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CONSTITUTION OF TINGENONE, A COMPONENT OF THE STEMBARK OF EUONYMUS TINGENS WALL (F. CELASTRACEAE)

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Earlier work on some plants of the family Celastraceae led to the isolation of dulcitol[1], lespedin[2] and celaxanthin[3]. More recently from the barks of Pristimera indica (Willd.) and Celastrus scandens., pristimerin[4] and celastrol[5] have been isolated and are found to have complex structures[6].

Euonymus tingens is a tree belonging to this family and is common in the upper heights of the Himalayas (6500 ft. - 10000 ft.). The inner stembark is orange yellow and has been used as a skin pigment and as a vegetable

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[1] H. Rogerson, J. Chem. Soc. 1040, (1912).

[2] M. Kanao and M.S. Koriyama, Chem. Abs. **45**, 616, (1951).

[3] A. Seybold, Chem. Abs. **48**, 13834, (1954).

[4] S.S. Bhatnagar and P.V. Divekar, J. Sci. Ind. Res. **10B**, 56, (1951).

[5] O. Gisvold, J. Amer. Pharm. Ass. **28**, 440, (1939).

[6] P.K. Grant, A.W. Johnson, P.F. Juby and T.J. King, J. Chem. Soc., 549, (1960).

drug. It is considered useful for diseases of the eye and for chronic constipation and dyspepsia.

An orange red pigment has now been isolated from the cold light petroleum (60-80°) extract of the air dried bark. It crystallised from benzene as orange yellow leaflets m.p. 171-2°. Elemental analysis indicated the molecular formula to be $C_{25}H_{30}O_4$; I.R. ($CHCl_3$) 1698(s), 1647(w), 1590(s), 1538(m), 1513(s), 1439(s), 1372(s), 1342(inf.), 1316(m), 1307(inf.), 1285(s), 1080 cm^{-1}(s). $\lambda_{max.}^{ethanol}$ 250(logϵ 3.83), 263(logϵ 3.64), 425(logϵ 5.02) and min. at 285(logϵ 2.18) mμ.

The pigment could be easily reduced by sulphur dioxide and reoxidised by air. An alcoholic solution of it liberates iodine from aqueous potassium iodide. A leucoacetate is formed with zinc dust and aceticanhydride. All these reactions show that it is a quinone. It failed to form a product with o-phenylenediamine ruling out the possibility of a 1:2-quinone structure. It gave a red colour with methanolic magnesium acetate and a deep green colour with alcoholic ferric chloride and also a stable copper chelate showing the presence of a chelated phenolic hydroxyl. It formed a monoacetate, monobenzoate and a leucoacetate which contained three acetoxyl groups. Though it was phenolic in nature it did not dissolve in aqueous sodium hydrioxide but gave a deep violet-red insoluble salt on warming the solution. The sodium salt on treatment with hydrochloric acid regenerated the original compound. These properties would suggest a p-quinone system along with an ortho hydroxy carbonyl function or group. The presence of a $-COCH_3$ group in tingenone was indicated by I.R. spectrum (1698 cm^{-1}) and in its leucoacetate at 1718 cm^{-1}, a positive iodoform test and also by the easy formation of 2:4-dinitrophenylhydrazone.

The ultraviolet spectrum of the leucoacetate (235 mμ log ε 5.51), (254 mμ inf. log ε 4.53), (292 mμ log ε 4.13), (302 mμ inf. log ε 4.02) and (328 mμ log ε 3.69) resembled closely that of 1:2:4-triacetoxy naphthalene[7] (235,282 and 330 mμ). Zinc dust distillation gave a hydrocarbon whose U.V. spectrum (λ_{max} 230, 258, 270, 282 and 330 mμ) resembles that of substituted naphthalene. These data show that tingenone is a naphthaquinone derivative.

On oxidation with hydrogen peroxide in acetic acid it gave a monosubstituted phthalic acid giving no ferric reaction and it did not respond to the iodoform test. This would suggest that the hydroxyl and acetyl groups are located in the quinone part. Ozonolysis of the pigment (in ethylacetate) gave besides formaldehyde and acetone, a non-steam volatile aldehydic compound whose 2:4-D.N.P., U.V. and I.R. spectra indicated the aliphatic nature of the compound.

In n.m.r. spectral data the integral curve of the compound corresponds to 30 protons. The spectrum indicates the presence of a phenolic hydroxyl (δ 7.37), three aromatic protons, a proton α- to the benzene ring (δ 2.97), 3

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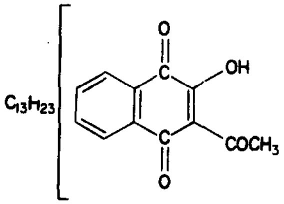
[7] R.C. Shah, A.B. Kulkarni and V.M. Thakore, J. Chem. Soc., 2515, (1955)

protons due to acetyl group (δ 2.27) and 9 protons due to three tertiary methyl groups (δ 1.52, 1.35 and 1.02). Based on the above observations the tentative structure (I) is suggested for the compound.



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