ABSORPTION SPECTRA OF PENTACYCLIC TRITERPENOIDS IN SULFURIC ACID

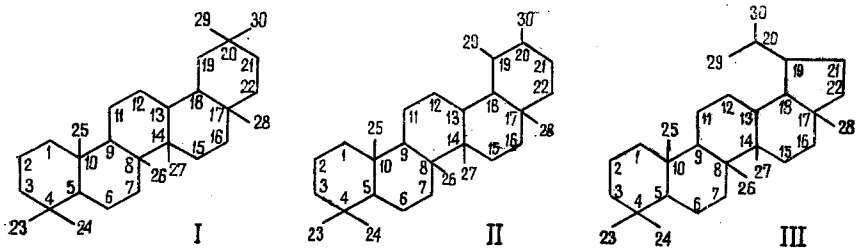
V. D. Ponomarev, É. T. Oganesyan, and V. F. Semenchenko

UDC 547.99

Various modifications of reactions with concentrated sulfuric acid are widely used for the qualitative determination of steroids and triterpenoids [1-3]. Because of the water-abstracting properties of sulfuric acid and the formation of complex compounds with the latter, chromophoric groups arise in the molecules of the steroids and triterpenoids, giving absorption bands both in the ultraviolet and in the visible regions of the spectrum [4, 5]. The UV absorption spectra of the compounds formed on interaction with concentrated sulfuric acid have been well studied for the steriods [2, 5]. It has been found that in various representatives of the steroid compounds UV absorption spectra characterisitc for each substance arise.

We have previously studied the reaction of triterpenoids with sulfuric acid and performed an analysis of the absorption spectra of some pentacyclic triterpenoids [3, 6, 7]. The preliminary results obtained showed a basic difference between the colors and absorption spectra arising in the case of the triterpene compounds and in the case of the steroid compounds.

The present paper reports the results of a study of the absorption spectra in concentrated sulfuric acid of representatives of three groups of pentacyclic triterpenoids: β-amyrane (I), ursane (II), lupane (III), and some representatives of other groups.



The experimental results presented (Table 1) permit the conclusion that all the triterpene compounds considered have a common absorption maximum at 310 nm in concentrated sulfuric acid. This maximum is extremely characterisitc, has a high extinction (Fig. 1), and does not change when various substituents are introduced into the molecule (Table 2).

At the same time, it must be observed that this maximum is not found in the spectra of the steroids [1, 2] and, therefore, it is specific for triterpene compounds. At the present time, reactions of low specificity (the Fontan Candela method, the reaction with vanillin and sulfuric acid, etc.) are used to determine qualitatively whether a substance belongs to the steroid or to the triterpenoid group. It can be said with some truth that the UV spectra of substances in concentrated sulfuric acid enable this question to be decided more accurately. The specific absorption maximum in concentrated sulfuric acid at 310 nm apparently shows that there is a single mechanism of the reaction of triterpenoids with concentrated sulfuric acid. Previously, Brieskorn and Kapuano [4], and also ourselves [3, 6], suggested that the action

Pyatigorsk Pharmaceutical Institute. Translated from Khimiya Prirodynykh Soedinenii, No. 2, pp. 147-150, March, 1971. Original article submitted December 14, 1970.

TABLE 1. Absorption Maxima of Solutions of Triterpenoids in Concentrated Sulfuric Acid, nm

Substance	Structure	λ_{max}	λ_{min} (plateau and inflections)
	α-Amyrane group		
Ursolic acid	3-Hydroxyursa-12-en-28-oic acid	310	250 pl. 305—307
Ursonic acid	3-Oxoursa-12-en-28-oic acid	310	247
Uvaol	Ursa-12-ene-3,28-diol	310	250 pl. 305—307
	β-Amyrane group		
18β-Glycirrhetic acid	3-Hydroxy-11-oxoamyra-12-en-30-oic acid	310	265
		400	380
18α-Glycirrhetic acid		310	245 pl. 385—400
Echinatic acid	3,15,22-Trihydroxyamyra-11,12-dien-28-oic acid	310	260
		405	375
Macedonic acid	3,19-Dihydroxyamyra-11,13-dien-28-oic acid	310	255
Erythrodiol	Amyra-12-ene-3,28-diol	310	255 pl. 385—405 infl. 245
Meristotropic acid	3-Hydroxy-6-oxoamyra-11,13-dien-30-oic acid	310	265 pl. 345—365
		410	395
Echinocystic acid	3,16-Dihydroxyamyra-12-en-28-oic acid	310	255 pl. 235—240
β-Amyrin acetate	3-Acetoxyamyra-12-ene	310	255 pl. 400—415 infl. 245
Oleanolic acid	3-Hydroxyamyra-12-en-28-oic acid	310	250
Hederagenin	3,23-Dihydroxyamyra-12-en-28-oic acid	310	260
		405	370
	Lupane group		
Betulinol	3,28-Dihydroxylupa-20-ene	310	250 pl. 312—315 pl. 385—400
Lupeol	3-Hydroxylupa-20-ene	240	225 pl. 315—320
Betulinic acid		310	255
Lupenone	3-Hydroxylupa-20-en-28-oic acid	310	245 pl. 315—320
	Lupa-20-en-3-one	310	250 pl. 315—320
	Various representatives of triterpenoids		
Zeorin	—	310	245
Taraxerol	—	310	250 pl. 390—415
Taraxerone	—	310	250 pl. 395—405
Myricadiol	—	310	255 pl. 390—405
Simiarenol	—	310	250 pl. 400—420
Simiarenone		310	250 pl. 395—405
Alnusenone	—	310	250 pl.

of concentrated sulfuric acid on triterpenoids forms conjugated diene groupings capable of giving complex compounds with sulfuric acid. Apparently, this maximum is due to complexes of sulfuric acid with conjugated dienes of the triterpenoid group, since on dilution with water the complex compounds with the absorption maximum at 310 nm disappear.

Simultaneously, compounds with absorption at 230-250 nm characteristic for conjugated dienes appear (ursadienecarboxylic acid).

EXPERIMENTAL

Weighed samples of the substances (0.3-0.4 mg) were each dissolved in 10 ml of concentrated sulfuric acid (sp. gr. 1.835), and the resulting solutions were thermostatted at 40° C for 2 h. After cooling, the solutions were studied spectroscopically in comparison with pure sulfuric acid. Since the reaction develops over 12-14 h [6], the spectra were taken 12 h after the substances had been dissolved in sulfuric acid, on an SF-4A spectrophotometer.

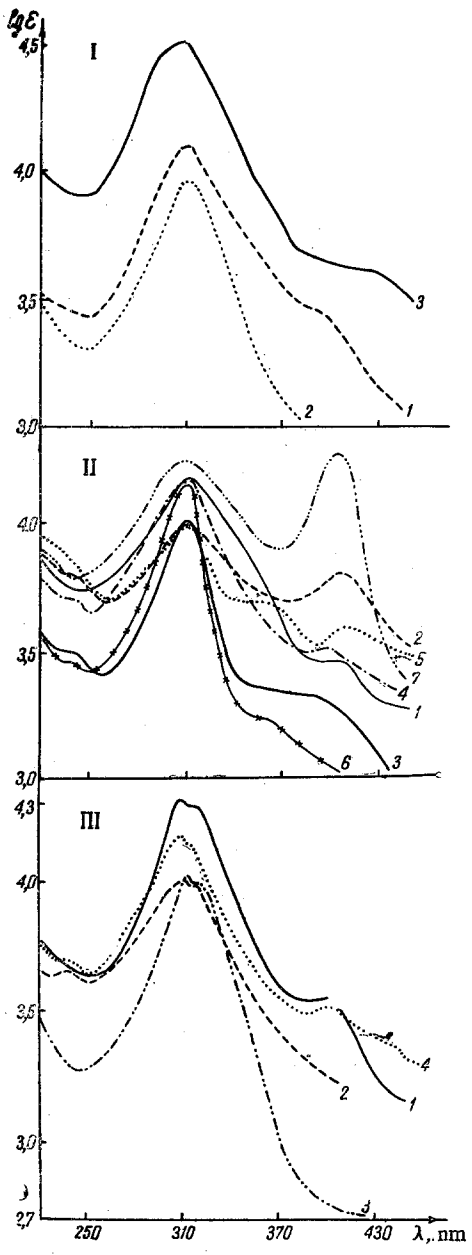


Fig. 1. Spectra of triterpenoids in sulfuric acid: I) α-amyrane group; 1) ursolic acid; 2) ursonic acid; 3) uvaol II) β-amyrane group; 1) 18α-glycirrhetic acid; 2) echinatic acid; 3) macedonic acid; 4) erythrodiol; 5) meristotropic acid; 6) echinocystic acid; 7) hederagenin; III) lupane group; 1) betulinol; 2) lupeol; 3) betulinic acid; 4) lupenone.

TABLE 2. Absorption Maxima of Triterpenoid Derivatives in concentrated Sulfuric Acid, nm

Substance	Me esters	Acetate	Ketone	Glycoside
Acid:				
glycirrhetic	310,405	—	—	310
meristotropic	310,410	—	—	—
echinatic	310,405	—	—	310
macedonic	310	310	—	310
oleanolic	310	310	—	—
ursolic	310	310	—	—
Hederagenin	310	—	—	310
Taraxerol	—	310	310	—
Myricadiol	—	310	—	—
Erythrodiol	—	310	—	—
Lupeol	—	310	310	—
β-Amyrin	—	310	—	—
Simiarenol	—	—	310	—

The samples of the triterpenoids were kindly given to us by N. P. Kir'yalov, A. A. Ryabinin (deceased), and C. Brieskorn (Wurzburg).

SUMMARY

In concentrated sulfuric acid, triterpene compounds have one common characteristic absorption maximum in the UV region of the spectrum at 310 nm; this maximum does not change with the introduction of various substituents into the molecule.

LITERATURE CITED

1. S. Bernstein and H. Lenhard, J. Org. Chem., 18 1146 (1953).
2. S. D. Nikonovich and N. K. Abubakirov, Zh. Obshch. Khim., 34, 2658 (1964).
3. V. D. Ponomarev, Zh. Analit. Khim., 18, 137 (1963).
4. C. H. Brieskorn and L. Kapuano, Chem. Ber., 86, 866 (1953).
5. S. Bernstein and H. Lenhard, J. Org. Chem., 19, 1269 (1954).
6. É. T. Oganesyan, A. L. Shinkarenko, and V. A. Bandyukova, Khim. Prirodn. Soedin., 4, 212 (1968).
7. I. A. Murav'ev and V. F. Semenchenko, 5, 17 (1969).