Anal. Calcd. for $C_{30}H_{52}O_2$ (444.72): C, 81.02; H, 11.79. Found: C, 80.92; H, 11.61.

3,4-Seco-4-methyl-4-methylenecholestan-3-oic Acid (XXa).—4-Oxa-4a,4a-dimethyl-A-homocholestan-3-one (XVIII) (71 mg.) was pyrolyzed in a sealed tube as described in the previous experiment. Recrystallization of the reaction mixture from methanol furnished 28 mg. of the crystalline acid (XXa): m.p. 117–119°; $[\alpha]^{23}\text{D}$ +15° (*c* 0.99); $\lambda_{\max}^{\text{CHCl}_3}$ 5.86, 6.10, 8.31, 11.10 μ; n.m.r. τ 5.13, 5.28 (4-CH_2=), 8.25 (4-CH_3), 9.09 (19-CH_3).

Anal. Calcd. for $C_{29}H_{50}O_2$ (430.69): C, 80.87; H, 11.70. Found: C, 80.81; H, 11.75.

Ozonolysis of Methyl 3,4-Seco-4-methyl-4-methylenecholestan-3-oate (XXb).—A solution of 10 mg. of methyl 3,4-seco-4-methyl-4-methylenecholestan-3-oate in 2 ml. of ethyl acetate was ozonized with an excess of ozonized oxygen at −40°. The solution was allowed to stand at −40° for 15 min., warmed to room temperature, and treated with 0.5 g. of zinc dust and 1 drop of glacial acetic acid. After stirring for 10 min., the reaction mixture was filtered, diluted with ethyl acetate, washed with water, dried over sodium sulfate, and evaporated to dryness. The reaction product was chromatographed on a thin layer of neutral alumina, activity V, and eluted with 1:1 benzene–hexane. The band corresponding to the known reaction product XIIIa (R_f 0.3) was isolated and rechromatographed in the same manner. Crystallization from methanol afforded 2 mg. of material, m.p. 74–76°, which on recrystallization from methanol had m.p. 75–76° (block). The infrared spectrum of this material was identical with that of an authentic sample of methyl 3,4-seco-4-keto-4-methyl-cholestan-3-oate (XIIIa).

3,4-Seco-25,26,27-trisnordammarane-4,20ξ-diol-3,24-dioic Acid 3→4,24→20-Dilactone (XXIII).—A solution of 1.35 g. of 25-26,27-trisnordammaran-3-on-20ξ-ol-24-oic acid lactone (XXII)[20] and 1.35 g. of *m*-chloroperbenzoic acid in 8 ml. of chloroform was kept at 25° for 23 hr. After dilution with 25 ml. of chloroform to dissolve precipitated *m*-chlorobenzoic acid, the solution was washed consecutively with 5% potassium iodide, 5% sodium thiosulfate, water, 5% potassium bicarbonate, and water, dried over sodium sulfate, and evaporated to dryness *in vacuo*. The residual 3,4-seco-25,26,27-trisnordammarane-4,20ξ-diol-3,24-dioic acid 3→4,24→20-dilactone (XXIII, 1.3 g.) on recrystallization from methanol furnished in two crops a total of 865 mg. of material, m.p. 173–176°. Analytical material had m.p. 178–180° or 192–194° (polymorphic modifications): $[\alpha]^{23}\text{D}$ +104° (*c* 0.75); $\lambda_{\max}^{\text{KBr}}$ 5.65, 5.80 μ.

Anal. Calcd. for $C_{27}H_{42}O_4$ (430.61): C, 75.31; H, 9.83. Found: C, 75.33; H, 9.78.

3,4-Seco-25,26,27-trisnordammarane-4,20ξ-diol-3,24-dioic Acid and Its 24→20-Monolactone.—A solution of 40 mg. of the dilactone XXIII in 8 ml. of 6% KOH in methanol was allowed to remain at 25° for 18 hr. Water was then added; the mixture was acidified to pH 3.0 and extracted with methyl isobutyl ketone. The organic phase was washed with water and dried over sodium sulfate, and the solvent evaporated to dryness. The residue (48 mg.) on crystallization from methanol–ethyl acetate furnished 14 mg. of the diacid: m.p. 195–197° with sintering at 158°; $\lambda_{\max}^{\text{KBr}}$ 2.87, 5.85 μ; neut. equiv. 235 (calcd., 233).

The mother liquor from the above crystallization was recrystallized from acetone–hexane and furnished 25 mg. of the monolactone acid: m.p. 205–207°; $[\alpha]^{23}\text{D}$ +61° (*c* 0.64); $\lambda_{\max}^{\text{KBr}}$ 2.92, 5.70, 5.76 μ.

Anal. Calcd. for $C_{27}H_{44}O_5$ (448.62): C, 72.28; H, 9.89. Found: C, 72.21; H, 9.84.

3,4-Seco-25,26,27-trisnor-$\Delta^{4(30)}$-dammaren-20ξ-ol-3,24-dioic Acid 24→20-Lactone (XXIVa).—3,4-Seco-25,26,27-trisnordammarane-4,20ξ-diol-3,24-dioic acid 3→4,24→20-dilactone (XXIII) (252 mg.) was heated *in vacuo* at 202–204° for 8 min. Crystallization of the melt from methanol yielded 176 mg. of fine needles, m.p. 143–144°. The analytical sample (from 95% ethanol, dried at 80°) had m.p. 146–148°; $[\alpha]^{23}\text{D}$ +44.5° (*c* 0.83); $\lambda_{\max}^{\text{Nujol}}$ 2.86, 5.69, 5.86, 11.22 μ; n.m.r. τ 5.11, 5.29 (1 proton each, 4-CH_2=), 8.26 (4-CH_3), 8.63 (21-CH_3), and 8.97, 9.08 and 9.13 (8β-, 14α- and 19-CH_3).

Anal. Calcd. for $C_{27}H_{42}O_4 \cdot H_2O$ (448.63): C, 72.28; H, 9.89. Found: C, 72.43; H, 9.98.

The methyl ester XXIVb was prepared with diazomethane, purified by chromatography on neutral alumina, and recrystallized from methanol: m.p. 119–121°; $[\alpha]^{23}\text{D}$ +44° (*c* 1.2); $\lambda_{\max}^{\text{Nujol}}$ 5.66, 5.76, 6.08, and 11.27 μ; n.m.r. τ 5.14, 5.33 (1 proton each, 4-CH_2=), 6.34 (OCH_3), 8.26 (4-CH_3), 8.63 (21-CH_3), 8.98, 9.09, and 9.14 (8β-, 14α- and 19-CH_3); lit. m.p. 125–128°; $[\alpha]\text{D}$ +43°,[20] and m.p. 125–126°, $[\alpha]\text{D}$ +51°.[21]

Anal. Calcd. for $C_{28}H_{44}O_4$ (444.63): C, 75.63; H, 9.97. Found: C, 75.57; H, 9.98.

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Sulfonation of Acetone with Fuming Sulfuric Acid and Some Reactions of Propanone-1,3-disulfonic Acid

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Propanone-1,3-disulfonic acid can be prepared easily by sulfonation of acetone with fuming sulfuric acid. Its reactions are in many respects similar to those of β-keto carboxylic acid derivatives.

While β-keto carboxylic acids and their esters have been studied extensively, comparatively little work has been done on β-keto sulfonic acids. Until recently the only general method for the preparation of this class of compounds has been the reaction of α-halogenated ketones with alkali sulfite. Only recently it has been reported that some β-keto sulfonic acids can be obtained by treating ketones with SO_3–dioxane.[1]

It now has been found that acetone can be sulfonated conveniently and in high yield by reaction with fuming sulfuric acid. The solid propanone-1,3-disulfonic acid (I) formed can be obtained by filtration and may be purified by recrystallization from nitromethane.

The reactions of I resemble in many respects those of ethyl acetoacetate. The acidifying effect of the sulfonic acid group on the α-hydrogen atoms is actually stronger than that of a carboxylic acid group. This is evident from the fact that dimethyl propanone-1,3-disulfonate is a moderately strong acid. When titrated using a pH meter, a pH of 5.5 is obtained for 50% neutralization. Even in the case of disodium propanone-1,3-disulfonate one of the hydrogen atoms exhibits a certain degree of acidity, although, because of the presence of the two negative charges, to a much smaller degree. The corresponding salt crystallizes

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(1) A. P. Terentev and L. A. Yanovskaya, *Zh. Obshch. Khim.*, **23**, 618, (1953).

out if a warm, concentrated solution of the disodium salt of I is treated with the theoretical amount of 50% NaOH solution. This salt formation on the methylene group is accompanied by a change of the infrared and ultraviolet spectra. In the infrared spectra the keto peak at 5.85 μ disappears and is replaced by two peaks at 6.1 and 6.4 μ. In the ultraviolet spectrum of the aqueous solution the absorption between 290 and 295 mμ is replaced by a 200 times stronger one at 243 mμ. The dimethyl ester of I has a peak at 5.85 μ in the infrared spectra. It absorbs ultraviolet light at 246 mμ in both neutral and alkaline media but does not give a color test with ferric chloride solution.

Cleavage.—The cleavage of salts of I in both alkaline and acid media is in complete analogy to the cleavage of ethyl acetoacetate.

$$O{=}C(CH_2SO_3Na)_2 + NaOH \xrightarrow{110^\circ} NaOCOCH_2SO_3Na + CH_3SO_3Na$$

$$O{=}C(CH_2SO_3Na)_2 + 2H_2O \xrightarrow[H^+]{190^\circ} (CH_3)_2CO + 2NaHSO_4$$

Although most of the acetone formed according to the second equation is converted to secondary products under these extreme conditions, it was possible to identify acetone among the reaction products.

The carbon–sulfur bond may also be cleaved under reducing conditions, the sulfonate group being removed as sulfite (zinc and caustic) or as sulfur, sulfur dioxide, and hydrogen sulfide (zinc and acid). The organic reaction products have not been identified except for trace amounts of acetone and isopropyl alcohol.

Reactions of the Methylene Groups.—The acidity of one of the hydrogen atoms of the methylene groups has been discussed above. The reversible replacement of hydrogen by halogen according to the following equation has been reported in the literature.[2] Equilibrium in this reaction is at a pH of approximately 2 in the case of bromine and 4 in the case of iodine.

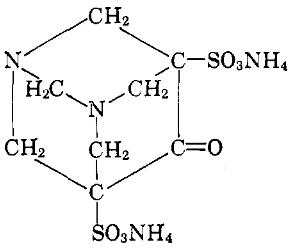
$$O{=}C(CH_2SO_3K)_2 + 2Br_2 \underset{H^+}{\overset{OH^-}{\rightleftarrows}} O{=}C(CHBrSO_3K)_2 + 2HBr$$

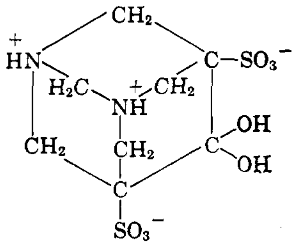
The sulfonation may be carried further by the use of chlorosulfonic acid or more concentrated oleum. Propanone-1,1,3-trisulfonic acid has been isolated among the reaction products. The third sulfonic acid group results in an increased acidity of the α-hydrogen atom and further weakening of the carbon–carbon bond. Shift of the ultraviolet absorption therefore occurs at a lower pH and to a slightly longer wave length (258 mμ) than in the case of I. Alkaline cleavage results in the formation of methionic acid and sulfoacetic acid.

Alkylation and acylation of the methylene group have been attempted under several different conditions. Acylation of the trisodium salt of I with acid chlorides in an inert solvent failed probably because of the insolubility of the salt in such solvents. Reaction of benzoyl chloride with an aqueous alkaline solution of the sodium salt resulted only in the formation of benzoic acid. There is some indication that acylation occurs if I is caused to react with acid halides or anhydrides in the presence of Friedel–Crafts catalysts. Aluminum chloride and ferric chloride cannot be used because they react with I with evolution of hydrogen chloride. Boron trifluoride and stannic chloride were found to be most effective as catalysts. Benzoyl chloride, acetyl chloride, and acetic anhydride have been used as acylating agents and the reaction products have been isolated as potassium salts. Although these products have not been positively identified, they appear to be completely enolized. They give a color formation with ferric chloride, do not show a carbonyl peak in the infrared, and titrate as weak acids. They undergo alkaline cleavage more easily than the starting material and the products of the alkaline cleavage show a carbonyl peak in their infrared spectra and do not give a ferric chloride test.

Salts of I undergo coupling reactions with diazonium salts in alkaline medium to form azo dyes.

Salts of I react with aldehydes or with aldehydes in combination with amines. The product formed upon reaction of diammonium propanone-1,3-disulfonate with formaldehyde and ammonia (or hexamethylenetetramine) has been tentatively identified as diammonium 1,3-diazaadamantan-6-one-5,7-disulfonate (II).


II


III

This structure is based on the analogy with the reaction product of dibenzyl ketone with formaldehyde and ammonia and on the fact that the corresponding free acid III is only slightly soluble in water and titrates as a dibasic acid with two distinctly different acidities (pH 1.3 and 4.5, respectively, for 50% neutralization), both the result of the formation of an internal salt. The hydrated carbonyl group of III is based on the comparison of the infrared spectra of II and III.

Reactions of the Keto Group.—Salts of I may be reduced to salts of 2-hydroxypropane-1,3-disulfonic acid by zinc dust in approximately neutral medium. Treatment with zinc in strongly acid or strongly alkaline media results in cleavage of the carbon–sulfur bond, as mentioned above.

Polymeric materials are formed in the reaction of I with phenols and formaldehyde. These polymers have the properties of ion-exchange resins.

Experimental

Propanone-1,3-Disulfonic Acid (I).—In the following procedure, fuming sulfuric acid was used in two different portions and in two different strengths in order to increase the amount of propanone-1,3-disulfonic acid that can be recovered by crystallization. If only 23% fuming sulfuric acid is used, a larger proportion of the product stays in the sulfuric acid mother liquor.

Into a round-bottom flask equipped with a mechanical stirrer, thermometer, and cooling bath was placed 190 g. of fuming sulfuric acid (23% SO_3). Acetone (17 g.) was added dropwise with stirring; the temperature was kept below 20°. The mixture was heated then to 70° for 15 min. and cooled again, 50 g. of fuming sulfuric acid (75% SO_3) was added, and 17 g. of acetone was dropped in as before. The mixture was heated again to 70–80° for 1 hr. During this period the crystallization of I began.

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[2] W. Prahl, German Patent 568,240 (Oct. 1930).

After several hours at room temperature the crystallization was complete, and the light yellow, nearly solid mixture was filtered and washed with nitromethane and petroleum ether giving 120 g. of crude propanone-1,3-disulfonic acid. The crude material may be purified by recrystallization from nitromethane. The recrystallized acid is a white, extremely hygroscopic solid, m.p. 140–150° dec., which is slightly soluble in nitromethane and nitrobenzene, very soluble in alcohols, ethers, nitriles, and most other oxygen- or nitrogen-containing solvents, and insoluble in hydrocarbons.

For the preparation of the salts it was easier to neutralize the crude filter cake without further purification and to purify the salt by recrystallization. Most convenient was the work-up as the ammonium salt, particularly because it can be converted easily into most other salts.

	Solubility, g. of salt/100 ml. of water	
Temp., °C.	$O{=}C(CH_2\text{-}SO_3NH_4)_2$	$O{=}C(CH_2\text{-}SO_3NH_4)_2$ and $(NH_4)_2SO_4$
20	46	3.5 and 63
90	62	29 and 76

The sodium salt is very soluble in water, the ammonium and potassium salts are moderately soluble, and the barium and silver salts are slightly soluble. All the salts mentioned are insoluble in methanol or acetone; the silver salt, however, is very soluble in acetonitrile.

Anal. Calcd. for $C_3H_{12}N_2O_7S_2$ (NH_4 salt): C, 14.26; H, 4.76; N, 11.12; S, 25.40. Found: C, 14.3; H, 4.9.

The infrared spectrum of the dipotassium salt of I had peaks at 2.9, 3.3, 3.4, 5.85, 7.15, 7.8–8.2, 8.7, 9.2, 9.5, 9.7, 10.75 (weak), 11.05 (weak), 12.0, 12.55, 13.4, and 14.7 μ.

The spectrum of the dimethyl ester of I is nearly identical with the above; the diammonium salt has additional broad bands at 3.2 and 7.0 μ.

The barium salt of I has infrared peaks at 2.9, 3.3, 3.4, 5.8, 7.05, 7.7, 7.9–8.55, 8.7, 9.3, 9.55, 9.7, 10.5 (weak), 11.1 (weak), 11.9, 13.5, and 14.15 μ.

The spectrum of the disodium salt of I is nearly identical.

The infrared spectrum of the trisodium salt of I has peaks at 2.9, 6.1, 6.4, 7.1, 7.8, 8.1–8.4, 8.75 (broad), 9.5, 9.7, 10.4, 10.8, 11.7, 12.3, 13.6, and 15.2 μ.

The structure of I was established by comparing the infrared spectra of the barium salt of I with that of an authentic sample obtained from the reaction mixture of 1,3-dichloroacetone and sodium sulfite and by the identification of the products of alkaline cleavage and reduction.

Disodium Sulfoacetate and Sodium Methanesulfonate by Alkaline Cleavage.—To a concentrated solution of 130 g. of sodium hydroxide in water were added 240 g. of diammonium propanone-1,3-disulfonate (caution, NH_3 evolution). The mixture was heated to 110° and enough water was added to dissolve all. After 3 hr. at 110° the solution was cooled; 118 g. of disodium sulfoacetate crystallized out. An additional 68 g. was obtained by precipitation with methanol. Upon concentration of the mother liquor 54 g. of sodium methanesulfonate was obtained. The infrared spectra of the two salts are identical with those of authentic samples of disodium sulfoacetate and sodium methanesulfonate.

Dipotassium 2-Hydroxypropane-1,3-Disulfonate.—A solution of 28 g. of potassium hydroxide in 50 ml. of water was added slowly with stirring to a hot mixture of 63 g. of diammonium propanone-1,3-disulfonate, 35 g. of zinc dust, and 200 ml. of water (caution, NH_3 evolution). After the evolution of ammonia had stopped, 35 ml. of water containing small amounts of volatile materials was distilled off. The residue was filtered hot and the zinc hydroxide was washed with hot water. Upon cooling, 36 g. of dipotassium 2-hydroxypropane-1,3-disulfonate crystallized from the filtrate. An additional 20 g. was obtained by concentrating the mother liquor. The infrared spectrum of the product is identical with that of an authentic sample obtained from the reaction of epichlorohydrin with potassium bisulfite.

Diammonium 1,3-Diazaadamantan-6-one-5,7-Disulfonate (II). A solution of 50 g. of diammonium propanone-1,3-disulfonate and 25 g. of hexamethylenetetramine in 200 ml. of water was heated. Evolution of ammonia started at about 60°. After 2 hr. at 90°, the solution was cooled; the precipitation was completed by addition of methanol. Slightly yellow crystals (65 g.) were obtained by filtration. Recrystallization from water gave a white product. Ten grams of this material was dissolved in 100 ml. of water and the corresponding free acid was precipitated by addition of 20 ml. of 50% sulfuric acid. The material was filtered, washed with water, and dried giving 7.2 g. of 1,3-diaza-6,6-dihydroxyadamantane-5,7-disulfonic acid.

Anal. Calcd. for $C_8H_{14}N_2O_8S_2$: C, 29.1; H, 4.24; neut. equiv., 165. Found: C, 28.9, 29.1; H, 4.3, 4.7; neut. equiv., 165.

The infrared spectrum of the ammonium salt of this acid is identical with that of the salt from which the acid was prepared, indicating that the acid treatment had not resulted in hydrolysis. The infrared spectrum for the NH_4 salt has peaks at 2.8–3.3, 5.8, 6.9 (broad), 7.4 (weak), 7.5 (weak), 8.0–8.6, 8.9, 9.65, 9.9, 10.3, 10.7, 11.9, 12.0, 12.8, 13.0, and 15.05 μ; that of the free acid, 2.9, 2.95, 3.3, 4.0 (broad), 6.1, 6.9, 7.05, 7.2, 7.5, 8.0–9.0, 9.6, 9.8, 10.2, 10.4, 10.75, 11.15 (weak), 12.4 (weak), 12.85, 14.6, and 14.8 μ.

Dimethyl Propanone-1,3-Disulfonate.—To a solution of 43 g. of the silver salt of 1 in 150 ml. of acetonitrile was added 35 g. of methyl iodide. Precipitation of silver iodide started almost instantaneously. The mixture was filtered after standing in the dark 10 hr. and the acetonitrile was evaporated from the filtrate under vacuum. The last trace of acetonitrile was removed by pouring the oily residue into ice–water. The dimethyl ester of I precipitated in the form of white needles and was immediately filtered and dried in a vacuum desiccator to avoid hydrolysis: 14 g.; m.p. 70°; infrared, 2.9, 5.85, 7.2, 7.8–8.5, 9.5, 9.65, 11.95, 12.5, 13.4, and 14.7 μ.

The silver salt of I, being only slightly soluble in water, may be conveniently prepared by mixing concentrated solutions of the ammonium salt of I and silver nitrate.

Reaction of Disodium Propanone-1,3-disulfonate with Diazonium Salts.—To an ice-cold solution of 4.3 g. (40 mmoles) of *p*-toluidine in 20 ml. of 6 *M* hydrochloric acid was added with cooling 20 ml. of 2 *M* sodium nitrite solution followed by 25 ml. of a 1.8 *M* solution of the disodium salt of I and a solution of 2 g. of sodium acetate in 10 ml. of water. Upon further neutralization with ice-cold 2 *N* sodium hydroxide solution an intense red color developed; at pH 7, a dark oily material precipitated which turned solid at pH ~10. The precipitate was filtered, washed with water, and dried; 2.6 g. of a red dye was obtained. The aqueous solution has an absorption maximum at 450 mμ.

Anal. Found: C, 47.0; H, 4.4; Na, 8.4.

Similar dyes have been prepared from aniline (λ_{max} 440 mμ) and N,N-dimethyl-*p*-phenylenediamine (λ_{max} 550 mμ). They dye wool and nylon directly.

This reaction may be used as a qualitative test for I by pouring a mixture of an ice-cold diazonium salt solution and the sample (0.2–1 mg. of I) into a mixture of excess 2 *N* sodium hydroxide and ice. If I is present, a deep red color develops instantaneously.

Reaction of Propanone-1,3-disulfonic Acid with Benzoyl Chloride.—A mixture of 25 g. of crude propanone-1,3-disulfonic acid and 30 g. of benzoyl chloride was saturated at room temperature with boron trifluoride (1.0 g.). Hydrogen chloride was evolved upon heating to 110°. The total weight loss after 30 min. was 2.5 g. (this includes some of the boron trifluoride). The mixture was cooled to room temperature and again saturated with boron trifluoride (3.5 g.). Heating at 130° for 30 min. resulted in an additional weight loss of 7.5 g. The mixture was cooled and filtered. Methanol (15 ml.) was added to the filtrate in order to convert any unchanged benzoyl chloride to methyl benzoate; 15 ml. of water was then added, resulting in the formation of two layers. The lower layer (56 g.) was neutralized with potassium carbonate and precipitated with methanol. A solid material (17.5 g.) was obtained which is, according to its infrared spectrum, the potassium salt of a sulfonic acid other than I. The material develops an intense red color with ferric chloride solution. The ability to give the ferric chloride test is destroyed reversibly by addition of concentrated hydrochloric acid, irreversibly by boiling with potassium hydroxide solution.