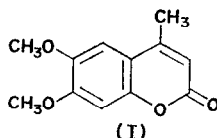


(M^+ 220), m.p. 196–197° (MeOH), is in accord with the proposed structure. In the IR (KBr) it presents the typical absorptions of coumarins at 1715, 1600 and 815 cm^{-1} , and in the UV (EtOH) at λ_{max} 235, 290 and 314 nm. The NMR spectrum shows singlets at 3.24 τ (2H, $W_{\frac{1}{2}}$ = 6 Hz; aromatic protons), 4.36 (1H; H-C₃), 6.02 and 6.12 (3H each; MeO-C₆, MeO-C₇) and at 7.35 τ (3H; Me-C₄). The position of the signals for the aromatic protons and the methoxyl groups agrees with that of the 6,7-dimethoxy-coumarins.⁴ On the other



hand, the peaks which correspond to the H-C₃ and Me-C₄ are similar to those found for 8-methoxy-4-methyl-coumarin.⁵ The MS, besides the molecular ion at m/e 220, has prominent peaks at m/e 205 (M^+ -Me), 192 (M^+ -CO), 177 (M^+ -Me-CO), 162 (M^+ -2 Me-CO), 149 (M^+ -Me-2 CO), 134 (M^+ -2 Me-2 CO) and 106 (M^+ -2 Me-3 CO).

From the same species we also isolated a lignan of m.p. 121–123° (MeOH), $[\alpha]_D +72^\circ$ (CHCl_3), NMR spectrum (CDCl_3): 3.08 τ (d, 6H; aromatic protons), 4.00 (s, 4H; 2 —OCH₂O—), 5.20 [d, 2H, J = 5 Hz; 2 —OCH(Ar)—CH<], 5.80 and 6.15 (each dd and 2H; 2 >CH—CH₂—O), and 6.90 τ (m, 2H; >CH—CH<), which by its physical and spectroscopic data was identified as (+)-sesamin.⁶ To our knowledge, *Sideritis canariensis* Ait. is the first Labiata from which a lignan has been isolated; moreover, the presence of coumarins is very rare in this family.

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⁵ C. W. L. BEVAN and D. E. U. EKONG, *Chem. & Ind.* 383 (1965).

⁶ W. KARRER, *Konstitution und Vorkommen der organischen Pflanzenstoffe*, p. 463, Birkhäuser Verlag, Basel (1958).

Key Word Index—*Sideritis canariensis*; Labiatae; coumarin; 6,7-dimethoxy-4-methylcoumarin; lignan; sesamin.

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LECYTHIDACEAE

STEROLS FROM *CAREYA ARBOREA*

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Plant. *Careya arborea* Roxb. **Uses.** Medicinal.¹ **Previous work.** On seeds,^{2,3} stem bark⁴ and leaves.⁵

¹ Council of Scientific & Industrial Research, in *The Wealth of India*, Vol. II, p. 76, Delhi (1950).

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³ J. GEDEON and F. A. KINCL, *Arch. Pharm.* **290**, 578 (1957).

⁴ L. R. ROW and C. S. P. SASTRY, *Indian J. Chem.* **2**, 510 (1964).

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Seeds. Preliminary chemical tests revealed the presence of saponin in the seeds. The seeds were successively extracted with light petroleum, CHCl_3 and EtOH. The EtOH extract was found to contain saponin. The crude saponin was hydrolysed with 5% ethanolic HCl and the acid hydrolysate on subsequent purification by chromatography yielded a number of polyhydroxy triterpenoid sapogenols. The report on the constitution of these compounds will be communicated later. The light petroleum extract on purification by chromatography over alumina was separated into two fractions: (i) The light petroleum–benzene (1:1) eluate on further chromatography followed by crystallization from acetone–MeOH mixture afforded α -spinasterol (m.p., m.m.p., $[\alpha]_D$; m.p., m.m.p. and $[\alpha]_D$ of acetate); (ii) The light petroleum eluate was purified by further chromatography and was crystallized from acetone when α -spinasterone was obtained as needles, m.p. 165–166°, $[\alpha]_D +24.7^\circ$ (CHCl_3). It could be reduced to α -spinasterol by NaBH_4 . The compound showed IR (Nujol) absorption bands at 1715 cm^{-1} (6-membered ring ketone), $1670, 845\text{ cm}^{-1}$ (trisubstituted double bond at $\text{C}_7\text{--C}_8$), 970 cm^{-1} (*trans* disubstituted double bond at $\text{C}_{22}\text{--C}_{23}$). The NMR spectrum (CDCl_3) showed a multiplet centred at $\delta\ 2.3$ (4H) which may be attributed to the protons α to the carbonyl group. The methyl signals appeared between $\delta\ 0.61$ and 1.12 . The C_{18} -methyl appeared at $\delta\ 0.61$ and that C_{19} methyl appeared at $\delta\ 1.04$. The multiplet centred at $\delta\ 5.2$ correspond to the three olefinic protons. The mass spectrum showed the molecular ion peak at $m/e\ 410$ (100%). The other major peaks were at $m/e\ 367$ (M^+ -isopropyl fragment, i.e. mass 43, 58.9%), 298 ($\text{M}^+\text{--C}_8\text{H}_{16}$, i.e. cleavage at $\text{C}_{21}\text{--C}_{22}$ bond⁶ and one H, 57%), 271 ($\text{M}^+\text{--C}_{10}$ side chain, 69%), 269 (M^+ -side chain and 2 H, 87%), 244 (11.5%) and 229 (M^+ -side chain and 42 mass units, 11%).

The isolation of α -spinasterone from a natural source (*Samanea saman*) has very recently been reported by Mitra *et al.*⁷ Their publication has prompted us to communicate our results. The CHCl_3 extract on chromatography over alumina yielded α -spinasterol (m.p., m.m.p., IR and co-TLC) and Δ^{22} -stigmastanol (m.p., m.m.p., MS, IR).

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⁶ S. G. WYLLIE and C. DJERASSI, *J. Org. Chem.* **33**, 305 (1968).

⁷ S. K. NIGAM, G. MISRA and C. R. MITRA, *Phytochem.* **10**, 1954 (1971).

Key Word Index—*Careya arborea*; Lecythidaceae; sterols; α -spinasterol; α -spinasterone.