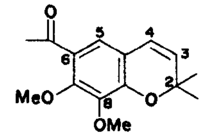
residue was chromatographed on Si gel. From the eluate with C_6H_6:EtOAc (100:3), there was obtained an oily compound (**1**) (0·3 g), ν_{max} 1660 cm^{-1} and no OH absorption ($CHCl_3$), λ_{max} 255 nm (inflexion 287 nm) (EtOH), MS M^+ 262 ($C_{15}H_{18}O_4$), which was proved to be homogeneous by GLC and TLC and formed a red 2,4-dinitrophenylhydrazone, mp 139–140°. PMR signals of I (100 MHz, $CDCl_3$, ppm from TMS) δ 1·49 (6H *s*, 2× Me), 2·56 (3H *s*, –CO–Me), 3·86 3·95 (3H *s* each, 2× OMe), 5·56, 6·24 (1H each, a pair of AB type doublets, *J* 10 Hz, *cis* R–CH=CH–R), and 7·16 (1H *s*, aromatic H) as well as the observation of NOE between the following pairs of signals, 1·49:5·56 and 6·24:7·16 (no observation of NOE between the signal at 7·16 and OMe signals) led to the formulation of **1** as 6-acetyl-7,8-dimethoxy-2,2-dimethylchromene which was isolated from *Eupatorium riparium* Regel (Compositae) and named methylripariochromene A [2,3]. This identification was further confirmed by CMR of I (25 MHz, $CDCl_3$, ppm from TMS) δ 28·3 (*q*, 2× Me), 31·1 (*q*, –CO–$\underline{C}H_3$), 60·8, 61·4 (*q* each, 2× OMe), 77·7 (*s*, C-2), 121·6 (*d*, C-4), 122·2 (*d*, C-5), 129·7 (*d*, C-3), 117·7, 124·7, 141·2, 150·8, 154·6 (*s* each, substituted aromatic carbons), and 197·8 (*s*, C=O).

Since *Stevia* is known to be closely related to *Eupatorium*, the present isolation of **1** is significant from the chemotaxonomic point of view. The chromene (**1**) could not be detected however, in the leaves of *Stevia paniculata* Lag., *S. purpurea* Peas., *S. rebaudiana* Bertoni, and *S. ovata* Lag., all of which were grown in this Experimental Station.



(**1**)

EXPERIMENTAL

GLC. Detector: FID. On 1·5% OV-1 2 m 2 mm, isothermal at 160°, injection temp. 200°. N_2: 1·2 kg/cm^2. R_t of **1**: 7·4 min. *TLC.* On Si gel. Solvent C_6H_6–AcOEt (6:1).

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SEMMLER'S HYDROCARBON FROM *EUPATORIUM AYAPANA*

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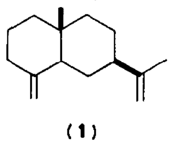
Recent interest in anti-tumor compounds [1, 2] from species of *Eupatorium* coupled with Semmler's report[3] on the isolation of a sesquiterpene hydrocarbon of unknown structure from *E. ayapana* prompted us to investigate this plant in a greater detail. We report here our results on the sesquiterpene hydrocarbon isolated by Semmler in 1908. The hydrocarbon analyzed for $C_{15}H_{24}$, absorbed two moles of hydrogen, and hence must be bicyclic. Its gross carbon skeleton was established by dehydrogenation to eudalene in 40% yield. This, coupled with the spectral data, led us to identify Semmler's hydrocarbon as β-selinene **1**, further confirmed by a comparative MS and GLC studies with an authentic sample prepared by dehydration of β-eudesmol [4].



(**1**)

EXPERIMENTAL

Rotations were determined in $CHCl_3$. NMR were obtained in $CDCl_3$ and MS were measured with a single focus spectrometer using an ionizing energy of 70 eV.

Semmler's hydrocarbon. Column chromatography of the essential oil (73 g) of *E. ayapana* yielded the hydrocarbon (3.1 g), bp 84–86°/0.4 mm, d_4^{26} 0.9089. n_D^{19} 1.5038, $[\alpha]_D^{24}$ +43.65° (neat); IR: 3090, 1645 and 884 cm^{-1}; MS: M^+ peak at *m/e* 204 ($\%\Sigma_{27} = 7.44$); NMR (τ): 9.28 (3H, *s*), 8.25 (3H, *t*, *J* 1.0 Hz), 5.56 (1H, broad singlet), and 5.30 (3H, *d*, *J* 1.0 Hz). (Found: C, 87.99; H, 11.68. $C_{15}H_{24}$ requires: C, 88.16; H, 11.84%). The hydrocarbon gave the crystalline di-HClide, mp 48–52°, $[\alpha]_D^{25}$ −78.70°; MS: M^+ peak at *m/e* 276 ($\%\Sigma_{27} = 0.34$) for $C_{15}H_{26}{}^{35}Cl_2$: this compound decomposed to a dark coloured gum within a few days of preparation, it could, however, be stored for several months at −20°.

Catalytic hydrogenation of Semmler's hydrocarbon in HOAc acid with Adam's catalyst yielding a tetrahydro derivative bp 135° (bath)/5.5 mm, $[\alpha]_D^{25}$ +12.94° (*c*, 0.51); IR and NMR spectra exhibited complete absence of unsaturation in the molecule; (Found: C, 86.19; H, 13.37. $C_{15}H_{28}$ requires: C, 86.46; H, 13.54%).

Dehydrogenation of Semmler's hydrocarbon with selenium powder at 300–320° for 4 hrs under N_2 yielded an oil which was shown by GLC comparison with an authentic sample to be 40% eudalene, which was characterized as its picrate, mp 94–95° (undepressed upon admixture with an authentic specimen).

β-selinene from β-eudesmol. β-Eudesmol was dehydrated with alumina impregnated with 2% pyridine [5] at 190° for 2 hr. The product was purified by chromatography over $AgNO_3$–Si gel, followed by distillation over Na gave β-selinene (**1**) pure by GLC. The IR, NMR, and MS of β-selinene **1** were identical with those of Semmler's hydrocarbon [4]. Their GLC behaviour on Carbowax 4000, SE-30 and APL columns confirmed their identity [4].

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DIACETYLNERIIFOLIN FROM *CERBERA ODOLLAM*

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Key Word Index—*Cerbera odollam*; Appocyanaceae; diacetylneriifolin.

Plant and source. Seed kernels of *Cerbera odollam* Gaertn. which grow wild in salt swamps or on the sea coast, particularly in Kerala State, South India. *Previous work*. Cardiac glycosides: cerebroside (thevetin B) [1–3], acetyl-thevetin B [4], cerberin [2,5], neriifolin [2]. *Uses*. Medicinal, Cardiac poison.

Present work. Fresh seed kernels were ground, extracted with 90% EtOH and the extract concentrated. During concentration, a crystalline solid separated which, on chromatography over Si gel, gave a fraction in $CHCl_3$-MeOH (49:1) mainly consisting of cerberin (2′-monoacetylneriifolin) and a faster moving compound. The fraction was rechromatographed on Si gel when the $CHCl_3$-MeOH (99:1) eluate gave the faster moving compound in pure form, crystallised from MeOH–Et_2O. It was identified as diacetylneriifolin by mp, colour reactions, elemental analysis, UV, IR, MS and direct comparison with diacetylneriifolin prepared from neriifolin.

Comment. The precursor for cerberin in *C. odollam* has been presumed to be acetylthevetin B (diglucomonoacetylneriifolin) as in *Thevetia neriifolia* [4,5]. The occurrence of diacetylneriifolin in fresh seed kernels of *C. odollam* suggests that this compound could also be a precursor of cerberin as it has been observed [6] that of the two acetyl groups attached to the sugar thevetose, the one attached to C_4 is more labile than that attached to C_2. It is possible that either through enzymatic action or change in pH during extraction and working up, the labile acetyl group is lost giving rise to cerberin. Furthermore, to our knowledge, this appears to be the first record of occurrence of a diacetylcardenolide in nature.

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