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MINOR TRITERPENE COMPONENTS FROM *QUERCUS ROBUR* GALLS

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The chemical composition of the resinous exudate covering the galls produced by the insect *Cynips mayri* on common oak (*Quercus robur*) has already been the object of research in our laboratory. As a result of these studies, it was shown that two triterpene seco-acids, roburic and nyctanthic acid¹ are the main components of the acidic fraction, while α - and β -amyrine and α - and β -amyrone are the main components of the neutral fraction.² Almost at the same time, the isolation from oak bark and leaves of a number of triterpenes with glutinane, taraxane and friedelane skeletons was reported.³

We have now examined the minor components of the resin with the purpose of checking the possible presence of triterpenes with these skeletons among gall components. The examination of the less abundant fractions, obtained by chromatography performed as described in previous papers,^{1,2} led to the isolation of small quantities of an acidic substance (6%) and of two neutral substances (3 and 2%).

The crystalline acid, m.p. 139–141°, $[\alpha]_D +45^\circ$, was identified as the already known dammarenolic acid⁴ on the basis both of its spectroscopic characteristics and by conversion of its methyl ester into the carbomethoxy-keto-lactone m.p. 154–156° $[\alpha]_D +31^\circ$, by CrO_3 .⁴ The two neutral substances were also crystalline, and had m.p. 142–144°, $[\alpha]_D +27^\circ$ and m.p. 135–136°, $[\alpha]_D +67^\circ$, respectively. On the basis of these physical constants and spectra, the first substance was identified as dammarenediol,⁵ identical with an authentic sample, while the second one was identified as dipterocarpol⁶ since its reduction with NaBH_4 gave dammarenediol.

Therefore, in the gall exudate, triterpenes having the skeletons found in the plant appear to be totally absent; this result is an indication of different metabolism in the galls as compared to the other parts of the plant. Furthermore, the large amount of seco-acids might be explained by the need of the galls to produce a resinous exudate and, therefore, using for this purpose triterpenes which are already present, simply by opening the A ring.

¹ MANGONI, L. and BELARDINI, M. (1963) *Tetrahedron Letters* 921; *idem.* (1964) *Gazz. Chim. Ital.* **94**, 382.

² MANGONI, L. and BELARDINI, M. (1963) *La Ric. Scient. (Rome)* II(A), **3**, 528.

³ WAZECIONO, U. (1963) *Roczniki Chem.* **37**, 1457, 1463; *idem.* (1964) *Chem. Abstr.* **60**, 8069f; *idem. ibid.* **38**, 79; *idem.* (1964) *Chem. Abstr.* **60**, 14548d.

⁴ ARIGONI, D. *et al.* (1960) *J. Chem. Soc.* 1900.

⁵ MILLS, J. (1956) *J. Chem. Soc.* 2196.

⁶ CRABBÉ, P., OURISSON, J. and TAKAHASHI, T. (1958) *Tetrahedron* **3**, 279.