

day and, particularly, from those that have only just opened. It was natural to assume that the anomalous distribution of the FAs in the PIs of the third-day flowers is either retained or increases. To elucidate this point, flowers of a cotton plant of variety S-4880 were gathered in three time intervals - 0, 24, and 48 hours after opening. The PIs were isolated by column chromatography and preparative thin layer chromatography and were subjected to enzymatic hydrolysis with phospholipase A₂ [11]. The position distribution of the FAs of the PIs of the flowers is shown in Table 1.

From the results of the experiment it must be noted that an increase in the content of FA 16:0 in PI is observed from 0 to 24 h, followed by a drop at 48h. At the same time, with regard to position, the distribution of FA 16:0 at the sn-2 position is roughly the same at 0 and 48 h, yet at 24 h the acid 16:0 in this position is about 4 times as great i.e., the anomaly of its distribution is revealed.

Also remarkable is the decrease almost to the minimum for acids 18:0 and 18:1 at 24 h, and reappearance at 48 h. The diene and triene FA 18:2 and 18:3 are distributed practically evenly at 24 h at both sn-1 and sn-2 positions, although at 0 and 48 h the traditional positional distribution of FA is observed.

The results obtained persuade us that the unusual position distribution of the FAs in the PIs at 24 h is necessary for the development of the flower. This may apparently be connected with a definite functional activity of the PIs in the development of the flowers, since PIs are responsible for a whole series of membrane functions. To these may be assigned chemical and electrical excitation, active ion transport, oxidative phosphorylation, the provision of selective permeability, and other functions of a more general order.

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UNUSUAL ALKALINE HYDROLYSIS OF GIBBERELLIN ISO-A₃

BY A B_{AL}² MECHANISM

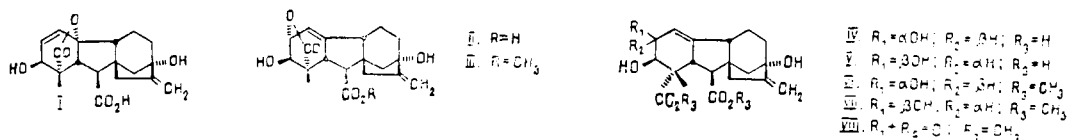
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In aqueous alkali, the phytohormone gibberellin A₃ (I) readily isomerizes into gibberellin iso-A₃ (II), which is quantitatively hydrolyzed to the diacid (IV) [1]. To synthesize substance (IV) we carried out the hydrolysis of acid (I) in 1 M aqueous Na₂CO₃ at 100°C and, together with the usual hydrolysis product (IV), we unexpectedly detected (by HPLC) in the reaction mixture a new compound (5:2) for which structure (V) has been proposed. To deter-

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mine the structure of (V), the mixture of hydrolysis products (IV) and (V) was methylated with CH_2N_2 and the resulting mixture of esters was separated by chromatography (silica gel; $\text{CHCl}_3\text{-EtOAc}$). The new ester (VII) was eluted first: mp 96-98°C, M^+ 392 (2.7%). The ^1H and ^{13}C NMR spectra of (VI) and (VII) were extremely close. Alcohols (VI) and (VII) were oxidized with $\text{Py}\cdot\text{HCrO}_3\text{Cl}$ in CH_2Cl_2 [2], and in each case the known ketol (VIII) [3] was obtained in high yield. In order to synthesize the epimers (IV) and (V) the ketol (VIII) was treated with NaBH_4 in EtOH (5 h). The main components of the reaction mixture proved to be (PMR, HPLC) the epimer (VII) and the methyl ester of gibberellin iso- A_3 (III) (8:10). It was found that the epimer (VI) was also formed in this reaction but already after 2 h it had lactonized completely into the ester (III). Thus, the hydrolysis of gibberellin A_3 does in fact form the new 2 β -hydroxy epimer (V) of the diacid (IV), characterized as the ester (VII). With a rise in the concentration of Na_2CO_3 from 0.25 to 4 M (with the acid (I) in a concentration of 1 mg/ml) the ratio of the epimers (IV) and (V) changed from 100:3 to 100:17, respectively. With an increase in the concentration of acid (I) to 100 mg/ml (1 M Na_2CO_3) the ratio of epimers became (100:40).



It was shown by the hydrolysis of gibberellin iso- A_3 (II) under the same conditions that the new epimer (V) was formed in the course of the opening of the γ -lactone ring of this gibberellin. Epimer (V) can be formed in the alkaline hydrolysis of lactone (II) only by the β -attack of an OH^- ion at C-2 of lactone (II), i.e., the very rare $\text{B}_{\text{AL}}2$ mechanism of alkaline hydrolysis [4] is realized. This hydrolysis mechanism has been described for β -lactones but this is the first time it has been detected for γ -lactones. The reaction described may be the first stage in a new three-stage synthesis of gibberellin A_8 from gibberellin A_3 (see [5]).

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A STUDY OF THE HERB *Aerva lanata*

II. FERULOYLAMINES

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Continuing the chemical study [1] of the phenolic components of the herb *Aerva lanata* Juss., family *Amaranthaceae*, we have separated the weakly polar components by chromatography on silica gel using as eluent chloroform with the addition of small amounts (1-3%) of methanol and on Sephadex LH-20 with the eluent chloroform-hexane (8:2-10:0). Eight individual substances were isolated, of which six have been identified with the aid of chemical transformations and spectral methods (UV, IR, PMR, and mass spectra). We also used comparison with authentic samples for the identification of substances (I)-(IV).

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