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^{13}C NMR SPECTROSCOPY OF SOLASODINE GLYCOSIDES FROM *SOLANUM LACINIATUM*

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Key Word Index—*Solanum laciniatum*; Solanaceae; roots; glycoalkaloids; solaradixine; solashabanine; solaradinine; ^{13}C NMR.

Abstract—The structures of the solasodine glycosides solaradixine, solashabanine and solaradinine isolated from the roots of *Solanum laciniatum* were determined by ^{13}C NMR spectroscopy.

INTRODUCTION

Solanum laciniatum has gained importance for its high content of solasodine, a substitute for diosgenin, which is used in the synthesis of hormonal steroids. Leaves and berries of this plant have been reported to contain the glycoalkaloids β-solamargine, solamargine and solasonine [1]. From the roots of this plant, in addition to solamargine and solasonine, solaradixine, solashabanine and solaradinine were isolated [2].

In a previous communication [3] based on chemical studies the structure of solaradixine, the main glycoalkaloid from roots of *S. laciniatum* was found to be *O*(3)-{α-L-rha*p*-(1→2$_{gal}$)-[β-D-glc*p*-(1→2$_{glu}$)-β-D-glc*p*-(1→3$_{gal}$)]-β-D-gal*p*}-solasodine.

Using GC analysis and action of various enzymes, Bite and Shabana gave a preliminary identification for solashabanine as solasodine bonded to five sugar units (one D-galactose, one L-rhamnose and three D-glucoses) and solaradinine with the same aglycone attached to six sugar units (one D-galactose, one L-rhamnose and four D-glucoses) [4].

^{13}C NMR spectra of solasodine, khasianine, solamargine, solasonine and their assignments have been reported [5]. As ^{13}C NMR data for for solaradixine, solashabanine and solaradinine are not available we report here the application of ^{13}C NMR spectroscopy to their structural elucidation.

RESULTS AND DISCUSSION

The ^{13}C NMR spectra of solasodine (**1**), solashabanine (**3**), solaradixine (**4**), solaradinine (**5**) and their assignments are shown in Table 1. The data for solasonine (**2**) [5] are also included for comparison.

The chemical shift values of the aglycones of **3**–**5** are in good agreement with those of solasodine. It is clearly seen from the number of anomeric signals and the total number of lines, that both solaradixine and solashabanine contain four sugar moieties while solaradinine contains five.

Comparing the 15–20 ppm region of the spectra with that of the aglycone, one new line is found in each case, at *ca* 17 ppm, which is characteristic of 6-desoxy sugars. The patterns of the chemical shifts show that each substance contains one α-rhamnose and that its chemical shifts are in good agreement with those of the respective unit of solasonine [5].

The chemical shift of C-6 in a pyranose ring is *ca* 60–63 ppm in the case of a free CH_2OH group and it is shifted downfield by *ca* 7 ppm in a diasaccharide linked at C-6.

It follows from the number of lines in the intervals mentioned, that **3**–**5** contain two, three and three sugar units, respectively, which are not linked at C-6.

The chemical shift values of the branched β-galactopyranose of solasonine can also be found in each compound. We conclude, that each molecule contains a branched β-galactopyranose unit, the linkage being to C-2 and C-3.

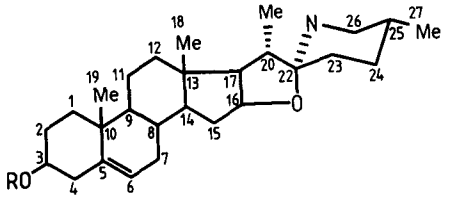
In the spectra of **3** and **5**, 12 lines can be identified belonging to a β-gentiobiose type subunit [6]. It is seen from the chemical shift values, that in the case of **5** another saccharide unit is linked to C-1 of the gentiobiose moiety, that can be indentified as β-glucopyranose linked at C-2, on the basis of the chemical shift values for β-sophorose [6]. The same unit can also be recognised in **4**.

According to the above results, solaradixine is *O*(3)-{α-L-rha*p*-(1→2$_{gal}$)-[β-D-glc*p*-(1→2$_{glu}$)-β-D-glc*p*-(1→3$_{gal}$)]-β-D-gal*p*}-solasodine (**4**) [3]; solaradinine is *O*(3)-{α-L-rha*p*-(1→2$_{gal}$)-[β-D-glc*p*-(1→6$_{glu}$)-β-D-glc*p*-(1→2$_{glu}$)-β-D-glc*p*-(1→3$_{gal}$)]-β-D-gal*p*}-solasodine (**5**) and solashabanine is *O*(3)-{α-L-rha*p*-(1→2$_{gal}$)-[β-D-glc*p*-(1→6$_{glu}$)-β-D-glc*p*-(1→3$_{gal}$)]-β-D-gal*p*}-solasodine (**3**). The structures of these molecules were corroborated by the action of β-glycosidase [4] and *Aspergillus japonicus* [7]: solaradinine (**5**)→ solaradixine (**4**) [4]→ solasonine (**2**) [7] and solashabanine (**3**)→ solasonine (**2**) [4].

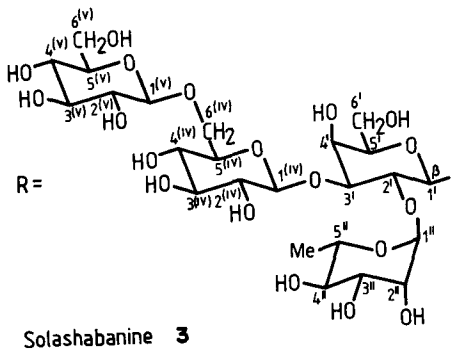
EXPERIMENTAL

Plant material was obtained from the Research Institute for Medicinal Plants, Budakalasz, Hungary.

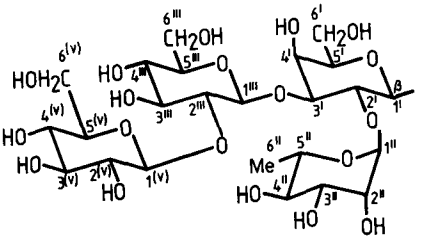
Mps: uncorr. TLC was performed on silica gel using $CHCl_3$–MeOH–H_2O (13:7:2). ^{13}C NMR spectra were measured in Py-d_5–CD_3OD soln at 70° and 25.16 MHz. Chemical shifts are measured relative to CD_3OD (48 ppm).



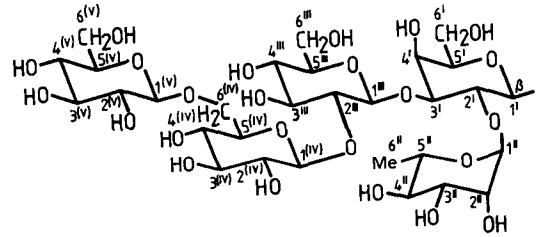
R=H : Solasodine **1**



Solashabanine **3**



Solaradixine **4**



Solaradinine **5**

Isolation of glycoalkaloids. Dried powdered root bark (2 kg) of *S. laciniatum* Ait. was defatted with petrol (60–80°) and then extracted ×3 with MeOH under reflux. The MeOH ext on removal of solvent gave a dark brown, semi-solid mass (115 g). The residue was treated with 0.5 % HNO_3 (1 l). The acidic soln was adjusted with NH_3 to pH 6, heated to 60°, basified with conc NH_3 to pH 9 and left overnight. The pptd glycoalkaloids were collected by centrifugation and dried (yield 52 g). The product was refluxed with MeOH and filtered. Evapn of the MeOH extract gave the purified mixt. of glycoalkaloids as yellowish-white crystals (22.5 g). TLC of the purified product showed 5 spots: R_f 0.46-solamargine, R_f 0.38-solasonine, R_f 0.30-solaradixine, R_f 0.24-solashabanine, R_f 0.20-solaradinine.

The mixt of glycoalkaloids was chromatographed on neutral Al_2O_3 (1.5 kg). Successive elution with *n*-BuOH satd with H_2O finally yielded solamargine, 80 mg (0.004% of root dry wt), mp 295–300° (dec), solasonine (**2**), 2.2 g (0.11%), mp 269–271° (dec) and solaradixine (**4**), 7.4 g (0.37%), mp 260–264°, besides a crude fraction (2.8 g) containing solashabanine and solaradinine contaminated with trace amounts of **4**. The latter fraction was

Table 1. ^{13}C NMR chemical shifts (ppm) of solasodine (**1**), solasonine (**2**) 15, solashabanine (**3**), solaradixine (**4**) and solaradinine (**5**) in Py-d_5–CD_3OD at 25.16 MHz and 70°

Carbon No.	1	2	3	4	5
1	37.4	37.4	37.2	37.2	37.2
2	32.0	30.1	29.7	29.6	29.6
3	71.0	78.3	77.7	77.6	77.7
4	42.5	38.8	38.5	39.4	38.3
5	141.5	140.7	140.8	140.8	140.7
6	120.7	121.6	121.1	121.1	121.1
7	32.0	32.5	32.0	31.9	31.9
8	31.5	32.5	31.4	31.4	31.4
9	50.4	50.3	50.3	50.1	50.3
10	36.7	37.1	36.8	36.7	36.7
11	20.9	21.1	20.8	20.7	20.7
12	39.9	40.1	39.8	39.5	39.7
13	40.4	40.6	*	40.5	40.3
14	56.5	56.7	56.4	56.2	56.3
15	31.6	31.7	32.0	31.8	31.4
16	78.7	78.7	78.6	80.0	78.7
17	63.2	63.5	63.2	63.5	63.0
18	15.9	16.5	15.8	15.6	15.8
19	18.9	19.3	18.9	18.4	18.8
20	41.4	41.5	41.3	41.5	41.4
21	14.7	15.6	14.5	14.5	14.7
22	97.9	98.2	*	*	*
23	34.2	34.6	36.8	36.7	36.7
24	30.4	31.1	30.2	29.6	30.2
25	31.0	31.7	30.5	29.6	30.7
26	47.5	47.9	47.2	47.0	47.4
27	18.9	19.7	18.9	18.8	18.8
1′		100.3	100.3	99.9	99.9
2′		76.3	76.3	75.1	76.1
3′		84.8	84.6	83.1	82.9
4′		70.2	69.7	69.9	69.9
5′		74.9	74.6	74.8	74.7
6′		62.4	62.2	61.7	62.0
1″		102.0	101.4	102.6	102.5
2″		72.4	72.0	71.8	71.7
3″		72.7	71.2	70.5	71.0
4″		74.0	73.5	73.2	73.1
5″		69.3	68.8	68.7	68.7
6″		18.5	17.7	17.3	17.3
1‴				100.3	100.3
2‴				82.8	82.3
3‴				74.6	74.3
4‴				69.9	69.9
5‴				77.2	77.3
6‴				61.3	61.3
1(IV)			104.5		104.5
2(IV)			74.6		74.8
3(IV)			77.7		77.5
4(IV)			71.6		71.0
5(IV)			75.2		74.8
6(IV)			69.3		69.7
1(V)		105.7	104.6	104.8	104.8
2(V)		74.8	74.6	74.8	74.8
3(V)		78.7	77.4	77.2	77.1
4(V)		71.4	71.2	71.4	71.5
5(V)		78.3	77.4	77.6	77.4
6(V)		61.8	61.7	61.6	61.6

*Not observed.

applied to a smaller column of neutral Al_2O_3 (100 g). Successive elution with EtOAc–*n*-BuOH (1:1) satd with H_2O afforded solashabanine (**3**), 65 mg (0.003%), mp 270–273° (MeOH–Et_2O) and solaradinine (**5**), 1.2 g (0.06%), mp 227–230° (EtOH).

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