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SELENIUM DIOXIDE OXIDATION OF SAUSSUREALACTONE

IN continuation of our studies on the selenium dioxide oxidation of sesquiterpenic lactones^{1,2,6} we now report our results on the selenium dioxide oxidation of saussurealactone.

Saussurealactone (I), obtainable from dihydrocostunolide (II) by thermal (Cope's) rearrangement³ possesses two double bonds of which, only the one at C₃-C₄, has methyl and methine groups in the allylic positions. The other double bond, however, does not have any such oxidisable groups in the allylic positions. When (I) is subjected to selenium dioxide oxidation (refluxing benzene, 20 h), a mixture containing five compounds (TLC) was obtained. Of these, three compounds have been isolated pure (TLC), by chromatography, followed by crystallisation.

The least polar of these, the major product of the reaction (30%) has been identified as the conjugated aldehydolactone (III), C₁₅H₂₀O₃, M⁺ 248, m.p. 150-2° (benzene + 10% hexane); (α)_D + 40° (c, 0.5; CHCl₃) IR* 1770 (γ-lactone), 1681, 2778 (ν_{C=O}) 1639, 1621, 900 (conj. and non-conj. >C=CH₂); NMR (CDCl₃): 8.97 (3H, s, C₁₀-CH₃); 8.8 (3H, d, J = 6 Hz, C₁₁-CH₃); 7.0 (1H, d, J = 12 Hz, C₅-allylic proton); 5.2 (2H, m, C₂ olefinic protons); 5.74 (1H, t, J = 12 Hz, C₆ proton); 4.44 (1H, m, C₁-olefinic proton); 3.75 (2H, s, conj. C₃-olefinic protons) and 0.52 (1H, s, aldehydo proton). UV λ_{max} 218 mμ, ε_{max} 8000; 2:4 DNP C₂₁H₂₄O₆N₄, m.p. 190-2°.

Sodium borohydride reduction of (III) gave the corresponding hydroxylactone (IV), C₁₅H₂₂O₃ (low melting solid m.p. < 40°); (α)_D + 44° (c, 2.2; CHCl₃); n_D^{31.5} 1.5037; IR, 3650 (OH), 1776 (γ-lactone), 1639, 892 (>C=CH₂); NMR (CCl₄): 8.92 (3H, s, C₁₀-CH₃); 6.14 (2H, s, -CH₂OH at C₄); 5.93 (1H, t, J = 10 Hz, C₆-proton); 6.67 (1H, d, J = 10 Hz, C₅-olefinic proton); 5.14 (4H, m, olefinic protons at C₂ and C₃); 4.27 (1H, m, C₁-olefinic proton) and at 7.4 exchangeable with D₂O (1H, hydroxyl proton). On acetylation, lactone (IV) gave a liquid acetate lactone (V), C₁₇H₂₄O₄

with the following spectral properties. IR, 1770 (γ-lactone), 1739, 1235 (acetate) 1639, 895 (>C=CH₂); NMR (CCl₄): 8.78, 8.92 (6H, C₁₀- and C₁₁-CH₃); 7.97 (3H, s, acetate methyl at C₄); 6.44 (1H, d, J = 15 Hz, C₅-olefinic proton); 6.0 (1H, t, J = 12 Hz, C₆ proton); 5.58 (2H, s, -CH₂ at C₄); 5.0 (4H,



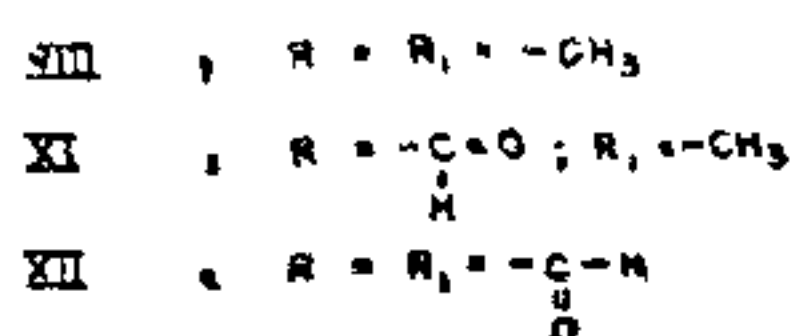
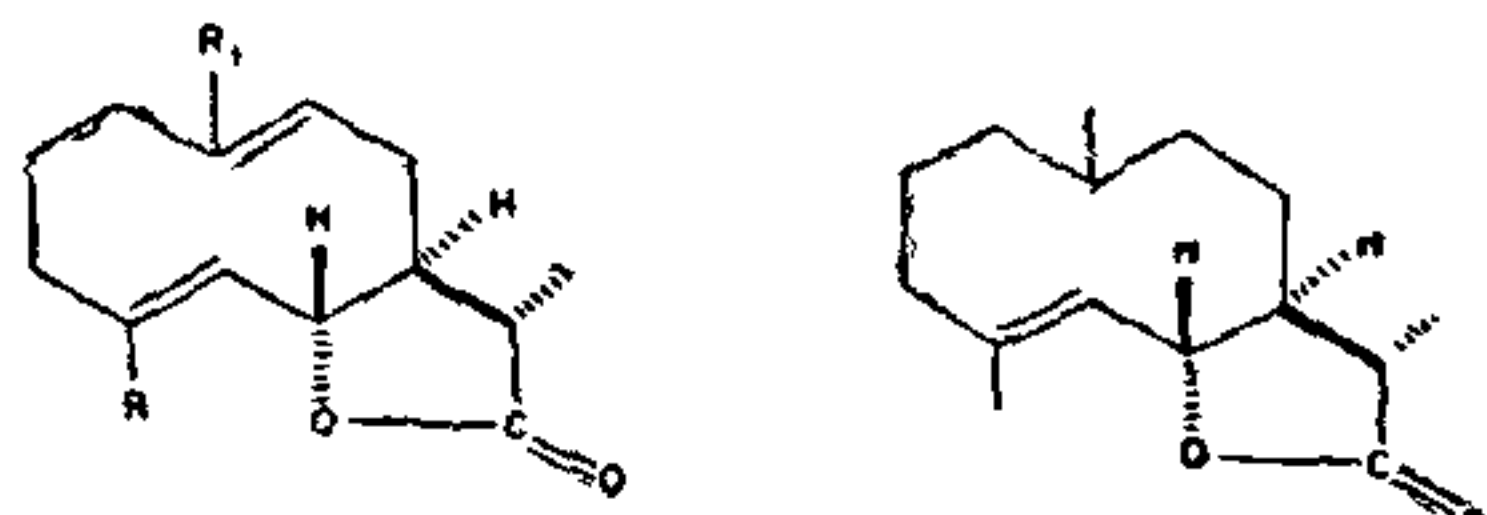
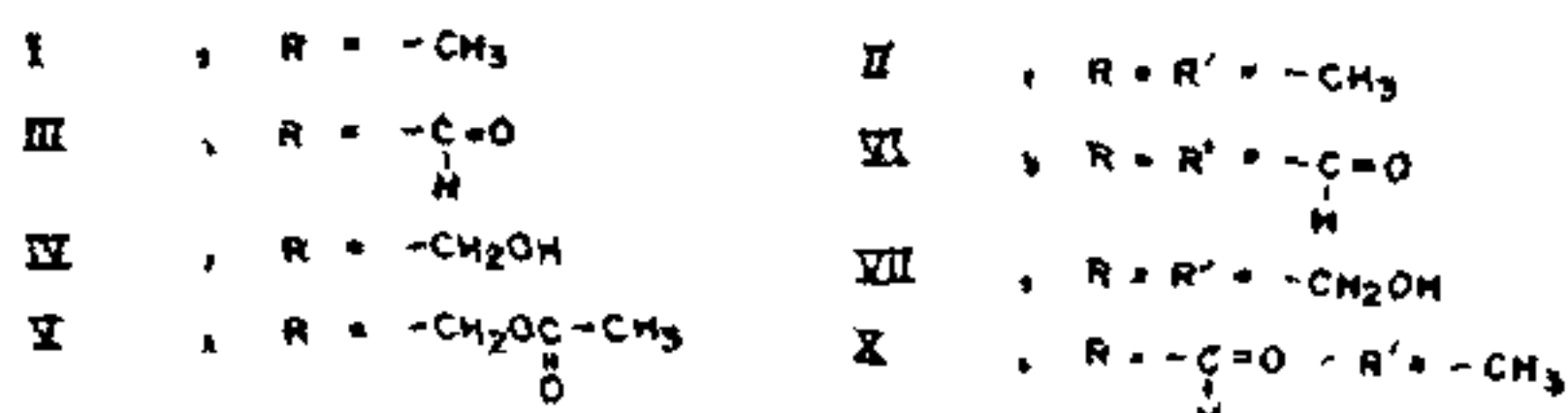
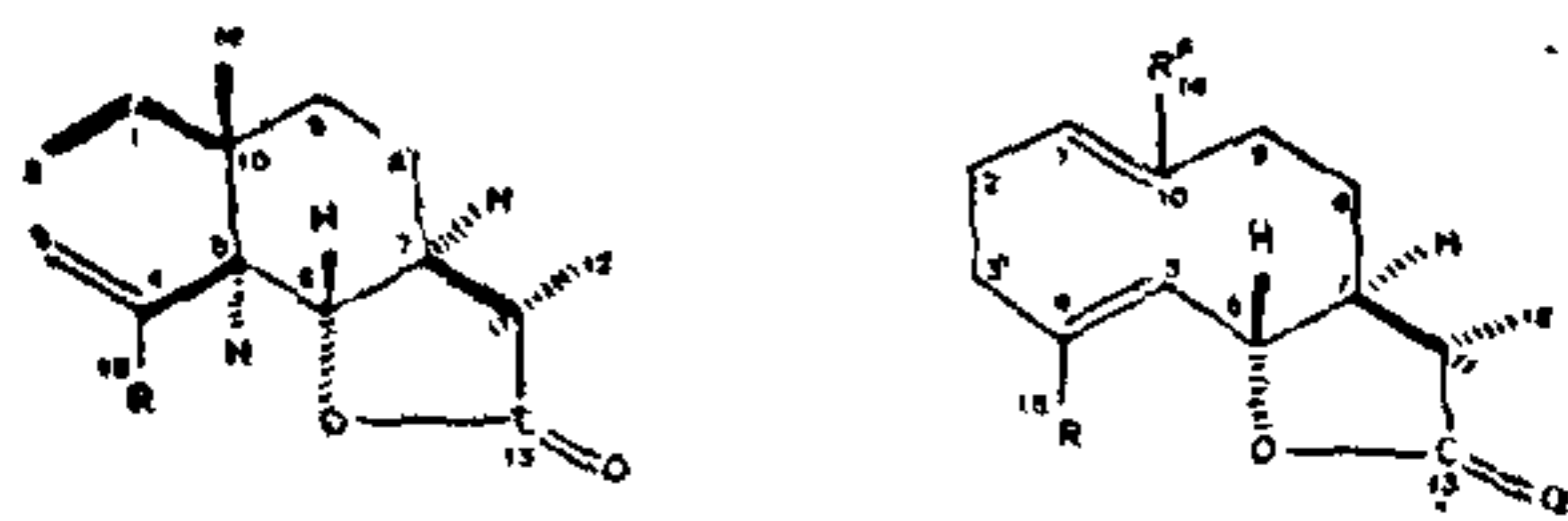
m, C₂ and C₃ olefinic protons), 4.24 (1H, m, C₁-olefinic proton).

The lactone (IV) could also be isolated from the tail fractions of chromatography (identified by IR NMR, TLC and (α)_D + 42° (c, 1.2; CHCl₃); n_D^{31.5} + 1.5034). The identity was further confirmed by converting it into acetate (V) and comparing the spectral properties.

From the middle fractions of chromatography a crystalline dialdehydo lactone, C₁₅H₁₈O₄, M⁺ 262, m.p. 200-2° (benzene + 30% hexane) has been isolated though in very low yields (<1%), which has been assigned structure (VI) on the basis of spectral data; IR 1776 (γ-lactone), 1681, 2786 (aldehyde), 1621 (conj. >C=C<); NMR (CDCl₃): 8.81 (3H, d, J = 7.2 Hz, C₁₁-CH₃); 4.73 (1H, t, J = 10.8 Hz, C₆-proton); 3.47 (1H, t, J = 7.8 Hz, C₁-olefinic proton); 3.87 (1H, d, J = 10 Hz, C₅-olefinic proton) and at 0.53-0.17 (2H, aldehydo protons); UV λ_{max} 225 mμ, ε_{max} 20,000; 2:4 DNP C₂₇H₂₆O₁₀N₈, m.p. 207°. The above spectral data indicated that compound (VI) contains two aldehydo groups, probably both of which are conjugated. The possibility of any conjugation between the double bonds was eliminated, from the fact, that the dihydroxylactone (VII), obtained by sodium-borohydride reduction of (VI) shows in its UV spectrum only the end absorption for isolated trisubstituted double bonds (ε₂₀₅, 3000). The NMR spectrum of (VI) indicated the presence of only one secondary methyl, viz., one at C₁₁. It therefore appeared that the two CH₃ groups (C₄ and C₁₀) of I are involved in allylic oxidation and must have been converted into the aldehydo groups. This, however, is not possible for a compound like (I), as such, without undergoing rearrangement. The appearance of the triplet for the C₆-proton in the NMR spectrum of VI, clearly suggested that there must be one proton on each side of C₆-which is available for coupling, viz., at C₅ and C₇. The C₆-proton in the spectra of compounds like I, III, IV appeared as triplets at 5.9, 5.74 and 6.0 respectively and even in compounds such as VIII and IX⁴ where the C₆-proton is allylic to the double bond at C₄-C₈, it is observed at 5.55 and 5.52 respectively. The significant down field shift of the C₆-proton from the normal value of 5.8 to 6.0τ to 4.73τ, suggests that it is in a different environment and such a down-field shift is possible only when it is allylic to a conjugated double bond as in (VI). Structure (VI) satis-

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 monochloroacetic acid (0.5 g) 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