IR SPECTRA OF METHYLTETROSIDES AND THEIR MONOMETHYL ETHERS IN THE REGION OF VALENCE VIBRATION OF HYDROXYL GROUPS

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IR Spectral absorption bands ν(OH) (3 700 to 3 400 cm^{-1}) of the both anomers of methyl D-threofuranoside, methyl D-erythrofuranoside, and their monomethyl ethers have been studied in dilute tetrachloromethane solution. For these 11 compounds positions and intensities of individual bands are discussed with respect to possible formation of intramolecular hydrogen bonds.

In the previous papers[1,2] we studied ^1H and ^{13}C NMR spectra of the synthetized methyl tetrosides; the present paper deals with their IR spectra in the region of valence vibrations of hydroxyl groups. Measurement of dilute solutions of the studied compounds in non-polar solvents, in which formation of intermolecular hydrogen bonds is suppressed[3-5], enabled to obtain useful information about existence of intramolecular hydrogen bonds and, hence, also about conformation of the given saccharide derivative. Position and intensity of IR absorption bands in this region depends on sterical conditions of formation of intramolecular hydrogen bonds whose strength is proportional to magnitude of the difference $\Delta\nu$ of the absorption wave numbers of the bonded and free OH group[3,4,6]. (If the bonded hydroxyl group is involved simultaneously in two hydrogen bonds (double bridge), then its vibration frequency shift towards lower wave number values is even more marked[7,8].)

EXPERIMENTAL

The substances measured, *i.e.* methyl α-D-threofuranoside (*I*), methyl 2-O-methyl-α-D-threofuranoside (*II*), methyl 3-O-methyl-α-D-threofuranoside (*III*), methyl β-D-threofuranoside (*IV*), methyl 2-O-methyl-β-D-threofuranoside (*V*), methyl 3-O-methyl-β-D-threofuranoside (*VI*), methyl α-D-erythrofuranoside (*VII*), methyl 2-O-methyl-α-D-erythrofuranoside (*VIII*), methyl 2-O-methyl-β-D-erythrofuranoside (*IX*), methyl 3-O-methyl-β-D-erythrofuranoside (*X*), and methyl β-D-erythrofuranoside (*XI*), were prepared by the known procedure[1].

The spectra were measured in tetrachloromethane solutions with a Perkin–Elmer 325 apparatus in 2 cm quartz cells Infrasil (the spectral slot width 1·2 cm^{-1} at 3 400 cm^{-1}). Concentration

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of the studied substances ($2 . 10^{-3}$ mol l^{-1}) was chosen in such a region as to secure the possibility of formation of intramolecular hydrogen bonds only. (In cases of analogous hydroxy derivatives the given values of concentrations preventing formation of intermolecular hydrogen bonds are $5 . 10^{-3}$ mol l^{-1} (ref.[3,9]) or even $1 . 10^{-2}$ mol l^{-1} (ref.[4,5]).)

RESULTS AND DISCUSSION

Positions of absorption bands ν(OH) of the compounds studied are given in Table I.

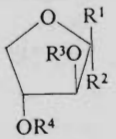
The IR spectrum of compound *I* contains the absorption bands at 3621 and 3545 cm^{-1}. The band with the higher wave number corresponds either to free hydroxyl group or possibly to a very weak intramolecular hydrogen bridge* which can be formed by the bond of hydroxyl group either at the third or at the second carbon atom with the electron pair of oxygen in furanoside ring. The second absorption band ν(OH) = 3 545 cm^{-1} is due to the substantially stronger intramolecular hydrogen bond $O_{(3)}$—H···$O_{(1)}$, whose assignment is given by possibility of formation of the sterically favourable six-membered ring. From this point of view it is interesting that a practically identical position of the absorption band ν(OH) = 3 544 to 3 548 cm^{-1} was found for intramolecular hydrogen bond of pyranoside derivatives[13,14] and 1,3-diaxial cyclohexanediols[15,16].

On the basis of formation of the said hydrogen bond it is possible to presume the arrangement $O_{(2)}$—H···$O_{(4)}$ for the value ν(OH) = 3 621 cm^{-1}. The intensive IR absorption band ν(OH) = 3 543 cm^{-1} found with the compound *II* is due to strong hydrogen bond $O_{(3)}$—H···$O_{(1)}$ (same as in the case of *I*). The IR spectrum of *III* contains similar vibration band ν(OH) at 3 619 cm^{-1} due to the hydrogen bond $O_{(2)}$—H···$O_{(4)}$.

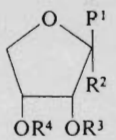
An intensive absorption band ν(OH) = 3 562 cm^{-1} was found in IR spectrum of *IV* corresponding to relatively strong hydrogen bond of *cis* vicinal arrangement $O_{(2)}$—H···$O_{(1)}$ with a five-membered ring. (For bonded hydroxyl groups in compound *XIV* the measured[10] value was ν(OH) = 3 585 cm^{-1}, that of *XVI* was[10] ν(OH) = 3 572 cm^{-1} or (ref.[3,11]) 3 573 and 3 579 cm^{-1}, that of *cis*-2-methoxycyclopentanol (*XVIII*) was[12] ν(OH) = 3 570 cm^{-1}.) The second intensive absorption band of vibration ν(OH) with the maximum at 3 616 cm^{-1} corresponds then probably to the substantially weaker hydrogen bond $O_{(3)}$—H···$O_{(4)}$. In case of compound *V* we found in the IR spectrum an intensive absorption band ν(OH) =

* Ref.[4] gives IR absorption at 3 629 cm^{-1} for free secondary hydroxyl groups of simple alcohols; the values observed[9] with tetrahydrofuran-3-ol (*XII*) was ν(OH) = 3 628 cm^{-1}, the value given[10] for free OH groups of 1,4-anhydro-L-threitol (*XIII*) and 1,4-anhydroerythritol (*XIV*) is 3 624 cm^{-1}. Similarly the values obtained for free hydroxyl groups of *trans*-cyclopentane-1,2-diol (*XV*) were ν(OH) = 3 624 cm^{-1} (ref.[10,11]) and 3 620 cm^{-1} (ref.[3]), those of *cis*-cyclopentane-1,2-diol (*XVI*) were (OH) = 3 624 cm^{-1} (ref.[10]), 3 633 cm^{-1}, 3 635 cm^{-1} (ref.[3,11]), that of *trans*-2-methoxycyclopentanol (*XVII*) was[12] 3 627 cm^{-1}.

$= 3\,630\ cm^{-1}$, *i.e.* a higher wave number value than with the compound *IV*. Due to *cis* vicinal arrangement of the two methoxyl groups, the furanoside ring conformation was probably partially changed, and the distance between $O_{(3)}$—H and $O_{(4)}$ was consequently increased. The measured value $\nu(OH) = 3\,630\ cm^{-1}$, therefore, is most probably due to free hydroxyl group $O_{(3)}$—H. In the IR spectrum of *VI* an intensive absorption band $\nu(OH) = 3\,574\ cm^{-1}$ was found due to the hydrogen bond $O_{(2)}$—H···$O_{(1)}$. A certain weakening of this bond (as compared with compound *IV*)



I, $R^1 = R^3 = R^4 = H$, $R^2 = OCH_3$
II, $R^1 = R^4 = H$, $R^2 = OCH_3$, $R^3 = CH_3$
III, $R^1 = R^3 = H$, $R^2 = OCH_3$, $R^4 = CH_3$
IV, $R^1 = OCH_3$, $R^2 = R^3 = R^4 = H$
V, $R^1 = OCH_3$, $R^2 = R^4 = H$, $R^3 = CH_3$
VI, $R^1 = OCH_3$, $R^2 = R^3 = H$, $R^4 = CH_3$



VII, $R^1 = R^3 = R^4 = H$, $R^2 = OCH_3$
VIII, $R^1 = R^4 = H$, $R^2 = OCH_3$, $R^3 = CH_3$
IX, $R^1 = OCH_3$, $R^2 = R^4 = H$, $R^3 = CH_3$
X, $R^1 = OCH_3$, $R^2 = R^3 = H$, $R^4 = CH_3$
XI, $R^1 = OCH_3$, $R^2 = R^3 = R^4 = H$

is due to substitution of OH group by methoxyl group at the third carbon atom, which could probably cause a certain change in conformation of the furanoside ring.

In the IR spectrum of compound *VII* a dominant absorption band was found for $\nu(OH) = 3\,533\ cm^{-1}$ accompanied by another intensive one, $\nu(OH) = 3\,631\ cm^{-1}$. For explanation of the former band (at $3\,533\ cm^{-1}$) a possibility of formation of a "double-bridge" $O_{(3)}$—H···$O_{(2)}$—H···$O_{(1)}$ could be presumed, but this interpretation is strongly contradicted by existence of intensive absorption band $\nu(OH) = 3\,631\ cm^{-1}$ of free hydroxyl group whose existence would be impossible in the case of the "double-bridge". Therefore, the said absorption band with the lowest wave number value is probably due by the very strong intramolecular hydrogen bond formed between $O_{(2)}$—H hydroxyl group and free electron pairs at oxygen atoms at

the first and the third carbon atoms. (An analogous strenghtening of intramolecular hydrogen bond was observed *e.g.* with 1,3-dioxan-5-ol as compared with tetrahydropyran-3-ol[9].) The proton of $O_{(3)}$—H group remains free in this case, being not involved in intramolecular hydrogen bond.

The IR spectrum of compound *VIII* contains an intensive absorption band $\nu(OH) = 3\,567\ cm^{-1}$ corresponding to a relatively strong hydrogen bond in the *cis* vicinal arrangement $O_{(3)}$—H···$O_{(2)}$. The absorption band $\nu(OH) = 3\,560\ cm^{-1}$ was found for analogous arrangement in compound *IX*. The IR spectrum of compound *X* contains the absorption band $\nu(OH) = 3\,550\ cm^{-1}$ corresponding to strong intramolecular hydrogen bond $O_{(2)}$—H···$O_{(3)}$. The IR spectrum of compound *XI* contains two intensive absorption bands $\nu(OH) = 3\,565\ cm^{-1}$ and $\nu(OH) = 3\,627\ cm^{-1}$. The former band can be explained by the intramolecular hydrogen bond $O_{(3)}$—H···$O_{(2)}$ or $O_{(2)}$—H···$O_{(3)}$, whereas the latter one represents a vibration value of free hydroxyl group $O_{(3)}$—H or $O_{(2)}$—H, respectively. From comparison of the

TABLE I

IR Spectra of methyltetrosides and their monomethyl ethers

Compound	Wave number of IR absorption cm^{-1}	The presumed intramolecular hydrogen bond
I	3 621	$O_{(2)}$—H...$O_{(4)}$
	3 545	$O_{(3)}$—H...$O_{(1)}$
II	3 543	$O_{(3)}$—H...$O_{(1)}$
III	3 619	$O_{(2)}$—H...$O_{(4)}$
IV	3 562	$O_{(2)}$—H...$O_{(1)}$
	3 616	$O_{(3)}$—H...$O_{(4)}$
V	3 630	$O_{(3)}$—H
VI	3 574	$O_{(2)}$—H...$O_{(1)}$
VII	3 533	$O_{(2)}$—H (...$O_{(1)}$, ...$O_{(3)}$)
	3 631	$O_{(3)}$—H
VIII	3 567	$O_{(3)}$—H...$O_{(2)}$
IX	3 560	$O_{(3)}$—H...$O_{(2)}$
X	3 550	$O_{(2)}$—H...$O_{(3)}$
XI	3 565	$O_{(3)}$—H...$O_{(2)}$
	3 627	$O_{(2)}$—H

measured values of valence vibrations of hydroxyl groups in compounds *IX* to *XI* and with respect to the published IR spectra of vicinal diols[3,10-12] and their monomethyl ethers (*e.g.* of compounds *XVI* and *XVIII*) it can be concluded that the absorption band $\nu(OH) = 3\,565\ cm^{-1}$ of compound *XI* is due to intramolecular hydrogen bond $O_{(3)}—H\cdots O_{(2)}$. This hydrogen bond changes the wave number value by $5\ cm^{-1}$ on going from compound *XI* to *IX*, which agrees well with analogous changes in similar compounds. On the contrary, if the said absorption band of compound *XI* were due to the intramolecular hydrogen bond $O_{(2)}—H\cdots O_{(3)}$, then a markedly greater wave number decrease would accompany the change from compound *XI* to its monomethyl ether *X*. Of course, such a wave number change would be possible in connection with changed conformation of the compounds *X* and *XI*. Therefore, for the above consideration concerning preference of intramolecular hydrogen bond $O_{(3)}—H\cdots O_{(2)}$ in compound *XI* to be justified it is necessary to know conformation of this compound and its monomethyl ethers *IX* and *X*.

The given results of IR spectra measurement of methyl tetrosides and their monomethyl ethers in the region of valence vibrations of hydroxyl groups provide useful information about possible existence and strength of intramolecular hydrogen bonds. However, a more detailed conformational analysis necessitates a combination of these results with further techniques used in conformational analysis.

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