O-METHYLFUMAROPHYCINE

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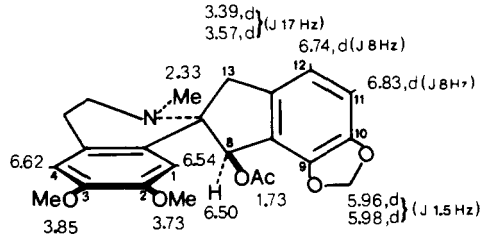
The alkaloid *O*-methylfumarophycine (**1**), which is present in *Fumaria officinalis* L. (Fumariaceae), has been described only briefly in the literature (1). We, therefore, became interested in studying its nmr spectrum at 360 MHz as opposed to an indenobenzazepine—and second, to establish its stereochemistry.

The proton nmr spectrum of *O*-methylfumarophycine has now been outlined around **1** and is in agreement



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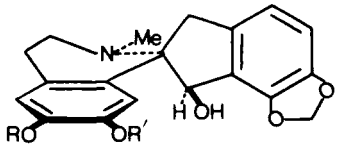
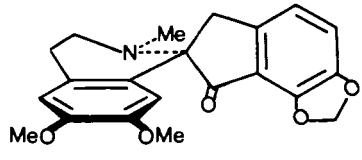


2 R=Me; R′=Me

3 R=Me; R′=H



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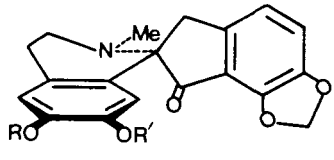

5 R+R′=$-CH_2-$

6 R=Me; R′=H

in deuteriochloroform solution, as well as its other spectral and optical properties. There was first a need to confirm its structure as a spirobenzylisoquinoline—with a spirobenzylisoquinoline structure. In particular, the two geminal hydrogens at C-13 appear as a doublet of doublets at δ 3.39 and 3.57 (J_{gem} 17 Hz). The downfield chemical shift of H-8 at δ 6.50 indicates that this hydrogen is *syn* to the nitrogen as shown, so that

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the alkaloid possesses the relative stereochemistry indicated. The C-2 methoxyl singlet is at δ 3.73, and the C-3 methoxy is further downfield at δ 3.85.

The ir spectrum of the alkaloid shows an ester carbonyl absorption at 1730 cm^{-1} ($CHCl_3$); while the uv spectrum, λ max (MeOH) 208, 232 sh, and 285 nm (log ε 4.79, 4.18, and 3.86) is congruent with a tetrahydroisoquinoline chromophore. The ms includes peaks *m/z* 411 (M^+, $C_{23}H_{25}O_6N$, 12), 368 (M^+-CH_3CO, 100), 351 (17), 338 (12), 336 (17), 322 (3), 206 (11), and 190 (12).

O-Methylfumarophycine (**1**) has a negative specific rotation, $[\alpha]^{22}D-30°$ (c 0.158, MeOH). Fumaricine (**2**), of established absolute configuration (2), also possesses a negative specific rotation, $[\alpha]^{22}D-16°$ (c 0.158, MeOH), suggesting that the two alkaloids possess the identical absolute configuration. This was ascertained by a comparative study of the cd curves in methanolic solution for the triad of alcoholic, or *O*-acetylated, spirobenzylisoquinolines *O*-methylfumarophycine (**1**), fumaricine (**2**), and fumaritine (**3**). Additionally, because the related ketonic spirobenzylisoquinolines parfumidine (**4**), fumariline (**5**), and parfumine (**6**) were available to us, their cd curves were also obtained. Of these six alkaloids, cd data for only furmaritine (**3**) and parfumine (**6**) had been previously recorded (3); but the present measurements are more detailed and complete. Table 1 summarizes the data collected.

It will be noted first that the curves for all six alkaloids show a positive tail near 212 nm. Both sets of cd curves, *i.e.*, those for alkaloids **1-3** and for **4-6**, display a minimum in the 217-233 nm range, and a maximum between 238 and 242 nm. For the alcoholic, or *O*-acetylated, alkaloids **1-3**, there is found within the 252-262 nm range a minimum at the shorter wave-length, followed immediately by a maximum at the longer wave-length. If the curve is recorded too rapidly, this minimum-maximum may take the shape of an inflection. For ketones **4-6**, however, there is always simply a minimum between 259 and 263 nm.

It would have been desirable at this stage to expand the present study to include the cd curves of other spirobenzylisoquinolines, particularly those originating from *Corydalis* species and bearing two oxygenated substituents on ring C. Unfortunately, most of these spirobenzylisoquinolines were unavailable to us.

A final comment should be made regarding specifically the 200 MHz nmr (ft) spectrum of fumariline (**5**). Careful analysis of the computer data showed that H-12 and H-13 have complex splittings that are undetectable through visual inspection of the spectrum. H-12 (δ 6.90) is not only split by H-11 (δ 7.11, J=8 Hz), but also by the C-13 protons ($J_{12,13}$=1 Hz). H-12 thus appears as a doublet of doublets, rather than as a simple doublet as had been reported previously (4). In turn, the protons at C-13 (δ 3.30 and 3.54) are split by H-12 (J=1 Hz) in addition to the geminal coupling (J=17 Hz). The result is a quartet of

TABLE 1. CD curves for spirobenzylisoquinolines in methanol, $\Delta\epsilon_{nm}$.

O-Methylfumarophycine (**1**) . .	$+5.0_{292}$	-2.9_{275}	-1.1_{261}	-1.3_{255}	$+1.2_{241}$	-7.0_{217}	Positive tail beyond 212 nm
Fumaricine (**2**) .	$+8.2_{290}$	-4.9_{275}	-1.1_{262}	-1.3_{260}	$+3.2_{242}$	-5.5_{225}	"
Fumaritine (**3**) .	$+3.0_{292.5}$	-1.4_{274}	-0.15_{256}	-0.17_{252}	$+1.2_{237.5}$	-1.6_{224}	"
Parfumidine (**4**) .	-2.7_{293}	-2.5_{283}	-8.3_{260}	—	$+1.7_{240}$	-2.0_{227}	"
Fumariline (**5**) .	-4.1_{297}	-3.3_{281}	-9.6_{259}	—	$+1.5_{238}$	$+0.8_{229}$	"
Parfumine (**6**) . .	-2.6_{293}	-2.4_{284}	-7.0_{263}	—	$+0.6_{242}$	-2.1_{235}	"

quartets for the two C-13 protons. The remaining peaks in the spectrum are at δ 2.36 (s, 3H, NCH_3), 5.83, and 5.86 (dd, J= 1 Hz, 2H, 2,3-OCH_2O), 6.17 (s, 2H, 9,10-OCH_2O), 6.18 (s, 1H, H-1), and 6.58 (s, 1H, H-4).

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