Tetrahedron Letters No.43, pp. 4211-4214, 1967. Pergamon Press Ltd. Printed in Great Britain.

A NEW CATECHIN AND A DIMERIC PROANTHOCYANIDIN FROM OURATEA SP.

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(Received in UK 12 June 1967)

The root of Ouratea sp. (Ochnaceae), a plant original from North East Brazil and known also as "Jerimum de porco" yielded a red powder by extraction with acetone. By paper chromatography five phenolic substances were detected, two of which were isolated by cellulose column chromatography. The more preponderant one (3% of the root weight)(I) crystallizes from water, m.p. 141-143°, $C_{16}H_{16}O_7$ (calc.%: C 60.00, H 5.04; found %: C 59.73, H 4.85), R_f = 0.33 (Whatman no. 1, water), $[\alpha]_D^{25}$ = - 62° (c = 1.5, ethanol), $[\alpha]_D^{25}$ = - 53° (c = 1.5 acetone).

In the molecule a methoxy group is present as shown by NMR spectrum 60Mc in $CDCl_3$ (δ = 4.35) and hydroxy groups are also evidenced by chemical and spectroscopical means. (I) gives the following derivatives:

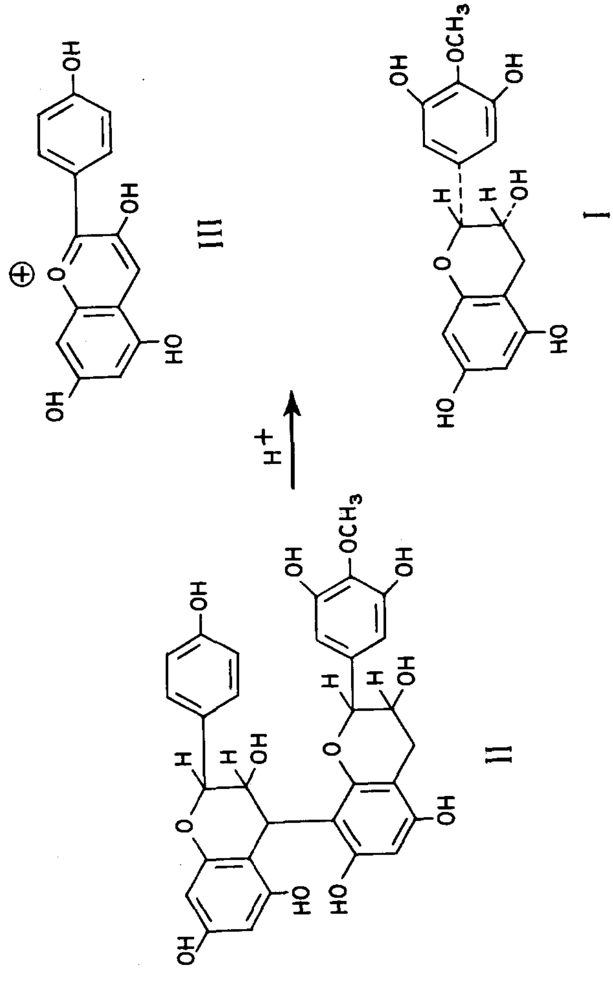
-Penta-O-acetyl derivative, amorphous powder, $C_{26}H_{26}O_{12}$ (calc.%: C 58.92, H 4.59; found %: C 58.86, H 4.74). $[\alpha]_D^{25}$ = - 19.7° (c = 2.5, acetone), $[\alpha]_D^{25}$ = - 11.3° (c = 2.5, sym. tetrachloroethane);

-Tetra-O-methyl derivative, crystallizes from methanol, m.p. 161-163°, $C_{20}H_{24}O_7$ (calc.%: C 63.82, H 6.43; found %: C 63.60, H 6.32), $[\alpha]_D^{25}$ =-66.0° (c = 2 acetone), $[\alpha]_D^{25}$ = - 57,3° (c = 2, sym. tetrachloroethane);

-Mono-O-acetyl-tetra-O-methyl derivative, crystallizes from methanol, m.p. 183-184°, $C_{22}H_{26}O_8$ (calc.%: C 63.15, H 6.26; found %: C 63.16, H 6.04 $[\alpha]_D^{25}$ = - 73.6° (c = 2.5 acetone), $[\alpha]_D^{25}$ = - 65.0°(c=2.5, sym. tetrachloroetane);

-Mono-O-tosyl-tetra-O-methyl derivative, crystallises from methanol, m.p. 165-176° dec, $C_{27}H_{30}O_9$ (calc.%: C 61.12, H 5.70, S 6.04; found %: C 61.08, H 5.67, S 5.97).

Therefore it can be assumed that in (II) a C_{15} skeleton is present and that of seven oxygen atoms present in (I), four are phenolic hydroxyls, one is an aliphatic hydroxyl, and one is a methoxy-group; the last oxygen there-


III
H+
II
I
OH
HO
OCH3
H

fore must be considered a part of a heterocyclic ring.

- Tetra-O-methyl derivative of (I) by oxydation with $KMnO_4$ in acetone yields 3-4-5-trimethoxy-benzoic acid, m.p. 165-168°, undepressed with authentic specimen.

Alkali-fusion of (I) gives phloroglucinol, 3-5-dihydroxy-4-methoxy benzoic acid, and traces of pyrogallol and 3-4-5-trihydroxy-benzoic acid. Thus we can attribute to compound (I) the structure of a catechin for which we propose the name of Ouratea-catechin.

The absolute configuration of this catechin has been determined examining both the coupling constants in NMR spectrum (J_{2-3} = 1 c.p.s.)(1) and the specific rotations of Ouratea-catechin and its derivatives compared to those of known derivatives of (-)epicatechin(2) Therefore Ouratea-catechin has to be considered the 3-5-7-3'-5'-pentahydroxy 4'-methoxy-(-)epicatechin.

The second substance (1% of the root weight)(II) was obtained as an almost colourless powder $C_{31}H_{28}O_{12}$ ($C_{31}H_{28}O_{12}\cdot 2H_2O$ calc. %: C 59.25, H 5.09; found %: C 58.94, H 5.02), R_f 0.67 (Whatman no. 1, water),$[\alpha]_D^{25}$= + 54° (c = 1.6, acetone).

Mild acid hydrolysis of (II) yields Ouratea-catechin (I) and pelargonidin chloride (III). Vigorous acid hydrolysis gave a good yield of pelargonidin chloride, identical with an authentic specimen (chromatographic behaviour, spectral properties, and colour reactions).

The following derivatives of (II) were obtained:

-Nona-O-acetyl derivative, crystallizes from benzene-cyclohexane, m.p. 134-135°, $C_{49}H_{46}O_{21}$ (calc.% C 60.62, H 4.77; found %: C 60.69, H 4.58), $[\alpha]_D^{20}$= + 43.9° (c = 2, acetone), $[\alpha]_D^{20}$ = + 22.8 (c = 2, chloroform);

-Epta-O-methyl derivative, crystallizes from benzene-cyclohexane, m.p. 120-122°, $C_{38}H_{42}O_{12}$ (calc.%: C 66.07, H 6.13; found %: C 66.02, H 5.92), $[\alpha]_D^{20}$= + 67.5 (c = 2, acetone),$[\alpha]_D^{20}$= + 77.5 (c = 2, chloroform). The substance does not react with sodium metaperiodate.

-Di-O-acetyl-epta-O-methyl derivative, crystallizes from methanol, m.p. 183-184°, $C_{42}H_{46}O_{14}$ (calc.%: C 65.10, H 5.45; found %: C 65.03, H 5.62).

-Di-O-tosyl-epta-O-methyl derivative, crystallizes from methanol, m.p. 126-128° dec, $C_{52}H_{54}O_{12}S_2$ (calc.%: C 62.58, H 5.45, S 6.51; found %: C 62.32, H 5.27, S 6.23).

It is evident that (II) is a dimeric proanthocyanidin. We propose therefore for this substance the structure (II) and the name of Ouratea-proanthocyanidin A. The NMR spectrum 100 Mc in $CDCl_3$ of Nona-O-acetyl derivative confirms the proposed formula. In this substance the following signals 7.88 δ , 7.12 δ (quartet, J=9 cps, four protons), and 6.49 δ , 6.10 δ , (quartet, J=2.4 cps, two protons), can be assigned to the aromatic hydrogens of the leucopelargonidin moiety; 6.70 , (singlet, two protons) and 6.60 δ , (singlet, one proton) to the aromatic hydrogens of catechin moiety; 5.60 δ , to 4.35 δ (complex multiplet, five protons) to two methine protons, two protons to the aliphatic acetoxyls, and to the proton at position 4 of leucopelargonidin moiety; 3.75 δ (singlet, three protons) to the methoxy-group; 2.85 δ (two protons) to the benzylic protons of the catechin moiety; 2.30 to 1.50 δ (twenty seven protons) to the aromatic and aliphatic acetoxy groups.

As the phloroglucinol proton quartet (6.49 δ , 6.10 δ) and the benzylic protons (2.85 δ) have both only two protons, this means that the two flavanic units are linked between the benzylic carbon of the leucopelargonidin moiety and the carbon 8 (or 6) of the catechin moiety.

In the last years several dimeric proanthocyanidins with C-C bond have been described, i.e. in *Persea gratissima* (3), in *Fragaria vesca* (4), in Cola acuminata (5), in *Eucalyptus camaldolensis* (6), in *Myrica nagi* (7), in *Acacia mearnsii* (8-9). The linkage in 8 was demonstrated for Cola proanthocyanidin by synthesis (10). Ouratea-proanthocyanidin is the first procyanidin with a methoxy group and the first which yields by hydrolysis pelargonidin chloride.

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