Tetrahedron Letters No.9, pp. 915-919, 1966. Pergamon Press Ltd.
Printed in Great Britain.

ALKALOIDS OF BUXUS SEMPERVIRENS L. - VI (1) - STRUCTURE OF BUXPSIINE.

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Alcaloïdes stéroïdiques - XLVIII (2)
(Famille des Buxacées ; 6ème communication).
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(Received 28 December 1965)

In a previous communication (1), the structure and absolute configuration of buxtauine and buxpiine, alkaloids extracted from Buxus sempervirens L., were reported. These are steroidal bases of a new type which have a single nitrogen atom, a cyclopropane ring, and a keto group in position 20.

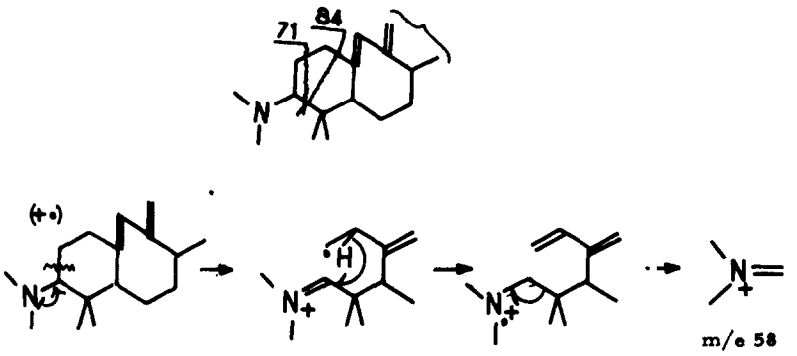
In the present note, we propose a structure for a new alkaloid to which we have given the trivial name buxpsiine (3).

Like buxpiine and buxtauine, buxpsiine I has a carbonyl group in position 20. However, it differs from these two bases by the presence of a conjugated double bond in position 16 and by the absence of a cyclopropane ring. The base has been isolated by chromatography on alumina of a mixture of alkaloids (fraction "C" (4)) originating from B. sempervirens.

Buxpsiine I has the formula $C_{26}H_{39}ON$ (calc. % C 81,83, H 10.36, N 3.67 ; found % C 81.96, H 10.79, N 3.52), molecular weight 381 (8), m.p. 176-178°, $[\alpha]_D^{24}$ + 105° ($CHCl_3$, c = 0,18). The U.V. spectrum has maxima at 240 (log. ε 4.73) and 247mμ (log. ε 4.62), and a shoulder at 255mμ (log. ε 4.43). This spectrum is the sum of the absorptions of two chromophores : a conjugated ketone and a conjugated diene. The ORD curve shows a positive multiple Cotton effect, $[\alpha]_{350}^{25}$ + 1050° corresponding to a conjugated carbonyl group. The I.R. spectrum has the two bands of an αβ-unsaturated ketone at 1612 and 1690 cm^{-1}. Hydroxyl bands are absent. The NMR spectrum has singlets at δ 0.73ppm (6 protons ; two tertiary methyls), δ 1.01ppm (3 protons ; one tertiary methyl), δ 2.26ppm (9 protons ; superimposed signals of the two groups $N(CH_3)_2$ and $COCH_3$), a signal with the appearance of a triplet centred on δ 6.64ppm (olefinic proton at position 16, β to a carbonyl group) ; a narrow signal (Δν at half height 4cps) at δ 5.88ppm (olefinic proton at position 9a) ; and a multiplet centred on δ 5.53 ppm (olefinic proton at position 11).

These data show that buxpsiine I has three double bonds, one conjugated with the carbonyl group, the other two constituting a conjugated diene.

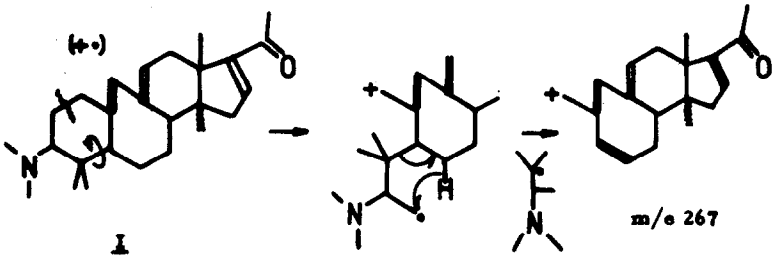
The mass spectrum of buxpsiine I reveals a molecular ion peak at m/e 381 (20% of the base peak). The dimethylamino group at position 3 is responsible for the presence of peaks at m/e 71 (base peak ; 27% Σ_{27}) and m/e 84 (23% of the base peak), whose mechanisms of formation are well known (5), and a peak at m/e 58 (33%) for which the following mechanism of formation is proposed (6) :



It may be noted that the conjugated diene renders more difficult the formation of the ion of mass 84 which is generally very important in the case of 3-dimethylamino steroids. On the other hand, the ion of mass 71 formed by homolytic rupture of the 1,2 bond is favoured. A similar situation is found in the series of Buxaceae alkaloids having a cyclopropane ring in position 9,10 (7).

Also noteworthy is the presence of a peak at m/e 43 (30% of the base peak) representing the ion $CH_3C \equiv O^+$, which comprises carbons 20 and 21, and a peak at m/e 338 (18% of the base peak) corresponding to the complementary ion (M-43) (M+ → M-43, metastable peak at m/e 299.8). The relative importance of this latter peak seems to be characteristic of Δ^{16}-20-oxo-pregnane derivatives (11).

The presence of a peak at m/e 336 (10% of the base peak ; M-45) is also of interest. A metastable peak at m/e 296.3 indicates the transition M+ → M-45. It is accompanied by peaks at m/e 321 (1%) (m/e 336 → m/e 321 metastable peak at 306.6) and m/e 293 (1%) (m/e 336 → m/e 293 metastable peak at 255.5) corresponding to the loss of the radicals. CH_3 and CH_3-$\dot{C}O$ (M-45-15 and M-45-43). The ion M-45 thus represents the loss of a molecule of dimethylamine from the molecular ion. Finally, there is a peak at m/e 267 (4%) which may be interpreted as follows :



The formation of this ion, stabilized by three conjugated double bonds, seems to be due to the presence of the diene and is a good confirmation of the proposed structure.

From these results, it is clear that buxpsiine I has the structure 3β-dimethylamino-4,4',14α-trimethyl-19 nor-B-homo-pregna-9a(10),9(11), 16-trien-20-one. It is a new type of mono-amino steroidal alkaloid of the 19-nor-B-homo series, to which also belong the diamines buxamines or buxegines described by Stauffacher (9) and Kupchan (10).

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