Aldobiouronic acids obtained from gum polysaccharides of the *Prunus* genus trees. V. Infrared spectroscopy

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Received 28 April 1972

Infrared spectra of three aldobiouronic acids: 6-*O*-β-D-glucuronopyranosyl-D-galactose, 2-*O*-β-D-glucuronopyranosyl-D-mannose, and 6-*O*-(4-*O*-methyl-β-D-glucuronopyranosyl)-D-galactose and of their methyl (methyl glycosid)-uronates were recorded and absorption bands in the 900—700 cm^{-1} range interpreted. The identified absorption bands at 935—925, 890—875, and 785—780 cm^{-1} were assigned to the reducing end in the aldobiouronic acids. This conclusion was confirmed also by the strong band at 830 cm^{-1} in the spectra of methyl (methyl glycosid)uronates of all three aldobiouronic acids where the influence of α anomer became evident. The absorption bands in the region of 810—800 cm^{-1} can be assigned to β-glycosidic bonds between the uronic acid residue and the hexose unit.

In our previous works [1, 2] we described the structure of three aldobiouronic acids: 6-*O*-β-D-glucuronopyranosyl-D-galactose, 2-*O*-β-D-glucuronopyranosyl-D-mannose, and 6-*O*-(4-*O*-methyl-β-D-glucuronopyranosyl)-D-galactose isolated from polysaccharide of peach-tree gum (*Prunus persica* (L.) BATSCH.). We discussed the infrared spectra of this polysaccharide in our previous work [3].

The purpose of this work was to record the i.r. spectra of the above-mentioned three aldobiouronic acids and correlate the specific bands in the spectra with their structure. We measured the spectra of free acids as well as of their methyl (methyl glycosid)uronates. However, our study was confined only to the 900—700 cm^{-1} range; on the basis of the so far published data we expected the bands belonging to α- and β-glycosidic bonds in this region.

Experimental

The aldobiouronic acids were prepared by hydrolysis of peach gum polysaccharide with 0.25 M sulfuric acid as described previously [4, 5]. Methyl (methyl glycosid)uronates were prepared according to *Timell* [6]. Optical rotations were measured on a JASCO ORD/UV-5 spectrophotometer at 589 nm and 25°C using spectral ethanol.

6-*O*-β-D-Glucuronopyranosyl-D-galactose (*I*): $[\alpha]_D^{25}$ −8.5° (*c* 0.518, 50% ethanol).

2-*O*-β-D-Glucuronopyranosyl-D-mannose (*II*): $[\alpha]_D^{25}$ −25.4° (*c* 0.508, 50% ethanol).

6-*O*-(4-*O*-Methyl-β-D-glucuronopyranosyl)-D-galactose (*III*): $[\alpha]_D^{25}$ −4.4° (*c* 0.498, 50% ethanol).

Methyl 6-*O*-(methyl β-D-glucopyranuronate)-D-galactoside (*IV*): $[\alpha]_D^{25}$ +56.8° (*c* 0.475, 50% ethanol).

Methyl 2-*O*-(methyl β-D-glucopyranuronate)-D-galactoside (*V*): $[\alpha]_D^{25}$ +3.2° (*c* 0.5, 50% ethanol).

Methyl 6-*O*-(methyl 4-*O*-methyl-β-D-glucopyranuronate)-D-galactoside (*VI*): $[\alpha]_D^{25}$ +70.7° (*c* 0.566, 50% ethanol).

KBr pellets containing 3 mg of aldobiouronic acids were used for recording the spectra on a Zeiss UR-10 spectrophotometer.

Results and discussion

In the spectra of aldobiouronic acids in the range of 900—700 cm^{-1}, many of the bands characteristic of mono-, oligo-, and polysaccharides are either absent or very weak. *Barker et al.* [7—9] studied this range with monosaccharides. They classified the absorption bands to three types. The stretching vibration of C—O—C bonds of α anomers exhibits type *1* absorption at 917 ± 13 cm^{-1} and that of β anomers at 920 ± ± 5 cm^{-1}. Type *3*, shown by α anomer at 766 ± 10 cm^{-1} and by β anomer at 774 ± ± 9 cm^{-1}, was suspected of being the ring deformation. Type *2a* (revealed by α anomer at 844 ± 8 cm^{-1}) and type *2b* (revealed by β anomer at 891 ± 7 cm^{-1}) were believed to be one of the C—H deformation modes. *Verstraeten* [10] specified this theory: only furanoses give type *2* absorption (850 ± 6 cm^{-1}) provided the ring can freely rotate. He stated further that the type *3* absorption appears if the two conditions are met: *a*) the sugar must have a pyranoid ring, and *b*) this pyranoid form must assume a conformation having at least one axial hydroxyl group. If the number of axial hydroxyl groups is increased, the pronounced type *3* absorption occurs. *Bajpaj et al.* [11] interpreted the i.r. spectra of some aldobiouronic acids. In the spectra of 2-*O*-α-D-galacturonopyranosyl-L-rhamnose and 4-*O*-α-D-galacturonopyranosyl-D-galactose, they observed two bands at 810 and 820 cm^{-1}, respectively. Although this absorption was very close to the type *2a* absorption for α-D-galactose and its derivatives (825 ± 11 cm^{-1}), assignment as α anomer might not be correct, as many other characteristic absorptions of the sugars were absent in the i.r. spectra of both aldobiouronic acids. This absorption probably arose from an α-glycosidic linkage between the uronic acid and the sugar moiety. With two other aldobiouronic acids 4-*O*-β-D-glucuronopyranosyl-D-galactose and 6-*O*-β-D-glucuronopyranosyl-D-galactose they identified only one band at 940 cm^{-1}; in the first case it was a very weak and in the second one a weak band. However, they did not discuss this band in their work.

Results of our measurements are summarized in Table 1. We attribute the measured wavenumbers of bands to end units in aldobiouronic acids. The steady state of both anomers of the same aldohexose is influenced by conformational stability of each anomer. It is known that different aldohexoses mutarotate differently. For instance, in the aqueous solution of D-mannose, there are 66.8% of α anomer and 31.2% of β anomer, while in the case of D-galactose, there are 29.6% of α anomer and 70.4% of β anomer present. These ratios were calculated during mutarotation [12]. The measured wavenumbers of bands of the compounds *I* and *III* at 925 and 930 cm^{-1}, respectively, point to the type *1* absorption. The absorption bands at 880 and 890 cm^{-1} occurring also in the compound *II*, we ascribe to the type *2b* absorption. It indicates that β anomer of D-galacto- and D-mannopyranose is involved because the hydrogen on C_1 in these hexoses is in axial position as these hexopyranoses are in C1 conformation [13]. The absorption bands of the compounds *I* and *III* at 785 and 780 cm^{-1} we attribute to the type *3* absorption. This proves the β anomer to be dominant in D-galactopyranose. This band is absent

Table 1

Infrared spectra of aldobiouronic acids

Compound	Wavenumbers [cm^{-1}]					
	1	*2b*		*2a*		*3*
I	925 w	880 w			805 vw	785 vw
IV		880 w		830 s		780 w
II		890 w	850 vw		810 w	
V		890 vw	845 vw	830 s	805 w	
III	930 vw	880 vw			880 vw	780 vw
VI	935 vw	875 vw		830 s	800 vw	785 w

s — strong, w — weak, vw — very weak.

with the compound *II*; however, another band at 850 cm^{-1} is present which we assign to the predominant α anomer of D-mannopyranose. The existence of the strong band of each methyl (methyl glycosid)uronate at 830 cm^{-1} provides unambiguous evidence that the reducing ends are responsible for the mentioned absorption bands. This band ought to be assigned to the type *2a* absorption because in these compounds the effect of α anomer is significant which, as known, predominates with methyl glycosides.

In the spectra of each aldobiouronic acid as well as in those of methyl (methyl glycosid)uronates, absorption bands of different intensity appeared in the 800—810 cm^{-1} region. These bands could be assigned to β-glycosidic bonds between the acid residue and the appropriate hexose unit. It is to be noted that we recorded the i.r. spectra of aldobiouronic acids obtained from different plant gums isolated earlier [1]. Results of those measurements correspond with the present ones.

Acknowledgements. We are indebted to R. Justhová for taking the spectra.

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Translated by A. Kardošová