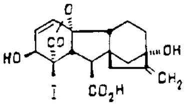
mine the structure of (V), the mixture of hydrolysis products (IV) and (V) was methylated with CH_2N_2 and the resulting mixture of esters was separated by chromatography (silica gel; $CHCl_3$–EtOAc). The new ester (VII) was eluted first: mp 96-98°C, M^+ 392 (2.7%). The ^1H and ^{13}C NMR spectra of (VI) and (VII) were extremely close. Alcohols (VI) and (VII) were oxidized with $Py \cdot HCrO_3Cl$ 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 2β-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).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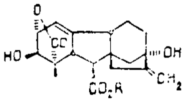
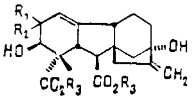

II. R=H
III. R=CH_3


IV. R_1=αOH; R_2=βH; R_3=H
V. R_1=βOH; R_2=αH; R_3=H
VI. R_1=αOH; R_2=βH; R_3=CH_3
VII. R_1=βOH; R_2=αH; R_3=CH_3
VIII. R_1+R_2=O; R_3=CH_3

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 $B_{AL}2$ 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

G. G. Zapesochnaya, V. A. Kurkin
and L. N. Pervykh

UDC 547.9

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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β-Sitosterol (I) – white crystals, mp 132-133°C, composition $C_{29}H_{50}O$, M^+ 414.

Daucosterol (II) – white crystals, mp 315-317°C, composition $C_{35}H_{60}O_6$. Hydrolysis with β-glucosidase formed β-sitosterol and glucose.

Syringic acid (III) – colorless crystals, mp 203-205°C, composition $C_9H_{10}O_5$, λ_{max} 216 and 274 nm. In the PMR spectrum (deuteroacetone) singlets at 7.34 ppm (2 H) and 3.90 ppm (6 H) showed symmetrical substitution of a benzene ring and confirmed the structure of substance (III) as did also the characteristic fragments of the mass spectrum: m/z 198 (M^+, 100%), 183 (83), 181 (27), 155 (27), 154 (8), 153 (16), 137 (23), 127 (79%). For its identification, substance (III) was also compared with an authentic sample of syringic acid.

Vanillic acid (IV) – colorless crystals, mp 210-212°C, composition $C_8H_8O_4$, M^+ 168 (100%) λ_{max} 260 and 290 nm. PMR spectrum (deuteroacetone), ppm: 7.62 (dd, 9 and 2 Hz, H-6), 7.56 (d, 2 Hz, H-2), 6.92 (d, 9 Hz, H-5), 3.90 (s, CH_3O). The facts presented and comparison with an authentic sample permitted substance (IV) to be identified as vanillic acid.

Feruloyltyramine (V) – colorless crystals, mp 146-148°C, composition $C_{18}H_{19}NO_4$, M^+ 313, λ_{max}^{EtOH}, nm 221, 290, 317; ν_{max}, cm^{-1} 1660 (amide C=O).

The NMR spectrum (100 MHz) in deuteroacetone included a triplet at δ 2.78 (2 H, 7 Hz) and a quartet at δ 3.52 (2 H, 7 Hz), which were assigned to the methylene protons in phenylethylamine. A singlet at δ 3.86 (3 H) belonged to an aromatic methoxy group. The presence of trans-olefinic protons was revealed by two doublets with constants of 16 Hz at δ 6.16 (1 H) and 7.54 (1 H). A multiplet at δ 7.00-7.20 (3 H) and two doublets with a constant of 8 Hz at δ 6.84 (2 H) and 6.75 (2 H) were due to seven aromatic protons.

In the mass spectrum at 15 eV the molecular ion M^+ 313 was the main peak, and the fragmentation at 70 eV (m/z 194, 193, 192, 177, 120, 107) corresponded to the scheme given in [2].

Acetylation gave a crystalline diacetate with mp 154-156°C (from water with the addition of alcohol), with the composition $C_{22}H_{23}O_6$, M^+ 397. The PMR spectrum ($CDCl_3$) contained the signals of two aromatic aceto groups: singlets at δ 2.30 (3 H) and 2.32 (3 H).

A comparison of the results obtained with the literature [2, 3] enabled the substance isolated to be identified as feruloyltyramine having the structure (V).

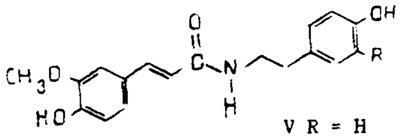
Feruloylhomovanillylamine (VI) – colorless crystals with mp 158-160°C, composition $C_{19}H_{21}NO_5$, M^+ 343; λ_{max}^{EtOH}, nm, 218, 232, 290, 318, ν_{max}, cm^{-1}, 1660 (C=O).

The nature of the NMR spectrum of the substance under investigation ($CDCl_3$) differed little from that of compound (V); there was an additional singlet of a methoxy group (δ 3.90), and the aromatic region (δ 6.6-7.0) included a multiplet of only six protons.

In the mass spectrum, fragmentation analogous to that of substance (V) was observed, only the masses of the fragments of the phenylethylamine moiety of the molecule being changed (m/z 150 and 137 instead of m/z 120 and 107).

Acetylation led to a diacetate with mp 131-133°C having the composition $C_{23}H_{25}NO_7$, M^+ 427.

A comparison of the results obtained with the literature [3] permitted the substance that had been isolated to be identified as feruloylhomovanillylamine, having the structure (VI).



V R = H

VI R = OCH_3

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