The N-hydroxy-imide was treated with toluene-*p*-sulphonyl chloride and then with 1*N* aqueous sodium hydroxide at 95°. This gave two *ketones*, $C_{16}H_{22}O_4$, (A) m.p. 110°, $[\alpha]_D$ – 79° (c, 0.90), $\lambda_{max}^{cyclohexane}$ 252 mμ ($\varepsilon = 4600$), ν_{max} 1860, 1760, and 1695 cm^{-1}, and (B) m.p. 155°, $[\alpha]_D$ + 6° (c, 0.95), $\lambda_{max}^{cyclohexane}$ 255 mμ ($\varepsilon = 5500$), ν_{max} 1845, 1760, and 1686 cm^{-1}. These compounds must be formed according to the sequence (XLVIII) and therefore have two out of the four formulae ((XLIX), (L), (LI), and (LII)). We are currently degrading these ketones further to establish their constitutions and to obtain evidence as to the absolute configuration of byssochlamic acid[27,28].

Zusammenfassung. Die Struktur der Pilzstoffwechselprodukte Glaucon- und Glaucansäure ($C_{18}H_{20}O_7$ bzw. $C_{18}H_{20}O_6$) aus *Penicill. purp.* wird in der Hauptsache durch das Studium der Reduktionsprodukte ermittelt. Diese Verbindungen enthalten zwei fünfgliedrige Säureanhydrid-Gruppierungen, die mit einem eigenartigen doppelt ungesättigten neungliedrigen Ringsystem gekuppelt sind, das unter verschiedenen Bedingungen in das Indangerüst übergeführt werden kann.

Wie schon früher beschrieben, wird Glauconsäure leicht pyrolytisch zu Diäthylacrolein und Glauconin abgebaut. Die Formel des Glauconins, die durch Spektralmessungen und Synthese bewiesen wurde, ist für die Konstitutionsaufklärung der Glauconsäure in gewisser Hinsicht irreführend, da das Kohlenstoffskelett des Glauconins nicht schon in der Glauconsäure vorliegt, sondern erst durch eine Umlagerung unter Bildung neuer C–C-Bindungen bei der Spaltung der Glauconsäure entsteht.

Die Biogenese der beiden Säuren wird diskutiert; sie scheint auf der Verknüpfung zweier Fragmente mit neun Kohlenstoffatomen und identischem Gerüst zu beruhen. Die Annahme einer andersartigen Verknüpfung der beiden Fragmente führt zu einer möglichen Struktur für Byssochlamsäure, $C_{18}H_{20}O_7$. Die so abgeleitete Konstitution wird durch röntgenkristallographische Strukturbestimmung bestätigt.

Byssochlamsäure, aus *Byssochlamys fulva*, enthält ebenfalls ein neungliedriges, doppelt ungesättigtes Ringsystem sowie zwei fünfgliedrige Säureanhydrid-Gruppierungen und zeigt die Tendenz, Indanderivate zu bilden. Ihr chemisches Verhalten wird anhand der durch Röntgenstrahlenkristallographie bestimmten Struktur diskutiert.

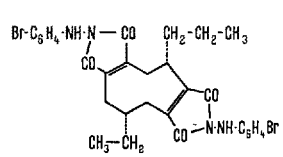
[27] Unless stated otherwise $[\alpha]_D$ were taken in $CHCl_3$, ultraviolet absorption spectra in ethanol and infrared spectra as Nujol mulls. All m.p.s. were determined on the Kofler block. N.M.R. spectra were determined in $CDCl_3$ and τ values given refer to the centre of multiple absorption where present. We thank Dr. J. W. LOWN and Mr. R. G. FOSTER for some of these determinations.

[28] *Acknowledgments.* We express our deep appreciation to Professor H. RAISTRICK, F.R.S., for his constant encouragement and for supplies of glauconic and byssochlamic acids. We thank Professor J. H. BIRKINSHAW, Mr. G. SMITH, and Dr. C. E. STICKINGS for very helpful advice on the culture of *Penicillium purpurogenum* and for facilities generously placed at our disposal. Dr. J. W. COOK, F.R.S., and Dr. J. D. LOUDON kindly permitted us to see, and to quote from, their unpublished experiments. Dr. E. R. S. WINTER of Messrs. J. and E. Sturge (Birmingham) is thanked for the supply of glauconic acid at critical moments. Dr. R. H. B. GALT, Dr. H. HOFMANN, Dr. H. H. A. LINDE, and Dr. J. C. E. PECHER made constructive contributions to attempted syntheses of glauconin and we thank them cordially. Dr. R. I. REED (Glasgow) kindly determined the M.W.s of glauconic acid acetate and of several other compounds described in this communication.

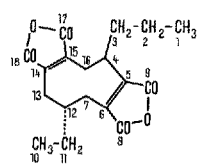
The Structure of Byssochlamic Acid

By T. A. HAMOR, I. C. PAUL, J. MONTEATH ROBERTSON, and G. A. SIM*

Byssochlamic acid, the characteristic metabolite of *Byssochlamys fulva*, was first isolated in 1933 by RAISTRICK and SMITH[1]. In the course of subsequent studies of the related byssochlamic, glauconic, and glaucanic acids BALDWIN, BARTON, BLOOMER, JACKMAN, RODRIGUEZ-HAHN, and SUTHERLAND[2] prepared a beautifully crystalline derivative of byssochlamic acid by reacting it with *p*-bromophenylhydrazine. We have elucidated the crystal structure of this derivative by detailed X-ray analysis and since our results define the constitution and relative stereochemistry of the derivative to be as in (I) it follows that the structure of byssochlamic acid is represented by (II). At the outset of the X-ray study the only chemical information available to us concerning byssochlamic acid was that it contains two anhydride rings and has molecular formula $C_{18}H_{20}O_6$[1,2].



(I)



(II)

* Chemistry Department, The University, Glasgow (Scotland).

[1] H. RAISTRICK and G. SMITH, Biochem. J. *27*, 1814 (1933).

[2] J. E. BALDWIN, D. H. R. BARTON, J. L. BLOOMER, L. M. JACKMAN, Miss L. RODRIGUEZ-HAHN, and J. K. SUTHERLAND, Experientia *18*, 345 (1962).

The *p*-bromophenylhydrazine derivative of byssochlamic acid crystallizes in the tetragonal system, space group $P4_12_12$ (or the enantiomorphous $P4_32_12$). Precession photographs taken with molybdenum Kα radiation ($\lambda = 0.7107$ Å) were analysed to obtain the cell dimensions $a = b = 10.07$, $c = 57.61$ Å. Determination of the crystal density, D (meas.) = 1.505 gcm^{-3},

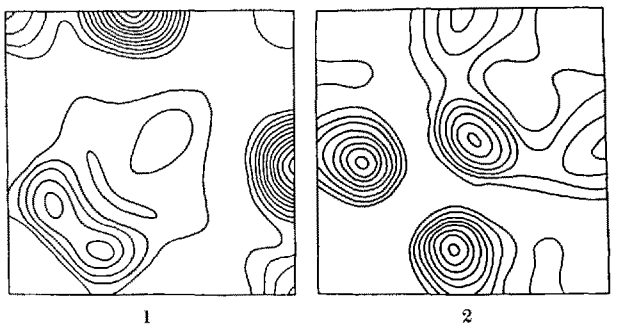


Fig. 1. Section through the three-dimensional sharpened Patterson function $P(uvw)$ at $w = {}^1/_4$. Contour scale arbitrary.
Fig. 2. Section through the three-dimensional sharpened Patterson function $P(uvw)$ at $w = {}^1/_2$. Contour scale arbitrary.

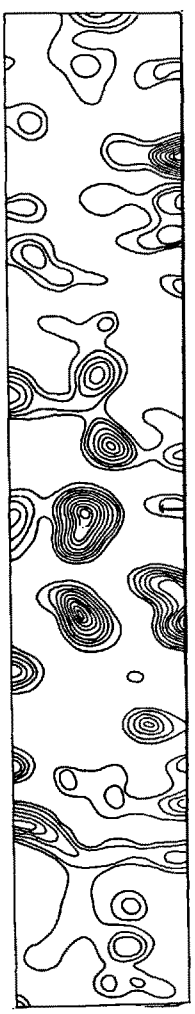


Fig. 3. Section through the three-dimensional sharpened Patterson function $P(uvw)$ at $v = {}^1/_2$. Contour scale arbitrary.

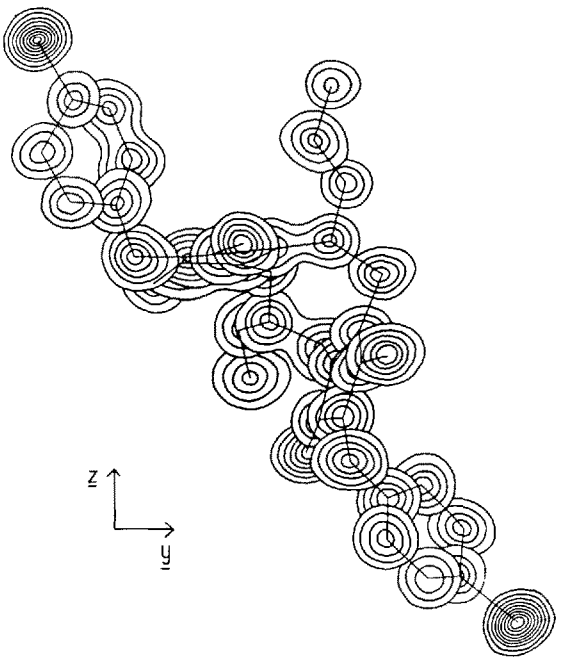


Fig. 4. The eighth three-dimensional electron-density distribution for the *p*-bromophenylhydrazine derivative of byssochlamic acid shown by means of superimposed contour sections drawn parallel to (100). Contour intervals 1 eÅ^{-3} except around the bromine atoms where it is 3 eÅ^{-3}.

showed that each molecule of byssochlamic acid had reacted with two molecules of *p*-bromophenylhydrazine; with eight molecules of $C_{30}H_{30}N_4O_4Br_2$ in the unit cell D (calc.) = 1.524 gcm^{-3}. In the space group $P4_12_12$ there are eight equivalent positions and the asymmetric crystal unit therefore consists of one molecule of $C_{30}H_{30}N_4O_4Br_2$. For the intensity measurements the X-ray reflexions were recorded on equi-inclination Weissenberg photographs taken with copper Kα radiation ($\lambda = 1.5418$ Å); in all 1128 independent structure amplitudes were evaluated.

The crystal-structure analysis proceeded on the basis of the usual phase-determining heavy-atom method[3]. In order to determine the positions of the bromine atoms in the asymmetric crystal unit we first calculated the three-dimensional sharpened Patterson function $P(uvw)$. The special (Harker) sections at $w = {}^1/_4$, $w = {}^1/_2$, and $v = {}^1/_2$, which contain peaks representing vectors between symmetry-related bromine atoms, are shown in Figures 1, 2, and 3, respectively. From a study of these sections and of the general Patterson peaks corresponding to vectors between non-related bromine atoms the positions of the two independent bromine atoms were deduced as

	x	*y*	*z*
Br(1)	0.643	0.372	0.532
Br(2)	0.887	0.456	0.266

[3] J. M. Robertson and I. Woodward, J. chem. Soc. *1937*, 219; *1940*, 36.—G. A. Sim, *Computing Methods and the Phase Problem in X-Ray Crystal Analysis* (Ed. by R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon Press, Oxford 1961), p. 227.

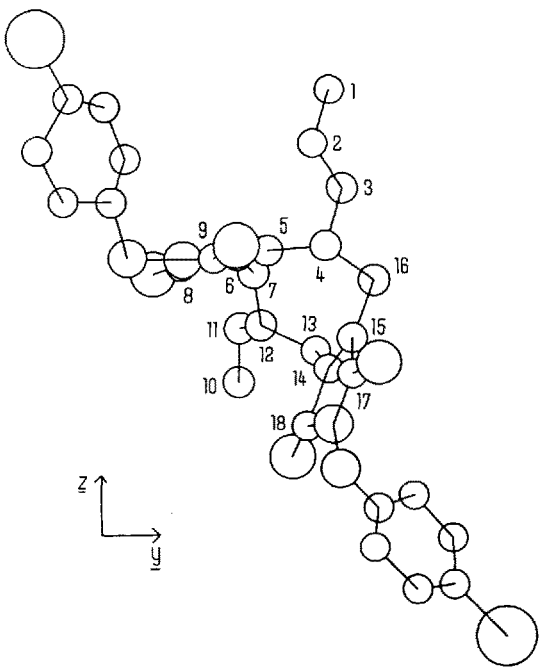


Fig. 5. Atomic arrangement corresponding to Figure 4.

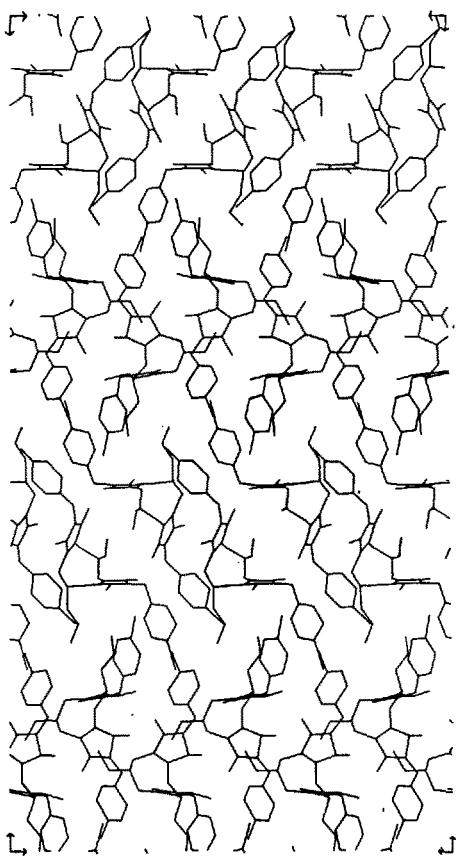


Fig. 6. Line drawing of the molecular framework of several unit cells projected along *a*.

The standard Fourier programme[4] for the DEUCE computer cannot be used in a straightforward manner when the space group $P4_12_12$ is involved. To overcome this difficulty the unit cell was treated in subsequent calculations as if it belonged to the orthorhombic space group $P2_12_12_1$ with two molecules in the asymmetric crystal unit.

The first Fourier synthesis was evaluated with the measured values of the structure amplitudes and phase angles appropriate to the bromine atoms alone. When the resulting three-dimensional electron-density distribution was drawn out sixteen atoms other than the bromine atoms were sufficiently well defined to be included in the calculation of an improved set of phase angles. These phase angles were used in turn to derive an improved electron-density distribution in which further atoms could be discerned. This iterative process of structure-factor and Fourier calculations with increasing numbers of atoms included in the structure-factor (phasing) calculations as they became clearly defined on the electron-density maps was continued and eventually all the atoms, other than hydrogen, in the asymmetric crystal unit were located. The eighth three-dimensional electron-density distribution over one molecule of the *p*-bromophenylhydrazine derivative of byssochlamic acid is shown in Figure 4 by means of superimposed contour sections drawn parallel to (100). The atomic arrangement corresponding to this electron-density distribution is illustrated in Figure 5. Some idea of the mutual arrangement of the molecules in the unit cell is given by Figure 6 which shows a line drawing of the molecular framework of several unit cells projected along the *a* axis.

The average discrepancy between calculated and observed structure amplitudes at the present stage is 18.1% and the atomic co-ordinates yield generally satisfactory bond lengths and valency angles[5].

Zusammenfassung. Die Struktur des *p*-Bromphenylhydrazids der Byssochlamsäure, des charakteristischen Stoffwechselproduktes von *Byssochlamys fulva*, wurde durch dreidimensionale Röntgenanalyse bestimmt. Die Resultate stellen eine Bestimmung der Konstitution und Stereochemie (abgesehen von der absoluten Konfiguration) des *p*-Bromphenylhydrazids als (I) und demnach der Byssochlamsäure als (II) dar.

[4] J. S. ROLLETT, *Computing Methods and the Phase Problem in X-Ray Crystal Analysis* (Ed. by R. PEPINSKY, J. M. ROBERTSON, and J. C. SPEAKMAN, Pergamon Press, Oxford 1961), p. 87.

[5] *Acknowledgments.* We are grateful to Professor D. H. R. BARTON, F.R.S., for suggesting the problem, and for making available supplies of the *p*-bromophenylhydrazine derivative. The calculations were carried out on the Glasgow University DEUCE computer using programmes devised by Dr. J. S. ROLLETT and Dr. J. G. SIME. We thank the Carnegie Trust for a Scholarship (to I. C. P.) and the University of Glasgow for an I.C.I. Research Fellowship (to T. A. H.).