The solvent was distilled to about 50 cc. and then extracted with ether and washed well with water. The ether was evaporated to a small volume and cooled overnight. The crystals were filtered and the product was crystallized from dilute methanol and finally from ether, m. p. and mixed m. p. with authentic chlorogenin, 274–276°.

The above product was refluxed with acetic anhydride for thirty minutes. The excess acetic anhydride was removed and the residue was crystallized from dilute methanol, m. p. and mixed m. p. with authentic chlorogenin diacetate, 154–155°.

Pseudomexogenin.—A solution of 30 g. of mexogenin in 50 cc. of acetic anhydride was treated as described for the preparation of pseudohecogenin. The product was crystallized from ether and from acetone, m. p. 145°; yield 22.8 g.

Anal. Calcd. for $C_{27}H_{42}O_5$: C, 72.6; H, 9.5. Found: C, 72.5; H, 9.4.

Neomexogenin.—A mixture of 20 g. of pseudomexogenin, 500 cc. of ethyl alcohol and 20 cc. of concentrated hydrochloric acid was treated as described for neokammogenin. The solvent was distilled to a small volume and allowed to stand overnight in a refrigerator. The crystals were filtered and recrystallized from ether, m. p. and mixed m. p. with mexogenin, 244–246°; yield 11.2 g. Upon acetylation with acetic anhydride a product was obtained which melted at 205–207° and gave no depression when mixed with the diacetate of mexogenin.

The ethereal mother liquors from the crystallization of mexogenin were evaporated and the residue was acetylated by refluxing with acetic anhydride for thirty minutes. The solvent was removed and the residue was crystallized from a small amount of methanol to give the diacetate of neomexogenin, m. p. 162–164°; yield 3.6 g.

Anal. Calcd. for $C_{31}H_{46}O_7$: C, 70.2; H, 8.7. Found: C, 70.4; H, 8.9.

The above product was hydrolyzed by refluxing with alcoholic potassium hydroxide for twenty minutes. It was crystallized from dilute methanol and from ether, m. p. 222°.

Anal. Calcd. for $C_{27}H_{42}O_5$: C, 72.6; H, 9.5. Found: C, 72.8; H, 9.2.

When neomexogenin was refluxed with alcoholic hydrochloric acid for forty hours a product was obtained melting at 246–247° which gave no depression in melting point when mixed with mexogenin.

Neosamogenin.—To a solution of 10 g. of sodium in 200 cc. of absolute ethanol was added 2 g. of neomexogenin diacetate and 10 cc. of 85% hydrazine hydrate. The product was heated at 200° for ten hours. Water was added and the precipitated product was filtered, dried and crystallized from acetone to give neosamogenin, m. p. 174–176°.

Anal. Calcd. for $C_{27}H_{44}O_4$: C, 75.0; H, 10.3. Found: C, 74.8; H, 10.1.

Neosamogenin upon refluxing with acetic anhydride gave a diacetate which was crystallized from methanol as needles, m. p. 173–175°.

Anal. Calcd. for $C_{31}H_{48}O_6$: C, 72.1; H, 9.4. Found: C, 71.9; H, 9.5.

The above product gave no depression in melting point with that prepared from pseudosamogenin.

Pseudosamogenin.—A solution of 30 g. of samogenin in 50 cc. of acetic anhydride was treated as described for the preparation of pseudomexogenin. After hydrolysis with alcoholic potassium hydroxide the product was crystallized from methanol, m. p. 182–184°; yield 21.6 g.

Anal. Calcd. for $C_{27}H_{44}O_4$: C, 75.0; H, 10.3. Found: C, 74.9; H, 10.5.

To a cold solution of 20 g. of pseudosamogenin in 500 cc. of ethyl alcohol was added 20 cc. of concentrated hydrochloric acid. The product was allowed to stand in a refrigerator overnight. It was then extracted with ether, washed well with water and the solvent removed to a small volume. It was allowed to stand overnight in a refrigerator and was then filtered. It was crystallized from ether, m. p. and mixed m. p. with samogenin, 212°; yield 10.6 g. Upon acetylation this product gave the diacetate of samogenin, m. p. and mixed m. p. 198°.

The mother liquors from the above crystallization of samogenin were distilled and the residue was acetylated by boiling for thirty minutes with acetic anhydride. The solvent was removed *in vacuo* and the residue was crystallized from methanol, m. p. and mixed m. p. with neosamogenin acetate, 173–175°; yield 4.1 g.

Anal. Calcd. for $C_{31}H_{48}O_6$: C, 72.1; H, 9.4. Found: C, 72.0; H, 9.4.

Hydrolysis with alcoholic potassium hydroxide gave a product m. p. and mixed m. p. with neosamogenin, 174–176°. This is identical with the product reported above.

When neosamogenin was refluxed with alcoholic hydrochloric acid for thirty hours it gave a product which gave no depression in melting point with samogenin. Acetylation gave a diacetate, m. p. and mixed m. p. with samogenin diacetate, 197–198°.

Summary

Neokammogenin, neomanogenin, neoyuccagenin, neogitogenin, neohecogenin, neotigogenin, neodiosgenin, neochlorogenin, neomexogenin and neosamogenin were prepared.

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[CONTRIBUTION FROM THE LABORATORY OF BOTANICA-MEX., S. A.]

Steroidal Sapogenins. No. 161. The Seasonal Variation of Sapogenins in Plants

BY RUSSELL E. MARKER AND JOSEFINA LOPEZ

A study has been made of the steroidal sapogenins present in various parts of *Yucca schottii*, *Samuela carnerosana* and *Agave striata* before and after fruiting. It was shown that after fruiting the plants contained no monohydroxy steroids, but contained only the complex polyhydroxy steroids. As the flowering and fruiting season approaches these polyhydroxy steroids are changed progressively to the simpler steroids which are discarded in the fruit or flower stem of the plant. It is interesting to note that the flowers of *Yucca schottii* contained manogenin, gitogenin, tigogenin and smilagenin, yet in the course of only a few weeks until the fruit was formed these were all changed into their side-chain isomers neomanogenin, neogitogenin, neotigogenin and sarsasapogenin. The only sapogenin that could be isolated from the flowers of *Samuela carnerosana* was smilagenin, yet when the fruit was formed this contained only its side chain isomer, sarsasapogenin. *Agave striata* medium aged plants contained only neo-manogenin, but the flower stems and flowers from old plants contained a mixture of neogitogenin and neoheco-

genin, whereas when the fruit was formed these were reduced to neotigogenin. These results are summarized in Table I.

TABLE I

Agave Striata

Young plants	Flowers and stems	Fruit
Neomanogenin	Neogitogenin	Neotigogenin
	Neohecogenin	

Samuela Carnerosana

Caudex before flowering[a]	Flowers	Fruit
Kammogenin	Smilagenin	Sarsasapogenin
Mexogenin		
Samogenin		
Smilagenin		

Caudex after fruiting	Leaves after fruiting
Mexogenin	Kammogenin
Samogenin	Mexogenin

Yucca Schottii

Caudex before flowering	Flowers	Fruit
Kammogenin	Manogenin	Neomanogenin
Manogenin	Gitogenin	Neogitogenin
Mexogenin	Tigogenin	Neotigogenin
Yuccagenin	Smilagenin	Sarsasapogenin
Gitogenin		
Samogenin		
Smilagenin		

Caudex after fruiting	Roots after fruiting	Leaves after fruiting
Kammogenin	Yuccagenin	Kammogenin
Yuccagenin		

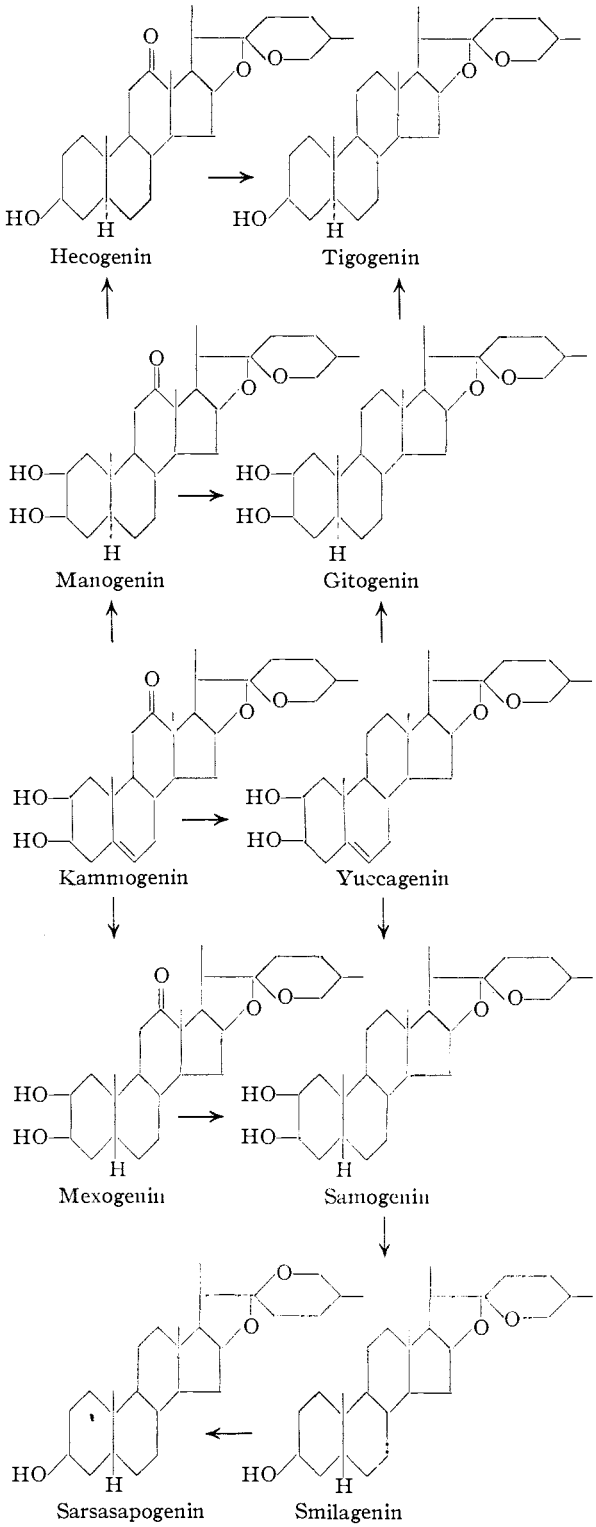
Fruit stems	Roots after flowering	Leaves before flowering
Yuccagenin	Yuccagenin	Kammogenin

[a] Unpublished results.

The structural formulas below will show the progressive biogenetic change in the plants from the more complex to the simpler steroidal sapogenins as the fruiting season approaches and passes. The simpler sapogenins which had been formed during the year in the plant from the more complex ones are discarded in the fruit and the cycle then commences over again. The process involved is merely one of reduction at various points in the molecule, its course depending upon the plant and its enzymes.

In the above table neomanogenin, neogitogenin and neotigogenin were omitted. These compounds differ from manogenin, gitogenin and tigogenin in the same manner that sarsasapogenin differs from smilagenin in their side-chain configurations.

In the case of *Yucca schottii* the most oxygenated sapogenin isolated was kammogenin. Only kammogenin and its reduction product yuccagenin were present in the plant after fruiting. To form yuccagenin the kammogenin lost its ketone group at C-12. Shortly before the flowers appeared the plant contained many other sapogenins; yuccagenin on reduction gave gitogenin



with the allo configuration at C-5 as well as samogenin which differs from gitogenin only in the configuration of the hydrogen at C-5. In the same manner, kammogenin upon reduction of the double bond gave manogenin and mexogenin

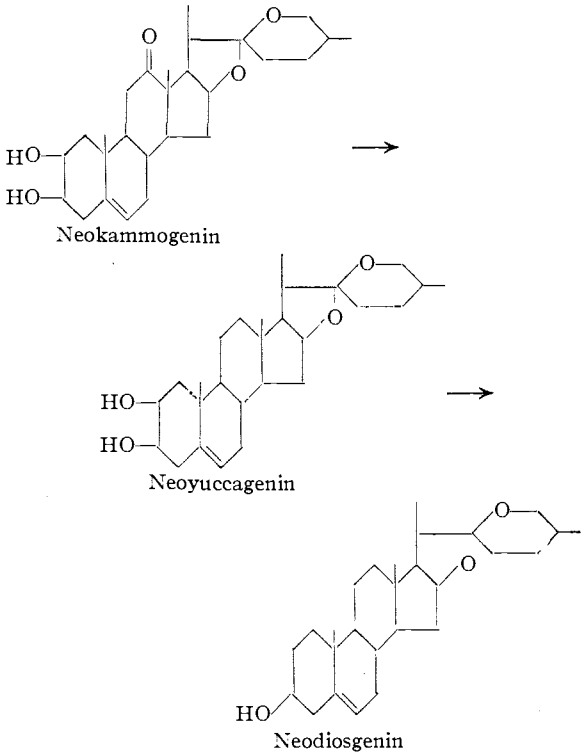
differing only in the configuration of the hydrogen at C-5. Production of gitogenin and samogenin from manogenin and mexogenin, respectively, can be brought about by the loss of the ketonic groups at C-12 in the same manner in which kammogenin is transformed into yuccagenin. Smilagenin is formed from samogenin and tigogenin from gitogenin. Evidence for this is the fact that before flowering a considerable amount of samogenin was present in the plant but after the fruit had formed this had disappeared entirely with an increase in the amount of smilagenin and sarsasapogenin. These products as they occur in the plant are combined with many sugars in the form of glycosides. As a great deal of this change in the sapogenins occurs near the flowering period it has been observed that very much free sugar is present in the flower, flower stalk and fruit. This could well be accounted for by the splitting off of the sugars from some of the hydroxyl groups during these reductions to the simpler steroids.

In the case of *Samuela carnerosana*, kammogenin was also isolated both before and after flowering. After the fruit was obtained the plant contained no smilagenin or sarsasapogenin. However, before flowering a considerable amount of smilagenin was formed. In this plant reduction of kammogenin goes in only one direction to give first saturation at C-5 with the coprostane configuration (mexogenin), which on further loss of the ketone at C-12 gives samogenin. The latter then goes to smilagenin which is discarded in the fruit in the form of sarsasapogenin.

Another type of biogenesis of steroidal sapogenins occurs in the formation of the unsaturated compounds at C-5 such as diosgenin and neodiosgenin. These compounds are generally found in the large rhizones of the plants, such as *Dioscoreas*. Careful study of the products in dioscorea rhizones gave no indication of their formation as only products with a hydroxyl group at C-3 could be found. However, a study of the steroids present in the leaves of *Dioscorea mexicana* showed the presence of neokammogenin and neoyuccagenin but the rhizones previously reported by us yielded only neodiosgenin and nologenin.[1] In the case of these types of plants the simpler steroids are not discarded in the fruit and flowers but are retained after their formation in the large tubers. All the steroids isolated from this plant had a side chain isomeric with kammogenin, yuccagenin, and diosgenin. In this type of biogenesis neokammogenin loses its ketone group with the formation of neoyuccagenin in the leaves. This is followed by the conversion of neoyuccagenin to the mono hydroxy steroid neodiosgenin in the same manner in which gitogenin and samogenin are converted to tigogenin and smilagenin in *Yucca schottii*. This takes place without the saturation of the double bond at C-5.

We have studied many other plants and all

(1) Marker and Lopez, THIS JOURNAL, **69**, 2386 (1947).



follow this general scheme of the complex steroids forming the simpler ones near flowering and fruiting time. The four examples presented here are typical of the ones we have observed in other plants.

We have accumulated much evidence in support of the non-existence of a C-12 ketone in kammogenin, manogenin, hecogenin and mexogenin when these products are present in the plant in the form of glycosides. Indications are that these products exist in the plant as glycosides at C-11 and C-12, which upon hydrolysis dehydrate to form a C-12 ketone.

Experimental Part

Sapogenins from Agave Striata.—Medium aged plants: The entire plant was ground and extracted with alcohol. The saponins were hydrolyzed in the usual manner and the sapogenin fraction was crystallized from acetone and from methanol. The total sapogenins were then converted into their acetates by refluxing with acetic anhydride for thirty minutes. Upon cooling the product was filtered and recrystallized from methanol, m. p. and mixed m. p. with neomanogenin diacetate, 222°. The yield was 8 g. from 20 kg. of plants.

Anal. Calcd. for $C_{31}H_{46}O_7$: C, 70.2; H, 8.7. Found: C, 70.4; H, 8.8.

Hydrolysis of the diacetate with alcoholic potassium hydroxide gave a product which was crystallized from ether, m. p. and mixed m. p. with neomanogenin, 242°.

Anal. Calcd. for $C_{27}H_{42}O_5$: C, 72.6; H, 9.5. Found: C, 72.5; H, 9.4.

When the above product was refluxed for seventy-two hours with an alcoholic solution of hydrochloric acid it gave a product, m. p. and mixed m. p. with manogenin, 254°. Acetylation of this product with acetic anhydride gave the diacetate of manogenin, m. p. and mixed m. p. 242°.

TABLE II

	M. p. and mixed m. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Sarsasapogenin Ac.	140	$C_{29}H_{46}O_4$	75.9	76.1	10.1	10.3
Sarsasapogenin	200–201	$C_{27}H_{44}O_3$	77.8	77.9	10.7	10.6
Neomanogenin Diac.	222	$C_{31}H_{46}O_7$	70.2	70.3	8.7	8.7
Neomanogenin	242	$C_{27}H_{42}O_5$	72.6	72.4	9.5	9.7
Neogitogenin Diac.	212	$C_{31}H_{48}O_6$	72.1	72.4	9.4	9.6
Neogitogenin	248	$C_{27}H_{44}O_4$	75.0	75.3	10.3	10.1
Neotigogenin Ac.	180	$C_{29}H_{46}O_4$	75.9	76.1	10.1	10.3
Neotigogenin	204	$C_{27}H_{44}O_3$	77.8	77.8	10.7	10.5

Anal. Calcd. for $C_{31}H_{46}O_7$: C, 70.2; H, 8.7. Found: C, 70.5; H, 8.7.

The sapogenins obtained from 5 kg. of the fruit of *Agave striata* were crystallized from methyl alcohol and acetylated. After removal of the excess acetic anhydride the residue was crystallized from methyl alcohol to give neotigogenin acetate, m. p. and mixed m. p. 180°; yield 4.2 g. No other sapogenins could be isolated.

Anal. Calcd. for $C_{29}H_{46}O_4$: C, 75.9; H, 10.1. Found: C, 76.0; H, 10.4.

Hydrolysis of the above acetate with alcoholic potassium hydroxide gave a product which was crystallized from ether, m. p. and mixed m. p. with neotigogenin, 204°.

Anal. Calcd. for $C_{27}H_{44}O_3$: C, 77.8; H, 10.7. Found: C, 77.7; H, 10.5.

The sapogenins obtained from 10 kg. of the flower stems and flowers of *Agave striata* were dissolved in alcohol and treated with Girard reagent. The ketonic sapogenins were acetylated by refluxing for thirty minutes with acetic anhydride. The excess acetic anhydride was removed and the residue was crystallized from methanol to give neohecogenin acetate, m. p. and mixed m. p. 228°. No other ketonic sterols could be isolated.

Anal. Calcd. for $C_{29}H_{44}O_5$: C, 73.7; H, 9.4. Found: C, 73.4; H, 9.7.

Hydrolysis of the above acetate with alcoholic potassium hydroxide gave a product which was crystallized from dilute methanol. This gave no depression in m. p. when mixed with neohecogenin, m. p. 238°.

Anal. Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.8. Found: C, 75.2; H, 10.0.

The non-ketonic fraction was crystallized from ether, m. p. and mixed m. p. with neogitogenin 248°.

Anal. Calcd. for $C_{27}H_{44}O_4$: C, 75.0; H, 10.3. Found: C, 75.0; H, 10.4.

The above product was converted to the acetate by refluxing for thirty minutes with acetic anhydride. It was crystallized from methanol to give neogitogenin diacetate, m. p. and mixed m. p. 212°. No other non-ketonic sapogenins could be isolated.

Anal. Calcd. for $C_{31}H_{48}O_6$: C, 72.1; H, 9.4. Found: C, 72.1; H, 9.7.

Sapogenins from the Fruit of Yucca Schottii.—The sapogenin fraction from 5 kg. of the dried fruit was crystallized from ether. The solvent was removed from the ether soluble fraction and the residue was crystallized from methanol. The product was acetylated and crystallized from ethyl acetate to give 32 g. of sarsasapogenin acetate. The m. p. and the m. p. of the mixture with an authentic sample and the analyses for all compounds isolated are given in Table I. Hydrolysis of the acetate gave sarsasapogenin which was crystallized from methanol.

The ether insoluble sapogenin fraction (14 g.) from the fruit was dissolved in boiling ethyl alcohol and treated with Girard reagent on a steam-bath for thirty minutes. Water and ether were added and the aqueous ketonic fraction was hydrolyzed by warming for twenty minutes with hydrochloric acid. The product was extracted with ether. Upon concentration of the ether, crystals separated. These were acetylated and crystallized from methanol to give 1.2 g. of neomanogenin diacetate. Crystallization from ether of the hydrolysis product gave neomanogenin.

The solvent was removed from the non-ketonic fraction until about 100 cc. remained. Upon cooling, a product crystallized and was separated by filtration. The product was acetylated and crystallized from methanol to give 2.3 g. of neogitogenin diacetate. Hydrolysis and crystallization from ether gave neogitogenin.

The ether soluble fraction from the crude neogitogenin was acetylated and crystallized from methanol to give 3.1 g. of neotigogenin acetate. Saponification of the acetate gave neotigogenin.

Sapogenins from the Flowers of Yucca Schottii.—The flowers of *Yucca schottii* were picked from the flower stems, dried and pulverized. An alcoholic extract of 5 kg. of these was hydrolyzed and the sapogenin fraction was crystallized from ether. The ether soluble fraction was acetylated, the solvent removed and the residue was crystallized from methanol to give 21 g. of smilagenin acetate. Hydrolysis of the acetate gave smilagenin.

The ether insoluble fraction of sapogenins was treated with Girard reagent to separate the ketonic steroids. The ketonic fraction, 6.6 g. was acetylated and the product was crystallized from methanol to give 3.4 g. of manogenin diacetate. Hydrolysis of the diacetate and crystallization from ether gave manogenin.

The non-ketonic ether insoluble fraction, 12.9 g., was crystallized from methanol to give 3.9 g. of tigogenin. Acetylation and crystallization from methanol gave tigogenin acetate.

The methanol mother liquors from the crystallization of tigogenin were concentrated to dryness and the residue was crystallized from ether to give 3.4 g. of gitogenin. Acetylation and crystallization from methanol gave gitogenin diacetate.

TABLE III

	M. p. and mixed m. p. °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Smilagenin ac.	130	$C_{29}H_{46}O_4$	75.9	76.0	10.1	10.3
Smilagenin	184	$C_{27}H_{44}O_3$	77.8	77.8	10.7	10.5
Manogenin diac.	242	$C_{31}H_{46}O_7$	70.2	70.4	8.7	8.9
Manogenin	255	$C_{27}H_{42}O_5$	72.6	72.7	9.5	9.7
Tigogenin ac.	202	$C_{29}H_{46}O_4$	75.9	76.1	10.1	10.3
Tigogenin	207	$C_{27}H_{44}O_3$	77.8	77.6	10.7	10.6
Gitogenin diac.	242	$C_{31}H_{48}O_6$	72.1	72.0	9.4	9.2
Gitogenin	268	$C_{27}H_{44}O_4$	75.0	75.0	10.3	10.0

Sapogenins from Yucca Schottii at Fruit Collecting Time.—At the time of the collection of the fruit of *Yucca schottii*, six plants which had borne fruit were collected. These were separated into the green leaves, roots, and a mid-section of the caudex or trunk. The section of the trunk examined represented about one-third of the caudex taken midway between the leaves and roots.

The sapogenin fraction from 10 kg. of dried leaves was crystallized from ether and acetylated. The acetates

were crystallized from methanol and from ether to give 18.2 g. of kammogenin diacetate. Hydrolysis and crystallization from ether gave kammogenin. No other sapogenins could be isolated from the leaves.

The sapogenin fraction from 10 kg. of dried roots was treated with Girard reagent in alcohol to remove ketones. There was no ketonic fraction present. The non-ketonic fraction was crystallized from ether and acetylated. The acetate was crystallized from methanol to give 24.8 g. of yuccagenin diacetate. Hydrolysis of this acetate and crystallization from ether gave yuccagenin. No other sapogenins could be isolated from the roots.

The sapogenin fraction from 10 kg. of the dried mid-section of the caudex of *Yucca schottii* fruiting plants was dissolved in alcohol and treated with Girard reagent to remove ketones. The ketone fraction was acetylated and the resulting product was crystallized from methanol and from ether to give kammogenin diacetate (18.6 g.). No other sapogenins could be found in the ketonic fraction. The non-ketonic fraction was extracted with ether and the solvent was removed. The residue was acetylated and the acetates were crystallized from methanol and from ether to give 24.7 g. of yuccagenin diacetate. Hydrolysis of this acetate and crystallization from ether gave yuccagenin. No other sapogenins could be isolated from the caudex of the fruiting plant.

TABLE IV

	M. p. and mixed m. p. °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Kammogenin diac.	258–260	$C_{31}H_{44}O_7$	70.4	70.5	8.4	8.6
Kammogenin	242	$C_{27}H_{40}O_6$	72.9	72.7	9.1	9.5
Yuccagenin diac.	178–180	$C_{31}H_{46}O_6$	72.2	72.5	9.0	9.2
Yuccagenin	248–250	$C_{27}H_{42}O_4$	75.3	75.3	9.8	9.6

Sapogenins in Yucca Schottii before Flowering.—Six plants were obtained before the stage of flowering had been reached. These were separated into leaves, roots and a mid-section of the caudex.

The sapogenins from 10 kg. of dried leaves were worked up as described for the leaves after fruiting. The only sapogenin which could be isolated from these was kammogenin, which was crystallized from ether (18.9 g.). Acetylation and crystallization from ether gave kammogenin diacetate.

The sapogenin fraction from 10 kg. of dried roots was worked up as previously described. The only product which could be isolated from this fraction was yuccagenin (19.4 g.). Acetylation and crystallization from methanol gave yuccagenin diacetate.

The sapogenin fraction from 20 kg. of the dried caudex of *Yucca schottii* before flowering was dissolved in ethanol and treated with Girard reagent to separate into a ketonic and a non-ketonic fraction. The ketonic fraction was crystallized from ether and the insoluble sterols were converted into their acetates. These were crystallized from ether to give 9.7 g. of kammogenin diacetate. Hydrolysis of this acetate and crystallization from ether gave kammogenin. The sterols from the acetate mother liquors of the crystallization of kammogenin diacetate were crystallized from methanol to give 2.1 g. of manogenin diacetate. Hydrolysis of this product and crystallization from ether gave manogenin.

The ether soluble sapogenins were acetylated and combined with those of the mother liquors from the crystallization of manogenin diacetate. The total was crystallized from ether to give an additional 4.1 g. of kammogenin diacetate. The mother liquors from these were hydrolyzed with alcoholic potassium hydroxide and crystallized from ether. The ether insoluble fraction was acetylated and the acetates were crystallized from pentane to give 6.2 g. of mexogenin diacetate. Hydrolysis of this acetate and crystallization from ether gave mexogenin.

The non-ketonic fraction from Girard treatment was crystallized from ether. The ether insoluble sterols were acetylated and crystallized from acetic anhydride. The crystalline portion was recrystallized from acetone to give 8.1 g. of gitogenin diacetate. Hydrolysis of this acetate and crystallization from ether gave gitogenin. The acetic anhydride mother liquors from the gitogenin diacetate were evaporated and the residue was crystallized from methanol to give 22.6 g. of yuccagenin diacetate. Hydrolysis of this acetate and crystallization from ether gave yuccagenin. The mother liquors from the yuccagenin diacetate were hydrolyzed and the product was crystallized from methanol to give an additional small fraction of yuccagenin. The methanol mother liquors were evaporated and the residue was crystallized from ether to give 12.6 g. of samogenin. Acetylation of this product and crystallization from methanol gave samogenin diacetate.

The ether soluble non-ketonic fraction was crystallized once from methanol and acetylated. This product was crystallized from methanol and from acetone to give 21.4 g. of smilagenin acetate. Hydrolysis and crystallization from methanol gave smilagenin.

TABLE V

	M. p. and mixed m. p. °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Kammogenin diac.	258–260	$C_{31}H_{44}O_7$	70.4	70.6	8.4	8.4
Kammogenin	242					
Yuccagenin diac.	178–180	$C_{31}H_{46}O_6$	72.3	72.3	9.0	9.1
Yuccagenin	248–250					
Manogenin diac.	242	$C_{31}H_{46}O_7$	70.2	70.2	8.7	8.8
Manogenin	254					
Mexogenin diac.	208	$C_{31}H_{46}O_7$	70.2	70.0	8.7	8.6
Mexogenin	247					
Gitogenin diac.	243	$C_{31}H_{46}O_6$	72.1	72.0	9.4	9.6
Gitogenin	268					
Samogenin diac.	200	$C_{31}H_{46}O_6$	72.1	72.4	9.4	9.6
Samogenin	206	$C_{27}H_{44}O_4$	75.0	75.2	10.3	10.2
Smilagenin ac.	150–152	$C_{29}H_{46}O_4$	75.9	76.0	10.1	9.9
Smilagenin	184					

Sapogenins from Yucca Schottii Fruit Stems.—The only sapogenin which could be isolated from the stems containing the fruit was yuccagenin, which was isolated as its diacetate, m. p. and mixed m. p. 178–180°.

Anal. Calcd. for $C_{31}H_{46}O_6$: C, 72.3; H, 9.0. Found: C, 72.4; H, 9.2.

Sapogenins from the Fruit of Samuela Carnerosana.—The sapogenin fraction was isolated from 10 kg. of the dried fruit. The total sapogenin fraction was crystallized from methanol and acetylated by refluxing for thirty minutes with acetic anhydride. The solvent was removed and the residue was crystallized from ethyl acetate to give 28 g. of sarsasapogenin acetate, m. p. and mixed m. p. 140°.

Anal. Calcd. for $C_{29}H_{46}O_4$: C, 75.9; H, 10.1. Found: C, 76.2; H, 10.4.

Hydrolysis of the acetate gave a product which was crystallized from methanol, m. p. and mixed m. p. with sarsasapogenin, 200–201°. No other sapogenins could be isolated from the fruit.

Sapogenins from the Flowers of Samuela Carnerosana.—The sapogenin fraction from 5 kg. of the dried flowers was acetylated and the product was crystallized from methanol to give smilagenin acetate, m. p. and mixed m. p. 130°. Yield was 19 g. No other product could be isolated.

Anal. Calcd. for $C_{29}H_{46}O_4$: C, 75.9; H, 10.1. Found: C, 75.7; H, 10.0.

Hydrolysis of this acetate and crystallization from methanol gave smilagenin, m. p. and mixed m. p. 184°.

Sapogenins from the Leaves of Samuela Carnerosana.—The sapogenin fraction from 5 kg. of the leaves of *Samuela carnerosana*, which were collected from plants which had just borne fruit, was treated with Girard reagent to separate into ketonic and non-ketonic sterols. There were no non-ketonic sapogenins present. The total sapogenin fraction was acetylated by refluxing for thirty minutes with acetic anhydride. The excess acetic anhydride was distilled and the residue was crystallized from ether to give the diacetate of kammogenin, m. p. and mixed m. p. 258–260°. Yield was 2.3 g.

Anal. Calcd. for $C_{31}H_{44}O_7$: C, 70.4; H, 8.4. Found: C, 70.4; H, 8.6.

Hydrolysis of the above acetate with alcoholic potassium hydroxide gave kammogenin, m. p. and mixed m. p. 242°.

The ether soluble fraction from the mother liquors of crystallization of the diacetate of kammogenin were hydrolyzed with alcoholic potassium hydroxide and the product was crystallized from ether. The ether insoluble fraction was acetylated by boiling with acetic anhydride for thirty minutes. The acetate was crystallized from methanol to give 5.8 g. of mexogenin diacetate, m. p. and mixed m. p. 208°.

Anal. Calcd. for $C_{31}H_{46}O_7$: C, 70.2; H, 8.7. Found: C, 70.1; H, 8.7.

Hydrolysis of the above acetate with potassium hydroxide gave mexogenin, which was crystallized from ether, m. p. and mixed m. p. 247°. No other sapogenins could be isolated from the leaves.

Sapogenins from Caudex and Roots of Samuela Carnerosana after Fruiting.—The sapogenins from 20 kg. of dried caudex and roots of *Samuela carnerosana* after fruiting were separated into a ketonic and a non-ketonic fraction by means of Girard reagent.

The ketonic fraction was acetylated and the product was crystallized from pentane to give 23 g. of the diacetate of mexogenin, m. p. and mixed m. p. 208°.

Anal. Calcd. for $C_{31}H_{46}O_7$: C, 70.2; H, 8.7. Found: C, 70.4; H, 8.7.

Hydrolysis of the above acetate and crystallization from ether gave mexogenin, m. p. and mixed m. p. 247°. No other ketonic sapogenins could be isolated from the caudex and roots.

The non-ketonic fraction from the caudex and roots was crystallized from ether to give samogenin, m. p. and mixed m. p. 206°; yield 18.3 g. Acetylation of this product and crystallization from methanol gave samogenin diacetate, m. p. and mixed m. p. 200°.

Anal. Calcd. for $C_{31}H_{48}O_6$: C, 72.1; H, 9.4. Found: C, 72.5; H, 9.7.

Sapogenins from Dioscorea Mexicana Leaves.—The crude sapogenins were isolated from 10 kg. of freshly dried leaves of *Dioscorea mexicana*. These were crystallized once from a small amount of ether to remove oily material. The total weight, 36 g., was refluxed for thirty minutes with 80 cc. of acetic anhydride. Upon cooling to room temperature the crystalline material was filtered. This consisted chiefly of neodiosgenin acetate. The mother liquors were evaporated and the residue was hydrolyzed with strong alcoholic potassium hydroxide. The sapogenin fraction was extracted with a large volume of ether, washed well and the solvent was removed to about 150 cc. Upon standing a week in a refrigerator the crystalline material was filtered, wt. 7.8 g. This was recrystallized several times from ether and from methanol to give a product, 2.1 g., m. p. and mixed m. p. with neokammogenin, 230°. Acetylation with acetic anhydride and crystallization from methanol gave the diacetate of neokammogenin, m. p. and mixed m. p. 203–205°.

Anal. Calcd. for $C_{31}H_{44}O_7$: C, 70.4; H, 8.4. Found: C, 70.6; H, 8.6.

When the neokammogenin was refluxed for seventy hours with an alcoholic solution of hydrochloric acid it gave a product which upon acetylation and crystallization from methanol was identical with kammogenin diacetate, m. p. 258–260°.

The mother liquors from the isolation of neokammogenin were treated with Girard reagent to remove ketones. From these a small additional quantity of neokammogenin was obtained. The non-ketonic fraction was crystallized from ether to give 1.7 g. of neoyuccagenin, m. p. and mixed m. p. 247°.

Anal. Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.8. Found: C, 75.0; H, 9.7.

Acetylation and crystallization from methanol gave the diacetate of neoyuccagenin, m. p. and mixed m. p. 157–159°.

Anal. Calcd. for $C_{31}H_{46}O_6$: C, 72.3; H, 9.0. Found: C, 72.0; H, 9.0.

Summary

A study has been made of the seasonal variation of the steroidal content of *Agave striata, Yucca schottii, Samuela carnerosana* and *Dioscorea mexicana*.

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[CONTRIBUTION FROM THE LABORATORY OF BOTANICA-MEX., S. A.]

Steroidal Sapogenins. No. 162. Kappogenin and Furcogenin

BY RUSSELL E. MARKER AND JOSEFINA LOPEZ

A preliminary announcement appeared in This Journal[1] on the isolation and tentative structures of a number of new steroidal sapogenins which were obtained from various plant sources. At the time it was submitted insufficient work was done on two of the products, "kappogenin" and "furcogenin," for complete characterization and structure proof.

A more careful study on "furcogenin" has shown it to be a mixture of smilagenin and hecogenin. Oxidation of "furcogenin" gave a diketone which is identical with hecogenone.

"Kappogenin" has been separated into nologenin and pseudodiosgenin. The latter is formed in small amounts upon refluxing diosgenin with acetic anhydride for thirty minutes. Its presence in the crude sapogenin mixture is accounted for by the fact that these were separated by means of their acetates. Its structure previously[1] was assumed because oxidation of the acetate gave 5,16-pregnadien-3-ol-20-one and treatment with

(1) Marker and co-workers, THIS JOURNAL, **65**, 1206 (1943).