χ^2 tests indicate planarity of two of the rings, but slight non-planarity of the third [C(17) through C(22)], with maximum deviation 0·019 (3) Å. Atoms of this ring also exhibit the largest thermal parameters of the structure, causing observed bond distances to be systematically shorter than those of the chemically equivalent ring, P1. The possibility that the apparent thermal motion is actually a static effect involving a slight crystal disorder cannot be discounted.

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Structural Studies of Colchicine Derivatives. IV. The Structure of Colchiceine Benzoate Monohydrate, $C_{28}H_{27}NO_7.H_2O$

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Abstract. $M_r = 507·5$, orthorhombic, $P2_12_12_1$, $a = 10·324$ (4), $b = 11·348$ (6), $c = 22·944$ (9) Å, $V = 2688$ (9) Å^3, $Z = 4$, $D_m = 1·24$ (2), $D_x = 1·254$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·86$ cm^{-1}, $F(000) = 1072$, $T = 293$ K, $R = 0·052$ for 1399 unique reflections. The troponoid ring *C* exhibits a definite bond-length alternation with an arrangement corresponding to an isocolchicine-like structure. The three shorter C—C bonds are of lengths 1·329 (8)–1·386 (8) Å, and the longer bonds are in the range 1·407 (8)–1·448 (10) Å. The other seven-membered ring has a similar conformation to those of similar compounds. The normals to the three rings *A, B, C* of colchiceine are $A–B = 43·7$ (4), $B–C = 36·3$ (4) and $A–C = 52·1$ (4)°. The molecules are held together by hydrogen bonds between molecules of colchiceine benzoate and the water.
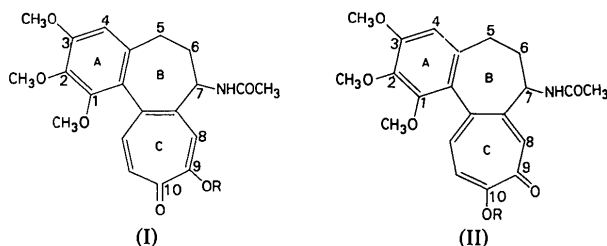

Introduction. As part of a study on the molecular geometry of some colchicine derivatives (Part I: Miravitlles, Solans, Bladé-Font, Germain & Declercq, 1982; Part II: Miravitlles, Rius, Bladé-Font & Germain, 1983; Part III: Rius, Molins, Miravitlles & Bladé-Font, 1984), the structure of colchiceine benzoate has been determined.

This derivative was synthesized in order to determine whether it belongs to the colchicine (II) or the isocolchicine series (I), and to study the equilibrium in solution of the two forms in relation to that of colchiceine acetate (Elguero, Muller, Bladé-Font, Faure & Vincent, 1980). The biological activity of colchicine derivatives depends, principally, on the position of the oxygen functions of the tropolonic ring *C*. Thus, the derivatives belonging to the colchicine series (II) are considerably more active biologically than those of the isocolchicine series (I) (Santavý, 1979).

The present structure determination has shown that the title compound belongs to the isocolchicine series [(I); $R = C_6H_5CO$].

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(I)   (II)

Experimental. Title compound prepared by treatment of colchiceine with benzoyl chloride in pyridine (Santavý, 1952). Yellow prismatic crystals from aqueous solution; size: $0.35 \times 0.20 \times 0.20$ mm. D_m by flotation. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$; unit-cell parameters by least squares from 25 reflections (θ between 10 and 20°); ω–2θ scan mode; $\theta_{max} = 25°$; range of hkl: $h \le 12$, $k \le 13$, $l \le 27$; three standard reflections measured after every 50 reflections (intensity variation $< 1\%$). Number of unique reflections measured: 2691; 1399 observed with $I > 2.5\sigma(I)$. Lorentz and polarization, no absorption correction. Structure solved with $MULTAN11/82$ (Main et al. 1982). Refinement with $SHELX$ (Sheldrick, 1976). Isotropic and weighted anisotropic full-matrix least-squares refinements on $\sum w(F_o-F_c)^2$ converged at $R = 0.07$ for all observed reflections: subsequent difference Fourier synthesis showed positions of 21 H atoms. Remaining methyl H atoms introduced in calculated positions. Final anisotropic full-matrix refinement with isotropic temperature factors for H atoms gave $R = 0.052$; $wR = 0.064$ with $w = K[\sigma^2(F) + 0.0003|F_o|^2]^{-1}$ [$\sigma(F)$ from counting statistics]; max. Δ/σ 0.25, $S = 1.1$. Max. and min. heights in final difference Fourier synthesis 0.19 and -0.22 e Å^{-3}. Atomic scattering factors from International Tables for X-ray Crystallography (1974).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1;* Fig. 1 shows the molecular structure and the numbering system ($PLUTO$; Motherwell & Clegg, 1978). The bond lengths and angles are shown in Table 2.

The r.m.s.d. of the benzene ring A is 0.01 (2) Å, $\delta_{max} = 0.014$ (7) Å for C(2) and C(4a). The methoxy groups C(1)–O(1)–C(1m), C(2)–O(2)–C(2m) and C(3)–O(3)–C(3m) form dihedral angles of 54.5 (3), 123.3 (3) and 24.3 (3)° respectively, with ring A, all of them pointing in the same direction.

The conformation of ring B is similar to that found in other colchicine derivatives as shown by the sum of the torsion angles of this ring: colchicine 305, iso-

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* Lists of structure factors, anisotropic thermal parameters, H atom coordinates and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39887 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

colchicine 300, colchiceine acetate 291, colchiceine 296, deacetamidocolchiceine 292, colchiceine benzoate 298°.

The troponoid ring C exhibits a definite bond-length alternation with an arrangement corresponding to an isocolchicine-like structure (I). The r.m.s.d. of the plane is 0.075 Å with a δ_{max} of 0.129 (7) Å for C(10).

Table 1. *Fractional atomic coordinates ($\times 10^4$) with standard deviations in parentheses and equivalent isotropic temperature factors (Å^2)*

	x	y	z	B_{eq}†
C(1)	3185 (6)	9447 (6)	789 (3)	4.29
C(2)	2085 (6)	10094 (6)	712 (3)	4.93
C(3)	882 (5)	9562 (6)	826 (3)	4.45
C(4)	851 (6)	8411 (6)	1026 (3)	4.93
C(4a)	1964 (5)	7767 (6)	1123 (3)	4.11
C(5)	1943 (6)	6556 (6)	1378 (3)	4.53
C(6)	2444 (6)	6558 (6)	2012 (3)	4.96
C(7)	3611 (6)	7350 (5)	2100 (3)	4.10
C(7a)	4628 (5)	7127 (5)	1614 (3)	3.52
C(8)	5722 (6)	6393 (5)	1765 (3)	3.97
C(9)	6811 (5)	6139 (6)	1482 (3)	4.19
O(9)	7707 (5)	5459 (4)	1799 (2)	5.08
C(10)	7305 (6)	6549 (6)	927 (3)	4.64
C(11)	6441 (5)	7085 (6)	514 (3)	4.46
C(12)	5231 (5)	7516 (5)	589 (3)	4.18
C(12a)	4412 (5)	7643 (5)	1075 (3)	3.47
C(12b)	3177 (5)	8305 (5)	991 (3)	3.38
C(13)	4902 (6)	8020 (6)	2937 (3)	4.70
O(13a)	5243 (5)	8884 (5)	2658 (2)	5.94
C(14)	5325 (6)	7782 (7)	3541 (3)	6.32
O(1)	4404 (4)	9957 (4)	720 (2)	4.64
C(1m)	4687 (7)	10484 (6)	162 (4)	6.14
O(2)	2189 (5)	11280 (4)	604 (2)	6.06
C(2m)	1518 (8)	11732 (7)	107 (4)	8.84
O(3)	−186 (5)	10249 (5)	760 (3)	7.13
C(3m)	−1390 (7)	9663 (8)	666 (5)	10.71
O(10)	8454 (4)	6429 (5)	801 (3)	6.40
N	4112 (5)	7210 (5)	2693 (2)	4.04
C(15)	8068 (5)	4433 (5)	1557 (3)	4.67
O(15)	7531 (5)	4010 (4)	1154 (2)	6.60
C(16)	9204 (5)	3912 (5)	1850 (3)	4.32
C(17)	9785 (5)	4426 (5)	2327 (3)	5.39
C(18)	10869 (6)	3900 (6)	2570 (3)	6.26
C(19)	11353 (6)	2895 (6)	2341 (4)	7.47
C(20)	10815 (7)	2384 (6)	1859 (4)	7.30
C(21)	9713 (6)	2875 (6)	1619 (3)	5.77
O	3768 (4)	4959 (5)	3315 (2)	5.91

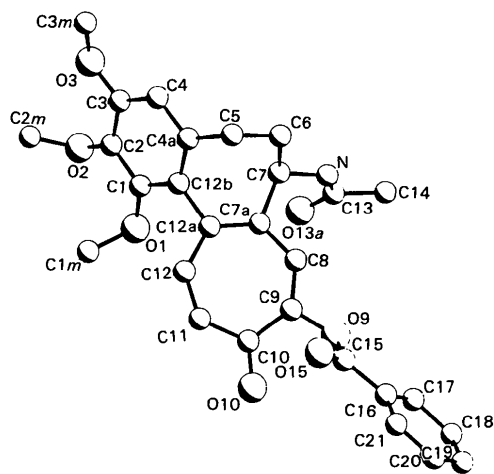† $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a^*_i a^*_j a_i \cdot a_j$.

Fig. 1. A view of the molecule with the atomic numbering.

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

C(2)–C(1)	1·363 (9)	C(11)–C(10)	1·437 (9)
C(12b)–C(1)	1·378 (9)	O(10)–C(10)	1·229 (7)
O(1)–C(1)	1·394 (7)	C(12)–C(11)	1·352 (8)
C(3)–C(2)	1·405 (9)	C(12a)–C(12)	1·407 (8)
O(2)–C(2)	1·374 (8)	C(12b)–C(12a)	1·493 (8)
C(4)–C(3)	1·383 (9)	O(13a)–C(13)	1·223 (8)
O(3)–C(3)	1·359 (8)	C(14)–C(13)	1·477 (10)
C(4a)–C(4)	1·380 (9)	N–C(13)	1·351 (8)
C(5)–C(4a)	1·495 (9)	C(1m)–O(1)	1·442 (10)
C(12b)–C(4a)	1·425 (8)	C(2m)–O(2)	1·430 (11)
C(6)–C(5)	1·543 (10)	C(3m)–O(3)	1·426 (9)
C(7)–C(6)	1·517 (9)	O(15)–C(15)	1·180 (8)
C(7a)–C(7)	1·553 (8)	C(16)–C(15)	1·477 (8)
N–C(7)	1·464 (8)	C(17)–C(16)	1·377 (9)
C(8)–C(7a)	1·446 (8)	C(21)–C(16)	1·394 (9)
C(12a)–C(7a)	1·386 (8)	C(18)–C(17)	1·385 (9)
C(9)–C(8)	1·329 (8)	C(19)–C(18)	1·351 (10)
O(9)–C(9)	1·406 (8)	C(20)–C(19)	1·365 (12)
C(10)–C(9)	1·448 (10)	C(21)–C(20)	1·381 (9)
C(15)–O(9)	1·342 (7)		

C(12b)–C(1)–C(2)	123·0 (6)	O(10)–C(10)–C(11)	119·3 (7)
O(1)–C(1)–C(2)	121·0 (6)	C(12)–C(11)–C(10)	130·0 (6)
O(1)–C(1)–C(12b)	115·8 (5)	C(12a)–C(12)–C(11)	133·9 (6)
C(3)–C(2)–C(1)	118·8 (6)	C(12)–C(12a)–C(7a)	124·6 (5)
O(2)–C(2)–C(1)	119·0 (6)	C(12b)–C(12a)–C(7a)	117·7 (5)
O(2)–C(2)–C(3)	121·6 (6)	C(12b)–C(12a)–C(12)	117·6 (5)
C(4)–C(3)–C(2)	119·2 (6)	C(4a)–C(12b)–C(1)	118·7 (5)
O(3)–C(3)–C(2)	116·7 (6)	C(12a)–C(12b)–C(1)	120·8 (5)
O(3)–C(3)–C(4)	124·0 (6)	C(12a)–C(12b)–C(4a)	120·5 (5)
C(4a)–C(4)–C(3)	122·3 (6)	C(14)–C(13)–O(13a)	123·6 (6)
C(5)–C(4a)–C(4)	122·6 (5)	N–C(13)–O(13a)	120·1 (6)
C(12b)–C(4a)–C(4)	118·1 (6)	N–C(13)–C(14)	116·3 (6)
C(12b)–C(4a)–C(5)	119·3 (5)	C(1m)–O(1)–C(1)	117·1 (5)
C(6)–C(5)–C(4a)	111·3 (5)	C(2m)–O(2)–C(2)	117·2 (6)
C(7)–C(6)–C(5)	113·1 (5)	C(3m)–O(3)–C(3)	117·2 (6)
C(7a)–C(7)–C(6)	110·2 (5)	C(13)–N–C(7)	121·7 (5)
N–C(7)–C(6)	109·9 (5)	O(15)–C(15)–O(9)	123·1 (6)
N–C(7)–C(7a)	114·2 (5)	C(16)–C(15)–O(9)	112·3 (5)
C(8)–C(7a)–C(7)	116·8 (5)	C(16)–C(15)–O(15)	124·6 (6)
C(12a)–C(7a)–C(7)	117·6 (5)	C(17)–C(16)–C(15)	122·5 (5)
C(12a)–C(7a)–C(8)	125·6 (5)	C(21)–C(16)–C(15)	117·7 (5)
C(9)–C(8)–C(7a)	132·0 (6)	C(21)–C(16)–C(17)	119·7 (5)
O(9)–C(9)–C(8)	115·0 (6)	C(18)–C(17)–C(16)	119·2 (6)
C(10)–C(9)–C(8)	131·0 (6)	C(19)–C(18)–C(17)	120·4 (7)
C(10)–C(9)–O(9)	113·5 (5)	C(20)–C(19)–C(18)	121·5 (6)
C(15)–O(9)–C(9)	116·4 (5)	C(21)–C(20)–C(19)	119·2 (6)
C(11)–C(10)–C(9)	119·9 (5)	C(20)–C(21)–C(16)	119·9 (6)
O(10)–C(10)–C(9)	120·8 (6)		

The benzene ring *D* of the benzoyl group is planar $\{\chi^2 = 11\cdot4[=\sum(\delta/\sigma)^2],$ r.m.s.d. $= 0\cdot01$ (1) Å, $\delta_{max} = 0\cdot017$ (8) Å for C(20)\}.

The geometry of the molecule is characterized by the angles between the normals to the following rings

A–$B = 43\cdot7$ (4), B–$C = 36\cdot3$ (4), A–$C = 52\cdot1$ (4), C–$D = 59\cdot8$ (4)° as well as by the twisting between ring A and ring C, given by the torsion angle C(12)–C(12a)–C(12b)–C(1) $= -57\cdot3$ (4)°.

The molecular packing in the crystal is determined by the presence of one water molecule, which forms a relatively strong H bond with O(13a) [O–H(O1)···O(13a) $= 2\cdot741$ (7) Å], and a short contact with O(1) [O–H(O3)···O(1) $= 2\cdot909$ (6) Å]. The occupation factor for H(O2) and H(O3) is 0·5. No other short intermolecular distances below 3·20 Å are found.

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Structure d'Agents Mutagènes. V. Le Nitro-2 Naphto[1,2-*b*]furanne, C₁₂H₇NO₃

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Abstract. $M_r = 213\cdot2$, $P2_1/c$, $a = 6\cdot500$ (1), $b = 19\cdot866$ (4), $c = 7\cdot375$ (3) Å, $\beta = 90\cdot77$ (3)°, $V = 952\cdot2$ Å³, $Z = 4$, $D_m = 1\cdot50$, $D_x = 1\cdot487$ g cm⁻³, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\bar{\mu} = 10\cdot3$ cm⁻¹, $F(000) = 440$, $T = 298$ K, $R = 0\cdot047$ for 1620 independent reflections. This is a weakly active mutagenic agent, whose geometry is close to that of 7-methoxy-2-nitronaphtho[2,1-*b*]furan (R7000) [Bravic, Bideau &