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MESOGENIC ANDROSTANE DERIVATIVES

By

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A homologous series of 4-alkoxybenzoic acid diesters with androst-5-ene-3β,17β-diol have been prepared and their mesogenic properties studied.

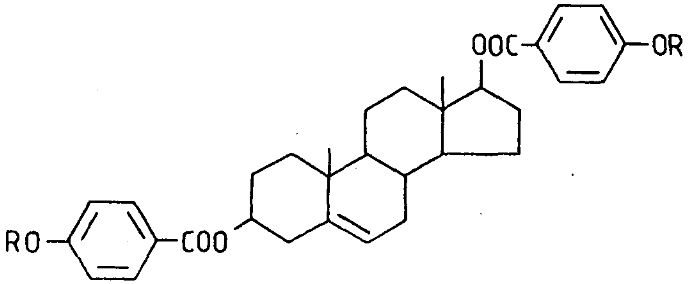
The literature contains a number of publications relating to the effects of the structure of the 17β-side-chain of sterols on the mesogenic properties of these compounds [1-3]. Most of these investigations concern the structural requirements of the cholesterol-like molecules, and relatively few articles deal with other biologically important steroidal compounds.

Therefore, we have synthetized a homologous series of diester derivatives of androst-5-ene-3β,17β-diol with 4-alkoxybenzoic acids, which are well-known mesogenic compounds. All compounds prepared exhibited mesogenic properties in relatively wide ranges of temperature. In the case of lower alkoxy derivatives, only a relatively simple phase sequence appeared: Cr——Ch——I (from methoxy- to heptyloxybenzoic acid esters), while for higher homologues the cholesteric mesophase was accompanied by a monotropic smectic phase. These derivatives showed the characteristic light reflexion. The cholesteric mesophases had oily-streaks in the textures, while the smectic phases appeared as

Table I

Thermal data from polarizing microscopic measurements on compounds investigated

Compound	R	Cr		S		Ch		I
1	methyl	•	198	•		•	277	•
2	ethyl	•	215	•		•	265	•
3	n-propyl	•	214	•		•	236	•
4	n-butyl	•	165	•		•	218	•
5	n-pentyl	•	110	•		•	155	•
6	n-hexyl	•	102	•		•	175	•
7	n-heptyl	•	103	•		•	173	•
8	n-octyl	•	105	•	(84)	•	165	•
9	n-nonyl	•	110	•	(82)	•	154	•
10	n-decyl	•	110	•	(84)	•	146	
11	n-undecyl	•	112	•	(108)	•	129	



Compounds $\underline{\underline{1}}$-$\underline{\underline{11}}$

(R varies from methyl to n-decyl)

schlieren textures. In the calorimetric measurements, all compounds showed nearly the same phase-transition temperatures as observed optically with a polarizing microscope in the case of the crystalline-cholesteric and the cholesteric-smectic transitions, but no thermal effect appeared at the cholesteric-isotropic transition. Therefore, this transition is considered to be of a higher (infinite)-order type [4]. The optically observed transition temperatures are listed in Table 1.

At higher temperatures (about 200 °C), the samples decomposed slowly (the 17 β -ester pyrolyzed) when the isotropic liquid state was reached. In the cholesteric region qualitative TLC observation indicated that the decomposition was absent.

Experimental

All esters were prepared in the usual way from specially purified 4-n-alkoxybenzoic acids [5] via the acid chlorides and androst-5-ene-3β,17β-diol in dry pyridine solution at room temperature. In the crude esters were contaminated with the corresponding acid anhydrides, which were hydrolyzed by boiling in aqueous pyridine solutions.

These samples were purified by low-pressure column chromatography on Kieselgel G (Merck) adsorbents, and were crystallized from rectified spirit. The purities were checked on precoated TLC plates (Kieselgel HF, Merck). The analytical data on compounds 1-11 are shown in Table 2. The IR and NMR spectra of the compounds were recorded with Carl Zeiss Jena 75/IR and JEOL 60 HL NMR spectrometers. The calorimetric investigations were performed with a Perkin-Elmer DSC-2 instrument. Microscopic investigations were conducted on a PMHK-5 (Dresden) hot-stage.

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Table II

Analytical data on compounds 1-11

Compound	Formula	Calcd.		Found	
		C	H	C	H
1	$C_{35}H_{42}O_6$	75.24	7.58	75.11	7.57
2	$C_{37}H_{46}O_6$	75.74	7.90	75.40	7.77
3	$C_{39}H_{50}O_6$	76.19	8.20	76.00	8.03
4	$C_{41}H_{54}O_6$	76.60	8.47	76.70	8.51
5	$C_{43}H_{58}O_6$	76.98	8.71	77.03	8.82
6	$C_{45}H_{62}O_6$	77.32	8.94	77.31	8.97
7	$C_{47}H_{66}O_6$	77.64	9.15	77.42	9.21
8	$C_{49}H_{70}O_6$	77.94	9.35	78.11	9.45
9	$C_{51}H_{74}O_6$	78.22	9.53	78.03	9.61
10	$C_{53}H_{78}O_6$	78.48	9.69	78.51	9.48
11	$C_{55}H_{82}O_6$	78.72	9.83	78.83	9.71

References

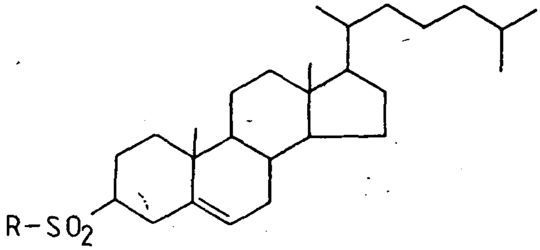
[1] *Gray, G.W.*: Molecular Geometry and the Properties of Non-Amphiphilic Liquid Crystals in Advances of Liquid Crystals (Ed: G.H. Brown) Vol. 2 pp. 62-67. Academic Press, New York (1976).

[2] *Elser, W., Ennulat R.D.*: Selective Reflection of Cholesteric Liquid Crystals, in Advances of Liquid Crystals (Ed: G. H. Brown) Vol. 2 pp. 99-121. Academic Press, New York (1976).

[3] *Demus, D., Zaschke H.*: Flüssige Kristalle in Tabellen. Vol. 1 pp. 276-307 VEB Deutscher Verlag für Grundstoffindustrie. Leipzig (1974). Vol. 2 pp. 408-436. VEB. Deutscher Verlag für Grundstoffindustrie, Leipzig. (1984).

[4] *Kelker, H., Hatz R.*: Handbook of Liquid Crystals Ch. 8. pp. 340-372 Verlag Chemie, Weinheim (1980).

[5] *Gray, G.W., Jones B.*: J. Chem. Soc. 1953, 4199.



Compounds 1-10
(R varies from methyl to n-decyl)

is a monotropic smectic substance, while the higher members (8-10) are enantiotropic smectic. These smectic phases exhibited characteristic focal-conic fan textures, and all of them were supercoolable to various extents, depending on the cooling rate, e.g. at a cooling rate, of about 10°sec^{-1} compounds 8 and 10 supercooled by nearly 30° under the observed C—S transition temperatures, while compound 9 did so by only 10°. The compounds displayed crystal polymorphism, frequently with metastable crystal modofications, e.g. compound 5 has a $Cr_I \longrightarrow Cr_{II}$ transition at about 105-115°, while compound 4 shows three modifications, with transition temperatures of about 110°, 136° and 146°.

Table I

The mesogenic properties of compounds 1-10

Compound	R	Cr		S		I
1	methyl		172	.		.
2	ethyl	.	161	.		.
3	n-propyl	.	157	.		.
4	n-butyl	.	166	.		.
5	n-pentyl	.	173	.		.
6	n-hexyl	.	159	.	(156)	.
7	n-heptyl	.	160	.		.
8	n-octyl	.	137	.	166	.
9	n-nonyl	.	142	.	167	.
10	n-decyl	.	143	.	169	.

Experimental

Preparation of sulphones: To a 0.01 M ethanolic solution of the thioether (about 30 cm^3), 3 cm^3 30 percent H_2O_2 (about 0.026M) and 1 cm^3 1 % aqueous ammonium molybdate solution (about 0.04 M based on $(NH_4)_2MoO_4$) were added. The samples were allowed to stand for 1-5 days at room temperature, then poured onto ice-water and the solid was filtered off, dried, and chromatographed on Kieselgel 60 (Merck) with benzene. The pure fractions were evaporated and crystallized from aqueous ethanolic solution.

The textural investigations were made a PMHK 5 (Dresden) polarizing microscope hot-stage. In the calorimetric measurements, a Perkin-Elmer DSC-2 instrument was applied. The spectra were recorded with Specord 75IR (Jena) and Jeol 60 HL NMR spectrometers.

Table II

Analytical data

Compound	Formula	Calcd. C	Calcd. H	Found C	Found H
1	$C_{28}H_{48}O_2S$	75.00	10.69	75.30	10.62
2	$C_{29}H_{50}O_2S$	75.26	10.81	75.15	10.91
3	$C_{30}H_{52}O_2S$	75.56	10.90	75.48	10.58
4	$C_{31}H_{54}O_2S$	75.85	11.00	75.91	10.93
5	$C_{32}H_{56}O_2S$	76.12	11.10	76.21	11.07
6	$C_{33}H_{58}O_2S$	76.38	11.18	76.05	11.34
7	$C_{34}H_{60}O_2S$	76.62	11.26	76.40	11.53
8	$C_{35}H_{62}O_2S$	76.85	11.33	76.62	11.27
9	$C_{36}H_{64}O_2S$	77.07	11.41	76.78	11.49
10	$C_{37}H_{66}O_2S$	77.28	11.48	76.85	11.61

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References

[1] *Szabó, J.A., A.I. Zoltai, P.M. Agócs and G. Motika*: in Advances in Liquid Crystal Research and Applications (Ed: L. Bata) Pergamon Press, Oxford; Akadémiai Kiadó Budapest (1979) pp. 1049-1058.

[2] *Demus, D. and H. Zaschke*: Flüssige Kristalle in Tabellen Vol. II p. 418, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (1984).

[3] *Kelker, H. and R. Hatz*: Handbook of Liquid Crystals Ch. 2.12. pp. 67-113. Verlag Chemie, Weinheim (1980).

ЖИДКОКРИСТАЛЛИЧЕСКИЕ ХОЛЕСТЕРИЛ-СУЛЬФОНЫ

Й.А. Сабо, А.И. Золтаи, Г. Мотика

Авторы синтетизировали серию тождественных н-алкилзамещенных холестерил-сульфонов и изучили мезогенные свойства этих соединений.