Crystallographic Determinations of Partial Stereochemistries of the Sesquiterpenoids Illudol and Marasmic Acid

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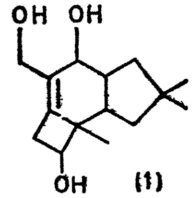
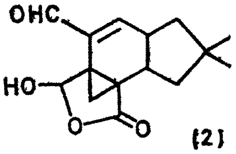
Summary *X*-Ray crystal-structure analyses show that illudol and marasmic acid have *cis*-fused hydrindane skeletons.

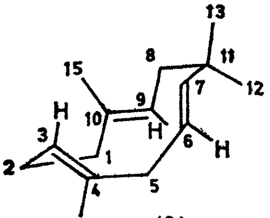
THE group of sesquiterpenoid fungal metabolites exemplified by illudol (**1**)[1] and marasmic acid (**2**)[2] may arise from a humulene-like precursor.[3] In the liquid phase humulene is conformationally mobile,[4] but in the solid complex with silver nitrate the hydrocarbon has the conformation (**3**) (and its mirror image),[5] and this conformation has been invoked to rationalize the stereochemical course of reaction with *N*-bromosuccinimide in aqueous acetone to yield product (4).[6] If the hypothetical cationic precursor (**5**) is postulated to arise from conformation (**3**) of humulene it will have the stereochemistry shown, and (**1**) and (**2**) and related sesquiterpenoids would be expected to have *cis*-fused hydrindane skeletons. To test this hypothesis we have determined the crystal structures of a pair of illudol and marasmic acid derivatives.[2,7] We find that these derivatives have the stereochemistries shown in (**6**) and (**7**), and these results accord with our suggestion.



(1)



(2)



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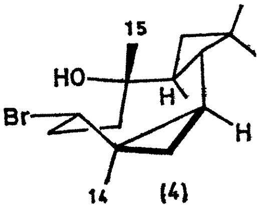
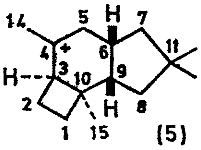
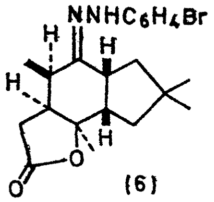


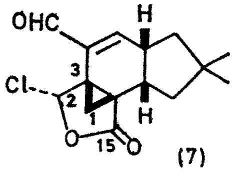
(4)



(5)



(6)



(7)

(**6**) crystallizes in the monoclinic space group $P2_1$, with $a = 9\cdot837$, $b = 15\cdot622$, $c = 13\cdot796$ Å, $\beta = 100\cdot2°$, and $Z = 4$; the X-ray diffraction data were recorded on a computer-controlled four-circle diffractometer with Cu-K_α radiation. (**7**) crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 8\cdot467$, $b = 9\cdot285$, $c = 18\cdot349$ Å, and $Z = 4$; the X-ray diffraction data were recorded photographically with Cu-K_α radiation and estimated with a flying-spot microdensitometer. The crystal structures were elucidated by the heavy-atom approach, with tangent-formula adjustment of phases[8] to overcome problems of pseudo-symmetry. The atomic co-ordinates were subsequently refined by least-squares calculations, and R is now 11·5% over 1193 reflections for (**6**) and 10·7% over 575 reflections for (**7**). The absolute configuration defined by (**6**) was unambiguously established when a correction for anomalous dispersion by the bromine atom ($\Delta f'' = 1\cdot5$ electrons) was incorporated in the structure-factor calculations. Direct measurements of the intensity differences caused by anomalous dispersion in the case of the marasmic acid derivative favour the absolute configuration shown in (**7**), but the results are not completely conclusive.

We thank the S.R.C. for financial support, and Dr. T. C. McMorris and Professor P. de Mayo for samples of (**6**) and (**7**).

(*Received, March 4th,* 1971; *Com.* 176.)

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