Tetrahedron Letters No.51, pp. 4669-4674, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE STRUCTURE OF CARBOHYDRATE CHAINS OF PANAXOSIDES D,E,F

G.B. Elyakov, N.I. Uvarova, R.P. Gorshkova
Institute of Biologically Active Substances in Vladivostok,
the Siberian Branch of Academy of Sciences of USSR,Moscow

(Received 28 October 1965)

In recent paper we reported the isolation of 6 individual glycosides-panaxosides A-F from Ginseng roots.[1] The structure of carbohydrate chain of panaxoside A has already been established.[1,2] In the present paper we report the data on the structure of carbohydrate chains of panaxosides D,E,F, having common genin that is different from genin of panaxosides A,B,C. On estimating the analytical data we took into account the structure of native genin, proposed by Shubata et al.[3]

Panaxosides D and F are penta -and hexaglucosides, respectively. Panaxoside E contains one arabinose* residue and four glucose** residues.[1] On partial hydrolysis of panaxosides D,E,F with mixture $CH_3OH-H_2O-H_2SO_4$ (50:50:2) at 60° (3hrs) progenin was isolated $[\alpha]_D^{20}$ +8.1 (c 2.47 in methanol)(Found: C 62.02,62.16; H 9.03,8.95; M.w. 890) that proved to be identical for all three glycosides according to IR spectra,chromotographic behaviour and analytical data. Progenin was shown to be a triglucoside by M.w. and hydrolysis data.

---

*arabinose -Ar; ** glucose- Gl.

In the products of hydrolysis of fully methylated progenin 2,3,4,6-tetra-O-Me-D-Gl and 2,4,6-tri-O-Me-D-Gl have been identified. Consequently in carbohydrate chain of progenin there are present only (1→3) linkages between Gl residues and structures I and II are possible for it. In the products of hydrolysis of panaxosides D,E,F , oxidized with the periodate, chromotography showed the presence of Gl therefore these three glycosides should have Gl residues linked by (1→3) bond. Oxidation resulted in consumption of two mols of periodate per mol of progenin (cf.4). This result is in agreement with structure I.

On partial hydrolysis of panaxoside D together with progenin is formed Gl, of panaxoside E - Gl and Ar, of panaxoside F - Gl and gentiobiose; t. decomp. 121-123° (from ethanol) $/\alpha/_D^{20}$ +9.08 (c 5.28 in water) (Found: C 41.91,41.98; H 6.56, 6.64; calcd for $C_{12}H_{22}O_{11}$: C 42.12, H 6.48). The isolation of gentiobiose shows the presence of (1→6) linkages in carbohydrate chain of panaxoside F.

The structures of carbohydrate chains of panaxosides D,E and F have been established by the method of methylation. The methylated products were obtained by double treatment according to Kuhn (45-50° in dimethyl formamide or in mixture of dimethyl formamide with dimethyl sulphoxide) followed by single one according to Purdie. Complete methylation was checked by IR spectra and thin layer chromotography on alumina and silica gel in toluol-ethanol system (10:1). Destruction of carbohydrate chains of panaxosides occurs on methylation.

The purification was carried out first on silica gel

(60–200 mesh) in chloroform-ethyl-acetate (100→0 ; 0→100) and then in ethyl-acetate-ethanol (100→0 ; 0→100). The data on the products of methylation of panaxosides D,E,F are given in table 1.

TABLE 1

Methylated product of a panaxoside	$/\alpha/^{20}_{D}$ $CHCl_3$	M.w.	FOUND			Methylated monosaccharides
			C	H	OCH_3	
D*	+ 4,5	1070	62.77	9.30	30,53	2,3,4,6-tetra-O-Me-D-Gl(2
	C 7.93	1218			30.47	2,3,4 -tri -O-Me-D-Gl(1
						2,4,6 -tri -O-Me-D-Gl(1
E	- 13,14	1260	61,60	9,00	31,27	2,3,4,6-tetra-O-Me-D-Gl(1
	C 5.95	1290	61.50	9.15	31.22	2,3,5 -tri- O-Me-D-Ar(1
						2,3,4 -tri -O-Me-D-Gl(1
						2,4,6 -tri -O-Me-D-Gl(1
F	– 0,66	1274	61,81	9,48	32,22	2,3,4,6-tetra-O-Me-D-Gl(2
	C 9.1	1236	61.77	9.40	32.39	2,3,4 -tri -O-Me-D-Gl(1
						2,4,6 -tri -O-Me-D-Gl(1

*We failed to obtain pure sample owing to unsufficient amount of the material.

Studies on hydrolysates (72% $HClO_4$ in methanol,1:10, 3hrs, 100°) of products of methylation of panaxosides (paper chromotography in 2-butanone saturated with 1% NH_4OH) established the absence of mono- and dimethylated monosaccharides and hence provided the evidence for the linear structure of carbohydrate chains of the three glycosides. From molecular weight and methoxyl content it follows that all the products of methylation obtained from panaxosides are the methyl esters of tetraoside with original panaxosides D,E being pentaoside and

F- hexaoside[1].

Taking into consideration the data on hydrolysis of products of methylation for panaxosides D,E as well as the structure of carbohydrate chain of progenin we suggest the following structure for carbohydrate chain of tetraoside D-Gl-1→6-D-Gl-1→3-D-Gl-1→3-D-Gl-1 → genin. However, the ratio 2,3,4,6-tetra-O-Me-D-Gl and trimethylated glucose in hydrolysates of products of methylation of panaxosides D,F, determined by the known method[5], is 0.87:1. On the basis of this evidence one may assume the presence of two carbohydrate linear chains in original panaxosides and suggest for tetraoside the following structure:

$$\begin{tikzcd} \text{D-Gl-1}\rightarrow\text{3-D-Gl-1} \arrow[dr] & \\ & \text{genin.} \\ \text{D-Gl-1}\rightarrow\text{6-D-Gl-1} \arrow[ur] & \end{tikzcd}$$

From the data of hydrolysis of methylated panaxoside E it follows that the latter also has two carbohydrate chains since there are two methylated terminal monosaccharides 2,3,4,6-tetra-O-Me-D-Gl and 2,3,5-tri-O-Me-D-Ar among the products of hydrolysis. In that case the only possible variation in the structure of carbohydrate chain of tetraoside from panaxoside E is

$$\begin{tikzcd} \text{D-Gl-1}\rightarrow\text{3-D-Gl-1} \arrow[dr] & \\ & \text{genin.} \\ \text{D-Ar-1}\rightarrow\text{6-D-Gl-1} \arrow[ur] & \end{tikzcd}$$

Structures

$$\begin{tikzcd} \text{D-Ar-1}\rightarrow\text{6-D-Gl-1}\rightarrow\text{3-D-Gl-1} \arrow[dr] & \\ & \text{genin} \\ \text{D-Gl-1} \arrow[ur] & \end{tikzcd}$$

and

$$\begin{tikzcd} \text{D-Gl-1}\rightarrow\text{3-D-Gl-1}\rightarrow\text{3-D-Gl-1} \arrow[dr] & \\ & \text{genin} \\ \text{D-Ar-1} \arrow[ur] & \end{tikzcd}$$

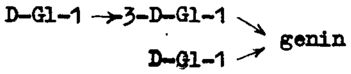
are removed since the former is not consistent with the structure of carbohydrate chain of progenin[1] and the latter does not explain the formation of 2,3,4-tri-O-Me-D-Gl.

The experimental data show that there are two linear carbohydrate chains in each of the three panaxosides; The formation of methylated tetraosides from panaxosides D,E which are pentaosides and from panaxoside F - hexaoside indicates the partial destruction during the process of methylation. Bearing in mind the structure of carbohydrate chains of tetraosides from panaxosides D,E and also the structure of carbohydrate chain of progenin one may propose structure III for panaxoside D and structure IY - for panaxoside E.

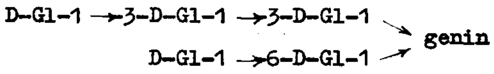
Partition chromotography /silica gel, chloroform (100→0) ethanol (0→100) / of mixture of methylated monosaccharides, formed on hydrolysis of crude product of methylation of panaxoside F, resulted in isolating one additional product which was rather easily oxidized with Bonner reagent[6] and gave complex with boric acid. These properties are characteristic of 3,4,6-tri-O-Me-D-Gl . The isolation of this glucose indicates the possible presence of (1→2) linkage in carbohydrate chains of panaxoside F. Hence, structures Y or YI may be proposed for carbohydrate chains of panaxoside F.

D-Gl-1 → 3-D-Gl-1 → 3-D-Gl-1 → genin

I


$$\begin{tikzcd} \text{D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[dr] & \\ & & \text{genin} \\ & \text{D-Gl-1} \arrow[ur] & \end{tikzcd}$$

II


$$\begin{tikzcd} \text{D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[dr] & \\ & & & \text{genin} \\ & \text{D-Gl-1} \arrow[r] & \text{6-D-Gl-1} \arrow[ur] & \end{tikzcd}$$

III

$$\begin{tikzcd}
\text{D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[dr] & \\
 & & & \text{genin} \\
 & \text{D-Ar-1} \arrow[r] & \text{6-D-Gl-1} \arrow[ur] &
\end{tikzcd}$$

IY

$$\begin{tikzcd}
\text{D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[dr] & \\
 & & & \text{genin} \\
\text{D-Gl-1} \arrow[r] & \text{2-D-Gl-1} \arrow[r] & \text{6-D-Gl-1} \arrow[ur] &
\end{tikzcd}$$

Y

$$\begin{tikzcd}
\text{D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[r] & \text{3-D-Gl-1} \arrow[dr] & \\
 & & & \text{genin} \\
\text{D-Gl-1} \arrow[r] & \text{2-D-Gl-1} \arrow[r] & \text{6-D-Gl-1} \arrow[ur] &
\end{tikzcd}$$

YI

REFERENCES

1. G.B. Elyakov et al., *Tetrahedron Letters*, *1964* ,3591

2. G.B. Elyakov, L.I. Strigina, N.K. Kochetkov
Chimiya Prirodnich Soedineni , *1965* ,149

3. Sh. Shibata, O. Tanaka, M. Sado and S. Tsushima,
Tetrahedron Letters , *1963* , 795

4. M.P. Khare, O. Schindler, T. Reichstein,
Helv. Chim. Acta, *45* , 1534 (1962)

5. M. Dubois, K.A. Gilles, J.K. Hamilton, P.A. Rebers, F. Smith,
Anal. Chem., *28* , 350 ,(1956)

6. T.G. Bonner, *Chem. and Ind.*, *1960* , 345