STRUCTURE OF A NEW SAPONIN FROM *ZIZYPHUS VULGARIS*

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ABSTRACT.—The structure of a major saponin obtained from the leaves and stems of *Zizyphus vulgaris* was obtained by C^{13}-nmr and confirmed by chemical degradation experiments. The structure was assigned as 3-*O*-[(2-*O*-α-D-fucopyranosyl-3-*O*-β-D-glucopyranosyl)-α-L-arabinopyranosyl]jajubogenin.

In a previous paper, we reported the elucidation of dammarane-type saponins isolated from the seeds of *Zizyphus jujuba*, mainly by C^{13}-nmr spectroscopy (1). This report deals with the identification of a major saponin isolated from the leaves of another *Zizyphus* species grown in Iran and Pakistan, *Z. vulgaris*. It was identified mainly by C^{13}-nmr and confirmed by chemical degradation experiments.

EXPERIMENTAL

Dry powdered leaves and stems were percolated with methanol at room temperature. The methanolic extract was fractionated between chloroform and water. The chloroform extract was further fractionated between petroleum ether and 90% methanol. The methanol extract was chromatographed through a silica gel column by elution with chloroform-methanol (gradient) to obtain a new saponin, **1**, mp 285–290°, $[\alpha]^{15}D-17.5°$ (C=1.0, MeOH), $C_{47}H_{74}O_{17}$. The C^{13}-nmr spectrum indicated that the aglycone was jujubogenin and that the sugar moiety was attached through a C-3 hydroxy group. All the C^{13}-signals due to the aglycone moiety were essentially identical to those of other *Zizyphus* saponins which are 3-*O*-glycosyl jujubogenins (table 1). Apart from the 30 signals, 3 signals in the "anomeric carbon region", 13

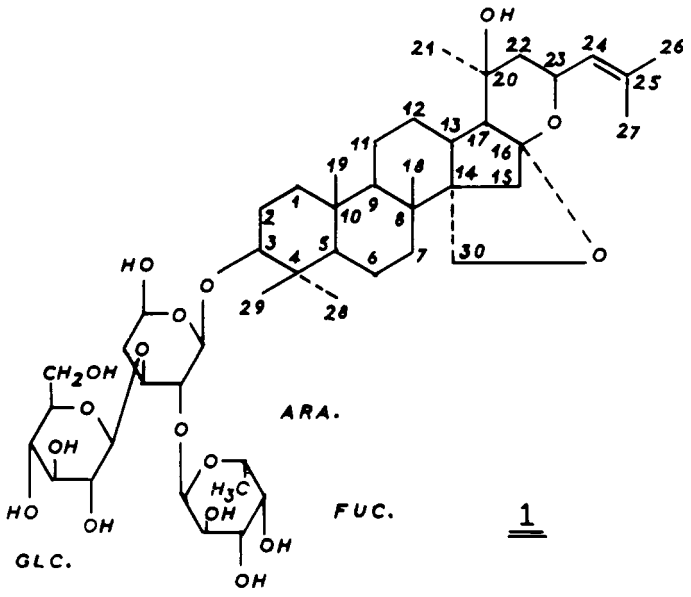
TABLE 1. C^{13} Chemical shifts (δ from TMS) in C_5D_5N[c]

Aglycone Carbons						Ara		Fuc		Glc	
1.	38.9	11	21.7	21	29.9	1	104.8	1	101.7	1.	104.8
2.	26.7	12	28.5	22	45.3	2	74.1	2	68.5	2	74.8
3.	87.9	13	36.8[a]	23	68.5	3	83.3	3	71.4	3	78.3
4.	39.5	14	53.7	24	126.9	4	67.7	4	73.9	4	71.8
5.	56.2	15	37.2[a]	25	134.3	5	65.5	5	66.9	5	78.3
6.	18.3	16	110.6	26	25.5			6	17.2	6	62.4
7.	36.0	17	53.9	27	18.9						
8.	37.5[b]	18	18.3	28	27.9			cf. Methyl fucosides			
9.	53.0	19	16.4	29	16.5						
10.	37.2[b]	20	68.5	30	65.9			α	β		
								1	101.7	105.8	
								2	70.0	72.0	
								3	71.6	75.3	
								4	73.2	72.6	
								5	66.9	71.3	
								6	17.1	17.1	

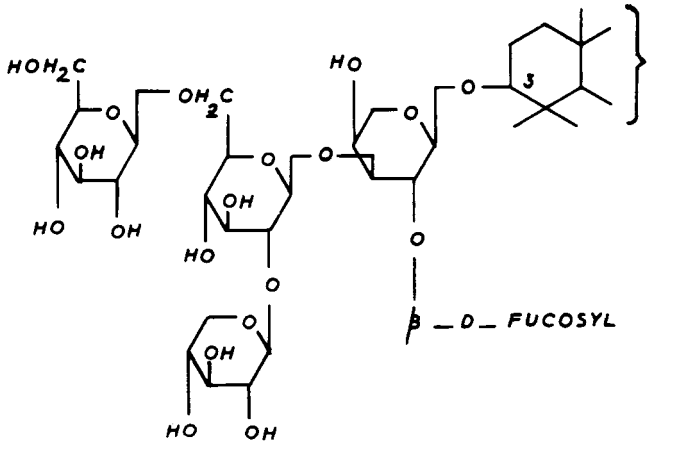
[a, b] Assignments may be reversed.
[c] Measured at 25° with a JEOL JNMPFT 100 spectrometer at 25.15 MHz.

signals between δ 62.4–83.3 and 1 signal (q) at δ 17.2 were observed; these signals could be attributed to three sugar parts. By comparison with other *Zizyphus* saponins, six signals, δ 104.8(d), 78.3(dx2), 74.8(d), and 62.4(t) were assigned to the carbon atoms of the terminal β-glucosyl. The isolated signal at δ 17.2(q) was characteristic to fucose and another five signals, δ 101.7, 73.9, 71.4, 68.5 and 66.9 (all d) could be assigned to a fucosyl carbon. The remaining five resonances arose from a 2,3-disubstituted arabinosyl carbon by the analogy of jujuboside B_1 (2). However, the previous structure for **2** should be revised from "β" to "α" -D-fucopyranosyl on the basis of a comparison of fucosyl signals of **1** with those of methyl α and β-fucosides (table 1).

The structure of the sugar unit of **1** was confirmed by the following experiments. The three sugars, glucose, arabinose and fucose, were identified by comparison of gc retention time (2% OV-17 at 150°) of their TMS derivatives with authentic samples. Methylation of **1** by Hakomori's method followed by methanolysis gave a mixture of methyl glycosides of partially methylated sugars. Gas chromatography (10% DECS, at 170°) of this mixture showed the presence of methyl 2,3,4,6 tetra-*O*-methyl glucoside and methyl 2,3,4 tri-*O*-methyl fucoside as well as methyl 4 *O*-methyl arabinoside. The decisive experiment was partial hydrolysis of **1**



1



2 (Jujuboside B)

to prove which sugar (glucose or fucose) was combined to the 2- or 3-position of the arabinose moiety. On partial hydrolysis, sugars at position 2 of the arabinose moiety were eliminated (2), and the remaining sugars at position 3 were identified by methylation followed by methanolysis. Compound (**1**) was partially hydrolyzed in dioxane –0.1N–HCl (1:3) under reflux for 6 hrs to give the hydrolysate which was extracted with butan-1-ol and purified by silica gel chromatography. The hydrolysate on methylation by the Kuhn method, followed by methanolysis (5% MeOH–HCl), gave a mixture of methyl glycosides of partially methylated sugars. In this mixture, methyl permethyl glucoside and methyl 2,4 di *O*-methyl arabinoside were detected by glc (as above); no fucose derivatives were detected (2). This evidence supported the supposition that the glucose was linked to the 3-position of arabinosyl moiety in **1**. Thus, **1** was identified as 3-*O*-[(2-*O*-α-D-fucopyranosyl-3-*O*-β-D-glucopyranosyl)-α-L-arabinopyranosyl]jujubogenin.

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