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4 November 1968

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UDC 547.992+543.42

NMR SPECTRA OF SUBSTITUTED PSORALENS

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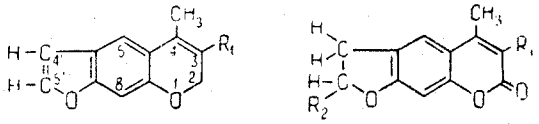
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 2, pp. 120–121, 1969

We have studied the NMR spectra of C-substituted derivatives of psoralen and of 4',5'-dihydropsoralen with the general formulas:

I. 4-Methylpsoralen (A; R_1 = H).
II. 3,4-Dimethylpsoralen (A; R_1 = CH_3).
III. 3-Ethyl-4-methylpsoralen (A; R_1 = C_2H_5).
IV. 3,4,5'-Trimethyl-4',5'-dihydropsoralen (B; R_1 = R_2 = CH_3).
V. 3-Ethyl-4,5'-dimethyl-4',5'-dihydropsoralen (B; R_1 = C_2H_5; R_2 = CH_3).



The spectra were obtained on a JNM-4-H-100 instrument at 100 MHz using hexamethyldisiloxane (HMDS) as internal standard, its signal being taken as 0 (δ scale). The spectra of compounds I–III were taken in deuterochloroform and those of compounds IV and V in carbon tetrachloride. The table gives the chemical shifts (in ppm) and the spin-spin coupling constants (J) of the protons of the compounds listed.

Substance	3C–CH_3 (S)*	3C–CH_2–CH_3 (K) (T)	4C–CH_3	5C–H (S)	4'C–H** 4'C–H***H	5'C–H** 5C'H–CH_3***	8C–H (S)
(I)	—	—	2.40 (D) 1.2****	7.70	6.77 (D) 2.0****	7.60 (D) 2.0****	7.33
(II)	2.15	—	2.40 (S)	7.72	6.77 (D) 2.0****	7.60 (D) 2.0****	7.35
(III)	—	2.61; 1.08 7.4; 7.3****	2.36 (S)	7.67	6.74 (D) 2.0****	7.57 (D) 2.0****	7.27
(IV)	1.93		2.12 (S)	7.06	3.25 (Q); 2.75 (Q)	4.86 (M); 1.42 (D) 6,4****	6.28
(V)	—	2.45; 1.02 7.1; 7.1****	2.18 (S)	7.12	3.25 (Q); 2.75 (Q)	4.87 (M); 1.41 (D) 6.2****	6.33

*S, singlet; D, doublet; T, triplet; Q, quartet; M, multiplet.
**For compounds I–III.
***For compounds IV and V.
****Spin-spin coupling constants, Hz.

It is known that in furocoumarin derivatives the signal of the H_4 proton is shifted to a weaker field (in psoralen it is at 7.93 ppm [1]). Since all the compounds under consideration are substituted by a methyl group at C_4, this signal is lacking for them. The signal for the proton at C_3 (6.14 ppm, not shown in the table) is seen only in the spectrum of 4-methylpsoralen (I).

As in all the furocoumarins, the protons at C_5 and C_8 are nonequivalent and give two singlets at 7.06–7.72 and 6.28–7.35 ppm, respectively. The chemical shift of the proton in the 5 position is affected by conjugation with the α,β-unsaturated carbonyl group of the α-pyrone ring.

Hydrogenation of the double bond of the furan ring markedly changes the nature of the spectrum. In compounds IV and V signals of the protons of the methyl group of C_4 and of the benzene ring undergo a considerable diamagnetic shift ($\Delta\delta_5$ = −0.66 ppm; $\Delta\delta_8$ = −1.07 ppm). A one-proton multiplet of the C'_5 methine group appears at 4.86 ppm. The protons of the C'_4 methylene group, being nonequivalent, form with the C'_5 methine proton a system of the AKX type with two well-separated quartets (in the AK part). A signal in the stronger field (2.75 ppm, J_{AK} = 15 Hz) must be ascribed to a proton present in the cis position relative to the methyl group at C'_5.

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4 December 1968

Institute of the Chemistry of Plant Substances AS UzSSR

UDC 547.972

HYPERIN FROM SORBUS TIANSCHANICA

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 2, p. 121, 1969

Sorbus tianschanica Rupr. (Tien-Shan mountain ash) is a small tree or shrub of the family Rosaceae which is distributed in the mountain regions of Central Asia and western China.

Branches freed from leaves (2.5 kg) collected in the fruit-bearing phase in the Irdyk gorge, Issyk-Kul'skaya basin were extracted with methanol. The residue after the methanol had been driven off was treated with 0.5 *l* of water and the filtrate was then extracted with benzene, ether, ethyl acetate, and butan-1-ol.

The total material from the ethyl acetate extract was dissolved in 10% ethanol and transferred to a column of polyamide. The column was washed with water, and then methanol—water (1 : 1) eluted 12 g (0.48% of the air-dry material) of a crystalline substance with mp 223–224° C. On the basis of qualitative reactions, the substance isolated is a flavonol glycoside. Its acid hydrolysis gave equimolar amounts of quercetin (mp 315–317° C; pentaacetate, mp 195–197° C) and galactose (thin-layer and paper chromatography in the presence of reference samples. The position of the sugar was determined by the exhaustive methylation of the glycoside by means of dimethyl sulfate, followed by acid hydrolysis. This gave 3-hydroxy-3',4',5,7-tetramethoxyflavone with mp 194–194.8° C, which shows that the galactose is attached to the 3-hydroxy group of the quercetin. Thus, the substance isolated is hyperin, as was also confirmed by the results of a direct comparison with an authentic sample [1].

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13 November 1968

All-Union Scientific-Research Institute for Medicinal Plants

UDC 547.918

FLAVONOLS OF SOLIDAGO CANADENSIS

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 2, pp. 121–122, 1969

Five substances of a flavonoid nature (table) have been isolated by chromatography on polyamide from the epigeal part of Solidago canadensis L., family Compositae (Canada goldenrod) collected in the flowering period.

By their qualitative reactions, physicochemical properties, UV spectra with complex-forming and ionizing additives, and their conversion products, substances I, II, and III have been identified as 3,5,7,3',4'-pentahydroxyflavone (quercetin), 3,5,7,4'-tetrahydroxyflavone (kaempferol), and 5,7,3',4'-tetrahydroxyflavone-3-rutinoside (rutin).