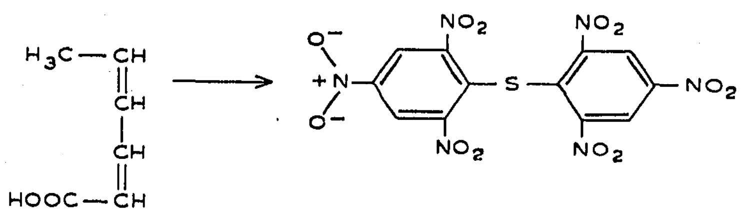
CHROM. 5363

Studies on charge transfer complexes of some conjugated compounds with explosives

According to DEWAR's molecular orbital theory[1] conjugated compounds are characterised as π donors. It is likely that in nature compounds such as sorbic acid, vitamin A, α-, β-, and γ-carotenes, lycopene, β-citraurin etc., function as $\pi\pi$, $n\pi$ or similar charge transfer complexes. Sorbic acid forms a complex with diaminooxidase[2]. Its inhibitory effect on the respiration rate in the cell is due to the formation of a sorbic acid–coenzyme A complex[3]; a vitamin A–rhodopsin complex is known[4]. Vitamin A and the hydrocarbon carotenoids exist as protein complexes and are transported by the serum lipoprotein[5–7]. Vitamin A in rats, as in man, is associated with α_1-globulin[8].

Although such compounds have been separated by thin-layer chromatographic (TLC) techniques, no work is reported where they have been demonstrated as π donors to nitro aromatic compounds, which are excellent π acceptors.



Sorbic acid–2,4,6,2′,4′,6′-hexanitrodiphenyl sulphide complex.

The present paper describes the resolution and identification of some conjugated compounds as π complexes with 2,4,6,2′,4′,6′-hexanitrodiphenyl sulphide (HNDPS) and 2,4,2′,4′-tetranitrodiphenyl sulphide (TNDPS) using TLC.

Experimental

Compounds and solvents. The compounds were purified by passing them through neutral alumina columns, eluting with petroleum ether–ethyl acetate (95:5), and repeated crystallisations. They gave single spots in two-dimensional TLC and were spectroscopically pure; sorbic acid, m.p. 133–134°; vitamin A, m.p. 63–64°; α-carotene, m.p. 187–188°; β-carotene, m.p. 184°; γ-carotene, m.p. 178°, lycopene, m.p. 175°; and β-citraurin, m.p. 146–147°. Both 2,4,2′,4′-tetranitrodiphenyl sulphide, m.p. 196–197° and 2,4,6,2′,4′,6′-hexanitrodiphenyl sulphide, m.p. 234°, were prepared according to the procedure of BIELIG AND REIDIES[9]. All irrigating solvents were freshly dried and distilled.

Preparation, spotting and irrigation of plates. Photographic glass plates 35 × 12 cm were employed for the preparation of chromatoplates. A fine slurry of the adsorbent (50 g) in water (100 ml) was prepared. The slurry was poured on the glass plates and uniformly spread by tilting them from side to side. The plates were left at room temperature overnight for drying and activated at 110° in an oven for 1 h before use. The average coating of the adsorbents was noted after weighing the

TABLE I

R_F VALUES OF THE CHROMATOGRAMS RUN UNDER VARIOUS CONDITIONS

Serial No.	Compound	*Silica Gel G*		*Silica Gel G–Kieselguhr G (3:1)*		*Neutral alumina–$CaSO_4$*	
		Petroleum ether–benzene (3:2)	*Petroleum ether–methylene dichloride (9:1)*	*Petroleum ether–benzene (3:2)*	*Petroleum ether–methylene dichloride (9:1)*	*Benzene*	*Chloroform*
Plates not treated with nitro compounds							
1	Sorbic acid	0.24	0.15	0.28	0.19	0.15	0.31
2	Vitamin A	0.30	0.20	0.33	0.24	0.18	0.38
3	β-Citraurin	0.53	0.47	0.58	0.52	0.49	0.66
4	Lycopene	0.67	0.52	0.72	0.57	0.66	0.81
5	γ-Carotene	0.80	0.70	0.83	0.75	0.79	0.92
6	β-Carotene	0.87	0.87	0.92	0.92	0.88	0.97
7	α-Carotene	0.89	0.91	0.92	0.96	0.89	0.97
Plates treated with 0.1 % hexanitrodiphenyl sulphide							
1	Sorbic acid	0.06	0.01	0.11	0.08	0.02	0.12
2	Vitamin A	0.15	0.10	0.20	0.18	0.06	0.20
3	β-Citraurin	0.39	0.38	0.43	0.42	0.33	0.48
4	Lycopene	0.59	0.45	0.59	0.49	0.49	0.63
5	γ-Carotene	0.63	0.61	0.66	0.66	0.60	0.72
6	β-Carotene	0.68	0.73	0.72	0.78	0.69	0.78
7	α-Carotene	0.74	0.88	0.77	0.88	0.78	0.84
Plates treated with 0.1 % tetranitrodiphenyl sulphide							
1	Sorbic acid	0.16	0.07	0.21	0.14	0.09	0.22
2	Vitamin A	0.25	0.17	0.30	0.22	0.12	0.30
3	β-Citraurin	0.49	0.45	0.53	0.50	0.43	0.58
4	Lycopene	0.65	0.50	0.69	0.55	0.59	0.78
5	γ-Carotene	0.73	0.68	0.76	0.73	0.70	0.82
6	β-Carotene	0.78	0.80	0.82	0.85	0.79	0.88
7	α-Carotene	0.84	0.90	0.87	0.95	0.86	0.94

respective plates. The adsorbent coatings in various cases were: Silica Gel G, 5.12 mg/cm^2; Silica Gel G–Kieselguhr G (3:1), 6.88 mg/cm^2; neutral alumina (M. Woelm) containing 20 % $CaSO_4$, 7.2 mg/cm^2. The plates were impregnated with the respective nitro compounds by irrigating them with a 0.1 % solution in acetone using an ascending technique. The plates were dried at room temperature and spotted with 2 μg of each poly-unsaturated compound (dissolved in 5 μl of ethanol) with a standard micro-capillary. At the same time, these compounds were spotted on untreated chromatoplates. Both treated and untreated plates, after spotting, were irrigated at 28 ± 1° with suitable solvents employing an ascending technique. The irrigating solvent for the treated plates also contained 0.1 % of the nitro compound. All the compounds were located by spraying the chromatoplates with 0.5 % potassium permanganate in 50 % sulphuric acid. The compounds could be seen as white spots against a brown background and were marked.

Fig. 1 is a typical chromatoplate showing the resolution of π complexes of conjugated compounds with TNDPS. The R_F values are given in Table I.

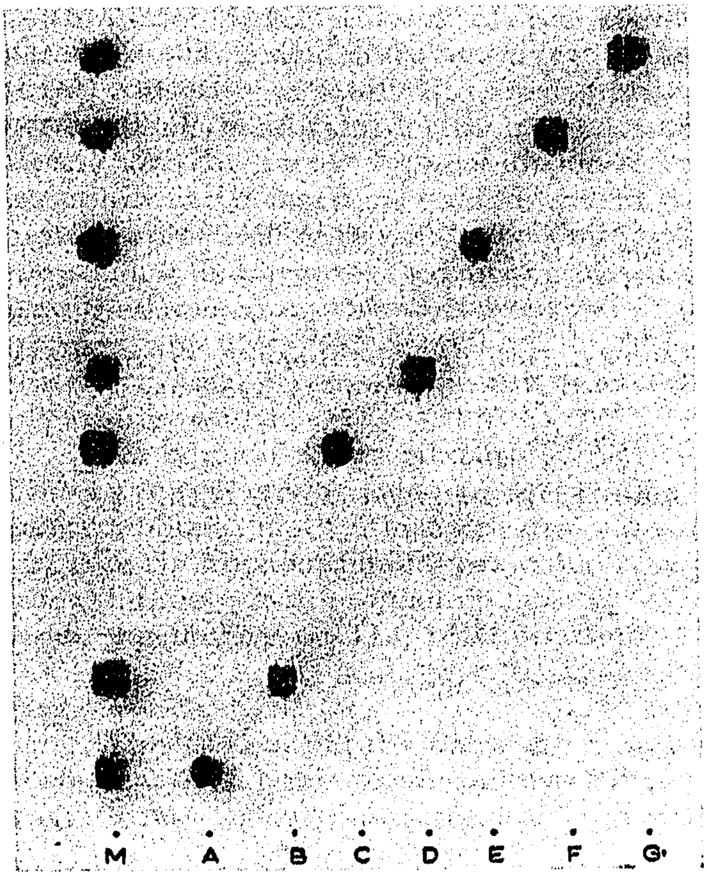


Fig. 1. Separation of conjugated compounds on a thin-layer chromatogram employing Silica Gel G, impregnated with 2,4,2',4'-tetranitrodiphenyl sulphide. M = mixture; A = sorbic acid; B = vitamin A; C = β-citraurin; D = lycopene; E = γ-carotene; F = β-carotene; G = α-carotene. Solvent, petroleum ether–methylene dichloride (9:1) containing 0.1 % of the nitro compound. Technique, ascending.

Discussion and results

It was interesting to observe that conjugated compounds like sorbic acid, vitamin A, α-, β-, and γ-carotene, lycopene and β-citraurin being π donors have better resolutions as complexes with π acceptors such as TNDPS and HNDPS. The spots of the complexes were quite distinct compared to when they were run as the uncomplexed materials. In general the R_F values of the complexes were lower than for the respective unsaturated compounds. The distance by which α- and β-carotenes are separated is far greater when they move as complexes than in the uncomplexed state. In addition to their conjugated nature, the presence of an α-ionone ring in α-carotene could be responsible for the stronger charge transfer and hence better resolution. Substitution of open chain in place of α- and β-ionone groups very much alters the migration of the complexes. The π complexes with γ-carotene have higher migration than those with lycopene. Again the number of conjugated double bonds plays a specific role. The differences in the mobilities of complexes with HNDPS and TNDPS are due to the enhanced π accepting properties of the first compound compared with the latter.

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