NATURAL QUINONES

I. A New Anthraquinone from Rubia iberica (Fisch. Ex D.C.) C. Koch

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As a result of the study of the chemical composition of the roots of Rubia iberica (Fisch. ex D. C.) C. Koch (Iberian madder) collected in the USSR we have isolated, in addition to known anthracene derivatives, an anthraquinone with the composition $C_{17}H_{14}O_5$, mp 182-183°C (decomp., from benzene), called ibericin.

The UV spectrum of ibericin (Fig. 1) shows that it is a hydroxyanthraquinone. The IR spectrum of ibericin (Fig. 2) has bands of a hydroxyl group not involved in an internal-complex hydrogen bond (3240 cm^{-1}), a free quinonoid carbonyl group (1673 cm^{-1}) and a quinonoid C=O group connected by an internal-complex hydrogen bond to a hydroxyl in the α position (1630 cm^{-1}). In addition, the spectrum contains a strong band at 1587 cm^{-1} due to the vibrations of the rings which is characteristic for anthraquinones. The band of the stretching vibrations of an OH group involved in an internal-complex hydrogen bond is generally absent from the IR spectra of α-hydroxyanthraquinones [1, 2]. Thus, ibericin has at least two hydroxyl groups. To determine their nature, mono- and diacetyl derivatives of ibericin were prepared.

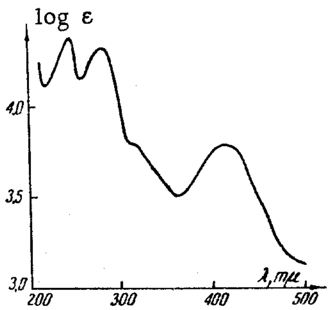
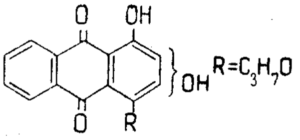


Fig. 1. UV spectrum of ibericin in 96% ethanol.

In the IR spectrum of ibericin monoacetate, the hydroxyl band had disappeared and a carbonyl band of a vinyl ester appeared in the 1770 cm^{-1} region. The band of the C=O group remained practically unchanged. It follows from this that one hydroxyl group attached to an aromatic nucleus and not in the α position to the carbonyl group had been acetylated. As was to be expected, in the spectrum of the diacetate the intensity of the ester band increased and the band of the bound carbonyl group disappeared, a strong maximum due to two free quinonoid carbonyl groups appearing in its place in the 1682 cm^{-1} region.

The NMR spectrum of ibericin (Fig. 3) has two groups of lines a and b in the region from 6.5 to 8.5 ppm corresponding respectively to the protons in the 5, 8 and 6, 7 positions and a singlet c (δ = 7.04) due to a proton in position 2 or 3 [3]. The analytical formula of ibericin may be as follows:



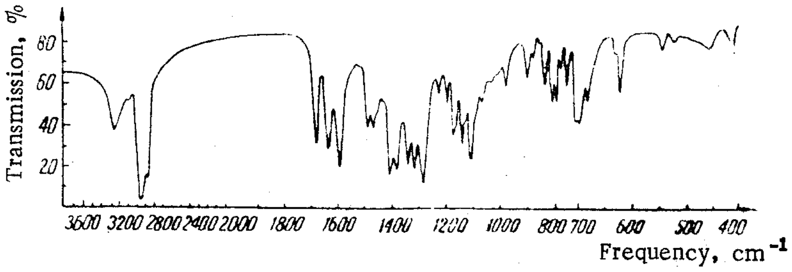


Fig. 2. IR spectrum of ibericin (mull in paraffin oil).

The structure of the C_3H_7O residue was determined from the NMR spectrum. The position of the singlet d (δ =4.83) corresponds to a methylene group located between an aromatic ring and an oxygen atom. The quadruplet e (δ = 3.70, j = 6.5 cps) and the triplet f (δ = 1.32, j = 6.5 cps) may belong to the methylene and methyl protons in the ethoxy group [4]. The proportional signal intensities a : b : c : d : e : f; 2 : 2 : 1 : 2 : 2 : 3) also agrees with these conclusions. The presence of one ethoxy group is confirmed, in addition, by the results of analysis (Zerewitinoff). Thus, R = $= -CH_2-O-CH_2-CH_3$.

The position of the second hydroxyl was established by means of the UV spectra of ibericin and model compounds in an alkaline medium. Because of the different degrees of conjugation of negatively charged oxygen atoms with carbonyl groups in phenoxide ions, the UV spectra of the phenoxides of 1, 2- and 1, 3-dihydroxyanthraquinones must differ substantially. We recorded the UV spectra of ibericin, alizarin (1, 2-dihydroxyanthraquinone), and rubiadin (1, 3-dihydroxy-2-methylanthraquinone) in 0.05 N caustic potash.

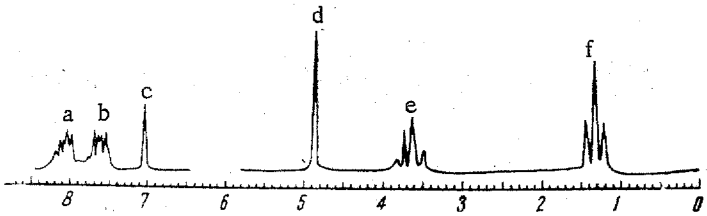
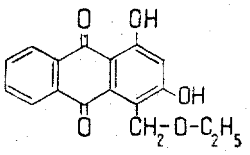


Fig. 3. NMR spectrum of ibericin taken at a frequency of 60 Mcps (region from 0 to 6.5 ppm in $CDCl_3$, 6.5-8.5 ppm region in dioxane).

Compound	λ_{max}, mμ (log ε)		
Alizarin (1, 2-dihydroxyanthraquinone)	261 (4.40)	560 (3.94)	
Rubiadin (1, 3-dihydroxy-2-methylanthraquinone)	245 (4.33)	309 (4.39)	480 (3.75)
Ibericin	250 (4.32)	310 (4.32)	482 (3.79)

The results given show that the UV spectra of the phenoxides of rubiadin and ibericin are very similar and, at the same time, differ substantially from the spectrum of alizarin phenoxide. Hence, it may be concluded that the second hydroxy group in ibericin is in position 3. Thus, the structural formula of ibericin is as follows:



Experimental

Isolation of ibericin. 40 kg of the dried and comminuted roots of Iberian madder was covered with 96% ethyl alcohol (1:5) and the mixture was boiled for 2 hr. The alcoholic extract was filtered off, evaporated to one tenth of its initial volume, and left for 12 hr. The precipitate which deposited was filtered off, and the mother liquor was evaporated to half bulk and allowed to stand for 12 hr, after which the resinous precipitate that had deposited was filtered off.

The residue (1.8 kg) was treated with three 1.5-*l* portions of ether. The residue from the ether treatment was dissolved in 200 ml of chloroform. The solution was transferred to a chromatographic polyamide column. Elution was carried out with chloroform. Six colored zones were found on the chromatogram. The eluate from the first zone was extracted twice with 500 ml of 2% caustic soda. The red alkaline solution was washed with two 200-ml portions of chloroform and was then acidified with 10% sulfuric acid to a weak acid reaction (pH 5). The precipitate which deposited (1.8 g) was filtered off, washed with water to neutrality, and dried at 60-70°C. The residue was dissolved in 100 ml of benzene, chromotographed on a polyamide column, and washed with benzene. Two zones were found. The fraction containing the second zone was investigated. It was brought to a volume of 10 ml by distilling off the solvent and was left for 12 hr. This gave a precipitate of 1.1 g of lemon-yellow crystals with mp 182-183°C (from benzene).

Found, %: C 68.53, 68.23; H 4.83, 4.82; $-OC_2H_5$ 15.06, 15.12 (Zerewitinoff); mol. wt. 275, 296 (Beckmann).

Calculated for $C_{17}H_{14}O_5$, %: C 68.45; H 4.70; mol. wt. 298; $-OC_2H_5$ 15.10.

The monoacetate was obtained by heating ibericin with acetic anhydride and crystalline sodium acetate for 2 hr. The melting point of the crystals was 129-131°C (from alcohol).

Found, %: C 67.40, 66.73; H 4.90, 4.85. Calculated for $C_{19}H_{16}O_6$, %: C 67.06; H 4.76.

The diacetate was formed by heating ibericin with acetic anhydride and fused sodium acetate for 2 hr. The melting point of the crystals was 163-164°C (from alcohol).

Found, %: C 66.13, 65.88; H 4.87, 4.68. Calculated for $C_{21}H_{18}O_7$, %: C 65.97; H 4.71.

The UV spectra of ibericin was obtained on a SF-4 spectrophotometer, the IR spectra on a UR-10 spectrophotometer, and the NMR spectrum on a JNM-C-60 instrument. The chemical shifts in ppm were calculated with respect to the signal of tetramethylsilane taken as 0. The NMR spectrum of ibericin was taken by G. Yu. Pek (IKhPS AN SSSR [Institute of the Chemistry of Natural Compounds, AS USSR]) and the analyses were performed by E. A. Nikonova.

Summary

A new anthraquinone of composition $C_{17}H_{14}O_5$, mp 182-183° (decomp., from benzene) has been isolated from the roots of Rubia iberica (Fisch. ex D.C.); it has been called ibericin and has the structure of 1, 3-dihydroxy-4-ethoxymethylanthraquinone.

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