THE STRUCTURE OF YUCCOSIDE E FROM *Yucca filamentosa*

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The present paper gives the results of a chemical study and a proof of the structure of a new glycoside of sarsasapogenin, yuccoside E (I), isolated from the roots of Yucca filamentosa (Adam's needle yucca) by the method described previously [1].

The acid hydrolysis of (I) gave an aglycone which was identical with sarsapogenin according to its melting point, specific rotation, IR and mass spectra, and chromatographic mobility. The gas–liquid chromatography of the aldononitriles of the sugars of (I) showed the presence in them of galactose and glucose in a ratio of 1:1.

To determine the type of bonds between the monosaccharides, compound (I) was methylated by Kuhn's method [2], and the resulting permethylated product (II) was subjected to methanolysis with perchloric acid. The methyl glycosides formed were chromatographed on a column of silica gel. Three individual substances (III, IV, and V) were obtained. By GLC in the presence of markers, substance (III) was identified as methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside. The demethylation of (IV) and (V) gave glucose. According to GLC and mass [3] and NMR [4] spectroscopy, substance (IV) is methyl 2,3,6-tri-O-methyl-β-D-glucopyranoside. From its chromatographic mobility, substance (V) was assigned to the dimethylated sugar derivatives. According to its mass [3] and NMR [4] spectra and GLC, substance (V) is methyl 3,4-di-O-methyl-α-D-glucopyranoside. After the removal of the methyl group at C_1, compound (V) gave a positive reaction with Bonner's reagent [5].

On the periodate oxidation of (I), not one sugar remained unchanged and this confirmed the results of methylation.

To prove the sequence of monosaccharides, compound (I) was partially hydrolyzed. Three progenins (VI, VII, and VIII) were obtained. The gas–liquid chromatography of the acetates of the aldononitriles of the sugar derivatives in the hydrolyzates of both (VI) and (VII) showed the presence of only glucose, and in the hydrolyzate of (VIII) the presence of galactose and glucose in molar ratios of 1:2.

When the permethylated progenins were hydrolyzed, in the case of (VI) methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside was isolated, in the case of (VII) methyl 2,3,6-tri-O-methyl-D-glucopyranoside as well,

TABLE 1

Methyl glycosides of the monosaccharides	$[M]^{20}$, deg		Glycosides	$[M]^{20}$, deg	ΔC	Form of the bond
	α	β				
			Progenin E	−425	−209	β
			Progenin VIII	−216		
Methyl D-galactopyranoside [11]	+380	0	Progenin VIII	−216		
	+380	0	Progenin VII	−495	+279	α
	+309	−66	Progenin VII	−495	−114	β
			Progenin VI	−381		
Methyl D-glucopyranoside [12]	+309	−66	Progenin VI	−381	−57	β
			Sarsasapogenin	−324		

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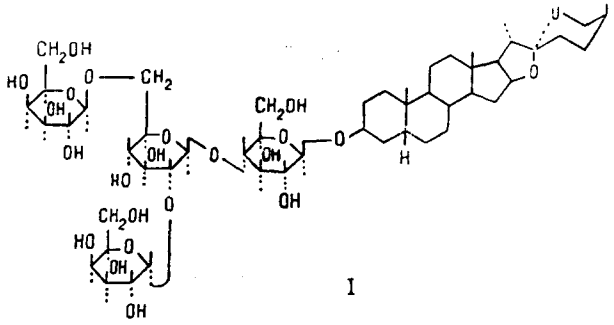
and in the case of (VIII) methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside, methyl 2,3,6-tri-O-methyl-D-glucopyranoside, and a new methyl glycoside (IX) which was characterized by GLC and by mass and NMR spectrometry [3, 4] as methyl 3,4,6-tri-O-methyl-α-D-glucopyranoside.

The configurations of the glycosidic centers were shown by means of Klyne's rule [6] (Table 1), and were additionally confirmed for the progenin (VI), (VII), and (VIII) by the NMR spectrometry of their methyl derivatives [7]. The NMR spectrum of methylated yuccoside E did not give convincing results because of the great number of monosaccharides in its molecule.

On the basis of the facts presented above, yuccoside E has the following structure:



I

EXPERIMENTAL

For chromatography we used silica gel L40/100 and L5/100, neutral alumina, FN-3 paper, and the solvent systems 1) chloroform–methanol–water (65 :25 :10, lower phase), 2) chloroform–methanol–water (65 :35 :7), 3) benzene–ether (7 :3), 4) benzene–ethanol (4 :1), 5) benzene–acetone (2 :1), and 6) butanol–benzene–pyridine–water (5 :1 :3 :3).

To free the saponins from sugars we used Sephadex G-25. On silica gel plates the steroid glycosides were revealed with Sannié's reagent [8] and with concentrated sulfuric acid, and on the paper chromatograms the sugars were revealed with aniline phthalate. Gas–liquid chromatograms of the aldononitrile derivatives of the sugars and methylated sugars were obtained on a Khrom-4 instrument (glass column 2 m long filled with 5% of XE-60 on Chromaton N-AW-HMDS at a temperature of 140°C with helium as the carrier gas, V_{He} = 45 ml/min). The IR spectra were obtained on a IR-Specord spectrophotometer and the UV spectra on a UV-Specord instrument, IR the mass spectra on an MKh-1303 instrument, and the NMR spectra on a RS-60 spectrometer. The substances were dissolved in CCl_4, and HMDS was used as standard.

Preparation of Pure Yuccoside E. The total saponins (butanol fraction, 150 g) were purified first by chromatography on alumina saturated with aqueous butanol, and then on Sephadex G-25 with elution by water. The pure combined saponins (48 g) were deposited in separate portions on a column of silica gel and eluted in system 1. The separation of the saponins was monitored by TLC in system 2. This gave 1.1 g of yuccoside E with mp 292-294°C, $[\alpha]_D^{20}$ –40° (c 1.0; pyridine).

Acid Hydrolysis of (I). Yuccoside E (50 mg) was hydrolyzed with 2.5% H_2SO_4 at 120°C for 24 h. After cooling, the reaction mixture was diluted with water and filtered. The precipitate was recrystallized from ethanol. This gave 20 mg of a genin, which, from its melting point, chromatographic mobility on TLC in system 3, and IR spectrum was identical with sarsasapogenin [9, 10]. Galactose and glucose were identified in the filtrate by paper chromatography in system 6. The GLC of the acetates of the aldononitriles of the sugars obtained showed a molar ratio of 2 :2.

Methylation and Hydrolysis of the Permethylated Products. The product of the Kuhn [2] methylation of (I) was chromatographed on a column of silica gel in system 4. This gave 0.55 g of the permethylated product (II) with mp 77-79°C, $[\alpha]_D^2$ –51° (c 6.41; chloroform), which was hydrolyzed with 72% perchloric acid in absolute methanol (1 :10) at 100°C for 5 h. After cooling, the mixture was diluted with water and filtered. The filtrate was neutralized with anion-exchange resin, evaporated, and chromatographed on a column of silica gel in the benzene–acetone system with a gradient of increasing concentrations of acetone in benzene from 15 to 35%. This gave compounds (III), (IV), and (V). By GLC in the presence of an authentic sample, compound (III) was identified a methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside. The separation of the methyl glycosides was monitored by TLC in system 5. The mass spectra of (IV) and (V) had characteristic peaks: for (IV) with m/e 71, 73, 75, 88, 101, 161, and for (V) with m/e 71, 73, 74, 75, 87, 88, 101, 161, and for (V)

with m/e 71, 73, 74, 75, 87, 88, 101, 161; their intensities corresponded to literature information [3]. The NMR spectrum of (IV) showed the following chemical shifts of the CH_3 groups (ppm): 3.42 (C_1), 3.48 (C_2), 3.51 (C_3), and 3.28 (C_6), and the doublet of the proton at C_1 (δ = 4.05 ppm, J = 7.42 Hz), and the NMR spectrum of (V) had, respectively (ppm): 3.23 (C_1), 3.56 (C_3), and 3.41 (C_4) and a doublet of the proton at C_1 (δ = 4.5 ppm, J = 4.0 Hz) [4].

Partial Hydrolysis of (I). Yuccoside E (0.5 g) was heated in 20 ml of 1.5 N HCl at 100°C for 2 h, and the mixture was then diluted with water and extracted with butanol. The extract was evaporated and was chromatographed on silica gel in system 1. This gave 150 mg of (VI) with mp 245-247°C, $[\alpha]_D^{20}$ −66° (c 0.70; methanol); 100 mg of (VII) with mp 256-258°C, $[\alpha]_D^{20}$ −67° (c 0.95; methanol); and 60 mg of (VIII) with mp 276-278°C, $[\alpha]_D^{20}$ −24° (c 1.65; chloroform−methanol (1 : 1)). Compound (VIII) was also detected in the combined saponins isolated from the roots of Yucca filamentosa and has been called yuccoside C. In addition to the progenins mentioned, ~50 mg of sarsasapogenin was isolated. All three progenins (20 mg each) were hydrolyzed with 2.5% H_2SO_4 by the method given above. Gas−liquid chromatography of the acetates of the aldononitriles of the sugar derivatives in the hydrolyzates of (VI) and (VII) showed the presence only of glucose, and in the case of (VIII) galactose and glucose were present in a molar ratio of 1 : 2.

Methylation of (VI), and (VII), and (VIII). Each compound (50 mg) was methylated and the product was purified as described above. The NMR spectra of the methylated progenins obtained showed doublets of protons at C_1 with the following constants: for (VI), δ = 3.97 ppm, J = 8.9 Hz; for (VII), δ = 4.05 ppm, J = 7.9 Hz; and for (VIII) δ = 4.62, 3.85 ppm; J = 3.5, 7.0 Hz. According to Parkhurst et al. [7], in (VI) and (VII) the glucose possesses the β configuration and in (VIII) the galactose the α configuration of the glycosidic center. The hydrolysis of the permethylated progenins yielded: for (VI), methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside; for (VII), in addition, methyl 2,3,6-tri-O-methyl-D-glucopyranoside; and for (VIII), methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside and methyl 2,3,6-tri-O-methyl-D-glucopyranoside, identified by GLC with markers, and the new methyl glycoside (IX). The mass spectrum of (IX) has the peaks characteristic for methyl 3,4,6-tri-O-methyl-D-glucopyranoside with m/e 71, 74, 75, 87, 88, 101, 102, 161, the intensities of which agree with those given in the literature [3]. The NMR spectrum of (IX) showed the following chemical shifts of the CH_3 groups (ppm): 3.28 (C_1), 3.41 (C_3), 3.39 (C_4), and 3.23 (C_6), and a doublet of the proton at C_1 (δ = 4.50 ppm, J = 4.00 Hz), which is characteristic of methyl 3,4,6-tri-O-methyl-α-D-glucopyranoside [4].

Periodate Oxidation of Yuccoside E. Compound (I) (20 mg), in solution in aqueous methanol, was oxidized with 80 mg of $NaIO_4$. The reaction products, worked up in the usual way, were hydrolyzed with sulfuric acid and, after neutralization, chromatographed in system 6. No monosaccharides were detected.

SUMMARY

From the roots of Yucca filamentosa L. we have isolated a new sarsasapogenin glycoside, yuccoside E, which is 3-O-{[O-α-D-galactopyranosyl(1 → 2)]-[-O-β-D-galactopyranosyl(1 → 6)]-O-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranosyl}-(25S), 5 β-spirostan-3β-ol.

LITERATURE CITED

1. P. K. Kintya, I. P. Dragalin, and V. Ya. Chirva, Khim. Prirodn. Soedin., 615 (1972).
2. R. Kuhn and H. Trischmann, Chem. Ber., 96, 284 (1963).
3. K. Heyns, K. R. Sperling, and H. F. Grutrmacher, Carbohydr. Res., 9, 79 (1969).
4. D. Gagnaire and L. Odier, Carbohydr. Res., 11, 33 (1969).
5. T. G. Bonner, Chem. Ind. (London), 345 (1960).
6. W. Klyne, Biochem. J. 47, No. 4, xli (1950).
7. R. M. Parkhurst, D. W. Thomas, and W. A. Skinner, Phytochemistry, 12, 1437 (1952).
8. M. Ch. Sannié and H. Lapin, Bull. Soc. Chem. Fr., 1082 (1952).
9. R. Tschesche, G. Wulff, and G. Bailé, Tetrahedron, (London), 18, 959 (1962).
10. M. E. Wall, C. R. Eddy, M. L. McLennan, and M. E. Klumpp, Anal. Chem., 24, 1337 (1952).
11. N. K. Kochetkov, A. F. Bochkov, B. A. Dmitriev, A. I. Usov, and O. S. Chizhov, and V. N. Shibaev, The Chemistry of the Carbohydrates [in Russian], Moscow (1967).
12. E. Fischer, Ber., 28, 1156 (1895).