Alkaloids of *Buxus sempervirens* L. VII.* Structure and Configuration of Cyclobuxine-B

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A structure elucidation of a new alkaloid isolated from common Box is described.

So far, there has been published not less than 44 structures of alkaloids isolated from the common Box (*Buxus sempervirens* L.). Now, we wish to report the structure elucidation of another alkaloid of this plant which has been proved to be 3β-dimethylamino-20α-methylamino-4-methylene-14α-methyl-9β,19-cyclo-5α-pregnane-16α-ol (*Ia*).

This alkaloid was isolated from the acetone-insoluble portion of the free bases obtained from the „strong" bases fraction (denoted by the letter „O" [2]) *via* ethanol-insoluble oxalate salts [3]. Benzene—methylene chloride fraction of the column chromatography over alumina (neutral, grade VI [4]) yielded *Ia* in form of colourless prisms, $C_{26}H_{44}N_2O$, m.p. 230—233°C (benzene—methylene chloride 1 : 1), $[\alpha]_D^{24}$ +119° (*c* 1.00, $CHCl_3$), mass spectral molecular ion 400. Its IR spectrum showing bands at 900 and 1655 cm^{-1} (terminal methylene), 1460 and 3032 cm^{-1} (cyclopropane ring), 1040 and 3580 cm^{-1} (secondary hydroxyl), 3310 cm^{-1} (monomethylamino group) and 1280 and 2777 cm^{-1} (dimethylamino group) was resembling that of cyclobuxine-D. The NMR spectrum reveals signals indicating the presence of a cyclopropyl methylene (δ 0.05 and 0.3, 2H, AB doublets, J = 4 cps), two tertiary *C*-methyl groups (δ 0.91, 1.06, 6H), one secondary *C*-methyl group (δ 0.96, 3H, doublet, J = 6 cps), a C-20-*N*-methyl group (δ 2.37, 3H), a C-3-*N*-dimethyl group (δ 2.23, 6H), a secondary hydroxyl group (δ 4.09, 1H, multiplet), and a terminal methylene group (δ 4.65 and 4.95, 2H).

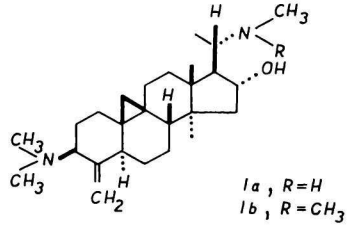

Chart 1

* For Part VI, see [1].

The foregoing data have led us to assume that the new isolated alkaloid should belong to the cyclobuxine type series. A further argument for this assignment was adduced from the mass spectrum. Besides the molecular ion peak a characteristic fragmentation pattern, indicative of the substitution at nitrogen atoms attached to carbon atoms C-3 and C-20, was observed. Thus ions at *m/e* M-15, M-30 and M-58 are due to the methylamino grouping at C-20, whereas those at *m/e* 58 (base peak), 71 and 84 refer to the dimethylamino group at C-3 [5]. Moreover, the physicochemical constants (m.p., $[\alpha]_D$) and NMR data of *Ia* were found to be consonant with those of *N*-methylcyclobuxine-D, prepared earlier by partial methylation of cyclobuxine-D [6].

To confirm this assumption and verify the stereochemistry *N*-methyl derivative $C_{27}H_{46}N_2O$ (*Ib*) was prepared the IR spectrum of which was lacking the band at 3310 cm^{-1}. A new band appeared at 2780 cm^{-1} (dimethylamino group) and the spectrum was found to be superimposable with that of *N,N'*-dimethylcyclobuxine-D prepared earlier in this Laboratory. The mass spectrum of *Ib* exhibited a molecular ion peak at 414 *m/e* and the fragmentation pattern M-15, M-44, M-72 *m/e* (dimethylamino group at C-20) and 58, 71 and 84 *m/e* (dimethylamino group at C-3) [5]. The m.p., R_F and $[\alpha]_D$ of *Ib* were in full accordance with those reported for *N,N'*-dimethylcyclobuxine-D (cf. *e.g.* [7]) and also the mixed m.p. of both alkaloid derivatives showed no depression.

According to convention accepted on the International Symposium in Kyoto [8] a systematic name cyclobuxine-B should be given to this new alkaloid as represented by formula *Ia*.

Apparatuses

Mass spectra were measured with a MCh 1306 spectrometer, infrared spectra were run with a UR-10 Zeiss spectrometer using KBr technique and NMR spectra were taken with a Tesla BS 487-80 MHz apparatus hexamethyldisiloxane being the internal standard.

References

1. Tomko J., Bauerová O., Votický Z., Goutarel R., Longevialle P., *Tetrahedron Lett.* ***1966***, 915.
2. Tomko J., Votický Z., Paulík V., Vassová A., Bauerová O., *Chem. Zvesti* ***18***, 721 (1964).
3. Schlittler E., Heusler K., Friedrich W., *Helv. Chim. Acta* ***32***, 2209 (1949).
4. Heřmánek S., Schwarz V., Čekan Z., *Collect. Czech. Chem. Commun.* ***26***, 3170 (1961).
5. Dolejš L., Hanuš V., Votický Z., Tomko J., *Collect. Czech. Chem. Commun.* ***30***, 2869 (1965).
6. Nakano T., Hasegawa M., *J. Chem. Soc.* ***1965***, 6688.
7. Brown K. S., Jr., Kupchan S. M., *J. Amer. Chem. Soc.* ***86***, 4414 (1964).
8. Brown K. S., Jr., Kupchan S. M., *Tetrahedron Lett.* ***1964***, 2895.

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