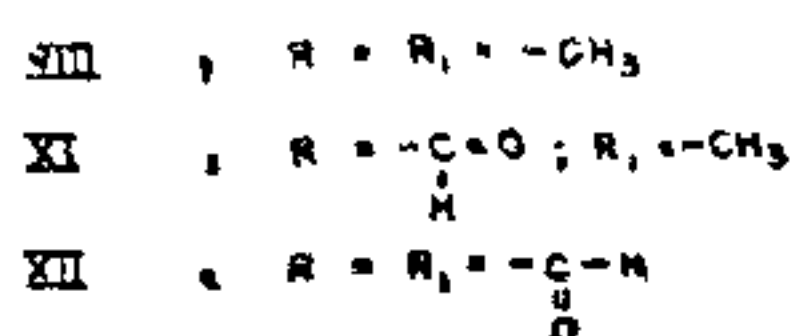
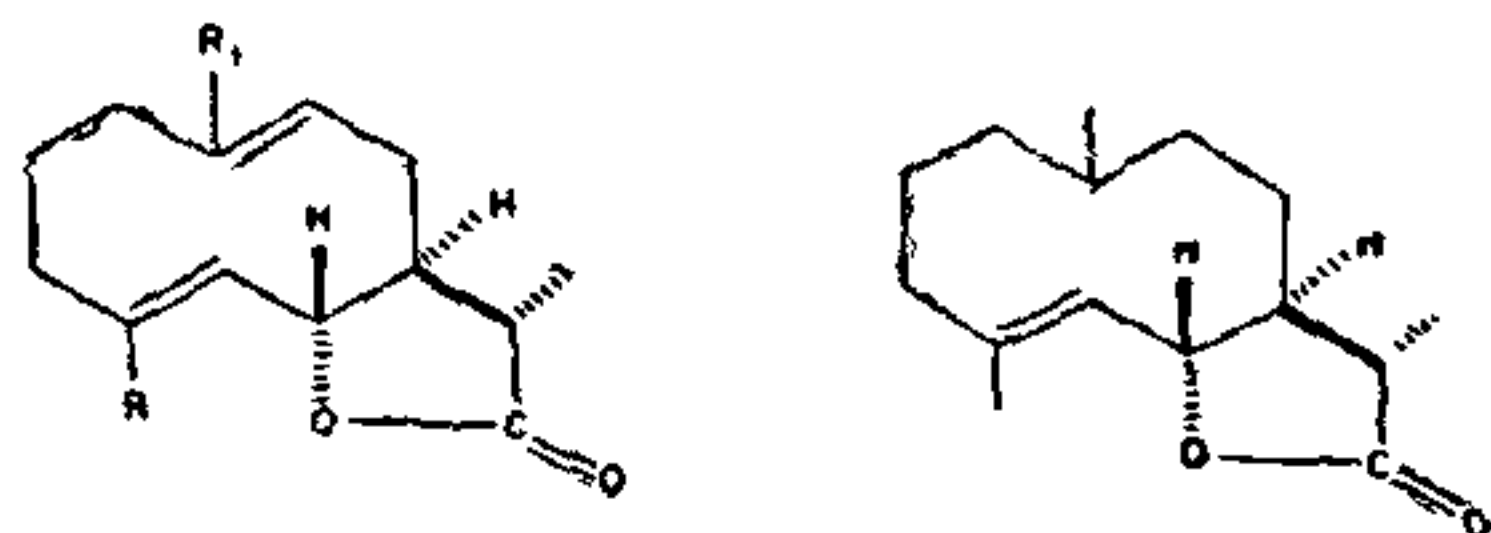
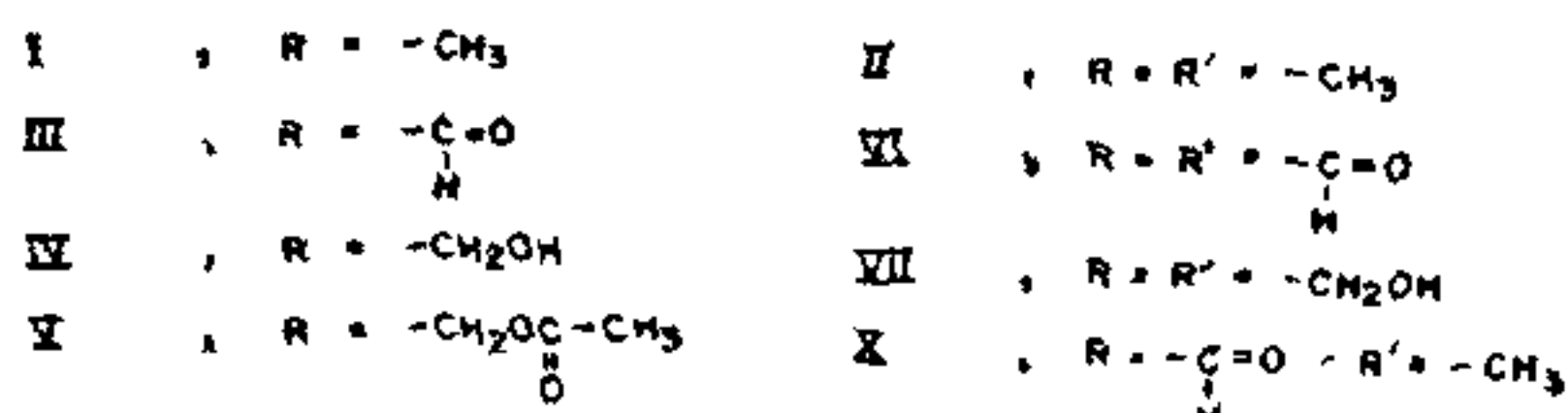
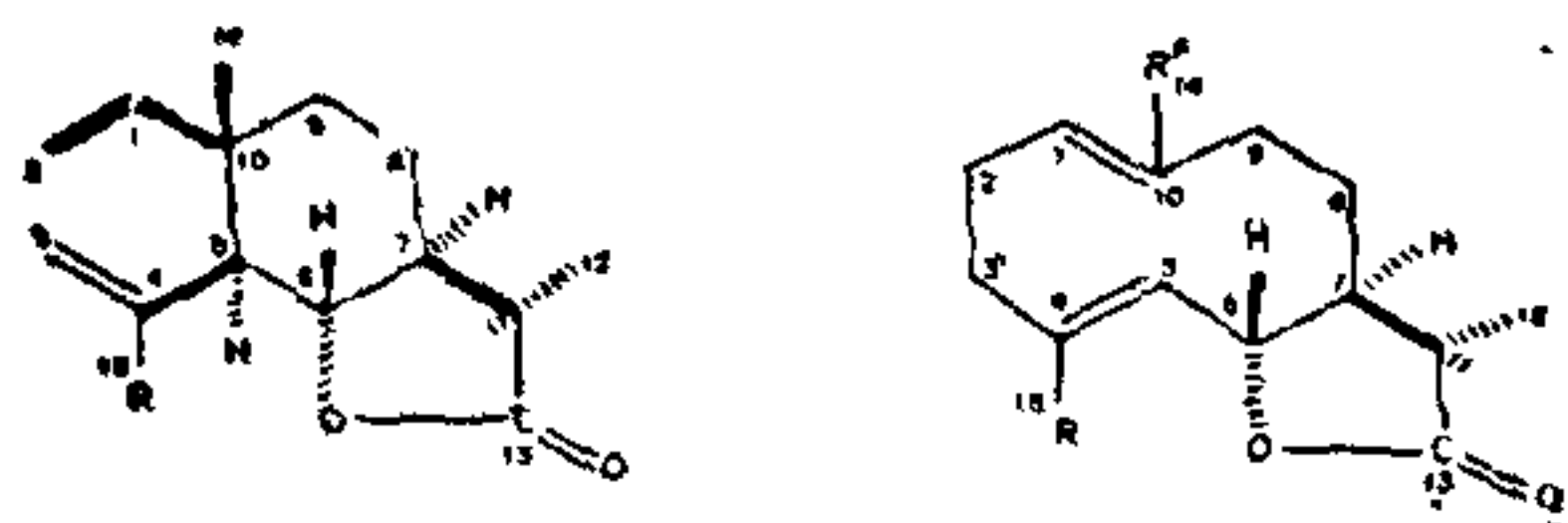


factorily explains the splitting patterns of C_1 and C_5 protons. From these considerations it appeared that the lactone (VI) possessed germacrane skeleton.

It is known⁵ that when lactone (I) is heated at 230 ± 10 for 3 minutes in nitrogen atmosphere a reproducible mixture containing (I) and (II) in the ratio 2:1 results, indicating that the conversion of (I) to (II) is a reversible reaction. Lactone (III), similarly, is capable of undergoing such a conversion to (X). At temperatures of refluxing benzene, such a conversion may be proceeding only at a very slow rate, to give ultimately lactone (VI), though in quite low yields.



That the lactone (III) is an intermediate in the formation of (VI) was demonstrated as follows. Lactone (III) was subjected to selenium dioxide oxidation, using two different solvents (1) benzene and (2) dioxan. In the case of reaction in benzene (20 hrs), (VI) was obtained in low yields, while in the case of reaction in dioxan, (VI) was obtained in about 50% yield (8 h.).

As reported⁶ earlier, germacronolides such as (II), when treated with selenium dioxide in benzene at room temperature, undergo double bond migration, the C_1-C_{10} double bond shifting to C_9-C_{10} position, to give the rearranged lactone (VIII). So under the conditions of the reaction employed, lactone (X) formed from (III) by reversible thermal (Cope's) rearrangement, is capable of undergoing a similar rearrangement to give (XI), which ultimately may get oxidised to give lactone (XII). The spectral data, reported for the dialdehydolactone, can also be satisfactorily explained by the alternative structure (XII),

The possibility of structure (XII) for the dialdehydolactone therefore cannot be ruled out completely. The exact structure of the dialdehydolactone needs further confirmation.

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* IR ν_{\max} in cm^{-1} and NMR chemical shifts in τ scale with TMS internal reference.

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A NOVEL SPRAY REAGENT FOR PLANT PIGMENTS

THE present investigation was carried out with a view to finding some new spray reagents for detecting the presence of hydroxyl groups adjacent to carbonyl groups in the quinones and flavones. This was achieved by paper chromatographic procedures involving the use of butanol : acetic acid : water (4 : 1 : 5 v/v) as solvent and phosphomolybdic acid (0.5 g) and mono-chloroacetic acid (0.5g) in water (25 ml) as spray reagent when the plant pigments were present in amounts of at least 5 μg each.

This reagent has shown better results on comparing with the following popular spray reagents¹⁻⁴ viz., ammonia vapours, *p*-toluene sulphonic acid, iodine vapours, methanolic sulphuric acid, methanolic aluminium chloride, 25% aqueous lead acetate basic, 5% aqueous sodium carbonate, 1% methanolic sodium hydroxide solution. Only ammonia vapours, aqueous sodium carbonate and methanolic sodium hydroxide were found almost equal in performance in comparison to that of phosphomolybdic acid and chloroacetic acid (1 : 1). The new reagent is specific for the detection of hydroxyl groups adjacent to carbonyl groups in quinones, flavones and their O-glycosides even at a concentration of 5 μg . The pigments having no hydroxyl groups adjacent to carbonyl groups and completely methylated flavonoids do not give colour reaction with the reagent. Interestingly it has been observed that 3', 4', 5, 7-tetra-O-methyl quercetin does not give colour reaction with the reagent

in spite of the fact that it contains a hydroxyl group at C₃ adjacent to carbonyl group.

The R_f values, colour with the spray reagent and colour in the UV light are given in Table I.

TABLE I

Substance	R _f	Colour observed	Fluorescence in UV light
2-hydroxy 1 : 4 Naphthaquinone	0.84	LY	BL
Chrysophanol	0.76	LY	LB
Emodin	0.64	LY	LB
Mono-methyl ether of Phycion	0.11	P	P
Phycion 1-O-arabino glucoside	0.68	P	P
Taxifoline	0.78	Y	LB
Taxifoline galactoside	0.73	Y	LB
5, 7 dihydroxy flavanone	0.57	Y	LB
Kaempferol	0.83	Y	LB
Quercetin	0.78	Y	DB
Rhamnetin	0.80	Y	DB
5, 7 dihydroxy flavone	0.67	LY	LY
5, 3' dihydroxy 7, 4' dimethoxy flavonol	0.52	LY	LB
5, 7', 4' trihydroxy 3, 6, 3' trimethoxy flavonol	0.61	LY	LY
5, 7 dihydroxy 4' methoxy flavone	0.50	Y	LB
5 hydroxy 7, 3', 4' trimethoxy flavone	0.43	Y	LB
7 hydroxy flavone	0.00	—	BL
Avicularin	0.70	Y	LB
Quercitrin	0.82	Y	LB
Rutin	0.56	Y	LB
Penta methyl quercetin	0.71	—	BL
3', 4', 5, 7 tetra methoxy quercetin	0.88	—	BL
5 hydroxy 7', 3', 4' trimethoxy flavonol	0.38	LY	LY

LY = light yellow; LB = light brown; DB = dark brown; BL = bluish; P = pink.

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SYNTHESIS AND STRUCTURAL STUDIES OF MALONYL AND SUCCINYL DIHYDRAZIDE COMPLEXES OF SOME FIRST ROW TRANSITION METAL IONS

ALTHOUGH there are a few papers¹⁻⁴ on the synthesis and structural studies of transition metal complexes of malonyl dihydrazide (MDH) and succinyl dihydrazide (SDH), yet there is disagreement among the various investigators regarding the composition of complexes formed and bonding sites of the ligands utilized therein. We have undertaken in continuation of our previous work⁵, the synthesis and structural investigations of the complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with the above dihydrazides and the results of these studies are reported in this note.

Preparation and Analysis of the Complexes

The complexes were prepared by mixing together cold/hot ethanolic solutions of the metal salts and ligand in 1 : 1 and/or 1 : 2 molar ratios. All the complexes precipitated immediately except [Ni(MDH)₂Cl₂].2H₂O and [Ni(SDH)₂Cl₂].2H₂O which were kept overnight to get the filterable precipitate. All the complexes thus obtained were filtered, washed with ethanol, ether and finally dried at room temperature. Experimental details pertaining to the analysis of the complexes, molar conductance, magnetic susceptibility, i.r. and electronic spectral measurements were the same as described in our earlier papers⁶.

MDH and SDH react with metal(II) chlorides and nickel(II) nitrate to yield the complexes of the empirical compositions MLC₂, ML₂Cl₂, [NiL₂Cl₂].2H₂O and [NiL₂(H₂O)₂](NO₃)₂ where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) and L = MDH and SDH. The complexes are insoluble in common organic solvents but the chloride complexes are slightly soluble in cold or hot DMSO. Most of the complexes melt in temperature range 131-238° and some decompose in the temperature range 148-241° but a few complexes do not melt or decompose up to 250°. The loss of water molecules in 100-115° temperature range in hydrated nickel(II) chloride complexes and in 140-160° temperature range in hydrated nickel(II) nitrate complexes shows that the water molecules are in lattice⁶ in the former complexes and coordinated⁶