X-Ray Structure of Mascaroside, A New Bitter Glycoside from Coffee Beans

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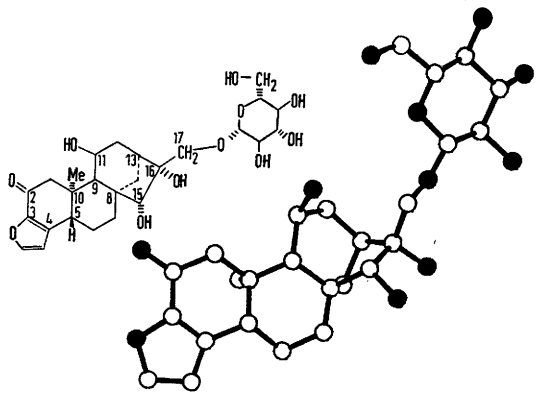
Summary The structure of mascaroside, a bitter glycoside from *Coffea vianneyi*, has been shown by spectroscopic methods and *X*-ray analysis to be a diterpene, of the (−)-kaurene type with a β-glucose unit attached to C-17.

MASCAROSIDE is a bitter principle from beans of Malagasy *Coffea vianneyi* Leroy[1] and the first glycoside found in coffee beans to have its structure determined: $C_{26}H_{36}O_{11}$, m.p. 277—278 °C, $[\alpha]_{578}$ −187° (H_2O). Extended hydrolysis provides glucose. A 2-furylcarbonyl group is present [λ_{max} 278 nm (log ε 4·13); ν_{max} 1650 cm^{-1}; δ 6·40 and 7·68 (AB, J 1·5 Hz)]. Two acetylatable hydroxy-groups, and one tertiary hydroxy-group are present, as shown by the mass spectrum of hexa-acetylmascaroside, $C_{38}H_{48}O_{17}$ [*m/e* 776 (M^+) and 758 ($M^+ - H_2O$)]. The structure was determined by *X*-ray crystallography.

Crystals of mascaroside were obtained by slow evaporation of a methanolic solution. The crystals are monoclinic, space group $P2_1$, with cell dimensions: a = 11·752, b = 7·704, c = 16·605 Å, β = 106·68° and Z = 2. 2823 reflexions were collected on a Philips automatic diffractometer and the structure was solved by direct methods.[2] The final R value is 0·06.

The molecule (Figure) is composed of a diterpene and a sugar unit. The diterpene portion is somewhat analogous to cafestol,[3] a (−)-kaurene-type diterpene, with the furan ring connected to C-3 and C-4, a *trans* C-5–C-10 junction, a cyclopentane unit attached to C-8 and C-13, and a 9–10 *anti* configuration.[4] However, it differs in the presence of a ketone group at C-2 and two hydroxy-groups at C-11 and C-15. The β-glucose sugar residue is attached to C-17.



FIGURE

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