Liquid Crystals

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First carbohydrate liquid crystals of columnar structure†

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S, S-Dialkylacetals of aldoses, tripodal in structure and recently synthesized in large numbers by three groups, do not exhibit thermotropically a smectic, but a columnar hexagonal mesophase (Hx) as we have proved by X-ray diffraction. The molecular organization in this mesophase is comparable with a similar one known for phasmidic molecules. These various multiols, although different in stereochemistry, form only one type of hydrogen-bonded disc-shaped multimer. Its mesophase structure is made up of about five molecules placed in columns with a skeleton of hydrogen-bridged sugar parts surrounded by thioalkyl groups in the periphery. Since three 6-deoxy sugar dithioacetals were shown to be non-thermomesomorphic the terminal hydroxyl function is essential for this molecular arrangement which seems not to be true for missing ones in the inner part of a sugar chain, as we have found in one case.

1. Introduction

Of the about 25 000 thermotropic mesogens synthesized and studied since the beginning of the liquid crystal research 100 years ago [1–3], there are not many derived from naturally occuring compounds as, for example, from cholesterol [1, 2, 4, 5] sugars [6–19], and inositols [8, 9, 20]. The members of this slowly growing subgroup also exhibit nematic, cholesteric, smectic or, in the case of derivatives of inositols [8, 9, 20] only, even discotic phase structures which, as usual, have been identified by their optical properties and/or by X-ray diffraction.

Hitherto, only carbohydrate liquid crystals with one alkyl chain (mono-tailed sugar mesogens) had been reported and all of them examined so far are of the smectic A type [11]. However, for about a year or so numerous other sugar derivatives, acyclic, tripodal in structure, and with two thioalkyl groups in geminal arrangement (double-tailed sugar mesogens) as shown by the selected examples in figure 1, have become known [15, 17, 18] which exhibit thermotropically an isomorphous, viscous mesophase. But, this mesophase is of another type to those so far known in the field of carbohydrate derivates. In contrast to two other statements [15, 17] in which the mesophase was assigned as smectic B^{15} or smectic A_d^{17} respectively, we can exclude these two possibilities on the basis of our findings which are a result of intensive microscopic studies [18].

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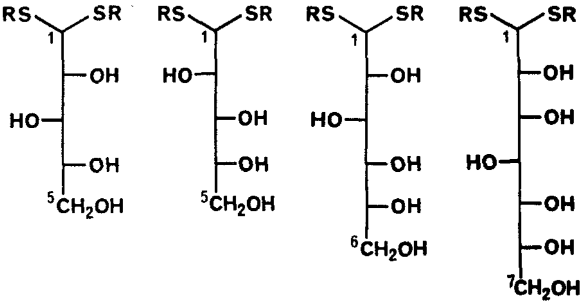
†Part XLIX on liquid crystalline and part LXXX on organic sulphur compounds; for parts XLVIII or LXXIX, see PRAEFCKE, K., KOHNE, B., GUTBIER, K., JOHNEN, N, and SINGER, D., 1989, *Liq. Crystals*, **5**, 233; and PRAEFCKE, K., KOHNE, B., and KRAUSE, J., 1988, pat. appl. P 3827046.3, 10 August 1988, by E. Merck, patent GmbH, Darmstadt, F.R. Germany, respectively.



1 **2** **3a–c** **4**

Figure 1. The formulas and sterochemistry of the six dialkyl dithioacetals [18], each tripodal in structure, studied here by X-ray diffraction: (1) 1 and 2, derivatives of the pentoses D-xylose and D-arabinose; (2) 3a–c, three derivatives of D-glucose; (3) 4, a derivative of D-gluco-D-guloheptose. Their phase transition temperatures [18] (°C, microscopic/thermoanalytic) and enthalpies [18] (kJ/mol given in parentheses) are:

Dithioacetal	*R*	C†		Hx‡		I§
1	C_8H_{17}	●	36·0/ 38·2 (39·3)	●	85·8/ 84·4 (1·5)	●
2	C_8H_{17}	●	92·1/ 92·8 (31·8)	●	100·7/100·8 (1·6)	●
3a	C_7H_{15}	●	102·6/102·8 (48·6)	●	104·6/104·6 (1·4)	●
3b	C_8H_{17}	●	102·4/102·4 (49·2)	●	117·6/117·6 (1·4)	●
3c	C_9H_{19}	●	101·6/101·4 (50·2)	●	125·8/125·9 (1·5)	●
4	C_8H_{17}	●	120·4/119·2 (44·1)	●	162·6/162·5 (1·6)	●

†The highest melting solid modification obtained after suitable thermal treatment, e.g. tempering or second heating. These dithioacetals exhibit a rich multimorphism in the sold state.

‡Hx = hexagonal columnar mesophase.

§I = isotropic phase.

For the applied instruments see [18]

In this paper we now present the results of X-ray diffraction studies of selected members **1**, **2**, **3a–c**. and **4** of our extensive series of the carbohydrate dithioacetals, published recently [18], which clearly give evidence for the columnar hexagonal type of their mesophase.

2. Results and discussion

The powder patterns for the five dithioacetals **1**, **2**, **3b**, **c** and **4** have been performed with a Guinier camera, whereas that for the glucose derivative **3a** has been recorded only with a point focus geometry because of its short mesophase range. All of the patterns for the mesophase of these dithioacetals are similar: three sharp rings at small angles and one diffuse ring for a scattering angle of about 20°; an example is shown in figure 2 for the D-glucose *S*,*S*-acetal **3b**. Since the lattice spacings corresponding to the three sharp rings are in the ratios 1, $1/\sqrt{3}$, and $1/\sqrt{4}$, their diffraction pattern is that of a hexagonal columnar mesophase. The unique diffuse ring is indicative of the disordered state of both the sugar chain and the geminal thialkyl groups. The columnar character is confirmed by the diffraction pattern of aligned samples, see figure 3(*c*) and (*d*). All of the diffraction rings of the two-dimensional hexagonal lattice lie in a plane perpendicular to the stretching direction,

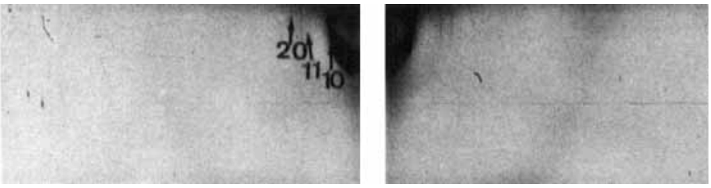


Figure 2. X-ray diffraction powder pattern of the mesophase of D-glucose *S*, *S*-dioctyl acetal (**3b**).

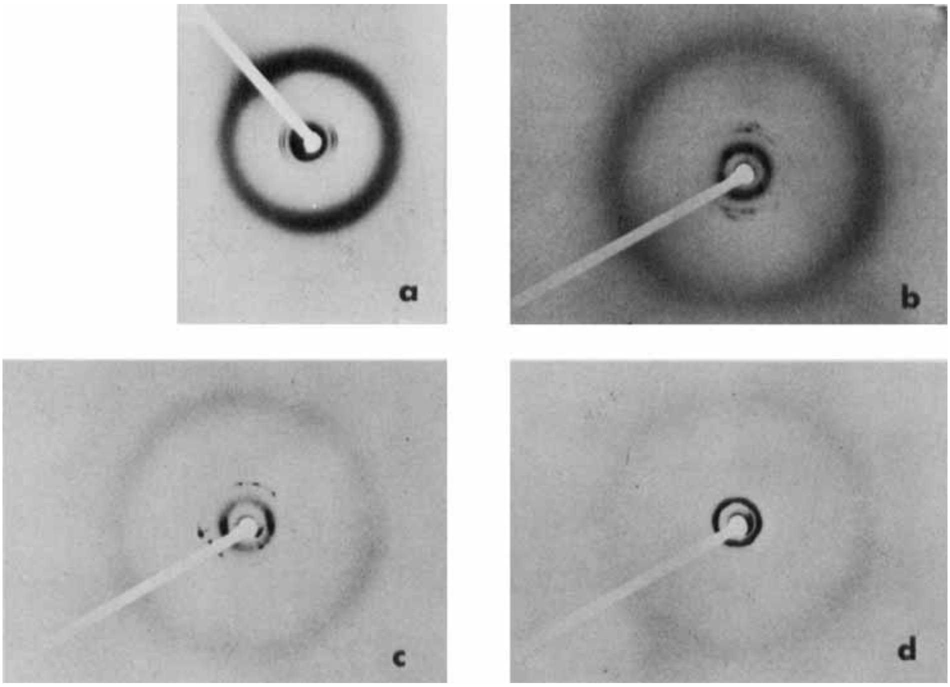


Figure 3. Examples of X-ray diffraction patterns of the aldose *S*, *S*-dialkyl acetals **1**, **2**, **3a** and **c** (compare figure 1) obtained with a point focusing geometry: (a) **1**, $T = 46°\mathrm{C}$, film to sample distance (f.t.s.d.) 40 cm; (b) **2**, $T = 98°\mathrm{C}$, f.t.s.d. 67 cm; (*c*) **3a**, $T = 104°\mathrm{C}$, f.t.s.d. 67 cm; (*d*) **3c** $T = 114°\mathrm{C}$, f.t.s.d. 67 cm. Comment: Two spots of very low intensity are seen close to the shadow of the beam stop on pattern *b*. They result from λ Cu Kα/2 X-ray reflection by the sample. Such a wavelength is selected from the continuous spectra of the target by the monochromator used in these experiments.

whereas the the outer diffuse ring is nearly isotropic: therefore, the column axis is parallel to the stretching direction, but, the orientational order of the chains is very poor. The hexagonal symmetry can be seen easily on some other patterns, e.g. figure 3 (*a*) and (*b*).

The table gives the lattice parameter *a* for the hexagonal networks of these compounds as measured from powder patterns. The unit cell parameter *a* equals the column diameters. In order to compare the different molecules we have reported the specific areas A/M, in which $A = a^2 \sqrt{3}/2$ stands for the column cross sectional area, and M is the molecular weight. As it has been noted [21] the equation $Ad/M = 1/\varrho$ relates the mean distance d between two molecules along the column axis to ϱ the

Table 1. Lattice parameter (measured on X-ray diffraction powder patterns) for the hexagonal networks of six selected aldose dithioacetals: **1**, **2**, **3a–c**, and **4** as shown in figure 1.

Aldose dithioacetal	Unit cell parameter $a/\text{Å}$	Specific area† $(A/M)/\text{cm}^2\ \text{g}^{-1}\ 10^{-8}$	Distance‡ $d/\text{Å}$
1	29·6	1·09	0·92
2	28·5	1·01	0·99
3a	28·4	0·96	1·04
3b	30·0	1·04	0·96
3c	30·7	1·06	0·94
4	32·1	1·12	0·89

†Unit cell area $A = a^2\sqrt{3}/2$, M = molecular weight. -

‡Mean axial molecular distance along the column axis assuming a specific gravity $\varrho = 1\,\text{g}\,\text{cm}^{-3}$.

specific gravity of the mesophase. If we assume that the specific gravity ϱ is nearly independent of the member of our series of compounds and equal to $\varrho = 1\,\text{g}\,\text{cm}^{-3}$ the mean linear intermolecular distance varies between 0·89 and 1·04 Å. Since a realistic distance between two molecules is about 4·6 Å, 4·7 molecules are expected to be located at the same level in a column slice of 4·6 Å. The sugar chains form the central part of the column whereas the thioalkyl groups are located in its peripheric zone (see figure 4).

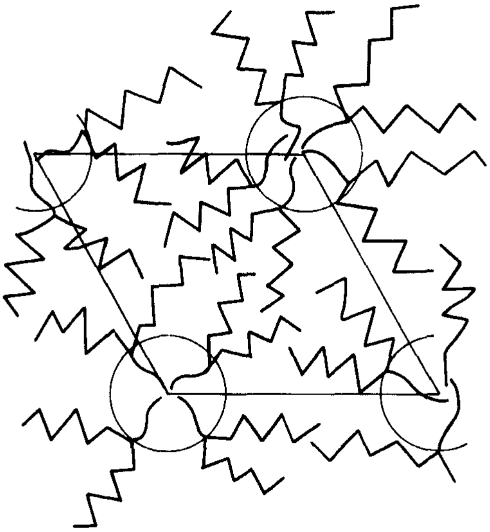
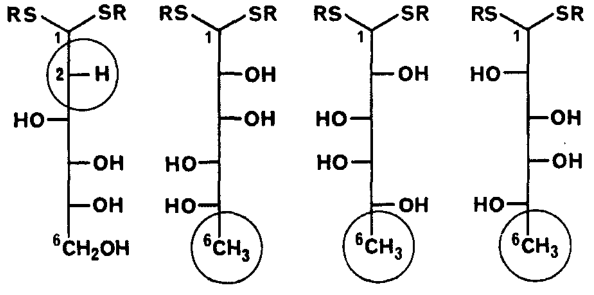


Figure 4. Schematic representation of the molecular array of the thermomesomorphic aldose dithioacetals of figure 1 in their columnar hexagonal mesophase.

In principle, more information could be extracted from the dependence of the lattice spacing versus the length of the alkyl chain or of the radius of the core formed by the sugar parts, respectively. But, since the increment in these two lengths is to small, dependable information cannot be derived from our present measurements. Let us just remark that if we assume that the mean volume of a methylene unit in this series is similar to that of discotic compounds (27 Å^3) [23], the radius of the sugar part should vary between 9·6 Å for the shortest sugar derivative and 11·4 Å for the largest one.

In conclusion, these X-ray diffraction results on a few selected members of this new family of liquid-crystalline sugar derivatives [18] as shown in figure 1 not only support our opinion, published recently [18], about their novel type of mesophase in the field of carbohydrates, developed from results obtained by polarizing microscopy, but, now prove their columnar hexagonal character unambiguously, as has been established already for liquid crystals of discotic [22] or phasmidic [21, 23] systems. Relative to the tripodal molecular architecture and orientational order of most of our sugar derivatives their molecular organization is comparable with that of phasmidic molecules in their columnar phases.

It is interesting to point out that a missing OH-function at the inner part of the sugar chain effects the capability to form the columnar hexagonal mesophase only slightly; see for instance the 2-deoxy example **5** (see figure 5) in comparison to **3b** (see figure 1) and to the corresponding dithioacetal of D-mannose [18] (C 114·1/114·4 Hx 143·1/143·0 I; °C, microscopically/thermoanalytically determined temperatures). On the other hand, a comparison of the clearing temperature of the 2-deoxy hexose derivative **5** with that of the corresponding pentose dithioacetal **2**, the stereochemistry and length of the hydrophilic part of these two tetrols are identical as shown in the figures 1 and 5, demonstrates the influence of a chain prolonging methylene group in the lipophilic part on the mesophase stability of this new type of sugar liquid crystals: the clearing temperatures (Hx → I) of **5** is increased over **2**



5 **6** **7** **8**

Figure 5. The formulas and sterochemistry of the four deoxy dioctyl dithioacetals **5**–**8**[18](R = C_8H_{17}) derived from 2-deoxy-D-glucose, 6-deoxy-L-rhamnose, 6-deoxy-D-fucose, or -L-fucose, respectively. The deoxy position in the tripodal structures are marked with circles. Their phase transition temperatures [18] (°C, microscopic/ thermoanalytic) and enthalpies [18] (kJ/mol given in round parentheses) are:

Dithioacetal	C†		Hx‡		I§
5	●	111·6/112·4 (57·0)	●	117·5/117·7 (1·8)	●
6	●	114·3/113·6 (48·1)	—		●
7	●	128·3/129·3 (51·1)	—		●
8	●	128·3/129·1 (52·4)	—		●

†The highest melting solid modification obtained after suitable thermal treatment, e.g. tempering or second heating. These dithioacetals exhibit a rich multimorphism in the sold state.

‡Hx = *hexagonal columnar mesophase*.

§I = isotropic phase.

For the applied instruments see [18]

by about 17 K. An analogous, even though weaker stabilizing effect by increasing the lipophilic chain length on the other side of the centre (C-1) of the molecule, now in the S-alkyl groups, can be seen in the homologous series of the D-glucose *S*, *S*-dialkyl acetals **3a–c** (figure 1 and [18]).

In contrast to the foregoing discussion, the presence of a terminal hydroxyl group in the sugar chain is essential for the occurrence of the columnar hexagonal (Hx) mesophase among such carbohydrate derivatives! In addition to one case (**6**, a dithioacetal of L-rhamnose), reported earlier [17, 18], the two new 6-deoxy dithioacetals **7** and **8** of D- and L-fucose, respectively, are non-thermomesomorphic too (see figure 5), which strongly supports our statement given before [18]. For example, from a mixture (clearing point 116·8°C) containing 20·8 mol % of the D-fucose derivative **7** and 79·2 mol % of the corresponding D-galactose derivative [18] (clearing point 141·9°C) we could derive via a linear extrapolation, assuming an ideal miscibility between the mesophase of the D-galactose dithioacetal and the potential mesophase of **7**, a virtual clearing point of 21·2°C for the pure **7**. Therefore, we consider the D-fucose dithioacetal **7** as non-mesomorphic; a 1 : 1 mixture with its L-isomer **8** melts at 126·4°C into the isotropic liquid.

These multiols represent a fascinating group of compounds which all form one type of multimer with liquid-crystalline properties, apparently based on hydrogen-bonded structures and arranged in columns. At least the influence of the stereochemistry, the number and positions of OH-functions at the hydrophilic part of this or similar types of carbohydrate derivatives on their ability for hydrogen-bond supported mesophase formation deserves further investigations.

3. Experimental

(1) The preparation of the D- and L-fucose *S*, *S*-dioctyl acetals **7** and **8** was carried out according to a known procedure [24] starting each from 1·00 g (6·1 mmol) D- or L-fucose, respectively. The raw materials obtained were recrystallized from ethanol yielding 0·46 g (17 per cent) **7** or 1·66 g (62 per cent) **8**, respectively. Their purities determined by D.S.C. (Mettler TA 3000/DSC 30 S) were up to 99·17 mol % for **7** and 99·76 mol % for **8**. Their phase transition data are summarized in figure 5, the values of the specific rotation (Perkin–Elmer 241 MC, $c = 1{\cdot}6$ [g/100 ml, DMSO]) $[\alpha]_D^{25}$ are: **7** −10·8° and **8** +11·1°. The following selected spectroscopic data support the two enantiomeric structures: (1) MS (Varian MAT 711) (a) **7**, DI at 155°C: m/z (per cent) = 438 (M^+, 4), 303 (M − C_5–sugar chain, $C_5H_{11}O_4$, α-cleavage, 100), identical with (*b*) **8**, DI at 145°C; (2); selected ^{1}H N.M.R. data (Bruker, 400 MHz, DMSO-d_6): δ (**7** ≡ **8**) = 2·59 (m; SCH_2), 1·08 (*d*, $J \approx 6{\cdot}5$ Hz; CH_3 at C-6) ppm; (3) selected ^{13}C N.M.R. data (Bruker, 270 MHz, DMSO-d_6): δ (**7** ≡ **8**) = 55·28 (*d*; C-1), 65·28, 69·74, 71·82, and 73·08 (4 ds; the 4 inner C-atoms of the sugar chain), 20·09 (*q*; C-6). Satisfactory elemental analyses were obtained (Perkin–Elmer 240 C Elemental Analyser).

(2) X-ray diffraction experiments. Two kinds of X-ray patterns have been recorded. (*a*) Powder patterns were obtained using a Guinier camera: the beam was provided by a linear focus (8 • 0·015 mm) tube with a copper target; a Johannson quartz crystal selected the CuKα_1 radiation; the sample was held in a Lindemann glass tube of 1 mm diameter rotating along a vertical axis parallel to the linear source; the temperatures of the samples were maintained to within ± 1 K; the diffraction pattern is recorded on a photographic film. With this device, the accuracy for

the measurement of the scattering angle is ± 0.02°. (*b*) Using a point focus geometry with a double bent graphite monochromator we can obtain diffraction patterns of oriented samples. The sample was in a fixed position and maintained at a constant temperature to within ± 0·2 K. With the compounds studied here we were able to obtain two kinds of orientations: the sample is held in a capillary tube, by cooling the sample from the isotropic liquid the mesophase can grow in large domains and therefore very few monodomains are illuminated by the X-ray beam (see figure 3(*b*), (*d*)). At a sufficiently low temperature the mesophase is very viscous and spreading the mesophase on the glass tube walls gives an aligned sample with the optic axis parallel to the stretching direction.

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References

[1] Reinitzer, F., 1888, *Mh. Chem.*, **9**, 421.

[2] Lehmann, O., 1889, *Z. phys. Chem.*, **4**, 462.

[3] On the History of liquid crystals see Kelker, H., 1973, *Molec. Crystals Liq. Crystals*, **21**, 1, as well as Knoll, P. M. and Kelker, H., 1988, *Otto Lehmann Erforscher der flüssigen Kristalle—Eine Biographie mit Briefen an Otto Lehmann*, copyright 1988, P. Knoll, Ettlingen and H. Kelker, Frankfurt. Kelker, H., and Knoll, P. M., 1989, *Liq. Crystals*, **5**, 19.

[4] Kelker, H., and Hatz, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemié, Deerfield Beach). Gray, G. W. (editor), 1987, *Thermotropic Liquid Crystals* (John Wiley & Sons Ltd.).

[5] Here it may be of interest to note that esters of the unnatural 19-norcholesterol exhibit wider cholesteric phase ranges than corresponding cholesteryl esters; see Sucrow, W., and Howard, S., 1985 *Chem. Ber.*, **118**, 4341.

[6] Fischer, E., and Helferich, B., 1911, *Liebigs Ann. Chem.*, **383**, 68, as well as liquid crystal investigations by Noller, C. R., and Rockwell, W. C., 1938, *J. Am. chem. Soc.*, **60**, 2076.

[7] Goodby, J. W., 1984, *Molec. Crystal. liq. Crystals*, **110**, 205.

[8] Praefcke, K., *et al.*, 1984–1988 (unpublished results).

[9] Kohne, B., and Praefcke, K., 1985, *Chemiker-Ztg.*, **109**, 121.

[10] Marcus, M. A., 1986, *Molec. Crystals liq. Crystals.*, **3**, 85.

[11] Jeffrey, G. A., 1986, *Accts chem. Res.*, **19**, 168, and earlier papers of J., G. A. cited here.

[12] Köll, P., and Oelting, M., 1986, *Angew. Chem.*, **98** 362, or 1986, *Angew. Chem. Int. Ed. Engl.*, **25**, 368, and 1986, *Tetrahedron Lett.*, **27**, 2837.

[13] Pfannemüller, B., Welte, J., Chin, E., and Goodby, J. W., 1986, *Liq. Crystals.*, **1**, 357.

[14] Kjaer, A., Kjaer, D., and Skrydstrup, T., 1986, *Tetrahedron*, **42**, 1439.

[15] Dahlhoff, W. V., 1987, *Z. Naturf.* (*b*), **42**, 661, and earlier papers of D., W. V. cited here.

[16] Morris, N. L., Zimmermann, R. G., Jameson, G. B., Dalziel, A. W., Reuss, P. M., and Weiss, R. G., 1988, *J. Am. chem. Soc.*, **110**, 2177.

[17] van Doren, H., Buma, T. J., Kellogg, R. M., and Wynberg, H., 1988, *J. chem. Soc. Chem. Commun.*, 460. van Doren, H. A., van der Geest, R., Keuning, C. A., Kellogg, R. M., and Wynberg, H., 1989, *Liq. Crystals*, **5**, 265.

[18] Eckert, A., Kohne, B., and Praefcke, K., 1988, *Z. Naturf.* (*b*), **43**, 878.

[19] Goodby, J. W., Marcus, M. A., Chin, E., Finn, P. L., and Pfannemüller, B., 1988, *Liq. Crystals*, **3**, 1569.

[20] Kohne, B., Praefcke, K., Ringsdorf, H., and Tschirner, P., 1989, *Liq. Crystals*, **4**, 165, and earlier papers by K. Praefcke *et al.* cited therein.

[21] LEVELUT, A.-M., MALTHÊTE, J., DESTRADE, C., and NGUYEN, H. T., 1987, *Liq. Crystals*, **2**, 877.
[22] LEVELUT, A.-M., 1983, *J. Chim. phys.*, **80**, 149.
[23] MALTHÊTE, J., NGUYEN, H.T., and LEVELUT, A.-M., 1986, *J. chem. Soc. Chem. Commun.*, 1540.
[24] GAUTHIER, B., and VANISCOTTE, C., 1956, *Bull. Soc. chim. Fr.*, 30, see also reference [18].