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Note

Jone's oxidation of terpenoids on thin-layer chromatographic plates

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A number of organic reactions in a solid matrix are known to occur[1–4]. For example, Singh *et al.*[5] described the use of pyridinium chromate on silica gel and chromic acid on silica gel and evaluated them as readily available reagents for the efficient oxidation of a variety of primary and secondary alcohols. Pyridinium chromate on silica gel can be safely used for the oxidation of alcohols containing acid labile functions. For example, El-Maghraby[6] carried out chemical reactions on thin-layer chromatographic (TLC) plates in order to solve several problems, particularly involving natural products. Samples obtainable from natural sources are often too small to prepare derivatives for comparison with known products or to carry out

TABLE I

R_F VALUES OF REACTION PRODUCTS OF TERPENOIDS WITH JONE'S REAGENT ON SILICA GEL G PLATES

Solvent: benzene–ethyl acetate (9:1 or 8:2, as indicated).

Compound	*Original compound*		*Reaction product*	
	9:1	*8:2*	*9:1*	*8:2*
Khusinol	0.54	0.64	0.79	0.80
Khusilal	0.55	0.53	0.85	0.78
Khusol	0.52	0.49	0.84	0.74
Isopulegol	0.60	0.57	0.86	0.88
Citronellol	0.52	0.51	0.83	0.77
Santonin	0.35	0.37	0.62	0.58
Daucol	0.49	0.52	0.78	0.74
Carotol	0.50	0.57	0.77	0.76
Costunolide	0.63	0.62	0.85	0.84
Khusinodiol	0.19	0.22	0.64	0.52
Nerol	0.48	0.45	0.75	0.70
Citral	0.50	0.47	0.78	0.75
Eugenol	0.63	0.62	0.42	0.46
Equol	0.31	0.28	0.65	0.51
Khusilol	0.56	0.58	0.75	0.74
Linalool	0.23	0.24	0.82	0.84
Methyleugenol	0.78	0.72	0.64	0.63
Cholesterol	0.38	0.59	0.76	0.91

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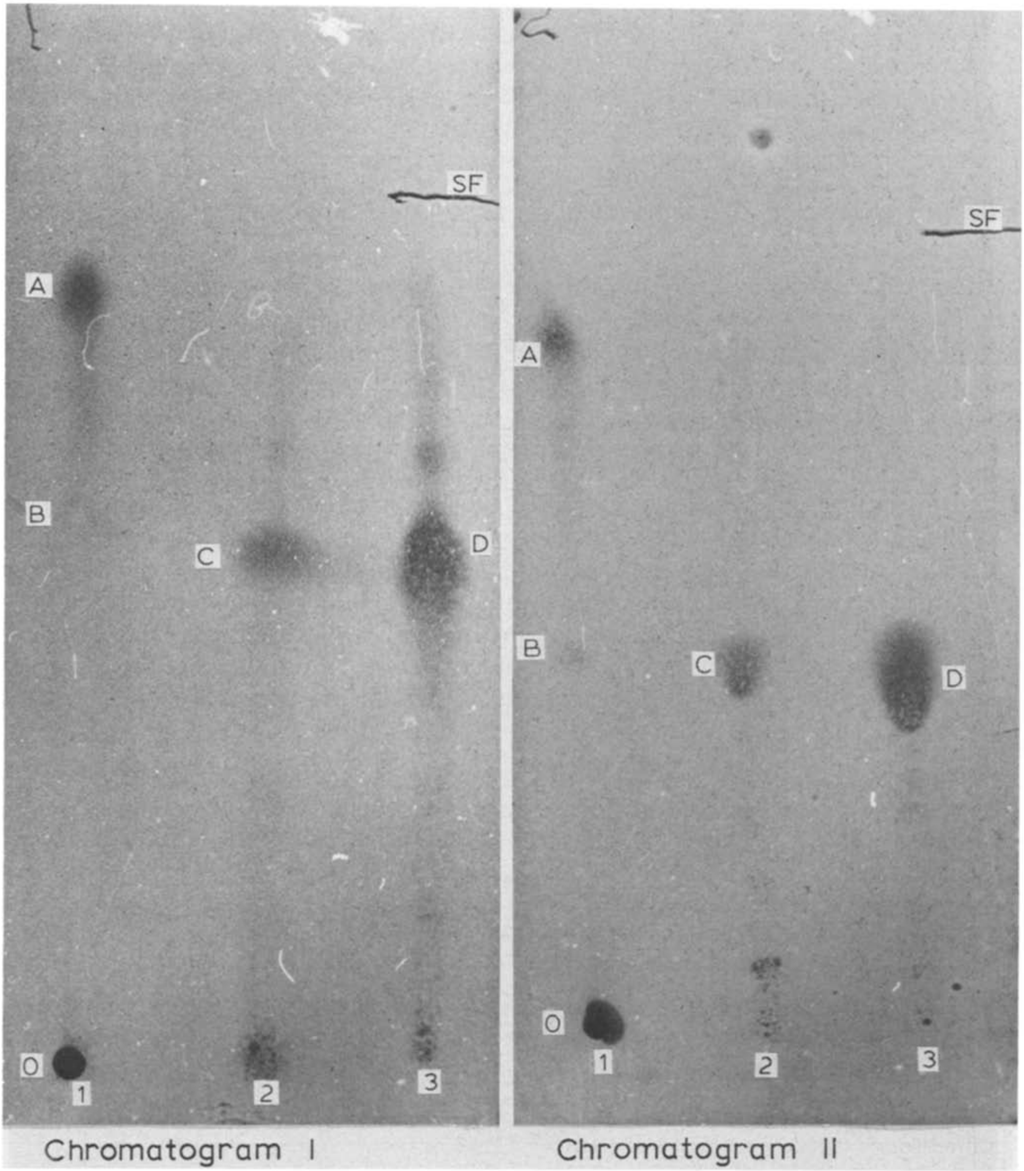

Fig. 1. Chromatogram of Jone's oxidation of khusinol. A, Product of Jone's oxidation; B, unreacted khusinol; C, khusinol after 24 h on active surface; D, khusinol at room temperature.

Fig. 2. Chromatogram of Jone's oxidation of cholesterol. A, Product of Jone's oxidation; B, unreacted cholesterol; C, cholesterol after 24 h on active surface; D, cholesterol at room temperature. SF = Solvent front; O = origin.

reactions in flasks. Therefore, in continuation of our earlier studies of organic reactions in a solid matrix[7], we now report Jone's oxidation of terpenoids on TLC plates for the convenient and facile oxidation of terpenoids.

EXPERIMENTAL AND RESULTS

Preparation of Jone's reagent

Jone's reagent of concentration *ca.* 8 *N* was prepared by dissolving pure chromium trioxide (66.7 g) in distilled water, adding concentrated sulphuric acid (53.3 ml) and diluting the mixture with water to 250 ml.

General method for carrying out the reaction on TLC plates

Terpenoids in the appropriate solvent were applied to a plate at the starting line together with Jone's reagent. The plates were kept at room temperature for 12 h in order to simulate, as far as possible, the normal reaction conditions in a flask. The adsorbed layer was then treated in the normal manner as a chromatographic medium for the resolution of the components of the reaction mixture. After development with a suitable solvent system, the plates were sprayed with concentrated sulphuric acid–methanol (1:1) and heated in an electric oven at 110°C in order to reveal the spots. The results are given in Table I.

It is interesting that Jone's reagent oxidizes khusol and cholesterol on the TLC plate. The products were isolated and identified as γ-cadinene and cholest-4-en-3-one by comparison with an authentic sample using TLC and IR spectroscopy. However, it is worth mentioning that Jone's reagent partially oxidizes the terpenoids, as indicated by some typical chromatograms (Figs. 1 and 2).

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