212. *Reactions of β-Methylarabinoside. Part II. 3 : 4-Acetone β-Methylarabinopyranoside. 3 : 4-Dimethyl Arabinose. The Conversion of Arabinose into Xylose.*

By JOHN HONEYMAN.

In the presence of a dehydrating agent, acetone condenses with β-methyl-*l*-arabinoside to yield liquid 3 : 4-*acetone β-methylarabinopyranoside*. This has been used as the starting material to prepare 3 : 4-*dimethyl arabinose* and also 3 : 4-*ditosyl* 2-*acetyl β-methylarabinoside* and 2-*tosyl* 3 : 4-*diacetyl β-methylarabinoside*. Alkaline hydrolysis leads, respectively, to 2 : 3-*anhydro β-methyl*-l-*lyxoside* and 2 : 3-*anhydro β-methyl*-l-*riboside* both of which yield, on further alkaline hydrolysis, β-methyl-*l*-arabinoside plus *β-methyl*-l-*xyloside*.

β-METHYLARABINOSIDE reacts with acetone in the presence of a dehydrating agent to form monoacetone β-methylarabinoside, the reaction being rapid and the yield good when phosphoric oxide is used. The product, after distillation, is a colourless liquid, the stability of which is similar to that of 3 : 4-ethylidene β-methylarabinoside (Part I). Benzoylation in the usual manner leads to a complex reaction which involves loss of the glycosidic methyl group, but under mild conditions an almost theoretical yield of a crystalline benzoate is obtained. Hydrolysis with 0·36% hydrochloric acid removes only the acetone residue to yield 2-benzoyl β-methylarabinoside (see Part I). The stability of the glycosidic group shows that the acetone compound is pyranosidic, and the formation of 2-benzoyl β-methylarabinoside proves that C_2 is unsubstituted. The high yield obtained on benzoylation shows that the liquid is a pure compound and not an azeotropic mixture of isomers. Hence the acetone derivative is 3 : 4-*acetone β-methylarabinopyranoside* and the benzoate is 2-*benzoyl* 3 : 4-*acetone β-methylarabinoside*. Thus when benzaldehyde, acetaldehyde, or acetone reacts with β-methylarabinoside the hydroxyls on C_3 and C_4 are involved. Further proof of the constitution of 3 : 4-acetone β-methylarabinoside is obtained by methylation and subjecting the monomethyl derivative (*i.e.*, 2-*methyl* 3 : 4-*acetone β-methylarabinoside*) to partial hydrolysis. The product so obtained is 2-methyl β-methylarabinoside crystallising as the monohydrate (identical with that described in Part I).

Methylation of 2-benzoyl β-methylarabinoside leads to 2-*benzoyl* 3 : 4-*dimethyl β-methylarabinoside* as a syrup which gives, on alkaline hydrolysis, 3 : 4-*dimethyl β-methylarabinoside* as a colourless liquid. From this 3 : 4-*dimethyl arabinose* is obtained, also as a liquid, by acid hydrolysis. The composition of 3 : 4-dimethyl β-methylarabinoside can be verified by treatment with tosyl chloride, which gives an excellent yield of crystalline 2-*tosyl* 3 : 4-*dimethyl β-methylarabinoside*. This compound, prepared also by an alternative route (see below), proves that no migration took place during the methylation of 2-benzoyl β-methylarabinoside.

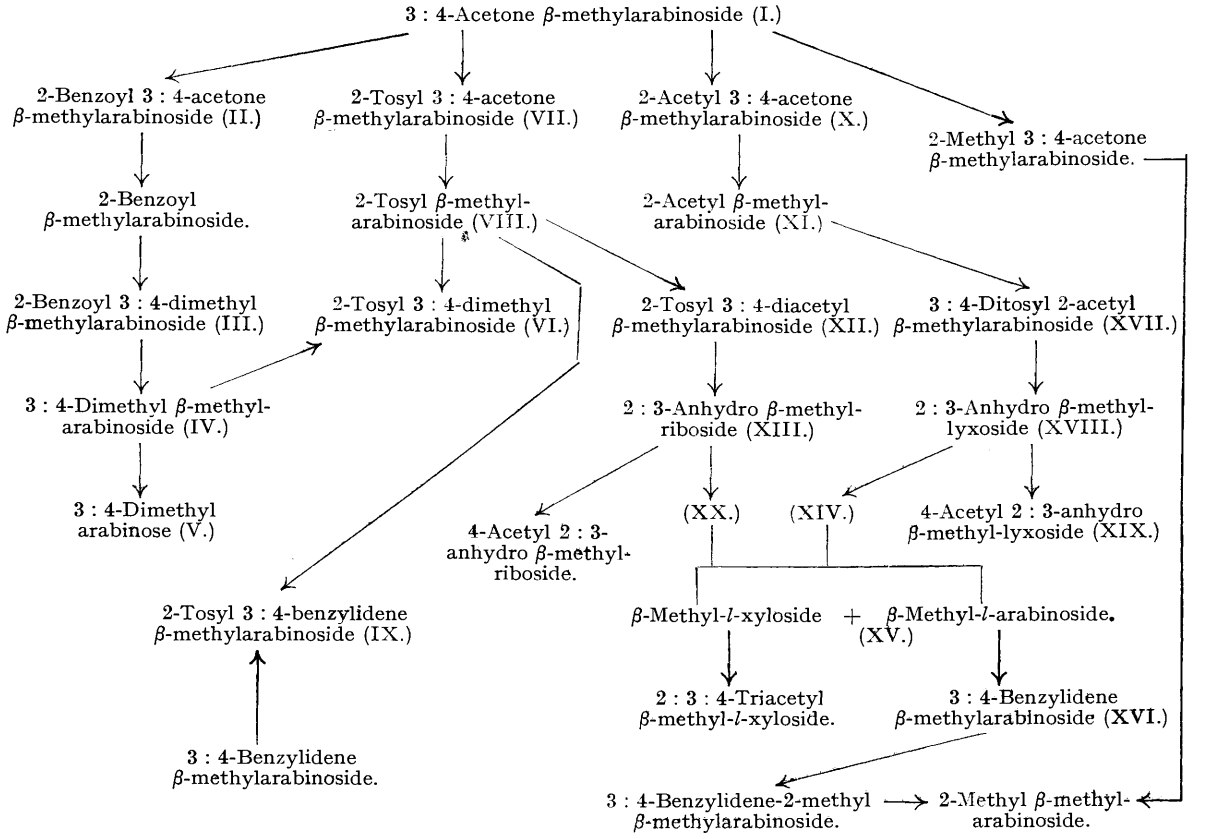
Reaction of 3 : 4-acetone β-methylarabinoside with tosyl chloride in pyridine leads to 2-*tosyl* 3 : 4-*acetone β-methylarabinoside* from which the acetone residue can be removed with acid to provide crystalline 2-*tosyl β-methylarabinoside*. It is to be noted that the stability of the acetone residue is greatly increased when C_2 carries a substituent other than the hydroxyl group. When 2-tosyl β-methylarabinoside is methylated the crystalline product obtained is 2-tosyl 3 : 4-dimethyl β-methylarabinoside identical with the compound already prepared. Condensation with benzaldehyde also yields a crystalline derivative which is 2-*tosyl* 3 : 4-*benzylidene β-methylarabinoside*. When freshly prepared 3 : 4-benzylidene β-methylarabinoside is treated with tosyl chloride a poor yield (25%) of the identical 2-tosyl 3 : 4-benzylidene β-methylarabinoside is obtained together with a larger amount of a syrup with the composition of an impure tritosyl β-methylarabinoside. It appears, therefore, that the slowness of the tosylation reaction results in only the more stable benzylidene β-methylarabinoside being substituted, the less stable form decomposing and yielding tritosyl β-methylarabinoside. Also, when 2-tosyl β-methylarabinoside condenses with benzaldehyde only the more stable 2-tosyl 3 : 4-benzylidene β-methylarabinoside is produced. The benzylidene group of this compound is unusually stable, resisting hydrolysis with 0·45% hydrochloric acid. In fact, no method was found to eliminate the benzaldehyde residue without simultaneously removing the glycosidic methyl group.

The crystalline 3 : 4-ethylidene β-methylarabinoside (see Part I) gives a high yield of 2-*tosyl* 3 : 4-*ethylidene β-methylarabinoside* from which the ethylidene group is readily removed leading to 2-tosyl β-methylarabinoside. However, the simplest method of preparing 2-tosyl β-methylarabinoside is through the acetone compound.

On acetylation of 2-tosyl β-methylarabinoside, crystalline 2-*tosyl* 3 : 4-*diacetyl β-methylarabinoside* is obtained in excellent yield. Mild alkaline hydrolysis produces a syrup with the analysis of an anhydro methylpentoside which forms a crystalline monoacetate in good yield. By analogy with similar reactions on hexoses (for a review see Peat, *Ann. Reports*, 1939, **36**, 259), it is thought that the tosyl group is removed with Walden inversion on C_2 accompanied by formation of an anhydro group between C_2 and C_3. The yield of crystalline monoacetate is noteworthy since it points to the syrup being one substance only, which is considered to be 2 : 3-*anhydro β-methyl*-l-*riboside* and hence the acetyl derivative is 4-*acetyl* 2 : 3-*anhydro β-methylriboside*. Further alkaline hydrolysis opens the anhydro ring to give a syrup with the composition of a methylpentoside. Treatment of this with benzaldehyde followed by addition of the syrupy product to benzene gives a precipitate of crystals with physical constants corresponding to *β-methyl*-l-*xyloside* [Fischer (*Ber.*, 1895, **28**, 1157) and Dale (*J. Amer. Chem. Soc.*, 1915, **37**, 2747) have prepared the corresponding *d*-xyloside] which on acetylation gives 2 : 3 : 4-*triacetyl β-methyl*-l-*xyloside*. [Hudson and Dale (*J. Amer. Chem. Soc.*, 1918, **40**, 1000) have prepared the *d*-compound.] The benzene solution yields a syrupy benzylidene methylpentoside which by methylation and hydrolysis gives 2-methyl β-methylarabinoside. Hence the syrupy methylpentoside obtained on ring scission must be a mixture of β-methyl-*l*-xyloside and β-methyl-*l*-arabinoside. It is known that β-methyl-

xyloside does not react with benzaldehyde under the conditions used (Robertson and Speedie, *J.*, 1934, 824). The yields point to there being about 75% of the former and 25% of the latter. These products are obtained from the 2 : 3-anhydro compound by opening the ethylene oxide ring at the two possible points accompanied in each case by Walden inversion. No trace could be found of a riboside which would be formed if the ring were opened without inversion. Since only the two products named are obtained, the 2 : 3-anhydro ring is the only one formed. This is striking proof of the great ease with which an ethylene oxide ring can be produced, since a 2 : 4-anhydro ring is also possible.

2-*Acetyl* 3 : 4-*acetone* β-*methylarabinoside*, prepared by acetylating 3 : 4-acetone β-methylarabinoside, leads on acid hydrolysis to 2-*acetyl* β-*methylarabinoside*, which can be tosylated to 3 : 4-*ditosyl* 2-*acetyl* β-*methylarabinoside*. Alkaline hydrolysis of this gives a syrupy anhydro methylpentoside which yields a crystalline monoacetate distinct from 4-acetyl 2 : 3-anhydro β-methylriboside. The syrupy anhydro compound is considered to be 2 : 3-*anhydro* β-*methyl*-l-*lyxoside*, and its crystalline acetate 4-*acetyl* 2 : 3-*anhydro* β-*methyl*-l-*lyxoside*. In this case further hydrolysis with alkali leads to a mixture of methylpentosides proved, in the same way as before, to consist of about 65% of β-methyl-*l*-xyloside and 35% of β-methyl-*l*-arabinoside. This is further proof that only the 2 : 3-anhydro ring is formed, that no 2 : 4-anhydro compound is present, and that no 3 : 4-anhydro ring is formed, *i.e.*, that elimination of *cis*-tosyl groups on adjacent carbons is not accompanied by anhydro ring formation.



Experimental.

Except where otherwise stated, solvents were removed under reduced pressure at $\not>45°$ and benzene and chloroform solutions were dried over anhydrous sodium sulphate. The light petroleum used had b. p. 60—80°.

l-*Arabinose*.—This was prepared by the acid hydrolysis of mesquite gum (*Org. Synth.*, Coll. Vol. I, p. 60).

Acetone β-Methylarabinoside.—β-Methylarabinoside (for preparation see Part I) condensed with acetone in the presence of zinc chloride, hydrogen chloride, sulphuric acid, anhydrous copper sulphate, or phosphoric oxide. The best yield was obtained using phosphoric oxide, and this was used in the standard method of preparation.

Excess of phosphoric oxide (10 g.) was added with vigorous agitation to a suspension of β-methylarabinoside (5 g.) in acetone (300 ml.). After being shaken for 5 minutes at room temperature the acetone solution was decanted and the inorganic residue washed with acetone (3 × 20 ml.). The combined extracts were neutralised with solid potassium carbonate. Filtration followed by distillation of the solvent left a pale yellow, slightly reducing syrup (5 g.) contaminated by a trace of acetone auto-condensation products. Distillation gave colourless, non-reducing, liquid acetone β-methylarabinoside (I) (11 g., 63%), b. p. 82°/0·1 mm., $[\alpha]_D^{20°}$ + 199·1° (c = 3·3 in chloroform) (Found: C, 52·2; H, 7·8; OMe, 15·1. $C_9H_{16}O_5$ requires C, 52·5; H, 7·8; OMe, 15·2%), soluble in water and most organic solvents except aliphatic hydrocarbons. Its stability was similar to that of 3 : 4-ethylidene β-methylarabinoside.

Benzoyl Acetone β-Methylarabinoside.—(i) (I) (0·5 g.) was dissolved in pyridine (10 ml.), and benzoyl chloride (0·5 g., 50% excess) added. After 12 hours at room temperature, the reaction mixture was poured into a large volume of water and the product extracted with chloroform, and the solution washed with 2% sulphuric acid, 2% potassium bicarbonate solution, and dried. Removal of the solvent left a mobile syrup (0·6 g.) which had a strong smell of methyl benzoate. The syrup reduced Fehling's solution confirming that loss of methoxyl group had taken place.

(ii) The above experiment was repeated under milder conditions. (I) (0·5 g.) was dissolved in pyridine (5 ml.) and to this was added a solution of benzoyl chloride (0·5 g.) in pyridine (5 ml.). The temperature was maintained at −5° for 12 hours, and the product isolated as before. A reducing syrup was again obtained (Found: OMe, 4·7. $C_{16}H_{20}O_6$ requires OMe, 10·0%).

(iii) (I) (0·5 g.) was dissolved in pyridine (5 ml.) and cooled to −5°. A solution of the theoretical quantity of benzoyl chloride (0·35 g.) in pyridine (5 ml.) was slowly dropped into this with efficient agitation. This operation took 35 minutes. After a further 5 minutes at −5° the solution was poured on crushed ice. The product, purified as before, was obtained in theoretical yield as non-reducing crystals. Recrystallisation was difficult as the substance was extremely soluble in all the common solvents except water. The solvent ultimately used was ethanol–water (10 : 90) at $>60°$. Five recrystallisations gave pure benzoyl acetone β-methylarabinoside (II), m. p. 78—79°, $[\alpha]_D^{18°}$ + 206·7° (*c* = 1·3 in chloroform) (Found: C, 61·8; H, 6·4; OMe, 10·0. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5; OMe, 10·0%).

Benzoyl β-Methylarabinoside.—(II) (0·45 g.) was dissolved in methanol (24·5 ml.) and hydrochloric acid (0·5 ml., 5N) added. Polarimetric observation showed that no reaction took place at room temperature. The solution was therefore refluxed until the rotation was constant (10 hours). After neutralising with silver carbonate, the solution was filtered and the solvent removed. The residue was dissolved in chloroform and dried. Evaporation yielded a non-reducing syrup (0·4 g.) which crystallised on stirring. Recrystallisation from ethanol–light petroleum gave pure 2-benzoyl β-methylarabinoside, m. p. 147° (Found: OMe, 11·5. Calc. for $C_{13}H_{16}O_6$: OMe, 11·6%), identical (m. p. and mixed m. p.) with that prepared in Part I.

These experiments show that (I) is 3 : 4-*acetone β-methylarabinopyranoside*, and (II) is 2-*benzoyl* 3 : 4-*acetone β-methylarabinoside*.

2-*Benzoyl* 3 : 4-*Dimethyl β-Methylarabinoside.*—Complete methylation of 2-benzoyl β-methylarabinoside (2·4 g.) required five treatments with methyl iodide–silver oxide to give syrupy 2-*benzoyl* 3 : 4-*dimethyl β-methylarabinoside* (III) (2·2 g., 83%), $[\alpha]_D^{18°}$ + 143·5° (*c* = 2·6 in chloroform) (Found: OMe, 30·9. $C_{15}H_{20}O_6$ requires OMe, 31·4%).

3 : 4-*Dimethyl β-Methylarabinoside.*—(III) (1·9 g.) was refluxed for one hour in a solution of aqueous sodium hydroxide (10 ml., 2N) and alcohol (10 ml.). Extraction with chloroform, followed by evaporation, gave 3 : 4-*dimethyl β-methylarabinoside* (IV) (1·1 g., 89%) as a pale yellow syrup, which distilled uniformly (b. p. 83—84°/0·1 mm.) to yield a colourless liquid (1·0 g.); $[\alpha]_D^{18°}$ + 210·6° (*c* = 3·8 in chloroform) (Found: C, 49·6; H, 8·3; OMe, 48·6. $C_8H_{16}O_5$ requires C, 50·0; H, 8·3; OMe, 48·4%).

3 : 4-*Dimethyl Arabinose.*—(IV) (2·5 g.) was refluxed with sulphuric acid (50 ml., N) for 4 hours and the solution then neutralised with barium carbonate, filtered through silica, and evaporated. Purification by chloroform extraction gave 3 : 4-*dimethyl arabinose* (V) (2·1 g., 91%) as a syrup, which distilled uniformly (b. p. 123—124°/0·1 mm.) to a colourless liquid; $[\alpha]_D^{18°}$ + 116° (*c* = 4·2 in water) (Found: OMe, 34·7. $C_7H_{14}O_5$ requires OMe, 34·8%).

2-*Tosyl* 3 : 4-*Dimethyl β-Methylarabinoside.*—(IV) (1·3 g.) was dissolved in pyridine (10 ml.) and tosyl chloride (1·7 g., 25% excess) added. After 4 days at room temperature the product was isolated in the usual way as a hard crystalline mass. A single recrystallisation from aqueous alcohol gave pure needles of 2-*tosyl* 3 : 4-*dimethyl β-methylarabinoside* (VI) (2·2 g., 94%), m. p. 111—112° (Found: C, 51·5; H, 6·4; S, 9·1; OMe, 26·5. $C_{15}H_{22}O_7S$ requires C, 52·0; H, 6·4; S, 9·2; OMe, 26·8%). The constitution assigned to (VI) was verified by its preparation by an alternative method (see below).

2-*Methyl* 3 : 4-*Acetone β-Methylarabinoside.*—Methylation of (I) by the method of Purdie and Irvine gave, after recrystallisation from alcohol–light petroleum, 2-methyl 3 : 4-acetone β-methylarabinoside, m. p. 62°, $[\alpha]_D^{20°}$ + 162·5° (*c* = 4·6 in chloroform). Acid hydrolysis [as descibed for (II)] followed by recrystallisation from ether gave 2-methyl β-methylarabinoside monohydrate, identical (m. p. and mixed m. p.) with that described in Part I.

2-*Tosyl* 3 : 4-*Acetone β-Methylarabinoside.*—(I) (0·58 g.) was dissolved in excess of pyridine (10 ml.), and tosyl chloride (0·86 g., 50% excess) added with cooling. After 4 days at room temperature the product (0·97 g., 93%) was isolated as usual. A single recrystallisation from ethanol–light petroleum (1 : 1) gave pure needles (0·83 g., 80%) of 2-*tosyl* 3 : 4-*acetone β-methylarabinoside* (VII), m. p. 136°, $[\alpha]_D^{18°}$ + 181·3° (*c* = 1·68 in chloroform) (Found: C, 53·5; H, 6·1; S, 8·7; OMe, 8·9. $C_{16}H_{22}O_7S$ requires C, 53·6; H, 6·1; S, 8·9; OMe, 8·7%). The substance is soluble in alcohol, acetone, benzene, chloroform, and pyridine, but insoluble in light petroleum and water.

The syrups obtained from the reactions of acetone with β-methylarabinoside in the presence of the various condensing agents mentioned were subjected individually to reaction with tosyl chloride. In each case a crystalline product was obtained which, after recrystallisation, was shown (m. p. and mixed m. p.) to be (VII).

Thus, irrespective of the agent used, acetone condenses with β-methylarabinoside to give (I).

2-*Tosyl β-Methylarabinoside.*—(VII) (0·5 g.) was hydrolysed as for (II) except that 8 hours' refluxing was necessary. A colourless glass (0·4 g., 88%) was obtained which crystallised after being stored for several years. Recrystallisation from aqueous alcohol gave needles of 2-*tosyl β-methylarabinoside* (VIII), m. p. 48—49°, $[\alpha]_D^{18°}$ + 110·9° (*c* = 1·14 in chloroform) (Found: S, 9·9; OMe, 9·7. $C_{13}H_{18}O_7S$ requires S, 10·6; OMe, 9·8%). The substance is soluble in chloroform, benzene, acetone, alcohol, and pyridine but insoluble in water and light petroleum.

Methylation of (VIII) (Purdie and Irvine) gave (VI).

Condensation of (VIII) with benzaldehyde, under the conditions described for the preparation of 3 : 4-benzylidene β-methylarabinoside in Part I, gave (IX) (identified by m. p. and mixed m. p.).

2-*Tosyl* 3 : 4-*Benzylidene β-Methylarabinoside.*—Since 3 : 4-benzylidene β-methylarabinoside (Part I) decomposed readily it was subjected as soon as isolated to treatment with tosyl chloride.

3 : 4-Benzylidene β-methylarabinoside (5 g.) was dissolved in pyridine and tosyl chloride (6·5 g.) added. After 4 days at room temperature the product was obtained in the usual manner as a light brown syrup. After being rubbed with a rod this yielded a hard, crystalline mass contaminated with syrup. The crystals were less soluble in hot alcohol than the syrup, which was removed by repeated treatment with this solvent. The crystals were tiled and recrystallised from absolute ethanol–light petroleum to give needles (2 g., 25%) of 2-*tosyl* 3 : 4-*benzylidene β-methylarabinoside* (IX), m. p. 144—145°, $[\alpha]_D^{18°}$ + 188·0° (*c* = 1·26 in benzene) (Found: C, 59·0; H, 5·4; S, 7·8; OMe, 7·5. $C_{20}H_{22}O_7S$ requires C, 59·1; H, 5·4; S, 7·9; OMe, 7·6%).

The syrup (4 g.) obtained was subjected to a further treatment with tosyl chloride but no further condensation took place. Analysis of the syrup showed it to be impure tritosyl β-methylarabinoside (Found: C, 51·2; H, 4·7; OMe, 4·3. Calc. for $C_{27}H_{30}O_{11}S$: C, 51·7; H, 4·8; OMe, 4·9%).

Acid Hydrolysis of 2-*Tosyl* 3 : 4-*Benzylidene β-Methylarabinoside.*—Prolonged boiling with methanolic hydrochloric acid in concentrations up to 0·45% led to no hydrolysis. More concentrated acid removed the glycosidic methyl as well as the benzylidene group.

2-*Tosyl* 3 : 4-*Ethylidene β-Methylarabinoside*.—Crystalline ethylidene β-methylarabinoside (Part I) (0·35 g.) was dissolved in pyridine (10 ml.) containing tosyl chloride (0·5 g., 50% excess). After 30 minutes at room temperature the product was isolated in the usual way to give crude crystals (0·65 g.) which when recrystallised from ethanol–light petroleum (50 : 50) yielded colourless plates of 2-*tosyl* 3 : 4-*ethylidene β-methylarabinoside* (0·55 g., 86%), m. p. 134—135°, $[\alpha]_D^{19°}$ + 188·4° (*c* = 1·8 in chloroform) (Found: C, 52·0; H, 5·9; S, 9·1; OMe, 8·9. $C_{15}H_{20}O_7S$ requires C, 52·3; H, 5·8; S, 9·3; OMe, 9·0%).

Hydrolysis as described for (II), except that 1 hour's refluxing was sufficient, gave (VIII) (m. p. and mixed m. p.).

2-*Tosyl* 3 : 4-*Diacetyl β-Methylarabinoside*.—(VIII) (0·35 g.) was dissolved in pyridine (5 ml.) containing acetic anhydride (0·35 g., 50% excess) and left at room temperature for 12 hours. The product (0·44 g., 98%) gave on recrystallisation from ethanol–light petroleum (15 : 85) pure 2-*tosyl* 3 : 4-*diacetyl β-methylarabinoside* (XII) (0·35 g.) as colourless prisms, m. p. 116°, $[\alpha]_D^{19°}$ +122·5° (*c* = 2·0 in chloroform) (Found: S, 8·0; OMe, 7·6. $C_{17}H_{22}O_9S$ requires S, 8·0; OMe, 7·7%). The crystals are soluble in all common solvents except water and light petroleum.

Alkaline Hydrolysis of 2-*Tosyl* 3 : 4-*Diacetyl β-Methylarabinoside*.—(XII) (5 g.) was added to methanol (100 ml.) containing sodium (2 g.) and the solution kept at room temperature for 48 hours. After careful neutralisation with acetic acid and dilution with water, the product was extracted with chloroform and isolated as a pale yellow syrup (1·6 g., 90%) with the composition of an anhydro methylpentoside, $[\alpha]_D^{18°}$ + 36·8° (*c* = 2·0 in chloroform) (Found: C, 49·0; H, 6·8; OMe, 21·1. $C_6H_{10}O_4$ requires C, 49·3; H, 6·8; OMe, 21·2%). By analogy with similar reactions on hexosides this is considered to be 2 : 3-*anhydro β-methylriboside* (XIII).

Acetylation of (XIII) (0·5 g.) with acetic anhydride in pyridine led to a crystalline product which on recrystallisation from aqueous alcohol gave needles (0·5 g., 78%) of 4-*acetyl* 2 : 3-*anhydro β-methylriboside*, m. p. 82—83°, $[\alpha]_D^{18}$ + 73·6° (*c* = 3·5 in chloroform) (Found: OMe, 16·3. $C_8H_{12}O_5$ requires OMe, 16·5%). No other substance was isolated.

Alkaline Hydrolysis of 2 : 3-*Anhydro β-Methylriboside*.—(XIII) (4·1 g.) was heated on a boiling water-bath for 48 hours with aqueous sodium hydroxide (250 ml., 5%). After neutralisation with acetic acid the solution was taken to dryness and the organic matter dissolved in absolute alcohol. Removal of the solvent gave a pale yellow syrup (4 g., 90%) having the composition of a methylpentoside (XIV), $[\alpha]_D^{18°}$ + 106·8° (*c* = 2·3 in water) (Found: C, 44·2; H, 7·4; OMe, 18·7. $C_6H_{12}O_5$ requires C, 43·9; H, 7·3; OMe, 18·9%).

Examination of (XIV).—The syrup (3·2 g.) was treated with benzaldehyde under the conditions described for the preparation of 3 : 4-benzylidene β-methylarabinoside (Part I). On pouring the product into benzene, crystals (XV) (2·3 g.) of a methylpentoside (Found: OMe, 18·8. $C_6H_{12}O_5$ requires OMe, 18·9%) were precipitated; these were filtered off. Evaporation of benzene left a syrup (XVI) (1·2 g.) with the composition of a benzylidene methylpentoside (Found: OMe, 12·4. $C_{13}H_{16}O_5$ requires OMe, 12·3%).

Examination of (XV).—The crystals after recrystallisation from alcohol had m. p. 155—156°, $[\alpha]_D^{18°}$ + 62·5° (*c* = 2·4 in water) and mixed m. p. with β-methylarabinoside (m. p. 169—170°) 130—135°. From the fact that the substance did not condense with benzaldehyde, and from the physical constants, the crystals were thought to be *β-methyl-l-xylo-pyranoside*. For β-methyl-*d*-xylopyranoside Fischer (*loc. cit.*) gives m. p. 156—157°, $[\alpha]_D$ − 65·8° (*c* = 9 in water), and Dale (*loc. cit.*) gives m. p. 155—156°, $[\alpha]_D^{20°}$ − 65·3°.

Acetylation of (XV) with acetic anhydride–sodium acetate gave 2 : 3 : 4-*triacetyl β-methyl-l-xyloside* which after recrystallisation from water had m. p. 115—116°, $[\alpha]_D^{18°}$ + 59·9° (*c* = 2·3 in chloroform) (Found: OMe, 10·6. $C_{12}H_{18}O_8$ requires OMe, 10·7%). Hudson and Dale (*loc. cit.*) give, for triacetyl β-methyl-*d*-xyloside, m. p. 115°, $[\alpha]_D^{20°}$ − 60·8° (*c* = 2·7 in chloroform). This verifies that (XV) is β-methyl-*l*-xyloside.

Examination of (XVI).—Methylation followed by acid hydrolysis (as described for the preparation of 2-methyl β-methylarabinoside in Part I) gave 2-methyl β-methylarabinoside monohydrate identified by m. p. and mixed m. p. (46—47°) with an authentic specimen.

Thus (XVI) is 3 : 4-*benzylidene β-methylarabinoside* and (XIV) is a mixture of approximately 75% of β-methyl-*l*-xyloside and 25% of β-methyl-*l*-arabinoside.

2-*Acetyl* 3 : 4-*Acetone β-Methylarabinoside*.—Acetic anhydride (0·38 g., 50% excess) was added to (I) (0·5 g.) in pyridine (5 ml.). After 2 hours the reaction mixture was flooded with saturated potassium chloride solution and the product extracted with chloroform. This solution was purified by shaking with 2% hydrochloric acid saturated with potassium chloride followed by saturated potassium carbonate solution, and dried. The chloroform was evaporated leaving almost the theoretical amount of crystalline product. Since the crystals were soluble in all the common solvents, including water, purification was difficult. However, recrystallisation from a small amount of boiling water, followed by a further recrystallisation from light petroleum, gave pure 2-*acetyl* 3 : 4-*acetone β-methylarabinoside* (X), m. p. 76—77°, $[\alpha]_D^{16°}$ + 123·6° (*c* = 1·2 in water) (Found: OMe, 12·4. $C_{11}H_{18}O_6$ requires OMe, 12·6%).

2-*Acetyl β-Methylarabinoside*.—Hydrolysis of (X) as for (VII) gave, on recrystallisation from ethanol–light petroleum, colourless prisms of 2-*acetyl β-methylarabinoside* (XI), m. p. 172°, $[\alpha]_D^{16°}$ + 252·2° (*c* = 1 in water) (Found: OMe, 15·1. $C_8H_{14}O_6$ requires OMe, 15·0%).

3 : 4-*Ditosyl* 2-*Acetyl β-Methylarabinoside*.—Treatment of (X) (0·4 g.) in pyridine with tosyl chloride (1 g., 25% excess) at room temperature for 4 days followed by the usual purification gave, after recrystallisation from ethanol–light petroleum, prisms (0·8 g., 80%) of 3 : 4-*ditosyl* 2-*acetyl β-methylarabinoside* (XVII), m. p. 62—63°, $[\alpha]_D^{18°}$ + 173·2° (*c* = 3·3 in chloroform) (Found: S, 12·4; OMe, 6·0. $C_{22}H_{26}O_{10}S_2$ requires S, 12·5; OMe, 6·0%).

Alkaline Hydrolysis of 3 : 4-*Ditosyl* 2-*Acetyl β-Methylarabinoside*.—This was carried out as for (XII). A similar yield was obtained of a syrupy *anhydro methylpentoside* (XVIII); $[\alpha]_D^{18°}$ + 127·6° (*c* = 1·3 in chloroform) (Found: C, 49·5; H, 6·8; OMe, 21·3. $C_6H_{10}O_4$ requires C, 49·3; H, 6·9; OMe, 21·2%).

Acetylation of (XVIII) showed it to be distinct from (XIII) since the crystalline product, considered to be 4-*acetyl* 2 : 3-*anhydro β-methyl-lyxoside* (XIX), had m. p. 112—114°, $[\alpha]_D^{18°}$ + 106·9° (*c* = 2·8 in chloroform) (Found: OMe, 16·6. $C_8H_{12}O_5$ requires OMe, 16·5%).

Alkaline Hydrolysis of 4-*Acetyl* 2 : 3-*Anhydro β-Methyl-lyxoside*.—When treated as described for (XIII), a pale yellow syrup (XX) (88% yield) was obtained; $[\alpha]_D^{18°}$ + 108·5° (*c* = 2·5 in water). Its composition was that of a methyl pentoside (Found: OMe, 18·8. Calc. for $C_6H_{12}O_5$: OMe, 18·9%).

Examination of (XX).—(XX) (4·2 g.) was treated with benzaldehyde as for (XIV) to give crystals (2·8 g.) shown to be β-methyl-*l*-xyloside [identical with (XV)] and a syrup shown by the same method as before to be 3 : 4-benzylidene β-methylarabinoside (1·7 g.).

Thus (XX) consists of approximately 65% β-methyl-*l*-xyloside and 35% β-methyl-*l*-arabinoside.

The author is indebted to the Carnegie Trust for the Universities of Scotland for a Research Scholarship, and to Principal Sir James C. Irvine for his constant interest and guidance.

UNITED COLLEGE, THE UNIVERSITY, ST. ANDREWS.
UNIVERSITY OF LONDON, KING'S COLLEGE.

[*Received, March 18th,* 1946.]