Eine Möglichkeit, Aussagen über das qualitative Verhalten der Lösungen von (1) zu gewinnen, sei durch folgende Bemerkungen angedeutet: man verschafft sich e ne Lösung von (2) $y = \bar{y}(x,t)$, drückt mit Hilfe dieses Ansatzes gemäss

$$\int_0^x \sqrt{1 + \ddot{\bar{y}}_x{}^2}\, dx \quad : \quad \int_0^{l_0} \sqrt{1 + \bar{y}_x{}^2}\, dx = s(x,t) \qquad (3)$$

s als Funktion von x und t aus und bringt so die zweite der beiden Gleichungen (1) in die Form

$$G[x,y] = H[y] - \zeta(x,t), \qquad (4)$$

wobei $H[y]$ den linearen Differentialausdruck (2) bedeutet und $\zeta(x,t)$ formal als Anregung interpretiert werden kann.

Um den Ausdruck $G[x,y]$ nach (4) aufzuspalten, wird er zunächst mit Hilfe von

$$y' = y_x x' \text{ und } y'' = x'^2 y_{xx} + x'' y_x$$

im Sinne von $y_x \ll 1$ vereinfacht. Für $\ddot{y}$ ergibt eine kurze Rechnung

$$\ddot{y} = y_{tt} + 2\, y_{xt}\dot{x} + y_{xx}\dot{x}^2 + y_x \ddot{x}.$$

Wenn der Ansatz $\bar{y}(x,t)$ zum Beispiel der Grundschwingung entspricht, also etwa

$$\bar{y}(x,t) = A \cos \omega t \sin \frac{\pi x}{l_0} \quad \text{mit} \quad \omega^2 = \frac{S_0 \pi^2}{l_0 M}$$

angenommen wird, so lassen sich die Ableitungen von x nach s und t gemäss (3) aus

$$F(x,s,t) \equiv E(p,\xi) - 2\, sE(p) = 0$$

bestimmen, wobei

$$p^2 = \frac{a^2}{1+a^2},\ a = \frac{\pi A}{l_0} \cos \omega t,\ \xi = \frac{\pi x}{l_0}$$

sind und $E(p,\xi)$ bzw. $E(p)$ das elliptisch bzw. vollständige elliptische Integral 2. Gattung bedeuten. Damit gewinnt der Differentialausdruck G schliesslich die Gestalt

$$G[x,y] = H[y] - \zeta(x,t).$$

Das heisst also: das Verhalten der gemäss (1) frei schwingenden Saite stimmt im Rahmen einer angenäherten Behandlung überein mit dem Verhalten einer angeregt schwingenden Saite, die sich unangeregt gemäss (2) bewegen würde.

H. MÜLLER

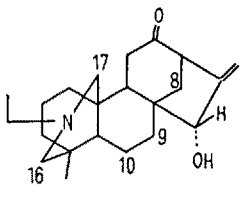
Institut für theoretische Physik der Johannes-Gutenberg-Universität Mainz, 19. Februar 1958.

Summary

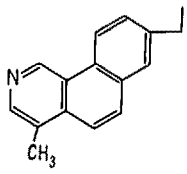
For the Cartesian coordinates of the elements of a vibrating string, which are introduced as functions of time and a parameter (similar to the Lagrangean method in hydrodynamics), a general, non-linear system of differential equations is offered. The behaviour of the freely vibrating string corresponding to this system agrees, approximately, with the behaviour of a string put in motion in a certain way, which string, if moving freely, would act according to the linear differential equation of the elementary theory.

The Structure of Napelline and Songorine

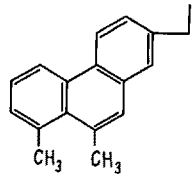
Some time ago[1] we have described the isolation of napellonine ($C_{22}H_{31}O_3N$) and napelline ($C_{22}H_{33}O_3N$) from amorphous aconitine. We have shown that napellonine contains the garrya skeleton and may be represented by the partial structure I.



I



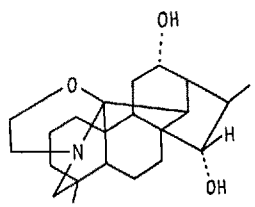
II



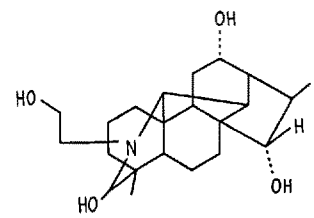
VI

Napelline may be obtained by $LiAlH_4$ reduction of napellonine and thus may be represented by I with an equatorial OH group in place of the keto group. The partial structure I was based on conclusive evidence on the structure and substitution of the C–D (1-2-3-bicyclo octane) ring system and on dehydrogenation data. These included the isolation of a good yi: ld of unidentified phenanthrenes and of the azaphenanthrene II which is a typical dehydrogenation product of veatchine[2].

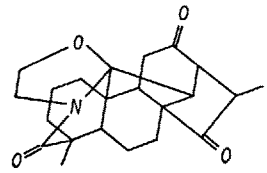
To complete the partial structure I it was still necessary to place a hydroxy group and form an additional carbon-carbon bond. The first point was regarded as settled when napelline was shown to give glyoxal by treatment with lead tetra-acetate. This, according to EDWARDS[3], demonstrates the presence of an ethanolamine group. The additional carbon-carbon bond was tentatively postulated to be a C_{17}-C_8 bond on the following evidence. Silver oxide oxidation of dihydronapelline (pK = 7·8) gave two compounds ($C_{22}H_{33}O_3N$ III and $C_{22}H_{35}O_4N$ IV) formulated as IIIa and IVa. Compound III was a carbinol-



IIIa pK = 6·8



IVa pK = 8·8



Va

amine-ether more weakly basic than dihydronapelline. On the other hand, it was shown by infrared evidence that the salts of III have quaternary Schiff salt character. The only explanation of this unprecedented behavior, that we have been able to think of at the time, was to place the

[1] K. WIESNER, Z. VALENTA, J. F. KING, R. K. MAUDGAL, L. G. HUMBER, and SHÔ ITÔ, Chem. and Ind. *1957*, 173.

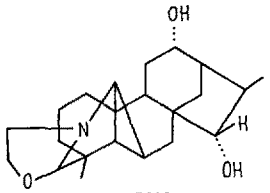
[2] M. F. BARTLETT and K. WIESNER, Chem. and Ind. *1954*, 542.

[3] O. E. EDWARDS and TARA SINGH, Canad. J. Chem. *32*, 465 (1954).

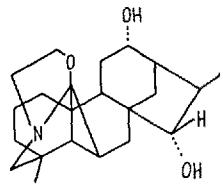
carbinolamine-ether group at a bridgehead of such a type, which would make the quaternary Schiff salt energetically unfavourable, but still possible.

The only way to create a bridgehead which would satisfy this requirement in the partial structure I is the assumption of a C_{17}-C_8 bond. The oxidation of the weakly basic carbinolamine-ether III with CrO_3 in pyridine gave then a lactam $C_{22}H_{27}NO_4$ (V) formulated as V*a*. However, it will be shown now that these conclusions were erroneous and that the reasons for the weak basicity of the carbinolamine-ether III are entirely different and, we believe, quite novel in their character.

We have recently sent a sample of napellonine to Dr. A. D. KUZOVKOV, Moscow. Dr. KUZOVKOV has kindly informed us that napellonine is identical with the alkaloid songorine, the dehydrogenation of which he has been studying[4]. KUZOVKOV was able to isolate from this reaction a $C_{18}H_{18}$ phenanthrene and identify it as VI by synthesis. If one takes this dehydrogenation result at its face value, it is obvious (as has been suggested also by Dr. KUZOVKOV) that the C_{17}–C_8 bond in napellonine and napelline must be replaced by a C_{17}–C_{10} linkage. (Of course, a C_{16}–C_{10} bond is also possible at this stage; we shall discuss the decision between the two possibilities at the end of this article.)



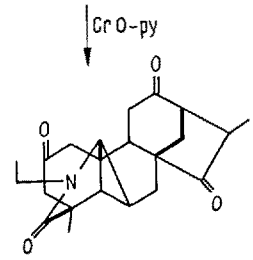
III*b*



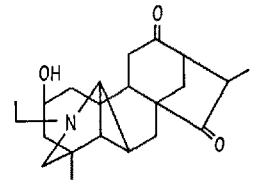
III*c*

If one assumes a C_{17}–C_{10} linkage, one can formulate the weakly basic carbinolamine-ether III only as III*b* or III*c*.

Both these structures are quite unsatisfactory since III*b* fails to explain the weak basicity (see garryine, pK = 8·8) and III*c* clearly rules out the existence of quaternary Schiff salts. We have reached, consequently, the conclusion that some of the evidence must be misleading. At this stage we have just ascertained that other aconite alkaloids, which definitely contain an N-ethyl group give glyoxal on treatment with lead tetra-acetate and that consequently this reaction[3] has no diagnostic value for the presence of an ethanol amine group. Furthermore, already YUNUSOV[4] has demonstrated the presence of an N-ethyl in songorine and also we have been able to prove now conclusively the presence of this group in napelline and napellonine in a manner similar to the method used by us previously for veatchine[5] (for details of this evidence, see forthcoming full publication). This finding enables us to formulate the weakly basic carbinolamine-ether as III*d*, its Schiff salts as VII and its oxidation product by CrO_3-pyridine as V*b* instead of V*a*. That this last compound is indeed a triketone follows clearly from the quantitative comparison of its infrared spectrum



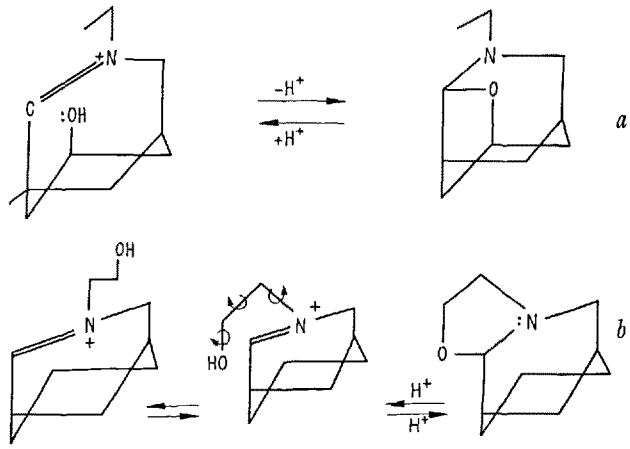
V*b*



VIII

with the spectrum of isonapellonine VIII. The intensity of the sixmembered ketonic peak (1712 cm^{-1}) in V*b* is much greater than the intensity of the five-membered ketonic peak (1740 cm^{-1}). In compound VIII both peaks are equal.

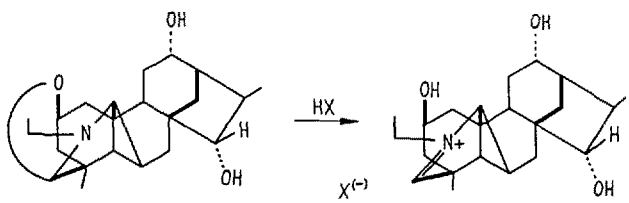
It still is necessary to show why III*d* should be, by two orders of magnitude, less basic than garryine. The following scheme which shows the equilibria between carbinolamine-ether and quaternary Schiff base forms for III*d* (*a*) and garryine (*b*) clearly illustrates this point.



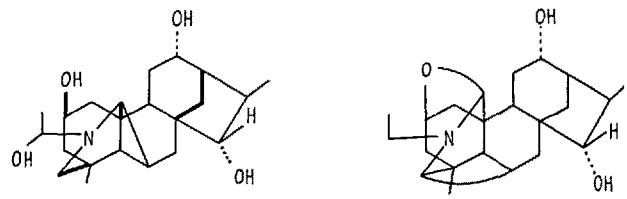
In (*a*) there is a rigid 1,3 diaxial interaction between the trigonal carbon and the hydroxy group which is relieved by ether formation. In (*b*) the free rotation around the three bonds of the ethanol amine group stabilizes the quaternary Schiff form.

The strongly basic oxidation product of dihydronapelline previously formulated as IV*a* must now be formulated as IV*b*.

This assignment is in agreement with the experimental demonstration that the N-alkyl group may be removed by vigorous hydrolysis.



III*d* VII



IV*b* IX

The skeletal structure as in IX for napelline and its derivatives is equally plausible and permits a quite analogous interpretation of all the data.

[4] S. YUNUSOV, J. gen. Chem. U.S.S.R. *18*, 515 (1948). – A. D. KUZOVKOV, J. gen. Chem. U.S.S.R. *23*, 521 (1953).

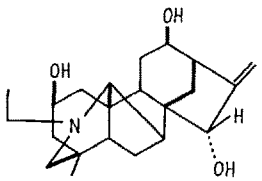
[5] K. WIESNER, W. I. TAYLOR, S. K. FIGDOR, M. F. BARTLETT, J. R. ARMSTRONG, and J. A. EDWARDS, Chem. Ber. *86*, 800 (1953).

However, the basicity of the weakly basic carbinolamine-ether III, if it is formulated as IX, cannot be equally well explained as for the structure III*d*.

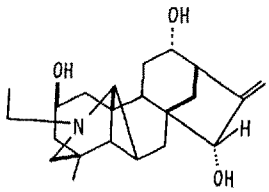
There is a strong tendency to maintain C_{17} in the trigonal state because of steric interaction with C_8. This effect would oppose the basicity weakening interaction with the axial hydroxy group. (For a detailed discussion of this effect in veatchine, see ref.[6].) This means that the interaction with the axial hydroxyl would have to lower the basicity not by two, but almost by five orders of magnitude (pK of veatchine = 11·5). This is considered unlikely and consequently the C_{17}–C_{10} bond is preferred to the C_{16}–C_{10} bond in the napelline skeleton. Also the oxidation of III*d* to V*b* is analogous to the course of such a reaction in garryine. The oxidation of veatchine has *never been observed to give C_{17} lactams*.

The structure of napelline and napellonine can of course not be regarded as rigorously proven, but the rather extensive evidence available at present is fully compatible with the structures discussed.

There is only one attractive hypothesis left. This is the possibility that in the last step of KUZOVKOV's synthesis, which was a dehydrogenation, the very plausible rearrangement of a methyl group into the less hindered 9 position has occurred and that the 'natural' phenanthrene is actually 1–9-dimethyl-7-ethyl phenanthrene. This possibility changes nothing in the interpretation of the chemistry of napelline, it only means that the biogenetically very plausible structure X is still a possibility for napelline besides the structure XI.



X



XI

We might mention that the skeleton as in X was considered by us ab origine, but discarded initially for the reasons we have discussed[1].

We have recently also sent a sample of napellonine to Professor E. OCHIAI, Tokyo, who has ascertained its identity with the Shimoburo base[7].

In conclusion, we wish to withdraw the name napellonine in favour of the name songorine, in deference to the first isolation of this compound by YUNUSOV[4].

We wish to thank Dr. A. D. KUZOVKOV and Professor E. OCHIAI for kindly communicating their results to us.

K. WIESNER, SHÔ ITÔ, and Z. VALENTA

Organic Chemistry Laboratory, University of New Brunswick, Canada.

Zusammenfassung

Für das Aconitum-Alkaloid Napellin wurden auf Grund einer eingehenden Diskussion des Tatsachenmaterials die Strukturen XI bzw. X vorgeschlagen. Das Alkaloid Songorin ist das dazugehörige Ring-D-Keton.

[6] K. WIESNER and J. A. EDWARDS, Exper. *11*, 255 (1955).

[7] TSUTOMU SUGASAWA, Pharmac. Bulletin *4*, 6 (1956).

Über die Atmungsenzyme des Seeigeleies

Die Information über die Atmungsenzyme des Seeigeleies erscheint lückenhaft, grossenteils veraltet und teilweise widersprechend[1]. Ungeklärt sind unter anderem folgende Fragen:

1. Inwieweit das Zytochrom-System operativ ist[2];
2. der Weg des Wasserstoff-Transportes, insbesondere inwieweit DPNH- und TPNH-dehydrierende Enzyme aktiv sind;
3. ob der Zitronensäurezyklus wirksam ist, besonders im Hinblick auf mehrfache Berichte über die Abwesenheit von Succinatsystemen[3], und
4. Natur und Abbauweise der Substrate der endogenen Atmung[4].

Zudem ist auch die intrazelluläre Verteilung der Atmungssysteme, ob Mitochondrien und Mikrosomen oder ihre Äquivalente existieren, bisher nicht untersucht worden. In einer Mitteilung[5] wurde kürzlich der Beweis für mitochondrienartige Teilchen, die das komplette Zytochrom-System enthalten, geführt. Unsere Untersuchungen ergaben folgende Hauptergebnisse:

Es gelang mittels photometrisch-kinetischer Methoden der Nachweis und die Messung von a) Zytochrom-Oxydase, b) hochaktiver DPNH[6]-Zytochrom-c-Reduktase-, c) Succinodehydrase- und d) schwacher TPNH-Zytochrom-c-Reduktase-Aktivitäten ($< {}^1/_{20}$ der DPNH-Reduktase-Aktivität) im Homogenat von unbefruchteten ebenso wie von befruchteten Seeigeleiern.

Fraktionierung mittels Zentrifugation zeigte enzymatische Profile, wie sie für Mitochondrien und Mikrosomen kennzeichnend sind (Tabelle I). Nur die Mitochondrienfraktion zeigte Zytochrom-Oxydase und Succinodehydrase-Wirkung; ihre Succinodehydrase und DPNH-Zytochrom-c-Reduktase war durch RÜ-Hemmstoff hemmbar (Tabelle II). Diese Eigenschaften der Mitochondrien sind also beim Seeigel und beim Säugetier gleich. Die Mikrosomen enthalten annähernd die Hälfte der gesamten DPNH-Zytochrom-c-Reduktase-Aktivität. Neben der Abwesenheit von Zytochrom-Oxydase und Succinodehydrase sind sie durch RÜ nicht beeinflussbar. Das Differenzspektrum (reduziert mittels DPNH und Dithionit gegen oxydiert) einer Mikrosomensuspension ähnelt dem Mikrosomenzytochrom (b_5) der Säugetiere, jedoch ist das Maximum[7] in der γ-Bande bei 428–30 mμ, also deutlich zum Langwelligen hin verschoben. Gegen eine Identität mit Zytochrom b_5 spricht auch die Abwesenheit einer katalytischen Wirkung bei Zugabe von Erythrozyten-Diaphorase, wie sie bei Zytochrom b_5 beobachtet wurde[8].

[1] J. RUNDSTRÖM, Adv. Enzymol. *9*, 241 (1949).

[2] E. G. BALL und B. MEYERHOF, J. biol. Chem. *134*, 483 (1940). – M. E. KRAHL, A. K. KELTCH, C. E. NEUBECK und G. H. A. CLOWES, J. gen. Physiol. *24*, 597 (1941).

[3] E. G. BALL und B. MEYERHOF, J. biol. Chem. *134*, 483 (1940). – I. M. GOLDINGER und E. S. G. BARRON, J. gen. Physiol. *30*, 73 (1943). – A. K. KELTCH *et al.* J. gen. Physiol. *33*, 547 (1950).

[4] M. E. KRAHL *et al.*, J. gen. Physiol. *38*, 31 (1954–55); Biochim. biophys. Acta *20*, 27 (1956).

[5] A. GHIRETTI-MAGALDI, Exp. Cell Res. (im Druck).

[6] Abkürzungen: DPNH: reduziertes Diphosphopyridinnukleotid; TPNH: reduziertes Triphosphopyridinnukleotid; RÜ: Retikulozytenhemmstoff.

[7] P. STRITTMATTER und S. F. VELICK, J. biol. Chem. *221*, 253 (1956). – D. GARFINKEL, Arch. Biochem. Biophys. *71*, 111 (1957).

[8] S. RAPOPORT und C. WAGENKNECHT, Naturwissenschaften *44*, 515 (1957).