Properties of the solid fluoro acid

This appeared to be not more than 5% of the toxic oil obtained after purification by precipitation as the calcium salt. The acid had m.p. 72.0–73.7° (corr.) with softening at 70.5°.

It has no double bond and the carboxyl-group titration gave a value for the equivalent weight of 286. The fluorine content was 6.8%. This could represent an acid with 17 carbon atoms but the acid inhibits aconitase in the guinea-pig-kidney-particle test (Table 2) and is toxic to rats; this indicates that it acts as an acid with an even number of carbon atoms (Peters, 1955) and is virtually as active as fluoro-oleic acid.

The infrared spectrum in carbon tetrachloride was similar to that of fluoro-oleic acid, except that the band at 1460 cm^{-1} was much more pronounced. The absence of the band at 970 cm^{-1} indicates that it is not a *trans*-isomer. The ultraviolet spectrum resembled that of oleic acid. The small peak at 270–275 $\text{m}\mu$ was absent.

DISCUSSION

The first experiments on the toxic fluoro oil from *D. toxicarium* (Peters, Wakelin, Birks, Martin & Webb, 1959) indicated that it was a long-chain fatty acid. The constitution of the main component is now proved, so far as this can be done without synthesis. That of the solid fluoro acid is not yet clear; its fluorine content, carboxyl-group titration and absence of $\text{CH}=\text{CH}$ suggest a saturated acid with possibly 17 carbon atoms. The biochemical

tests indicate that it behaves to the enzymes concerned as an acid with an even number of carbon atoms. This suggests either a branched-chain ω -fluoro acid with an even number of carbon atoms in the fluorine-containing chain or an ω -fluoro hydroxy acid with 16 carbon atoms. Hansen, Shorland & Cooke (1953, 1954) have shown that some branched-chain fatty acids found in mutton fat all have low optical rotations. With the small amount of the solid fluoro acid available, the optical rotation in propan-1-ol was not measurable, from which we concluded that the compound was optically inactive or had $[\alpha_D] < 2.0$. This observation did not confirm the presence of a branched-chain structure or a hydroxyl group but the subject is being investigated.

The fluorine content of the soil in which plants that contain organic fluorine compounds grow raises some points requiring investigation. *Dichapetalum cymosum*, the leaves of which contain fluoroacetate, is stated to grow in a soil rich in fluorine (Saunders, 1957*b*). On the other hand, in a personal communication, Dr Dagmar Wilson said that she saw no evidence of fluorosis in Sierra Leone, where *Dichapetalum toxicarium* grows, from which she concluded that the soil content in this part was low in fluorine. If this is so, *Dichapetalum toxicarium* must concentrate fluorine compounds.

We now know the main compound responsible for the condition of 'broke back' (Peters, 1955) in Sierra Leone and also for the circumstance that causes the seeds of *Dichapetalum toxicarium* to be called 'ratsbane'.

APPENDIX

Notes on the Nuclear-Magnetic-Resonance Spectrum of ω -Fluorodecanoic Acid and of a Fluoro-Octadecenoic Acid of Unknown Structure

By N. SHEPPARD

The hydrogen (proton-) resonance spectra of the two compounds were obtained in chloroform solution with a Varian V-4300B spectrometer at 40 Mc/sec. Fig. 3 shows those parts of the spectra where resonances are expected to occur for CH bonds adjacent to the electronegative fluorine atom, as in $\text{CH}_2\text{F}\cdot$ or $\text{CHF}\cdot$. The remainder of the spectra were typical of long-chain carboxylic acids.

This part of the spectrum of ω -fluorodecanoic acid is essentially as expected for a $[\text{F}]-\text{CH}_2-[\text{CH}_2]$ group. It consists of a widely spaced pair of bands (separation 48 cyc./sec., centre of gravity σ 0.95) each with triplet contours (fine structure spacing ~ 6 cyc./sec.), one being sharp and the other blurred. The separation of 48 cyc./sec. is of the size expected for spin-spin splitting of the methylene

resonance by the magnetic F nucleus (spin 1/2); the smaller triplet spacing is of the magnitude and type to be anticipated for spin-spin interaction with the second CH_2 group along the chain. The only unusual and unexplained feature of the spectrum is the blurred nature of the triplet at higher field.

The spectrum of the unknown fluoro-octadecenoic acid shows two bands (a triplet at ν 14 cyc./sec. with spacing 6.1 cyc./sec. and a blurred triplet at 61 cyc./sec.) of the same position and appearance as those shown in the first spectrum, with an additional stronger triplet centred at $\nu + 1$ cyc./sec. and with a spacing of 3.6 cyc./sec. The first two bands clearly show the presence of the $\text{F}\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ group in the molecule. The third

Fig. 3. Nuclear-magnetic-resonance spectra of (A) ω -fluorodecanoic acid and (B) the unknown fluoro-octadecenoic acid. The spectra are given in frequency units (ν , cyc./sec.) and in chemical-shift units [σ , p.p.m. relative to a water zero defined relative to *cyclohexane* ($\sigma + 3.9$) as an internal standard]. To convert into alternative units (τ , relative to silicon tetramethyl as an internal standard), 4.66 should be added to each value.

additional one is undoubtedly caused by the two ethylenic CH bonds ($\text{HC}=\text{CH}$). In this case the triplet structure is caused by spin-spin interaction with adjacent CH_2 groups.

If the fluorine atom on the acid of unknown structure had not been attached to the end of the chain, the groups giving rise to the resonance under discussion would probably have been of the type

There are three experimental criteria for considering this formulation to be extremely unlikely. First, the band centred at ν 14 cyc./sec. would then have had a pentuplet rather than a triplet contour; secondly the combined intensity of the bands at ν 14 and 61 cyc./sec. is, by comparison with the hydrogen resonance of the CO_2H group (not illustrated) at $\sigma - 4.7$, too great to correspond to only one CH bond contributing to the resonance, and thirdly a resonance caused by a terminal CH_3 group should then have been observable at $\sigma \sim 4.3$, next to the very strong band of chain methylene groups at σ 4.1 (not illustrated), whereas there is no band at this position in the spectrum.

SUMMARY

1. Fluoro-oleic acid from the seeds of *Dichapetalum toxicarium* (Sierra Leone) has been isolated pure in gram quantities.

2. The terminal position of the fluorine has been proved by nuclear magnetic resonance. The *cis*-structure was confirmed by infrared spectrophotometry and the position of the double bond by the identification of ω -fluorononanoic acid and of azelaic acid by gas chromatography after ozonization. The identification of ω -fluorononanoic acid confirmed the position of the fluorine.

3. In the final purification another fluoro-fatty acid of much higher melting point has been separated in small amounts. It contains no double bond, and possibly 17 carbon atoms, but behaves biochemically as a long-chain fatty acid with an even number of carbon atoms.

4. Observations have been made of the ultra-violet spectra and of the toxicity to rats and to guinea-pig-kidney particles of both acids.

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