FLAVONOIDS OF Aflatunia ulmifolia. II

G. G. Zapesochnaya and A. I. Ban'kovskii

UDC 547.972

We have previously reported the isolation from branches freed from leaves of Aflatunia ulmifolia of a flavanone (I) with mp 227-229°C [1]. A study of the IR spectra and the UV spectra of (I) with additives showed that it was a flavanone with free OH groups in positions 5 and 7. A Zeisel determination showed that it contained methoxy (10%) or ethoxy (14%) groups.

A further study has shown that the molecular weight of the substance (288) (determined mass spectrometrically) does not agree with the presence in the molecule of methoxy or ethoxy groups and corresponds to the formula $C_{15}H_{12}O_6$. The presence of these groups was not confirmed in the NMR spectrum, either. We assumed that the substance isolated was a solvate and had the composition $C_{15}H_{12}O_6 \cdot C_2H_5OH$. This was also shown by microanalysis. The NMR spectrum showed the signals of ethanol: triplet at 1.13 ppm and quartet at 3.35 ppm.

An analysis of the NMR spectrum taken on a Varian HA 100D instrument with a frequency of 100 MHz (using tetramethylsilane as internal standard) enabled the positions of the substituents in ring B (solution in methyl sulfoxide) and C (solution in pyridine) to be determined. It is known that in the 5,7-dihydroxyflavanones the protons at C-6 and C-8 give a single signal close to 5.95 ppm and, when they contain a 3-hydroxy group, a pair of doublets [2], which was in fact found in our case ($\delta = 5.89$ ppm for H-6 and $\delta = 5.95$ ppm for H-8, J = 2.5 Hz). The signals of the aromatic protons of ring B appeared in the form of two doublets with an intensity of 2 H each at 6.82 ppm (H-3' and H-5') and 7.34 ppm (H-2' and H-6') with a constant J = 8 Hz (ortho protons); they show the 4'-OH substitution of the B ring. The spectrum has two doublets at 4.9 ppm (H-3) and 5.35 ppm (H-2), which confirms the 3-OH substitution of ring C, while the constant J = 11 Hz shows the trans arrangement of the protons at C-2 and C-3 [2, 3].

Thus it has been established that the substance (I) isolated previously is 3,4',5,7-tetrahydroxyflavanone (aromadendrin). From an evaporated ethereal extract of (I) by chromatography on polyamide and elution with water we obtained a colorless substance, $C_{15}H_{14}O_6$, mp 166-170°C, yield 0.06%, giving no cyanidin reaction but giving a bright crimson color with a 1% solution of vanillin in hydrochloric acid, which is characteristic for catechins. On Whatman-2 paper in the butan-1-ol—acetic acid—water (4 : 1 : 5) system it had R_f 0.72. Its UV spectrum had a single absorption maximum at 281 nm (log ε 3.57), which is characteristic of the catechins [4]. NMR spectrum: two doublets at 6.19 ppm (H-6) and 6.26 ppm (H-8) with J = 2 Hz (meta protons); singlet (2 H) at 7.06 ppm (H-5', 6'), and a signal at 7.16 ppm (H-2') showing the 5,7-dihydroxy substitution of ring A and a 3',4'-dihydroxy grouping in ring B of catechin [2]. Acetylation with acetic anhydride in the presence of sodium acetate (100°C) formed a pentaacetate of the composition $C_{25}H_{24}O_{11}$ with mp 132-133°C, R_f 0.55 [TLC on silica gel, Merck plates, in the toluene—ethyl formate—formic acid (5 : 4 : 1) system], $[\alpha]_D^{20}$ +36° (c 0.67; chloroform) [5]. The results of a comparison of the physicochemical constants with literature data showed that the substance isolated was (+)-catechin.

LITERATURE CITED

1. G. G. Zapesochnaya, A. I. Ban'kovskii, and I. A. Gubanov, Khim. Prirodn. Soedin., 5, 122 (1969).
2. W. Olechnowicz-Stepien and H. Rzadkowska-Bodalska, Herba Polonica, 14, No. 3, 179 (1968).
3. J. W. Clark-Lewis, L. M. Jackman, and T. M. Spotswood, Austr. J. Chem., 17, No. 6, 632 (1964).

All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 665, September-October, 1971. Original article submitted May 24, 1971.

4. L. Jurd, in: The Chemistry of Flavonoid Compounds, T. A. Geissman (editor), Pergamon Press, Oxford (1962).
5. L. T. Pashinina and T. K. Chumbalov, in: Phenolic Compounds and Their Biological Functions [in Russian], Moscow (1968).