CHEMICAL EXAMINATION OF JACK TREE LATEX AND JACK FRUIT GUM

Part II. Occurrence of a-Artostenone

BY K. J. BALAKRISHNA AND T. R. SESHADRI, F.A.Sc. (From the Department of Chemistry, Andhra University, Waltair)

Received July 15, 1947

In an earlier communication it was concluded that artostenone does not occur in the tree latex and fruit gum of the Jack tree, but that its isomer, a-artostenone occurs in the form of its enol-wax esters and the change takes place to artostenone during the saponification with alcoholic potash. This was supported by the behaviour of a-artostenone enol-benzoate which under the same conditions of saponification yielded artostenone. a-Artostenone would thus be a remarkable example of a ketone belonging to the steroid group and occurring in nature as a stable enol-wax ester. If this should be correct this compound itself should be capable of isolation directly from the gum by employing suitable methods.

As a mild alkaline reagent the use of sodium methoxide in cold methyl alcoholic solution has been examined to bring about the hydrolysis without isomeric change to artostenone. Employing first α -artostenone enol-benzoate α -artostenone was obtained by this process. Applying it to the waxy matter obtained from Jack fruit gum a good yield of α -artostenone could be obtained with ease. It has been identified by comparison with an authentic sample and by conversion into its benzoate. Thus the occurrence of α -artostenone in the Jack fruit gum and tree latex is established.

 α -artostenone-enol-wax-ester $\rightarrow \alpha$ -artostenone \rightarrow artostenone.

EXPERIMENTAL

a-Artostenone from a-artostenone benzoate

a-Artostenone benzoate¹ (0.5 g.) was dissolved in dry benzene (2 c.c.) and sodium methoxide (0.3 g.) in dry methyl alcohol (10 c.c.) was added. The mixture was shaken well and left aside overnight. The solvent was then distilled off over a water-bath and the residue, after cooling, was stirred up with water. A colourless solid separated out which was filtered and crystallised from alcohol. It was obtained as silvery white plates melting at 99–100°. The mixed melting point with an authentic sample of α -artostenone was undepressed.

a-Artostenone from the fruit gum

The following method of isolating the waxy matter was adopted. The crude fruit gum was digested with boiling acetone and the hot solution filtered under suction to remove suspended impurities. When the filtrate was allowed to cool down, the colourless non-steroid solid melting at 84° separated out. It was filtered and the filtrate was concentrated over a boiling water-bath until all acetone was removed. The residue was a brown viscous semi-solid giving all reactions of sterols. It was dried in a vacuum over sulphuric acid when it set into a reddish-brown solid.

This substance $(2 \cdot 0 \text{ g.})$ was dissolved in dry benzene (5 c.c.) and sodium methoxide $(1 \cdot 2 \text{ g.})$ in dry methyl alcohol (40 c.c.) was added. The mixture was shaken well and left aside overnight. The solvent was then distilled off over a water-bath and after cooling, the residue was stirred up with water. A pale yellow solid separated out and was filtered. It was recrystallised from alcohol twice when it was obtained as glistening colourless plates melting at 99–100°. (Found: C, $84 \cdot 5$; H, $11 \cdot 8$; $C_{30}H_{50}O$ requires C, $84 \cdot 5$; H, $11 \cdot 7\%$.) The mixed melting point with an authentic sample of α -artostenone was undepressed.

The benzoate was prepared from the above sample of α -artostenone (0.5 g.) obtained direct from the fruit gum, by treatment with benzoyl chloride (10 c.c.) and refluxing the mixture for 20 minutes. It was worked up as described in Part I¹ and crystallised from a mixture of benzene and alcohol. It was obtained as fine short needles melting at $157-59^{\circ}$. The mixed melting point with the benzoate of an authentic sample of α -artostenone was not depressed.

SUMMARY

a-Artostenone has been prepared directly from Jack fruit gum by saponification using sodium methoxide in cold methyl alcoholic solution. In preliminary tests a-artostenone enol-benzoate was found to yield a-artostenone under these conditions. Thus the conclusion that a-artostenone occurs in the plant in the form of enol-wax-esters is confirmed.

REFERENCES

1. Balakrishna and Seshadri

.. Proc. Ind. Acad. Sci., A, 1947, 26, 46.