Barakol, a Novel Dioxaphenalene Derivative from *Cassia siamea*

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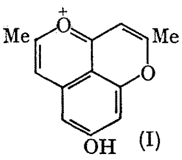
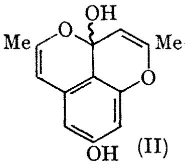
Summary An extractive from the leaves of *Cassia siamea* has been named barakol and identified as 3a,4-dihydro-3a,8-dihydroxy-2,5-dimethyl-1,4-dioxaphenalene.

THE ethanol extract of the leaves of *Cassia siamea* (vern: Mbaraka) contains a phenol, $C_{13}H_{12}O_4$, which we call barakol. Barakol crystallises from aqueous methanol or ethanol as pale yellow needles m.p. 165° (decomp.) and is stable in hydroxylic solvents or in a moist atmosphere. When dried, even at room temperature, or when dissolved in non-hydroxylic solvents, *e.g.* chloroform, the phenol rapidly turns bright green and insoluble polymeric material is formed. The phenol is very rapidly degraded by base but, with strong acids, it reversibly forms anhydro-salts which may be dried and which do not decompose at room temperature in the solid state.



(I)



(II)

Chemical degradation of barakol did not lead to any immediately recognisable products so the structure of the derived bromide was determined by *X*-ray crystallography.

The bromide crystallised from aqueous ethanol as monoclinic prisms free from solvent. Oscillation and equi-inclination Weissenberg photographs (Cu-K_α radiation) revealed the space group as $P2_1/c$. The unit cell parameters are:—$a = 9{\cdot}58 \pm 0{\cdot}02$, $b, = 13{\cdot}25 \pm 0{\cdot}03$, $c = 10{\cdot}90 \pm 0{\cdot}02$ Å, $\beta = 118° \ 11' \pm 8'$, $U = 1220$ Å^3, $D_m = 1{\cdot}606$, $Z = 4$, $D_c = 1{\cdot}618$.

Intensity measurements were made on a Hilger and Watts linear diffractometer using Mo-K_α radiation with the crystal rotating about its *c*-axis. Intensity data were collected for the layers *hk*0—*hk*14 and 1482 reflections were used in the structure determination. The bromide ions were located from a three-dimensional Patterson synthesis and a three-dimensional Fourier synthesis phased on these ions revealed the position of all the carbon and oxygen atoms. Refinement by full-matrix least-squares with anisotropic temperature factors for the bromide ion confirmed the structure of barakol bromide, one canonical form of which is represented by (I). The final *R* value was 8·6%.

The free phenol is assumed to be one of the possible corresponding carbinol bases and the n.m.r. spectrum is in agreement with its formulation as (II). We attribute the instability of the phenol to ready dehydration to the derived methylenequinone. The possible biogenesis of the molecule by a novel polyketide cyclisation is obvious. The synthesis of barakol is in hand.

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