hours at 50°. Addition of 50 ml. of methanol did not precipitate polymer; only a trace of flocculent white solid separated. On standing overnight in an open heater, the solvent evaporated off, leaving a clear yellow sticky wax, evidently very low molecular weight polymer or air oxidation product of monomer.

All other reactions were quenched by chilling the tubes before opening and pouring the contents into a 2% sol. of PBNA in absolute ethanol. Where solid polymers were obtained, they precipitated as gummy particles which on stirring balled up into one mass. After drying at room temperature *in vacuo* the solids were hard, brittle white resins. They were found to be completely insoluble and generally unswollen in all common organic solvents.

Where oils were obtained, unreacted monomer could be recovered as its maleic anhydride adduct from an ether extract of the coagulating solution. The presence of monomer rather than dimer, even after heating at 50° for 50 hours (see Table I), indicates further the decreased activity of this diene. 1,2-Dimethylenecyclopentane, in comparison, dimerizes very readily above 90° or on contact with silica gel to form a self Diels–Alder adduct.[3]

The homopolymers obtained as oils were not further investigated.

Anal. of polymer (solid). Calcd. for $(C_8H_{12})_x$: C, 88.82; H, 11.18. Found: C, 89.09; H, 10.98.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES]

Preparation and Properties of Some Hexadecyl Hydrogen Esters of Dibasic Acids

BY W. FREDERICK HUBER AND E. S. LUTTON

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Hexadecyl hydrogen esters of the dibasic acids succinic, glutaric, pimelic, maleic and itaconic were prepared and their crystallization behavior studied by means of X-ray diffraction. The compounds melt in the range of 59–77° and show only one crystal form whether from solvent or melt. Each appears to crystallize in double chain-length structure; each shows rather individualistic diffraction behavior except the similar homologous pair, the glutarate and the pimelate.

Introduction

Little is known of the preparation and properties of the longer monoalkyl hydrogen esters of dibasic acids. The preparation of hexadecyl hydrogen succinate by the reaction of succinic anhydride with hexadecanol has been reported.[1] Herein are reported the preparation and X-ray diffraction patterns of the hexadecyl hydrogen esters of succinic, glutaric, pimelic, maleic and itaconic acid.

Experimental

M.p.'s and analyses of the products appear in Table I.

TABLE I

M.P.'S AND ANALYSES OF HEXADECYL HYDROGEN ESTERS

n-Hexadecyl hydrogen ester	M.p., °C.	Analyses, % Neut. equiv. Calcd.	Analyses, % Neut. equiv. Found	Analyses, % Sapn. equiv. Calcd.	Analyses, % Sapn. equiv. Found
Succinate	63.5–64.5	342.5	340.0	171.3	172.2
Maleate	70–71.5	340.5	338.8	170.3	172.1
Itaconate	76–76.5	354.5	356.0	177.3	175.8
Glutarate	68.5–69.5	356.5	356.7	178.3	177.7
Pimelate	58–59	384.6	382.5	192.3	191.4

The succinate, maleate and itaconate were prepared by heating molar equivalents of the requisite acid anhydride with hexadecyl alcohol at 130–140° for 10 minutes. Hexadecyl hydrogen glutarate and pimelate were obtained by refluxing hexadecanol with excess dibasic acid for about 10 hr. in benzene with *p*-toluenesulfonic acid as a catalyst. The products were purified by recrystallization from hexane. In the case of the pimelate it was necessary to wash the hexane solution with warm water to remove pimelic acid. The structure of the products is unequivocal with the exception of hexadecyl hydrogen itaconate. In this case, esterification can open the anhydride to form either hexadecyl hydrogen α-methylenesuccinate or hexadecyl β-methylenesuccinate. The chemical structure of the itaconate was not explored.

Thermal and X-Ray Diffraction Technique.—Rapid complete m.p.'s and regular complete m.p.'s[2] were determined, the latter on both melted-chilled and solvent-crystallized samples. The single melting-level has been reported under sample preparation. "Rod pellets" of both solvent-crystallized and melted-chilled samples were X-rayed and found to have substantially identical patterns. Flat-film patterns were obtained with a General Electric XRD-1 unit employing nickel-filtered CuKα radiation and a 0.025-in. pinhole system. Sample-to-film distance was normally 10 cm.

X-Ray diffraction data are listed in the following order: compound; long spacing, L.S. (in Å.); short spacings, S.S. (in Å.). Relative intensities of diffraction lines are indicated by (V.S.) = very strong, (S) = strong, (M) = medium, (W) = weak.

Hexadecyl H succinate: L.S. 42.8; S.S. 4.54(S+), 3.98(S), 3.77(W), 3.63(S+)
Hexadecyl H glutarate: L.S. 45.2; S.S. 4.63(W), 4.4(W), 4.11(V.S.), 3.76(S)
Hexadecyl H pimelate: L.S 50.8; S.S. 4.60(W), 4.14(V.S.), 3.79 (S)
Hexadecyl H maleate: L.S. 29.4; S.S. 5.28(W), 4.64(S), 3.78(V.S.)
Hexadecyl H itaconate: L.S. 40.7; S.S. 4.68(M), 4.44(W), 4.16(V.S.), 3.74(S)

Discussion

While the dibasic acids from which these hexadecyl monoesters were made show a range of m.p.'s covering 90°, the esters show a spread of only 18° with little correlation between relative melting level in the acid and ester series. Each ester shows the same single solid phase whether from solvent or from melt. The several compounds are quite individualistic in X-ray diffraction behavior except for the glutarate and pimelate which are adjacent odd homologs; they show a beta prime-type of pattern rather similar to those exhibited by palmitic and stearic acids. It is a little surprising that the higher homolog melts 10° lower, especially when the acid m.p.'s are in the reverse order.

The chain lengths of these hexadecyl esters should be of the order 28–30 Å. The long spacings which mostly run from 40–50 Å. bespeak tilted double-chain length structures. The maleate long

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(1) J. T. Davies and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A194**, 417 (1948).

(2) E. S. Lutton, F. L. Jackson and O. T. Quimby, THIS JOURNAL, **70**, 2441 (1948).

spacing is remarkably short at 29 Å. and may signify a single-chain-length structure, but the fact that the intensities of various orders of long spacing follow a sequence similar to those of the succinate suggests a double-chain-length structure.

CINCINNATI 31, OHIO

COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF RUSCOGENIN[1]

Sir:

Ruscogenin, isolated by Lapin and Sannié[2] in 1955 from *Ruscus aculeatus L.*, was identified as 19-hydroxydiosgenin.[3] However, we wish to report recent evidence which invalidates the structure proposed by the French workers. For purpose of clarity we shall assume that this new sapogenin is x-hydroxydiosgenin and later in this communication arrive at the most probable structure.

Recrystallized ruscogenin[4] diacetate (m.p. 191–194°, $[\alpha]^{25}\text{D}$ $-80.5°$, 1.03% in $CHCl_3$; diol,[5] m.p. 205–211°, $[\alpha]^{25}\text{D}$ $-118°$, 1% in $CHCl_3$) was degraded[6] by methods well established in the sapogenin field[3,7] to the oily diacetate of 5,16-pregnadiene-x,3-diol-20-one I in 70% yield. Beckmann rearrangement[8] of the oxime (m.p. 188–197° dec.; C, 69.82; H, 8.02), followed by mild acid treatment yielded x-acetoxydehydroepiandrosterone acetate II (m.p. 97–99°) and 147–149°; C, 71.44; H, 8.31), which on vigorous alkaline hydrolysis afforded x-hydroxydehydroepiandrosterone III (m.p. 195–197°; C, 74.71; H, 8.99). Diol III was stable to acid and reverted to II on acetylation. Controlled acid-catalyzed methanolysis of the diacetate II led, after chromatography, to x-acetoxydehydroepiandrosterone IV (m.p. 136.5–138°; C, 72.91; H, 8.97) in about 65% yield.

When the diol III was treated with aluminum isopropoxide and cyclohexanone in refluxing toluene, 1,4-androstadiene-3,17-dione[9] (m.p. 139.5–140.5°; $\lambda_{\max}^{\text{MeOH}}$ 243 mμ, ε 16,000) was obtained in approximately 30% yield, as shown by comparison (infrared and mixed m.p.), with an authentic sample prepared according to Djerassi and Scholz.[9b] The monoacetate IV was carefully oxidized with chromic acid in acetone[10] to an oily ketone V, which on treatment with potassium acetate in refluxing ethanol or aqueous potassium hydroxide in methanol at room temperature, again afforded 1,4-androstadiene-3,17-dione (m.p. 139–140.5°) in approximately 40% and 50% yield respectively. These results could best be rationalized by assuming the additional hydroxyl to be situated on carbon 1 of the steroid nucleus.

In order to obtain additional information as to the position and configuration of the functional groups, the diol III was reduced with sodium borohydride in methanol to 5-androstene-1,3β,17β-diol VIa (m.p. 275–280° dec.; C, 74.24; H, 9.97; triacetate VIb, m.p. 145–147°; C, 69.24; H, 8.57), which on catalytic hydrogenation in presence of Adams catalyst in ethanol containing a trace of hydrochloric acid, afforded in 93% yield androstane-1,3β,17β-triol VII (m.p. 217–219°; C, 74.01; H, 10.47). Triol VII was found to be different (infrared and mixed m.p.) from authentic androstane-1α,3β,17β-triol (m.p. 236–238°; C, 73.71; H, 10.54), obtained from 1-androstene-3,17-dione by α-epoxidation with alkaline hydrogen peroxide, followed by stepwise reduction with sodium borohydride and lithium aluminum hydride.[11]

Conclusive proof of structure was finally obtained when the triol VIa and its triacetate VIb were compared with authentic samples[12] of 5-androstene-1β,3β,17β-triol, m.p. 270–278° dec. and its triacetate m.p. 147.5–148.5°. They were respectively found to be identical in all respects (infrared and mixed m.p.).

The positions of the two hydroxyl groups and of the double bond in ruscogenin are thus firmly established. In light of our results and the conversion of ruscogenin to diosgenin by Lapin and Sannié,[2] we conclude that this new sapogenin is very likely 1β-hydroxydiosgenin.

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[1] After this work was completed a recent communication—D. Burn, B. Ellis and V. Petrow, *Proc. Chem. Soc.*, 119 (1957)—dealing with this subject, came to our attention.

[2] H. Lapin and C. Sannié, *Bull. Soc. Chim.*, 1552 (1955).

[3] C. Sannié and H. Lapin, *ibid.*, 1556 (1955).

[4] We wish to thank Mr. J. Monnet of Société des Usines Chimiques Rhône-Poulenc, for a generous supply of a mixture—as shown by paper chromatography and infrared analysis—of ruscogenin and its ring-F isomer.

[5] This sample of ruscogenin, derived from the diacetate, belonged to the "iso" series as shown by its infrared absorption spectrum.

[6] We are indebted to Dr. G. P. Mueller of this laboratory for his advice and help in this degradation.

[7] G. P. Mueller, R. E. Stobaugh and R. S. Winniford, THIS JOURNAL, **75**, 4888 (1953); M. E. Wall, H. E. Kenney and E. S. Rothman, *ibid.*, **77**, 5665 (1955); A. F. B. Cameron, R. M. Evans, J. C. Hamlet, J. S. Hunt, P. G. Jones and A. G. Long, *J. Chem. Soc.*, 2807 (1955).

[8] G. Rosenkranz, O. Mancera, F. Sondheimer and C. Djerassi, *J. Org. Chem.*, **21**, 520 (1956).

[9] (a) H. H. Inhoffen, G. Zühlsdorff and Huang-Minlon, *Ber.*, **73B**, 451 (1940); (b) C. Djerassi and C. R. Scholz, *J. Org. Chem.*, **13**, 697 (1948).

[10] C. Djerassi, R. R. Engle and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

[11] *Cf.* the extensive work of Tamm and co-workers—F. Salmann and C. Tamm, *Helv. Chim. Acta*, **39**, 1340 (1956), and earlier references on analogous systems, where it was shown that a similar sequence of reactions always led to the 1α,3β-diol as the major product.

[12] R. M. Dodson, A. H. Goldkamp, R. D. Muir, THIS JOURNAL, **79**, 3920 (1957).