

TABLE I
 ACID HYDROLYSIS OF STEROIDAL SAPONINS

Saponin and derived sapogenin	Hydrochloric acid normality	Percentage of total sapogenin (based on 4 N)									Time for 90% hydrolysis, hours	
		1/6	1/2	1	2	3	4	5	6	8		72
Sarsasaponin spirostan-3 β -ol	1				27	47	53	60	67			>6
	2			47	73	87	93		93			3-4
	4		80	87	93	93	93		100			1-2
Dioscin Δ^5 -isospirosten-3 β -ol	1			13	17	17	17	26				>5
	2			9	35	70	74	78				>5
	4		74		83	91	100	100				3
Chloronin isoallospirostan-3 β ,6 α -diol	2						41			57	99	>8
	4				93		98			100		1-2
	6	93					61			63		<1
Digitonin isoallospirostan-2,3 β ,15(?) -triol	1				12	18	30	35				>5
	2				47	65	80	84				>5
	4			89	91	100	100	100				1/2-1
Gitonin isoallospirostan-2 α ,3 β -diol	2			82	89		94					2
	4			89	98		100					1
	6	100	77									<1

longer than the comparable 4 N period, and as shown in Table I, the times varied from 2 hours to more than 8 hours.

In all the experiments, use of 1 N hydrochloric acid was ineffective, as was also hydrolysis with 1 and 2 N sulfuric acid (not shown in table). Destruction of sapogenins with excess heating time apparently occurred only when 6 N hydrochloric acid was used.

The limited data indicate that the structure of the steroidal aglucone portion of the molecule does not influence the rate of hydrolysis (*i.e.*, isomerism at C₅ or C₂₂ or number of hydroxyl groups). This is best shown by the data obtained with 2 N acid hydrolysis. Sarsasaponin, yielding spirostan-3 β -ol and gitonin, the precursor of isoallospirostan-2 α ,3 β -diol, are the most rapidly hydrolyzed saponins. Dioscin, yielding Δ^5 -isospirosten-3 β -ol, and digitonin forming isoallospirostan-2,3 β ,15(?) -triol, were more resistant to hydrolysis. Chloronin, forming isoallospirostan-3 β ,6 α -diol, was the most difficultly hydrolyzable saponin tested.

The results discussed above suggest that the routine use of 2 N hydrochloric acid for the hydrolysis of *unknown saponins* in crude plant extracts can result in *low sapogenin yields*. Crude plant extracts such as those used by Marker, *et al.*,⁵ contain proteins and sugars. It is not surprising therefore, that when we attempted to hydrolyze such extracts with 4 N acid, large quantities of tar were produced, from which little sapogenin could be isolated. Subsequently, a procedure was developed at this Laboratory⁶ in which saponins could be routinely separated from proteins and carbohydrates by extraction from the aqueous phase with butanol. After this treatment, the saponin preparations could be hydrolyzed by refluxing with 4 N acid for 3-4 hours with little tar formation. The sapogenins thus formed are readily isolated. A number of experiments comparing the direct 2 N hydrolysis⁵ with the butanol purified 4 N hydrolysis⁶ have invariably shown that the latter procedure gives 25-100% higher yields of sapogenin.

(6) Paper I, M. E. Wall, M. M. Krider, E. S. Rothman and C. R. Eddy, *J. Biol. Chem.*, in press.

Experimental

Purified saponin preparations were prepared as described previously^{1,8} with the exception of digitonin, which was obtained from a commercial source. The saponin yielding isoallospirostan-3 β ,6 α -diol was obtained from bulbs of *Chlorogalum pomeridianum*; the saponin yielding Δ^5 -isospirosten-3 β -ol was obtained from rhizomes of *Dioscorea composita*; the saponin yielding isoallospirostan-2 α ,3 β -diol⁷ was obtained from leaves of *Yucca gloriosa*; and the saponin yielding spirostan-3 β -ol was obtained from the leaves of *Yucca baccata*.⁸

Stock solutions of saponins were prepared in 1:1 ethanol-water (by volume) so that 3.34-ml. aliquots contained 100 mg. of saponin. To the aliquots were added sufficient concentrated hydrochloric acid, water and alcohol to bring the final volume of 5.00 ml. to the desired normality. Two ml. of benzene, previously equilibrated with an equal volume of 1:1 ethanol-water was added, and the hydrolyses were conducted at reflux temperature in centrifuge tubes immersed in a water-bath at 75-78° as described previously⁹ and the sapogenins, as acetates, were assayed by the infrared method,^{9,10} or in some cases gravimetrically.

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(7) A small quantity of isoallospirostan-3 β -ol was also present.

(8) We wish to thank C. O. Erlanson, D. S. Correll and H. S. Gentry of the Division of Plant Exploration and Introduction, Bureau of Plant Industry, Soils, and Agricultural Engineering for procuring the various plant specimens.

(9) Paper 11, M. E. Wall, C. R. Eddy, M. L. McClennan and M. E. Klumpp, submitted to *Anal. Chem.*

(10) The infrared assays were conducted by C. R. Eddy and M. E. Klumpp.

(11) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. This work was done as part of a cooperative arrangement between the Bureau of Plant Industry, Soils and Agricultural Engineering and the Bureau of Agricultural and Industrial Chemistry, United States Department of Agriculture, and the National Institutes of Health, Federal Security Administration.

Fluorination of Carbon Disulfide and Carbonyl Sulfide

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The fluorination of methyl mercaptan or carbon disulfide has been shown under certain conditions to produce trifluoromethylsulfur pentafluoride, CF₃SF₅.¹ A continuation of the study of fluorina-

(1) G. A. Silvey and G. H. Cady, *THIS JOURNAL*, **72**, 3624 (1950).

tion processes has revealed another way to prepare this compound and has given some additional information about the behavior of carbon disulfide and carbonyl sulfide.

Electrolytic Preparation of Trifluoromethylsulfur Pentafluoride.—An electrolytic cell of 2.5 liters volume similar to those of Simons and his co-workers² was constructed from a piece of four-inch iron pipe. The electrodes were of nickel and it was possible to collect gas separately from the anode and from the cathode. The cell was filled with liquid hydrogen fluoride to a level about 6 cm. below the top; then 150 ml. of carbon disulfide and 1 ml. of water were added, the latter to increase the electrical conductivity. A bath of ice and water surrounded the cell. As electrolysis took place the potential difference between electrodes was kept between six and seven volts and the current was held close to five amperes. At times it was necessary to add more water to maintain the electrical conductivity. A total of 5.6 faradays of electricity was passed.

No gaseous product was set free at the anode. Hydrogen was produced at the cathode at a rate of 0.41 mole per faraday. The gas stream from the cathode passed through a trap cooled by liquid oxygen. At the end of the run the condensed material was filtered at about -123° to obtain sulfur hexafluoride as a solid phase, and the other components as a liquid mixture which was later fractionally distilled. The volume of trifluoromethylsulfur pentafluoride obtained was 1.75 liters, at 0° (760 mm.). Approximately 4.5 liters of sulfur hexafluoride and 1 liter of carbon tetrafluoride were found. One or more other products boiling below -40° were also present. These substances were not identified but they were found to hydrolyze rapidly in 6 N NaOH.

At the end of the run carbon disulfide no longer remained as a separate liquid phase in the cell. It must have reacted to give a soluble product, for it is not very soluble in liquid hydrogen fluoride. When the liquid from the cell was allowed to evaporate in a vessel standing in the room, all but about 1 g. of the material boiled away. The interior walls of the cell were thinly coated with an unidentified dark colored material.

Reaction of Carbon Disulfide with Fluorine Highly Diluted by Nitrogen.—When a stream of carbon disulfide vapor diluted with some nitrogen is passed into an atmosphere of fluorine it burns with a blue flame. As the degree of dilution becomes larger the flame becomes larger but less easily visible. The purpose of the experiment now to be described was to carry out the reaction with the gases so highly diluted that only a small temperature rise would occur and no flame would be visible. Under these conditions it was hoped that the carbon-sulfur bonds would not break and that compounds of carbon, sulfur and fluorine would be produced. No evidence was found for the presence of such compounds among the products.

A one-liter glass flask was used as the reaction vessel. Fluorine diluted with 30 times its volume of nitrogen entered at the center of the flask, and carbon disulfide vapor diluted with 12 times its volume of nitrogen entered at the top. The products left the flask through a tube at the bottom and were passed through a trap cooled by liquid oxygen. As the reaction occurred no flame could be seen, even in a dark room. Heat was liberated but the warmest spot on the flask was not over 40° . A total of two grams of carbon disulfide was caused to react in a six-hour run with a sufficient excess of fluorine to permit one easily to detect the unreacted halogen in the effluent gases.

At the end of the run the product in the cold trap was distilled, from bulb to bulb, and gas densities along the way were found to be 99, 104, 106 g. per g.m.v (sulfur tetrafluoride has a molecular weight of 108). The vapor pressure of the last of the liquid to distil was about the same as that of sulfur tetrafluoride. Like sulfur tetrafluoride the product had a bad odor and it fumed in moist air. No attempt was made to purify this material, because a previous trial with sulfur tetrafluoride had resulted in severe corrosion of the metal packing in the fractionating column. No trifluoromethylsulfur pentafluoride was found in the product. If SF_6 and CF_4 were present, the amounts were small. The latter substance was probably one of the principal products,

(2) J. H. Simons and co-workers, *Trans. Electrochem. Soc.*, **95**, 47 (1949).

but nitrogen must have carried it through the cold trap without condensation.

Under the above conditions the action of fluorine upon carbon disulfide broke carbon-sulfur bonds and gave rise to products which appeared to be sulfur tetrafluoride and, probably, carbon tetrafluoride.

Fluorination of Carbonyl Sulfide by Cobalt Trifluoride.—A 7.5-g. sample of carbonyl sulfide was fluorinated by a large excess of cobalt trifluoride at about 200° using apparatus described in other publications.^{1,3} Nitrogen was used as a diluent and carrier, and the product was condensed in a trap cooled by liquid oxygen. The product was warmed without appreciable loss to -110° and it was filtered at this temperature. The solid collected on the filter was found to be nearly pure sulfur hexafluoride and the liquid to be a mixture of sulfur hexafluoride and carbonyl fluoride. Since these two substances made up all or nearly all of the product, the reaction may be represented by the equation



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(3) E. J. Barber, L. L. Burger and G. H. Cady, *THIS JOURNAL*, **73**, 4241 (1951).

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Decyanoation by Grignard Reagent

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In view of the smooth reaction of 4-dimethylamino-2,2-diphenylpentanenitrile with ethylmagnesium bromide to form the expected compound, 6-dimethylamino-4,4-diphenyl-2-heptanone (Methadon),¹ an observation made in this Laboratory is of interest. When ethylmagnesium bromide reacted with 4,5-bis-(dimethylamino)-2,2-diphenylpentanenitrile (I) in xylene solution the product was not the expected aminoketone but the oxygen-free base, 3,4-bis-(dimethylamino)-1,1-diphenylbutane (II), formed from (I) by the replacement of the cyano group by hydrogen. The decyanoation of amines in which a cyano group is linked to a quaternary carbon has been reported previously^{2,3} but heretofore very strong bases such as sodamide² or potassium hydroxide³ have been employed to accomplish the degradation. Cleavage by the Grignard reagent in preference to addition to the cyano group was, therefore, unexpected. That the structure of the oxygen-free base corresponds to II was demonstrated by the decyanoation of I by the action of potassium hydroxide in boiling "polyethylene glycol 200"³ to obtain a base identical with II.

The 4,5-bis-(dimethylamino)-2,2-diphenylpentanenitrile (I) used in this work was prepared from 2,2-diphenyl-4-pentenenitrile⁴ which was brominated to give 4,5-dibromo-2,2-diphenylpentanenitrile (III).⁵ This upon heating with ethanolic dimethylamine gave a small yield of I. The

(1) Office of the Production Board, Department of Commerce, Report No. PB-981, p. 96-A, October 1, 1945.

(2) M. Bockmuhl and G. Ehrhardt, *Ann.*, **561**, 71 (1949).

(3) E. L. May and E. Mosettig, *J. Org. Chem.*, **13**, 459 (1948).

(4) E. M. Schultz, C. M. Robb and J. M. Sprague, *THIS JOURNAL*, **69**, 2454 (1947).

(5) J. Attenburrow, J. Elks, B. A. Hems and K. N. Speyer, *J. Chem. Soc.*, 512 (1949).