BRIEF COMMUNICATIONS

IMPROVED METHOD OF SYNTHESIZING 4,6-O-BENZYLIDENE ACETALS OF METHYL GLYCOSIDES

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Benzylidene derivatives of monosaccharides have found wide use as protected components in the synthetic chemistry of carbohydrates [1] because of their relatively high stability in alkaline and neutral media and the ease of eliminating the protective groups by hydrolysis or hydrogenolysis. However, in spite of the great diversity of methods proposed [2-8], the synthesis of benzylidene acetals of monosaccharides has certain difficulties.

We propose an improved method for the synthesis of 4,6-O-benzylidene derivatives of certain methyl glycosides using benzaldehyde dimethyl acetal in the presence of catalytic amounts of sulfuric acid without a solvent. This permits a considerable shortening of the reaction time and the isolation of the desired products. For the practically complete occurrence of the reaction a 50-100% excess of the dimethyl acetal is sufficient; the use of a larger excess of acetal or a higher concentration of catalyst does not increase the yield of product. The time of occurrence of the reaction at 100°C does not exceed 2-5 min, and longer heating leads only to an accumulation of by-products. In the acetalization of methyl α-D-mannopyranoside by this method, no formation of the 4,6-O-benzylidene derivative was observed and the only product was methyl 2,3:4,6-di-O-benzylidene-α-D-mannopyranoside.

To perform the reaction, a mixture of 5 g of ground methyl glycoside, 10 ml of benzaldehyde dimethyl acetal [9], and 0.5 ml of a 10% solution of sulfuric acid in methanol was heated in an oil bath (100°C) with continuous stirring. After the methyl glycoside had dissolved and the mixture had begun to boil (1 min), it was heated with stirring for another 1-3 min, and then 100 ml of hexane was poured into the resulting viscous syrup with vigorous stirring. The precipitate of the benzylidene acetal was carefully triturated under a layer of hexane, cooled, and filtered off. The following derivatives have been obtained in this way:

7.0 g (96%) of methyl 4,6-O-benzylidene-α-galactopyranoside, with mp 174-175°C (methanol), $[\alpha]_D$ +160°C (c 1.2; chloroform) [10];

7.1 g (98%) of methyl 4,6-O-benzylidene-β-D-galactopyranoside, mp 194-195°C (methanol), $[\alpha]_D$ −34° (c 1.6; chloroform) [10];

7.2 g (99%) of methyl 4,6-O-benzylidene-α-D-glucopyranoside, mp 158-160°C (methanol), $[\alpha]_D$ +117° (c 1.5; chloroform) [10];

7.0 g (96%) of methyl 4,6-O-benzylidene-β-D-glucopyranoside, mp 196-197°C (methanol), $[\alpha]_D$ −61° (c 1.3; chloroform) [10]; and

6.4 g (67%) of methyl 2,3:4,6-di-O-benzylidene-α-D-mannopyranoside, mp 184-186°C (benzene), $[\alpha]_D$ 0° (c 2.0; chloroform) [8].

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MINOR PHOSPHOLIPIDS OF THE KERNELS OF THE SEEDS OF THE COTTON PLANT OF VARIETY 159-F

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We have previously reported [1, 2] that in the cotton plant at various stages of development a phosphatidic acid (PA) has been detected which has been identified by qualitative reactions and chromatographic mobility and on the basis of spectrometric information. It must be mentioned that contradictory information is given in the literature on the chromatographic mobilities of the phosphatidic acids. Some authors give high values of R_f in an ammonia system of silica gel — 0.75 [3], 0.68 [4], 0.8 [5]; others indicate a low mobility under the same conditions — 0.04 [6], 0.07 [7], 0.05 [8]. For a more rigid identification of the phosphatidic acid isolated we have obtained the corresponding compound from phosphatidylcholine by enzymatic hydrolysis with phospholipase D [8]. The phosphatidic acid obtained was compared with that isolated from the cotton plant and their complete identity was established. R_f values of phosphatidic acids given in the second set of publications mentioned [6-8] have been fully confirmed.

We also isolated a phosphatidic acid from ripe cotton seeds. The amount of phosphatidic acid in the total phospholipids was 0.3% in terms of phosphorus, and its fatty acid composition was: 16:0 — 50.2%; 18:0 — traces; 18:1 — 24.4%; 18:2 — 25.4%; 18:3 — traces.

With the aid of one-dimensional and two-dimensional TLC on silica gel in systems 1 and 2 [1] a phosphorus-containing compound with R_f 0.15 (system 1) and 0.12 (system 2) was detected in, and was then isolated from, the total phospholipids of cottonseed kernels, its proportion amounting to 0.1% in terms of phosphorus of the total phospholipids and its fatty acid composition being: 14:0 — traces; 16:0 — 58.8%; 18:0 — traces; 18:1 — 19.8%; 18:2 — 21.4%. From the results of chromatographic mobility, qualitative reactions, IR spectra, products of acid hydrolysis, information in the literature [6], and comparison with lysophosphatidylinositol obtained by enzymatic hydrolysis from phosphatidylinositol by phospholipase A_2, we established that this phospholipid is identical with lysophosphatidylinositol.

To confirm the presence of phosphatidic acid and lysophosphatidylinositol in the cottonseed kernels we isolated the total phospholipids from samples of cotton seeds harvested in different years. We detected phosphatidic acid and lysophosphatidylinositol in all the combined phospholipids from which it follows that these phospholipids are component parts of the biological membranes and not artifacts.

We have detected phosphatidic acid and phosphophatidylinositol among the phospholipids of cottonseed kernels from variety 159-F for the first time.

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