ISOLATION OF AN INDANONE FROM *Equisetum arvense* AND ITS CRYSTAL AND MOLECULAR STRUCTURE

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UDC 547.665

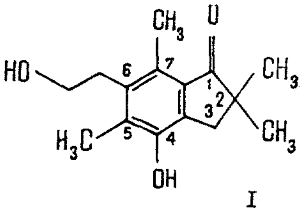
In a study of the chemical composition of the field horsetail *Equisetum arvense* L. we have isolated a colorless optically active crystalline compound with mp 210-212°C and the molecular formula $C_{15}H_{20}O_3$ deduced from the results of elementary analysis and mass spectrometry (M^+ 248). The compound is soluble in methanol, ethanol, and pyridine, partially solubl in chloroform, and insoluble in water.

As follows from the IR spectrum, two of the oxygen atoms of this compound are present i hydroxy groups (broad bands at 3400 and 3300 cm^{-1}) and the third belongs to a conjugated ketone group (1690 cm^{-1}).

The PMR spectrum of the trimethylsilyl ether of this compound has the signals of four methyl groups, two of which are equivalent (δ = 1.08 ppm, singlet) and two are located in an aromatic ring. In addition, the spectrum has the signal of an isolated methylene group (δ = 2.62 ppm, singlet) and two triplets with δ = 2.84 and 3.54 ppm and J = 8 Hz, belonging to a hydroxyethyl group.

The PMR spectrum contains no signals of aromatic protons, but the presence of a benzene ring followed from the ^{13}C NMR spectrum (six signals in the 125-150 ppm region) and the results of UV and IR spectroscopy. The combination of the facts given permitted us to assign the compound isolated to the class of indanones. The arrangement of the substituents in the benzene ring was made on the basis of a comparison with the structures of known natural compounds of the pterosin type [1]. For the compound isolated we have suggested the structure of 4-hydroxy-6-(2-hydroxyethyl)-2,2,5,7-tetramethylindanone (I). The position of the phenol hydroxyl on the C_4 atom also followed from the agreement of the observed absorption band in the UV spectrum (270 nm) with the calculated position (272 nm). However, the presence of a strong hydrogen bond, which is shown in the IR spectrum of the compound, did not exclude the possibility of the presence of the hydroxyl at C_7 (of the isopterosin type) [2].

The results of an x-ray structural analysis confirmed the structure (I) and provided an explanation of the features of the vibrational spectrum that have been mentioned.



I

The crystals for x-ray structural analysis were grown from methanol. The colorless cry tals were monoclinic with the following unit cell parameters: a = 9.276, b = 8.532, c = 16.887 Å, γ = 97.1°. The cell contained four formula units with the composition $C_{15}H_{20}O_3$. The systematic extinctions of the intensities unambiguously fixed the space group at $P2_1/b$.

The cell contained one crystallographically independent indanone molecule, the interatom distances and valence angles in which are given in Fig. 1 and below:

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Institute of Applied Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 508-513, July-August, 1978. Original article submitted March 22, 1978.

0009-3130/78/1404-0432$07.50

Atom	Angle, degree	Atom	Angle, degrees
$O_3—C_{15}—H_{20}$	112	$H_{13}—C_{12}—H_{11}$	86
$C_2—C_3—H_3$	113	$H_{12}—C_{12}—C_5$	109
$C_9—C_3—H_4$	115	$H_{14}—C_{13}—H_{16}$	114
$C_2—C_{10}—H_6$	110	$C_7—C_{13}—H_{15}$	108
$H_5—C_{10}—H_7$	103	$H_{17}—C_{14}—C_6$	109
$C_{12}—C_{11}—H_9$	113	$H_{18}—C_{14}—C_{15}$	113
$H_{10}—C_{11}—H_8$	116	$C_{14}—C_{15}—H_{19}$	110

Each of the two linked rings of the molecule is planar, and the rings themselves are almost in the same plane: the angle between them is 3.2°. The equations of the planes and the deviations of the atoms from them are given in Table 1.

The C_2 bonds with the carbon atoms of the methyl groups lie in a plane perpendicular to the plane of the five-membered ring. The hydroxyethyl chain $CH_2—CH_2—OH$ has a zigzag shape determined by the tetrahedral coordination of the carbon atoms. The four atoms C_6, C_{14}, C_{15}, and O_3 lie in one plane which makes an angle of 86.5° with the six-membered ring.

The packing of the molecules in the cell is shown in Fig. 2, which gives a projection of the structure along the b axis. The molecules are joined into a layer parallel to the zx coordinate plane by means of hydrogen bonds of the OH···O type, which are shown in Fig. 2 by dashed lines. Each molecule forms an H bond with four neighboring molecules connected with it by two-fold screw axes. All three oxygen atoms participate in these bonds, the hydroxy group of the hydroxyethyl chain forming two bonds in one of which — with the ketonic oxygen — it is the proton donor while in the other — with the hydroxy group in the six-membered ring — it acts as the proton acceptor. The distances are: O—H = 0.9 Å, H···O = 1.97 and 1.92 Å, O···O = 2.80 and 2.77 Å. The angles at the H atoms in the O—H···O bonds are 153°.

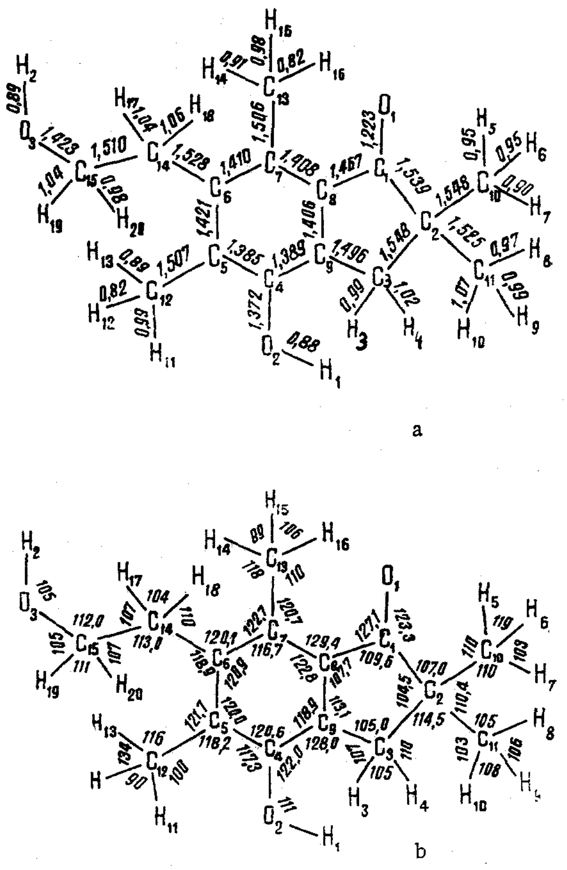


Fig. 1. Interatomic distances (a) and valence angles (b) in the indanone studied. Standard deviations for distances of the C—O type 0.003 Å, of the C—C type 0.004 Å, and of the C—H and O—H types 0.04 Å, and in the angles not containing hydrogen atoms 0.3° and those containing hydrogen atoms 4-9°.

TABLE 1. Equations of the Planes Ax + By + Cz — D = 0 Least Deviating from the Group of Atoms

Plane	Atoms defining the plane	Coefficients of the equation				Deviation of the atoms, Å
		A	B	C	D	
I	$C_4, C_5, C_6, C_7, C_8, C_9$	1,0408	8.1781	2.7867	3,6218	C_4(−0,001) C_5(0,000) C_6(0,004) C_7(—0,007) C_8(0,007) C_9(—0,002)
II	C_1, C_2, C_3, C_8, C_9	0.7007	8,2982	2.0811	3.2849	C_1(—0,009) C_2(0,016) C_3(—0,019) C_8(—0,004) C_9(0,015)
III	C_2, C_{10}, C_{11}	8.392	−1,0372	−7.1936	−1,659	
IV	C_6, C_{14}, C_{15}, O_3	9,086	—2.613	1.289	1,475	C_6(−0,04) C_{14}(0,04) C_{15}(0,04) O_3(−0,04)

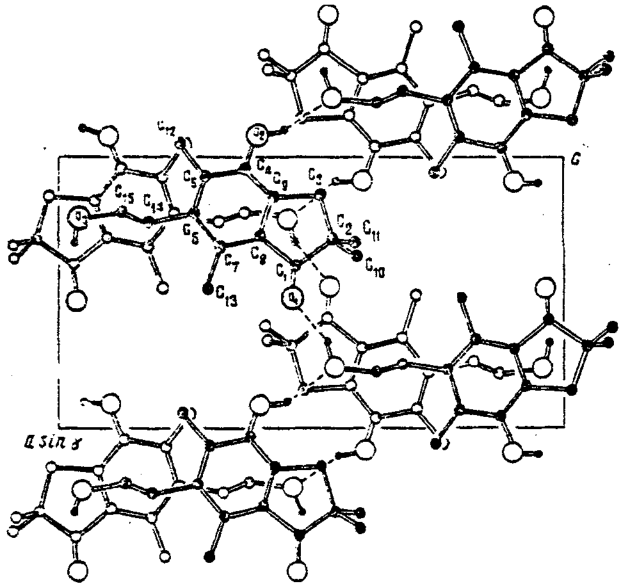


Fig. 2. Projection of the structure on the xz plane.

The molecules from the different layers, which are displaced with respect to one another by reflection glide planes (which pass through the points z = 0.25 and 0.75), form a peculiar type of stack. In each of them, the hydroxyethyl chains are located between the bicyclic nuclei of the molecules of the neighboring layers, and the C_{15} atom is "countersunk" in the six-membered ring of the molecule of the neighboring layer lying below it in some stacks and above it in others. Thus, in the structure alternating polar antiparallel stacks of molecules bound weakly to one another are observed. There are no close contacts between the molecules of the neighboring layers (the shortest distance for the nonhydrogen atoms is 3.54 Å) and the bond between them is made by van der Waals forces.

In recent years, more than 30 indanones have been isolated from ferns [1-4].

Indanones have not been found previously in the horsetail family. The finding of representatives of the indanones in a horsetail permits the hypothesis that this rare class of natural substances was distributed in the ancient flora of the earth. When the present work was close to completion a report appeared [5] of the isolation of the indanone (I), which was called onitin from the fern *Onichium auratum*. Since we did not have available information on the physicochemical properties and methods of establishing the structure it is not possible to speak with complete certainty of the identity of these compounds.

EXPERIMENTAL

The IR spectra were taken on a UR-10 spectrophotometer in KBr, the UV spectra on an SF-4A instrument in methanol, the PMR spectra on a Varian HA-100D spectrometer at 100 MHz (with HMDS as internal standard), the ^{13}C spectra on a Brüker Spectrospin in DMSO-d_6 (with TMS as

TABLE 2. Coordinates and Anisotropic Temperature Parameters ($\times 10^4$) in the Form of $\exp -[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{23}kl + B_{13}hb]$ of the Nonhydrogen Atoms in the Structure

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
O_1	0,5163 (2)	0,2340 (3)	0,4635 (1)	78 (2)	229 (5)	26 (1)	98 (4)	8 (3)	− 4 (2)
O_2	0,9032 (2)	0,3226 (3)	0,4005 (1)	70 (2)	244 (5)	22 (1)	79 (5)	20 (3)	5 (2)
O_3	0,2207 (2)	0,2424 (3)	0,0459 (1)	80 (2)	236 (5)	15 (1)	37 (5)	− 3 (3)	0 (2)
C_1	0,3853 (3)	0,2448 (4)	0.4653 (2)	73 (3)	113 (5)	19 (1)	40 (5)	− 7 (3)	− 5 (3)
C_2	0,7033 (3)	0,2635 (4)	0.0423 (2)	72 (3)	113 (5)	17 (1)	43 (6)	1 (3)	11 (3)
C_3	0,8601 (3)	0,2478 (4)	0,0153 (2)	73 (3)	208 (7)	16 (1)	48 (7)	− 7 (4)	0 (2)
C_4	0,0421 (3)	0,3091 (4)	0,3756 (2)	63 (3)	126 (6)	18 (1)	34 (6)	1 (3)	2 (3)
C_5	0,0717 (3)	0,3330 (4)	0,2956 (2)	81 (3)	120 (5)	17 (1)	25 (6)	− 7 (3)	−11 (3)
C_6	0,2139 (3)	0,3255 (3)	0,2662 (2)	91 (3)	99 (5)	15 (1)	13 (6)	− 6 (3)	2 (3)
C_7	0,3263 (3)	0,2920 (3)	0,3172 (2)	73 (3)	99 (5)	16 (1)	12 (6)	−11 (3)	9 (2)
C_8	0,2910 (3)	0,2714 (3)	0,3978 (2)	68 (3)	106 (5)	17 (1)	32 (6)	−10 (3)	− 5 (2)
C_9	0,1505 (3)	0 2780 (3)	0,4273 (2)	68 (3)	109 (5)	14 (1)	20 (6)	−11 (3)	4 (2)
C_{10}	0,6869 (3)	0.4170 (4)	0,0844 (2)	148 (4)	149 (6)	32 (2)	105 (8)	−32 (5)	−24 (4)
C_{11}	0,6421 (3)	0,1221 (4)	0,0937 (2)	111 (4)	162 (6)	31 (1)	33 (7)	47 (5)	6 (3)
C_{12}	0.4771 (3)	0,2769 (4)	0,2879 (2)	82 (3)	197 (7)	22 (1)	55 (19)	−10 (4)	15 (2)
C_{13}	0,9500 (3)	0,3715 (5)	0,2428 (2)	121 (4)	219 (7)	19 (1)	121 (8)	7 (4)	−18 (3)
C_{14}	0,2440 (3)	0,3550 (4)	0 1783 (2)	104 (3)	124 (6)	15 (1)	−5 (6)	6 (3)	11 (3)
C_{15}	0,2088 (3)	0,2086 (4)	0.1283 (2)	99 (3)	136 (6)	15 (1)	31 (7)	− 5 (4)	2 (3)

TABLE 3. Coordinates of the Hydrogen Atoms in the Structure

Atom	x	y	z
H_1	0,891 (5)	0,304 (5)	0,451 (3)
H_2	0,313 (4)	0,235 (5)	0.033 (3)
H_3	0.069 (4)	0.157 (5)	0,524 (3)
H_4	0,101 (4)	0,345 (5)	0.547 (3)
H_5	0,266 (4)	0,076 (5)	0.637 (3)
H_6	0,260 (5)	0.000 (5)	0,552 (2)
H_7	0,427 (4)	0,072 (5)	0,592 (3)
H_8	0,341 (5)	0.470 (5)	0,571 (3)
H_9	0,303 (4)	0,376 (5)	0.644 (3)
H_{10}	0,461 (4)	0.387 (5)	0.595 (3)
H_{11}	0,481 (4)	0,213 (5)	0.243 (3)
H_{12}	0,519 (4)	0,377 (5)	0,266 (3)
H_{13}	0,529 (4)	0,259 (5)	0,327 (3)
H_{14}	−0,004 (5)	0,473 (6)	0,215 (3)
H_{15}	0,954 (4)	0,325 (5)	0,201 (3)
H_{16}	0,883 (4)	0,426 (5)	0,265 (3)
H_{17}	0,181 (4)	0,437 (5)	0,160 (3)
H_{18}	0,355 (4)	0,410 (5)	0.170 (3)
H_{19}	0,100 (4)	0,161 (5)	0,137 (3)
H_{20}	0,275 (4)	0,135 (5)	0,146 (3)

internal standard), and the mass spectra on a Varian CH-8 instrument at 70 eV at a recording temperature of 155°C. The purity of the substances was checked by TLC in "Woelm" silica gel and on Silufol in the ethyl acetate—benzene—methanol (5:6:1), ethyl acetate—benzene (2:3), and chloroform—methanol (9:1) systems.

The results of elementary analysis corresponded to the calculated figures.

Isolation of the Indanone. The epigeal part of the field horsetail (moisture content 70-73%) was extracted with methanol, and the extract was partially evaporated and was extracted successively with chloroform, ether, and ethyl acetate. Saponaretin and kaempferol 3-sophoroside [6, 7] were isolated from the aqueous residue by chromatography on polyamide with elution by water and methanol—water (1:9). Further elution with methanol—water (15:85 and 20:80) gave a fraction from which compound (I) was isolated by chromatography on silica gel in benzene—ethyl acetate and benzene—chloroform systems, the compound also being detected in the ethereal extract.

4-Hydroxy-6-(2-hydroxyethyl)-2,2,5,7-tetramethylindanone. $C_{15}H_{20}O_3$, mp 210-212°C (methanol); ν (KBr) 3400, 3300, 1690, 1600 cm^{-1}; λ_{max} (methanol) 270, 323 nm (log ε 3.66, 3.06). PMR spectrum (TMS ether, δ, ppm): 1.08 (singlet, two CH_3 groups at C_6, 6 H); 2.62 (singlet,

$-CH_2-$, 2 H); 2.18 and 2.3 (singlets, two CH_3 groups at C_5 and C_7, respectively 3 H each); two triplets with centers at 2.84 and 3.54 ($HO-CH_2-CH_2-$ at C_6, 2 H each, J = 8 Hz). ^{13}C NMR ($DMSO-d_6$) δ, ppm: 12.6 (2C); 25.4 (2C); 32.0; 44.8: 38.3; 60.0; 127.6; 130.2; 130.6; 136.8 136.9; 149.9; 211.5.

Preparation of the TMS Ether. A solution of 30 mg of (I) in 0.5 ml of pyridine was treated with 0.5 ml of chlorotrimethylsilane and 0.5 ml of hexamethyldisiloxane. The mixtur was kept in a closed flask at room temperature for 25-30 min, and then the excess of reagent was distilled off, CCl_4 was added, the precipitate was separated off, and the filtrate was evaporated until the smell of pyridine had disappeared. The resulting TMS ether of the indanone was used for recording the PMR spectra.

Interpretation of the Crystal Structure. The experimental material for the x-ray structural analysis was obtained on a DAR-UMB automatic x-ray diffractometer in monochromatized Mo Kα radiation ($\sin \Theta/\lambda$ 0.8 $Å^{-1}$). The intensities of 3140 independent reflections were measured, of which 1890 proved to be nonzero ($J > 3\sigma$). In the recalculation of the intensities two structural factors, polarization and kinematic factors, were taken into account. No correction was made for absorption.

The structure was interpreted by the direct method under automatic conditions according to the programs of Andrianov et al. [8]. At this stage, we localized the nonhydrogen atoms with an initial R factor of 31.3%. The refinement of the structure by the method of least squares according to the "Kristall" group of programs [9] in the isotropic approximation reduced the R factor to 14.9%. Several cycles of refinement taking the isotropic thermal vibrations of the atoms and the individual weight factors of the structural amplitudes into account reduced the R factor to 9.2%. After this, a difference synthesis was calculated from which all the 20 hydrogen atoms appeared. The final refinement of the structure taking all the atoms into account led to a value R = 6.5% (for the hydrogen atoms, an isotropic temperature factor B = 5 $Å^2$ was adopted and only the position parameters were refined). The coordinates and anisotropic temperature parameters of the basis atoms are given in Tables 2 and

SUMMARY

From the herb *Equisetum arvense* L. an indanone compound has been isolated for the first time for which the structure of 4-hydroxy-6-(2-hydroxyethyl)-2,2,5,7-tetramethylindanone has been established by spectroscopy and x-ray structural analysis.

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