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ROBURIC ACID, A NEW TRITERPENE 3,4-SECO-ACID

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The very characteristic red-purple galls produced by the insect Cynips Mayri on common oak (Quercus robur) are found frequently in central and southern Italy (1).

The galls are covered with a colorless, smelling resinous exudate, which may be easily extracted by light petroleum. This exudate has now be shown to consist mainly of a mixture of triterpene acids.

Acidic components were isolated from crude extract as insoluble barium salts; treatment of these with diluted hydrochloric acid gave free acids, which were then chromatographated on acid-washed silica.

Elution with benzene yielded a colorless crystalline fraction (almost 50% of crude extract). This is a mixture of two acids which we have been able to separate by fractional crystallisation.

The less soluble one, m.p. 221-222° (from ethanol), $[\alpha]_D = +84°$ has a molecular formula $C_{30}H_{48}O_2$ [1]. Its infrared

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[1] Satisfactory analyses were obtained for all compounds reported. Melting points were determined on a Kofler block and have not be corrected. Infrared spectra were made in CCl_4 solution. Specific rotations were determined on chloroform solutions at room temperature. NMR spectra were determined on a Varian A60 spectrometer in carbon tetrachloride using tetramethyl-silane as internal reference.

spectrum showed carboxyl bands [3300-2500 cm^{-1} (broad) and 1710 cm^{-1}] and $>C=CH_2$ bands (1635 cm^{-1} and 900 cm^{-1}).

On hydrogenation at atmospheric pressure it yielded a dihydroacid $C_{30}H_{50}O_2$ m.p. 194-195°, $[\alpha]_D = +80°$, end adsorption in the ultraviolet.

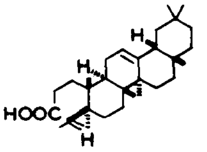
On the grounds of the above data and by comparison with an autenthic sample the acid m.p. 221-222° was identified with known nyctanthic acid (I) (2,3).

The more soluble acid m.p. 181-182° (from ethanol), $[\alpha]_D = +78°$, to which we have given the name "roburic acid", has the same molecular formula $C_{30}H_{48}O_2$. Its IR spectrum showed the bands of $>C=CH_2$ group at 1640 cm^{-1} and 900 cm^{-1}. The presence of this group was confirmed by NMR spectrum where there are peaks at 5.34 and 5.16 τ ; in addition a peak corresponding to another olefinic proton is present at 4.85 τ . On catalytic hydrogenation, it yielded dihydroroburic acid m.p. 171-172°, $[\alpha]_D = +70°$, which still shows the peak at 4.85 τ in its NMR spectrum.

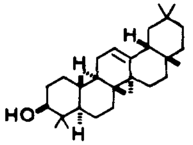
The presence of an inert trisubstituted double bound in roburic acid was deduced.

As β-amyrine (II) and α-amyrine (III) are very often found together in nature, the occurrence of roburic acid besides nyctanthic acid suggested the hypothesis that the former may be (IV), a new triterpene seco-acid of nyctanthic type with α-amyrine skeleton.

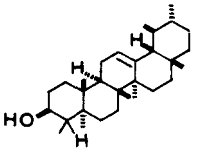
Structure (IV) was in good accord with all the aforementioned chemical and spectroscopic properties of roburic acid and was strongly supported by the comparison between the physical constants of dihydroroburic acid and of 3,4-seco-urs-12-ene-3-carboxylic acid (V), prepared by D.Arigoni, D.H.R.Barton, C.Djerassi et al. (3) by photochemical cleavage of β-amyrone.



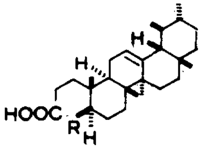
I



II



III



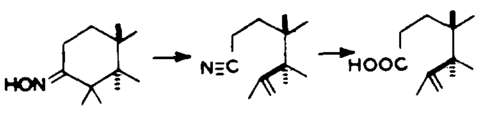
IV $R = \overset{CH_3}{\overset{|}{C}}{=}CH_2$

V $R = CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$

That roburic acid actually has structure (IV) was proved by its partial synthesis from α-amyrine.

α-Amyrine was oxidized to α-amyrone and this converted into corresponding oxime (VI). By refluxing (VI) with tosyl chloride in pyridine (2,4), unsaturated seco-nitrile (VII) m.p. 199-200° (from benzene-ligroin), $[\alpha]_D = +80°$ was obtained [IR bands at 2245 cm^{-1} ($C{\equiv}N$); at 1635 and 900 cm^{-1} ($>C{=}CH_2$)].

Alkaline hydrolysis of nitrile (VII) yielded acid (IV) m.p. 181-182°, $[\alpha]_D = +81°$, identical in all respects with natural roburic acid (mixed melting point, infrared spectra).



VI VII IV

Research to establish the nature of minor components of crude extract is in progress.

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