268. *The Partial Esterification of Polyhydric Alcohols. Part XIV. The Iodohydrins.*

By ARTHUR FAIRBOURNE and DAVID WILLIAM STEPHENS.

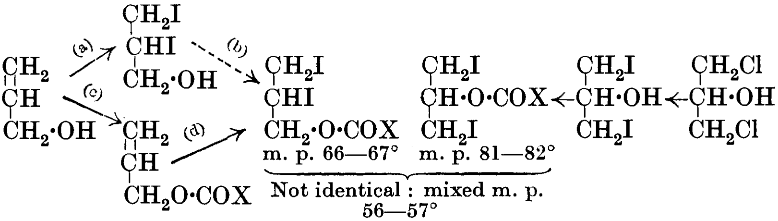
REBOUL is incorrectly reported in Beilstein's " Organische Chemie " (ed. III, **1**, 262; ed. IV, **1**, 475) as having prepared α-monoiodohydrin, d^{13° 2·03, by treating monochlorohydrin with potassium iodide: reference to the original statement cited (*Jahresber.*, 1860,

459) reveals that a preparation of epi-iodohydrin has been mistaken for one of monoiodohydrin, probably owing to a misinterpretation of the old formula "$C_6H_5IO_2$." Abderhalden (*Z. physiol. Chem.*, 1910, **65**, 53) employed an "α-mono-iodohydrin," b. p. 94°/0·3 mm., but gave no description of how it was obtained or identified. Lüders and Emmert (*Deutsch. med. Woch.*, 1915, **41**, 648) concluded that the pharmaceutical product "Alival" is the true α-monoiodohydrin, m. p. 48—49°, and, apparently without realising the nature of Beilstein's mistake (*op. cit.*), noted that the properties of the drug differed from those recorded for this compound in the chemical literature. Fischer and Pfähler (*Ber.*, 1920, **53**, 1606) synthesised α-monoiodohydrin from βγ-*iso*propylidenemonochlorohydrin.

p-Nitrobenzoates of specimens of α-monoiodohydrin obtained from different sources have now been proved identical by the mixed melting point process.

β-Mono-iodohydrin thus remains unknown.

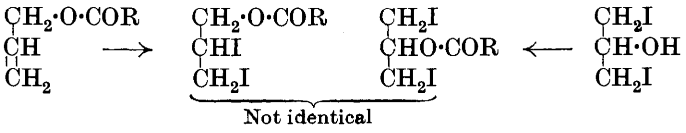
Both di-iodohydrins have been prepared, one by the addition of iodine to allyl alcohol, and the other by the action of potassium iodide on dichlorohydrin. That the products are respectively the αβ- and the αγ-isomeride is now made clear in a similar manner to that adopted by Conant and Quayle (*J. Amer. Chem. Soc.*, 1923, **45**, 2771) and in Part VII (J., 1929, 129) for the establishment of the structures of the corresponding dichloro- and dibromo-hydrins :



[$X = p\text{-}NO_2{\cdot}C_6H_4{\cdot}$]

Owing to the instability of αβ-di-iodohydrin, reaction (b) could not be realised on this occasion.

The laurates, palmitates, and stearates of these isomeric di-iodohydrins have also been prepared, and their identities independently established (compare *Ann. Reports*, 1929, **26**, 76) as follows :



Their melting points are given below, in comparison with those of similar pairs of substituted glycerols which have been identified in this way.

	Unsym.	Sym.	Mixed.	Ref.
Di-iodohydrin *p*-nitrobenzoate	66—67°	81—82°	56—57°	p. 1976
,, laurate	38—39	34—35	29—30	p. 1976
,, palmitate	55	48—49	43	p. 1976
,, stearate	55—56	49—50	46—47	p. 1977
Dibromohydrin *p*-nitrobenzoate ...	57—58	77—78	—	[1]
,, palmitate	34	35·5	28	[2]
Dichlorohydrin *p*-nitrobenzoate ...	35·5—37	58—59	26—48	[3]
,, salicylate	56—58	50	—	[4]
Glycerol mono-*p*-nitrobenzoate ...	107	120—121	—	[5]
,, dibenzoate mono-*p*-nitrobenzoate	114	86—87	—	[6]
,, ,, ,,	113·5—114	89	—	[7]
,, di-*p*-nitrobenzoate monobenzoate	122—123	152—152·5	115	[8]
,, di-*p*-nitrobenzoate monoacetate	129—130	161	110—112	[9]
,, distearate monoacetate ...	59	64	56—58	[10]
,, distearate mono-*p*-nitrobenzoate	74·5	61	60	[11]
,, dimethyl ether *p*-nitrobenzoate	43—44	43	26	[12]
,, monopalmitate :				
(lower-melting form of the α-isomeride)	74—75	68·5	64—66	p. 1977
(higher-melting form of the α-isomeride)	78	69	70—75	[13]

[1] J., 1926, 3146, 3148. [2] J., 1929, 129. [3] Conant and Quayle, *J. Amer. Chem. Soc.*, 1923, **45**, 2771. [4] Humniki, *Rocz. Chem.*, 1931, **11**, 670. [5] Fischer, Bergmann, and Bärwind, *Ber.*, 1920, **53**, 1597; Helferich and Sieber, *Z. physiol. Chem.*, 1928, **175**, 311. [6] Fischer, Bergmann, and Bärwind, *Ber.*, 1920, **53**, 1597; Bergmann, Brand, and Dreyer, *Ber.*, 1921, **54**, 963. [7] Helferich and Sieber, *Z. physiol. Chem.*, 1927, **170**, 31; 1928, **175**, 311. [8] Fischer, *Ber.*, 1920, **53**, 1621; Helferich and Sieber, *Z. physiol. Chem.*, 1927, **170**, 31. [9] Fischer, *Ber.*, 1920, **53**, 1621. [10] *Idem, ibid.* [11] *Idem, ibid.* [12] J., 1931, 445. [13] Bergmann and Carter, *Z. physiol. Chem.*, 1930, **191**, 211.

Fischer noted in the case of three of the four pairs of compounds which he so examined that the symmetrical isomeride melted at the higher temperature. The increased number of examples now available shows that the unsymmetrical compound may melt above, at the same temperature as, or below, its symmetrical isomeride (compare Robinson, Roche, and King, *J. Amer. Chem. Soc.*, 1932, **54**, 705).

EXPERIMENTAL.

α-Monoiodohydrin, $CH_2I\cdot CH(OH)\cdot CH_2\cdot OH$.—A specimen prepared by Fischer and Pfähler's method (*Ber.*, 1920, **53**, 1606) from βγ-*iso*propylidenemonochlorohydrin was proved to be identical with "Alival" by the m. p. of the mixed *p*-nitrobenzoates. Such a proof is the more desirable in consequence of the mistake regarding monoiodohydrin (p. 1973), and of the occasional great similarity in melting point of isomeric glycerol derivatives (see table) (Found : I, 62·6. Calc. for $C_3H_7O_2I$: I, 62·9%).

α-Monoiodohydrin (Fischer and Pfähler, *loc. cit.*) on *p*-nitrobenzoylation gave the di-*p*-nitrobenzoate, m. p. 102° alone or mixed with the di-*p*-nitrobenzoate of " Alival " obtained by Fischer's method (*Ber.*, 1920, **53**, 1625) (Found : I, 25·9. Calc. for $C_{17}H_{13}O_8N_2I$: I, 25·4%).

αβ-*Di-iodohydrin* p-*Nitrobenzoate*, $CH_2I{\cdot}CHI{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$.—To 3 g. of allyl *p*-nitrobenzoate (J., 1926, 3146), 3·5 g. of iodine dissolved in chloroform were added with stirring. After evaporation of the solvent, the residue was washed with *N*/100-sodium hydroxide and then with water, dried with absorbent paper, and recrystallised from alcohol; m. p. 66—67° (decomp.) (Found : C, 26·2; H, 2·2; I, 55·3. $C_{10}H_9O_4NI_2$ requires C, 26·0; H, 2·0; I, 55·1%).

αβ-Di-iodohydrin melted at 43° (compare Hübner and Lellmann, *Ber.*, 1880, **13**, 460; 1881, **14**, 207).

αγ-*Di-iodohydrin* p-*Nitrobenzoate*, $(CH_2I)_2CH{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$.—The pharmaceutical product " Jothion " and αγ-di-iodohydrin (Claus, *Annalen*, 1873, **168**, 21) were *p*-nitrobenzoylated as described by Fischer (*loc. cit.*, p. 1633). Only after repeated treatment with potassium iodide did the latter yield a p-*nitrobenzoate* melting, alone or mixed with that from " Jothion," at 81—82° (Found : I, 55·0. $C_{10}H_9O_4NI_2$ requires I, 55·1%).

αβ-*Di-iodohydrin Laurate*, $CH_2I{\cdot}CHI{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_{11}H_{23}$.—6·2 G. of iodine, added gradually, were ground in a mortar with 10 c.c. of chloroform containing 6 g. of allyl laurate (Rewadikar and Watson, *J. Indian Inst. Sci.*, 1930, **13A**, 132). The product was extracted with ether, washed with dilute sodium thiosulphate solution and with water, dried over sodium sulphate, concentrated, and crystallised at 0°. It formed pale yellow crystals, m. p. 38—39° from ice-cold light petroleum (Found: C, 36·8; H, 5·8; I, 51·8. $C_{15}H_{28}O_2I_2$ requires C, 36·4; H, 5·7; I, 51·4%).

αβ-*Di-iodohydrin palmitate* was prepared in the same way as the laurate, 6 g. of allyl palmitate (J., 1929, 129) being used; pale yellow crystals were obtained from light petroleum and then alcohol, m. p. 55° (Found : C, 41·5; H, 6·8; I, 46·5. $C_{19}H_{36}O_2I_2$ requires C, 41·5; H, 6·6; I, 46·2%).

αγ-*Di-iodohydrin Palmitate*, $(CH_2I)_2CH{\cdot}O{\cdot}CO{\cdot}C_{15}H_{31}$.—7·3 G. of palmitic acid were warmed at 60° with 15 c.c. of thionyl chloride for 1 hour, the excess of the latter removed under reduced pressure, 8·9 g. of αγ-di-iodohydrin (see above) added, and the mixture heated at 60° for 90 minutes. (Decomposition with evolution of iodine occurred at higher temperatures.) The product was extracted, washed (dilute sodium bicarbonate solution), and dried (sodium sulphate) in ether and crystallised from light petroleum and repeatedly from alcohol, forming pale yellow crystals, m. p. 48—49° (Found: C, 41·8; H, 6·7; I, 46·5. $C_{19}H_{36}O_2I_2$ requires C, 41·5; H, 6·6; I, 46·2%).

αβ-*Di-iodohydrin Stearate*, $CH_2I{\cdot}CHI{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35}$.—This was prepared (5 g. of iodine; 20 c.c. of chloroform; 6·5 g. of allyl stearate, *loc. cit.*, p. 131) and purified in the same way as the laurate; it formed pale yellow crystals, m. p. 55—56° (Found: C, 43·7; H, 7·1; I, 44·3. $C_{21}H_{40}O_2I_2$ requires C, 43·6; H, 6·9; I, 43·9%).

αγ-*Di-iodohydrin Stearate*, $(CH_2I)_2CH{\cdot}O{\cdot}CO{\cdot}C_{17}H_{35}$.—(a) 15 G. of stearyl chloride were stirred with a mixture of 4 c.c. of dry pyridine and 4 c.c. of chloroform, and 15 g. of αγ-di-iodohydrin in 10 c.c. of chloroform added, followed, after 12 hours, by water and ether. The extract was washed (sodium carbonate solution; water), concentrated, and repeatedly crystallised from alcohol, giving pale yellow crystals, m. p. 49—50°.

(b) 5 G. of αγ-di-iodohydrin and 5 g. of stearyl chloride were heated at 70—80° for 1 hour; higher temperatures caused decomposition. The product was isolated as above, m. p. 49—50° (Found: C, 43·9; H, 7·1; I, 43·5. $C_{21}H_{40}O_2I_2$ requires C, 43·6; H, 6·9; I, 43·9%).

Glycerol β-*Monopalmitin*, $CH_2(OH){\cdot}CH(O{\cdot}CO{\cdot}C_{15}H_{31}){\cdot}CH_2{\cdot}OH$.—A sample of this compound, m. p. 69°, was kindly sent to one of the authors by Dr. Carter (compare Bergmann and Carter, *Z. physiol. Chem.*, 1930, **191**, 211). Mixed with the monopalmitin described in Part V (J., 1926, 3151), which had m. p. 74—75° in accordance with the lower-melting form observed by Fischer (*Ber.*, 1920, **53**, 1605), it melted at 64—66°. This result confirms the view, stated in Part V, that no true β-monoglyceride had then been isolated, and also supports Dr. Carter's claim that his product has the true β-structure.

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