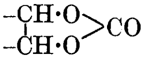
# CCXXXI.—*Sugar Carbonates. Part II. Derivatives of Arabinose and Xylose.*

By Walter Norman Haworth and William Maw.

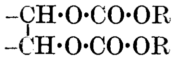
The wide distribution of arabinose and xylose in vegetable products, and their importance in relation to constitutional studies of the hexoses have led us to extend our studies of the formation of sugar carbonates to these examples of the pentose group. As yet no partially substituted members of the pentose series which might be available for synthetic work have been prepared, but in this communication we describe the isolation of fully substituted sugar carbonates which are similar in properties to the hexose carbonates (compare Allpress and Haworth, J., 1924, **125**, 1223), differing from the latter in that they can be purified by distillation in a high vacuum.

The two expected types of carbonate linking are illustrated in the pentose carbonates, namely, the normal carbonate (A) and the ester of the acid carbonate (B) :

(A.)



$$\begin{array}{l} -\mathrm{CH{\cdot}O} \\ \;\;| \\ -\mathrm{CH{\cdot}O} \end{array} \!\!>\! \mathrm{CO}$$



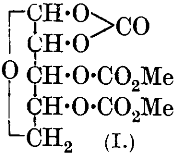
$$\begin{array}{l} -\mathrm{CH{\cdot}O{\cdot}CO{\cdot}OR} \\ \;\;| \\ -\mathrm{CH{\cdot}O{\cdot}CO{\cdot}OR} \end{array}$$

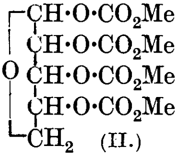
(B.)

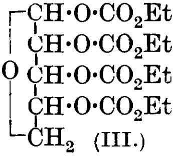
All the products isolated were prepared by condensation of the pentose with a chloroformic ester, and it was again observed that the use of aqueous alkali as the medium gave rise to a normal carbonate linking (A) in the pentose. Most of the compounds were obtained, however, by conducting the condensation in the presence of dry pyridine, and all the carbonates derived by the use of the latter method were of the type (B). In a third method of condensation in which metallic sodium was used in a dry solvent, a carbonic ester of arabinose was isolated having different properties from those of the other compounds. This was lævorotatory, whereas the substances derived by the use of either sodium hydroxide or pyridine as reagent were all dextrorotatory. To this series of fully substituted pentoses the amylene oxide structure has been ascribed, since we are not able to detect any of the properties which would lead us to regard these products as $\gamma$-sugars. The several compounds which we have prepared by these methods are tabulated below :—

| | | $[\alpha]_D$. |
|---|---|---|
| Dicarbomethoxy *l*-arabinose monocarbonate (I) | M. p. 137° | + 39·5° |
| Tetracarbomethoxy *l*-arabinose (II) .............. | M. p. 123° | +126·6° |
| Tetracarbomethoxy *l*-arabinose (II) .............. | M. p. 186° | − 16·4° |
| Tetracarbethoxy *l*-arabinose (III) .................. | B. p. 230°/0·4 mm. | + 98·8° |
| Tetracarbomethoxy *l*-xylose (II) .................. | B. p. 215°/0·5 mm. | + 59·5° |
| Tetracarbethoxy *l*-xylose (III) ...................... | B. p. 222°/0·4 mm. | + 62·1° |

Excluding considerations of stereochemical distribution of the groups, we propose to allocate the following provisional formulæ to these compounds:


(I.)


(II.)


(III.)

All these products are insoluble in water, but readily soluble in acetone and less soluble in alcohol or ether. They are completely hydrolysed in presence of warm dilute alkali, whilst barium hydroxide gives a copious precipitate of barium carbonate. This phenomenon is probably due to the intermediate formation of barium salts of the sugar carbonates. It is interesting to note that Siegfried and Howwjanz (*Z. physiol. Chem.*, 1909, **59**, 376) have obtained carbonic acid derivatives of arabinose and xylose in the form of their calcium salts. The method adopted by these workers was to add milk of lime to an ice-cold solution of the sugar and admit carbon dioxide, and the aqueous solutions obtained in this way gave optically active calcium salts. Since these sugars have the capacity of combining with carbon dioxide, it seems probable that changes analogous to the formation of sugar carbonates may occur in the leaf of plants.

## EXPERIMENTAL.

*Dicarbomethoxy Arabinose Monocarbonate* (I).—*l*-Arabinose (10 g. dissolved in a little water) was mixed with methyl chloroformate (37·9 g.) and the mixture was cooled by means of ice and salt, and vigorously stirred during the succeeding operations. To the mixture 2*N*-sodium hydroxide was gradually admitted, and when the solution became permanently alkaline after 3 hours the stirring was discontinued and the solution kept over-night. A semi-solid mass separated, which was collected and dried in a vacuum. This product was purified from alcohol and isolated as colourless, silky needles, m. p. 137°. The substance showed in acetone $[\alpha]_D + 39{\cdot}5°$. It dissolved also in chloroform or alcohol, but was insoluble in water, and readily yielded barium carbonate in contact with cold, aqueous barium hydroxide [Found: C, 41·5; H, 4·3; OMe, 20·6; *M*, ebullioscopic, 235. $C_8H_6O_8(OMe)_2$ requires C, 41·1; H, 4·1; OMe, 21·2%; *M*, 292].

*Tetracarbomethoxy* l-*Arabinose* (II).—To a chloroform solution containing pyridine (31·5 g.) and finely sieved *l*-arabinose (10 g.), which was well cooled, there was gradually added with frequent agitation over a period of 1¼ hours a chloroform solution of methyl chloroformate (38 g.). The mixture was again placed on a shaking machine for 3½ hours until the constituents had dissolved. The solution was concentrated under diminished pressure, and pyridine hydrochloride separated. Water was added to the filtrate, producing the separation of a syrup, which was washed repeatedly with water until free from acidity. After keeping for several days in a vacuum desiccator, a glassy mass (18·5 g.) was isolated. Digestion with hot ether yielded a solution, which on cooling deposited syrups (A), and on concentration of the mother-liquor colourless crystals separated, which were purified from ether and obtained in plates, m. p. 123°. This substance was strongly dextrorotatory; in acetone, $[\alpha]_D + 126{\cdot}6°$. It dissolved easily also in chloroform or benzene, but was less soluble in alcohol or ether. It would appear to be insoluble in water. It readily gave a precipitate of barium carbonate on treatment with cold barium hydroxide solution [Found: C, 40·9; H, 4·8; OMe, 31·8, 31·9. Calc. for $C_9H_6O_9(OMe)_4$: C, 40·8; H, 4·7; OMe, 32·5%].

The above syrups (A) were again dissolved in ether, and on concentration of the solution a purified specimen of a syrupy product separated which distilled at 219—220°/0·4 mm. On cooling, this distillate formed a glass which could readily be powdered, and this substance appeared to contain isomeric forms of the preceding crystalline product. It showed $[\alpha]_D$ (in acetone) $+ 89{\cdot}3° \longrightarrow 95{\cdot}4°$ after 92 hours. It was slightly more soluble in ether than the crystalline variety, which it resembled in its general behaviour (Found: C, 41·45; H, 4·7; OMe, 29·6, 29·8%).

A specimen of arabinose (7·6 g.) and finely divided sodium (5 mols.) in anhydrous ether were digested with methyl chloroformate (44 g.) for a period of 10 hours. On removal of the solvent a small quantity of liquid distilled, but a portion remained as a crystalline residue, which was purified from ether and melted at 186° with previous softening at 174°. It was insoluble in water, readily soluble in acetone, and showed $[\alpha]_D - 16{\cdot}4°$. From the analytical data it appeared to be an isomeric form of the above tetracarbomethoxy arabinose (Found: OMe, 33·4. Calc.: OMe, 32·5%). Its behaviour with barium hydroxide corresponded with that of the compounds already described, but as the amount of this substance did not admit of its complete characterisation its examination is being continued.

*Tetracarbethoxy* l-*Arabinose* (III).—A similar procedure to that described above (using the pyridine method) was adopted for the preparation of this derivative. The product was a viscid syrup which distilled at 230°/0·4 mm., giving an almost theoretical yield. It was more soluble in the usual solvents than the corresponding carbomethoxy-derivative, and was insoluble in water; $[\alpha]_D + 98{\cdot}8° \longrightarrow 96{\cdot}9°$ after 168 hours; $n_D$ 1·4475. From a solution in acetone barium carbonate was precipitated on the addition of cold barium hydroxide solution [Found: C, 46·2; H, 5·9; OEt, 41·6; *M*, cryoscopic, 463·7. $C_9H_6O_9(OEt)_4$ requires C, 46·6; H, 5·9; OEt, 41·1%; *M*, 438].

*Tetracarbomethoxy* l-*Xylose* (II).—The procedure already described in the case of the carbomethoxy-derivatives of arabinose being imitated, the analogous compounds of xylose were isolated as follows: The ethereal extract of the viscid product of the reaction between xylose and methyl chloroformate yielded a yellow, viscid syrup, which distilled readily, b. p. 215°/0·5 mm.; and showed $[\alpha]_D$ (in acetone solution) + 59·5°. It dissolved in the usual organic solvents, especially acetone, but was insoluble in light petroleum or water. It gave the usual test for a carbonate with barium hydroxide [Found: C, 41·1; H, 4·9; OMe, 30·1. $C_9H_6O_9(OMe)_4$ requires C, 40·85; H, 4·7; OMe, 32·5%].

*Tetracarbethoxy* l-*Xylose* (III).—This compound was prepared by using a method similar to that described above for the corresponding carbethoxy-derivative of arabinose. It was isolated as a viscid syrup, b. p. 221—222°/0·4 mm., $n_D$ 1·4450, and showed in acetone, $[\alpha]_D + 62{\cdot}1° \longrightarrow 52{\cdot}4°$ (after 18 hours). Its behaviour towards solvents was similar to that of the corresponding derivative of arabinose, and it exhibited the characteristic behaviour with barium hydroxide [Found: C, 46·4; H, 6·1; OEt, 39·7. $C_9H_6O_9(OEt)_4$ requires C, 46·6; H, 5·9; OEt, 41·1%].

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