THE SAPOGENINS OF POLYGALA SENEGA

BY WALTER A. JACOBS AND OTTO ISLER*

(From the Laboratories of The Rockefeller Institute for Medical Research, New York)

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Although a number of references to the saponin of *Polygala senega* or senega-root are to be found in the older literature, it has not been possible to uncover anything of importance relating to its structural chemistry. The more recent work of Wedekind and Krecke represents apparently the first real attempt in this regard. The latter, working with a saponin obtained as such from E. Merck, Darmstadt, found it to yield on hydrolysis a genin, senegenin, to which the formula $C_{26}H_{46}O_{6}$ was assigned. It was shown to be dibasic. The presence of two OH groups was indicated by the formation of a diacetyl derivative, the nature of which was concluded from its titration. A dimethyl ester (m.p. 206–208°) was also mentioned, but without analytical data.

Our own interest in the subject began before the recent developments in the chemistry of the sapogenins in which the method of dehydrogenation has so helped to sharpen their division into members of the triterpene and sterol groups. It was of importance then to determine in which of these categories the polybasic sapogenins would fall, if in either. Recently it has been possible to resume this study, but in the meantime the interesting series of papers by Wieland and coworkers on quinovic acid, another polybasic sapogenin, has appeared and, as will become apparent, senegenin has been found to belong apparently in the same general group.

The saponin studied by us was prepared in this laboratory from

* Holder of a fellowship from the Swiss-American Student Exchange.


commercial senega-root by extraction with alcohol. The partly purified saponin yielded on hydrolysis first a gelatinous prosapogenin which on further treatment with acid gave a sapogenin mixture. It soon became apparent that a number of substances were produced, and considerable study was required to find a suitable method of isolation and purification. Two of these were obtained in pure form and are the subject of the present report. The results obtained differed materially from those of Wedekind and Krecke, so that either their material was of different origin or it was not homogeneous.

One of our substances, which will be called senegenin, melted at 290–292°, was separated because of its lower solubility, and gave on analysis figures which agreed with the formula $C_{30}H_{46}O_8$ or $C_{36}H_{44}O_8$. Titration showed it to be dibasic and on heating with alkali a third equivalent was consumed, undoubtedly owing to cleavage of a lactone group. Although it resisted well the action of acids, it could not be recovered from the saponification mixture because of deep seated alteration. An amorphous dimethyl ester was prepared with diazomethane and in this derivative, although the lactone group was still readily saponified, the ester groups proved to be very resistant to saponification. Senegenin readily formed a diacetyl derivative. A high melting by-product of unexplained nature was simultaneously produced. Senegenin could not be hydrogenated and it is not certain whether a very weakly positive test obtained with tetranitromethane indicates unsaturation. The functions of the 8 oxygen atoms have been explained, since 4 are contained in two COOH groups, 2 in a lactone group, and 2 in two OH groups. From the analytical figures it is not possible to decide directly between the two possible formulas $C_{30}H_{44}O_8$ and $C_{36}H_{44}O_8$. In the former case, if no double bond occurs in the sapogenin, it would be pentacyclic, and in the latter case tetracyclic; but if the color with tetranitromethane means unsaturation, then it would be tetracyclic even in the former case.

In the more soluble sapogenin fraction crystalline material was contained from which it was possible to isolate a second sapogenin derivative which analysis indicated to possess the formula $C_{31}H_{50}O_8$ or $C_{33}H_{48}O_8$. It was found to be a monobasic acid. Contrary to senegenin, however, no lactone group could be detected on boiling with dilute alkali. However, further investigation showed that
the substance contained an ethyl group and was the monoethyl ester of a dibasic acid, $\text{C}_{29}\text{H}_{48}\text{O}_6$ ($\text{C}_{29}\text{H}_{48}\text{O}_6$). The latter was obtained from the ester by vigorous treatment with alkali. The ethyl ester group undoubtedly was formed by partial esterification of the dibasic acid during the hydrolysis of the saponin in dilute alcohol. The neutral mixed methyl ethyl ester was amorphous and, like senegenin ester, proved to be very resistant to saponification. This sapogenin also gave a diacetyl derivative. As in the case of senegenin diacetate, a small amount of a high melting by-product, likewise of unexplained nature, was formed. A di-$p$-bromobenzoate of the acid ester was also prepared. The acid $\text{C}_{29}\text{H}_{48}\text{O}_6$, therefore, is a dihydroxydibasic acid. The acid ester gave a positive test with tetranitromethane in chloroform solution and more pronounced than in the case of senegenin, but no double bond could be directly detected by hydrogenation. Although not definite, the available data as in the case of senegenin might appear to favor a tetracyclic structure.

The thought at once occurred of a possible relationship between senegenin and the second sapogenin. Attempts to prepare the latter by the continued action of alcoholic or dilute alcoholic acid on senegenin were unsuccessful. However, it is still possible that senegenin and its companion product do not occur as such but as a common precursor, perhaps of tribasic character ($\text{C}_{29}\text{H}_{48}\text{O}_6$), and that during the hydrolysis a labile carboxyl and a labile hydroxyl group are protected by lactonization (perhaps after preliminary stereoisomerization) with the formation of the dibasic lactone acid, senegenin. On the other hand, a portion of such a hypothetical acid, $\text{C}_{29}\text{H}_{48}\text{O}_6$, could lose both CO$_2$ and water to give the unsaturated dibasic acid $\text{C}_{29}\text{H}_{48}\text{O}_6$. Further work will be necessary to test such a suggestion.

The dehydrogenation of senegenin and the companion monoethyl ester was also studied. In these cases the dehydrogenation with selenium proceeded smoothly and with no evidence of the formation of naphthalin hydrocarbons as usually occurs with triterpene derivatives. In the case of senegenin, the largest fraction yielded a hydrocarbon which crystallized as lustrous leaflets and melted at 246.5°. The analysis agreed with the formulation $\text{C}_{22}\text{H}_{20}$ or $\text{C}_{22}\text{H}_{22}$. Its solubilities and other properties resembled closely those of chrysene. These properties suggest
that it is perhaps a homologue of the latter. A hydrocarbon $C_{26}H_{26}$ with a melting point of 245° was described by Ruzicka and Ehmann\(^3\) as produced in small amount on dehydrogenation of hederagenin. A sample of this substance kindly sent to us by Professor Ruzicka resembled closely our hydrocarbon and gave no melting point depression. There is therefore a possibility that they are identical. However, in the case of senegenin it is produced in much larger amount and in fact appears to be a principal dehydrogenation product. This was especially evident in the case of the dehydrogenation of the companion sapogenin.

The highest boiling fraction yielded in very small amount a hydrocarbon which melted at 298° and gave analytical figures corresponding to a trimethylpicene, $C_{25}H_{26}$. It showed no depression in melting point when mixed with the trimethylpicene from oleanolic acid, for which we are also indebted to Professor Ruzicka. The ultraviolet absorption curves obtained with both were indistinguishable (Fig. 1).

The dehydrogenation of the companion sapogenin appeared to proceed even more smoothly than in the case of senegenin. Hydrocarbon fractions which amounted to at least 25 per cent of the sapogenin used consisted principally of the chrysene hydrocarbon which melted at 246.5° and was indistinguishable from the substance obtained from senegenin. Finally, again a very small amount of the $C_{25}H_{26}$ hydrocarbon (trimethylpicene) was isolated, which melted at 297.5° and again proved to be apparently identical with the second hydrocarbon from senegenin. The trimethylpicene is a substance which Ruzicka and coworkers\(^4\) have obtained on dehydrogenation of a number of triterpenes and its formation has therefore given weight to the interpretation of these substances as picene derivatives.

It is premature to attempt to present a possible structure for the sapogenins of senega-root, and the question must be left open as to whether they are tetracyclic chrysene derivatives or pentacyclic picene derivatives. It is of interest that Wieland, Hartmann, and Dietrich\(^2\) on dehydrogenation of quinovic acid

\(^3\) Ruzicka, L., and Ehmann, L., Helv. chim. acta, 15, 447 (1932).

(pyroquinovic acid) obtained upwards of about 10 per cent of a hydrocarbon, $C_{25}H_{50}$, apparently identical with Ruzicka's trimethyl-

![Graph]

$\lambda$ in Å.

$\log \varepsilon$ is the molecular extinction coefficient; chloroform, the solvent

FIG. 1

picene, and a smaller yield of a second hydrocarbon, $C_{26}H_{44}$, melting at 202°. There was no mention, however, of a substance corresponding to our $C_{26}H_{42}$ hydrocarbon, although it is possible that
the $C_nH_m$ hydrocarbon may also be a chrysene derivative and a homologue of our substance. There is undoubtedly a significance in the fact that senegenin should give principally a chrysene hydrocarbon, while quinovic acid gives principally a picene derivative. This might perhaps support the tetracyclic nature of the former. However, many more data must be obtained before such a conclusion is justified, and we hope in further work to go more critically into this question.

We are especially indebted to Dr. Alexandre Rothen of this Institute for the ultraviolet absorption spectra determinations (as well as the plotting of the curves) which were generously carried out by him.

**EXPERIMENTAL**

The senega-root (*Polygala senega*) employed in our studies was the commercial material. A number of samples obtained at separate times from different crude drug houses gave essentially the same results. For the preparation of the crude saponin the following method was employed.

2 kilos of the ground root were refluxed in 6 liters of 95 per cent alcohol for 3 hours and then filtered hot. The extraction was repeated twice, each time with 4 liters of alcohol. The combined alcoholic filtrates were kept at 0° for 48 hours during which a copious precipitate of crude saponin mixed with fats separated. The collected material was dried and then thoroughly defatted in a Sohxtet apparatus with ether. The crude saponin was dissolved in about 30 parts of alcohol and refluxed with bone-black and then filtered hot. After standing 24 hours at 0° the colorless, amorphous saponin was collected. More material was recovered from the mother liquor by concentration to one-third volume. The two fractions were joined for further purification by reprecipitation from alcohol.

From 45 kilos of senega-root 950 gm. of crude senegin were thus obtained. On repeated fractionation from alcohol no crystalline saponin could be obtained. On rapid heating, it colored between 220-230° and decomposed towards 250°. The degree of homogeneity of this material could not be decided. All fractions ob-
tained on attempting repeated fractionation gave a similar sapo-
genin mixture on hydrolysis.

Hydrolysis of Senegin—100 gm. of twice “recrystallized” senegin
were dissolved in 800 cc. of hot 50 per cent alcohol and then treated
with 200 cc. of HCl (sp. gr. 1.19). A voluminous brown precipitate
of prosapogenin soon began to form on further heating. For com-
pletion, the mixture was refluxed for 30 minutes and then allowed
to cool. The prosapogenin precipitate was centrifuged from a
dark colored mother liquor which was then decanted. The precip-
itate was resuspended in 30 per cent alcohol and recentrifuged.
This process was then repeated several times with water. The
prosapogenin without drying was further hydrolyzed by refluxing
in a mixture which consisted of 6 parts of alcohol, 2 of water, and
2 of concentrated HCl based on the weight of the original saponin.
After 2 hours the solution was rapidly filtered from a small amount
of flocculent material and the heating resumed for another 2 hours,
during which crystalline senegenin separated. The mixture was
cooled to 60° and filtered at this temperature.

The collected sapogenin melted at 280–290° and was quite pure.
The mother liquor left overnight at 0° gave a good amount of a
mixture which melted at 230° after preliminary sintering. When
the filtrate from this material was heated to boiling and carefully
treated with water and cooled, more crystalline material was
obtained; but as the process was repeated, the final precipitates
became amorphous. The sapogenin fractions were carefully
washed in each case and recrystallized from dilute alcohol. In
this manner there were obtained from 920 gm. of senegin 35 gm.
of senegenin, 74 gm. of mixed crystals, and 40 gm. of amorphous
sapogenin.

Senegenin—The above high melting, first sapogenin fraction was
purified by dissolving in hot 60 per cent alcohol and then slowly
boiling the solution down. The first precipitate containing a
sparingly soluble impurity was filtered off hot and discarded. The
filtrate was concentrated further until most of the senegenin
separated as needles and prisms. It was collected while hot.
The mother liquor contained mostly low melting sapogenin
mixtures.

Pure senegenin melts at 290–292°.

$$\alpha = +19° \ (c = 0.84 \text{ in } 95\% \text{ alcohol})$$
It is easily soluble in alcohol, acetone, and acetic acid and practically insoluble in chloroform and benzene. In aqueous alcohol it is more soluble than the companion sapogenin, but mixtures of the two form mixed crystals which are extremely difficult to separate by recrystallization alone.

For analysis three different preparations of senegenin were repeatedly recrystallized from alcohol and dried at 120° and low pressure.

\[
\begin{align*}
C_{10}H_{16}O_8 & \quad \text{Calculated.} \quad \text{C 67.37, H 8.68} \\
C_{10}H_{14}O_8 & \quad \text{Found.} \quad \begin{align*}
& \quad \text{(a) 67.51, 67.44, } 8.56, 8.58 \\
& \quad \text{(b) 67.20, } 8.50 \\
& \quad \text{(c) 67.45, 67.34, } 8.52, 8.62
\end{align*}
\end{align*}
\]

9.455 mg. of substance dissolved in 1 cc. of alcohol were titrated against phenolphthalein with 0.1 N NaOH. Calculated for 2 equivalents, 0.354 cc.; found, 0.335 cc. 3 cc. of alkali were then added and after boiling for 2 hours the mixture was titrated back. Calculated for 1 equivalent, 0.177; found, 0.172 cc.

11.820 mg. of substance on direct titration required 0.416 cc. Calculated for 2 equivalents, 0.454 cc. On saponification, as given above, an additional 0.212 cc. of alkali was consumed.

Senegenin could not be recovered from the above saponification mixtures. The product proved to be an amorphous, apparently dibasic decomposition product. Its analysis (C 69.1, H 8.8) suggested loss of CO₂ after saponification of the lactone group.

Senegenin in acetic acid solution gives a very weak yellow color with tetranitromethane. Although altered by alkalies, it is quite stable on boiling with dilute acids. On heating in a current of nitrogen, 2 moles of CO₂ are split off.

The Dimethyl Ester—A suspension of senegenin in ether was esterified with diazomethane. The ester could not be obtained crystalline. The amorphous material obtained by careful dilution of the methyl alcoholic solution was dried for analysis at 80° and low pressure.

\[
\begin{align*}
C_{12}H_{14}O_8 & \quad \text{Calculated.} \quad \text{C 68.28, H 8.97, OCH₃ 11.04} \\
C_{12}H_{12}O_8 & \quad \text{Found.} \quad \begin{align*}
& \quad \text{68.64, } 8.64, \quad 11.08 \\
& \quad \text{68.22, } 8.94, \quad 10.51
\end{align*}
\end{align*}
\]
The ester gave a weak yellow color with tetranitromethane. The ester groups proved to be difficult to saponify since only 1 equivalent of alkali was consumed (by the lactone group) on saponification.

12.255 mg. of substance were refluxed in 2 cc. of alcohol and 3 cc. of 0.1 N NaOH for 2 hours and titrated back against phenolphthalein. Calculated for 1 equivalent, 0.218 cc.; found, 0.207 cc.

Senegenin Diacetate—0.2 gm. of senegenin was heated at 100° for 1 hour with a mixture of 2 cc. of acetic anhydride and 0.1 gm. of fused sodium acetate. On decomposition of the mixture with water, a colorless resin deposited. After decantation from the latter and washing, the resin was dissolved in a small volume of alcohol. On careful dilution a sandy, crystalline deposit formed in small amount, which will be described below. The mother liquor was evaporated to dryness. The resinous residue on treatment with a small volume of ether crystallized as flat prisms. It was collected with ether in which it was appreciably soluble. It softened above 260° and melted with effervescence at 270°.

\[
\begin{align*}
C_{40}H_{32}O_{16} & \quad \text{Calculated.} \quad C \ 65.98, \ H \ 8.15 \\
C_{40}H_{32}O_{16} & \quad \text{"} \quad C \ 66.19, \ H \ 7.85 \\
& \quad \text{Found. (a) "} \quad 65.80, \ 8.08 \\
& \quad \text{"} \quad \text{(b) "} \quad 66.21, \ 8.07
\end{align*}
\]

13.092 mg. of substance were titrated with 0.1 N NaOH against phenolphthalein. Calculated for 2 equivalents, 0.424 cc.; found, 0.395 cc. After addition of 3 cc. of 0.1 N NaOH and refluxing for 2 hours, the mixture was again titrated. Calculated for 3 equivalents (lactone and two acetyl groups), 0.636 cc.; found, 0.671 cc.

The above sparingly soluble by-product of the acetylation was recrystallized by concentration of its hot alcoholic solution. It formed minute prisms which melted at 313° after preliminary sintering. Found, C 66.76, H 7.90.

The Dihydroxydicarboxylic Acid Monoethyl Ester, \(C_{31}H_{50}O_6\)—20 gm. of the sapogenin mixture, which represented the second crystal crop from the hydrolysis of senegin, were dissolved in a liter of alcohol. To this were added 8 gm. of NaOH dissolved in 1 liter of water. The mixture was refluxed for 2 hours. The residual high melting sapogenin was thus decomposed. The hot solution was then acidified to Congo red with 10 per cent HCl. On cooling,
the new sapogenin derivative crystallized as long needles. For purification it was suspended in 400 cc. of water and treated, with stirring, with 130 cc. of 20 per cent Na₂CO₃ solution. The sparingly soluble sodium salt separated. After standing the salt was collected, dissolved in alcohol, and decomposed with an excess of HCl. When the hot solution was treated with an equal volume of water and allowed to cool, the sapogenin derivative separated as a voluminous mass of thin needles. It was recrystallized from 50 per cent alcohol. The mother liquor yielded material which was less pure. The yield was 6.7 gm.

This monoethyl ester is easily soluble in alcohol, acetone, chloroform, ether, acetic acid, and hot benzene. It is insoluble in ligroin. It melts on rapid heating at 257° after preliminary sintering, although samples were frequently obtained which melted at 215–218°. The sodium salt is very sparingly soluble in the presence of excess Na ions.

\[ \alpha = +24.5° \ (c = 0.53 \text{ in } 95\% \text{ alcohol}) \]

C₃₃H₆₂O₆. Calculated. C 71.76, H 9.72, OC₅H₄ 8.69

C₄₃H₄₄O₄. " 72.04, " 9.37, " 8.72

Found. (a) 71.96, 71.91, " 0.58, 0.54, " 0.12

(b) 71.58, " 9.36

12.040 mg. of substance were dissolved in 10 cc. of alcohol and titrated against phenolphthalein with 0.1 N NaOH. Calculated for 1 equivalent, 0.232 cc.; found, 0.225 cc.

12.850 mg. of substance were titrated in the same way. Calculated, 0.248 cc.; found, 0.243 cc.

On refluxing with N NaOH no additional alkali than that required by the free carboxyl group was consumed.

This acid ester in chloroform solution gave a good yellow color with tetranitromethane. It is very stable towards acids. The ester group is very resistant to saponification. When heated in a nitrogen stream at 300–320°, approximately 1 mole of CO₂ besides H₂O was split off.

The Methyl Ethyl Ester, C₆₂H₆₄O₆—The above acid ester was esterified with diazomethane in ether solution. The resulting neutral mixed ester proved difficult to crystallize. The amorphous precipitate obtained from aqueous acetone was dried to constant weight and analyzed.
C_{32}H_{52}O_4. Calculated. C 72.13, H 9.84, OCH_{3} + OC_{6}H_{5} 14.29
C_{32}H_{52}O_4. " " 72.40, " 9.50, " + " 14.34
Found. " 71.85, " 9.49, " + " 14.61

The neutral ester was not appreciably saponified on boiling with 0.1 N NaOH.

The Ethyl Ester Diacetate—0.2 gm. of the acid ester was refluxed for 2 hours with 2 cc. of acetic anhydride and 0.1 gm. of sodium acetate. After decomposition with water the precipitate was collected. The amorphous material was dissolved in alcohol and the solution boiled down to small bulk. On cooling, a small fraction of minute needles separated, which will be described below. On further concentration of the filtrate and careful dilution a second substance, the diacetate, slowly crystallized. This was collected with 50 per cent alcohol and recrystallized from dilute alcohol. It formed needles which are readily soluble in the usual solvents. For analysis it was dried at 100° and 15 mm.

C_{32}H_{52}O_4. Calculated. C 69.72, H 9.04
C_{32}H_{52}O_4. " " 69.95, " 8.73
Found. (a) " 69.67, " 8.52
 " (b) " 69.51, " 8.57

The above sparingly soluble substance, which first crystallized from alcohol, was recrystallized by solution in acetone, with addition of alcohol, followed by concentration to remove the acetone. It formed needles which did not melt on heating up to 340°. It did not dissolve in alkali.

Found. (a) C 70.91, H 8.55, OC_{6}H_{5} 7.71
 " (b) " 70.78, " 8.69

The Di-p-Bromobenzoate of the Ethyl Ester—The acid ester was acylated in pyridine solution with p-bromobenzoyl chloride. The acyl derivative was separated in the usual manner. After two recrystallizations from alcohol, it formed needles which melted at 213°.

C_{45}H_{39}O_{2}Br_{2}. Calculated. C 61.07, H 6.38, Br 18.07, OC_{6}H_{5} 5.09
C_{45}H_{39}O_{2}Br_{2}. " " 61.20, " 6.17, " 18.12, " 5.10
Found. " 60.74, " 6.20, " 18.08, " 5.17

The Dibasic Acid, C_{29}H_{46}O_6—0.3 gm. of the acid ester was refluxed for 20 hours in a mixture of 50 cc. of amyl alcohol and 2.5
The acid is very easily soluble in alcohol, acetone, and acetic acid, appreciably so in ether, and practically insoluble in chloroform and benzene. In dilute alcohol it is more soluble than its precursor. It gives a pronounced yellow color with tetranitromethane. The alkyl determination was negative.

\[
\text{C}_{23} \text{H}_{44} \text{O}_6. \quad \text{Calculated. } C \ 70.97, \ H \ 9.45 \\
\text{C}_{23} \text{H}_{44} \text{O}_6. \quad \text{" } \ 71.26, \ " \ 9.08 \\
\text{Found. } \quad \ " \ 71.27, \ " \ 8.99
\]

10,365 mg. of substance were dissolved in 5 cc. of alcohol and titrated against phenolphthalein with 0.1 N NaOH. Calculated for 2 equivalents, 0.506 cc.; found, 0.483 cc.

**Dehydrogenation of Senegenin**

30 gm. of senegenin (m.p. 280–290°) were intimately mixed with 45 gm. of selenium and heated in a 500 cc. long necked flask. The latter was provided with a meter-long vertical reflux tube fitted at the end with a bent tube leading to a bulb for collection of water and more volatile reaction products. The mixture was heated in a NaNO$_3$–KNO$_3$ bath quickly to 340° and kept at this temperature for 48 hours. At first water was liberated and collected in the collecting bulb with some selenium and a little oil. The reaction then quieted and apparently no naphthalene hydrocarbons refluxed steadily as is usual during the dehydrogenation of other triterpenes. On the other hand, there was a gradual accumulation of an amorphous sublimate on the cooler portions of the tube. During these experiments this accumulation was not constantly melted back into the flask, so that the reaction product therefore contained more incompletely dehydrogenated or oxygen-containing tars and a smaller amount of crystalline hydrocarbons than in the case of the dehydrogenation of the companion sapogenin.
described later on. After cooling, the flask and its contents were broken and glass and all were extracted in a Soxhlet apparatus with ether for 24 hours. The undissolved portion was then extracted 14 hours more with dioxane. The two extracts were separately concentrated and the residual tars in each case fractionated by distillation or sublimation as follows:

The ether extract gave 13.5 gm. of yellow residue. The latter gave 3 gm. of a greenish yellow, soft resin from 200-280° at 5 mm. (Fraction I) and 6.2 gm. of a yellow resin at 270-300° and 3 mm. (Fraction II).

The dioxane extract gave 3.1 gm. of a green residue. Sublimation of the latter for 3 hours at 260-280° and 3 mm. gave 0.3 gm. of a white sublimate (Fraction III). Finally, on sublimation for 10 hours at 260-280° and 3 mm., 0.2 gm. more of a yellow sublimate was collected (Fraction IV). Longer sublimation gave but a trace of poorly defined material. Fraction I on refractionation was separated into two further fractions. The first was a viscous oil which boiled at 220-240° and 5 mm. No picrate could be obtained from it and all attempts to isolate Diels' hydrocarbon from it were fruitless. It possibly contained mostly incompletely dehydrogenated material. The higher fraction was collected at 260-280° and 5 mm. as a yellow tar resembling Fraction II.

Fraction II (1 gm.) was dissolved in ethyl acetate and treated with petroleum ether. After standing overnight at 0° the crystalline precipitate was collected, dissolved in benzene, and the latter was extracted with small amounts of H₂SO₄ until it no longer became colored. After washing with water, any precipitated material was redissolved by addition of ether and the extract was dried with sodium sulfate. The residue left on concentration was successively recrystallized from toluene, acetic anhydride, and butyl acetate and then sublimed at 220° and 0.2 mm. (The fraction subliming towards the end contained some higher melting dehydrogenation product and was therefore kept separate.) The substance (A) now formed lustrous leaflets which melted at 246.5° after preliminary softening. When mixed with chrysene with a melting point of 250°, a depression of 10° was noted.

In order to determine whether this hydrocarbon was the only crystalline component of this fraction, the first acetic ester mother liquors were concentrated and the residue was treated with petro-
leum ether and filtered. The amorphous substance was put through the same procedure described above. After repeated recrystallization the melting point of the substance (B) again remained constant at 246.5° and gave no depression with substance (A).

\[ \text{C}_{23} \text{H}_{22} \text{O} \]

Calculated. C 92.56, H 7.44, mol. wt. 298.17

Found. (A) 92.38, 7.30

(B) 92.40, 92.43, 7.36, 7.44

1.705 mg. of substance in 17.265 mg. of camphor gave a depression of 12.6°. Mol. wt. found, 282.

1.257 mg. of substance in 24.855 mg. of camphor gave a depression of 6.7°. Mol. wt. found, 272.

This hydrocarbon fluoresced a blue-violet in ultraviolet light. It resembled closely chrysene in its properties, which suggests that it may be a chrysene homologue. The crystalline forms appeared to be the same, and both substances exhibited a blue fluorescence in camphor solution. The solubilities were also indistinguishable. Finally, the ultraviolet absorption spectrum resembles that of chrysene (cf. Fig. 1). The maxima are, however, definitely displaced and at 3800 \( \lambda \) there occurs a band which is not present in the chrysene spectrum. This may be due either to an additional double bond or to a mixture with some trimethylpicene described below.

Like chrysene, the new hydrocarbon gave an unstable picrate. In attempts to prepare a dibromide, nitro derivative and quinone crystalline substances could not be isolated. The red oxidation product gave with concentrated \( \text{H}_2\text{SO}_4 \) an intensive blue color like chrysoquinone, but with a tinge, however, in the green.

This hydrocarbon was indistinguishable in appearance and properties from the hydrocarbon with a melting point of 245° obtained by Ruzicka and coworkers from hederagenin and which was kindly placed at our disposal by Professor Ruzicka for comparison. No melting point depression could be detected when the two were mixed.

Fraction III was extracted with boiling ether and the extract was decanted. The residue was dissolved in 1 liter of benzene and the solution was shaken with concentrated \( \text{H}_2\text{SO}_4 \) until the latter no longer became colored. After washing with water, any precipitated substance was redissolved by addition of sufficient
acetic ether and the solution was dried with Na$_2$SO$_4$. The residue which remained after concentration was recrystallized in succession from butyl acetate and xylene. It was then extracted with hot acetic anhydride and then sublimed twice at 230$^\circ$ and 0.2 mm. The substance (C) now melted constantly at 298$^\circ$.

Fraction IV was purified in the same manner as Fraction III and the resulting substance (D) melted at 297.5$^\circ$. The two substances (C and D) showed no depression when mixed.

\[ \text{C}_{29}H_{20} \]

Calculated. C 93.80, H 6.20, mol. wt. 320.15

Found. (C) " 93.84, " 6.04 (D) " 93.70, " 6.06

1.005 mg. of substance in 25.347 mg. of camphor gave a depression of 4.7$^\circ$. Mol. wt. found, 304.

The hydrocarbon (C) was compared with trimethylpicene (m.p. 297$^\circ$) from oleanolic acid which was kindly placed at our disposal by Professor Ruzicka. No depression was obtained in a mixed melting point determination. The appearance and solubilities of the substances seemed to be identical, as well as the intense blue fluorescence shown in ultraviolet light. Finally, the ultraviolet absorption curves of the two substances in chloroform solution were identical (Fig. 1).

Dehydrogenation of the Companion Sapogenin, \( \text{C}_{21}\text{H}_{30}\text{O}_6 \)

14 gm. of the sapogenin acid ester were dehydrogenated with 21 gm. of selenium at a bath temperature of 320–330$^\circ$ for 48 hours. The reaction proceeded smoothly, since no appreciable liquid products formed. A crystalline substance sublimed constantly on the cooler exposed walls of the flask and were now and then melted back into the reaction mixture. The cooled mass was broken and glass and all were placed in a Soxhlet apparatus and extracted first with ether for 12 hours and then with dioxane once for 5 hours and a second time for 40 hours. The residues obtained on concentration of each of these extracts were then fractionated as given below. The dioxane residues, however, were first washed with ether or water to remove persistent amounts of solvent.

The ether extract residue (5 gm.) was a soft tar which was fractionally sublimed and divided into a number of fractions. The major portion, 2 gm., was collected as a light colored sublimate at 230–240$^\circ$ and 3 mm. This material was dissolved in a small
volume of hot xylene and placed in the refrigerator. The material which separated was collected and then shaken up in 1 liter of warm benzene. The solution was filtered from a small portion which remained undisolved (40 mg.). The clear benzene solution was repeatedly extracted with concentrated sulfuric acid and then after washing with water was concentrated to dryness. The residue was recrystallized first from acetic anhydride and then sublimed at 210° and 0.2 mm. The sublimate was recrystallized from butyl acetate. 0.43 gm. of lustrous leaflets was obtained, which melted at 246-247.5°. This gave no depression with the hydrocarbon (m.p. 246.5°) from senegenin. Found, C 92.73, H 7.44. The succeeding fraction which sublimed after the previous fraction at 3 mm. and 240-250° weighed 0.51 gm. and contained somewhat more contaminated material. It was not investigated in detail.

The residue from the first dioxane extract was crystalline. It was very slowly sublimed and separated into fractions each of which was recrystallized separately from xylene. At 230° and 3 mm. 0.52 gm. of lustrous platelets was obtained, which melted at 240° after recrystallization. At 240° and 3 mm. 0.65 gm. of leaflets was collected, which melted at 242° after recrystallization. Finally, at 250-260° and 3 mm. 0.1 gm. of gray powder deposited.

The second dioxane extract contained appreciable amounts of the higher melting hydrocarbon and was amorphous. On sublimation, followed by recrystallization from xylene, the following fractions were obtained.

One at 200-220° and 3 mm. which weighed 0.6 gm. and melted at 240-245° after preliminary softening. It has not been investigated further.

The higher fraction was collected at 220-240° at 3 mm. and amounted to only 0.1 gm. This material was dissolved in 1 liter of benzene and was freed from impurities by extraction with H₂SO₄. Ether was then added and the solution was washed with water and concentrated. The residue was recrystallized successively from xylene and acetic anhydride, giving 6 mg. of substance which were then sublimed at 230° and 0.2 mm. After a final recrystallization from butyl acetate a small amount was recovered which melted at 297.5° and gave no depression with the hydrocarbon (trimethylpicene) from senogenin.
THE SAPOGENINS OF POLYGALA SENEGA
Walter A. Jacobs and Otto Isler


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