

THE STRUCTURE OF ECHINATIC ACID

N. P. Kir'yalov and V. F. Bogatkina

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, pp. 447-448, 1969

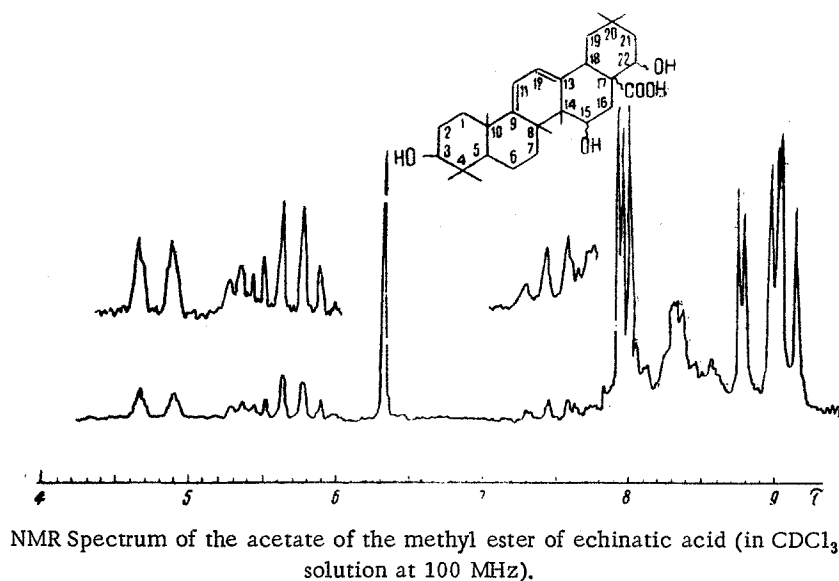
As shown previously [1, 2], echinatic acid $C_{30}H_{46}O_5$ with mp 298-300° C, mol. wt. 500 belongs to the β -amyrin series. On the basis of its mass and NMR spectra it may be assumed that echinatic acid contains three hydroxyl groups. In the τ 7.9-8 region there are nine protons of three acetyl groups the secondary nature of which is confirmed by signals with a total area of 3H (τ 5.3-5.9) corresponding to the protons of acetyl groups.

In the NMR spectrum there are signals in the τ 4.6 and 4.9 regions (two protons) corresponding to olefinic protons, apparently in ring C, in which the presence of two conjugated double bonds is confirmed by the UV spectrum: λ_{max} 280-282 (log ϵ 3-3.3).

The tertiary nature of the COOH group is shown by the ready splitting off of CO_2 in the saponification of the triketo derivative of the methyl ester of echinatic acid (mp 220-225° C). This reaction simultaneously shows that one of the hydroxyl groups is adjacent to the carboxyl group. A second hydroxyl group is possibly in the γ position with respect to the carboxyl since the oxidation of the acetate of echinatic acid with CrO_3 forms a substance having a lactone group (band at 1780 cm^{-1} in the IR spectrum). At the same time, the two OH groups mentioned are not adjacent to one another, since echinatic acid does not contain an α -glycol system.

The oxidation of the triacetate of the methyl ester of echinatic acid with SeO_2 first gives a heteroangular diene with mp 192° C; UV spectrum λ_{max} $m\mu$: 258, 249, 240; IR spectrum, cm^{-1} : 1735 (CO of ester groups). Subsequently, the substance with mp 192° C was oxidized by the SeO_2 to a dienedione with mp 212-214° C; UV spectrum, λ_{max} $m\mu$: 280 (on 12-fold dilution); IR spectrum, cm^{-1} : 1625 (double bond), 1665 (conjugated CO group of a six-membered ring), 1700 (CO of a keto group), and 1735 (CO of ester groups).

Echinatic acid does not form a bromolactone under the usual conditions (like morolic acid) [3], which is due to the absence of a COOH group at $C_{(17)}$ or to steric hindrance.



The reactions of echinatic acid and its derivatives are explained in a comparatively simple manner if it is assumed that one of the OH groups is located at $C_{(3)}$ and the other two at $C_{(15)}$ and $C_{(22)}$ or at $C_{(16)}$ and $C_{(21)}$ (figure) and the COOH group at $C_{(17)}$.

REFERENCES

1. N. P. Kiryalov and T. N. Naugol'naya, ZhOKh, **34**, 8, 1963.
2. N. P. Kir'yalov, Questions of the Study and Use of Licorice in the USSR [in Russian], Leningrad, p. 123, 1966.
3. J. Simonsen and W. C. J. Ross, The Terpenes, **5**, 209, 1957.

14 May 1969

Komarov Botanical Institute AS USSR