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CARDIOSPERMINSULFATE - A SULPHUR CONTAINING CYANOGENIC GLUCOSIDE FROM CARDIOSPERMUM GRANDIFLORUM

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Summary: Isolation and structure elucidation of cardiospermin-5-sulfate, the first reported sulphur containing cyanogenic glycoside is described. The compound cooccurs with cardiospermin in Cardiospermum grandiflorum Sw.(Sapindaceae).

Cardiospermin (1, 2-ß-D-glucopyranosyloxy-3-hydroxymethylbutyronitril-3-en) was reported as the only cyanogenic glucoside in the vegetative portion of Cardiospermum grandiflorum Sw.(Sapindaceae)[1]. Controlling the ontogenetic variability of all parts of C.grandiflorum with respect to 1 and the enzymatically releasible hydrocyanic acid it was shown especially for leaves that at distinct times significant differences are found in the yield of 1 and total cyanide liberated by treatment with ß-glucosidase[2]. Chromatography of methanolic extracts on silica gel showed 1 and a second cyanogenic band with a smaller Rf-value.

This second cyanogenic compound was purified from 180 g freeze dried leaves by column chromatography on cellulose (iPropOH/nButOH/H_2O 60:30:10) followed by preparative thin layer chromatography on silica gel (EtOAc/MeOH/H_2O 60:30:10). The resulting polar compound (50 mg) still contained silica gel and some water after lyophilization. Enzymatic hydrolysis by ß-glucosidase (Serva 22830) yielded glucose, hydrocyanic acid and sulfate. Hydrolysis by UV-light in acid solution[3] (254 nm, 2 x 40 W, 5 cm distance, 0.2 N HCl, 5 - 30 min) resulted in glucose, traceable amounts of 1 and sulfate. Sulfate was also produced by treatment with aryl sulfatase (Sigma 8629). These results indicate the new compound to be a cardiospermin derivative. The production of sulfate during alkaline and acid hydrolysis proves the existence of a sulfuric ester. Elementary analysis resulted in a C:N:S ratio of 11:1:0.7 indicating one sulfate group per molecule (O and H were not evaluated, as the compound still contained silica gel and water). FD-MS showed a M^+ at 400 (cardiosperminsulfate-anion + Na^+ + Na^+).

As shown in table 1 in many respects the ^{1}H-NMR spectrum is similar to that of 1 and cardiospermin-5-p-hydroxybenzoate[4]. Compared to cardiospermin the paramagnetic shift of the C_5-methylenprotons indicates a substitution at the primary hydroxy group; a coupling constant of 7.5 Hz of the doublet of the

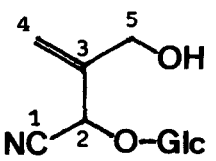
anomeric glucose proton proves ß-configuration of the glycosidic linkage. Integration of the C_2- and C_4-protons and those of the glucose moiety obtained in D_2O/TFA-d_1 results in a ratio of 1:2:6 demonstrating a ratio of 1:1 for aglycon and glucose.

	C_2-H	C_4-H_2	C_5-H_2	Glc-H_1	other Glc-H_s
cardiospermin	5.45 s	5.55 s 5.51 s	4.22 s	4.51 d J=7.5 Hz	3.2 - 4
new glucoside	5.64 s	5.73 s 5.64 s	4.68 s	4.60 d J=7.5 Hz	3.2 - 4
cardiospermin-5-p-OH-benzoate	5.65 s	5.70 s 5.75 s	4.90 s	4.65 d J=7.5 Hz	3.2 - 4

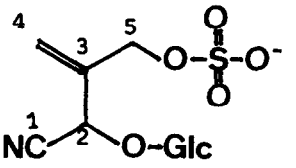
Table 1: ^{1}H-NMR-data of cardiospermin, cardiospermin-5-p-hydroxybenzoate and the new polar glucoside. All spectra recorded in MeOH-d_4 using a Varian XL 100 spectrometer. All chemical shifts given in δ-values relative to TMS.

The proton decouplet ^{13}C-NMR of the polar compound exhibits the entire 11 carbon atoms in agreement with the proposed structure at the following resonances: δ=136.32 (=CH-), δ=121.97 (CH_2=), δ=116.76 (-CN), δ=100.2 (Glc-C_1), δ=76.04 (Glc-C_3), δ=75.04 (Glc-C_5), δ=72.50 (Glc-C_2), δ=69.25 (Glc-C_4), δ=67.36 (-CH_2-O-), δ=66.67 (-CH-O-), δ=60.47 (Glc-C_6). D_2O, Varian XL 100.

With respect to the results discussed above we propose structure 2 for the new cyanogenic glucoside.



cardiospermin (1)



cardiospermin-5-sulfate (2)

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