

(c) 4,4', 6,6'-Tetramethoxy-2,2'-dihydroxy-3,3'-di(ω -benzoylacetyl)-biphenyl

A mixture of 4,4', 6,6'-tetramethoxy-2,2'-dibenzoyloxy-3,3'-diacetyl biphenyl (5 g), acetone (200 ml) and potassium carbonate (50 g) was refluxed on a water bath for 30 hr. Acetone was removed by distillation on water bath. The residue was added to water. The precipitated 4,4', 6,6'-tetramethoxy-2,2'-dihydroxy-3,3'-di(ω -benzoylacetyl)-biphenyl was filtered and recrystallised from dilute alcohol as yellow needles, m.p. 178°–179° (found: C, 67.86; H, 4.95; $C_{34}H_{30}O_{10}$ requires C, 68.23; H, 5.017%).

(d) I-5, II-5, I-7, II-7-Tetramethoxy [I-8, II-8] biflavone

4,4', 6,6'-tetramethoxy-2,2'-dihydroxy-3,3'-di(ω -benzoylacetyl)-biphenyl (2 g) was dissolved in concentrated sulphuric acid (20 ml) and kept at room temperature. After 8 hr the solution was poured into water. The precipitated biflavone was filtered and recrystallised from dilute alcohol as yellow needles, m.p. 203°–204°, λ_{max} in ethanol at 270 and 310 nm. (Found: C, 72.35; H, 4.55; OMe, 21.2; Mol. wt. (Mass spectrometry), 562; $C_{34}H_{28}O_8$ requires C, 72.61; H, 4.63; OMe, 22.07%; Mol. wt., 562).

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Chemical Investigation of *Canthium diococcum*

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THE benzene extract of the bark of the plant *Canthium diococcum* after column chromatography yielded a number of terpenoids. One of these compounds, $C_{30}H_{50}O$, m.p. 185°–86°, formed

an acetate, $C_{32}H_{52}O_2$, m.p. 225°, and these have been characterized as α -amyrin and its acetate respectively by comparison of m.p., TLC and IR spectra with authentic samples. The alcoholic extract of the bark yielded a saponin which on acid hydrolysis gave an acid, $C_{30}H_{48}O_3$, m.p. 306°–8°, which formed a methyl ester, $C_{31}H_{50}O_3$, m.p. 196°–8°. These have been characterized as oleanolic acid and methyl oleanolate respectively by comparison of m.p., TLC and IR spectra with authentic samples.

Experimental

Air-dried powdered bark (1 kg) was extracted successively with benzene and ethanol (95%) for 48 hr in a Soxhlet apparatus. The benzene extract was separated into acid and neutral fractions in the usual way and the latter was subjected to column chromatography over silica gel (200 g) and eluted with different solvents. Benzene eluate gave a fraction which was crystallized from ethanol, $C_{30}H_{50}O$, m.p. 185°–86°. It was heated with acetic anhydride and pyridine on steam bath and worked up in the usual way. Crystallization from ethanol gave an acetate, $C_{32}H_{52}O_2$, m.p. 225°.

The ethanolic extract was concentrated by distillation and the crude saponin was precipitated by addition of excess ether. The crude saponin gave copious lather when shaken with water. It was dissolved in ethanol (200 ml) and 40 ml of conc. hydrochloric acid was added and refluxed on steam bath for an hour. This was then diluted with water and the precipitated sapogenin was extracted with ether which was separated into acid and neutral fractions in the usual way with 1% aqueous caustic potash solution. The acid fraction was chromatographed over silica gel and the $CHCl_3/MeOH$ (95:5 v/v) eluate gave a fraction which crystallized from methanol, $C_{31}H_{50}O_3$, m.p. 196°–8°.

Satisfactory analytical data were obtained for the compounds reported.

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Triterpenoids. XLII. Further Studies on the Structure of Lantanolic Acid

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BARUA and co-workers earlier^{1,2} proposed the structure (I) for lantanolic acid, a new triterpene

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acid isolated from the leaves of *Lantana camara*. Lantanolic acid was converted to 3-deoxy methyl oleanolate. The potential keto group in lantanolic acid was considered to be at C-3 because the keto-aldehyde (III)² obtained by oxidation of the diol gave positive Zimmermann colour test³. But the possibility of the keto group being at C-2 cannot be completely overruled on this basis only and another alternative structure (II) had to be considered for lantanolic acid. Investigation has been carried out to decide finally between the two structures (I) and (II) and the result is presented here.

The keto aldehyde (III), prepared according to the method of Barua *et al.*² on refluxing with ethylene glycol and *p*-toluene sulphonic acid in benzene in the usual way furnished a monoketal (IV), C₃₃H₅₀O₅, m.p. 204°-6°, (M⁺, 526). The keto-aldehyde (III) gave positive Zimmermann colour reaction but the monoketal (IV) did not give any Zimmermann colour reaction. This indicated that the keto group and not the aldehyde group was blocked by ketalization. Wolff-Kishner reduction of the monoketal (IV) under anhydrous condition⁴ followed by esterification with diazomethane furnished (V), C₃₃H₅₂O₄, m.p. 220°-24°, which on refluxing with ethanolic hydrochloric acid yielded (VI), C₃₁H₄₈O₃, m.p. 184°-85°.

The compounds (V) and (VI) were found to be identical with the ketal of 3-keto methyl oleanolate and 3-keto methyl oleanolate respectively by comparison of m.p., mixed m.p., tlc and IR spectra. 3-Keto methyl oleanolate (VI) and its ketal (V) were prepared from methyl oleanolate in the usual way.

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