

transitions in Hf^{180} ; for the first three transitions they found experimental values to be $(10 \pm 8)\%$ lower than theory and for the last transition $(6 \pm 8)\%$ higher than theory. This situation, if confirmed, clearly calls for an explanation.

Summarising, it may be said that there is general agreement between theory and experiment when finite size effects are taken into account. The observed deviations from theory in the case of unhindered E2 transitions are interesting in that they are, in the first place, unexpected and secondly, pose a challenge to theoreticians. More precise data in the rare-earth region may be expected in the near future which should help to clear up the question of whether or not there is any correlation between nuclear deformation and deviations in α_K from theory. Finally it would be highly welcome if independent checks on the results from

the IEC method can be made. However, at the present time such a prospect does not appear bright.

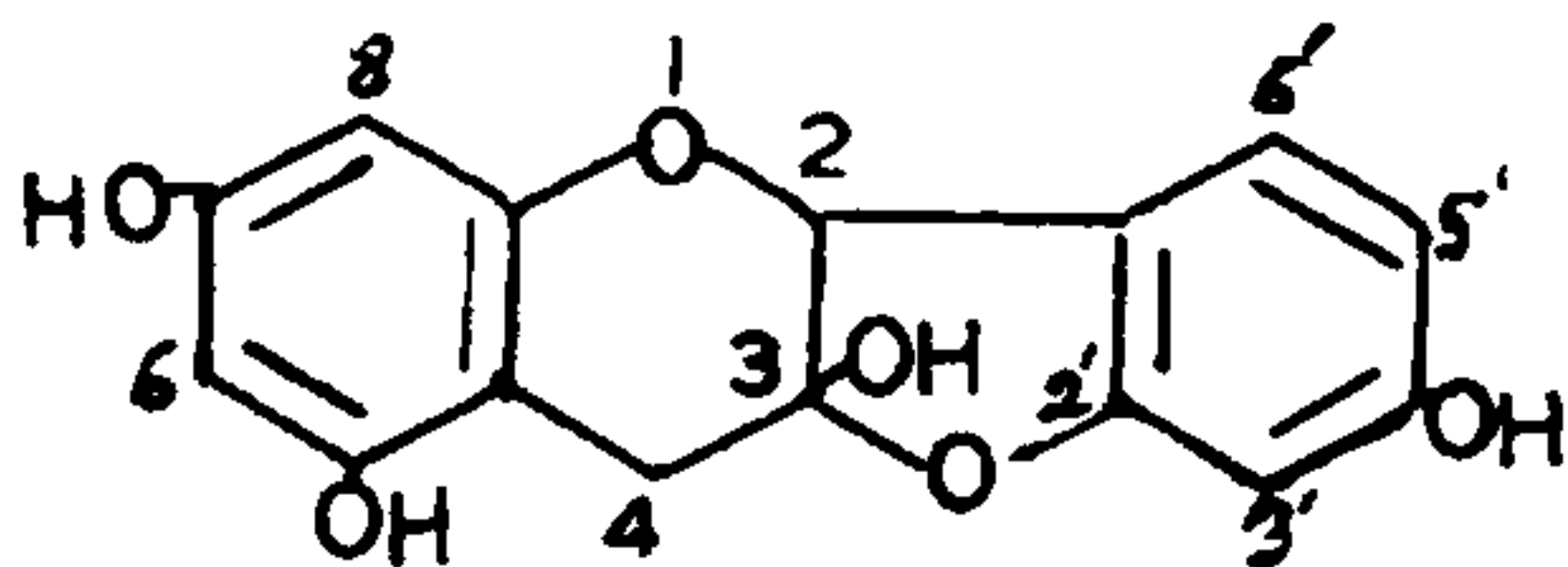
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STRUCTURE OF CYANOMACLURIN

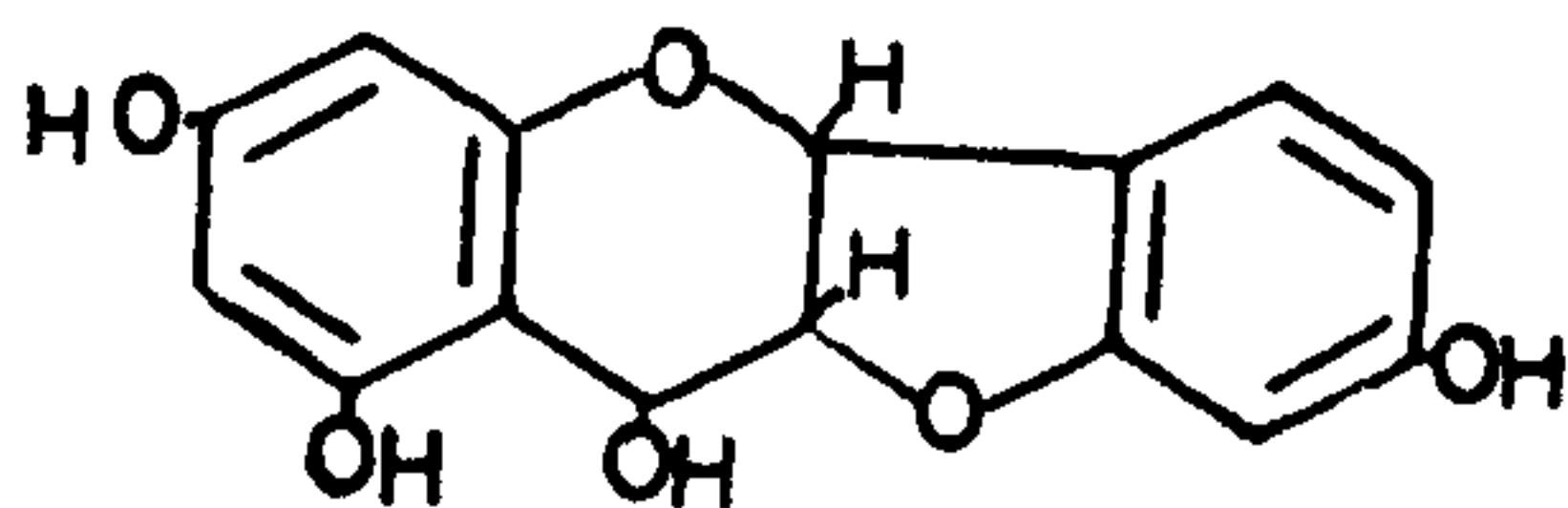
GEETA CHAKRAVARTY AND T. R. SESHADRI

Chemistry Department, University of Delhi, Delhi

IN an earlier publication¹ chemical and spectral data were provided in order to show that cyanomaclurin is a derivative of a flavan-3,4-diol. Close comparison with the catechins definitely established the absence of a $>\text{CH}_2$ group in the 4-position as embodied in the original structure of Appel and Robinson² (I).

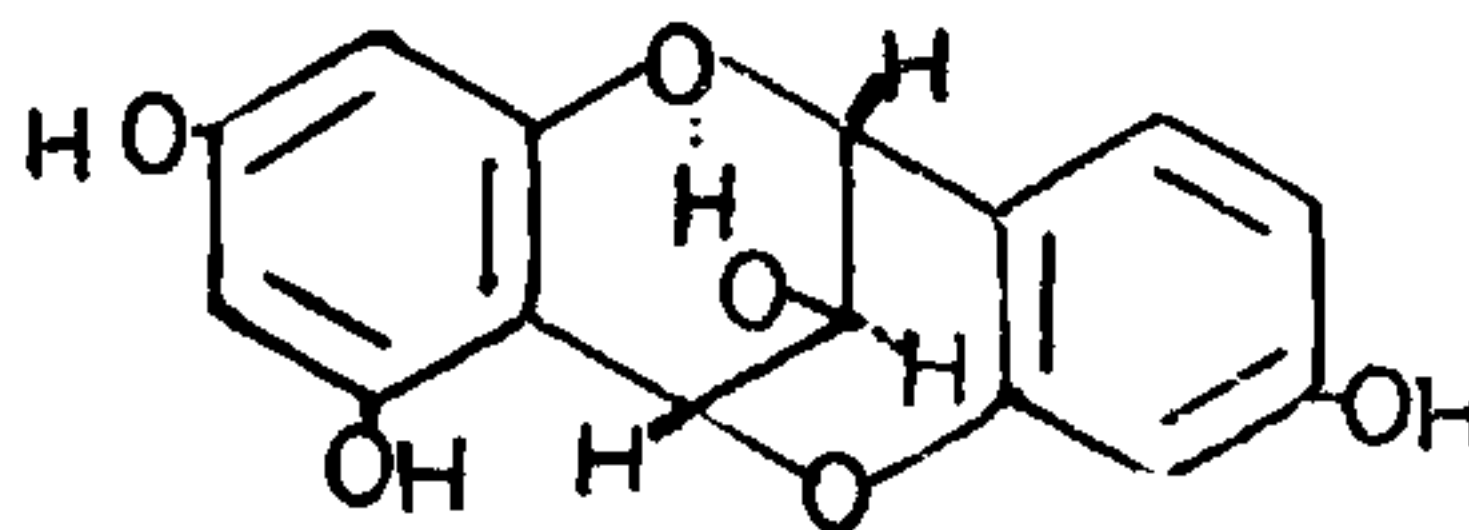


I



II

There was no definite way of fixing up the oxygen involved in the formation of the fourth ring. Established analogies would support dihydrofuran ring formation (II) using the adjacent 3-position; homopterocarpin and rotenone may be cited as well-known examples. There are certain reactions which could be expected from a benzyl alcoholic compound of structure (II) such as oxidation with manganese dioxide or catalytic reduction; but they could not be effected successfully. This was considered to be due to simultaneous substitution in both 5 and 3-positions. Similar lack of oxidation with manganese dioxide is found in compounds like leucocyanidin methyl ether.



III

More recently a modified structure (III) has been proposed by Nair and Venkataraman.³ This contains a dihydropyran ring involving the benzylic hydroxyl in the 4-position. The chief

arguments given by the above workers are the following: (1) failure of cyanomaclurin trimethyl ether to be oxidised with manganese dioxide and chromium trioxide; (2) lack of reduction even by drastic treatment with Raney nickel; (3) in cyanomaclurin methyl ether the benzylic protons in 2 and 4-positions have more or less the same τ values (4.61 and 4.88) and that in the 3-position have a markedly different value 5.67. The acetate of this ether gives for the 3-proton a lower value which is nearly the same as for the other protons in the 2 and 4-positions which are unaffected. This effect could be explained only by placing the free hydroxyl in position 3. It was also brought out by them that there was no coupling between the protons in the 3 and 4 positions as is found in the case of flavan 3 : 4-diols (axial-equatorial)⁴ and the absence of such coupling indicates that the H in the 3 position is *trans* to the protons in the 2 and 4 positions.

indicating the existence of a 3-OH grouping which is hydrogen bonded more markedly than in the case of the catechins.

(c) A study has now been made of the I.R. spectra of a number of compounds having both 5- and 6-atom oxide rings in their structures just as in cyanomaclurin. Homopterocarpin, rotenone, dihydrorotenone and dehydrorotenone show the presence of a fairly strong band around 1280 cm^{-1} and this band may be attributed to the presence of a dihydrofuran ring in the molecule. Cyanomaclurin does not show any prominent band around this region. On the other hand the characteristic peak for a pyran ring comes as a strong band around 1075 cm^{-1} in these compounds; cyanomaclurin has a strong doublet in this region and dehydrorotenone in which this 6-atom ring has undergone change has not got the absorption. The peaks around these two regions are tabulated below for all the above-mentioned compounds.

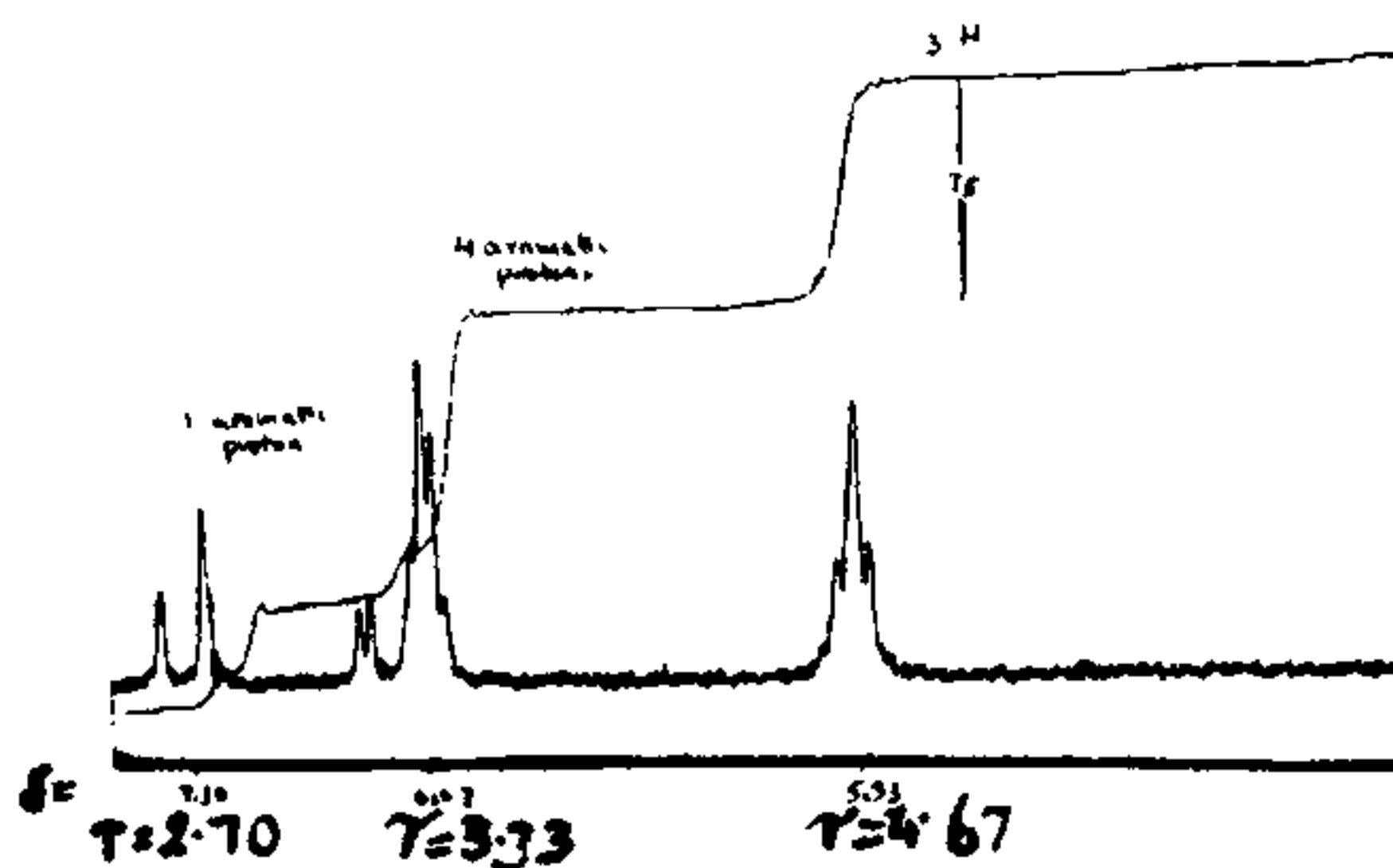
Cyanomaclurin	Homopterocarpin	Rotenone	Dihydrorotenone	Dehydrorotenone
1081 (s)	1075 (m)	1090 (s)	1050 (m) cm^{-1}	..
1070	1266 (s)	1280 (m)	1270 (m)	1279 (m) cm^{-1}
..				

The above structure (III) seems to be reasonable and we have examined its validity further in the following manner.

(a) We have constructed molecular models in accordance with both the alternative structures II and III; the former seems to involve some strain, the latter is free from strain and is easily constructed using Catalin models. This is brought out in the photographs. The side phenyl has to be axial in this structure and so also the oxygen link in the 4-position. As mentioned in the next para the hydroxyl in the 3-position is also axial facilitating hydrogen bonding with the oxygen in position 1. Consequently the three protons in the 1, 2 and 3 positions are equatorial, protons in the 1, 2 positions *trans* and those in the 2, 3 positions *trans*.

(b) In the case of catechins it was earlier established that the hydroxyl in the 3-position is involved in intramolecular hydrogen bond formation. This is shown by the I.R. absorptions of the hydroxyl groups of (+) catechin and (–) epicatechin tetramethyl ethers in CCl_4 which occur at 3594 and 3587 cm^{-1} respectively.⁵ These low hydroxyl stretching frequencies and the absence of a free OH band near 3630 cm^{-1} indicate intramolecular hydrogen bonding of axial hydroxyl groups as originally postulated by Roberts.⁶ In the I.R. spectrum of cyanomaclurin trimethyl ether in CHCl_3 solution, the hydroxyl group absorbs at 3450 cm^{-1} (doublet)

(d) The NMR spectra of cyanomaclurin and its derivatives along with those of catechins have now been reconsidered. In cyanomaclurin and its trimethyl ether the protons in the 2 and 4 positions are indistinguishable and have τ values between 4.61 and 4.92. On the other hand the proton in position 3 has almost the same value in both compounds, $\tau = 5.73$ and 5.67 respectively. Acetylation of either cyanomaclurin or its methyl ether does not affect the values for proton in 2 and 4 positions whereas τ value for the hydrogen in the 3 position is lowered by nearly a unit. Nair and Venkataraman³ have recorded the lowering for the methyl ether acetate. In our record for cyanomaclurin acetate (see chart) the τ values for the protons



NMR spectra of cyanomaclurin tetraacetate.

in 2, 3 and 4 positions are quite close being round about 4.7. Another point may also be mentioned and it relates to a comparison with the NMR spectrum of catechin tetramethyl ether. The proton in the 3 position has the τ value 5.71 which is almost the same as the value of the corresponding proton in cyanomaclurin.

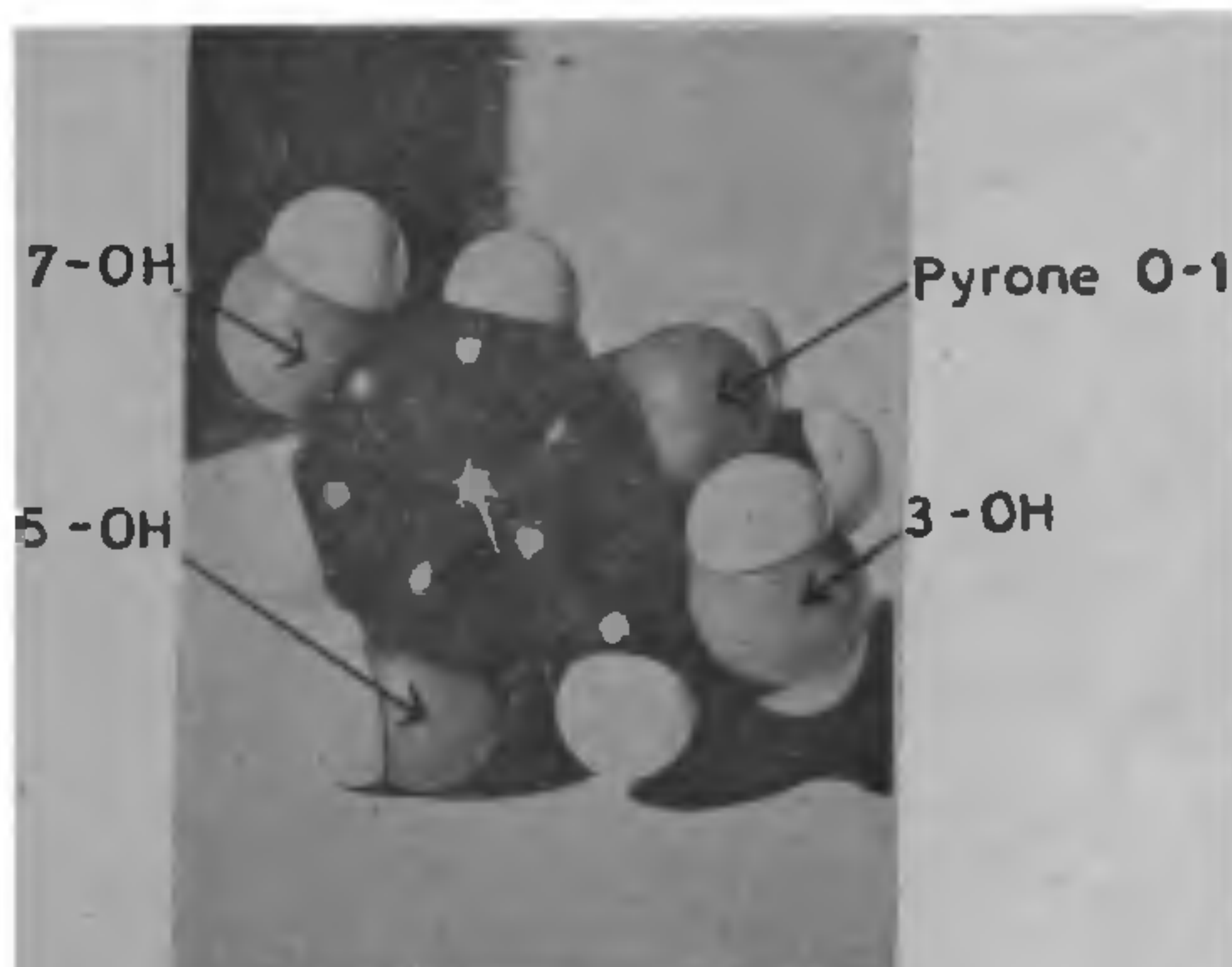


FIG. 1. Facing condensed benzene.

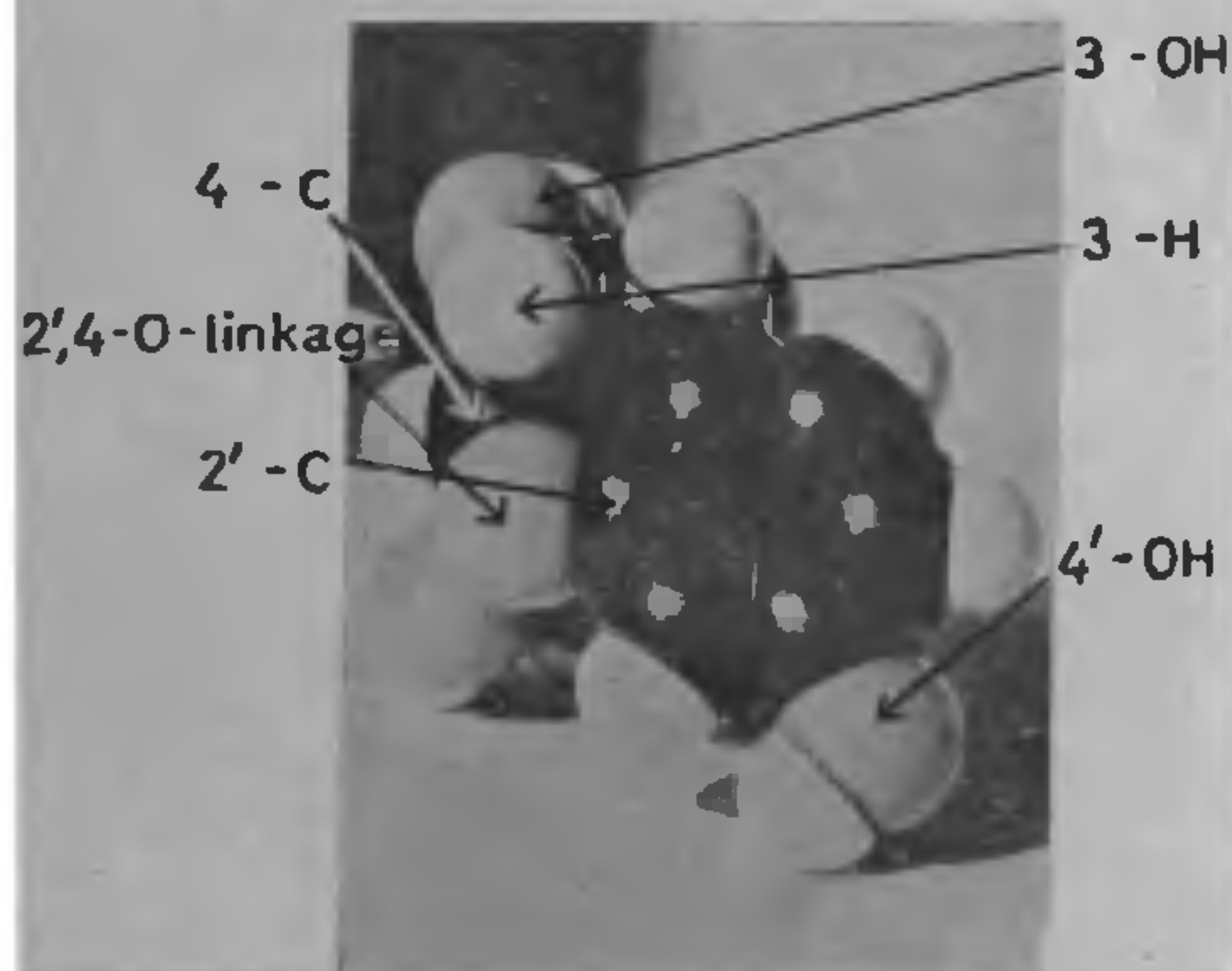
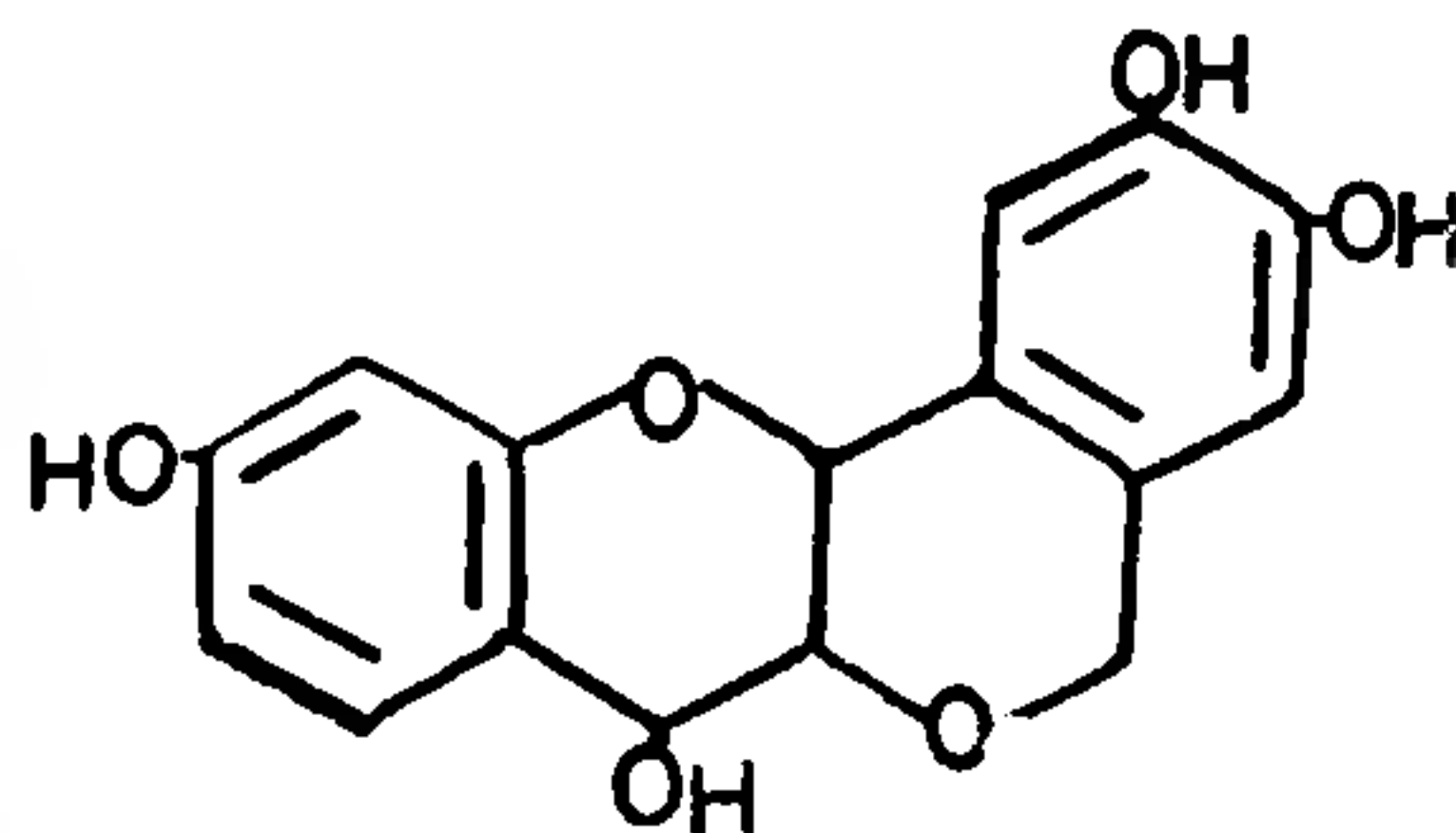


FIG. 2. Facing the side phenyl.

(e) Among the chemical properties of cyanomaclurin which favour the new structure (III) a few may be recorded here. (i) Cyanomaclurin and its methyl ether when subjected to acetylation under drastic conditions do not undergo dehydration as normally happens with

3 : 4-diols and flavan-4-ols but yield the normal acetates. As a very near example may be mentioned 5 : 7 : 4'-flavan-4-ol, which under hot acetylation condition undergoes dehydration yielding the corresponding flavene.⁷ (ii) There seems to be some difference in solubility of hydroxyflavan derivatives depending on the presence of free hydroxyl group in the 3- or 4-positions. 3-ols like the catechins are fairly soluble in water whereas 4-ols are not. Cyanomaclurin is quite soluble in water. This behaviour is in agreement with the 3-ol structure. (iii) Attempts to convert cyanomaclurin into the corresponding tetracyclic anthocyanidin chloride have met with failure indicating the possible absence of a hydroxyl group in the 4-position. The closely related peltogynol (IV) which has a hydroxyl group in the 4-position could be converted into peltogynidin chloride⁸ with all the rings intact.



IV

We convey our thanks to Dr. Norman S. Bhacca of Varian Associates, California, for the NMR spectrum of cyanomaclurin acetate.

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