

not been detected previously in urine is doubtless due to the fact that the usual method of working up urine for its steroidal content (acid hydrolysis) must lead to the rearrangement of much or all of the *i*-steroids contained therein.

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¹ Dingemans, E., Huisin 't Veld, L. G., and Hartogh-Katz, S., *Nature*, **161**, 848 (1948).

² Butenandt, A., and Suranyi, L. A., *Ber.*, **75**, 591 (1942).

³ Butenandt, A., and Dannenbaum, H., *Z. physiol. Chem.*, **229**, 192 (1934).

⁴ Rosenheim, O., *Nature*, **147**, 776 (1941).

Deodorization of Shark Liver Oil

SHARK liver oil, which is one of the cheapest and most plentiful sources of vitamin A in Nature, has a highly disagreeable odour which is very much more pronounced than that of cod liver oil. On account of its unpalatability it does not easily find favour with the consumers. The deodorization of the oil has to be effected in such a manner that the highly susceptible vitamin A is retained intact. Among the various methods that we have tried to achieve this result are: (i) steam-'distillation' of the oil under normal and reduced pressure in which the malodorous substances pass over with the steam; (ii) agitation of the oil with fermenting milk and toddy; and (iii) selective hydrogenation of the oil in the presence of a nickel catalyst.

Steam-treated oils are fairly free from odour when freshly prepared, but revert in the course of a few days to their original character. Oils, deodorized by agitation with fermenting milk or toddy, have been found to remain bland for several months. The

Chemical characteristics

| | Milk-deodorized | | Toddy-deodorized | |
|----------------------|-----------------|---------|------------------|---------|
| | Control | Treated | Control | Treated |
| Acid value | 0.2 | 0.3 | 2.0 | 2.2 |
| Saponification value | 188 | 199 | 191 | 191 |
| Iodine value | 128 | 128 | 109 | 108 |

Vitamin A potency in international units per gram

| Species of shark | Milk-deodorized | | Toddy-deodorized | |
|----------------------------|-----------------|---------|------------------|---------|
| | Control | Treated | Control | Treated |
| <i>Stegostoma tigrinum</i> | 1,200 | 1,100 | 3,800 | 3,800 |
| <i>Pristis cuspidatus</i> | 5,900 | 5,900 | | |
| Hammerhead | 37,000 | 36,900 | | |
| Bulk sample | 11,200 | 11,100 | 9,600 | 9,600 |

Stability of the oil

| Time, days | Peroxide value | | | |
|------------|-----------------|---------|------------------|---------|
| | Milk-deodorized | | Toddy-deodorized | |
| | Control | Treated | Control | Treated |
| 0 | 9.4 | 9.8 | 6.0 | 4.5 |
| 1 | 17.8 | 15.9 | | |
| 2 | | | 21.4 | 23.6 |
| 3 | 47.8 | 46.4 | | |
| 4 | 57.5 | 60.4 | 60.8 | 62.4 |
| 6 | 94.5 | 96.8 | 103.9 | 110.1 |
| 8 | 198.0 | 210.4 | | |

accompanying data with regard to the chemical constants, potency and stability of oils deodorized with fermenting milk and toddy as compared with those of the original oil show that very little change in these vital characteristics is involved in the process.

Brocklesby¹ has indicated that hydrogenation of fish liver oils under carefully controlled conditions would eliminate the malodorous factors while the vitamin A itself may be kept unimpaired. Working with 0.1, 0.25, and 0.4 per cent concentrations of nickel catalysts prepared by the method of Adkins, Covert and Connor², we have obtained results which are quite promising. While 0.1 per cent of catalyst is not sufficient to effect complete deodorization (organoleptic test) within a temperature range of 100–180° C., 0.25 per cent of the catalyst effected fairly complete deodorization of the oil at 120° C. within 30–45 min. The percentage loss of vitamin A by this process is about 7, and stability studies have shown that the keeping quality of the oil has improved very considerably. 0.4 per cent of the catalyst caused increased destruction of the vitamin.

The accompanying table, giving results obtained with 0.25 per cent nickel catalyst at temperatures between 100° and 180° C. and reaction periods from 30 to 180 min., shows that the loss of vitamin increases progressively with increase in temperature and time of exposure.

| | Time (min.) | Temperature (°C.) | | | | |
|------------|-------------|-------------------|--------|--------|-------|------|
| | | 100 | 120 | 140 | 160 | 180 |
| Vitamin A* | 30 | 97.1†f | 84.0ff | 93.0ff | 89.0b | 87.0 |
| Vitamin A | 60 | 92.9f | 90.0b | 85.5 | 74.8 | 71.2 |
| Vitamin A | 90 | 91.4ff | 86.9b | 76.4 | 68.0 | 56.9 |
| Vitamin A | 120 | 88.0b | 80.2 | 70.7 | 56.7 | 43.0 |
| Vitamin A | 150 | 84.5b | 74.3 | 64.3 | 48.0 | 31.3 |
| Vitamin A | 180 | 82.0b | | 57.0 | 42.1 | 20.2 |

* Percentage of original content.

†f = fishy; ff = faintly fishy; b = bland.

Further studies are in progress, and full details will be published as soon as they are completed. We are grateful to the University of Travancore for research scholarships awarded to two of us (P. K. M. and H. S.).

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¹ Brocklesby, H. N. "The Chemistry and Technology of Marine Animal Oils", Ministry of Fisheries, Canada, Bull. No. 59.

² Covert, Connor and Adkins, *J. Amer. Chem. Soc.*, **54**, 1651 (1932).

Activities of Associating Solutes

THERE are comparatively few cases of binary mixtures in which the activity or fugacity of one component has been interpreted in terms of molecular properties. Well-known instances of such treatments are the Debye-Hückel theory of electrolytes and Hildebrand's theory of regular solutions. We have examined the case of a binary mixture where interaction between the two components is negligible, but where one of the components (the solute) has a tendency to form multiplets of any degree of complexity by means of association. Since interaction is