FOMENTARIC ACID, A NOVEL TYPE OF ALKYL SUCCINIC ACID FROM FOMES FOMENTARIUS (L) Fr.

Pratap Singh and S. Rangaswami

Department of Chemistry, University of Delhi, Delhi.7, India

(Received 31 October 1966)

While working with the chemical components of the woodrotting fungus Fomes fomentarius (L.) Fr., it was found in the case of one sample that the petroleum ether extract contained an appreciable quantity (0.035% calculated on weight of dry fungus) of an organic acid. It was conveniently isolated via its sparingly soluble sodium salt. Purification was effected by chromatographing the methyl ester on alumina. The major part of the compound was eluted with petroleum ether and it constituted a single substance (T.L.C.), $c_{43}H_{84}o_4^*$ m.p. 46-47°, $[\alpha]_D^{**}$ -29.5°. Saponification of the ester (II) gave the acid (I), colourless stout prisms, m.p. 78-80°, $C_{41}H_{80}O_{4}$, $[\alpha]_{D} \stackrel{+}{=} 0^{\circ}$. It was found to be a long chain aliphatic acid [I.R. absorptions at 1715 cm (COOH) and 1300, 1240, 729, 719 cm⁻¹ (polymethylene)]. dibasic (conductometric titration) and saturated (no reaction with bromine or permanganate). Micro-titration employing thymol blue as indicator gave the molecular weight as ca 648.

The acid gave a fluorescent compound on fusion with

^{*} All the compounds whose formulae are given in this communication analysed correctly for C and H.

^{**} All rotations were taken in chloroform solution.

resorcinol and sulphuric acid, indicating that it was a glutaric acid or succinic acid derivative. Under the conditions of the Schmidt reaction, the acid yielded the diamine which was initially obtained in the form of the sulphate, m.p. $230-32^{\circ}$, $\left[\alpha\right]_{D}^{-2}0^{\circ}$. The diamine (IIIa), m.p. $37-39^{\circ}$, $C_{39}H_{82}N_{2}$ regenerated therefrom, on treatment with nitrous acid gave the diol (IIIb), $C_{39}H_{80}O_{2}$, m.p. $45-47^{\circ}$. Acetylation of the diol under mild conditions revealed that in it one hydroxyl was secondary and the other tertiary. The diol consumed one mole of periodate showing that it was a vicinal glycol; the parent acid should therefore be a substituted succinic acid.

The steam volatile part of the periodate oxidation product was identified as acetaldehyde through its DNP derivative. The non-volatile product of the periodate oxidation was further oxidised with neutral permanganate and the resulting acid (IV) converted into the methyl ester and examined by vapour phase chromatography. The principal compound was found to be a C_{19} straight chain saturated aliphatic ester.

The two ester groups in (II) were reduced to hydroxyls by means of lithium aluminium hydride to give the diol (Va) ${}^{C}_{41}{}^{H}_{84}{}^{O}_{2}$, m.p. 75-78°, ${}^{O}_{1}{}^{O}_{1}$ -9.2°, and subsequently converted into the methyl groups via the iodide (Vb), ${}^{C}_{41}{}^{H}_{82}{}^{I}_{2}$, m.p. 41-43°, ${}^{O}_{1}{}^{O}_{1}$. In the mass spectrum of the resulting hydrocarbon (VI), ${}^{C}_{41}{}^{H}_{84}$, m.p. 39-41°, ${}^{O}_{1}{}^{O}_{1}$, the highest molecular species that could be detected was ${}^{C}_{18}{}^{H}_{38}$ and the series of smaller fragments accompanying it showed that it was a straight chain aliphatic hydrocarbon.

Based on the above data and the N.M.R. spectrum of the diester (II), the structure of the parent acid, which being new has been called fomentaric acid, is deduced as (I) and the several reactions mentioned above may be

represented as below:

Structure (I) for fomentaric acid has further been confirmed by synthesis. The ethyl ester of a-bromodistearylacetic acid (VII) was condensed with sodio monomethyl malonic acid ester (VIII) giving rise to the trisubstituted tricarboxylic acid ester (IX).

Hydrolysis and decarboxylation of this ester yielded the dicarboxylic acid (I). This was converted into the dimethyl ester and subjected to enromatographic purification on a silica gel column. The major compound eluted from the column, m.p. $48-49^{\circ}$, $\left[\alpha\right]_{D}$ -32.7°, was identical with the dimethyl ester of the natural acid (mixed melting point, T.L.C. and superimposable infra-red spectrum). The dicetyl analogue, which was also synthesised for special reasons, following the same route, differed from the natural compound in melting point and infra-red spectrum.

The structure of fomentaric acid as α -methyl- α' , α' -distearyl succinic acid represents a type which has not been met with in nature so far. Full details of the investigation will be published elsewhere.

Acknowledgement:

The authors are grateful to Prof.T.R.Seshadri,F.R.S. for his kind interest, Dr.B.K.Bakshi for identification of the fungus, Prof.T.R.Govindachari for the N.M.R. spectrum, Dr. Jagdish Shankar for the Mass spectrum, Dr.T.A.V.Subramaniam for the vapour phase chromatogram and Dr.K.G.Sarma and Dr.P.S.Rao for help in the collection of the fungus.