l'ouverture du cycle C de II se produit, comme dans III et IV, selon un mécanisme de type retro-Diels–Alder. La double liaison de II ne peut donc se trouver que dans le cycle D. D'autre part, la faible intensité du fragment à *m/e*: 208 dans le SM de II par rapport aux spectres de III et IV, suggère que la double liaison n'est pas en $\Delta^{(3-14)}$ car cette position, favorisant un clivage allylique, augmenterait l'intensité relative de ce pic. D'autre part, cette structure énamine devrait laisser prévoir une réduction facile de II par les borohydrures de sodium ou de potassium qui n'est pas observée. La double liaison de II doit donc être placée en Δ^{14-15}.

Plusieurs alcaloïdes à squelette éburnane et possédant une double liaison en Δ^{14}, comme dans la tabersonine dont ils doivent biogénétiquement dériver, ont déjà été rencontrés.[7,8]

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FLAVONOLS AND OTHER COMPONENTS OF THE LEAVES OF *CALYCOPTERIS FLORIBUNDA*

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Plant. Calycopteris floribunda (N.O. Combretaceae). *Uses.* Leaves as anthelmintic and in cholic and dyspepsia. Juice from young twigs for diarrhoea and dysentry. Fruits in jaundice.

Previous work. Calycopterin (5,4'-dihydroxy-3,6,7,8-tetramethoxyflavone) was isolated,[1] its constitution established[2,3] and it was synthesized.[4] Recently Mabry *et al.*[5] felt that there was some ambiguity about the free 5-hydroxyl and therefore confirmed the structure by NMR, UV and MS data, although the presence of this 5-hydroxyl had been earlier proved by ethylation[3] experiments and by synthesis.[4]

Present work. Air-dried leaves (0·5 kg) were obtained from Kerala State, India. (a) Light petrol. (b.p. 60–80°) extract when chromatographed on silica gel column yielded n-*octacosanol* (0·005%), m.p. 82–83° and confirmed by comparison with an authentic sample (m.m.p., TLC and IR); *sitosterol* (0·020%), flakes from $CHCl_3$–MeOH, m.p.

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135–137°, $[\alpha]_D$ −32·5°, acetate m.p. 132–133°, $[\alpha]_D$ −40·3° in $CHCl_3$ and identity confirmed by comparison with an authentic sample. (b) C_6H_6 *extract. 4′-O-Methylcalycopterin* (5-hydroxy-3,6,7,8,4′-pentamethoxyflavone) (0·003%), earlier known in Citrus aurantium[6] and synthetically,[2] brownish yellow needles from MeOH, m.p. 122–123°, green ferric reaction, positive Mg–HCl test; spectral data are in agreement with the structure. UV: λ_{max} (MeOH): 276, 334 nm; λ_{max} (MeOH–$AlCl_3$): 290, 310, 357, 415 (sh) nm; λ_{max} (MeOH–$AlCl_3$–HCl): 238 (sh), 286, 307, 355, 415 (sh) nm; λ_{max} (NaOAc–MeOH); 280, 330 nm; λ_{max} (MeOH–NaOAc–boric acid): 276, 330 nm; λ_{max} (MeOH–NaOMe); 296, 400 nm. NMR signals (δ values) (solvent $CDCl_3$): 3·90–4·13 (m) for 5 methoxyls, 7·1 (*d*, *J* 9Hz) for H-3′ and 5′, 8·23 (*d*, *J* 9Hz) for H-2′ and 6′ and 10·36 (s) for a hydrogen bonded 5-OH proton. The identity was further confirmed by comparison with an authentic sample. *Calycopterin* (0·03%), bright yellow needles from MeOH, m.p. 225–226°, green ferric reaction, positive Mg–HCl test; the diacetate, colourless plates from EtOH, m.p. 126–127°; NMR signals, (δ values) (solvent $CDCl_3$): 3·85–4·11 (4*s*) for 4 methoxyl groups, 2·36 (*s*) for 4′-O.CO.Me protons, 2·52 (*s*) for 5-O.CO. Me protons, 7·25 (*d*, *J* 9Hz) for H-3′ and 5′, 8·17 (*d*, *J* 9Hz) for H-2′ and 6′. These fully agree with its structure; earlier, Mabry *et al.*[5] recorded NMR of the trimethylsilyl ether. (c) *Acetone extract.* The concentrated extract deposited a polymeric proanthocyanidin (0·25%). The mother liquor yielded sitosterol (0·005%) and calycopterin (0·01%). (d) *EtOH extract.* The concentrated extract deposited an inorganic material. The mother liquor after dilution with water was extracted with ether and ethyl acetate. Ether soluble portion: *Ellagic acid* as sparingly soluble solid, crystallized as pale yellow needles (0·005%) from aqueous pyridine, m.p. > 300°, bluish green ferric reaction, blood-red colour in Griessmeyer's test. It was confirmed by direct comparison with an authentic sample. *Quercetin* (0·005%), m.p. > 300°, green ferric reaction, crimson red with Mg–HCl; confirmed by direct comparison. The ethyl acetate soluble part: proanthocyanidin, converted into cyanidin chloride, R_f: (HOAc–HCl–H_2O, 30:3:10) 0·5; R_f: (HCOOH–HCl–H_2O, 5:2:3) 0·2 on Whatman No. 1 paper; visible λ_{max} (MeOH–HCl); 535 nm.

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