specimen of *Belemnites virgatus* from the Toarcian of Deux Sèvres gave a reading of 24.9°C. An Aalenian specimen from Alsace was found to have a temperature of 20.1°C. Three Bajocian specimens from Normandy gave temperatures of 19.5°C, 20.6°C and 21.4°C respectively. From England, 3 Toarcian specimens from Northampton gave temperatures of 23.8°C, 25.7°C and 29.6°C respectively while another Toarcian specimen from Yorkshire gave a temperature of 31.7°C. These data have been plotted on Table IV together with the data recorded in this paper.

The consistency of data derived from 4 countries covering a considerable area of Western Europe is apparent and some comments are necessary. Firstly, an overall climatic change from moderately warm water conditions in the Plienbachian to hot conditions in the Toarcian occurred and was succeeded by a decline in temperatures until rather cool conditions are reached in the Upper Bajocian. The range of temperatures varies from 8 or 9°C in the Lias and Aalenian to 4°C in the Upper Bajocian. A point made by one of us earlier (R. Bowen) is that the inference made by some workers based upon the scarcity of limestones and coral reefs in the Lias that cooler conditions prevailed then than later in the Jurassic is erroneous. The analyses listed herein amply confirm this since at least the Upper Lias is shown to be very warm and hot (in the Toarcian). It is apparent that limestones are not reliable indices of warm-water conditions since their formation may be influenced by many factors not dependent on temperature.

Secondly a word must be said about the amplitude of the climatic variations. A 6°C rise of temperature occured from Pliensbachian into Toarcian time and the subsequent decline was through 11°C into the Upper Bajocian. Of course these are approximate figures but they nevertheless indicate the indisputable directions of temperature trends and the order of magnitude to which they belong.

It is necessary to add some comments on the Pelecypod and Echinoid results also. With reference to Pelecypoda, it must be remembered that Lowenstam and Epstein[5] have observed that where they are associated with Belemnoids in the post-Aptian Cretaceous they give temperatures higher than the Belemnoids. Our specimens—of *Trigonia navis* and *Gervillea pernoides*— give temperatures considerably in excess of the associated Belemnoids. The actual figures are reasonable, but of course much too high for the low-temperature Dogger δ. Possibly secondary alteration has taken place in the shells, but this seems improbable in view of their different physical structures. It is more likely that a biological fractionation effect ('vital' effect) occurs among Pelecypods rendering them less suitable for temperature determinations than the Belemnoids. It is in any case interesting that as in the Cretaceous, higher temperatures are recorded by the Pelecypoda than by associated Belemnoidea. With reference to the Cidarid spines analysed, clearly the result is not a temperature record.

The authors hope to continue their investigations into the climatic history of Germany during the Jurassic by investigating the Lower Lias and the period Callovian to Kimeridgian. The results obtained will be published at a later stage[6].

Zusammenfassung. In der vorliegenden Arbeit werden Temperaturbestimmungen an 22 Belemniten, 2 Muscheln und Seeigelstacheln aus dem mittleren und oberen Lias, sowie dem mittleren und unteren Dogger angegeben. Die Proben wurden in der Umgebung von Pliensbach (Württemberg) gesammelt.

Aus diesen Analysen geht hervor, dass für die Zeit des Toarcian ein Temperaturmaximum angenommen werden muss, während im mittleren Lias sowie im mittleren Dogger niedrigere Temperaturen vorherrschten. Die Temperaturschwankungen betragen zwischen Lias γ und Lias ε ca. 6°C und zwischen Lias ε und Dogger δ ca. 11°C.

R. Bowen[7] and P. Fritz[8]

Laboratorio di Geologia Nucleare dell'Università di Pisa (Italy) and Geologisch-Paläontologisches Institut der Technischen Hochschule Stuttgart (Germany), April 25, 1963.

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[6] *Acknowledgments.* The authors are indebted to Prof. E. Tongiorgi, director of the Laboratorio di Geologia Nucleare del C.N.E.N., Pisa, at which this work was carried out, for facilities.

[7] Present address: Institut für Kernchemie der Universität, Köln (Germany).

[8] Present address: Laboratorio di Geologia Nucleare, Via S. Maria 22, Pisa (Italy).

Heterocyclic Steroids. Steroidal Pyrimidines[1]

In continuing our search for novel heterocyclic steroids we have synthesized steroids in which ring A has a pyrimidine structure, i.e. carbons 2 and 4 are replaced by nitrogen. Although several heterocyclic steroids have been prepared, none have the pyrimidine moiety incorporated directly in the steroid ring system.

Condensation of 19-nortestosterone with ethyl formate by the sodium hydride procedure[2] and acetylation of the product gave 17β-acetoxy-2-acetoxymethylene-estr-4-en-3-one (1); m.p. 134–137°; λ_{max}^{MeOH} 261 mμ (ε 12900); ν_{max}^{KBr} 1760, 1730, 1670, 1610, 1240, 1185 cm^{-1}. Found: C, 71.20; H, 7.86. (Calcd. for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82.) Ozonolysis of 1 resulted in the γ-ketoacid 2a; m.p. 151–153°; ν_{max}^{KBr} 3420, 1730, 1690, 1250 cm^{-1}. Found: C, 66.68, 66.70; H, 8.49, 8.33. (Calcd. for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13.) Treatment of acid 2a with diazomethane followed by ketalization with ethylene glycol yielded the γ-ethylenedioxyester 2b; m.p. 107–109°; ν_{max}^{KBr} 1740, 1735, 1265, 1245, 1040 cm^{-1}. Found: C, 66.65; H, 8.64. (Calcd. for $C_{21}H_{32}O_6$: C, 66.30; H, 8.48.)

The diphenylene ketosteroid 3a, m.p. 156–160°, was realized from the reaction of 3b with phenyl magnesium bromide, then dehydration with glacial acetic acid[3]. The product 3a had λ_{max}^{MeOH} 250 mμ (ε 16100); ν_{max}^{KBr} 1730, 1700, 1600, 1495, 1245 cm^{-1} (found: C, 81.58; H, 7.65 – calcd. for $C_{30}H_{34}O_3$: C, 81.41; H, 7.74) and on treatment with

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[1] (a) This research was supported by U.S. Public Health Service Grant No. A-5326; (b) Part IV of Heterocyclic Steroids. Part III, see E. Caspi, P. K. Grover, and D. M. Piatak, Chem. and Ind., in press.

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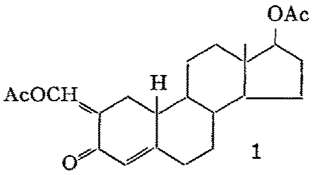
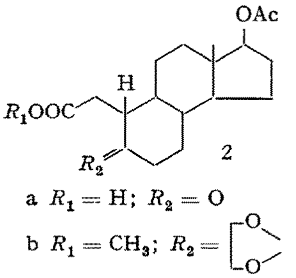


1



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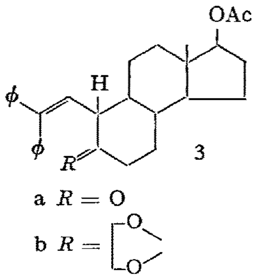

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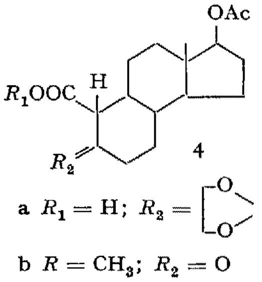

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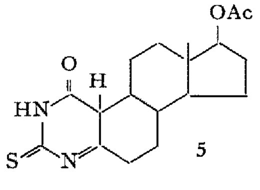

5

ethylene glycol was readily converted to ketal 3b; m.p. 117–120°; λ_{max}^{MeOH} 250 mμ (ε 16500); ν_{max}^{KBr} 1735, 1600, 1495, 1250, 1040 cm^{-1}. Found: C, 79.19; H, 7.88. (Calcd. for $C_{32}H_{38}O_4$: C, 78.98; H, 7.87.) The diphenylene ketal 3b was cleaved by ruthenium tetroxide-sodium periodate[4] to the β-ethylenedioxy-acid 4a; m.p. 201–207° (dec.); ν_{max}^{KBr} 1755, 1735, 1720, 1245, 1050 cm^{-1}. Found: C, 64.86; H, 7.86. (Calcd. for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01.) Methylation of 4a with diazomethane and subsequent regeneration of the C-5 ketone with hydrochloric acid gave the β-ketoester 4b; m.p. 152–155°; ν_{max}^{KBr} 1735, 1700, 1260, 1250 cm^{-1}. Found: C, 67.28; H, 8.16. (Calcd. for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13.)

Fusion of β-ketoester 4b with thiourea gave rise to 17β-acetoxy-2,4-diazaestr-4-en-1-one-3-thione (5); m.p. above 300°; λ_{max}^{MeOH} 219 mμ (ε 12000), 280 mμ (ε 21000); ν_{max}^{KBr} 3100, 1730, 1670, 1615, 1565, 1235 cm^{-1}. Found: C, 62.18; H, 6.85. (Calcd. for $C_{18}H_{24}N_2O_3S$: C, 62.05; H, 6.94.)

The synthesis of derivatives and other pyrimidine steroids is in progress.

Zusammenfassung. Die erste Synthese eines Steroid-Analogen, in welchem Ring A zu einem Pyrimidin umgewandelt wurde, wird beschrieben. Die wichtigste Zwischenstufe 4b wurde durch Abbau von 19-nor-Testosteron gewonnen. Kondensation von 4b mit Thioharnstoff führte zu 17β-Acetoxy-2,4-diazaestr-4-en-1-on-3-thion (5).

E. Caspi[5] and D. M. Piatak

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Zur polarographischen Untersuchung von Peroxiden und oxydierten Fetten

Die Polarogramme oxydierter Fette und Fettsäurederivate zeigen in dem bisher meist verwendeten Grundelektrolyten 0,3 m-LiCl in Methanol/Benzol (1:1)[1] bis zu drei oder vier Stufen[1–4]. Die vierte Stufe bei etwa –1,6 V (gegen Boden-Hg), die erst in späteren Oxydationsstadien auftritt, wird Carbonylverbindungen zugeordnet[2,4]. Die anderen Stufen entstehen bei Anwesenheit von Peroxiden: Die Potentiale bei etwa –0,7 und –1,1 V (gegen Boden-Hg) entsprechen – wie an Reinsubstanzen gezeigt wurde[5,6] – Hydroperoxiden, z.T. auch Peroxiestern[5]. Die Natur der ersten Stufe A bei 0 bis –0,2 V, die aus den beiden voneinander abhängigen Komponenten A_1 und A_2 besteht, ist noch ungeklärt. Nach Kuta und Quackenbush[5] werden in diesem Bereich Diacylperoxide und Persäuren reduziert. Figur 1 zeigt Stufe A in autoxydiertem und bestrahltem Fett.

Zur Aufklärung der Stufe A wurden Untersuchungen mit einem Kathodenstrahlpolarographen ('single sweep method') durchgeführt und die Lösungen genau 5 min nach Durchleiten von N_2 gemessen. Diese Versuche haben folgendes ergeben:

Die Grösse der Spitzenströme A_1 und A_2, sowie das Verhältnis A_2/A_1 wachsen bei Dibenzoylperoxid (Figur 2)

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