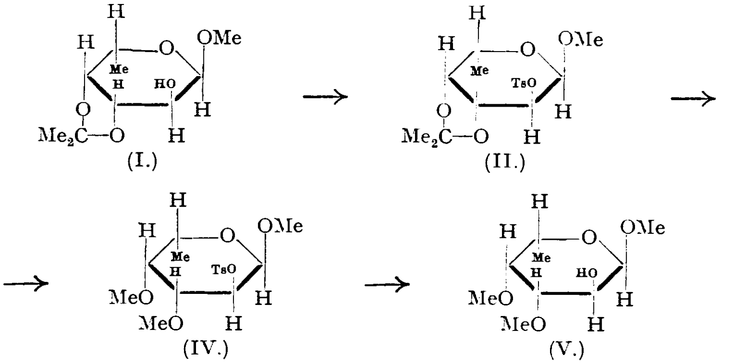
137. 3 : 4-*Dimethyl* L-*Fucose and* 2 : 3-*Dimethyl* L-*Rhamnose.*

By E. E. Percival and E. G. V. Percival.

From 2-*toluene*-p-*sulphonyl* 3 : 4-iso*propylidene* α-*methyl*-L-*fucoside* by mild hydrolysis, methylation, and reduction, 3 : 4-*dimethyl* α-*methyl*-L-*fucoside* and 3 : 4-*dimethyl* L-*fucose* have been prepared. 2 : 3-Dimethyl L-rhamnose has been prepared by a similar route.

The isolation of a dimethyl L-fucose from methylated fucoidin made it desirable to prepare synthetic dimethyl fucoses of known structure. The preparation and properties of the 3 : 4-dimethyl isomer are now recorded.

α-Methyl-L-fucoside was converted into the 3 : 4-*iso*propylidene derivative (I) (MacPhillamy and Elderfield, *J. Org. Chem.*, 1939, **4**, 150) from which 2-*toluene*-p-*sulphonyl* 3 : 4-iso*propylidene* α-*methyl*-L-*fucoside* (II) was prepared. Methanolysis removed the acetone residue (to give III), and methylation then gave 2-*toluene*-p-*sulphonyl* 3 : 4-*dimethyl* α-*methyl*-L-*fucoside* (IV). Reductive fission of the toluene-*p*-sulphonyl residue gave 3 : 4-*dimethyl* α-*methyl*-L-*fucoside* (V) from which by hydrolysis 3 : 4-*dimethyl* L-*fucose* was obtained as the monohydrate, m. p. 75°, $[\alpha]_D$ −118°.


(I.) (II.) (III.) (IV.) (V.)

(Ts = p-$C_6H_4Me{\cdot}SO_2$)

By a similar process 2 : 3-*iso*propylidene α-methyl-L-rhamnoside was converted into 4-*toluene*-p-*sulphonyl* 2 : 3-*dimethyl* α-*methyl*-L-*rhamnoside* from which, by reductive hydrolysis followed by the removal of the glycosidic methyl group, 2 : 3-dimethyl L-rhamnose was prepared as a syrup, $[\alpha]_D$ +40°. This compound prepared by another route (Schmidt, Plankenhorn, and Kübler, *Ber.*, 1942, **75**, 579) is reported to have $[\alpha]_D$ +47·6°. Crystalline 2 : 3-*dimethyl* L-*rhamnose anilide* has been prepared.

By the paper chromatogram the R_G values (Hirst, Hough, and Jones, *J.*, 1949, 928) of both dimethyl 6-deoxyhexoses have been determined and compared with those of 2-methyl fucose and 4-methyl rhamnose, prepared by the methylation and hydrolysis of the corresponding *iso*propylidene α-methylglycosides. Certain differences between the results obtained and those previously published (Hirst, Hough, and Jones, *loc. cit.*) (in parentheses) emphasise the point made in that publication that such figures are useful as an indication of the methylated sugar concerned, but that direct comparisons on the same chromatogram are essential before identity (in the chromatographic sense) can be established, because of the difficulty of the rigid standardisation of all the variables between different laboratories.

Sugar.	R_G.	Sugar.	R_G.
4-Methyl L-rhamnose	0·64; 0·65 (0·57)	2-Methyl L-fucose	0·56 (0·51)
2 : 3-Dimethyl L-rhamnose ...	0·82; 0·83	3 : 4-Dimethyl L-fucose	0·67; 0·68

Experimental.

3 : 4-iso*Propylidene* α-*Methyl*-L-*fucoside*.—α-Methyl-L-fucoside (1 g.) in acetone (50 c.c.) containing two drops of acetaldehyde was shaken with anhydrous copper sulphate (11 g.) for 120 hours. One drop of concentrated sulphuric acid was then added, and shaking continued for a further 14 hours. After filtration and neutralisation with potassium carbonate, the solvent was evaporated; the product (0·9 g.), distilled at 95°/0·01 mm., had n_D^{15} 1·4621, $[\alpha]_D^{15}$ −160° (*c*, 1·0 in water). On storage in the refrigerator the product solidified.

2-*Toluene*-p-*sulphonyl* 3 : 4-iso*Propylidene* α-*Methyl*-L-*fucoside*.—The above derivative (0·51 g.) in pyridine (5 c.c.) was treated with powdered toluene-*p*-sulphonyl chloride (1 g.) and kept for 2 days at 15°.

When the mixture was poured on ice a white crystalline solid was obtained which was combined with the product obtained on extraction of the filtrate with chloroform, which was washed with dilute sulphuric acid, aqueous sodium hydrogen carbonate, and water, dried, and evaporated. On recrystallisation from methanol a crystalline *product* (0·37 g.), m. p. 182°, $[\alpha]_D^{15}$ −146° (*c*, 1·0 in $CHCl_3$), was obtained (Found : C, 54·7; H, 6·5; OMe, 8·5. $C_{17}H_{24}O_7S$ requires C, 54.8; H, 6·45; OMe, 8·3%).

2-*Toluene*-p-*sulphonyl* 3 : 4-*Dimethyl* α-*Methyl*-L-*fucoside*.—Crystalline 2-toluene-*p*-sulphonyl 3 : 4-*iso*-propylidene α-methylfucoside (0·5 g.) was treated with methanolic hydrogen chloride (10 c.c.; 1%) at 70° for 1 hour. After neutralisation with silver carbonate and extraction of the silver residues with ethanol, 2-*toluene*-p-*sulphonyl* α-*methyl*-L-*fucoside* (0·36 g.), m. p. 158°, $[\alpha]_D^{15}$ −85° (*c*, 1·0 in chloroform), was obtained. This substance was then methylated 4 times with methyl iodide and silver oxide, to give a crystalline *product* (0·4 g.) which, recrystallised from chloroform–light petroleum (b. p. 60—80°), had m. p. 103°, $[\alpha]_D^{15}$ −84° (*c*, 0·7 in chloroform) (Found : C, 53·6; H, 6·8; OMe, 16·6; S, 8·2. $C_{16}H_{24}O_7S$ requires C, 53·3; H, 6·7; OMe, 17·2; S, 8·9%).

3 : 4-*Dimethyl* α-*Methyl*-L-*fucoside*.—The above compound (0·5 g.) in methanol (11 c.c.) and water (5 c.c.) was treated with sodium amalgam (10 g.; 4%) with stirring at 35° during 17 hours. After filtration and extraction with chloroform, the extracts were treated with carbon dioxide for 15 minutes, dried (Na_2SO_4), and freed from organic solvents under diminished pressure. The aqueous residue was neutralised with carbon dioxide, evaporated to dryness, and extracted with ether. From these operations a crystalline *fucoside* was obtained (0·2 g.) which was recrystallised from boiling light petroleum (b. p. 40—60°), to give crystals, m. p. 100°, $[\alpha]_D^{20}$ −213° (*c*, 1·3 in water) (Found : C, 52·1; H, 8·5; OMe, 44·6. $C_9H_{18}O_5$ requires C, 52·4; H, 8·6; OMe, 45·1%).

3 : 4-*Dimethyl* L-*Fucose*.—3 : 4-Dimethyl α-methyl-L-fucoside (0·13 g.) was hydrolysed at 100° with sulphuric acid (15 c.c.; 4%) for 3 hours, whereafter the rotation was constant. After neutralisation with barium carbonate, evaporation to dryness, and extraction with acetone, a crystalline *ether* (0·1 g.) was obtained, having m. p. 82° (from ethanol), m. p. 76° (from chloroform–light petroleum), $[\alpha]_D^{15}$ −118° (*c*, 1·1 in water) (Found : C, 45·9; H, 8·9; OMe, 27·9. $C_8H_{16}O_5,H_2O$ requires C, 45·6; H, 8·6; OMe, 29·5%).

4-*Toluene*-p-*sulphonyl* 2 : 3-iso*Propylidene* α-*Methyl*-L-*rhamnoside*.—Anhydrous rhamnose (12 g.) was boiled with methanolic hydrogen chloride (150 c.c.; 0·25%) until non-reducing (40 hours) and the syrupy α-methylrhamnoside ($[\alpha]_D$ −48°) isolated. Treatment with acetone as previously described gave a good yield of the *iso*propylidene derivative which distilled at 110°/0·05 mm., n_D^{11} 1·4563, $[\alpha]_D^{12}$ −14° (*c*, 1·1 in acetone). Treatment of this product (3 g.) with toluene-*p*-sulphonyl chloride (5·5 g.) and pyridine (14 c.c.) as described above gave, on pouring of the mixture into ice-water, a crystalline substance which was recrystallised (2·7 g.) from methanol and had m. p. 60°, $[\alpha]_D^{15}$ +22·5° (*c*, 2·9 in methanol) (cf. Levene and Compton, *J. Amer. Chem. Soc.*, 1935, **57**, 2306, who quote m. p. 61—62°, $[\alpha]_D$ +22° in methanol).

4-*Toluene*-p-*sulphonyl* 2 : 3-*Dimethyl* α-*Methylrhamnoside*.—Removal of the *iso*propylidene residue as described above gave a syrupy *rhamnoside*, $[\alpha]_D$ −73·5° (*c*, 1·4 in chloroform), n_D^{12} 1·5208 (Found : S, 8·9; OMe, 8·0. $C_{14}H_{20}O_7S$ requires S, 9·6; OMe, 9·3%). Methylation with methyl iodide and silver oxide in 3 operations gave a crystalline *ether* (1·9 g.) which, recrystallised from chloroform–light petroleum (b. p. 60—80°), had m. p. 111°, $[\alpha]_D$ −33° (*c*, 2·0 in chloroform) (Found : C, 52·8; H, 6·4; OMe, 25·0. $C_{16}H_{24}O_7S$ requires C, 53·3; H, 6·7; OMe, 25·8%).

2 : 3-*Dimethyl* α-*Methylrhamnoside and* 2 : 3-*Dimethyl Rhamnose*.—Treatment of the above derivative (1 g.) with sodium amalgam as described previously gave 2 : 3-*dimethyl* α-*methylrhamnoside* as a syrup (0·5 g.) which distilled at 110°/0·05 mm. and had n_D^{16} 1·4538, $[\alpha]_D$ −6° (*c*, 2·0 in water) (Found : OMe, 43·2. $C_9H_{18}O_5$ requires OMe, 45·1%). Hydrolysis with sulphuric acid (4%) was complete in 6 hours; 2 : 3-dimethyl rhamnose isolated as above had $[\alpha]_D$ +40° (*c*, 0·7 in water) (Found : OMe, 30·0. Calc. for $C_8H_{16}O_5$: OMe, 32·3%). Treatment of the syrup (0·4 g.) in ethanol (5 c.c.) with aniline (0·4 g.) at 80° for 2 hours followed by evaporation at room temperature gave an *anilide*, m. p. 138—139° (Found : C, 62·3; H, 7·9; N, 4·9; OMe, 21·4. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·9; N, 5·2; OMe, 23·2%).

Periodate Oxidation [with A. G. Ross].—Estimation of the acetaldehyde liberated on oxidation with periodate (Cameron, Ross, and Percival, *J. Soc. Chem. Ind.*, 1948, **67**, 161) gave only 5·6% of the theoretical amount.

Thanks are expressed to Imperial Chemical Industries Limited for grants.

KING'S BUILDINGS, UNIVERSITY OF EDINBURGH.

[*Received, December* 13*th*, 1949.]