Furylidene derivatives of carbohydrates. II.* Mass spectrometric fragmentation of some monosaccharide furylidene acetals and its analytical applications

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Dedicated to Professor Dr J. Hostomský in honour of his 70th birthday

Furylidene acetals of methyl glycopyranosides and glycofuranosides have been studied by low and high resolution mass spectrometry. Differences in the fragmentation of compounds substituted at various positions with the furylidene residue and deuteration of substances with free hydroxyl groups permitted elucidation of the mechanisms of the fragmentation and of the formation of structurally significant ions. Using the established fragmentation patterns the structures of some products of condensation of 2-furaldehyde with D-glucose and D-xylose, formed under the conditions of the formation of 2-furaldehyde itself, have been determined.

Furylidene derivatives of sugars may play an important role in systems containing carbohydrates, 2-furaldehyde and an acid catalyst [1]. This is the case, *inter alia*, with pulp cooking, prehydrolysis, dimensional stabilization of wood, and the production of 2-furaldehyde itself. The determination of the structure of furylidene acetals by conventional methods is quite difficult and time consuming [2]. With the aim to elaborate a rapid and precise method for structural characterization of this class of compounds which, in addition, would require only micro quantity of a pure substance we have prepared different types of furylidene acetals of methyl glycosides and used these as model compounds for mass spectrometric studies. Based on the found criteria of fragmentation the structure of condensation products of 2-furaldehyde with D-glucose and D-xylose, formed under the conditions of acid-catalyzed dehydration of saccharides [3] has been determined. The two substances have been identified as 4,6-*O*-furylidene-D-glucopyranose (*VII*) and 3,5-*O*-furylidene-D-xylofuranose (*VIII*).

Experimental

Methyl 4,6-*O*-furylidene-α-D-glucopyranoside (*I*), methyl 4,6-*O*-furylidene-α-D-galactopyranoside (*II*), methyl 4,6-*O*-furylidene-α-D-mannopyranoside (*III*), methyl 3,4-*O*-furylidene-β-L-arabinopyranoside (*V*), and methyl 2,3:4,6-di-*O*-furylidene-α-D-mannopyranoside (*VI*) were prepared by the modified method of *Irvine* and *Scott* [2, 4, 5].

* For Part I see Ref. [3].

Methyl 3,5-*O*-furylidene-α-D-xylofuranoside (*IV*) was prepared by condensation of freshly distilled 2-furaldehyde (5 ml) with methyl α-D-xylofuranoside [6] (0.5 g) in the presence of anhydrous copper sulfate (2 g). The mixture was stirred for 2 hours at room temperature, filtered, and 2-furaldehyde was removed under vacuum (10^{-1} torr) at 35°C. The product (0.53 g; 72%) crystallized from ether—hexane and after recrystallization from the same solvent melted at 71—72°C and had $[\alpha]_D^{22}$ +52° (*c* 1, chloroform).

For $C_{11}H_{15}O_6$ (242.08) calculated: 54.53% C, 5.83% H, 12.81% CH_3O; found: 54.12% C, 6.18% H, 12.90% CH_3O.

Preparation of *VII* and *VIII* has been described [3].

Mass spectra were obtained on an MCh 1306 instrument at 70 eV. Compound *I* was studied also at 12 eV. The temperature in the site of evaporation was 30—40°C and that in the ionization chamber 120°C. Exact mass measurements were done using an MS 902 S instrument (resolution 20 000). The results are presented in terms of the empirical formulae of the ions. During these measurements the temperature in the ionization chamber was 120—150°C. *O*-Deuteration of *I*—*V* was accomplished directly in the MCh 1306 spectrometer by evaporation of the solutions (in D_2O). The *m/e* values of *O*-deuterated compounds are given in parentheses.

Results and discussion

An important feature of the mass spectra of furylidene derivatives of monosaccharides (Figs. 1—6), as well as of 4,6-*O*-benzylidene acetals of methyl glycosides [7] (in contrast to acyclic, monocyclic [8], and isopropylidene [9—11] derivatives of mo-

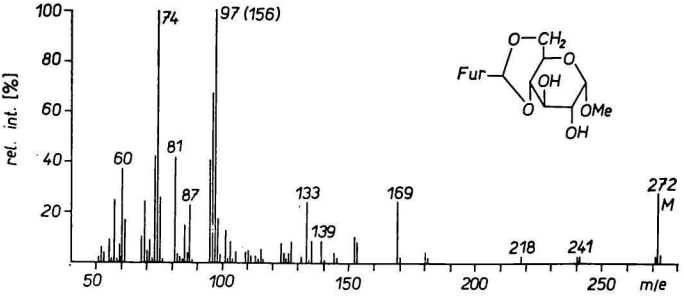


Fig. 1. Mass spectrum of methyl 4,6-*O*-furylidene-α-D-glucopyranoside.

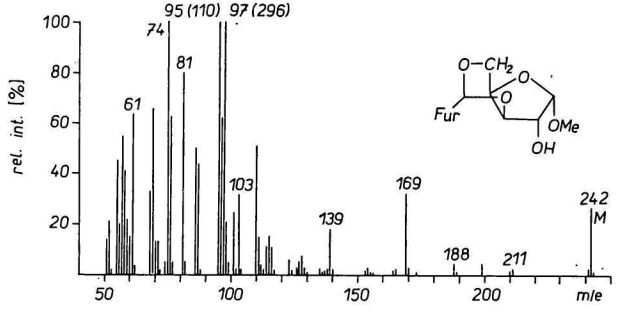


Fig. 2. Mass spectrum of methyl 3,5-*O*-furylidene-α-D-xylofuranoside.

nosaccharides) is the presence of well pronounced peaks of the molecular ions. This naturally permits direct determination of molecular weight of this class of substances. The formation of $[M - \dot{H}]^+$ ions, unlike the *O*-benzylidene acetals, occurs only in a negligible extent. The glycosidic methoxyl group of methyl glycosides (*I*—*VI*) (Figs. 1—4) is cleaved either in the form of a radical to give $[M - \dot{O}Me]^+$ ions (*m/e* 319, Fig. 4; 271

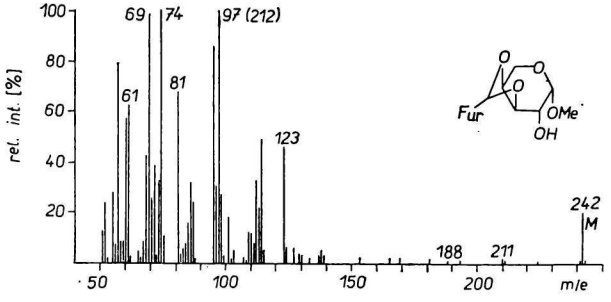


Fig. 3. Mass spectrum of methyl 3,4-*O*-furylidene-β-L-arabinopyranoside.

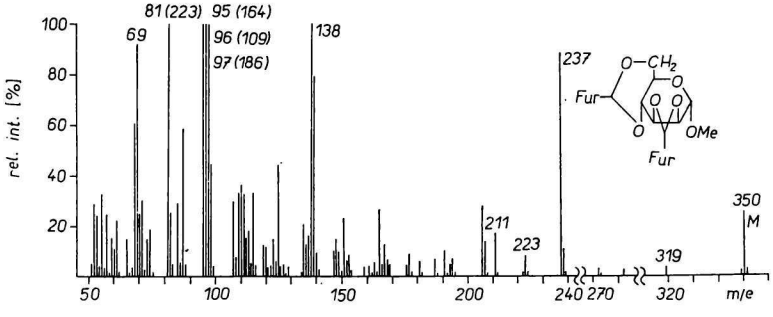


Fig. 4. Mass spectrum of methyl 2,3:4,6-di-*O*-furylidene-α-D-mannopyranoside.

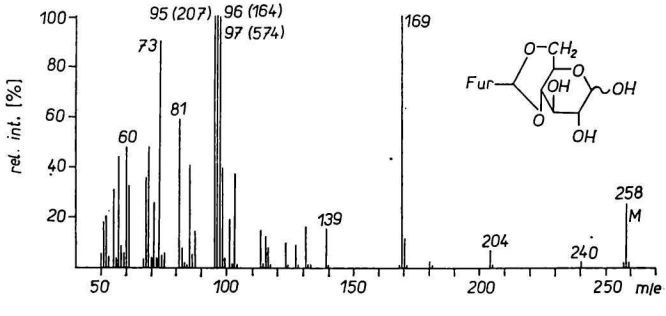


Fig. 5. Mass spectrum of 4,6-*O*-furylidene-D-glucopyranose.

(273), Fig. 1; 241 (242), Figs. 2 and 3), or it interacts with the free hydroxyl group at the C(2) position to give $[M - MeOH]^+$ ions (*m/e* 270 (271), Fig. 1; 240 (240), Figs. 2 and 3).

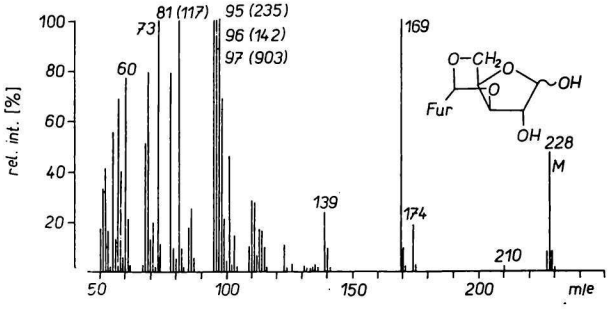


Fig. 6. Mass spectrum of 3,5-*O*-furylidene-D-xylofuranose.

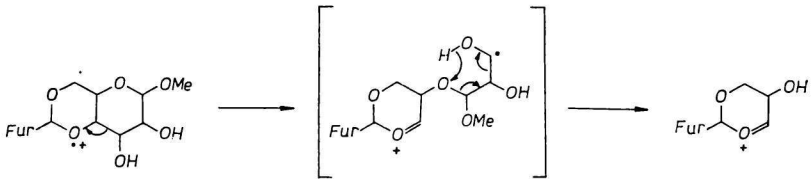
The presence of the furylidene arrangement is proved by the peaks at *m/e* 95—97 which are the most intense in the spectra. These correspond to the ions $Fur-C\equiv\overset{+}{O}$ at *m/e* 95 (95), $Fur-\dot{C}H\overset{+}{O}$ at *m/e* 96 (96), and $Fur-CH=\overset{+}{O}H$ at *m/e* 97 (98). Another characteristic feature of the furylidene arrangement is the formation of the furyl ions at *m/e* 81 (81), which are rearranged into pyronium ions in a manner analogous to the rearrangement of benzyl ions to tropylium ions [12]. The furylidene arrangement undergoes, in addition, a slightly pronounced fission comprising hydrogen transfer to give the ions $[M - C_3H_2O]^+$ at *m/e* 218 (220) in the case of *I*—*III* (Fig. 1 for *I*) and at *m/e* 188 (189) in the case of *IV* and *V* (Figs. 2 and 3). The elimination of C_3H_2O molecule (probably propargylaldehyde) was proved by exact mass measurements of the ions at *m/e* 218 and 188 which correspond to the elemental composition $C_9H_{14}O_6$ and $C_8H_{12}O_5$, respectively.

In all furylidene derivatives studied the "*h*-rupture", described by *Chizhov et al.* [13, 14] was observed. Since this mode of fragmentation varies with the type of the derivative, it will be discussed below.

Methyl 4,6-O-furylidene hexopyranosides (I—III)

The mass spectra of methyl 4,6-*O*-furylidene-α-D-glucopyranoside are shown in Fig. 1. The spectra of the stereoisomers *II* and *III* differ merely quantitatively. No rules for distinguishing between the stereochemistry of these compounds could be found under the conditions of the measurements.

Two modes of fragmentation characteristic of the fragmentation of 4,6-*O*-furylidene derivatives could be found. The first one (marked as *r*-rearrangement) is started by the rupture of the C(3)—C(4) linkage and proceeds by the transfer of the hydrogen of the hydroxyl group at C(3) to the oxygen of the pyranoid ring. The rupture of the O—C(1) and C(2)—C(3) linkages gives rise to the ions of the elemental composition $C_8H_9O_4$ at *m/e* 169 (170) (Scheme 1).

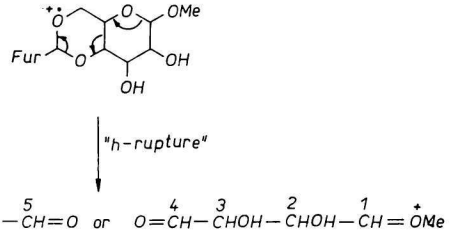


$\dot{M}^+$ *m/e* 272 (274)

r m/e 169 (170)
$C_8H_9O_4$

Scheme 1

A pair of the ions h_1 and h_2 at *m/e* 139 (139) and at *m/e* 133 (135) is formed by "*h*-rupture" (Scheme 2).



h_1 *m/e* 139 (139)
$C_7H_7O_3$

h_2 *m/e* 133 (135)
$C_5H_9O_4$

Scheme 2

Further fissions, most intense in the fragmentation of monosaccharide methyl ethers [8, 15, 16], give rise to the ions $MeO{=}CH{-}\dot{C}H{-}OH$ at *m/e* 74 (75), $HO{=}CH{-}\dot{C}H{-}OH$ at *m/e* 60 (62) (H_1 according to the nomenclature introduced by *Kochetkov* [8]), $MeO{=}{=}CH{-}CH{=}CH{-}OH$ at *m/e* 87 (88) (F_1) and $MeO{=}CH{-}OH$ at *m/e* 61 (62) (J_1).

The fragmentation described here is supported also by low energy (12 eV) mass spectrum of methyl 4,6-*O*-furylidene-α-D-glucopyranoside. The spectrum contained only the peak of the molecular ions and those of primary fragments: *m/e* 272 (100%), 271 (4.5%), 241 (1.5%), 240 (3.0%), 169 (30.3%), 139 (6.1%), 133 (19.7%), 97 (124.2%), 96 (6.1%), 87 (1.5%), 81 (6.1%), 74 (30.3%), 61 (2.0%), and 60 (3.0%). Other peaks in the spectrum on Fig. 1 are thus those of the disintegration products of the primary fragments.

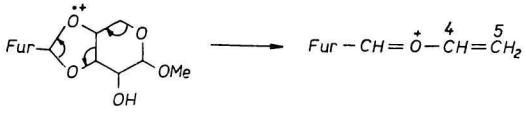
Methyl 3,5-O-furylidene-α-D-xylofuranoside (IV) (Fig. 2)

The fragmentation of methyl pentofuranoside 3,5-*O*-furylidene acetals proceeds in general in the same pattern as that found for the fragmentation of methyl 4,6-*O*-furylidene hexopyranosides. The *r* ions at *m/e* 169 (170) are given rise to by the cleavage

of $MeO-\dot{C}H-CH=O$ radicals from the molecular ions. A pair of h_1 ions *i.e.* $Fur-CH=\overset{+}{O}-CH_2-CH=O$ and $O=CH-CH(OH)-CH=\overset{+}{O}Me$ at *m/e* 139 (139) and 103 (104), respectively, is formed *via* "*h*-rupture". The disintegration of the furanoid cycle gives, as the most intense, the ions H_1 at *m/e* 74 (75) and J_1 at 61 (62).

Methyl 3,4-O-furylidene-β-L-arabinopyranoside (V) (Fig. 3)

The absence of *r* ions in the spectra is characteristic of the fragmentation of 3,4-*O*-furylidene derivatives of pyranosides. The "*h*-rupture", on the other hand, occurs also here to give rise to the ions h_1 at *m/e* 123 (123). The other part of the molecule remains uncharged (the peak of the ions at *m/e* 119 is not present in the spectrum) (Scheme 3).



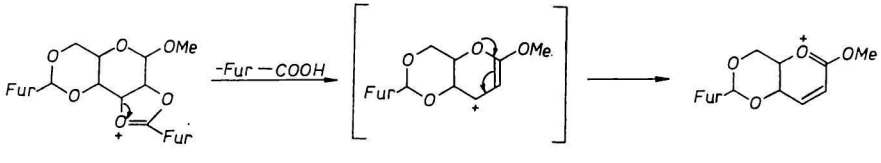
$\dot{M}^+$ *m/e* 242 (243) — h_1 *m/e* 123 (123), $C_7H_7O_2$

Scheme 3

Of the ions formed through the cleavage of the pyranoid ring the ions H_1 at *m/e* 74 (75) are the most intense; very intense are also ions at *m/e* 69 (69) of the elemental composition C_4H_5O. Their structure is probably that of a protonized furan.

Methyl 2,3:4,6-di-O-furylidene-α-D-mannopyranoside (VI) (Fig. 4)

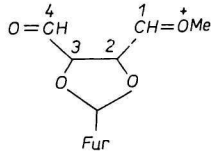
In addition to the fragmentation discussed above the fragmentation of the di-*O*-furylidene derivative *VI* is characterized by fissions caused by the presence of the furylidene cycle at C(2)—C(3). From the ions $[M - \dot{H}]^+$ at *m/e* 349 a molecule of 2-furoic acid is eliminated to give rise to the ions at *m/e* 237 of the elemental composition $C_{12}H_{13}O_5$ (Scheme 4).



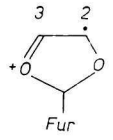
$[M - \dot{H}]^+$ *m/e* 349 — $C_{12}H_{13}O_5$ *m/e* 237

Scheme 4

After the elimination of a molecule of 2-furaldehyde from the position C(2)—C(3) the ions $[M - \dot{O}Me]^+$ give rise to the ions at *m/e* **223** of the elemental composition $C_{11}H_{11}O_5$. As a result of "*h*-rupture" the ions h_1 at *m/e* **139** or h_2 at *m/e* 211 are produced. The ions at *m/e* 138 are of H_1 series, containing the carbon atoms C(2) and C(3) together with their substituents (Scheme 5).



h_2 *m/e* 211
$C_{10}H_{11}O_5$



H_1 *m/e* 138
$C_7H_6O_3$

Scheme 5

Determination of the structure of condensation products of D-*glucose and* D-*xylose with 2-furaldehyde (VII and VIII)*

The molecular weight of the condensation product of D-glucose with 2-furaldehyde is given by the peak of the molecular ions at *m/e* 258 (Fig. 5). The presence of the intense peaks at *m/e* 81, 95, 96, and 97 together with the peak of the ions $[M - 54]^+$ at *m/e* 204 proved the presence of the furylidene arrangement. The peak of the ions $[M - H_2O]^+$ at *m/e* 240 indicates that the glycosidic hydroxyl group is unsubstituted. The presence of *r* ions at *m/e* 169 and h_1 ions at *m/e* 139 proves that the furylidene group occupies the positions C(4) and C(6). The ions F_1, J_1, and H_1, formed from C(1)—C(3), bearing unsubstituted hydroxyl groups, are at *m/e* 73, 61, and 60. Hence, the compound *VII* can be formulated as 4,6-*O*-furylidene-D-glucopyranose.

The structure of the condensation product of 2-furaldehyde with D-xylose (Fig. 6) was unequivocally established by the presence of the peaks $\dot{M}^+$ at *m/e* 228, $[M - 18]^+$ at *m/e* 210, $[M - 54]^+$ at *m/e* 174, *r* at *m/e* 169, h_1 at *m/e* 139, F_1 at *m/e* 73, H_1 at *m/e* 60. The structure of 3,5-*O*-furylidene-D-xylofuranose (*VIII*) is supported also by the presence of the peaks of the ions at *m/e* 81, 95, 96, and 97.

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