The Isopavine Structure of Amurensine and Amurensinine

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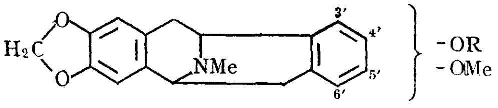
FROM *Papaver alpinum*, *P. tatricum*, *P. pyrenaicum*, *P. suaveolens*, and some varieties of *P. nudicaule*, the alkaloids amurensine $C_{19}H_{19}NO_4$ (I) and amurensinine $C_{20}H_{21}NO_4$ (II) were isolated.[1–4] Amurensinine has two methoxyl groups, one methylenedioxy-group, and one *N*-methyl group. By two steps of Hofmann exhaustive methylation it afforded an optically inactive nitrogen-free substance $C_{19}H_{16}O_4$ (m.p. 179—181°). Alkaline permanganate oxidation of amurensine (I) gave hydrastic acid which was identified as its ethylimide (m.p. 164—166°). The n.m.r. spectrum (60 Mc./sec.) of amurensinine revealed two aromatic protons in the *ortho*-position (τ 3·37 and 3·47), two aromatic protons in the *para*-position (τ 3·27), a singlet for the *N*-methyl group (τ7·50), a quartet for the methylenedioxy-group (τ4·17; 4·15; 4·10; 4·07), and unresolved signals for six further protons (τ6·25—7·45). The n.m.r. signal of amurensinine (II) shows two methoxyls (τ6·14 and 6·22) whereas amurensine (I) has only the one (τ 6·14) not shielded by the other part of the molecule. The n.m.r. spectrum (100 Mc./sec.) of amurensininebismethine gives a singlet of the terminal methylene group (τ 4·84) and a singlet of the methylenedioxy-group (τ 4·09).

The ultraviolet spectra of *N*-methylamurensininemethine and amurensininebismethine are similar to those of the substituted 1-methyl- and 1-methylene-2,3,6,7-dibenzocycloheptatriene, respectively. The latter two substances were obtained by Battersby *et al.*[5–6] from Hofmann exhaustive methylation of isopavine which they also synthesised. The ultraviolet spectrum of amurensininebismethine does not correspond to that of the substituted dibenzocyclo-octatetraene[7] obtained on exhaustive methylation of the pavine alkaloids. The ultraviolet spectrum of amurensinine is also similar to isopavine but not to pavine alkaloids. Amurensininebismethine shows bands at 990 and 910 cm.$^{-1}$ which are attributed to a terminal methylene group.

A comparison of the infrared spectra (in the range 900—800 cm.$^{-1}$) of amurensinine (II) with those of other alkaloids (chelidonine or rhoeadine)[8] indicates that the molecule has one aromatic nucleus substituted at the 1,2,4,5-positions whilst the other is 1,2,3,4-tetrasubstituted. The n.m.r. singlet of the terminal methylene group of amurensininebismethine indicates, however, that the molecule is symmetrical. Since the signals for the two aromatic protons of amurensinine (II) in the *para*-position overlap, it follows that the methylenedioxy-group in the two alkaloids is located on the ring A (these signals differ when the two protons are in non-equivalent positions[9]). Consequently the two methoxyl groups of amurensinine may be placed 3′, 4′; or 4′, 5′; or 5′, 6′ on ring B; one of the first two positions is preferred on biogenetic grounds.

From our results it appears that amurensinine exhibits a shift in its optical rotation depending on the solvents used similar to that of the pavine alkaloid (—)-argemonine,[10] and also a similar o.r.d. curve (first and second Cotton effect negative). On the basis of these results amurensine and amurensinine are assigned the isopavine structure (I) and (II), respectively.



(I) R=H (II) R=Me

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