(1)—C(14)	−149·2 (3)	C(10)—C(11)—C(12)—O(3)	−172·3 (6)	C(16)—C(17)—C(18)—C(14)	−56·0 (4)
C(1)—C(2)—C(3)—C(4)	−41·1 (5)	O(1)—C(14)—C(18)—C(17)	176·3 (3)	C(16)—C(17)—C(18)—O(10)	−173·9 (3)
C(1)—C(2)—C(3)—C(7)	77·3 (5)	O(1)—C(14)—C(18)—O(10)	−66·1 (4)	O(8)—C(17)—C(18)—C(14)	−175·7 (3)
C(1)—C(2)—C(3)—C(8)	−162·1 (4)	O(4)—C(14)—C(18)—C(17)	58·1 (4)	O(8)—C(17)—C(18)—O(10)	66·4 (4)
C(2)—C(3)—C(4)—C(5)	9·6 (6)	O(4)—C(14)—C(18)—O(10)	175·7 (3)	C(16)—C(17)—O(8)—C(22)	120·1 (6)
C(2)—C(3)—C(4)—C(10)	−147·4 (4)	C(18)—C(14)—O(1)—C(1)	155·1 (3)	C(18)—C(17)—O(8)—C(22)	−118·7 (6)
C(2)—C(3)—C(4)—O(2)	76·4 (5)	O(4)—C(14)—O(1)—C(1)	−86·6 (4)	C(14)—C(18)—O(10)—C(24)	120·9 (4)
C(7)—C(3)—C(4)—C(5)	−110·8 (4)	C(18)—C(14)—O(4)—C(15)	−65·5 (4)	C(17)—C(18)—O(10)—C(24)	−121·7 (4)
C(7)—C(3)—C(4)—C(10)	92·3 (5)	O(1)—C(14)—O(4)—C(15)	176·2 (3)	C(15)—C(19)—O(5)—C(26)	−174·8 (5)
C(7)—C(3)—C(4)—O(2)	−43·9 (5)	C(19)—C(15)—C(16)—C(17)	−177·0 (4)	C(15)—C(19)—O(105)—C(126)	87·6 (14)
C(8)—C(3)—C(4)—C(5)	128·7 (4)	C(19)—C(15)—C(16)—O(6)	66·0 (5)	C(21)—C(20)—O(6)—C(16)	−175·0 (5)
C(8)—C(3)—C(4)—C(10)	−28·3 (5)	O(4)—C(15)—C(16)—C(17)	−58·6 (4)	O(7)—C(20)—O(6)—C(16)	3·2 (9)
C(8)—C(3)—C(4)—O(2)	−164·4 (4)	O(4)—C(15)—C(16)—O(6)	−175·6 (3)	C(23)—C(22)—O(8)—C(17)	−175·9 (7)
C(3)—C(4)—C(5)—C(6)	−1·8 (6)	C(16)—C(15)—C(19)—O(5)	−167·5 (4)	O(9)—C(22)—O(8)—C(17)	−0·5 (12)
C(3)—C(4)—C(5)—C(9)	−156·5 (5)	C(16)—C(15)—C(19)—O(105)	168·2 (9)	C(25)—C(24)—O(10)—C(18)	180·0 (5)
C(10)—C(4)—C(5)—C(6)	155·2 (4)	O(4)—C(15)—C(19)—O(5)	74·0 (5)	O(11)—C(24)—O(10)—C(18)	−1·3 (8)
C(10)—C(4)—C(5)—C(9)	0·5 (6)	O(4)—C(15)—C(19)—O(105)	49·7 (11)	C(27)—C(26)—O(5)—C(19)	174·1 (6)
C(3)—C(4)—C(10)—C(11)	−109·5 (6)	C(16)—C(15)—O(4)—C(14)	65·4 (4)	O(12)—C(26)—O(5)—C(19)	−4·2 (9)
C(5)—C(4)—C(10)—C(11)	92·5 (6)	C(19)—C(15)—O(4)—C(14)	−173·7 (4)	C(127)—C(126)—O(105)—C(19)	177·7 (15)
O(2)—C(4)—C(10)—C(11)	26·7 (7)	C(15)—C(16)—C(17)—C(18)	56·3 (4)	O(112)—C(126)—O(105)—C(19)	−1·7 (21)

methyl 6-*O*-acetyl-*β*-D-glucopyranoside (Lindberg, 1976). The torsion angles O(4)—C(15)—C(19)—O(5) and O(4)—C(15)—C(19)—O(105) are 74 and 50°, respectively.

All ester groups derived from secondary alcohols have an H—C—O—C torsion angle close to zero, again in accord with the statistics of Schweizer & Duntiz (1982).

The structure consists of discrete molecules held together by van der Waals forces. The epoxycyclohexane ring has an unsymmetrical conformation which can be described as a C(1)-sofa distorted towards a C(1), C(2)-half-chair. The mirror symmetry about the plane through C(1) and C(4) has asymmetry parameter (Duax, Weeks & Rohrers, 1976) $\Delta C_s = 12{\cdot}5°$. The pseudoaxis C_2 passing through bond C(4)—C(5) has asymmetry parameter $\Delta C_2 = 14{\cdot}2°$. The half-chair conformation which was found in 1-(*p*-bromophenyl)-1,2-epoxycyclohexane seems to be the ground-state conformation for the isolated epoxycyclohexane ring (Merlino, Lami, Macchia, Macchia & Monti, 1972). A 1*β*-sofa conformation, on the other hand, was found in 4*β*,5*β*-epoxycholestan-6-one (van Niekerk, Nassimbeni & Cragg, 1977). The substituents on the six-membered ring are pseudoequatorial except for C(7). The epoxy O(2) can also be regarded as the axial substituent because the angle between the mean plane of the cyclohexane ring and the plane of the epoxy ring is 97·6 (4)°.

The pyranose ring has almost exact mirror symmetry normal to the mean plane of the ring and passing through the ring atoms O(4) and C(17). The ring is more puckered at O(4) and least puckered at C(17), as shown by the torsion angles given in Table 3. The same general trend was noted, for a wide range of carbohydrates containing the pyranose ring, by Jeffrey, McMullan & Takagi (1977). The asymmetry parameter $\Delta C_s = 0{\cdot}33°$ is almost negligible, and the ring is more symmetric than those found in *β*-glucose, methyl 6-*O*-acetyl-*β*-glucoside or methyl *β*-glucoside (Chu & Jeffrey, 1968; Lindberg, 1976; Jeffrey & Takagi, 1977).

References

CHU, S. S. C. & JEFFREY, G. A. (1968). *Acta Cryst.* B**24**, 830–838.
DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Top. Stereochem.* **9**, 271.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JEFFREY, G. A., MCMULLAN, R. K. & TAKAGI, S. (1977). *Acta Cryst.* B**33**, 728–737.
JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1974). *Carbohydr. Res.* **38**, 81–95.
JEFFREY, G. A. & TAKAGI, S. (1977). *Acta Cryst.* B**33**, 738–742.
LINDBERG, K. B. (1976). *Acta Cryst.* B**32**, 642–645.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
MERLINO, S., LAMI, G., MACCHIA, B., MACCHIA, F. & MONTI, L. (1972). *J. Org. Chem.* **37**, 703–706.
NIEKERK, J. C. VAN, NASSIMBENI, L. R. & CRAGG, G. M. L. (1977). *Acta Cryst.* B**33**, 3582–3584.
PAVELČIK, F., KETTMANN, V., ZEMAN, J. & MAJER, J. (1983). *XRC*83 program package for the determination of crystal structures by X-ray diffraction. Tech. Rep. V-5-1/16. Department of Analytical Chemistry, Faculty of Pharmacy, Komenský Univ.
SCHWEIZER, W. B. & DUNITZ, J. D. (1982). *Helv. Chim. Acta*, **65**, 1547–1554.