Phytochemistry, 1971, Vol. 10, pp. 441 to 442. Pergamon Press. Printed in England.

BORAGINACEAE

ALKALOIDAL AND OTHER CONSTITUENTS OF *SYMPHYTUM ORIENTALE*

AYHAN ULUBELEN and SOLMAZ DOĞANCA
Faculty of Pharmacy, University of Istanbul, Turkey

(*Received* 30 *June* 1970)

Plant. Symphytum orientale L.*

Source. Central Anatolia and Istanbul, Turkey.

Uses. Antitumor activity against cell culture 9KB test system[1] ED_{50} 3.Oxl.

Previous work. On sister species, *S. officinalis* L. [2–6] and *S. asperum* Lepech.[7]

Whole plant. Extracted with ethanol, upon concentration of alcoholic extract allantoin crystallized out. Alchohol was then removed completely, the residue was taken up in 10% H_2SO_4. The H_2SO_4-soluble part was reduced with Zn dust, made alkaline with NH_3 and extracted with $CHCl_3$ (I). Fraction I was chromatographed on an Al_2O_3 (activity III) column. In addition to anadoline[8] three other alkaloids were isolated. The H_2SO_4-insoluble part II was dissolved in $CHCl_3$ and separated on a silica gel column, three compounds were obtained, two of which were identified.

Allantoin. M.p. 230–231°. Calc. $C_4H_6O_3N_4$: C, 30·37; H, 3·97; N, 35·44%. Found: C, 30·45; H, 3·86; N, 35·56%. Mixed m.p. and i.r. curve comparison as well as the R_f comparison.

Part I

Symphytine.† Oil. Calc. $C_{20}H_{31}O_6N$: C, 62·99; H, 8·13; N, 3·93%. Found: C, 62·85; H, 7·95; N, 3·70%. R_f and i.r. comparison.

Echimidine. M.p. of echimidine picrate 142–143°. Calc. $C_{20}H_{31}O_7N$: C, 60·45; H, 7·8; N, 3·52%. Found: C, 60·4; H, 7·88; N, 3·48%. Mixed m.p. of the picrates, i.r. and R_f comparison.

Unknown alkaloid. $CHCl_3$–EtOH (95:5) washings of the column yielded a yellowish oil, which TLC showed to be a single compound. This was resubmitted to silica gel column

* The plant was identified by Prof. Dr. A. Baytop (Istanbul). Samples are deposited in Herbarium of Faculty of Pharmacy, University of Istanbul.

† Standard sample of symphytine was obtained from *S. officinalis* according to Furuya.[2]

[1] Protocols for screening chemical agents and natural products against animal tumors and other biological systems. *Cancer Chemotherapy Rep.* No. 25 (1962).
[2] T. FURUYA and K. ARAKI, *Chem. Pharm. Bull Tokyo* **16**, 2512 (1968).
[3] K. STAESCHE, *Univ. of Tuebingen, Ger. Planta* **71**, 268 (1966); CA, 66, 171207.
[4] F. KACZMAREK and A. WALICKA, *Biol. Inst. Roslin Lecziczych* **4**, 273 (1958); CA, 53, 15487 h.
[5] F. KACZMAREK and A. WALICKA, *Biol. Inst. Roslin Lecziczych.* **5**, 89 (1959); CA, 54, 3606 e.
[6] M. REPTA, *Farmacia* (Bucharest) **10**, 645 (1962); CA, 58, 13713 f.
[7] S. Ya. ZOLOTNITSKAYA, *Izv. Akad. Nauk Arm. SSR Biol. i Sel'skokhoz. Nauki* **7**, 27 (1954); CA, **48**, 11727 e.
[8] A. ULUBELEN and S. DOĞANCA, *Tetrahedron Letters* 2585 (1970).

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.

Acknowledgements—This investigation was supported by the Scientific and Technical Research Council of Turkey (TAG-96). The authors thank Prof. Dr. C. C. J. Culvenor (Melbourne) for a supply of several senecio alkaloids and acids. We also thank Prof. Dr. H. Wagner (Munich) for NMR curves.

Phytochemistry, 1971, Vol. 10, pp. 442 to 445. Pergamon Press. Printed in England.

BUXACEAE

ALKALOID C OF *SARCOCOCCA PRUNIFORMIS*[1]

J. M. KOHLI, A. ZAMAN and A. R. KIDWAI

Department of Research in Unani Medicine, Tibbiya College and Department of Chemistry, Aligarh Muslim University, Aligarh, India

(*Received* 29 *May* 1970)

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).