

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

THE NUMBER OF STRUCTURALLY ISOMERIC ALCOHOLS OF THE METHANOL SERIES

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Although several attempts have been made by Cayley and others¹ to calculate the number of isomeric hydrocarbons of the methane series, little attention has been given to the similar problem of calculating the number of isomeric alcohols of the methanol series. This limited treatment^{1g} undoubtedly depended upon the fact that the methanol homologs were considered as typical mono-substitution products of the paraffins; hence, it was logical to assume that the number of isomeric alcohols should be conditioned by the number of hydrocarbons from which, theoretically, the former might be derived. Such formulas as have been advanced for determining the number of isomeric alcohols of any given carbon content actually prove to be inadequate and erroneous. Hence, it seemed desirable to derive a formula which would estimate accurately the number of isomeric alcohols.

Our initial attempt sought to establish a simple mathematical relationship between the total number of isomers and their carbon content. It was soon realized that no such simple relationship exists, and the problem was solved only by recognition of the fact that the alcohols might be classified according to simple types, for each of which the number of isomers could be computed. The types into which the alcohols were divided were those commonly recognized in organic chemistry, namely, (1) primary, (2) secondary and (3) tertiary. The scheme for calculating the number of isomers of each type depends upon the method of forming their structural formulas.

(1) The structural formulas of the primary alcohols, RCH_2OH , of n total carbon atom content, may be formed from those of the alcohols of $n - 1$ carbon atoms, ROH , by removing the OH group from each and attaching the resulting alkyl radical, $R-$, to the $-CH_2OH$ group. Obviously, the number of primary alcohols that may be formed in this way will equal the total number of alcohols of all types containing $n - 1$ carbon atoms. This may be expressed as

$$p_n = T_{(n-1)} \quad (I)$$

where p_n is the number of primary alcohols of n carbon atoms, and T_{n-1} is the total number of alcohols of all types containing $n - 1$ carbon atoms.

¹ (a) Cayley, *Ber.*, **8**, 1056 (1875); (b) Schiff, *ibid.*, **8**, 1542 (1875); (c) Hermann, *ibid.*, **13**, 792 (1880); **30**, 2423 (1897); **31**, 91 (1898); (d) Tiemann, *ibid.*, **26**, 1605 (1893); (e) Delannoy, *Bull. soc. chim.*, [3] **11**, 239 (1894); (f) Losanitsch, *Ber.*, **30**, 1917, 3059 (1897); (g) Goldberg, *Chem.-Ztg.*, **22**, 395 (1898); (h) David, *Rev. gen. Sci.*, **39**, 142 (1928); (i) Trautz, "Lehrbuch der Chemie," Berlin, 1924, Vol. III, p. 23.

(2) The structural formulas of the secondary alcohols, $RR'>CHOH$, of n total carbon atom content, may be formed from those of the alcohols ROH and $R'OH$ (the carbon content of $R-$ plus $R'-$ always equaling $n - 1$) by removing the OH group from each and attaching the resulting alkyl radicals, $R-$ and $R'-$, to the $>CHOH$ group. The number of secondary alcohols that may be thus formed will equal the total number of possibilities, without exception or repetition, of combining simultaneously with the $>CHOH$ group every value of $R-$ taken one at a time and every complementary value of $R'-$ also taken one at a time. These possibilities are theoretically of two types: (a) in which the two alkyl radicals, $R-$ and $R'-$, are of unequal carbon content; and (b) in which these are of equal carbon content. Type (b) is actually impossible with an alcohol of an even number of carbon atoms for in that type $n - 1$ should be divisible by two. The number of isomeric secondary alcohols may be calculated by the following (finite) recursion formulas according to whether the carbon content is even or odd.

$$\text{Even} \quad s_n = T_1 \cdot T_{(n-2)} + T_2 \cdot T_{(n-3)} + \dots + T_{(n-2)/2} \cdot T_{(n/2)} \quad (\text{IIa})$$

Odd

$$s_n = T_1 \cdot T_{(n-2)} + T_2 \cdot T_{(n-3)} + \dots + T_{(n-3)/2} \cdot T_{(n+1)/2} + \frac{T_{(n-1)/2} \cdot (1 + T_{(n-1)/2})}{2} \quad (\text{IIa}')$$

where T is the total number of alcohols of all types containing the number of carbon atoms represented by its subscript. Note that the subscripts in each term add up to $n - 1$, and that the number of terms is $(n - 1)/2$ for odd carbon atom content and $(n - 2)/2$ for even.

(3) The structural formulas of the tertiary alcohols, $RR'>C<OHR''$, of n total carbon atom content, may be formed from those of the alcohols ROH , $R'OH$ and $R''OH$ (the carbon content of $R-$ plus $R'-$ plus $R''-$ always equaling $n - 1$) by removing the OH group from each and attaching the resulting alkyl radicals, $R-$, $R'-$ and $R''-$, to the $>C<OH$ group. The number of tertiary alcohols that may be thus formed will equal the total number of possibilities, without exception or repetition, of combining simultaneously with the $>C<OH$ group every value of $R-$ taken one at a time and all complementary values² of $R'-$ and $R''-$ also taken one at a time. These possibilities are theoretically of three types: (a) in which the three alkyl radicals are of different carbon content; (b) in which two of the alkyl radicals are of equal carbon content and different from that of the third; and (c) in which the three alkyl radicals are of equal carbon content. Type (c) is actually possible only when $n - 1$ is divisible by three. The number of alcohols of each type may be calculated by the following (finite) recursion formulas for that particular type:

² The values of $R'-$ and $R''-$ complementary to $R-$ satisfy the relationship that the total carbon content of $R-$ plus $R'-$ plus $R''-$ equal $n - 1$.

The number of isomeric tertiary alcohols of type (a) equals

$$\sum T_i \cdot T_j \cdot T_k \quad (\text{IIIa})$$

where i, j and k are integers, distinct, and greater than zero; $i + j + k = n - 1$; $i > j > k$.

The number of terms of type (a) depends on whether n is even or odd. Even: if $n/6$ or $(n - 2)/6$ is an integer, the number of terms of type (a) is $(n - 2)(n - 6)/12$; and if $(n + 2)/6$ is an integer the number of terms is $(n - 4)^2/12$.

Odd: if $(n + 1)/6$ or $(n + 3)/6$ is an integer, the number of terms is $(n - 3)(n - 5)/12$; and if $(n - 1)/6$ is an integer the number of terms is $(n^2 - 8n + 19)/12$.

The number of isomeric tertiary alcohols of type (b) equals

$$\frac{1}{2} \sum T_i \cdot (1 + T_i) \cdot T_j \quad (\text{IIIb})$$

where i and j are integers, distinct, and greater than zero, and $2i + j = n - 1$.

The number of terms of type (b) also depends on whether n is even or odd. Even: if $n/6$ or $(n - 2)/6$ is an integer, the number of terms of type (b) is $(n - 2)/2$; and if $(n + 2)/6$ is an integer, the number of terms is $(n - 4)/2$.

Odd: if $(n + 1)/6$ or $(n + 3)/6$ is an integer, the number of terms is $(n - 3)/2$; and if $(n - 1)/6$ is an integer, the number of terms is $(n - 5)/2$.

The number of isomeric tertiary alcohols of type (c) equals

$$\frac{T_i(1 + T_i)(2 + T_i)}{6} \quad (\text{IIIc})$$

where i is an integer, greater than zero, and $3i = n - 1$.

Obviously, there will never be more than one term of type (c) for any given value of n .

Grateful acknowledgment is made to Dr. Leo Zippin³ and to Professor Orrin Fink, Jr., of Pennsylvania State College for their aid in checking the recursion formulas.

The actual use of these formulas may be illustrated in the calculation of the number of isomeric heptyl alcohols, $C_7H_{16}OH$.⁴ Primary alcohols: $n = 7$

$$p_7 = T_6 = 17$$

Secondary alcohols: number of terms equals $(n - 1)/2 = 3$

$$\begin{aligned} s_7 &= T_1T_6 + T_2T_4 + T_3(1 + T_3)/2 \\ &= 1 \cdot 8 + 1 \cdot 4 + 2 \cdot 3/2 = 15 \end{aligned}$$

Tertiary alcohols: type (a), number of terms (for $(n - 1)/6 =$ an integer) equals $[(n - 4)^2 + 3]/12 = 1$

³ National Research Fellow in Mathematics.

⁴ It is of interest to note that the total number of heptyl alcohols is erroneously stated as being 38 in Richter's "Organic Chemistry" (Spielmann), second edition, Vol. I, p. 121.

$$T_3 \cdot T_2 \cdot T_1 = 2 \cdot 1 \cdot 1 = 2$$

Type (b), number of terms (for $(n - 1)6 = \text{an integer}$) equals $(n - 5)/2 = 1$

$$T_1(1 + T_1)T_4/2 = 1(1 + 1)4/2 = 4$$

Type (c), number of terms (for $(n - 1)/3 = \text{an integer}$) equals 1

$$T_2(1 + T_2)(2 + T_2)/6 = 1(1 + 1)(2 + 1)/6 = 1$$

$$t_7 = 2 + 4 + 1 = 7$$

$$T_7 = p_7 + s_7 + t_7 = 17 + 15 + 7 = 39$$

The following table indicates the number of isomeric alcohols of the methanol series as calculated by the use of the recursion formulas.⁵

TABLE I
NUMBER OF ISOMERIC ALCOHOLS

Carbon content	Primary	Secondary	Tertiary	Total
1	1	0	0	1
2	1	0	0	1
3	1	1	0	2
4	2	1	1	4
5	4	3	1	8
6	8	6	3	17
7	17	15	7	39
8	39	33	17	89
9	89	82	40	211
10	211	194	102	507
11	507	482	249	1,238
12	1,238	1,188	631	3,057
13	3,057	2,988	1,594	7,639
14	7,639	7,528	4,074	19,241
15	19,241	19,181	10,443	48,865
16	48,865	49,060	26,981	124,906
17	124,906	126,369	69,923	321,198
18	321,198	326,863	182,158	830,219
19	830,219	849,650	476,141	2,156,010
20	2,156,010	2,216,862	1,249,237	5,622,109

Summary

1. No direct or simple relationship appears to exist between the total number of isomeric alcohols of the methanol series and their carbon content.

2. Formulas of the (finite) recursion type are advanced which permit the calculation from their carbon content of the number of primary, secondary and tertiary alcoholic isomers. In using these recursion formulas to calculate the total number of such alcohols of any given carbon content, the total number of isomers of every lesser carbon content must be known.

3. The totals so obtained agree exactly through the dodecyl alcohols

⁵ The structural formulas of the homologs of methanol, inclusive of the dodecyl alcohols, were written in connection with the derivation of these recursion formulas. The totals obtained from actual count of these structural formulas agreed exactly with those derived from the use of the recursion formulas.

with the numbers required by theory as tested by actually writing all the possible structural formulas.

4. The usefulness of the formulas advanced is not limited to the calculation of the number of structurally isomeric alcohols. Since the latter are typical mono-substituted derivatives of the paraffins, the figures recorded in Table I more generally represent the number of structurally isomeric mono-substitution products of the saturated hydrocarbons inclusive of the eicosanes.

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SOME ORGANIC ACIDS IN BARLEY, MAIZE, OATS AND RYE PLANTS

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In continuation of the work on the organic acids of cereal plants, which began with a study of the acids of wheat plants,¹ an investigation has been made of the non-volatile acids in the green parts of the growing plants of barley, maize, oats and rye. The maize was raised in the field. The barley, oats and rye plants were grown in the greenhouse. All plants were beginning to head when cut. As in the case of wheat plants the investigation was confined to the non-volatile acids, extracted by boiling water from the dried, ground plants. These have not been previously reported in the literature.

Aconitic acid, previously reported as present in sugar cane² and in sorghum³ and found in the wheat plant,¹ is present also in these plants of the grass family. Other acids in some of these plants which have not been found in numerous investigations of the acids of fruits are tricarballylic acid and malonic acid.

The Acids of Barley Plants.—The acids were separated from one hundred pounds of barley plants and converted into the ethyl esters, yielding 84 g. of crude esters. Fractionation at 10 mm. yielded: 1, 80–95°, 0.4 g.; 2, 95–105°, 0.6 g.; 3, 105–115°, 1.5 g.; 4, 115–125°, 5.2 g.; 5, 125–135°, 42.2 g.; 6, 135–150°, 1.1 g.; 7, 150–165°, 2.8 g.; 8, 165–173°, 21.9 g.; residue, 8 g.

Fraction 1 yielded oxalic dihydrazide, melting at 235° and further identified by optical crystallographic data.⁴ The filtrate, seeded with malonic hydrazide, yielded a second crop of crystals, melting at 148–149° and further identified as malonic hydrazide by optical data.

¹ Nelson and Hasselbring, *THIS JOURNAL*, 53, 1040–1043 (1931).

² Behr, *Ber.*, 10, 35 (1877).

³ Parsons, *Jahresb.*, 1444 (1882).

⁴ Optical crystallographic examinations were made by G. L. Keenan of the Food and Drug Administration.