ISSN (Print) 2794-7629 Received 02/01/2025
ISSN (Online) 2794- 4549 Accepted 16/01/2026

FULL PAPER

Some Naturally Oxolane-2-one and 2-(5H) Furanone with Substituted Aliphatic Open Chains, Mini Review

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Abstract

Five membered ring carboxylic esters are called □-Lactone, which are a group of important compounds produced from an intramolecular esterification reaction of saturated and unsaturated hydroxycarboxylic acids. There are also known butyro-lactone corresponding to the numbers of carbons in the precursor carboxylic acid (butyric acid). The other suffix that can be used instead of lactone is –olide. □-Lactone can be containing open short or long side chains, which may be saturated or unsaturated. Both oxolane-2-one and 2-(5H) furanone derivatives are two classes of □-lactones that can be obtained from natural sources. Sometimes the branched chains of them contain hydroxy and or carbonyl groups. They showed a number of biological activities and have been considered as anti-bacteria and anti-toxicity. The spectra of these type of ϒ- lactones exhibited the character features that confirmed the presence of (C-C=O)-O and (O-C-C) and suggested the five-membered lactone in oxolane-2-one, also revealed the presence of an □,□-unsaturated □-lactone moiety in 2-(5H) furanone.

Keywords: □-Lactones, Oxolane-2-one, Furan-(5H)-2-one, butyro-lactones, Spectroscopy Analysis, Biological Activity.

1. Introduction

□-Lactones compounds that are five membered cyclic carboxylic esters are produced from an intramolecular esterification reaction of saturated or unsaturated hydroxycarboxylic acids. These □-lactones are crucial in many different areas, from their essential physiological functions in living organism to possess different biological activities. □-Lactones are called butyro-lactone corresponding to the numbers of carbons in the precursor carboxylic acid (butyric acid), and the suffix –olide also can be used instead of lactone. There are some naturally □-lactone with short or long open side chains which are saturated or unsaturated, and sometimes containing hydroxy and or carbonyl functional groups. These molecules are secondary metabolites having an important biological activity as a source of pharmaceuticals, cytotoxicity, antibiotics, antitumoral, antifungal agents, and some of them are sex pheromones.[1-7] Oxolane-2-one **1** and 2-(5H) furanone **2** and their derivatives are crucial classes of □-lactones that can be obtained from natural sources. The figure 1. Shows oxola-2-one 1, and 2-(5H) Furanone **2** which is considered as butenolide compound and may be possess 2(5H) and 2(3H) furanones carbon skeleton. These butenolide lipids are identified more than 30 years ago.[8-10] As part of our studies, we reviewed here a number of naturally □-lactone derivatives that having one ring oxola-2-one **1** and furan-(5H)-2-one **2** with saturated and unsaturated open chains.

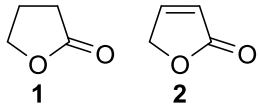


Figure 1. The chemical structure of oxola-2-one **1** and furan-(5H)-2-one **2**

2. Results

2.1. Naturally Obtained

2.1.1. Oxolane-2-one Derivatives

A number of Oxolane-2-one 1 ring derivatives were obtained naturally with different substituents. Butanolide which called 3- or α-substituted oxolan-2-one 3 was isolated as monoterpene from Mold Mite, *Tyrophagus putrescentiae*.[11] While □- substituted oxolan-2-one 4 reported from marine bacteria, *Anomala cuprea*,[12] besides 3,5-, 4,5-oxolan-2-one and several β-,□□ -lactones that were 5a-h,6-12 and extracted from two marine bacteria in the North Sea, also some of them isolated from the giant honey bee, *Apis dorsata*, and *Osmoderma eremita*.[13-21] The (R,Z)-7,15-hexadecadien-4-olide 13 and (R,Z)-9-octadecen-4-olide 14 were isolated from the yellowish elongate chafer *Heptophylla picea*, and *Janus integer* (Hymenoptera), respectively.[22-25]While lactones 15a-d were found in the males of the danaine butterfly *Idea leuconoe*, [26] Figure 2.

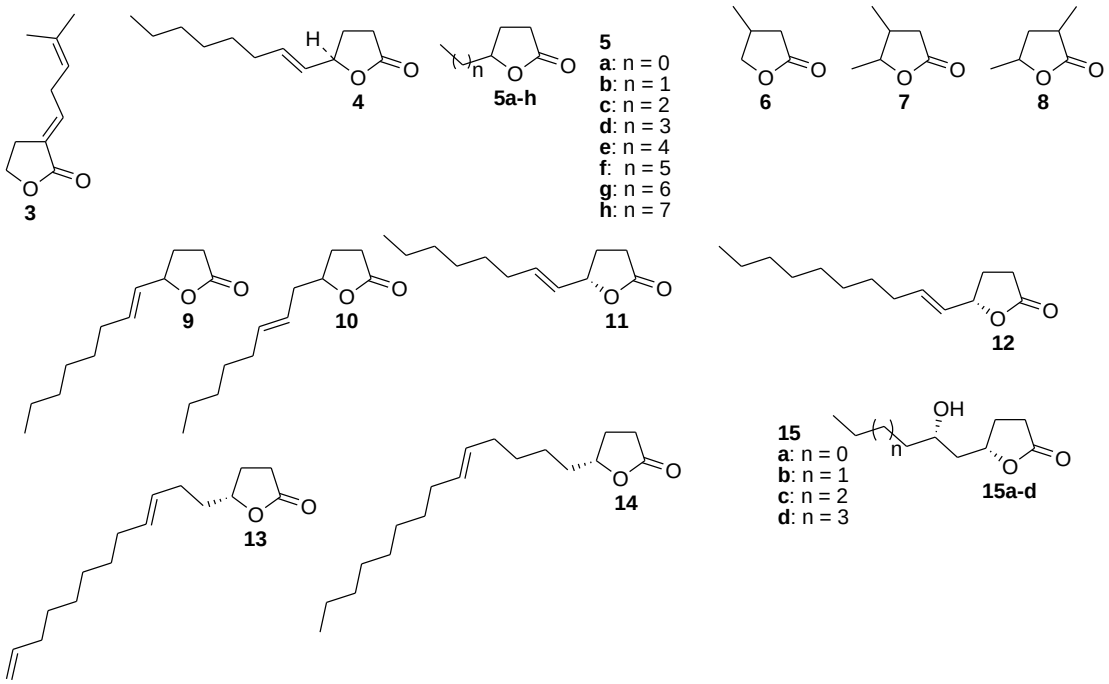


Figure 2. Some chemical structures of oxola-2-one derivatives

Some 3,4-disubstituted oxolane-2-one lactones with terminal OH functional group as enantiomeric derivatives 16-18 were extracted from soil bacteria.[27-29] There are also, 5-substituted and 5,5-disubstituted oxolane-2-one natural products compounds containing hydroxy functional group in the side chain 19-20 that were isolated from the soft corals *Sarcophyton trocheliophorum* and *Lithophyton arboretum*.[30] Additionally, 4,5-disubstituted oxolane-2-one compounds 21a-c and Eldanolide 22 were obtained from a fungal *endophytes* and borer *Eldana saccharina*, respectively,[31-34] Figure 3.

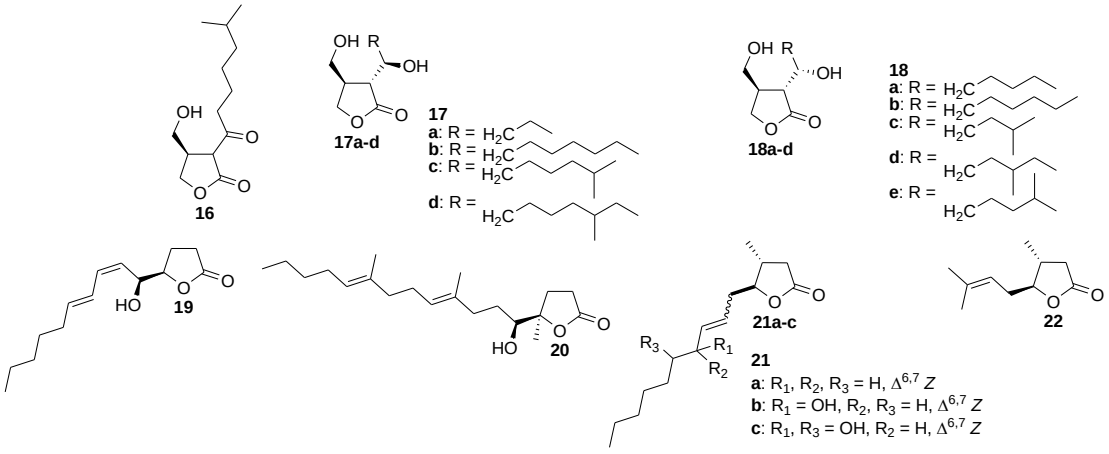


Figure 3. Some chemical structures of oxola-2-one lactones with terminal OH functional group

2.1.2. Furan-(5H)-2-one Derivatives

Some unsaturated □-lactones ring derivatives were extracted as terpenoid lactone 23from *Schwiebea araujoae*, and 24 from *Rhizoglyphus sp*. The 5-substituted of furan-(5H)-2-one 25 produced by litchi seeds.[34-36] Isomeric furanones Versicolactones A 26 and B 27 were identified from a *coral-associated* fungus.[37-39] There were 3,5-disubstituted furan-(5H)-2-one 28-33 were isolated from a Cup Fungus Plectania sp,[40] and acyltetronic acid derivatives 34-35 were identified from strain *A. niger* ATCC1015, Figure 4.[41]

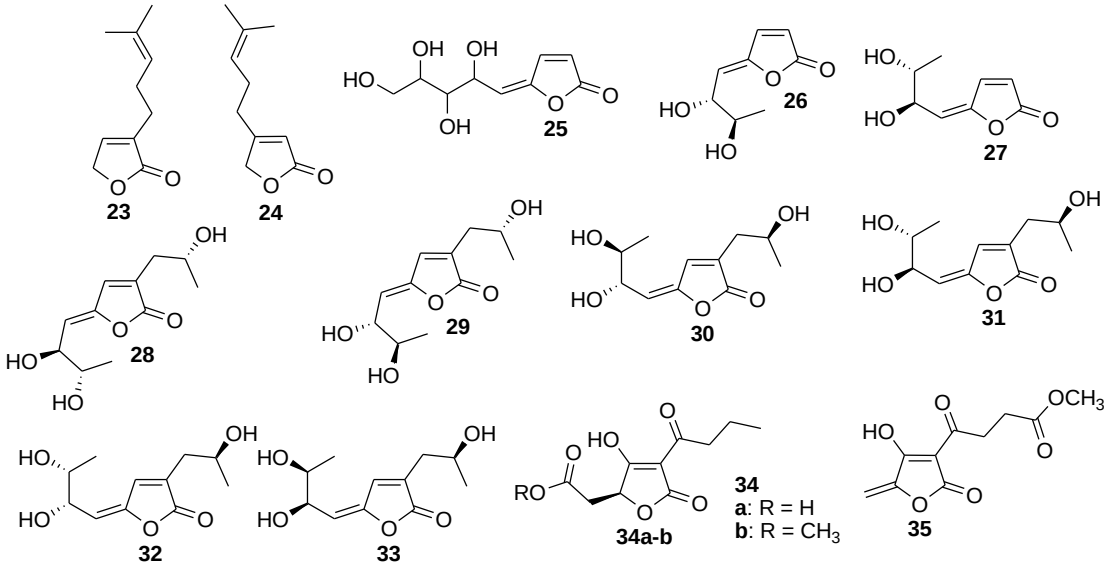


Figure 4. Some chemical structures of substituted furan-(5H)-2-one

Marine sponge *Ircinia variabilis* gave 2-carboxymethyl-3-hexylmaleic acid anhydride 36.[42] As for Gregation B 37 was produced by *A. flavus*,[43] and *A. ochraceus* MA-15 gave Asperochrins B 38 and its derivative 39.[44] Asperochratide F 40 was derived from the deep-sea-derived fungus *A. ochraceus*.[45] Dihydrofuranone 41-44a-e were resulted from *Aspergillus sp*.,[46] while □-lactones 45a-b,46a-b were derived from *Aspergillus sp.*[47] Some 3,5-disubstituted unsaturated side chains with or without hydroxyl functional groups were extracted. Which were compound 47 that isolated from Spruce *endophytes*,[31] □ -lactones (48-51) from a fungus *Plectania sp.*,Figure 5. [36] Compounds 52-55 from the soft corals *Sarcophy*,[22] and 56-58 lactones derived from the fungus *Penicillium sp.* TGM112, Figure 6.[48]

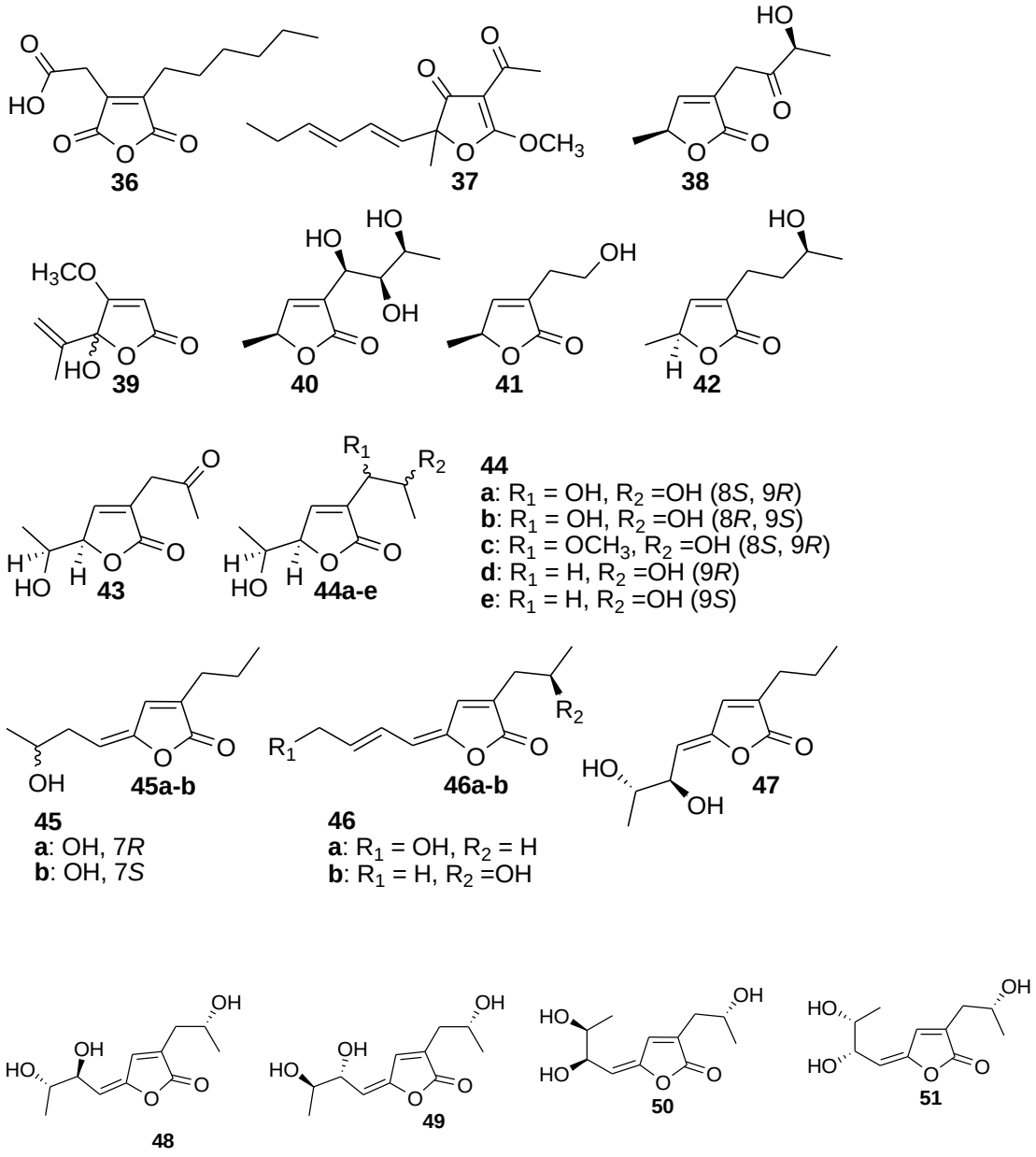


Figure 5. Some derived of furan-(5H)-2-one from natural products.

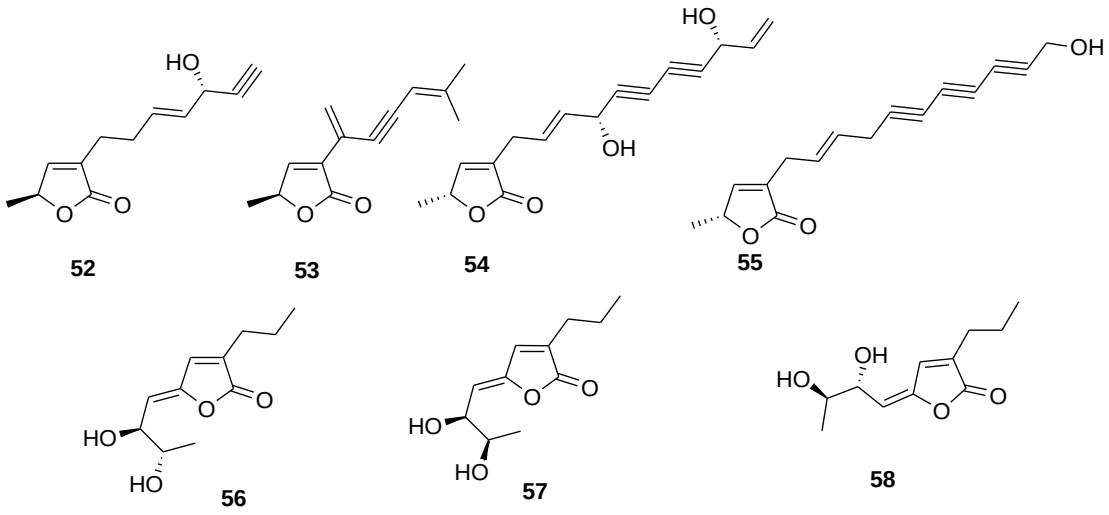


Figure 6. Some derived of furan-(5H)-2-one from natural products.

.2. Spectroscopy Identification

2.2.1. FTIR Spectra

The IR spectra have several advantages to confirm the five-ring lactone. The most characteristic absorptions were strong higher C=O band of □-lactone in the range 1811-1765 cm^{-1} together with signals C-O bands around 1195-1157 and 1041-1027 cm^{-1} that suggested the presence of [C-C=O)-O], (O-C-C) and confirmed the five-membered lactone ring in these molecules (□-lactone).[11-12,30] Since there were absorptions at 1735-1645 cm^{-1} revealed the presence of an □,□-unsaturated □-lactone moiety.[36-37,49] The spectra showed signals around 3020 cm^{-1} indicate the stretching of C-H in the double bonds (C=C-H) in the side chains.[2] In Addition to dienes and hydroxyl functional groups around 1650 cm^{-1} and in the range 3314-3490 cm^{-1}, respectively.[30,36]

.2.2. NMR Spectra

^{1}H and ^{13}C NMR are the most useful tools for structure determination of oxolane-2-one lactones derivatives. ^{13}CNMR spectra consistent all chemical shifts corresponding to all carbons. The chemical shift in the range 171.4-177.4 ppm, which is very typical for carbonyl C=O, *s*.[11,30] This together with the one at 65.4 ppm -CH_2-O-, *t*, corresponding to the lactone moiety in these compounds of five membered □-lactone.[11] The olefinic carbons around 149 ppm are corresponding to the lactone moiety in these compounds of five membered □-lactone.[30] In general, the ^{13}CNMR spectral also showed those of other secondary hydroxylated carbon at interval from 65-84 ppm, and showed methyl and methylene functional groups at 14.1-30 ppm.[11,30] ^{1}HNMR spectra suggested the structural features of all protons in these lactones.[11,30,50] The chemical shifts of the methylene protons of the ring of □-lactone derivatives appear in the range □□□ 2.05-2.88 ppm.[11,30,49-50] The ^{1}HNMR spectra exhibited signals for vinyl hydrogen around □□□ 6.94, a methyl signals at □□□ 1.46 and

methine at □□□ 5.05 ppm suggesting an □,□-unsaturated □-lactone.[22] ^{1}HNMR spectrum of compound **25** showed two *cis Z* olefinic proton signals (□*H* = 5.72 ppm, *d*, *J* = 8.5 Hz and 8.04 pmm, *d*, *J* = 8.5 Hz) which were characteristic signals of an □,□-unsaturated □-lactone moiety.[35] The ^{1}HNMR showed resonances for two methyl signals (□*H* = 1.08 and 1.00 ppm), three oxygenated methines (□*H* = 4.27, 3.85 and 3.56 ppm), and two olefinic protons (□*H* = 7.51 and 5.37 ppm).[32] Sometimes the complete configurations by the CD spectroscopic data.[49] ^{1}HNMR demonstrated the structural features, such as the type of the substitution in the isoprenoid, methylene protons in the side chains, and *cis Z* or *trans E* substituted dienes that confirmed from the splitting of the signals and the value of and *J* coupling constant.[30] ^{1}HNMR showed the methyl functional group on side chained at 1.65 ppm (3*H*), and the resonance of these protons become around □*H* = 4.39-4.85 ppm in the case oxygenated carbon atoms that carried protons. Olefinic protons were observed at chemical shifts in the range □*H* = 5,15-6.71 ppm.[30]

2.2.3. Mass Spectra

In general, the MS spectra of these compounds have the M^+ ion confirmed the molecular formulas of these lactones.[11-21,30,36] The MS spectra showed of almost the typical fragments of the substituted oxolane-2-one **1** or furan-(5H)-2-one **2**. Including, the fragment ions that results from the loss of aldehyde group CHO, or unusual cleavage with double bond migration as a major fragment, or the fragment ion obtained due to the missing of water, or, methylene and alkyl groups. Sometimes the MS exhibited the typical fragments of a substituted hydroxy □-lactone as well as fragmentation of a substituted □-lactone derivatives having a hydroxyl functional group. In addition to fragmentation of degrees of unsaturation. [11,30,36]

2.2.4. UV-Vis. Spectra

In general, the conjugated diene system was improved by UV. The UV spectra that consisted a characteristic maximum absorption □$_{max}$ which were agree with the theoretical values.[11,30,35] Such as the UV spectrum of compound **25**showed □$_{max}$ (MeOH) 208 nm,[35] and UV data of compounds **28-33** are exhibited that □$_{max}$ in the range 279-288 nm,[36] while □$_{max}$ at 228 nm in lactones **19**.[30] The compounds can be showed UV and carbonyl functional group.[11]

2.3. Biological Activity

Compounds **4-14** were utilized as the Scarabae Beetle sex pheromone.[12-24] Other compounds **16-18** used to regulate the production of secondary metabolites in *Streptomycetes*.[27-29] The rare lactones **18-19** and **52-54** showed positive results against the toxicity of *Artemia salina* shrimp bioassay.[30] 4,5- disubstituted oxolane-2-one compounds **21a-c** were obtained from a fungal *endophytes*.[31] Eldanolide **22** is a sex pheromone in the wing gland of the male African sugar-cane borer *Eldana saccharina*, Lepidoptera.[33-34] Compound **27** displayed pronounced cytotoxicity on

human pancreatic cancer cells.[38-39] Compound **36** showed an inhibitory effect against *Neurospora crassa*.[41]

3. Conclusions

Oxolane-2-one **1** and 2-(5H) furanone **2** derivatives are two important classes of □-lactones that having five membered cyclic carboxylic esters. 2-(5H) furanone **2** contains unsaturated ring, while oxolane-2-one **1** contains saturated □-lactone moiety ring. An -olide suffix is known and used instead of lactone. 2-(5H) Furanone derivatives are also called butanolide compounds, and sometimes have 2(5H) or 2(3H) furanones carbon skeleton. Derivatives of 2-(5H) furanone **2** and oxolane-2-one **1** are wildly spread as natural product compounds. They showed a variety of biological activities such as anti-bacteria, anti-toxicity, anti-fungi and some of them are sex pheromones. The NMR spectroscopic of them are studied and characterized by the chemical shifts of the methylene protons of the ring of □-lactone which appear in the rang □ 2.05-2.88 ppm in oxolane-2-one **1**. While the signals for vinyl hydrogen around □ 6.94 ppm, a methyl signals at □ 1.46 ppm and methine at □ 5.05 ppm suggesting an □,□-unsaturated □-lactones in 2-(5H) furanone derivatives. On the other hand, the most characteristic absorptions in the IR spectra of oxolane-2-one **1** were exhibit strong band of C=O bond in the range 1811-1765 cm^{-1} together with signals C-O bands around 1195-1157 and 1041-1027 cm^{-1} revealed the presence of C-C=O)-O and O-C-C and suggested the five-membered lactone in it. Since the absorptions at 1735-1645 cm^{-1} confirmed the presence of an □,□-unsaturated □-lactone moiety in 2-(5H) furanone **2**.

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