TABLE I

Values of relaxation time (τ) and free energy of activation

Polar components	$\tau \times 10^{12}$ sec.	H_τ (K.cal./mole)	Dipolar mixture	$\tau \times 10^{12}$ sec.	H_τ (K.cal./mole)	H_η (K.cal./mole)
Anisaldehyde ..	14·94	2·63	Anisaldehyde + salisaldehyde	11·62	2·48	2·90
Salisaldehyde ..	6·87	2·18	Salisaldehyde + *o*-chlorobenzaldehyde	9·54	2·37	2·90
Chlorobenzaldehyde ..	11·60	2·48	Anisaldehyde + *o*-chlorobenzaldehyde	14·79	2·62	2·90

Kadaba[2] has suggested that when the absorption regions of two polar liquids are quite close to each other, one may expect a single relaxation time for their mixture in non-polar solvents. Keeping this in view, the relaxation times of mixtures of anisaldehyde, salisaldehyde and o-chlorobenzaldehyde have been determined.

Five solutions of increasing concentrations were made by mixing equal volumes of the two components of the dipolar liquids in benzene. The relaxation time and activation energy for these dipolar mixtures and for their components as observed are given in Table I.

The experimental results for mixtures suggest that for every pair of dipolar mixture in benzene, the relaxation time obtained is the average of two individual relaxation times. These results also show that there is no association in the mixture. This conclusion is in conformity with the fact that in dilute solutions, dipole-dipole interaction is considerably reduced.

The authors are thankful to Dr. P. N. Sharma for encouragement and interest in the work.

Physics Department, Lucknow University, Lucknow, *March* 9, 1966.

N. K. MEHROTRA.
M. C. SAXENA.

1. Mehrotra, N. K., Shukla, J. P. and Saxena, M. C. *Curr. Sci.*, 1966, **35**, 120.
2. Kadaba, P. K., *J. Phys. Chem.*, 1958, **62**, 887.

CHEMICAL COMPONENTS OF *VATERIA INDICA* SEEDS

Vateria indica (dipterocarpacea) is a large ever-green tree indigenous to South-Western India, Kanara and Travancore. It is the source of the Indian Copal resin of commerce. The seeds which are enclosed in a thick hard shell contain usually from 22 to 27% of what is called Malabar or Piney Tallow (Dhupa fat). This oil is credited with medicinal properties. It is used as a local application in chronic rheumatism and other painful afflictions.[1]

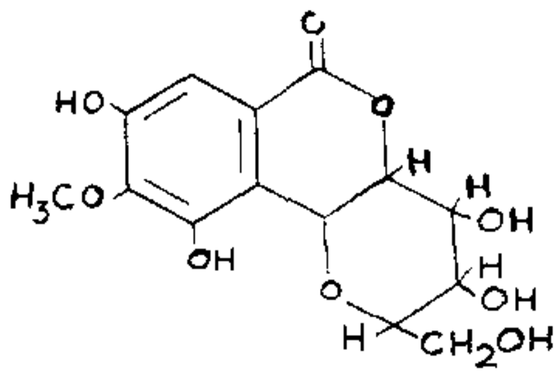
With a view to study the non-fatty components of this oil, a sample of the seeds was obtained from Shimoga, Mysore. The shell was separated from the kernel and the latter (2·5 kg.) coarsely ground and extracted with a succession of solvents in an extractor. (*i*) Light petroleum (b.p. 60–80°) yielded only the fat (250 g., 10%). (*ii*) Subsequent ether extraction at room temperature afforded a small amount (*ca.* 0·5 g.) of a compound which had no definite m.p. but charred and left a residue on ignition. (*iii*) Extraction with acetone at room temperature yielded a deep red extract. On partial concentration a viscous brown-red mass was obtained which deposited a small amount of fat and a colourless crystalline compound. The fat was removed by repeated washing with ether and the crystalline compound collected by decantation and washing with methanol (Yield 7 g.; m.p. 155–156°). Complete removal of acetone from the decanted solution gave a dark brown resinous solid which could not be crystallised. The colourless compound crystallised from water or aqueous ethanol in stout rectangular prisms, m.p. 155–156°. Drying at 120° in vacuum for three hours raised the m.p. to 226–228° (Found on dried material: C, 48·9; H, 5·4 Calc. for $C_{14}H_{16}O_9$, $1H_2O$: C, 48·5; H, 5·2%). The compound did not give Molisch test and dissolved in cold sodium hydroxide solution from which it could be recovered on acidification. It dissolved slowly in aqueous sodium bicarbonate and more easily in sodium carbonate, the colourless solution becoming violet on keeping. An alcoholic solution of the compound gave a light green colour with ferric chloride.

Acetylation with sodium acetate and acetic anhydride (140°, 3 hr.) yielded a pentaacetate which crystallised from methanol as colourless hexagonal plates, m.p. 205–206° (Found: C, 53·7; H, 5·0; COMe, 40·9. Calc. for $C_{14}H_{11}O_9(COMe)_5$: C, 53·5; H, 4·8; COMe, 39·9%).

A solution of the compound in ethanol showed blue fluorescence in UV light; $\lambda_{max.}$ 275 mμ, λ_{inflex} 310 mμ (Methanol medium). The IR spectrum had the following peaks: 2·85, 3·02 μ (hydroxyl); 3·35, 3·62 μ (chelated hydroxyl);

5·84 μ (carbonyl) ; 6·18, 6·52 μ (aromatic). The NMR spectrum of the acetate in deutero chloroform indicated the presence of five acetoxyl groups, two of which were phenolic (at τ 7·66) and the other three alcoholic (at τ 7·9). Signals at τ 6·08 and τ 2·2 were attributed to the 3 protons of the methoxyl group and a lone aromatic proton respectively.

The above properties indicated close resemblance of the colourless compound with bergenin (I).[2-6] Comparison of the acetate with an authentic sample[4] confirmed the identity. Dean *et al.*,[6] found bergenin to be inactive at a concentration of 1 : 1000 *in vitro* against *Entamœba histolytica*. However, an aqueous decoction from three herbal plants, *viz.*, *Didymocarpus pedicellata, Bergenia ciliata* and *Bergenia ligulata* has been claimed to be successful for dissolving stone in kidney and bladder by Ayurvedic experts. The role of bergenin in this as well as in other drugs is yet unknown.



I. Bergenin

(*iv*) Continued extraction with ethanol of the residual seeds yielded an extract which on concentration yielded a very small amount of sucrose. Complete removal of the solvent afforded a brown-red viscous resin. Paper chromatography of the concentrate using *n*-butanol-pyridine-water (6 : 4 : 3) and aniline hydrogen phthalate as spraying reagent indicated the presence of glucose and mannose in it.

Since the commercial oil is obtained by boiling the crushed seeds with water there was a possibility of its containing bergenin. A sample of it was therefore extracted in a liquid-liquid extractor with ethanol. The ethanolic extract was tested for the presence of bergenin and it was found to be absent.

The results indicate that the seeds of *Vateria indica* contain a solid fat, a novel C-glucoside bergenin besides sucrose and traces of other sugars but the oil extracted from it by means of solvents or by the crude village process is free from polyphenols.

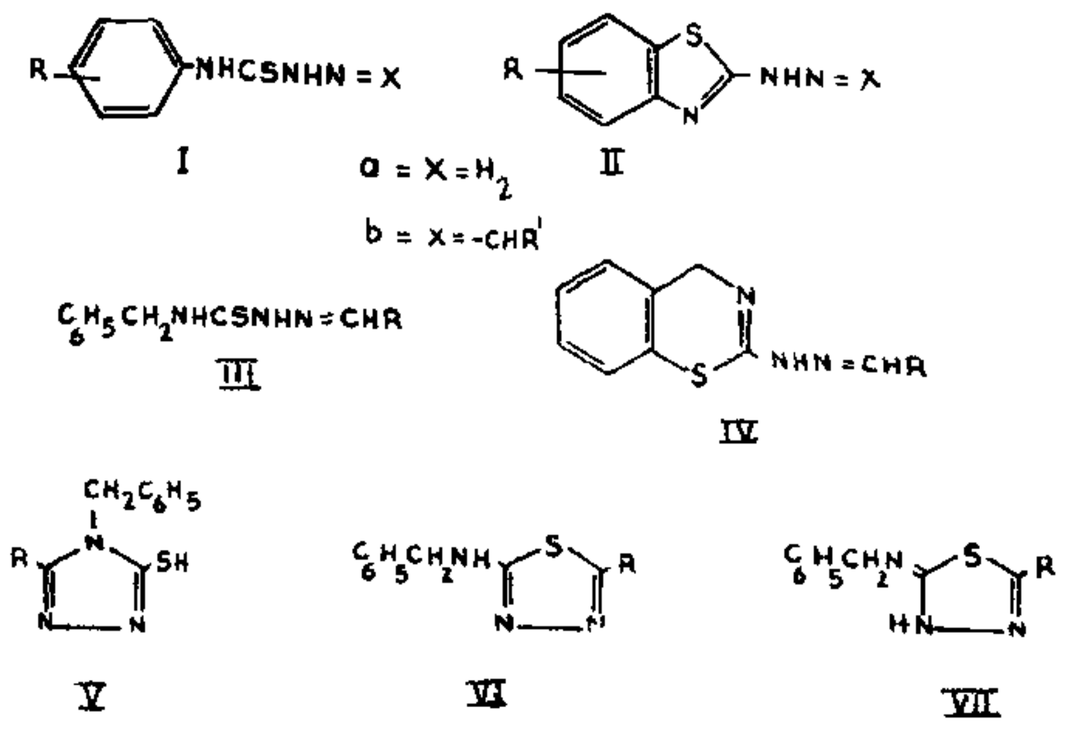
Dept. of Chemistry,
University of Delhi,
Delhi-7, *June* 2, 1966.

S. C. Bhrara.
T. R. Seshadri.

1. Nadkarni, K. M. and Nadkarni, A. K., *Indian Materia Medica*, Vol. **1**, p. 1265.
2. Posternak, T. and Durr, K., *Helv. Chem. Acta*, 1958, **41**, 1159.
3. Hay, J. E. and Haynes, L. J., *J. Chem. Soc.*, 1958, p. 2231.
4. Aiyar, S. N., Jain, M. K., Krishnamurti, M. and Seshadri, T. R., *Phytochemistry*, 1964, **3**, 335.
5. Carruthers, W. R., Hay, J. E. and Haynes, L. J., *Chem. and Ind.*, 1957, p. 76.
6. Dean, B. M. and Walker, J., *Ibid.*, 1958, p. 1696.

OXIDATIVE CYCLISATION OF SOME 4-BENZYLTHIOSEMICARBAZONES

During the course of an extended study[1-4] of the oxidative cyclisation of 4-arylthiosemicarbazides (I *a*) and 4-arylthiosemicarbazones (I b) under different conditions, it was demonstrated[4] that the oxidation of 4-arylthiosemicarbazides and-thiosemicarbazones by bromine in chloroform leads respectively to the formation of 2-hydrazinobenzthiazoles (II *a*) and their benzylidene derivatives (II b). It was thus of interest to investigate whether 4-benzylthiosemicarbazones (III) would undergo such a cyclisation to yield the benzo-1, 3-thiazine system (IV) in addition to the other three conventionally obtainable products, *viz.*, 3-mercapto-*s*-triazoles (V), 2-benzylamino-1, 3, 4-thiadiazoles (VI) and 2-benzylamino-Δ^4-1, 3, 4-thiadiazolines (VII).



I a = X = H_2; b = X = -CHR'; II; III $C_6H_5CH_2NHCSNHN=CHR$; IV; V; VI; VII

It has now been shown that the oxidation of III (R = aryl residues) by bromine in chloroform gave only two sets of products in varying proportions ; alkali-soluble components to which the 3-mercapto-*s*-triazole structure (V) was assigned and the other—alkali-insoluble products—characterised as 2-benzylamino-5-aryl-1, 3, 4-thiadiazoles (VI). The latter structure was also authenticated by the direct obstention of VI through ferric chloride oxidation[1,5] of III (R = aryl residues). The yields of the 3-mercapto-*s*-triazoles (V) varied between 50–80%, while the thiadiazoles were formed in