

HELIANGOLIDES FROM *STEVIA ORIGANOIDES*¹

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In continuation of our chemical investigations of Mexican *Stevia* species (1-3), we report the isolation and identification of three sesquiterpene lactones of the heliangolide type from the aerial parts of *Stevia origanoides* H.B.K. (Compositae, tribe Eupatorieae). They have been identified as eucannabinolide, hiyodorilactone F, and eucannabinolide-19-*O*-acetate. The structures and stereochemistry were determined by comparison of spectroscopic data with literature values (4-7) and partial hydrolysis of eucannabinolide. To our knowledge, from 29 *Stevia* species studied chemically, heliangolides have been isolated only from *Stevia monardaefolia* (2).

Hiyodorilactone F has previously been isolated from *Eupatorium sachalinense* (5), but the ¹H-nmr data were incompletely published; later the isolation of eucannabinolide-20-*O*-acetate from *Disynaphia multicrenulata* (6) was reported. An examination of the ¹H-nmr data reported in Bohlmann *et al.* (6) with those of our hiyodorilactone F clearly showed their identity, but the assignments for H-3 α and H-6 were interchanged. Therefore, there is no doubt in our minds that hiyodorilactone F and eucannabinolide-20-*O*-acetate are identical.

Recently these three heliangolides were also isolated from *Isocarpus oppositifolia* var. *achyrantes* (7). This finding may be of chemotaxonomic value, since *Isocarpus* has been placed both in the Eupatorieae (8) and the Heliantheae tribes (9).

EXPERIMENTAL

PLANT MATERIAL.—*S. origanoides* was collected in México City at Ciudad Universitaria on November 1979. A voucher specimen Calderón-30 is deposited in the Herbarium of the Instituto de Biología, UNAM, México.

EXTRACTION AND ISOLATION.—The air-dried leaves and flowers (1.41 kg) were extracted with petroleum-ether and CHCl₃. The CHCl₃ extract (60 g) was column chromatographed on Si gel (400 g) using CHCl₃ and CHCl₃/Me₂CO as eluents. Fractions eluted with CHCl₃-Me₂CO (9:1) were combined (5.56 g) and rechromatographed on Si gel and further purified by tlc to give hiyodorilactone F, colorless oil: $[\alpha]^{25}_D = -111.3$ (c 2.5, CHCl₃) [lit. (5) $[\alpha]^{25}_D = -141$ (c 0.21, EtOH)], ir, and ¹H-nmr data identical to those previously published (5,6) and eucannabinolide-19-*O*-acetate: ir, eims, and ¹H-nmr data identical with literature values (7,10). Fractions eluted with CHCl₃-Me₂CO (3:2) were rechromatographed on Si gel. Further purification of the fractions from the above column by tlc afforded eucannabinolide whose ir, eims, ¹H-nmr, and optical rotation data were identical with those published in the literature (4,10).

Full details of the isolation and identification are available from the authors on request.

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