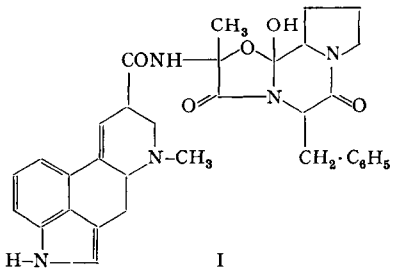
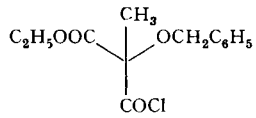
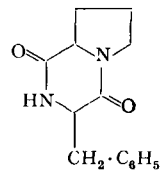


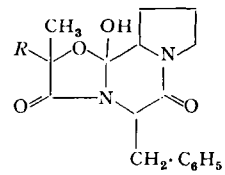
I



II



III



IV a/b – IX

Drehvermögen, Schmelzpunkt, Mischschmelzpunkt, UV- und IR-Spektrum, im chromatographischen Verhalten und im pharmakologischen Test als vollkommen identisch erwies.

Die ausführliche Publikation wird später in den Helv. chim. Acta erscheinen.

Summary. The total synthesis of the Ergot alkaloid Ergotamine is described.

A. Hofmann, A. J. Frey und H. Ott

Pharmazeutisch-chemisches Laboratorium, Sandoz A.G., Basel, 17. April 1961.

Natural Chromatography and the Accumulation of Petroleum in Rocks in View of Analyses of Bitumen from the Athabasca Deposit in Canada

Petroleum is the only organic liquid which occurs in sedimentary rocks in significant quantities. Petroleum consists mainly of hydrocarbons; whereas its ultimate source, the organic matter in marine sediments, is composed of small quantities of a large variety of different compound types. It is known that fluids, mainly water solutions, flow within sedimentary rocks, percolating through the maze of capillary pores. Colloidal mineral particles in the pores may selectively filter out polar compounds from the flowing fluids.

Figure 1 shows a photomicrograph of a thin section of a common, graywacke type sandstone, prepared from a drill core from the Woodbine formation of East Texas, taken from a depth of approximately 4800 feet. The clay mineral aggregates are visible in the pore channel. Laboratory chromatographic columns and sandstones often have similar compositions and textures.

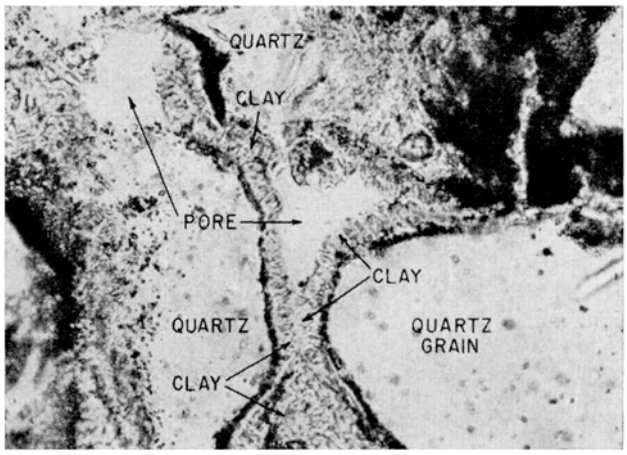


Fig. 1. Photomicrograph of a thin section of a sandstone. Woodbine formation, East Texas. Depth approximately 4800 feet, Magnification approximately 300×.

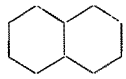
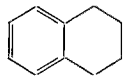
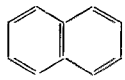
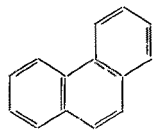
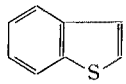
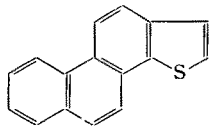
It has been long known that beds of clay minerals act as selective filters removing asphaltic and polar substances from petroleum[1]. It is also known that certain non-hydrocarbon constituents may be preferentially distributed in petroleum deposits[2,3] in a pattern which resembles chromatographic bands. It was found in the laboratory that among a group of organic compounds the hydrocarbons move with the least restraint through clay packed columns[4]. Furthermore, organic ions have been eluted in quartz sand and clay columns with sea water only[5], in accordance with the chromatographic principles of Martin and Synge[6]. The chromatographic 'plate' theory can be used to predict the movement of the bands in beds of sand and clay[7]. Consequently, one may conclude that chromatography is both a laboratory process and a natural phenomenon.

The Table lists some of the components of the semi-solid Athabasca bitumen from northeastern Alberta (Canada). This analysis[8] further substantiates the fact that this is the largest known petroleum deposit. Geological field relationships show that the petroleum in the Athabasca deposit was brought into its present resting place by percolating fluids. These two observations, together with the fact that most of the bituminous sandstones lie exposed on the surface, make the Athabasca deposit well suited for a study in natural chromatography.

The saturated hydrocarbon content of approximately 100 bituminous rock samples was determined. The samples came from three bore holes from the northeastern part of the deposit; the two holes which were the farthest were approximately 40 miles apart. If fluid flow was operational for a prolonged period of time, the chromatographic concept requires that the saturated hydrocarbons be evenly distributed over a large area in the deposit. This was found to be the case, because the saturated hydrocarbon contents of the samples showed only minor variations.

[1] J. E. Gilpin and M. P. Cram, Amer. Chem. J. *40*, 495 (1908).
[2] L. C. Bonham, Bull. AAPG *40*, 897 (1956).
[3] G. W. Hodgson and B. L. Baker, Bull. AAPG *43*, 311 (1959).
[4] C. E. Legate, Bull. GSA *69*, 1603 (1958).
[5] B. Nagy and J. P. Wourms, Bull. GSA. *70*, 655 (1959).
[6] A. J. P. Martin and R. L. M. Synge, Biochem. J. *35*, 1358 (1941).
[7] B. Nagy, Geochim. cosmochim. Acta *19*, 289 (1959).
[8] B. Nagy and G. C. Gagnon, Geochim. cosmochim. Acta, in print.

Composition of the Athabasca petroleum from the Abasand Quarry, in the vicinity of McMurray, Alberta (Canada)

Constituent	Type	Amount	Method of Analysis
Total petroleum[a]	glossy, brownish-black, semi-solid organic matter	16.47 weight% of dry rock	extraction with CH_2Cl_2 at room temperature
Asphaltenes	colloidal particles in the petroleum	22.3 weight% of total petroleum	precipitation and digestion with *n*-pentane
Saturated hydrocarbons	*n*-paraffins, *iso*-paraffins and naphthenes	approx. 11 weight% of total petroleum	elution chromatography mass spectrometry
n-Paraffins	———	approx. 1 weight% of saturated hydrocarbons	elution chromatography, urea adduction, ultraviolet spectroscopy
Monocyclic naphthenes		relatively common	elution chromatography mass spectrometry
Condensed naphthenes		common constituents	elution chromatography mass spectrometry
Alkyl benzenes		common constituents	elution chromatography mass spectrometry
Cyclo-alkyl benzenes		common constituents	elution chromatography mass spectrometry
Naphthalenes		present in sample	elution chromatography mass spectrometry
Phenanthrenes		present in sample	elution chromatography mass spectrometry
Pyridines		possible constituents	elution chromatography mass spectrometry
Benzothiophenes		possible constituents	elution chromatography mass spectrometry
Thiophenophenanthrenes		possible constituents	elution chromatography mass spectrometry

[a] An elementary analysis of the petroleum gave the following results: C = 80.10%; H = 10.68%; N = 0.54%; S = 6.63%; O (by difference) = 2.05%; C/H = 0.63.

To be able to use the Athabasca deposit for a study of natural chromatography, one must account for the presence of the asphaltene colloids in the petroleum. The colloids seem to be chiefly responsible for the high viscosity of the petroleum. Some of the colloidal particles and/or their aggregates are too large to have flowed through the smaller pores in shales and sandstones. Asphaltenes can be separated from petroleum[9], but their sizes and molecular weights vary, depending on the environment and on the means of study[10]. It is known that asphalt can be prepared from petroleum residues by air oxidation. Figure 2 illustrates such an effect, using crude petroleum in a simulated geological environment. The asphaltene colloids are, apparently, the products of chemical reactions taking place after the petroleum reached its reservoir.

The concept of natural chromatography may help to explain the accumulation of petroleum even when the exact origin of petroleum components, is still being debated. It points to the preferential accumulation of

[9] P. A. WITHERSPOON, Report of Investigations *206*, Illinois State Geol. Survey (1958).

[10] R. S. WINNIFORD, Preprint, Div. Pet. Chem. ACS *5*, A-11 (1960).

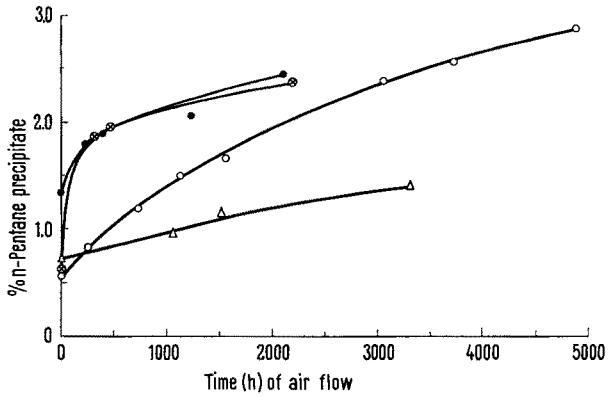


Fig. 2. The development of asphaltic matter in petroleum by prolonged exposure to air. Asphaltenes were determined by precipitation with *n*-pentane. Temperature: 50° ± 1°C; rate of air flow: approx. 2.5 ml air/min/ml of liquid crude oil; ○ crude oil, Perry, Oklahoma; △ crude oil, Pembina Field, Alberta; ● crude oil, Perry, Oklahoma, with 0.1% surface active agent added (Poly-Tergent B-300, Olin Mathieson Co., ethoxylated nonyl phenol, containing 9–10 moles of ethylene oxide); ⊗ crude oil, Perry, Oklahoma, with 5 weight % colloidal sulfur added.

hydrocarbons in rocks, regardless of whether they were synthesized in 'source rocks'[11] or derived with minor alterations only from living matter[12,13].

Résumé. La matière organique contenue dans les sédiments récents offre une grande variété de composants. Le pétrole, cependant, est constitué essentiellement d'hydrocarbures. Le déplacement des fluides dans les roches se traduit par une chromatographie, où les particules colloïdales séparent sélectivement de la phase mobile les composants polaires. La répartition des hydrocarbures saturés dans une partie du gisement de l'Athabasca, au Canada, répond à la notion de chromatographie naturelle.

B. NAGY[14] and JOSEFINA LUGAY

Department of Chemistry, Fordham University, New York, October 20, 1960.

[11] G. T. PHILIPPI, Preprints, 42nd Annual Meeting AAPG. *36*, (1957).
[12] W. G. MEINSCHEIN, Bull. AAPG. *43*, 925 (1959).
[13] E. G. BAKER, Science *129*, 871 (1959).
[14] The work which is reported here is sponsored by the National Science Foundation.

Voacanga-Alkaloide V[1]. Verknüpfung von Vobasin mit Dregamin und Tabernaemontanin

Vobasin, $C_{21}H_{24}N_2O_3$, ein Nebenalkaloid aus der Stammrinde von *Voacanga africana* Stapf[2], gehört dem gleichen Spektraltyp an wie Tabernaemontanin, $C_{20}H_{26}N_2O_3$ [3] oder $C_{21}H_{28}N_2O_3$[4], Voacafrin, $C_{22}H_{26}N_2O_4$, Voacafricin, $C_{22}H_{24}N_2O_4$[5] und Dregamin, $C_{21}H_{28}N_2O_3$[6]. Als Chromophor wurde in diesen Stoffen ein Strukturelement der Art eines 2-Phenyl-indols[2] oder eines 2-Acyl-indols[4] vermutet.

Im Vobasin konnte nun eine dem 2-Acylindol entsprechende konjugierte Carbonylgruppe nachgewiesen werden: Vobasin bildet ein granatrotes *2,4-Dinitrophenylhydrazon*, $C_{27}H_{28}N_6O_6$[7], Smp. 172–175° (Zers.), dessen langwellige UV-Absorption (λ_{max}^{MeOH} 217,5; 317 und 413 mμ; log ε 4,43; 3,96 und 4,13) und dessen IR-Spektrum (in CH_2Cl_2 Banden bei 3,03 (NH) und 6,20 (C=N) μ) auf eine stark konjugierte Ketimingruppierung hinweisen. Reduktion von Vobasin mit Kaliumborhydrid führt zu *Vobasinol*, $C_{21}H_{26}N_2O_3$[7], Smp. 100–102° (Solvat), dessen UV-Spektrum demjenigen eines nicht konjugierten 2,3-Dialkylindols entspricht (λ_{max}^{MeOH} 224; 279; 285 und 294 mμ; log ε 4,48; 3,89; 3,90 und 3,85). Die neuentstandene Hydroxylgruppe ist im IR-Spektrum nicht erkennbar, lässt sich aber durch Acetylierung nachweisen: *O-Acetylvobasinol*, $C_{23}H_{28}N_2O_4$[7], Smp. 160–162°, im IR-Spektrum (KBr) Acetylbanden bei 5,73 (CO-Acetat), 8,15 und 9,75 mμ.

Vobasin enthält eine C-Methyl-[2], aber keine C-Äthylgruppe (Mikrochromsäure-Oxydation). Durch Mikrohydrierung[2] sind in Vobasin zwei ungesättigte Gruppierungen nachweisbar, wovon eine mit der Ketogruppe identisch ist. Die andere entspricht einer Äthylenfunktion, die durch selektive Hydrierung abgesättigt werden kann: in Abhängigkeit vom verwendeten Katalysator entsteht aus Vobasin unter Aufnahme von 1 Mol H_2 entweder in nahezu einheitlicher Reaktion Dregamin[8], oder aber ein Gemisch aus Dregamin und Tabernaemontanin (Smp. 215–216°, $[\alpha]_D^{22} = -58°$ in $CHCl_3$), aus dem die reinen Alkaloide[9] durch Gegenstromverteilung und/oder fraktionierte Kristallisation abgetrennt werden können. In Dregamin wie in Tabernaemontanin ist eine C-Methylgruppe als Teil einer C-Äthylgruppierung nachweisbar. Somit ist in Vobasin an der entsprechenden Stelle eine Äthylidengruppe vorhanden. In Übereinstimmung mit der durch zahlreiche Derivate gesicherten Summenformel des Vobasins ergeben die Analysen der Dihydroderivate Dregamin und Tabernaemontanin die Zusammensetzung $C_{21}H_{26}N_2O_3$[7]. Es darf angenommen werden, dass sich diese beiden Alkaloide nur in der räumlichen Lage ihrer Äthylseitenketten unterscheiden.

Während Vobasin bis heute nur in *V. africana* und Tabernaemontanin nur in *Ervatamia coronaria*[3,4,10] gefunden wurden, konnte Dregamin sowohl in *E. coronaria*[4] wie auch in *V. dregei* E.M.[6] festgestellt werden.

Summary. Chemical proof is adduced for the 2-acylindole moiety in vobasine. Reduction of the ethylidene moiety present in vobasine furnishes the diastereomeric 2-acylindole alkaloids dregamine and tabernaemontanine, whose correct molecular composition, $C_{21}H_{26}N_2O_3$, is thus established.

U. RENNER und D. A. PRINS[11]

Wissenschaftliche Laboratorien der J. R. Geigy A.G., Basel, 9. Februar 1961.

[1] IV. Mitt. vgl. U. RENNER und D. A. PRINS, Exper. *17*, 106 (1961).
[2] U. RENNER, Exper. *15*, 185 (1959).
[3] A. N. RATNAGIRISWARAN und K. VENKATOCHALOM, Quart. J. Pharm. Pharmacol. *12*, 174 (1939).
[4] M. GORMAN, N. NEUSS, N. J. CONE und J. A. DEYRUP, J. Amer. chem. Soc. *82*, 1142 (1960).
[5] K. V. RAO, J. org. Chem. *23*, 1455 (1958).
[6] N. NEUSS und N. J. CONE, Exper. *15*, 414 (1959).
[7] Die angegebenen Formeln sind analytisch gesichert. Die Smp. wurden auf dem Kofler-Block bestimmt und sind korrigiert.
[8] Die Identität unseres Dregamins mit dem von NEUSS et al.[6] beschriebenen Alkaloid wurde durch Vergleich der IR-Spektren der freien Basen und der Röntgen-Pulverdiagramme der Basen sowie ihrer Hydrochloride bestätigt. Herrn Dr. NEUSS sei auch an dieser Stelle für die freundliche Durchführung der Vergleichsbestimmungen bestens gedankt.
[9] Vgl. N. NEUSS, *Physical Data of Indole and Dihydroindole Alkaloids*, 4th ed. (Eli Lilly & Co., Indianapolis, Ind., 1960), Nr. 26 und 73.
[10] S. A. WARSI und BASHIN AHMED, Pakistan J. Sci. *1*, 128 (1949).
[11] Den HH. Dres. E. GIROD und H. WAGNER und ihren Mitarbeitern danken wir für Spektren und Mikroanalysen.