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STRUCTURE OF CACCIGENIN, A NEW TRITERPENOID SAPOGENIN FROM CACCINIA GLAUCA SAVI.

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From the leaves of Caccinia glauca Parthasarathy and Seshadri[1] reported the isolation of rutin and an acid saponin. The latter was isolated by the lead salt method and the reported yield was moderate. Using the butanol method we have now been able to isolate an acid saponin (mixture) m.p. 230-257° (d); ν_{max} 1700 cm^{-1} (COOH) in better yields (from 2 to 10 g. per kg. depending on the quality of the material). It was hydrolysed by boiling with 7% methanolic sulphuric acid. Glucose and rhamnose were identified in the water soluble part of the hydrolysate. The aglycone which was obtained in ester form was not identical with any known genin and is therefore given the name caccigenin. A study of the genin has been made by chemical and spectral methods and the results which lead to the tentative structure (I) are mentioned below.

The ester $C_{31}H_{50}O_6$, m.p. 273-275°, $[\alpha]_D^{18}$ +77° (methanol) contained one ester group (micro-Zeisel). It could be hydrolysed to the acid genin by boiling with 10% potassium hydroxide in 50% aqueous methanol for one hour, and the

acid could be reesterified using 7% methanolic sulphuric acid. The genin gave positive Liebermann-Burchard reaction and tetranitromethane colour reaction. The I.R. spectrum of the ester showed the following absorption bands: 3448 cm^{-1} (OH), 1735 cm^{-1} ($COOCH_3$), 1381 cm^{-1} (gem dimethyl), 855 cm^{-1} and 820 cm^{-1} (trisubstituted double bond[2]). These indicated that it could be a pentacyclic triterpene of the α or β-amyrin series. The acid genin $C_{30}H_{48}O_6$, ν_{max} 1700 cm^{-1} (COOH), formed a bromolactone, ν_{max} 1760 cm^{-1} (γ-lactone), giving negative tetranitromethane colour reaction[3]. The ester readily formed a tetraacetate; the ease of acetylation suggests that the hydroxyl groups are either primary or equatorially oriented secondary or both. The ester tetraacetate on refluxing with selenium dioxide in glacial acetic acid yielded a pale yellow dehydro product having in its U.V. spectrum triple absorption maxima at 241.5, 249 and 259 mμ (log ε : 4.169, 4.183 and 3.927 respectively) associated with a heteroannular diene; formation of structures of this type is a well known characteristic of compounds of the β-amyrin group[4]. The acid genin thus seems to be an oleanolic acid with three additional acylable hydroxyl groups.

The positions of the hydroxyl groups were deduced as follows: The ester genin on pyrolysis with copper at 300° yielded formaldehyde identified as its dimedone derivative, thus indicating the presence of a 3,23 diol system[5].

In quantitative periodate oxidation experiments the ester genin consumed one mole of the reagent indicating the presence of a 1:2 glycol system. It should be a trans glycol because it did not form a cyclic derivative with phosgene or thionyl chloride.

The glycol unit should be at one of the following positions: 2,3; 6,7; 15,16 or 21,22. The easy acylability of all the hydroxyls ruled out 6,7. The 2,3 positions were also eliminated since the dialdehyde obtained by the periodate oxidation of the methyl ester failed to cyclise[6,7]. Hence the choice is limited to 15,16 or 21,22. This agrees with the observation that the ester could be hydrolysed without difficulty. Esters of oleanolic and related C_{28} acids are known to be difficult to hydrolyse, unless there is a hydroxyl group in the β or γ-position to the COOR[8]. A choice between the two alternatives (15,16 and 21,22) could be made on the basis of NMR data. The spectral data[9] of the ester acetate taken in $CDCl_3$ solution are shown in table I. The pattern of the CH_3 protons (2:1:2:1) shows that C-29 and C-30 carry equivalent protons. On the other hand in a 21,22 glycol, the C-29 and C-30 protons would not be equivalent and the spectrum would be expected to show a 2:1:1:1:1 pattern for these protons.

TABLE I

NMR Spectral Data for the Genin Ester Acetate*

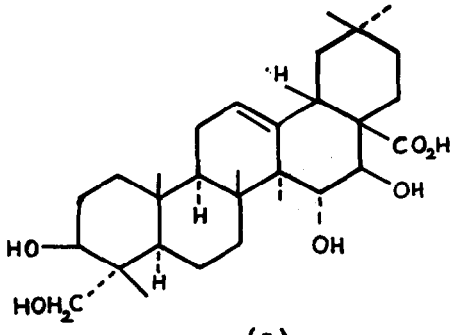
Chemical shifts in ppm (δ)	Splitting** pattern	Number of protons	Assignment of the protons
5.37	m	1	C-12
5.1-5.2	m	2	C-15 and C-16
4.5-4.8	m	1	C-3
3.79	q	2	C-23
3.62	s	3	C-28(1-OCH_3)
2.08	s	3	4 CH_3-C-O (O)
2.01	s	6	
1.96	s	3	
1.11	s	6	C-24 and C-27
1.0	s	3	C-25 or C-26
0.90	s	6	C-29 and C-30
0.733	s	3	C-26 or C-25

(tert. CH_3)

** m = multiplet; q = quartet; s = singlet.

* Taken in $CDCl_3$ on a Varian A-60 instrument with tetramethylsilane as internal standard.

This conclusion falls in line with the general observation that hydroxylation incidence in the β-amyrin group is more in ring D than in ring E. The 15α, 16β-configuration is given for the hydroxyls in question to explain their chemical reactivity.



(I)

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