than mannosamine) but more likely due to the known differences in the acyl groups.

While D-mannosamine has been synthesized previously, this apparently is the first report of its natural occurrence. Nevertheless, the compound may be widespread in nature; most of the techniques employed for characterization of D-glucosamine would not distinguish it from D-mannosamine.[14]

[14] We are deeply grateful to Drs. Edwin A. Popenoe and Ruth Drew who informed us that extracts of *Cl. perfringens* exhibited the desired enzymatic activity with NANA and who supplied us with a culture of the organism. Dr. G. Blix kindly supplied the sialic acid samples from bovine, pig and sheep submaxillary mucins; the methoxyneuraminic acid was a gift of Dr. E. Klenk.

[15] Postdoctoral fellow, American Cancer Society.

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RECEIVED NOVEMBER 29, 1957

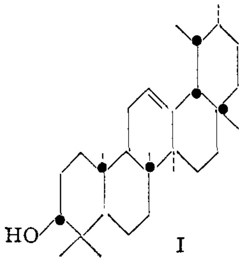
PROOF OF THE STRUCTURE AND STEREOCHEMISTRY OF α-AMYRIN BY SYNTHESIS FROM A β-AMYRIN DERIVATIVE, GLYCYRRHETIC ACID

Sir:

The gross structure of α-amyrin which had been determined by Ruzicka, Jeger and co-workers[1] (I without stereochemical connotations) was elaborated to the complete stereochemical description I in 1954 on the basis of extensive chemical and physical data.[2] Subsequently a number of other formulations were advanced.[3–5]

We now report the unambiguous confirmation of expression I by synthesis of α-amyrin from glycyrrhetic acid,[6] a known derivative of β-amyrin having structure II.

Hydrogenation of methyl glycyrrhetate, m.p. 242.5–249.5°, [α]D +153, afforded the 11-desoxy derivative, m.p. 233–245°, [α]D +115°, which was saponified and acetylated to 11-desoxyacetylglycyrrhetic acid, m.p. 305–307°, [α]D +117°. This was converted to the isocyanate (III, R_1 = OAc, R_2 = N=C=O), strong infrared max. 2265 cm.$^{-1}$, via the acid chloride and the azide.[7] Reduction of the isocyanate ($LiAlH_4$) yielded the amine III, R_1 = OH, R_2 = $NHCH_3$, m.p. 216–229.5°, [α]D +99°; found: C, 81.29; H, 11.90; N, 3.40, which was methylated to the quaternary iodide III, R_1 = OH, R_2 = $^{\oplus}N(CH_3)_3$. The olefin IV, R_1 = OH, R_2 = CH_2, m.p. 166–169°, [α]D +157°; found: C, 84.28; H, 11.21; infrared max. 890 cm.$^{-1}$ (strong), 1652 cm.$^{-1}$, 3620 cm.$^{-1}$, formed from the quaternary salt with potassium *t*-butoxide, was acetylated (acetate, m.p. 196.5–197.5°, [α]D + 164°; found: C, 82.42; H, 10.80), and degraded to the ketone IV, R_1 = OAc, R_2 = O, by hydroxylation of the terminal double bond with osmium tetroxide and cleavage with periodic acid (found for IV, R_1 = OAc, R_2 = O: m.p. 242.5–244°, [α]D +85.5°; C, 79.22; H, 10.22, infrared max., 1724, 1740 cm.$^{-1}$ (both strong)). The acetoxy ketone was saponified and benzoylated to give IV, R_1 = OBz, R_2 = O, m.p. 229.5–231.5°, [α]D +100°, found: C, 81.48; H, 9.70, which was monomethylated using trityl sodium and methyl iodide to V, R = O, m.p. 248–250.5°, [α]D +115°; found: C, 81.56; H, 9.65.[8] The attachment of the added methyl to C_{19} and not C_{21}, anticipated from analogy to the coprostanone series, was established by rotatory dispersion measurements.[9] Reaction of V, R = O, with methylene-triphenylphosphine[10,11] led to the terminal olefin V, R = CH_2, m.p. 224–226°, infrared max. 1718, 1644, 888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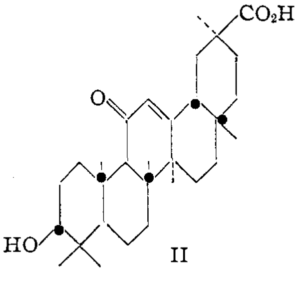
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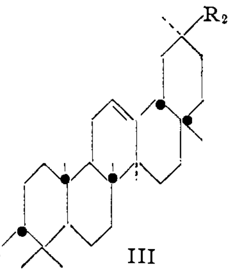
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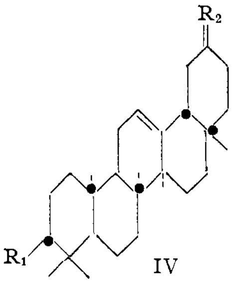
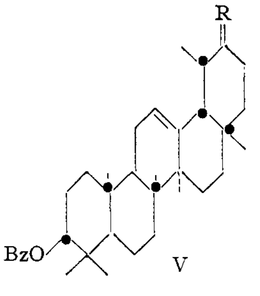

IV


V

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[1] A. Meisels, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1075 (1949); see also O. Jeger, *Fortschritte der Chemie Organische Naturstoffe*, **7**, 1 (1950).

[2] E. J. Corey and J. J. Ursprung, *Chem. and Ind.*, 1387 (1954), THIS JOURNAL, **78**, 183 (1956). Previously the configurations at C_9, C_{14}, C_{17}, C_{18}, C_{19} and C_{20} were unknown, although the configuration at C_{17} opposite to that in I had been considered as proved on the basis of lengthy degradative sequences [O. Jeger, *Angew. Chem.*, 196 (1951); see also *Ann. Rep.*, **48**, 198 (1951)].

[3] J. L. Beton and T. G. Halsall, *Chem. and Ind.*, 1560 (1954).

[4] F. S. Spring and co-workers, *ibid.*, 281 (1955); *J. Chem. Soc.*, 2606, 2610, 3072, 3371, 3378, 3992 (1955); *ibid.*, 456, 465 (1956). These papers also describe correlation of α- and β-amyrin at C_{14} and C_{17}. See also D. D. Phillips and D. E. Tuites, THIS JOURNAL, **78**, 5438 (1956).

[5] G. D. Meakins, *Chem. and Ind.*, 1353 (1955).

[6] L. Ruzicka and co-workers, *Helv. Chim. Acta*, **19**, 1402 (1936); **20**, 312, 1271 (1937); **22**, 195 (1939); J. M. Beaton and F. S. Spring, *J. Chem. Soc.*, 3126 (1955).

[7] See H. H. Zeiss and W. B. Martin, THIS JOURNAL, **75**, 5935 (1953).

[8] This technique is recommended for the monomethylation of ketones in high yield. The excess trityl sodium rapidly and completely converts ketone to mono-enolate and is rapidly destroyed by the excess methyl iodide.

[9] *Viz.* by comparison of IV, R_1 = OBz, R_2 = O and V, R = O with coprostanone and 2- and 4-methylcoprostanones, kindly made by Dr. Carl Djerassi.

[10] G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

[11] F. Sondheimer and R. Mechoulam, Abstracts, A.C.S. Meeting, April 1957, p. 35-O.

cm.$^{-1}$, which was reduced by lithium in ethylenediamine[12,13] and acetylated to give α-amyrin acetate, m.p. 223.5–225°, undepressed upon admixture with an authentic sample.[14] The X-ray powder diffraction patterns, infrared spectra and optical rotatory dispersion curves of synthetic I acetate and α-amyrin acetate were found to be identical.

The establishment of stereoformula I for α-amyrin renders the proposed[2,15] biosynthetic path from the lupanyl cation all the more attractive.

It is a pleasure to thank Dr. C. K. Swift, MacAndrews–Forbes Co., for a supply of ammonium glycyrrhizinate and the National Science Foundation, Alfred P. Sloan Foundation, Procter and Gamble Co. and Ethyl Corp. for fellowships.

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(12) R. A. Benkeser, G. Schroll and D. M. Sauve, THIS JOURNAL, **77**, 3378 (1955).

(13) L. Reggel, R. A. Friedel and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).

(14) The equatorial (α) orientation of the 20-methyl group produced by this reduction follows from data on reduction of model compounds of known configuration (3-methylene cholestane → 3β-methylcholestane stereospecifically). See also D. H. R. Barton, A. Campos-Neves and R. C. Cookson, *J. Chem. Soc.*, 3500 (1956), and *cf.* reduction of cyclohexanones by metals.

(15) A. Eschenmoser, L. Ruzicka, O. Jeger and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955); A. Melera, D. Arigoni, A. Eschenmoser, O. Jeger and L. Ruzicka, *ibid.*, **39**, 441 (1956). The latter publication describes an elegant proof of configuration at C$_{18}$ in α-amyrin.

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REVERSIBLE CONTRACTILE PROCESSES IN FIBROUS MACROMOLECULES

Sir:

It is known that the crystallization of an oriented polymer fiber is accompanied by an increase in length, while contraction will occur on melting such a system.[1-3] In previous reports[2,3] the orientation has always been imposed by the application of a tensile stress, and the dimensional changes that occur during the melting–crystallization cycle can be considered reversible only if an equilibrium stress is maintained. We wish to report that by appropriately cross-linking a fibrous polymer a material is obtained which has the property of not only contracting on melting and spontaneously elongating on crystallization but does so in a cyclic manner *without* the application of any external force.

A highly oriented sample of fibrous poly-(ethylene)[4] was cross-linked by the action of γ-ray irradiation from a Co^{60} source. The wide angle X-ray pattern of the fiber prior to cross-linking indicates almost perfect alignment of the polymer chains along the fiber axis, and the pattern is not significantly altered by the introduction of cross-links. The high state of orientation is further evidenced by the fact that about a forty-fold irreversible shrinkage[5,6] occurs on melting the non-cross-linked material. After being cross-linked, the fibers were melted and then allowed to recrystallize at room temperature. Three distinct states of the cross-linked fiber can then be distinguished: the initial state, the liquid state, and the final state achieved by recrystallization from the liquid state. Each of these states is further characterized by the fact that no external force is applied. The change which occurs in going from the initial state to the liquid state represents an irreversible process[5,6] since the original cross-linked fibers can no longer be regenerated merely by cooling. In accord with theoretical considerations[7] and previous experimental results[6,8] the lengths of the recrystallized fibers increase as the cross-linking density is increased. For the range of cross-linking encompassed by these experiments a twenty-five fold increase in length is observed in this state.

An X-ray diffraction analysis of the recrystallized materials at room temperature indicates that the crystallites are randomly arranged in the specimen into which no cross-links have been introduced. However, as the cross-linking density is increased, the concomitant increase in length that occurs manifests itself in the fact that an axial orientation of the crystallites begins to develop. Thus a specimen which has received a radiation dose of 650 megareps. possesses a rather marked axial orientation. Hence by sufficiently cross-linking a highly oriented fiber a large proportion of the order of the system is maintained even after melting and subsequent recrystallization.[6,7] It should be emphasized that the orientation is present without the imposition of any external force and is a sole consequence of a sufficient number of cross-linkages being appropriately introduced.

It is then found that the fibers which display crystallite orientation contract on melting and when slightly under-cooled spontaneously elongate back to their equilibrium length. This process can be repeated indefinitely without any external force being applied, and, depending on the cross-linking density, dimensional changes of from 5 to 30% have been observed. This contractile process is reversible and sharp, and is a consequence of the basic principle that an oriented macromolecular system will contract on melting and reelongate on cooling. As Flory already has pointed out,[1] fibers such as have been described here can serve as the working substance of an engine which converts thermal energy into mechanical energy.

A more thorough discussion and analysis of these and related observations will appear in a forthcoming paper.[9]

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(1) P. J. Flory, *Science*, **124**, 53 (1956).

(2) W. H. Smith and C. P. Saylor, *J. Research Natl. Bur. Standards*, **21**, 257 (1938).

(3) A. V. Tobolsky and G. M. Brown, *J. Polymer Sci.*, **17**, 547 (1955).

(4) We wish to thank the Research Department of the American Viscose Corporation for supplying this material.

(5) J. M. Oth and P. J. Flory, THIS JOURNAL, **80**, in press (1958).

(6) D. E. Roberts and L. Mandelkern, *ibid.*, **80**, in press (1958).

(7) P. J. Flory, *ibid.* **78**, 5222 (1956).

(8) D. E. Roberts, L. Mandelkern and P. J. Flory, *ibid.*, **79**, 1515 (1957).

(9) L. Mandelkern, D. E. Roberts and A. F. Diorio, in preparation.

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