802. *Further Crystalline Constituents of Gum Mastic.*

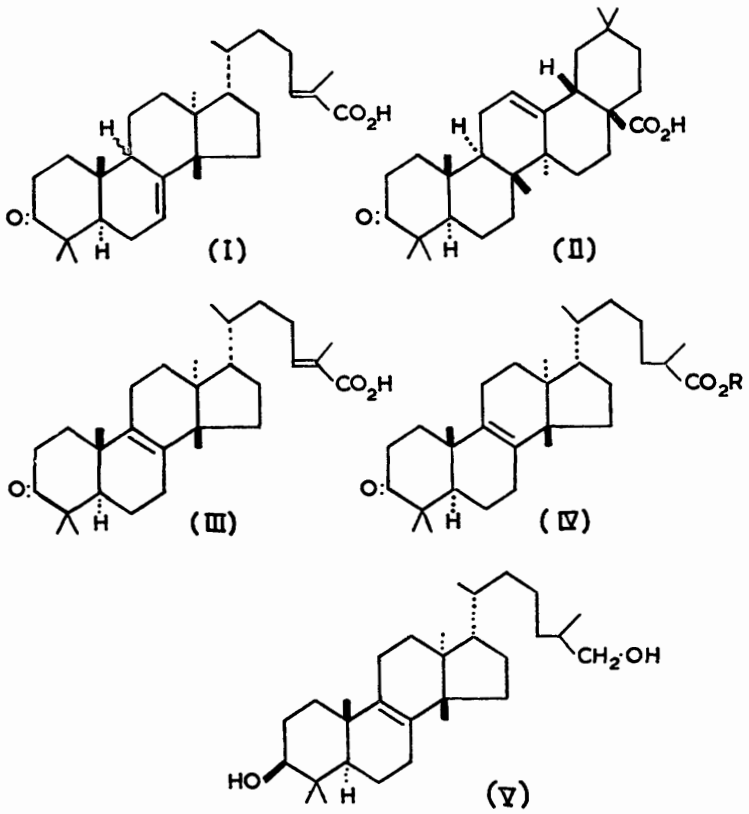
By Eliseo Seoane.

From the acid fraction of gum mastic oleanonic acid and a new triterpenoid keto-acid have been isolated. The latter acid has been related to masticadienonic acid from which it differs only in the position of one ethylenic linkage.

In a recent paper [1] an investigation of the constituents of gum mastic was reported. From the neutral fraction tirucallol was isolated, whilst from the acidic fraction a new triterpenoid acid, masticadienonic acid (I), was obtained. The present paper deals with two further crystalline constituents of the resin, both isolated from the acidic fraction.

As already briefly mentioned,[1] the portion of the acidic fraction soluble in dilute sodium hydroxide solution contains a crystalline acid. This has now been identified as oleanonic acid (II).

From the less strongly acidic fraction a new crystalline triterpenoid keto-acid, characterised as its methyl ester, has also been isolated. For reasons outlined below this is designated



*iso*masticadienonic acid and has the constitution and stereochemistry summarised in (III). This acid, $C_{30}H_{46}O_3$, was very similar in many respects to masticadienonic acid. Thus it contained, from its ultraviolet absorption spectrum, an $\alpha\beta$-unsaturated carboxylic acid function. Ozonolysis gave one mol. of acetic acid as with masticadienonic acid (I). The presence of the ketone grouping was indicated by a positive Zimmermann test,[2] by reduction with sodium borohydride to *iso*masticadienoloic acid, and by reduction with

[1] Barton and Seoane, preceding paper.
[2] Zimmermann, *Z. physiol. Chem.*, 1935, **233**, 257; 1936, **245**, 47; Barton and de Mayo, *J.*, 1954, 887.

lithium aluminium hydride to *iso*masticadienediol. As with masticadienonic acid,[1] hydrogenation over palladium proceeded smoothly with uptake of one mol. of hydrogen to furnish dihydro*iso*masticadienonic acid (IV; R = H), further characterised as the methyl ester (IV; R = Me). Reduction of this dihydro-acid (IV; R = H) with sodium borohydride afforded dihydro*iso*masticadienoloic acid whilst reduction with lithium aluminium hydride gave dihydro*iso*masticadienediol (V) identical with an authentic specimen [1] of established structure.

These facts enable one to deduce the correctness of formula (III) for *iso*masticadienonic acid and suggest [3] that mild acid treatment of masticadienonic acid should afford the new *iso*-acid. This was confirmed experimentally. In an analogous series of experiments methyl masticadienolate acetate was transformed into dihydro*iso*masticadienoloic acid identical with material prepared by the route indicated above.

Experimental

Rotations were determined in $CHCl_3$ solution. Ultraviolet absorption spectra were taken in EtOH solution with the Unicam S.P. 500 Spectrophotometer. Infrared spectra were kindly determined by Dr. G. Eglinton and his associates. Silica gel for chromatography was obtained from Messrs. Hopkin and Williams Ltd. Light petroleum of b. p. 40—60° was used throughout, unless stated to the contrary.

Isolation of Oleanonic Acid.—The acidic fraction (10 g.) extracted with 0·5N-sodium hydroxide in 5 : 1 light petroleum–benzene (200 ml.) was chromatographed over silica gel (400 g.), elution being with increasing proportions of benzene and then with 3 : 1 benzene–ether (25 fractions). Crystallisation of the material eluted with benzene from ether–light petroleum and from methanol gave oleanonic acid (2·5 g.), identified by m. p., mixed m. p., rotation {$[\alpha]_D$ +101° (*c* 1·63)}, and analysis (Found: C, 79·05; H, 10·45. Calc. for $C_{30}H_{46}O_3$: C, 79·25; H, 10·2%). The identity was confirmed by conversion into the methyl ester {m. p., mixed m. p., and rotation, $[\alpha]_D$ +94° (*c* 1·26)} (Found: C, 79·3; H, 10·8. Calc. for $C_{31}H_{48}O_3$: C, 79·45; H, 10·3%) and into methyl oleanolate acetate.

Isolation of iso*Masticadienonic Acid.*—The mother-liquors from the crystallisation of masticadienonic acid (see Barton and Seoane [1]) gave on long storage further crystalline material (14 g. from about 800 g. of gum mastic). This material in benzene (150 ml.) was chromatographed over silica gel (600 g.), which was eluted with up to 1 : 9 ether–benzene (18 fractions of approx. m. p. 140—150° and $[\alpha]_D$ −11°). These fractions were combined and systematically triangulated from 1 : 3 ether–light petroleum. In this way the 14 g. of crystals were separated into pure masticadienonic acid (3·0 g.) and pure iso*masticadienonic acid* (1·12 g.). Recrystallised from the same solvent mixture, this had m. p. 166—167°, $[\alpha]_D$ +34° (*c* 1·10), $\lambda_{max.}$ 212 mμ (ε 15,000) (Found: C, 79·05; H, 9·9. $C_{30}H_{46}O_3$ requires C, 79·25; H, 10·2%). Treatment with diazomethane gave *methyl* iso*masticadienonate*, m. p. (from methanol) 111°, $[\alpha]_D$ +36° (*c* 1·05) (Found: C, 79·15; H, 10·0. $C_{31}H_{48}O_3$ requires C, 79·45; H, 10·3%). Ozonolysis of *iso*masticadienonic acid as described by Barton and Seoane [1] gave the same result (acetic acid identified as the *p*-bromophenacyl ester).

iso*Masticadienoloic Acid.*—*iso*Masticadienonic acid (200 mg.) in methanol (40 ml.) was treated with sodium borohydride (100 mg.) in the minimum of water at room temperature overnight. Crystallisation from methanol gave iso*masticadienoloic acid*, m. p. 171—172°, $[\alpha]_D$ −3° (*c* 1·14) (Found: C, 78·9, 78·8; H, 10·5, 10·65. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%).

iso*Masticadienediol.*—*iso*Masticadienonic acid (130 mg.) in dry ether (30 ml.) was refluxed overnight with lithium aluminium hydride (140 mg.) in the same solvent. Crystallisation from methanol gave iso*masticadienediol*, m. p. 157—158°, $[\alpha]_D$ −5° (*c* 1·02) (Found: C, 80·8; H, 11·1. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%).

*Dihydro*iso*masticadienonic Acid.*—*iso*Masticadienonic acid (400 mg.) in ethyl acetate (200 ml.) was hydrogenated over palladised charcoal as for masticadienonic acid.[1] Crystallisation from aqueous methanol afforded *dihydro*iso*masticadienonic acid*, m. p. 155—157°, $[\alpha]_D$ +27° (*c* 1·01) (Found: C, 79·35, 79·45; H, 10·5, 10·45. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%). This acid was also obtained by acid-catalysed isomerisation of dihydromasticadienonic acid by the procedure detailed below. Treatment with diazomethane in the usual way afforded *methyl dihydro*-iso*masticadienonate*, m. p. 75—77°, $[\alpha]_D$ +26° (Found: C, 79·05; H, 10·1. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·7%).

[3] Cf. Irvine, Lawrie, McNab, and Spring, *Chem. and Ind.*, 1955, 626; Dawson, Halsall, Jones, Meakins, and Phillips, *ibid.*, p. 918.

Dihydroisomasticadienoloic Acid.—Dihydro*iso*masticadienonic acid (124 mg.) in methanol (20 ml.) was treated with sodium borohydride (excess) in the minimum of water and left overnight. Crystallisation from aqueous methanol furnished *dihydroisomasticadienoloic acid*, m. p. 210—213°, $[\alpha]_D$ −6° (*c* 1·00) (Found: C, 78·65, 78·75; H, 10·8, 10·8. $C_{30}H_{50}O_3$ requires C, 78·55; H, 11·0%).

Dihydroisomasticadienediol.—Dihydro*iso*masticadienonic acid (400 mg.) in dry ether (50 ml.) was treated with lithium aluminium hydride (300 mg.) in the same solvent under reflux overnight. Chromatography of the product over silica gel (20 g.) and elution with benzene and with 1 : 4 ether–benzene gave dihydro*iso*masticadienediol identical {m. p., mixed m. p., rotation, $[\alpha]_D$ +3° (*c* 1·75)} with material described in the earlier paper as "*iso*dihydromasticadienediol."

Isomerisation of Masticadienonic Acid.—The acid (103 mg.) in chloroform (10 ml.) was treated at 0° with dry hydrogen chloride for 2 hr. Crystallisation of the product from ether–light petroleum gave masticadienonic acid, identified by m. p., mixed m. p., rotation, and infrared spectrum.

In a similar correlation methyl masticadienolate acetate (100 mg.) in chloroform (10 ml.) was isomerised in the same way. The product was hydrolysed with 5% ethanolic potassium hydroxide. Crystallisation from methanol gave dihydro*iso*masticadienoloic acid (see above), identified by m. p., mixed m. p., and rotation {$[\alpha]_D$ −6° (*c* 1·40)}.

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