Table 4. *Hydrogen bonds*

D H *A*	H···*A* (Å)	∠*DHA* (°)
O–H···Cl	2·28 (3)	171 (2)
N–H···O	1·89 (2)	165 (2)
N–H···Cl	2·16 (2)	174 (2)
N–H···Cl	2·36 (2)	170 (2)

The constraints imposed by the two-carbon bridge and the fusion to the aromatic ring force the six-membered ring into a half-chair conformation. In the crystal lattice, the chloride anion appears to be hydrogen-bonded to the hydroxy proton and two of the amino protons of three different neighboring molecules. The third amino proton is hydrogen-bonded to the hydroxy oxygen of an adjacent molecule. Table 4 summarizes the pertinent parameters for the hydrogen bonds.

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16,18-Dihydroxy-8-oxo-8-demethyl-5α-kolava-3,13-diene-15,17-dioic Acid 15,16:17,18-Dilactone (Desmethyl-marrubiaketone)

By A. Kirfel

Lehrstuhl für Mineralogie und Kristallographie am Mineralogischen Institut der Universität Bonn, D-5300 Bonn, Poppelsdorfer Schloss, Federal Republic of Germany

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Abstract. $C_{19}H_{22}O_5$, orthorhombic, $P2_12_12_1$, a = 12·825 (2), b = 13·545 (1), c = 9·855 (1) Å, V = 1665·6 (5) Å^3, Z = 4, D_x = 1·317 g cm^{-3}. The stereochemical configuration of a new natural compound which was unclear from chemical and spectroscopic methods has been established unambiguously by X-ray structure analysis. The molecules are held together by packing forces only.

Introduction. The specimen was provided by Professor R. Tschesche and B. Streuff, Institute of Organic Chemistry and Biochemistry, Universität Bonn. For the present investigation a clear crystal of irregular shape with a maximum diameter of 0·2 mm was used. Systematic absences were $h00$, h odd, $0k0$, k odd and $00l$, l odd. Intensities were measured in the θ–2θ mode on an automatic Syntex $P2_1$ four-circle diffractometer with Mo $K\alpha$ radiation (λ = 0·71069 Å) monochromatized by a graphite crystal.

With a 2° plus ($\alpha_1\alpha_2$)-dispersion scan range for positive h, k, l and a maximum $2\theta = 45°$, 1267 unique reflexions were recorded of which 527 were regarded as unobserved ($I < 3\sigma$) owing to the small sample size and the high overall temperature factor (B = 4·1 Å^2). No absorption correction was applied (μ = 1·0 cm^{-1}).

The structure (24 heavy atoms) was solved with *MULTAN* (Germain, Main & Woolfson, 1971) using 180 $|E|$'s $\geq$ 1·4, 2340 Σ_2 relationships, $|E_hE_kE_{h-k}| \geq$ 3·0. The starting set with the highest CFOM fixed the positions of 23 heavy atoms. The position of the missing methyl group C atom was calculated as well as derived from a difference electron density map at R = 0·27. Refinement was by full-matrix least-squares calculations with anisotropic temperature factors. Except for the methyl group H atoms, which were ignored, all H positions were calculated. The H atoms were allocated the isotropic temperature factors of their carrier atoms, and refined for positional parameters.

Table 1. *Positional parameters (non-hydrogen atoms* × 10^4, *hydrogen atoms* × 10^3) *with standard deviations in parentheses*

	x	*y*	*z*
C(1)	2164 (5)	7443 (5)	2411 (7)
C(2)	1104 (5)	6957 (5)	2050 (8)
C(3)	1001 (5)	5939 (5)	2663 (8)
C(4)	1788 (5)	5481 (5)	3250 (7)
C(5)	2883 (5)	5880 (5)	3441 (6)
C(6)	3038 (5)	6235 (4)	4926 (6)
C(7)	4111 (6)	6697 (5)	5118 (8)
C(8)	4309 (5)	7509 (5)	4070 (8)
C(9)	4152 (5)	7231 (4)	2524 (7)
C(10)	3085 (5)	6706 (5)	2364 (6)
C(11)	5034 (5)	6520 (5)	2081 (7)
C(12)	6153 (5)	6887 (5)	2297 (9)
C(13)	6962 (5)	6214 (5)	1738 (8)
C(14)	6883 (6)	5431 (6)	904 (8)
C(15)	7936 (7)	5057 (6)	713 (9)
C(16)	8069 (6)	6378 (6)	2121 (8)
C(17)	1796 (7)	4431 (6)	3607 (7)
C(18)	3483 (5)	4900 (5)	3202 (7)
C(19)	4218 (5)	8182 (5)	1616 (8)
O(1)	4631 (4)	8316 (4)	4415 (5)
O(2)	8632 (4)	5615 (5)	1434 (6)
O(3)	8242 (4)	4361 (4)	57 (6)
O(4)	2794 (4)	4113 (3)	3705 (5)
O(5)	1071 (4)	3849 (4)	3777 (6)
H1(C1)	218 (4)	770 (4)	316 (6)
H2(C1)	230 (4)	817 (4)	161 (6)
H1(C2)	41 (4)	733 (4)	230 (6)
H2(C2)	120 (4)	702 (4)	66 (5)
H(C3)	40 (4)	562 (4)	250 (7)
H1(C6)	286 (3)	559 (3)	549 (4)
H2(C6)	249 (3)	674 (4)	516 (5)
H1(C7)	482 (4)	624 (4)	489 (6)
H2(C7)	417 (5)	720 (5)	594 (6)
H(C10)	316 (4)	639 (3)	131 (5)
H1(C11)	490 (3)	647 (4)	122 (5)
H2(C11)	500 (4)	583 (4)	269 (6)
H1(C12)	603 (4)	698 (4)	349 (6)
H2(C12)	626 (4)	760 (4)	172 (6)
H(C14)	627 (4)	520 (4)	32 (6)
H1(C16)	833 (4)	649 (4)	302 (6)
H2(C16)	833 (5)	697 (5)	188 (7)
H1(C18)	416 (4)	492 (4)	372 (6)
H2(C18)	365 (4)	486 (4)	217 (5)

Owing to the large number of parameters (275) refinement had to take place in overlapping cycles. The reflexions were weighted with $w = 1/\sigma(F_{\text{obs}})$. An isotropic extinction factor (Zachariasen, 1963) was included (final value $2{\cdot}7 \times 10^{-6}$).

With eight reflexions omitted from the calculation the refinement was stopped when the parameter shifts were well below the standard deviations. The final *R* was 0·097 (0·045 omitting unobserveds) and R_w = 0·044 (0·032 omitting unobserveds). The goodness of fit was 1·54.*

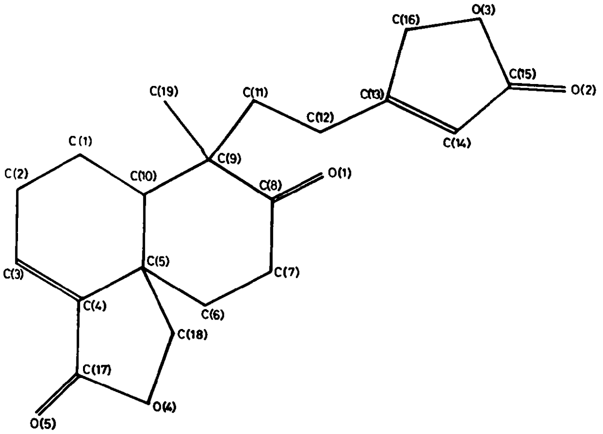

Fig. 1. Numbering scheme of atoms.

Discussion. From blossoms and leaves of *Leonorus marrubiastrum* L. (Labiatae) a small amount of a new natural compound with the molecular formula $C_{19}H_{22}O_5$ has been isolated.

From spectroscopic methods, *e.g.* IR, UV, ^{1}H-NMR, ^{13}C-NMR, MS, the molecule was found to consist of two six-membered rings (*A*) and (*B*), (*A*) being connected to a lactone group. Referring to the conventional chemical numbering scheme a tertiary methyl group and a side chain with a butenolide ring were found to be bound to C(9) of ring (*B*). In addition, a ketone group was found to be connected to (*B*). However, the ketone-group position, the stereochemical position of the methyl group, and whether the two six-membered rings were *cis* or *trans* could not be established. Because of the small amount of substance a further structure analysis by chemical methods was impossible; instead the molecular structure of the title compound (Fig. 1) was established by X-ray diffraction analysis.

Tables 1 and 2 give the final fractional atomic coordinates, bond distances, and angles of the molecule. All distances and angles are normal and the distances C(3)–C(4), 1·311 (9) Å, and C(13)–C(14), 1·332 (11) Å, clearly establish these as double bonds,

Fig. 2. Stereoscopic view of the molecule.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33087 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Selected distances* (Å) *and angles* (°)

C(1)–C(2)	1·551 (9)	C(9)–C(19)	1·556 (9)
C(1)–C(10)	1·547 (9)	C(9)–C(11)	1·545 (9)
C(1)–C(3)	1·504 (10)	C(11)–C(12)	1·531 (9)
C(3)–C(4)	1·311 (9)	C(12)–C(13)	1·481 (10)
C(4)–C(5)	1·515 (9)	C(13)–C(14)	1·332 (11)
C(4)–C(17)	1·463 (11)	C(13)–C(16)	1·485 (11)
C(5)–C(6)	1·518 (9)	C(14)–C(15)	1·454 (12)
C(5)–C(10)	1·544 (9)	C(15)–O(2)	1·360 (10)
C(5)–C(18)	1·551 (9)	C(15)–O(3)	1·199 (11)
C(6)–C(7)	1·521 (10)	C(16)–O(2)	1·423 (10)
C(7)–C(8)	1·512 (10)	C(17)–O(4)	1·354 (10)
C(8)–C(9)	1·542 (10)	C(17)–O(5)	1·232 (10)
C(8)–O(1)	1·214 (8)	C(18)–O(5)	1·465 (10)
C(9)–C(10)	1·551 (9)		
C(2)–C(1)–C(10)	112·8 (5)	C(10)–C(9)–C(19)	111·8 (5)
C(1)–C(2)–C(3)	112·2 (6)	C(11)–C(9)–C(19)	108·8 (5)
C(2)–C(3)–C(4)	122·3 (6)	C(9)–C(10)–C(1)	112·0 (5)
C(3)–C(4)–C(5)	126·5 (6)	C(9)–C(10)–C(5)	114·5 (5)
C(3)–C(4)–C(17)	124·5 (7)	C(5)–C(10)–C(1)	108·6 (5)
C(5)–C(4)–C(17)	108·1 (6)	C(9)–C(11)–C(12)	116·6 (6)
C(4)–C(5)–C(6)	110·4 (5)	C(11)–C(12)–C(13)	114·1 (6)
C(4)–C(5)–C(10)	109·5 (5)	C(12)–C(13)–C(14)	130·8 (7)
C(4)–C(5)–C(18)	97·9 (5)	C(12)–C(13)–C(16)	119·3 (6)
C(6)–C(5)–C(10)	112·0 (5)	C(14)–C(13)–C(16)	109·9 (7)
C(6)–C(5)–C(18)	110·1 (5)	C(13)–C(14)–C(15)	106·4 (7)
C(10)–C(5)–C(18)	116·0 (5)	C(14)–C(15)–O(2)	110·6 (7)
C(5)–C(6)–C(7)	111·3 (5)	C(14)–C(15)–O(3)	130·1 (8)
C(6)–C(7)–C(8)	111·8 (6)	O(2)–C(15)–O(3)	119·2 (8)
C(7)–C(8)–C(9)	116·1 (6)	C(15)–O(2)–C(16)	107·9 (6)
C(7)–C(8)–O(1)	122·0 (7)	O(2)–C(16)–C(13)	105·2 (6)
C(9)–C(8)–O(1)	121·7 (6)	C(4)–C(17)–O(4)	109·5 (7)
C(8)–C(9)–C(10)	108·8 (5)	C(4)–C(17)–O(5)	130·3 (8)
C(8)–C(9)–C(11)	108·7 (5)	O(4)–C(17)–O(5)	120·2 (7)
C(8)–C(9)–C(19)	109·2 (5)	C(17)–O(4)–C(18)	108·3 (5)
C(10)–C(9)–C(11)	109·5 (5)	O(4)–C(18)–C(5)	106·0 (5)

Table 3. *Atom-to-plane distances* (Å) *and angles* (°) *between planes*

Plane *A*

C(1)	C(2)	C(3)	C(4)	C(5)	C(10)
0·231	−0·014	−0·049	0·012	0·156	−0·336

Plane *B*

C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
−0·229	0·233	−0·224	0·205	−0·191	0·206

Plane *C*

C(4)	C(5)	C(17)	C(18)	O(4)
−0·131	0·185	0·018	−0·184	0·111

Plane *D*

C(13)	C(14)	C(15)	C(16)	O(2)
0·000	−0·001	0·001	0·001	−0·001

Angles between planes

	B	*C*	*D*
A	55	21	61
B	–	76	78
C	–	–	45

Fig. 3. Stereoscopic view of the unit cell along **c**.

thus confirming the chemical information. The unclear ketone position was located at C(8). The distances involving H vary between 0·80 and 1·34 Å with a mean value of 1·04 (14) Å. An *ORTEP* drawing (Johnson, 1965) of the molecule is depicted in Fig. 2.

Table 3 contains results of least-squares-plane calculations and includes the angles between the defined planes.

Both six-membered rings (planes *A*, *B*) are in chair configurations oriented *cis*, with an angle between their mean planes of 55°. The methyl group [C(19)] and the lactone-ring [C(17)–C(18), plane *C*] are in *α* positions whereas the side chain with the planar butenolide-ring [C(15)–C(16), plane *D*] is in the *β* position.

Closest distances between atoms of adjacent molecules are greater than 3·2 Å; hence the cohesion of the molecules is due solely to van der Waals forces. Fig. 3 shows a stereoscopic *ORTEP* drawing of the arrangement of the molecules in the unit cell viewed along **c**.

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