A REVISION OF THE PENTANOLS.*

BY S. M. GORDON AND EDWARD KREMERS.

The special interest which the plant chemist attaches to these alcohols lies in their biochemical significance. The question is not so much one of wide distribution of amyl alcohol, valeric aldehyde and valeric acid in the plant kingdom, but which of the isomeric primary alcohols with its corresponding aldehyde and acid is thus found. Again, the principal interest lies not only in the occurrence of this group of related compounds with five carbon atoms, but in the possible genesis of compounds with ten carbon atoms that may be derived from one of the iso valeric aldehydes. The peculiar grouping of many compounds with ten carbon atoms found so widely distributed in plants is too significant to be overlooked.[1] In an attempt to make certain which of the isomeric pentanols occurs in peppermint, it was found that our knowledge of this group of alcohols was insufficient to establish the identity of the compound isolated, hence this revision.

The Pentanols.—The alcohols of the formula $C_5H_{11}OH$, known formerly as amyl alcohols, now as pentanols, exist in eight isomeric forms. Of these three contain an asymmetric carbon atom, hence the number of isomers is thus theoretically raised to eleven.

Historical Introduction.—The formula $C_5H_{12}O$ was assigned to the amyl alcohol of fermentation by Dumas in 1834 (*Ann.*, 13, 80), though Scheele had obtained such a product in an impure state as early as 1785 (*Crell's Ann.* (1), 61, 1785). Its analogy with ethyl alcohol was first pointed out by Cahours in 1839 (*Ann.*, 30, 288; *Ibid.*, 35, 312 (1840); *Ibid.*, 37, 164 (1841)), who also assigned to it the name amyl alcohol, because of its supposed relation to starch. This was confirmed by Dumas and Stas in 1840 (*Ann.*, 35, 143) and by others. The optical behavior of amyl alcohol of fermentation was first studied by Biot (*Compt. rend.*, 41, 296 (1855)) and later more particularly by Pasteur (*Ann. de Chem.*, 96, 255 (1855)), Le Bel (*Bull. de la Soc. Chem.* (2), 21, 542 (1874) and 25, 545 (1876)), and Marckwald (*Ber.*, 34, 479 (1901); 35, 1596 (1902), and *Ber.*, 37, 1049 (1904)).

Thus there were foreshadowed, firstly the position of amyl alcohol in the homologous series of alcohols of which ethyl alcohol was the principal member; and secondly, the isomerism of the alcohols $C_5H_{11}OH$ (*Limpricht, Org. Chem.*, p. 125). Kolbe's carbinol hypothesis had already revealed the possibility of primary, secondary and tertiary alcohols (*Kolbe's Lehrbuch*, p. 412 (1856)). These then found complete structural expression in Kekule's structural theory (*Kekule, Lehrbuch*, p. 433 (1861)). From now on it became a question of identifying alcohols $C_5H_{11}OH$, already in hand, with the hypothetical formulas of the carbinol and structural theories, seeking the remaining ones and to prove the correctness of the several assertions by synthesis.

Isomerism.—The isomeric alcohols of the formula $C_5H_{11}OH$ may be arrived at in one of the several ways.

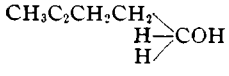
I. According to Kolbe's carbinol hypothesis:

---

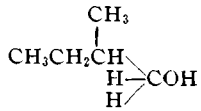
* Read before Scientific Section, A. PH. A., Philadelphia meeting, 1926.

[1] R. E. Kremers, *J. Biol. Chem.*, 50, p. 31 (1923).

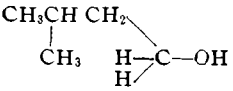
A. Primary: the four butyl carbinols:

a. 

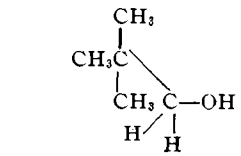
Primary normal butyl carbinol

b. 

Secondary normal butyl carbinol

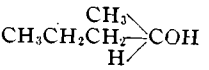
c. 

Primary isobutyl carbinol

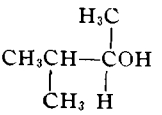
d. 

Tertiary isobutyl carbinol

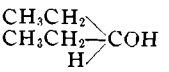
B. Secondary: the two methyl propyl carbinols:



Methyl *p*-propyl carbinol

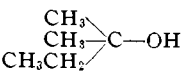


Methyl *s*-propyl carbinol



Diethyl carbinol

C. Tertiary: Dimethyl ethyl carbinol:



II. The methyl homologues of the butyl alcohols.

Butyl alcohols

A. $CH_3CH_2CH_2CH_2OH$
p-n-butyl alcohol

B. $CH_3CH_2CHCH_3$ (OH)
S-N-butyl alcohol

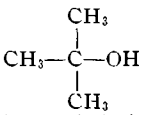
C. $CH_3CH(CH_3)CH_2OH$
p-isobutyl alcohol

Pentyl alcohols

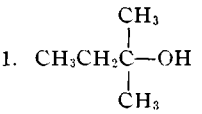
1. $CH_3CH_2CH_2CH_2CH_2OH$
2. $CH_3CH(CH_3)CH_2CH_2OH$
3. $CH_3CH_2CH(CH_3)CH_2OH$
4. $CH_3CH_2CH_2CH(CH_3)OH$

1. $CH_3CH_2CH_2CH(OH)CH_3$ = A, 4
2. $CH_3CH(CH_3OH)CH_3$
3. $CH_3CH_2C(CH_3)(OH)CH_3$
4. $CH_3CH_2CH(OH)CH_2CH_3$

1. $CH_3CH_2CH(CH_3)CH_2OH$ = A, 3
2. $CH_3C(CH_2OH)(CH_2)$
3. $CH_3CH(CHOH)CH_3CH_3$ = B, 2

D. 

t-isobutyl alcohol



= B, 3

III. In accordance with the Geneva Congress Nomenclature.

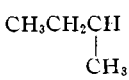
A. Alcohols referable to pentane

$CH_3CH_2CH_2CH_2CH_2OH$
Pentanol-1

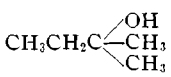
$CH_3CH_2CH_2CHOHCH_3$
Pentanol-2

$CH_3CH_2CHOH\ CH_2CH_3$
Pentanol-3

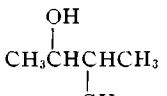
B. Alcohols referable to methyl butane



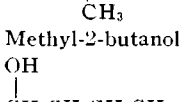
Methyl 2, butanol-1



Methyl 2, butanol-2

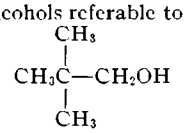


Methyl-2-butanol-3



Methyl-2-butanol-4

C. Alcohols referable to dimethyl propane



Dimethyl-2,2-propanol-1

No matter by which method the isomeric alcohols $C_5H_{11}OH$ may be derived, the number of structural isomers is the same, *viz.*, 8. It will be seen, however, that three of these structural isomers have an asymmetric carbon atom, hence exist in two optically isomeric forms, *viz.*, dextro and laevo gyrate. The asymmetric carbon atoms are found in pentanol 2, methyl-2-butanol-3 and methyl-2 butanol-1. When referring to the optically active amyl alcohol textbook writers commonly refer to methyl-2 butanol-1.

(To be continued)

OFFICERS OF THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Arthur A. Noyes of the California Institute of Technology, Pasadena, Cal., is the President of the American Association for the Advancement of Science. The Secretary is Burton E. Livingston whose home address is c/o The Smithsonian Institution Building, Washington, D. C. The general officers of the Committee of One Hundred on Scientific Research are Chairman A. A. Noyes, President of the Association, and Secretary, Rodney H. True, of the University of Pennsylvania. The dates of the annual meetings for this and next year have been fixed. The meeting this year will be held at Nashville beginning December 26th and the one of the year following in New York City beginning on December 28th.

LIMITATION OF PHARMACISTS IN TURKEY.

The proposed pharmacy law of Turkey will necessitate the closing of about three hundred businesses and is seriously disturbing the pharmacists of that country, most of whom are opposing the provision which limits the number of stores.

INDIA'S EXPORT TRADE IN CINCHONA, NUX VOMICA AND SENNA.

Exports of nux vomica and senna, from India, increased during the first six months of last year. However, shipments of cinchona during the same period were very much less than during the previous year; namely, 410,528 against 456,069 pounds.