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CRABBOGENIN, 1β-HYDROXYCRABBOGENIN, STRICTAGENIN AND POMPEYGENIN, FOUR NEW STEROIDAL SAPOGENINS FROM *CORDYLINE STRICTA* LEAVES

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Abstract—From the leaves of *Cordyline stricta* Endl. four new steroidal sapogenins crabbogenin {5α-spirost-25(27)-en-3α-ol}, 1β-hydroxycrabbogenin, strictagenin {(20S, 22S, 25S)-5α-furostan-22, 25-epoxy-1β, 3α, 26-triol} and pompeygenin {(25S)-5α-spirostane-1β, 3α-25-triol} have been isolated and their structures determined by chemical and spectroscopic methods.

From the leaves of *Cordyline stricta* Endl. (Agavaceae) 3-*epi*-tigogenin {(25R)-5α-spirostan-3α-ol}, 3-*epi*-neotigogenin {(25S)-5α-spirostan-3α-ol}, cannigenin {(25R)-5α-spirostane-1β, 3α-diol} and its 25S-epimer cordylagenin have been isolated.[1,2] Chromatographic evidence was obtained also for the presence of tigogenin {(25R)-5α-spirostan-3β-ol}, its 25S-epimer neotigogenin, diosgenin {(25R)-spirost-5-en-3β-ol}, its 25S-epimer yamogenin, ruscogenin {(25R)-spirost-5-ene-1β, 3β-diol} and brisbagenin {(25R)-5α-spirostane-1β, 3β-diol}. Other sapogenins were detected in small quantities, but these were not identified.[2] Further study has resulted in the isolation and characterisation of four of these compounds, which are reported in this paper.

RESULTS AND DISCUSSION

The saponins of *Cordyline stricta* leaves have been hydrolysed, the liberated sapogenins extracted and separated into three fractions by column chromatography. The first fraction contained the monohydroxy sapogenins, the second the dihydroxy compounds and the third the polyhydroxy sapogenins. The monohydroxy compounds have been separated further into three fractions by preparative tlc: A1 contained 3-*epi*-tigogenin, 3-*epi*-neotigogenin and crabbogenin; A2 was a minor component which has not been characterised; and A3 contained diosgenin, yamogenin, tigogenin and neotigogenin.[2] The three components of A1 have been separated on preparative thin-layers of $AgNO_3$ impregnated silica gel.

Crabbogenin (**1a**), $C_{27}H_{42}O_3$. (M^+, *m/e* 414.3128; calculated 414.3134), m.p. 203–204°, has been obtained in low yield (1.4 mg). Its MS displays prominent fragment peaks in the high mass range at *m/e* 347, 302, 287 and 273 characteristic of saturated monohydroxy spirostanes.[3] However, the presence of the base peak at *m/e* 137 and ions at *m/e* 124 and 113, and the lack of an ion at *m/e* 357, is indicative of an exocyclic methylene group attached to C_{25}.[3,4] Calculation of the degree of water elimination from the major ions at *m/e* 347, 302, 287 and 273 shows that crabbogenin behaves in a similar manner to 5β-spirostan-3β-ols and 5α-spirostan-3α-ols on electron bombardment.[5] The IR spectrum of crabbogenin shows absorption at 3420 cm^{-1} (hydroxyl), but lacks the characteristic bands of the spirostane ring; absorptions at 870 and 918 cm^{-1} are indicative of an exocyclic methylene group.[6,7] The NMR spectrum contains resonances at δ 0.76† (3H, s; C_{18}-Me), 0.78 (3H, s; C_{19}-Me), 0.95 (3H, d, $J \simeq 6.5$ Hz; C_{21}-Me), 3.80 (1H, d, $J_{26\beta,26\alpha} \simeq 12.5$ Hz; $C_{26\alpha}$ – H), 3.97 (1H, broad s, $W_{1/2} \simeq 7.5$ Hz; $C_{3\beta}$–H), 4.24 (1H, d, $J_{26\alpha,26\beta} \simeq 12.5$ Hz; $C_{26\beta}$–H), 4.37 (1H, q, $J \simeq 7.5$ Hz; C_{16}–H), 4.65 (1H, s, $J_{gem_{AB}} \simeq 0$ Hz; C_{27_A}–H) and 4.70 (1H, s, $J_{gem_{BA}} \simeq 0$ Hz; C_{27_B}–H). The spectrum lacks the doublet normally observed for a C_{27}-methyl group and the C_{26}-protons appear as an AB quartet. These properties confirm the presence of an exocyclic methylene group at C_{25}. The geminal protons ($C_{27_{A\&B}}$) of the C_{25}-methylene group were resolved as two singlets, the coupling constant of approximately 0 Hz being characteristic of an exocyclic methylene.[8,9] The C_{18}- and C_{19}- methyl signals are consistent with crabbogenin being a 5α-spirostan-3α-ol.[10]

Hydrogenation of crabbogenin gives two components, which have the same tlc characteristics as 3-*epi*-tigogenin and 3-*epi*-neotigogenin. From all the data available,

†All chemical shifts are given in δ-values.

crabbogenin has been concluded to be 5α-spirost-25(27)-en-3α-ol. To our knowledge, this is the first record of this steroid, which has been named in honour of Dr. T. A. Crabb. Chromatographic evidence suggests the presence of crabbogenin in extracts of *C. rubra* leaves also.[2]

The dihydroxy sapogenins have been separated by preparative tlc into three fractions: B1 comprised cordylagenin, cannigenin and 1β-hydroxycrabbogenin; B2 and B3 contained compounds with chromatographic characteristics identical to ruscogenin and brisbagenin respectively. After acetylation of the B1 sapogenins, 1β-hydroxycrabbogenin diacetate was separated from cordylagenin and cannigenin diacetates by preparative tlc using $AgNO_3$ impregnated layers of silica gel.

1β-Hydroxycrabbogenin diacetate (**1c**) has been obtained as an oil. Its IR spectrum is very similar to that of crabbogenin, but shows absorption also at 1725 cm^{-1} (carbonyl). The characteristic bands of the spirostane ring are absent, but absorptions at 870 and 918 cm^{-1} indicate the presence of an exocyclic methylene group.[6,7] The NMR spectrum displays resonances at δ 0.77† (3H, s; C_{18}–Me), 0.94 (3H, d, $J \simeq 6.5$ Hz; C_{21}–Me), 0.95 (3H, s; C_{19}–Me), 1.96 (3H, s; 1β-OCO$\underline{CH_3}$), 2.05 (3H, s; 3α-OCO$\underline{CH_3}$), 3.80 (1H, d, $J_{26\beta,26\alpha} \simeq 12.5$ Hz; $C_{26\alpha}$–H), 4.24 (1H, d, $J_{26\alpha,26\beta} \simeq 12.5$ Hz; $C_{26\beta}$–H), 4.37 (1H, q, $J \simeq 7.5$ Hz; C_{16}–H), 4.66 (1H, s, $J_{gem_{AB}} \simeq 0$ Hz; C_{27_A}–H), 4.70 (1H, s, $J_{gem_{BA}} \simeq 0$ Hz; C_{27_B}–H), 4.81 (1H, dd, $J_{1\alpha,2\beta} \simeq 12$ Hz and $J_{1\alpha,2\alpha} \simeq 5$ Hz; $C_{1\alpha}$–H) and 4.96 (1H, broad s, $W_{1/2} \simeq 7.5$ Hz; $C_{3\beta}$–H). The spectrum resembles that of crabbogenin in exhibiting the C_{26}-protons as an isolated AB quartet, the C_{27}-protons as two broad singlets, and in the absence of resonances for the C_{27} secondary methyl protons. These results are consistent with the presence of an exocyclic methylene group in place of a C_{27} methyl group.

Hydrolysis of the diacetate affords 1β-hydroxycrabbogenin (**1b**), $C_{27}H_{42}O_4$, (M^+, *m/e* 430.3082; calculated 430.3083), which did not crystallise, but was obtained as a fatty material. The fragmentation pattern of its MS is similar to the spectra exhibited by saturated dihydroxy spirostanes, with the exception of ring F fragments at *m/e* 137 (base peak), *m/e* 124 and 113. These indicate the presence of an exocyclic double bond associated with that ring;[3,4] an ion at *m/e* 373 is observed, but its intensity is very low.[4] The IR spectrum of 1β-hydroxycrabbogenin is consistent with it being a 25(27)-dehydrospirostane.

The NMR spectrum closely resembles that of crabbogenin with the exception of the C_{19}-methyl and $C_{3\beta}$–H signals, both of which suffer a paramagnetic shift. The 0.04 ppm downfield shift of the C_{19}-methyl group is consistent with an additional 1β-hydroxyl group.[10] From all the data obtained 1β-hydroxycrabbogenin has been proved to be 5α-spirost-25(27)-ene-1β, 3α-diol, which, to our knowledge, is the first record of this compound. This assignment has been confirmed by hydrogenation of 1β-hydroxycrabbogenin diacetate over Adams' catalyst; the product is a mixture of cordylagenin and cannigenin diacetates.

From the solution of the polyhydroxy sapogenins in chloroform, strictagenin (**2a**) has been obtained, on standing, as a solid floating on the surface of the liquid. After recrystallisation from methanol, crystals have been isolated with m.p. 271–273°, $[\alpha]_D$–25° (C. 0.16). The IR spectrum shows absorption at 3460 cm^{-1} (hydroxyl), but diverges in the spiroketal region from the spectra of normal spirostanes and 25(27)-dehydrospirostanes. Absorptions at 1000, 924, 900, 867 and 844 cm^{-1} indicate the presence of a hydroxy group in ring F.[6,11] This assumption is confirmed by MS; the base peak is observed at *m/e* 155, 16 mass units higher than the base peak of normal spirostanes.[3] Additional F ring fragments are observed at *m/e* 142 and 131, which are 16 mass units higher than those produced by normal spirostanes. Major ions are detected at *m/e* 418 and 417, both of which have been recorded for F ring hydroxylated spirostanes.[4,12] No molecular ion is observed, but major fragments are recorded at *m/e* 360, 318, 303 and 289, showing the presence of two hydroxy groups in rings A to D. The MS of strictagenin lacks an ion at *m/e* 373 and shows only a small peak at *m/e* 363. Both these fragments would have arisen through hydrogen transfer reactions which are probably affected by ring size.[12] Analogous fragments have not been observed in the MS of cholegenin, a compound which bears a $-CH_2OH$ group attached to C_{25} of a "furanose" F ring, whereas both fragments have been recorded for reineckiagenin,[4,12] which has a tertiary hydroxy group at C_{25} of a "pyranose" F ring. From the IR and MS features strictagenin has been concluded to be a trihydroxy saturated spirostane resembling compounds of the reineckiagenin and cholegenin types, the latter with a "furanose" F ring being the more favoured.

The NMR spectrum of strictagenin shows singlets at δ 0.76 and δ 0.82 which have been assigned to the C_{18}- and C_{19}- tertiary methyl groups, respectively. Instead of the two doublets of the secondary methyl groups (C_{21} and C_{27}) a doublet at δ 0.97 and a singlet at δ 1.13 are observed. Since the MS analysis situates one of the three hydroxy groups in the F ring, the doublet has been assigned to the C_{21}-methyl group and the singlet to the C_{27}-methyl group attached at C_{25}; the latter carbon atom bears a tertiary hydroxy group if in a "pyranose" F ring or a $-CH_2OH$ if it is situated in a "furanose" F ring. Comparison of the resonance of the C_{27}-methyl group of strictagenin with spirostanes possessing a hydroxy group attached to ring F in both the "pyranose" and "furanose" series favours the latter structure with the C_{27}-tertiary methyl group in the β-position.[11,13–16]

On dilution and subsequent addition of D_2O to the solution of strictagenin used to prepare the original NMR spectrum, no change is observed in the chemical shifts of the methyl groups. However, the resonances associated with those of the hydroxy protons and the two protons on C_{26} show interesting features. The latter absorbs as a complex multiplet in the region between δ 3.48 and δ 3.12 (Fig. 1A) which alters on dilution (Fig. 1B), but on the addition of D_2O collapses to a simple AB quartet at δ 3.46 (1H, d, $J_{AB} \simeq 11$ Hz; C_{26_A} –H) and δ 3.29 (1H, d, $J_{BA} \simeq 11$ Hz; C_{26_B}–H) (Fig. 1C). Double irradiation at δ 3.46 results in a simplification of the signal at δ 3.29 to a near singlet and confirms that the protons on C_{26} are coupled. The behaviour of the C_{26}-protons is consistent with the F ring hydroxy group being hydrogen bonded to the oxygen in the E ring in the "furanose" series or the oxygen in the F ring in the "pyranose" series. For bonding to take place the hydroxy group is restricted to an α-conformation (α-CH_2OH) in the former case and to a β-configuration (β-C_{25}–OH) in the latter. The calculated lengths of the H-bridge in the former and latter cases (0.25 nm and 0.09 nm, respectively)[13] are in accord with the measured values (0.24 nm and 0.13 nm, respectively) on a Dreiding model. The changes in the pattern and chemical shifts of the two protons on C_{26} in the three NMR spectra are regarded therefore as being due to the variations in the proportions of inter and in-

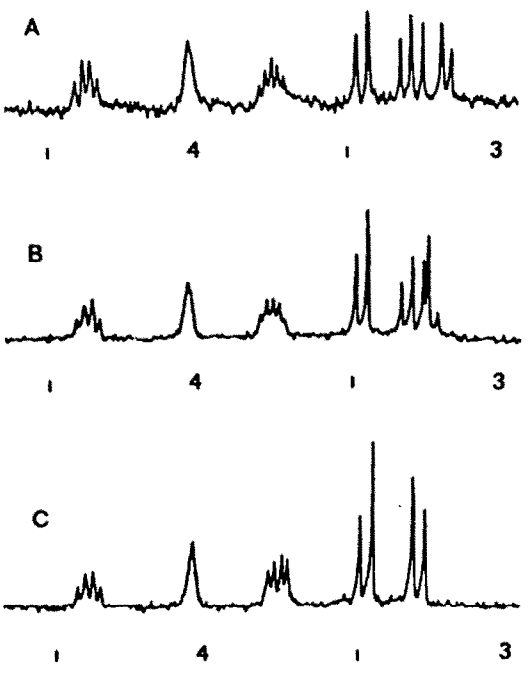


Fig. 1. NMR spectra (270 MHz), from δ 3.0 to δ 4.5, of strictagenin (A) showing the effects of dilution (B) and D_2O addition (C).

tramolecular hydrogen bonding on dilution of the sample.

The chemical shift of the C_{19}-tertiary methyl group is consistent with the presence of 1β- and 3α-hydroxy groups in a 5α-sapogenin. The resonance for the 3β-proton is observed at δ 4.04 (1H, broad s, $W_{1/2} \simeq 8$ Hz), but the signal for the $C_{1\alpha}$-proton appears as a multiplet at δ 3.75 (1H, $W_{1/2} \simeq 20$ Hz), which collapses to the normal double doublet at δ 3.76 (1H, $J_{1\alpha,2\beta} \simeq 11$ Hz and $J_{1\alpha,2\alpha} \simeq 5$ Hz) on addition of D_2O. This suggests that the multiplet obtained initially is due to coupling ($\simeq 5$ Hz) between the $C_{1\alpha}$-proton and the proton of the hydroxy group attached to C_1. The large peak around δ 1.5, which is not observed on addition of D_2O, has been assigned to resonances of the hydroxy group protons also. In all three spectra the signal for the C_{16}-proton is recorded around δ 4.38 (1H, q, $J \simeq 7.5$ Hz).

From all the data obtained strictagenin appears to be either (20S, 22S, 25S)-5α-furostan-22, 25-epoxy-1β, 3α, 26-triol or (25S)-5α-spirostane-1β, 3α, 25-triol, the results being more consistent with the former compound.

Strictagenin triacetate (**2b**), $C_{33}H_{50}O_8$ (M^+, *m/e* 574.3513, calculated 574.3503), has been obtained as an oil which would not crystallise. The MS verifies the conversion of strictagenin into the triacetate and localises one of the acetoxy groups in ring F (base peak *m/e* 197), as expected. The other F ring fragments occur at *m/e* 184, 173 and 137. Other fragments, for example at *m/e* 373 and 253 (*m/e* 373 − $2CH_3COOH$), show that the additional acetoxy groups are located in rings A–D. As in the MS of strictagenin, that of the triacetate lacks the ions analogous to those at *m/e* 373 and 363 of normal dihydroxy spirostanes and this suggests the presence of a "furanose" F ring.

The NMR spectrum of strictagenin triacetate shows resonances at δ 0.74† (3H, s; C_{18}–Me), 0.94 (3H, s; C_{19}–Me), 0.95 (3H, d, $J \simeq 6.5$ Hz; C_{21}–Me), 1.16 (3H, s; C_{27}–Me), 1.95 (3H, s; 1β-OCO$\underline{CH_3}$), 2.05 (3H, s; 3α-OCO$\underline{CH_3}$), 2.07 (3H, s; C_{26}-OCO$\underline{CH_3}$), 3.85 (1H, d, $J_{AB} \simeq 12$ Hz; C_{26}–H), 4.10 (1H, d, $J_{BA} \simeq 12$ Hz; C_{26_B}–H), 4.27 (1H, q, $J \simeq 7.5$ Hz; 4.80 (1H, dd, $J_{1\alpha,2\beta} \simeq 11$ Hz and $J_{1\alpha,2\alpha} \simeq 5$ Hz; $C_{1\alpha}$–H) and 4.94 (1H, broad s, $W_{1/2} \simeq 7.5$ Hz; $C_{3\beta}$–H). The chemical shift of the C_{27}-methyl group is consistent only with it being attached to a "furanose" F ring in an equatorial position.[11,16] The marked downfield shift of the two protons on C_{26} after acetylation favours also the presence of a primary hydroxy group on C_{26} ("furanose" series $-CH_2OH$) rather than a tertiary hydroxy group attached to C_{25} ("pyranose" series). Double irradiation at δ 3.85 causes the signal at δ 4.10 to collapse to a singlet which shows that the protons on C_{26} are coupled. The downfield shift of the C_{19}-methyl group is similar to that of 1β-hydroxycrabbogenin diacetate and confirms the presence of 1β- and 3α-acetoxy groups in the 5α-series. From all the data obtained strictagenin is shown to be (20S, 22S, 25S)-5α-furostan-22, 25-epoxy-1β, 3α, 26-triol. To our knowledge, this is the first record of this compound.

Similar compounds with hydroxylated "furanose" F rings have been noted to isomerise, stereospecifically, under mildly acidic conditions and at room temperature to the 6-membered F ring series.[17,18] The reaction is thought to proceed through opening of the 5-membered F ring to give a carbonium ion at C_{22} and the posterior recyclisation to a 6-membered ring.[19]

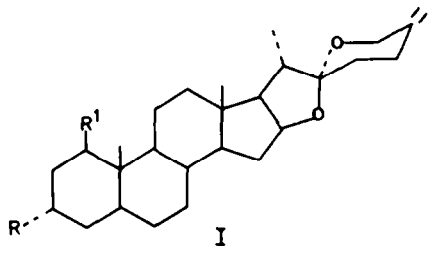
The structure of strictagenin has been confirmed by acid isomerisation to its 6-membered analogue, to which the trivial name pompeygenin has been given. Although in some previous studies[17,18] nearly 100% conversion has been achieved in the transformation of the "furanose" to the "pyranose" F ring series, in our case the transformation has been incomplete. Tlc examination of the mixture reveals two compounds, which have been separated by preparative tlc. One compound is strictagenin and the second pompeygenin.

Pompeygenin (**3**), m.p. 260°, crystallises as needles from acetone. Its IR spectrum shows absorption at 3440 cm^{-1} (hydroxyl) and at 984, 941, 908, 893 and 842 cm^{-1} (spiroketal region), with the absorption at 893 cm^{-1} being of greater intensity than that at 908 cm^{-1}. The spectrum is indicative of 25S-hydroxy spirostanes,[6] such as iso-reineckiagenin, *iso*-androgenin A and *iso*-caelagenin. A sharp band observed in the spectrum of pompeygenin at 941 cm^{-1} has been recorded at 938 cm^{-1} for *iso*-reineckiagenin[6] and *iso*-caelagenin[14], and at 940 cm^{-1} for *iso*-androgenin A.[19]

The NMR spectrum of pompeygenin exhibits resonances for the methyl groups at δ 0.76† (3H, s; C_{18}–Me), 0.82 (3H, s; C_{19}–Me), 1.00 (3H, d, $J \simeq 6.5$ Hz; C_{21}–Me) and 1.09 (3H, s; C_{27}–Me). The chemical shift of the C_{27}-methyl group is consistent only with 25S-hydroxyspirostanes.[13–15] Addition of D_2O does not affect the shifts of the methyl groups nor those of the C_{26}-protons. The resonances of the latter protons are observed at δ 3.20 (1H, dd, $J_{26_\alpha,26_\beta} \simeq 12$ Hz and $J_{26_\beta,24_\beta} \simeq 2$ Hz; C_{26}–H) and at δ 3.68 (1H, d, $J_{26_\beta,26_\alpha} \simeq 12$ Hz; C_{26_α}–H), the assignments of which are aided by the long range coupling observed between the equatorial C_{26_β}- and C_{24_β} protons. Double irradiation at δ 3.68 causes the signal at δ 3.20 to collapse to a broad singlet ($W_{1/2} \simeq 5$ Hz) and confirms that the C_{26}-protons are coupled.

The data obtained reveals that the conversion of strictagenin to pompeygenin had been achieved. As pompeygenin has identical chromatographic characteristics to a component present in *C.stricta* leaf extract it seems likely that this spirostane is present in the plant extract.

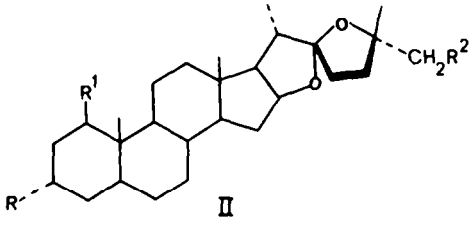
However, because this compound and other similar F ring hydroxylated "pyranose" compounds can be obtained by acid isomerisation of their "furanose" F ring analogues, doubt is cast on whether the former compounds exist in the plant or have been formed during the acid hydrolysis of the glycoside.



I

(1)

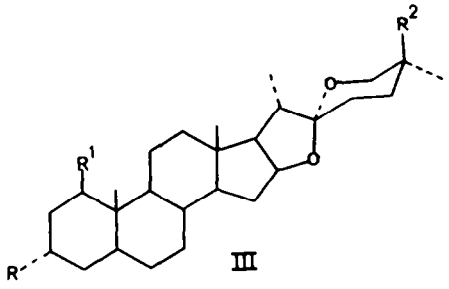
(a) R=OH; R^1=H = crabbogenin
(b) R=R^1=OH = 1β-hydroxycrabbogenin
(c) R=R'=OAc = 1β-hydroxycrabbogenin dicetate



II

(2)

(a) R=R^1=R^2=OH = strictagenin
(b) R=R^1=R^2=OAc = strictagenin triacetate



III

(3)

R=R^1=R^2=OH = pompeygenin

EXPERIMENTAL

The m.ps, determined on a Kofler block, are uncorrected. IR spectra have been obtained from KBr discs using a Perkin-Elmer 377 Grating Infra-Red Spectrophotometer. The MS have been recorded on a Kratos MS 50 Spectrometer. NMR spectra have been determined in $CDCl_3$ using a Bruker 270 MHz machine and the optical rotation in MeOH using an Optical Activity -AA-10 Polarimeter.

Isolation of the sapogenins. Air-dried leaves of *Cordyline stricta*† (3 kg), collected from Unumgar State Forest No. 540, Northern New South Wales in July, were powdered and extracted by the method used by Griffin *et al.*[20] This involved hot percolation with 85% aqueous EtOH. The extract was concentrated to 3l under reduced pressure, H_2O (1l) was added and the mixture was shaken with 2 × 2l of Et_2O. To the aqueous extract, combined with 2 × 1l aqueous washing of the mixed Et_2O extracts, an equal volume of EtOH was added and the mixture concentrated under reduced pressure to 1l. NaCl (100 g) was added, the pH adjusted to 4.5 by adding 1M H_2SO_4, and the mixture extracted ×3 with equal volumes of *n*-BuOH saturated with H_2O. To the combined *n*-BuOH extracts was added an equal volume of H_2O and the mixture was concentrated to 800 ml. HCl was added to make the solution 4M, the mixture was refluxed for 4 hr and filtered. The insoluble material, after drying, was dissolved in toluene (1l) and refluxed with 20% methanolic KOH solution (250 ml) for 1 hr before filtration. The insoluble material was washed with hot toluene and the filtrates combined. The toluene solution, after washing with 1l H_2O was evaporated to dryness to yield a mixture of crude sapogenins.

The sapogenin extract was chromatographed on a column of silica gel (4 × 45 cm) using successively *n*-hexane-EtAc (4:1, 1l), *n*-hexane-EtAc (3:1, 0.6l), *n*-hexane-EtAc (2:1, 0.9l), *n*-hexane-EtAc (1:1, 2.6l), EtAc (1l) and EtOH (0.6l). The collected fractions were screened for sapogenins by tlc using air-dried layers of silica gel G(250 mμ) and CH_2Cl_2–MeOH-formamide as the solvent system. The steroidal compounds were located by spraying with 50% aq. H_2SO_4 and heating at 100° until the characteristic colours developed. *n*-Hexane-EtAc (4:1) and *n*-hexane-EtAc (3:1) eluted the monohydroxy sapogenins only, *n*-hexane-EtAc (2:1) and the earlier fractions of the *n*-hexane-EtAc (1:1) eluate afforded the dihydroxy sapogenins and the rest of the solvents furnished the polyhydroxy compounds.

The monohydroxy sapogenins were separated initially into fractions A1, A2 and A3 by preparative tlc on air-dried layers of silica gel G (500 mμ) using *n*-hexane-EtAc (4:1) (system 1). The chromatograms were sprayed with H_2O to locate the sapogenin bands, which were dried, separately removed and eluted with $CHCl_3$. The components of A1 were separated by preparative tlc on layers of silica gel G containing 2% $AgNO_3$. The layers, 500 mμ thick, had been activated at 100° for 1 hr before use. The chromatograms were developed three times in CH_2Cl_2-acetone (49:1) (system 2).

The dihydroxy sapogenins were separated initially into fractions C, D and E on air-dried layers of silica gel G (500 mμ) using two-fold development in $CHCl_3$–EtOH (95:5) (system 3). The components of C were acetylated by dissolving them in pyridine and refluxing with acetic anhydride for 15 min. 1β-Hydroxycrabbogenin diacetate was separated from cordylagenin and cannigenin diacetates by preparative tlc using system 2.

1β-Hydroxycrabbogenin diacetate was refluxed with 5% methanolic potassium hydroxide for 15 min to yield 1β-hydroxycrabbogenin. NMR: δ 0.76† (3H, s; C_{18}-Me), 0.82 (3H, s; C_{19}-Me), 0.95 (3H, d, $J \simeq 6.5$ Hz; C_{21}-Me), 3.75 (1H, dd, $J_{1\alpha,2\beta} \simeq 11$ Hz and $J_{1\alpha,2\alpha} \simeq 5$ Hz; $C_{1\alpha}$-H), 3.79 (1H, d, $J_{26\beta,26\alpha} \simeq 12.5$ Hz; $C_{26\alpha}$-H), 4.02 (1H, broad s, $W_{1/2} \simeq 8$ Hz; $C_{3\beta}$-H), 4.24 (1H, d, $J_{26\alpha,26\beta} \simeq 12.5$ Hz; $C_{26\beta}$-H, 4.36 (1H, q, $J \simeq 7.5$ Hz; C_{16}-H), 4.65 (1H, s; $J_{gem_{AB}} \simeq 0$ Hz; C_{27A}-H), and 4.68 (1H, s, $J_{gem_{BA}} \simeq 0$ Hz; C_{27_B}-H).

Conversion of strictagenin to pompeygenin. A solution of strictagenin (4 mg) in 4% HCl in MeOH (2 ml) was allowed to stand at room temp for 1 hr. H_2O was added and the mixture extracted with three volumes of $CHCl_3$. The combined extracts were concentrated to small volume and the pompeygenin formed was separated (≃ 1.5 mg) by preparative tlc using three-fold development in system 3.

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