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REVISED STRUCTURE OF CERIFERIC ACID

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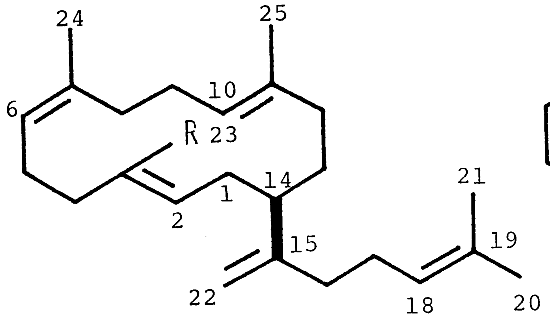
The structure of ceriferic acid, a scale insect sesterterpene secretion, has been revised from 10 to 5. Naturally occurring ceriferol has been correlated with ceriferic acid.

We recently reported the structures of a series of 14-membered monocyclic sesterterpenoids isolated from the secretion of a Japanese scale insect *Ceroplastes ceriferus* Anderson (Coccidae).[1,2] Eight of these possess the 2-t/6-c/10-t skeletal framework as exemplified by cericerol-I (1), $[\alpha]_D^{27}$ -84.1°, for which the absolute configuration at C-14 was established by chemical correlations;[1] two minor congenors possibly have 2-t/6-c/10-c and 2-t/6-t/10-t skeletons.[2]

The arrangement of annular double bonds in these compounds is in contrast to that of albocerol (2) which was isolated from the Mexican species *C. albolineatus* by Veloz et al.[3] It should be noted that the skeletons of 1 and 2 are derived, respectively, from two opposing cyclization modes of the biogenetic precursor geranylfarnesyl pyrophosphate (3) and (4).[2,3] It was thus quite remarkable that spectral data of ceriferic acid isolated from the Japanese species *C. ceriferus* (collected in Tokyo area) led to the albocerol- or Mexican-type structure (10);[4] it even implied necessity for a taxonomic reinvestigation. In the following, however, we show that ceriferic acid should after all be represented by the cericerol-I type structure (5).

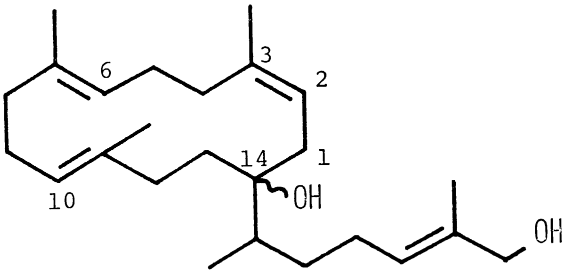
The evidence leading to the revised structure is as follows:

1) Ceriferic acid showed no CD Cotton effect. Therefore, the α,β-unsaturated carboxylic acid group, which from ^{1}H- and ^{13}C-NMR data is clearly part of a *cis*

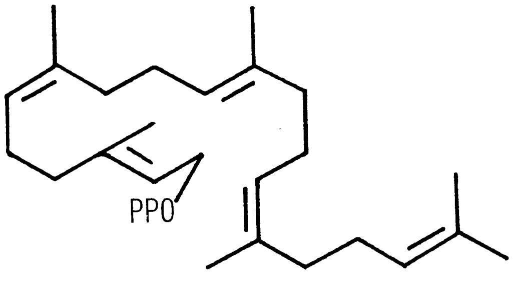


(1): R=CH_2OH
(cericerol-I)

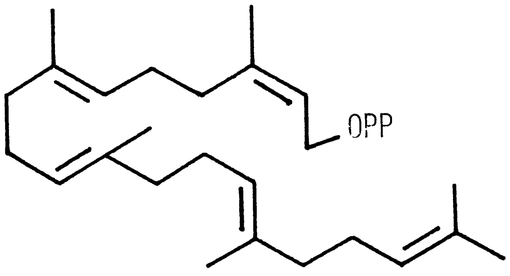
(11): R=CH_3



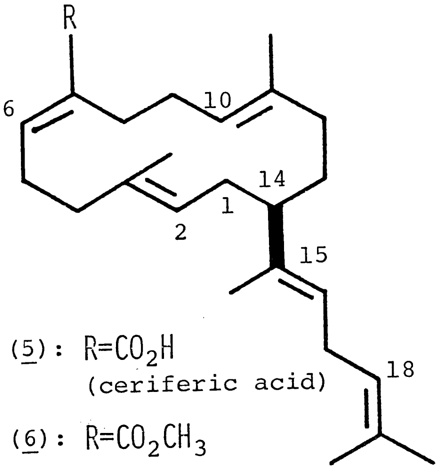
(2)
(albocerol)



(3)



(4)



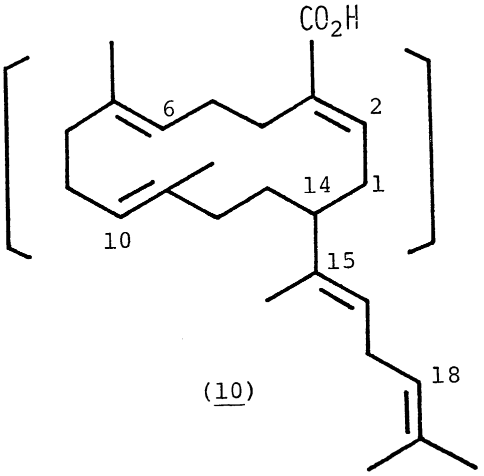
(5): R=CO_2H
(ceriferic acid)

(6): R=CO_2CH_3

(7): R=CH_2OH
(ceriferol)

(8): R=CH_2OTs

(9): R=CH_3



(10)

Table 1. ^{13}C-NMR chemical shifts of methyl ceriferate (6), ceriferol (7), "α-cericerene" (9), and cericerene (11) in $CDCl_3$. Peak assignments are based on measurements of T_1 and ^{13}C-NOE[1] in addition to the more conventional techniques.

C-atom	6	7	9	11
C-1	29.8^a	29.6^a	29.4^a	30.5^a
C-2	125.3^b	125.0^b	125.2^b	125.1^b
C-3	133.7^c	133.2^c	133.8^c	134.1^c
C-4	31.2^a	29.9^a	30.4^a	31.1^a
C-5	26.9	27.2	31.0^a	31.4^a
C-6	142.4	127.6	124.9^b	125.1^b
C-7	131.3^d	137.6	133.1^c	132.9^c
C-8	36.0	35.8	35.8	36.2
C-9	26.0	24.6^d	24.5	24.6
C-10	125.4^b	125.0^b	124.9^b	125.0^b
C-11	132.9^c	133.1^c	132.9^c	133.0^c
C-12	40.3	30.2	40.2	40.3
C-13	24.5	24.5^d	24.5	24.6
C-14	49.9	46.4	46.6	44.6
C-15	136.4	136.8	137.1	153.0
C-16	123.4	123.5	123.7	33.7
C-17	26.9	26.9	26.8	26.6
C-18	124.6	124.8^b	124.5	124.6^b
C-19	131.1^d	131.2	131.0	131.3
C-20	25.7	25.6	25.6	25.7
C-21	17.7	17.7	17.7	17.8
C-22	12.3	12.0	12.0	108.9
C-23	15.6^e	15.6^e	15.6^d	15.6^d
C-24	168.4	66.6	22.4	22.5
C-25	15.3^e	15.4^e	15.4^d	15.5^d
$-COOCH_3$	51.3			

a-e) Assignments denoted by same alphabet are interchangeable.

skeleton framework,[4] must be remote from the sole chiral center at C-14; if it were as in 10 , the CD should have shown a Cotton effect at the λ_{max} of ceriferic acid. Of the two 14-membered skeletal possibilities, 5 (or 1) and 10 , it is only structure 5 which satisfies the two criteria underscored above.

2) Reduction of methyl ceriferate (6) with LiAlH$_4$ gave "ceriferol" (7), which was further converted into the tosylate (8) by careful treatment with TsCl/py at 0 °C. Tosylate 8 with its strongly absorbing chromophore also lacked a CD Cotton effect, thus confirming the deductions described above.

3) Acid treatment of tosylate 8 simply resulted in hydrolysis to alcohol 7 . In contrast, acid treatment of the tosylate derived from cericerol-I 1 underwent transannular cyclization to a bicyclocericerene.[5]

4) The neutral fraction of *C. ceriferus* collected around Kyoto in 1979 has given, in addition to cericerol-I 1 , an alcohol, $[\alpha]_D^{24}$ -83.5° (c, 1.33), the physical constants (MS, NMR, IR, and rotation) of which were identical with those of allyl alcohol 7 (ceriferol). Furthermore, the acidic fraction[1] gave ceriferic acid, $[\alpha]_D^{26}$ -97.6° (c, 1.02); these findings are in line with the taxonomical identify of the Tokyo and Kyoto species.

5) The ^{13}C-NMR data of ceriferic acid 5 derivatives are in good agreement with cericerol-I 1 derivatives, a further support for the skeletal identity. This is exemplified by a comparison of the data for hydrocarbons (9), $[\alpha]_D^{19}$ -28.8° (c, 0.24) (derived from tosylate 8 by LiAlH$_4$ treatment) and (11),[1] $[\alpha]_D^{27}$ -48.3° (c, 0.48) (derived from cericerol-I) (Table 1). The data for methyl ceriferate 6 and ceriferol 7 given in Table 1 are in accord with the structural variations.

Finally, in analogy with other cericerol-I 1 derivatives, we assign an R-configuration (or "β" as depicted) to the C-14 of ceriferic acid 5 .

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5) To be published elsewhere.

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