700. 4-*Methyl* β-*Methylglucoside and Some Further Derivatives of* β-*Methylglucoside.*

By D. I. McGilvray.

A compound designated 4(?)-methyl β-methylglucoside has been described as a liquid (Helferich and Lang, *J. pr. Chem.*, 1932, **132**, 332) but, as the authors indicated, the method of its preparation is open to some doubt. It has now been isolated crystalline following an unequivocal synthesis, which is a development of that previously reported for the preparation of 4 : 6-dimethyl β-methylglucoside (Dennison and McGilvray, *J.*, 1951, 1616).

Experimental.—2 : 3-*Dibenzyl* 6-*trityl* β-*methylglucoside.* 2 : 3-Dibenzyl β-methylglucoside (Dennison and McGilvray, *loc. cit.*) (11·0 g.) and triphenylmethyl chloride (8·0 g.) in dry pyridine (200 ml.) were heated at 100—105° for 5½ hours. After the solution had cooled, toluene was added until no further precipitation occurred, and the filtrate was poured, with stirring, into aqueous sodium hydrogen carbonate (4 l.; 0·25%). The layers were separated and washed, the aqueous layer once with toluene, and the combined toluene solutions twice with more sodium hydrogen carbonate solution. After drying (Na_2SO_4) of the solution and evaporation of the solvent, the *trityl* derivative remained as a viscous syrup (19·0 g.), $[\alpha]_D^{20}$ −12·6° (in chloroform) (Found : C, 77·5; H, 6·45; OMe, 4·9. $C_{40}H_{40}O_6$ requires C, 77·9; H, 6·5; OMe, 5·0%).

2 : 3-*Dibenzyl* 4-*methyl* 6-*trityl* β-*methylglucoside.* The foregoing compound (7·2 g.) was twice methylated with Purdie's reagents. The syrupy *glucoside* (7·86 g.) had $[\alpha]_D^{20}$ +20·4° (in chloroform) (Found : C, 77·8; H, 6·6; OMe, 9·7. $C_{41}H_{42}O_6$ requires C, 78·1; H, 6·7; OMe, 9·8%).

2 : 3-*Dibenzyl* 4-*methyl* β-*methylglucoside.* The trityl derivative (15 g.) was treated with acetic acid (300 ml.; 80%) for 1 hour at 95—100°. On cooling a crystalline precipitate of triphenylmethanol separated and was removed by filtration, the filtrate dropping directly into ice-water (4 l.). The *glucoside* was recrystallised from light petroleum (b. p. 60—80°), forming fine white needles (5·35 g.), m. p. 87·5—88·5°, $[\alpha]_D^{20}$ +42·9° (in chloroform) (Found : C, 67·6; H, 7·2; OMe, 16·1. $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·2; OMe, 15·95%).

4-*Methyl* β-*methylglucoside.* The benzyl groups were removed from the benzyl derivative (1·7 g.) with sodium ethoxide [from sodium (3 g.)] in ethanol (50 ml.; 97%) (cf. Bell and Lorber, *J.*, 1940, 453). After being heated and then diluted with an equal volume of water, the solution was passed through a column of Amberlite resin IRC 50. Evaporation of the effluent gave a syrup (1·08 g.; OMe, 31%). The product crystallised from ethyl acetate as white needles, m. p. 98—100°. Recrystallisation from *cyclo*hexane–ethanol (4 : 1) gave needles (600 mg.), m. p. 102—103° (not raised by further recrystallisation), $[\alpha]_D^{20}$ −17·6° (in water) (Found: C, 45·8; H, 7·7; OMe, 29·7. Calc. for $C_8H_{16}O_6$: C, 46·1; H, 7·7; OMe, 29·8%).

British Rayon Research Association,
Urmston, Nr. Manchester.

[*Received, May* 19*th*, 1952.]

---

701. *The Bromination Product of Acridone.*

By S. Kruger.

The bromination of acridone in glacial acetic acid readily yields a dibromo-derivative, which was considered to be 2 : 3-dibromoacridone (Tananescu and Ramontianu, *Bull. Soc. chim.*, 1939, **6**, 486; Heilbron, "Dictionary of Organic Compounds," 1946, Eyre and Spottiswoode, London; Albert, "The Acridines," 1951, Edward Arnold and Co., London). Since Lehmstedt (*Ber.*, 1931, **64**, 2386) has clearly shown that the nitration of acridone leads principally to the 3 : 7-dinitro-compound, it was felt that bromination would be more likely to give an analogous compound rather than the product suggested by Tananescu and Ramontianu.

As these acridones melt above 360°, the 5-*p*-diethylaminophenyl-derivatives, which have lower melting points and are more amenable to purification, were prepared for purposes of comparison. Thus 3 : 7-dibromoacridone, prepared from authentic 3 : 7-diaminoacridone (Goldberg and Kelly, *J.*, 1946, 102) by means of a double Sandmeyer reaction, was converted into 3 : 7-dibromo-5-*p*-diethylaminophenylacridine, which gave no depression of melting point when mixed with the corresponding derivative of Tananescu and Ramontianu's dibromo-compound.

Authentic 3-bromoacridone similarly gave a dibromo-derivative, identical with synthetic 3 : 7-dibromoacridone.

Experimental.—Bromination of acridone. Acridone (5 g.) was dissolved in glacial acetic acid (500 ml.), and bromine (5·2 g.) in glacial acetic acid (50 ml.) added with shaking at room temperature. The bright yellow precipitate, which formed almost immediately, was filtered off, washed, dried, and recrystallised from nitrobenzene. The yield was almost quantitative. The yellow needles, m. p. >360°, gave a violet-blue fluorescence in alcohol, which became greenish-yellow on the addition of a few drops of alkali (Found : C, 44·3; H, 2·1. Calc. for $C_{13}H_7ONBr_2$: C, 44·2; H, 2·1%).

Bromination of 3-*bromoacridone.* Bromine (2·4 g.) in glacial acetic acid (20 ml.) was added with shaking to 3-bromoacridone (4 g.) (Ullmann and Tedesco, *Annalen*, 1907, **355**, 341) in glacial acetic acid (600 ml.) The bright yellow precipitate was filtered off, washed, dried, and recrystallised from boiling nitrobenzene; it formed yellow needles, m. p. >360°.

3 : 7-*Dibromoacridone.* 3 : 7-Diaminoacridone (Goldberg and Kelly, *J.*, 1946, 102) (10 g.) was dissolved in excess of aqueous hydrobromic acid and diazotised with a slight excess of sodium nitrite at 5—10°. Excess of nitrite was destroyed by the addition of a small quantity of urea. During the diazotisation a pale yellow precipitate (probably the diazonium salt) was formed, which was dissolved by slightly raising the temperature. The solution was then filtered and a solution of cuprous bromide (13 g.) in hydrobromic acid (100 ml.) was added slowly with stirring; nitrogen was evolved and a brown precipitate was formed. The reaction was completed by warming the mixture on a water-bath till the evolution of nitrogen had ceased (about 4 hours). The solid was filtered off, dried, and recrystallised from boiling nitrobenzene; 3 : 7-dibromoacridone formed small greyish-yellow needles (6 g., 39%), m. p. >360° (Found : Br, 44·9. Calc. for $C_{13}H_7ONBr_2$: Br, 45·3%).

3 : 7-*Dibromo*-5-p-*diethylaminophenylacridine.*—Each of the above-mentioned dibromoacridones was treated as follows : Dibromoacridone (1 g.), freshly distilled diethylaniline (2 g.), and phosphorus oxychloride (1 g.) were heated in a water-bath for 2 hours. The mixture was then poured into excess of sodium hydroxide solution, and the diethylaniline removed by steam-distillation. The remaining solid was filtered off, dried, and recrystallised, first from benzene and then from toluene; it formed orange prisms, m. p. 278—279°, in each case. None of these samples of *dibromodiethylaminophenylacridine* gave a depression of melting point when mixed with either of the others (Found : C, 57·3; H, 4·4; N, 6·1. $C_{23}H_{20}N_2Br_2$ requires C, 57·0; H, 4·1; N, 5·8%).

I am indebted to Burroughs Wellcome and Co. (Australia) Ltd. for a grant with which this work was carried out, and also to Professor R. H. Thorp for his encouragement and interest.

DEPARTMENT OF PHARMACOLOGY, UNIVERSITY OF SYDNEY. [*Received, May 27th,* 1952.]

---

702. *The "Cross and Bevan" Cellulose of* Posidonia australis.

By D. J. BELL.

Posidonia australis, a monocotyledon of terrestrial character, inhabits sheltered shallow seas off South Australia. Fibrous remains of the plant accumulate in quantity on the beaches where only slow natural decomposition takes place. Earl (*J.*, 1924, **125**, 123) and Arneman and Earl (*J. Roy. Soc. N.S.W.*, 1929, **63**, 44) prepared acetates {$[\alpha]_D$ *ca.* —40° (in chloroform)} (Barnett, *J. Soc. Chem. Ind.*, 1921, **40**, 8T) from "Cross and Bevan" celluloses derived from both leaves and residual fibres, and obtained from them mixed α- and β-methyl-D-glucosides, in 77·5% yield (cf. Irvine and Hirst, *J.*, 1922, **121**, 1588). They suggested that the chief polyglucose of *Posidonia* fibre differed in some way from the usual form of cellulose which yields an acetate with $[\alpha]_D$ *ca.* 22°. Subsequently, celluloses from wood (Barsha and Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 1006; Bell, *Biochem. J.*, 1938, **32**, 699), pear cell-wall (Hirst, Isherwood, Jermyn, and Jones, *J.*, 1949, S182), and marine algae (Percival and Ross, *J.*, 1949, 3041) have been shown to be based on the same fundamental chemical plan as cotton. It therefore appeared of interest to re-examine the *Posidonia* polysaccharide. Through the kind co-operation of Dr. H. B. S. Womersley of the University of Adelaide Botanical Department, generous supplies of both the freshly gathered leaves and the residual fibres were made available.

" Cross and Bevan " celluloses were prepared from both sources, as described by Dorée (" The Methods of Cellulose Chemistry," London, 1947, p. 352); the materials contained appreciable amounts of pentosan. Acetylation (Barnett, *loc. cit.*) gave triacetyl derivatives (pentosan-free) having, in chloroform, $[\alpha]_D$ $-22°$ ($\pm 2°$) from the residual fibre, and $-24°$ ($\pm 2°$) from the leaves. Six treatments, at room temperature, of the acetate (5·0 g.) suspended in dioxan with large excesses of methyl sulphate and 30% (w/v) sodium hydroxide solution gave a trimethyl hexosan (2·2 g.) (Found, OMe, 44·7%), $[\alpha]_D$ $-6°$ (in chloroform); the average loss per methylation treatment was therefore 4·65%. Hirst *et al.* (*loc. cit.*) found $[\alpha]_D$ $-7°$ for pear trimethyl cellulose, and Bell (*loc. cit.*) found wood trimethyl cellulose to be inactive. Haworth, Hirst, Peat, and Averill (*J.*, 1939, 1885) found values between $-3°$ and $-8°$ for specimens of cotton trimethyl cellulose, prepared under different conditions.

Hydrolysis (Bell, *Biochem. J.*, 1935, **29**, 2031) of trimethyl cellulose from *Posidonia* gave 94% recovery of an almost entirely crystalline trimethyl hexose which was freed from traces of lower homologues by chromatography (Bell, *J.*, 1944, 473). Paper chromatography indicated the presence of 2 : 3 : 6-trimethyl glucose uncontaminated by any isomers. Dissolved in dry methanol, containing 2% (w/v) of dry hydrogen chloride, the substance showed $[\alpha]_D$ $+60°$ (2 minutes) falling to $-35°$ (constant) in 450 minutes (cf. Irvine and Hirst, *J.*, 1922, **121**, 1213), thus confirming the 2 : 3 : 6-structure.

The acetates prepared by Earl may have retained some xylan derivatives. Although no reference can be found to the magnitude of the $[\alpha]_D$ of xylan acetates, xylan itself and its methylated derivative have large negative rotations. It is therefore concluded that *Posidonia* cellulose, when exhaustively " delignified," is not significantly different from celluloses of other plants.

The resistance to natural decomposition may be associated with the manner in which the fibres are impregnated by " lignin." The leaves and the residual fibre were not attacked by either snail-gut enzymes or the rumen flora of the sheep. The " Cross and Bevan " celluloses from each source were rapidly attacked by both digestive systems.

The author is grateful to Dr. I. A. McDonald for carrying out ruminant digestion tests and to Dr. D. H. Northcote for providing snail-gut preparations.

THE BIOCHEMICAL LABORATORY, CAMBRIDGE.

[*Received, June 17th*, 1952.]