spp. (Ochnaceae). Identifications were confirmed by direct comparison (mmp, NMR, MS, IR) with authentic samples.

Ouratea-proanthocyanidins (2) are formed by the linkage of one molecule of (−)epiafzelechin C_4-C_8 to one of (−)-4′-*O*-methylepigallocatechin. Their occurrence in the Celastraceae with (1) is of particular interest both on taxonomic and biogenetic grounds, since they are the only so-far known methylated proanthocyanidins. Their structure could throw light on the mechanism of the formation of proanthocyanidins in plants [6].

REFERENCES

1. Delle Monache F., Marini-Bettolo G. B., Gonçalves de Lima O., D'Albuquerque I. L. and De Barros Coelho J. S. (1973) *J. Chem. Soc. Perk. I*, 2725.
2. Marini-Bettolo G. B. (1974) *Farmaco, Ed. Sci.* **29**, 551.
3. Delle Monache F., De Mello J. F., Marini-Bettolo G. B., Gonçalves de Lima O. and D'Albuquerque I. L. (1972) *Gazzetta* **102**, 636.
4. Delle Monache F., D'Albuquerque I. L., Ferrari F. and Marini-Bettolo G. B. (1967) *Tetrahedron Letters* 4211.
5. Delle Monache F., Ferrari F., D'Albuquerque I. L. and Marini-Bettolo G. B. (1970) *Farmaco, Ed. Sci.* **25**, 96.
6. Weinges K., Bähr W., Ebert W., Göritz K. and Marx H. D. (1969) *Fortschr. Chem. Org. Natur.* **27**, 158.

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ARISTOTELINE AND ARISTOTELONE, UNUSUAL INDOLE ALKALOIDS FROM *ARISTOTELIA CHILENSIS*

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In continuation of our general screening programme of Chilean flora[1], an examination of the alkaloids of *Aristotelia chilensis* (Eleocarpaceae) has been initiated. Extraction of the basic components of this plant with ethanol, followed by isolation of the acid soluble fraction, afforded a mixture containing alkaloids (< 0·01%). Separation by chromatography through silica gel afforded two of these alkaloids (positive test to Dragendorff's reagent).

The major compound, aristoteline (1) (0·003%) analysed for $C_{20}H_{26}N_2$, and had mp 164–165°. Its UV spectrum was typical for the presence of an indole chromophore [2], but the compound gave a negative Ehrlich test, indicating substitution at both positions 2 and 3 of this nucleus. This deduction was confirmed by its ^1H NMR spectrum which contained only four aromatic protons, the pattern of which was similar to that in 3-methylindole [3]. The NMR spectrum also showed the presence of three quaternary methyl groups with chemical shifts indicating attachment to saturated carbon atoms. Since the molecular formula of this compound was indicative of combination between a tryptamine unit and a monoterpene group, the presence of these methyl signals suggested that aristoteline was a conjugate between tryptamine and an *unrearranged* terpene unit.

Further analysis of the spectral data confirmed this suspicion. The system Ar CH_2CH N was present in aristoteline, the geminal protons occurring at τ7·50 and 7·06 (J_{ab} 16·5 Hz) [4], each coupled with the proton adjacent to the secondary amino group at τ6·46 (J_{ax} 1 Hz, J_{bx} 5·5 Hz). The structure around the secondary amine function was established with the aid of the lanthanide shift reagent, Eu(fod)$_3$ [5]. Addition of just a small quantity of the reagent caused the proton, originally at τ6·46 and two of the methyl groups to rapidly move downfield, and with the onset of distinct paramagnetic broadening, thus establishing the part structure Ar CH_2CH NH-CMe_2.

A detailed mass spectral examination allowed the assignment of the unique structure (1) to aristoteline. The principal fragmentations are depicted in Scheme 1 and all processes were checked both by accurate mass measurements and metastable defocusing experiments. Only one relative configuration is feasible for this bridged structure, the most stable conformation (from Dreiding models) having ring C present in a half-chair form and with rings D and E adopting chair conformations. This formulation is identical to that obtained for the same alkaloid recently isolated independently from *Aristotelia serrata*, the New Zealand 'wineberry' [6]. A direct comparison with an authentic sample, kindly supplied by Professor Bick, confirmed the identity of these two alkaloids.

The minor alkaloid, aristotelone (2) (0·0001%), mp 218–222° analysed as $C_{20}H_{26}N_2O$ (viz. aristoteline + one O). Its UV spectrum [7] (λ_{max} 229, 260 nm (ϵ19500, 4500) and IR absorption [8] at ν_{max} 1660 cm^{-1} were consistent with a ψ-indoxyl derivative. Paucity of pure material precluded a detailed NMR examination but the mass spectral fragmentation pattern (Scheme 2) is consistent with the suggested structure (2).

Aristoteline (1), and its oxidation product, aristotelone (2) are relatively rare members of the indole alkaloids, since most of these arise by combination of a tryptophan unit with a terpene skeleton derived from loganin [9]. Members of the genus *Aristotelia* thus appear to be the source of interesting indolic alkaloids which do not conform with the loganin type. Besides the above two alka-

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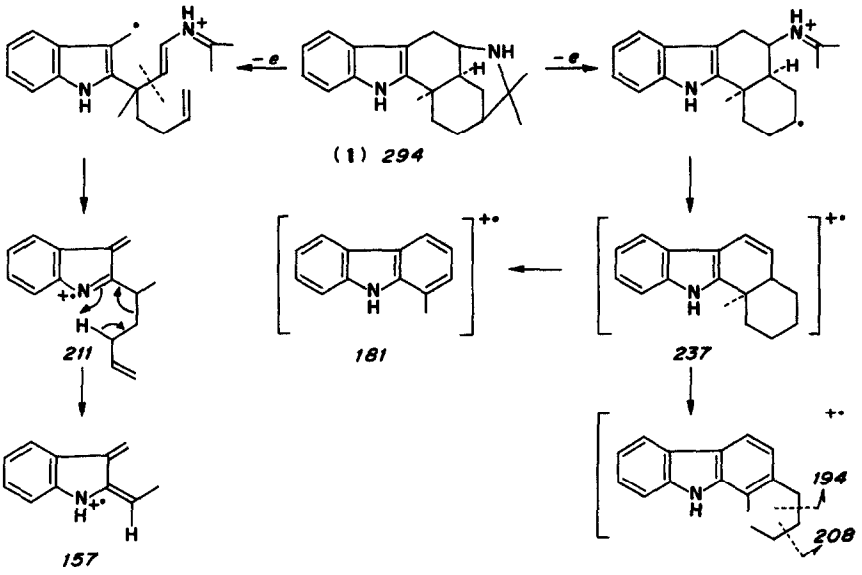

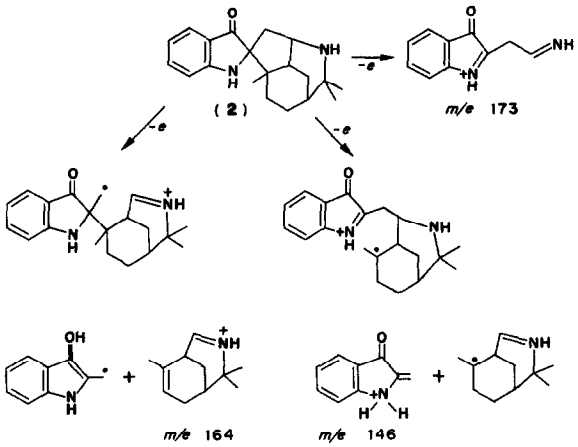

loids, a novel structure has also been assigned to peduncularine, isolated from *A. peduncularis* Hook. f. [10].

EXPERIMENTAL

Samples of *A. chilensis* were collected from near Concepcion, Chile in the summer. Dried leaves and stems (12 kg) were extracted with warm EtOH (20 l.), filtered, and the extract evaporated to dryness, treated with 2N HCl, the mixture extracted with $CHCl_3$ and the aq layer adjusted to pH 9·5 (aq NH_3) and re-extracted with chloroform, to give, eventually, the crude fraction (3 g). Chromatography of a portion (1·2 g) through Al_2O_3 (180 g, grade II) afforded with $CHCl_3$, aristoteline (200 mg, crude) (0·003%). mp (MeOH) 83–85° (solvate), 164–5° (after drying) $[\alpha]_D^{25}$ −23° (0·3, $CHCl_3$), ν_{max} (Nujol) 3220, 3200, 1640 cm^{-1}, (EtOH) 228, 282, 291 (ε22500, 5450, 4800), τ (100 MHz, $CDCl_3$) 2·2 (1H, broad *s*, exchanged with D_2O), 2·70–3·15 (4H, *m*), 6·46 (1H, *dd*, *J* 1, 5·5 Hz), 6·8 (1H, broad *s*, exchanged by D_2O), 7·06 (1H *dd*, *J* 5·5, 16·5 Hz), 7·50 (1H *dd*, *J* 1, 16·5 Hz), 8·60 (3H, *s*), 9·78 (3H, *s*), 9·02 (3H, *s*), besides an envelope at 7·8–9·1 (8H). *m/e* 294 (M^+, 100%), 279, 237, 222, 211, 194, 182, 18 , 167, 143, 130, 120, 118, 47, 35. (Found: M^+ 294·2080. $C_{20}H_{26}N_2$ requires 294·2096.) Mmp, mp and TLC comparison with an authentic sample indicated identity. Further elution of the column ($CHCl_3$) afforded the second alkaloid, aristotelone (70 mg crude) as an oil. This eventually crystallised to give the Ψ-indoxyl (10 mg, 0·0001%), mp (MeOH) 218–222°, ν_{max} (Nujol) 3320, 1660, 1620 cm^{-1}, λ_{max} (EtOH) 229, 260 (ε19500, 4500), *m/e* 310 (M^+), 295, 174, 173, 164 (100), 146, 84.

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REFERENCES

1. For the previous paper in this series, see Bhakuni, D. S., Gonzalez, C., Sammes, P. G. and Silva, M. (1974) *Rev. Latinoamer. Quim.* **5**, 158.
2. Jones, G. and Stevens, T. S. (1953) *J. Chem. Soc.* 2344.
3. Cohen, L. A., Daly J. W., Kay, H. and Witkop, B. (1960) *J. Am. Chem. Soc.* **82**, 2184.
4. *cf.* Abraham, R. J. (1967) *Nuclear Magnetic Resonance for Organic Chemists*, p. 129 (Mathieson D. W., ed.), Academic Press, London.
5. Rondeau, R. E. and Sievers, R. E. (1971) *J. Am. Chem. Soc.* **93**, 1522.
6. Anderson, B. F., Robertson, G. B., Avey, H. P., Donovan, W. F. Bick, I. R. C., Brenner, J. B., Finney A. J. J., Preston, N. W., Gallagher, R. T. and Russell, G. B. (1975) *J. Chem. Soc. Chem. Commun.* 511.
7. Scott, A. I. (1964) *Ultraviolet Spectra of Natural Products*, Pergamon Press, Oxford, p. 297.
8. Witkop B. and Ek, A. (1951) *J. Am. Chem. Soc.* **73**, 5666.
9. Möthes, K. and Schute, H. R. (1969) *Biosynthese der Alkaloide*, VEB Deutscher Verlag der Wissenschaften, Berlin.
10. Bick, I. R. C., Brenner, J. B., Preston N. W. and Calder, I. C. (1971) *J.C.S. Chem. Commun.* 1155.