ration and washings with MeOH, led to pure 3,5,7-tri-*O*-methoxyflavone (tri-*O*-methylgalangin, 36%), mp 199–200°, previously unreported as a natural product. The structure was elucidated from its ^{13}CMR spectrum. The carbonyl chemical shift (δ 173.6) and the four peaks (two of double intensity) in the 128–131 ppm region suggested a flavone unsubstituted in the B ring [3–5]. The two high field methines (δ 92.1, 95.5) could be accommodated by a 5,7-dioxygenated ring A. This accounts for the two methoxy carbons absorbing at higher field (δ 55.4, 56.0) and therefore not *ortho*-disubstituted [6], as opposed to the third methoxy carbon (δ 59.7) which can only be located at the highly hindered C-3 position. IR [ν_{max}^{KCl} (cm^{-1}):1638, 1616, 1462, 1450, 1360, 1240, 1223, 1180, 1160, 1125, 1022, 835, 800, 720], ^{1}HMR [δ ($CDCl_3$): 3.83 (*s*, OMe), 3.88 (*s*, OMe), 3.91 (*s*, OMe), 6.26 (*d*, *J* 1.0 Hz), H-6), 6.43 (*d*, *J* 1.0 Hz, H-8), 7.42 (*m*, H-3′,4′,5′), 8.00 (*m*, H-2′,6′)] and MS [*m/e* (%): 312 (25) M, 311 (27), 284 (28), 181 (100), 180 (74), 152 (10), 137 (17), 77 (21)] corroborated the identification.

Comment. The conspicuous secondary metabolites of all *Aniba* species which have so far been analysed are either 2-pyrones or neolignans [2]. *A. riparia*, thus, becomes the first exception.

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A METHYLATED CATECHIN AND PROANTHOCYANIDINS FROM THE CELASTRACEAE

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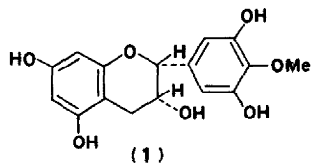
(*Received* 10 *April* 1975)

Key Word Index—*Prionostemma aspera*; *Maytenus rigida*; Celastraceae; (−)-4′-*O*-methyl-epigallocatechin; Ouratea-proanthocyanidins *A* and *B*.

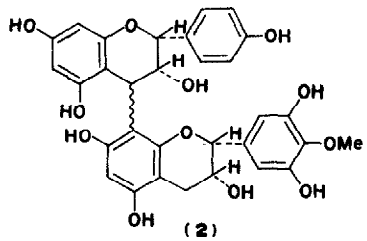
Plant. Prionostemma aspera and *Maytenus rigida.* Voucher specimens Nos. 1374 and 1750 respectively are deposited in the Herbarium of Institute of Antibiotics, UFePe, Recife, (Brasil). *Previous work.* From these and sister species tingenone [1] and/or pristimerin were isolated from the $CHCl_3$-soluble fraction of the methanolic extract of root bark. (For a review of previous studies on Celastraceae, see [2]). No study on the flavanol composition of this family has been reported.

Present work. MeOH extraction of the powdered root bark of *Prionostemma aspera*, or *Maytenus rigida*, and concentration of the extract gave a solid, which was treated with $CHCl_3$ to remove tingenone, pristimerin and other triterpenes [1,3]. The chloroform-insoluble residue was dissolved in acetone, poured into H_2O and extracted with EtOAc. Removal of the solvent gave a pale pink powder, which was chromatographed on silica (deactivated with 5% H_2O). Elution with EtOAc gave a catechin and a mixture of two proanthocyanidins (+ve HCl–vanillin test).

The catechin, $C_{16}H_{16}O_7$, mp 142–4° (H_2O), $[\alpha]_D = -60°$ (EtOH) showed a methoxy group by NMR. An amorphous pentaacetate, a tetra-*O*-methyl ether, mp 160–2°, and a mono-*O*-acetyl-tetra-*O*-methyl derivative were obtained. The above data indicated catechin to be (−)-4′-*O*-methyl-epigallocatechin (**1**), an unusual catechin previously isolated by us [4,5]. Identification was confirmed (mmp NMR, IR, TLC) by comparison with authentic samples of (**1**) and its derivatives.



(1)



(2)

The mixture of the two proanthocyanidins was separated on cellulose with H_2O. Proanthocyanidin *A*, amorphous powder showing a methoxy group by NMR, gave a nona-*O*-acetylderivative, $C_{49}H_{46}O_{21}$, mp 134–5°, $[\alpha]_D = +25$ ($CHCl_3$); a hepta-*O*-acetylderivative, $C_{38}H_{42}O_{14}$, (M^+ 774), mp 125–7° dec. Proanthocyanidin *B*, amorphous powder, gave a nona-*O*-acetylderivative $C_{49}H_{46}O_{21}$, mp, 171–4°, $[\alpha]_D = +55$ ($CHCl_3$); a hepta-*O*-methyl derivative $C_{38}H_{42}O_{12}$, mp 165–67°, and a di-*O*-acetyl-hepta-*O*-methyl derivative $C_{42}H_{46}O_{14}$ (M^+ 774), mp 164–66°. The above data indicate the two proanthocyanidins to be the C_4-epimeric Ouratea-proanthocyanidin *A* na *B* respectively, isolated by us from *Ouratea*

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].

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Phytochemistry, 1976, Vol 15, pp. 574–575 Pergamon Press Printed in England.

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

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(*Revised Received* 10 *August* 1975)

Key Word Index—*Aristotelia chilensis*; Eleocarpaceae; indole alkaloids; aristoteline; aristotelone.

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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