THE STRUCTURE OF ECHINATIC AND ISOECHINATIC ACIDS

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It has been shown previously [1, 2], that echinatic and isoechinatic acids, $C_{30}H_{46}O_5$, belong to the β-amyrin series. Differing from one another by the positions of the two double bonds, these acids have the same positions of the one carboxy group and three hydroxy groups in the molecule. In the present work we have accurately determined the position of these groups in the acids concerned.

The carboxy group in the acids under investigation is present at C_{20}, since on saponification the dienedione (M^+ 654, mp 212-214°C) gives a decarboxylation product [3] with mp 275°C. The PMR spectra of the triacetates of methyl isoechinatate and dihydroisoechinatate each show the presence of four protons at acetyl groups and not three, as was erroneously found for the triacetate of methyl echinatate [1]. Apparently, the signal of the fourth proton in the spectrum coincides with the signal of olefinic protons. One of the hydroxy groups in these acids is therefore primary. Thus, in the PMR spectra of derivatives of the acids the signals of only six CH_3 groups are well distinguished and there is a quartet of the AB type for $AcOC\underline{H}_2$ with δ 4.25 ppm (J = 12 Hz), which is characteristic for acetates of the methyl esters of 24-hydroxyglycyrrhetic and liquiridiolic and other acids [5]. The δ value of 4.25 ppm shows the axial position of the $AcOC\underline{H}_2$ group in all these compounds [6]. The positions of all the two OH groups at C_3 and C_{24} in the molecules of echinatic and isoechinatic acids were confirmed by the production of acetonides of the methyl esters by the method of Kubota et al. [7] (mp 192 and 252°C, respectively).

The position of the third OH group was investigated on the basis of chemical reactions. Methyl echinatate was oxidized with chromium trioxide in pyridine and the oxidation product was saponified with 2% KOH in ethanol to give a mixture of bisnordiketones, $C_{28}H_{40-42}O_2$, mp 201-204°C (M^+ 408, M^+ 410, C 81.71, H 10.62%), UV spectrum: λ_{max} 282 nm; IR spectrum: 1716 cm^{-1}. These facts show that the OH groups are located at C_3, C_{21}, and C_{24} in the original

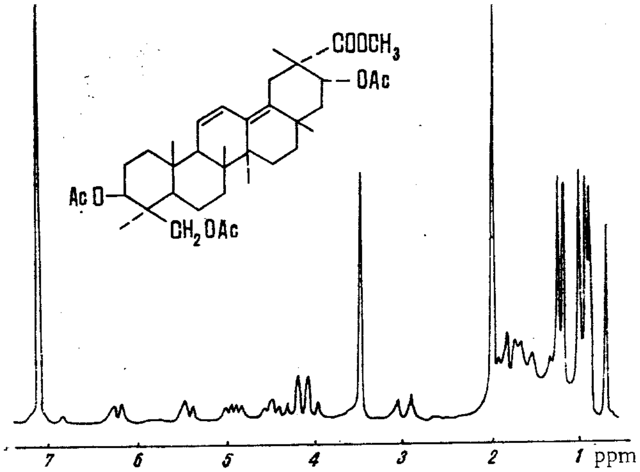

Fig. 1. PMR spectrum of the triacetate of methyl isoechinate ($CDCl_3$, Varian HA-100).

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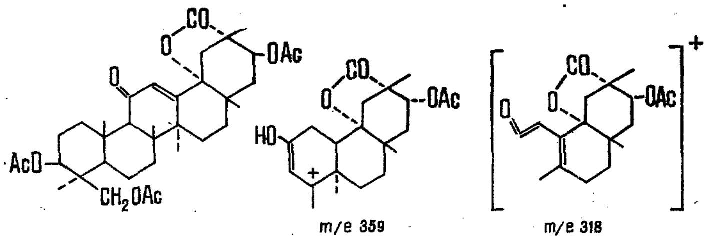
acid, and keto groups at C_3 and C_{21} in the bisnordiketone. The presence of a substance with M^+ 410 as an impurity shows that the initial acid is a mixture of acids with one and with two double bonds, but with the same positions of the functional groups.

The suggested structures of echinatic and isoechinatic acids were confirmed by the formation of the triacetate of the ketolactone with mp 314-318°C (UV spectrum: λ_{max} 236 nm; IR spectrum: 1250, 1675, 1720, 1785 cm^{-1}) when the triacetate of isoechinatic acid (mp 297°C) was oxidized with chromium trioxide in acetic acid. The mass spectrum of the triacetate of the ketolactone had the peaks M^+ 626 and strong peaks of ions with m/e 359 and 318. The last-mentioned two peaks are also characteristic for the mass spectrum of the diacetate of 21α-hydroxyisoglabrolide [8].



Thus, the structure of echinatic acid corresponds to 3β,21α,24-trihydroxyoleane-9(11),-12-dien-29-oic acid and that of isoechinatic acid to 3β,21α,24-trihydroxyoleane-11,13(18)-dien-29 oic-acid.

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