^{13}C NMR SPECTRAL ANALYSIS OF ANTHRAQUINONE DERIVATIVES FROM Rumex Alpinus

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Physcion, chrysophanol, and emodin isolated from the plant Rumex alpinus L. [1-3] growing in the Georgian SSR have been investigated by the ^{13}C NMR method. To improve their solubility, the compounds were acetylated with acetic anhydride in pyridine.

The spectra were recorded in the pulsed regime on a BS-497 spectrometer with a BP-4970 adaptor at a resonance frequency of 25.412 MHz, the pulse length of 7 (at 12 μsec μsec for a 90-degree pulse) at a frequency of once per second, accumulation of the interferograms in 8 K with expansion to 16 K with deuterochloroform (V/O "Izotop") as solvent, at a temperature of 30°C. Below we give details of the ^{13}C NMR spectra of chrysophanol diacetate (I) and emodin triacetate (II):

Carbon atom	*I*		*II*	
	Calc.	Exp.	Calc.	Exp.
C-1	150.2	150.2	150.2	150.2
C-2	130.8	130.7	131.1	130.9
C-3	145.8	146.3	145.8	146.3
C-4	125.9	125.8	126.0	125.9
C-5	125.5	125.3	118.2	118.2
C-6	134.6	134.4	155.8	154.6
C-7	130.3	130.2	123.6	123.3
C-8	150.1	150.2	152.0	151.6
C-9	180.1	180.3	179.6	179.6
C-10	182.2	182.1	180.9	181.0
C-11	123.0	123.1	122.6	123.0
C-12	134.2	134.2	134.2	134.0
C-13	134.5	134.6	136.0	135.6
C-14	125.7	125.7	123.1	123.2
Other peaks	169.4; 21.1; 22.2	169.4; 21.1; 22.0	~19; 21.5; 21.1	19.3; 18.9; 167.8; 21.5; 20.9

The values of the chemical shifts of the resonance lines obtained for the diacetate form of physcion agreed with information in the literature [4, 5]. Emodin and chrysophanol have not been investigated by the ^{13}C NMR method previously, and we are the first to have done this. The ^{13}C NMR spectra of chrysophanol diacetate and emodin tricetate were recorded. As the initial basis for the assignment of the resonance lines of the experimental spectrum of chrysophanol diacetate we used figures for 1,8-diacetoxy-9,10-anthraquinone and 1,8-diacetoxy-3-methoxy-6-methylanthraquinone [4, 5]. A comparison of these results permitted the following values of the increments to be calculated: $\delta_{C-1} = +11.2$ ppm; $\delta_{ortho} = +0.5$ ppm; $\delta_{meta} = \pm 0.2$ ppm; $\delta_{para} = -2.7$ ppm. In this approach it was assumed that the influence of a substituent extends only to one ring. The values of the increments that were obtained were in good qualitative and quantitative agreement with literature figures [6] on the influence of a methyl group on the chemical shifts of carbon nuclei in a benzene ring. For a definitive calculation of the chemical shifts of chrysophanol diacetate we also considered the increments for an OAc group in [4]. A comparison of the calculated and experimental spectra showed their agreement.

For the assignment of the spectrum of emodin tricetate we used the values of the increments of a CH_3 group given above and literature figures [4] for the OAc group. The spectrum calculated in this way agreed with the experimental spectrum.

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FLAVONE C-GLYCOSIDES OF Begonia erythrophylla. II

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We have previously [1] reported on the isolation of flavonols and flavones from the leaves of Begonia erythrophylla Neum. In a continuation of a study of this species, we used the same methodological means [1], namely: extraction, chromatographic separation, and the preparative isolation of individual substances. As a result we isolated four compounds (I-IV). They were purified by paper chromatography in water and 2% CH_3COOH systems. Substances (I-IV) had a brown coloration in UV light, which changed to yellow or pale green in NH_3 vapor, gave a yellow fluorescence with $AlCl_3$ and an orange-red color with Mg + HCl, and showed weak fluorescence under the action of Benedict's reagent, i.e., they exhibited the properties characteristic for flavonoids with free hydroxy groups in positions 5, 3', and 4'. They also had low R_f values of 0.42, 0.54, 0.32, and 0.39, respectively in the BAW (3:1:1 system and 0.27, 0.50, 0.15, and 0.33 in the 15% CH_3COOH system). Components (I-IV) each had two similar absorption maxima in UV light – 334 and 270 nm (for components I and II) and 348 and 270 nm (for components III and IV). Spectral investigations using diagnostic reagents showed the presence of free hydroxy groups in positions 5, 7, 3', and 4'. The glycosidic nature of flavonoids (I-IV) was shown by the cyanidin reaction with octyl alcohol. Their acid hydrolysis in 10% in HCl in a boiling water bath for 6 h followed by extraction of the hydrolysates with ethyl acetate gave mixtures of two substances in each case, as was shown by paper chromatography in the solvents BAW (3:1:1) and 15% CH_3COOH. No carbohydrate component was detected in the hydrolysates of substances (I-IV). Furthermore, substances (I), (II), (III), and (IV) were isomeric compounds. When substances (II) and (IV) were boiled in 5% HCl for 1.5 h, compounds were formed that were identified as vitexin and orientin, which is an additional proof of the structures of these substances [2]. A comparison of the chromatographic chemical and spectral properties of the substances isolated with literature information [3-7] and also with authentic samples identified compound (I) as vitexin, (II) as isovitexin (saponaretin), (III) as orientin, and (IV) as isoorientin (homoorientin). This is the first time that these known flavone C-glycosides have been detected in the family Begoniaceae.

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