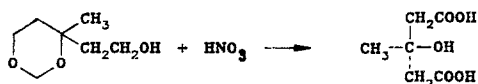


OXIDATION OF 4-METHYL-4-(2-HYDROXYETHYL)-1,3-DIOXANE TO
2-HYDROXY-2-METHYLGLUTARIC ACIDA. B. Devekki, A. N. Egor'kov, I. B. Blanshtein,
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2-Hydroxy-2-methylglutaric acid, which is an intermediate in the biosynthesis of cholesterol [1], is prepared by very complex preparative methods [2, 3].

We showed that 4-methyl-4-(2-hydroxyethyl)-1,3-dioxane, a by-product of isoprene synthesis, is converted directly to 2-hydroxy-2-methylglutaric acid (yield $\leq 90\%$) in its reaction with conc. HNO_3 .



To 640 ml of 58% HNO_3 , 56 g (0.38 mole) of 4-methyl-4-(2-hydroxyethyl)-1,3-dioxane was added dropwise for 7 h; after nitrogen oxides were no longer evolved, the mixture was heated for 1 h at 50-60°C. Then low-boiling products and an azeotrope of water with nitric acid were driven off at 12 kPa, and crystals that precipitated in the residue were filtered off and washed with water and ethanol, with mp 107-109°C (from water and acetone) and bp 119-120°C (17.3 hPa) for dimethyl ether [2].

During the oxidation, α -methylmalic (yield 5%) and oxalic (yield 4%) acids were also formed.

The oxidation product was methylated with an ether solution of diazomethane and then analyzed by GLC and chromatography-mass spectrometry. The main component of the investigated mixture was dimethyl 2-hydroxy-2-methylglutarate. The molecular ion was absent in the mass spectrum of this compound, but its structure was determined on the basis of characteristic ions with m/z (relative intensity, %): 175 (4), 141 (14), 118 (6), 117 (95), 101 (22), 85 (60), 74 (11), 59 (12), 43 (100). Together with the above-mentioned compound, dimethyl β -methoxy- β -methylglutarate was detected in the methylation products.

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