β,β-DIMETHYLACRYLIC ACID

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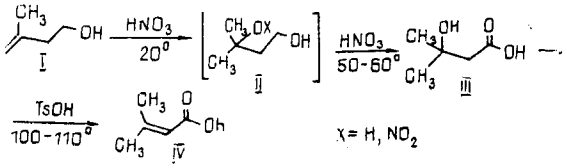
A method has been developed for obtaining β,β-dimethylacrylic acid from 3-methylbut-3-en-1-ol — a multitonnage product of the production of isoprene by the Prins method.

β,β-Dimethylacrylic acid is the starting material for a number of important substances and, in particular, the antibiotic carbomycin, the odoriferous substances lavandulic acid and verbenol, and the pesticide binapacryl, and also components of certain pheromones [1].

We have developed a simple two-state method of obtaining β,β-dimethylacrylic acid from the readily available 3-methylbut-3-en-1-ol (I), a multitonnage intermediate in the production of isoprene by the Prins method [2]. The reaction takes place on the interaction of the alcohol (I) with 62% nitric acid.

The first stage of the reaction (which is a two-stage one-pot process), according to PMR, at a temperature of 20°C the adduct (II) is formed, and this is then oxidized at 50-60°C to β-hydroxyisovaleric acid (III) with a yield of 65%. The acid (III) obtained is converted by reaction with p-toluenesulfonic acid at 100-110°C with a yield of 76% into β-β-dimethylacrylic acid (IV).



EXPERIMENTAL

PMR spectra were taken on a Perkin—Elmer R-12B instrument with a working frequency of 60 MHz.

β-Hydroxyisovaleric Acid (III). At 20°C, 8.6 g (0.1 mole) of 3-methylbut-3-en-1-ol (I) was added to 100 ml of 62% nitric acid (d 1.377), and the reaction mixture was stirred at the same temperature for 4 h. Then 0.1 g of sodium nitrite was added and the temperature was gradually raised to 50°C. In this process, oxides of nitrogen were evolved. Stirring was continued at 50-60°C until the evolution of oxides ceased (4 h). After this, the bulk of the nitric acid was distilled off and then 20 ml of water was added to the residue and this was distilled off completely. The final residue was dissolved in carbon tetrachloride, and the solution was dried with magnesium sulfate and evaporated, to give 7.6 g (65%) of the acid (III) in the form of a syrup, n_D^{20} 1.4520 [3]. PMR spectrum (in H_2O), δ, ppm: 1.12 s (6 H, CH_3CCH_3); 2.4 s (2 H, CH_2).

β,β-Dimethylacrylic Acid (IV). A mixture of 5.9 g (0.05 mole) of the acid (III) and 0.1 g of p-toluenesulfonic acid was heated at 100-110°C for 1 h. Then the water was driven off, and 3.8 g (76%) of the acid (IV) with mp 68-69°C [4] was isolated by distillation. PMR spectrum (in CCl_4), δ, ppm; 1.85 d (3 H, CH_3); 2.1 d (3 H, CH_3); 5.6 m (1 H, =CH).

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LIPID COMPLEX OF THE KERNELS OF SEEDS OF COTTON PLANTS OF THE WILT-RESISTANT VARIETY 175-F

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The amount, qualitative and class compositions, and total fatty acid composition of the free, bound, and strongly bound lipids of kernels of the seeds of cotton plant of variety 175-F have been determined, and with the aid of enzymatic hydrolysis the strongly bound lipids have been isolated from the cottonseed kernels in the native form. It has been established that more than half the weight of the lipids comprises neutral varieties and the remainder are polar components. The lipids of the more stable lipid-protein complexes possess a higher degree of saturation.

As is well known, the polar lipids of plants are integral components of cell membranes and, in a complex with protein and other compounds, determine their structure and properties. In order to break down the lipid-protein components and to extract the lipids it has been proposed to use ethanol [1] or alcohol-containing extractants [2]. By these solvents, lipids bound to proteins by Van der Waals hydrophobic interaction or hydrogen bonds are isolated from the plant tissues. However, there is a group of lipids strongly bound with protein by covalent bonds which are not extracted by organic solvents. They can be extracted only by breaking down the complex with the aid of acid or alkaline hydrolysis [1], during which the strongly bound lipids (SBLs) lose their native state. Their approximate composition and amount must therefore be judged from the fatty acids (FAs) isolated from alkaline hydrolysates. The SBLs have been isolated from cottonseed kernels [3] and from rice grains [4] in this way.

In recent years, it has been proposed to use proteolytic enzymes to cleave the lipid-protein bonds [5]. After enzymatic hydrolysis, the lipids liberated from the complexes, which have, in the main, retained their native form, are readily extracted by solvents. The glycolipids strongly bound with the protein in sunflowerseed kernels have been isolated by this method [6]. Among the glycolipids, the authors concerned found seven classes, the predominating ones being monogalactosyldiacylglycerols (MGDGs), digalactosyldiaclyglycerols (DGDGs), (acylmonogalactosyl)diacylgycerols (AMDGs), and sulfoquinovosyldiacylglycerols (SQDGs).

There is no information on the native SBLs of the cotton plant.

We have made a comparative study of the bound lipids (BLs) and SBLs of the seed kernels of a cotton plant of the variety 175-F isolated by two methods. The first method [I] was the official method [1] and consisted in the successive extraction from the ground kernels first of the free lipids (FLs) with hexane in a Soxhlet apparatus, then of the SBLs by breaking down the lipoproteins with boiling ethanol followed by extraction with diethyl ether in a Soxhlet apparatus, and then of the SBLs by severe alkaline hydrolysis in the form of FAs.

In the second method (II) the BLs were isolated by exhaustive extraction with a mixture of chloroform and methanol in a Soxhlet apparatus, and the SBLs by enzymatic hydrolysis.

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