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RESEARCH ARTICLE

SYNTHESIS OF COUMARIN DERIVATIVES BASED ON MELDRUM ACID AND ITS ANALOGUES.

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Abstract

The article studied the interaction of malonic acid and acetic anhydride with ketones, aldehydes of the fatty, aromatic and carbocyclic series (yields from 16 to 76%). Based on experimental and physical data, it is proved that Meldrum acid exists in solutions in the form of an equilibrium mixture of rapidly convertible conformers.

Introduction:-

As is known, the condensation of acetone with malonic acid under the action of a mixture of sulfuric and acetic acids leads to the formation of a substance with acidic properties, which was attributed to the structure of 3,3 – dimethyl - 2 - carboxy - β - propiolactone. Only 40 years later there was evidence that this substance, called Meldrum acid, has the structure of a six-link ester of 2,2 - dimethyl - 4,6 - dioxo - 1,3 - dioxane [1]. This peculiar substance has a significant CH - acidity comparable with the acidity of acetic acid, and the degree of its anolization under ordinary conditions is extremely small (the ratio of phenolic form to oxoform is 4.5 • 10-5) [2].

An analysis of the structural features and properties of the Meldrum acid derivatives has allowed us to predict the possibility of obtaining coumarins (benzo - α - pyrons) from them - an important class of natural compounds that are lactones.

Connection	Temp., ^{0}C	Exit, %	IK – spectrum, ν^{-1}	Found, %		Gross Formula	Calculated, %	
				C	H		C	H
XLVIII	189-190	54	1780, 1740, 1715	62,00	3,10	$C_{10}H_6O_4$	63,16	3,16
XLIX	233-234	36	1780, 1740, 3600	68,82	3,23	$C_{14}H_8O_4$	70,0	3,33
L	205-207	26	1665, 1640, 1580	64,65	6,20	$C_{12}H_{14}O_3$	64,86	6,31
LI	204-205	20	3180, 1740, 1695, 1580	60,54	4,30	$C_{14}H_{12}O_6$	60,87	4,35
LII	175-176	56	1750, 1720	63,99	5,21	$C_{17}H_{17}O_6$	64,35	5,36
LIII	243-244	8	1670, 1660, 1650	75,34	8,47	$C_{19}H_{26}O_3$	75,50	8,61
LIV	304-306	30	1715	73,44	3,54	$C_{22}H_{14}O_5$	73,74	3,91

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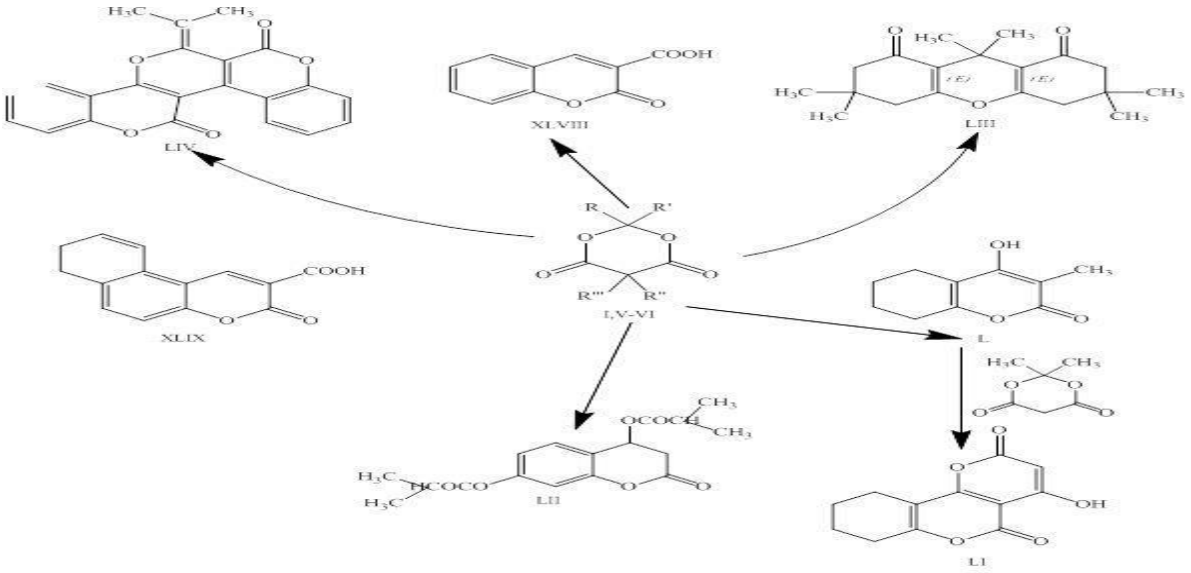


The reaction of 2,2,5-trimethyl-4,6-dioxo-1,3-dioxane with cyclohexanone gave 3-methin-4-hydroxy 11,12-cyclohexylpyrone (L).

In the IR spectrum (L) there are absorption bands of hydroxyl groups (3125 cm-1), carbonyl group of the α-pyrone ring at (1665, 1640 cm-1), C = C - bonds of the α - pyrone ring at (1580 cm-1) In the PMR spectrum of the base there are proton signals in the form of a multiplet of methylene groups 4H (1.6-1.9 ppm), a singlet of methyl groups (1.95 ppm), -CH2-C-protons of the cyclohexane ring (2 , 25-2.55 ppm), single-flow singlet hydroxyl group (6.9 ppm).

The reaction of 3-methyl-4-hydroxyl-11,12-cyclohexylpyro c (I) yields 16-hydroxy-11-12 cyclo octyl bis / 3,4 / - pyrone (L1).

In the IR spectrum (L1), there are absorption bands of the hydroxyl group (3180 cm-1), C = O α - pyrone (1740-1720 cm-1). The aromatic core associated with vibrations of C = C bonds is in the region (1650-1620 and 1650-1600 cm-1). The PMR spectrum recorded in CHCl3 contains signals of protons of the methylene group (1.65-1.95 and 2.40-2.55 ppm) and a single-flow singlet of the methyl group (5.47 ppm) and single-flow singlet from the hydroxyl group (10.73 ppm).

In the reaction of 4,7-dihydroxecoumarin with 2,2,5,5-tetramethyl-4,6-dioxo-1,3-dioxane, we obtained 4,7-diisobutylate benzopyrone (LP), in 56% yield. In its IR spectrum, absorption is observed at (1780 and 1750 cm -1), characteristic of stretching vibrations of the –CO - group of esters, absorption of carbonyl α - pyrone in the region (1720 cm –1). The PMR spectrum recorded in CC14 contains a quartet from the proton of the methyl group (1.3 ppm), a multiplet from the methylene group (2.8 ppm), a singlet from the proton of the methine group (6.35 m. d) and a multiplet of intensity 3H from aromatic protons (6.8 and 7.6 ppm).

The reaction of dimedone with 2,2,5,5-tetramethyl-4,6-dioxo-1,3-dioxane leads to the formation of 3,3,9,9 II, II hexa methyl bi-cyclo-γ-pyrandion 5.7 (Liii).

In the IR spectrum of LIII, there are absorption bands of carbonites of ester groups (1670, 1660, 1650 cm-1). Signals in the form of a singlet from the sixth methyl groups (0.8 ppm) and a singlet from methylene protons with an intensity of 8H (2.15 ppm) appear in the PMR spectrum recorded by CH3COOH. The mass spectrum contains peaks of the most intense ions with m / z 302 (M +, 1, 3%), 288 (M-74) + (1.2%), 287 (M-1) + (100%), 270 (M-17) + (1.2%), 244 (M-26) + (), 230 (M-14) + (13.4%), 174 (M-56) + (5.3%) 146 (M-28) + ().

During thermolysis, 4-hydroxycoumarin reacts with 2,2,5,5-tetramethyl-4,6-dioxo-1,3-dioxone, with the formation of 2-isopropylidene / bis-3,4,5,6-benzopyrone / - α - Piron (LIU).

The absorption spectrum of the carbonyl groups of the α-pyrone ring (1715 cm-1) and the aromatic ring (1595 cm-1) are present in the IR spectrum (LIU).

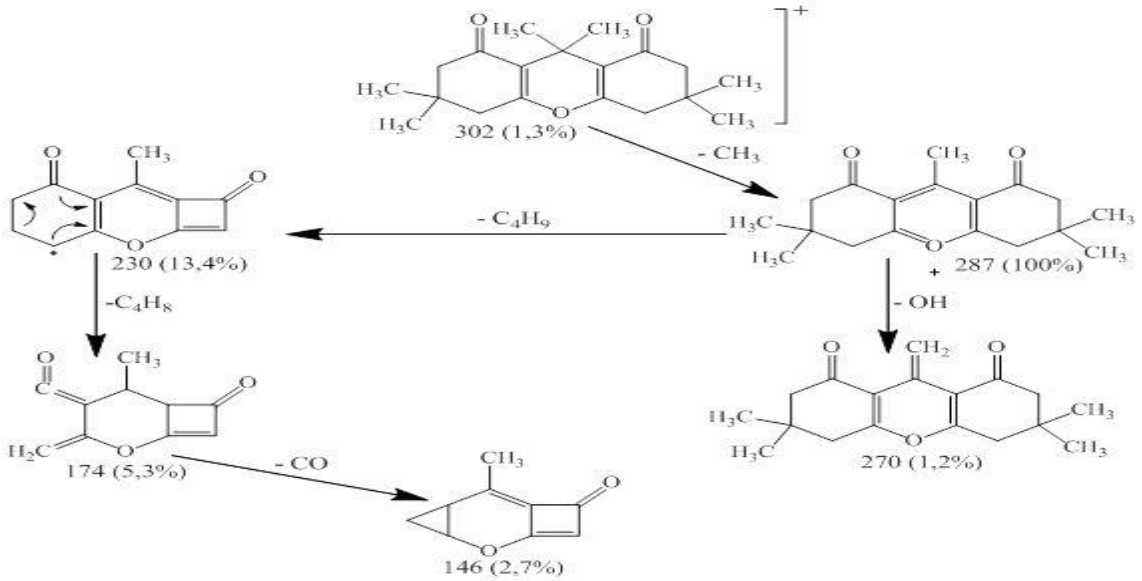
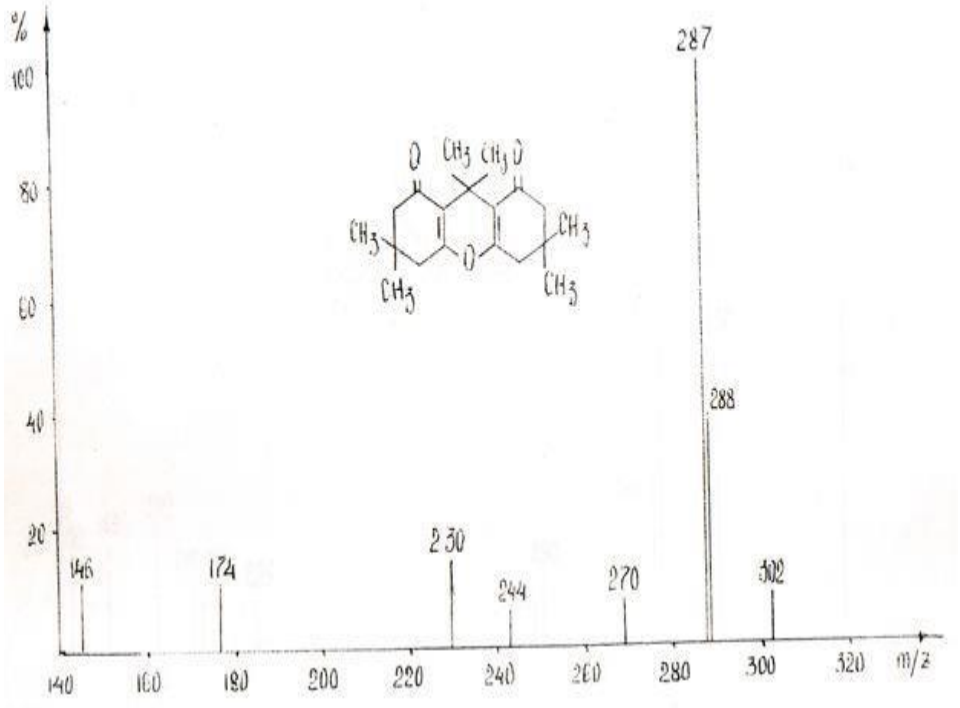


Figure 1:-Mass spectrum 3,3,9,9, II, II - hexamethyl - hexamethylbicyclo - γ - pyrondione - 5.7 (LIII)



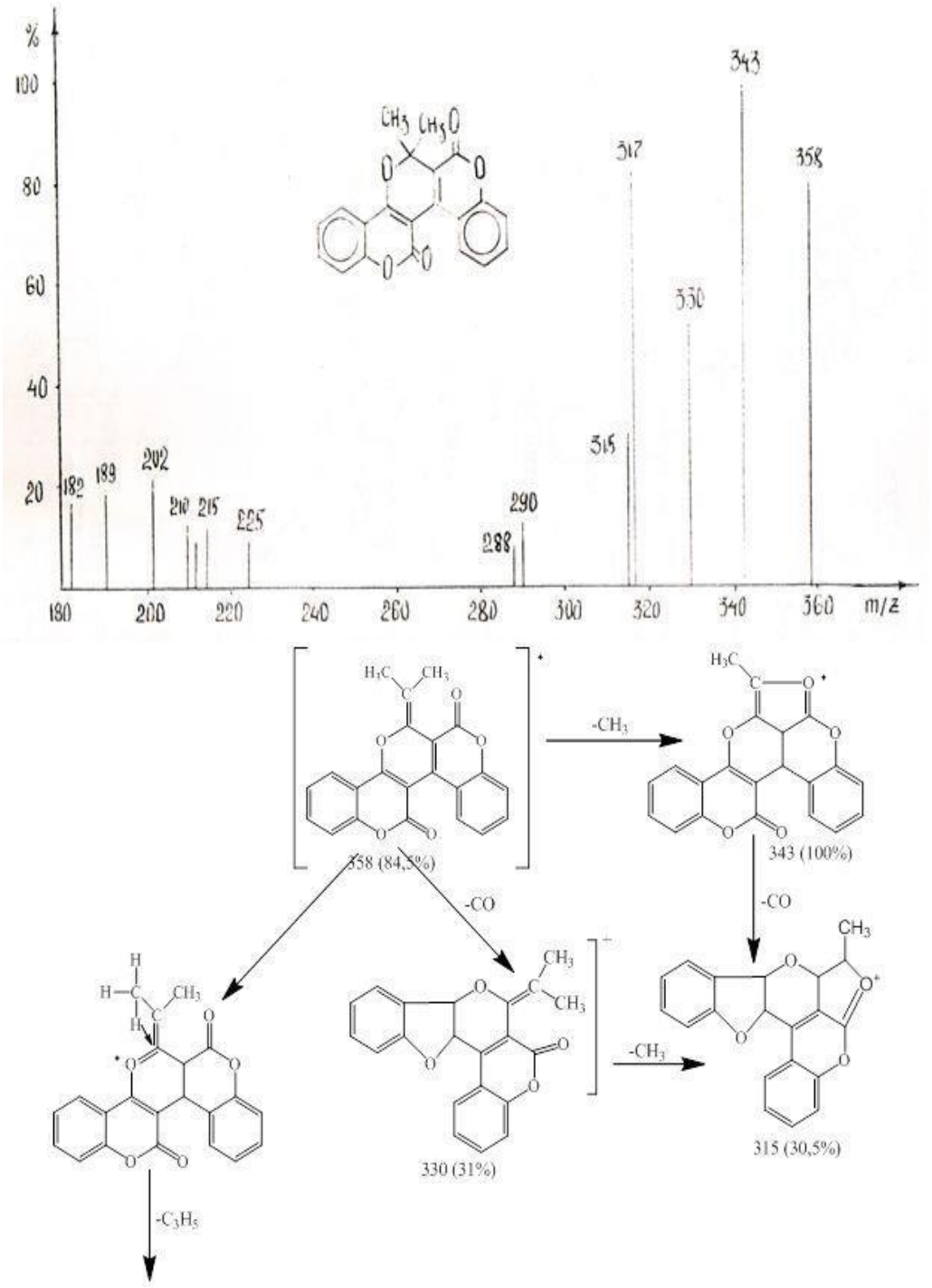
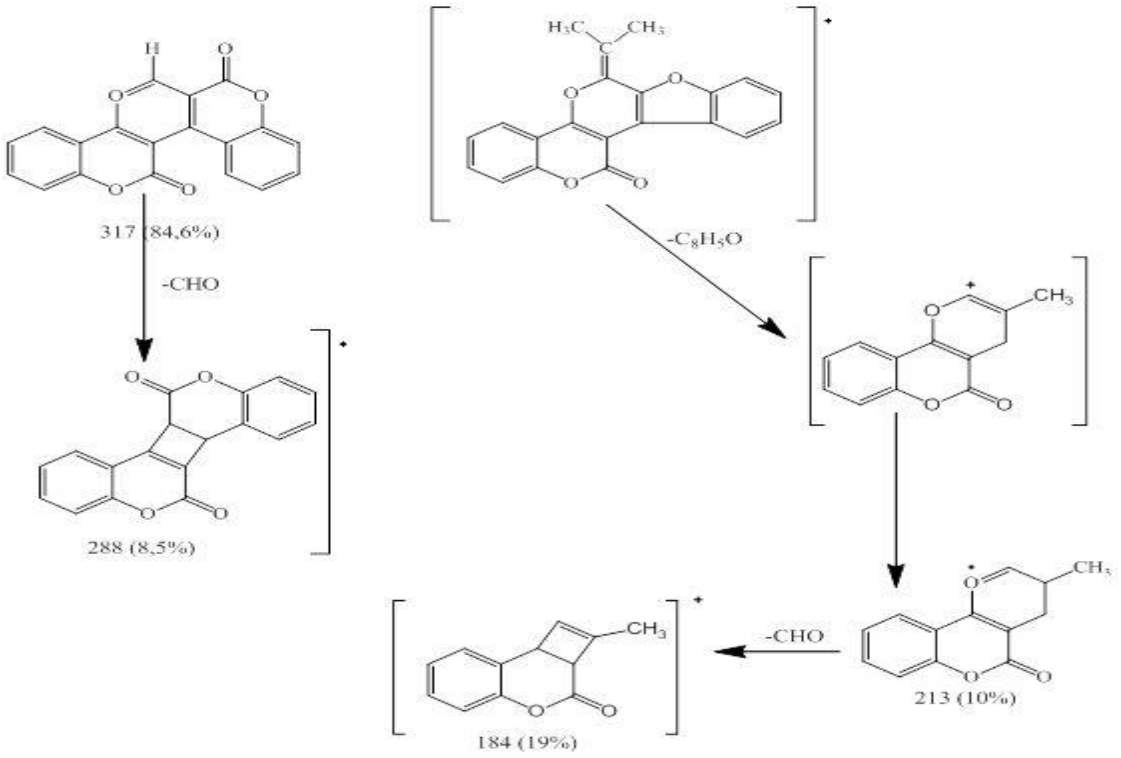


Figure 2:-Mass spectrum 2 - isopropylidene / bis - (3,4,5,6) - benzopyrone / - α - pyrone (LIV).

The decay of 2-isopropylidene / bis (3,4,5,6) - benzopyrone / -α - pyrone (LIU) under electron impact.



Signals in the form of singlets from two methyl groups (1.8 ppm), a multiplet from 7H aromatic ring protons (7.3-7.9 ppm) and a bis aromatic proton (8 , 35 ppm); the most intense ion peaks with mz 358 (M +, 84.5%), 343 (M-15) + (100%), 330 (M-13) + (44.6%), 317 (M -13) + (84.6%), 315 (M-2) + (30.8%), 290 (M-25) + (8.5%), 288 (M-2) +, (8, 5%), 233 (M-55) + (7.7%), 215 (M-18) + (10%), 213 (M-2) + (10%), 210 (M-3) + (11.5%), 202 (M-8) + (21.5%), 189 (M-13) +, (19.2%), 182 (M-7) + (15.4%).

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1. Davidson D., Bernhard A. The Structure of Meldrum's supposed β - Lactonic acid // J. Amer.Chem.Soc. 1948. - Vol. 70. - P.3426-3428.
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