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## CARBON SKELETON

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(Received in UK 12 November 1970; accepted for publication 13 January 1971) In previous papers (1, 2) we have reported the composition of the acidic fraction of the oleoresin from "Copaifera multijuga" Hayne (Leguminosae Caesalp.). We now report the composition of the neutral fraction which constitutes the 50% of the oleoresin which comprises sesquiterpenoid hydrocarbons (33%) and oxygenated sesquiterpenes (17%).

Among the sesquiterpenoid hydrocarbons we have identified by IR, NMR, MS and specific rotation,  $\beta$  -caryophyllene,  $\gamma$ -humulene,  $\beta$  -bisabolene,  $\alpha$  -copaene and  $\alpha$ -ylangene. From the oxygenated fraction we have isolated caryophyllene-oxide (8%) and a new alcohol (2%) for which we propose the name of  $\alpha$  -multijugenol (C<sub>15</sub>H<sub>24</sub>O, viscous oil, M. W. 220 by MS,  $[\alpha]_D^=$  + 115<sup>O</sup>). Its NMR spectrum shows two singlets at 1.0 and 1.05 (3H each) and a doublet at 1.65 (3H, J<1 cps), due to two tertiary methyl groups and a vinyl methyl group respectively; three vinyl protons at 5.66, 4.83 and 4.58  $\delta$ ; a signal, located between 5.0-4.6 and partially obscured by winylic protons, assignable to a proton on a carbon bearing an oxygen (acetylation displaces this proton 0.3 ppm downfield); a hydroxyl group at 3.4 (which disappears by deuteration); and a broad multiplet located between 3.0-2.5, probably due to an allylic proton. IR spectrum of  $\alpha$  -multijugenol exhibites hydroxyl bands (3450 and 1020 cm<sup>-1</sup>). Mass spectrum shows significant peaks at 205 (M-15), 202 (M-18), 187 (M-18-15), 177 (M-43), 159 (M-18-43), and 41 (base peak).

Acetylation gives a monoacetylderivative (MS 262, 202, 187, 159, 43;  $[\alpha]_D^{=+139}$ ). Catalytic hydrogenation gives a mixture of a tetrahydroalcohol,  $C_{15}H_{28}O$ , and a saturated hydrocarbon,  $C_{15}H_{28}$ , which was identified with caryophyllane. Presumably caryophyllane is formed by hydrogenolysis of an allylic hydroxyl group; this hypothesis is supported by the easy MnO<sub>2</sub>oxidation of  $\alpha$ -multijugenol to an  $\alpha$ - $\beta$ -unsaturated ketone  $\alpha$ -multijugenon  $C_{15}H_{22}O$ , low melting solid,  $[\alpha]_D^{=-38}$ ,  $\lambda_{max}$  238, log  $\xi = 3.94$ ;  $\gamma_{max}$  1680 cm<sup>-1</sup>).  $\alpha$ -Multijugenon has an MS peak at 176 (M-42) and in its NMR spectrum the vinyl methyl group resonates at  $\delta$  1.9 indicating the presence of the  $\alpha$ - $\beta$ -unsaturated cyclic ketone system. (3)

The above results suggest that  $\alpha$ -multijugenol has a caryophyllane carbon skeleton with two double bonds and an allylic secondary hydroxyl group.



Two alcohols,  $\alpha$  - and  $\beta$ -Betulenol (I and II) (4), with such structural characteristics have been reported but their specific rotation (-7° and -55° respectively) differ from that of  $\alpha$  multijugenol, although the IR spectrum of  $\alpha$ -betulenol is similar to that of  $\alpha$  -multijugenol. The tetrahydroketone (C<sub>15</sub>H<sub>26</sub>O), obtained by oxidation with pyridine/CrO<sub>3</sub> from the tetrahydroalcohol, is identical (IR and MS) with that prepared in the same way from  $\alpha$ -betulend Therefore, it appears that  $\alpha$  -multijugenol differs from  $\alpha$ -betulenol only in the position of double bonds. This has been confirmed by synthesis of  $\alpha$ -multijugenol from caryophyllene-ox ide. Caryophyllene-oxide with pyridinium bromide in pyridine gives a mixture of unsaturated alcohols (IV, R=H) and (V, R=H), (4, 5), which can be separated by chromatography of their acetylderivatives (IV, R=COCH<sub>3</sub>) and (V, R=COCH<sub>3</sub>) on silica gel (6). Deacetylation of IV (R=COCH<sub>3</sub>) gives the alcohol IV (R=H), which was demonstrated to be identical (IR, MS, NMR, [ $\alpha$ ]<sub>D</sub>) with  $\alpha$ -multijugenol. Therefore we can ascribe structure IV (R=H) to  $\alpha$ -multijugenol.

## References.

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- 6. C<sub>17</sub>H<sub>26</sub>O<sub>2</sub>; NMR spectrum 5.20(1H), 5.12(1H), 4.97(2H), 5.4-5.1(3H), 1.05(6H); mass spectrum 262, 202, 118, 43 (base peak)