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PUTRANJIVA ROXBURGHII WALL - IV

STRUCTURE OF PUTRANJIC ACID

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The triterpenic hydroxy acid, Putranjic acid, isolated from *P. roxburghii* bark[1], has been characterised by physical and chemical methods to be a hydroxy *seco* acid (I) of the friedelane series and its molecular formula corrected from $C_{30}H_{50}O_3$ to $C_{30}H_{52}O_3$ (M^+ 460) and that of the derived diol (II) from $C_{30}H_{52}O_2$ to $C_{30}H_{54}O_2$ (M^+ 446). The putranjic acid methyl ester, $C_{31}H_{54}O_3$ showed the presence of eight C-methyl groups in the region δ 0.71, to 1.18 ppm. and the carbomethoxy methyl signal at δ 3.75 ppm in its nmr spectra. Thus the nmr spectra accounting for eight methyl groups in the molecule as well as its mass spectra suggest the acid to be a friedelan-3-*seco* acid rather than a true tetra-cyclic triterpenoid.

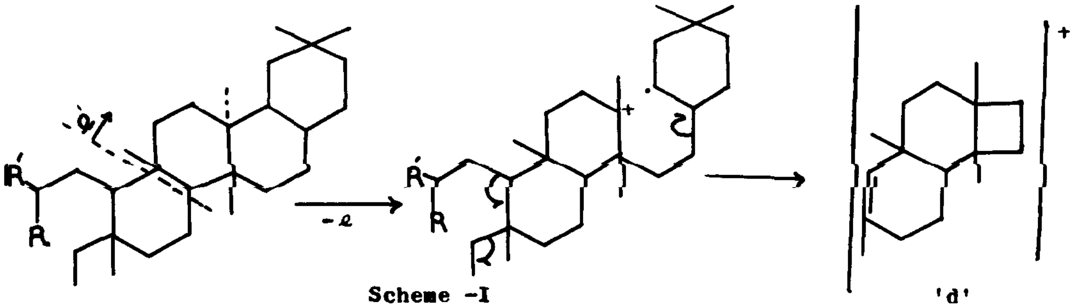
The downfield absorption of the carbomethoxy methyl signal and the lability of the methyl ester[1] to hydrolysis (even on the alumina column) indicated it to be in the side chain of an open ring rather than attached to an angular carbon atom. But interestingly the nmr spectra of methyl putranjate does not show the presence of any proton α to the carboxyl group (cf. putranjivic acid[2]) in the region δ 2-3 ppm and this may be attributed to the presence of a vicinal hydroxyl group.

The use of trichloroacetyl isocyanate (TAI) in the nmr studies[3] helped in determining the nature of the hydroxyls in methyl-putranjate and its derived diol (II). In the case of Me-putranjate (Ia), the broad signal at δ 2.75 ppm disappeared after addition of TAI and the one proton signal α to the hydroxyl

group at δ 4.20 ppm shifted downfield to δ 5.20 ppm (a shift of 1 ppm characteristic of a secondary alcohol)[3]. The carbamate N-$\underline{H}$ signal at δ 9.7 ppm of one prpton area indicated the presence of only one hydroxyl group in putranjic acid. The proton α to the hydroxyl having the restricted rotation about C-2 due to its asymmetric nature splitted into a pair of doublets (J, 9 c/s) being coupled with C-1 methylene group. This is further substantiated by the nmr spectra of the diol (II), showing the presence of eight C-methyl in the region δ 0.71 to 1.18 ppm, the two hydroxyl protons at δ 2.0 ppm and the C-3 methylene protons as a pair of two symmetrical quartets centred at δ 3.55 ppm. The nmr spectra of the diol (II) after addition of TAI showed the two O-$\underline{H}$ signal at δ 2.0 ppm to appear as a two-protons singlet at δ 9.8 ppm and the carbinol protons having characteristic downfield shift of 1.00 ppm to δ 5.35 ppm in case of the secondary hydroxyl and that of 0.8 ppm to δ 4.35 ppm in case of the primary hydroxyl[3]. The proton α to the secondary hydroxyl now appeared as broad multiplet centred at δ 5.3 ppm indicating the presence of additional vicinal protons due to newly generated -C$\underline{H}_2$OH which was recorded as a pair of symmetrical quartet centred at δ 4.35 ppm, showing three distinct couplings $J_{ab(gem)}$, 12 c/s, J_{ac}, 7 c/s and J_{bc}, 2 c/s of an ABC pattern. Thus the newly generated methylene in II showed the presence of a proton in its vicinity which was not evident in the parent methyl ester because of the presence of the α hydroxyl group and has shifted to the region δ 4.2 ppm. This is in agreement with the placement of the hydroxyl, α to the primary hydroxyl *vis a vis* α to the carboxyl in putranjic acid.

However an attempted dehydration of Ia with $POCl_3$ in pyridine or PCl_5 in petroleum ether at room temperature, resulted in both the cases into 2-chloro-Me-putranjate (III). The nmr spectra showed a triplet at δ 4.2 (J, 7 c/s) for the proton α to the halogen indicating a methylene group in its vicinity. The Me-putranjate on oxidation with CrO_3 in AcOH yielded a keto ester IV, $C_{31}H_{52}O_3$ m.p. 148-149°. The nmr spectra of IV shows a triplet of one proton area at δ 1.9 ppm (J, 5.5 c/s) and a two protons quartet like a pair of doublets at δ 2.75 ppm of an ABX system with $J_{ax} = J_{bx}$, 5.5 c/s and J_{ab} 4.5 c/s. The one proton triplet is assigned to C-10 proton and the quartet to those of C-1 methylene. This confirms the structure of the keto ester (III) as 2-keto friedelan-3-seco acid methyl ester and thus putranjic acid is 2-OH-friedelan-3-seco carboxylic acid (I).

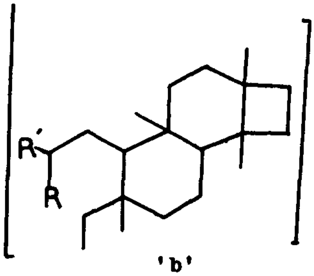
The structure of putranjic acid (I) is further supported by spectral data showing the cracking pattern similar to that of friedelane series[4,5,6]. The important fragments of putranjic acid (I), its acetate (Ib) and the diol (II) corresponding to the abundant peaks are listed in table I. The $\overset{+}{M} - 29$ ion peak shows the presence of an ethyl side chain being knocked off the seco friedelane skeleton. The abundant m/e 205 ion peak[4,5] corresponds to the fragment 'a' constituting rings D and E having no substituent groups present therein. The fragment 'b' arises by the cracking of ring D identical to that



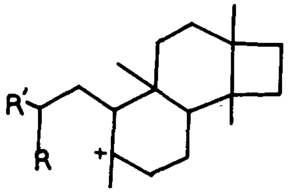
Scheme -I

'd'

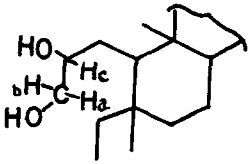
I R = COOH, R' = OH
Ia R = $COOCH_3$, R' = OH
Ib R = COOH, R' = OAc
II R = CH_2OH, R' = OH
III R = $COOCH_3$, R' = O
IV R = $COOCH_3$, R' = Cl



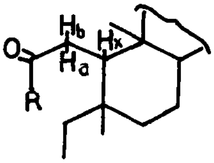
'b'



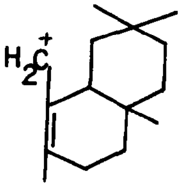
'c'



II



III



'a'

of putranjivadione[4]. The loss of the C-5 ethyl side chain is also evident from 'b' to give fragment 'c'. The fragment 'e' of m/e 273 arises by the cracking of ring B as reported in case of shionanone[6].

TABLE - I

Compound	Fragments m/e							
	M^+	M^+-15	M^+-29	a	b	c	d	e
I	460	445	431	205	336	307	218	273
Ib	502	487	473	205	378	349	218	273
II	446	431	417	205	322	-	218	273

The base ion peak in all the three compounds appearing at m/e 218 is assigned structure 'd' constituting rings B and C and may possibly arise as shown in scheme I. This confirms the placement of the hydroxyl as well as carboxyl groups in *seco* ring A.

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