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Molecular Formula and Identity of β–Guttiferin and α–Gambogic Acid

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Despite possible identity of β-guttiferin (I) with α-gambogic acid (II),[1] the molecular formula, $C_{29}H_{34}O_6$, proposed by Amorosa and Lipparini[2] for the latter seemed unlikely from its reactions. That akin to morellin[3] and α-guttiferin, (I) should be represented by $C_{33}H_{36\text{-}38}O_7$ follows from the crystallographic data of β-guttiferin-pyridine complex (III) and of the *dimethyl ether* (IV), m.p. 125–126°, prepared from (I) by exhaustive methylation (by methyl iodide in acetone solution in presence of potassium carbonate for 60 hours).

Apart from compounds (III) and (IV), the other derivatives of (I) did not appear satisfactory for crystallographic purposes. The analytical data of (IV) [(Found: C, 71·8, 71·9; H, 7·7, 7·4; OMe, 9·1. $C_{38}H_{48}O_8$ requires C, 72·14; H, 7·65; OMe, 9·81; $C_{38}H_{46}O_8$ requires C, 72·38; H, 7·35; OMe, 9·84%); $\lambda_{max.}^{MeOH}$ 280 mμ (log K=1·587) and 355 mμ (log K= 1·258); monoclinic symmetry; space group $P2_1$ or $P2_1/m$; unit cell dimensions: $a = 7{\cdot}91 \pm 0{\cdot}02$ A (rotation photograph), $b = 17{\cdot}04 \pm 0{\cdot}02$ A and $c \sin \beta = 13{\cdot}23 \pm 0{\cdot}01$ A (Weissenberg photographs); $\beta = 104 \pm 2°$ and $c = 13{\cdot}69 \pm 0{\cdot}15$A); volume of the unit cell (V) = 1783 ± 8 A^3; $d_{meas.} = 1{\cdot}206 \pm 0{\cdot}02$ g. cm.$^{-3}$; number of molecules per unit cell (n) = 2 and found M.W. 646 ± 18 ($d_{calc.} = 1{\cdot}179$ g. cm.$^{-3}$)] indicate $C_{38}H_{46\text{-}48}O_8$ (M.W. 630·76 + 2) which is, however, incompatible with the assumption of a straightforward methylation of (I) to (IV) since the corresponding formula $C_{36}H_{42\text{-}44}O_8$ for (I) is excluded on analytical grounds. While an addition of a molecule of acetone during the methylation as in the case of pristimerin[4] [*cf.*, satd. aliphatic C=O band 1725 cm.$^{-1}$ in the infrared-spectrum of (III)] is thereby suggested, the uncertainty of the course of this reaction renders the observed molecular weight of (IV) of dubious value in settling the issue of molecular formula of (I). Nonetheless, it excludes $C_{29}H_{34}O_6$.

On the other hand, the formula $C_{33}H_{36\text{-}38}O_7$ is supported by crystallographic data of the pyridine complex (III); unit cell dimensions: $a = 22{\cdot}23 \pm 0{\cdot}02$ A, $b = 18{\cdot}50 \pm 0{\cdot}02$ A, $c = 9{\cdot}61 \pm 0{\cdot}02$ A; V = 3954 ± 16 A^3; $d_{meas.} = 1{\cdot}196 \pm 0{\cdot}02$ g. cm.$^{-3}$; orthorhombic symmetry; number of molecules per unit cell (n) = 4 and found M.W. 712 ± 10; ($d_{calc.} = 1{\cdot}184$ g. cm.^{3}); $C_{33}H_{36\text{-}38}O_7{\cdot}2C_5H_5N$, (M.W. 702·8 + 2). Compound (III) crystallises from methanol-pyridine mixture with two molecules of pyridine, one of which is very labile and lost on drying. The dried material thus analyses for $C_{33}H_{36\text{-}38}O_7{\cdot}C_5H_5N$. The postulate of Amorosa and Lipparini[2] as to the presence of a free carboxylic moiety in (II) could not be substantiated by examination of preparations from gamboge of diverse origin, thus justifying the assumption of identity of (I) and (II). Further, identity of (II) with any of the free organic acids[5] of the guttiferin series occurring in *Garcinia morella* is excluded since they do not form the characteristic pyridine complex (III).

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