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PINOCEMBRIN AND (+)-β-EUDESMOL FROM *HYMENOCLEA MONOGYRA* AND *BACCHARIS GLUTINOSA*

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Key Word Index—*Hymenoclea monogyra*; *Baccharis glutinosa*; Compositae; pinocembrin; (+)-β-eudesmol; *Alternalia* fungi; antimicrobial activity.

Pinocembrin (5,7-dihydroxyflavanone) has been obtained from *Hymenoclea monogyra* and *Baccharis glutinosa* and (+)-β-eudesmol also obtained from *H. monogyra*. Pinocembrin has been previously isolated mainly from the family Pinaceae [1]; this is the first report of its isolation from members of the Compositae. (+)-β-Eudesmol has already been obtained from *Eucalyptus* oil [2] and other plants but its isolation from *Hymenoclea monogyra* species has not yet been reported.

Pinocembrin and (+)-β-eudesmol [3] show considerable anti-microbial activity to *Alternalia* fungi.

EXPERIMENTAL

Plants and source. Hymenoclea monogyra Torr and Gray was collected April 10, 1973 by R. Hartmen (No. 1140) near La Paz, Baja California Sur, Mexico and *Baccharis glutinosa* (R. & P.) Pers. was collected by M. D. Whalen (No. 68) October 21, 1974 near Coyame, Chihuahua, Mexico; vouchers of both species are deposited in the University of Texas Herbarium (TX). *H. monogyra.* 200 g dried ground plant material were extracted with $CHCl_3$. Chromatography of the crude extract (6.95 g) on Si gel using a gradient from $CHCl_3$ to 10% MeOH–$CHCl_3$ yielded two components. The first component was (+)-β-eudesmol [$C_{15}H_{26}O$, mp 81°, M^+ 222, $[\alpha]_D^{22.5}$ + 61.5° (*c*, 0.4, $CHCl_3$)] which was identical in all respects with authentic material (mmp, NMR, IR and $[\alpha]_D$) [4]. The second component was pinocembrin (5,7-dihydroxyflavanone) ($C_{15}H_{12}O_4$, mp 193–196° (decomp.), M^+ 256) which was identical in all respects with synthetic material (UV, NMR and MS) [5–8]. *B. glutinosa.* Pinocembrin was also isolated from *B. glutinosa* by chromatography of the $CHCl_3$ crude extract on Si gel using 2% MeOH–$CHCl_3$. The inhibitory values of pinocembrin at 100 ppm to *Alternalia mali*, *A. kikuchiana* and *A. brassicicola* were 57, 47 and 39% and those of (+)-β-eudesmol to the same organisms were 57, 38 and 64%, respectively. The method of testing was as follows: the compound in MeOH was added to a potato sucrose agar medium held at 45–55° to give the desired concentration. After 10 ml of the media was poured into a 9 cm petri dish, 5 mm mycelial discs of each fungus were placed on the agar plate and cultured at 27°. The diameter of mycelial colony was measured after 5 days. The inhibitory values were calculated by comparison with a control.

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METHYLRIPARIOCHROMENE A FROM *STEVIA SERRATA*

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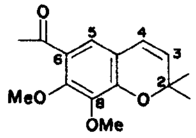
Key Word Index—*Stevia serrata*; Compositae; methyl-ripariochromene A.

Plant. Stevia serrata Cav. *Source.* The seeds supplied by Ente Giadini Botanici Vila Taranto, 28048 Pallanza (Lago Maggiore Italia) (Catalogo dei Semi 1971–1972 No. 2389) were sown in October, 1971 and cultivated at this Experimental Station. The aerial parts were harvested in July, 1973. *Previous work.* Christinine (sesquiterpene lactone) [1].

Present work. The MeOH extract of the dried leaves (10 g) was suspended in H_2O and extracted with Et_2O. The ethereal layer was concentrated to dryness and the 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*, $-CO-C\underline{H}_3$), 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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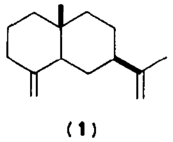
Recent interest in anti-tumor compounds [1, 2] from species of *Eupatorium* coupled with Semmler's report[3] on the isolation of a sesquiterpene hydrocarbon of unknown structure from *E. ayapana* prompted us to investigate this plant in a greater detail. We report here our results on the sesquiterpene 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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