further between hexane and a MeOH-H_2O (4:1) mixture. Evaporation of the MeOH from the MeOH/H_2O fraction and subsequent extraction of the residue with $CHCl_3$ yielded a gummy extract (12.6 g). Purification of this extract by column and preparative tlc on silica gel using an EtOAc/$CHCl_3$ gradient (2-100%) and toluene-EtOAc (4:1), respectively, as eluents afforded hildecarpin (320 mg), *trans*-tephrostachin (53 mg), and *trans*-anhydrotephrostachin (45 mg). The identification of the flavones was based on their physical and spectroscopic data (mp, ^1H and ^{13}C nmr, ms, ir, uv) and by comparison of the data with literature values.

TRANS-ANHYDROTEPHROSTACHIN.—^{13}C nmr δ ppm 18.27 (Me-3″), 55.95, 56.20 (5 and 7-OMe), 91.63 (C-6), 107.69, 108.64 (C-4a, C-8, C-3), 117.06, 117.79 (C-4″, C-1″), 126.16 (C-2′, C-6′), 129.00 (C-3′, C-5′), 131.23, 131.86 (C-4′, C-1′), 136.04, 142.98 (C-3″, C-2″), 159.19 (C-8a), 159.89, 160.84, 161.44 (C-5, C-2, C-7), 178.09 (C-4).

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C-GLYCOSIDES OF *RHYNCHOSIA CANA*

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The *C*-glycosides of the leaves of *Rhynchosia cana* DC. (Leguminosae) are reported here.

EXPERIMENTAL

PLANT MATERIALS.—The leaves of *R. cana* were collected during the winter on 15 January 1985, from Kalyan Dam, Andhra Pradesh, India. The plant was identified by Dr. K.N. Rao, Reader in Botany, S.V.University, Tirupati, India. Vouchers of the plant (RC-IV) are deposited in the Herbarium of the Botany Department, S.V.University, Tirupati, India.

EXTRACTION AND ISOLATION OF PHENOLICS.— Dried leaves of *R. cana* (500 gm) were extracted with Me_2CO and MeOH. Separation of constituents was carried out by preparative tlc (cellulose, 15% aqueous HOAc) and pc (*n*-BuOH-HOAc-H_2O, 4:1:5, upper phase) (1, 2). The compounds obtained were orientin, isoorientin, vitexin, isovitexin, and vicenin-2. All the *C*-glycosides were identified by standard procedures and hydrolytic data as well as by comparison with authentic samples (mmp included) earlier obtained from *Rhynchosia* species (3, 4). The isolation of mono- and di- *C*-glycosides is common with other *Rhynchosia* species except in the case of *Rhynchosia cyanosperma*, in which *C*-glycosides were absent (5, 6).

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METHYL β-ORCINOLCARBOXYLATE AND ATRANOL FROM THE LICHEN *STEREOCAULON VESUVIANUM*

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Extracts of *Stereocaulon vesuvianum* Pers. showed strong activity against *Bacillus subtilis* and *Escherichia coli* and a distinct activity against *Penicillium digitatum* and *Saccharomyces cerevisiae*. By preparative hplc, methyl β-orcinolcarboxylate (strongly antifungal) and atranol (strongly antibacterial) were isolated, and it was shown that both compounds are present as natural products and are not artifacts formed during work-up. Methyl β-orcinolcarboxylate was recently suggested to be present in *S. vesuvianum* by the revision (1) of an isomeric structure previously reported (2) in this species. Sizable amounts of the common cortical depside atranorin (inactive) were also isolated.

EXPERIMENTAL

PLANT MATERIAL.—*S. vesuvianum* was collected on the middle slopes (ca. 1300 m) of Mt. Etna. It grows abundantly only on the ancient (2-3 centuries old) lava flows. A voucher specimen is deposited at the University of Catania.

EXTRACTION AND ISOLATION OF METHYL β-ORCINOLCARBOXYLATE, ATRANOL, AND ATRANORIN.—The air-dried and ground lichen thalli (100 g) were extracted by stirring at room temperature with 500 ml of *n*-hexane. The extract was concentrated in vacuo (49 mg), and it was fractionated by hplc on a Hypersil column 25 cm×3.9 mm i.d. (eluent *n*-heptane-iPrOH, 95:5). Methyl β-orcinolcarboxylate and atranol, in order of elution, were identified by spiking their peaks with authentic materials and by mass spectral comparisons. Thus, the presence of these compounds derives from the plant material, although the yield from this hexane extraction is low due to their limited solubility. These compounds are not artifacts formed during work-up (3) or due to improper extraction solvent (i.e., $CHCl_3$ stabilized with EtOH) that can cause alcoholysis of atranorin, as recently cautioned (1). Atranorin may serve as a storage compound from which the plant slowly produces the other two bioactive compounds to protect itself from attack by pathogenic microorganisms.

A similar extraction of 100 g of the lichen in CH_2Cl_2, stabilized with amylene, yielded a residue (807 mg) that, after washing with *n*-hexane, was identified as atranorin (0.56% yield). Methyl β-orcinolcarboxylate and atranol were also obtained in the hexane washing. All compounds were identified by direct comparison (hplc, ms, ^1H nmr) with authentic samples.

To isolate atranol, 500 g of *S. vesuvianum* were extracted with H_2O by heating at 120° at 1.2 kg/cm^2 in a sterilizing autoclave for 30 min. The obtained aqueous suspension was filtered and partitioned with $CHCl_3$. The $CHCl_3$ concentrate (0.907 g) was stirred with CH_2Cl_2-*n*-hexane (2:1). Preparative hplc of the dissolved material (0.481 g) on a Magnum Partisil column 25 cm× 9 mm id (eluent *n*-hexane-*t*-butylmethylether, 75:25) gave, besides methyl β-orcinolcarboxylate (105 mg), atranol (60 mg) which was identified by comparison of the mp and ir spectrum with those reported in the literature (4, 5).