Tetrahedron Letters No. 8, pp. 519-521, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE SYNTHESIS OF D-CHALCOSE

N.K. Kochetkov and A.I. Usov

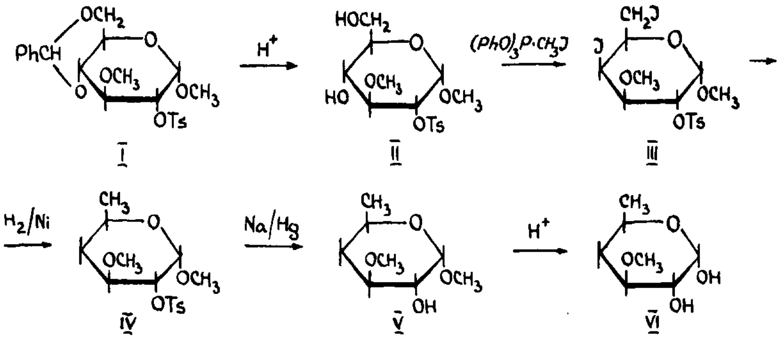
Institute for Chemistry of Natural Products
Academy of Sciences, Moscow, U.S.S.R.

(Received 23 December 1962)

CHALCOSE, one of the antibiotic chalcomycin acid degradation products, was isolated in 1961. This sugar being 4,6-dideoxy-3-O-methyl-D-glucose was confirmed by a series of chemical transformations as well as by NMR-spectra both of chalcose and methyl **β**-chalcoside[1,2]. Lankavose isolated later from the acid hydrolysate of lankamycin proved to be identical with chalcose[3].

Detailed investigation of the reaction of triphenyl phosphite methiodide and related compounds with monosaccharide derivatives[4] made it possible for us to develop a new method for deoxysugar synthesis[5]. The present communication describes the application of the method to the synthesis of chalcose. This synthesis may be considered as a final confirmation of the chalcose structure proposed.

The synthesis was accomplished according to the following scheme:



Methyl 4,6-O-benzylidene-3-O-methyl-2-O-tosyl-α-D-glucopyranoside[6] (I) was subjected to acid hydrolysis to give sirupy methyl 3-O-methyl-2-O-tosyl-α-D-glucopyranoside (II), $[\alpha]_D^{20}$+79.5°(c 1.11 in $CHCl_3$) in an almost quantitative yield. Treatment of II with excess $(PhO)_3P{\cdot}CH_3J$ in anhydrous benzene (30 hr, 50°) afforded diiodide III, which was isolated from the reaction mixture by chromatography on alumina, 85.5%, m.p. 99-99.5° (from methanol), $[\alpha]_D^{20}$+115,5°(c 1.0 in $CHCl_3$). (Found: C, 30.97; H, 3.45; J, 43.45; S, 5.50. $C_{15}H_{20}J_2O_5S$ requires:C, 30.94; H, 3.46; J, 43.60; S, 5.51%).

Hydrogenolysis of III in methanol in the presence of Raney nickel with simultaneous addition of methanolic alkali gave methyl 4,6-dideoxy-3-O-methyl-2-O-tosyl-α-D-glucopyranoside (IV), 93.5%, sirup, $[\alpha]_D^{20}$+102.5°(c 0.5 in $CHCl_3$). Treatment of IV with sodium amalgam in methanol led to sirupy methyl α-D-chalcoside (V), 80%, b.p.80° (bath)/0.1 mm, $[\alpha]_D^{20}$+184.5°(c 1.0 in $CHCl_3$). (Found: C, 54.56; H, 9.16. $C_8H_{16}O_4$ requires: C, 54.53; H, 9.15%).

V on heating with 1.5% sulphuric acid in aqueous dioxan (4 hr, 100°) gave rise to D-chalcose (95%), which after sublimation at 60°/0.01 mm crystallized, m.p. 92-93°, $[\alpha]_D^{20}$+96° (15 min) ⟶ +75°(3 hr or 24 hr; c 1.35 in water), R_F 0.60 (aq. butanol), 0.71 (butanol-acetic acid-water 4:1:1), Leningrad factory N2 "M" chromatographic paper. (Found: C, 52.05; H, 8.75. Calc. for $C_7H_{14}O_4$: C, 51.84; H, 8.70%).

The physical properties and the IR-spectrum of the substance obtained are identical with those published for natural chalcose[1,3].

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