

CARBONYL COMPOUNDS AS POSSIBLE CAUSE OF ODOUR IN VEGETABLE OILS

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THE presence of odour in vegetable oils has been known for a long time. In order to remove undesirable odour, steam distillation and vacuum heating have been recommended. But comparatively little work has been done on the isolation and characterisation of the chemical components responsible for odour. A search into the literature reveals that the main interest has been on the odour components of butter and of the strongly smelling mustard oil and the related Cruciferae oils. However, some work has been done on the volatile components of palm kernel¹ and coconut oil.^{2,3} The former is reported to contain methyl nonyl ketone; oil from fresh coconut contains mainly δ -lactones having the characteristic coconut odour. The crude coconut oil where some microbiological decomposition had set in, contains also ketones with odd number of carbon atoms.

In the course of our investigation on the non-fatty components of minor oil-seeds and oils, it was noticed that many of them have marked odour and colour. Nahor oil is one such having a dark brown colour and a strong unpleasant odour. It is obtained from the seed kernel of *Mesua ferrea*. When the oil was subjected to steam distillation, the distillate had the characteristic smell and gave 2,4-dinitrophenyl hydrazone (DNPH). Ether extraction of the distillate failed since the extracted components were highly volatile and escaped with ether. A better method was to pass the steam distillate directly into an alc. HCl solution of 2,4-dinitrophenyl hydrazine. The product was a mixture that could be separated into a major ether soluble fraction which contained two components identified as DNPH's of acetaldehyde and *n*-hexaldehyde along with some other component which has not been identified. The ether insoluble fraction after further purification was identified as glyoxal DNPH. Thus nahor seed oil contains as steam volatile components acetaldehyde, *n*-hexaldehyde and glyoxal. Nahor oil obtained from a second sample of *Mesua ferrea* seed kernel yielded only acetaldehyde.

The main experimental details with sample (I) are given below:

(a) Nahor seed oil (50 g.) obtained by extracting the seed kernel with petroleum ether was subjected to steam distillation for about 8 hr. and the steam distillate extracted with ether in a continuous extractor and the ether extract concentrated. No residue was left. The aqueous solution left after ether extraction was treated with excess of alc. HCl solution of 2,4-dinitrophenyl hydrazine and the solution kept overnight. The yellow bulky ppt. of DNPH was filtered, dried, dissolved in benzene and passed through a column of silica gel. The column was washed with benzene, the benzene solution evaporated and DNPH crystallised from alcohol; 160–63°; λ_{max} , 428 m μ in aq. methanolic potash⁴; m.wt (Rast) 205. (Found: C, 42.9; H, 3.8; N, 25.1; C₈H₈N₄O₄ requires C, 42.8; H, 3.5; N, 25.0.) Its identity as acetaldehyde DNPH was confirmed by comparison with an authentic sample prepared from acetaldehyde.

(b) Nahor oil (23 g.) was subjected to steam distillation for about 10 hr. and the steam distillate directly passed into an alc. HCl solution of 2,4-dinitrophenyl hydrazine at ordinary temperature. The solution was kept overnight and the DNPH formed was filtered and dried. On tlc. using silica gel and ethyl acetate-benzene (1 : 19), it was found to be a mixture of six components with three of R_f values 0.86, 0.75 and 0.40 in comparatively larger proportion. It was treated with ether and the ether solution evaporated to dryness. The residue was dissolved in benzene, passed through a column of silica gel and eluted with benzene. Different fractions in 4 c.c. lots were collected. Tlc. examination of the first two fractions indicated them to be rich in the compound having R_f value 0.86. The solvent was removed and the residue obtained was repeatedly crystallised from alcohol, m.p. 98–100°. Its properties agreed with those of *n*-hexaldehyde DNPH and the identity was confirmed by comparison with an authentic sample using R_f value and I.R. spectrum; mixed m.p. was undepressed. The later eluates

yielded acetaldehyde DNPH (R_f 0.75) already described. The ether insoluble portion of DNPH (R_f 0.40) was first washed with a little alcohol to remove excess of reagent. The residue thus obtained crystallised from nitro-benzene as scarlet needles, m.p. over 300°. (Found: C, 40.6; H, 2.7; N, 26.5; C₁₄H₁₀N₈O₈ requires C, 40.0; H, 2.3; N, 26.7.) Its identity as glyoxal DNPH was confirmed by comparison with an authentic sample using chromatography and I.R. spectrum. Glyoxal required for comparison was prepared by the hydrolysis of dichloro dioxane.⁵

Bisulphite extraction was also possible. A sample of the oil was dissolved in ether and extracted with a saturated solution of sodium bisulphite repeatedly. The bisulphite extract was decomposed with hydrochloric acid and treated with alc. HCl solution of 2,4-dinitrophenyl hydrazine. The product could be fractionated in the same way as mentioned above and all the three DNPH's were obtained. The residual ether solution on evaporation yielded the oil free from odour.

In continuation of the above work we had occasion to test a few other minor oils. Pongamia oil has also smell though it is not so unpleasant as that of nahor seed oil. In this case also steam distillation and bisulphite extraction removed the carbonyl compounds and they have been identified as acetone and glyoxal. Essential details are given below:

Pongamia oil was subjected to steam distillation and DNPH was collected as described in the case of nahor oil. It was fractionated

into ether soluble and ether insoluble portions. The former was passed through a column of silica gel and crystallised from alcohol; m.p. 121–23°. Its identity as acetone DNPH was confirmed by comparison with an authentic sample using co-chromatography and m.m.p. The ether insoluble portion of DNPH was washed with a little alcohol and crystallised from nitrobenzene yielding scarlet needles, m.p. over 300°; $\lambda_{m,x}$ 580 m μ in aq. methanolic potash.⁴ (Found C, 40.4; H, 2.8; N, 27.0; C₁₄H₁₀N₈O₈ requires C, 40.0; H, 2.3; N, 26.7.) Its identity as glyoxal DNPH was confirmed by comparison with an authentic sample.⁵

Neem oil is notorious for its markedly unpleasant odour. Steam distillation however removes most of the odour. The DNPH from the oil steam distillate was collected as in the above cases, and fractionated into ether soluble and ether insoluble portions. The former was a mixture of 4 DNPH's which have not been identified; but its spectrum is characteristic of mono-DNPH. The ether insoluble fraction after washing with a little alcohol was repeatedly crystallised from nitrobenzene. It was identical with the DNPH of glyoxal obtained from nahor oil and also synthetically prepared.⁵ In the bisulphite extract of the oil only glyoxal could be obtained.

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URANIUM DISEQUILIBRIUM IN ARABIAN SEA

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SINCE the discovery of high U²³⁴/U²³⁸ activity ratios in natural waters percolating through uranium ore beds by Russian workers,¹ the attention of many scientists²⁻⁵ has been directed towards the disequilibrium studies of uranium in other natural materials. The disequilibrium of uranium in nature is significant since this anomaly may be used as a geochemical tool in the study of rocks, soils and natural waters. The first encouraging results of Thurber,² on Einwetok corals which gave a value of $1.17 \pm$

0.03 for the U²³⁴/U²³⁸ activity ratio, accelerated the work by other workers⁶⁻⁸ in looking for uranium isotopic composition in sea-waters, shells and marine carbonates. Most of the sea-water studies are confined to the Pacific and the Atlantic Oceans and the accepted value for these waters is 1.15 ± 0.02 . Recently Veeh⁹ has determined the U²³⁴/U²³⁸ ratio in Red Sea and reported also the same value. There is no data on Indian Ocean waters, especially on coastal waters. It is the objective