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# DEXTROROTATORY HARDWICKIIC ACID.
# AN EXTRACTIVE OF COPAIFERA OFFICINALIS

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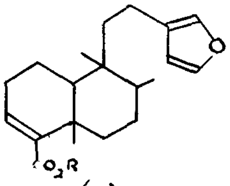
ALTHOUGH work has been carried out on the chemistry of Congo copal,[1,2] a fossilised resin obtained from Copaifera species (family Leguminosae), little attention has been given to extractives from the heartwoods of these species.

A ligroin extract of 46 lbs. of Copaifera officinalis gave us 1 g. of a dextrorotatory diterpene acid (I; R=H), $C_{20}H_{28}O_3$ (E=311; m.p. 104-106°; $[\alpha]_D^{20}$ +125°). The acid exhibited maxima at 2150Å and at 1680, 1650, 1580, 1490 and 873 $cm^{-1}$, but a doublet at 1375 $cm^{-1}$ characteristic of a gem dimethyl group was absent from the infrared region. These spectra are characteristic of an α,β- unsaturated acid and of a furan.[3] Parts of the infrared spectrum reminded us of that of marrubiin.[4]

With diazoethane the acid gave an ester (I; R=Et) (m.p. 45°; $[\alpha]_D^{20}$ +110°), which absorbed maximally at 2170Å and at 1721, 1640, 1565, 1500 and 874 $cm^{-1}$. The n.m.r. spectrum ($CCl_4$) of the ester had the following characteristics. A triplet at τ 2.68 and a singlet at 2.83 can be assigned to α-protons on a furan ring, whilst a singlet at τ 3.77 corresponds to a β-proton on a furan ring. A triplet at τ 3.41 (J,3.6 c/s) can be assigned to the ringed hydrogen of the system $-C\textcircled{H}=\overset{|}{C}-CO_2R$, whilst a quartet at τ 5.83 (J,7.3 c/s) and a triplet at τ 8.7 (J,7.5 c/s) correspond to the methylene and the methyl groups respectively of the ethoxycarbonyl group. Singlets at τ 8.72 and 9.22 can be assigned to two quaternary methyl groups whilst a doublet at τ 9.14 (J,8.1 c/s) corresponds to a methyl group α- to a methylene group in the system $\textcircled{CH_3}-\overset{|}{C}H-CH_2-$.



(I)

Hydrogenation of the ester with Adams's catalyst gave a liquid product lacking the furan bands at 1580, 1490 and 873 $cm^{-1}$, but bands at 1721 and 1640 $cm^{-1}$ showed the presence of $C=C-CO_2Et$ in the product. Dehydrogenation of the ester (100 mg.) with palladised charcoal afforded a mixture containing 1,2-dimethyl-, and 1,2,5-trimethylnaphthalene which were readily identified by g.l.c. on Apiezon L, Castorwax, D.E.G.S and S.A.I.B. columns.

The spectra and chemical properties of the new acid reminded us strongly of those of (−) hardwickiic acid (I; R=H), recently isolated[5] from <u>Hardwickia pinnata</u> (leguminosae). Through the kindness of Dr. Dev we were able to compare specimens of the two acids. A mixed m.p. of equal quantities of each was some 50° higher than the m.ps. of the components, a property typical of a racemic compound. The infrared spectra, in KBr discs, of the two acids were superimposable. A trace of (-)- hardwickiic acid when reacted with diazoethane gave an ester indistinguishable from our ester by g.l.c., on Apiezon L and S.E. 30 columns.

There can be no doubt therefore that the acid extracted from Copaifera officinalis is (+) hardwickiic acid. The spectra and chemical properties of the two enantiomers support the assigned[5] structure (I; R=H), and biogenetic considerations also lend support to it.

The formation of 1,2,5-trimethylnaphthalene on dehydrogenation of the ester no doubt results from methyl group migration from $C_5$ to $C_4$, a most likely possibility in view of the position of the double bond.

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