chromatography, eluted with methanol. Light yellow oil, $(\alpha)_D$ + 4·5 (in MeOH), i.r. 3350 (OH), 1725 and 1690 (two ester carbonyl), 1380 cm^{-1} (isopropyl group). NMR curve shows five methyl groups at 0·82 δ (3H, d, J=6·5 c/s), at 0·92 δ (3H, d, J=6·5 c/s) (—CH$\langle^{CH_3}_{CH_3}$), at 1·17 δ (3H, d, J=6 c/s) (—CH CH_3), at 1·86 δ (3H, d, J=6 c/s), and at 1·95 δ (3H, s) (CH_3CH=CCH_3—). A sharp singlet at 3·65 δ corresponds to six H_2O and two OH groups as shown by CF_3COOD exchange (the water molecules probably came from solvent), vinylic protons are at 6·9 δ (1H, q) and 5·8 δ (1H, s), other protons are at 5·1; 4·6 and 4·2 δ. NMR spectrum of this alkaloid is quite similar to that of echimidine, symphytine and anadoline. Analytical values, Found: C, 63·50, 62·96; H, 7·19, 7·61; N, 3·95, 3·93%. Calc. $C_{20}H_{27-29}O_6N$: C, 63·66; H, 7·16 (27 H) and 7·69 (29 H); N, 3·97%. Hydrolysis of the alkaloid with 20% NaOH, yielded a crystalline acid m.p. 64°, standard sample comparison proved that it was tiglic acid. The second acid and the amino alcohol part were not obtained in crystalline form. Since the amount was small, no further study was performed.

Part II

n-*Octacosane*. M.p. 61°, $(\alpha)_D$ ± 0° (in $CHCl_3$). Calc. $C_{28}H_{58}$: C, 85·28; H, 14·72%. Found: C, 85·55; H, 14·41%. U.v. (no peaks), i.r. (2850, 1450, 1380, 730 and 720 cm^{-1}).

β-*Sitosterol*. M.p. 137°, $(\alpha)_D$−36 (in $CHCl_3$). Calc. $C_{29}H_{50}O$: C, 84·05; H, 12·07%. Found: C, 84·15; H, 11·97%. Mixed m.p. and i.r. comparison with standard sample.

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BUXACEAE

ALKALOID C OF *SARCOCOCCA PRUNIFORMIS*[1]

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Abstract—Alkaloid C isolated earlier from *Sarcococca pruniformis* has been shown to be 3α-methoxy-20α-dimethylamino-pregn-5-ene.

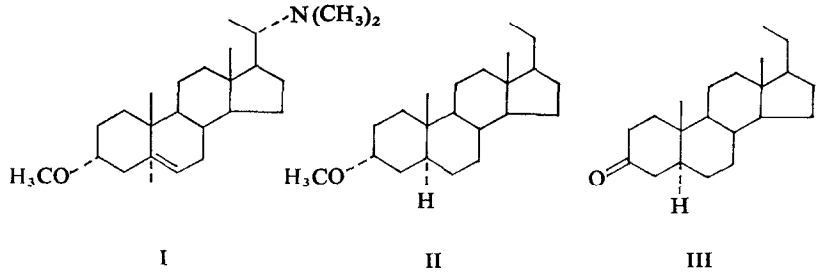
IN AN earlier communication[1] dealing with alkaloids of *Sarcococca pruniformis*, we reported the isolation of alkaloids A, B, C and D. The structure assigned to alkaloids A and B have

[1] Part II in the series "Alkaloids of *Sarcococca pruniformis*"; for Part I see J. M. KOHLI, A. ZAMAN and A. R. KIDWAI, *Tetrahedron* **23**, 3829 (1967).

since been confirmed by synthesis.[2] Alkaloid C is a minor component of the above mixture of bases and was separated and purified by repeated chromatography and fractional crystallization.

Elemental analysis and mol. wt. (359, mass spectrum) suggested the formula $C_{24}H_{41}ON$. The i.r. spectrum had bands at 7·35 and 9·15 μ suggestive of N-Me and O-Me groupings; the u.v. spectrum was featureless apart from some end absorption. The NMR spectrum showed a total of 40 $\pm$ 1 protons, corresponding to the assigned formula, and signals at 4·6 (IH, multiplet), 6·62 (3H), 7·82 (6H), 9·12 (3H), doublet J 6 cycles/sec and 8·98, 9·32 τ (3H, each). On the assumption of a 20-dimethylamino-Δ^5-pregnene skeleton, the signals at 9·12, 8·98, 9·32 τ can be assigned to the secondary C methyl at C_{20} and the 19-CH_3 and 18-CH_3 respectively. The value for the secondary C-methyl signal is the same as in pachysandrine-D[3] and other 20-dimethylamino steroids.[4] The values for the tertiary C-methyl groups are in agreement with those of irehdiamine-A and irehdiamine-B and suggest a -Δ^5-steroid; the signal for the olefinic proton at C_6 occurring at the same position as in alkaloid B and related unsaturated bases.[5] The signals at 7·82, 6·62 τ from the $N(CH_3)_2$ and OCH_3 resonances respectively confirm the presence of these groupings in the molecule.

The mass spectrum provided further proof for the presence of a C_{20}-dimethylamino group, by peaks at *m/e* 72 and 344 generally obtained in the 20-dimethylamino steroids.[6] The spectroscopic evidence therefore favours the formulation of alkaloid C as a 20-dimethylamino-Δ^5-pregnene derivative having a OCH_3 substituent. The most likely position for the methoxyl group appeared by analogy with similar alkaloids, such as irehine,[7] to be C_3.



I II III

Owing to the small amount of alkaloid available, degradation was not attempted, and structure I is assigned to this compound on the following basis. Emde's degradation gave a compound which, assuming the presence of a methoxyl at C_3, could be either 3α- or 3β-methoxy-Δ^5-pregnene. It was shown to be different, by comparative TLC and mixed m.p. determination, from 3β-methoxy-Δ^5-pregnene. Catalytic hydrogenation of this compound led to a product which was shown to have structure II by comparison with a synthetic sample obtained by the following sequence of reactions.

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[3] T. KIKUCHI, S. UYEO, JR., M. ANDO and YAMAMOTO, *Tetrahedron Letters* 1817 (1964).
[4] T. KIKUCHI, S. UYEO and T. NISHINGA, *Tetrahedron Letters* 3169 (1965).
[5] M. TRUONG-HO, Q. KHUONG-HUU and R. GOUTAREL, *Bull. Soc. Chim.* 594 (1963).
[6] Z. PELAH, D. H. WILLIAMS, H. BUDZIKIEWICZ and C. DJERASSI, *J. Am. Chem. Soc.* **87**, 574 (1965).
[7] M. TRUONG-HO, X. MONSEUR, Q. KHUONG-HUU and R. GOUTAREL, *Bull. Soc. Chim.* 2332 (1963).

Huang-Minlon reduction of pregnenolone afforded 3β-hydroxy-Δ^5-pregnene, which was hydrogenated to 3β-hydroxy-5α-pregnane. CrO_3 oxidation of this gave the corresponding ketone III. Reduction of the 3-keto group in the 5α series is known to give predominantly 3α-hydroxy-5α-pregnane along with some of the corresponding 3β isomer.[8] No attempt was made at this stage to resolve the mixture and it was methylated to the corresponding 3-methoxy compounds. TLC of the methylated product showed it to consist largely of one isomer which, therefore, must have the 3α-configuration. It was purified by column chromatography over silica gel. Co-TLC of the purified product with II showed the two to be identical, confirmation being obtained by mixed m.p. and comparison of the i.r. spectra.

EXPERIMENTAL

The m.ps were taken on a Kofler block and are not corrected. The NMR spectrum was measured in $CDCL_3$ at 60 Mc/sec.

Extraction. Air dried leaves of *Sarcococca pruniformis* (5 kg) were percolated at room temp. with light petroleum, the extract evaporated to dryness, taken up in light petroleum, kept over night in ice chest and filtered from betulin. The filtrate was extracted with dilute HCl and worked up according to the procedure outlined earlier[1] to give 150 mg of a mixture of alkaloids A, B and C. Crystallization of this from benzene–light petroleum gave first a mixture of alkaloids A and B then on concentration a second crop of crystals consisting of a mixture of alkaloids A, B and C. The minor alkaloid C (I) was isolated by repeated chromatography of the mixture over alumina and crystallized from benzene–light petroleum m.p. 151·53° (6–7 mg). Alkaloid C (I) m.p. 152–53° (Acetone), $(\alpha)_D^{30} = -32°$ (chf.) (Found: C, 79·84; H, 11·22; N, 3·77; $C_{24}H_{41}ON$ requires: C, 80·15; H, 11·49; N, 3·9%.)

Emde's degradation of I. I (250 mg) in $CHCl_3$ (5 ml) was refluxed with MeI (5 ml) for 3 hr. The methiodide (300 mg) was crystallized from MeOH, m.p. 268–75° (with decomposition) and converted to methochloride by refluxing with AgCl (400 mg) in MeOH for 4 hr. The methochloride was taken up in water and treated with freshly prepared Na/Hg 5% at 40–50° on a water bath for 4 hr, kept overnight and worked up to give product (120 mg) m.p. 126–28° (Acetone) (Found: C, 83·41; H, 11·40; $C_{22}H_{36}O$ requires: C, 83·48; H, 11·47%.)

Hydrogenation. The above product (100 mg) in glacial AcOH (10 ml) was hydrogenated over Adam's catalyst (25 mg) at atmospheric pressure for 5 hr and worked up to give (II) colourless needles (70 mg) m.p. 92–94°, undepressed on admixture with authentic 3α-methoxy-5α-pregnane m.p. 93–94° (Found: C, 82·92; H, 12·01; $C_{22}H_{38}O$ requires C, 82·95; H, 12·03%.)

Synthesis of 3α-methoxyl-5α-pregnane (II). (a) Reduction—Pregnenolone (500 mg) was taken in diethylene glycol (20 ml) containing NaOH (2 g) and freshly distilled hydrazine hydrate (100%, 2 ml). The reaction mixture was refluxed for 2 hr at 180°, the condenser was then removed and the temp. of the boiling mixture raised to 210°. Refluxing was continued after replacing the condenser for another 10 hr. The reaction mixture was cooled to room temp. diluted with water and extracted five times with ether. The combined ether extract was washed free of alkali, dried and the solvent evaporated. The colourless residue was crystallized from MeOH m.p. 133–4° (400 mg) (Found: C, 83·53; H, 11·02; $C_{21}H_{34}O$ requires: C, 83·38, H, 11·33%.)

(b) Hydrogenation—The above compound (400 mg) was dissolved in AcOH (20 ml) hydrogenated over Adam's catalyst (100 mg) at atmospheric pressure for 5 hr and worked up to give 3β-hydroxy-5α-pregnane colourless needles (360 mg), m.p. 139–40° (MeOH).

(c) Oxidation—3β-hydroxy-5α-pregnane (855 mg) in AcOH (49 ml) and $CHCl_3$ (39 ml) was treated with CrO_3 (855 mg) in AcOH (63 ml) and allowed to stand for 45 hr at room temp. Excess CrO_3 was destroyed by addition of MeOH, dried in vacuum, residue taken in water and extracted 5 times with 50 cc. $CHCl_3$–Et_2O (3:1). Work up of the extract gave a coloured solid which after several crystallizations from MeOH gave (III) m.p. 122–23° (Found: C, 83·31; H, 11·32; $C_{21}H_{34}O$ requires: C, 83·38, H, 11·33%.)

(d) Hydrogenation—III (200 mg) was dissolved in AcOH (150 ml) and reduced over Adam's catalyst at 45 lb/in^2 and 20° during a period of 4 hr and yielded a compound m.p. 144–46° (light petroleum) (Found: C, 82·52, H, 12·01; $C_{21}H_{36}O$ requires: C, 82·82; H, 11·92%.)

(e) Methylation—The above compound (1 g) in dry benzene (47 ml), K (0·59 g) was added and the mixture was refluxed for 1 hr, with vigorous shaking at intervals to disperse the molten K into small globulets. MeI (18 ml) was added and the refluxing continued for 3 hr during which time KI gradually separated out. Excess of K was destroyed with MeOH and the solvent removed in vacuum. The residue was extracted with light petroleum (500 ml) and the extract passed through a column of alumina (40 gm). The eluate on evapora-

[8] D. H. R. BARTON and R. C. COOKSON, *Quart. Rev.* **10**, 44 (1956).

tion and crystallization from MeOH afforded (II) m.p. 93–94°. (Found C, 82·73; H, 12·23; $C_{22}H_{38}O$ requires: C, 82·95; H, 12·03%.) TLC of the synthetic material with product obtained from I, over silica gel using light petroleum for elution showed the two to be identical. This was further confirmed by i.r. comparison of the synthetic and degradation products.

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CAMPANULACEAE

PLATYCONIN, A NEW ACYLATED ANTHOCYANIN IN CHINESE BELL-FLOWER, *PLATYCODON GRANDIFLORUM**

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Abstract—The anthocyanin in bluish-purple flowers of *Platycodon grandiflorum* A.DC. was crystallized in the form of chloride and identified as delphinidin 3-di-caffeoylrutinosido-5-glucoside.

A NUMBER of acylated anthocyanin based on delphinidin are known:[1] delphanin (violanin) in *Solanum*,[2,3] *Viola*[4] and *Petunia*,[5] awobanin in *Commelina*,[4] floridorin in *Iris*,[6] and delphinin in *Delphinium*,[7,8] although the last pigment may not be acylated as was originally suggested.[2]

A preliminary examination has revealed that a single anthocyanin is present in the bluish-purple flowers of Chinese bellflower ('kikyo' in Japanese).[9] For further study, this pigment was extracted from fresh petals of this plant, and precipitated in the form of lead

* Part LXIII in the Series "Studies on Anthocyanins"; for Part LXII, see *Proc. Japan Acad.* **46**, 535 (1970).

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