

**(+)-OXOTURKIYENINE: AN ISOQUINOLINE-DERIVED ALKALOID
FROM *HYPECOUM PENDULUM***

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*Department of Pharmacognosy, Faculty of Pharmacy, Ege University, Bornova, Izmir, Turkey*ABSTRACT.—(+)-Oxoturkiyenine [**2**], a more highly oxygenated analogue of the known (+)-turkiyenine [**1**], has been found in *Hypecoum pendulum*.

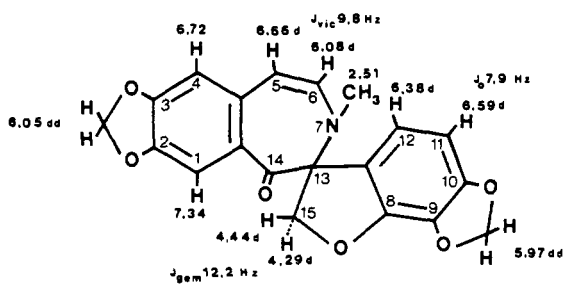
The plant genus *Hypecoum* (Papaveraceae) is represented by 15 species distributed from the Mediterranean to northern China (1). So far, fewer than half of these species have been investigated for their chemical content. Sufficient data have been gathered, however, to establish the presence of isoquinoline alkaloids as major components, particularly that of protopine (2-14), along with a variety of secondary constituents (15, 16).

In the course of our research on the Papaveraceae of Turkey, a number of *Hypecoum* species were subjected to phytochemical investigation. One of these, *Hypecoum procumbens* L., yielded two new alkaloids, (-)-corydalisol (9) and (+)-turkiyenine [**1**], the latter being the first example of a new skeleton among the isoquinoline-derived alkaloids (11).

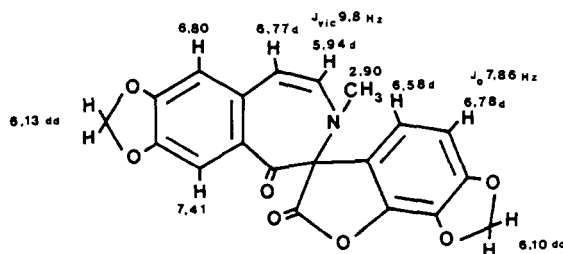
Presently, in continuation of our work on *Hypecoum* species, an investigation of *Hypecoum pendulum* L. has afforded, in addition to (+)-turkiyenine [**1**], the closely related base (+)-oxoturkiyenine [**2**].

(+)-Oxoturkiyenine [**2**], $C_{20}H_{13}NO_7$, was obtained as an amorphous white powder. The molecular composition indicated one oxygen atom more and two hydrogens less than in (+)-turkiyenine [**1**].

The 200-MHz nmr spectrum in $CDCl_3$, as summarized around expression **2**, immediately suggested the presence of the turkiyenine nucleus. In particular, the characteristic absorptions of two adjacent vinylic protons were in evidence, the first at δ 5.94



1



2

and the second at 6.77, each as a doublet with $J_{vic} = 9.8$ Hz. The other signals also resembled those for **1** but with a tendency toward a downfield shift of 0.1–0.2 ppm. Very significantly, the two one-proton doublets at δ 4.29 and 4.44 representing the C-15 methylene hydrogens in the spectrum of (+)-turkiyenine [**1**] were absent in the spectrum of (+)-oxoturkiyenine [**2**]. This feature suggested that in (+)-oxoturkiyenine [**2**] the two hydrogens in question had been replaced by an oxygen atom as part of a γ -lactone. Another telling feature of the spectrum of (+)-oxoturkiyenine [**2**] was the downfield chemical shift of the *N*-methyl singlet at δ 2.90, due in part to the presence of the extra carbonyl at C-15. The corresponding *N*-methyl absorption in (+)-turkiyenine [**1**] falls at δ 2.51.

As expected, the ir spectrum of (+)-oxoturkiyenine [**2**], obtained in CHCl_3 solution, displayed two strong and distinct carbonyl bands, one at 1730 cm^{-1} for the γ -lactone carbonyl and the other at 1695 cm^{-1} due to the conjugated ketone.

The mass spectrum of (+)-oxoturkiyenine [**2**] showed a small molecular ion m/z 379 (0.4%) and a base peak m/z 363 formed by loss of oxygen from the molecular ion. This pattern is reminiscent of that encountered in the spectrum of (+)-turkiyenine [**1**].

The uv spectrum of (+)-oxoturkiyenine [**2**] showed maxima at 217 and 259 nm. A closely related pattern had been observed in the case of (+)-turkiyenine [**1**].

It is quite likely that (+)-oxoturkiyenine [**2**] results from the *in vivo* enzymatic oxidation of (+)-turkiyenine [**1**].

EXPERIMENTAL

PLANT MATERIAL.—*H. pendulum* (8 kg dry wt) was collected on April 26, 1985, at the intersection of the state highway from Kula to Usak and the village road to Kisikkoy, Turkey. A voucher specimen, No. 926, was deposited in the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Ege University.

ISOLATION.—The powdered plant material was extracted with EtOH at room temperature to afford 1.1 kg of crude extract. This material was extracted with diluted HCl. The acid extracts were basified with NH_4OH and extracted into CHCl_3 . Evaporation of the organic solvent supplied the crude alkaloids (25 g). These were fractionated on a Si gel column (Si gel 60, 70–230 mesh). Elution was with CHCl_3 gradually enriched with MeOH. Final purification was by tlc on Si gel and provided (+)-turkiyenine [**1**], 14 mg, and (+)-oxoturkiyenine [**2**], 7 mg. A substantial quantity of protopine (13 g) was also obtained.

(+)-OXOTURKIYENINE [2].— $[\alpha]_D^{+75}$ ($c = 0.08$, CHCl_3), $[\alpha]_D^{+38}$ ($c = 0.11$, MeOH); uv λ max (MeOH) 217, 254 sh, 259, 308 nm ($\log \epsilon$ 4.37, 4.25, 4.29, 3.77); ir ν max (CHCl_3) 3005, 2920, 2355, 1730, 1690, 1640, 1600, 1510, 1495, 1465, 1415, 1355, 1210, 1175, 1020, 905 cm^{-1} ; ms m/z $[M]^+$ 379 (0.4), 378 (0.1), 363 (100), 334 (83), 305 (19), 277 (16), 276 (11).

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