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RESEARCH ON AFRICAN MEDICINAL PLANTS—IV†

BOONEIN, A NEW C-9 TERPENOID LACTONE FROM *ALSTONIA BOONEI*: A POSSIBLE PRECURSOR IN THE INDOLE ALKALOID BIOGENESIS

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Abstract—From the bark of *Alstonia boonei* De Wild (Apocynaceae) a new monoterpenoid δ-lactone 1, named boonein, was isolated. The structure was established by chemical and spectroscopical methods and by X-ray analysis.

In the course of our investigation on medicinal plants used in Africa, we examined the bark of *Alstonia boonei* De Wild (Apocynaceae) from Nigeria and isolated echitamidine and two new alkaloids, N-formylechitamidine and 12 - methoxy - N - formylechitamidine.[1]

We now report the isolation of a new lactone from the same plant, a derivative of the iridane series, named boonein, 1 (Fig. 1) $C_9H_{14}O_3$, m.p. 95–6°, $[\alpha]_D^{20} = +28.6$ ($c = 0.5$, $CHCl_3$), found in 0.04% against 0.12 of the alkaloid compounds. Probably this substance is identifiable with the lactone isolated from *A. congensis* (=*boonei*).[2]

The occurrence of a monoterpenoid together with alkaloids is of biogenetic interest. Indole alkaloids of the *Strychnos* and Apocynaceae were considered to be derived from tryptamine plus a C-9 (or C-10) isoprenoid unit, according to various hypotheses.[3–5]

Loganin, 2, an iridoid present in several *Strychnos* species and Apocynaceae, was proposed for its structure and occurrence as the biogenetic isoprenoid precursor. The incorporation into monoterpenoid indole alkaloids was demonstrated for loganin.[6]

The results of a complete X-ray analysis using direct methods enabled a full rationalization of the ^1H and ^{13}C NMR spectra in terms of structure 1. The vicinal Me and OH groups and the two *cis*-fused rings are stereochemical features of boonein which are common to loganin.

Boonein, 1, M^+ at *m/z* 170 (6%), showed IR bands ($CHCl_3$) at 3610 (narrow) and 3440 (broad) cm^{-1} (ν_{OH}) and a two edged CO stretching band (1718 and 1726 cm^{-1}). UV spectrum of 1 exhibited some absorption at the extreme limit of the wavelength range, only the very beginning of which could be recorded. ^1H NMR spectrum showed the clear signals corresponding to a secondary group (δ 1.20, d, J = 7 Hz) and to a methine (δ 2.00, broadened d, J = 6 Hz). Overlapped signals of three hydrogens lie between 4.0–4.4 ppm, and only one of them moved downfield (δ 5.20, broadened t, J = 4 Hz) in monoacetyl derivative 3§ (oily compound, M^+ at *m/z* 212 (3), corresponding to $C_{11}H_{16}O_4$). In a comparison of ^{13}C NMR spectra of 1 and 3, the upfield shifts of a methylenic and a methine group (40.7 and 43.8 in 1 and 39.0 and 42.4 ppm in 3, respectively) accounted for their position vicinal to the secondary OH group. The H adjacent to the OH group showed an identical coupling constant with two of the vicinal H's, whereas it was weakly coupled with the third H.

By oxidation with chromium trioxide, boonein gave the ketone 4, $C_9H_{12}O_3$, M^+ at *m/z* 168 (58%), m.p. 105–107°. The IR stretching band of the CO (ν 1740 cm^{-1}) and the ^{13}C NMR chemical shift of the same group (215.8 ppm) are accounted for by a cyclopentanone ring. In agreement with the sequence CH_2–CO–CH, the chemical shifts of the methylenic and the methine groups in 4 (43.4 and 44.9 ppm, respectively) were downfield with respect to the corresponding values in 1.

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†Part III: see Ref. 1.

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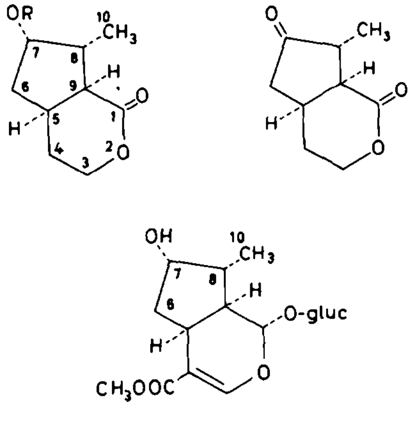
§Compound 3 on mild alkaline conditions regenerated

		R
1	boonein	H
3	acetylboonein	Ac



4 7-oxo-boonein

2 loganin

Fig. 1.

Table 1. Final coordinates $(\times 10^4)$ for non-hydrogen atoms. E.s.d.'s from the final refinement are given in parentheses as units on the last digit

(a) Molecule A

	x	y	z
O(1)	5578 (4)	6931 (6)	5047 (5)
O(2)	5339 (4)	5401 (6)	4335 (5)
O(3)	-938 (4)	7102 (6)	4170 (4)
C(1)	4655 (5)	6274 (6)	4598 (5)
C(3)	4192 (8)	4600 (7)	3900 (8)
C(4)	2680 (8)	4618 (6)	5003 (8)
C(5)	1576 (6)	5511 (6)	4607 (6)
C(6)	426 (6)	5880 (6)	5913 (6)
C(7)	168 (5)	6952 (6)	5525 (6)
C(8)	1998 (5)	7293 (6)	5104 (5)
C(9)	2731 (5)	6416 (6)	4236 (5)
C(10)	2051 (7)	8233 (6)	4192 (9)

(b) Molecule B

	x	y	z
O(1)	-398 (4)	993 (6)	9457 (5)
O(2)	-46 (4)	2501 (5)	10202 (5)
O(3)	6028 (3)	860 (5)	9620 (4)
C(1)	584 (5)	1672 (6)	9653 (5)
C(3)	1144 (8)	3325 (7)	10549 (8)
C(4)	2355 (7)	3428 (6)	9226 (8)
C(5)	3515 (5)	2524 (6)	9143 (6)
C(6)	5064 (6)	2486 (6)	10325 (7)
C(7)	5251 (5)	1431 (6)	10801 (5)
C(8)	3361 (5)	1085 (6)	10900 (5)
C(9)	2506 (4)	1569 (6)	9429 (5)
C(10)	3122 (7)	0000	11030 (9)

Table 2. Bond lengths (Å). E.s.d.'s from the final refinement are given in parentheses as units on the last digit

Bond lengths	Molecule A	Molecule B
O(1) - C(1)	1.201 (9)	1.208 (9)
O(2) - C(1)	1.327 (11)	1.324 (10)
O(2) - C(3)	1.450 (11)	1.479 (10)
O(3) - C(7)	1.422 (6)	1.419 (7)
C(1) - C(9)	1.526 (6)	1.518 (5)
C(3) - C(4)	1.526 (9)	1.494 (9)
C(4) - C(5)	1.521 (10)	1.532 (10)
C(5) - C(6)	1.531 (8)	1.537 (7)
C(5) - C(9)	1.566 (10)	1.545 (10)
C(6) - C(7)	1.512 (11)	1.502 (11)
C(7) - C(8)	1.549 (6)	1.547 (6)
C(8) - C(9)	1.526 (10)	1.538 (7)
C(8) - C(10)	1.499 (11)	1.498 (8)

From IR stretching frequency of the CO group and the ^{13}C NMR chemical shift of the same group (175.0 ppm in **1**, 174.1 in **3** and 171.6 in **4**) the two other oxygens of boonein belong to a δ-lactonic ring. The two ^{13}C NMR signals of **4** at relatively low field still to be considered (68.1 and 47.1 ppm) belong unambiguously to methylenic and methine groups, adjacent to O and CO group of the lactonic functions. The sequence could be further extended to $CH–CO–O–CH_2–CH_2$ since ^1H NMR signals of CH_2O, between δ 4.1 and 4.5 in **3** and **4**, consist of two partially overlapped AB portions of an ABX type thus accounted for a system ABXY.[7]

Of the three remaining ^{13}C NMR signals of **4**, the methine at 30.9 ppm is the second bridge head between the cyclopentane and the tetrahydropyranic ring, the methylene group at 27.9 ppm belongs to the δ-lactonic ring, as shown, and the Me group at 14.7 ppm (13.3 in **1**) is obviously bound to the methine close to the ketonic group.

On the basis of known biogenetic considerations,[8] an α-configuration could be assigned to H-5, whereas the *cis* ring junction could be assigned on the basis of the coupling constant with H-9, $J = 6$ Hz, at δ 2.00, for **1**.

There is a Cotton effect of **4** of considerable amplitude at 290 nm, due to the weak extinction band of the ketonic group and associated with the $n \rightarrow \pi^*$ transition (ORD: $\Phi + 3150$ at 262 nm and -1430 at 309 nm). The negative sign indicated a 6β or 8α position for the Me group on the basis of the octant rule.

The good accordance between ^{13}C NMR chemical shifts of C(6), C(7) and C(10) of boonein and loganin[9] (40.7, 74.4, 13.3 for **1** and 41.2, 74.8 and 12.8 for **2**) suggested an identical 8α-position for the Me group and α-configuration for the OH group. The *trans* relationship between Me and OH groups should have involved deshielding of C(7) and C(10) as it resulted by comparison of ^{13}C NMR data of *trans*- and *cis*-2-methylcyclopentanols[10] (CHOH and CH_3 at 80.9 and 19.4, respectively, in *trans* isomer and 76.3 and 14.8 ppm in *cis* isomer).

Table 1 reports the final atomic parameters from the X-ray analysis.† Bond lengths and angles are given in Tables 2 and 3; no correction has been applied for the effects of thermal motion. Torsion angles are reported in Table 4. Details of important molecular planes are given in Table 5.

The asymmetric unit contains two crystallographically independent molecules, **A** and **B** respectively (Fig. 2); each of them consists of a 6-membered ring *cis*-fused with a disubstituted 5-membered ring. The OH substituent at C(7) is on the same side of the Me group at C(8) for both molecules.

Although OH and CO groups are present, the closest intermolecular contacts are Van der Waals interactions.

The 6-membered ring. The average values for $C(sp^3)$–$C(sp^3)$ bonds are 1.54(1) Å and 1.52(1) Å and for the $C(sp^3)$–$C(sp^3)$–$C(sp^3)$ angles are 109.7(5)° and 111.0(5)° for molecules **A** and **B**, respectively.

The lactonic group is substantially planar, and the angle between the least-squares plane through O(2), C(1), C(9) and O(1) [planes (1) in Table 5] and that of the ring [planes (2) in Table 5] is 24.8° and 16.8°.

The distribution of the torsion angles around the ring is irregular and clearly corresponds to an unsymmetrical conformation. The signs of torsion angles and the deviations from the least-squares plane of the ring of the

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†Lists of structure factors, anisotropic thermal parameters and H atoms coordinates for both molecules have been deposited with the British Library Lending Division as Supplementary Publication No. (pages).

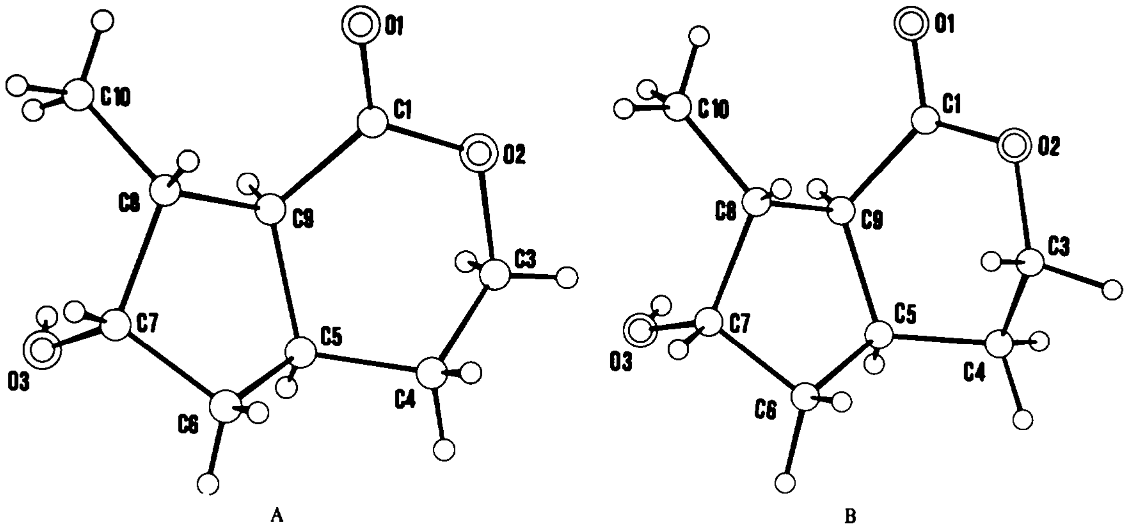

Fig. 2. Projection of the content of the asymmetric unit on the plane defined by O(1), C(5) and C(9) of each molecule: (a) molecule *A*, (b) molecule *B*. The atom numbering system is also shown. It should be noted the different conformation of the six-membered ring in molecule *A* and in molecule *B*.

defining atoms [planes (2) in Table 5] show that the **A** and **B** molecules adopt an opposite distorted twistboat conformation.

The 5-membered ring. The average values for $C(sp^3)$–$C(sp^3)$ bonds are 1.53(1) Å and 1.53(1) Å and for the $C(sp^3)$–$C(sp^3)$–$C(sp^3)$ angles are 104.3(5)° and 104.4(5)° for the two independent molecules in the asymmetric unit. Both molecules show an envelope-type conformation with four atoms approximately coplanar and C(7) 0.621 and 0.616 Å out of plane [planes (3) in Table 5].

The Me and OH substituents are on the same side of the 5-membered ring, with a distance of 0.814 Å and

Table 3. Bond angles (degrees). E.s.d.'s from the final refinement are given in parentheses as units on the last digit

Bond angles	Molecule A	Molecule B
O(1) - C(1) - O(2)	119.1 (5)	117.7 (4)
O(1) - C(1) - C(9)	122.5 (7)	122.0 (7)
O(2) - C(1) - C(9)	118.4 (6)	120.0 (6)
O(2) - C(3) - C(4)	108.2 (6)	109.2 (6)
O(3) - C(7) - C(6)	112.7 (6)	112.2 (5)
O(3) - C(7) - C(8)	107.7 (4)	107.4 (5)
C(1) - O(2) - C(3)	118.3 (4)	119.0 (4)
C(1) - C(9) - C(5)	115.0 (6)	116.6 (6)
C(1) - C(9) - C(8)	112.5 (5)	109.7 (4)
C(3) - C(4) - C(5)	108.6 (6)	110.2 (6)
C(4) - C(5) - C(6)	116.4 (5)	116.4 (6)
C(4) - C(5) - C(9)	110.8 (4)	111.8 (4)
C(5) - C(6) - C(7)	103.8 (5)	105.8 (5)
C(5) - C(9) - C(8)	107.3 (4)	106.4 (4)
C(6) - C(5) - C(9)	103.8 (6)	105.0 (5)
C(6) - C(7) - C(8)	103.0 (5)	103.0 (5)
C(7) - C(8) - C(9)	103.6 (6)	102.0 (4)
C(7) - C(8) - C(10)	114.7 (5)	115.3 (5)
C(9) - C(8) - C(10)	114.0 (5)	115.7 (5)

Table 4. Torsion angles (degrees). E.s.d.'s from the final refinement are given in parentheses as units on the last digit. Sings for the torsion angles have been given according to the convention of Klyne & Prelog (1960)[18]

Torsion angles	Molecule A	Molecule B
O(1) - C(1) - O(2) - C(3)	175.8 (5)	176.2 (5)
O(1) - C(1) - C(9) - C(5)	-146.7 (5)	159.5 (5)
O(1) - C(1) - C(9) - C(8)	-23.4 (7)	-79.5 (7)
O(2) - C(1) - C(9) - C(5)	36.5 (6)	-26.1 (6)
O(2) - C(1) - C(9) - C(8)	159.7 (5)	94.9 (7)
O(2) - C(3) - C(4) - C(5)	69.7 (7)	-65.2 (6)
O(3) - C(7) - C(6) - C(5)	72.1 (4)	77.0 (4)
O(3) - C(7) - C(8) - C(9)	-82.5 (6)	-76.8 (6)
O(3) - C(7) - C(8) - C(10)	42.5 (8)	49.3 (6)
C(1) - O(2) - C(3) - C(4)	-45.5 (7)	44.3 (8)
C(1) - C(9) - C(5) - C(4)	-9.4 (6)	3.0 (6)
C(1) - C(9) - C(5) - C(6)	116.2 (5)	130.1 (4)
C(1) - C(9) - C(8) - C(7)	-143.8 (5)	-157.0 (6)
C(1) - C(9) - C(8) - C(10)	90.8 (5)	77.2 (7)
C(3) - O(2) - C(1) - C(9)	-7.3 (7)	1.6 (7)
C(3) - C(4) - C(5) - C(6)	-157.9 (6)	-80.0 (7)
C(3) - C(4) - C(5) - C(9)	-39.7 (7)	40.6 (6)
C(4) - C(5) - C(6) - C(7)	154.8 (5)	143.4 (5)
C(4) - C(5) - C(9) - C(8)	-135.4 (5)	-119.7 (5)
C(4) - C(9) - C(8) - C(10)	-141.8 (4)	-155.9 (4)
C(5) - C(6) - C(7) - C(8)	-43.7 (5)	-38.1 (5)
C(5) - C(9) - C(8) - C(7)	-16.4 (5)	-30.0 (6)
C(6) - C(5) - C(9) - C(7)	-9.8 (5)	7.4 (6)
C(6) - C(7) - C(8) - C(9)	36.8 (5)	41.8 (6)
C(6) - C(7) - C(8) - C(10)	161.8 (5)	168.0 (5)
C(7) - C(6) - C(5) - C(9)	32.9 (5)	19.1 (5)

0.581 Å for C(10), and 2.032 and 2.020 Å for O(3) to the least-squares plane through C(5), C(6), C(8) and C(9) [planes (3) in Table 5].

EXPERIMENTAL

A Craig Post apparatus (200 stages, 10:10 ml, upper and lower phase) was used for countercurrent distribution (CCD). The separation was monitored by tlc analysis on silica gel F_{254} (solvent, $CHCl_3$/MeOH 95:5). Mass spectra were recorded on a LKB 9000 S spectrometer, ^1H and ^{13}C NMR spectra were registered with a Varian XL 100 spectrometer (using $CDCl_3$ as solvent and TMS as internal standard), and ORD curve was registered with a Cary 60 spectrophotometer.

Material and extraction. Stem bark of *Alstonia boonei* De Wild was collected in the State of Anambra (Nigeria). The dried powdered material was eluted with 2% aqueous AcOH three times. The liquid was made alkaline with $NaHCO_3$ and extracted twice with $CHCl_3$. The pooled extracts after evaporation yielded a residue which amounted to 1.4% of the starting material.

Separation. The extract was submitted to CCD between $CHCl_3$ and phosphate–citric acid buffer (mobile phase) at pH 5.6. A substance, negative to Dragendorff reagent and not detectable by quenching fluorescence under short wavelength UV light, was revealed by anisaldehyde–sulphuric acid reagent. It was purified by CCD between H_2O and $CHCl_3$, K_r ($H_2O/CHCl_3$) = 0.6 and recovered from the aqueous phase by extraction with $CHCl_3$ (0.04% of the starting material).

Boonein 1. Crystals from AcOEt and n-hexane, m.p. 95–96°, IR ($CHCl_3$), ν_{max} 3610, 3440, 1726 and 1718 cm^{-1}, $[\alpha]_D^{20} = +28.6$ ($c = 0.5$, $CHCl_3$), MS, *m/z* (%): 170(M^+, 6), 152(6), 141(18), 139(9), 99(100), 55(67); ^1H NMR, δ: 4.5–4.1 (3H, m, 2H-3 and H-7), 2.00(1H, bd, J = 6 Hz, H-5), 1.20(3H, d, J = 7 Hz, 3H-10); ^{13}C NMR: 175.0, C(1); 74.4, C(7); 66.9, C(3); 46.8, C(9); 43.8, C(8); 40.7, C(6); 33.3, C(5); 29.4, C(4); 13.3, C(10). (Found: C, 63.49; H, 8.45. Calc. for $C_9H_{14}O_3$: C, 63.51; H, 8.29%).

Acetylboonein 3. 1 (200 mg) was acetylated with a mixture of pyridine and Ac_2O (3 ml, 1:1 v/v) and the soln allowed to stand for 12 hr. The reagents were evaporated and the residue was purified by CCD (H_2O:cyclohexane:acetone:AcOEt 10:10:10:1.5, $K_r = 0.30$) to obtain pure 3 (210 mg), as oily compound. MS, *m/z* (%): 212 (M^+, 3), 170(34), 154(70), 153(100), 99(68), 43(43); ^1H NMR, δ: 5.20(1H, bt, J = 4 Hz, H-7), 4.1–4.5(2H, m, 2H-3), 2.08(3H, s, $CO\underline{CH_3}$), 2.00(1H, bd, J = 6 Hz, H-5), 1.20 (3H, d, J = 7 Hz, 3H-10); ^{13}C NMR: 174.1, C(1); 170.4, $\underline{CO}CH_3$; 77.8, (C7); 67.0, C(3); 47.7, C(9); 42.4, C(8); 39.0, C(6);

Table 5. Equations of least-squares best planes referred to the crystal axes. Distances (Å) of atoms from the planes are given in square brackets

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(a) Molecule A[1]

Plane (1) : $-1.633\,\underline{x} - 3.485\,\underline{y} + 8.036\,\underline{z} = 0.719$

[O(1)* = 0.006, O(2)* = 0.005, C(1)* = −0.016,
C(9)* = 0.005]

Plane (2) : $0.915\,\underline{x} + 0.154\,\underline{y} + 8.358\,\underline{z} = 4.124$

[O(1) = −0.172, O(2)* = −0.071, C(1)* = −0.242,
C(3)* = 0.410, C(4)* = −0.374, C(5)* = 0.044,
C(9)* = 0.234]

Plane (3) : $5.073\,\underline{x} - 2.758\,\underline{y} + 5.968\,\underline{z} = 2.086$

[O(3) = 2.032, C(5)* = 0.057, C(6)* = −0.037,
C(7) = 0.621, C(8)* = 0.038, C(9)* = 0.058,
C(10) = 0.814]

(b) Molecule B[1]

Plane (1) : $0.893\,\underline{x} - 4.148\,\underline{y} + 7.960\,\underline{z} = 7.070$

[O(1)* = −0.010, O(2)* = −0.009, C(1)* = 0.028,
C(9)* = −0.008]

Plane (2) : $2.702\,\underline{x} - 1.769\,\underline{y} + 7.743\,\underline{z} = 7.521$

[O(1) = 0.482, O(2)* = 0.077, C(1)* = 0.185,
C(3)* = −0.368, C(4)* = 0.348, C(5)* = −0.062,
C(9)* = −0.179]

Plane (3) : $-4.448\,\underline{x} + 7.245\,\underline{y} + 5.457\,\underline{z} = 5.211$

[O(3) = 2.020, C(5)* = −0.043, C(6)* = 0.028,
C(7) = 0.616, C(8)* = −0.028, C(9)* = 0.044,
C(10) = 0.581]

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(1) The e.s.d.'s in the atomic positions are 0.004-0.005 Å for O atoms, 0.005-0.007 Å for C atoms.

(*) Atoms defining the plane.

34.1, C(5); 29.4, C(4); 21.0, <u>CH</u>$_3$CO; 14.0, C(10). (Found: C, 62.12; H, 7.80. Calc. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%).

Saponification of 3. 3 (30 mg) dissolved in MeOH (5 ml) was added to 1% K_2CO_3 aq (5 ml). After 3 days the mixture was diluted with water and extracted with $CHCl_3$. After purification by CCD, as reported for boonein, and crystallization from AcOEt and n-hexane, 1 (16 mg) was obtained; the product was confirmed by comparison of m.p., rotatory power and spectroscopical data.

7-Oxo-boonein 4. CrO_3 (94 mg) was added to a soln of 1 (160 mg) in AcOH (10 ml) and the mixture vigorously stirred for 2 days. Few drops of MeOH were added to the green soln, which was then concentrated *under vacuum*. The residue was dissolved between 0.5 N HCl and $CHCl_3$ and the residue of the organic phase crystallized, without further purification, from AcOEt, m.p. 105–107°, IR ($CHCl_3$), ν_{max}: 1740, 1726, and 1718 cm^{-1}, MS, *m/z* (%): 168(M$^+$, 58), 148(31), 126(11), 99(16), 55(100). ^{1}H NMR, δ: 4.5–4.1 (2H, m, 2H-3), 1.28 (3H, d, J = 7 Hz, 3H-10). ^{13}C NMR: 215.8, C(7); 171.6, (C(1); 68.1, C(3); 47.1, C(9); 44.9, C(8); 43.4, C(6); 30.9, C(5); 27.9, C(4); 14.7, C(10). ORD (MeOH), $\Phi(\lambda_{max}$, nm): −1430(309), +3150(262). (Found: C, 64.41; H, 7.33. Calc for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.)

X-ray crystallography

Crystal data. $C_9H_{14}O_3$. Mol. wt. = 170.21. Monoclinic, a = 7.764(5), b = 13.660(3), c = 8.459(2) Å; β = 92.07(3)°, V = 896.5 Å,^{3} Z = 4, D_c = 1.261 g cm^{-3}. Space group $P2_1$, from systematic absences: 0k0 for K odd. Mo $K\ \alpha$ radiation, λ = 0.71069 Å; μ = 1.006 cm^{-1}.

Crystallographic measurements. Colourless prisms were grown by slow evaporation of boonein in a mixture of benzene and acetone (*ca* 1:1). After survey photography by oscillation and Weissenberg techniques a transparent well-shaped cyrstal, *ca* $1.14 \times 0.38 \times 0.46$ mm, was mounted on a Nonius CAD-4F, *K*-geometry diffractometer, which used graphite monochromatized Mo*K* α radiation.

Cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 25 reflexions. Intensities were collected at room temperature with an $\omega/2\theta$ scan, a variable scan speed according to the intensity, and an ω scan angle of $(1.20 + 0.35 \tan \theta)°$. The reciprocal space was explored up to $\theta = 29°$. Three periodically-monitored reflexions showed no significant crystal deterioration. 1519 reflexions with $I > 2\sigma(I)$, where $\sigma(I)$ is the e.s.d. based on simple counting statistics, were considered as non-zero. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Structure analysis. The structure was solved by direct methods with MULTAN 78[11] and all non-H atoms for the two independent molecules were revealed in the E-map with the highest figure of merit. Isotropic and then anisotropic least-squares refinement, followed by the introduction of the H atoms as given by a difference synthesis, yielded an *R*-value of 0.0609. The final refinement was carried out with a two-block approximation of the normal-equations matrix, using one block for the positional coordinates and one block for the temperature factors and the scale factor. The H-atoms were maintained in fixed positions, with B equal to 4.3 Å^2 for all the H(C) and to 8.0 Å^2 for the two H(O). Refinement converged at $R = 0.0538$, $R_W = 0.0662$. Weights were given according to the function $w = 1/(a + b|F_o| + c|F_o|^2)$, with $a = 47.2$, $b = 1.0$ and $c = 0.1$.[12] The number of observations per refined parameter was 7.0.† All parameter shifts during the final cycle were less than 0.2 σ, and a final difference map showed no peak larger than 0.16 eÅ^{-3}.

The scattering factors of Cromer & Mann[13] were used for O and C and of Hanson *et al.*[14] for H. Calculations were carried out on the Oxford University ICL 2980 computer with *CRYSTALS* package;[15] on the UNIVAC 1100/82 computer of the University of Rome and on the HP 21MX minicomputer of the CNR Research Area with local crystallographic programs.[16,17]

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†The 020 and 002 reflexions, which were seriously affected by secondary extinction, were excluded from the last refinement.