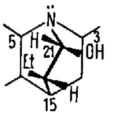
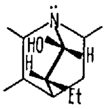
iso series. Alternatively if the substituent at C-21 was replaced by hydrogen (deoxyajmaline and isodeoxyajmaline in Run E) the two rates were almost identical but with a very slight advantage in favor of deoxyajmaline.

A study of molecular models revealed that the quinuclidine system in both ajmaline and isoajmaline is strained. If one looks at this system directly facing carbons 20 and 21, one observes a situation represented by expressions III or IV, where the hydrogen atom and the hydroxyl group on C-21 are not in a horizontal plane. Because of the bulk of the C-21 hydroxyl group in IV, it would be expected that the approach of the ethyl iodide molecule from the top would be slightly hindered, so that form IV should ethylate slower than III. This was indeed found to be the case since isoajmaline II or IV was half as slow as ajmaline I or III. As expected, this steric effect became more pronounced when the bulkier acetoxy derivatives were used (Runs C and D), and less important when the acetoxy group was replaced by the much smaller hydrogen atom (Run E).



III



IV

These results are therefore in complete agreement with the earlier conclusions[2]. The data also point out the usefulness of rate measurements to study relatively small steric differences in the structures of alkaloids and their derivatives.

Experimental. The apparatus used consisted of a conventional conductivity cell with black platinized electrodes purchased from the Fisher Scientific Co., a Hewlett Packart Model 200 AB audio-oscillator to furnish a 1000 cps current, a Leeds & Northrup Model 1553 shielded ratio box, a Leeds & Northrup Model 4754 a-c decade resistance box in series with a fabricated 100 Kohm step type resistance box, a Leeds & Northrup air capacitor (nom. max. 0.001 M.F.) to balance the cell capacitance, and a Heath oscilloscope, Model 10-12, to act as a galvanometer in detecting the balance point. The equipment was assembled so that the resistance of the cell could be measured using the classical Wheatstone bridge arrangement.

The temperature was maintained at 25.0 ± 0.1° by suspending the cell in a constant temperature bath. The nitrogenous base (3 mg in each case) was dissolved in 10 ml of acetonitrile, and the solution introduced in the cell. 1 ml of ethyl iodide was then injected into the cell by using a graduated syringe, and a timer was started. The bridge was balanced at appropriate intervals, and the resistance and time were recorded until the reaction had gone practically to completion. The rates were calculated using the equations given in Ref.[1a].

Résumé. Les auteurs ont mesuré les vitesses de réaction entre l'ajmaline plus dérivés et l'iodure d'éthyle. Les conclusions stéréochimiques de TAYLOR au C-21 en ont été confirmées.

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[3] *Acknowledgments.* The authors wish to thank Dr. W. I. TAYLOR of CIBA Pharmaceutical Company for the generous gift of the compounds used in this study, and the National Institutes of Health (Grant No. GM-10608-01) for financial assistance.

Oxygen Isotope Paleotemperature Analyses of Lower and Middle Jurassic Fossils from Pliensbach, Württemberg (Germany)

I. Introduction. Utilizing the established techniques of O^{18}/O^{16} paleotemperature analysis[1], 22 Belemnoid specimens, 2 Pelecypod specimens and several Echinoid spines from the German Lias γ, δ and ζ and Dogger α and δ were examined. The analyses were made on an Atlas-Werke M86 mass-spectrometer using Carrara marble standard and the resultant data were corrected to refer directly to the PDB-1 Chicago standard[2]. One of us (P. FRITZ) collected the material from the Pliensbach area near Stuttgart (Germany). The stratigraphy, lithology and thicknesses of the relevant strata are shown in Table I. The taxonomy of the speciment is included in the Table of Results (Table II).

II. Data obtained (see Tables II and III).

III. Interpretation of Data. From the Belemnoid results listed in Table II, it is evident that (assuming the mean ocean δ to have been zero in the Jurassic) the sea temperatures attained a maximum in the Upper Toarcian and Lower Bajocian from initially cooler conditions in the Pliensbachian. This maximum was followed by a decline in Upper Bajocian times. It is interesting to compare this picture with data obtained by one of us (R. BOWEN) elsewhere in Germany[3] and in some other countries of Western Europe[4] (which were interconnected by seas during the part of the Jurassic under consideration). Lias ε (Lower Toarcian) Belemnoids from the Trimeusel locality on the Main River near Bamberg, Bavaria (Germany) gave three temperatures. These are 24.2°C, 27°C and 28.4°C. One of these is the same as an Upper Toarcian result listed in this paper, but the smallest figure is 2.8°C below the present minimum (which is derived from the Upper Toarcian). This is consistent with a gradual rising of temperature from Lower into Upper Toarcian times. From Switzerland, 3 previous determinations have been made — 2 on *Belemnites tripartitus* from the Toarcian of Kanton Aargau and Canton de Vaud (readings of 27.3°C and 23.4°C respectively being obtained) and 2 on an unidentified Belemnoid from the Toarcian of Canton de Fribourg (giving 23.5°C). From France, from the Pliensbachian of the Vendée, 2 specimens of *Hastites umbilicatus* gave temperatures of 24.3°C and 24.6°C respectively. A

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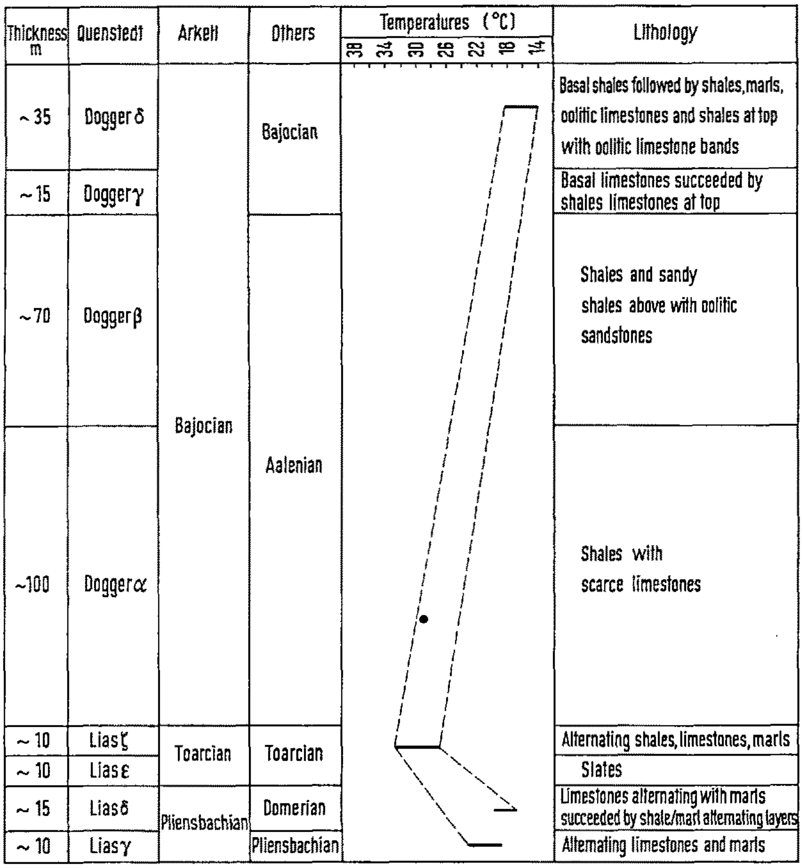
[1] S. EPSTEIN, R. BUCHSBAUM, H. A. LOWENSTAM, and H. C. UREY, Bull. Geol. Soc. Amer. *62*, 417 (1951); *64*, 1315 (1953). – H. C. UREY, H. A. LOWENSTAM, S. EPSTEIN, and C. R. MCKINNEY, Bull. Geol. Soc. Amer. *62*, 399 (1951).

[2] The Carrara Standard has a value of $-1.6^0/_{00}$ relative to PDB-1.

[3] R. BOWEN, Experientia *19*, 401 (1963).

[4] R. BOWEN, J. Geol. *69*, 309 (1961).



Thickness m	Quenstedt	Arkell	Others	Lithology
~35	Dogger δ	Bajocian	Bajocian	Basal shales followed by shales, marls, oolitic limestones and shales at top with oolitic limestone bands
~15	Dogger γ			Basal limestones succeeded by shales limestones at top
~70	Dogger β		Aalenian	Shales and sandy shales above with oolitic sandstones
~100	Dogger α			Shales with scarce limestones
~10	Lias ζ	Toarcian	Toarcian	Alternating shales, limestones, marls
~10	Lias ε			Slates
~15	Lias δ	Pliensbachian	Domerian	Limestones alternating with marls succeeded by shale/marl alternating layers
~10	Lias γ		Pliensbachian	Alternating limestones and marls

Table I. This shows the relevant formations, their various classifications, thicknesses and lithologies together with the temperatures obtained

Table II. Numbers 1–22 are Belemnoidea; 23 several Echinoid spines and 24, 25 Pelecypoda

(i) *Lower Pliensbachian* (*Lias γ*)

Specimen number	Taxonomy	δO^{18} (‰) relative to PDB-1	Average δO^{18} (‰) relative to PDB-1	Temperature in °C
1	?	−0.44		
		−0.56		
		−0.64	−0.54	18.8
2	?	−0.59		
		−0.75		
		−0.97	−0.77	18.9
3	*Passaloteuthis sp.*	−0.41		
		−0.69		
		−0.82	−0.64	19.3
4	*Hastites sp.*	−0.58		
		−0.67		
		−0.71	−0.65	19.4
5		−0.79		
		−1.01		
		−1.08	−0.96	20.6
6	*Passaloteuthis sp.*	−0.95		
		−1.15		
		−1.28	−1.12	21.5
7	*Passaloteuthis sp.*	−1.15		
		−1.25		
		−1.31	−1.23	22.0
8	*Passaloteuthis sp.*	−1.17		
		−1.35	−1.26	22.1
9	*Passaloteuthis sp.*	−1.50		
		−1.50		
		−1.55	−1.51	23.3
10	*Nannobelus sp.*	−1.57	−1.57	23.6

(ii) *Upper Pliensbachian* (*Lias δ: Domerian*)

Specimen number	Taxonomy	δO^{18} ($^0/_{00}$) relative to PDB-1	Average δO^{18} ($^0/_{00}$) relative to PDB-1	Temperature in °C
11	*Passaloteuthis paxillosus*	+0.14 −0.03 −0.09	+0.01	16.5
12	*Passaloteuthis paxillosus*	+0.04 −0.25	−0.10	16.9
13	*Passaloteuthis paxillosus*	−0.59 −0.95 −1.01	−0.85	20.2

(iii) *Upper Toarcian* (*Lias ζ*)

Specimen number	Taxonomy	δO^{18} ($^0/_{00}$) relative to PDB-1	Average δO^{18} ($^0/_{00}$) relative to PDB-1	Temperature in °C
14	*Acrocoelites sp.*	−2.25 −2.30 −2.31	−2.28	27.0
15	*Acrocoelites sp.*	−3.25 −3.26	−3.25	32.9

(iv) *Lower Bajocian* (*Dogger α: Aalenian*)

Specimen number	Taxonomy	δO^{18} ($^0/_{00}$) relative to PDB-1	Average δO^{18} ($^0/_{00}$) relative to PDB-1	Temperature in °C
16	*Acrocoelites sp.*	−2.47 −2.62 −2.92	−2.67	29.0

(v) *Upper Bajocian* (*Dogger δ*)

Specimen number	Taxonomy	δO^{18} ($^0/_{00}$) relative to PDB-1	Average δO^{18} ($^0/_{00}$) relative to PDB-1	Temperature in °C
17	*Belemnopsis canaliculatus*	+0.37 +0.50 +0.75	+0.54	14.2
18	*Belemnopsis sp.*	+0.53 +0.81 +0.82	+0.72	16.2
19	*Belemnopsis canaliculatus*	+0.05 −0.11	−0.03	16.6
20	*Megateuthis giganteus*	−0.44 +0.30	−0.05	16.7
21	*Belemnopsis canaliculatus*	−0.14 −0.15 −0.22	−0.17	17.2
22	*Belemnopsis canaliculatus*	−0.02 −0.73	−0.37	18.1
23	*Rhabdocidaris sp.*	−6.94 −6.95 −7.01	−6.91	43.2
24	*Trigonia navis*	−3.15 −3.33	−3.24	31.9
25	*Gervillea pernoides*	−3.42 −3.53	−3.47	33.1

The Belemnoid data are presented graphically on Table III.

Table III. This shows the data obtained from specimens collected in the Pliensbach area

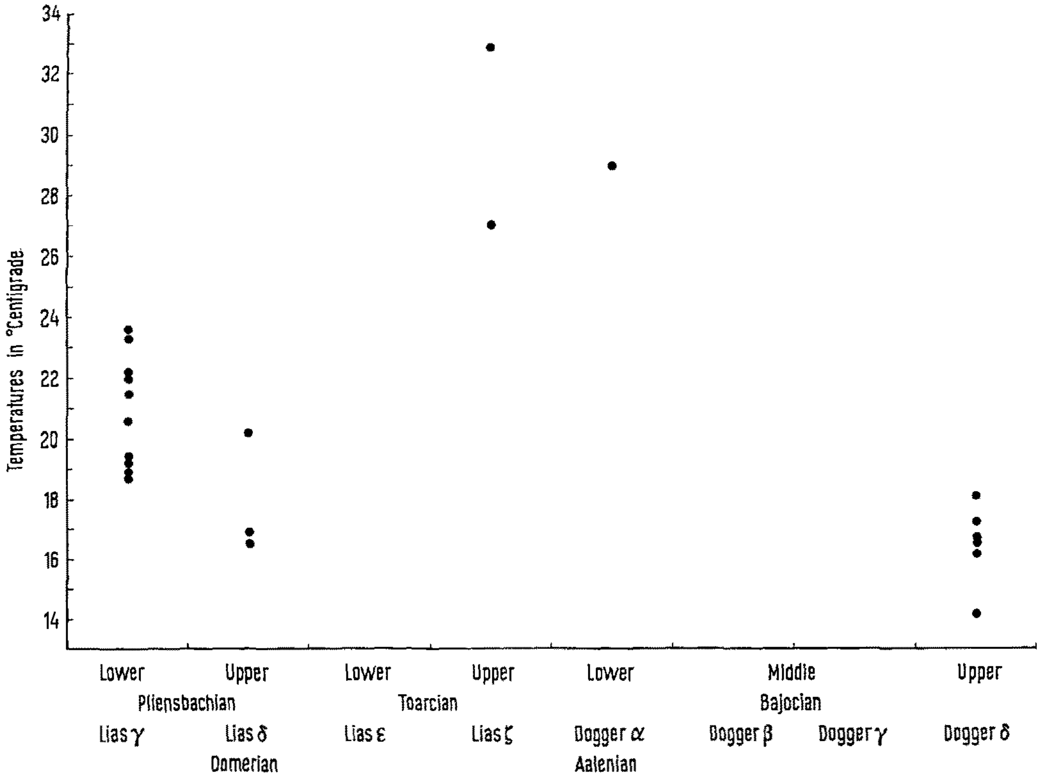
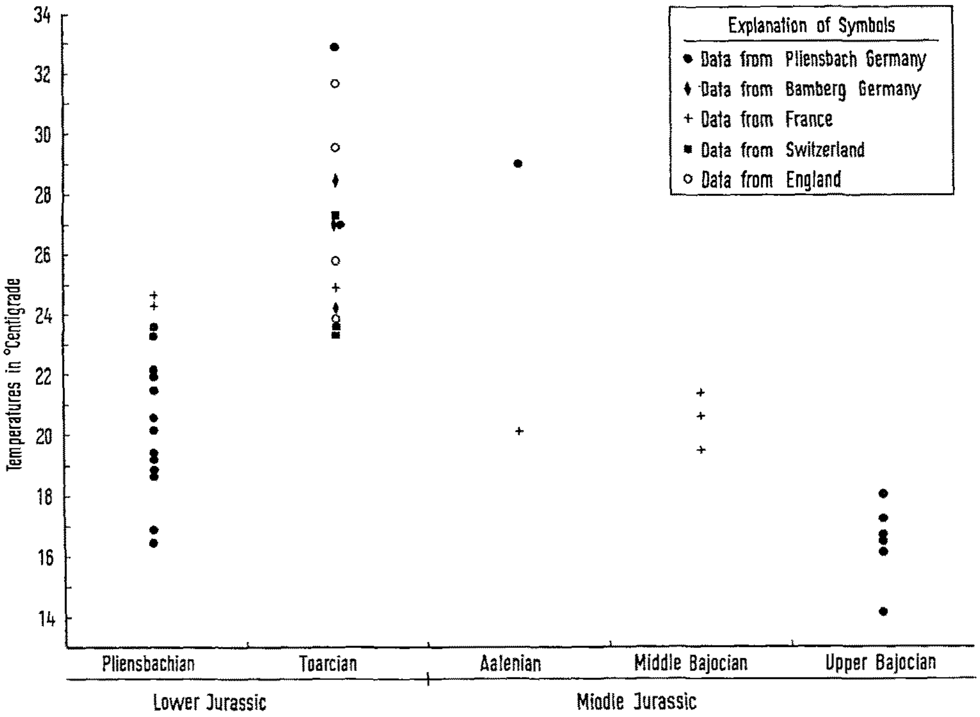


Table IV. This shows the data from western Europe



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.

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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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[5] H. A. Lowenstam and S. Epstein, J. Geol. *62*, 207 (1954).

[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.

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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°; $\lambda_{\max}^{\mathrm{MeOH}}$ 261 mμ (ε 12900); $\nu_{\max}^{\mathrm{KBr}}$ 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°; $\nu_{\max}^{\mathrm{KBr}}$ 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°; $\nu_{\max}^{\mathrm{KBr}}$ 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 $\lambda_{\max}^{\mathrm{MeOH}}$ 250 mμ (ε 16100); $\nu_{\max}^{\mathrm{KBr}}$ 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.

[2] F. L. Weisenborn, D. C. Remy, and T. L. Jacobs, J. Amer. chem. Soc. *76*, 552 (1959).

[3] N. Pappas and H. R. Nace, J. Amer. chem. Soc. *81*, 4556 (1959).